LAVOISIER

1743-1794

THE

PRINCIPLES OF CHEMISTRY

By D. MENDELÉEFF

THIRD ENGLISH EDITION

TRANSLATED FROM THE RUSSIAN (SEVENTH EDITION) BY

GEORGE KAMENSKY, A.R.S.M.

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THOMAS H. POPE, B.Sc., F.I.C.

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TRANSLATOR'S PREFACE

As in the previous English editions of these 'Principles,' so also in the present translation, it has been the aim of the Translator to give, as nearly as possible, a literal rendering of the Russian work.

All the more important of the new figures in the original have been reproduced, the only omissions, which are few in number, being either portraits or illustrations of well-known apparatus.

Of the Appendices issued with the first English edition, two have been retained; for permission to print the first of these we have to thank the Managers of the Royal Institution, while, for allowing the Faraday Lecture to appear, we are indebted to the Council of the Chemical Society of London. The matter of Appendix III. of the former English edition has now been incorporated into the text of the book, so that this appendix has been omitted. Its place is taken by an article, recently written by Professor Mendeléeff, on 'A Chemical Conception of the Ether.'

G. K.
T. H. P.

November, 1904.

AUTHOR'S PREFACE

TO

THE SEVENTH RUSSIAN EDITION

THIS work was written during the years 1868–1870, its object being to acquaint the student not only with the experimental facts and laws of chemistry, but also with the insight given by this science into the unchangeable substratum underlying the varying forms of matter.

If statements of fact themselves depend upon the person who observes them, how much more distinct is the reflection of the personality of him who gives an account of methods and philosophical speculations forming the essence of a science! For this reason there will inevitably be much that is subjective —bearing the stamp of time and locality—in every objective exposition of science. And as an individual production is only significant in virtue of that which has preceded and that which is contemporary with it, it resembles a mirror, which in reflecting exaggerates the size and clearness of neighbouring objects, and causes a person near it to see reflected most plainly those objects which are on the side to which it is directed, and sometimes even the person holding the mirror. Although I have endeavoured to make my book a true mirror directed towards the whole domain of chemical changes and of the elements taking part in them, yet involuntarily those influences near to me being the most clearly reflected and the most brightly illuminated have tinted the entire work with their colouring. In this way the chief peculiarity of the book has been determined. Experimental and practical data and their application in life and industry occupy their place, but the philosophical principles of our science form the chief theme of the work. In former times sciences, like bridges, could only be built up by supporting them on a few broad buttresses and long girders. In addition to the exposition of the principles of chemistry, it has been my desire to show how this science has now been built up like a suspension bridge, supported by the united strength of a number of slender, but firmly fixed, chains—individually of little strength—and has thus been carried over difficulties which before appeared insuperable. In comparing the science of the past, the present, and the future, in placing the particulars of its restricted experiments side by side with its aspirations after unbounded and infinite truth, and in restraining myself from yielding to a bias towards the most attractive path, I have endeavoured to incite in the reader a spirit of inquiry which, dissatisfied with speculative reasonings alone, should subject every idea to experiment, to encourage the habit of stubborn work, and to excite a search for fresh chains of evidence to complete the bridge over the bottomless unknown. History proves that it is possible by this means to avoid three equally pernicious extremes: the Utopian—a visionary contemplation which strives to create all from an impulse of thought alone—the stagnant realism which is content with bare facts, and presumptuous scepticism, irresolute about everything. Sciences like chemistry, which deal with ideas as well as with material substances, and create a possibility of immediately verifying that which has been or may be discovered or assumed, demonstrate at every step that the work of the past has availed much, and that, without it, it would be impossible to advance into the ocean of the unknown. They also show the possibility of becoming acquainted with fresh portions of this unknown, and compel us, while duly respecting the teachings of history, to cast aside classical illusions, and to engage in the work of tranquil and systematic investigation,

which is not only the sole means of attaining mental satisfaction, but is also practically useful to ourselves and all our fellow-creatures.[1]

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[1] Chemistry, like every other science, is at once a means and an end. It is a means of attaining certain practical results. Thus, by its assistance, the obtaining of matter in its various forms is facilitated; it shows new possibilities of availing ourselves of the forces of nature, indicates the methods of preparing many substances, points out their properties, &c. In this sense chemistry is closely connected with the work of the manufacturer and the artisan, it plays a useful part, and is a means of promoting the general welfare. Besides this honourable vocation, chemistry has another. With it, as with every other elaborated science, there are many lofty aspirations, the contemplation of which serves to inspire its workers and adherents. This contemplation comprises not only the principal data of the science, but also the generally accepted deductions, together with hypotheses which refer to phenomena as yet but imperfectly known. In this latter sense scientific contemplation varies much with times and persons, it bears the stamp of creative power, and embraces the highest forms of scientific progress. In that pure enjoyment experienced on approaching to the ideal, in the eagerness to draw aside the veil from the hidden truth, and even in that discord which exists between the various workers, we ought to see the surest pledges of further scientific progress. Science thus advances, discovering new truths, and at the same time obtaining practical results. The edifice of science not only requires material, but also a plan, and necessitates the work of preparing the materials, putting them together, working out the plans and the symmetrical proportions of the various parts. To conceive, understand, and grasp the whole symmetry of the scientific edifice, including its unfinished portions, is equivalent to tasting that enjoyment only conveyed by the highest forms of beauty and truth. Without the material, the plan alone is but a castle in the air, a mere possibility; whilst the material without a plan is but useless matter. All depends on the concordance of the materials with the plan and execution, and the general harmony thereby attained. In the work of science the artisan, architect, and creator are very often one and the same individual; but sometimes, as in other walks of life, there is a difference between them; sometimes the plan is preconceived, sometimes it follows the preparation and accumulation of the raw material. Free access to the edifice of science is not only allowed to those who devised the plan, worked out the detailed drawings, prepared the materials, or piled up the brickwork, but also to all those who are desirous of making a close acquaintance with the plan, and wish to avoid dwelling in the vaults or in the garrets where the useless lumber is stored.

Knowing how contented, free, and joyous is life in the realm of science, one fervently wishes that many would enter its portals. On this account many pages of this treatise are unwittingly stamped with the earnest desire that the habits of chemical contemplation which I have endeavoured to instil into the minds of my readers will incite them to the further study of science. Science will then flourish in them and by them, on a fuller acquaintance not only with that little which is enclosed within the narrow limits of my work, but with the further learning which they must imbibe in order to make themselves masters of our science and partakers in its further advancement.

Those who enlist in the cause of science have no reason to fear when they remember the urgent need for practical workers in the spheres of agriculture, arts, Thus the desire to direct those thirsting for truth to the pure source of the science of the forces acting throughout nature forms the first and most important aim of this book. The time has arrived when a knowledge of physics and chemistry forms as important a part of education as that of the classics did two centuries ago. In those days the nations which excelled in classical learning stood foremost, just as now the most advanced are those which are superior in the knowledge of the natural sciences, for they represent the strength as well as the signs of our times. If the universe clearly exhibits a unity of purpose, the cause of this is surely first seen in the unity of the principles of science, which inevitably become more and more uniform and progressive, and, although individually untrammelled, are bound to submit to the yoke of laws conceived and revealed. And chemistry, as the youngest branch of natural science, promises in the future a richer harvest than it has already given. One of the chief aims of this book is to attract and retain fresh, unshackled forces for this youthful science by pointing out what has been achieved, what remains to be achieved, and in what directions advances may be made. Only by gradually extending the conquests already made can the coming generation of chemists benefit mankind and disperse the shades of ignorance and superstition. The seeds sown by science are reaped by mankind. In contemplating the infinite, science has no limits.

Although I feel confident that 'good will' will be awakened by our science, I know that time is long, and that many efforts, conditions, and circumstances are needed for the fruits to ripen.

While following the above and chief aim, I set myself also a second object: to furnish a text-book giving an elementary knowledge of chemistry, and so satisfy a want which undoubtedly exists among students and those who have recourse

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and manufacture. By summoning adherents to the work of theoretical chemistry, I am confident that I call them to a most useful labour, to the habit of dealing correctly with nature and its laws, and to the possibility of becoming truly practical men.

to chemistry either as a source of truth or as a means of living.[2] Hence, although the fundamental object of this work was to express and embrace the general chemical teaching of the present day from a personal point of view, I have nevertheless striven throughout to maintain such a level as would render the 'Principles of Chemistry' accessible to the beginner.

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[2] I recommend those who are commencing the study of chemistry with my book *to first read only what is printed in large type*, because in that part I have endeavoured to concentrate all the fundamental, indispensable knowledge required for that study. In the footnotes, printed in small type (which should be read only after the large text has been mastered), certain details are discussed; they are either further examples, or debatable questions on existing ideas which I thought useful to lay before those entering into the sphere of science, or certain historical and technical details which might be withdrawn from the fundamental portion of the book. Without intending to attain in my treatise to the completeness of a work of reference, I have still endeavoured to express the principal developments of science as they concern the chemical elements viewed in that aspect in which they appeared to me after long-continued study of the subject and participation in the contemporary advance of knowledge.

I have also placed my personal views, suppositions, and arguments in the footnotes, which are chiefly designed for details and references. But I have endeavoured to avoid here, as in the text, not only all that I consider doubtful, but also those details which belong either to special branches of chemistry (for instance, to analytical, organic, physical, theoretical, physiological, agricultural, or technical chemistry) or to different branches of natural science which are gradually coming into closer and closer contact with chemistry. Chemistry, I am convinced, must occupy a place among the natural sciences side by side with mechanics; for mechanics treats of matter as a system of ponderable points having scarcely any individuality and only standing in a certain state of mobile equilibrium. For chemistry, matter is an entire world of life, with an infinite variety of individuality both in the elements and in their combinations. In studying the general uniformity from a mechanical point of view, I think that the highest point in the knowledge of nature cannot be attained without taking into account the individuality of things in which chemistry is set to seek for general higher laws. Mechanics forms the classical basis of natural philosophy, while chemistry, as a comparatively new and still young science, already strives to—and will, in the future—introduce a new, living aspect into the philosophy of nature; all the more is this so, as chemistry alone is never at rest or anywhere dead—its vital action has universal sway, and inevitably determines the general aspect of the universe. Just as the microscope and telescope enlarge the scope of vision, and discover life in seeming immobility, so chemistry, in discovering and striving to discern the life of the invisible world of atoms and molecules and their ultimate limit of divisibility, will clearly introduce new and important problems into our conception of nature. And I think that its *rôle*, which is now considerable, will increase more and more in the future; that is, I think that, in its further development, it will occupy a place side by side with mechanics for the comprehension of the secrets of nature. But here we require some second Newton; and I have no doubt but that he will soon appear.

Many aspects of this work are determined by this combination of requirements, which frequently differ widely. In the preparation of such a book it is necessary not to be carried away by what appears to be a plausible theory in explaining individual facts and to always endeavour to transmit the simple truth of a given fact, extracting it from the vast store of the literature of the subject and from tried personal experience. In publishing a new edition of this work I have striven to add any facts of importance recently discovered and to revise the former edition in the above spirit. With this object I have gone entirely over this edition, and a comparison of it with the former one will show that the additions and alterations have, in many instances, cost as much labour as their original compilation. I also wished to show in an elementary treatise on chemistry the striking advantages gained by the application of the periodic law, which I first saw in its entirety in the year 1869, when I was engaged in writing the first edition of this book, in which, indeed, the law was first enunciated. At that time, however, this law was not established so firmly as now, when so many of its consequences have been verified by the researches of numerous chemists. The, to me, unexpectedly rapid success with which the teaching of the periodicity of the elements has spread in our science, and perhaps, also, the perseverance with which I collected in this work, and upon a new plan, the most important data respecting the elements and their mutual relations, explained sufficiently the fact that the former editions of my work have been translated into English[3] and German.[4] Deeply touched by the favourable opinions expressed by English and American men of science upon my book, I ascribe them chiefly to the periodic law placed at the basis of my treatise, and especially of the second part of the book, which contains a large amount of data having a special, and sometimes unexpected, bearing from the point of view of this law. As the entire scheme of this work is subordinated to the law of periodicity, which may be illustrated in a tabular form by placing the elements in series, groups, and periods, such tables are given at the end of this Preface.

But the thought that this book might fall not only into the hands of the beginner for whom it is intended, but also of authorities who might wish to know the views held by an old disciple of science on the current problems of chemistry, greatly complicated the preparation of a new edition, for it necessitated making a selection of the most essential of the vast number of new researches published year by year, and explaining my views on them without greatly enlarging the bulk of the work.[5] After having closely followed all the chief conquests of chemical science since the days of Berzelius, Liebig, Dumas, and Gerhardt, and having seen the triumph of much that lay neglected and the fall of much that was exalted, I involuntarily acquired a tendency to analyse new facts and a desire to transmit to my readers the results of such analysis, if it could, in my opinion, help towards a proper explanation and generalisation of the chemical elements. In carefully preparing this

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[3] The English translation was made by G. Kamensky, and edited by A. J. Greenaway; published by Longmans, Green & Co.

[4] The German translation was made by L. Jawein and A. Thillot; published by Ricker (St. Petersburg).

[5] A mere dry and impersonal statement of facts and of the opinions of others, although new and important, would in no way correspond with the spirit of this book, which is mainly designed for the beginner, and for the expression of my personal views on the chemical elements. In my opinion, only a connection of ideas with facts, and of observations with a line of thought, can act in the right direction; otherwise reality slips away and fiction easily supersedes it, as has been, is, and will be frequently the case, and this I strenuously wish to avoid in this book. My chief desire is to inspire a spirit of inquiry, and if I often express my personal opinions, I do not wish to hide either the reasons which guide others in another direction or views which are contrary to my own. Of these views I may mention those which recognise an 'electrolytic dissociation' in saline solutions, the formation of the chemical elements from a single primary matter, &c. In shortly, but as far as possible exactly and objectively, stating observed facts, I endeavour, as well as I am able, to elucidate their sense and to group them in a precise and real manner, revealing further horizons for future scientific research. I have tried to exclude nothing which I knew and considered reliable and instructive, although it might have contradicted my views. Notwithstanding the care I have taken in collecting the difficult data cited in this book, I am far from thinking that it contains a complete review of all that is instructive in the doctrine of the chemical elements.

edition, I have not lost sight of the fact that I am hardly likely to publish another, and I have therefore, in many cases, spoken more definitely than formerly. After having been an insignificant but zealous worker in chemistry for almost half a century, I wished that my book should retain some traces of how a confirmed disciple of Gerhardt regards the fundamental problems of the theory of the chemical elements at the beginning of the twentieth century. As an example, I may mention that the more I have thought on the nature of the chemical elements, the more decidedly have I turned away from the classical notion of a primary matter, and from the hope of attaining the desired end by a study of electrical and optical phenomena, and the more clearly have I recognised that first and foremost are needed truer conceptions of 'mass' and 'ether' than those in vogue at the present time.[6] The return to electro-chemism

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[6] When I consider the undoubtedly real and all-permeating 'ether,' and involuntarily ask myself of what it consists, I cannot admit the idea that its atoms or matter are only composed of a 'primary matter' of which all atoms are built up, for if that were so one might expect not only cases of the appearance and disappearance of the 'mass' of a substance, but also of the transformation of one element into another, and all we know forces us to deny that this is possible, although thousands—from the spiritualists to Emmens (the conversion of silver into gold, 1897) and Fittica (the conversion of phosphorus into arsenic, 1900)—have tried and are trying to prove the contrary. And, of course, no one except a metaphysician would permit himself, and will hardly ever consent, to deny the presence of matter, 'atoms,' and mass in 'ether.' And if we recognise the materiality and mass of 'ether,' it seems to me first of all necessary to admit that it is a substance without power of chemical reaction on other substances. Not so long ago such an idea might have appeared most unreal; but now, when instances of substances incapable of reacting have been discovered in argon and its analogues, this view is quite possible. Besides being admissible, a light substance deprived of all chemical force should apparently certainly exist and is to be foreseen. Moreover, the distribution of the elements according to groups and series (Preface, tables I. and II.) in the periodic system, and the fact that a zero group must be recognised besides groups I.–VIII., give reason for thinking that there is also a zero series of elements lighter than hydrogen, and even an element in the hydrogen series of the zero group (is not this coronium or one of the volcanic gases, the spectra of which were observed by Nasini, Anderlini, and Salvadori in 1898?), and an element of the zero series and zero group should be many times lighter than hydrogen in its atomic weight. Let us call this weight x. It should be an unliquefiable gas, and its density with respect to hydrogen under like conditions should be $x/2$, i.e. its molecule should contain one atom like that of helium, argon, &c. The extremely small density of the gas, i.e. the extremely rapid motion proper to its molecules, their very small weight, and also the position in the zero

which is so evident in the supporters of the hypothesis of 'electrolytic dissociation,' and the notion of a splitting up of atoms into 'electrons,' in my opinion only complicate and in no way explain so real a matter (since the days of Lavoisier) as the chemical changes of substances, which led to the recognition of the invariable and ponderable atoms of simple bodies. The definition of mass gave a means for analysing and grasping chemical transformations of substances, and for arriving at the atom, while the mass of the atom was shown by the periodic law to influence all its chief chemical properties. Thus chemistry in its principles stood on the firm foundations laid by Galileo, Newton, and Lavoisier, and in order to gain further insight and knowledge of the atoms themselves, the fundamental conceptions of mass, gravity, and ether will have to be explained by a method of experiment alone, otherwise the realism of science will again open its doors to such metaphysical and 'metachemical' conceptions as phlogiston and other mystical dreams. For my part, I endeavour to remain true to the testament of realism left by Newton and Lavoisier, and it is my wish to instil this sentiment into my young readers.

In this seventh edition I have not found it necessary to alter any of the essential features of previous editions, and have only completed them by the addition of many new details. In this respect invaluable assistance has been rendered me by my dear friend, Professor Brauner, of the University of Prague, by his complete and concise contribution on the 'Elements of the Rare Earths,' which he wrote at my request. Many data have been added thereto in recent years, and it needs such an authority on the 'rare earths' as Professor Brauner to interpret this complex, difficult, and yet unfinished subject, where the obtaining

group, should contribute to the fact that this gas should permeate and penetrate everywhere; that it should occupy space, but not attach itself stably to anything with the harmonious motion of chemical combination, so that it cannot accumulate anywhere. And these imaginary properties should also be those of the substance 'ether.' In endeavouring to clothe the conception of 'ether' with a chemical dress, and so render it an actual, real possibility in harmony with the purely realistic periodic law, I think I am serving the cause of unity in natural philosophy.

of reliable data is complicated not only by the peculiarities and analogies of many facts, but also by the rareness of the earths themselves. Professor Brauner has himself contributed largely to the history of these metals, and his description of them contains much of his individual work. I offer him my most grateful thanks for his contribution. I am also greatly indebted to Mr. V. D. Saposhnikoff for revising the sheets for the press and for compiling the Index, which will be found of great help to those seeking for any special subject in this book.

D. MENDELÉEFF.

St. Petersburg: *November* 27, 1902.

THE PERIODS OF THE CHEMICAL ELEMENTS, TAKING THE ATOMIC WEIGHT OF O = 16.

Higher saline oxides.	Groups.	Elements of even series.				
R$_2$O	I	K=39·1	Rb= 85·4	Cs=132·9	—	—
RO	II	Ca=40·1	Sr= 87·6	Ba=137·4	—	Rd=224[7]
R$_2$O$_3$	III	Sc=44·1	Y= 89·0	La=139	Yb=173	—
RO$_2$	IV	Ti=48·1	Zr= 90·6	Ce=140[6]	—	Th=232
R$_2$O$_5$	V	V=51·4	Nb= 94·0	—	Ta=183	—
RO$_3$	VI	Cr=52·1	Mo= 96·0	—	W=184	U=239
R$_2$O$_7$	VII	Mn=55·0	?= 99[4]	—	—	
	VIII	Fe=55·9	Ru=101·7	—	Os=191	
		Co=59	Rh=103·0	—	Ir=193	
		Ni=59[3]	Pd=106·5	—	Pt=194·9	

Gaseous hydrogen compounds.	Higher saline oxides.	Groups.	Typical elements.						
	R$_2$O	I	**H=1·008**	Li= 7·03	Na=23·05	Cu=63·6	Ag=107·9	—	Au=197·2
	RO	II		Be= 9·1	Mg=24·3	Zn=65·4	Cd=112·4	—	Hg=200·0
	R$_2$O$_3$	III		B=11·0	Al=27·0	Ga=70·0	In=114·0	—	Tl=204·1
RH$_4$	RO$_2$	IV		C=12·0	Si=28·4	Ge=72·3	Sn=119·0	—	Pb=206·9
RH$_3$	R$_2$O$_5$	V		N=14·04	P=31·0	As=75·0	Sb=120·0	—	Bi=208
RH$_2$	RO$_3$	VI		O=16·00	S=32·06	Se=79	Te=127[5]	—	—
RH	R$_2$O$_7$	VII		F=19·0	Cl=35·45	Br=79·95	I=127	—	—
0	0	0[1]	**He=4·0**	Ne=19·9	Ar=38[2]	Kr=81·8	Xe=128	—	—

Elements of uneven series.

D. MENDELÉEFF.
1869–1902.

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[1] The atomic weights of helium, argon, and the analogous gases, judging from their densities (pp. 247–253), are greater than those of the halogens and less than those of the metals of the alkalies, but no compounds of these elements are known.

[2] The density of argon indicates an atomic weight 39·9; but, judging from the preceding note, it is probably greater than that of Cl but less than that of K, i.e. about 38.

[3] The atomic weight of Ni is given as 58·7; but as this metal, judging from its properties, should follow after Co = 59, its atomic weight should not be less but greater than that of Co. Therefore it is probable that further research will prove these atomic weights to be slightly different from the above.

[4] The discovery of a metal resembling Mn (ekamanganese) with an atomic weight 99 may be expected.

[5] Judging by its properties and the periodic law, tellurium should have an atomic weight less than that of iodine, but so far experiment proves the contrary—the values obtained for Te varying from 126·4 (Steiner) to 127·9 (Metzner) with an average of 127·7, that of iodine being slightly less—126·96 (Stas), and 126·98 (Ladenburg). Both these latter figures are near 127, and it is therefore likely that further research will prove that the atomic weight of iodine is greater than 127 (which is possible because the iodine was dried with CaCl$_2$, which might introduce chlorine), or else a figure smaller than 127 may be afterwards found for tellurium.

[6] A whole large period is wanting between Ce = 140 and Ta = 183, but the series of rare elements (they have not been fully investigated)—for instance, Pr = 140·5, Nd = 143·6, Gd = 156, Er = 166, Yb = 173, &c.—have, as far as is now known, atomic weights which exactly fill this interval, and therefore this portion of the periodic system is, in a way, broken and requires fresh researches.

[7] According to Madame Curie (1902), *radium* (Vol. II., p. 328) (one of the radio-active elements) resembles barium and has an atomic weight lying between 223 and 225.

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES.

Series	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Hydrogen **H** 1·008	—	—	—	—	—	—	
2	Helium **He** 4·0	Lithium **Li** 7·03	Beryllium **Be** 9·1	Boron **B** 11·0	Carbon **C** 12·0	Nitrogen **N** 14·04	Oxygen **O** 16·00	Fluorine **F** 19·0	
3	Neon **Ne** 19·9	Sodium **Na** 23·05	Magnesium **Mg** 24·3	Aluminium **Al** 27·0	Silicon **Si** 28·4	Phosphorus **P** 31·0	Sulphur **S** 32·06	Chlorine **Cl** 35·45	
4	Argon **Ar** 38	Potassium **K** 39·1	Calcium **Ca** 40·1	Scandium **Sc** 44·1	Titanium **Ti** 48·1	Vanadium **V** 51·4	Chromium **Cr** 52·1	Manganese **Mn** 55·0	Iron Cobalt Nickel **Fe Co Ni** (Cu) 55·9 59 59
5		Copper **Cu** 63·6	Zinc **Zn** 65·4	Gallium **Ga** 70·0	Germanium **Ge** 72·3	Arsenic **As** 75	Selenium **Se** 79	Bromine **Br** 79·95	
6	Krypton **Kr** 81·8	Rubidium **Rb** 85·4	Strontium **Sr** 87·6	Yttrium **Y** 89·0	Zirconium **Zr** 90·6	Niobium **Nb** 94·0	Molybdenum **Mo** 96·0	—	Ruthenium Rhodium Palladium **Ru Rh Pd** (Ag) 101·7 103·0 106·5
7		Silver **Ag** 107·9	Cadmium **Cd** 112·4	Indium **In** 114·0	Tin **Sn** 119·0	Antimony **Sb** 120·0	Tellurium **Te** 127	Iodine **I** 127	
8	Xenon **Xe** 128	Cæsium **Cs** 132·9	Barium **Ba** 137·4	Lanthanum **La** 139	Cerium **Ce** 140	—	—	—	— — —
9		—	—	—	—	—	—	—	
0	—	—	—	Ytterbium **Yb** 173	—	Tantalum **Ta** 183	Tungsten **W** 184	—	Osmium Iridium Platinum **Os Ir Pt** (**Au**) 191 193 194·9
11		Gold **Au** 197·2	Mercury **Hg** 200·0	Thallium **Tl** 204·1	Lead **Pb** 206·9	Bismuth **Bi** 208	—	—	
2	—	—	Radium **Rd** 224	—	Thorium **Th** 232	—	Uranium **U** 239		
HIGHER SALINE OXIDES									
	R	R_2O	**RO**	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
HIGHER GASEOUS HYDROGEN COMPOUNDS									
					RH_4	RH_3	RH_2	**RH**	

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PRINCIPLES OF CHEMISTRY

INTRODUCTION

THE rapid development of the study [1] of the external universe, dating from the days of Galileo (†1642) and Newton (†1727), led to the

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[1] The investigation of a substance or a natural phenomenon consists: (*a*) in determining the relation of the object under examination to that which is already known, either from previous researches, or from experiment, or from the knowledge of the common surroundings of life—that is, in determining and expressing the quality of the unknown by the aid of that which is known; (*b*) in measuring all that which can be subjected to measurement, and thereby indicating the quantitative relation of that under investigation to that already known—to time and space, temperature, mass, &c.; (*c*) in determining the position held by the object under investigation in the system of known objects, taking into account both qualitative and quantitative data; (*d*) in determining, from the quantities which have been measured, the empirical (visible) dependence (function, or 'law,' as it is sometimes termed) of variable factors—for instance, the dependence of the composition of a substance on its properties, of temperature on time, of properties on mass (weight), &c.; (*e*) in framing hypotheses or suppositions as to the actual cause and nature of the relation of that studied to that which is known or to the categories of time, space, &c.; (*f*) in experimentally verifying the logical consequences of such hypotheses; and (*g*) in advancing a theory which shall account for the nature of the properties of that studied in its relations with things already known and with the conditions under which it exists. It is manifest that it is only possible to carry out these investigations when we have taken as a basis something which is incontestable and self-evident to our understanding; such, for instance, as number, time, space, matter, form, motion, or mass. Hence it follows that in the investigation of anything, there always remains something which is accepted without investigation, or admitted as a known and recognised factor; the axioms of geometry may be taken as an example. Thus in the science of biology it is necessary to admit the faculty of organisms for multiplying themselves, as a conception whose meaning is as yet unknown. In the study of chemistry, too, the notion of elements must be accepted almost without any further analysis. However, by investigating and describing what is visible and open to direct observation by the organs of the senses, we may hope to arrive, first at hypotheses, and afterwards at theories, of what has now to be taken as the basis of our investigations. The minds of the ancients strove to seize at once the very fundamental categories of investigation, whilst all the successes of recent knowledge are based on the above-cited method of investigation, without the determination of 'the beginning of all beginnings.' By following this inductive method, the *exact sciences* have already succeeded in becoming accurately acquainted with much of the invisible world, not directly perceptible to the organs of sense (for example, the molecular motion of all bodies, the composition of the heavenly luminaries, and the paths of their motion, the necessity for the existence

separation of Chemistry as a special branch of natural philosophy. Not only was this owing to the increasing store of observations and experiments relating to the transformations of substances, but more especially because, in addition to gravity, cohesion, heat, light, and electricity, it became necessary to recognise the existence of peculiar internal forces in the ultimate parts of all substances, forces which make themselves manifest in the transformations of substances into one another, but remain hidden (latent) under ordinary circumstances, and whose existence cannot therefore be directly apprehended, and so for a long time remained unrecognised. The primary object of chemistry is the study of the homogeneous substances [2] of which all the objects of the universe are made up, of the transformations of these substances [3] into each other, and of the phenomena [4] which accompany such transformations. Every chemical change, or reaction,[5] as it is called, can only take place under a condition of most intimate and close contact of the reacting substances,[6] and is determined by forces peculiar to the smallest invisible

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of substances as yet unknown to experiment, &c.), and have verified the knowledge thus obtained, and employed it for increasing the interests of humanity. It may therefore be safely said that *the inductive method of investigation* is a more perfect mode of acquiring knowledge than the deductive method alone (which from a little of the unknown accepted as incontestable arrives at much which is visible and observable) by which the ancients strove to embrace the universe. By investigating the universe by an inductive method (endeavouring from the much which is observable to arrive at a little which may be verified and is indubitable), the new science refuses to recognise dogma as *truth*, but through *reason*, by a slow and laborious method of investigation, strives for and attains to true deductions.

[2] Substance or matter is that which occupies space and has weight; that is, which presents a mass attracted by the earth and by other masses of matter, and of which the *objects* of nature are composed, and by means of which the motions and *phenomena* of nature are accomplished. It is easy to discover, by examining and investigating in various ways the objects met with in nature and in the arts, that some of these are *homogeneous*, whilst others are composed of a *mixture* of several homogeneous substances. This is most clearly apparent in solid substances. The metals used in the arts (for example, gold, iron, copper) must be homogeneous, otherwise they are brittle and unfit for many purposes. *Homogeneous matter exhibits similar* properties in all its parts. By breaking up a homogeneous substance we obtain parts which, although different in form, resemble each other in their properties. Glass, pure sugar, marble, salt, &c., are examples of homogeneous substances. Examples of non-homogeneous substances are, however, much more frequent in nature and the arts. Thus the majority of the rocks are not homogeneous. In porphyries bright pieces of a mineral called 'orthoclase' are often seen interspersed amongst the dark mass of the rock. In ordinary red granite it is easy to distinguish large pieces of orthoclase mixed with dark semi-transparent quartz and flexible laminæ of mica. Similarly, plants and animals are non-homogeneous. Thus, leaves are composed of skin, fibre, pulp, sap, a green colouring matter, &c. As an example of non-homogeneous substances artificially produced, gunpowder may be cited, which is prepared by mixing together sulphur, nitre, and charcoal. Many liquids, also, are not homogeneous, as may be observed by the aid of the microscope, when drops of blood are seen to consist of a colourless liquid in which red corpuscles, invisible to the naked eye owing to their small size, are floating about. It is these corpuscles which give blood its peculiar colour. Milk is also a transparent liquid, containing microscopic drops of fat, which rise to the top and form cream when the milk is left at rest. It is possible to extract from every non-homogeneous substance those homogeneous substances of which it is made up. Thus orthoclase may be separated from porphyry by breaking it off. So also gold is extracted from auriferous sand by washing away the mixture of clay and sand. Chemistry deals only with the homogeneous substances met with in nature, or extracted from natural or artificial non-homogeneous substances. The various mixtures found in nature form the subjects of other natural sciences—such as geology, botany, zoology, anatomy, &c. Substances can only be investigated by their *properties* or by their relations to our organs of sense and to other substances and bodies, but of itself matter is beyond the grasp of our understanding; for there is something in its nature which is self-existent and foreign to our understanding and spirit. If at the present day matter is represented as composed of individual mobile atoms, this is, in my opinion, only a scheme (a method or expedient for facilitating study) based originally on the structure of the visible (sidereal, solar) universe, which is actually composed of separate stars, like the sun, of planets and their satellites, of meteorites, and of the special ether which has the faculty of transmitting light and other forms of energy and motion, all of these being united in one harmonious whole. There is a great charm in the idea that the most minute parts of nature should be constructed on the same plan as the most gigantic, but it is far from proved that such is actually the case. It does not follow, however, because matter in itself is incomprehensible to us, that the study of matter is beyond our faculties if we follow the path of inductive reasoning (inaugurated by Bacon). This is evident from the fact that, by gradually investigating matter, man gains a greater and greater mastery over it, makes more and more accurate predictions concerning it, and finds wider and more frequent applications of it for satisfying his needs. In fact, there is no reason to anticipate any limit to our knowledge of, and dominion over, matter.

[3] The name 'body' is given to a substance bounded by a surface or possessing shape. The earth, as a part of the solar system, is a body. A crystal, a plant, a house, are all bodies. It is evident that, in general, knowledge concerning matter is knowledge concerning bodies. Chemistry does not deal with bodies but with substances. However in ordinary usage the words 'body' and 'substance' are very often confused. Thus we speak of chemically simple and compound 'bodies' when we should, of course, use the word 'substances.'

[4] All those events which are accomplished by substances in time are termed 'phenomena.' Phenomena in themselves form the fundamental subject of the study of physics. Motion is the primary and most easily understood form of phenomenon, and therefore we endeavour to reason about other phenomena as clearly as when dealing with motion. For this reason mechanics, which treats of motion, forms the fundamental science of natural philosophy, and in all other sciences endeavour is made to reduce the phenomena with which they are concerned to mechanical principles. Astronomy was the first to take to this path of reasoning, and succeeded in many cases in resolving astronomical into purely mechanical phenomena. And so, under the present state of knowledge, it is inevitably necessary to recognise the separate categories, motion and matter; and as chemistry is more closely concerned with the various forms of the latter, it should, together with mechanics, or the study of motion, lie at the basis of natural science.

[5] The verb 'to react' means to act or change chemically.

[6] If a phenomenon proceeds at visible or measurable distances (as, for instance, magnetic attraction or gravity), it cannot be described as chemical, since these phenomena only take place at distances immeasurably small and undistinguishable to the eye or the microscope; that is to say, they are purely molecular. Even Newton recognised, however, that it was impossible to comprehend the influence of bodies on each other (for instance attraction) without the agency of some medium situated between them. And this still holds good. Therefore a 'vacuum' is not admitted in modern science, but all so-called vacua, or spaces void of air, are considered to be filled with 'ether,' which was first regarded as the medium transmitting light waves, and afterwards as a means of

particles (molecules) of matter. We must distinguish three chief classes of chemical transformations.

1. *Combination* is a reaction in which the union of two substances yields a new one, or generally, from a given number of substances, a lesser number is obtained. Thus, by heating a mixture of iron and sulphur[7] a single new substance is produced, iron sulphide, in which the constituent substances cannot be distinguished even under the highest magnification. Before the reaction the iron could be separated from the mixture by a magnet, and the sulphur by dissolving it in certain oily liquids;[8] in general, before combination they might be mechanically separated from each other, but after combination the two substances penetrate into each other, and are then neither mechanically separable nor individually distinguishable. As a rule, reactions of direct combination are accompanied by an evolution of heat, and the common case of combustion, evolving heat, consists in the combination of the combustible substance with a portion (the oxygen) of the atmosphere, the gases and vapours contained in the flame and smoke representing the products of the combination.

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explaining the action of attractions at a distance as well as magnetic and electrical phenomena. Without entering into these conceptions, which are more or less hypothetical (like that of the chemical elements), it may not be superfluous to mention that chemical theories lie beyond the hypothesis of ether, and that, judging from our present knowledge, chemical reactions do not proceed through the medium of ether, as they only take place by actual contact. It appears to me, therefore, that the chemism of substances possesses a certain simplicity and elementary character, and I foresee that chemistry may some day lead to an explanation of our conception regarding matter. In this sense chemical phenomena are more real to the understanding than physical or mechanical phenomena. Taking into consideration the comparative youth of this branch of natural science and the speciality of the phenomena it treats of, it seems to me that the province of chemical generalisations will rapidly extend, just as the applications of chemistry to the industries are extending at the present day. This forms the peculiar charm of chemistry, and especially of physico-chemical research. If the astronomer grasps the infinitely great in its highest reality, the chemist embraces the infinitely small, and science strives to attain the infinite and everlasting, unfettered by the finite and temporal.

[7] For this purpose a piece of iron may be made red-hot in a forge, and then placed in contact with a lump of sulphur, when iron sulphide will be obtained as a molten liquid, the combination being accompanied by an appreciable increase in the glow of the iron. Or else iron filings are mixed with powdered sulphur in the proportion of 5 parts of iron to 3 of sulphur, and the mixture placed in a glass tube, which is then heated at one part. Combination does not commence without the aid of external heat, but when once started in any portion of the mixture it extends throughout the entire mass, because the portion first heated, in forming iron sulphide, evolves sufficient heat to raise the adjacent parts of the mixture to the temperature required for starting the reaction. The rise in temperature thus produced is so high as to soften the glass tube.

[8] Sulphur dissolves slightly in many thin oils, and to a greater extent in carbon bisulphide and some other liquids. Iron is insoluble in carbon bisulphide, and the sulphur can therefore be dissolved away from the iron, so long as the two are not chemically combined.

2. Reactions of *decomposition* are the reverse of those of combination, that is, one substance gives two, or, in general, a given number of substances yields a greater number. Thus, by heating wood (and also coal and many animal or vegetable substances) without access to air, a combustible gas, a watery liquid, resin or tar, and carbon are obtained. It is in this way that tar, illuminating gas, and charcoal are prepared on a large scale.[9] All limestones, for example, flagstones, chalk, or marble, when heated to redness are decomposed into lime and a peculiar gas called carbonic anhydride. A similar decomposition, taking place, however, at a much lower temperature, proceeds with the green copper carbonate which is contained in natural malachite. This example will be studied more in detail presently. Whilst heat is evolved in the ordinary reactions of combination, it is, on the contrary, generally absorbed in reactions of decomposition.

3. The third class of chemical reactions—where the number of reacting substances is equal to the number of substances formed—may be considered as a simultaneous decomposition and combination. If, for instance, two compounds A and B are taken and they react on each other, forming the substances C and D; then supposing that A is decomposed into D and E, and that E combines with B to form C, we have a reaction in which two substances A (or D E) and B were taken and two others C (or E B) and D were produced. Such reactions ought to be classed under the general term of reactions of '*rearrangement*,' and the particular case where two substances give two fresh ones, reactions of '*substitution*' or '*double decomposition*.'[10] Thus, if a piece of iron be immersed in a solution of blue vitriol (copper sulphate), copper is formed—or, rather, separated out, and green vitriol (iron sulphate), which only differs from the blue vitriol in that the iron has replaced the copper, is obtained in solution. In this manner iron may be coated with copper, or copper with silver; such reactions are frequently made use of in practice.

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[9] Decomposition of this kind is termed 'dry distillation,' because, just as in distillation, the substance is heated and vapours are given off which, on cooling, condense into liquids. In general, decomposition, in absorbing heat, presents much in common with a physical change of state—such, for example, as that of a liquid into a gas. Deville likened complete decomposition to boiling, and compared partial decomposition, in which a portion of a substance is not decomposed in the presence of its products of decomposition (or dissociation), with evaporation.

[10] A reaction of rearrangement may in certain cases take place with one substance only; that is to say, a substance may by itself change into a new *isomeric* form. Thus, for example, if hard yellow sulphur be heated to a temperature of 250° and then poured into cold water, it gives, on cooling, a soft brown variety. Cases of isomerism indicate the possibility of an internal rearrangement in a substance, and are the result of an alteration in the grouping of the same elements, just as a certain number of balls may be grouped in figures and forms of different shapes.

The majority of the chemical changes which occur in nature and are made use of technically are very complicated, as they consist of an association of many separate and simultaneous combinations, decompositions, and replacements. It is chiefly due to this natural complexity of chemical phenomena that for so many centuries chemistry did not exist as an exact science; that is to say, that although many chemical changes were known and made use of,[11] yet their real nature was unknown, and they could not be predicted or directed at will. Another reason for the tardy progress of chemical knowledge is the participation of gaseous substances, especially air, in many reactions. The true comprehension of air as a ponderable substance, and of gases in general as peculiar elastic and dispersive forms of matter, was only arrived at in the sixteenth and seventeenth centuries, and it was only after this that the transformations of substances could form a science. Up to that time, without understanding the invisible, but ponderable, gaseous and vaporous forms of matter, it was impossible to obtain any fundamental chemical knowledge, because the gases formed or used up in any reaction escaped notice. It is easy, from the impression conveyed to us by the phenomena we observe, to form the opinion that matter is created and destroyed; a whole mass of trees burn, and there only remains a little charcoal and ash, whilst from one small seed there grows little by little a majestic tree. In one case matter seems to be destroyed, and in the other to be created. This conclusion is arrived at because the formation or consumption of gases, being under the circumstances invisible to the eye, is not observed. When wood burns, it undergoes a chemical change into gaseous products, which escape as smoke. The substance of the wood is not lost; it is only converted into gaseous form by a chemical process. A very simple experiment will prove this. By collecting the smoke it may be observed that it contains gases which differ entirely from air, being incapable of supporting either combustion or respiration. These gases may be weighed, and it will then be seen that their weight exceeds that of the wood taken. This increase in weight arises from the fact that, in burning, the component parts of the wood combine with a portion of the air; in like manner iron increases in weight by rusting. When gunpowder is burnt its substance is not destroyed, but only converted into gases and smoke. So also in the growth of a tree: the seed does not increase in mass of itself and from itself, but grows because it absorbs gases from the atmosphere and sucks water and substances dissolved therein from the earth through its roots. The sap and solid substances which give plants their form are produced from these absorbed gases and liquids by complicated chemical processes directed by forces acting in the living organism. Plants not only do not increase in size, but die, in a gas which does not contain the nutrient constituents of air. When moist substances dry they decrease in weight; when water evaporates we know that it does not disappear, but will return from the atmosphere as rain, dew, and snow. When water is absorbed by the earth, it does not disappear there for ever, but accumulates somewhere underground, whence it afterwards flows forth as a spring. Thus matter does not disappear and is not created, but only undergoes various physical and chemical transformations—that is to say, changes its locality and form. Matter remains in the same quantity as before; in a word it is, so far as we are concerned, everlasting. It was difficult to submit this simple and primary chemical principle to investigation, but when once made clear it rapidly spread, and now seems as natural and simple as many truths which have been acknowledged for ages. The philosophers of ancient Greece, and also Mariotte and other savants of the seventeenth century, suspected the indestructibility or conservation of matter, but they made no efforts to express it, or to make use of it for scientific purposes. The experiments by means of which this simple law was arrived at were made during the latter half of the eighteenth century by the founder of modern chemistry, LAVOISIER, the French Academician and tax farmer.[11a] The numerous experiments of this savant were conducted with the aid of the balance, which is the only means of directly and accurately determining the quantity of matter.

By weighing all the substances, and also the apparatus, used in every experiment, and then weighing the substances obtained after the chemical change, Lavoisier found that the sum of the weights of the substances formed was always equal to the sum of the weights of the substances taken; or, in other words: **Matter is not created and does not disappear**—i.e., *matter is everlasting*—so that the mass (weight) of matter in nature remains unchanged or constant. This

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[11] For example, the conversion of the juice of grapes, containing a saccharine principle (glucose), into wine or vinegar, and the extraction of metals from the ores found in the earth's crust.

[11a] The portrait of Lavoisier is placed at the beginning of this work because he established the fundamental law of our science on an indestructible basis, and should be regarded as the founder of modern scientific chemistry. Lavoisier was born on August 26, 1743, soon after the death of Newton, and his name must rank with those of Galileo and Newton. The closing days of his life were passed during the Reign of Terror, and he was beheaded at Paris, together with 27 other tax-farmers, on May 8, 1794; but his works and ideas have rendered him immortal. A monument, the cost of which was defrayed by international subscription, was erected in his honour in Paris in the year 1900.

expression naturally includes a hypothesis, but it serves to express concisely the following lengthy period: That in all experiments, and in all the investigated phenomena of nature, it has never been observed that the weight of the substances formed was less or greater (as far as accuracy of weighing permits [12]) than the weight of the substances originally taken, and as weight is proportional to mass [12a] or quantity of matter, it follows that no one has ever succeeded in observing a disappearance of matter or its appearance in fresh quantities. The law of the indestructibility of matter endows all chemical investigations with exactitude, as on its basis an equation may be formed for every chemical reaction. If in any reaction the weights of the substances taken be designated by the letters A, B, C, &c., and the weights of the substances formed by the letters M, N, O, &c., then

$$A + B + C + \dots \dots \dots = M + N + O + \dots \dots \dots$$

Therefore, should the weight of one of the reacting or resultant substances be unknown, it may be determined by solving this equation.

By applying the law of the indestructibility of matter, and by making use of the chemical balance, the chemist can never lose sight of any one of the reacting or resultant substances. Should such an oversight be made, it will at once be remarked that the sum of the weights of the substances taken is unequal to the sum of the weights of the substances formed. It is absolutely necessary, in beginning the study of chemistry, to become familiar with the simple truth which is expressed by this law, and for this purpose several examples illustrating its application will now be cited.

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[12] The experiments conducted by the Belgian savant Stas (described in detail in Chap. XXIV. on Silver) form some of the most accurate of the researches which go to prove that the weight of matter is not altered in chemical reactions, as he weighed extremely accurately (introducing all the necessary corrections) the reacting and resultant substances. Landolt (1893) carried on various reactions in inverted and sealed glass U-tubes, and on weighing the tubes before reaction (when the reacting solutions were separated in each of the branches of the tubes) and afterwards (when the solutions had been well mixed by shaking) found either that the weight remained perfectly constant or that the variation was so small (for instance, 0·2 milligram) that it must be ascribed to the inevitable errors of weighing. It is now possible to weigh weights (like the Russian standard platino-iridium pound) with an accuracy of one ten-millionth part of their weight, as is done in the St. Petersburg Weights and Measures Department. Such a degree of accuracy (greater than in any other relative but direct measurement) can only be attained by observing a great many precautions, and only when dealing with such hard and invariable bodies as platino-iridium weights. In ordinary chemical works, especially when weighing glass vessels, liquids or gases, an accuracy of one millionth (that is, a milligram in a kilogram) is scarcely attainable owing to the effect of various corrections in weighing (reducing to vacuum), friction of surfaces, &c., on the ultimate result.

[12a] The idea of the mass of matter was first given an exact form by Galileo (died 1642), and more especially by Newton (born 1643, died 1727), in the glorious epoch marking the development of the principles of inductive reasoning enunciated by Bacon and Descartes in their philosophical treatises.

1. It is well known that iron rusts in damp air,[13] and that when heated to redness in air it becomes coated with scale (oxide) which has, like rust, the appearance of an earthy substance and resembles some of the iron ores from which metallic iron is extracted. If the iron is weighed before and after the formation of the scale or rust, it will be found that the metal has increased in weight during the operation.[14] It can easily be proved that this increase in weight is accomplished at the expense of the atmosphere, and mainly, as Lavoisier proved, at the expense of that portion which is called oxygen, and which supports combustion. In fact, in a vacuum, or in gases which do not contain oxygen, for instance, in hydrogen or nitrogen, iron neither rusts nor becomes coated with scale. Had the iron not been weighed, the participation of the oxygen of the atmosphere in its transformation into an earthy substance might easily have passed unnoticed, as was the case prior to the time of Lavoisier, when phenomena like the above were, for this reason, misunderstood. It is evident from the law of the indestructibility of matter that as iron increases in weight in its conversion into scale, the latter must be a more complex substance than iron itself, and its formation is due to a reaction of combination. We might form an entirely wrong opinion about this transformation, and might consider, for instance, the scale to be a simpler substance than iron, and explain the formation of scale as due to the removal of something from the iron. Such, indeed, was the general opinion prior to Lavoisier, when it was held that iron contained a certain unknown substance called 'phlogiston,' and that scale was iron deprived of this supposed substance.

2. When copper carbonate (in the form of a powder, or as the well-known green mineral called 'malachite,' which is used both for making ornaments and as an ore for the extraction of copper) is heated to

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[13] By covering iron with enamel, varnish, an unrustable metal (such as nickel), a coating of paraffin, or some similiar substance, it may be protected from the air and moisture, and so kept from rusting.

[14] Such an experiment may easily be made by taking the finest (unrusted) iron filings (ordinary filings must be first washed in ether to remove traces of grease, then dried, and passed through a very fine sieve). The filings thus obtained are capable of burning directly in air (by oxidising or forming scale), especially when they hang (attracted) from a magnet. A compact piece of iron does not burn in air, but spongy iron glows and smoulders like tinder. In making the experiment, a horseshoe magnet is fixed, with the poles downwards, on one arm of a fairly sensitive balance, and the iron filings are applied to the magnet (on a sheet of paper) so as to form a beard or fringe about the poles. The balance pan should be exactly under the filings on the magnet, in order that any filings which might fall should not alter the weight. The filings, having been weighed, are ignited by applying the flame of a candle or lamp: they easily take fire, and go on burning by themselves, forming scale. When the combustion is ended, it will be clear that the iron has increased in weight; from 5½ parts by weight of iron filings taken, there are obtained, by complete combustion, about 7½ parts by weight of scale.

redness it changes into a black substance called 'copper oxide.'[15] This black substance is also obtained by heating copper to redness in air—that is, it is the scale or oxidation product of copper. The weight of the black oxide of copper left is less than that of the copper carbonate originally taken, and therefore we consider the reaction which occurred to have been one of decomposition, and that by it something was separated from the green copper carbonate; in fact, by closing the orifice of the vessel in which the copper carbonate is heated, with a well-fitting cork, through which passes a gas delivery tube[16] the end of which is immersed under water, it will be observed that during the heating a gas is formed which bubbles through the water. This gas can be easily collected, as will presently be described, and it will be found to differ essentially from air in many respects; for instance, a burning taper is extinguished in it just as if it had been plunged into water. If weighing had not proved to us that some substance had been separated, the formation of the gas might easily have escaped our notice, as it is colourless and transparent like air. The carbonic anhydride evolved may be weighed,[17] and it will be seen that the sum of the

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[15] For the purpose of experiment it is most convenient to take copper carbonate, which may be prepared by the experimenter himself, by adding a solution of sodium carbonate to a solution of copper sulphate. The precipitate (deposit) so formed is collected on a filter, washed, and dried. The decomposition of copper carbonate into copper oxide and carbonate anhydride is effected by so moderate a heat that it may be carried out in a glass vessel heated by a lamp. For this purpose a thin glass tube closed at one end, and called a 'test tube,' may be employed, or else a vessel called a 'retort.' The experiment is carried on, as described in example 3 on p. 11, by collecting the carbonic anhydride over water, as will be afterwards explained.

[16] Gas delivery tubes are usually made of glass tubing of various diameters and thicknesses. If of small diameter and thickness, a glass tube is easily bent by heating in a gas jet or the flame of a spirit lamp, and it may also be easily divided at a given point by making a scratch with a file and then breaking the tube at this point with a sharp jerk. These properties, together with their impermeability, transparency, hardness, and regularity of bore, render glass tubes most useful in experiments with gases. A glass gas delivery tube may be hermetically fixed into a vessel by fitting it into a perforated cork, which should be soft and free from flaws, and fixing the cork into the orifice of the vessel. To protect the cork from the action of gases it is sometimes previously soaked in melted paraffin wax, or else replaced by an indiarubber stopper.

[17] Gases, like all other substances, may be weighed, but, owing to their extreme lightness and the difficulty of dealing with them in large masses, they can only be weighed on very sensitive balances; that is, on such as, with a considerable load, indicate a very small change in the weight—for example, a milligram on a load of 1,000 grams. In order to weigh a gas, a glass globe furnished with a tight-fitting stop-cock is first of all exhausted of air by an air-pump (a Sprengel pump is the best), after which the stop-cock is closed, and the exhausted globe weighed. If the gas to be weighed is then let into the globe, its weight can be determined from the increase in the weight of the globe. It is necessary, however, that the temperature and pressure of the air about the balance should remain the same for both weighings, as the weight of the globe in air varies (according to the laws of hydrostatics) with the density of the latter. The volume of the air displaced, and its weight, must therefore be determined by observing the temperature, density, and moisture of the atmosphere during the time of the experiment. This will be partly explained later, but may be studied more in detail by physics. Owing to the complexity of all these operations, the mass of a gas is usually determined from its volume and its density, i.e. the weight of unit volume.

weights of the black copper oxide and the carbonic anhydride is equal to the weight of the copper carbonate[18] originally taken.

3. When red oxide of mercury (which is formed as mercury rust by heating mercury in air) is heated, it is decomposed, like copper carbonate (only by heating more slowly and at a somewhat higher temperature), with the formation of the peculiar gas, oxygen. For this purpose the oxide of mercury is placed in a glass tube or retort,[19] to which a gas delivery tube is attached by means of a cork. This tube is bent downwards, as shown in the drawing (fig. 1), and its open end

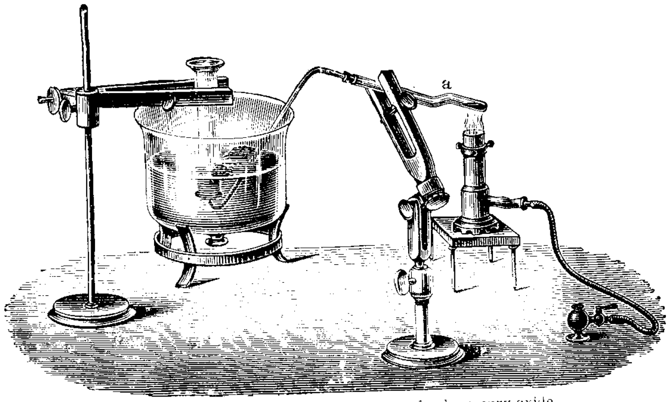

Fig. 1.—Apparatus for the decomposition of red mercury oxide.

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[18] The copper carbonate should be dried before weighing, as otherwise—besides copper oxide and carbonic anhydride—water will be obtained in the decomposition. Water enters into the composition of malachite, and has therefore to be allowed for. The water produced in the decomposition may be all collected by absorbing it in sulphuric acid or calcium chloride, as will be described further on. In order to dry a salt it must either be heated at about 100° until its weight remains constant, or be placed under an air-pump over sulphuric acid, as will also be presently described. As water is met with almost everywhere, and as it is absorbed from the air by many substances, the possibility of its presence should never be lost sight of in weighing.

[19] As the decomposition of red oxide of mercury requires so high a temperature—approaching a red heat—as to soften ordinary glass, it is necessary for this experiment to take a retort (or test tube) made of hard glass, which is able to stand high temperatures without softening. For the same reason the lamp used must give a strong heat and a large flame, capable of embracing the whole of the bottom of the retort, which should be as small as possible for the convenience of the experiment.

immersed in a vessel filled with water, called a pneumatic trough.[20] When the gas begins to be evolved in the retort it is obliged, having no other outlet, to escape through the gas delivery tube into the water in the pneumatic trough, and its evolution will therefore be rendered visible by the bubbles coming from this tube. On heating the retort containing the mercury oxide, the air contained in the apparatus is first partly expelled, owing to its expansion by heat, and after this the peculiar gas called 'oxygen' is evolved and may be easily collected as it comes off. For this purpose a vessel (an ordinary cylinder, as in the drawing) is filled quite full with water and its mouth closed; it is next inverted and the mouth dipped under the water in the trough and then opened. The cylinder will remain full of water—that is, the water will remain

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[20] The pneumatic trough may naturally be made of any material (china, earthenware, metal, &c.), but a glass one, as shown in the drawing, is generally used, as it allows the progress of the experiment to be better observed. For this reason, and on account of the ease with which they are kept clean, and also owing to the fact that glass is not acted on by many substances which affect other materials (for instance, metals), glass vessels of all kinds are preferred to any others for chemical experiments. A glass vessel may be heated without any danger if the following precautions be observed: 1st, it should be made of thin glass, as otherwise it is liable to crack from the bad heat-conducting power of glass; 2nd, it should be surrounded by a liquid or by sand (fig. 2), or sand bath as it is called; or else it should stand in a current of hot gases without touching the fuel from which they proceed, or in the flame of a smokeless lamp. A common candle or lamp forms a deposit of soot on a cold object placed in the flame. The soot interferes with the transmission of heat, so that a glass vessel when covered with soot often cracks. And for this reason spirit lamps, which burn with a smokeless flame, or gas burners of a peculiar construction, are used. In the Bunsen burner the gas is previously mixed with air, after which it burns with a non-luminous and smokeless flame. On the other hand, if an ordinary lamp (petroleum or benzine) does not smoke it may be used without danger for heating a glass vessel, provided the glass is placed well above the flame in the current of hot gases. In all cases the heating should be begun very carefully and the temperature gradually raised.

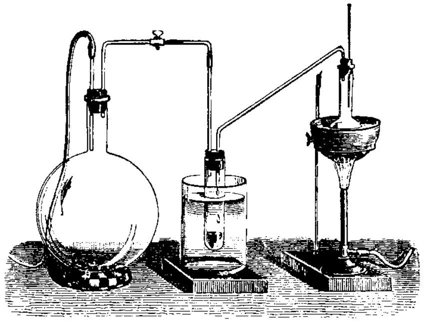

Fig. 2.—Apparatus for distilling, under a diminished pressure, liquids which decompose at their boiling-points under the ordinary pressure. The apparatus in which the liquid is distilled is connected with a large globe from which the air is pumped out; the liquid is heated, and the receiver cooled.

at a higher level in it than in the surrounding vessel, owing to the atmospheric pressure. The mouth of the cylinder is placed over the end of the gas delivery tube,[21] and the bubbles issuing from the latter will rise into the cylinder and displace the water contained in it. Gases are generally collected in this manner. When a sufficient quantity of gas has accumulated in the cylinder it can be clearly shown that it is not air, but another gas which is distinguished by its capacity for vigorously supporting combustion. In order to show this, the cylinder is closed under water, and removed from the bath; its mouth is then turned upwards, and a smouldering taper plunged into it. As is well known, a smouldering taper will be extinguished in air, but in the gas which is given off from red mercury oxide it burns clearly and vigorously, showing the property possessed by this gas for supporting combustion more energetically than air, and thus enabling it to be distinguished from the latter. It may be observed in this experiment that, besides oxygen, there is also formed metallic mercury, which, volatilising at the high temperature required for the reaction, condenses on the cooler parts of the retort in the form of a mirror or in globules. Thus two substances, mercury and oxygen, are obtained by heating red mercury oxide. In this reaction, from a single substance, two new ones are produced—that is, a decomposition has taken place. The means of collecting and investigating gases were known before Lavoisier's time, but he first showed the real part they played in the processes of many chemical changes which before his era were either wrongly understood (as will be afterwards explained) or not explained at all, but only observed in their superficial aspects. This experiment on red oxide of mercury has a special significance in the history of chemistry contemporary with Lavoisier, because the oxygen gas which is here evolved is contained in the atmosphere, and plays a most important part in nature, especially in the respiration of animals, in combustion in air, and in the formation of rusts or scoriæ (earths, as they were then called) from metals—that is, of earthy substances, like the ores from which metals are extracted.

4. In order to illustrate by experiment one more example of chemical change and the application of the law of the indestructibility of matter, we will consider the reaction between common table salt and lunar caustic, which is well known from its use in cauterising

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[21] In order to avoid the necessity of holding the cylinder, its open end is widened (and also ground so that it may be tightly closed with a ground-glass plate when necessary), and placed on a stand below the level of the water in the bath. This stand is called 'the bridge.' It has several circular openings cut through it, and the gas delivery tube is placed under one of these, and the cylinder for collecting the gas over it.

wounds. Both these substances are soluble in water. By taking clear solutions of each of these and mixing them together, it will at once be observed that a solid white substance is formed which settles to the bottom of the vessel, and is insoluble in water. This substance may be separated from the solution by filtering. This is at once evident from the fact that it does not dissolve in water. On evaporating the liquid which passes through the filter, it will be found to contain a new substance differing from both table salt and lunar caustic, but, like them, soluble in water. Thus table salt and lunar caustic, two substances soluble in water, produce, by their mutual chemical action, two new substances, one of which is insoluble in water whilst the other remains in solution. The water serves only to convert the reacting substances into a liquid and mobile state. If the lunar caustic and salt be dried [22] and weighed, and if about 58½ grams [23] of the latter and 170 grams of the former be taken, then 143½ grams of insoluble silver chloride and 85 grams of soluble sodium nitrate will be obtained. The sums of the weights of the reacting and of the resultant substances are seen to be similar (228½ grams), which follows necessarily from the law of the indestructibility of matter.

Accepting the truth of the above law, the question naturally arises as to whether there is any limit to the various chemical transformations, or are they unrestricted in number—that is to say, is it possible from a given substance to obtain an equal quantity of any other substance? In other words, does there exist a perpetual and infinite change of one kind of material into every other kind, or is the cycle of these transformations limited? This is the second essential problem of chemistry, a question concerning the quality of matter, and one, it is evident, more complicated than the question of quantity. It cannot be solved by a mere superficial glance at the subject. Indeed, on seeing how all the varied forms and colours of plants are built up from air and the elements of the soil, and how metallic iron can be transformed into colours such as inks and Prussian blue, we might be led to think that there is no end to the qualitative changes to which matter is susceptible. But, on the other hand, everyday experience compels us to acknowledge that food cannot be made out of a stone, nor gold out of copper. Thus a definite answer can only be looked for in a close and diligent study of the subject, and the problem has been solved in different ways at different times. In ancient times the opinion most generally held was that everything visible was composed of four elements—Air, Water, Earth, and Fire. The origin of this doctrine can be traced far back into the confines of Asia, whence it was handed down to the Greeks, and very fully expounded by Empedocles, who lived before 460 B.C. This doctrine was not the result of exact research, but apparently owes its origin to the clear division of bodies into gases (like air), liquids (like water), and solids (like the earth), and to the recognition of the changes brought about in these by fire, i.e. heat. The Arabs attempted to solve the question by experimental methods, and, by way of Spain, they introduced a taste for the study of similar problems into Europe, where from that time there appear many adepts in chemistry, which was regarded as an unholy art, and called 'alchemy.' As the alchemists were ignorant of any exact law which could serve as a starting-point for their researches, they obtained most anomalous results. Their chief service to chemistry was that they made a number of experiments, and discovered many new chemical transformations; but it is well known how they solved the fundamental problem of chemistry. Their view may be taken as a positive acknowledgment of the infinite transmutability of matter, for they aimed at discovering the Philosopher's Stone, capable of converting everything into gold and diamonds, and of making the old young again. This solution of the question was afterwards completely overthrown, but it must not be thought that the hopes held by the alchemists were only the fruit of their imaginations. The first chemical experiments might well lead them to such conclusions. They took, for instance, the bright metallic mineral galena, and extracted metallic lead from it. Thus they saw that from a metallic substance which is unfitted for use they could obtain another metallic substance which is ductile and valuable for many technical purposes. Furthermore, they took this lead and obtained silver, a still more valuable metal, from it. Thus they might easily conclude that it is possible to ennoble metals by means of a series of transmutations—that is to say, to obtain from them those which are more and more precious. Having got silver from lead, they assumed that it would be possible to obtain gold from silver. The imperfection of their work is to be ascribed to the fact that, as a rule, they paid little attention to quantities, and qualitative data are very often subjective

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[22] Drying is necessary in order to remove any water which may be held in the salts (see note 18).

[23] The exact weights of the reacting and resulting substances are determined with the greatest difficulty, not only from possible inexactitude of the balance (every weighing is only correct within the limits of sensitiveness of the balance) and weights used, not only from the difficulty in making corrections for the weight of air displaced by the vessels containing the substances weighed and by the weights themselves, but also from the hygroscopic nature of many substances (and vessels) causing absorption of moisture from the atmosphere, and from the difficulty of not losing any of the substance to be weighed in the several operations (filtering, evaporating, drying, &c.) which have to be performed before arriving at a final result. All these circumstances have to be taken into consideration in exact researches.

and conditional. Had they done so, they would have learnt that the weight of the lead was much less than that of the galena from which it was obtained, and the weight of the silver infinitesimal compared with that of the lead. Had they looked more closely into the process of the extraction of silver from lead (and silver at the present time is chiefly obtained from lead ores), they would have seen that the lead does not change into silver, but that it only contains a certain small quantity of the latter, and this amount having once been separated from the lead it cannot by any further operation give more. The silver which the alchemists extracted from the lead was in the lead, and was not obtained by a chemical change of the lead itself. This is now well known from experiment, but the first view of the nature of the process was very likely to be an erroneous one.[24] The methods of research adopted by the alchemists could give but little success, for they did not set themselves clear and simple questions, the answers to which would aid them to make further progress. But although they did not arrive at any exact law, they nevertheless left many new experimental data as an inheritance to chemistry; they investigated, in particular, the transformations proper to metals, and for this reason chemistry was for long afterwards entirely confined to the study of metallic substances.

In their researches the alchemists made frequent use of two chemical processes which are now termed 'reduction' and 'oxidation.' The rusting of metals, and in general their conversion from a metallic into an earthy form, is called 'oxidation,' whilst the extraction of a metal from an earthy substance is called 'reduction.' Many metals—for instance, iron, lead, and tin—are oxidised by simply heating in air, and may be again reduced by heating with carbon. Such oxidised metals are found in the earth and represent one type of metallic ores. Metals such as tin, iron, and copper, may be extracted from these ores by heating them together with carbon. All these processes were studied by the alchemists. Thus the alchemists knew of two forms of chemical change: the oxidation of metals and the reduction of the oxides so formed into metals. The explanation of the nature of these

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[24] Indeed, in the majority of cases, the first explanation of a phenomenon which does not repeat itself in everyday experience under various aspects, but always in one form, or only at intervals and infrequently, is wrong. Thus the daily rising and setting of the sun and stars evoke the erroneous idea that the heavens move and that the earth stands still. This apparent truth is far from being the real one, and, as a matter of fact, is contradictory to it. Similarly, everyday experience concludes that iron is incombustible, whereas it burns not only as filings (see note 14) but even as wire, as we shall see later. In ordinary life we often reason at first sight with perfect accuracy, only because we are taught a right judgment by our daily experience. Naturally, experiment itself cannot give truth, but it makes it possible to destroy erroneous representations and to confirm in all their consequences those which are true.

two classes of chemical phenomena was the means for the discovery of the most important chemical laws. The first hypothesis on their nature is due to Becker, and more particularly to Stahl, a surgeon to the King of Prussia. In his 'Fundamenta Chemiæ,' 1723, Stahl states that all substances consist of an imponderable fiery substance called 'phlogiston' (materia aut principium ignis non ipse ignis), and of another element having particular properties for each substance. The greater the capacity of a body to undergo oxidation or combustion, the richer it is in phlogiston. Carbon contains it in great abundance. In oxidation or combustion phlogiston is emitted, and in reduction it is consumed or enters into combination. Carbon reduces earthy substances because it is rich in phlogiston, a portion of which it gives up to the substance reduced. Thus Stahl supposed a metal to be a compound substance consisting of phlogiston and an earthy substance or oxide. This hypothesis is distinguished for its very great simplicity, and for this and other reasons it acquired many supporters.[25]

Lavoisier proved by means of the balance that every case of rusting

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[25] It is true that Stahl was acquainted with a fact which directly disproved his hypothesis. It was already known (from the experiments of Geber, and more especially those of Ray in 1630) that metals increase in weight on oxidation, whilst, according to Stahl's hypothesis, they should decrease in weight because phlogiston is given up. Stahl speaks on this point as follows:—'I am well aware that on oxidation (transformation into earths) metals increase in weight. Not only does this fact not disprove my theory, but, on the contrary, it confirms it, for phlogiston is lighter than air, and, in combining with substances, strives to lift them, and so decreases their weight; consequently a substance which has lost phlogiston must be heavier.' This argument, it will be seen, is founded on a confused idea of phlogiston itself, since it was first defined as imponderable. The conception of imponderable phlogiston tallies well with the habit and methods of the past century, when recourse was had to imponderable fluids for explaining a large number of phenomena. Heat, light, magnetism, and electricity were explained as being peculiar imponderable fluids. In this sense the doctrine of Stahl corresponds entirely with the spirit of his time. If heat be now regarded as motion or energy, then phlogiston also should be considered in this light. In fact, in combustion, of coals, for instance, heat and energy are evolved and not combined with the coal, although the oxygen and coal do combine. Consequently the doctrine of Stahl contains the essence of a true representation of the evolution of energy, but naturally this evolution is only a consequence of the combination occurring between the coal and oxygen. As regards the history of chemistry prior to Lavoisier, besides Stahl's work, Priestley's *Experiments and Observations on different Kinds of Air* (London, 1790), and also Scheele's *Opuscula Chimica et Physica* (Lips., 1788–89, 2 vols.), must be recommended as the two leading works of the English and Scandinavian chemists showing the condition of chemical learning before the propagation of Lavoisier's views, and containing also many important observations which lie at the basis of the chemistry of our times. A most interesting memoir on the history of phlogiston is that of Radwell, in the *Philosophical Magazine*, 1868, in which it is shown that the idea of phlogiston dates very far back, that Basil Valentine (1394–1415), in the *Cursus Triumphalis Antimonii*, Paracelsus (1493–1541), in his work *De Rerum Natura*, Glauber (1604–1668), and especially John Joachim Becher (1625–1682), in his *Physica Subterranea*, all referred to phlogiston, but under different names.

of metals or oxidation, or of combustion, is accompanied by an increase in weight at the expense of the atmosphere. He formed, therefore, the natural opinion that the heavier substance is more complex than the lighter one.[26] Lavoisier's celebrated experiment, made in 1774, gave indubitable support to his views, which in many respects were contradictory to Stahl's doctrine. Lavoisier poured four ounces of pure mercury into a glass retort (fig. 3), the neck of which was bent as shown in the drawing and dipped into the vessel R S, also full of mercury, the projecting end of the neck being covered with a glass bell-jar P. The weight of all the mercury taken, and the volume of air remaining in the apparatus, that is, in the upper portion of the retort and under the bell-jar, were determined before beginning the experiment. It was most important in this experiment to know the volume of air, in order to learn what part it played in the oxidation of the mercury, because, according to Stahl, phlogiston is emitted into the air, whilst, according to Lavoisier, the mercury in oxidising absorbs a portion of the air; consequently it was absolutely necessary to determine whether the amount of air increased or decreased during the oxidation of the metal. It was therefore most important to measure the volume of the air in the apparatus both before and *after* the

experiment. For this purpose it was necessary to know the total capacity of the retort, the volume of the mercury poured into it, the volume of the bell-jar above the level of the mercury, and also the temperature and pressure of the air at the time of its measurement. From these data the volume of air contained in the apparatus and isolated from the surrounding atmosphere could be determined. Having arranged his apparatus in this manner, Lavoisier heated the retort for a period of twelve days at a temperature near the boiling point of mercury. The mercury became covered with a quantity of small red scales; that is, it was oxidised or converted into an earth (like lime). This substance is the same mercury oxide which has already been mentioned (example 3). After the lapse of twelve days the apparatus was cooled, and it was then seen that the volume of the air in the apparatus had diminished during the time of the experiment; a result directly contradictory to the views of the German investigator. Out of 50 cubic inches of air originally taken, there only remained 42. Lavoisier's experiment led to other equally important results. The weight of the air taken decreased by as much as the weight of the mercury increased in oxidising; that is, part of the air was not destroyed, but only combined with mercury. This portion of the air may be again separated from the mercury oxide, and has, as we have seen (example 3), properties different from those of air. It is called 'oxygen.' That portion of the air which remained in the apparatus and did not combine with the mercury does not oxidise metals, and cannot support either combustion or respiration, so that a lighted taper is immediately extinguished if it be dipped into the gas which remains in the bell-jar. 'It is extinguished in the residual gas as if it had been plunged into water,' writes Lavoisier in his memoirs. This gas is called 'nitrogen.' Thus air is not a simple substance, but consists of two gases, oxygen and nitrogen, and therefore the opinion that air is an elementary substance is erroneous. The oxygen of the air is absorbed in combustion and in the oxidation of metals, and the earths produced by the oxidation of metals are substances composed of oxygen and a metal. By mixing the oxygen with the nitrogen the same air as was originally taken is re-formed. It has also been shown by direct experiment that on reducing an oxide with carbon the oxygen contained in the oxide is transferred to the carbon, and gives the same gas as is obtained by the combustion of carbon in air. This gas is therefore a compound of carbon and oxygen, just as the earthy oxides are composed of metals and oxygen.

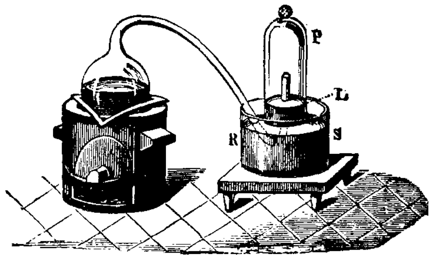

FIG. 3.—Lavoisier's apparatus for determining the composition of air and the reason of the increase in weight of metals when they are calcined in air.

The many examples of the formation and decomposition of substances which are met with convince us that the majority of substances

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[26] An Englishman named Mayow, who lived a whole century before Lavoisier (in 1666), understood certain phenomena of oxidation in their true aspect, but was not able to develop his views with clearness or to support them by conclusive experiments; he cannot therefore be considered, like Lavoisier, as the founder of contemporary chemical learning. Science is a universal heritage, and therefore it is only just to give the highest honour in science, not to those who first enunciate a certain truth, but to those who are first able to convince others of its authenticity and to establish it for the general welfare. But scientific discoveries are rarely made all at once; as a rule, the first teachers do not succeed in convincing others of the truth they have discovered; with time, however, a true herald comes forward, possessing every means for making the truth apparent to all; but it must not be forgotten that such are indebted to the labours of many others and to the mass of data accumulated by them. Such was Lavoisier, and such are all the great founders of science.

with which we have to deal are compounds made up of several other substances. By heating chalk (or else copper carbonate, as in the second example) we obtain lime and the same carbonic acid gas which is produced by the combustion of carbon. On bringing lime into contact with this gas and water, at the ordinary temperature, we again obtain the compound, carbonate of lime, or chalk. Therefore chalk is a compound. So also are those substances from which it may be built up. Carbonic anhydride is formed by the combination of carbon and oxygen, and lime is produced by the oxidation of a certain metal called 'calcium.' By resolving substances in this manner into their component parts we arrive at last at such as are indivisible into two or more substances by any means whatever, and which cannot be formed from other substances. All we can do is to make such substances either combine with one another or act on other substances. Substances which cannot be formed from or decomposed into others are termed **simple substances** (elements). Thus all homogeneous substances may be classified into simple and compound substances. This view was introduced and established as a scientific fact during the lifetime of Lavoisier. The number of these elements is very small in comparison with the number of compound substances which are formed by them. At the present time only seventy-five elements are known with certainty to exist. Some of them are very rarely met with in nature, or are found only in very small quantities. The number of elements with whose compounds we commonly deal in everyday life does not exceed twenty-five at the present time.

Elements cannot be transmuted into one another—at least up to the present not a single case of such a transformation has been met with; it may therefore be said that as yet it is impossible to transmute one metal into another. And, notwithstanding the number of attempts which have been made in this direction, no fact has been discovered which could in any way support the idea of the complexity of such well-known elements[27] as oxygen, iron, sulphur, &c. Therefore, from its very conception, an element is not susceptible to reactions of decomposition.[28]

The quantity, therefore, of each element remains constant in all chemical changes; a fact which may be deduced as a consequence of the law of the indestructibility of matter, and of the conception of the elements themselves. Thus the equation expressing the law of the indestructibility of matter acquires a new and still more important signification. If we know the quantities of the elements occurring in the reacting substances which yield, by means of chemical changes, a series of new compound substances, then the latter will together contain the same quantity of each of the elements as originally existed in the reacting substances. The essence of chemical change is embraced in the study of how and with what each element is combined before and after change.

In order to be able to express chemical changes by equations, it has been agreed to represent each element by the first or some two letters of its (Latin) name. Thus, for example, oxygen is represented by the letter O; nitrogen by N; mercury (hydrargyrum) by Hg; iron (ferrum) by Fe; and so on for all the elements, as is seen in the tables given later on. A compound substance is represented by placing side by side the symbols representing the elements of which it is made up. For example, red mercury oxide is represented by HgO, which shows that it is composed of oxygen and mercury. Besides this, the symbol of every element corresponds with a certain relative quantity of it by weight, called its 'combining' weight, or the weight of an atom; so that the chemical formula of a compound substance designates not only the nature of the elements of which it is composed, but also their quantitative proportion. Every chemical process may be expressed by an equation composed of the formulæ corresponding with the reacting and resulting substances. The amount by weight of each element in a chemical equation must be the same on either side of the equation, since no element is either formed or destroyed in a chemical change.

On pages 24 and 25 is given a list of the elements and their symbols, while the preface contains a table of the elements, with their combining or atomic weights, and we shall see later, on what basis the atomic weights are determined. At present we will only point out that a compound containing the elements A and B is designated by the formula $A_n B_m$, where m and n are the coefficients or multiples in which the combining weights of the elements enter into the composition of

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[27] Many of the ancient philosophers assumed the existence of one elementary form of matter. This idea still appears in our times, in the constant efforts which are made to reduce the number of the elements; to prove, for instance, that bromine contains chlorine, or chlorine, oxygen. By many methods, founded both on experiment and theory, has it been tried to prove the compound nature of the elements. All labour in this direction has as yet been in vain, and the assurance that elementary matter is not so homogeneous (single) as the mind would desire in its first transport of rapid generalisation is strengthened from year to year.

[28] The weakest point in the idea of elements is the negative character of the determinative signs given them by Lavoisier, and from that time ruling in chemistry. They do *not decompose*, they do *not change* into one another. But it must be remarked that elements form the limiting horizon of our knowledge of matter, and it is always difficult to *determine a positive side on the borderland* of what is known. However, there is no doubt (from the results of spectrum analysis) that the elements are distributed as far as the most distant stars, and that they support the highest attainable temperatures without decomposing.

the substance. If we represent the combining weight of the substance A by a, and that of the substance B by b, then the composition of the substance A_nB_m will be expressed thus: it contains na parts by weight of the substance A and mb of B, and consequently 100 parts of our compound contain $\frac{na\,100}{na+mb}$ parts by weight of the substance A and $\frac{mb\,100}{na+mb}$ of the substance B. It is evident that, as a formula shows the relative amounts of all the elements contained in a compound, the actual weights of the elements contained in a given weight of the compound may be calculated from its formula. For example, the formula of table salt, NaCl, shows (since Na=23 and Cl=35·5) that 100 parts of it contain 39·3 parts of sodium and 60·7 of chlorine.

What has been said above clearly limits the range of chemical changes, because from substances of a given kind there can be obtained only such as contain the same elements. Even with this limitation, however, the number of possible combinations is infinitely great. Only a comparatively small number of compounds have yet been described or subjected to research, and anyone working in this direction may easily discover new compounds which have not before been obtained. It often happens, however, that such newly discovered compounds were foreseen by chemistry, whose object is the apprehension of that uniformity which rules over the multitude of compound substances, and the comprehension of the laws which govern their formation and properties. The conception of elements having been established, the next objects of chemistry were the determination of the properties of compound substances on the basis of the quantity and nature of the elements of which they are composed; the investigation of the elements themselves; the determination of the compound substances which can be formed from each element and the properties exhibited by these compounds; and the apprehension of the nature of the connection between the elements in the different compounds. An element thus serves as the starting-point, being taken as the primary conception on which all other substances are built up.

When we state that a certain element enters into the composition of a given compound (when we say, for instance, that mercury oxide contains oxygen), we do not mean that it contains oxygen as a gaseous substance, but only desire to express those transformations which mercury oxide is capable of undergoing; that is, we wish to say that it is possible to obtain mercury and oxygen from mercury oxide, and that it can give up oxygen to various other substances; in a word, we desire only to give expression to those transformations of which mercury oxide

is capable. Or, more concisely, it may be said that the **composition** of a compound is the expression of those transformations of which it is capable. It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous *substance* and as a *material part* or *element* of a compound. Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, which, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is present in mercury oxide, which only contains the substance of these elements, just as steam only contains the substance of ice, but not ice itself; or as bread contains the substance of the corn, but not the corn itself. The existence of an element may be recognised without knowing it in the uncombined state by merely investigating its combinations, and by the knowledge that it gives, under all possible conditions, substances which are unlike other known combinations of substances. Fluorine is an example of this kind. It was for a long time unknown in the free state, but nevertheless was recognised as an element because its combinations with other elements were known, and their difference from all other similar compound substances was determined. In order to grasp the difference between the conceptions of the visible form of an element as we know it in the free state and of the intrinsic **element** (or 'radicle,' as Lavoisier called it), it should be remarked that compound substances also combine together, forming yet more complex compounds. The original compound may often be extracted from these new compounds by exactly those methods by which elements are extracted from their corresponding combinations. Further, many elements exist under various visible forms, whilst the intrinsic element contained in these various forms is something which is not subject to change. Thus carbon appears as charcoal, graphite, and diamond, but yet the element carbon, of which each consists, is one and the same. Carbonic anhydride contains carbon, and not charcoal, or graphite, or the diamond.

Many elements, although not all of them, have the peculiar lustre, opacity, malleability, and the high thermal and electrical conductivities peculiar to the metals and their mutual combinations known as alloys. But elements are far from all being **metals**. Those which do not possess the physical properties of metals are called **non-metals**. These two classes of elements are clearly distinguished in certain definite examples, but in some cases the distinction is not clear, and hence cannot serve as a basis for the exact division of the elements into two groups.

The conception of elements forms the basis of chemical knowledge, and in giving a list of them at the very beginning of our work we wish to tabulate our present knowledge on the subject. Altogether about 80 elements are now authentically known, some of them—about six—are so rarely met with in nature, and have been obtained in such small quantities, that we possess but a very insufficient knowledge of them. The substances most widely distributed in nature contain a very small number of elements, and these have been more completely studied than the others, because a greater number of investigators have been able to make experiments and observations on them. The elements most widely distributed in nature are :—

Hydrogen,	H.	In water, and in animal and vegetable organisms.
Carbon,	C.	In organisms, coal, limestones.
Nitrogen,	N.	In air and in organisms.
Oxygen,	O.	In air, water, earth. It forms the greater part of the mass of the earth.
Sodium,	Na.	In common salt and in many minerals.
Magnesium,	Mg.	In sea-water and in many minerals.
Aluminium,	Al.	In minerals and clay.
Silicon,	Si.	In sand, minerals, and clay.
Phosphorus,	P.	In bones, ashes of plants, and soil.
Sulphur,	S.	In pyrites, gypsum, and in sea-water.
Chlorine,	Cl.	In common salt and in sea-water.
Potassium,	K.	In minerals, ashes of plants, and in nitre.
Calcium,	Ca.	In limestones, gypsum, and in organisms.
Iron	Fe.	In the earth, iron ores, and in organisms.

Besides these, the following elements, although not very largely distributed in nature, are all more or less well known from their applications to the requirements of everyday life or the arts, either in the free state or as compounds :—

Lithium	Li.	In medicine (Li_2CO_3), and in photography (LiBr).
Boron	B.	As borax, $B_4Na_2O_7$, and as boric acid, BH_3O_3.
Fluorine,	F.	As fluor spar, CaF_2, and as hydrofluoric acid, HF.
Chromium,	Cr.	As chromic anhydride, CrO_3, and potassium dichromate, $K_2Cr_2O_7$.
Manganese,	Mn.	As manganese peroxide, MnO_2, and potassium permanganate, $MnKO_4$.
Cobalt,	Co.	In smalt and blue glass.
Nickel,	Ni.	For electro-plating other metals.
Copper,	Cu.	The well-known red metal.
Zinc,	Zn.	Used for the plates of batteries ; in **brass, &c.**

Arsenic,	As.	White arsenic (poison), As_2O_3.
Bromine,	Br.	A brown volatile liquid ; sodium bromide, NaBr.
Strontium,	Sr.	In coloured fires (SrN_2O_6).
Silver,	Ag.	The well-known white metal.
Cadmium,	Cd.	White metal. Yellow paint (CdS).
Tin,	Sn.	The well-known metal.
Antimony,	Sb.	In alloys such as type metal.
Iodine,	I.	In medicine and photography ; free, and as KI.
Barium,	Ba.	'Permanent white,' and as an adulterant in white lead, and in heavy spar, $BaSO_4$.
Platinum,	Pt.	Well-known metals.
Gold,	Au.	
Mercury,	Hg.	
Lead,	Pb.	
Bismuth,	Bi.	In medicine and fusible alloys.

The compounds of the following elements have fewer applications, but are well known, and are fairly frequently met with in nature, although in small quantities :—

Beryllium,	Be.	Palladium,	Pd.	Titanium,	Ti.
Cerium,	Ce.	Vanadium,	V.	Tungsten,	W.
Selenium,	Se.	Osmium,	Os.	Zirconium,	Zr.
Iridium,	Ir.	Molybdenum,	Mo.	Thallium,	Tl.
Thorium,	Th.	Uranium,	U.		

The compounds of the following elements are still more seldom met with in nature. They have no applications, but have been studied somewhat fully :—

Scandium,	Sc.	Germanium,	Ge.	Gallium,	Ga.
Rubidium,	Rb.	Yttrium,	Y.	Cæsium,	Cs.
Niobium,	Nb.	Lanthanum,	La.	Ruthenium,	Ru.
Neodymium,	Nd.	Praseodymium,	Pr.	Samarium,	Sm.
Rhodium,	Rh.	Ytterbium,	Yb.	Indium,	In.
Tantalum,	Ta.	Tellurium,	Te.	Erbium,	Er.

Then a special group is formed by those gaseous substances discovered by Ramsay which enter in small quantities into the composition of air, and differ from all others in that they, so far, have given no compounds with other elements ; Helium, He ; Neon, Ne ; Argon, Ar ; Krypton, Kr ; and Xenon, Xe. There are also grounds for recognising the individuality of the metals : Actinium, Polonium, and Radium (discovered by Madame Curie), which enter into the composition of the so-called radio-active compounds, occurring in small quantities in the native compounds of Uranium and Thorium.

Besides these 77 elements may be enumerated:—Gadolinium, Terbium, Thulium, Holmium, Karolinium, and several others. But owing to their extreme rarity, their properties and combinations are very little known, and even the existence of some of them as independent substances [29] is doubtful.

It has been incontestably proved, from observations on the spectra of the heavenly bodies, that many of the commoner elements (such as H, Na, Mg, Fe) occur on the far-distant stars. This fact confirms the belief that those forms of matter which appear on the earth as elements are widely distributed throughout the entire universe. But we do not yet know why the mass of some elements in nature should be greater than that of others.[29a]

The capacity of an element to combine with other elements, and to form with them more or less stable compounds which are in a greater or less degree prone to give new and yet more complex substances, forms the fundamental character of that element. Thus sulphur combines readily with the metals, oxygen, chlorine, or carbon, whilst gold and silver enter into combination with difficulty, and form unstable compounds, which are easily decomposed by heat. We must now consider the cause or force which induces the elements to enter into chemical change, and also that which holds different substances in combination—that is, which endows the substances formed with their particular degree of stability. This cause or force is called **affinity** (affinitas, affinité, Verwandtschaft), or chemical affinity.[30] Since this force must be regarded exclusively as an attractive force like gravity, many writers (for instance, Bergmann at the end of the eighteenth, and Berthollet at the beginning of the nineteenth century) supposed affinity

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[29] There can be no mention of such contestable and doubtful elements in a short general handbook of chemistry.

[29a] Clark in America made an approximate calculation of the amounts of the different elements contained in the earth's crust (to a depth of 15 kilometres), and found that the chief mass (about 50 per cent.) is composed of oxygen; then come silicon (about 25 per cent.), Al, Fe, &c., while the amount of hydrogen is less than 1 per cent., carbon scarcely 0·21 per cent., nitrogen even less than 0·03 per cent. The relative masses of such metals as Cu, Ni, and Au are very minute. Judging from the density (see Chapter VIII.) of the earth, a large proportion of its mass must be composed of iron.

[30] This word, first introduced into chemistry, if I mistake not, by Glauber, is based on the idea of the ancient philosophers that combination can only take place when the substances combining have something in common. As is generally the case, another idea evolved itself in antiquity, and has lived until now, side by side with the first, to which it is exactly contradictory: this considers union as dependent on contrast, on polar difference, on an effort to fulfil a want.

to be essentially similar to the universal force of gravity, from which it only differs in that the latter acts at observable distances, whilst affinity only evinces itself at the smallest possible distances. But chemical affinity cannot be entirely identified with the universal attraction of gravity, for the latter is dependent only on mass and distance, and not on the quality of the material acting, whilst it is by the quality of matter that affinity is most forcibly influenced. Neither can it be entirely identified with cohesion, which gives to homogeneous solid substances their crystalline form, elasticity, hardness, ductility, and other properties, and to liquids their surface tension, drop formation, capillarity, and other properties, because affinity acts between the component parts of a substance and cohesion on a substance in its homogeneity, although both these forces act at imperceptible distances (by contact) and have much in common. Nor can chemical force, which makes one substance penetrate into another, be entirely identified even with those attracting forces which make different substances adhere to each other or hold together (as when two plane-polished surfaces of solid substances are brought into close contact), or which cause liquids to soak into solids or adhere to their surfaces, or gases and vapours to condense on the surfaces of solids. These forces must not be confounded with chemical forces, which cause one substance to penetrate into the substance of another and form a new substance, which is never the case with cohesion. But it is evident that the forces which determine cohesion form a connecting-link between mechanical and chemical forces, because they only act by intimate contact. For a long time, and especially during the first half of the nineteenth century, chemical attraction and chemical forces were identified with electrical forces. There is certainly an intimate relation between them, for electricity is evolved in chemical reactions, and has also a powerful influence on chemical processes—for instance, compounds are decomposed by the action of an electric current. And the exactly similar relation which exists between chemical phenomena and the phenomena of heat (heat being developed by chemical phenomena, and being able also to decompose compounds) only proves the unity of the forces of nature, the capability of one force to produce and to be transformed into others. But for this reason the identification of chemical force with electricity will not bear experimental proof.[31] As of all the (molecular) phenomena

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[31] Especially conclusive are those cases of so-called metalepsis (Dumas, Chapter II.). Chlorine, in combining with hydrogen, forms a very stable substance called 'hydrochloric acid,' which is split up by the action of an electric current into chlorine and hydrogen, the chlorine appearing at the positive and the hydrogen at the negative pole. Hence electro-chemists considered hydrogen to be an electro-positive and chlorine an electro-negative element, the two being held together by virtue of their opposite electrical charges.

of nature those of heat are at present the best (comparatively) known, having been reduced to the simplest fundamental principles of mechanics (of energy, equilibrium, and movement), which since Newton have been subjected to strict mathematical analysis, it is quite natural that an effort, which has been particularly pronounced during the last ten years, should have been made to bring chemical phenomena into strict correlation with the already investigated phenomena of heat, without, however, aiming at any identification of chemical with thermal phenomena. The true nature of chemical force is still a secret to us, just as is the nature of the universal force of gravity; and yet, without knowing what gravity really is, by applying mechanical conceptions, astronomical phenomena have not only been subjected to exact generalisation, but have also been employed for the detailed prediction of a number of particular facts; and so, also, although the true nature of chemical affinity may be unknown, there is reason to hope for considerable progress in chemical science by applying to it the laws of the mechanical theory of heat. As yet this portion of chemistry has not been fully worked out, and therefore, while forming a current problem of the science, it is treated more fully in a particular branch which is termed either 'theoretical' or 'physical' chemistry, or, more correctly, *chemical mechanics*. As this province of chemistry requires a knowledge, not only of the various homogeneous substances which have as yet been obtained and of the chemical transformations which they undergo, but also of the phenomena (thermal and other kinds) by which these transformations are accompanied, it is only possible to enter on the study of chemical mechanics after becoming acquainted with the fundamental chemical conceptions and substances which form the subject of this book.[32]

It appears, however, from metalepsis that chlorine can replace hydrogen (and, inversely, hydrogen can replace chlorine) without in any way either changing the grouping of the other elements in a compound or altering its chief chemical properties. For instance, acetic acid in which hydrogen has been replaced by chlorine is still capable of forming salts. It must be observed, while considering this subject, that the explanation suggesting electricity as the origin of chemical phenomena is unsound, since it attempts to explain one class of phenomena whose nature is almost unknown by another class which is no better known. It is most instructive to remark that together with the electrical theory of chemical attraction there arose and still survives a view which explains the galvanic current as being a transference of chemical action through the circuit—i.e. regards the origin of electricity as a chemical one. It is evident that the connection is very intimate, although the two phenomena are independent and represent different forms of molecular (atomic) motion, whose real nature is not yet understood. Nevertheless, the connection between the phenomena of both categories is not only in itself very instructive, but it extends the applicability of the general idea of the unity of the forces of nature, conviction of the truth of which held so important a place in the science of the last decade.

[32] I consider that in an elementary textbook of chemistry, like the present, it is only

As the chemical changes to which substances are liable proceed from internal forces peculiar to these substances, as chemical phenomena certainly consist of motions of material parts, and as the investigation of mechanical and physical phenomena proves the **law of the indestructibility of forces**, or conservation of energy, we are inevitably obliged to acknowledge in all substances (and especially in the elements) the presence of a store of **chemical energy** or invisible motion inducing them to enter into combinations. If heat is evolved in a reaction, it means that a portion of the chemical energy is transformed into heat;[33] if heat is absorbed in a reaction,[34] that it is partly transformed (rendered latent) into chemical energy. The store of force or energy which can be used for the formation of new compounds may, after several combinations accomplished with loss of heat, finally diminish to such a degree that indifferent compounds will be obtained, although these, by combining with energetic elements or compounds, give more complex compounds capable of entering into chemical combination. Among elements, gold, platinum, and nitrogen have but little energy, whilst potassium, oxygen, and chlorine possess it in a very marked degree. When dissimilar substances enter into combination they often form substances of diminished energy. Thus sulphur and potassium when heated readily burn in the air, but when combined together they yield a compound which is neither inflammable nor capable of burning in air like its component parts. Part of the energy

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advisable, or even possible, to mention, in reference to chemical mechanics, a few general ideas and some particular examples referring more especially to gases and such equilibrated systems as are met with in dissociation and in the passage from one physical or chemical state to another. However, during recent times, owing mainly to the labours of van't Hoff and Gibbs, this province has expanded so largely that it forms a vast section of physical (theoretical) chemistry. The present work, in treating of the general principles of chemistry, and more particularly of the theory of the elements, can only serve as an introduction to such branches of our science as organic, analytical, physical, and technical chemistry.

[33] The theory of heat gave the idea of a store of internal motion or energy, and it therefore became necessary to recognise also chemical energy, but there is no foundation whatever for identifying thermal with chemical energy. It may be assumed, but not positively affirmed, that heat motion is peculiar to molecules and chemical motion to atoms, but as molecules are made up of atoms, the motion of the one passes to the other, and for this reason heat strongly influences chemical reactions during which it also appears or disappears (is absorbed). These relations, which are apparent and hardly subject to doubt on general lines, still present much that is doubtful in detail, because all forms of molecular and atomic motion are able to pass into each other.

[34] The reactions which take place (at ordinary or at high temperatures) directly between substances may be clearly divided into exothermal, which are accompanied by an evolution of heat, and endothermal, which are accompanied by an absorption of heat. It is evident that for the latter to take place a source of heat is necessary, and this is furnished either by the surrounding medium, by a secondary reaction proceeding simultaneously, or by some other form of energy.

of the potassium and sulphur was evolved during their combination in the form of heat. Just as in the passage of substances from one physical state to another a portion of their store of heat is absorbed or evolved, so in combinations or decompositions, and in all other chemical processes, there occurs a change in the store of chemical energy and at the same time an evolution or absorption of heat.

For the comprehension of chemical phenomena as mechanical processes—i.e. the study of the *modus operandi* of chemical phenomena—it is most important to consider (1) the facts gathered from *stoïchiometry*, or that part of chemistry which treats of the quantitative relations, by weight or volume, of the reacting substances; (2) the distinction between the different forms and classes of chemical reactions; (3) the changes in properties produced by alteration in composition; (4) the phenomena which accompany chemical transformation; (5) a generalisation of the conditions under which reactions occur. As regards stoïchiometry, this branch of chemistry has been worked out most thoroughly, and comprises laws (of Dalton, Avogadro-Gerhardt, and others) which bear so deeply on all parts of chemistry that at the present time the chief problem of chemical research consists in the application of general stoïchiometrical laws to concrete examples. Even the very signification of reactions of combination, decomposition, and rearrangement, acquired, as we shall see, a new and special character under the influence of the progress of exact ideas concerning the quantitative relations of substances entering into chemical changes. Furthermore, in this sense there arose a new—and, till then, unknown—division of compound substances into **definite** and **indefinite compounds**. Even at the beginning of the nineteenth century Berthollet had not made this distinction. But Prout showed that many compounds contain the substances of which they are composed or into which they break up, in exact definite proportions by weight, which are unalterable under any conditions. Thus, for example, red mercury oxide always contains sixteen parts by weight of oxygen for every 200 parts by weight of mercury, and this relation is expressed by the formula HgO. But in an alloy of copper and silver one or the other metal may be added at will, and in an aqueous solution of sugar the relative proportions of the sugar and water may be altered and yet a homogeneous whole with the sum of the independent properties will be obtained—i.e., in these cases there is indefinite chemical combination. Although in nature and chemical practice the formation of indefinite compounds (such as alloys and solutions) plays as essential a part as the formation of definite chemical compounds, yet, as the stoïchiometrical laws at present apply chiefly to the latter, all data concerning indefinite compounds suffer from inexactitude, and it is only during recent years that the attention of chemists has been directed to this province of chemistry.[34a]

In chemical mechanics it is very important to distinguish clearly between **reversible** and **non-reversible reactions**. Substances capable of reacting on each other at a certain temperature produce substances which at the same temperature either can or cannot give back the original substances. For example, salt dissolves in water at the ordinary temperature, and the solution so obtained is capable of breaking up at the same temperature, the water being separated by evaporation and salt left behind. Carbon bisulphide is formed from sulphur and carbon at the same temperature as that at which it can be resolved into sulphur and carbon. At a certain temperature iron separates hydrogen from water, forming iron oxide, which, in contact with hydrogen at the same temperature, is able to produce iron and water. It is evident that if two substances, A and B, give two others C and D, and the reaction be reversible (that is, C and D form A and B), then, by taking definite masses of A and B, or corresponding masses of C and D, we shall obtain, in either case, all four substances—that is to say, there will be a state of **chemical equilibrium** (or distribution) existing between the reacting substances. By increasing the mass of one of the substances we obtain a new condition of equilibrium, so that reversible reactions present a means of studying the **influence of mass** on the *modus operandi* of chemical changes. Many of those reactions which occur with very complicated compounds or mixtures may serve as examples of non-reversible reactions. Thus, many of the compound substances of animal and vegetable organisms

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[34a] The question of indefinite chemical compounds, particularly of solutions and alloys and their intimate connection with definite compounds, deeply interested me from the very beginning of my scientific career (in the fifties and sixties of the nineteenth century), when but slight attention was being paid to these matters. Several of my investigations had reference to such subjects (for instance, *Specific Volumes*, 1856; *The Compounds of Alcohol with Water*, 1865; *The Study of Aqueous Solutions*, 1887, &c.), which have therefore a special charm for me. But the *Principles of Chemistry*, which deals mainly with the elements and is a textbook for beginners, can only just touch the subject. Consequently I only consider solutions and alloys cursorily in passing, and chiefly in the notes, although since the publication of van't Hoff and Gibbs's work they have formed the object of extensive research. Their study occupies an important place in recent physical and theoretical chemistry, to which I refer my readers for further details. Moreover, I am of the opinion that the position of contemporary knowledge in the sphere of indefinite compounds has not the requisite completeness and generality for it to have much influence on the general principles of chemistry (although I am convinced that in time this will be accomplished), and therefore it will be best for the beginner to attack this subject after he has become acquainted with so-called general inorganic chemistry. I therefore refrain from burdening my book with a detailed discussion of my views on the subject.

are broken up by heat, but can at no temperature be re-formed from their products of decomposition. Gunpowder, as a mixture of sulphur, nitre, and carbon, on being exploded forms gas and a powdery smoke from which the original substance cannot be re-formed at any temperature. In order to obtain them, recourse must be had to an indirect method **of combination at the moment of separation.** If A does not under any circumstances combine directly with B, it does not follow that it cannot give a compound A B. For A can often combine with C, and B with D, and if C has a great affinity for D, then the action of A C on B D produces not only C D, but also A B. As, on the formation of C D, the substances A and B (previously in A C and B D) are left in a peculiar state of separation, it is supposed that their mutual combination occurs because they meet together in this **nascent state** (*in statu nascendi*). Thus chlorine does not directly combine with charcoal, graphite, or diamond; there are, nevertheless, compounds of chlorine with carbon, and many of them are distinguished by their stability. They are obtained in the action of chlorine on hydrocarbons, as the separation products from the direct action of chlorine on hydrogen. Chlorine takes up the hydrogen, and the carbon liberated at the moment of its separation enters into combination with another portion of the chlorine, so that in the end the chlorine is combined with both the hydrogen and the carbon.

As regards the phenomena accompanying chemical action, the most important circumstance in reference to chemical mechanics is that not only do chemical processes produce mechanical displacement (a motion of particles), heat, light, electrical potential and current, but that all these agents are themselves capable of changing and governing chemical transformations. This reciprocity or reversibility naturally depends on the fact that all the phenomena of nature are only different kinds and forms of visible and invisible (molecular) motions. First sound, and then light, were shown to consist of vibratory motions, as the laws of physics have proved and developed beyond a doubt. The connection of heat with mechanical motion and work has ceased to be a supposition, and has become an accepted fact, the mechanical equivalent of heat (425 kilogram-metres of mechanical work correspond with one kilogram unit of heat, or calorie) giving a mechanical measure for thermal phenomena. It is known that both statical and dynamical electricity are produced by mechanical means (e.g. in the dynamo machines of Gramme and others), and, conversely, a current (in electric motors) can produce mechanical motion. Thus by passing a current between the poles of a Gramme dynamo it may be made to revolve, and, conversely, by rotating it an electric current is produced, which

demonstrates the reversibility of electricity and mechanical motion. Accordingly chemical mechanics must look for the fundamental lines of its advancement in the correlation of chemical with physical and mechanical phenomena. But this subject, owing to its complexity and comparative novelty, has not yet been expressed by an harmonious theory, or even by a satisfactory hypothesis, and we shall therefore not linger over it, but leave this province of physical chemistry as a special branch of our science.

A chemical change in a certain direction is accomplished not only by reason of the difference of masses, the composition of the substances concerned, the distribution of their parts, and their affinity or chemical energy, but also by reason of the **conditions** under which the substances occur. In order that a certain chemical reaction may take place between substances capable of reacting on each other, it is often necessary to have recourse to conditions which are very different from those under which the substances usually occur in nature. For example, not only is the presence of air (oxygen) necessary for the combustion of charcoal, but the latter must also be heated to redness. The red-hot portion of the charcoal burns—i.e. combines with the oxygen of the atmosphere—and in so doing evolves heat, which raises the temperature of the adjacent parts of the charcoal, so that they burn. Just as the combustion of charcoal is dependent on its being heated to redness, so also every chemical reaction only takes place under certain physical, mechanical, or other conditions. The following are the chief conditions which exert an influence on the progress of chemical reactions.

(*a*) *Temperature.*—Chemical reactions of combination only take place within certain definite limits of temperature, and cannot be accomplished outside these limits. We may cite as examples that the combustion of charcoal begins only at a red heat, whilst chlorine or salt only combines with water at a temperature below 0°. These latter compounds cannot be formed at a higher temperature, for they are then wholly or partially broken up into their component parts. In certain cases of combination the effect of a rise of temperature may be explained as causing one of the reacting bodies to change from a solid into a liquid or gaseous form. This conversion into the fluid state facilitates the progress of the reaction, because it aids the intimate contact of the particles reacting on each other. Another cause, and to this must be ascribed the chief influence of heat in exciting chemical action, is that the physical cohesion, or the internal chemical union, of the homogeneous particles is thereby weakened, and in this way the separation of the particles of the original substances and their transference into new compounds are rendered easier. When a reaction absorbs heat—as in decomposition—the reason why heat is necessary is self-evident.

At the present day it may be asserted, upon the basis of existing data respecting the action of high temperatures, that all compound bodies undergo decomposition at a more or less high temperature. We have already seen examples of this in describing the decomposition of mercury oxide into mercury and oxygen, and the decomposition of wood under the influence of heat. Many substances are decomposed at very moderate temperatures; for instance, the fulminating salt employed in cartridges is decomposed at a little above 120°. The majority of those compounds which constitute the mass of animal and vegetable tissues are decomposed at 200°. On the other hand, at very low temperatures, no reaction whatever can take place. Thus plants cease to carry on their chemical processes during the winter. Raoul Pictet (1892), employing the very low temperatures (as low as −200° C.) obtained by the evaporation of liquefied gases (see Chap. II.), has proved that at temperatures below −120°, even such reactions as these between sulphuric acid and caustic soda or metallic sodium do not take place, while the coloration of litmus by acids only commences at temperatures above −80°. Every chemical reaction requires a temperature between certain limits for its accomplishment, and there is no doubt that many of the chemical changes observed by us cannot take place in the sun, where the temperature is very high, or on the moon, where it is very low.

The influence of heat on reversible reactions is particularly instructive. If, for instance, a compound which is capable of being reproduced from its decomposition products be heated up to the temperature at which decomposition begins, the decomposition of a mass of the substance contained in a definite volume will not be immediately completed. Only a certain fraction of the substance is decomposed, the other portion remaining unchanged; and if the temperature be raised, the quantity of the substance decomposed will increase. Furthermore, for a given volume the ratio between the part decomposed and the part unaltered has a certain value for every definite temperature up to that at which the compound is entirely decomposed. This partial decomposition under the influence of heat is called **dissociation**. It is possible to distinguish between the temperatures at which dissociation begins and ends. Should dissociation proceed at a certain temperature, yet should the product or products of decomposition not remain in contact with the still undecomposed portion of the compound, then decomposition will go on to the end. Thus, in a lime-kiln, limestone is completely decomposed into lime and carbonic anhydride, because the latter is carried off by the draught of the furnace. But if a certain mass of limestone be enclosed in a definite volume—for instance, in a gun-barrel in which it is sealed up—and heated to redness, then, as the carbonic anhydride cannot escape, only a certain proportion of the limestone will be decomposed at each definite temperature higher than that at which dissociation begins. Decomposition will cease when the carbonic anhydride evolved exerts a maximum *dissociation pressure* corresponding with each temperature. If the pressure be increased by increasing the quantity of gas, then combination begins afresh; if the pressure be diminished decomposition will recommence. Decomposition in this case is exactly similar to evaporation; if the steam given off by evaporation cannot escape, its pressure will reach a a maximum corresponding with the given temperature, and then evaporation will cease. Should steam be added it will be condensed in the liquid; if its quantity be diminished—i.e. if the pressure be lessened, the temperature being constant—then evaporation will go on. We shall afterwards discuss more fully these phenomena of dissociation, which were first discovered by Henri St. Claire Deville. We will only remark that the products of decomposition recombine with greater facility the nearer their temperature is to that at which dissociation begins, or, in other words, that the initial temperature of dissociation is near to the initial temperature of combination. In certain instances chemical change proceeds at a fixed temperature which may be determined like (and compared to) the melting or boiling point. A given compound will decompose above this temperature, while below it combination or formation of the compound takes place. This may be observed, not only with the aid of a thermometer, but also by the rapid change of volume (by the dilatometer) which takes place at this *critical temperature.* Thus, gypsum or dihydrated calcium sulphate ($CaSO_4,2H_2O$) decomposes at 107° (in a closed vessel, otherwise the water escapes as steam) into a pasty liquid mass containing three-fourths of its water in a free state and hemi-hydrated calcium sulphate ($CaSO_4,\frac{1}{2}H_2O$). At lower temperatures the solid dihydrated salt is again formed.

(*b*) *The influence of an electric current*, and of electricity in general, on the progress of chemical transformations is very similar to the influence of heat. The majority of compounds which conduct electricity are decomposed by the action of a galvanic current, and as there is great similarity in the conditions under which decomposition and combination proceed, combination often proceeds under the influence of electricity. Electricity, like heat, must be regarded as a peculiar form of molecular motion, and all that refers to the influence of heat also refers to the phenomena produced by the action of an electric current, only with this difference, that a substance can sometimes be separated into its component parts with much greater ease by electricity, since the process goes on at the ordinary temperature. The most stable compounds may be decomposed by this means, and a very important fact is then observed—namely, that the component parts appear at the different poles or electrodes by which the current passes through the substance. Those substances which appear at the positive pole (anode) are called 'electro-negative,' and those which appear at the negative pole (cathode) 'electro-positive.' The majority of non-metallic elements, such as chlorine, oxygen, &c., and also acids and substances analogous to them, belong to the first group, whilst the metals, hydrogen, and analogous products of decomposition or ions, appear at the negative pole. Chemistry is indebted to the decomposition of compounds by the electric current for many most important discoveries. Many elements have been discovered by this method, the most important being potassium and sodium. Lavoisier and the chemists of his time were not able to decompose the oxygen compounds of these metals, but Davy showed that they might be decomposed by an electric current, the metals sodium and potassium appearing at the negative pole. Now that the dynamo gives the possibility of producing an electric current by the combustion of fuel, by water power, &c., this method of Davy is advantageously employed for obtaining metals, &c., on a large scale; for instance, sodium from fused caustic soda, or chlorine from solutions of salt.

(*c*) *The action of light* also decomposes certain unstable compounds. Photography is based on such a decomposition of certain substances (for instance, the salts of silver). The mechanical energy of those vibrations which determine the phenomena of light is very small, and therefore only certain generally unstable compounds can be decomposed by light—at least under ordinary circumstances. But there is one class of chemical phenomena dependent on the action of light which forms as yet an unsolved problem in chemistry—viz., the processes accomplished in plants under the influence of light. We find here the most varied decompositions and combinations, which are often unattainable by artificial means. For instance, carbonic anhydride, which is so stable towards the influence of heat and electricity, is nevertheless decomposed, and evolves oxygen in plants under the influence of light. Chlorine combines with hydrogen, under the influence, not only of heat, but also of light, which shows that combination, as well as decomposition, can be determined by its action.

(*d*) *Mechanical influences*, like the foregoing agents, exert an action on the processes of both chemical combination and decomposition. Many substances are decomposed by friction or by a blow—as, for example, the compound called iodide of nitrogen (which is composed of iodine, nitrogen, and hydrogen) and silver fulminate. Mechanical friction causes sulphur to burn at the expense of the oxygen contained in potassium chlorate. Pressure affects both the physical and chemical states of the reacting substances, and, together with the temperature, determines the condition of a substance. This is particularly evident when the substance occurs in an elastic-gaseous form, since the volume and hence also the number of points of encounter between the reacting substances are greatly altered by a change of pressure. Thus, if the temperature be kept constant, hydrogen when compressed acts more powerfully upon iodine and on the solutions of many salts than at the ordinary pressure.

(*e*) The *influence of time* on the progress of chemical reactions is manifested, not only by the fact that the interpenetration of bodies, giving the possibility of their reacting together, requires a mechanical translation which can only proceed with a certain velocity (thus the combustion of a solid in air is determined by the removal from it and access to it, of air, and these actions only take place with a certain limited velocity), but also in the fact that after perfect contact has taken place the internal translation, determining chemical reactions, requires time, or proceeds at a certain rate. The ageing of wine is a well-known instance, a peculiar 'bouquet' or aromatic essences appearing in the wine after the course of time. These essences proceed from the acids and alcohol, present in the new wine in a free state, reacting together (a double decomposition), and in the course of time forming water and aromatic esters. This reaction, which proceeds slowly at the ordinary temperature, is one of the reversible reactions (i.e. an ester and water are able to give an alcohol and an acid), taking place with a distinctly limited velocity whose value depends upon the temperature and other conditions. There are many such retardative reactions, but the majority of the more distinct chemical changes (which should form the first object of study for the beginner) proceed so rapidly that the element of time is not, as a rule, taken into consideration in their investigation.[35]

(*f*) The progress of chemical reactions is also accelerated or retarded by the *condition of contact* in which the reacting bodies occur. Other conditions remaining constant, the rate of progress of a chemical reaction is accelerated by increasing the number of points of contact.

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[35] The rate of reaction is considered more fully in *Physical Chemistry*. In the present work it is only touched upon cursorily.

It will be enough to point out the fact that sulphuric acid does not absorb ethylene under ordinary conditions of contact, but only after continued shaking, by which means the number of points of contact is greatly increased. To ensure complete action between solids, it is necessary to reduce them to very fine powder and to mix them as thoroughly as possible. Spring, the Belgian chemist, has shown that finely powdered solids which do not react on each other at the ordinary temperature may, however, do so under an increased pressure. Thus, under a pressure of 6,000 atmospheres, sulphur combines with many metals at the ordinary temperature, and mixtures of the powders of many metals form alloys.[35a] It is evident that an increase in the number of points or surfaces must be regarded as the chief cause producing reaction, which is doubtless accomplished in solids, as in liquids and gases, in virtue of an internal motion of the particles, which motion must exist, although in different degrees and forms, in all the states of matter. It is very important to direct attention to the fact that the internal motion or condition of the particles of matter must be different on the surface of a substance from what it is inside; because in the interior of a substance similar particles are acting on all sides of any particle, whilst at the surface they act on one side only. Therefore the condition of a substance at its surfaces of contact with other substances must be more or less modified by them—possibly in a manner similar to that caused by an elevation of temperature. These considerations throw some light on the action in the large class of **contact reactions**; that is, such as appear to proceed owing to the mere presence (contact, catalysis) of certain special substances. Porous or powdery substances are very prone to act in this way, especially spongy platinum and charcoal. For example, sulphurous anhydride does not combine directly with oxygen; but this reaction takes place in the presence of spongy platinum.[36]

[35a] Spring, in 1888, showed that a mixture of finely powered dry non-hygroscopic salts—acetate of sodium, $C_2H_3NaO_2$, and nitrate of potassium, KNO_3—forms a hygroscopic mass, even under the ordinary atmospheric pressure (by simply lying in dry air), owing to the formation by substitution, of a new hygroscopic salt, acetate of potassium, $C_2H_3KO_2$, and nitrate of sodium, $NaNO_3$, thus proving that solids are capable of reacting on each other.

[36] Contact phenomena are considered in detail in the work of Professor Konovaloff (1884). In my opinion the state of the internal motions of the atoms in molecules is modified at the points of contact of substances, and this state determines chemical reactions, so that reactions of combination, decomposition, and rearrangement are accomplished by contact. Professor Konovaloff showed that a number of substances, under certain conditions of their surfaces, act by contact; for instance, finely divided silica (from the hydrate) acts just like platinum, decomposing certain compound ethers. As reactions only take place when the reacting substances are in close contact, it is probable that those modifications in the distribution of the atoms in molecules which

The above general and introductory chemical conceptions cannot be thoroughly grasped in their true sense without a knowledge of the detailed facts of chemistry to which we shall now turn our attention. It was, however, absolutely necessary on the very threshold to become acquainted with such fundamental principles as the laws of the indestructibility of matter and the conservation of energy; since it is only by their acceptance, and under their direction and influence, that the examination of particular facts can give practical and fruitful results.

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come about by contact phenomena prepare the way for them. By this the rôle of contact phenomena is considerably extended. Such phenomena should explain the fact that a mixture of hydrogen and oxygen yields water (explodes) at different temperatures, according to the nature of the heated substance which transmits the temperature. In chemical mechanics, phenomena of this kind have great importance; but as yet they have been but little studied. It must not be forgotten that contact is a necessary condition for every chemical reaction.

CHAPTER I

ON WATER AND ITS COMPOUNDS

WATER is found almost everywhere in nature, and in all three physical states. As vapour, water occurs in the atmosphere over the entire surface of the earth. The vapour of water in condensing forms snow, rain, hail, dew, and fog. One cubic metre (or 1,000 litres, or 35·316 cubic feet) of air can contain at 0° only 4·8 grams of water, at 20° about 17·0 grams, and at 40° about 50·7 grams; but ordinary air only contains about 60 per cent. of this amount. Air containing less than 40 per cent. of the possible amount of moisture is felt to be dry, whilst air which contains more than 80 per cent. is considered as distinctly damp.[1] Water in the liquid state, falling as rain and snow, soaks into the soil, and collects together into springs, lakes, rivers, seas, and oceans.

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[1] In practice the chemist has to deal continually with gases, and gases are often collected over water; in this case a certain amount of water passes into vapour which mixes with the gases. It is therefore most important that he should be able to calculate the amount of **moisture in air and other gases**. Let us imagine a cylinder standing in a mercury bath, and filled with a dry gas whose volume equals v, temperature $t°$, and pressure h mm. (h millimetres of a column of mercury at 0°). We will introduce water into the cylinder in such quantity that a small part remains in the liquid state, and consequently the gas becomes saturated with aqueous vapour; the volume of the gas will then increase (if a large quantity of water be taken, some of the gas will be dissolved in it, and the volume may therefore be diminished). We will further suppose that, after the addition of the water, the temperature remains constant; then the pressure and volume are increased. In order to investigate the phenomenon we will artificially increase the pressure and reduce the volume to the original volume v. Then the pressure will be greater than h, namely, $h+f$, which means that by the introduction of aqueous vapour the pressure of the gas is increased. The researches of Dalton, Gay-Lussac, and Regnault showed that this increase f is equal to the maximum possible pressure of aqueous vapour at the temperature at which the observation is made. The maximum pressure f for all temperatures may be found in the tables made from observations on the pressure of aqueous vapour. This may be expressed thus: The maximum pressure of aqueous vapour (and of all others) is the same, no matter whether the space containing it is a vacuum or filled with a gas. This rule is known as **Dalton's law**. Thus we have a volume of dry gas v, under a pressure h, and a volume of moist gas, saturated with vapour, under a pressure $h+f$. The volume v of the dry gas under a pressure $h+f$ occupies, from Boyle's law, a volume $\frac{vh}{h+f}$; consequently the volume occupied by the aqueous vapour under the pressure $h+f$ equals $v - \frac{vh}{h+f}$, or $\frac{vf}{h+f}$. Thus the volumes of the dry gas and of the moisture which occurs in it, at a pressure $h+f$, are in the ratio $f : h$; and, therefore, if the aqueous vapour saturates a space at a pressure H, the volumes of the dry air and of the moisture which is contained in it are in the ratio $H - f : f$, where f is the pressure of the vapour according to the tables of vapour pressure. Thus, if a volume N of a gas saturated with moisture be measured at a pressure H, then the volume of the gas when dry will be equal to $N \frac{H-f}{H}$. We thus obtain the following practical rule: If a volume of a gas saturated with aqueous vapour be measured at a pressure H mm., the volume of dry gas contained in it will be obtained by finding the volume corresponding with a pressure equal to H less the pressure due to the aqueous vapour at the temperature observed.

The preceding ratio gives the maximum quantity of water which can be held in a gas, and the degree of moisture shows what fraction of this maximum quantity occurs in any given case when the vapour does not saturate the space occupied by the gas. Thus, if it is required to measure the volume of a moist gas, it must be either thoroughly dried or quite saturated with moisture, or else the degree of moisture determined. The first and last methods are inconvenient, so that recourse is usually had to the second. For this purpose water is introduced into the cylinder holding the gas to be measured; it is left for a certain time so that the gas may become saturated, care being taken that a portion of the water remains in a liquid state; then the volume of the moist gas is determined, from which that of the dry gas may be calculated.

In order to find the **weight of the aqueous vapour** in a gas it is necessary to know the weight of a cubic measure at 0° and 760 mm. Knowing that one cubic centimetre of air under these conditions weighs 0·001293 gram, and that the density of aqueous vapour is 0·62, we find that one cubic centimetre of aqueous vapour at 0° and 760 mm. weighs 0·0008 gram, and at a temperature $t°$ and pressure h the weight of 1 cubic centimetre will be $0{\cdot}0008 \times \frac{h}{760} \times \frac{273}{273+t}$ gram. We already know that v volumes of a gas at a temperature $t°$ and pressure h contain $v \times \frac{f}{h}$ volumes of aqueous vapour when saturated, so that the weight of the aqueous vapour held in v volumes of a gas will be

$$v \times 0{\cdot}0008 \times \frac{f}{760} \times \frac{273}{273+t}.$$

Accordingly the weight of water which is contained in unit volume of a gas depends only on the temperature and not on the pressure (this is **Dalton's law**). From this it is clear that if the weight of the vapour, p, contained in a given volume of a gas be known, it is easy to determine the degree of moisture, $r = \frac{p}{v \times 0{\cdot}0008} \times \frac{760}{t} \times \frac{273+t}{273}$. On this is founded the very exact determination of the degree of moisture of air from the weight of water contained in a given volume. It is easy to calculate from the preceding formula the number of grams, p, of water contained at any pressure in 1 cubic metre of a gas saturated with vapour at various temperatures; for instance, at 30°, $f = 31{\cdot}5$; hence $p = 29{\cdot}84$ grams.

The laws of Mariotte, Dalton, and Gay-Lussac, which are here applied to gases and vapours, are not perfectly exact, but are approximately true. In fact the pressure of aqueous vapour is slightly less in a gas than in a vacuum, and the weight of aqueous vapour held in a gas is slightly less than it should be according to Dalton's law, as was shown by the experiments of Regnault and others. The difference does not, however, exceed 5 per cent. of the total pressure of the vapours. This **decrement in vapour pressure** which occurs in the intermixture of vapours and gases, although small, indicates that there is then already, so to speak, a beginning of chemical change. The essence of the matter is that in this case there occurs, as on contact (see preceding

It is absorbed from the soil by the roots of plants, which when fresh contain from 40 to 80 per cent. of their weight of water. Animals contain about the same proportion of water. In a solid state, water appears as snow or ice, or in a state intermediate between these two, which is seen on mountains covered with perpetual snow. The water of rivers,[2] springs, oceans and seas, lakes and wells, contains various substances in solution, mostly salts—that is, substances resembling common

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footnote), an alteration in the motions of the atoms in the molecules, and therefore also a change in the motion of the molecules themselves.

In the uniform intermixture of air and other gases with aqueous vapour, and in the ability of water to pass into vapour and form a uniform mixture with air, we have an instance of a physical phenomenon which is analogous to chemical phenomena, and forms indeed a transition from the one class of phenomena to the other. Between water and dry air there exists a kind of affinity which obliges the water to saturate and mix with the air. But such a homogeneous mixture is formed (almost) independently of the nature of the gas into which evaporation takes place; even in a vacuum the phenomenon occurs in exactly the same way as in a gas, and therefore it is not the property of the gas, nor its relation to water, but the property of the water itself, which compels it to evaporate, so that in this case chemical affinity is not yet operative—or at least its action is not clearly pronounced. That it does, however, play a certain part is seen from the deviation from Dalton's law.

[2] In falling through **the atmosphere, water** dissolves the gases of the air, nitric acid, ammonia, organic compounds, salts of sodium, magnesium, and calcium, and mechanically washes out a mixture of dust and microbes suspended in the atmosphere. The amount of these and certain other constituents is very variable. Even between the beginning and end of the same rainfall a variation which is often very considerable may be remarked. Thus, for example, Bunsen found that rain collected at the beginning of a shower contained 8·7 grams of ammonia per cubic metre, whilst that collected at the end of the same shower contained only 0·64 gram. The water of the entire shower contained an average of 1·47 gram of ammonia per cubic metre. In the course of a year rain supplies an acre of ground with as much as 15 kilos of nitrogen in a combined form. Marchand found in one cubic metre of snow water 15·63, and in one cubic metre of rain water 10·07, grams of sodium sulphate. Angus Smith showed that after thirty hours' rainfall at Manchester the rain still contained 34·3 grams of salts per cubic metre. A considerable amount of organic matter, namely, 25 grams per cubic metre, has been found in rain water. The total amount of solid matter in rain water reaches 50 grams per cubic metre. Rain water generally contains very little carbonic acid, whilst in river water there is a considerable quantity of it. In considering the nourishment of plants it is necessary to keep in view the substances which are carried into the soil by rain.

River water contains from 50 to 1,600 parts by weight of salts in 1,000,000 parts. The amounts of solid matter per 1,000,000 parts by weight contained in the chief rivers are as follows:—The Don 124, the Loire 135, the St. Lawrence 170, the Rhone 182, the Dnieper 187, the Danube from 117 to 234, the Rhine from 158 to 317, the Seine from 190 to 432, the Thames at London from 400 to 450, in its upper parts 387, and in its lower parts up to 1,617, the Nile 1,580, and the Jordan 1,052. The Neva is characterised by the remarkably small amount of solid matter it contains. From the investigations of Prof. G. K. Trapp, a cubic metre of Neva water contains 32 grams of incombustible and 23 grams of organic matter, or altogether about 55 grams. This is one of the purest waters met with in a river. The large amount of impurities in river water, and especially of organic impurity produced by pollution with putrid matter, makes the water of many rivers unfit for use.

The chief part of the soluble substances in river water consists of calcium salts. A hundred parts of the solid residues contain the following amounts of calcium carbonate: from the water of the Loire 53, from the Thames about 50, the Elbe 55, the Vistula 65, the Danube 65, the Rhine from 55 to 75, the Seine 75, the Rhone from 82 to 94. The Neva contains 40 parts of calcium carbonate per 100 parts of saline matter. The considerable amount of calcium carbonate which river water contains is very easily explained from the fact that water which contains carbonic acid in solution easily dissolves calcium carbonate, which occurs all over the earth. Besides calcium carbonate and sulphate, river water contains the chlorides and other salts of magnesium, sodium, potassium, aluminium, iron, and manganese. The presence of nitrates has been proved with certainty in almost all kinds of well-investigated river water. The quantity of calcium phosphate does not exceed 0·4 gram in the water of the Dnieper, and the Don does not contain more than 5 grams. The water of the Seine contains about 15 grams of nitrates, and that of the Rhone about 8 grams. The amount of ammonia is much less: thus in the water of the Rhine there is about 0·5 gram in June and 0·2 gram in October. The water of the Seine contains the same amount. This is less than in rain water. Notwithstanding this insignificant quantity, the water of the Rhine alone, which is not so very large a river, carries about 16 tons of ammonia into the ocean every day. The difference between the amounts of ammonia in rain and river water depends on the fact that the soil through which the rain water passes is able to retain the ammonia and also many other substances, such as phosphoric acid, potassium salts, &c.

The water of springs, rivers, wells, and in general of those places from which it is taken for drinking purposes, may be injurious to health if it contains much organic pollution, the more so as in such water the lower organisms (bacteria) may rapidly develop, and these organisms often serve as the carriers or causes of infectious diseases. For instance, certain pathogenic (disease-producing) bacteria are known to produce typhoid, the Siberian plague, and cholera. Thanks to the work of Pasteur, Metchnikoff, Koch, and many others, this province of research has made considerable progress. It is possible to investigate the number and properties of the germs in water. *In bacteriological researches* a gelatinous medium in which the germs can develop and multiply is prepared with gelatine and water, which has previously been heated several times, at intervals, to 100° (it is thus rendered sterile; that is to say, all the germs in it are killed). The water to be investigated is added to this prepared medium in a definite and small quantity (sometimes diluted with sterilised water to facilitate the calculation of the number of germs), protected from dust (which contains germs), and then left at rest until whole families of lower organisms are developed from the separate germs. These families (colonies) are visible to the naked eye (as spots), and may be counted; and by examining them under the microscope, and observing the number of organisms they produce, their significance may be determined. The majority of bacteria are harmless, but there are undoubtedly pathogenic kinds whose presence is one of the causes of malady and of the spread of certain diseases. The number of bacteria in 1 cubic centimetre of water sometimes attains the immense figures of hundreds of thousands and millions. Certain well, spring, and river waters contain very few bacteria, and are free from disease-producing bacteria under ordinary circumstances. By boiling water the bacteria in it are killed, and therefore boiled water is less harmful for drinking purposes than fresh water. The best kinds of water for drinking purposes do not contain more than 300 bacteria in a cubic centimetre.

The amount of the gases dissolved in river water is much more constant than that of its solid constituents. One litre, or 1,000 grams, of water contains 40 to 55 c.c. of gas measured at normal temperature and pressure. In winter the amount of gas is greater than in summer or autumn. Assuming that a litre contains 50 c.c. of gases, it may be admitted that these consist on an average of 20 vols. of nitrogen, 20 vols. of carbonic anhydride (proceeding in all likelihood from the soil and partly from the atmosphere), and 10 vols. of oxygen. If the total amount of gases be less, the constituent gases are still in about the same proportion; in most cases, however, carbonic anhydride predominates. The water of many deep and rapid rivers contains less carbonic anhydride, which shows that they have been rapidly formed from atmospheric water, and that they table salt in their physical properties and chief chemical transformations.[3] Further, the quantity and nature of these salts differ in different waters. Everybody knows that there are salt, fresh, iron, and other waters. The presence of about 3½ per cent. of salts renders sea water[4] bitter to the taste and increases its specific gravity. Fresh water also contains salts, but only in a comparatively small quantity (not above 1 per cent.) Their presence may be easily proved by simply evaporating water. On evaporation the water passes away as vapour, whilst the salts are left behind. This is why a crust consisting of salts, previously in solution, is deposited on the insides of kettles, boilers, and other vessels in which water is boiled. Running water (rivers &c.) is charged with salts, owing to its being formed from the collection of rain water percolating through the soil. During this percolation the water dissolves certain parts of the soil. Thus water which filters or passes through saline or calcareous soils becomes charged with salts or calcium carbonate (chalk). Rain water and snow are much purer than river or spring water. Nevertheless, in passing through the atmosphere, rain and snow succeed in

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have not succeeded during a long and slow course in absorbing a greater quantity of carbonic anhydride. Thus, for instance, the water of the Rhine, near Strassburg, according to Deville, contains 8 c.c. of carbonic anhydride, 16 c.c. of nitrogen, and 7 c.c. of oxygen per litre. From the researches of Prof. M. R. Kapoustin and his pupils, it appears that in determining the quality of a water for drinking purposes it is most important to investigate the composition of the dissolved gases, more especially as regards the oxygen present.

[3] **Spring water** is formed from rain water percolating through the soil. Naturally a part of the rain water is evaporated directly from the surface of the earth and from the vegetation on it. It has been shown that out of 100 parts of water falling on the earth only 36 parts flow to the ocean; the remaining 64 are evaporated or percolate far underground. After flowing underground along some impervious strata, water comes out at the surface in many places as springs whose temperature is determined by the depth from which the water has flowed. Springs penetrating to a great depth may become considerably heated, and this is why hot mineral springs, with a temperature of 30° and higher, are often met with. When a spring water contains substances which endow it with a peculiar taste, and especially if these substances are such as are only found in minute quantities in river and other flowing waters, it is termed **a mineral water**. Many such waters are employed for medicinal purposes. Mineral waters are classed according to their composition into—(*a*) saline waters, which often contain a large amount of common salt; (*b*) alkaline waters, which contain sodium carbonate; (*c* bitter waters, which contain magnesia; (*d*) chalybeate waters, which hold iron carbonate in solution; (*e*) aërated waters, which are rich in carbonic anhydride; (*f*) sulphuretted waters, which contain hydrogen sulphide. Sulphuretted waters may be recognised by their smell of rotten eggs, and by their giving a black precipitate with lead salts, and also by their tarnishing silver objects. Aërated waters, which contain an excess of carbonic anhydride, effervesce in the air, have a sharp taste, and redden litmus paper. Saline waters leave a large residue of soluble solid matter on evaporation, and have a salt taste. Chalybeate waters have an inky taste, and are coloured black by an infusion of galls; on being exposed to the air they usually give a brown precipitate. The character of a mineral water is generally a mixed one. In the table below, analyses are given of certain mineral springs which are valued for their medicinal properties. The quantity of the substances present in the water is expressed in millionths by weight.

—	Calcium salts	Sodium chloride	Sodium sulphate	Sodium carbonate	Potassium iodide and bromide	Other potassium salts	Iron carbonate	Magnesium salts	Silica	Carbonic anhydride	Sulphuretted hydrogen	Total solid contents
I.	1,928	—	152	—	—	24	—	448	152	1,300	80	2,609
II.	816	386	1,239	26	—	43		257	46	1,485	—	2.812
III.	1,085	1,430	1,105	—	4	90	—	187	65	1,326	11	3,950
IV.	343	3,783	16	3,431	—	14	—	251	112	2,883	—	7.950
V.	3,406	15,049	—	—	2	—	7	1,587	229	—	76	20,290
VI.	352	3,145	—	95	35	50	1	260	11	20	—	3,970
VII.	308	1,036	2,583	1,261	—	—	4	178	75	—	—	5,451
VIII.	1,726	9,480	—	—	40	120	26	208	40	—	—	11,790
IX.	551	2,040	1,150	999	—	1	30	209	50	2,740	—	4.070
X.	285	558	279	3,813	—	—	7	45	45	2,268	—	5,031
XI.	340	910	Iron and aluminium sulphates				1,020 1,660	940	190	2,550 330	Sulphuric and hydrochloric acids	

I. Sergieffsky, a sulphur water, Gov. of Samara (temp. 8° C.), analysis by Clause. II. Geléznovodskya water source No. 10, near Patigorsk, Caucasus (temp. 22·5°), analysis by Fritzsche. III. Aleksandroffsky, alkaline-sulphur spring, Patigorsk (temp. 46·5°), average of analyses by Herman, Zinin, and Fritzsche. IV. Bougountouksky, alkaline spring No. 17, Essentoukah, Caucasus (temp. 21·6°), analysis by Fritzsche. V. Saline water, Staro-Russi, Gov. of Novgorod, analysis by Nelubin. VI. Water from artesian well at the factory of State papers, St. Petersburg, analysis by Struve. VII. Sprüdel, Carlsbad (temp. 83·7°), analysis by Berzelius. VIII. Kreuznach spring (Elisenquelle), Prussia (temp. 8 8°), analysis by Bauer. IX. Eau de Seltz, Nassau, analysis by Henry, X. Vichy water, France, analysis by Berthier and Puvy. XI. Paramo de Ruiz, Colombia, analysis by Levy. This water is distinguished by the amount of free acids present.

[4] **Sea water** contains more non-volatile saline constituents than the common types of fresh water. This is explained by the fact that the waters flowing into the sea supply it with salts, and whilst a large quantity of vapour is given off from the surface of the sea the salts remain behind. Even the specific gravity of sea water differs considerably from that of pure water. It is generally about 1·02, but in this, and also in the amount of salts present, samples of sea water *from different localities* and *from different depths* present rather remarkable variations. It will be sufficient to point out that 1 cubic metre of water from the undermentioned localities contains the following quantity in grams of solid constituents:—Gulf of Venice, 19,122; Leghorn Harbour, 24,312; the Mediterranean, near Cetta, 37,665; the Atlantic Ocean, from 32,585 to 35,695; and the Pacific Ocean, from 34,708 to 35,233. In closed seas which do not communicate, or are in very distant communication, with the ocean, the difference is often still greater. Thus the Caspian Sea contains 6,300 grams; the Black Sea and Baltic, 17,700. Common salt forms the chief constituent of the saline matter of sea or ocean water; thus in 1 cubic metre of sea water there are 25,000–31,000 grams of common salt, 2,600–6,000 grams of magnesium chloride, 1,200–7,000 grams of magnesium sulphate, 1,500–6,000 grams of calcium sulphate, and 10–700 grams of potassium chloride. The small amount of the organic matter and of the salts of phosphoric acid in sea water is very remarkable. Sea water (the composition of which is partially discussed in Chapter X.) contains, in addition to salts of common occurrence, a certain and sometimes minute amount of the most varied elements, even gold and silver; and as the mass of water of the oceans is so enormous these 'traces' of rare substances amount to large quantities, so that it may be hoped that in time methods will be found to extract even gold from sea water, which by means of the rivers forms a vast reservoir for the numerous products of the changes taking place on the earth's surface.

catching the dust held in it and in dissolving air, which is found in every water. When water is heated the dissolved gases of the atmosphere are partly disengaged, as bubbles, and, after long boiling, water is quite freed from these gases.

In general terms water is called pure when it is clear and free from insoluble particles held in suspension and visible to the naked eye, from which it may be freed by filtration through charcoal, sand, or porous (natural or artificial) stones, and when it possesses a clean fresh taste. It depends on the absence of any taste of decomposing organic matter, on the quantity of air[5] and atmospheric gases in solution, and on the presence of mineral substances to the amount of about 300 grams per ton (or 1,000 kilograms per cubic metre, or, what is the same, 300 milligrams to a kilogram or a litre of water), and of not more than 100 grains of organic matter.[6] Such water is suitable for drinking and every practical application, but evidently it is not pure in a chemical sense. A **chemically pure water** is necessary not only for scientific purposes, as an independent substance having constant and definite properties, but also for many practical purposes—for instance, in photography and in the preparation of medicines—because many properties of substances in solution are changed by the impurities of natural waters. Water is usually purified by distillation, because the solid substances in solution are not transformed into vapours in this process, and any gases in solution are driven off during the boiling. Such **distilled** water is prepared by chemists and in laboratories by boiling water in closed metallic boilers or stills, and causing the steam produced to pass into a condenser—that is, through tubes (which should be made of tin, or, at all events, tinned, as water and its impurities do not act on tin) surrounded by cold water, and in which the steam, being cooled, condenses into water which is collected[7] in a receiver. By standing exposed to the atmosphere, however, the water in time absorbs air, and dust carried in the air. Nevertheless, in distillation, water retains, besides air, a certain quantity of volatile impurities (mostly organic), and the walls of the distillation apparatus are partly

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[5] The taste of water is greatly dependent on the quantity of dissolved gases it contains. These gases are given off on boiling, and it is well known that, even when cooled, boiled water has, until it has absorbed gaseous substances from the atmosphere, quite a different taste from fresh water containing a considerable amount of gas. The dissolved gases, especially oxygen and carbonic anhydride, have an important influence on the health. The following instance is very instructive in this respect. The Grenelle artesian well at Paris when first opened supplied a water which had an injurious effect on men and animals. It appeared that this water did not contain oxygen, and was in general very poor in gases. As soon as it was made to fall in a cascade, by which it absorbed air, it proved quite fit for consumption. In long sea voyages fresh water is sometimes not taken at all, or only taken in a small quantity, because it spoils by keeping and becomes putrid, owing to the decomposition of the organic matter it contains. Fresh water may be obtained directly from sea water by distillation. The distilled water no longer contains sea salts, and is therefore fit for consumption, but it is very tasteless, and has the properties of boiled water. In order to render it palatable certain salts, which are usually present in fresh water, are added to it, and it is made to flow in thin streams exposed to the air in order that it may become saturated with the component parts of the atmosphere—that is, absorb gases.

[6] **Hard water** is such as contains much mineral matter, and especially a large proportion of calcium salts. Such water, owing to the amount of lime it contains, does not form a lather with soap, prevents vegetables boiled in it from softening properly, and forms a large amount of incrustation on vessels in which it is boiled. When of a high degree of hardness it is injurious for drinking purposes, as is evident from the fact that in several large cities the death-rate has been found to decrease after introducing a soft water in place of a hard one. Water containing decomposed organic matter may be purified by means of Condy's fluid (potassium permanganate). A solution of this substance, even if very dilute, is of a red colour; on adding it to a putrid water the permanganate oxidises and destroys the organic matter. It is added to water in such a quantity as to impart to it an almost imperceptible rose colour. It is especially salutary to add a small quantity of Condy's fluid to impure water in times of epidemic.

The presence in water of 1 gram per litre, or 1,000 grams per cubic metre, of any substance whatsoever renders it unfit, and even injurious, for consumption, and this is so, no matter whether organic or mineral matter predominates. The presence of 1 per cent. of chlorides makes water quite salt, and produces thirst instead of assuaging it. A large amount of nitrates is only found in impure and usually injurious water, as they often indicate the presence of decomposing organic matter.

[7] Distilled water may be prepared on a small scale in the laboratory in a glass retort (fig. 4) heated by a lamp. Fig. 4 illustrates the main parts of the usual glass laboratory apparatus used for distillation. The steam issuing from the retort (on the right-hand side) passes through a glass tube surrounded by a larger tube, through which passes a stream of cold water, by which the steam is condensed and runs into a receiver (on the left-hand side).

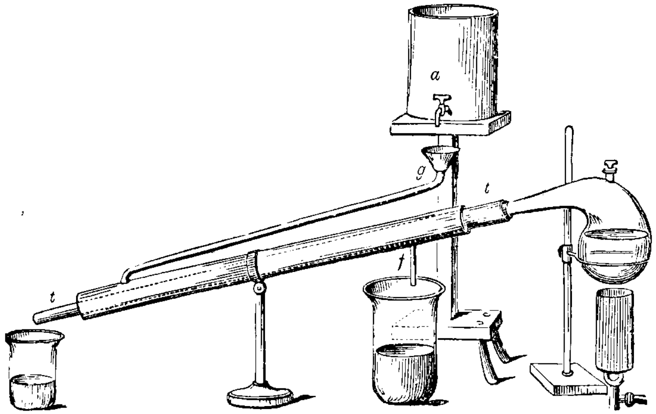

Fig. 4.—Distillation from a glass retort. The neck of the retort fits into the inner tube of the Liebig's condenser. The space between the inner and outer tubes of the condenser is filled with cold water, which enters by the tube *g* and flows out at *f*.

corroded by the water, and a portion, although only a small one, of their substance renders the water not entirely pure, so that a residue is left on evaporation.[8]

For certain physical and chemical researches, however, it is necessary to have perfectly pure water. To obtain it, a solution of potassium permanganate is added to distilled water until the whole has a faint rose colour. By this means the organic matter in the water is destroyed (converted into gases or non-volatile substances). An excess of potassium permanganate does no harm, because in the next distillation it is left behind in the distillation apparatus. This second distillation should take place in a platinum retort with a platinum receiver. Platinum is a metal which is not acted on either by air or water, and therefore nothing passes from it into the water. The water obtained in the receiver still contains air. It must then be boiled for a long time, and afterwards cooled in a vacuum under the receiver of an air-pump, and must be kept in air-tight vessels. Pure water does not leave any residue on evaporation; does not in the least change, however long it is kept; does not decompose like water only once distilled or impure; and does not give bubbles of gas on heating, nor does it change the colour of a solution of potassium permanganate.

Water, purified as above described, has constant **physical** and **chemical properties.** For instance, it is of such water only that one cubic centimetre weighs one gram at 4° C.—i.e. it is only such pure water whose specific gravity equals 1 at 4° C.[9] Water in a solid state

forms crystals of the hexagonal system,[10] seen in snow, which generally consists of starlike clusters of several crystals, and also in the half-melted scattered ice floating on rivers in spring time. But ice also occurs, like many solids, in an amorphous (non-crystalline) form.

The temperatures at which water passes from one state to another are taken as fixed points on the thermometer scale; namely, the zero corresponds with the temperature of melting ice, and the temperature of the steam disengaged from water boiling at the normal barometric pressure (that is, 760 millimetres measured at 0°, at the latitude of 45°, at the sea level) is taken as 100° of the Celsius scale. Thus, the facts that ice liquefies at 0° and water boils at 100° are taken as characteristics of a definite chemical compound. The weight of a litre of water at 4° is 1,000 grams, and at 0°, 999·87 grams. The weight of a litre of ice at 0° is less—namely, 916 grams (according to Vincenna, 1902, the coefficient of cubical expansion of ice is 0·000152); the weight of the same cubic measure of water vapour at 760 mm. pressure and 100° is only 0·60 gram; the density of the vapour compared with that of air is 0·62, and compared with that of hydrogen, 9.

These data briefly characterise the physical properties of water as

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[8] One of Lavoisier's first memoirs (1770) referred to this question. He investigated the formation of the earthy residue in the distillation of water in order to prove whether it was possible, as was affirmed, to convert water into earth, and he found that the residue was produced by the action of the water on the sides of the vessel containing it, and not from the water itself. He proved this to be the case by direct weighing.

[9] Taking the generally accepted specific gravity of water at its greatest density—i.e. at 4°—as unity, it has been shown by experiment that the specific gravity of water at different temperatures is as follows:—

At	0°	0·99987	At	20°	0·99823
„	+ 10°	0·99973	„	30°	0·99568
„	15°	0·99913	„	100°	0·95859

A comparison of all the data at present known shows that the variation of **the** specific gravity S_t with the temperature t (determined by the hydrogen **thermometer**) may be expressed (Mendeléeff, 1896) between − 5° and + 40° C. by the formula

$$S_t = 1 - \frac{(t-4)^2}{118932 + 1366{\cdot}75t - 4{\cdot}13t^2}.$$

If the temperature be determined by the mercurial thermometer, whose indications between 0° and 100° are slightly higher than those of the hydrogen thermometer (for example, about 0·1° C. at 20°), then a slightly higher sp. gr. will be obtained for a given t.

Water at 4° is taken as the basis for reducing measures of length to measures of weight and volume. The **metric** or **decimal system** of measuring weights and volumes is universally employed in science. The starting-point of this system is the metre (39·37 inches) divided into decimetres (= 0·1 metre), centimetres (= 0·01 metre), millimetres (= 0·001 metre), and microns (= one millionth of a metre). A cubic decimetre is called a **litre,** and is used for the measurement of volumes. The weight of a litre of water in a vacuum at 4° is called a kilogram. Platino-iridium standard samples of the **kilogram** and metre have been established by international treaty, and their prototypes have been distributed in many countries, with the object of establishing a uniformity of weights and measures. In Russia the law (1899) sanctions the use of the metric system on a par with the Russian by the mutual consent of the negotiating parties. The thousandth part of a kilogram weighs one **gram.** It is divided into decigrams, centigrams, and milligrams (= 0·001 gram). An English pound equals 453·59 grams. The great advantage of this system is that it is a decimal one, and that it is universally adopted in science and in international relations. *All the measures cited in this work are metric.* The units most often used in science are:—Of length, the centimetre; of weight, the gram; of time, the second; of temperature, the degree Centigrade of the hydrogen thermometer.

According to the most trustworthy determinations the weight of a c. dcm. of water at 4° in vacuo is about 1 decigram less than a kilogram. For ordinary purposes the weight of a c. dcm. may be taken as equal to a kg. Hence the litre (or more truly the weight of water it holds) is equal to about 1000·1 cub. decimetres.

[10] As solid substances appear in individual regular crystalline forms which are dependent, *judging* from their cleavage or lamination (in virtue of which mica breaks up into laminæ, and Iceland spar, &c., into pieces bounded by faces inclined to each other at angles which are definite for each substance), on an inequality of attraction (cohesion elasticity) in different directions which intersect at definite angles, the determination of crystalline form affords one of the most important characteristics for identifying definite chemical compounds. The elements of crystallography, which is a special science, should therefore be familiar to all who desire to work in scientific chemistry. In this work we shall only have occasion to speak of a few crystalline forms, some of which are shown in figs. 5 to 11. But solids not only occur in crystalline forms determined by inequalities of cohesion and elasticity in different directions, by which (as also by their

a separate substance. To this may be added that water is a mobile liquid, colourless, transparent, without taste or smell, &c. Its latent

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optical and electrical properties) they differ distinctly from liquids (which are of uniform structure in all directions, or isotropic), but also in an amorphous or isotropic state—without any difference of structure in different directions—which is best illustrated by

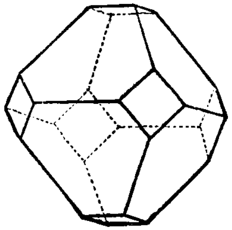

FIG. 5.—Example of the form belonging to the regular system. Combination of an octahedron and a cube. The former predominates. Alum, fluor spar, suboxide of copper, and others.

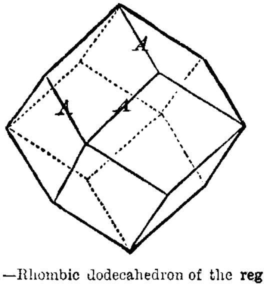

FIG. 6.—Rhombic dodecahedron of the **regular** system. Garnet.

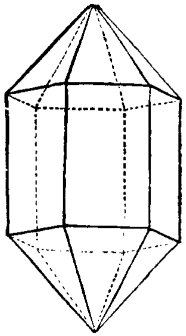

FIG. 7.—Hexagonal prism **terminated by hexagonal** pyramids. Quartz, &c.

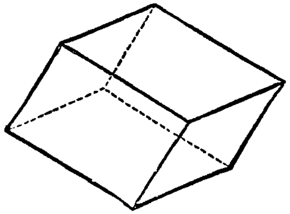

FIG. 8.—Rhombohedron. Calc spar, &c.

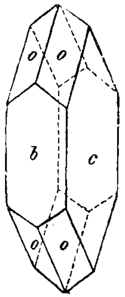

FIG. 9.—Rhombic **system.** Desmine.

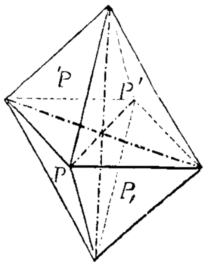

FIG. 10.—Triclinic pyramid.

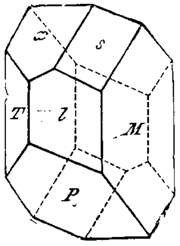

FIG. 11.—Triclinic **system.** Albite &c.

heat of vaporisation is 538 units, and that of liquefaction 79 units of heat.[11] The large amount of heat stored up in water vapour and also in

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glass. When a solid forms by solidification from a liquid (i.e., from a molten state) it generally appears in an amorphous state, and only passes into a crystalline form by the agency of other bodies (especially crystals and such like substances) or under certain conditions of temperature and pressure. This subject, especially since Prof. Tamman's (Yurieff University, 1890–1902) recent researches, is of great interest, not only from a physico-mechanical, but also from a chemical point of view.

[11] Of all known liquids, water exhibits the greatest **cohesion** of particles. Indeed, it ascends in capillary tubes to a greater height than other liquids; for instance, two and a half times as high as alcohol, nearly three times as high as ether, and to a much greater height than oil of vitriol, &c. In a tube 1 mm. in radius, water at 0° ascends 15·3 mm., measuring from the height of the liquid to two-thirds of the height of the meniscus, and at 100° it rises 12·5 mm. The cohesion varies very uniformly with the temperature; thus at 50° the height of the capillary column equals 13·9 mm.—that is, the mean between the heights at 0° and 100°. This uniformity is not destroyed even at temperatures near the freezing-point, and hence it may be assumed that at high temperatures cohesion will vary as uniformly as at ordinary temperatures; so that at some temperature near 370° water should not ascend in a capillary tube. The cohesion between the particles of water would then be nil, and a peculiar critical state is attained of which mention will be made presently. Only certain solutions (sal-ammoniac and lithium chloride)—and these only with a great excess of water—rise higher than pure water in capillary tubes. The great cohesion of water doubtless determines many of both its physical and chemical properties.

The quantity of heat required to raise the temperature of one part by weight of water from 0° to 1°, i.e., by 1° C., is called the *unit of heat* or calorie; the **specific heat of liquid water** at 0° is taken as equal to unity. The variation of this specific heat with rise of temperature is inconsiderable in comparison with the variation exhibited by the specific heats of other liquids. The specific heat of water at 20° is 0·993, and at 100°, 1·073. The specific heat of water is greater than that of any other known liquid; for example, the specific heat of alcohol at 0° is 0·55—i.e., the quantity of heat which raises the temperature of 55 parts of water 1° raises that of 100 parts of alcohol 1°. The specific heat of oil of turpentine at 0° is 0·41, of ether 0·53, of acetic acid 0·5274, and of mercury 0·033. Hence water is the best condenser or absorber of heat. This property of water has an important significance in practice and in nature. Water prevents rapid cooling or heating, and thus tempers cold and heat. The specific heats of ice and aqueous vapour are much less than that of water, that of ice being 0·504, and that of steam 0·48.

With an increase in pressure equal to one atmosphere, the compressibility of water is 0·000047, of mercury 0·00000352, and of ether 0·00012 at 0°. The addition of various substances to water generally decreases both its compressibility and cohesion. The compressibility of other liquids increases with a rise of temperature, but for water it decreases up to 53° and then increases as with other liquids.

The **expansion of water** by heat (note 9) also exhibits many peculiarities which are not found in other liquids. The expansion of water at low temperatures is very small compared with that of other liquids: at 4° it is almost zero, and at 100° it is equal to 0·0008; below 4° it is negative—i.e., water on cooling does not then decrease in volume, but expands. In passing into the solid state, the specific gravity of water decreases; at 0° 1 c.c. of water weighs 0·99987 gram, and 1 c.c. of ice at the same temperature weighs only 0·916 gram. The ice formed, however, contracts on cooling like the majority of other substances. Thus 100 volumes of ice are produced from 92 volumes of water—that is, water expands considerably on freezing, which fact determines a number of natural phenomena. The freezing-point of water falls with an increase in pressure (0·007° per atmosphere), because water in freezing expands (Thomson), whilst with substances which contract in solidifying, the melting-point rises with an increase in liquid water (for its specific heat is greater than that of other liquids)

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pressure; thus, paraffin under one atmosphere melts at 46°, and under 100 atmospheres at 49°. The above proves that, under very considerable pressures, the densities of water and ice tend to become equal, and that a point may be reached where ice will sink under water. This has been confirmed by Tamman's researches (1890-1902) on the influence of temperature and pressure on the formation of amorphous and crystalline solids from liquids.

When liquid water passes into vapour the cohesion of its particles must be destroyed, as the particles are removed to such a distance from each other that their mutual attraction no longer exhibits any influence. As the cohesion of aqueous particles varies at different temperatures, the quantity of heat which is expended in overcoming this cohesion—or the **latent heat of evaporation**—will for this reason alone be different at different temperatures. The quantity of heat which is consumed in the transformation of one part by weight of water, at different temperatures, into vapour was determined with great accuracy by Regnault, Griffiths (1895), and others. It is found that one part by weight of water at 0°, in passing into vapour having a temperature $t°$, consumes $640 + (t - 100)\ 0{\cdot}6$ units of heat; that is, at 100°, 640, and at 200°, 700 heat units. But this quantity includes also the quantity of heat required for heating the water from 0° to $t°$—i.e., besides the latent heat of evaporation, also that heat which is used in heating the water in a liquid state to a temperature $t°$. On deducting this amount of heat, we obtain the latent heat of evaporation of water as 598 at 0°, 538 at 100°, and 478 at 200°. From this we may conclude that at a certain temperature no heat would be required for the conversion of water into vapour. At this temperature, water passes into vapour, whatever be the pressure (see Chap. II. The absolute boiling-point of water is about 365°). It must here be remarked that water, in presenting a greater cohesion, requires a larger quantity of heat for its conversion into vapour than other liquids.

The whole amount of heat which is consumed in the conversion of water into vapour is not used in overcoming the cohesion—that is, in internal work accomplished in the liquid. A part of this heat is employed in moving the aqueous particles; in fact, aqueous vapour at 100° occupies a volume 1,650 times greater than that of water (at the ordinary pressure); consequently a portion of the heat or work is employed in lifting the aqueous particles, in overcoming pressure, or in external work, which may be usefully employed, and which is so employed in steam engines. In order to determine this work let us consider the variation of the maximum **vapour pressure of steam** at different temperatures. The observations of Regnault in this connection, as on those preceding, deserve special attention owing to their comprehensiveness and accuracy. The pressure of aqueous vapour at various temperatures is given in the subjoined table, and is expressed in millimetres of the barometric column reduced to 0°.

Temperature	Pressure	Temperature	Pressure
−20°	0·9	70°	233·3
−10°	2·1	90°	525·4
0°	4·6	100°	760·0
+ 10°	9·1	105°	906·4
15°	12·7	110°	1075·4
20°	17·4	115°	1269·4
25°	23·5	120°	1491·3
30°	31·5	150°	3581·0
50°	92·0	200°	11689·0

This table shows the boiling-points of water at different pressures. Thus on the summit of Mont Blanc, where the average pressure is about 424 mm., water boils at 84·4°; and at a pressure of five atmospheres (five times the ordinary atmospheric pressure—i.e., $5 \times 760 = 3{,}800$ mm.) the temperature of the water would be 152°. As a column of mercury 1 mm. high exerts a pressure of 13·596 grams on a

renders it available in both forms for heating purposes.[12] The chemical reactions which water undergoes, and by means of which it is formed,

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surface of 1 sq. cm., the pressure of the atmosphere, 760 mm., corresponds with a pressure of 1033·28 grams per square centimetre. This means that if a cylinder be taken whose sectional area equals 1 sq. cm., and if water be poured into it and it be closed by a piston weighing 1,033 grams, then on heating it *in a vacuum* to 100° no steam will be formed, because the steam cannot overcome the pressure of the piston; and if at 100° 538 units of heat be transmitted to each unit of weight of water, then the whole of the water will be converted into vapour having the same temperature. The question now arises, *to what height does the piston rise under these circumstances*; that is, in other words, what is the volume occupied by the steam under a known pressure? For this we must know the weight of a cubic centimetre of steam at various temperatures. It has been shown by experiment that the density of steam, with reference to air at the same temperature and pressure, is 0·62. Steam which saturates a space varies in density at different temperatures, but this difference is very small, and its average density with reference to air is 0·64. Now one cubic centimetre of air at 0° and 760 mm. weighs 0·001293 gram, while at 100° and under the same pressure it will weigh $\frac{0{\cdot}001293}{1{\cdot}368}$ or about 0·000946 gram, and consequently one cubic centimetre of steam whose density is 0·64 will weigh 0·000605 gram at 100°, and one gram of aqueous vapour will occupy a volume of about 1,653 c.c. *Consequently the piston in the cylinder of 1 sq. cm. sectional area, and in which the water occupied a height of 1 cm., will be raised 1,653 cm. on the conversion of this water into steam.* This piston, as has been mentioned, weighs 1,033 grams, therefore the **external work of the steam**—that is, that work which the water does in its conversion into steam at 100°—is equal to lifting a piston weighing 1,033 grams to a height of 1,653 cm., or 17·07 kilogram-metres of work—i.e., is capable of lifting 17 kilograms 1 metre, or 1 kilogram 17 metres. One gram of water requires for its conversion into steam 538 gram units of heat or 0·538 kilogram unit of heat—i.e., the quantity of heat absorbed in the evaporation of one gram of water is equal to the quantity of heat which is capable of heating 1 kilogram of water 0·538°. Each unit of heat, as has been shown by accurate experiment, is capable of doing 425 kilogram-metres of work. *Hence, in evaporating, one gram of water expends* $425 \times 0{\cdot}538 =$ (almost) 227 kilogram-metres of work. The external work was found to be only 17 kilogram-metres; therefore 210 kilogram-metres are expended in overcoming the internal cohesion of the aqueous particles, and consequently about 92 per cent. of the total heat or work is consumed in overcoming the internal cohesion.

The work necessary for overcoming the internal cohesion of water in its passage into vapour decreases with the rise in temperature; that is, corresponds with the decrease of cohesion; and the variations which take place in this case are very similar to those which are observed in the heights to which water rises in capillary tubes at different temperatures. It is evident, therefore, that the amount of external—or, as it is termed, useful—work which water can supply by its evaporation is very small compared with the amount *which it expends in its conversion into vapour*.

It is evident from the above considerations that, even in a physical change of state, the greatest part of the work done is employed in overcoming cohesion, but an enormous amount of internal energy must be expended in overcoming chemical cohesion or affinity.

[12] When it is necessary to heat a considerable mass of liquid in different vessels, it would be very uneconomical to make use of metallic vessels and to construct a separate furnace for each. Such cases are continually met with in practice. Steam from a boiler is introduced into the liquid, or, in general, into the vessel which it is required to heat. The steam, in condensing and passing into a liquid state, parts with its latent heat; and as this is very considerable a small quantity of steam will produce a considerable heating effect. *If it be required, for instance,* to heat 1,000 kilos of water from 20° to 50°, which requires approximately 30,000 units of heat, steam at 100° is passed into the water

are so numerous, and so closely allied to the reactions of many other substances, that it is impossible to describe the majority of them at this early stage of chemical exposition. We shall become acquainted with many of them afterwards, but at present we shall only cite certain compounds formed by water. In order to see clearly the nature of the various kinds of compounds formed by water, we will begin with the most feeble, which are determined by purely mechanical superficial properties of the reacting substances.

Water is mechanically attracted by many substances: it adheres to their surfaces just as dust adheres to objects, or one piece of polished glass adheres to another. Such attraction is termed 'moistening,' 'soaking,' or 'absorption of water.' Thus water is absorbed by the soil, sand, and clay, and does not flow away from them, but lodges itself between their particles. Similarly, water soaks into a sponge, cloth, hair, or paper, &c.; but fat and greasy substances in general are not moistened. Attraction of this kind does not alter the physical or chemical properties of water. For instance, under these circumstances water, as is known from everyday experience, may be expelled from objects by drying. Water which is in any way held mechanically may be dislodged by mechanical means, by friction, pressure, centrifugal force, &c. Thus water is squeezed from wet cloth by pressure or centrifugal machines. But objects which in practice are called dry (because they do not feel wet) often still contain moisture, as may be proved by heating the object in a glass tube closed at one end. On placing a piece of paper, dry earth, or any similar object (especially porous substances) in such a glass tube, and heating that part of the tube where the object is situated, it will be remarked that water condenses on the cooler portions of the tube. The presence of such absorbed, or 'hygroscopic,' water is generally best detected in non-volatile substances by drying them either at 100°, or under the receiver of an air-pump and over substances which attract water chemically. By weighing a substance before and after drying, it is easy to determine the amount of hygroscopic water from the loss in weight.[13] But in

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from a boiler. Each kilogram of water at 50° contains about 50 units of heat, and each kilogram of steam at 100° contains 640 units of heat; therefore each kilogram of steam in cooling to 50° gives up 590 units of heat, and consequently 51 kilos of steam are capable of heating 1,000 kilos of water from 20° to 50°. Water is very often applied for heating in chemical practice. For this purpose metallic vessels or pans, called 'water-baths,' are made use of. They are closed by a cover formed of concentric rings lying on each other. The vessels—such as beakers, evaporating basins, retorts, &c.—containing liquids, are placed on these rings, and the water in the bath is heated. The steam given off heats the bottom of the vessels to be heated, and thus effects the evaporation or distillation.

[13] In order to dry any substance at about 100°—that is, at the boiling-point of water

this case the amount of water must be judged with care, because the loss in weight may sometimes proceed from the decomposition of the

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(hygroscopic water passes off at this temperature)—an apparatus called a 'drying-oven' is employed. It consists of a double copper box; water is poured into the space between the internal and external boxes, and the oven is then heated over a stove or by any other means, or else steam from a boiler is passed between the walls of the two boxes. When the water boils, the temperature inside the inner box will be approximately 100° C. The substance to be dried is placed inside the oven, and the door is closed. Several holes are cut in the door to allow the free passage of air, which carries off the aqueous vapour by the chimney on the top of the oven. Often, however, desiccation is carried on in copper ovens heated directly over a lamp (fig. 12). In this case any desired temperature may be obtained, and is determined by a thermometer fixed in a special orifice. In order to determine directly the amount of water in a substance which does not part with anything except water at a red heat, the substance is placed in a bulb tube. By first weighing the tube empty and then with the substance to be dried in it, the weight of the substance taken may be found. The tube is then connected on one side with a gas-holder full of air, which, on opening a stop-cock, passes first through a flask containing sulphuric acid, and then into a vessel containing lumps of pumice-stone moistened with sulphuric acid. In passing through these vessels

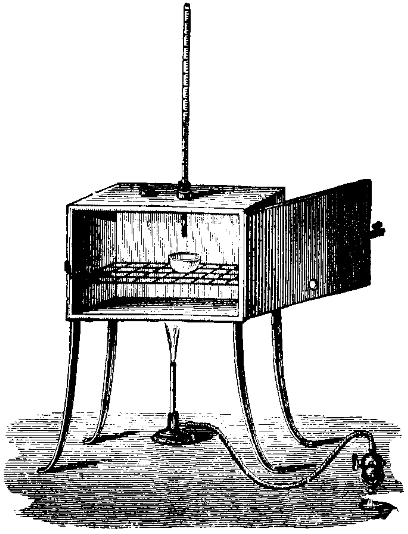
FIG. 12.—Drying oven, constructed of brazed copper. It is heated by a lamp. The object to be dried is placed on the gauze inside the oven. The thermometer indicates the temperature.

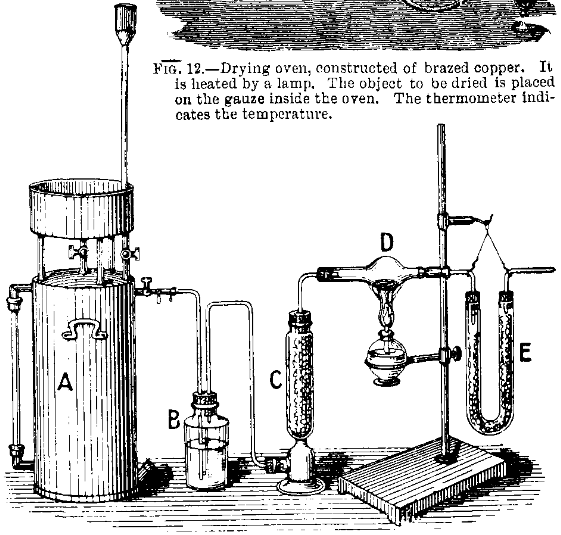

FIG. 13.—Determination of the quantity of water in a substance by heating it (in D) in a stream of air proceeding from A and dried in B and C; the water from the substance in D is collected in E and weighed.

substance itself, with disengagement of gases or vapour. In making exact weighings the hygroscopic capacity of substances—that is, their capacity to absorb moisture—must be continually kept in view, as otherwise the weight will be untrue owing to the presence of moisture. The quantity of moisture absorbed depends on the degree of moisture of the atmosphere (that is, on the pressure of the aqueous vapour in it) in which a substance is situated. In a perfectly dry atmosphere, or in a vacuum, the hygroscopic water is expelled, being converted into vapour; therefore substances containing hygroscopic water may be completely dried by placing them in a dry atmosphere or in a vacuum. The process is aided by heat, which increases the pressure of the aqueous vapour. Phosphoric anhydride (a white powder), liquid sulphuric acid, solid and porous calcium chloride, and the white powder of ignited copper sulphate, are most generally employed in drying gases. They absorb the moisture contained in air and all gases to a considerable, but not unlimited, extent. Phosphoric anhydride and calcium chloride deliquesce, become damp, sulphuric acid changes from a thick oily liquid into a more mobile one, and ignited copper sulphate becomes blue; after which changes these substances partly lose their capacity of holding water, and can, if it be in excess, even give up their water to the atmosphere. We may remark that the order in which these substances are placed above corresponds with the order in which they stand in respect to their capacity for absorbing moisture. Air dried by calcium chloride still contains a certain amount of moisture, which it can give up to sulphuric acid. The most *complete desiccation takes place with phosphoric anhydride.* Water is also removed from many substances by placing them in a dish over a vessel containing a substance absorbing water under a glass bell jar.[14]

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the air is thoroughly dried, having given up all its moisture to the sulphuric acid. Thus dry air will pass into the bulb tube. The moisture given up by the substance in the tube will be carried off by the air passing through it. This damp air then passes through a **U**-shaped tube full of pieces of pumice-stone moistened with sulphuric acid, which absorbs all the moisture given off from the substance in the bulb tube. Thus all the water expelled from the substance will collect in the **U**-tube; and so, if this be weighed before and after, the difference will show the quantity of water expelled from the substance. If only water (and no gases) come over, the increase of the weight of the **U**-tube will be equal to the decrease in the weight of the bulb tube.

[14] Instead of under a glass bell jar, drying over sulphuric acid is often carried on in a desiccator consisting of a shallow wide-mouthed glass vessel, closed by a well-fitting ground-glass cover. Sulphuric acid is poured over the bottom of the desiccator, and the substance to be dried is placed on a glass stand above the acid. A lateral glass tube with a stop-cock is often fused into the desiccator in order to connect it with an air pump, and so allow drying under a diminished pressure, when the moisture evaporates more rapidly. The fact that, in the usual form of desiccator, the desiccating substance (sulphuric acid) is placed beneath the substance to be dried has the disadvantage that the moist air, being lighter than dry air, distributes itself in the upper portion of the desiccator and not below.

The bell jar, like the receiver of an air pump, should be hermetically closed. In this case desiccation takes place because the sulphuric acid, for instance, first dries the air in the bell jar by absorbing its moisture, the substance to be dried then parting with its moisture to the dry air from which it is again absorbed by the sulphuric acid, &c. Desiccation proceeds still better under the receiver of an air pump, for then the aqueous vapour is formed more quickly than in a bell jar full of air.

From what has been said above, it is evident that the transference of moisture to gases and the absorption of hygroscopic moisture present great resemblance to, but still are not, chemical combinations with water. Water, when combined as hygroscopic water, does not lose its properties and does not form new substances.[15]

The attraction of water for substances which dissolve in it is of a different character. In the solution of substances in water a peculiar kind of indefinite combination goes on, a new homogeneous substance being formed from the two substances taken. But here also the bond connecting the substances is very unstable. Water containing different substances in solution boils at a temperature near to its usual boiling-point. From the solution of substances which are lighter than water itself, there are obtained solutions of a less density than water; as, for example, in the solution of alcohol in water; whilst a heavier substance in dissolving in water gives it a higher specific gravity. Thus salt water is heavier than fresh.[16]

Aqueous solutions have a special interest because they are constantly being formed on the earth and in the waters of the earth, in plants and in animals, in chemical processes and in the arts; and these solutions play an important part in the chemical transformations which are everywhere taking place, because a substance in solution presents the most favourable conditions for the execution of chemical changes, which require a mobility of parts and a possible distension of

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Hempel, in his desiccator (1891), avoids this by placing the absorbent above the substance to be dried. The process of desiccation can be further accelerated by cooling the upper portion of the desiccator, and so inducing ascending and descending currents of air within the apparatus.

[15] Chappuis, however, determined that in the wetting of 1 gram of charcoal with water, 7 units of heat are evolved, and on pouring carbon bisulphide over 1 gram of charcoal as much as 24 units of heat are evolved. Alumina (1 gram), when moistened with water, evolves 2½ calories. This indicates that in respect to evolution of heat moistening already represents a step towards exothermal combinations (those evolving heat in their formation).

[16] Strong acetic acid ($C_2H_4O_2$), whose specific gravity at 15° is 1·055, does not become lighter on the addition of water (a lighter substance, sp. gr. = 0·999), but heavier, so that a solution of 80 parts of acetic acid and 20 parts of water has a specific gravity of 1·074; and even a solution containing equal parts of acetic acid and water (50 per cent.) has a sp. gr. of 1·065, which is still greater than that of acetic acid itself. This shows the high degree of contraction which takes place on solution. In fact, solutions—and, in general, liquids—on mixing with water, usually decrease in volume.

parts. In dissolving, a solid substance acquires a mobility of parts, and a gas loses its elasticity, and therefore reactions which do not proceed in the undissolved substances often take place in solutions. Further, a substance, distributed in water, evidently breaks up—that is, becomes more like a gas. All these considerations require that, in describing the properties of substances, particular attention should be paid to their relation to water as a universal solvent.

To demonstrate the solubility of gases in water, a gas should be taken which has a high coefficient of solubility—for instance, ammonia. This is introduced into a bell jar (or cylinder, as in fig. 14), which is previously filled with mercury and stands in a mercury bath. If water be then introduced into the cylinder, the mercury will rise, owing to the water dissolving the ammonia gas. If the column of mercury be less than the barometric column, and if there be sufficient water to dissolve the gas, all the ammonia will be absorbed by the water. The water is introduced into the cylinder by a glass pipette with a bent end. The bent end is put into water, and the air is sucked out from the upper end. When full of water, its upper end is

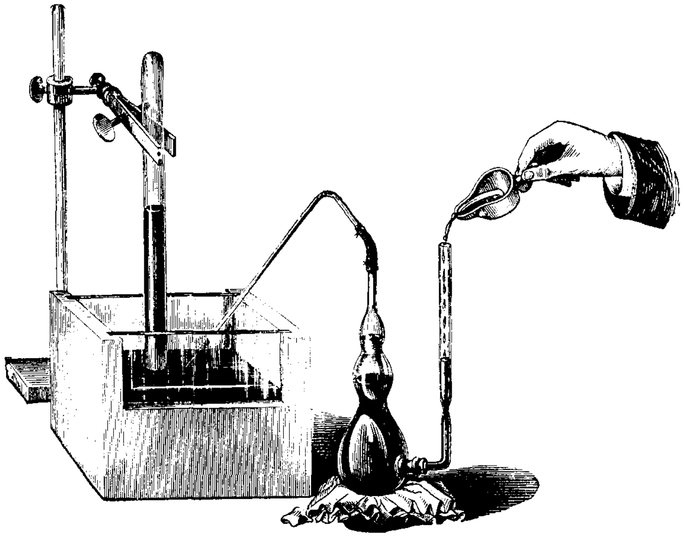

FIG. 14.—Method of transferring a gas into a cylinder filled with mercury, the open end of which is immersed under the mercury in a bath having two glass sides. The apparatus containing the gas is represented on the right. Its upper extremity is furnished with a tube extending under the cylinder. The lower part of the vessel communicates with a vertical tube. If mercury be poured into this tube, the pressure of the gas in the apparatus is increased, and it passes through the gas-conducting tube into the cylinder, where it displaces the mercury, and can be measured or subjected to the action of absorbing agents, such as water.

closed with the finger, and the bent end placed in the mercury bath under the orifice of the cylinder. On blowing into the pipette the water will rise, owing to its lightness, to the surface of the mercury in the cylinder. The solubility of a gas like ammonia may be demonstrated by taking a flask full of the gas, and closed by a cork with a tube passing through it. On placing the tube under water, the water will rise into the flask (this may be accelerated by previously warming the flask), and begin to play like a fountain inside it. Both the rising of the mercury and the fountain clearly show the considerable affinity of water for ammonia gas, and the force acting in this dissolution is rendered evident. A certain period of time is required both for the homogeneous intermixture of gases (diffusion) and the process of solution, which depends not only on the extent of the surface of the participating substances, but also on their nature. This may be seen from experiment. Solutions of different substances heavier than water, such as salt or sugar, are poured into tall jars. Pure water is then very carefully poured into these jars (through a funnel) on to the top of the solutions, so as not to disturb the lower stratum, and the jars are then left undisturbed. The line of demarcation between the solution and the pure water will be visible, owing to the difference of their coefficients of refraction. Notwithstanding, however, that the solutions taken are heavier than water, after some time complete intermixture will ensue. Gay-Lussac convinced himself of this fact by this particular experiment, which he conducted in the cellars under the Paris Astronomical Observatory. These cellars are well known as the locality where numerous interesting researches have been conducted, because, owing to their great depth under ground, they have a uniform temperature during the whole year; the temperature does not change during the day, and this was indispensable for the experiments on the diffusion of solutions, in order that no doubt as to the results should arise on account of a daily change of temperature (the experiment lasted several months), which would set up currents in the liquids and intermix their strata. Notwithstanding the uniformity of the temperature, the substance in solution in time ascended into the water and distributed itself uniformly through it, proving that there exists between water and a substance dissolved in it a particular kind of attraction or striving for mutual interpenetration in opposition to the force of gravity. Further, this effort, or rate of diffusion, is different for salt or sugar or other substances.[16a] It follows therefore that a

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[16a] Graham in the jelly formed by gelatine, and De Vries in gelatinous silica (Chapter XVIII.), most frequently employed coloured (tinted) substances, for instance, $K_2Cr_2O_7$, which showed the rate of diffusion with very great clearness. Prof. Oumoff

peculiar force acts in solution, just as in actual chemical combinations, and solution is determined by a particular kind of motion (by the chemical energy of a substance) which is proper to the substance dissolved and to the solvent.

Graham made a series of experiments similar to those described above, and showed that the **rate of diffusion of solutions**[17] into water is very variable—that is, a uniform distribution of a substance in the water dissolving it is attained in different periods of time with different solutions. Graham compared diffusive capacity with volatility. There are substances which diffuse easily, and there are others which diffuse with difficulty, just as there are more and less volatile substances. Seven hundred cubic centimetres of water were poured into a jar, and by means of a siphon (or a pipette) 100 cubic centimetres of a solution containing 10 grams of a substance were cautiously poured in so as to occupy the lower portion of the jar. After a lapse of several days successive layers of 50 cubic centimetres were taken from the top downwards, and the quantity of substance dissolved in the different layers determined. Thus, common table salt, after fourteen days, gave the following amounts (in milligrams) in the respective layers, beginning from the top: 104, 120, 126, 198, 267, 340, 429, 535, 654, 766, 881, 991, 1,090, 1,187, and 2,266 in the remainder; whilst albumin in the same time gave a very small amount in the first seven layers, and beginning from the eighth layer, 10, 15, 47, 113, 343, 855, 1,892, and in the remainder 6,725 milligrams. Thus, the diffusive power of a solution depends on time and on the nature of the substance dissolved; which fact may serve not only for explaining the process of solution, but also for distinguishing one substance from another. Graham showed that substances which diffuse rapidly through liquids are able to pass rapidly through membranes and to crystallise, whilst substances which diffuse slowly and do not crystallise are **colloids**, that is, resemble glue, and penetrate through a membrane

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employed for this purpose glass bulbs of known density which were heavier than water and lighter than the liquid whose diffusion was being studied, and observed the rate of diffusion from the position of the bulbs, which showed the density of the solution and its composition in a given layer.

[17] The researches of Graham, Fick, Nernst, and others showed that the quantity of a dissolved substance which is transmitted (rises) from one stratum of liquid to another in a vertical cylindrical vessel is not only proportional to the time and to the sectional area of the cylinder, but also to the amount of the substance dissolved in a stratum of liquid, so that to every dissolved substance there corresponds its own coefficient of diffusion. The cause of the diffusion of solutions must be considered as essentially the same as that of the diffusion of gases—that is, as dependent on motions peculiar to *their molecules*—but here most probably those purely chemical, although feebly developed, forces, which incline the substances dissolved to the formation of indefinite compounds with the water, also play their part.

slowly,[18] and form jellies, as will be explained in speaking of silica (Chapter XVIII.)

Hence, if it be desired to increase the rate of solution, recourse must be had to *stirring, shaking, or some such mechanical motion.*

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[18] The rate of diffusion—like the rate of transmission—through membranes, or **dialysis** (which plays an important part in the vital processes of organisms and also in technical processes), presents, according to Graham's researches, a sharply defined change in passing from such crystallisable substances as the majority of salts and acids to substances which are capable of giving jellies (gum, gelatin, &c.) The former diffuse into solutions and pass through membranes much more rapidly than the latter, and Graham therefore distinguishes between **crystalloids**, which diffuse rapidly, and **colloids**, which diffuse slowly. On breaking solid colloids into pieces, a total absence of cleavage is remarked. The fracture of such substances is like that of glue or glass, and is termed 'conchoidal.' Almost all the substances of which animal and vegetable bodies consist are colloids, and this is, at all events partly, the reason why animals and plants have such varied forms, which have no resemblance to the crystalline forms of the majority of mineral substances. The colloid solid substances in organisms—that is, in animals and plants—almost always contain water, and take most peculiar forms, such as networks, granules, hairs, shapeless mucous masses, &c., which are quite different from the forms taken by crystalline substances. When colloids separate out from solutions, or from a molten state, they present a form which is similar to that of the liquid from which they are formed. Glass may be taken as the best example of this. Colloids are distinguishable from crystalloids, not only by the absence of crystalline form, but by many other properties which admit of clearly distinguishing these two classes of solids, as was shown by Graham. Nearly all colloids are capable of passing, under certain circumstances, from a soluble into an insoluble state. The best example is shown by white of eggs (albumin) in the raw and soluble form, and in the hard-boiled and insoluble form. The majority of colloids, on passing into an insoluble form in the presence of water, give substances having a gelatinous appearance, which is familiar to everyone in starch, *solidified glue, jelly,* &c. Thus gelatine or common carpenter's glue, when soaked in water, swells up into an insoluble jelly. If this jelly is heated, it melts, and is then soluble in water, but on cooling it again forms a jelly which is insoluble in water. One of the properties which distinguish colloids from crystalloids is that the former pass very slowly through a membrane, whilst the latter penetrate very rapidly. This may be shown by taking a cylinder, open at both ends, and by covering its lower end with a bladder or with vegetable parchment (unsized paper immersed for two or three minutes in a mixture of sulphuric acid and half its volume of water, and then washed), or any other membranous substance (all such substances are themselves colloids in an insoluble form). The membrane must be firmly tied to the cylinder, so as not to leave any opening. Such an apparatus is called a **dialyser** (fig. 15), and the process of separation of crystalloids from colloids by *means of such a membrane* is termed **dialysis**. An aqueous solution of a crystalloid or colloid, or a mixture of both, is poured into the dialyser, which is then placed in a vessel containing water, so that the bottom of the membrane is covered with

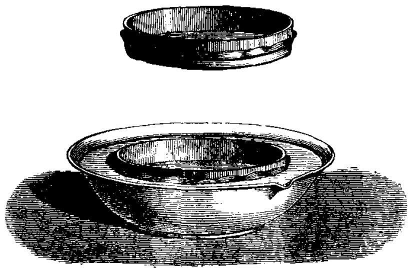

FIG. 15.—Dialyser. Apparatus for the separation of substances which pass through a membrane from those which do not. Description in text.

But if once a uniform solution is formed, it will remain uniform, no matter how heavy the dissolved substance, or how long the solution be left at rest; *which fact again shows the presence of a force holding* together the particles of the dissolved body and of the solvent.[19]

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water. Then, *after a certain period of time, the crystalloid passes through the membrane*, whilst the colloid, if it does pass through at all, does so at an incomparably slower rate. The crystalloid passes through into the water until finally the solution attains the same strength on both sides of the membrane. By replacing the outside water with fresh water, a fresh quantity of the crystalloid may be separated from the dialyser. While the crystalloid is passing through the membrane the colloid remains almost entirely in the dialyser, and therefore mixed solutions of these two kinds of substances may be separated from each other by a dialyser.

[19] The formation of solutions may be considered in two aspects, from a physical and from a chemical point of view; and it is more evident in solutions than in any other department of chemistry how closely these provinces of natural science are allied. On the one hand solutions form a particular case of a physico-mechanical interpenetration of homogeneous substances, and a juxtaposition of the molecules of the substance dissolved and of the solvent, similar to the juxtaposition which is exhibited in homogeneous substances. From this point of view the diffusion of solutions is exactly similar to the diffusion of gases, with only this difference, that the nature and store of energy are different in gases from what they are in liquids, and that in the latter there is considerable friction, whilst in gases there is comparatively little. The penetration of a dissolved substance into water is likened to evaporation, and solution to the formation of vapour. This resemblance was clearly expressed even by Graham, and the Dutch chemist van't Hoff has developed this view of solutions in great detail, having shown (in a memoir in the *Transactions of the Swedish Academy of Science*, 'Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous,' 1886) that for dilute solutions the *osmotic pressure* follows the same laws (of Boyle, Mariotte, Gay-Lussac, and Avogadro-Gerhardt) as do gases. The **osmotic pressure** of a substance dissolved in water is determined by means of membranes which allow water, but not a substance dissolved in it, to pass through them. This property is found in animal protoplasmic membranes and in porous substances covered with an amorphous precipitate, such as is obtained by the action of copper sulphate on potassium ferrocyanide (Pfeffer, Traube). If a 1 per cent. solution of sugar is placed in such a vessel, which is then closed and placed in water at 70°, the water passes through the walls of the vessel and increases the pressure by 50·5 cm. of the barometric column (= *0·664 atmosphere*). *If the pressure be artificially increased inside* the vessel, then the water will be expelled through the walls. De Vries found a convenient method of determining *isotonic* solutions (those presenting a similar osmotic pressure) by means of the cells of plants. For this purpose a portion of the soft part of the leaves of the *Tradescantia discolor*, for instance, is cut away and moistened with the solution of a given salt and of a given strength. If the osmotic pressure of the solution taken be less than that of the sap contained in the cells, the latter will change their form or shrink; if, on the other hand, the osmotic pressure be *greater than that of the* sap, then the cells will expand, as can easily be seen under the microscope. By altering the amount of the different salts in solution it is possible to find for each salt the strength of solution at which the cells begin to swell, and at which they will consequently have an equal osmotic pressure. As it increases in proportion to the amount of a substance dissolved per 100 parts of water, it is possible, knowing the osmotic pressure of a given substance—for instance, sugar at various degrees of concentration of solution—and also the composition of isotonic solutions compared with sugar, to determine the osmotic pressure of all the substances investigated. The osmotic pressure of dilute solutions determined in this manner directly or indirectly (from observations made by Pfeffer and De Vries) was shown to follow the same laws as those of the pressure of gases; (1) by doubling or increasing the quantity of a salt (in a given volume) *n* times, the pressure is

In the consideration of the process of solution, besides the conception of diffusion, another fundamental conception is necessary—namely, that of **saturated solutions.**

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doubled or increases *n* times. Thus, for example, in a solution containing one part of sugar per 100 parts of water, the osmotic pressure (according to Pfeffer) is 53·5 cm. of mercury; if 2 parts of *sugar are present*, 101·6; if 4 parts, 208·2, and so on; which proves that the ratio is true within the limits of experimental error. (2) Equally concentrated solutions of different substances show very different osmotic pressures, just as equal weights of gases in equal volumes show different pressures. (3) If, for a given dilute solution at 0°, the osmotic pressure equal p_0, then at $t°$ it will be greater and equal to $p°\ (1+0{\cdot}00367t)$, i.e., it increases with the temperature in exactly the same manner as the pressure of gases increases. (4) If in dilute solutions of such substances as do not conduct an electric current (*for instance, sugar, acetone, and many other* organic bodies) the substances be taken in the ratio of their molecular weights (expressed by their formulæ, see Chapter VII.), then not only will the osmotic pressure be the same in all cases, but its magnitude will be determined by that pressure which would be exerted by the vapours of the given substances if they were contained in the space occupied by the solution, just as the pressure of the vapours of molecular quantities of the given substances in equal volumes will be equal, and determined by the laws of Gay-Lussac, Mariotte, and Avogadro-Gerhardt. Those formulæ (Chapter VII., Notes 23 and 24) by which the gaseous state of matter is determined, may also be applied in the present case. Thus, for example, the osmotic pressure p, in centimetres of mercury, *of a 1 per cent. solution of* sugar, may be calculated according to the formula for gases—

$$Mp = 6200\ s\ (273 + t),$$

where M is the molecular weight, s the weight in grams of a cubic centimetre of vapour, and t its temperature. For sugar M = 342 (*because its molecular composition* is $C_{12}H_{22}O_{11}$). The specific gravity of the solution of sugar is 1·003, so that the weight of sugar s contained in a 1 per cent. solution = 0·01003 gram. The observation was made at $t=14°$. Hence, according to the formula, we find $p=52{\cdot}2$ centimetres. And experiments carried on at 14° gave 53·5 centimetres, which is very near to the above number. (5) For the solutions of salts, acids, and similar substances, which conduct an electric current, the calculated pressure is usually (but not always) a definite or multiple number of times i less than the observed value, and this i for dilute solutions of $MgSO_4$ is nearly 1; for CO_2, 1; for KCl, NaCl, KI, KNO_3 greater than 1 and approximating to 2; for $BaCl_2$, $MgCl_3$, K_2CO_3, and others between 2 and 3; for HCl, H_2SO_4, $NaNO_3$, CaN_2O_6 and others nearly 2, and so on. It should be remarked that the above deductions are only applicable (with any degree of accuracy) to dilute solutions. Nevertheless, the arithmetical relation found by van't Hoff between the formation of vapours and the transition into dilute solutions forms an important scientific discovery, which should facilitate the explanation of the nature of solutions, while the osmotic pressure of solutions already forms a very important aspect of their study. In this respect it is necessary to mention that Prof. Konovaloff (1891, and subsequently others also) discovered the dependence (*and it may be a sufficient explanation*) of the osmotic pressure upon the differences of the pressures of aqueous vapours and aqueous solutions; this, however, takes us into a special province of physical chemistry (certain data are given in Note 49 and following), and to this physical side of the question belongs also one of the extreme consequences of the resemblance of osmotic pressure to gaseous pressure, which is that the concentration of a uniform solution varies in parts which are heated or cooled. Soret (1881) indeed observed that a solution of copper sulphate containing 17 parts of the salt at 20° only contained 14 parts *after heating the upper portion* of the tube to 80° for a long period of time; that is to say, the lower portion of the solution was richer in salt.

This aspect of solution, which is now being very carefully and fully worked out, may be called the *physical* side. Its other aspect is purely *chemical*, for solution does not take place between any two substances, but requires a special and particular attraction or

Just as moist air may be diluted with any desired quantity of dry air, so also an indefinitely large quantity of a liquid solvent may be taken, and yet a uniform solution will be obtained. But more than a definite quantity of aqueous vapour cannot be introduced into a certain volume of air at any given temperature. The excess above that re-

chemical affinity between them. A vapour or gas permeates any other vapour or gas, but a salt which dissolves in water may not be in the least soluble in alcohol, and is quite insoluble in mercury. In considering solutions as a manifestation of chemical force (and of chemical energy), it must be acknowledged that they are here developed to so feeble an extent that the definite compounds (that is, those formed according to the law of multiple proportions) formed between water and a soluble substance dissociate even at the ordinary temperature, forming a homogeneous system—that is, one in which both the compound and the products into which it decomposes (water and the aqueous compound) occur in a liquid state. The chief difficulty in the comprehension of solutions depends on the fact that the mechanical theory of the structure of liquids has not yet been so fully developed as the theory of gases. The conception of solutions as dissociated definite liquid chemical compounds is based on the following considerations: (1) that there exist certain undoubtedly definite crystallised chemical compounds (such as H_2SO_4,H_2O; or $NaCl,2H_2O$; or $CaCl_2,6H_2O$, &c.) which melt on a certain rise of temperature, and then form true solutions; (2) that metallic alloys in a molten condition are real solutions, but on cooling they often give entirely distinct and definite crystallised compounds; (3) that between the solvent and the substance dissolved there are formed, in a number of cases, many undoubtedly definite compounds, such as compounds with water of crystallisation; (4) that the physical properties of solutions, and especially their specific gravities (a property which can be very accurately determined), vary with a change in composition, and in such a manner as would be required by the formation of one or more definite but dissociating compounds. Thus, for example, on adding water to fuming sulphuric acid its density is observed to decrease until it attains the definite composition H_2SO_4, or $SO_3 + H_2O$, when the specific gravity increases, although on further diluting with water it again falls. Moreover (Mendeléeff, *The Investigation of Aqueous Solutions from their Specific Gravities*, 1887), the increase in specific gravity (ds) varies in all well-known solutions with the proportion of the substance dissolved (dp), and this dependence can be expressed by a formula ($\frac{ds}{dp} = A + Bp$) between the limits of definite compounds whose existence in solutions must be admitted. Thus, for instance, from H_2SO_4 to $H_2SO_4 + H_2O$ (both of which substances exist as definite compounds in a free state), the fraction $\frac{ds}{dp} = 0{\cdot}0729 - 0{\cdot}000749p$ (where p is the percentage amount of H_2SO_4 present). For alcohol, C_2H_6O, whose aqueous solutions have been more accurately investigated than all others, the definite compound, $C_2H_6O + 3H_2O$, and others must be acknowledged in its solutions.

The two aspects of solution above mentioned and the hypotheses which have up to the present time been applied to the examination of solutions, although they have somewhat different starting-points, will doubtless lead to a general theory of solutions, because the same general laws govern both physical and chemical phenomena, inasmuch as the properties and motions of molecules, which determine physical properties, depend on the motions and properties of atoms, which determine chemical reactions. For details of the questions dealing with theories of solution, recourse must now be had to special memoirs and to works on physical chemistry; for this subject forms one of special interest at the present epoch of the development of our science. In working out chiefly the chemical side of solutions, I consider it to be necessary to reconcile the two aspects of the question: this seems to me to be all the more possible, as the physical side is limited to dilute solutions only, whilst the chemical side deals mainly with strong solutions (see Note 49 and Chap. VII.)

quired for saturation will remain in the liquid state.[20] The relation between water and substances dissolved in it is similar. More than a definite quantity of a substance cannot, at a certain temperature, dissolve in a given quantity of water; the excess does not unite with the water. Just as air or a gas becomes saturated with vapour, so water becomes saturated with a substance dissolved in it. If an excess of a substance be added to water which is already saturated with it, it will remain in its original state, and will not diffuse through the water. The quantity of a substance (by volume with gases, or by weight with solids and liquids) which is capable of saturating 100 parts of water is called its **coefficient of solubility** or **its solubility**. In 100 grams of water at 15°, there can be dissolved not more than 35·86 grams of common salt. Consequently its solubility at 15° is equal to 35·86.[21]

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[20] In the case of limited solution of liquids in liquids **the difference between the solvent and the substance dissolved** is clearly seen. The former (that is, the solvent) may be added in an unlimited quantity, and yet the solution obtained will always be uniform, whilst only a definite saturating proportion of the substance dissolved can be taken. Let us take water and ordinary (sulphuric) ether. On shaking the ether with the water, it will be remarked that a portion of it dissolves in the water. If the ether be taken in such a quantity that it saturates the water and a portion of it remains undissolved, then this remaining portion will act as a solvent, and water will become diffused through it and form a saturated solution of water in the ether. Thus two saturated solutions will be obtained. One solution will contain ether dissolved in water, and the other, water dissolved in ether. These two solutions will arrange themselves in two layers, according to their density, the ethereal solution of water being at the top. If the upper ethereal solution be poured off from the aqueous solution, any quantity of ether may be added to it: this shows that the dissolving substance is ether. If water be added to it, it will no longer be dissolved in it, indicating that water saturates the ether; so that here water is the substance dissolved. If we deal in the same way with the lower layer, we shall find that water is the solvent and ether the substance dissolved. By taking different amounts of ether and water, the degree of solubility of ether in water, and that of water in ether, may be easily determined. Water dissolves approximately $\frac{1}{10}$ of its volume of ether, and ether dissolves a very small quantity of water. According to Schuncke (1894) the ethereal solution contains 2·7 per cent. of water at 10°–20°, while the aqueous solution contains 9·6 per cent. of ether at 10°, and 7·5 per cent at 20°. Let us now imagine that the liquid poured in dissolves a considerable amount of water, and that water dissolves a considerable amount of the liquid. Two layers could not be formed, because the saturated solutions would resemble each other, and would therefore intermix in all proportions, as occurs with alcohol and water. This is, consequently, a case of a phenomenon where two liquids present considerable coefficients of solubility in each other, but where it is impossible to say what these coefficients are because it is impossible to obtain a saturated solution.

[21] The solubility, or coefficient of solubility, of a substance may be determined by various methods. Either a solution is expressly prepared at a given temperature, and using an evident excess of the soluble substance and the quantity of water and of the substance dissolved in it determined by evaporation, desiccation, or other means; or else, as is done with gases, definite quantities of water and of the soluble substance are taken, the amount of the latter remaining undissolved being then determined. So that the solubility is always determined by the presence of an excess of the soluble substance, i.e., it corresponds with a state of equilibrium between the solution, taken in a known quantity (which is one 'phase' or homogeneous substance), and the soluble body (the

It is most important to turn attention to the **existence of the solid insoluble substances of nature**, because on them depends the shape of

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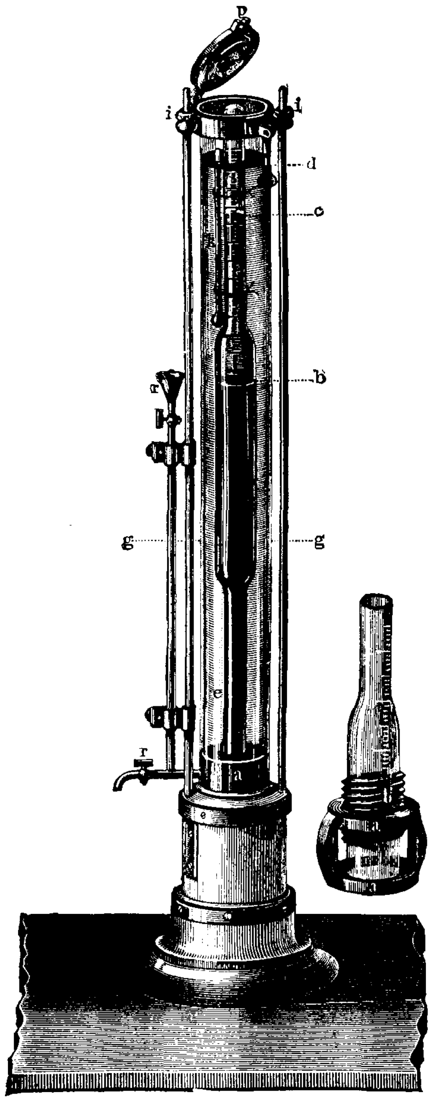

FIG. 16.—Bunsen's absorptiometer. Apparatus for determining the solubility of gases in liquids.

other 'phase,' according to the prevalent nomenclature regarding the equilibrium of substances in contact). The theory of solutions and the practical methods of determining the solubility of substances in water and other liquids must be sought for in works on physical chemistry, as this subject now forms a considerable section of itself, and cannot be treated in sufficient detail in the present work, which is chiefly devoted to the study of the chemical elements.

The following description of the mode of determining the solubility of gases must therefore be regarded as an individual example to give the student some idea of the methods practised in the complicated subject of solutions.

The solubility of a gas in water is determined by means of an apparatus called an **absorptiometer** (fig. 16). It consists of an iron stand *f*, on which rests an indiarubber ring. A wide glass tube is placed on this ring, and is pressed down on it by the ring *h* and the screws *i i*. The tube is thus *firmly fixed on the stand.* A cock *r*, communicating with a funnel *r*, passes into the lower part of the stand. Mercury can be poured into the wide tube through this funnel, which is therefore made of steel, as copper would be affected by the mercury. The upper ring *h* is furnished with a cover *p*, which can be firmly pressed down on to the wide tube, and hermetically closes it by means of an indiarubber ring. The tube *r r* can be raised at will, and so by pouring mercury into the funnel the height of the column of mercury, which produces a pressure inside the apparatus, can be increased. The pressure can also be diminished at will, by letting mercury out

the substances of the earth's surface, and of plants and animals. There is so much water on the earth's surface that were the surface of

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through the cock *r*. A graduated tube *e*, containing mercury and also the gas and liquid to be experimented on, is placed inside the wide tube. This tube is graduated in millimetres for determining the pressure, and it is calibrated in volumes, so that the number of volumes occupied by the gas and liquid dissolving it can be readily calculated. This tube can also be easily removed from the apparatus. The lower portion of this tube when removed from the apparatus is shown to the right of the figure. It will be observed that its lower end is furnished with a male screw *b*, fitting into a nut *a*. The lower surface of the nut *a* is covered with indiarubber, so that on screwing up the tube its lower end presses upon the indiarubber, and thus hermetically closes the whole tube, for its upper end is fused up. The nut *a* is furnished with arms *c c*, and in the stand *f* there are corresponding spaces, so that when the screwed-up internal tube is fixed into the stand *f*, the arms *c c* fix into these spaces, thus enabling the internal tube to be fixed on to the stand *f*. When the internal tube is fixed in the stand, the wide tube is placed in position, and mercury and water are poured into the space between the two tubes, communication being then opened between the inside of the tube *e* and the mercury between the interior and exterior tubes. This is done by either revolving the inner tube *e*, or by a key turning the nut about the bottom part of *f*. The tube *e* is filled with gas and water as follows: the tube is removed from the apparatus, filled with mercury, and the gas to be experimented on is passed into it (over a pneumatic trough). The volume of the gas is measured, the temperature and pressure determined, and the volume it would occupy at 0° and 760 mm. calculated. A known volume of water is then introduced into the tube. The water must be previously boiled, so as to be quite freed from air in solution. The tube is then closed by screwing it down on to the india-rubber on the nut. It is then fixed on to the stand *f*, mercury and water are poured into the intervening space between it and the exterior tube, which is then screwed up and closed by the cover *p*, and the whole apparatus left at rest for some time, so that the tube *e* and the gas in it may attain the same temperature as that of the surrounding water, which is marked by a thermometer *k* tied to the tube *e*. The inner tube is then again closed by turning it in the nut, the cover *p* again shut, and the whole apparatus shaken in order that the gas in the tube *e* may completely saturate the water. After several shakings, the tube *e* is again opened by turning it in the nut, and the apparatus left at rest for a certain time; it is then closed and again shaken, this being repeated until the volume of the gas does not diminish after a fresh shaking—that is, until saturation ensues. Observations are then made of the temperature, the height of the mercury in the inner tube, and the level of the water in it, and also of the level of the mercury and water in the outer tube. All these data are necessary in order to calculate the pressure under which the solution of the gas takes place, and what volume of gas remains undissolved, and also the quantity of water which serves as the solvent. By varying the temperature of the surrounding water, the amounts of gas dissolved at different temperatures may be determined. By means of this apparatus Bunsen, Carius, and many others determined the solubilities of various gases in water, alcohol, and certain other liquids. If in a determination of this kind it is found that *n* cubic centimetres of water at a pressure *h* dissolve *m* cubic centimetres of a given gas, measured at 0° and 760 mm., when the temperature at which solution took place was $t°$, then it follows that at the temperature *t* **the coefficient of solubility of the gas** in 1 volume of the liquid will be equal to $\frac{m}{n} \times \frac{760}{h}$.

This formula is very clearly understood from the fact that the coefficient of solubility of a gas is that quantity (by volume or weight) measured at 0° and 760 mm., which is absorbed at a pressure of 760 mm. by 1 part or 100 parts of a liquid. If *n* cubic centimetres of water absorb *m* cubic centimetres of a gas, then one cubic centimetre absorbs $\frac{m}{n}$. If $\frac{m}{n}$ c.c. of a gas are absorbed under a pressure of *h* mm., then, according to the law of substances formed of soluble matters it would constantly change, and, however substantial their forms might be, mountains, river banks and sea shores, plants and animals, or the habitations and coverings of men, could not exist for any length of time.[22]

Substances which are easily soluble in water bear a certain resemblance to it. Thus sugar and salt in many of their superficial features remind one of ice. Metals, which are not soluble in water, have no points in common with it, whilst on the other hand they dissolve each other in a molten state, forming alloys, just as oily substances dissolve each other; for example, tallow is soluble in petroleum and in olive oil, although they are all insoluble in water. From this it is evident that the **analogy between the substances forming a solution** is of some

importance, and as aqueous and all other solutions are liquids, there is good reason to believe that in the process of solution solid and gaseous substances change physically and pass into a liquid state. These considerations elucidate many points of solution—as, for instance, the variation of the coefficient of solubility with the temperature and the evolution or absorption of heat in the formation of solutions.

The solubility—that is, the quantity of a substance necessary for saturation—**varies with the temperature**, and, further, with a rise in temperature the solubility of solid substances generally increases, whilst that of gases decreases: this might be expected, as solid substances by heating, and gases by cooling, approach to a liquid or dissolved state.[23] A graphic method is often employed to express the variation of solubility with temperature. On the axis of abscissæ or on a horizontal line, temperatures are marked out and perpendiculars are raised corresponding with each temperature and having lengths determined by the solubilities of the salt at the various temperatures—expressing, for instance, one part by weight of a salt in 100 parts of water by one unit of length, such as a millimetre. By joining the summits of the perpendiculars, a curve is obtained which expresses the degree of solubility at different temperatures. For solids, the curve is generally an ascending one—i.e., it recedes from the horizontal line as the temperature rises. These curves clearly show by their inclination the degree of rapidity of increase in solubility with the temperature. Having determined several points of a curve—that is, having made determinations of the solubilities for several temperatures—the solubilities at intermediate temperatures may be determined from the form of the curve so obtained: in this way the empirical law of solubility may be examined.[23a]

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the variation of solubility of a gas with the pressure, there would be dissolved, under a pressure of 760 mm., a quantity standing in the same ratio to $\frac{m}{n}$ as 760 : h. In determining the residual volume or weight of gas, its moisture (note 1) must be taken into consideration. L. Winkler (1888–1902) of Buda-Pesth determined the solubility of gases by a more perfect method.

The solubility (expressed in volumes) of many gases in water is given in note 30. Below are given the numbers of grams of several substances saturating 100 grams of water—that is, their coefficients of solubility by weight at three different temperatures under a pressure of 760 mm.

	—	At 0°	At 20°	At 100°
Gases	Oxygen, O_2	$\frac{6}{1000}$	$\frac{4}{1000}$	—
	Carbonic anhydride, CO_2	$\frac{35}{100}$	$\frac{18}{100}$	—
	Ammonia, NH_3	90·0	51·8	7·3
Liquids	Phenol, C_6H_6O	4·9	5·2	∞
	Amyl alcohol, $C_5H_{12}O$	4·4	2·9	—
	Sulphuric acid, H_2SO_4	∞	∞	∞
Solids	Gypsum, $CaSO_4$, $2H_2O$	$\frac{1}{5}$	$\frac{1}{4}$	$\frac{1}{5}$
	Alum, $AlKS_2O_8$, $12H_2O$	3·3	15·4	357·5
	Anhydrous sodium sulphate, Na_2SO_4	4·5	20	43
	Common salt, NaCl	35·7	36·0	39·7
	Nitre, KNO_3	13·3	31·7	246·0

Sometimes a substance is so slightly soluble that it may be considered as insoluble. Many such substances are met with both in solids and liquids, and such a gas as oxygen, although it does dissolve, does so in so small a proportion by weight that it might be considered as zero did not the solubility of even so little oxygen play an important part in nature (as in the respiration of fishes), and were not an infinitesimal quantity of a gas by weight so easily measured by volume. The sign ∞, which stands on a line with sulphuric acid in the above table, indicates that it intermixes with water in all proportions. This is the case with many liquids.

[22] Just as the existence must be admitted of substances which are completely undecomposable (chemically) at the ordinary temperature—and of substances which are entirely non-volatile at such a temperature (as wood and gold), although capable of decomposing (wood) or volatilising (gold) at a higher temperature—so also the existence must be admitted of substances which are totally insoluble in water. It must be remarked, besides, that water in a number of cases does not dissolve a substance as such, but acts on it chemically and forms a soluble substance. Thus glass and many rocks, especially if taken as powder, are chemically changed by water, but are not directly soluble in it.

[23] Beilby (1883) experimented on paraffin, and found that one litre of solid paraffin at 21° weighed 874 grams, and in the liquid state at its melting-point, 38°, 783 grams; at 49°, 775 grams, and at 60°, 767 grams; hence the weight of a litre of liquefied paraffin would be 795·4 grams at 21°, supposing that it could remain liquid at that temperature. By dissolving solid paraffin in lubricating oil at 21°, Beilby found that 795·6 grams occupy one cubic decimetre, from which he concluded that the solution contained liquefied paraffin.

[23a] Gay-Lussac was the first to have recourse to such a graphic method of expressing solubility, and he considered, in accordance with the general opinion, that by joining up the summits of the ordinates in one harmonious curve it is possible to express the entire change of solubility with the temperature. Now, there are many reasons for doubting the accuracy of such an admission, for there are undoubtedly critical points in curves of solubility (for example, of sodium sulphate, as shown further on), and it may be that definite compounds of dissolved substances with water, in decomposing within known limits of temperature, give critical points more often than would be imagined; it may even be, indeed, that, instead of a continuous curve, solubility should be expressed—if not always, then not infrequently—by straight or broken lines. The modern theory of phases (which is treated more fully in *Physical Chemistry*; see also Chap. XXIV., note 9a) fully explains such breaks in the curve of solubility, which occur when the soluble substance and water are able to form crystals of various compositions (different crystallohydrates) and crystalline forms (see note 24). According to Ditte, the solubility of

The results of research have shown that the solubility of certain salts—as, for example, common table salt—varies comparatively little with the temperature, whilst for other substances the solubility increases by equal amounts for equal increments of temperature. Thus, for example, for the saturation of 100 parts of water by potassium chloride there is required 29·2 parts of the salt at 0°, 34·7 at 20°, 40·2 at 40°, 45·7 at 60°, and so on, the solubility increasing by 2·75 parts by weight of the salt for every 10°. Therefore the solubility of the potassium chloride in water may be expressed by a simple equation: $a=29{\cdot}2+0{\cdot}275t$, where a represents the solubility at $t°$. For other salts more complicated equations are required. For example, for nitre: $a=13{\cdot}3+0{\cdot}574t+0{\cdot}01717t^2+0{\cdot}0000036t^3$, which shows that when $t=0°$, $a=13{\cdot}3$; when $t=10°$, $a=20{\cdot}8$, and when $t=100°$, $a=246{\cdot}0$.

The variation in the solubility of salts, &c., with a rise or fall of temperature is often taken advantage of, especially in technical work, for the separation of salts mixed with each other. Thus a mixture of potassium and sodium chlorides (a mixture met with in nature at Stassfurt) is separated by subjecting a saturated solution alternately to boiling (evaporation) and cooling. The sodium chloride separates out in proportion to the amount of water expelled from the solution by

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sodium nitrate, $NaNO_3$, per 100 parts of water is expressed by the following figures:—

0°	4°	10°	15°	21°	29°	36°	51°	68°
66·7	71·0	76·3	80·6	85·7	92·9	99·4	113·6	125·1

In my opinion (1881) these data should be expressed with exactitude by a straight line, $67{\cdot}5+0{\cdot}87t$. The experiments made by Ditte showed that all saturated solutions between 0° and $-15{\cdot}7°$ have such a composition, and that at the latter temperature the solution completely solidifies into one homogeneous whole whose composition is approximately $NaNO$ $,7H_2O$. Thus the solubility of sodium nitrate is expressed by a broken straight line. Étard (1888) discovered a similar phenomenon in many of the sulphates. Brandes, in 1830, showed a diminution in solubility below 100° for manganese sulphate. The percentage by weight (i.e., per 100 parts of the solution, and not of water) of saturated ferrous sulphate ($FeSO_4$) solution from $-2°$ to $+65°$ is given by $13{\cdot}5+0{\cdot}3784t$—that is, the solubility of the salt increases. From 65° to 98° the solubility remains constant, and from 98° to 150° it falls and is expressed by $104{\cdot}35-0{\cdot}6685t$. Hence, at about $+156°$ the solubility should become zero; and this has been confirmed by experiment. I find that Étard's formula gives 38·1 per cent. of salt at 65° and 38·8 per cent. at 92°, and this maximum amount of salt in solution corresponds very nearly with the composition $FeSO_4,14H_2O$, which requires 37·6 per cent. From what has been said, it is evident that the data concerning solubility require a new method of investigation, which should take into account the entire scale of solubility—from the formation of completely solidified solutions (cryohydrates, which we shall speak of presently) to either the separation of salts from their solutions, should this take place at a higher temperature (for manganese and cadmium sulphates there is complete separation, according to Étard), or the attainment of a constant solubility (for potassium sulphate the solubility, according to Étard, remains constant from 163° to 220° and equals 24·9 per cent.). The following are Étard's data for several salts (parts of salt per 100 parts of solution). KNO_3: up to 70°, $24{\cdot}0+0{\cdot}7100t$; from 70° to 125°, $59{\cdot}5+0{\cdot}3727t$; from 125° to 338°, $80{\cdot}0+0{\cdot}0938t$. For $NaNO$: from 5° to 64°, $39{\cdot}0+0{\cdot}2825t$; from 64° to 313°, $58{\cdot}5+0{\cdot}1666t$. For NaCl: from 0° to 250°, $25{\cdot}8+0{\cdot}0248t$ (see Chap. XII., note 4, &c.)

boiling, and is removed, whilst the potassium chloride separates out on cooling, as the solubility of this salt decreases rapidly as the temperature falls. Nitre, sugar, and many other soluble substances are purified (refined) in a similar manner.

Although in the majority of cases the solubility of solids increases with rise of temperature, yet there are some solid substances whose solubilities decrease on heating. A particularly instructive example is found in the case of Glauber's salt, or sodium sulphate. If this salt be taken after ignition (deprived of its water of crystallisation), its solubility in 100 parts of water varies with the temperature in the following manner: at 0°, 5 parts of the salt form a saturated solution; at 20°, 20 parts of the salt, while at 33° more than 50 parts are required. The solubility, as will be seen, increases with the temperature, but above 33° it suddenly diminishes, and at a temperature of 40° less than 50 parts, at 60° only 45 parts, and at 100° about 43 parts, dissolve in 100 parts of water. This phenomenon may be traced to the following facts: First, this salt forms various compounds with water, as will be afterwards explained; secondly, at 33° the compound $Na_2SO_4+10H_2O$, formed from the solution at lower temperatures, melts; and thirdly, on evaporation at a temperature above 33° an anhydrous salt, Na_2SO_4, separates out, while at lower temperatures the anhydrous salt converts the water into a solid state without itself passing into solution (see Chap. XII., note 8). It will be seen from this example how complicated such an apparently simple phenomenon as solution really is; and all data concerning solutions lead to the same conclusion.[24] This complexity becomes evident also

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[24] First of all we must remember that saturation of a solution can only refer to the substance which is present in the solution, and not to that which was originally taken for making the solution. Thus, for instance, if a given salt occurs in two crystalline forms A and B (that is, it is dimorphous), stable within certain limits of temperature, these will possess different solubilities. Suppose A to be more soluble than B. A saturated solution of B will be able to dissolve a further amount of A until saturation be reached. If we now pour off this solution from the excess of A, and add a further quantity of B, then a portion of the salt will separate out from the solution in the form B, although the same solution, if evaporated in the presence of an excess of A, would deposit the variety A; and since many anhydrous salts deposit solid, frequently dimorphous, compounds with water from their solutions, it is evident that the different phenomena concerned in saturation may be most complex (see, for instance, Chap. XIV., note 50, for $CaCl_2$; Chap. XXII., note 23, for Fe_2Cl_6). As an instance of this, we may take the solubility of sodium carbonate calculated as parts of anhydrous salt per 100 parts of water:

Solid phase	At 0°	At 20°
$Na_2CO_3,10H_2O$	7	22
$Na_2CO_3,7H_2O$ – cubic	20	39
$Na_2CO_3,7H_2O$ – rhombic	31	46

The solubility of the anhydrous salt, Na_2CO , cannot be given, because at these

on investigating the **heat of solution.** If solution consisted of a physical change only, then in the solution of gases there would be evolved—and in the solution of solids there would be absorbed—just that amount of heat corresponding with the change of state; but in reality a larger amount of heat is always evolved in the solution of gases, and less is absorbed in the solution of solids than is required by theory, owing to the fact that in the process of solution chemical combination takes place, accompanied by an evolution of heat. Seventeen grams of ammonia (this weight corresponds with its formula NH_3), in passing from a gaseous to a liquid state, evolve 4,400 units of heat (latent heat), that is, the quantity of heat necessary to raise the temperature of 4,400 grams of water 1°. The same quantity of ammonia, in dissolving in an excess of water, evolves twice as much heat—namely, 8,800 units—showing that the combination with water is accompanied by the evolution of 4,400 units of heat. Further, the chief part of this heat is generated when the gas dissolves in small quantities of water, so that 17 grams of ammonia, in dissolving in 18 grams of water (this weight corresponds with its composition H_2O), evolve 7,535 units of heat, and therefore the formation of the solution NH_3+H_2O evolves 3,135 units of heat beyond that due to the change of state. Since in the solution of gases the heats of liquefaction (of physical change of state) and of chemical combination with water are both positive (+), it follows that in the *solution of gases* in water *heat is* always *evolved.* This phenomenon is different in the solution of solid substances, because the passage from a solid to a liquid state is accompanied by an absorption of heat (−heat), whilst their chemical combination with water is accompanied by an evolution of heat (+heat); consequently their sum may either be a cooling effect, when the positive (chemical) portion of the heat is less than the negative (physical), or it may be, on the contrary, a heating effect. This is actually found to be the case. 124 grams of sodium thiosulphate (employed in photography), $Na_2S_2O_3,5H_2O$, in melting (at 48°) absorb 9,700 units of heat, but in dissolving in a large quantity of water at the ordinary temperature they absorb 5,700 units of heat, which shows that, notwithstanding the cooling effect observed in the process of solution, an evolution of heat (about +4,000 units) takes place in the act of the chemical combination of the salt with water.[25] But in most cases

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temperatures it forms a solid crystallohydrate, and *if brought into solution in excess, it precipitates a portion of the salt from the solution* in the form of the solid phase of the crystallohydrate (compare Chap. XII., note 8).

[25] The latent heat of fusion is determined at the temperature of fusion, whilst solution takes place at the ordinary temperature; and one must think that at this temperature the latent heat would be different, just as the latent heat of evaporation varies with

solid substances in dissolving in water evolve heat, notwithstanding the passage into a liquid state, indicating so considerable an evolution of (+) heat in the act of combination with water as to exceed the absorption of (−) heat dependent on the passage into a liquid. Thus, for instance, calcium chloride, $CaCl_2$, magnesium sulphate, $MgSO_4$, and many other salts evolve heat in dissolving; for example, 60 grams of magnesium sulphate evolve about 10,000 units of heat. Therefore, *in the solution of solids or liquids in water either a cooling*[26] *or a*

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the temperature (see note 11). Besides which, in the process of solution, disintegration of the particles of both the solvent and the substance dissolved takes place; a change which in its mechanical aspect resembles evaporation, and must therefore consume much heat. The heat emitted in the solution of a solid must therefore be considered (Personne) as composed of three factors: (1) positive, the effect of combination; (2) negative, the effect of transference into a liquid state; and (3) negative, the effect of disintegration. In the solution of a liquid by a liquid the second factor is removed; and therefore if the heat evolved in combination is greater than that absorbed in disintegration a heating effect is observed, and in the reverse case a cooling effect; and, indeed, sulphuric acid, alcohol, and many other liquids evolve heat in dissolving in each other. But the solution of chloroform in carbon bisulphide (Bussy and Binget), or of phenol (or aniline) in water (Alexéeff) produces cold. In the solution of a small quantity of water in acetic acid (Abasheff), or hydrocyanic acid (Bussy and Binget), or amyl alcohol (Alexéeff), cold is produced, whilst when these substances are dissolved in an excess of water heat is evolved.

The relation existing between the solubility of solid bodies and the heat and temperature of fusion and solution has been studied by many investigators, and more especially (1893) by Schröder, who states that in the solution of a solid body in a solvent which does not act chemically upon it a very simple process takes place, which differs but little from the intermixture of two gases which do not react chemically upon each other. To such a case the following relation between the heat of solution Q and the heat of fusion p is applicable: $\frac{p}{T_0}=\frac{Q}{T}=$ constant, where T_0 and T are the absolute (from −273°) temperatures of fusion and saturation. In the case of naphthalene, for instance, the calculated and observed magnitudes of the heat of solution differ but slightly from each other.

The fullest information concerning the solution of liquids in liquids has been obtained by W. T. Alexéeff (1883–1885); but these data are, however, far from being sufficient to solve the mass of problems respecting this subject. He showed that the solubility of phenol, C_6H_6O, in water, and the converse, is limited up to 70°, whilst above this temperature the two intermix in all proportions. This is seen from the following figures, where p is the percentage amount of phenol and t the temperature at which the solution becomes turbid—that is, that at which it is saturated:—

$p=7{\cdot}12$	10·20	15·31	26·15	28·55	36·70	48·86	61·15	71·97
$t=1°$	45°	60°	67°	67°	67°	65°	53°	20°

It is exactly the same with the solutions of benzene, aniline, and other substances in molten sulphur. Alexéeff discovered a similar complete intermixture for secondary butyl alcohol and water at about 107°; at lower temperatures the solubility is not only limited, but between 50° and 70° it is at its minimum, both for solutions of the alcohol in water and for water in the alcohol; and at a temperature of 5° both solutions exhibit a fresh change in their scale of solubility, so that a solution of the alcohol in water, which is saturated between 5° and 40°, will become turbid when heated to 60°. In the solution of liquids in liquids Alexéeff observed a lowering in temperature (an absorption of heat) and an absence of change in specific heat (contrary to the calculated results for the mixture) much more frequently than had been done by previous observers.

[26] The cooling effect produced in the solution of solids (and also in the expansion of gases and in evaporation) is applied to the **production of low temperatures.** Ammonium

heating[27] *effect* is produced, according to the difference of the reacting affinities. When they are considerable—that is, when water is with difficulty separated from the resultant solution, and only with a rise of temperature—then much heat is evolved in the process of solution, just as in many reactions of direct combination, and therefore a considerable heating of the solution is observed. Of such a kind, for instance, are the solutions of sulphuric acid (oil of vitriol, H_2SO_4), and of caustic soda (NaHO), &c., in water.[28]

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nitrate is very often used for this purpose; in dissolving in water it absorbs 77 units of heat for each part by weight. On evaporating the solution thus formed, the solid salt is re-obtained. The application of the different **freezing mixtures** is based on the same principle. Snow or broken ice frequently enters into the composition of these mixtures, advantage being taken of its latent heat of fusion in order to obtain the lowest possible temperature (without altering the pressure or employing heat, as in other methods of obtaining a low temperature). For laboratory work recourse is most often had to a mixture of three parts of snow and one part of common salt, which causes the temperature to fall from 0° to −21° C. Potassium thiocyanate, KCNS, mixed with water (¾ by weight of the salt) gives a still lower temperature. By mixing ten parts of crystallised calcium chloride, $CaCl_2,6H_2O$, with seven parts of snow, the temperature may even fall from 0° to −55°.

[27] The heat which is evolved in solution, or even in the dilution of solutions, is also sometimes made use of in practice. Thus caustic soda (NaHO), in dissolving or on the addition of water to a strong solution of it, evolves so much heat that it can replace fuel. In a steam boiler, which has been previously heated to the boiling-point, another boiler is placed containing caustic soda, and the exhaust steam is made to pass through the latter; the formation of steam then goes on for a fairly long time without any further heating. Norton makes use of this for smokeless street locomotives.

[28] The temperatures obtained by mixing monohydrated sulphuric acid, H_2SO_4, with

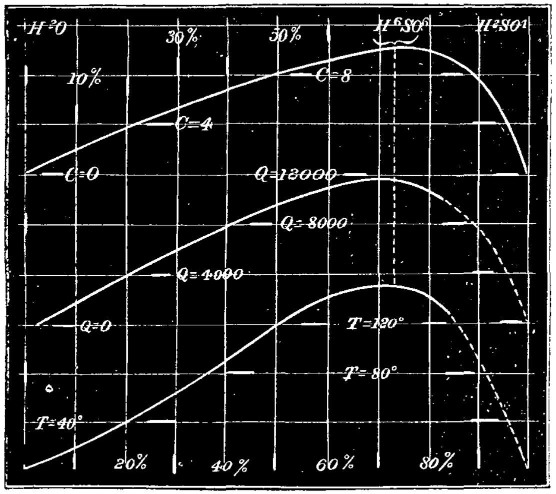

Fig. 17.—Curves expressing the contraction, quantity of heat, and rise of temperature produced by mixing sulphuric acid with water. Percentage of H_2SO_4 is given along the axis of abscissæ.

Solution is a reversible reaction; for, if the water be expelled from a solution, the substance originally taken is obtained again. But it must be borne in mind that the expulsion of the water taken for solution is not always accomplished with equal facility, because water has different degrees of chemical affinity for the substance dissolved. Thus, if a solution of sulphuric acid, which mixes with water in all proportions, be heated, it will be found that very varying temperatures are required to expel the water. When in a large excess, water is given off at a temperature slightly above 100°; but if it be in only a small proportion, there is such an affinity between it and the sulphuric acid that at 120°, 150°, 200°, and even at 300°, water is still retained by the sulphuric acid. The bond between the remaining quantity of water and the sulphuric acid is evidently stronger than that between the sulphuric acid and the excess of water. The force acting in solutions is consequently of different intensity, starting from so feeble an attraction that the properties of water—as, for instance, its power of evaporation—are but very little changed, and ending with strong attraction between the water and the substance dissolved in or chemically combined with it.

The solubility of gases, which is usually measured by the volume of gas[29] (at 0° and 760 mm. pressure) per 100 volumes of water, varies

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different quantities of water are shown on the lowest curve in fig. 17, the relative proportions of the two substances being expressed in percentages by weight along the horizontal axis. The greatest rise of temperature is 149°. It corresponds with the greatest evolution of heat (given on the middle curve) for a definite volume (100 c.c.) of the solution produced. The top curve expresses the degree of contraction corresponding with 100 volumes of the solution produced. The greatest contraction, as also the greatest rise of temperature, corresponds with the formation of a trihydrate, $H_2SO_4,2H_2O$ (containing 73·1 per cent. H_2SO_4). Similar relations probably hold for other solutions, although all the phenomena (contraction, evolution of heat, and rise of temperature) are very complex, and are dependent on many circumstances. One would think, however, judging from the above examples, that all other influences are feebler in their action than chemical attraction, especially when this is so considerable as it is between sulphuric acid and water.

[29] If a volume of gas v be measured under a pressure of h mm. of mercury (at 0°) and at a temperature t° Centigrade, then, according to the combined laws of Boyle, Mariotte, and Gay-Lussac, its volume at 0° and 760 mm. will equal the product of v into h divided by the product of 760 into $1+at$, where a is the coefficient of expansion of gases, which is equal to 0·00360. The weight of the gas will be equal to its volume at 0° and 760 mm., multiplied by its density referred to air and by the weight of one volume of air at 0° and 760 mm., the weight of a litre of air under these conditions being 1·293 gram. If the density of the gas be given in relation to hydrogen, this must be divided by 14·4 to make it refer to air. If the gas be measured when saturated with aqueous vapour, then it must be reduced to the volume and weight of the gas when dry, according to the rules given in note 1. If the pressure be determined by a column of mercury having a temperature t°, then by dividing the height of the column by $1+0·00018t$ the corresponding height at 0° is obtained. If the gas be enclosed in a tube in which a liquid stands above the level of the mercury, the height of the column of the

not only with the nature of the gas (and also of the solvent), and with the temperature, but also with the pressure, because gases themselves change their volume considerably with change of pressure. As might be expected, (1) gases which are easily liquefied (by pressure and cold) are more soluble than those which are liquefied only with difficulty. Thus, in 100 volumes of water only two volumes of hydrogen or nitrogen dissolve at 0° and 760 mm., three volumes of carbonic oxide, four volumes of oxygen, &c., for these are gases which are liquefied with difficulty; whilst there dissolve 180 volumes of carbonic anhydride, 130 of nitrous oxide, and 437 of sulphurous anhydride, for these are gases which are fairly easily liquefied. (2) The solubility of a gas is diminished by heating, this being easily intelligible from what has been said previously—the elasticity of a gas becomes greater, that is, it is removed further from a liquid state. Thus 100 volumes of water at 0° dissolve 2·5 volumes of air, but at 20° only 1·7 volume. For this reason cold water, when brought into a warm room, parts with a portion of the gas dissolved in it.[30] (3) The quantity of the gas

dissolved varies directly with the pressure. This rule is called the **law of Henry and Dalton**, and is applicable to those gases which are slightly soluble in water. Therefore in a vacuum a gas becomes separated from its solution in water, and water saturated with a gas under great pressure parts with it if the pressure is diminished. For instance, many mineral springs are saturated underground with carbonic anhydride under the great pressure of the column of water above them. On coming to the surface, the water of these springs boils and foams on giving up the excess of dissolved gas. Sparkling wines and aërated waters are saturated under pressure with the same gas. They retain the gas so long as they are kept in a well-corked vessel. When the cork is removed, and the liquid comes into contact with air at a lower pressure, part of the gas, unable to remain in solution at a lower pressure, is separated as froth with the hissing sound familiar to all. It must be remarked that the law of Henry and Dalton belongs to the class of '*approximate laws*, like the laws of gases (Gay-Lussac's and Mariotte's)—that is, it expresses only a portion of a complex phenomenon or the limit towards which the phenomenon tends. The matter is rendered complicated by the influence exerted by the degree of solubility and by the affinity of the dissolved gas for water. Gases which are little soluble—for instance, hydrogen, oxygen, and nitrogen—follow the law of Henry and Dalton the most closely. Carbonic anhydride exhibits a decided deviation from the law (Wroblewski, 1882); at 0° a cubic centimetre of water absorbs 1·8 cubic centimetre of the gas under a pressure of one atmosphere; under 10 atmospheres, 16 cubic centimetres (and not 18, as it should be according to the law); under 20 atmospheres, 26·6 cubic centimetres (instead of 36); and under 30 atmospheres, 33·7 cubic centimetres.[31] However, as is shown by the researches of Sechenoff, the absorption of carbonic anhydride within certain limits of change of pressure, and at the ordinary temperature, by water —and even by solutions of salts which are not chemically changed by

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liquid being H and its density D, then the gas will be under a pressure equal to the barometric pressure less $\frac{HD}{13{\cdot}59}$, 13·59 being the density of mercury. By these methods the **quantity of a gas** is determined, and its observed volume reduced to normal conditions or to parts by weight. The physical data concerning vapours and gases must be continually kept in sight in dealing with and measuring gases. The student must become perfectly familiar with the calculations relating to gases.

[30] According to Bunsen, Winkler, Timoféeff, and others, 100 vols. of water under a pressure of one atmosphere absorb the following volumes of gas (measured at 0° and 760 mm.):—

	1	2	3	4	5	6	7	8	9	10	11
0°	4·82	2·35	2·15	179·7	3·54	130·5	437·1	688·6	5·4	104960	7·38
20°	3·10	1·54	1·83	90·1	2·32	67·0	290·5	362·2	3·5	65400	4·71

1, oxygen; 2, nitrogen; 3, hydrogen; 4, carbonic anhydride; 5, carbonic oxide; 6, nitrous oxide; 7, hydrogen sulphide; 8, sulphurous anhydride; 9, marsh gas; 10, ammonia; 11, nitric oxide. The decrease of solubility with rise of temperature varies for different gases and increases with the molecular weight of the gas. It is shown by calculation that this decrease varies (Winkler at Buda-Pesth) as the cube root of the molecular weight of the gas. This is seen from the following table:

Decrease of solubility per 20° in per cent.		Cube root of molecular weight	Ratio between decrease and cube root of mol. wt.
H_2	15·32	1·259	12·17
N_2	34·33	3·037	11·30
CO	34·44	3·037	11·34
NO	36·24	3·107	11·66
O_2	36·55	3·175	11·51

The decrease in the coefficient of absorption with rise of temperature must be connected with a change in the physical properties of the water. Winkler (1891) observed a certain relation between the internal friction and the coefficient of absorption at various temperatures.

[31] These figures show that the coefficient of solubility decreases with an increase of pressure, notwithstanding that the carbonic anhydride approaches more nearly to a liquid state. As a matter of fact, liquefied carbonic anhydride does not mix with water. This indicates, in the first place, that solution does not consist in liquefaction, and in the second place that the solubility of a substance is determined by a peculiar attraction of water for the substance dissolving. Wroblewski even considered it possible to admit that a dissolved gas retains its properties as a gas. This he deduced from experiments showing that the rate of diffusion of gases in a solvent is, for gases of different densities, inversely proportional to the square roots of their densities, as is the case with the velocities of gaseous molecules (see note 34). Wroblewski demonstrated the affinity of water, H_2O, for carbonic anhydride, CO_2, by showing that on expanding moist carbonic anhydride, compressed at 0° under a pressure of 10 atmospheres (a fall in temperature takes place from the expansion), a very unstable definite crystalline compound, CO_2+8H_2O, is obtained.

it, or do not form compounds with it—follows very closely the law of Henry and Dalton, the chemical bond between this gas and water being so feeble that the breaking up of the solution with separation of the gas is accomplished by a decrease of pressure alone.[32] The case is different if a considerable affinity exists between the dissolved gas and the water. It might then be even expected that the gas would not be entirely separated from water in a vacuum, as should be the case with gases following the law of Henry and Dalton. As examples, ammonia and hydrochloric acid gas may be taken. The former is separated by boiling and decrease of pressure, while the latter is not; but they both deviate distinctly from the law.

Pressure in mm. of mercury	Ammonia disolved in 100 grams of water at 0°	Hydrochloric acid gas dissolved in 100 grams of water at 0°
	Grams	Grams
100	28·0	65·7
500	69·2	78·2
1,000	112·6	85·6
1,500	165·6	—

It will be remarked, for instance, from this table that, whilst the pressure increases ten times, the solubility of ammonia only increases 4 times.

A number of examples might be cited of cases of the absorption of gases by liquids which do not in any way, even approximately, agree with the law of Henry and Dalton. Thus, for instance, carbonic anhydride is absorbed by a solution of caustic potash in water, and if sufficient caustic potash be present the gas will not be evolved from the solution by decreasing the pressure. This is a case of more intimate chemical combination. A correlation less patent, but similar and clearly chemical, appears in certain cases of the solution of gases in water, and we shall afterwards find an example of this in the solution of hydrogen iodide; but we will first stop to consider a remarkable application of the law of Henry and Dalton[33] to the case of the solution

of a mixture of two gases, this being all the more necessary because the phenomena which there take place cannot be foreseen without a clear theoretical representation of the nature of gases.[34]

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[32] As, according to the researches of Roscoe and his collaborators, ammonia exhibits a considerable deviation at low temperatures from the law of Henry and Dalton, whilst at 100° the deviation is small, it would appear that the dissociating influence of temperature affects all gaseous solutions; that is, at high temperatures the solutions of all gases will follow the law, whilst at lower temperatures there will in all cases be a deviation from it.

[33] The ratio between the pressure and the amount of gas dissolved was discovered by Henry in 1805, while Dalton in 1807 pointed out the applicability of this law to cases of gaseous mixtures, introducing the conception of partial pressures which is absolutely necessary for a right comprehension of Henry's law. The conception of partial pressures enters essentially into that of the diffusion of vapours in gases (footnote 1); for the pressure of damp air is equal to the sum of the pressures of dry air and of the aqueous vapour in it, and it is admitted as a corollary to Dalton's law that evaporation in dry air takes place as in a vacuum. It is, however, necessary to remark that the volume of a mixture of two gases (or vapours) is only approximately equal to the sum of the volumes of its constituents (the same, naturally, also refers to their pressures)—that is to say, in mixing gases a change of volume occurs, which, although small, is quite apparent when carefully measured. For instance, in 1888 Brown showed that on mixing equal volumes of sulphurous anhydride (SO_2) and carbonic anhydride (at the same pressure—760 mm. —and temperature) a decrease of pressure of 3·9 millimetres of mercury takes place. The possibility of chemical action in such mixtures is evident from the fact that equal volumes of sulphurous and carbonic anhydrides at −19° form, according to Pictet's researches in 1888, a liquid which may be regarded as an unstable chemical compound, or as a solution similar to that given when sulphurous anhydride and water combine to an unstable chemical whole.

[34] The origin of the now generally accepted **kinetic theory of gases**, according to which their molecules are animated by a rapid progressive motion, is very ancient (Bernouilli and others in the last century had already developed a similar representation), but it was only generally accepted after the mechanical theory of heat had been established, and after the work of Krönig (1855), and especially after its mathematical side had been worked out by Clausius and Maxwell. The pressure, elasticity, diffusion, and internal friction of gases, the laws of Boyle, Mariotte, and of Gay-Lussac and Avogadro-Gerhardt are not only explained (deduced) by the kinetic theory of gases, but also expressed with perfect exactitude; thus, for example, the magnitude of the internal friction of different gases was foretold with exactitude by Maxwell by applying the theory of probabilities to the impact of gaseous particles. The kinetic theory of gases must therefore be considered as one of the most brilliant acquisitions of the latter half of the nineteenth century. The velocity of the progressive motion of the particles of a gas, one cubic centimetre of which weighs d grams, is found, according to the theory, to be equal to the square root of the product of $3p \,.\, D \,.\, g$ divided by d, where p is the pressure under which d is determined expressed in centimetres of the mercury column, D the weight of a cubic centimetre of mercury in grams ($D = 13·59$, $p = 76$; consequently the normal pressure $= 1,033$ grams on a sq. cm.), and g the acceleration of gravity in centimetres ($g = 980·5$ at the sea level and lat. 45° and 981·92 at St. Petersburg; in general it varies with the latitude and altitude of the locality). Therefore at 0° the velocity of hydrogen is 1,843, and that of oxygen 461, metres per second. This is the average velocity, and (according to Maxwell and others) it is probable that the velocities of individual particles are different; that is, they occur, as it were, in different conditions of temperature, which it is very important to take into consideration in investigating many phenomena proper to matter. It is evident from the above determination of the velocity that different gaseous molecules, at the same temperature and pressure, have average velocities inversely proportional to the square roots of their densities: this is also shown by direct experiment on the flow of gases through a fine orifice, or through a porous wall. This *dissimilar velocity of flow* for different gases is frequently taken advantage of in chemical researches (see Chap. II. and also Chap. VII.) in order to separate two gases having different densities and velocities. The difference of the velocity of flow of gases also determines the phenomenon cited in the following footnote for demonstrating the existence of an internal motion in gases.

If for a certain mass of a gas which follows exactly the laws of Mariotte and Gay-Lussac the temperature t and the pressure p be changed simultaneously, then the entire change would be expressed by the equation $pv = C\ (1 + at)$, or, what is the same, $pv = RT$, where $T = t + 273$ and C and R are constants which vary not only with the units taken but also with the nature of the gas and its mass. But as there are

The law of partial pressures is as follows:—The solubility of gases mixed with each other does not depend on the influence of the total pressure acting on the mixture, but on the influence of that portion of the total pressure which is due to the volume of each separate gas in the mixture. Thus, for instance, if oxygen and carbonic anhydride were mixed in equal volumes and exerted a pressure of 760 millimetres, then water would dissolve as much of each of these gases as would be dissolved if each separately exerted a pressure of half an atmosphere, and in this case, at 0°, one cubic centimetre of water would dissolve 0·90 cubic centimetre of carbonic anhydride. If the pressure of a gaseous mixture equal h, and in n volumes of the mixture there be a volumes of a given gas, then its solution will proceed as though this gas were dissolved under a pressure $\frac{h \times a}{n}$. That portion of the pressure under the influence of which the solution proceeds is termed the 'partial' pressure.

In order to clearly understand the cause of the law of partial pressures, an explanation must be given of the fundamental properties of gases according to the views of contemporary science. Gases are elastic and disperse in all directions. We are led, from what we know of gases, to the assumption that these fundamental properties are due to a rapid progressive motion, in all directions, proper to the smallest particles (molecules) of the gases.[35] These molecules in impinging against an obstacle produce a pressure, and the greater the number of molecules impinging against an obstacle in a given time, the greater the pressure. The pressure of a separate gas or of a gaseous mixture depends on the sum of the pressures of all the molecules—on the number of blows in a unit of time on a unit of surface, and on the mass and velocity (or the *vis viva*) of the impinging molecules. The nature of the different molecules is of no account; the obstacle is acted on by a pressure due to their total *vis viva*. But in a chemical action such as the solution of gases, the nature of the impinging molecules plays, on the contrary, a most important part. In impinging against a liquid, a portion of the gas enters into the liquid itself, and is held by it so long as other gaseous molecules impinge against the liquid, that is, exert a pressure on it. As regards the solubility of a given gas, for the number of blows it makes on the surface of a liquid, it is immaterial whether other molecules of gases impinge side by side with it or not. Hence, the solubility of a given gas will be proportional, not to the total pressure of a gaseous mixture, but to that portion of it which is due to the given gas separately. Moreover, the saturation of a liquid by a gas depends on the fact that the gaseous molecules that have entered the liquid do not remain at rest in it—although they enter into an harmonious kind of motion with the molecules of the liquid—but throw themselves off from its surface (just like the vapour of a volatile liquid). If in a unit of time an equal number of molecules penetrate into (leap into) and leave (or leap out of) a liquid, it is saturated. It is in a condition of mobile equilibrium, and not of rest. Therefore, if the pressure be diminished, the number of molecules departing from the liquid will exceed the number of molecules entering into the liquid, and a fresh state of mobile equilibrium only takes place on the attainment of a fresh equality between the number of molecules departing from and entering the liquid. In this manner are explained the main features of solution, and furthermore of that special (chemical) attraction

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discrepancies from both the fundamental laws of gases (which will be discussed in the following chapter), and as, on the one hand, a certain attraction between the gaseous molecules must be assumed, while, on the other hand, the molecules of gases themselves must occupy a certain portion of space, hence for ordinary gases, within any considerable variation of pressure and temperature, recourse should be had to **van der Waals' formula**—

$$\left(p + \frac{a}{v^2}\right)(v-b) = R(1+\alpha t),$$

where α is the coefficient of expansion of gases.

The formula of van der Waals has an especially important significance in the case of the passage of a gas into the liquid state, because the fundamental properties of both gases and liquids are equally well expressed by it, although only in their general features.

The further development of the questions referring to the subjects here touched upon, which are of especial interest for the theory of solutions, must be looked for in special memoirs and works on theoretical and physical chemistry. A small part of this subject will be partially considered in the footnotes of the following chapter.

[35] Although the actual motion of gaseous molecules, which is accepted by the kinetic theory of gases (note 34), cannot be seen, yet its existence may be rendered evident by taking advantage of the difference in the velocities, undoubtedly belonging to different gases which are of different densities, under equal pressures. The molecules of a light gas must move more rapidly than the molecules of a heavier gas in order to produce the same pressure. Let us take, therefore, two gases, hydrogen and air: the former is 14·4 times lighter than the latter, and hence the molecules of hydrogen must move almost four times more quickly than air (more exactly 3·8). Consequently, if a porous cylinder containing air is introduced into an atmosphere of hydrogen, then, in a given time, the volume of hydrogen which succeeds in entering the cylinder will be greater than the volume of air leaving the cylinder, and therefore the pressure inside the cylinder will rise until the gaseous mixture (of air and hydrogen) attains an equal density both inside and outside of the cylinder. If now the experiment be reversed and air surround the cylinder, and hydrogen be inside the cylinder then more gas will leave than enter the cylinder, and hence the pressure inside the cylinder will be diminished. In these considerations we have replaced the idea of the number of molecules by the idea of volumes. We shall learn subsequently that equal volumes of different gases contain the same number of molecules (the law of Avogadro-Gerhardt), and therefore instead of speaking of the number of molecules we can speak of the number of volumes. If the cylinder be partially immersed in water the rise and fall of the pressure can be observed directly, and the experiment consequently rendered self-evident.

(penetration and harmonious motion) of a gas for a liquid which determines both the measure of the solubility and the degree of stability of the solution produced.

The consequences of the law of partial pressures are exceedingly numerous and important. In nature all liquids are in contact with the atmosphere, which, as we shall afterwards see more fully, consists of a mixture of gases, chiefly four in number—oxygen, nitrogen, carbonic anhydride, and aqueous vapour. A hundred volumes of air contain, approximately, 78 volumes of nitrogen and about 21 volumes of oxygen; the quantity of carbonic anhydride, by volume, does not exceed 0·05. Under ordinary circumstances, the amount of aqueous vapour is much greater than this, but it varies with climatic conditions. We conclude from these numbers that the solution of nitrogen in a liquid in contact with the atmosphere will proceed under a partial pressure of $\frac{78}{100} \times 760$ mm. (if the atmospheric pressure equal 760 mm.), that is, under a pressure of 600 mm. of mercury; whilst the solution of the oxygen will proceed under a partial pressure of about 160 mm., and the solution of the carbonic anhydride under the very small pressure of 0·4 mm. As, however, the solubility of oxygen in water is twice that of nitrogen (note 30), the ratio of oxygen to nitrogen dissolved in water will be greater than the ratio in air. It is easy to calculate what quantity of each of the gases will be contained in water, and taking the simplest case we will calculate what quantities of these gases will be dissolved from air containing 21 per cent. of oxygen and 79 per cent. of nitrogen at 0° and 760 mm. pressure. Under a pressure of 760 mm., 1 cubic centimetre of water dissolves 0·0235 cubic centimetre of nitrogen, and under the partial pressure of 600 mm. it will dissolve $0{\cdot}0235 \times \frac{600}{760}$, or 0·0185 cubic centimetre; of oxygen, $0{\cdot}0482 \times \frac{160}{760}$, or 0·0102 cubic centimetre, will be dissolved. Hence 100 cubic centimetres of water will contain at 0° altogether 2·87 cubic centimetres of atmospheric gases, containing about 65 per cent. of nitrogen and 35 per cent. of oxygen by volume—i.e., about $\frac{1}{3}$ by volume of oxygen, although in the atmosphere this gas only occupies $\frac{1}{5}$ by volume.[35a]

According to the law of partial pressures, whatever gas be dissolved in water will be expelled from the solution in an atmosphere of another gas. This depends on the fact that gases dissolved in water escape from it in a vacuum, because the pressure is nil, and an atmosphere of another gas acts like a vacuum towards a gas dissolved in water.

[35a] The amount of carbonic anhydride held (dissolved) in river water is usually greater than the amount obtained by calculation from its content in air. This is due to the oxidation of organic matter and to the exhalations of the fish, &c., in the water, with the consequent formation of carbonic anhydride.

Evolution of gas then proceeds, because molecules of the dissolved gas no longer impinge upon the liquid, and are therefore not dissolved in it, and those previously held in solution leave the liquid in virtue of their elasticity.[36] For the same reason a gas may be entirely expelled from a gaseous solution by boiling—at least, in many cases, when it does not form particularly stable compounds with water. In fact, on the surface of the boiling liquid there will be aqueous vapour, and therefore all the pressure acting on the gas will be due to the aqueous vapour. On this account the partial pressure of the dissolved gas will be very inconsiderable, and this is the sole reason why *a gas separates from solution on boiling the liquid containing it.* At the boiling-point of water the solubility of gases in water is still sufficiently great for a considerable quantity of a gas to remain in solution. The gas dissolved in the liquid is carried away, together with the aqueous vapour, and if boiling be continued for a long time, all the gas will finally be given up.[37]

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[36] Here two cases occur: either the atmosphere surrounding the solution may be limited, or it may be proportionally so vast as to be unlimited, like the earth's atmosphere. If a gaseous solution be brought into an atmosphere of another gas which is limited—for instance, as in a closed vessel—then a portion of the gas held in solution will be expelled, and thus pass over into the atmosphere surrounding the solution, and will produce its partial pressure, under the influence of which a portion of the gas will remain in solution. But where the atmosphere into which the gaseous solution is introduced is not only that of another gas but also unlimited, then the gas dissolved will, on passing out from the solution, diffuse into this atmosphere, and produce an infinitely small pressure in the unlimited atmosphere. Consequently, no gas can be retained in solution under this infinitely small pressure, and it will be entirely expelled from the solution. For this reason water saturated with a gas which is not contained in air, will be entirely deprived of the dissolved gas if left exposed to the air. Water also passes off from a solution into the atmosphere, and it is evident that there might be such a case as a constant proportion between the quantity of water vaporised and the quantity of a gas expelled from a solution, so that not the gas alone, but the entire gaseous solution, would pass off. A similar case to this is met with in solutions which are not decomposed by heat (such as those of hydrogen chloride and iodide), as will afterwards be considered.

[37] However, in those cases where the variation of the coefficient of solubility with the temperature is not sufficiently great, and where certain quantities of aqueous vapour and gas pass off from a solution at the boiling-point, an atmosphere may be obtained having the same composition as the liquid itself. In this case the amount of gas passing over into such an atmosphere will not be greater than that held by the liquid, and therefore such a gaseous solution will distil over unchanged. The solution will then represent, like a solution of hydriodic acid in water, a liquid which is not altered by distillation, while the pressure under which this distillation takes place remains constant. Thus, in all its aspects, solution presents gradations from the most feeble affinity to intimate chemical combination between the solvent and dissolved substance. The **amount of heat** evolved in the solution of equal volumes of different gases stands in direct relation to these variations of stability and solubility of the gases. 22·3 litres of the following gases (at 760 mm. pressure) evolve the following numbers of (gram) units of heat on dissolving in a large mass of water; carbonic anhydride 5,600; sulphurous anhydride 7,700; ammonia 8,800; hydrochloric acid 17,400; and hydriodic acid 19,400. The last two gases, which are not expelled from their solutions by boiling, evolve approximately twice as

It is evident that the conception of the partial pressures of gases should be applied not only to the formations of solutions, but also to all cases of chemical action of gases. Especially numerous are its applications to the physiology of respiration, for in these cases it is only the oxygen of the atmosphere that acts.[38]

The solution of **solids**, while depending in a small measure on the pressure under which solution takes place (because solids and liquids are almost incompressible), is very often greatly dependent on the temperature. In the majority of cases the solubility of solids in water increases as the temperature rises; and, further, the rapidity of solution increases also. The latter is determined by the rapidity of diffusion of the solution formed into the remainder of the water. The solution of a solid in water, although it is, as with gases, a physical change into a liquid state, is determined by its chemical affinity for water: this is clearly shown from the fact that in solution there occurs a diminution in volume, changes in the boiling-point of the water, in the pressure of its vapour, in the freezing point, and in many similar properties. If solution were a physical, and not a chemical, phenomenon, it would naturally be accompanied by an increase and not by a diminution of volume, because, in melting, solids generally increase in volume (their density diminishes). **Contraction** is the usual phenomenon accompanying solution, and takes place even on the addition of solutions to water,[39] and on the solution of liquids in water,[40] just as happens in the combination of substances with the production of chemically new substances.[41] The contraction which takes place in solution is, however, very small; a fact which depends on the small compressibility of solids and liquids, and on the insignificance of the compressing force acting in solution.[42] The change of volume which takes place in the solution of solids and liquids, or the alteration in specific gravity[43] and many other physical properties corresponding with it, depends on

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much heat as gases like ammonia, which are separated from their solutions by boiling, whilst gases which are only slightly soluble evolve very much less heat.

[38] With regard to the numerous researches treating of this subject, certain results obtained by Paul Bert are cited in Chapter III., and we will here point out that Prof. Sechenoff, in his researches on the absorption of gases by liquids, investigated very fully the phenomena of the solution of carbonic anhydride in solutions of various salts, and arrived at many important results, which showed that, on the one hand, in the solution of carbonic anhydride in solutions of salts on which it is capable of acting chemically (for example, sodium carbonate, borax, ordinary sodium phosphate), there is not only an increase of solubility, but also a distinct deviation from the law of Henry and Dalton; whilst, on the other hand, solutions of salts which are not acted on by carbonic anhydride (for example, the chlorides, nitrates, and sulphates) absorb less of it, owing to the 'competition' of the salt already dissolved, and follow the law of Henry and Dalton, but at the same time show undoubted signs of a chemical action between the salt, water, and carbonic anhydride. Sulphuric acid (whose coefficient of absorption is 92 vols. per 100), when diluted with water, absorbs less and less carbonic anhydride, until the hydrate H_2SO_4,H_2O is formed, when the coefficient of absorption equals 66 vols.; then, on further addition of water, the solubility again rises.

[39] Kremers made this observation in the following simple way:—He took a narrow-necked flask with a mark on the narrow part (like that on a litre flask used for accurately measuring liquids), poured water into it, and then inserted a funnel, having a fine tube which reached to the bottom of the flask. Through this funnel he carefully poured a solution of any salt, and (having removed the funnel) allowed the liquid to attain a definite temperature (in a water-bath); he then filled the flask up to the mark with water. In this manner two layers of liquid were obtained, the heavy saline solution below and water above. The flask was then shaken in order to accelerate diffusion, and

it was observed that the volume became less if the temperature remained constant. This can be proved by calculation, if the specific gravity of the solutions and water be known. Thus at 15°, 1 c.c. of a 20 per cent. solution of common salt weighs 1·1500 gram, so that 100 grams of it occupy a volume of 86·96 c.c. As the sp. gr. of water at 15° is 0·99916, 100 grams of water occupy a volume of 100·08 c.c. The sum of the volumes is 187·04 c.c. After mixing, 200 grams of a 10 per cent. solution are obtained. Its specific gravity is 1·0725 (measured at 15° and referred to water at its maximum density); hence the 200 grams will occupy a volume of 186·48 c.c. The contraction is consequently equal to 0·56 c.c.

[40] The contractions produced in the case of the solution of sulphuric acid in water are shown in the diagram, fig. 17 (page 74). The maximum is 10·1 c.c. per 100 c.c. of the solution formed. A maximum contraction of 4·15 at 0°, 3·78 at 15°, and 3·50 at 30° takes place on dissolving 46 parts by weight of anhydrous alcohol in 54 parts of water. This signifies that if, at 0°, 46 parts by weight of alcohol be taken and 54 parts by weight of water, then the sum of their separate volumes will be 104·15, whilst after mixing their total volume will be 100.

[41] This subject will be considered later in this work, and we shall then see that the contraction produced in reactions of combination (of solids or liquids) is very variable in its amount, and that there are, although rarely, reactions of combination in which contraction does not take place, or when an increase of volume is produced. Solutions exhibit a similar phenomenon.

[42] The compressibility of solutions of common salt is less, according to Grassi, than that of water. At 18° the compression of water is 48 vols. per million for a pressure of one atmosphere; for a 15 per cent. solution of common salt it is 32, and for a 24 per cent. solution 26 vols. Similar determinations were made by Brown (1887) for saturated solutions of sal-ammoniac (38 vols.), alum (46 vols.), common salt (27 vols.), and sodium sulphate at + 1°, when the compressibility of water is 47 per million volumes. This investigator also showed that substances which dissolve with an evolution of heat and with an increase in volume (as, for instance, sal-ammoniac) are partially separated from their saturated solutions by an increase of pressure (this experiment was particularly conclusive in the case of sal-ammoniac), whilst the solubility of substances which dissolve with an absorption of heat or diminution in volume increases, although very slightly, **with an increase of pressure.** Sorby observed the same phenomenon with common salt (1863).

[43] The most trustworthy data relating to the variation of the specific gravity of solutions with a change of their composition and temperature are collected and discussed in my work cited in footnote 19. The practical (the amount of a substance in solution being determined by the aid of the specific gravities of solutions, both in works and in laboratory practice) and the theoretical (for specific gravity can be more accurately observed than other properties, and because a variation in specific gravity governs the variation of many other properties) interest of this subject, besides the strict rules and laws to which it is liable, make one wish that this province of data concerning solutions may soon be enriched by further observations of as accurate a nature as possible. Their carrying out does not present any great difficulty, although requiring much time and attention.

peculiarities of the dissolving substances and of water, and, in the majority of cases, is not proportional to the quantity of the substance dissolved,[44] showing the existence of a chemical force between the solvent and the substance dissolved, which is of the same nature as in all other forms of chemical reaction.[45]

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[44] Owing to the degree of change, exhibited in many properties on the formation of solutions, not being large, and to the insufficient accuracy of observations, a proportionality between this change and change of composition may, especially within narrow limits of change of composition, easily be imagined in cases where it does not exist. The conclusion of Michel and Kraft is particularly instructive in this respect; in 1854, on the basis of their researches, they assumed that the increment of the specific gravity of solutions was proportional to the increment of salt in a given volume of a solution, which is only true for determinations of specific gravity exact merely to the second decimal place—an accuracy insufficient even for technical determinations. Accurate measurements do not confirm a proportionality either in this case or in many others where such has been generally accepted; as, for example, in the rotatory power (of the plane of polarisation) of solutions, and in their capillarity, &c. Judging by the results obtained in my researches on the specific gravity of solutions, I think that in many cases it would be nearer the truth to take the change of properties as proportional, not to the amount of a substance dissolved, but to the product of this quantity and the amount of water in which it is dissolved; the more so since many chemical relations vary in proportion to the reacting masses, and a similar ratio has been established for many phenomena of attraction studied by mechanics.

[45] All the different forms of chemical reaction may be said to take place in the process of solution: (1) *Combinations* between the solvent and the substance dissolved, yielding compounds more or less stable (more or less dissociated). This form of reaction is the most likely to occur, and is that most often observed. (2) Reactions of *substitution* or of *double decomposition* between the molecules. Thus it may be supposed that in the solution of sal-ammoniac, NH_4Cl, the action of water produces ammonia, NH_4HO, and hydrochloric acid, HCl, which are dissolved in the water and simultaneously attract each other. As these solutions and many others do indeed exhibit signs, sometimes indisputable, of such double decompositions (thus solutions of sal-ammoniac yield a certain amount of ammonia), it is probable that this form of reaction is more often met with than is generally thought. (3) *Isomeric changes* also probably take place in solution, all the more so since here molecules of different kinds come into intimate contact, and it is very likely that under these influences the configuration of the atoms in the molecules is somewhat different from what it was in its original and isolated state. One is led to this supposition especially from observations made on solutions of substances which rotate the plane of polarisation (and observations of this kind are very sensitive with respect to the atomic structure of molecules), because they show, for example (according to Schneider, 1881), that strong solutions of malic acid rotate the plane of polarisation to the right, whilst its ammonium salts in all degrees of concentration rotate to the left. (4) Reactions of *decomposition* under the influences of solution are not only rational in themselves, but have in recent years been recognised by Arrhenius, Ostwald, and others, particularly on the basis of electrolytic determinations. If some of the molecules of a solution occur in a condition of decomposition, the rest may occur in a still more complex state of combination, just as the velocities of different gaseous molecules may be far from being the same (see note 34).

It is, therefore, very probable that the reactions taking place in solution vary both quantitatively and qualitatively with the mass of water in the solution, and the great difficulty of arriving at a definite conclusion as to the nature of the chemical relations in solution will be understood; and as also the existence of a physico-mechanical process like the sliding between and interpenetration of two homogeneous liquids must also be recognised in solution, the complexity of the problem as to the actual nature of solutions, which is now to the fore, appears in its true light. But it would not be expedient to discuss this complex subject and the numerous researches upon it in a short exposition of the principles of chemistry. It requires to be specially and fully treated in physical chemistry (see Chapter VII., note 27).

The feeble development of the chemical affinities acting in solutions of solids becomes evident on considering the different methods by which **their solutions are decomposed**, with the separation of either their component parts or their definite compounds with water. The water contained in solutions is removed from them as vapour, or, by freezing, in the form of ice,[46] but **the pressure of the vapour of the water**[47] present in a solution is less than that of water in a free state, and the **temperature of the formation of ice** from solutions is lower than 0°. Further, both the diminution of vapour pressure and the lowering of the freezing-point are, in dilute solutions, very nearly proportional to the amount of a substance dissolved.[48] Thus, if for every 100 grams of water there be in solution 1, 5, or 10 grams of common salt (NaCl), then at 100° the vapour pressure of the solution will be 4, 21, or 43 mm. less than 760 mm.—the vapour pressure of water—while the freezing-points are $-0{\cdot}58°$, $-2{\cdot}91°$, and $-6{\cdot}10°$ respectively. The above figures[49] are almost proportional to the amounts

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[46] In separating as ice or vapour, water makes, with a solution, a heterogeneous system (made up of substances in different physical states) similar, for instance, to the formation of a precipitate or volatile substance in reactions of double decomposition.

[47] If the substance dissolved is non-volatile (like salt or sugar), or only slightly volatile, then the whole of the pressure of the vapour given off is due to the water; but if a solution of a volatile substance—for instance, a gas or a volatile liquid—evaporates, then only a portion of the pressure belongs to the water, and the whole pressure observed consists of the sum of the pressures of the vapours of the water and of the substance dissolved. The majority of researches bear on the first case, which will be spoken of presently, whilst the observations of D. P. Konovaloff (1881) refer to the second case. He showed that in the case of two volatile liquids, mutually soluble in each other, forming two layers of saturated solutions (for example, ether and water, note 20, p. 65), both solutions have an equal vapour pressure (in the case in point the pressure of each is equal to 431 mm. of mercury at 19·8°). Further, he found that for solutions which are formed in all proportions, the pressure is either greater (solutions of alcohol and water) or less (solutions of formic acid) than that corresponding with the rectilinear change (proportional to the composition) from the pressure of water to the pressure of the substance dissolved; thus the pressure, for example, of a 70 per cent. solution of formic acid is less, at all temperatures, than the pressure of water or that of formic acid. In this case the pressure of a solution is never equal to the sum of the pressures of the dissolving liquids, as Regnault already showed when he distinguished this case from that in which a mixture of liquids, which are insoluble in each other, evaporates. From this it is evident that a mutual action occurs in solution, which diminishes the vapour pressure proper to the individual substances, as would be expected on the supposition of the formation of compounds in solutions, because the elasticity then always diminishes.

[48] This amount is usually expressed by the weight of the substance dissolved per 100 parts by weight of water. Probably it would be better to express it by the quantity of the substance in a definite volume of the solution for instance, in a litre—or by the ratio of the numbers of molecules of water and of the dissolved substance.

[49] The variation of the vapour pressure of solutions has been the subject of many

of salt in solution (1, 5, and 10 per 100 of water). Furthermore, it has

investigations. The best known researches are those of Wüllner in Germany (1858–1860) and of Tamman in Russia (1887). The researches on the temperature of the formation of ice by various solutions are also very numerous; Blagden (1788), Rüdorff (1861), and De Coppet (1871) were the first to start such work, which, however, takes its chief interest from the work of Raoult, begun in 1882 on aqueous solutions, and afterwards continued with solutions in various other easily frozen liquids—for instance, benzene, C_6H_6 (melts at 4·96°), acetic acid, $C_2H_4O_2$ (16·75°), and others. Especial interest is attached to these **cryoscopic** investigations made by Raoult, in France, on the *depression* of the freezing-point, because he took solutions of many well-known carbon-compounds and discovered a simple relation between the molecular weights of the substances and the temperatures of crystallisation of the solvent, which enabled this method of research to be applied to the investigation of the nature of substances. We shall meet with the application of this method later on (see also Chapter VII.), and at present will only cite the deduction arrived at from these results. The solution of one-hundredth part of that molecular gram weight which corresponds with the formula of a substance (for example, NaCl = 58·5, C_2H_6O = 46, &c.) in 100 parts of a solvent lowers the freezing-point of water 0·185°, of benzene 0·49°, and of acetic acid 0·39° or twice as much as with water. And as in dilute solutions the depression or fall of freezing-point is proportional to the amount of the substance dissolved, the fall of freezing-point for all other solutions may be calculated by means of this rule. Thus, for instance, the weight which corresponds with the formula of acetone, C_3H_6O, is 58; solutions containing 2·42, 6·22, and 12·35 grams of acetone per 100 grams of water form ice (according to the determinations of Beckmann) at −0·770°, −1·930°, and −3·820°, and these figures show that with a solution containing 0·58 gram of acetone per 100 of water the fall of the temperature of the formation of ice will be 0·185°, 0·180°, and 0·179°. It must be remarked that the law of proportionality between the fall of temperature of the formation of ice and the concentration of a solution is in general only approximate, and is only applicable to weak solutions (Pickering and others).

We may here remark that the theoretical interest of this subject was strengthened on the discovery of the connection existing between the fall of vapour pressure, the depression of the temperature of the formation of ice, the diminution of osmotic pressure (van't Hoff, note 19), and the electrical conductivity of solutions, and we shall therefore supplement what we have already said on the subject by some short remarks on the method of cryoscopic investigations, although the details of the matter form the subject of more special works on physical chemistry.

In order to determine the **temperature of the formation of ice** (or of crystallisation of other solvents), a solution of known strength is prepared and poured into a cylindrical vessel surrounded by a second similar vessel, leaving between the two a layer of air which, being a bad conductor, prevents any rapid change of temperature. Still better results are obtained if the air be exhausted from the space between the two vessels and the sides of both be silvered. The transfer of heat then proceeds very slowly. The bulb of a sensitive and corrected thermometer is immersed in the solution, and also a bent platinum wire for stirring the solution; the whole is then cooled (by immersing the apparatus in a freezing mixture), and the temperature at which ice begins to separate observed. The temperature may fall slightly below its final value, but it rises and remains constant when ice begins to form. By then allowing the liquid to become slightly warmer, and again observing the temperature of the formation of ice, an exact determination may be arrived at. It is still better to take a large mass of solution, and induce the formation of the first crystals by dropping into the solution, already partially over-cooled, a small lump of ice, which only imperceptibly changes the composition of the solution. The observation should be made at the point of formation of only a very small amount of crystals, as otherwise the composition of the solution will become altered owing to their separation. Every precaution must be taken to prevent the access of moisture to the interior of the apparatus, as this might also alter the composition of the solution or the properties of the solvent (for instance, when using acetic acid).

been shown by experiment that the ratio of the diminution of vapour

With respect to the depression of dilute solutions it is known: (1) That the depression increases in almost direct proportion to the amount of the substance in solution (always per 100 parts of water); for example, for KCl when the solution contains 1 part of salt (per 100 parts of water) the depression is 0·45, when it contains 2 parts of salt, 0·90°, or with 10 parts of salt, 4·4°. (2) The greater the molecular weight expressed by the formula (see Chapter VII.), and designated by M, the less, under similar conditions, will be the depression d, and therefore if the concentration of a solution (the amount by weight of substance dissolved per 100 parts of water) be designated by p, then the fraction $M\frac{d}{p}$ or the molecular depression for a given class of substances will be a constant quantity; for example, in the case of methyl alcohol in water 17·3, for acetone about 18·0, and for sugar about 18·5. (3) In general the molecular depression for substances whose solutions do not conduct an electric current is about 18·5, while for acids, salts, and such like substances whose solutions do conduct electricity, it is i times greater; for instance, for HCl, KI, HNO_3, KHO, &c., about 36 (i being nearly 2), for borax about 66, and so on, i varying in the same manner as it does in the case of the osmotic pressure of solutions (note 19). (4) Different solvents (water, acetic acid, benzene, &c.) have each their corresponding constants of molecular depression (which have a certain remote connection with their molecular weight); for example, for acetic acid the molecular depression is about 39 and not 19 (as it is for water); for benzene, 49; for methyl alcohol about 17, &c. (5) If the molecular weight M of a substance be unknown, then in the case of non-conductors of electricity or for a given group, it may be found by determining the depression, d, for a given concentration, p; for example, in the case of peroxide of hydrogen, which is a non-conductor of electricity, the molecular weight, M, was found to be nearly 34, corresponding with the formula H_2O_2 (see Chapter VII.).

Similar results have also been found for the fall in the vapour pressure of solutions (note 51), and for the rise of their boiling-points and for other properties of the substances dissolved (Chapter VII.), and for the osmotic pressure (note 19). A variation in the magnitude of i, in passing from solutions which do not conduct an electric current to those which do conduct electricity, is everywhere remarked, so that it was natural to seek here that causal connection which Arrhenius (1888), Ostwald, and others think they have found in the supposition that a portion of the substance of the electrolyte is decomposed, in the very act of solution, into its ions (for example, NaCl into Na and Cl), or into the atoms of those individual substances which make their appearance in electrolysis, and in this way to explain the fact that i is greater for those bodies which conduct an electric current. We will not here consider this supposition, known as the hypothesis of 'electrolytic dissociation,' not merely because it belongs entirely to the special branch of physical chemistry, and gives scarcely any help towards explaining the chemical relations of solutions (particularly their passage into definite compounds, their reactions, and their very formation), but also because: (1) all the above data (for constant depression, osmotic pressure, &c.) refer only to dilute solutions, and are not applicable to strong solutions; whilst the chemical interest in strong solutions is not less than in dilute solutions, and the transition from the former to the latter is consecutive and inevitable; (2) because in any homogeneous body (although it may be insoluble and not an electrolyte) some of the atoms may always be supposed (Clausius) to be in the act of passing from one molecule to another (Chap. X. note 20), and hence in a dissociated state, but there are no reasons for believing that such a phenomenon is peculiar to the solutions of electrolytes; (3) because no essential difference is observed between the solution of electrolytes and non-conductors, although this might well be expected, according to Arrhenius's hypothesis; (4) because it is more reasonable to assume, in the act of solution, the formation of new, more complex, but unstable and easily dissociated compounds, than a decomposition even partial, of the substances taken; (5) because, if Arrhenius's hypothesis be accepted, it becomes necessary to admit the existence in solutions of free ions, like the atoms Cl or Na, without any pressure in a given solution to the vapour pressure of water is an

almost constant quantity at different temperatures,[50] and that for every (dilute) solution the ratio between the depressions of the vapour pressure and of the freezing-point is also a tolerably constant quantity.[51]

The diminution of the vapour pressure of solutions explains the rise in boiling-point occasioned by the solution of solid non-volatile bodies in water. The temperature of a vapour is the same as that of the solution from which it is generated, and therefore it follows that the aqueous vapour given off from a solution will be superheated. A saturated solution of common salt boils at 108·4°, a solution of 335 parts of nitre in 100 parts of water at 115·9°, and a solution of 325 parts of potassium chloride in 100 parts of water at 179°, if the temperature of ebullition be determined by immersing the thermometer bulb in the liquid itself. This is another proof of the bond which exists between the water and the dissolved substance. And this bond is indicated still more clearly in those cases (for example, in the solution of nitric or formic acid in water) where the solution boils at a higher temperature than either water or the volatile substance dissolved in it. For this reason the solutions of certain gases—for instance hydriodic or hydrochloric acid—boil above 100°.

The separation of ice from solutions[52] explains both the phenomenon, well known to sailors, that the ice formed from salt water gives

apparent expenditure of the energy necessary for their disruption; and although on this supposition it can be explained why i then = 2, it is not at all clear why solutions of $MgSO_4$ give i = 1, although they also conduct an electric current; (6) because in dilute solutions, the approximative proportionality between the depression and concentration may be recognised, while admitting the formation of hydrates, with as much right as in admitting the solution of anhydrous substances, and if the formation of hydrates be recognised it is easier to assume that these are partially decomposed than to accept the breaking up into ions; (7) because the best conductors of electricity are solutions of substances like the sulphates, in which it is necessary to recognise the formation of associated systems or hydrates; (8) because the cause of electro-conductivity can be sooner looked for in this affinity and this combination of the substance dissolved with the solvent, as is seen from the facts that (D. P. Konovaloff) neither aniline nor acetic acid alone conducts an electric current, a solution of aniline in water conducts it badly (and here the affinity is very small), while a solution of aniline in acetic acid forms a good electrolyte, in which, without doubt, chemical forces are acting, bringing aniline, like ammonia, into combination with the acetic acid; and, lastly, (9) because I, together with many of the chemists of the present day, cannot regard the hypothesis of electrolytic dissociation, in the form given to it up to now by Arrhenius and Ostwald, as accounting for the sum total of the chemical data respecting solutions and dissociation in general. The hypothesis of 'electrolytic dissociation' (of the electrolytes dissolved, i.e., their splitting up on solution into imaginary ions, which, according to this hypothesis, are formed even without a current) which is lamely applied to explain the increase of the value of i, but which adds nothing to our comprehension of solutions in general, suffers, moreover, in its endeavour to penetrate into the province of ordinary chemical phenomena by affirming that reaction proceeds, as a rule, only between free ions; for instance, that in the action of $AgNO_3$ on NaCl, the free ions of Ag, on meeting the ions of Cl, give AgCl. The followers of the hypothesis have applied this view to a number of phenomena (such as coloration, distribution, &c.) and reactions. For my part I consider this side of the question still less satisfactory and less in accordance with fact, and in illustration of this I will cite the following two (out of many) instances. (1) Liveing (1900) showed that the absorption spectrum (see Chap. XIII.) of solutions of a certain salt of didymum remains unchanged, notwithstanding a variation in the amount of water (concentration), if only the ray of light passing through the solution encounters the same quantity of the didymum salt (for instance, if in one case A grams of salt per litre be taken and the column of solution be n centimetres long, and in another case xA grams of the salt be present per litre and the column be n/x centimetres long). But according to the followers of the electrolytic dissociation hypothesis, the more diluted the solution the greater the proportion of free ions, and the coloration and absorption spectra of solutions are determined by these free ions. (2) L. Kahlenberg (1902) showed that on mixing a solution of dry oleate of copper, Cux_2 (where $x = C_{18}H_{33}O_2$), in dry benzene with a benzene solution of perfectly dry hydrochloric acid, 2HCl (non-conductors of electricity, and therefore, according to the hypothesis, containing no free ions), they immediately give a precipitate of chloride of copper, $CuCl_2$, because the latter is insoluble in benzene. But according to the hypothesis of electrolytic dissociation, this could in nowise be expected, because as the above solutions do not conduct an electric current they should contain no free ions, and therefore instantaneous reaction should not take place. I do not consider the hypothesis in question to be in accordance with fact, and therefore refrain from giving a detailed exposition of it in this work. Thus, although I consider it superfluous to discuss further the evolution of the above theory of solutions, still I think that it would be most useful for students of chemistry to consider all the data referring to this subject, which can be found in the *Zeitschrift für physikalische Chemie*, first published in 1887. Besides which, I think it well to point out that in my opinion (note 45) the nature of solutions is very complex, and there is reason for recognising a portion of the substances present to be in a state of combination and another portion in a state of dissociation, having nothing in common with the still obscure force of electricity. I consider that the recognition of dissociation and association in solutions will become necessary for their right comprehension, and I think that the modern conception of electrolytic dissociation, although retarding the progress of the theory of solution, is useful in giving the motive for collecting a store of experimental data to be embraced by a true theory in the future.

[50] This fact, which was established by Gay-Lussac, Pierson, and v. Babo, is confirmed by the latest observations, and enables us to express not only the fall of pressure $(p-p')$ itself, but its ratio to the pressure of water $\left(\frac{p-p'}{p}\right)$. It is to be remarked that in the absence of any chemical action, the pressure is equal, according to the law of Dalton, to the sum of the pressures of the substances taken. Hence liquids which are insoluble in each other (for example, water and chloride of carbon) present a pressure equal to the sum of their individual pressures, and therefore such a mixture boils at a lower temperature than the more volatile liquid (Magnus, Regnault).

[51] If, in the example of common salt, the fall of pressure is divided by the pressure of water, a figure is obtained which is nearly 105 times less than the magnitude of the fall of temperature of formation of ice. This correlation was theoretically deduced by Goldberg, on the basis of the mechanical theory of heat, and has been experimentally confirmed for many solutions. But here again I must refer the reader to works on physical chemistry, because it is impossible to go into all the theoretical and practical details of the subject here.

[52] Fritzsche showed that solutions of certain colouring matters yield colourless ice, clearly proving that the water alone without any intermixture of the substance dissolved passes into a solid state, although the possibility of the admixture in certain other cases cannot be denied.

fresh water,[52a] and also the fact that by freezing, just as by evaporation, a solution is obtained which is richer in salts than before. In cold countries this is taken advantage of for obtaining from sea water a liquor, which is then evaporated for the extraction of salt.

On the removal of part of the water from a solution (by evaporation or the separation of ice), a saturated solution should be obtained, and the solid substance dissolved should then separate out. Solutions saturated at a certain temperature should also deposit a corresponding portion of the substance dissolved if they be reduced, by cooling,[53] to a temperature at which the water can no longer hold in solution the quantity of the substance originally present. If this separation, by cooling a saturated solution or by evaporation, takes place slowly, **crystals** of the substance dissolved are in many cases formed; and this is the method by which crystals of soluble salts are usually obtained. Certain solids very easily separate out from their solutions in perfectly formed crystals, which may attain very large dimensions. Such are nickel sulphate, alum, sodium carbonate, chrome-alum, copper sulphate, potassium ferricyanide, and a whole series of other salts. The most remarkable circumstance in this is that many solids in separating out from an aqueous solution retain a portion of water, forming crystallised solid substances which contain water. Water which is thus retained is called **water of crystallisation.** Alum, copper sulphate, Glauber's salt, and magnesium sulphate contain such water, but neither sal-ammoniac, common salt, nitre, potassium chlorate, silver nitrate, nor sugar contains water of crystallisation in its crystals. One and the same substance may separate out from a solution with or without water of crystallisation, according to the temperature at which the crystals are formed. Thus common salt when crystallised from its solution in

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[52a] If the ice be gradually formed in a continuous mass. But if it occurs as frozen fragments, it will enclose a portion of the salt water.

[53] As the solubility of certain substances (for example, coniine, cerium sulphate, &c.) decreases with a rise of temperature (between certain limits—see, for example, note 24), these substances separate from their saturated solutions, not on cooling, but on heating. Thus a solution of manganese sulphate, saturated at 70°, becomes cloudy on further heating. The observation of the point at which a substance separates from its solution with a change of temperature gives an easy means of determining the coefficient of solubility, and this was taken advantage of by Prof. Alexéeff for determining the solubility of many substances. The phenomenon and method of observation are here essentially the same as in the determination of the temperature of formation of ice. If a solution of a substance which separates out on heating be taken (for example, sulphate of calcium or manganese), then on a certain fall of temperature ice will separate out from it, and on a certain rise of temperature the salt will separate out. From this example, and from general considerations, it is clear that the separation of a dissolved substance from a solution presents a certain analogy to the separation of ice from a solution. In both cases a heterogeneous system of a solid and a liquid is formed from a homogeneous (liquid) system.

water at the ordinary or at a higher temperature does not contain water of crystallisation. But if it separates from solution at a low temperature, namely, below −10°, then 100 parts of the crystals contain 38 parts of water. Crystals of the same substance which separate out at different temperatures may contain different amounts of water of crystallisation. This proves to us that a solid dissolved in water may form various compounds with it, differing in their properties and composition, and capable of appearing in a separate solid form like many ordinary definite compounds. This is indicated by the numerous properties and phenomena connected with solutions, and gives reason for thinking that there exist in solutions themselves either such compounds of the dissolved substance with the solvent or compounds similar to them, only in a liquid and partly decomposed form. Even the **colour of solutions** may often confirm this opinion. Copper sulphate forms crystals having a blue colour and containing water of crystallisation. If the water of crystallisation be removed by heating the crystals to redness, a colourless anhydrous substance—a white powder—is obtained. From this it may be seen that the blue colour belongs to the compound of the copper salt with water. Solutions of copper sulphate are all blue, and consequently they contain a compound similar to the compound formed by the salt with its water of crystallisation. Crystals of cobalt chloride when dissolved in an anhydrous liquid—like alcohol, for instance—give a blue solution; but when they are dissolved in water a red solution is obtained. Crystals from the aqueous solution, according to Professor Potilitzin, contain six times as much water ($CoCl_2,6H_2O$) for a given weight of the salt as the violet crystals ($CoCl_2,H_2O$) formed by the evaporation of an alcoholic solution.

Further light on the nature of solutions is given by supersaturated solutions, by the so-called cryohydrates, by solutions of certain acids having constant boiling-points, and by the properties of compounds containing water of crystallisation, to the consideration of which we now turn.

Supersaturated solutions exhibit the following phenomena:—On cooling a saturated solution of certain salts,[54] the excess of the solid

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[54] Salts which separate out with water of crystallisation and form several crystallohydrates yield supersaturated solutions with the greatest facility, and the phenomenon is much more common than was previously imagined. The first data were given in the eighteenth century by Loewitz in St. Petersburg. Numerous researches have proved that supersaturated solutions do not differ from ordinary solutions in any of their essential properties. The variations in specific gravity, vapour pressure, formation of ice, &c., take place according to the ordinary laws, and their formation depends on the absence of solid particles (of the solid phase), about which crystallisation readily takes place (as has been partially explained in note 24).

may, under certain conditions, remain in solution and not separate out. A great number of substances, and more especially sodium sulphate, Na_2SO_4, or Glauber's salt, readily form supersaturated solutions. If boiling water be saturated with this salt, and the *solution be poured off from any salt remaining undissolved*, and be kept boiling while the vessel containing it is well closed either with a plug of cotton wool, or by fusing it in the flame, or if the solution be covered with a layer of oil, it will be found that this saturated solution does not deposit any Glauber's salt whatever on cooling down to the ordinary or even to a much lower temperature; without, however, the above precautions, the salt separates out on cooling in the form of crystals of the composition $Na_2SO_4,10H_2O$—that is, containing 180 parts of water for every 142 parts of anhydrous salt. The supersaturated solution may be moved about or shaken inside the vessel holding it, and no crystallisation will take place; the salt remains in the solution in as large an amount as at a higher temperature. If the vessel holding the supersaturated solution is opened, and a crystal of Glauber's salt thrown in, crystallisation suddenly takes place.[55] A considerable rise in temperature is noticed during this rapid separation of crystals, and this is due to the fact that the salt, previously in a liquid state, passes into a solid one. This bears some resemblance to the fact that, under certain circumstances, water may be cooled below 0° (even to −10°) if it be left at rest, and then evolves heat in suddenly crystallising. Although from this point of view there is a resemblance, yet in reality the phenomenon of supersaturated solutions is much more complicated. Thus, on cooling, a saturated solution of Glauber's salt deposits crystals of the composition $Na_2SO_4,7H_2O$,[56] and not $Na_2SO_4,10H_2O$. The

crystals containing $7H_2O$ are distinguished for their instability: if they stand in contact not only with crystals of $Na_2SO_4,10H_2O$, but with many other substances, they immediately become opaque, forming a mixture of the anhydrous and deca-hydrated salts. It is evident that between water and a soluble substance there may be established various kinds of more or less stable equilibrium, of which solutions form a particular case.[57]

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[55] Inasmuch as air, as has been shown by direct experiment, contains, although in very small quantities, minute crystals of salts, and among them sodium sulphate, air can bring about the crystallisation of a supersaturated solution of sodium sulphate in an open vessel, but it has no effect on saturated solutions of certain other salts, for example, lead acetate. According to the observations of de Boisbaudran, Gernez, and others, isomorphous salts (analogous in composition) are capable of inducing crystallisation. Thus, a supersaturated solution of nickel sulphate crystallises by contact with crystals of other sulphates analogous with it, such as those of magnesium, cobalt, copper, and manganese. The crystallisation of a supersaturated solution, set up by the contact of a minute crystal, starts from it in rays with a definite velocity, and it is seen that the crystals as they form propagate the crystallisation in definite directions. This phenomenon recalls the evolution of organisms from germs. An attraction of similar molecules ensues, and they dispose themselves in definite similar forms.

[56] At the present time a view is very generally accepted, which regards supersaturated solutions as homogeneous systems, which pass into heterogeneous systems (composed of a liquid and a solid substance) in a manner exactly resembling the passage of water, cooled below its freezing-point, into ice and water, or the passage of crystals of rhombic sulphur into monoclinic crystals, and of the monoclinic crystals into rhombic. Although many phenomena of supersaturation are thus clearly understood, yet the spontaneous formation of the unstable hepta-hydrated salt, in the place of the more stable deca-hydrated salt, indicates that the phenomenon is essentially a complex one, and is most probably determined by the fact that chemical forces act between the water and the dissolved substance, tending to the formation of compounds of the two in different proportions and with different distribution of parts (structure). Stcherbacheff asserts, on the basis of his researches, that a solution of the deca-hydrated salt gives, on evaporation without the aid of heat, the deca-hydrated salt, whilst after heating above 33° it forms a supersaturated solution and the hepta-hydrated salt. But in order that this view should be accepted, indications must be found distinguishing solutions (which are, according to this view, isomeric) containing the hepta-hydrated salt from those containing the deca-hydrated salt, and all efforts in this direction (the study of the properties of the solutions) have given negative results. As some crystallohydrates of salts (alums, sugar of lead, calcium chloride) melt directly, without depositing anything, whilst others (like $Na_2SO_4,10H_2O$) are broken up, it may be that the latter are in a state of equilibrium which does not persist at a temperature higher than the melting-point. It may here be observed that, on melting crystals of the deca-hydrated salt, there is formed, besides the solid anhydrous salt, a saturated solution giving the hepta-hydrated salt, so that this passage from the deca- to the hepta-hydrated salt, and the reverse, take place with the formation of the anhydrous (or, it may be, mono-hydrated) salt.

Moreover, supersaturation (Potilitzin, 1889) only takes place with those substances which are capable of giving several modifications or several crystallohydrates, i.e., supersaturated solutions deposit, besides the stable normal crystallohydrate, hydrates containing less water and also the anhydrous salt. Sulphate of nickel solution at 15°–20° deposits rhombic crystals containing $7H_2O$, at 30°–43° cubical crystals with $6H_2O$, at 50°–70° monoclinic crystals, also containing $6H_2O$. The ability to deposit slightly hydrated or anhydrous salts by the introduction of a crystal into the solution is common to all supersaturated solutions. If a salt forms a supersaturated solution, then one would expect, according to this view, that it should exist in the form of several hydrates or in several modifications. Thus Potilitzin concluded that strontium chlorate, which readily gives supersaturated solutions, should be capable of forming several hydrates, besides the anhydrous salt known; and he succeeded in discovering the existence of two hydrates, $Sr(ClO_3)_2,3H_2O$ and apparently $Sr(ClO\ )_2,8H_2O$. Further, three modifications of the common anhydrous salt were obtained, differing from each other in crystalline form. It seems to me that the following fact throws most light on the nature of supersaturated solutions; if crystals of two forms be simultaneously thrown into a supersaturated solution (for instance, of Na_2CO_3, note 24) capable of depositing either of them, then only the less soluble form (solid phase) will crystallise out, whilst the more soluble form will pass into solution.

[57] **Emulsions**, such as milk, are composed of a solution of glutinous or similar substances, or of oily liquids suspended in a liquid in the form of drops, which are clearly visible under a microscope, and form an example of a mechanical formation resembling solution. But the difference from solutions is here evident. There are, however, solutions which approach very near to emulsions in the facility with which the dissolved substance separates from them. It has long been known, for example, that a particular kind of Prussian blue, $KFe_2(CN)_6$, dissolves in pure water, but, on the addition of the smallest quantity of any one of a number of salts, it coagulates and becomes quite insoluble. If

Solutions of salts, on cooling below 0°, deposit ice or crystals (which frequently contain water of crystallisation) of the salt dissolved, and on reaching a certain degree of concentration they solidify in their entire mass. These solidified masses are termed *cryohydrates.* My researches on solutions of common salt (1868) showed that its solution solidifies when it reaches a composition $NaCl+10H_2O$ (180 parts of water per 58·5 parts of salt), which takes place at about −23°. The solidified solution melts at the same temperature, and both the portion melted and the remainder preserve the above composition. Guthrie (1874–1876) prepared the cryohydrates of many salts, and he showed that certain of them are formed like the above at comparatively low temperatures, whilst others (for instance, those of corrosive sublimate, potassium chlorate and various colloids, and also the alums) are formed on a slight cooling—to −2° or even before.[58] In the case of common

salt *the cryohydrate with 10 molecules of water, and in the case of sodium nitrate that*[59] *with 7 molecules of water* (i.e., 126 parts of water per 85 of salt), should be accepted as established substances, capable of passing *from a solid to a liquid state, and conversely;* and therefore *it may be thought* that in cryohydrates we have solutions which are not only undecomposable by cold, but also have a definite composition representing a fresh case of definite equilibrium between the solvent and the dissolved substance.

The formation of definite compounds in the process of solution becomes evident from the marked decrease of vapour pressure, or from the rise of the temperature of ebullition which occurs in the solution of certain volatile liquids and gases in water. As an example, we may take hydriodic acid, HI, a gas which liquefies, giving a liquid boiling at −34°. A solution of it containing 57 per cent. of hydriodic acid is distinguished by the fact that, if it is heated, the hydriodic acid and water volatilise together in the proportions in which they occur in the solution, so that such a solution may be distilled unchanged. The solution boils at a higher temperature than water, namely, at 127°. Some of the physical properties of the gas and water have in this case

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copper sulphide (CuS), cadmium sulphide (CdS), arsenious sulphide (As_2S_3) (the experiments with these substances proceed with great ease, and the solution obtained is comparatively stable), or one of many other metallic sulphides be obtained by a method of double decomposition (by precipitating salts of these metals by hydrogen sulphide), and be then carefully washed (by allowing the precipitate to settle, pouring off the liquid, and again adding hydrogen sulphide solution), then, as was shown by Schulze, Spring, Prost, and others, the previously insoluble sulphides pass into transparent (for mercury, lead, and silver, reddish brown; for copper and iron, greenish brown; for *cadmium and indium, yellow; and for zinc, colourless*) solutions, which may be preserved (the weaker they are, the longer they keep), and even boiled, but which, nevertheless, in time coagulate—that is, separate in an insoluble form, and then sometimes become crystalline and quite incapable of redissolving. Graham and others observed the power shown by colloids (*see note 18*) *of forming similar* **hydrosols or solutions of gelatinous colloids**, and, in describing alumina and silica, we shall again have occasion to speak of such solutions.

In the existing state of our knowledge concerning solution, such solutions may be regarded as a transition between emulsions and ordinary solutions.

[58] Offer (1880) concludes, from his researches on cryohydrates, that they are simple mixtures of ice and salts, having a constant melting-point, just as there are alloys having a constant point of fusion, and solutions of liquids with a constant boiling-point (see note 60). This does not, however, explain in what form a salt is contained, for instance, in the cryohydrate $NaCl+10H_2O$. At temperatures above − 10 common salt separates out in anhydrous crystals, and at temperatures near − 10°, in combination with water of crystallisation, as $NaCl+2H_2O$; so that it is very improbable that at still lower temperatures it would separate without water. If the possibility of the solidified cryohydrate containing $NaCl+2H_2O$ and ice be admitted, then it is not clear why one of these substances does not melt before the other. If alcohol extracts water from the solid mass leaving the salt behind, this does not prove the presence of ice, because alcohol also takes up water from the crystals of many hydrated substances (for instance, from $NaCl+2H_2O$) at about their melting-points. Besides which, a simple observation on the cryohydrate, $NaCl+10H_2O$, shows that with the most careful cooling it does not, on the addition of ice, deposit ice, if, as should be the case on solidification, ice were formed intermixed with the salt.

I may add with regard to cryohydrates, that many of the solutions of acids solidify completely on prolonged cooling (for example, H_2SO_4,H_2O), and then form perfectly definite compounds. From solutions of sulphuric acid (see Chapter XX.), for instance, Pickering obtained a hydrate, $H_2SO_4,4H_2O$ at − 25 . Hydrochloric, nitric, and other acids also give similar crystalline hydrates, melting at low temperatures and presenting many similarities with the cryohydrates. It is my personal opinion that there exist the most varied and diverse stages of transition between molecular-physical and chemical reactions, and even between the mechanical juxtaposition of particles and their chemical interaction, and that cryohydrates (like solutions in general) form one of these stages. I therefore expect the most fruitful scientific results, not only from the application of physical conceptions to chemistry, but also from indications of the manifestation of chemical forces in the operations of molecular phenomena of a physico-mechanical order. This would bring about reconciliation between conceptions now in discord. To his researches on the heat evolved in the formation of the alloys of sodium and potassium, Joannis (1887) recognises the alloy NaK_2 as a definite compound (melting at − 12·5°), as it is the most fusible and evolves the most heat. In 1901 N. S. Kurnakoff and N. A. Pushin showed in their researches on the melting-points that the alloy NaK_2 does indeed fuse at a lower temperature than all the other alloys of sodium and potassium, but came to the conclusion that this is only an instance of a cryohydrate or eutectic point and not of a definite compound, as in the case of cryohydrates (see Chap. XIII., note 21). The conception of the cryohydrate (in the case of solutions) or eutectic (in the case of alloys) point, according to the views of Le Chatelier and others, takes the following form. Imagine a solution or alloy of simple or compound substances A in B or conversely. The addition of B to A causes the melting-point of the latter to fall by an amount increasing with the amount of B added, although the melting-point of B may be higher than that of A, just as the temperature of formation of ice in solutions falls on the addition of a salt. But the same takes place on the addition of A to B (for instance, in alloys of tin and lead), only in the first instance A separates out in the solid state, and in the second B, which predominates. Evidently there must be some proportions of A and B, at which *the decrements of the melting-points will coincide, and then the solidified alloy will contain both A and B.* I cannot say for certain, but I think in general (there are probably different cases) that further study of this subject will elucidate certain aspects of the theory of solutions (see Chap. XVIII.)

[59] See *note 24.*

already disappeared—a new substance is formed, which has its definite boiling-point. To put it more correctly, this is not the temperature of ebullition, but the temperature at which the compound formed decomposes, yielding the vapours of the products of dissociation, which, on cooling, recombine. Should a less amount of hydriodic acid than the above be dissolved in water, then, on heating such a solution, water at first distils over alone, until the solution attains the above-mentioned composition; it will then distil over unaltered. If more hydriodic acid be passed into such a solution, a fresh quantity of the gas will dissolve, but it passes off with great ease, like air from water. It must not, however, be thought that those forces which determine the formation of ordinary gaseous solutions have no part whatever in the formation of a solution having a definite boiling-point; that they do come into play is shown by the fact that such constant gaseous solutions vary in their composition under different pressures.[60] It is not, therefore, at every, but only at the ordinary, atmospheric pressure that a constant boiling solution of hydriodic acid will contain 57 per cent. of the gas. At another pressure the proportions of water and hydriodic acid will be different. Judging, however, from observations made by Roscoe, the composition varies very little for considerable variations of pressure. This variation in composition indicates directly that pressure exerts an influence on the formation of unstable chemical compounds which are

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[60] For this reason (the inconstancy of the composition of constant boiling solutions with a change of pressure), the existence of definite hydrates formed by volatile substances—for instance, by hydrochloric acid and water—is frequently denied. It is generally argued as follows: If there did exist a constancy of composition, then it would be unaltered by a change of pressure. But the distillation of constant boiling hydrates is undoubtedly accompanied (judging by the vapour densities determined by Bineau), like the distillation of sal-ammoniac, sulphuric acid, &c., by a complete decomposition of the original compound—that is, these substances do not exist in a state of vapour, but their products of decomposition (hydrochloric acid and water) are gases at the temperature of volatilisation and dissolve in the volatilised and condensed liquids; but the solubility of gases in liquids depends on the pressure, and therefore the composition of constant boiling solutions may, and even ought to, vary with a change of pressure; and, further, the smaller the pressure and the lower the temperature of volatilisation, the more likely is a true compound to be obtained. Sulphuric acid, H_2SO_4, presents an instance of an undoubted chemical compound, and yet, as we shall see in Chap. XX., it gives off sulphuric anhydride on heating and decomposes when distilled. According to the researches of Roscoe and Dittmar (1859), the constant boiling solution of hydrochloric acid proved to contain 18 per cent. of hydrochloric acid at a pressure of 3 atmospheres, 20 per cent. at 1 atmosphere, and 23 per cent. at $\frac{1}{10}$ of an atmosphere. On passing air through the solution until its composition became constant (i.e., forcing the excess of aqueous vapour or of hydrochloric acid to pass away with the air) acid was obtained containing about 20 per cent. at 100°, about 23 per cent. at 50°, and about 25 per cent. at 0°. From this it is seen that either by decreasing the pressure or by lowering the temperature of evaporation one arrives at the same limit, where the composition must be taken as $HCl + 6H_2O$, which requires 25·26 per cent. of hydrochloric acid. Fuming hydrochloric acid contains more than this.

easily dissociated (with formation of a gas), just as it influences the solution of gases, the latter being, however, influenced to a greater degree than the former.[61] Hydrochloric, nitric, and other acids form **solutions having definite boiling-points**, like that of hydriodic acid. They show, further, the common property, if containing but a small proportion of water, that they **fume in air**. Strong solutions of nitric, hydrochloric, hydriodic, and similar acids are even termed 'fuming acids.' The fuming liquids contain a definite compound whose temperature of ebullition (decomposition) is higher than 100°, and contain also an excess of the volatile substance dissolved, which exhibits a capacity to combine with water and form a hydrate the vapour pressure of which is less than that of aqueous vapour. On evaporating in air, this dissolved substance meets the atmospheric moisture and forms with it a visible vapour (fumes), consisting of the above-mentioned compound. The attraction or affinity which binds, for instance, hydriodic acid to water is evinced, not only in the evolution of heat and the diminution of vapour pressure (rise of boiling-point), but also in many purely chemical relations. Thus hydriodic acid is produced from iodine and hydrogen sulphide in the presence of water; but unless water is present this reaction does not take place.[62]

Many **compounds containing water of crystallisation** are solid substances (when melted they are already solutions—i.e., liquids); furthermore, they are capable of being formed from solutions, like ice or aqueous vapour. They may be called **crystallo-hydrates**. Inasmuch as the direct presence of ice or aqueous vapour cannot be admitted in solutions, although the presence of water may be, so also there is no basis for acknowledging the presence in solutions of crystallo-hydrates, although they are obtained from solutions as such.[63] It is evident that

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[61] The essence of the matter may be thus represented. A gaseous or easily volatile substance, A, forms with a certain quantity of water, nH_2O, a definite complex compound, A,nH_2O, which is stable up to a temperature $t°$, higher than 100°. At this temperature it is decomposed into two substances, A and H_2O. Both boil below $t°$ at the ordinary pressure, and therefore at $t°$ they distil over and recombine in the receiver. But if a part of the substance A,nH_2O is decomposed or volatilised, there still remains in the vessel a portion of the undecomposed liquid which can partially dissolve one of the products of decomposition, and that in quantity varying with the pressure and temperature, so that the constant boiling-point solution will have a slightly different composition at different pressures.

[62] For solutions of hydrochloric acid in water there are still greater differences in reaction. For instance, strong solutions decompose antimony sulphide (forming hydrogen sulphide, H_2S), and precipitate common salt from its solutions, whilst weak solutions do not act in this way.

[63] Supersaturated solutions give an excellent proof of this point. Thus a solution of copper sulphate generally crystallises in penta-hydrated crystals, $CuSO_4 + 5H_2O$, and a saturated solution gives such crystals when it is brought into contact with the minutest possible crystal of the same kind. But, according to the observations of Lecoq de

such substances present one of the many forms of equilibrium between water and a substance dissolved in it. This form, however, reminds one, in all respects, of solutions—that is, aqueous compounds which are more or less easily decomposed, with separation of water and the formation of a less aqueous or an anhydrous compound. In fact, there are not a few crystals containing water which lose a part of this water at the ordinary temperature. Such, for instance, are the crystals of soda, or sodium carbonate, which, when separated from an aqueous solution at the ordinary temperature, are quite transparent; but when left exposed to air, they lose a portion of their water, becoming opaque, and in the process lose their crystalline appearance, although preserving their original form. This process of the separation of water at the ordinary temperature is termed the **efflorescence** of crystals. Efflorescence takes place more rapidly under the receiver of an air-pump, and especially at a gentle heat. This breaking-up of a crystal is dissociation at the ordinary temperature. Solutions are decomposed in exactly the same manner.[64] The pressure of the aqueous vapour given off from crystallo-hydrates is naturally, as with solutions, less than the vapour pressure of water itself [65] at the same temperature, and therefore many

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Boisbaudran, if a crystal of ferrous sulphate (an isomorphous salt; see note 55), $FeSO_4 + 7H_2O$, be placed in a saturated solution of copper sulphate, then crystals of hepta-hydrated salt, $CuSO_4 + 7H_2O$, will be obtained. It is evident that neither the penta- nor the hepta-hydrated salt is contained as such in the solution. The solution presents its own particular liquid form of equilibrium (see note 24).

[64] Efflorescence, like evaporation, always proceeds from the surface. In the interior of crystals which have effloresced there is usually found a non-effloresced mass, so that the majority of effloresced crystals of washing soda show, in their fracture, a transparent nucleus coated by an effloresced, opaque, powdery mass. It is a remarkable circumstance that efflorescence proceeds in a perfectly regular and uniform manner, so that the angles and planes of similar crystallographic character effloresce simultaneously, and in this respect the crystalline form determines on which parts of crystals efflorescence starts, and the order in which it continues. In solutions, evaporation also proceeds from the surface, and the first crystals which appear when the required degree of saturation is reached are also formed at the surface. After falling to the bottom the crystals naturally continue to grow (see Chapter X., note 12).

[65] According to Lescœur (1883), at 100° a concentrated solution of barium hydroxide, BaH_2O_2, on first depositing crystals (with $1H_2O$), has a pressure of about 630 mm. (instead of 760 mm., the pressure of water), which decreases (because the solution evaporates) to 45 mm., when all the water is expelled and only the crystals, $BaH_2O_2 + H_2O$ left; the latter then also lose water (dissociate, effloresce at 100°), leaving the hydroxide, BaH_2O_2, which at 100° is perfectly undecomposable; that is, does not part with water. At 73° (the pressure of water is then 265 mm.) a solution containing $33H_2O$, on crystallising, has a pressure of 230 mm. and the crystals $BaH_2O_2 + 8H_2O$, which separate out, have a pressure of 160 mm., and on losing water give $BaH_2O_2 + H_2O$. This substance does not decompose at 73°, and therefore its pressure = 0. In those crystallo-hydrates which effloresce at the ordinary temperature, the pressure of dissociation approximates closely to that of the aqueous vapour, as was shown by Lescœur (1891). To this category of compounds belong $B_2O_3,(3 + x)H_2O$; $C_2O_4H_2,(2 + x)H_2O$; $BaO, (9 + x)H_2O$, and $SrO,(9 + x)H_2O$. And a still greater pressure is possessed

anhydrous salts which are capable of combining with water absorb aqueous vapour from moist air; that is, they act like a cold body, on which steam condenses. It is on this that the desiccation of gases is based, and it must further be remarked in this respect that certain substances—for instance, potassium carbonate (K_2CO_3) and calcium chloride ($CaCl_2$)—not only absorb the water necessary for the formation of a solid crystalline compound, but also give solutions, or **deliquesce**, as it is termed, in moist air. Many crystals do not effloresce in the least at the ordinary temperature; for example, copper sulphate, which may be preserved for an indefinite length of time without efflorescing (because its vapour pressure is less than that of the moisture in the air), but if it be placed under the receiver of an air-pump, and efflorescence be once started, it goes on at the ordinary temperature. The temperature at which the complete separation of water from crystals takes place varies considerably, not only for different substances, but also for different portions of the contained water of any one substance. Very often the temperature at which dissociation begins is very much higher than the boiling-point of water. Thus, for example, copper sulphate, which contains 36 per cent. of water, gives up 28·8 per cent. at 100°, and the remainder, namely, 7·2 per cent., only at 240°. Alum, out of the 45·5 per cent. of water which it contains, gives up 18·9 per cent. at 100°, a further 17·7 per cent. at 120°, 7·7 per cent. at 180°, and 1 per cent. at 280°; it only loses the remainder (1 per cent.) at its temperature of decomposition. These examples clearly show that the taking-up of water of crystallisation is accompanied by a rather profound, although, in comparison with instances which we shall consider later, still inconsiderable, change of its properties. In certain cases the water of crystallisation is only given off when the solid form of the substance is destroyed, i.e., when the crystals melt on heating. The crystals are then said **to melt in their water of crystallisation.** Further, after the separation of the water, a solid substance remains behind, so that by further heating of the molten mass it acquires a solid form. This is seen most clearly in

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by $Na_2SO_4,10H_2O$; $Na_2CO_3,10H_2O$, and $MgSO_4,(7 + x)H_2O$. Müller-Erzbach (1884) determines the pressure (with reference to liquid water) by placing tubes of the same length containing water and the substances experimented with in a desiccator, the rate of loss of water giving the relative pressure. Thus, at the ordinary temperature, crystals of sodium phosphate, $Na_2HPO_4 + 12H_2O$, present a pressure of 0·7 compared with that of water, until they lose $5H_2O$, then 0·4 until they lose $5H_2O$ more, and on losing the last portions of water the pressure falls to 0·04 compared with that of water. It is clear that the different molecules of water are held by unequal forces. Of the five molecules of water in copper sulphate the first two are comparatively easily separated, even at the ordinary temperature (but only after several days in a desiccator, according to Latchinoff); the next two are more difficultly separated, and the last equivalent is retained even at 100°. This is another indication of the capacity of $CuSO_4$ to form three hydrates, $CuSO_4,5H_2O$, $CuSO_4,3H_2O$, and $CuSO_4,H_2O$. The crystals of sugar of lead or lead acetate, which melt in their water of crystallisation at a temperature of 56·25°, and in so doing begin to lose water. On reaching a temperature of 100° the sugar of lead solidifies, having lost all its water; and then, at a temperature of 280°, the anhydrous and solidified salt again melts.[65a]

It is most important to recognise, in respect to the water of crystallisation, that its ratio to the quantity of the substance with which it is combined is always constant. However often we may prepare copper sulphate, we shall always find 36·07 per cent. of water in its crystals, and these crystals always lose four-fifths of their water at 100°, while one-fifth of the whole amount of the contained water remains in the crystals at 100°, and is only expelled from them at a temperature of about 240°. What has been said about copper sulphate crystals applies also to all other crystals containing water of crystallisation. It is impossible in any of these cases to increase the relative proportion either of the salt or of the water without changing the homogeneity of the substance. If once a portion of the water is lost—for instance, if once efflorescence takes place—there is obtained not a homogeneous substance, but a mixture consisting of a substance deprived of water and one which has not yet lost water, i.e., decomposition has already commenced. This constant ratio is an example of the fact that in chemical compounds the proportions of the component parts are quite definite; that is, it is an example of the so-called **definite chemical compounds**. These may be distinguished from solutions, and from all other so-called indefinite chemical compounds, in that at least one, and sometimes both, of the component parts may be added in large quantity to an indefinite chemical compound without destroying the homogeneity, as in the case of solutions; whilst it is impossible to add to a definite chemical compound any one of its component parts without destroying the homogeneity of the entire mass. Definite chemical compounds only decompose on a certain rise in temperature; on lowering the temperature they do not, at least in but few cases, yield their components, as do solutions, which form ice or compounds containing water

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researches of Andreae on the pressure of dissociation of hydrated copper sulphate showed (1891) the existence of three regions, characterised at a given temperature by constant pressures: (1) between 3 and 5, (2) between 1 and 3, and lastly (3) between 0 and 1 molecule of water, again confirming the existence of three hydrates of this salt having the above compositions.

[65a] Sodium acetate ($C_2H_3O_2Na,3H_2O$) melts at 58°, but resolidifies only on contact with a crystal, otherwise it may remain liquid even at 0°, and may be used for obtaining a constant temperature. According to Jeannel, the latent heat of fusion is about 28 calories, and according to Pickering the heat of solution is 35 calories. When melted, this salt boils at 123°, that is, the pressure of the vapour given off at that temperature equals the atmospheric pressure.

of crystallisation. This leads to the assumption that solutions contain water as water,[66] although it may sometimes be in very small quantity. So that solutions which are capable of solidifying completely (for instance, crystallo-hydrates capable of melting), such as the compound of 84½ parts of sulphuric acid, H_2SO_4, with 15½ parts of water, H_2O, or H_2SO_4,H_2O (or H_4SO_5), appear as true definite chemical compounds. If, then, we imagine such a definite compound in a liquid state, and admit that in this state it partially decomposes, with the separation of water—not as ice or vapour (for then the system would be heterogeneous, containing substances in different physical states), but in a liquid form, when the system will be homogeneous—we shall form an idea of a solution as an unstable, dissociating fluid state of equilibrium between water and the substance dissolved.[66a] Moreover, it should be remarked that, judging by experiment, many substances give with water not one but several *different* compounds,[67] as is seen in the capacity of one substance to form with water many different **crystallo-hydrates**, or compounds with water of crystallisation, showing diverse and independent

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[66] Such a phenomenon frequently presents itself in purely chemical actions. For instance, let a liquid substance *A* give, with another liquid substance *B*, under certain experimental conditions, only a minute quantity of a solid or gaseous substance *C*. This small quantity will separate out (pass away from the sphere of action, as Berthollet expressed it), and the remaining masses of *A* and *B* will again give *C*; consequently under these conditions action will go on to the end. Such, it seems to me, is the action in solutions when they yield ice or vapour indicating the presence of water.

[66a] A difficulty in understanding solutions is here met with in the fact that it is necessary to admit the interpenetration (entire uniform intermixture) of two liquids, water and the liquid compound. But if gases and vapours of all kinds intermix in all proportions by virtue of the mobility of their particles, of their elasticity, and of the radical similarity of their structure, there is no reason why these properties should be denied to liquids, as much in them is akin to gases; and if liquids resemble each other, the intermixture or interpenetration of their particles is also admissible, more especially as particles of different substances are found mixed together in the crystals of similar (isomorphous) substances.

[67] Certain substances on combining are capable of forming together only one compound, whilst others yield several, and these of the most varied degrees of stability. The compounds of water are instances of this kind. In solutions the existence of several different definite compounds must be acknowledged, but many of these have not yet been obtained in a free state, and it may be that they cannot be obtained in any other than a liquid form—that is, dissolved—just as there are many undoubted definite compounds which only exist in one physical state. Such instances occur among the hydrates. The compound CO_2+8H_2O (see note 31), according to Wroblewski, only occurs in a solid form. Hydrates like H_2S+12H_2O (De Forcrand and Villard), $HBr+H_2O$ (Roozeboom), are recognised only by a decrease of pressure and are very transient substances, incapable of stable existence in a free state. Even sulphuric acid, H_2SO_4, itself, which is undoubtedly a definite compound, fumes in a liquid form, giving off the anhydride, SO_3, and this exhibits a very unstable equilibrium. The crystallo-hydrates of chlorine, Cl_2+8H_2O, of hydrogen sulphide, H_2S+12H_2O (formed at 0°, and completely decomposed at +1°, when 1 vol. of water only dissolves 4 vols. of hydrogen sulphide, while at 0·1 it dissolves about 100 vols.), and of many other gases, are instances of hydrates which are very unstable.

properties. From these considerations, *solutions*[68] *may be regarded as definite, unstable liquid chemical compounds in a state of dissociation.*[69]

Regarding solutions from this point of view, they come under the head of those definite compounds with which chemistry is mainly concerned.[70]

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[68] Of such a kind are also other indefinite chemical compounds, for example, metallic alloys. These are solid substances or solidified solutions of metals. They also contain definite compounds, and may contain an excess of one of the metals. According to the experiments of Laurie (1888), the alloys of zinc with copper behave, in respect to their electromotive force in galvanic batteries, just like zinc, if the proportion of zinc does not exceed a certain percentage—that is, so long as a definite compound is not formed—for in that case particles of free zinc are present; but if a copper plate be taken, and only one-thousandth part of its area be covered by zinc, then the zinc alone will act in a galvanic battery.

[69] According to the above supposition, the condition of solutions in the sense of the kinetic hypothesis of matter (that is, on the supposition of an internal motion of molecules and atoms) may be represented in the following form:—In a homogeneous liquid—for instance, water—the molecules occur in a certain state of equilibrium, which, although mobile, is stable. When a substance *A* dissolves in water, its molecules form, with several molecules of water, systems, A,nH_2O, which are so unstable that when surrounded by molecules of water they decompose and re-form, so that *A* passes from one group of water molecules to another, and the molecules of water which were at one moment in harmonious motion with *A* in the form of the system A,nH_2O, in the next instant may have already succeeded in getting free. The addition of water or of molecules of *A* may either only alter the number of free molecules, which in their turn enter *into systems* A,nH_2O, *or it may introduce conditions for the possibility of building up* new systems A,mH_2O, where *m* is either greater or less than *n*. If the relation of the molecules in the solution were the same as in the system A,mH_2O, then the addition of fresh molecules of water or of *A* would be followed by the formation of new molecules A,nH_2O. The relative quantity, stability, and composition of these systems or definite compounds will vary in one or another solution. I adopted this view of solutions in 1887 (Pickering subsequently putting forward a similar view) after a most intimate study of the variation of their specific gravities, to which my book, cited in note 19, is devoted. Substances *A*, which give solutions, are distinguished by the fact that they can form such unstable systems, A,nH_2O, but besides these they may give other much more stable systems, A,n_1H_2O. Thus ethylene, C_2H_4, in dissolving in water probably forms a system, C_2H_4,nH_2O, which easily splits up into C_2H_4 and H_2O, but it gives also the system alcohol, C_2H_4,H_2O or C_2H_6O, which is comparatively stable. Further, oxygen can dissolve in water, and it can also combine with it, forming peroxide of hydrogen. Turpentine, $C_{10}H_{16}$, does not dissolve in water, but it combines with it, giving a comparatively stable hydrate. In other words, the chemical structure of hydrates or of the definite compounds contained in solutions, is distinguished, not only by its peculiar characters, but also by a diversity of stability.

[70] The above representation of solutions and other indefinite compounds, considering them as a particular state of definite compounds, excludes the independent existence of indefinite compounds; in this way, that unity of chemical conception is obtained which cannot be arrived at by admitting the physico-mechanical conception of indefinite compounds. The gradual transition from typical solutions (such as those of gases in water and weak saline solutions) to sulphuric acid, and from it and its definite but yet unstable and liquid compounds, to clearly defined compounds, such as salts and their crystallo-hydrates, is so imperceptible that in denying that solutions belong to the number of definite but dissociating compounds we risk denying the definiteness of the atomic composition of such substances as sulphuric acid or molten crystallo-hydrates. I repeat, however, that

We saw above that copper sulphate loses four-fifths of its water at 100° and the remainder at 240°. This means that there are two definite compounds of water with the anhydrous salt. Washing soda or carbonate of sodium, Na_2CO_3, separates out from its solutions at the ordinary temperature as crystals, $Na_2CO_3,10H_2O$, containing 62·9 per cent. of water by weight. When a solution of the same salt deposits crystals at a low temperature, about −20°, these crystals contain 71·8 parts of water to 28·2 of the anhydrous salt. Further, the crystals are obtained together with ice, and are left behind when the latter melts. If ordinary soda, with 62·9 per cent. of water, be cautiously melted in its own water of crystallisation, there remains a salt, in a solid state, containing only 14·5 per cent. of water, and a liquid is obtained which at 34° deposits crystals which contain 46 per cent. of water and do not effloresce in the air. Lastly, if a supersaturated solution of soda be prepared at temperatures below 8°, it deposits crystals containing 54·3 per cent. of water. Hence as many as five compounds of anhydrous soda with water are known, and they are dissimilar in their properties and crystalline forms, and even in their solubilities. There is apparently no relation between the above quantities of water and salt, but this is only because in each case the amounts of water and anhydrous salt were given in percentages; if the amounts of water be calculated for one and the same quantity of anhydrous salt, great regularity will be observed in the proportions of the component parts in all these compounds. It appears that for 106 parts of anhydrous salt there are, in the crystals separated out at −20°, 270 parts of water; in the crystals obtained at 15°, 180 parts of water; in those obtained from a supersaturated solution, 126 parts; in the crystals which separate out at 34°, 90 parts; and in the crystals with the smallest amount of water, 18 parts. On comparing these quantities of water it will readily be seen that they are very simply related to each other, for they are all divisible by 18, and are in the ratio 15 : 10 : 7 : 5 : 1. Naturally, direct experiment, however carefully it be conducted, is hampered with errors; but taking these unavoidable experimental errors into consideration, it will be seen that for a given quantity of the anhydrous salt there occur, in its various compounds with water, quantities of water which are in very simple multiple proportion. This is observed in,

for the present the theory of solutions cannot be considered as firmly established. The above opinion concerning them is nothing more than an hypothesis. By submitting solutions to the Daltonic conception of atomism, I hope that we may not only attain to a general harmonious chemical doctrine, but also that new motives for investigation and research will appear in the problem of solutions, which must either confirm the proposed theory or replace it by another, fuller and truer; and I, for my part, cannot consider this to be the case with any of the other present doctrines of solutions (note 49).

and is common to, all definite chemical compounds. This rule is called **the law of multiple proportions**. It was discovered by Dalton, and will be evolved in further detail subsequently in this work. For the present we will only state that the law of definite composition enables the composition of substances to be expressed by formulæ, and the law of multiple proportions permits the application of whole numbers as coefficients of the symbols of the elements in these formulæ. Thus the formula $Na_2CO_3,10H_2O$ shows directly that in this crystallo-hydrate there are 180 parts of water to 106 parts by weight of the anhydrous salt, because the formula of soda, Na_2CO_3, corresponds with a weight of 106, and the formula of water to 18 parts by weight, which are here taken ten times.

In the above examples of the combinations of water, we saw the gradually increasing intensity of the bond between water and a substance with which it forms a homogeneous compound. There is a series of such compounds with water, in which the latter is held with very great force, and is only given up at a very high temperature, and indeed, in some cases, cannot be separated by any degree of heat without completely decomposing the substance. In these compounds there is generally no outward sign whatever that they contain water. A perfectly new substance is formed from an anhydrous substance and water, in which sometimes the properties of neither one nor the other component are observable. In the majority of cases a considerable amount of heat is evolved in the formation of such compounds with water. Sometimes this evolution is so intense that a red heat is produced and light emitted. After this it is hardly to be wondered at that stable compounds are formed by such combinations. Their decomposition requires much heat; a large amount of work is necessary to separate them into their component parts. All such compounds are definite, and, as a rule, quite distinctly definite. Such definite compounds with water are called **hydrates**. The water contained in these compounds is often called **water of constitution**, i.e., water which enters into the structure or composition of the given substance. By this it is desired to express that in other cases the molecules of water are, as it were, separate from the molecules of the substance with which it is combined. It is supposed that, in the formation of hydrates, this water, even in the smallest particles, forms one complete whole with the anhydrous substance. Many examples of the formation of such hydrates might be cited. The most familiar example in practice is the hydrate of lime, or so-called 'slaked' lime. Lime is prepared by burning limestone, by which the carbonic anhydride is expelled from it and there remains a white stony mass, which is dense, compact, and somewhat tenacious. Lime is usually sold in this form, which bears the name of 'quick' or 'unslaked' lime. If water be poured over such lime, a considerable rise in temperature is remarked either directly or after a certain time. The whole mass becomes hot, part of the water is evaporated, the stony mass in absorbing water crumbles into powder, and if the water be taken in sufficient quantity, and the lime be pure and well burnt, not a particle of the original stony mass is left—it all crumbles into powder. If the water be in excess, then naturally a portion of it remains and forms a solution. This process is called 'slaking' lime. Slaked lime is used in practice mixed with sand as mortar. Slaked lime is a definite hydrate of lime. If it is dried at 100°, it retains 24·3 per cent. of water. This water can only be expelled at a temperature above 400°, and then quicklime is obtained again. The heat evolved in the combination of lime with water is so intense that it can set fire to wood, sulphur, gunpowder, &c. Even on mixing lime with ice, the temperature rises to 100°. If lime is moistened with a small quantity of water in the dark, a luminous effect is observed. The reaction which takes place is as follows: $CaO+H_2O=CaH_2O_2$. But, nevertheless, water may still be separated from this hydrate.[71] If phosphorus be burnt in dry air, a white substance called 'phosphoric anhydride' is obtained. This combines with water with such energy that the experiment must be conducted with great caution. A red heat is produced in the formation of the compound, and it is impossible to separate the water from the resultant hydrate at any temperature. The hydrate formed by phosphoric anhydride is a substance which is totally undecomposable into its original component parts by the action of heat. Almost as energetic a combination occurs when sulphuric anhydride, SO_3, combines with water, forming its hydrate, sulphuric acid, H_2SO_4. In both cases definite compounds are produced, but the latter substance, as a liquid, and capable of decomposition by heat, forms an evident link with solutions. If 80 parts of sulphuric anhydride combine with 18 parts of water, this water cannot be separated from the anhydride, even at a temperature of 300°. It is only by the addition of phosphoric anhydride, or by a series of chemical transformations, that water can be separated from its combination with sulphuric anhydride. This compound is oil of vitriol, or sulphuric acid. If a larger proportion of water be taken, it will combine with the H_2SO_4; for instance, if 36

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[71] In combining with water, one part by weight of lime evolves 245 units of heat. A high temperature is obtained, because the specific heat of the resulting product is small. Sodium oxide, Na_2O, in reacting on water, H_2O, and forming caustic soda (sodium hydroxide), $NaHO$, evolves 552 units of heat for each part by weight of sodium oxide, and the resulting hydrate decomposes entirely on ignition, without the separation of water.

parts of water per 80 parts of sulphuric anhydride be taken, a compound is formed which crystallises in the cold, and melts at +8°, whilst oil of vitriol does not solidify even at −30°. If still more water be taken, the oil of vitriol will dissolve in the remaining quantity of water. An evolution of heat takes place, not only on the addition of the water of constitution, but in a less degree on further additions of water;[72] and therefore there is no distinct boundary, but only a gradual transition, between those chemical phenomena which are expressed in the formation of solutions and those which take place in the formation of the most stable hydrates.[73]

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[72] The diagram given in note 28 shows the evolution of heat on mixing sulphuric acid, or the mono-hydrate (H_2SO_4, i.e., SO_3+H_2O), with different quantities of water per 100 vols. of the resultant solution. Every 98 grams of sulphuric acid (H_2SO_4) evolve, on the addition of 18 grams of water, 6,379 units of heat; with twice or three times the quantity of water 9,418 and 11,137 units of heat, and with an infinitely large quantity of water 17,860 units of heat, according to the determinations of Thomsen. The latter also showed that when H_2SO_4 is formed from SO_3 (=80) and H_2O (=18), 21,308 units of heat are evolved for every 98 parts by weight of the resultant sulphuric acid.

[73] Thus for different hydrates the stability with which the water is held is very dissimilar. Certain hydrates hold water very loosely, and in combining with it evolve little heat. From other hydrates the water cannot be separated by any degree of heat, even if they are formed from anhydrides (i.e., anhydrous substances) and water with but little evolution of heat; for instance, acetic anhydride in combining with water evolves an inconsiderable amount of heat, but the water cannot afterwards be expelled. If the hydrate (acetic acid) formed by this combination be strongly heated, it either volatilises without change, or decomposes into new substances, but it does not again yield the original substances, namely, the anhydride and water, at least in a liquid form. Here is an instance which gives the reason for calling the water entering into the composition of the hydrate 'water of constitution.' Such, for example, is the water entering into the so-called caustic soda or sodium hydroxide (see note 71). But there are hydrates which easily part with their water; yet this water cannot be considered as water of crystallisation, not only because sometimes such hydrates have no crystalline form, but also because in perfectly analogous cases very stable hydrates are formed, capable of particular kinds of chemical reactions, as we shall subsequently learn. Such, for example, is the unstable hydrated oxide of copper, which is not formed from water and oxide of copper, but which is obtained just like far more stable hydrates, for example, the hydrated oxide of barium, BaH_2O_2, or $BaO+H_2O$, by the double decomposition of the solution of salts with alkalies. In a word, there is no distinct boundary either between the water of hydrates and of crystallisation, or between solution and hydration.

It must be observed that, in separating from an aqueous solution, many substances, without having a crystalline form, hold water in the same unstable state as in crystals; but this water cannot be termed 'water of crystallisation' if the substance which separates out has no crystalline form. The hydrates of alumina and silica are examples of such unstable hydrates. If these substances are separated from an aqueous solution by a chemical process, they always contain water. The formation of a new chemical compound containing water is here particularly evident, for alumina and silica in an anhydrous state have chemical properties differing from those they show when combined with water, and do not combine directly with it. The entire series of colloids on separating from water form with it similar compounds, which have the aspect of solid gelatinous substances. Water is held in considerable quantity in solidified glue or boiled albumin. It cannot be expelled from them by pressure; hence in this case there has ensued some kind of combination of the substance with water. This water is, however, easily separated

We have thus considered many aspects and degrees of combination of various substances with water, or instances of the **compounds of water**, when it and other substances form new homogeneous substances, which in this case will evidently be complex, i.e., made up of different substances; and although they are homogeneous, yet it must be admitted that there exist in them those component parts which entered into their composition, inasmuch as these parts may be again obtained from them. It must not be imagined that water really exists in hydrate of lime, any more than that ice or steam exists in water. When we say that water occurs in the composition of a certain hydrate, we only wish to point out that there are chemical transformations in which it is possible to obtain that hydrate by means of water, and other transformations in which this water may be separated out from the hydrate. This is all simply expressed by saying that water enters *into the composition* of this hydrate. And the study of the composition of compounds, that is, the expression of their transformations, forms one of the chief problems of chemistry, when our study is limited to the elements, or simple substances.

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on drying; but not the whole of it, as a portion is retained, and this portion is considered to belong to the hydrate, although in this case it is very difficult, if not impossible, to obtain definite compounds. The absence of any distinct boundary lines between solutions, crystallo-hydrates, and ordinary hydrates above referred to is very clearly seen in such examples.

CHAPTER II

THE COMPOSITION OF WATER; HYDROGEN

THE question now arises, Is not **water** itself a **compound substance?** Can it not be formed by the mutual reaction of some component parts? Can it not be broken up into its component parts? There cannot be the least doubt that if it does split up, and if it is a compound, then it is a **definite** one characterised by the stability of the union between those component parts from which it is formed. From the fact alone that water passes into all physical states as a homogeneous whole, without in the least varying chemically in its properties and without splitting up into its component parts (neither solutions nor many hydrates can be distilled—they are split up), we must conclude, that if water is a compound, then it is a stable and definite chemical compound capable of entering as a whole into many other combinations. As with all other great discoveries in the province of chemistry, it is to the end of the eighteenth century that we are indebted for the important discovery that water is not a simple substance, but that, like a number of other compound substances, it is composed of two separate substances. This was proved by two of the methods by which the compound nature of bodies may be directly determined: by analysis and by synthesis, that is, by the decomposition of water into, and by the formation of water from, its component parts. In 1781 Cavendish first obtained water by burning hydrogen in oxygen, both of which gases were already known to him. He concluded from this that water was composed of two substances. But he did not make more accurate experiments, which would have shown the relative quantities of the component parts in water, and which would have determined its complex nature with certainty. Although his experiments were the first, and although the conclusion he drew from them was a true one, yet such novel ideas as the complex nature of water are not easily recognised so long as there is no series of researches which completely and indubitably proves the truth of such conclusions. The fundamental experiments which really proved the complexity of water by the method

of synthesis, and its formation from other substances, were made in 1789 by Monge, Lavoisier, Fourcroy, and Vauquelin. They obtained four ounces of water by burning hydrogen, and found that 100 parts of water contain 15 parts of hydrogen and 85 parts of oxygen. It was also proved that the weight of water formed was equal to the sum of the weights of the component parts entering into its composition; consequently water contains all the matter entering into oxygen and hydrogen, and no other. The compound nature of water was proved in this manner by a method of synthesis. But we will turn to its analysis, i.e., to its decomposition into its component parts. The analysis may be more or less complete. Either both component parts may be obtained in a separate state, or else only one is separated and the other converted into a new compound in which its amount may be determined by weighing. This will be a reaction of substitution such as is often taken advantage of in analysis. The first analysis of water was conducted in this way by Lavoisier and Meusnier in 1784. The apparatus they employed consisted of a glass retort containing water previously purified, of which the weight had been determined. The neck of the retort was inserted into a porcelain tube, placed inside an oven, and heated to a red heat by means of charcoal. Iron filings, which decompose water at a red heat, were placed inside this tube, the end of which was connected with a worm, for the purpose of condensing any water which might pass through the tube undecomposed. This condensed water was collected in a separate flask. The gas formed by the decomposition was collected over water in a bell jar. The aqueous vapour in passing over the red-hot iron was decomposed, and a gas was formed from it whose weight could be determined from its volume and its known density. Besides the water which passed through the tube unaltered a certain quantity of water disappeared in the experiment, and this quantity, in the experiments of Lavoisier and Meusnier, was equal to the weight of gas collected in the bell jar plus the increase in weight of the iron filings. Hence the water was decomposed into a gas, which was collected in the bell jar, and a substance, which combined with the iron, and is consequently composed of these two component parts. This was the first analysis of water ever made; but here only one (and not both) of the gaseous components of water was collected separately. Both the component parts of water can, however, be simultaneously obtained in a free state. For this purpose the decomposition is brought about by a galvanic current or by heat, as we shall learn directly.[1]

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[1] The first experiments on the synthesis and decomposition of water did not afford, however, an entirely convincing proof that water was composed of hydrogen and oxygen

Water is a bad conductor of electricity, that is, pure water is incapable of transmitting a feeble current; but if any salt or acid be dissolved in it, its conductivity increases, and **on the passage of a current** through acidified water **it is decomposed** into its component parts. A little sulphuric acid is generally added to the water. By immersing platinum plates (electrodes) in this water (platinum is chosen because it is not attacked by acids, which act chemically on many other metals) and connecting them with a galvanic battery it will be observed that bubbles of gas appear on these plates. The gas which separates is called **detonating gas**,[2] because on ignition it very readily explodes.[3] What takes place is as follows. The water, by the action of the current, is decomposed into two gases. The mixture of these gases forms detonating gas, and when this is brought into contact with an incandescent substance—for instance, a lighted taper—the gases recombine, forming water, the combination being accompanied by a great evolution of heat, so that the vapour of the water formed expands considerably and very rapidly, and as a consequence an explosion takes place—that is, sound and increase of pressure, and atmospheric disturbance, as in the explosion of gunpowder.

In order to discover what gases are obtained by the decomposition of water, the gases which are given off at the two electrodes must be collected separately. For this purpose a **V**-shaped tube is taken, one end being open and the other fused up. A platinum wire, terminating inside the tube in a plate, is fused into the closed end, which is entirely

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alone. Davy, who investigated the decomposition of water by the galvanic current, thought for a long time that, besides these gases, an acid and alkali were also obtained. He was only convinced of the fact that water contains nothing but hydrogen and oxygen by a long series of researches, which showed him that the appearance of an acid and alkali in the decomposition of water proceeds from the presence of impurities (especially ammonium nitrate) in the water. A final comprehension of the composition of water is obtained from the accurate determination of the quantities of the component parts which enter into its composition. It will be seen from this how many data are necessary for proving the composition of a substance—that is, of the transformations of which it is capable. What has been said of water refers to all other compounds; the investigation of each one, the entire proof of its composition, can only be obtained by the accumulation of a large mass of data referring to it.

[2] This gas is collected in a voltameter.

[3] In order to observe this explosion without the slightest danger, it is best to proceed in the following manner. Some soapy water which easily forms soap bubbles is prepared and poured into an iron trough. In this water the end of a gas-conducting tube is immersed. This tube is connected with any suitable apparatus in which detonating gas is evolved. In this way soap bubbles full of this gas are formed. If the apparatus in which the gas is produced be then removed (otherwise the explosion might travel into the interior of the apparatus), and a lighted taper be brought to the soap bubbles, a very sharp explosion will take place. The bubbles should be small to avoid any danger; ten, each about the size of a pea, suffice to give a sharp report like a pistol-shot.

filled with water[4] acidified with sulphuric acid, and another platinum wire, terminating in a plate, is immersed in the open end. If a current from a galvanic battery be now passed through the wires, an evolution of gases will be observed, that obtained in the open branch passing into the air, while that in the closed branch accumulates above the water. As this latter gas accumulates it displaces the water, which continues to descend in the closed and ascend in the open branch of the tube. When the water in this way reaches the top of the open end, the passage of the current is stopped, and the gas evolved from one of the electrodes only is obtained in the apparatus. By this means it is easy to prove that a distinct gas appears at each electrode. If the closed end be the cathode, i.e., be connected with the negative pole of the battery (the zinc), then the gas collected in the apparatus is capable of burning. This may be demonstrated by the following experiment. The bent tube is taken from the stand, its open end stopped up with the thumb and the tube inclined in such a manner that the gas passes from the closed into the open end. It will then be found, on applying a lighted lamp or taper, that the gas burns. This combustible gas, which collects at the cathode or negative electrode, is **hydrogen.** If the same experiment be carried on with a current passing in the opposite direction—that is, if the closed end be joined up with the positive pole, (i.e., with the carbon, copper, or platinum)—then the gas which is evolved from it does not itself burn, but it supports combustion very vigorously, so that a smouldering taper placed in it immediately bursts into flame. This gas, which is collected at the anode or positive pole, is

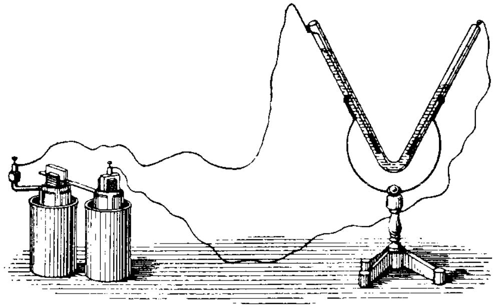

FIG. 18.—Decomposition of water by the galvanic current.

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[4] In order to fill the tube with water it is turned up, so that the closed end points downwards and the open end upwards, water acidified with sulphuric acid being then poured into it.

oxygen, which is obtained, as we saw before (in the Introduction,, from mercury oxide, and is contained in air.

Thus, in the decomposition of water, oxygen appears at the positive pole and hydrogen at the negative pole[4a]; so that detonating gas will be a mixture of both. Hydrogen burns in air from the fact that in doing so it forms water with the oxygen of the air. Detonating gas explodes owing to the hydrogen burning in the oxygen mixed with it. It is very easy to measure the relative quantities of one and the other gas which are evolved in the decomposition of water. For this purpose a funnel is taken whose orifice is closed by a cork through which pass two platinum wires connected with a battery. Acidified water is poured into the funnel and a glass cylinder full of water is placed over the end of each wire (fig. 19). On passing a current, hydrogen and oxygen collect in these cylinders, and it will easily be seen that two volumes of hydrogen are evolved for every one volume of oxygen. This signifies that in decomposing, water gives two volumes of hydrogen and one volume of oxygen.

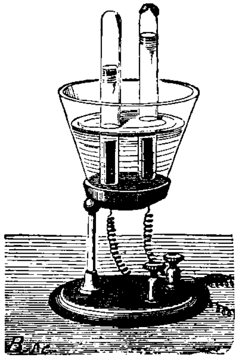

FIG. 19.—Decomposition of water by the galvanic current, for determining the relation between the volumes of hydrogen and oxygen.

Water is also decomposed into its component parts by **the action of heat**. At the melting-point of silver (950°), and in its presence, water is decomposed and the oxygen absorbed by the molten silver, which dissolves it so long as it is liquid. But directly the silver solidifies the oxygen is expelled from it. This experiment is, however, not entirely convincing; it might be thought that in this case the

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[4a] Owing to the gradual but steady progress made during the last quarter of the nineteenth century in the production of an electric current from the dynamo and its transmission over considerable distances, the electrolytic decomposition of many compound bodies has acquired great importance, and the use of the electric current is making its way into many chemical manufactures. Hence Prof. D. A. Lachinoff's proposal to obtain hydrogen and oxygen (both of which have many applications) by means of electrolysis (of either a 10 to 15 per cent. solution of caustic soda or a 15 per cent. solution of sulphuric acid) may find a practical application, at all events at some future time. Owing to their simplicity, electrolytic methods of decomposition have a great future; but as yet, so long as the production of an electric current remains so costly, their application is limited. And for this reason, although certain of these methods are mentioned in this work, they are not specially considered, the more so since a profitable and proper use of the electric current for chemical purposes requires special electro-technical knowledge which beginners cannot be assumed to have, and therefore an exposition of the principles of electro-technology as applied to the production of chemical transformations, although referred to in places, does not come within the scope of the present work.

decomposition of the water did not proceed from the action of heat, but from the action of the silver on water—that silver decomposes water, taking up the oxygen. If steam be passed through a red-hot tube, the interior of which is at a temperature of 1,000°, a portion[5] of the water decomposes into its component parts, forming detonating gas. But on passing into the cooler portions of the apparatus this detonating gas again forms water, since the hydrogen and oxygen obtained combine at a lower temperature.[6] The problem of showing the decomposability of water at high temperatures is apparently unsolvable. It was considered as such before Henri Sainte-Claire Deville (in the fifties) introduced into chemistry the conception of dissociation; that is, a change of chemical state resembling evaporation (if decomposition be likened to boiling), and before he had demonstrated the decomposability of water by the action of heat in an experiment which will presently be described. In order to demonstrate clearly the **dissociation** of water, or its decomposability by heat, at a temperature approaching that at which it is formed, it was necessary to separate the hydrogen from the oxygen at a high temperature without allowing

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[5] As water is formed by the combination of oxygen and hydrogen, with a considerable evolution of heat, and as it can also be decomposed, this reaction is a reversible one (see Introduction), and consequently at a high temperature the decomposition of water cannot be complete—it is limited by the opposite reaction. Strictly speaking, it is not known how much water is decomposed at a given temperature, although many efforts (by Bunsen and others) have been made in various directions to solve this question. Our small knowledge of the coefficient of expansion, and of the specific heat of gases at such high temperatures, renders all calculations (from observations of the pressure on explosion) of doubtful value.

[6] Grove, in 1847, observed that a platinum wire fused in the oxy-hydrogen flame—that is, having acquired the temperature of the formation of water—forms at its end a molten drop which in falling into water evolves detonating gas, that is, decomposes the water. It therefore follows that water decomposes at the temperature of its formation. At that time this formed a scientific paradox, which we shall unravel only with the development of the conceptions of dissociation, introduced into science by Henri Sainte-Claire Deville in 1857. These conceptions form an important epoch in science, and their development is one of the problems of modern chemistry. The essence of the matter is that, at high temperatures, water exists, but also decomposes, just as a volatile liquid, at a certain temperature, exists both as a liquid and as a vapour. Similarly as a volatile liquid saturates a space, attaining its maximum pressure, so also the products of dissociation have their maximum pressure; and when once that is attained decomposition ceases, just as evaporation does. Under like conditions, if the vapour be allowed to escape (and therefore its partial pressure be diminished) evaporation will recommence; so also if the products of decomposition be removed decomposition again proceeds. These simple conceptions of dissociation introduce infinitely varied consequences into the mechanism of chemical reactions, and we shall therefore have occasion to return to them very often. We may add that Grove also concluded that water is decomposed at a white heat from the fact that he obtained detonating gas by passing steam through a tube containing a wire heated strongly by an electric current, and that by passing steam over molten oxide of lead he obtained, on the one hand, minium (=oxide of lead plus oxygen), and, on the other, metallic lead, formed by the action of the hydrogen

the mixture to cool. To do this, Deville took advantage of the difference between the densities of hydrogen and oxygen.

A wide porcelain tube P (fig. 20) is placed in a furnace, which can be raised to a high temperature (it should be heated with small pieces of good coke). In this tube there is inserted a second tube, T, of smaller diameter, made of unglazed earthenware, and therefore porous. The ends of the tube are luted to the wide tube, and two tubes, C and C′, are inserted into the ends, as shown in the drawing. With this arrangement it is possible for a gas to pass into the annular space between the walls of the two tubes, whence it can be collected. Steam from a retort or flask is passed through the tube D into the inner porous tube T. This steam on entering the red-hot space is decomposed into hydrogen and oxygen. The densities of these gases are very different, hydrogen being sixteen times lighter than oxygen.

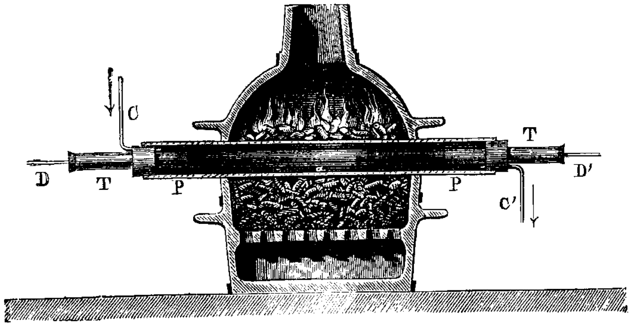

FIG. 20.—Decomposition of water by the action of heat, and the separation of the hydrogen formed by its diffusion through a porous tube.

Light gases, as we saw above, penetrate through porous surfaces very much more rapidly than denser ones, and therefore the hydrogen passes through the pores of the tube into the annular space very much more rapidly than the oxygen (about four times quicker, judging by the results of experiment). The hydrogen which separates out into the annular space can only be collected when this space does not contain any oxygen. If any air remains in this space, then the hydrogen which passes out will combine with its oxygen and form water. For this reason a gas incapable of supporting combustion—for instance, nitrogen or carbonic anhydride—is previously passed into the annular space. Thus the carbonic anhydride is passed through the tube C, and the hydrogen, separated from the steam, is collected through the tube C′, and will be partly mixed with carbonic anhydride. A certain portion of the carbonic anhydride will penetrate through the pores of the

unglazed tube into the interior of the tube T. The oxygen will remain in this tube, and the volume of the remaining oxygen will be half that of the hydrogen which separates out from the annular space.[6a]

The decomposition of water is effected much more easily by a method of substitution, advantage being taken of the affinity of substances for either the oxygen or the hydrogen of water. If a substance be added to water, which takes up the oxygen, that is, which replaces the hydrogen, we shall then obtain the latter gas from the water. Thus with sodium, water gives hydrogen, whilst with chlorine, which takes up the hydrogen, oxygen is obtained.

Hydrogen is evolved from water by many metals, which are capable of forming oxides in air; that is, which are capable of burning or combining with oxygen. The capacity of metals for combining with oxygen, and therefore for decomposing water, or for the evolution of hydrogen, is very varied.[7] Among metals potassium and sodium

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[6a] Part of the oxygen will also penetrate through the pores of the tube, but, as was said before, in much smaller quantity than the hydrogen; and as the density of oxygen is sixteen times greater than that of hydrogen, the volume of oxygen which passes through the porous walls will be four times less than that of the hydrogen (the quantities of gases passing through porous walls being inversely proportional to the square roots of their densities). The oxygen which separates out into the annular space will combine, when the temperature falls a certain amount, with the hydrogen; but as each volume of oxygen only requires two volumes of hydrogen, whilst four volumes of hydrogen will pass through the porous walls for every volume of oxygen that passes, part of the hydrogen will remain free, and can be collected from the annular space. A corresponding quantity of oxygen remaining from the decomposition of the water can be collected from the inner tube.

[7] In order to demonstrate the differences between the affinities of oxygen for different elements, it suffices to compare the amounts of heats evolved in their combination with 16 parts by weight of oxygen; in the case of sodium (when Na_2O is formed, or 46 parts of Na combine with 16 parts of oxygen, according to Beketoff) 100,000 calories (or kilogram units of heat) are evolved, for hydrogen (when water, H_2O, is formed) 69,000 calories, for magnesium (MgO is formed) about 140, for aluminium ($\frac{1}{3}$ Al_2O_3 is formed) about 130, for iron (when the oxide FeO is formed) 69,000, or (if the oxide Fe_2O_3 is formed) 64,000 calories, for zinc (forming ZnO) 86,000 calories, for lead (when PbO is formed) 51,000 calories, for copper (when CuO is formed) 38,000 calories, and for mercury (HgO being formed) 31,000 calories.

These figures cannot correspond directly with the magnitudes of the affinities, for the physical and mechanical side of the matter is very different in the different cases. Hydrogen is a gas, and, in combining with oxygen, gives a liquid; consequently it changes its physical state, and in doing so evolves heat. But zinc and copper are solids, and, in combining with oxygen, give solid oxides. The oxygen, previously a gas, now passes into a solid or liquid state, and so must also give up its store of heat in forming oxides. Therefore the figures expressing the heat of combination cannot depend only upon the affinities, i.e., only on the loss of internal energy previously in the elements. Nevertheless the figures above cited correspond, in a certain degree, with the order in which the elements stand in respect to their affinity for oxygen, as may be seen from the fact that mercury oxide, which evolves the least heat (among the above examples), is the least stable and is easily decomposed, giving up its oxygen; whilst sodium, the formation of whose oxide is accompanied by the greatest evolution of heat, is able to decompose all exhibit considerable energy in this respect. The first occurs in potash, the second in soda. They are both lighter than water, soft, and readily change in air. By bringing one or the other of them into contact with water at the ordinary temperature[8] a quantity of hydrogen, corresponding with the amount of the metal taken, may be directly obtained. One gram of hydrogen, occupying a volume of 11·16 litres at 0° and 760 mm., is evolved for every 39 grams of potassium or 23 grams of sodium taken. The phenomenon may be observed in the following

way. A solution of sodium in mercury—or 'sodium amalgam,' as it is generally called—is poured into a vessel containing water, where, owing to its weight, it sinks to the bottom; the sodium held in the mercury then acts on the water like pure sodium, liberating hydrogen. The mercury does not act here, and the same amount of it as was taken for dissolving the sodium is obtained in the residue. The hydrogen is evolved gradually in the form of bubbles, which pass through the liquid.

Beyond the hydrogen evolved and a solid substance which remains in solution (and may be obtained by evaporating the resultant liquid) no other products are here obtained. Consequently from the two substances (water and sodium) taken the same number of new substances (hydrogen and the substance dissolved in water, namely, caustic soda) have been obtained, from which we may conclude that the reaction which here takes place is one of double decomposition or of substitution. The resultant solid is nothing else than the so-called caustic soda (sodium hydroxide), which is made up of sodium, oxygen, and half of the hydrogen contained in the water. The substitution, therefore, takes place between the hydrogen and the sodium, half of the hydrogen in the water being replaced by the sodium and evolved in a free state. Hence the reaction which takes place here may be expressed by the equation: $H_2O + Na = NaHO + H$; the meaning of this is clear from what has already been said.[9]

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the other oxides, taking up their oxygen. In order to generalise the connection between affinity and the evolution and absorption of heat, which is evident in its main features, and was firmly established by the researches of Favre and Silberman (about 1840), and then of Thomsen (in Denmark) and Berthelot (in France), many investigators, especially the one last mentioned, established the *law of maximum work*. This states that only those chemical reactions take place of their own accord in which the greatest amount of chemical (latent, potential) energy is transformed into heat. But, in the first place, we are not able, judging from what has been said above, to distinguish that heat which corresponds with purely chemical action from the sum total of the heat observed in a reaction (in the calorimeter); in the second place, there are evidently endothermal reactions which proceed under the same circumstances as exothermal ones (carbon burns in the vapour of sulphur with absorption of heat, whilst in oxygen it evolves heat); and, in the third place, there are reversible reactions, which when taking place in one direction evolve heat, and when taking place in the opposite direction, absorb it; and, therefore, the principle of maximum work in its elementary form is not supported by science. But the subject continues to be developed, and will probably lead to a general law, such as thermal chemistry does not at present possess. And now thermochemical data clearly show that the chemical affinity of sodium for oxygen is greater than that of hydrogen, whilst mercury and copper have less affinities for oxygen than hydrogen has. Hence sodium easily decomposes water, which neither mercury nor copper can do. If aluminium does not decompose water directly, it is only because the oxide Al_2O_3 is insoluble in water, and a coating of the hydrogen formed prevents the reaction (Ditte). This and many other instances show that the course of chemical reactions is determined, not only by the properties and energy of the reacting substances, but also by the nature of those produced.

[8] If a piece of metallic sodium be thrown into water, it floats on it (owing to its lightness), keeps in a state of continual motion (owing to the evolution of hydrogen on all sides), and immediately decomposes the water, evolving hydrogen, which can be ignited. This experiment may, however, lead to an explosion should the sodium stick to the walls of the vessel, and begin to act on the limited mass of water immediately adjacent to it (probably in this case the NaHO and Na yield Na_2O, which acts on the water, evolving much heat and rapidly forming steam), and the experiment should therefore be cautiously performed. The decomposition of water by sodium may be demonstrated better, and with greater safety, in the following manner. Into a glass cylinder filled with mercury, and immersed in a mercury bath, water is first introduced, and owing to its lightness rises to the top, and then a piece of sodium wrapped in paper is introduced into the cylinder by means of forceps. The metal rises through the mercury to the surface of the water, on which it remains, and evolves hydrogen, which collects in the cylinder and may be tested after the experiment has been completed. The safest method of making this experiment is, however, as follows. The sodium (cleaned from the naphtha in which it is kept) is either wrapped in fine copper gauze and held by forceps or else held in forceps to the end of which a small copper cage is attached, and is then held under water. The evolution of hydrogen goes on quietly, and the gas may be collected in a bell jar and then lighted.

[9] This reaction is vigorously exothermal, i.e., it is accompanied by the evolution of heat. If a sufficient quantity of water be taken, the whole of the sodium hydroxide, NaHO, formed is dissolved, and about 42,500 kilogram units of heat are evolved per 23 grams of sodium taken. As 40 grams of sodium hydroxide are produced, and they in dissolving, judging from direct experiment, evolve about 10,000 calories, the reaction would evolve about 32,500 calories, supposing no excess of water to be present and no solution to be formed. We shall afterwards learn that hydrogen contains, in its smallest isolable particles, H_2 and not H, so that the reaction should be written thus, $2Na + 2H_2O = H_2 + 2NaHO$, and it then corresponds with an evolution of heat of + 65,000 calories. And as N. N. Beketoff showed that Na_2O, or anhydrous oxide of sodium, combines with water, forming the hydrate, or sodium hydroxide (caustic soda), 2NaHO, with the evolution of about 35,500 calories, the reaction $2Na + H_2O = H_2 + Na_2O$ corresponds to 29,500 calories. This quantity of heat is less than that which is evolved by the oxide in combining with water and forming caustic soda, and therefore it is not to be wondered at that the hydrate, NaHO, is always formed and not the anhydrous substance Na_2O. That such a conclusion, agreeing with the facts, is inevitable is also seen from the fact that, according to Beketoff, the anhydrous sodium oxide, Na_2O, acts directly on hydrogen, with separation of sodium, $Na_2O + H = NaHO + Na$. This reaction is accompanied by an evolution of heat equal to about 3,000 calories, because $Na_2O + H_2O$ gives, as we saw, 35,500 calories and $Na + H_2O$ evolves 32,500 calories. However, an opposite reaction also takes place—$NaHO + Na = Na_2O + H$ (both with the aid of heat)—in which of course heat is absorbed. In this we see an example of calorimetric calculations and the limited application of the law of maximum work to the general phenomena of reversible reactions, to which the case just considered belongs.

Sodium and potassium act on water at the ordinary temperature. Other heavier metals only act on it at higher temperatures, and even then not so rapidly or vigorously. Thus magnesium and calcium only liberate hydrogen from water at its boiling-point, and zinc and iron only at a red heat; whilst a whole series of heavy metals, such as copper, lead, mercury, silver, gold, and platinum, do not in the least decompose water at any temperature, and do not replace its hydrogen.

From this it is clear that hydrogen may be obtained by the decomposition of steam by the action of iron (or zinc) at a high temperature. The experiment is conducted in the following manner. Pieces of iron (filings, nails, &c.) are placed in a porcelain tube, which is then subjected to a strong heat and steam passed through it. The steam, coming into contact with the iron, gives up its oxygen to it, the hydrogen being thus set free and passing out at the other end of the tube, together with undecomposed steam. This method, which is historically of great importance,[10] is practically inconvenient, as it requires a rather high temperature. Further, this reaction, as a reversible one (a red-hot mass of iron decomposes a current of steam, forming oxide and hydrogen; and a mass of oxide of iron, heated to redness in a stream of hydrogen, forms iron and steam), does not proceed in virtue of the comparatively small difference between the affinities of oxygen for iron (or zinc) and for hydrogen, but only because the hydrogen escapes, as it is formed, by virtue of its elasticity.[11] If the oxygen compounds—that is, the oxides—which are obtained

[10] The composition of water, as we saw above, was determined by passing steam over red-hot iron. The same method was formerly used for making hydrogen for filling balloons. An oxide having the composition Fe_3O_4 is formed in the reaction, which is hence expressed by the equation, $3Fe + 4H_2O = Fe_3O_4 + 8H$.

[11] The reaction between iron and water (notes 7 and 10) is reversible. By heating the oxide in a current of hydrogen, water and iron are obtained. From this it follows, from the principle of chemical equilibria, that if iron and hydrogen be taken, and also oxygen in such quantity that it is insufficient for combination with both substances, then it will divide itself between the two: part of it will combine with the iron and the other part with the hydrogen, but a portion of both of these will remain in an uncombined state.

Therefore, if iron and water be placed in a closed space, decomposition of the water will proceed on heating to the temperature at which the reaction, $3Fe + 4H_2O = Fe_3O_4 + 8H$, commences; it does not go on to the end but ceases, because the conditions for the reverse reaction are attained, and a state of equilibrium will ensue after the decomposition of a certain quantity of water. Here, again, the reversibility is connected with the small heat effect, and again both reactions (direct and reverse) proceed at a red heat. But if, in the above-described reaction, the hydrogen escapes as it is evolved, then its partial pressure does not increase with its formation, and therefore all the iron can be oxidised by the water. In this we see the elements of that influence of mass to which we shall have occasion to return later. With copper and lead there will be no decomposition, either at the ordinary or at a high temperature, because the affinities of these metals for oxygen are much less than that of hydrogen.

from the iron or zinc be able to pass into solution, then the affinity acting during solution is added, and the reaction may become non-reversible and proceed with comparatively much greater facility.[12] As the oxides of iron and zinc, by themselves insoluble in water, are capable of combining with (have an affinity for) acid oxides (as we shall afterwards fully consider), and form saline and soluble substances with acids or hydrates having acid properties, these metals are able by the action of such acid hydrates, or of their aqueous solutions,[13] to liberate hydrogen with great ease at the ordinary temperature; that is, they act on solutions of acids just as sodium acts on water.[14] Sulphuric acid, H_2SO_4, is usually chosen for this purpose; the hydrogen is displaced from it by many metals with much greater facility than directly from water, and such a displacement is accompanied by the evolution of a large amount of heat.[15] When the hydrogen in sulphuric acid

[12] In general, if reversible as well as non-reversible reactions can take place between substances acting on each other, then, judging by our present knowledge, the non-reversible reactions take place in the majority of cases, which obliges one to acknowledge the action, in this case, of comparatively strong affinities. The reaction, $Zn + H_2SO_4 = H_2 + ZnSO_4$, which takes place in solutions at the ordinary temperature, is scarcely reversible under these conditions, but at a certain high temperature, it becomes reversible, because then zinc sulphate and sulphuric acid decompose, and the action must take place between the water and zinc. From the preceding proposition results proceed which are in some cases verified by experiment. If the action of zinc or iron on a solution of sulphuric acid is a non-reversible reaction, we may by its means obtain hydrogen in a very compressed state, and compressed hydrogen will not act on solutions of sulphates of the above-named metals. This was actually verified as far as it was possible, in the experiments, to keep up the compression or pressure of the hydrogen. Those metals which do not evolve hydrogen with acids, on the contrary, should, at least with increase of pressure, be displaced by hydrogen. And in fact Brunner showed that gaseous hydrogen displaces platinum and palladium from the aqueous solutions of their chlorine compounds, but not gold, and Beketoff succeeded in showing that silver and mercury, under a considerable pressure, are separated from the solutions of certain of their compounds by means of hydrogen. Reaction commences under a pressure of only six atmospheres if a weak solution of silver sulphate be taken; with a stronger solution a much greater pressure is, however, required for the separation of the silver.

[13] For the same reason, many metals in acting on solutions of the alkalies displace hydrogen. Aluminium acts particularly well in this respect, because its oxide gives a soluble compound with alkalies. For the same reason tin, in acting on hydrochloric acid, evolves hydrogen, and silicon does the same with hydrofluoric acid.

[14] It is acknowledged that zinc itself acts on water, even at the ordinary temperature, but that the action is confined to small masses and only proceeds at the surface. In reality, zinc, in the form of a very fine powder, or so-called 'zinc dust,' is capable of decomposing water with the formation of oxide (hydrated) and hydrogen. The oxide formed acts on sulphuric acid, water then dissolves the salt produced, and the action continues because one of the products of the action of water on zinc, namely, the zinc oxide, is removed from the surface. One might naturally imagine that the reaction does not proceed directly between the metal and the water, but between the metal and the acid; but such a simple representation, which we shall notice later, hides the mechanism of the reaction, and does not permit of its actual complexity being seen.

[15] According to Thomsen, the reaction between zinc and a very weak solution of sulphuric acid evolves about 38,000 calories (zinc sulphate being formed) per 65 parts

is replaced by a metal, a substance is obtained which is called a salt of sulphuric acid or a sulphate. Thus, by the action of zinc on sulphuric acid, hydrogen and zinc sulphate, $ZnSO_4$,[15a] are obtained. The latter is a solid substance, soluble in water. In order that the action of the metal on the acid should go on regularly, and to the end, it is necessary that the acid should be diluted with water, which dissolves the salt as it is formed; otherwise the salt in a solid state covers the metal and prevents the acid from attacking it. Usually the acid is diluted with from three to five times its volume of water, and the metal is covered with this solution. In order that the metal may act rapidly on the acid it should present a large surface, so that a maximum amount of the reacting substances may come into contact in a given time. For this purpose the zinc is used as strips of sheet zinc, or in the granulated form (that is, zinc which has been poured from a height, in a molten state, into water). The iron should be in the form of wire, nails, filings, or cuttings.

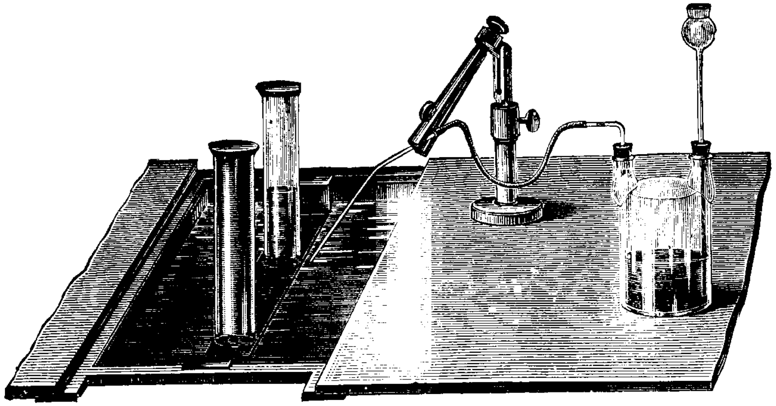

FIG. 21.—Apparatus for the preparation of hydrogen from zinc and sulphuric acid.

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by weight of zinc; and 56 parts by weight of iron—which combine, like 65 parts of zinc, with 16 parts by weight of oxygen—evolve about 25,000 calories (forming ferrous sulphate, $FeSO_4$). Paracelsus observed the action of metals on acids in the seventeenth century; but it was not until the eighteenth century that Lémery determined that the gas evolved in this action is a particular one which differs from air and is capable of burning. Even Boyle confused it with air. Cavendish determined the chief properties of the gas discovered by Paracelsus. At first it was called 'inflammable air;' later, when it was recognised that in burning it gives water, it was called hydrogen, a word derived from the Greek terms for water and generator.

[15a] If, when the sulphuric acid is poured over the zinc, the evolution of the hydrogen proceed too slowly, it may be greatly accelerated by adding a small quantity of a solution of copper sulphate or platinum chloride to the acid. The reason of this is explained in Chap. XVI., note 10a.

The usual method of obtaining hydrogen is as follows. A certain quantity of granulated zinc is put into a double-necked, or Woulfe's, bottle. Into one neck a funnel is placed, reaching to the bottom of the bottle, so that the liquid poured in may prevent the hydrogen from escaping through it. The gas escapes through a special gas-conducting tube, which is firmly fixed, by a cork, into the other neck, and ends in a water-bath (fig. 21), under the orifice of a glass cylinder full of water.[16] If sulphuric acid be now poured into the Woulfe's bottle it will

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[16] As laboratory experiments with gases require special methods of manipulation, we will describe certain of them here. When in laboratory practice an intermittent supply of hydrogen (or other gas which is evolved without the aid of heat) is required, the apparatus represented in fig. 22 is the most convenient. It consists of two bottles, having at the bottom orifices, in which corks with tubes are placed, and these tubes are connected by an indiarubber tube (sometimes furnished with a spring clamp). Zinc is placed in one bottle and dilute sulphuric acid in the other. The neck of the former is closed by a cork fitted with a gas-conducting tube with a stopcock. If the two bottles be connected with each other, and the stopcock be opened, the acid will flow to the zinc and evolve hydrogen. If the stopcock be closed, the hydrogen will force out the acid from the bottle containing the zinc, and the action will cease. Or the vessel containing the acid may be placed at a lower level than that containing the zinc, when all the liquid will flow into it; and in order to start the action the acid vessel may be placed on a higher level than the other, when the acid will flow to the zinc. It can also be employed for collecting gases (as an aspirator or gasometer).

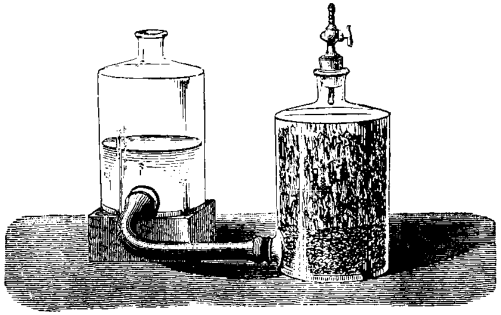

FIG. 22.—A very convenient apparatus for the preparation of gases obtained without heat. It may also replace an aspirator or gasometer.

An *aspirator* (for collecting and delivering gas) usually consists of a vessel furnished with a stopcock at the bottom. A stout cork, through which a glass tube passes, is fixed into the neck of this vessel. If the vessel be filled up with water to the cork, and the bottom stopcock opened, the water will run out and draw gas in. For this purpose the glass tube is connected with the apparatus from which it is desired to pump out or exhaust the gas.

The aspirator represented in fig. 23 may be recommended for its continuous action. It consists of a tube, *d*, which widens out at the top, the lower part being long and narrow. In the expanded upper portion, *c*, two tubes are sealed: one, *e*, is for drawing in the gas, whilst the other, *b*, is connected with the water supply, *w*. The amount of water supplied through the tube *b* must be less than the amount which can be carried off by the tube *d*.

soon be seen that bubbles of a gas are evolved, which is hydrogen. The first part of the gas evolved should not be collected, as it is mixed

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Owing to this the water in the tube *d* will flow through it in cylindrical portions alternating with cylindrical gas bubbles, which will be thus carried away. The gas which is drawn through may be collected from the end of the tube *d*; but this form of pump is usually employed where the air or gas aspirated is not to be collected. If the tube *d* is of considerable length, say 40 ft. or more, a very fair vacuum will be produced, the amount being shown by the gauge *g*: it is often used for filtering under reduced pressure, as shown in the figure. If the water be replaced by mercury, and the length of the tube *d* be greater than 760 mm., the aspirator may be employed as an air-pump, and all the air may be exhausted from a limited space; for instance, by connecting *g* with a hollow sphere.

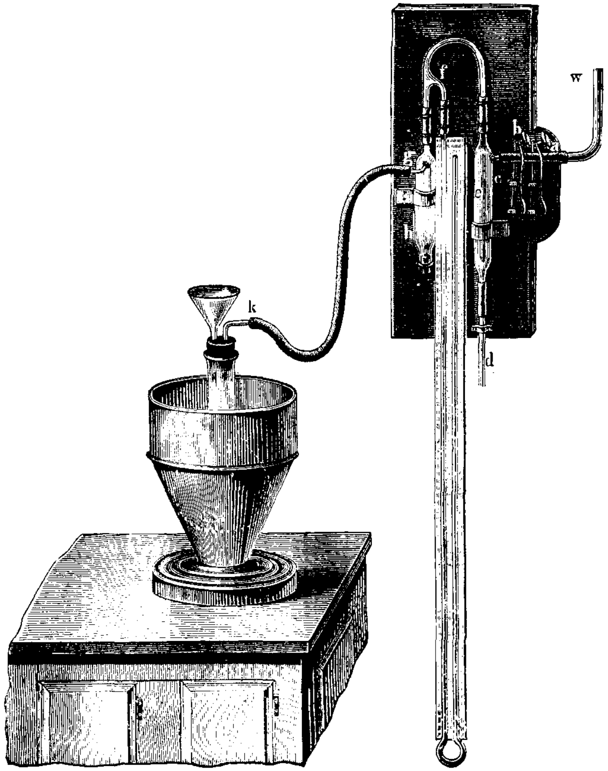

Fig. 23.—Continuous aspirator. The tube *d* should be more than 32 feet long.

Gasholders are often used for collecting and holding gases. They are made of glass, copper, or tin plate. The usual form is shown in fig. 24. The lower vessel *B* is made hermetically tight—i.e., impervious to gases—and is filled with water. A funnel is attached to this vessel (by several supports). The vessel *B* communicates with the

with the air originally in the apparatus. This precaution should be taken in the preparation of all gases. Time must be allowed for the gas evolved to displace all the air from the apparatus, otherwise in testing the combustibility of the hydrogen an explosion may occur owing to the formation of detonating gas (the mixture of the oxygen of the air with the hydrogen).[17]

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bottom of the funnel by a stopcock *b* and a tube *a*, reaching to the bottom of the vessel *B*. If water be poured into the funnel, and the stopcocks *a* and *b* be opened, the water will run through *a*, and the air escape from the vessel *B* by *b*. A glass tube *f* runs up the side of the vessel *B*, with which it communicates at the top and bottom, and shows the amount of water and gas the gasholder contains. In order to fill the gasholder with a gas, it is first filled with water, the cocks *a*, *b*, and *e* are closed, the nut *d* unscrewed, and the end of the tube conducting the gas from the apparatus in which it is generated is passed into *d*. As the gas fills the gasholder the water runs out at *d*. If the pressure of a gas be not greater than the atmospheric pressure, and it be required to collect it in the gasholder, then the stopcock *e* is put into communication with the space containing the gas. Then, having opened the orifice *d*, the gasholder acts like an aspirator; the gas will pass through *e*, and the water run out at *d*. If the cocks be closed, the gas collected in the gasholder may be easily preserved and transported. If it be desired to transfer this gas into another vessel, a gas-conducting tube is attached to *e*, the cock *a* opened, *b* and *d* closed, and the gas will then pass out at *e*, its pressure in the apparatus being greater than the atmospheric pressure, owing to the pressure of the water poured into the funnel. If it be required to fill a cylinder or flask with the gas, it is filled with water and inverted in the funnel, and the stopcocks *b* and *a* opened. Then water will run through *a*, and the gas will escape from the gasholder into the cylinder through *b*.

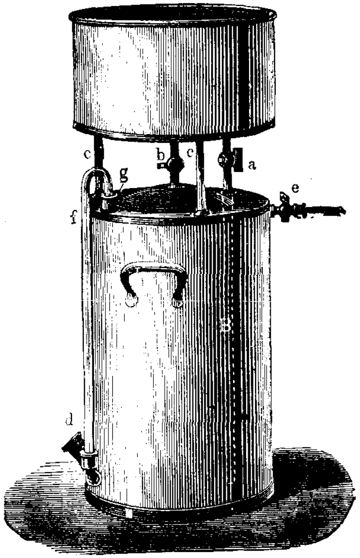

Fig. 24.—Gasholder.

[17] When it is required to prepare hydrogen in large quantities for filling balloons, copper vessels or wooden casks lined with lead are employed: they are filled with scrap iron over which dilute sulphuric acid is poured. The hydrogen generated from a number of casks is carried through lead pipes into special casks containing water (in order to cool the gas) and lime (in order to remove acid fumes). To avoid loss of gas all the joints are made hermetically tight with cement or tar. In order to fill his gigantic balloon (of 25,000 cubic metres capacity), Giffard, in 1878, constructed a complicated apparatus for giving a continuous supply of hydrogen, in which a mixture of sulphuric acid and water was run continuously into vessels containing iron, and from which the solution of iron sulphate formed was continually drawn off. When coal gas, extracted from coal, is employed for filling balloons, it should be as light, or as rich in hydrogen, as possible. For this reason, only the last portions of the gas coming from the retorts are collected,

Besides being contained in water, hydrogen is also present in many other substances,[18] and may be obtained from them. As examples of this it may be mentioned: (1) that a mixture of formate of sodium, $CHNaO_2$, and caustic soda, NaHO, when heated to redness, forms sodium carbonate, Na_2CO_3, and hydrogen, H_2;[19] (2) that a number of organic substances are decomposed at a red heat, forming hydrogen, among other gases; and thus it is that hydrogen is contained in ordinary coal gas; (3) charcoal liberates hydrogen from steam at a high temperature,[20] but the reaction which here takes place is distinguished by its complexity, and will therefore be considered later; (4) that a certain amount of hydrogen is formed, together with other gases, in the process of decay (change under the influence of micro-organisms) of certain organic substances (for instance, of plants under water).

Gaseous hydrogen is rarely met with in nature. It has been found in the gases of volcanoes (and fumaroles), in small cavities in crystals of rock salt (under pressure and mixed with other gases), and it even occurs in small quantities in the atmosphere, according to the careful researches of Armand Gautier (1900). The spectroscope has proved that hydrogen is also undoubtedly present in the atmospheres of the sun and many of the stars (Chap. XIII.).

The properties of hydrogen.—Hydrogen presents us with an example of a gas which at first sight does not differ from air. It is not surprising, therefore, that Paracelsus, having discovered that an aëriform substance is obtained by the action of metals on sulphuric acid, did not determine exactly its difference from air.[20a] In fact, hydrogen, like air, is colourless, and has no smell;[21] but a more intimate acquaintance with its properties proves it to be entirely different from air. The first sign which distinguishes hydrogen from air is its combustibility. This property is so easily observed that it is the one to which recourse is usually had in order to recognise if hydrogen is evolved in a reaction, although there are many other combustible gases. But before speaking of the combustibility and other chemical properties of hydrogen, we will first describe the physical properties of this gas, as we did in the case of water. It is easy to show that it is one of the lightest gases.[22]

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and, besides this, it is then sometimes passed through red-hot vessels, in order to decompose the hydrocarbons as much as possible. Charcoal is deposited in these vessels, and hydrogen remains as gas. Coal gas may be yet further enriched in hydrogen, and consequently rendered lighter, by passing it over an ignited mixture of charcoal and lime.

L. Mond (London) proposes to manufacture hydrogen on a large scale from water gas (see *infra*, and Chapters VIII. and IX.), which contains a mixture of oxide of carbon (CO) and hydrogen, and is produced by the action of steam upon incandescent coke ($C + H_2O = CO + H_2$). He destroys the oxide of carbon by converting it into carbon and carbonic anhydride, $2CO = C + CO_2$, which is easily done by means of incandescent finely divided metallic nickel; the carbon then remains with the nickel, from which it may be removed by burning it in air, and the nickel can then be used over again (see Chapter IX., note 24a). The CO_2 formed is removed from the hydrogen by passing it through milk of lime. This process should apparently give hydrogen on a large scale more economically than any of the methods hitherto proposed. Hydrogen is formed in many other ways. We shall meet many reactions which are accompanied by the formation of hydrogen gas. The methods here mentioned are the most convenient and easily adopted.

[18] Of the metals, only a very few combine with hydrogen (for example, palladium and sodium), and give substances which are easily decomposed, and some metals, especially platinum and iron, absorb this gas (see Occlusion, note 37). Of the non-metals, the halogens (fluorine, chlorine, bromine, and iodine) most easily form hydrogen compounds: of these the hydrogen compound of chlorine, and still more that of fluorine, are stable, whilst those of bromine and iodine are easily decomposed, especially the latter. The other non-metals—for instance, sulphur, carbon, and phosphorus—give hydrogen compounds of varying composition and properties, but they are all less stable than water.

[19] This reaction, expressed by the equation, $CNaHO_2 + NaHO = CNa_2O_3 + H_2$, may be effected in a glass vessel, like the decomposition of copper carbonate or mercury oxide (see Introduction): it is non-reversible, and takes place without the presence of water, and therefore Pictet (see later) made use of it to obtain hydrogen under great pressure.

[20] The reaction between charcoal and superheated steam is a double one—that is, there may be formed either carbonic oxide, CO (according to the equation, $H_2O + C = H_2 + CO$), or carbonic anhydride, CO_2 (according to the equation $2H_2O + C = 2H_2 + CO_2$), and the resulting mixture is called *water-gas*, but of this we shall speak in Chapter IX.

[20a] Considering the immense velocity of the hydrogen molecules—about 1,800 metres a second (see Chapter I., note 34)—they may, perhaps, travel away from the terrestrial atmosphere into space. The absence of any considerable quantity of hydrogen in the atmosphere of the earth is also probably due to its being converted into water by electrical discharges, &c., in the presence of an excess of oxygen.

[21] Hydrogen obtained by the action of zinc or iron on sulphuric acid generally smells of hydrogen sulphide (like rotten eggs), which it contains in admixture. As a rule, such hydrogen is not so pure as that obtained by the action of an electric current or of sodium on water. The impurity of the hydrogen depends on the impurities contained in the zinc, or iron, and sulphuric acid, and on secondary reactions which take place simultaneously with the main reaction. Impure hydrogen may be freed from the impurities it contains: some of them—namely, those having acid properties—are absorbed by caustic soda, and may therefore be removed by passing the gas through a solution of this substance; another series of impurities is absorbed by a solution of mercuric chloride; and, lastly, a third series is absorbed by a solution of potassium permanganate. If absolutely **pure hydrogen** be required, it is sometimes obtained by the decomposition of water (previously boiled to expel all air, and mixed with pure sulphuric acid) by the galvanic current. Only the gas evolved at the negative electrode is collected. Or else an apparatus like that which gives detonating gas is used, the positive electrode, however, being immersed under mercury containing zinc in solution. The oxygen which is evolved at this electrode then combines immediately, at the moment of its evolution, with the zinc, and this compound dissolves in the sulphuric acid and forms zinc sulphate, which remains in solution, so that the hydrogen generated will be free from oxygen. Quite pure hydrogen (and oxygen) is obtained by decomposing a solution of caustic baryta by electricity. Caustic soda gives hydrogen containing some carbonic anhydride, and sulphuric acid also does not give perfectly pure gases. (Becker, 1902.)

[22] An inverted beaker is attached to one arm of the beam of a tolerably sensitive balance, and its weight counterpoised by weights in the pan attached to the other arm. If the beaker be then filled with hydrogen it rises, owing to the air being replaced by hydrogen. At the ordinary temperature of a room, a litre of air weighs about 1·2 gram, and on replacing the air by hydrogen a decrease in weight of about 1 gram per litre is obtained. Moist hydrogen is heavier than dry—for aqueous vapour is nine times heavier than hydrogen. In filling balloons it is usually calculated (as it is impossible to have

If passed into the bottom of a flask full of air, hydrogen will not remain in it, but, owing to its lightness, rapidly escapes and mixes with the atmosphere. If, however, a cylinder whose orifice is turned downwards be filled with hydrogen, it will not escape, or, more correctly, it will only slowly mix with the atmosphere. This may be demonstrated by the fact that a lighted taper sets fire to the hydrogen at the orifice of the cylinder, and is itself extinguished inside the cylinder. Hence hydrogen, being *itself combustible, does not support combustion.* The great lightness of hydrogen is taken advantage of for balloons. Ordinary coal gas, which is often also used for the same purpose, is only about twice as light as air, whilst hydrogen is fourteen times lighter than air. A very simple experiment with soap bubbles illustrates very well the application of hydrogen to the filling of balloons. Charles, of Paris, showed the lightness of hydrogen in this way, and constructed a balloon filled with hydrogen almost simultaneously with Montgolfier. One litre of pure and dry hydrogen [23] at 0° and 760 mm. pressure weighs 0·08995 *gram ; that is, hydrogen is almost* 14½ *times lighter* than air. It is the lightest of all gases. The small density of hydrogen determines many remarkable properties which it shows ; thus hydrogen passes exceedingly rapidly through fine orifices, its molecules (Chap.

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perfectly dry hydrogen or to obtain it quite free from air) that the *lifting* force due to the difference between the weights of equal volumes of hydrogen and air is equal to 1 kilogram (=1,000 grams) per cubic metre (=1,000 litres).

[23] The density of hydrogen in relation to the air has been repeatedly determined. The first determination, made by Lavoisier, was not very exact. Taking the density of air as unity, he obtained 0·0769 for that of hydrogen ; that is, this gas is thirteen times *lighter than air. More accurate determinations are due to* Thomsen, *who obtained* the figure 0·0693 ; Berzelius and Dulong, who obtained 0·0688 ; and Dumas and Boussingault, who obtained 0·06945. Regnault, and more recently Le Duc, took two spheres of considerable volume, having equal capacities and displacing equal volumes of air (thus avoiding the necessity of any correction for weighing them in air). Both spheres were attached to the scale pans of a balance. One was sealed up, and the other weighed first *empty* and *then full of hydrogen.* Thus, knowing the weight of the hydrogen filling the sphere, and the capacity of the sphere, it was easy to find the weight of a litre of hydrogen ; and, knowing the weight of a litre of air at the same temperature and pressure, it was easy to calculate the density of hydrogen. Regnault found the average density of hydrogen to be 0·06926 ; Le Duc, 0·06948. In 1892 and 1895 Rayleigh, Morley, and Thomsen made fresh determinations, and obtained results very nearly equal to the above. The mean of their results is equal to 0·06956, and this latter figure must now be looked upon as near the truth. Hydrogen is therefore 14·4 times lighter than air. In other words a litre of hydrogen at 0°, under the normal pressure of 760 mm., at the sea level and latitude 45°, weighs 0·08995 gram, or at $t°$, and under the pressure **H**, at latitude 45°, the weight of a litre of hydrogen is equal to

$$0{\cdot}08995\frac{H}{760}\times\frac{1}{1+0{\cdot}00367t}\text{ grams.}$$

In this book we shall always refer the density of gases to that **of hydrogen, as it is the lightest of all gases and vapours under the same conditions.**

I.) being endowed with the greatest velocity.[24] At pressures somewhat higher than that of the atmosphere, all other gases exhibit a greater compressibility and coefficient of expansion than they should, according to the laws of Mariotte and Gay-Lussac ; whilst hydrogen, on the contrary, is compressed to a less degree than it should be from the law of Mariotte,[25] and with a rise of pressure it expands slightly

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[24] If a cracked flask be filled with hydrogen, and its neck immersed under water or mercury, the liquid will rise up into the flask, *owing to the hydrogen passing out* through the cracks about 3·8 times quicker than the air is able to pass through these cracks into the flask. The same phenomenon may be better observed if, instead of a flask, a tube be employed whose end is closed by a porous substance, such as graphite, unglazed earthenware, or a gypsum plate.

[25] According to Boyle and Mariotte's law, for a given gas at a constant temperature the volume decreases by as *many times* as *the pressure increases;* that is, the product of the volume v and the pressure p for a given gas is a constant quantity : $pv=C$, which does not vary with a change of pressure. This equation does very nearly and exactly express the observed relation between the volume and pressure, but only within comparatively small variations of pressure. If these variations be in any degree considerable, the quantity pv proves to be dependent on the pressure, and it either increases or diminishes with an increase *of pressure.* In the former case the compressibility is less than it should be according to Mariotte's law—in the latter case it is greater. We will call the first case a positive discrepancy (because then $d(pv)/d(p)$ is greater than zero), and the second case a negative discrepancy (because then $d(pv)/d(p)$ is less than zero). Determinations made by myself (in the seventies), M. L. Kirpicheff, and V. A. Hemilian showed that all known gases at low pressures—i.e., when considerably rarefied—present positive discrepancies. *On the other hand,* it appears from the researches of Cailletet, Natterer, and Amagat that all gases under great pressures (when the volume obtained is 500–1,000 times less than under the atmospheric pressure) also present positive discrepancies. Thus under a pressure of 2,700 atmospheres air is compressed, not 2,700 but only 800 times, and hydrogen 1,000 times. Hence the positive kind of discrepancy is, so to speak, normal to gases. And this is easily intelligible. If a gas followed Mariotte's law, *or if it were* compressed to a greater extent than is shown by this law, then under great pressures it would attain a density greater than that of solid and liquid substances, which is in itself improbable and even impossible by reason of the fact that solid and liquid substances are themselves but little compressible. For instance, a cubic centimetre of oxygen at 0° and under the atmospheric pressure weighs about 0·0014 gram, and at a pressure of 3,000 atmospheres (this pressure is attained in guns) it would, if it followed Mariotte's law, weigh 4·2 grams—that is, would be about four times heavier than water—and at a pressure of 10,000 atmospheres it would be heavier than mercury. Besides this, positive discrepancies are probable because the molecules of a gas themselves must occupy a certain volume. Considering that Mariotte's law, strictly speaking, applies only to the intermolecular space, we can understand the necessity of positive discrepancies. If we designate the volume of the molecules of a gas by b (like van der Waals, see Chapter I., note 34), then it must be expected that $p\ (v-b)=C$. Hence $pv=C+bp$, which expresses a positive discrepancy. Supposing that for hydrogen, $pv=1{,}000$, at a pressure of one metre of mercury, we obtain b, according to the results of Regnault's, Amagat's, and Natterer's experiments, as approximately 0·7 to 0·9.

Thus the increase of pv with increase of pressure must be considered as the normal law of the compressibility of gases. Hydrogen presents such a positive compressibility at all pressures, for it presents positive discrepancies, according to Regnault, at all pressures slightly above the atmospheric pressure. Hence hydrogen is, so to speak, a model gas. No other gas behaves so simply with a change of pressure. All other gases at pressures from 1 to 30 atmospheres present negative discrepancies ; that is, they are less than at the atmospheric pressure.[26] However, hydrogen, like air and many other gases which are permanent at the ordinary temperature,

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then compressed to a greater degree than should follow from Mariotte's law, as was shown by the determinations of Regnault, which were verified when repeated by myself and Boguzsky. Thus, for example, on changing the pressure from 4 to 20 metres of mercury—that is, on increasing the pressure five times—the volume of hydrogen only decreased 4·93 times, and that of air 5·06 times.

The positive discrepancies from the law at low pressures are of particular interest, and, according to the above-mentioned determinations made by myself, Kirpicheff, and Hemilian, and verified (by two methods) by K. D. Kraevitch and Ramsay (London, 1894), they are common to all gases (even to those which are easily compressed into a liquid state, such as carbonic and sulphurous anhydrides). These discrepancies coincide with a very high rarefaction of the gas, where it is near a condition of maximum dispersion of its molecules, and perhaps presents a passage towards the substance termed 'luminiferous ether' which fills up interplanetary and interstellar space. If we suppose that gases are rarefiable only to a definite limit, after having attained which they (like solids) hardly alter in volume with a decrease of pressure, then on the one hand the passage of the atmosphere at its upper limits into a homogeneous ethereal medium becomes comprehensible, and on the other hand it would be expected that gases would, in a state of high rarefaction, present positive discrepancies from Boyle and Mariotte's law. Our present acquaintance with this province of highly rarefied gases is very limited (because direct measurements are exceedingly difficult to make, and are hampered by possible errors of experiment, which may be considerable), and its further development promises to elucidate much in respect to natural phenomena. To the three states of matter (solid, liquid, and gaseous) perhaps a fourth may yet be added, the ethereal or ultra-gaseous (as Crookes proposed), by which is understood matter in its highest possible state of rarefaction.

[26] The law of Gay-Lussac states that all gases in all conditions present one coefficient of expansion, 0·00367; that is, when heated from 0° to 100° they expand like air, 1,000 volumes of a gas at 0° occupying 1,367 volumes at 100°. Regnault, about 1850, showed that Gay-Lussac's law is not entirely correct, and that different gases, and also one and the same gas at different pressures, have not quite the same coefficients of expansion. Thus the expansion of air between 0° and 100° is 0·367 under the ordinary pressure of one atmosphere, but at three atmospheres it is 0·371, whilst that of carbonic anhydride is 0·37. Regnault, however, did not directly determine the change of volume between 0° and 100°, but measured the variation of pressure with the change of temperature. But since gases do not entirely follow Mariotte's law, the change of volume cannot be directly judged by the variation of pressure. The investigations carried on by myself and Kayander, about 1870, showed the variation of volume on heating from 0° to 100° under a really constant pressure. These investigations confirmed Regnault's conclusion, that Gay-Lussac's law is not absolutely accurate, and further showed (1) that the expansion per unit volume from 0° to 100° under a pressure of one atmosphere is for air 0·368, for hydrogen 0·367, for carbonic anhydride 0·373, for hydrogen bromide 0·386, &c.; (2) that for gases which are more compressible than should follow from Mariotte's law, the expansion by heat increases with the pressure—for example, for air at a pressure of three and a half atmospheres, it equals 0·371, for carbonic anhydride, at one atmosphere 0·373, at three atmospheres 0·389, and at eight atmospheres 0·413; (3) that for gases which are less compressible than should follow from Mariotte's law, the expansion by heat decreases with an increase of pressure—for example, for hydrogen at one atmosphere 0·367, at eight atmospheres 0·369, for air at a quarter of an atmosphere 0·370, at one atmosphere 0·368; and hydrogen like *air* (and other gases) is less compressed *at low pressures* than should follow from Mariotte's law (see note 25). Hence, hydrogen, starting from zero and rising to the highest pressures, exhibits a gradually, although only slightly, varying coefficient of expansion, whilst for air and other gases at the atmospheric and higher pressures the coefficient of expansion increases with the

does not pass into a liquid state even under the greatest possible pressures,[27] but is compressed into a lesser volume than would follow

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increase of pressure, so long as their compressibility is greater than should follow from Mariotte's law. But when at considerable pressures this kind of discrepancy passes into the normal (see note 25), then the coefficient of expansion of all gases decreases with an increase of pressure, as is seen from the researches of Amagat. The difference between the two coefficients of expansion, for a constant pressure and for a constant volume, is explained by these relations. Thus, for example, for air at a pressure of one atmosphere the true coefficient of expansion (the volume varying at constant pressure) = 0·00368 (according to Mendeléeff and Kayander) and the variation of pressure (at a constant volume, according to Regnault) = 0·00367.

[27] Permanent gases are those which cannot be liquefied by an increase of pressure alone. With rise of temperature, all gases and vapours become permanent gases. As we shall afterwards learn, carbonic anhydride becomes a permanent gas at temperatures above 31°, and at lower temperatures it has a maximum pressure, and may be liquefied by pressure alone.

The liquefaction of gases, accomplished by Faraday (see Ammonia, Chapter VI.) and others, in the first half of the last century, showed that a number of substances are capable, like water, of assuming all three physical states, and that there is no essential difference between vapours and gases, the only distinction being that the boiling-points (or the temperatures at which the pressure = 760 mm.) of liquids lie above the ordinary temperature, and those of liquefied gases below, and that consequently a gas is superheated vapour, or vapour heated above the boiling-point, or removed from saturation and rarefied, having a lower pressure than that maximum which is proper to a given temperature and substance. We will here cite the **maximum pressures** of certain liquids and gases **at various temperatures**, because they may be taken advantage of for obtaining constant temperatures by changing the pressures at which boiling or the formation of saturated vapours takes place. The temperatures (according to the air thermometer) are placed on the left, and the pressures in millimetres of mercury (at 0°) on the right-hand side. Carbon bisulphide, CS_2; 0°, 127·9; 10°, 198·5; 20°, 298·1; 30°, 431·6; 40°, 617·5; 50°, 857·1. Aniline, C_5H_7N; 150°, 283·7; 160°, 387·0; 170°, 515·6; 108°, 677·2; 185°, 771·5. Mercury, Hg; 300°, 246·8; 310°, 304·9; 320°, 373·7; 330°, 454·4; 340°, 548·6; 350°, 658·0; 359°, 770·9. Sulphur, S; 395°, 300; 423°, 500; 443°, 700; 452°, 800; 459°, 900. These figures were obtained by Ramsay and Young. We may add the following boiling-points under a pressure of 760 mm. (according to the air thermometer, *Callendar and Griffiths*, 1891: *aniline*, 184°, 13; naphthalene, 217°, 94; benzophenone, 305°, 82; mercury, 356°, 76; sulphur, 444°, 53. And melting-points: tin, 231°, 68; bismuth, 269°, 22; lead, 327°, 69; and zinc, 417°, 57. These data may also be used for obtaining a constant temperature and for verifying thermometers. The pressures of liquefied gases are expressed *in atmospheres*. Sulphurous anhydride, SO_2: − 30°, 0·4; − 20°, 0·6; − 10°, 1; 0°, 1·5; + 10°, 2·3; 20°, 3·2; 30°, 5·3. Ammonia, NH_3: − 40°, 0·7; − 30°, 1·1; − 20°, 1.8; − 10°, 2·8; 0°, 4·2; + 10°, 6·0; 20°, 8·4. Carbonic anhydride, CO_2: − 115°, 0·033; − 80°, 1; − 70°, 2·1; − 60°, 3·9; − 50°, 6·8; − 40°, 10; − 20°, 23; 0°, 35; + 10°, 46; 20°, 58. Nitrous oxide, N_2O: − 125°, 0·033; − 92°, 1; − 80°, 1·9; − 50°, 7·6; − 20°, 23·1; 0° 36·1; + 20°, 55·3. Ethylene, C_2H_4: − 140°, 0·033; − 130°, 0·1; − 103°, 1; − 40°, 13; − 1°, 42., Air: − 191°, 1; − 158° 14; − 140°, 39. Nitrogen: N_2: − 203°, 0·085; − 193°, 1; − 160°, 14; − 146°, 32. The methods of liquefying gases (by pressure and cold) will be described under ammonia, nitrous oxide, sulphurous anhydride, and in later footnotes. We will now turn our attention to the fact that the evaporation of volatile liquids, under various, and especially under low, pressures, gives an easy means for obtaining **low temperatures**. Thus, liquefied carbonic anhydride, under the ordinary pressure, reduces the temperature to − 80°, and when it evaporates in a rarefied atmosphere (under an air-pump) at 25 mm. (= 0·033 atmosphere) the temperature, judging by the above-cited figures, falls to − 115° (Dewar). Even the evaporation of from Mariotte's law.[28] From this it may be concluded that the critical temperature (absolute boiling-point) of hydrogen, and of gases resembling it,[29] lies very much below the ordinary temperature; that is, that the **liquefaction** of this **gas** is only possible at low temperatures, and under great pressures.[30] This conclusion was verified (1877) by the experiments of Pictet and Cailletet.[31] They compressed gases at a very

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liquids of common occurrence, under low pressures easily attainable with an air-pump, may produce low temperatures, which may be again taken advantage of for obtaining still more volatile liquids. Water boiling in a vacuum becomes cold, and under a pressure of less than 4·5 mm. it freezes, because its pressure at 0° is 4·5 mm. A sufficiently low temperature may be obtained by forcing fine streams of air through common ether, carbon bisulphide, CS_2, or methyl chloride, CH_3Cl, and other similar volatile liquids. In the adjoining table are given, for certain gases, (1) the number of atmospheres necessary for their liquefaction at 15°, and (2) the boiling-points of the resultant liquids under a pressure of 760 mm.

	C_2H_2	C_2H_4	N_2O	CO_2	H_2S	AsH_3	NH_3	HCl	CH_3Cl	C_2N_2	SO_2
(1)	39	56	45	50	10	8	7	25	4	4	3
(2)	−75°	−104°	−90°	−79°	−74°	−58°	−34°	−84°	−24°	−21°	−10°

[28] Natterer's determinations (1851–1854), together with Amagat's results (1880–1888), show that the compressibility of hydrogen, under high pressures, may be expressed by the following figures:—

p =	1	100	1000	2500
v =	1	0·0107	0·0019	0·0013
pv =	1	1·07	1·9	3·25
s =	0·11	10·3	58	85

where p is the pressure in metres of mercury, v the volume (that under a pressure of 1 metre being taken as 1), and s the weight in grams of a litre of hydrogen at 20°. If hydrogen followed Mariotte's law, then under a pressure of 2,500 metres one litre would contain not 85, but about 265 grams. It is evident from the above figures, that as the pressure increases, the weight of a litre of the gas approaches a limit which is doubtless the density of the gas when liquefied, and therefore the weight of a litre of liquid hydrogen would be near 100 grams (density about 0·1, which is less than that of all other liquids) at 20°, if liquid hydrogen could exist at that temperature.

[29] Cagniard de Latour, on heating ether in a closed tube to about 190°, observed that at this temperature the liquid is transformed into vapour occupying the original volume—that is, having the same density as the liquid. The further investigations made by Drion and by myself showed that every liquid has such an **absolute boiling-point**, above which it cannot exist as a liquid, and is transformed into a dense gas. In order to grasp the true signification of this absolute boiling temperature, it must be remembered that the liquid state is characterised by a cohesion of the particles which does not exist in vapours and gases. The cohesion of liquids is expressed in their capillary phenomena (drop formation, rise in capillary tubes, &c.), and the product of the density of a liquid into the height to which it rises in a capillary tube (of a definite diameter) may serve as the measure of the magnitude of cohesion. Thus, in a tube of 1 mm. diameter, water at 15° rises (the height being corrected for the meniscus) 14·8 mm., and ether at $t°$ to a height ($5·35 - 0·028\ t$) mm. The cohesion of a liquid is lessened by heating, and therefore the capillary heights are also diminished. It has been shown by experiment that this decrement is proportional to the temperature, and hence by the aid of capillary observations we are able to form an idea that at a certain temperature the cohesion may vanish. For ether, according to the above formula, this would occur at 191°. If the cohesion disappears from a liquid it becomes a gas, for cohesion is the only point of difference between these two states. A liquid in evaporating and overcoming the force of cohesion, absorbs heat. Therefore the absolute boiling-point was defined by me (1861) as that temperature at which: (*a*) a liquid cannot exist as a liquid, but forms a gas which cannot pass into a liquid state under any pressure whatever; (*b*) its cohesion is zero; and (*c*) the latent heat of evaporation = 0.

This definition was but little known until Andrews (1869) explained the matter from another aspect by starting from gases. He discovered that carbonic anhydride cannot be liquefied by any degree of compression at temperatures above 31°, whilst at lower temperatures it can be liquefied. He called this temperature the *critical temperature*. It is evident that it is the same as the absolute boiling-point. We shall afterwards designate it by *tc*. At low temperatures a gas which is subjected to a pressure greater than its maximum pressure is transformed into a liquid, which, in evaporating, gives a saturated vapour possessing this maximum pressure; whilst at temperatures above *tc*, the pressure to which the gas is subjected may increase indefinitely. However, under these conditions the volume of the gas does not change indefinitely but approaches a definite limit (see notes 25 and 28)—that is, it resembles in this respect a liquid or a solid which is altered but little in volume by pressure. The volume which a liquid or gas occupies at *tc* is termed the **critical volume**, and corresponds with the **critical pressure**, which we will designate by *pc* and express in atmospheres. It is evident from what has been said that the discrepancies from Mariotte and Boyle's law, the absolute boiling-point, the density in the liquid and compressed gaseous states, and the properties of liquids, must all be intimately connected together. We shall consider these relations in one of the following notes. At present we will supplement the above observations by the values of *tc* and *pc* for certain liquids and gases which have been investigated in this respect—

	tc	*pc*		*tc*	*pc*
H_2	− 240°	15	CH_3COOH	+ 322°	57
N_2	− 146°	33	H_2S	+ 108°	92
CO	− 140°	39	C_2N_2	+ 124°	62
O_2	− 119°	50	NH_3	+ 131°	114
CH_4	− 100°	50	CH_3Cl	+ 141°	73
NO	− 93°	71	SO_2	+ 155°	79
C_2H_6	− 40°	50	C_5H_{10}	+ 192°	34
C_2H_4	+ 10°	51	$C_4H_{10}O$	− 194°	36
CO_2	+ 32°	77	$CHCl_3$	+ 268°	55
N_2O	+ 39°	78	CS_2	+ 273°	88
C_2H_2	+ 37°	68	C_6H_6	+ 288°	48
HCl	+ 52°	86	C_6H_5F	+ 287°	45
H_2O	+ 365°	200	C_6H_5Cl	+ 360°	45
CH_3OH	+ 240°	79	C_6H_5Br	+ 397°	45
C_2H_5OH	+ 243°	63	C_6H_5I	+ 448°	45

Young and Guy (1891) showed that *tc* and *pc* clearly depend upon the composition and molecular weight.

[30] I came to this conclusion in 1870 (*Ann. Phys. Chem.* **141**, 623).

[31] **Pictet**, in his researches, effected the direct liquefaction of many gases, which up to that time had not been liquefied. He employed the apparatus used for the manufacture of ice on a large scale, employing the vaporisation of liquid sulphurous anhydride, which may be liquefied by pressure alone. This anhydride is a gas which is transformed into a liquid at the ordinary temperature under a pressure of several atmospheres (see note 27), and boils at −10° at the ordinary atmospheric pressure. The liquid, like all others, boils at a lower temperature under a diminished pressure, and by continually pumping out the gas which comes off by means of a powerful air-pump its boiling-point falls as low as −75°. Consequently if, on the one hand, liquid sulphurous anhydride be forced into a vessel, and on the other hand the gas be pumped from the same vessel by powerful air-pumps, the temperature falls to −75°. If a second vessel is placed inside this one, then another gas may be easily liquefied in it at the low temperature

low temperature, and then allowed them to expand, either by directly decreasing the pressure or by allowing them to escape into the air, by which means the temperature fell still lower, and then, just as steam

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produced, if the latter is less than its critical temperature. Pictet in this manner easily liquefied carbonic anhydride, CO_2 (at −60° under a pressure of from four to six atmospheres). This gas is more refractory to liquefaction than sulphurous anhydride, but for this reason it gives on evaporating a still lower temperature than can be attained by the evaporation of sulphurous anhydride. A temperature of −80° may be obtained by the evaporation of liquid carbonic anhydride at a pressure of 760 mm., and in an atmosphere rarefied by a powerful pump the temperature falls to −140°. By employing such low temperatures it was possible, with the aid of pressure, to liquefy the majority of the other gases, but not hydrogen. It is evident that special pumps which are capable of rarefying gases are necessary to reduce the pressure in the chambers in which the sulphurous and carbonic anhydrides boil; and that, in order to recondense the resultant gases into liquids, special force pumps are required for pumping the liquid anhydrides into the refrigerating chamber. Thus, in Pictet's apparatus (fig. 25), the carbonic anhydride was liquefied by the aid of the pumps E A F, which compressed the gas (at a pressure of 4–6 atmospheres) and forced it into the tube K, vigorously cooled by being surrounded with boiling liquid sulphurous anhydride, which was condensed in the tube C by the pump B, and rarefied by the pump A. The liquefied carbonic anhydride flowed down the tube K into the tube H, in which it was subjected to a low pressure by the pump E, and thus gave a very low temperature of about −140°. The pump E carried off the vapour of the carbonic anhydride, and conducted it to the pump F, by which it was again liquefied. The carbonic anhydride thus made an entire circuit—that is, it passed from a rarefied vapour of small pressure and low temperature into a compressed and cooled gas, which was transformed into a liquid, which again vaporised and produced a low temperature.

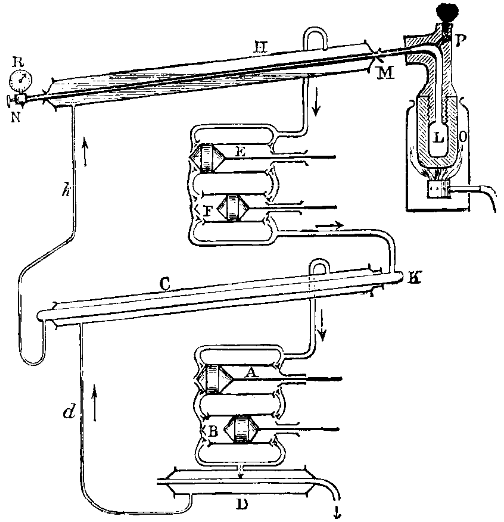

Fig. 25.—General arrangement of the apparatus employed by Pictet for liquefying gases.

Inside the wide inclined tube H, where the carbonic acid evaporated, was placed a

when rapidly rarefied [32] deposits liquid water in the form of a fog, hydrogen in expanding forms a fog, thus indicating its passage into

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second and narrow tube, M, containing hydrogen, which was generated in the vessel L by heating a mixture of sodium formate and caustic soda ($CHO_2Na + NaHO = Na_2CO_3 + H_2$). This vessel and the tube M were made of thick copper, and could withstand great pressures. They were, moreover, hermetically connected together and closed up. Thus the gas evolved had no outlet, accumulated in a limited space, and its pressure increased in proportion to the amount of it evolved. This pressure was recorded on a metallic manometer, R, attached to the end of the tube M. As the hydrogen in this tube was submitted to a very low temperature and a powerful pressure, all the necessary conditions were present for its liquefaction. When the temperature had fallen to −140° and the manometer R indicated a pressure of 600 atmospheres in the tube M, this pressure did not apparently rise with a further evolution of hydrogen in the vessel L. Pictet regarded this as an indication that the pressure of the vapour of the hydrogen had attained a maximum corresponding with −140°, and that consequently all the excess of the gas was condensed to a liquid. As a matter of fact Pictet could not possibly have obtained liquid hydrogen, for −140° was far too high a temperature, considering that the critical point of hydrogen lies at about −240°; but he obtained oxygen, nitrogen, and many other gases in a liquid state, and this was a great novelty in those days.

[32] At the same time (1879) as Pictet was working on the liquefaction of gases in Switzerland, **Cailletet**, in Paris, was occupied with the same subject, and his results, although not so convincing as Pictet's, still showed that the majority of gases, previously unliquefied, were capable of passing into a liquid state. Cailletet subjected gases to a pressure of several hundred atmospheres in narrow thick-walled glass tubes (fig. 26) and then cooled the compressed gas as far as possible by surrounding it with a freezing mixture; a cock was then rapidly opened for the outlet of mercury from the tube containing the gas, which consequently rapidly and vigorously expanded. This rapid expansion of the gas would produce great cold, just as the rapid compression of a gas evolves heat and causes a rise in temperature. This cold was produced at the expense of the gas itself, for in rapidly expanding its particles were not able to absorb heat from the walls of the tube, and in cooling a portion of the expanding gas was transformed into liquid. This was seen from the formation of cloud-like drops like a fog which rendered the gas opaque. Thus Cailletet proved the possibility of the liquefaction of gases, but he did not isolate the liquids.

The methods of Pictet and Cailletet were afterwards improved by Olszewski, Wroblewski, Dewar, and others. In order to obtain a still lower temperature they employed, instead of carbonic acid gas, liquid ethylene (C_2H_4) or nitrogen and oxygen, whose evaporation at low pressures produces a much lower temperature (as low as −200°). They also improved on the methods of determining such low temperatures without, however, essentially altering the principle.

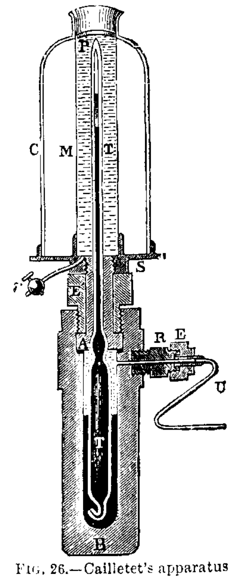

Fig. 26.—Cailletet's apparatus for liquefying gases.

The most instructive results have been obtained in recent years by Professor Dewar in the Royal Institution of London, which is glorified by the names of Davy, Faraday, and Tyndall. Dewar, by working with large quantities and powerful pumps, obtained many kilograms of oxygen and air (the boiling-point under the atmospheric pressure = −190°) in a liquid state, and kept them in this state for a length of time by means of open glass vessels (constructed as seen in the drawing) a liquid state. But the first of these experimenters was unable to preserve this liquid, even for a short time, to determine its properties,

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with double walls (silvered inside to reflect the rays of heat) having a vacuum between them, which prevented the rapid transference of heat, and so gave the possibility of maintaining very low temperatures inside the vessel for a long period of time. The liquefied oxygen or air can be poured from one vessel into another and used for any investigations. Thus, in June 1894, Professor Dewar showed that at the low temperature produced by liquid oxygen many substances become phosphorescent (self-luminous; for instance, oxygen on passing into a vacuum) and fluoresce (emit light after being illuminated; for instance, paraffin, glue, &c.) much more powerfully than at the ordinary temperature; also that solids then greatly alter in their mechanical properties, &c. The liquid gas poured into the above vessel only remains as such at the ordinary temperature, because it preserves its own low temperature (with air, for instance, this is −191° under the corresponding pressure) and does not evaporate to any extent, because that would require the absorption of heat (so-called latent) which penetrates with difficulty and but slowly through the double walls, just as the heat of a warm room passes with difficulty through a double window. It was the employment of such vessels with double (and even treble) walls which enabled Dewar (1898) not only to obtain liquid hydrogen but to keep it as such for a sufficient length of time to determine its properties and even its transition into a solid state. A scheme of the apparatus, used by Dewar for this purpose, is given in the accompanying drawings. *A* is a metallic reservoir containing hydrogen under a pressure of 180–200 atmospheres, *B* and *C* are double-walled vessels, with a vacuum between the walls, in which liquid carbonic anhydride and air are evaporated under a diminished pressure and cool the hydrogen passing through the spiral tube to −203°. In the third double-walled vessel, *D*, the refrigerated and liquefied hydrogen expands on opening the cock *F*, which causes its temperature to fall yet further, and it is then obtained as a colourless liquid whose chief properties are given in the text.

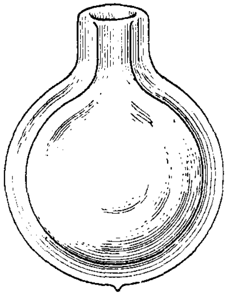

FIG. 27.—Dewar's vacuum-jacketed vessel for liquefied gases.

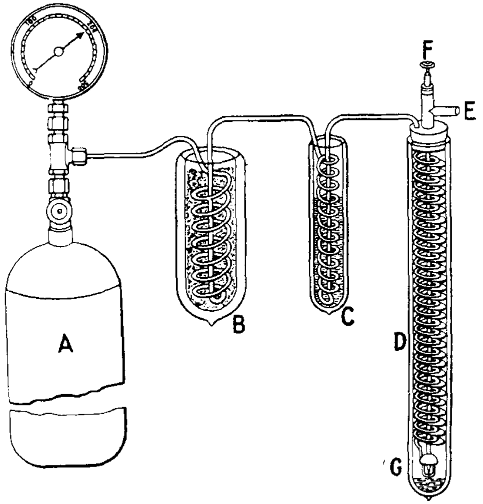

FIG. 28.—Dewar's apparatus for liquefying hydrogen.

notwithstanding the employment of a temperature of −200° and a pressure of 200 atmospheres,[33] although by these means the gases of the atmosphere may be easily liquefied. This is due to the fact that the absolute boiling-point of hydrogen lies lower than that of all other known gases, a fact which also depends on the extreme lightness of hydrogen.[34]

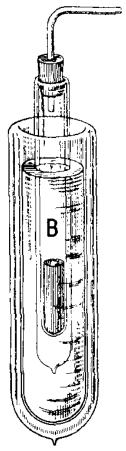

FIG. 29.—Dewar's apparatus for solidifying hydrogen. The inner vacuum vessel, B, contains liquid hydrogen, and the outer one liquid air. By pumping gas out of both of these vessels, the temperature of the hydrogen falls to −256°, when it solidifies.

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[33] The investigations of S. Wroblewski in Cracow clearly show that Pictet could not have obtained liquid hydrogen in the interior of his apparatus, and that if he did obtain it, it could only have been at the moment of its exit due to the fall in temperature following its sudden expansion, as hydrogen is not liquefied by any pressure at −140° because its critical temperature (absolute boiling-point) lies much lower—at about −240°. However, on expansion a fog is formed and a liquid state attained, but the liquid does not separate.

[34] After the idea of the absolute temperature of ebullition (*tc*, note 29) had been worked out (about 1870), and its connection with the deviations from Mariotte's law had become evident, and especially after the liquefaction of permanent gases, general attention was turned to the development of the fundamental conceptions of the gaseous and liquid states of matter. Some investigators directed their energies to the further study of vapours (for instance, Ramsay and Young), gases (Amagat), and liquids (Zaencheffsky, Nadeschdin, and others), especially to liquids near the critical temperature and pressure; others (Konovaloff and De Heen) endeavoured to discover the relation between liquids under ordinary conditions (far removed from the critical temperature and pressure) and gases; whilst a third class of investigators (van der Waals, Clausius, and others), starting from the generally accepted principles of the mechanical theory of heat and the kinetic theory of gases, and assuming in gases the existence of those forces which certainly act in liquids, deduced the connection between the properties of one and the other. It would be out of place in an elementary handbook (see Physical Chemistry) like the present to enunciate the whole mass of conclusions arrived at by this method; but it is well to give an idea of the results of van der Waals's considerations, for they explain the gradual uninterrupted passage from a liquid into a gaseous state in the simplest manner, and, although the deduction cannot be considered as complete and decisive (see note 25), nevertheless it penetrates so deeply into the essence of the matter that its signification is not only reflected in a great number of physical investigations, but also in the province of chemistry, where instances of the passage of substances from a gaseous to a liquid state (and conversely) are so common, and where the very processes of dissociation, decomposition, and combination must be identified with a change of physical state of the participating substances, which has been elaborated by Gibbs, Liveing, and others.

For a *given quantity* (weight, mass) *of a definite substance*, its state is expressed by three variables—volume v, pressure (elasticity, tension) p, and temperature t.

Dewar, who obtained and investigated liquid hydrogen in 1898, showed that the critical temperature of this gas lies at about −240°,

i.e., at a temperature difficult to attain even by evaporating other liquefied gases under diminished pressure. Dewar succeeded in liquefying hydrogen by cooling it to −220° (which he obtained in liquid oxygen under diminished pressure) under a pressure of 200 atmospheres, and then making it expand rapidly (by letting it flow from an orifice in the vessel holding it) when its temperature fell to −252°, at which temperature liquid hydrogen boils under the ordinary pressure (about 760 mm.) Liquid hydrogen then occurs as a colourless liquid, a litre of which weighs about 0·086 gram at its melting-point, −256° (it is thus the lightest liquid known), and which freezes (on lowering the

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Although the compressibility—[i.e., $d(v)/d(p)$]—of liquids is small, still it is clearly expressed, and varies not only with the nature of the liquids, but also with their pressure and temperature (the compressibility of liquids at a low temperature is very considerable; for instance, for hydrogen 0·024, nitrogen 0·0056, and oxygen 0·0046). Although, according to Mariotte's law, with small variations of pressure, gases are uniformly compressed, nevertheless the dependence of their volume v on t and p is very complex. This also applies to the coefficient of expansion $[=d(v)/d(t)$, or $d(p)/d(t)]$, which also varies with t and p, both for gases (see note 26) and for liquids (at tc it is very considerable, and often exceeds that of gases, 0·00367). Hence, the **equation of condition** must include three variables, v, p, and t. For a so-called perfect (ideal) gas or for inconsiderable variations of density, the elementary expression, $pv=R\,(273+t)$ should be accepted, where R is a constant varying with the mass and nature of a gas. In its simplest form the equation may be expressed thus:

$$pv=RT:$$

where T denotes what is termed the absolute temperature, or the ordinary temperature + 273, that is, $T=t+273$.

Starting from the supposition of the existence of an attraction or internal pressure (expressed by a) proportional to the square of the density (or inversely proportional to the square of the volume) and of the existence of a real volume or diminished length of path (expressed by b) for each gaseous molecule, **van der Waals** gives for gases the following complex **equation** of condition:—

$$\left(p+\frac{a}{v^2}\right)(v-b)=1+0{\cdot}00367t,$$

if at 0° and under a pressure $p=1$ (for example, under the atmospheric pressure), the volume (for instance, a litre) of a gas or vapour be taken as 1, and v and b be therefore expressed by the same units as p and a. The above equation **expresses the deviations** from the laws both of Mariotte and Gay-Lussac. Thus, for hydrogen a must be taken as infinitely small, and $b=0{\cdot}0009$, judging by the data for 1,000 and 2,500 metres pressure (note 28). For other permanent gases these deviations may be expressed by giving definite magnitudes of a and b (although van der Waals's formula is not applicable in the case of very small pressures) with sufficient accuracy for present requirements. It is evident that van der Waals's equation can also express the variation of the coefficients of expansion of gases with change either of pressure or of the method of determination (note 26). Besides this, van der Waals's formula shows that the absolute boiling-point $(tc)=273\left(\frac{8a}{27b}-1\right)$. This is found from the fact that all three possible volumes (the three roots of van der Waals's cubic equation) are then similar and equal, i.e. $(vc)=3b$. The pressure in this case is given by $(pc)=\frac{a}{27b^2}$. These ratios between the constants a and b and the conditions of the critical state, i.e. (tc) and (pc), give the possibility of determining one pair of these magnitudes from the others. Thus for ether (note 29), $(tc)=193°$, $(tp)=40$; hence $a=0{\cdot}0307$, $b=0{\cdot}00533$, and $(vc)=0{\cdot}016$. That mass of ether which at a pressure of one atmosphere at 0° occupies one volume—for instance, a litre—occupies, according to the above-mentioned condition, this critical volume. And as the density of the vapour of ether compared with that of hydrogen is 37, and a litre of hydrogen at 0° and under the atmospheric pressure weighs 0·0896 gram, then a litre of ether vapour weighs 3·32 grams; therefore in a critical state (at 193° and 40 atmospheres) 3·32 grams occupy 0·016 litre, or 16 c.c.; so that 1 gram occupies a volume of about 5 c.c., and the weight of 1 c.c. of ether will then be 0·21. According to the investigations of Ramsay and Young (1887), the critical volume of ether is approximately such at about the absolute boiling-point; but the compressibility of the liquid is so great that the slightest change of pressure or temperature has a considerable effect on the volume. But the investigations of the above savants gave another indirect demonstration of the truth of van der Waals's equation. They also found for ether that the isochords, or the lines of equal volumes (if both t and p vary), are generally straight lines, which is a direct result of van der Waals's formula.

When, in 1883, I demonstrated that the specific gravity of liquids decreases *approximately* in proportion to the rise of temperature $[S_t=S_0-Kt$ or $S_t=S_0\,(1-kt)]$, where k is the modulus of expansion, which varies with the nature of the liquid, then, in general, not only does a connection arise between gases and liquids with respect to a change of volume, but also it would appear possible, by applying van der Waals's formula, to judge, from the phenomena of the expansion of liquids, as to their transition into vapour, and to connect together all the principal properties of liquids, which up to this time had not been considered to be in direct dependence. Thus Thorpe and Rücker found that $2(tc)+273=1/k$, where k is the *modulus* of expansion in the above-mentioned formula. For example, the expansion of ether is expressed with sufficient accuracy from 0° to 100° by the equation: $S_t=0{\cdot}736\,(1-0{\cdot}00154t)$, or $V_t=1/(1-0{\cdot}00154t)$, where 0·00154 is the modulus of expansion, so that $(tc)=188°$, direct observation giving 194°. For silicon tetrachloride, $SiCl_4$, the modulus equals 0·00136, whence $(tc)=231°$, the experimental value being 230°. On the other hand, D. P. Konovaloff, admitting that the external pressure, p, in liquids is insignificant when compared with the internal (a in van der Waals's formula), and that the work in the expansion of liquids is proportional to their temperature (as in gases), deduced directly from van der Waals's equation, the above-mentioned formula for the expansion of liquids, and also the magnitudes of the latent heat of evaporation, of the cohesion, and of the compressibility. In this way van der Waals's formula embraces the gaseous, critical, and **liquid states** of substances, and shows the connection between them. On this account, although van der Waals's formula cannot be considered as perfectly general and accurate, yet it is not only very much more exact than $pv=RT$, but it is also more comprehensive, because it applies both to gases and liquids. Further research will naturally give a closer proximity to truth, and will show the connection between composition and the constants (a and b); but this form of the equation of state marks great scientific progress.

Clausius (in 1880), taking into consideration the variability of a in van der Waals's formula with the temperature, gave the following equation of condition:—

$$\left(p+\frac{a}{T\,(v+c)^2}\right)(v-b)=RT.$$

Sarrau (1882) applied this formula to Amagat's data for hydrogen, and found $a=0{\cdot}0551$, $c=-0{\cdot}00043$, $b=0{\cdot}00089$, and therefore calculated its absolute boiling-point to be −174°, and $(pc)=99$ atmospheres. But as similar calculations for oxygen (−105°), nitrogen (−124°), and marsh gas (−76°) gave tc higher than it really is, the absolute boiling-point of hydrogen must lie below −174°, and as a matter of fact it is about −240°. Further details on the subjects here touched upon must be sought in physical chemistry.

pressure and temperature) into colourless crystals, melting at about −256°.

Although a substance which passes with great difficulty into a liquid or solid state by the action of physico-mechanical forces, hydrogen loses its gaseous state (that is, its elasticity, or the physical energy of its molecules, or their rapid progressive motion) with comparative ease under the influence of chemical attraction,[35] as is seen, not only from the fact that hydrogen and oxygen (two permanent gases) form liquid water, but also from many phenomena of the absorption of hydrogen.

Hydrogen is vigorously absorbed by certain solids; for example, by charcoal and by spongy platinum. If a piece of freshly ignited charcoal be introduced into a cylinder full of hydrogen standing in a mercury bath, the charcoal will absorb as much as twice its volume of hydrogen. Spongy platinum condenses still more hydrogen. But **palladium,** a grey metal which is found with platinum, **absorbs** more **hydrogen** than any other metal. Graham showed that, when heated to a red heat and cooled in an atmosphere of hydrogen, palladium retains as much as 600 volumes of the gas. When once absorbed, the hydrogen is retained at the ordinary temperature, and is only given up at a red heat.[36] This capacity of certain metals for the absorption of hydrogen explains the property of hydrogen of passing through metallic tubes made, for instance, of iron or platinum.[37] This property is termed

occlusion, and is very similar to solution: it is based on the capacity of metals of forming with hydrogen unstable, easily dissociating compounds,[38] similar to those which salts form with water. Some of these direct compounds of hydrogen with metals have been isolated by Winkler, Moissan, and others (see Chaps. XII., XIV. &c.).

At the ordinary temperature hydrogen enters very rarely and feebly into chemical reaction. The capacity of gaseous **hydrogen** for reaction becomes evident only under a change of circumstances—by compression, heating, or the action of light, or at the moment of its evolution. However, even under these circumstances it **combines** directly with only a very few of the elements. Hydrogen combines directly with oxygen, sulphur, fluorine, carbon, potassium, and certain other elements, but not with the majority of the metals, nor with nitrogen, phosphorus, &c. Compounds of hydrogen with certain elements on which it does not act directly are, however, known, and are obtained by reactions of decomposition, or of double decomposition, of other hydrogen compounds. The property possessed by hydrogen of combining with oxygen at a red heat determines its combustibility. We have already seen that hydrogen easily takes fire, and that it then burns with a pale—that is, non-luminous—flame.[39] Hydrogen does not combine with the oxygen of the atmosphere at the ordinary temperature; but this combination takes place at a red heat,[40] and is accompanied by the evolution of

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[35] This and a number of similar cases clearly show how great are internal chemical forces compared with physical and mechanical forces.

[36] The property of palladium of absorbing hydrogen, and of increasing in volume in so doing, may be easily demonstrated by taking a sheet of palladium, varnished on one side, and using it as a cathode. The hydrogen which is evolved by the action of the current is retained by the unvarnished surface, as a consequence of which the sheet curls up. By attaching a pointer (for instance, a quill) to the end of the sheet, this bending effect is rendered strikingly evident, and on reversing the current (when oxygen will be evolved and will combine with the absorbed hydrogen, forming water) it may be shown that on losing the hydrogen the palladium regains its original form.

[37] Deville discovered that iron and platinum become pervious to hydrogen at a red heat. He speaks of this in the following terms:—'The permeability of such homogeneous substances as platinum and iron is quite different from the passage of gases through such non-compact substances as clay and graphite. The permeability of metals depends on their expansion, brought about by heat, and proves that metals and alloys have a certain porosity.' However, Graham proved that it is only hydrogen which is capable of passing through the above-named metals in this manner. Oxygen, nitrogen, ammonia, and many other gases only pass through in extremely minute quantities. Graham showed that at a red heat about 500 c.c. of hydrogen per minute pass through a surface of one square metre of platinum 1·1 mm. thick, but that with other gases the amount transmitted is hardly perceptible. Indiarubber has the same capacity for allowing the transference of hydrogen through its substance (see Chapter III.), and at the ordinary temperature one square metre, 0·014 mm. thick, transmits about 127 c.c. of hydrogen per minute. In the experiment on the decomposition of water by heat in porous tubes the clay tube may be exchanged for a platinum one with advantage. Graham showed that by placing a platinum tube containing hydrogen under these conditions, and surrounding it by a tube containing air, the transference of the hydrogen may be observed by the decrease of pressure in the platinum tube. In one hour almost all the hydrogen (97 per cent.) had passed from the tube, without being replaced by air. It is evident that the occlusion and passage of hydrogen through metals capable of occluding it are not only intimately connected together, but are dependent on the capacity of metals to form compounds of various degrees of stability with hydrogen-like solutions.

[38] It appeared on further investigation that palladium gives a definite compound, Pd_2H (see Chapter XXIII.), with hydrogen; but what was most instructive was the investigation of sodium hydride, Na_2H.

Molten iron absorbs hydrogen, but in solidifying it expels it. The solution of hydrogen by metals is to a certain degree based on its affinity for metals, and must be likened to the solution of metals in mercury and to the formation of alloys.' In its chemical properties hydrogen, as we shall see later, has much of a metallic character. The metallic properties of hydrogen are also evinced in the fact that it is a good conductor of heat, which is not the case with other gases (Magnus).

[39] If it be desired to obtain a perfectly colourless hydrogen flame, the gas must issue from a platinum nozzle, as the glass end of a gas-conducting tube imparts a yellow tint to the flame, owing to the presence of sodium in the glass.

[40] Let us imagine that a stream of hydrogen passes along a tube, and let us mentally divide this stream into several parts, consecutively passing out from the orifice of the tube. The first part is lighted—that is, brought to a state of incandescence, in which state it combines with the oxygen of the atmosphere. A considerable amount of heat is evolved in the combination. The heat evolved then ignites the second part of hydrogen coming from the tube, and, therefore, when once ignited, the hydrogen continues to burn, if there is a continual supply of it, and if the atmosphere in which it burns is unlimited and contains oxygen.

much heat. The product of this combination is water—that is, a compound of oxygen and hydrogen. This is the **synthesis of water**, and we have already noticed its analysis or decomposition into its component parts. The synthesis of water may be very easily observed if a cold glass bell jar be placed over a burning hydrogen flame, or, better still, if the hydrogen flame be lighted in the tube of a condenser. The water will condense in drops, as it is formed, on the walls of the condenser and trickle down.[41]

Light does not aid the combination of hydrogen and oxygen, so that a mixture of these two gases does not change when exposed to the action of light; but an electric spark acts just like a flame, and this is taken advantage of for inflaming a mixture of oxygen and hydrogen, or detonating gas, inside a vessel, as will be explained in the following chapters. As hydrogen (and oxygen also) is condensed by spongy platinum, with rise of temperature, and as platinum acts by contact (Introduction), therefore hydrogen also combines with oxygen, under the influence of platinum, as was shown by Döbereiner. If spongy platinum is thrown into a mixture of hydrogen and oxygen, an explosion takes place; and if a mixture of the gases be passed over spongy platinum, combination will also ensue, and the platinum become red-hot.[42] Hydrogen exhibits its greatest affinity for direct reaction, with fluorine and chlorine, forming hydrofluoric, HF, and hydrochloric acids, HCl, which will be considered more fully in Chapter XI.

Although gaseous hydrogen does not act directly[43] on many substances, yet in a **nascent state** reaction often takes place. Thus, for instance, water on which sodium amalgam is acting contains hydrogen in a nascent state. The hydrogen is here evolved from a liquid, and at the first moment of its formation must be in a condensed state.[44] In this condition it is capable of reacting on substances on which it does not act in a gaseous state. Reactions of substitution or **displacement of metals by hydrogen** at the moment of its formation are particularly numerous.[45]

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[41] The combustibility of hydrogen may be shown by the direct decomposition of water by sodium. If a pellet of sodium is thrown into a vessel containing water, it floats on the water and evolves hydrogen, which may be lighted. The presence of sodium imparts a yellow tint to the flame. If potassium be taken, the hydrogen bursts into flame spontaneously, because sufficient heat is evolved in the reaction to ignite the hydrogen. The flame is coloured violet by the potassium. If sodium be thrown, not on to water, but on to an acid, it will evolve more heat, and the hydrogen will then also burst into flame. These experiments must be carried on with caution, as, sometimes towards the end, a mass of sodium oxide (note 8) is produced, and flies about. It is therefore best to cover the vessel in which the experiment is carried on.

[42] This property of spongy platinum is made use of in the so-called hydrogen cigar-lighter. It consists of a glass cylinder or beaker, inside which there is a small lead stand (which is not acted on by sulphuric acid), on which a piece of zinc is laid. This zinc is covered by a bell, which is open at the bottom and furnished with a cock at the top. Sulphuric acid is poured into the space between the bell and the sides of the outer glass cylinder, and will thus compress the gas in the bell. If the cock of the cylinder be opened the gas will escape by it, and will be replaced by the acid, which, coming into contact with the zinc, evolves hydrogen, and this will escape through the cock. If the cock be closed, then the hydrogen evolved will increase the pressure of the gas in the bell, and thus again force the acid into the space between the bell and the walls of the outer cylinder. Thus the action of the acid on the zinc may be stopped or started at will by opening or shutting the cock, and consequently a stream of hydrogen may be turned on at any time. Now, if a piece of spongy platinum be placed in this stream, the hydrogen will take fire, because the spongy platinum becomes hot in condensing the hydrogen and inflames it. The considerable rise in temperature of the platinum depends, among other things, on the fact that the hydrogen condensed in its pores comes into contact with previously absorbed and condensed atmospheric oxygen, with which hydrogen combines with great facility in this form. In this manner the hydrogen cigar-lighter gives a stream of burning hydrogen when the cock is open. In order that it should work regularly it is necessary that the spongy platinum should be quite clean, and it is best enveloped in a thin sheet of platinum foil, which protects it from dust. In any case, after some time it will be necessary to clean the platinum, and this may be easily done by boiling it in nitric acid, which does not dissolve the platinum, but frees it from all dirt. This imperfection has given rise to several other forms, in which an electric spark is made to pass in front of the orifice from which the hydrogen escapes. This is arranged in such a manner that the zinc of a galvanic element is immersed when the cock is turned, or a small coil giving a spark is put into circuit on turning the hydrogen on.

[43] Under conditions similar to those in which hydrogen combines with oxygen it is also capable of combining with chlorine. A mixture of hydrogen and chlorine explodes on the passage of an electric spark through it, or on contact with an incandescent substance, or in the presence of spongy platinum; but, besides this, the action of light alone is enough to bring about the combination of hydrogen and chlorine. If a mixture of equal volumes of hydrogen and chlorine is exposed to the action of sunlight, complete combination rapidly ensues, accompanied by a report. Hydrogen does not combine directly with carbon, either at the ordinary temperature or under the action of heat and pressure. But if an electric current be passed through carbon electrodes at a short distance from each other (as in the electric light or voltaic arc), so as to form an electric arc in which the particles of carbon are carried from one pole to the other, then, in the intense heat to which the carbon is subjected in this case, it is capable of combining with hydrogen. A gas of peculiar smell called acetylene, C_2H_2, is thus formed from carbon and hydrogen.

[44] There is another explanation of the facility with which hydrogen reacts in a nascent state. We shall afterwards learn that the molecule of hydrogen contains two atoms, H_2, but there are elements the molecules of which contain only one atom—for instance, mercury. Therefore every reaction of gaseous hydrogen must be accompanied by the disruption of that bond which exists between the atoms forming a molecule. At the moment of evolution, however, it is supposed that free atoms exist, and in this condition, according to the hypothesis, act energetically. This hypothesis is not based upon facts, and the idea that hydrogen is condensed at the moment of its evolution is more natural, and is in accordance with the fact (note 12) that compressed hydrogen displaces palladium and silver (Brunner, Beketoff)—that is, acts as at the moment of its liberation. It is impossible at present to form any idea of the properties of the isolated atoms (ions) of hydrogen, for certain of the elements whose molecules contain one atom are chemically very active (for instance, Na) while others (such as argon) are perfectly inert.

[45] When, for instance, an acid and zinc are added to a salt of silver, the silver is reduced; but this may be explained as a reaction of the zinc, and not of the hydrogen at the moment of its formation. There are, however, examples to which this explanation is entirely inapplicable; thus, for instance, hydrogen, at the moment of its liberation,

Metals, as we shall afterwards see, are in many cases able to replace each other; they also, and in some cases still more easily, replace and are replaced by hydrogen. We have already seen examples of this in the formation of hydrogen from water, sulphuric acid, &c. In all these cases the metal sodium, iron, or zinc displaces the hydrogen which occurs in these compounds. Hydrogen may be displaced by metals from many of its compounds in exactly the same manner as it is displaced from water; thus, for example, hydrochloric acid, which is formed directly by the combination of hydrogen with chlorine, gives hydrogen by the action of a great many metals, just as sulphuric acid does. Potassium and sodium also displace hydrogen from its compounds with nitrogen; it is only from its compounds with carbon that hydrogen is not displaced by metals. Hydrogen, in its turn, is able to replace metals: this is accomplished most easily on heating, and with those metals which do not themselves displace hydrogen. If hydrogen be passed over the compounds of many metals with oxygen maintained at a red heat, it takes up the oxygen from the metals and displaces them just as it is itself displaced by metals. If hydrogen is passed over the compound of oxygen with copper at a red heat, then metallic copper and water are obtained—$CuO + H_2 = H_2O + Cu$. This kind of double decomposition is called **reduction**, with reference to the metal, which is thus reduced to a metallic state from its combination with oxygen. But it must be recollected that all metals do not displace hydrogen directly from its compound with oxygen; and, conversely, hydrogen is not able to displace all metals from their compounds with oxygen, &c.; thus it does not displace potassium, calcium, or aluminium from its compounds with oxygen. If the metals be arranged in the following series: K, Na, Ca, Al . . . Fe, Zn, H . . . Cu, Pb, Ag, Au, then the first are able to take up oxygen from water—that is, displace hydrogen—whilst the last do not act thus, but are, on the contrary, reduced by hydrogen—that is, have, as is said, a less affinity for oxygen than hydrogen, whilst potassium, sodium, and calcium have more. This is also expressed by the amount of heat evolved in the act of combination with oxygen (see note 7), and is shown by the fact that potassium and sodium and other similar metals evolve heat in decomposing water; but copper,

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easily takes up oxygen from its compounds with nitrogen if they be in solution, and converts the nitrogen into its hydrogen compound. Here the nitrogen and hydrogen, so to speak, meet at the moment of their liberation, and in this state combine.

It is evident from this that the elastic gaseous state of hydrogen fixes the limit of its energy and prevents it from entering into those combinations of which it is capable. In the nascent state we have hydrogen which is not in a gaseous state, and its action is then much more energetic. At the moment of evolution that heat which would be latent in the gaseous hydrogen is transmitted to its molecules, and consequently they are in a state of strain, and hence capable of acting on many substances.

silver, and the like do not do this, because in combining with oxygen they evolve less heat than hydrogen does, and therefore it happens that when hydrogen reduces these metals heat is evolved. Thus, for example, if 16 grams of oxygen combine with copper, 38,000 units of heat are evolved; and when 16 grams of oxygen combine with hydrogen, forming water, 69,000 units of heat are evolved; whilst 23 grams of sodium, in combining with 16 grams of oxygen, evolve 100,000 units of heat. This example clearly shows that chemical reactions which proceed directly and unaided evolve heat. Sodium decomposes water, and hydrogen reduces copper, because they are **exothermal** reactions, or such as evolve heat; copper does not decompose water, because such a reaction would be accompanied by an absorption (or secretion) of heat, or belongs to the class of **endothermal** reactions in which heat is absorbed; and such reactions do not generally proceed directly, although they may take place with the aid of energy (electrical, thermal, &c.) borrowed from some foreign source.[46]

The reduction of metals by hydrogen is taken advantage of for **determining the composition of water by weight.** Copper oxide is usually chosen for this purpose. It is heated to redness in hydrogen, and the quantity of water thus formed is determined, while the quantity of oxygen which occurs in it is found from the loss of weight of the copper oxide. The copper oxide must be weighed immediately before and after the experiment. The difference shows the weight of the oxygen which entered into the composition of the water formed. In this manner only solids have to be weighed, which is a very great gain in the accuracy of the results obtained.[47] Dulong and Berzelius (1819) were the first to determine the composition of water by this method, and they found that water contains 88·91 parts of oxygen and 11·09 of hydrogen in 100 parts by weight, or 8·008 parts of oxygen per one part of hydrogen. Dumas (1842) improved on this method,[48] and found that

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[46] Several numerical data and ideas bearing on this matter are given in notes 7, 9, and 11. It must be observed that the action of iron or zinc on water is reversible. But the reaction $CuO + H_2 = Cu + H_2O$ is not reversible; the difference between the degrees of affinity is very great in this case, and, therefore, so far as is at present known, no hydrogen is liberated even in the presence of a large excess of water. If definite amounts of a metal and acid be taken and their reaction be carried on in a closed space, the evolution of hydrogen will cease when its pressure equals that at which compressed hydrogen displaces the metal. The result depends upon the nature of the metal and the strength of the solution of acid. Tammann and Nernst (1892) found that the metals stand in the following order in respect to this limiting pressure of hydrogen:—Na, Mg, Zn, Al, Cd, Fe, Ni.

[47] This determination may be carried on in an apparatus like that mentioned in note 13 of Chapter I.

[48] We will proceed to describe Dumas's method and results. For this determination, pure and dry copper oxide is necessary. In each determination Dumas took a sufficient

water contains 12·575 parts of hydrogen per 100 parts of oxygen—that is, 7·990 parts of oxygen per 1 part of hydrogen—and it is therefore

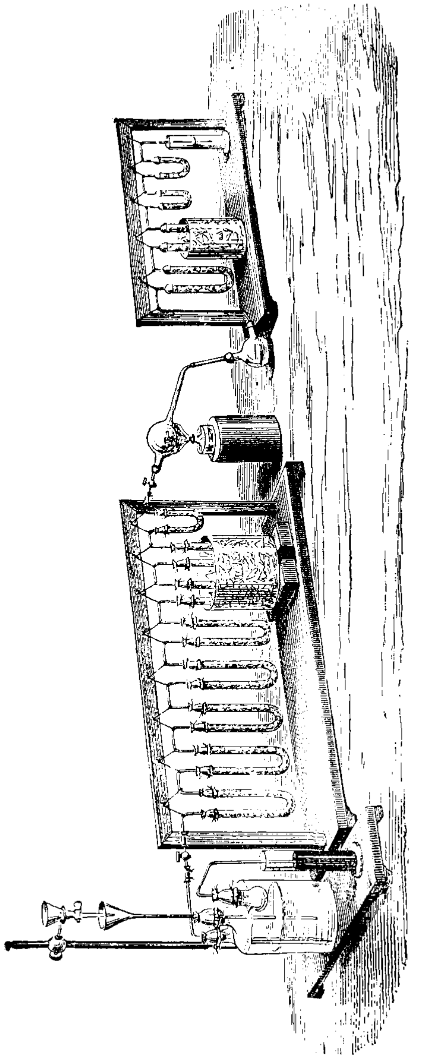

FIG. 30.—Apparatus employed by Dumas for determining the composition of water. Described in text.

quantity of copper oxide for the formation of 50 grams of water. As the oxide of copper was weighed before and after the experiment, and as the amount of oxygen contained in water was determined by the difference between these weights, it was essential that no other substance besides the oxygen forming the water should be evolved from the oxide of copper during its ignition in hydrogen. It was necessary also that the hydrogen should be perfectly pure, and free not only from traces of moisture, but from any other impurities which might dissolve in the water or combine with the copper and form some other compound with it. The bulb containing the oxide of copper (fig. 30), which was heated to redness, should be quite free from air, as otherwise the oxygen in the air might, in combining with the hydrogen passing through the vessel, form water in addition to that formed by the oxygen of the oxide of copper. The water formed should be entirely absorbed in order to accurately determine its quantity. The hydrogen was evolved in a three-necked bottle. The sulphuric acid, for acting on the zinc, is poured through funnels into the middle neck. The hydrogen evolved in the Woulfe's bottle passes through U-tubes, in which it is purified, to the bulb, where it comes into contact with the incandescent copper oxide, forms water, and reduces the oxide to metallic copper; the water formed is condensed in the second bulb, and any passing off is absorbed in the second set of U-tubes. This is the general arrangement of the apparatus. The loss in weight of the bulb containing the copper oxide shows the

accepted that *water contains eight parts by weight of oxygen to one part by weight of hydrogen.* And as the most exact determinations

quantity of oxygen which entered into the composition of the water formed, the weight of the latter being shown by the gain in weight of the absorbing apparatus. Knowing the amount of oxygen in the water formed, we also know the quantity of hydrogen contained in it, and consequently we can determine the composition of water by weight. This is the essence of the determination. We will now turn to certain details. In one neck of the three-necked bottle a tube is placed dipping under mercury. This serves as a safety-valve to prevent the pressure inside the apparatus becoming too great owing to the rapid evolution of hydrogen. If the pressure rose to any considerable extent, the current of gases and vapours would be very rapid, and, as a consequence, the hydrogen would not be perfectly purified nor the water entirely absorbed in the tubes placed for this purpose. In the third neck of the Woulfe's bottle is a tube conducting the hydrogen to the purifying apparatus, consisting of eight U-tubes, destined for the purification and testing of the hydrogen. The hydrogen, evolved from zinc and sulphuric acid, is purified by passing it first through a tube full of pieces of glass moistened with a solution of lead nitrate and then through silver sulphate; the lead nitrate retains sulphuretted hydrogen, while arseniuretted hydrogen is retained by the silver sulphate tube. Caustic potash in the next U-tube retains any acid which might come over. The two following tubes are filled with lumps of dry caustic potash in order to absorb any carbonic anhydride and moisture which the hydrogen might contain. The next two tubes, to *remove* the last traces of moisture, are filled with phosphoric anhydride, mixed with lumps of pumice-stone. They are immersed in a freezing mixture. The small U-tube contains hygroscopic substances, and is weighed before the experiment: it is used in order to ascertain whether the hydrogen passing through still retains any moisture. If it does not, then the weight of this tube will not vary during the whole experiment, but if the hydrogen evolved still retains moisture, the tube will increase in weight. The copper oxide is placed in the bulb, which, previous to the experiment, is dried with the copper oxide for a long time. The air is then exhausted from it in order to weigh the oxide of copper in a vacuum, and so avoid the need of a correction for weighing in air. The bulb is made of infusible glass, that it may be able to withstand a lengthy (20 hours) exposure to a red heat without changing in form. The *weighed* bulb is *only connected* with the purifying apparatus after the hydrogen has passed through for a long time, and after experiment has shown that the hydrogen passing from the purifying apparatus is pure and does not contain any air. The first U-tube contains pieces of ignited potash, and the second and third tubes, phosphoric anhydride or pumice-stone moistened with sulphuric acid. The last tube is employed for determining whether all the moisture is absorbed, and is therefore weighed separately. The glass cylinder contains sulphuric acid, through which the excess of hydrogen passes: it enables the rate at which the hydrogen is evolved to be seen, and shows whether its amount should be decreased or increased.

When the apparatus is fitted up it must be seen that all its parts are hermetically tight before commencing the experiment. When the previously weighed parts are connected together, and the *whole* apparatus put into communication, the bulb containing the copper oxide is heated with a spirit or other lamp, and the reduction of the copper oxide then takes place, and water is formed. When nearly all the copper oxide is reduced the lamp is removed and the apparatus allowed to cool, the current of hydrogen being kept up all the time. When cool, the drawn-out end of the bulb is fused up, and the hydrogen remaining in it exhausted, in order that the copper may be again weighed in a vacuum. The absorbing apparatus remains full of hydrogen, and would therefore present a less weight than if it were full of air, as it was before the experiment; and for this reason, having disconnected the copper oxide bulb, a current of dry air is passed through it until the gas passing from the glass cylinder is quite free from hydrogen. The condensing bulb and the two tubes next to it are then weighed in order to determine the quantity of water formed. Dumas repeated this experiment of the composition of water in recent times (Keiser 1888, Morley 1895, Thomsen 1896, &c.) concur in showing that it contains not more than 7,945, and not less than 7,935 parts of oxygen per 1 part by weight of hydrogen, the mean of these, or 7,940 parts of oxygen per 1 part by weight of hydrogen, or, what is almost the same, 8 parts of oxygen per 1·0076 parts of hydrogen, is now adopted wherever great accuracy is required. This corresponds with 88·81 parts of oxygen and 11·19 parts of hydrogen per 100 parts of water; but as the approximate ratio 1 : 8 only differs from this in hundredth parts of 1 per cent. of the amounts of the elements, the composition of water may be approximately expressed by the above easily remembered ratio 1 : 8, or more correctly 1·008 : 8, which is adopted in this work and in most researches of the present day. By whatever method water be obtained, it will always present the same composition. Whether it be taken from nature and purified, or whether it be obtained from hydrogen by oxidation, or whether it be separated from any of its compounds, or obtained by some double decomposition, it will in every case contain 1 part by weight of hydrogen and about 8 parts of oxygen. This is because water is a definite chemical compound. Detonating gas, from which it may be formed, is a simple mixture of oxygen and hydrogen, although a mixture of the same composition as water. All the properties of both constituent gases are preserved in detonating gas. Either one or the other gas may be added to it without destroying its homogeneity. The fundamental properties of oxygen and hydrogen are not found in water, and neither of the gases can be directly combined with it. But they may be evolved from it. In the formation of water there is an evolution of heat; for the decomposition of water heat is required. All this is expressed by saying that *water is a definite chemical compound of hydrogen with oxygen.* Taking the symbol of hydrogen, H, as expressing a unit quantity (or more exactly 1·008) by weight of this substance, and expressing 16 parts by weight of oxygen by O, we can formulate all the above statements by the chemical symbol of water, H_2O. As only definite chemical compounds are denoted by formulæ, having indicated the formula of a compound substance we express by it the entire series of properties which go to make up our conception of a definite compound, and at the same time the quantitative composition of the substance by weight. Further, as we shall see later, formulæ express the volume of the gases contained in a substance. Thus the formula of water shows that it contains two volumes of hydrogen and one volume of oxygen. Besides which, we shall find that the formula expresses the density of the vapour of a compound, and on this many properties of substances depend, and, as we shall learn, determine the quantities of the bodies entering into reactions. This vapour density we shall see determines also the quantity of a substance entering into a reaction. Thus the letters H_2O tell the chemist the entire history of the substance. This is an international language, which endows chemistry with a simplicity, clearness, stability, and trustworthiness founded on the investigation of the laws of nature.

many times. The average result was that water contains 1253·3 parts of hydrogen per 10,000 parts of oxygen. Making a correction for the amount of air contained in the sulphuric acid employed for producing the hydrogen, Dumas obtained the average figure 1251·5, the extreme values being 1247·2 and 1256·2. This proves that per 1 part of hydrogen, water contains 7·9904 parts of oxygen, with an error of not more than $\frac{1}{250}$, or 0·03, in the amount of oxygen per 1 part of hydrogen.

Erdmann and Marchand, in eight determinations, found that, per 10,000 parts of oxygen, water contains an average of 1,252 parts of hydrogen, the separate values ranging from 1258·5 to 1248·7; hence for 1 part of hydrogen there would be 7·9952 of oxygen, with an error of at most 0·05.

Keiser (1888), in America, by employing palladium hydride, and by introducing various fresh precautions for obtaining accurate results, found the composition of water to be 15·95 parts of oxygen per 2 of hydrogen.

The latest determinations of the composition of water, as also those made by Dumas, always give less than 8, and on the average from 7·93 to 7·95 of oxygen per 1 part of hydrogen, as has been mentioned in the text, and the final mean may be taken as 7·936, with a possible error of not more than 1 in the last decimal figure.

CHAPTER III

OXYGEN AND THE CHIEF ASPECTS OF ITS SALINE COMBINATIONS

On the earth's surface there is no other element which is so widely distributed as is oxygen in its various compounds.[1] It constitutes eight-ninths of the weight of water, which occupies the greater part of the earth's surface. Nearly all earthy substances and rocks consist of compounds of oxygen with metals and other elements. Thus, the greater part of sand is formed of silica, SiO_2, which contains 53 per cent. of oxygen; while clay and the earthy substances and rocks contain about 40 per cent. by weight of oxygen; animal and vegetable substances are also very rich in oxygen. Without counting the water present in them, plants contain up to 40, and animals up to 20, per cent. by weight of oxygen. Thus, oxygen compounds predominate on the earth's surface. Besides this, a portion exists in a free state, and is contained in admixture with nitrogen in the atmosphere, forming about one-fourth of its mass, or one-fifth of its volume.

Being so widely distributed in nature, oxygen plays a very important part in it, for a number of the phenomena which take place around us are mainly dependent on it. **Animals breathe** air in order to obtain from it only the **oxygen**, which enters their respiratory organs (the lungs of human beings and animals, the gills of fishes, and the tracheæ of insects); they, so to say, drink in air in order to absorb the oxygen. The oxygen contained in the air (or dissolved in water) passes through the membranes of the respiratory organs into the blood, is retained in it by the blood corpuscles, is transmitted by their means to all parts of the body, aids their transformations, bringing about chemical processes in them, and extracting from them chiefly carbon, in the form of carbonic anhydride, the greater part of which passes into the blood, is dissolved by it, and is thrown off by the lungs during the absorption of the oxygen. Thus, in the process of respiration, carbonic anhydride (and water) is given off and the oxygen of the air absorbed, by which means the blood is changed from the red venous to the dark-red arterial form. The cessation of this process causes death, because then all these chemical processes, and the consequent heat and work which the oxygen introduced into the system gives rise to, cease. For this reason suffocation and death ensue in a vacuum, or in a gas which does not contain free oxygen, i.e., which does not support combustion. If an animal is placed in an atmosphere of free oxygen, at first its movements are very active and a general invigoration is remarked, but a reaction soon sets in, and death may ensue. The oxygen of the air when it enters the lungs is diluted with four volumes of nitrogen, which is not absorbed into the system, so that the blood absorbs but a small quantity of oxygen from the air, whilst in an atmosphere of pure oxygen a large quantity of oxygen would be absorbed, and would produce a very rapid change of all parts of the organism, and destroy it. From what has been said, it will be understood that pure oxygen gas may be employed in respiration, at any rate for a limited time. When the respiratory organs suffer under certain forms of suffocation and impediment to breathing, pure oxygen is frequently had recourse to.[2]

The combustion of organic substances—that is, substances which make up the composition of plants and animals—proceeds in the same manner as the combustion of many inorganic substances, such as sulphur, phosphorus, iron, &c., from the combination of these substances with oxygen, as was described in the Introduction. The decomposition, rotting, and similar transformations of substances, which proceed around us, are also very often dependent on the action of the oxygen of the air, and reduce this gas from a free to a combined state. The majority of the compounds of oxygen are, like water, very stable, and

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[1] As regards the interior of the earth, it probably contains far less oxygen compounds than the surface, judging by the accumulated evidences of the earth's origin, of meteorites, of the earth's density, &c. (see Chapter VIII., note 58, and Chapter XXII., note 2).

[2] It is evident that the partial pressure (see Chapter I.) acts in respiration. The researches of Paul Bert showed this with particular clearness. Under a pressure of one-fifth of an atmosphere, consisting of oxygen only, animals and human beings remain under the ordinary conditions of the partial pressure of oxygen, but organisms cannot support air rarefied to one-fifth, for then the partial pressure of the oxygen falls to one-twenty-fifth of an atmosphere. Even under a pressure of one-third of an atmosphere the regular life of human beings is impossible, because of the impossibility of respiration (owing to the decrease of solubility of oxygen in the blood), on account of the small partial pressure of the oxygen, and not from any mechanical effect of the decrease of pressure. Paul Bert illustrated all this by many experiments, some of which he conducted on himself. This explains, among other things, the discomfort felt in the ascent of high mountains or in balloons, when the height reached exceeds eight kilometres, and at pressures below 250 mm. It is evident that an artificial atmosphere has to be employed in the ascent to great heights, just as in submarine work. The cure by compressed and rarefied air which is practised in certain illnesses is based partly on the mechanical action of the change of pressure and partly on the alteration in the partial pressure of the respired oxygen.

do not give up their oxygen under the ordinary conditions of nature. As the above-mentioned influences are at work everywhere, it might be expected that the amount of free oxygen in the atmosphere should decrease, and that this decrease should proceed somewhat rapidly. This is, in fact, observed where combustion or respiration proceeds in a closed space. Animals suffocate in a closed space because in consuming the oxygen the air remains unfit for respiration. In the same manner combustion, after a time, ceases in a closed space, as may be proved by a very simple experiment. An ignited substance—for instance, a piece of burning sulphur—has only to be placed in a glass flask, which is then closed with a stout cork to prevent the access of the external air; combustion will proceed for a certain time, so long as the flask contains any free oxygen, but it will cease when the oxygen of the enclosed air has entirely combined with the sulphur. From what has been said, it is evident that regularity of combustion or respiration requires a constant renewal of air—that is, that the burning substance or respiring animal should have access to a fresh supply of oxygen. This is attained in dwellings by having many windows, outlets, and ventilators, and by the current of air produced by fires and stoves. As regards the air over the entire earth's surface its proportion of oxygen hardly decreases at all, because in nature there is a process going on which renews the supply of free oxygen. **Plants**, or rather their leaves, during the daytime,[3] under the influence of light, absorb carbonic anhydride, CO_2, and **evolve free oxygen.** Thus the loss of oxygen which occurs in consequence of the respiration of animals and of combustion is made good by plants. If a leaf be placed in a bell jar containing water, and carbonic anhydride (because this gas is absorbed and oxygen evolved from it by plants) be passed into the bell, and the whole apparatus placed in sunlight, then oxygen will accumulate in the bell jar. This experiment was first made by Priestley at the end of the last century. Thus the life of plants on the earth not only serves for the formation of food for animals, but also for keeping up a constant percentage of oxygen in the atmosphere. In the long period of the life of the earth an equilibrium has been attained between the processes absorbing and evolving oxygen, by which a definite quantity of free oxygen is preserved in the entire mass of the atmosphere.[4]

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[3] At night, without the action of light, without the absorption of that energy which is required for the decomposition of carbonic anhydride into free oxygen and carbon (which is retained by the plants), they breathe like animals, absorbing oxygen and evolving carbonic anhydride. This process also goes on side by side with the reverse process in the daytime, but it is then far feebler than that which gives oxygen.

[4] The earth's surface has an area of about 510 million square kilometres, and the mass of the air (at a pressure of 760 mm.) on each kilometre of surface is about $10\frac{1}{3}$ thousand millions of kilograms, or about $10\frac{1}{3}$ million tons; therefore the whole weight of the atmosphere is about 5,100 million million ($= 51 \times 10^{14}$) tons. Consequently there are about 2×10^{15} tons of free oxygen in the earth's atmosphere. The innumerable series of processes which absorb a portion of this oxygen are compensated for by the plant processes. Assuming that 100 million tons of vegetable matter, containing 40 per cent. of carbon, formed from carbonic acid, are produced (and the same process proceeds in water) per year on the 100 million square kilometres of dry land (ten tons of roots, leaves, stems, &c., per hectare, or $\frac{1}{100}$ of a square kilometre), we find that the plant life of the dry land gives about 100,000 tons of oxygen, which is an insignificant fraction of the entire mass of the oxygen of the air.

Oxygen was obtained as an independent gas in 1774 by Priestley in England and in the same year by Scheele in Sweden, but its nature and great importance were only perfectly elucidated by Lavoisier.

Free oxygen may be obtained by one or another method from all the substances in which it occurs. Thus, for instance, the oxygen of many substances may be transferred into water, from which, as we have already seen, oxygen may be obtained.[5] We will first consider the methods of extracting oxygen from air as being a substance everywhere distributed. The separation of oxygen from it is, however, hampered by many difficulties.

From air, which consists of a *mixture* of oxygen and nitrogen, the nitrogen alone cannot be removed, because it has no inclination to combine directly or readily with any substance; and although it does combine with certain substances (boron, magnesium, titanium), these substances combine simultaneously with the oxygen of the atmosphere.[6]

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[5] The extraction of oxygen from water may be effected by two processes: either by the decomposition of water into its constituent parts by the action of a galvanic current (Chapter II.), or by means of the removal of the hydrogen from water. But, as we have seen and already know, hydrogen enters into direct combination with very few substances, and then only under special circumstances; whilst oxygen, as we shall soon learn, combines with a great many substances. Only gaseous chlorine (and, more especially, fluorine) is capable of decomposing water, taking up the hydrogen from it, without combining with the oxygen. Chlorine is soluble in water, and if an aqueous solution of chlorine, so-called chlorine water, be poured into a flask, and this be inverted in a basin containing the same chlorine water, we shall then have an apparatus by means of which oxygen may be extracted from water. At the ordinary temperature, and in the dark, chlorine does not act on water, or only acts very feebly; but under the action of direct sunlight chlorine decomposes water, with the evolution of oxygen. The chlorine then combines with the hydrogen, and gives hydrochloric acid, which dissolves in the water, and therefore free oxygen will be separated from the liquid, together with a small quantity of chlorine in admixture, which can be easily removed by passing the gas through a solution of caustic potash.

[6] Differences in the physical properties of the two gases cannot be here taken advantage of, because they are very similar in these properties. Thus the density of oxygen is 16 times and that of nitrogen 14 times greater than the density of hydrogen, so that porous vessels cannot be employed, the difference between the times of their passage through a porous surface being too insignificant.

Graham, however, succeeded in enriching air in oxygen by passing it through india-rubber. This may be done in the following way.—A common indiarubber cushion, E (fig. 81), is taken, and its orifice hermetically connected with an air-pump, or, better

However, oxygen may be separated from air by causing it to combine with substances which may be easily decomposed by the action of heat, and in so doing give up the oxygen absorbed—that is, by making use of reversible reactions. Thus, for instance, the oxygen of the atmosphere may be made to oxidise sulphurous anhydride, SO_2 (by passing directly over ignited spongy platinum), and so form sulphuric anhydride, or sulphur trioxide, SO_3; and this substance (which is a solid and volatile, and therefore easily separated from the nitrogen and sulphurous anhydride), on further heating, gives oxygen and sulphurous anhydride. Caustic soda or lime extracts (absorbs) the sulphurous anhydride from this mixture, whilst the oxygen is not absorbed, and is hence isolated from the air. On a large scale in works, as we shall afterwards see, sulphurous anhydride is transformed into hydrate of sulphur trioxide, or sulphuric acid, H_2SO_4; if this is allowed to drop on to red-hot flagstones, water, sulphurous anhydride, and oxygen may be obtained. The oxygen is easily isolated from this mixture by passing the gases over lime. The extraction of oxygen from oxide of mercury (Priestley, Lavoisier), which is obtained from mercury and the oxygen of the atmosphere, is also a reversible reaction by which oxygen may be obtained from the atmosphere (see Introduction). So also, by passing dry air through a red-hot tube containing barium oxide, it is made to combine with the oxygen of the air. In this reaction the so-called barium peroxide, or dioxide, BaO_2, is formed from barium oxide, BaO, and at a higher temperature the former evolves the absorbed oxygen, and leaves the barium oxide originally taken.[7]

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still, a mercury aspirator (the Sprengel pump, designated by the letters A, C, B). When the aspirator (Chapter II., note 16) has pumped out the air, which will be seen by the mercury running out in an almost uninterrupted stream and by its standing approximately at the barometric height, then it may be clearly observed that gas passes through the indiarubber. This is also seen from the fact that bubbles of gas continually pass along with the mercury. A minus pressure may be constantly maintained in the cushion by pouring mercury into the funnel A, and screwing up the pinchcock C, so that the stream flowing from it is small, and then a portion of the air passing through the indiarubber will be carried down with the mercury. This air may be collected in the cylinder R. Its composition is found to be about 42 volumes of oxygen, 57 volumes of nitrogen, and 1 volume of carbonic anhydride, whilst ordinary air contains only 21 volumes of oxygen in 100 volumes. A square metre of indiarubber surface (of the ordinary thickness) passes about 45 c.c. of such air per hour. Such an experiment clearly shows that indiarubber is permeable to gases. This may, by the way, be observed in common toy balloons filled with coal-gas. They fall after a day or two, not because there are holes in them, but because air penetrates into, and the gas from, their interior, through the surface of the indiarubber of which they are made. As was shown by Mitchell and Graham, the rate of the passage of gases through indiarubber does not depend on their densities, and consequently its permeability is not determined by orifices. It more resembles dialysis (Chap. I., note 18) and occlusion (Chap. II., note 37). Equal volumes of gases penetrate through indiarubber in periods of time related to each other as follows:—carbonic anhydride, 100; hydrogen, 247; oxygen, 532; marsh gas, 633; carbonic oxide, 1,220; nitrogen, 1,358. Hence nitrogen penetrates more slowly than oxygen, and carbonic anhydride more quickly than other gases. 2·556 volumes of oxygen and 13·585 volumes of carbonic anhydride pass through in the same time as one volume of nitrogen. By multiplying these ratios by the amounts of these gases in air, we obtain figures which are in almost the same proportion as the volumes of the gases penetrating from air through indiarubber. If the process of dialysis be repeated on the air which has already passed through indiarubber, then a mixture containing 65 per cent. by volume of oxygen is obtained. It may be thought that the cause of this phenomenon is the absorption or occlusion (see Chap. II., note 37) of gases by indiarubber and the evolution of the gas dissolved in a vacuum; and, indeed, indiarubber does absorb gases, especially carbonic anhydride. Graham called the above method of the decomposition of air *atmolysis*.

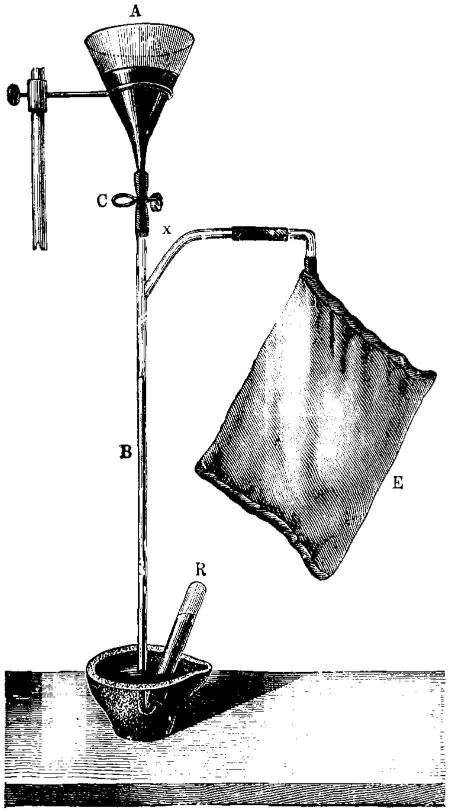

Fig. 31.—Graham's apparatus for the decomposition of air by pumping it through indiarubber.

Now that *liquid air* can be produced in large quantities (Chap. V.), the difference between the boiling-points of nitrogen (about −194°) and oxygen (about −181°), i.e., the greater elasticity (vapour pressure) of the nitrogen, can be taken advantage of for isolating the oxygen of the air. If liquid air be kept in a double-walled vessel (Chap. II., note 32), the nitrogen will evaporate to a greater extent than the oxygen, and a liquid far richer in oxygen than nitrogen will be obtained in the residue. If the mixture be carefully distilled (or only partially liquefied) it may be reduced to a residue containing 80 per cent. of oxygen. And as the evaporation of such liquids produces the low temperatures needed for liquefying air, this method may serve as a cheap means for obtaining from the air a gas rich in oxygen, combustion in which would give a very high temperature which might be advantageously employed for many purposes (for lighting or metallurgy). The day may come when this mode of enriching the air in oxygen may be employed on a large scale in works, &c., and so crown the many efforts which have been made in this direction.

[7] The preparation of oxygen by this method, which is due to **Boussingault,** is conducted in a porcelain tube, placed in a stove heated by charcoal. Barium oxide (which may be obtained by igniting barium nitrate, previously dried) is placed in the tube, through which a current of air passes. The air is previously passed through a solution of caustic potash, to remove all traces of carbonic anhydride, and is very carefully dried (for the

Oxygen is evolved with particular ease by a whole series of unstable oxygen compounds, of which we shall proceed to take a general survey, remarking that certain of these reactions, although not all, belong to the class of reversible reactions;[8] so that in order to obtain many of these substances (for instance, potassium chlorate) rich in oxygen, recourse must be had to indirect methods (see Introduction) with which we shall become acquainted in the course of this book.

1. **The compounds of oxygen** with certain metals, namely, mercury, silver, gold, and platinum, having once been obtained, retain their oxygen at the ordinary temperature, but part with it at a red heat. These compounds are solids, generally amorphous and infusible, and are easily decomposed by heat into the metal and oxygen. We have seen an example of this in the decomposition of mercury oxide. Priestley, in 1774, obtained pure oxygen for the first time by heating mercury oxide by means of a burning-glass. He showed its difference from air and its characteristic property of supporting combustion 'with remarkable vigour,' and he named it dephlogisticated air.

2. The substances called **peroxides**[9] evolve oxygen at a greater or less heat (and also by the action of many acids). They usually contain metals combined with a large quantity of oxygen. Peroxides are the highest oxides of certain metals which generally give several compounds with oxygen. Those of the lowest degrees of oxidation, containing the least amount of oxygen, are generally substances capable of reacting easily with acids, for instance, with sulphuric acid. Such low oxides are called bases. Peroxides contain more oxygen than the bases formed by the same metals. For example, lead oxide contains 7·1 parts of oxygen in 100 parts, and is basic, but lead peroxide contains 13·3 parts of oxygen in 100 parts. **Manganese peroxide or dioxide** is a similar substance, and is a solid of a dark brown colour, which occurs in nature. It is employed for technical purposes under the name of black oxide of manganese (in German 'Braunstein,' the 'pyrolusite' of the mineralogist). Peroxides are able to evolve oxygen at a more or less elevated temperature. They do not then part with all their oxygen, but with only a portion of it, and are converted into a lower oxide or base. Thus for example, lead peroxide, on heating, gives oxygen and lead oxide. The decomposition of this peroxide proceeds tolerably easily on heating, even in a glass vessel, but manganese peroxide only evolves oxygen at a strong red heat, and therefore oxygen can only be obtained from it in iron or clay vessels. This was formerly the method for obtaining oxygen. Manganese peroxide only parts with one-third of its oxygen (according to the equation, $3MnO_2 = Mn_3O_4 + O_2$), two-thirds remaining

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hydrate, BaH_2O_2, does not give the peroxide). At a *dark-red heat* (500–600°), the oxide of barium absorbs oxygen from the air, so that the gas leaving the tube consists chiefly of nitrogen. When the absorption ceases, the air will pass through the tube unchanged, which may be recognised from the fact that it supports combustion. Under these circumstances, the barium oxide is converted into peroxide and eleven parts of the oxide absorb about one part of oxygen by weight. When the absorption ceases, one end of the tube is closed, a cork with a gas-conducting tube is fixed into the other end, and the heat of the stove is increased to a *bright-red heat* (800°). At this temperature the peroxide gives up all that oxygen which it acquired at a dark-red heat,—i.e., about one part of oxygen is evolved from twelve parts of barium peroxide. After the evolution of the oxygen there remains the barium oxide which was originally taken, so that air may be again passed over it, and thus the preparation of oxygen from one and the same quantity of barium oxide may be repeated many times. Oxygen has been produced one hundred times from one mass of oxide by this method, all the necessary precautions being taken as regards the temperature of the mass and the removal of moisture and carbonic acid from the air. Unless such precautions be taken, the mass of oxide soon becomes spoilt.

As oxygen may become of considerable technical use, from its capacity for giving high temperatures and intense light in the combustion of substances, its preparation directly from air by practical methods forms a problem, whose solution many investigators are continuing to work at up to the present day (note 6). The most practical methods are those of **Tessié du Motay and Kassner**. The first is based on the fact that a mixture of equal weights of manganese peroxide and caustic soda at an incipient red heat (about 350°) absorbs oxygen from air, with the separation of water, according to the equation: $MnO_2 + 2NaHO + O = Na_2MnO_4 + H_2O$. If superheated steam, at a temperature of about 450°, be then passed through the mixture, the manganese peroxide and caustic soda originally taken are regenerated, and the oxygen held by them is evolved, according to the reverse equation: $Na_2MnO_4 + H_2O = MnO_2 + 2NaHO + O$. This mode of preparing oxygen may be repeated an infinite number of times. The oxygen in combining liberates water, and steam, acting on the resultant substance, evolves oxygen. Hence all that is required for the preparation of oxygen by this method is fuel and the alternate cutting off of the supplies of air and steam. In Kassner's process (1891) a mixture of oxide of lead and lime ($PbO + 2CaO$) is heated to redness in the presence of air, oxygen being thus absorbed and calcium plumbate, Ca_2PbO_4, formed. The latter is of a chocolate colour, and on further heating evolves oxygen and gives the original mixture, $PbO + 2CaO$, so that the phenomenon is essentially the same as in Boussingault's process (with BaO), but according to Le Chatelier (1893) the dissociation pressure of the oxygen evolved from Ca_2PbO_4 is less than with BaO_2 at the same temperatures; for instance, at 940°, it is 112 mm. of mercury for the first, and for the latter 210 mm. at 720°, and 670 mm. at 790°, while for Ca_2PbO_4 this last pressure is only reached at 1,080°. However, in Kassner's process the oxygen is absorbed more rapidly, and the influence of the presence of moisture and carbonic anhydride in the air is not so marked, so that this process, like that of Tessié du Motay, deserves consideration.

[8] Even the decomposition of manganese peroxide is reversible (under certain changes in the conditions of reaction), and it may be re-obtained from that suboxide (or its salts), which is formed in the evolution of oxygen (Chap. XI., note 6). The compounds of chromic acid containing the trioxide, CrO_3, in evolving oxygen, give chromium oxide, Cr_2O_3, but they re-form the salt of chromic acid when heated to redness in air with an alkali.

[9] We shall afterwards see that it is only substances like barium peroxide (which give hydrogen peroxide) which should be counted as true peroxides, and that MnO_2, PbO_2, &c., should be distinguished from them (they do not give hydrogen peroxide with acids), and therefore it is best to call these dioxides. This we generally do in the context, only retaining the old nomenclature in a few instances, on account of its historical interest, and to enable our readers to refer to former treatises. Peroxide of hydrogen (Chap. IV.) easily parts with half of its oxygen, leaving water as a residue.

in the solid residue after heating. Metallic peroxides are also capable of evolving oxygen on heating with sulphuric acid. They then evolve just that amount of oxygen which is in excess of that necessary for the formation of the base, which latter reacts on the sulphuric acid forming a compound (salt) with it. Thus barium peroxide, when heated with sulphuric acid, forms oxygen and barium oxide, which gives a compound with sulphuric acid termed barium sulphate ($BaO_2 + H_2SO_4 = BaSO_4 + H_2O + O$).[9a] For the purposes of experiment, powdered manganese peroxide is usually taken and mixed with strong sulphuric acid in a flask, and the apparatus set up as shown in fig. 32.

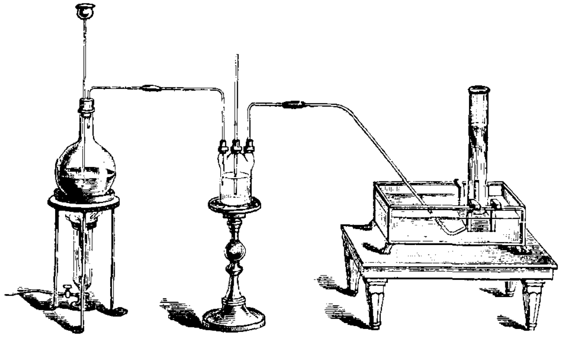

FIG. 32.—Preparation of oxygen from manganese peroxide and sulphuric acid. The gas evolved is passed through a Woulfe's bottle containing caustic potash solution.

[9a] Peroxide of barium also gives oxygen at the ordinary temperature in the presence of the solutions of many substances in a higher degree of oxidation. In this connection we may mention that Kassner (1890) proposes to obtain oxygen for laboratory purposes by mixing BaO_2 with $FeK_3(CN)_6$ (red prussiate of potash, Chapter XXII.); the reaction proceeds with the evolution of oxygen on the addition of even a very small quantity of water. In order to ensure a gradual evolution of gas, the author proposes to introduce the two substances into the reaction, little by little, instead of all at once; and this may be done with the following arrangement (Gavaloffsky). Finely powdered peroxide of barium is placed in an ordinary flask and sufficient water is added to fill the flask one-third full. The cork closing the flask has three holes: (1) for the gas-conducting tube; (2) for a rod to stir the BaO_2; and (3) *for a glass rod terminating in a perforated glass* vessel containing crystals of $FeK_3(CN)_6$. When it is desired to start the evolution of the oxygen, the vessel is lowered until it is immersed in the liquid in the flask, and the BaO_2 is stirred with the other rod. The reaction proceeds according to the equation, $BaO_2 + 2FeK_3(CN)_6 = FeK_4(CN)_6 + FeK_2Ba(CN)_6 + O_2$. The double salt, $FeBa_2(CN)_6$, crystallises out from the mother liquor. To understand the course of the reaction, it must be remembered that BaO_2 is of a higher degree of oxidation, and that it parts with oxygen and gives the base BaO, which enters into the complex salt $FeK_2Ba(CN)_6 = Fe(CN)_2 + 2KCN + Ba(CN)_2$, and this latter $= BaO + 2HCN - H_2O$. Moreover, $FeK_3(CN)_6$ contains the salt $Fe_2(CN)_6$, which also corresponds with the higher degree of oxidation of iron, Fe_2O_3, whilst after the reaction a salt is obtained which contains $Fe(CN)_2$, and corresponds with the lower degree of oxidation, FeO, so that (in the presence of water) oxygen is set free on this side also, i.e., the reaction gives compounds of lower degrees of oxidation and oxygen.

The gas which is evolved is passed through a Woulfe's (two-necked) bottle containing a solution of caustic potash, to purify it from carbonic anhydride and chlorine, which accompany oxygen from commercial manganese peroxide, and the gas is not collected until a thin smouldering taper placed in front of the escape orifice bursts into flame, and so shows that the gas coming off is oxygen. By this method of decomposition of the manganese peroxide by sulphuric acid there is evolved, not, as on heating, one-third, but one-half of the oxygen contained in the peroxide ($MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$); that is, 50 grams of peroxide gives about 7⅓ grams, or about 5½ litres, of oxygen,[10] whilst by heating only about 3½ litres are obtained. The chemists of Lavoisier's time generally obtained oxygen by heating manganese peroxide. At the present time more convenient methods are known.

3. A third source to which recourse may be had for obtaining oxygen is afforded by **acids** and **salts** containing much oxygen, which are capable, by parting with a portion or all of their oxygen, of being converted into other more difficultly decomposable compounds (lower products of oxidation). These acids and salts (like peroxides) evolve oxygen either on heating alone, or only when in the presence of some other substance. Sulphuric acid may be taken as an example of an acid which is decomposed by the action of heat alone,[11] for it breaks up at a red heat into water, sulphurous anhydride, and oxygen, as was mentioned before. Priestley, in 1772, and Scheele, somewhat later, obtained oxygen by heating nitre to a red heat. The best example of the formation of oxygen by the heating of salts is given by **potassium chlorate**, or Berthollet's salt, so called after the French chemist who discovered it. Potassium chlorate is a salt composed of the elements potassium, chlorine, and oxygen: $KClO_3$. It occurs as transparent colourless plates, is soluble in water, especially in hot water, and resembles common table salt in some of its reactions and physical properties; it melts on heating, and in melting begins to decompose, evolving oxygen gas. This decomposition ends in all the oxygen being evolved from the potassium chlorate, potassium chloride being left as a

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[10] Scheele, in 1785, discovered the method of obtaining oxygen by treating manganese peroxide with sulphuric acid.

[11] *All acids rich in oxygen*, and especially those whose elements form lower oxides, evolve oxygen either directly at the ordinary temperature (for instance, ferric acid), or on heating (nitric, manganic, chromic, chloric, and others), or, if lower basic oxides are formed from them, by heating with sulphuric acid. Thus the salts of chromic acid (for example, potassium dichromate, $K_2Cr_2O_7$) give oxygen with sulphuric acid; first potassium sulphate, K_2SO_4, is formed, and then the chromic acid set free gives a sulphuric acid salt of the lower oxide, Cr_2O_3. This is a convenient method for obtaining oxygen in small quantities in the laboratory.

residue, according to the equation, $KClO_3 = KCl + O_3$.[12] This decomposition proceeds at a temperature which allows of its being conducted in a glass vessel. However, in decomposing, the molten potassium chlorate swells up and boils, and gradually solidifies, so the evolution of the oxygen is not regular, and the glass vessel may crack. In order to overcome this inconvenience, the potassium chlorate is crushed and mixed with the powder of a substance which is infusible, incapable of combining with the oxygen evolved, and a good conductor of heat. Usually it is mixed with manganese peroxide.[13] The decomposition of the potassium chlorate is then considerably facilitated, and proceeds at a lower temperature (because the entire mass is then better heated, both externally and internally) and without swelling up, so that this method is more convenient than the decomposition of the salt alone. This method for the preparation of oxygen is very convenient, and is generally employed when a small quantity of oxygen is required. Further, potassium chlorate is easily obtained pure, and evolves much oxygen: 100 grams of the salt give as much as 39 grams, or 30 litres, of oxygen. This method is so simple and easy[14] that a course of practical chemistry is often commenced by the preparation of oxygen by this method, and of hydrogen by the aid of zinc and sulphuric acid, since by means of these gases many interesting and striking experiments may be performed.[15]

Bleaching powder, which contains calcium hypochlorite, $CaCl_2O_2$, evolves oxygen when gently heated in presence of a small quantity of

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[12] This reaction is not reversible, and is exothermal—that is, it does not absorb heat, but, on the contrary, evolves 9,713 calories per molecular weight of $KClO_3$, equal to 122 parts of salt (according to the determination of Thomsen, who burnt hydrogen in a calorimeter either alone or with a definite quantity of potassium chlorate mixed with oxide of iron). It does not proceed at once, but first forms perchlorate, $KClO_4$ (see Chlorine and Potassium). It is to be remarked that potassium chloride melts at 766°, potassium chlorate at 359°, and potassium perchlorate at 610°. (Concerning the decomposition of $KClO_3$, see Chapter II., note 47.)

[13] The peroxide does not evolve oxygen in this case (the temperature is not high enough). It may be replaced by many oxides—for instance, by oxide of iron. It is necessary to take the precaution that no combustible substances (such as bits of paper, splinters, sulphur, &c.) fall into the mixture, as they might cause an explosion.

[14] The decomposition of a mixture of fused and well-crushed potassium chlorate with powdered manganese peroxide proceeds at so low a temperature (the salt does not melt) that it may be effected in an ordinary glass flask. The apparatus is arranged in the same manner as in the decomposition of mercury oxide (Introduction), or as shown in the last drawing. As the reaction is exothermal, the decomposition of potassium chlorate with the formation of oxygen may probably be accomplished, under certain conditions (for example, under contact action), at very low temperatures. Substances mixed with the potassium chlorate act partially in this manner.

[15] Many other salts evolve oxygen on heating, like potassium chlorate, but they only part with it either at a very high temperature (as, for instance, common nitre) or else are unsuited for use on account of their cost (potassium manganate), or evolve impure oxygen at a high temperature (zinc sulphate at a red heat gives a mixture of sulphurous anhydride and oxygen).

certain oxides, for instance, cobalt oxide, which in this case acts by contact (see Introduction). When heated by itself, a solution of bleaching powder does not evolve oxygen, but it oxidises the cobalt oxide to a higher degree of oxidation; this higher oxide of cobalt in contact with the bleaching powder decomposes into oxygen and lower oxidised products, and the resultant lower oxide of cobalt with bleaching powder again gives the higher oxide, which again gives up its oxygen, and so on.[16] The calcium hypochlorite is here decomposed according to the equation, $CaCl_2O_2 = CaCl_2 + O_2$. In this manner a small quantity of cobalt oxide[17] is sufficient for the decomposition of an indefinitely large quantity of bleaching powder. Bleaching powder gives oxygen with still greater facility (without the aid of heat) by the action of an aqueous solution of peroxide of hydrogen (Chap. IV.), which then evolves oxygen, $CaCl_2O_2 + H_2O_2 = CaCl_2 + H_2O + 3O$. Permanganate of potassium acts in a similar way.

The properties of oxygen.[18]—It is a permanent gas—that is, it cannot be liquefied by pressure at the ordinary temperature, and, further, is only liquefied with difficulty (although more easily than hydrogen) at temperatures below −120°, because this is its absolute (critical) boiling-point. As its critical pressure[19] is about 50 atmospheres, it can be easily

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[16] Such is at present the only possible method of explaining the phenomenon of contact action. In many cases, such as the present one, it is supported by observations based on facts (see Chap. IV.) To this class of phenomena may also be referred the evolution of oxygen at the ordinary temperature from a mixture of barium peroxide and potassium manganate with water and sulphuric acid (note 9a). The essence of phenomena of this kind is purely a property of contact; the distribution of the atoms is slightly changed along the planes of contact; and if the equilibrium be unstable it is destroyed. This is more especially frequent with those substances which change exothermally—that is, for those reactions which are accompanied by an evolution of heat. The decomposition $CaCl_2O_2 = CaCl_2 + O_2$ belongs to this class, like the decomposition of potassium chlorate and peroxide of hydrogen.

[17] Generally a solution of bleaching powder is alkaline (containing free lime), and, therefore, a solution of cobalt chloride is added directly to it, the oxide of cobalt required for the reaction being thus formed.

[18] It must be remarked that in all the reactions above mentioned the formation of oxygen may be prevented by the admixture of substances capable of combining with it—for example, charcoal, many carbon (organic) compounds, sulphur, phosphorus, and various lower oxidation products, &c. These substances absorb the oxygen evolved, combining with it, forming a compound containing oxygen.

The oxygen obtained by any of the above-described methods is therefore rarely pure. It generally contains aqueous vapour, carbonic anhydride, and sometimes small traces of chlorine. The oxygen may be freed from these impurities by passing it through a solution of caustic potash, and by drying it. If the potassium chlorate be dry and pure, it gives almost pure oxygen. However, if the oxygen be required for respiration in cases of sickness, it should be washed by passing it through a solution of caustic alkali and through water. The best way to obtain pure oxygen directly is to take potassium perchlorate ($KClO_4$), which can be well purified and evolves pure oxygen on heating.

[19] With regard to the absolute boiling-point, critical pressure, and the critical state in general, see Chap. II., notes 29 and 34.

liquefied under pressures greater than 50 atmospheres at temperatures below $-120°$. According to Dewar, the density of oxygen in a critical state is 0·65 (water=1); but, like all liquids near this point,[20] it varies considerably in density with a change of pressure and temperature, and at $-181°$ its density is 1·13 under the ordinary pressure. Liquefied oxygen is an exceedingly mobile transparent liquid, with a faint blue tint [20a] and boiling (at a pressure of 760 mm.) at $-181°$ or $-182.°$ Oxygen solidifies at the temperature obtained by liquid hydrogen (probably at about $-250°$), forming a transparent blue ice, which, at a pressure of 55 mm., *gives a temperature of* $-258°$. Oxygen, like all gases, is transparent, and, like the majority of gases, colourless. It has no smell or taste, which is evident from the fact of its being a component of air. The weight of one litre of oxygen gas at 0° and 760 mm. pressure, at latitude 45°, is 1·4290 gram (Regnault, Morley, Thomsen, and others); it is slightly denser than air, so that its density in respect to air is 1·1051, and in respect to hydrogen, 16.[21]

In its chemical properties oxygen is remarkable from the fact that it very easily—and, in a chemical sense, vigorously—reacts on a number of substances, forming oxygen compounds. However, only a few substances and mixtures of substances (for example, phosphorus, copper with ammonia, decomposing organic matter, aldehyde, pyrogallol with

an alkali, &c.) combine directly and rapidly with oxygen at the ordinary temperature, whilst many substances easily combine with oxygen at a red heat, and this combination often presents a rapid chemical reaction accompanied by the evolution of a large quantity of heat. Every reaction which takes place rapidly, if accompanied by so great an evolution of heat as to produce incandescence, is termed **combustion.** Thus combustion ensues when many metals are plunged into chlorine, or oxide of sodium or barium into carbonic anhydride, or when a spark falls on gunpowder. A great many substances are combustible in oxygen, and, owing to its presence, in air also. In order to start combustion it is generally necessary [22] that the combustible substance should be brought to a state of incandescence. The continuation of the process does not require the aid of fresh external heat, because sufficient heat [23] is evolved to raise the temperature of further portions of the combustible substance to the required degree. Examples of this are familiar to all from every-day experience. Combustion proceeds in oxygen with greater rapidity, and is accompanied by a more powerful incandescence, than in ordinary air. This may be demonstrated by a number of very convincing experiments. If a piece of charcoal, attached to a wire and previously brought to red-heat, be plunged into a flask full of oxygen, it burns rapidly at a white heat—i.e., it combines with the oxygen, forming a gaseous product of combustion called carbonic anhydride, carbonic acid gas, or carbon dioxide, CO_2. This is the same gas as is evolved in the act of respiration, for charcoal is one of the substances which are obtained by the decomposition of all organic substances which contain them, and in the process of respiration part of the constituents of the body, so to speak, slowly burn. If a piece of burning sulphur be placed in a small cup attached to a wire and introduced into a flask full of oxygen, then the sulphur, which burns in air with a very feeble flame, will burn in the oxygen with a violet flame, which,

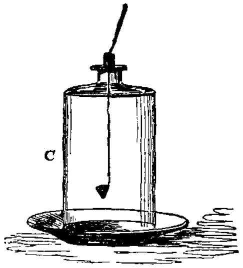

FIG. 33.—Mode of burning sulphur, phosphorus, sodium, &c., in oxygen.

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[20] Judging from what has been said in note 34 of the last chapter, and also from the results of direct observation, it is evident that all substances in a critical state have a large coefficient of expansion, and are very compressible.

[20a] Even a thin layer of liquid oxygen (or liquid air) *gives a perfect absorption* spectrum (see Chap. XIII., note 32).

[21] As water consists of 1 volume of oxygen and 2 volumes of hydrogen, and contains about 16 parts by weight of oxygen per 2 parts by weight of hydrogen, it therefore follows directly that oxygen is nearly 16 times denser than hydrogen. Conversely, the composition of water by weight may be deduced from the densities of hydrogen and oxygen and the volumetric composition of water. This method of mutual and reciprocal correction strengthens the practical data of the exact sciences, the conclusions of which require the greatest possible exactitude and variety of corrections.

It must be observed that the specific heat of oxygen at constant pressure is 0·2175; consequently it is to the specific heat of hydrogen (3·409) as 1 is to 15·6. Hence, the specific heats are inversely proportional to the weights of equal volumes, so that equal volumes of the two gases have (nearly) equal specific heats—that is, they require an equal quantity of heat for raising their temperature by 1°. We shall afterwards consider the specific heat of different substances more fully in Chap. XIV. According to Dewar, the specific heat of liquid hydrogen (between $-198°$ and $-182°$) is 0·32.

Oxygen, like the majority of difficultly liquefiable gases, is but slightly soluble in water and other liquids. The solubility is *given in note* 30, Chap. I. *From this it* is evident that water standing in air must absorb—i.e., dissolve—oxygen. This oxygen serves for the respiration of fishes. Fishes *cannot* exist in boiled water, because it does not contain the oxygen necessary for their respiration (see Chap. I.) I may also remark that repeated observations (Bore 1886, Baly and Ramsay 1894) on the *positive* discrepancies of oxygen from Boyle's law at low pressures show a rapid change in the law at pressures of about 0·7 mm., although the discrepancies remain positive even before and after this critical pressure.

[22] Certain substances (with which we shall afterwards become acquainted), however, *ignite spontaneously in air*; for example, impure phosphoretted hydrogen, silicon hydride, zinc ethyl, and pyrophorus (very finely divided iron, &c.) This signifies that the temperature of ignition is below the ordinary temperature.

[23] If so little heat is evolved that the adjacent parts are not heated to the temperature of combustion, then combustion will cease. Thus combustion may be stayed not only by stopping the access of oxygen, but also by cooling the burning body, i.e., by lowering its temperature. This is what occurs when a candle is blown out, or a fire extinguished by water.

although pale, is much larger than in air. If the sulphur be exchanged for a piece of **phosphorus**,[24] then, unless the phosphorus be heated, it will combine very slowly with the oxygen; but, if heated, even if in one spot only, it burns with an exceedingly brilliant white flame. In order to heat the phosphorus inside the flask, the simplest way is to bring a red-hot wire into contact with it. As regards charcoal, this cannot burn until it is brought to a state of incandescence. Sulphur also will not burn under 100°, whilst phosphorus inflames at 40°. Phosphorus which has been already lighted in air cannot so well be introduced into the flask, because it burns very rapidly and with a large flame in air. If a small lump of metallic **sodium** be put into a small cup made of lime,[25] melted, and ignited,[26] it burns very feebly in air. But if burning sodium be introduced into oxygen, the combustion is invigorated and is accompanied by a brighter yellow flame. Metallic **magnesium**, which burns yet more brightly in air, continues to burn with still greater vigour in oxygen (i.e., the temperature rises still higher), forming a white powder, which is a compound of magnesium with oxygen (magnesium oxide or magnesia). A strip of **iron** or steel does not burn in air, but an iron wire or steel spring may be easily burnt in oxygen.[27] The combustion of steel or iron in oxygen is not accompanied by a flame, but sparks of oxide fly in all directions from the burning portions of the iron.[28]

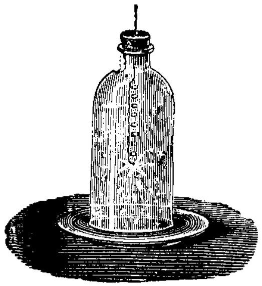
FIG. 34.—Mode of burning a steel spring in oxygen.

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[24] The phosphorus must be dry; it is usually kept in water, as it oxidises in air. It should be cut under water, as otherwise the freshly cut surface oxidises. It must be dried carefully and quickly by wrapping it in blotting-paper. If damp, it splutters on burning. A small piece should be taken, as otherwise the iron spoon will melt. In this and the other experiments on combustion, water should be poured over the bottom of the vessel containing the oxygen, to prevent it from cracking. The cork closing the vessel should not fit tightly, in order to allow for the expansion of the gas due to the heat of the combustion.

[25] An iron cup will melt with sodium in oxygen.

[26] In order to rapidly heat the lime crucible containing the sodium, it is heated in the flame of a blowpipe described in Chap. VIII.

[27] In order to burn a watch-spring, it is first tempered (made red-hot and then slowly cooled) in order to soften it, and then a piece of tinder (or paper soaked in a solution of nitre, and dried) is attached to one end. The tinder is lighted, and the spring then plunged into the oxygen. The burning tinder heats the end of the spring, the heated part burns, and in so doing heats the further portions of the spring, which then burns completely if sufficient oxygen be present.

[28] The sparks of rust are produced, owing to the fact that the volume of the oxide of iron is nearly twice that of the iron, and as the heat evolved is not sufficient to entirely

In order to demonstrate by experiment the **combustion of hydrogen** in oxygen, a gas-conducting tube, bent so as to form a convenient jet, is led from the vessel evolving hydrogen. The hydrogen is first ignited in air, and then the gas-conducting tube is let down into a flask containing oxygen. The combustion in oxygen will be similar to that in air; the flame remains pale, notwithstanding the fact that its temperature rises considerably. It is instructive to remark that oxygen may burn in hydrogen, just as hydrogen does in oxygen. In order to show the combustion of oxygen in hydrogen, a tube bent vertically upwards and ending in a fine orifice is attached to the stopcock of a gas-holder full of oxygen. Two wires placed at such a distance from each other as to allow of the passage of a series of sparks from a Ruhmkorff's coil, are fixed in front of the orifice of the tube. This is in order to ignite the oxygen, which may be also done by attaching tinder round the orifice, and burning it. When the wires are arranged at the orifice of the tube, and a series of sparks passes between them, an inverted (because of the lightness of the hydrogen) jar full of hydrogen is placed over the gas-conducting tube. When the jar covers the orifice of the gas-conducting tube (and not before, as otherwise an explosion might take place) the cock of the gasometer is opened, and the oxygen flows into the hydrogen and is set light to by the sparks. The flame obtained is similar to that formed by the combustion of hydrogen in oxygen.[29] From this it is evident that the flame is the locality where

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melt the oxide or the iron, the particles must be torn off and fly about. Similar sparks are also formed in the combustion of iron in other cases. We called attention in the Introduction to the combustion of iron filings. In the welding of iron, small iron splinters fly off in all directions and burn in the air, as is seen from the fact that whilst flying through the air they remain red-hot, and also because, on cooling, they are seen to be no longer iron, but a compound of it with oxygen. The same thing takes place when the hammer of a gun strikes against the flint. Small scales of steel are heated by the friction, and glow and burn in the air. The combustion of iron is still better seen by taking it as a very fine powder, such as is obtained by the decomposition of certain of its compounds, for instance, by heating Prussian blue, or by the reduction of its compounds with oxygen by hydrogen; when this fine powder is strewn in air, it burns by itself, even without being previously heated (it forms pyrophorus). This depends on the physical state of the surface of the powder after reduction and on the fact that the powder of iron presents a larger surface of contact with air than an equal weight in a compact form.

[29] The experiment may be conducted without the wires, if the hydrogen be lighted in the orifice of an inverted cylinder, and at the same time the cylinder be brought over the end of a gas-conducting tube connected with a gas-holder containing oxygen. Thomsen's method may be adopted for a lecture experiment. In this, two glass tubes with platinum ends are passed through orifices, about 1–1½ centimetre apart, in a cork. One tube is connected with a gas-holder containing oxygen and the other with a gas-holder full of hydrogen. Having turned on the gases, the hydrogen is lighted, and a common lamp glass, tapering towards the top, is placed over the cork. The hydrogen continues to burn inside the lamp glass, at the expense of the oxygen. If the current of oxygen is then decreased little by little, a point is reached when, owing to the insufficient supply of

the oxygen combines with the hydrogen, so that a flame of burning oxygen can be obtained as well as a flame of burning hydrogen.

If, instead of hydrogen, any other combustible gas be taken—for example, ordinary coal gas—then the phenomenon of combustion will be exactly the same, only a bright flame will be obtained, and the products of combustion will be different. However, as coal gas contains a considerable amount of free and combined hydrogen, it will also form a considerable quantity of water in its combustion.

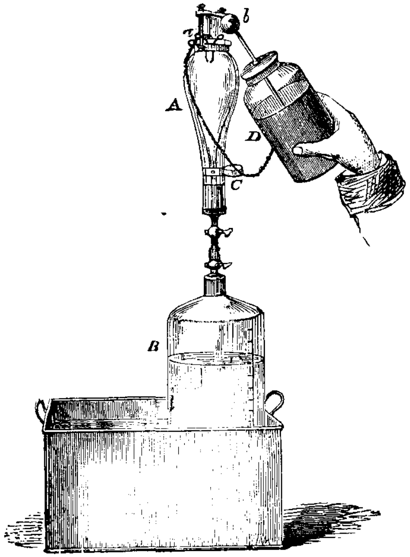

Fig. 35.—Cavendish's apparatus for exploding detonating gas. The bell jar standing in the bath is filled with a mixture of two volumes of hydrogen and one volume of oxygen, and the thick glass vessel A is then screwed on to it. The air is first pumped out of this vessel, so that when the stopcock C is opened, it becomes filled with detonating gas. The stopcock is then re-closed, and the explosion produced by means of a spark from a Leyden jar. After the explosion has taken place the stopcock is again opened, and the water rises into the vessel A.

If hydrogen be mixed with oxygen in the proportion in which these gases form water—i.e., if two volumes of hydrogen be taken for each volume of oxygen—the mixture will then be the same as that obtained by the decomposition of water by a galvanic current, i.e., detonating gas.

We have already mentioned in the last chapter that the combination of these gases, or their explosion, may be brought about by the action of an electric spark, because the spark heats the space through which it passes, and consequently acts in a manner similar to ignition by means of contact with an incandescent or burning substance.[30] Cavendish made this experiment on the ignition of detonating gas at the end of the eighteenth century, in the apparatus shown in fig. 35. Ignition of gases by the aid of the electric spark is convenient, for the reason that it may then be brought about in a closed vessel, and hence chemists employ this method when it is required to ignite a mixture of oxygen with a combustible gas in a closed vessel. For this purpose, especially since Bunsen's time,[31] a **eudiometer** is employed. It consists of a thick glass tube graduated along its length in millimetres (for indicating the height of the mercury column), and calibrated for a definite volume (weight of mercury). Two platinum wires are fused into the upper closed end of the tube, as shown in fig. 36.[32] By the aid of the eudiometer we may not only determine the volumetric composition of water,[33] and the quantitative content of oxygen in air, but may also make a number of experiments explaining the phenomenon of combustion.

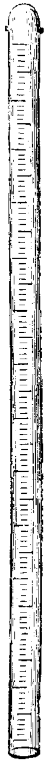

Fig. 36. Eudiometer

Thus, for example, it may be demonstrated, by the aid of the eudiometer, that, **for the ignition** of detonating gas (like all combustible bodies), a **definite temperature** is required. If the temperature be below that required, combination will not take place, but if at any spot within the tube it rises to the temperature of inflammation, then combination will ensue at that spot, and evolve enough heat for the ignition of the adjacent portions of the detonating mixture. If to 1 volume of detonating gas there be added 10 volumes of oxygen, or 4 volumes of hydrogen, or 3 volumes of carbonic anhydride, we shall not *then obtain an explosion by passing a spark through the diluted mixture.* This depends on the fact that the temperature falls with dilution of the detonating gas by another gas, because the heat evolved by the combination of the small quantity of hydrogen and oxygen brought to incandescence by the spark is transmitted, not only to the water proceeding from the combination, but also to the foreign substance mixed

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oxygen, the flame of the hydrogen increases in size, disappears for several moments, and then reappears at the tube supplying the oxygen. If the flow of oxygen be now increased again the flame reappears at the hydrogen tube. Air may be taken instead of oxygen, and ordinary coal-gas instead of hydrogen, and it will then be shown how air burns in an atmosphere of coal-gas, and it can easily be proved that the lamp glass is full of a gas combustible in air, because it may be lighted at the top.

[30] In fact, instead of a spark, a fine wire may be taken, and an electric current passed through it to bring it to a state of incandescence; in this case there will be no sparks, but the gases will inflame if the wire be fine enough to become red-hot by the passage of the current.

[31] At the present time, a great many other different forms of apparatus, sometimes designed for special purposes, are employed in the laboratory for the investigation of gases. Detailed descriptions of the methods of gas analysis and of the apparatus employed must be looked for in works on *analytical and applied chemistry.*

[32] They must be sealed into the tube in such a manner as to leave no aperture between them and the glass. In order to test this, the eudiometer is almost filled with mercury, and its open end placed in mercury. If there be the smallest orifice at the wires, the external air will enter the cylinder and the mercury will fall, although not rapidly if the orifice be very fine.

[33] Concerning this application of the eudiometer, see the chapter on Nitrogen. It may be mentioned, as illustrating the various uses of the *eudiometer, that Professor* Timerasеff employed microscopically small eudiometers to analyse the bubbles of gas given off from the leaves of plants.

with the detonating gas.[34] The necessity of a definite temperature for the ignition of detonating gas is also seen from the fact that pure detonating gas explodes in the presence of a red-hot iron wire, or of charcoal heated to 275°; but with a lower degree of incandescence there is no explosion. It may also be brought about by rapid compression, when, as is known, heat is evolved.[35] Experiments made in the eudiometer showed that the ignition of detonating gas takes place at a temperature between 450° and 560°.[36]

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[34] Further, ½ volume of carbonic oxide, an equal volume of marsh gas, two volumes of hydrogen chloride or of ammonia, or six volumes of nitrogen or twelve of air added to one volume of detonating gas prevent its explosion.

[35] If the compression be brought about slowly, so that the heat evolved succeeds in passing to the surrounding space, then the combination of the oxygen and hydrogen does not take place, even when the mixture is compressed 150 times, for the gases are not heated. If paper soaked with a solution of platinum (in aqua regia) and sal-ammoniac is burnt, the ash obtained contains very finely divided platinum, and in this form it is best fitted for igniting hydrogen and detonating gas. Platinum wire requires to be heated, but *platinum* in so finely divided a state as it occurs in this ash inflames hydrogen, even at – 20°. Many other metals, such as palladium (175°), iridium, and gold, act on a slight rise of temperature, like platinum; but mercury, at its boiling-point, does not inflame detonating gas, although the slow formation of water begins at 305°. All data of this kind show that the explosion of detonating gas forms one of the many cases of contact phenomena. This conclusion is further confirmed by the researches of V. Meyer (1892). He showed that only a very slow formation of steam begins at 448°, and that it only proceeds *more rapidly at* 518°. The *temperature* of the explosion of detonating gas, according to the same author, varies according to whether the explosion is produced in open vessels or in closed tubes. In the first case the temperature of explosion lies between 530°–606°, and in the second between 630°–730°. In general it may be remarked that the temperature of explosion of gaseous mixtures is always lower in closed vessels than when the detonating mixture flows freely through tubes. According to Freyer and V. Meyer, the following gases when mixed with the requisite amount of oxygen explode at the following temperatures:

—	When flowing freely	In closed vessels
H_2 with oxygen	630°–730°	530 –606°
CH_4 ,,	650 –730°	606 –650
C_2H_6 ,,	606°–650°	530°–606°
C_2H_4 ,,	606°–650°	530°–606°
CO ,,	650°–730°	650°–730°
H_2S ,,	315°–320°	250°–270°
$H_2 + Cl_2$	430°–440°	240°–270°

Baker (1892) showed that perfectly pure detonating gas, prepared by the action of an electric current on a solution of caustic baryta (BaH_2O_2) and very carefully dried by volatilised phosphoric anhydride, does not give water or explode at those temperatures (even at 950°) at which moist detonating gas immediately forms water (compare Chap. IX., note 29). Besides which, Baker proved that the moist gas gradually gives water when exposed to sunlight, but that the dry gas does not react at all. In my opinion, all such instances are due to phenomena of contact; that is, in other words, they are determined by changes in the distribution of the atoms in the molecules which take place to a greater or less degree at all the planes of contact of different bodies. This is particularly clear in the above influence of metals.

The velocity of the transmission of explosion in gaseous mixtures is as characteristic a magnitude for gaseous systems as the velocity of the transmission of sound. Berthelot showed that this velocity depends neither upon the pressure nor upon the size of the tubes in which the gaseous mixture is contained, nor upon the material of which the tube is made. Dixon (1891) determined the magnitude of these velocities for various mixtures, and his results agreed well with those previously given by Berthelot. For comparison we give the velocities expressed in metres per second:

—	Dixon	Berthelot
$H_2 + O$	2,821	2,810
$H_2 + N_2O$	2,305	2,284
$CH_4 + 4O$	2,322	2,287
$C_2H_2 + 6O$	2,364	2,210
$C_2H_4 + 5O$	2,391	2,482
$C_2N_2 + 4O$	2,321	2,195

The addition of oxygen to detonating gas lowers *the velocity of the transmission* of explosion almost as much as the introduction of nitrogen. An excess of hydrogen, on the contrary, raises the velocity of transmission. It is remarked that the explosion of mixtures of oxygen with marsh gas, ethylene, and cyanogen is transmitted more quickly if the oxygen be taken in such a proportion that the carbon should burn to oxide of carbon, i.e., the velocity of the explosion is less if the oxygen be taken in sufficient quantity to form carbonic anhydride. Observations upon liquid and solid explosives (Berthelot) show that, in these cases, the velocity of transmission of explosion is dependent upon the material of the tube. Thus the explosion of liquid nitro-methyl ether in glass tubes travels at the rate (with variation of the diameter from 1 mm. to 45 mm.) of from 1,890 to 2,482 metres, and in tubes of Britannia metal (3 mm. in diameter) at the rate of 1,230 metres. The harder the tube the greater the velocity of transmission of explosion. The following are the velocities for certain bodies:

	metres per second
Nitro-glycerine	1,300
Dynamite	2,500
Nitro-mannite	7,700
Picric acid	6,500

In conclusion we may add that Mallard and Le Chatelier (1882) observed that in the explosion of a mixture of 1 volume of detonating gas with *n* volumes of an inert gas, the pressure is approximately equal to *9·20 – ·9n atmospheres.*

[36] From the very commencement of the promulgation of the idea of dissociation, it might have been imagined that reversible reactions of combination (the formation of H_2O from H_2 and O belongs to this class) commence at the same temperature as that at which dissociation begins. And in many cases this is so, but not always, as may be seen from the facts: (1) that at 450–560°, when detonating gas explodes, the density of aqueous vapour not only does not vary (and it hardly varies at higher temperatures, probably because the amount of the products of dissociation is small), but there are not, as far as is yet known, any traces of dissociation; (2) that under the influence of contact the temperature at which combination takes place falls even to the ordinary temperature, at which water and similar compounds are, of course, not dissociated; and, judging from the data communicated by D. P. Konovaloff (Introduction, note 39) and others, it is impossible to escape the phenomena of contact. All vessels, whether of metal or glass, show the same influence as spongy platinum, although to a much less degree. The phenomena of contact, judging from a review of the data referring to it, must be especially *sensitive in* reactions which are powerfully exothermic, and the explosion of detonating gas is of this kind.

The combination of hydrogen with oxygen is accompanied by the evolution of a very considerable amount of heat; according to the determinations of **Favre** and **Silbermann**,[37] 1 part by weight of hydrogen in forming water evolves 34,462 units of heat. Many later determinations agree closely with this figure, so that it may be taken that in the formation of 18 parts of water (H_2O) there are evolved 69 major calories (each 1,000 times greater than the normal calorie, and therefore called kilogram-calories), or 69,000 units of heat.[38] *If the specific heat of aqueous vapour* (0·48) *remained constant from the ordinary temperature to that at which the combustion of detonating gas takes place* (and there is now no doubt that it increases rapidly, especially beyond 1,000°), were the combustion concentrated at one point [39] (but it occurs in the whole region of a flame), were there no loss from radiation and heat conduction, and *did dissociation* (which absorbs heat and consequently increases the apparent specific heat) *not take place*—that is, did not a state of equilibrium between the hydrogen, oxygen, and water come about—*then it would be possible to calculate the temperature of the flame of detonating gas.* It would then be 7,700°.[40] In reality it is

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[37] The amount of heat evolved in the combustion of a known weight (for instance, 1 gram) of a given substance is determined by the rise in temperature of a quantity of water, to which the whole of the heat evolved in the combustion is transmitted. A **calorimeter**, for example that shown in fig. 37, is employed for this purpose. It consists *of a thin* (*in order that it may absorb less heat*), *polished* (*that it should transmit a minimum of heat*) metallic vessel, surrounded by down (*c*), or some other bad conductor of heat, and an outer metallic vessel. This is necessary in order that the least possible amount of heat should be lost from the vessels; nevertheless, there is always a certain loss, the magnitude of which is determined by preliminary experiment (by taking warm water, and determining its fall in temperature after a definite period of time) as a correction for the results of observations. The water to which the heat of the burning substance is transmitted is poured into the vessel. The stirrer *g* allows of all the layers of water being brought to the same temperature, which is determined by the thermometer. The heat evolved passes, naturally, not to the water only, but to all the parts of the apparatus. The quantity of water corresponding with the whole amount of those objects (the vessels, tubes, &c.) to which the heat is transmitted is previously determined, and in this manner another most important correction is made in the calorimetric determinations. The combustion itself is carried on in the vessel *a*. The ignited substance is introduced through the tube at the top, which closes tightly. In fig. 37 the apparatus is arranged for the combustion of a gas, introduced by a tube. The oxygen required for the combustion is led into *a* by the tube *e*, and the products of combustion either remain in the vessel *a* (if liquid or solid), or escape by the tube *f* into an apparatus in which their quantity and properties can easily be determined. Thus the heat evolved in combustion passes to the walls of the vessel *a*, and to the gases which are formed in it, and these transmit it to the water of the calorimeter.

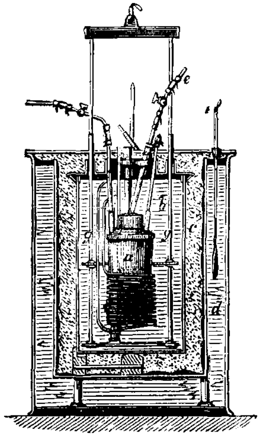

FIG. 37.—Favre and Silbermann's calorimeter for determining the heat evolved in combustion.

The construction of the calorimeter and even the method of determination vary considerably in different cases. Since the beginning of the nineties, a large number of determinations of the heat of combustion have been conducted in closed bombs containing compressed oxygen. The greatest number of calorimetric determinations were made by Berthelot and by Thomsen. They are given in their works: *Essai de mécanique chimique fondée sur la thermochimie*, by M. Berthelot, 1879 (2 vols.), and *Thermochemische Untersuchungen*, by J. Thomsen, 1886 (4 vols.) The most important methods of recent thermochemistry, and all the trustworthy results of experiment, are given in Professor W. F. Louginin's *Description of the different Modes of determining the Heat of Combustion of Organic Compounds*, Moscow, 1894. The student must refer to works on theoretical and physical chemistry for a description of the elements and methods of **thermochemistry**, into the details of which it is impossible to enter in this work. One of the originators of thermochemistry, Hess, was a member of the St. Petersburg Academy of Sciences. Since 1870 a large amount of research has been carried out in this province of chemistry, especially in France and Germany, after the investigations of the French Academician, Berthelot, and Professor Thomsen, of Copenhagen. Among Russians, Beketoff, Werner, Louginin, Cheltzoff, Chroustchoff, and others are known by their thermochemical researches. The present epoch of thermochemistry must be considered rather as a collective one, wherein the material of facts is being amassed, and the first consequences arising from them are being noticed. In my opinion two essential circumstances prevent the possibility of deducing any exact consequences, of importance to chemical mechanics, from the immense store of thermochemical data already collected: (1) The majority of the determinations are conducted in weak aqueous solutions, and, the heat of solution being known, are referred to the substances in solution; yet there is much (Chap. I.) which leads to the conclusion that water in solution does not play the simple part of a diluting medium, but of itself acts independently in a chemical sense on the substance dissolved. (2) Physical and mechanical changes (decrease of volume, diffusion, and others) invariably proceed side by side with chemical changes, and for the present it is impossible, in a number of cases, to distinguish the thermal effects of the one and the other kind of change. It is evident that the one kind of change (chemical) is essentially inseparable and incomprehensible without the other (mechanical and physical); and therefore it seems to me that thermochemical data will only acquire their true meaning when the connection between the phenomena of both kinds (on the one hand chemical and atomic, and on the other, mechanical and molecular or between entire masses) is explained more clearly and fully than is at present the case. As there is no doubt that the simple mechanical contact, or the action of heat alone, on substances sometimes causes an evident and always a latent (incipient) chemical change—that is, a different distribution or motion of the atoms in the molecules—it follows that purely chemical phenomena are inseparable from physical and mechanical phenomena. A mechanical change may be imagined without a physical change, and a physical without a chemical change; but it is impossible to imagine a chemical change without a physical and mechanical one, for without the latter we should not be able to recognise the former, and it is by their means that we are enabled to do so.

[38] This quantity of heat corresponds with the formation of water at the ordinary temperature from detonating gas at the same temperature. If the water be as vapour, the heat evolved is 58 major calories (because the latent heat of evaporation takes 600 calories per 1 part by weight of water, and there are 18 parts); if as ice, 70·4 major calories.

[39] This flame, or locality where the combustion of gases and vapours takes place, is a complex phenomenon, 'an entire factory,' as Faraday says, and therefore we will consider flame in some detail in one of the following notes.

[40] If 34,500 units of heat are evolved in the combustion of 1 part of hydrogen, and

very much lower, but it is nevertheless higher than the temperature attained in furnaces and flames, and is as high as 2,000°. The explosion of detonating gas is explained by this high temperature, because the aqueous vapour formed must occupy a volume at least five times greater than that occupied by the detonating gas at the ordinary temperature. Detonating gas emits a sound, not only as a consequence of the commotion which occurs from the rapid expansion of the heated vapour, but also because it is immediately followed by a cooling effect, the conversion of the vapour into water, and a rapid contraction.[41]

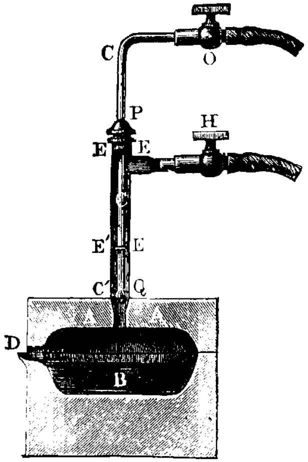

FIG. 38.—Safety burner for detonating gas, described in text.

Mixtures of hydrogen and of various other combustible gases and vapours with oxygen are taken advantage of for obtaining high temperatures. By the aid of such high temperatures, metals like platinum may be melted on a large scale, which cannot be performed in furnaces heated with charcoal and fed by a current of air of the ordinary temperature.[41a] The burner shown in fig. 38 is constructed for the application of detonating gas to the purpose. It consists of two brass tubes, one fixed inside the other, as in the drawing. The inner central tube C C conducts the oxygen, and the outer, enveloping, tube, E′ E′, the hydrogen. Previous to their egress the gases do not mix together, so that there can be no explosion inside the apparatus. When the burner is in use, C is connected with a gas-holder containing oxygen, and E with a gasholder containing hydrogen (or sometimes coal-gas). The flow of the gases can be easily regulated by the stopcocks O and H. The flame is shortest and evolves the greatest heat when the gases burning are in the proportion of 1 volume of oxygen to 2 volumes of hydrogen. The degree of heat may be easily judged from the fact that a thin platinum wire placed in the flame of a properly proportioned mixture readily melts. By placing the burner in the orifice of a hollow piece of lime, a crucible A B is obtained in which platinum may be readily melted, even in large quantities, if the current of oxygen and hydrogen be sufficiently great (Deville). The flame of detonating gas may also be used for illuminating purposes. By itself it is very pale, but owing to its high temperature, it serves for rendering infusible objects incandescent, and at the very high temperature produced by the detonating gas the incandescent substance gives a most intense light. For this purpose, lime, magnesia, or oxide of zirconium is used, as these are not fusible at the very high temperature generated by the detonating gas. A small cylinder of lime placed in the flame of detonating gas, if regulated to the required point, gives a very brilliant white light, which was at one time proposed for illuminating lighthouses. At present, in the majority

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this heat is transmitted to the resulting 9 parts by weight of aqueous vapour, then we find that, taking the specific heat of the latter as 0·475, each unit of heat raises the temperature of 1 part by weight of aqueous vapour 2·1° and 9 parts by weight (2·1÷9) 0·23°; hence the 34,500 units of heat raise its temperature 7,935°. If detonating gas is converted into water in a closed space, then the aqueous vapour formed cannot expand; and therefore, in calculating the temperature of combustion, the specific heat at constant volume must be taken into consideration; for aqueous vapour this is 0·36. This figure gives a still higher temperature for the flame. In reality it is much lower, but the results given by different observers are very contradictory (from 1,700° to 2,400°), the discrepancies depending on the fact that flames of different sizes are cooled by radiation to a different degree, but mainly on the fact that the methods and apparatus (pyrometers) for the determination of high temperatures, although they enable relative changes of temperature to be judged, are of little use for determining their absolute magnitudes. By taking the temperature of the flame of detonating gas as 2,000°, I give, I think, the average of the most trustworthy determinations and calculations based upon the determination of the variation of the specific heat of aqueous vapour and other gases.

The determination of the temperature of combustion or heating power (pyrometric effect, as it is often called) is considered more fully in speaking of combustion in my work, *The Principles of Industry. Fuel*, 1897, pp. 93–98. Why only 2,000° is attained instead of 8,000° is explained by the fact that between 0° and 2,500° the *mean* apparent (combined with dissociation) specific heat of steam probably exceeds (judging from Mallard and Le Chatelier's observations, 1888) the specific heat of liquid water, and if the mean specific heat of steam be taken as about 1·9, it is evident that only about 2,000° will be obtained instead of 8,000°. Mallard and Le Chatelier showed that the mean specific heat of aqueous vapour up to the distinct commencement of dissociation may be taken as $0·4 + 0·0002t$. Dissociation is very considerable at the temperature of the flame of detonating gas, and this lowers the temperature or increases the apparent specific heat.

[41] It is evident that not only hydrogen, but every other combustible gas and vapour, can give an explosive mixture with oxygen. For this reason coal-gas mixed with air explodes when the mixture is ignited. The pressure obtained in the explosions serves as the **motive power of gas engines.** In this case advantage is taken, not only of the pressure produced by the explosion, but also of the contraction which takes place after the explosion. On this is based the construction of several motors, of which Lenoir's was formerly, and Otto's is now, the best known. The explosion is usually produced by coal-gas and air, but of late the vapours of combustible liquids (kerosene, benzine, naphtha) and the combustible gases of blast furnaces are also being employed (Chap. XXII.) In Lenoir's engine a mixture of coal-gas and air is ignited by means of sparks from a Ruhmkorff's coil; but in the most recent machines the gases are ignited by the direct action of a gas jet, or by contact with the hot walls of a side tube.

[41a] However, if the air used for combustion be previously strongly heated, and charcoal or some combustible gas (lighting or generator, see Chap. IX., note 19) be burnt in it, then the melting-point of platinum (1,780°) and iron (1,450°) may be attained; and this is now taken advantage of in works in the so-called regenerator furnaces (see Chap. IX., note 19).

of cases, the electric light, owing to its constancy and other advantages, has replaced it for this purpose. The light produced by the incandescence of lime in detonating gas is called the **Drummond light** or **limelight.**

The above cases form examples of the combustion of elements in oxygen, but exactly similar phenomena are observed in the **combustion of compounds.** Thus, for instance, the solid, colourless, shiny substance, naphthalene, $C_{10}H_8$, burns in the air with a smoky flame, whilst in oxygen it continues to burn with a very brilliant flame. Alcohol, oil, and other substances burn brilliantly in oxygen on conducting the oxygen by a tube to the flames of lamps burning these substances. A high temperature is thus evolved, which is sometimes made practical use of in chemistry.

In order to understand why combustion in oxygen proceeds more rapidly, and is accompanied by a more intense heat effect, than combustion in air, it must be recollected that air is oxygen diluted with nitrogen, which does not support combustion, and therefore fewer particles of oxygen flow to the surface of a substance when burning in air than when burning in pure oxygen, and the heat evolved has, moreover, to heat the mass of nitrogen accompanying the oxygen as well as the products of combustion (and the oxygen).[42]

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[42] Let us consider as an example the combustion of sulphur in air and in oxygen. If 1 gram of sulphur burns in air or oxygen it evolves in either case 2,250 units of heat, i.e., sufficient heat for heating 2,250 grams of water 1° C. This heat is first of all transmitted to the sulphurous anhydride, SO_2, formed by the combination of sulphur with oxygen. In its combustion, 1 gram of sulphur forms 2 grams of sulphurous anhydride—i.e., 1 gram of the sulphur combines with 1 gram of oxygen. In order that 1 gram of sulphur should have access to 1 gram of oxygen in air, it is necessary that 3·4 grams of nitrogen should simultaneously reach the sulphur, because air contains 77 parts of nitrogen (by weight) per 23 parts of oxygen. Thus, in the combustion of 1 gram of sulphur, the 2,250 units of heat are transmitted to 2 grams of sulphurous anhydride and at least 3·4 grams of nitrogen. As 0·155 unit of heat is required to raise the temperature of 1 gram of sulphurous anhydride 1° C., 2 grams will require 0·31 unit. So also, 3·4 grams of nitrogen require $3{\cdot}4 \times 0{\cdot}244$ or 0·83 unit of heat, and therefore, in order to raise both gases 1° C., $0{\cdot}31 + 0{\cdot}83$ or 1·14 unit of heat is required; but as the combustion of the sulphur evolves 2,250 units of heat, the gases might be heated (if their specific heats remained constant) to $\frac{2250}{1{\cdot}14}$ or 1,974° C. That is, the maximum possible temperature of the flame of sulphur burning in air will be 1,974° C. In the combustion of the sulphur in oxygen the heat evolved (2,250 units) can only pass to the 2 grams of sulphurous anhydride, and therefore the highest possible temperature of the flame of sulphur in oxygen will be $= \frac{2250}{0{\cdot}31}$ or 7,258°. This formation of gaseous products in conbustion must also lower the temperature of combustion. Therefore when a reaction takes place between solid bodies with the formation of solid bodies (or in general when the volume does not increase or varies but little, and all the more if contraction takes place), the heating effect may be very great. This is illustrated by a powdered mixture of molecular proportions of oxide of iron and metallic aluminium,

Among the phenomena accompanying the combustion of certain substances, the **phenomenon of flame** attracts attention. Sulphur, phosphorus, sodium, magnesium, naphthalene, &c. burn, like hydrogen, with a flame, whilst in the combustion of other substances no flame is observed, as, for instance, in the combustion of iron and of charcoal. The appearance of flame depends on the capacity of the combustible substance to yield gases or vapours at the temperature of combustion. At the temperature of combustion, sulphur, phosphorus, sodium, and naphthalene pass into vapour, whilst wood, alcohol, oil, &c. are decomposed into gaseous and vaporous substances. The combustion of gases and vapours forms flames, and therefore *a flame is composed of the hot incandescent gases and vapours produced by combustion.* It may easily be proved, by placing a tube in the flame connected with an aspirator, that the flames of such non-volatile substances as wood contain volatile and combustible substances formed from them. Besides the products of combustion, combustible gases and liquids, previously in the flame as vapours, collect in the aspirator. For this experiment to succeed—i.e., in order to really extract combustible gases and vapours from the flame—it is necessary that the suction tube should be placed *inside* the flame. The combustible gases and vapours can only remain unburnt inside the flame, for at its surface they come into contact with the oxygen of the air and burn.[42a] Flames are of different degrees of **brilliancy**, according to whether *solid* incandescent particles occur in the combustible gas or vapour, or not. Incandescent gases and vapours emit but little light by themselves, and therefore give a paler flame.[43] If a flame does not contain solid particles it is transparent, pale, and emits but little light.[44] The flames of burning

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Goldschmidt's thermite, which after ignition (by a magnesium wire bent into the mixture) burns and gives a temperature as high as 3,000° (according to the equation $Fe_2O_3 + Al_2 = Al_2O_3 + Fe_2$) at which the resultant iron melts. The temperature is undoubtedly higher than in the hydrogen flame.

[42a] Faraday proved this by a very convincing experiment on a candle flame. If one arm of a bent glass tube be placed in a candle flame in the dark portion of the flame above the wick, then the products of the partial combustion of the stearin will pass up the tube, condense in the other arm, and collect in a flask placed under it (fig. 39) as heavy white fumes which burn when lighted. If the tube be raised into the upper luminous portion of the flame, a dense black smoke which will not inflame accumulates in the flask. Lastly, if the tube be let down until it touches the wick, little but stearic acid condenses in the flask.

[43] All transparent substances which transmit light with great ease (that is, which absorb but little light) are but slightly luminous when heated; so also substances which absorb but few heat rays, when heated, transmit few rays of heat.

[44] There is, however, no doubt but that very heavy dense vapours or gases under pressure (according to the experiments of Frankland) are luminous when heated, because, as they become denser, they approach a liquid or solid state. Thus, detonating gas, when exploded under pressure, gives a brilliant light.

alcohol, sulphur, and hydrogen are of this kind. A pale flame may be rendered luminous by placing fine particles of solid matter in it. Thus, if a very fine platinum wire be placed in the pale flame of burning alcohol—or, better still, of hydrogen—the flame emits a bright light. This is still better seen by sifting the powder of an incombustible substance, such as fine sand, into the flame, or by placing a bunch of asbestos threads in it. A brilliant flame always contains some kind of solid particles, or at least some very dense vapour. The flame of sodium burning in oxygen has a brilliant yellow colour, from the presence of particles of solid sodium oxide. The flame of magnesium is brilliant from the fact that, in burning, it forms solid magnesia, which becomes white hot, and similarly the brilliancy of the Drummond light is due to the heat of the flame raising the lime to a state of incandescence. The flames of a candle, wood, and similar substances are brilliant, because they contain particles of charcoal or soot. It is not the flame itself which is luminous, but the incandescent soot it contains. These particles of charcoal which occur in flames may be easily observed by introducing a cold object, like a knife, into the flame.[45] The particles of charcoal burn at the outer surface of the flame if the supply of air is sufficient; but if the supply of air—that is, of oxygen—be insufficient for their combustion the flame will smoke, because the

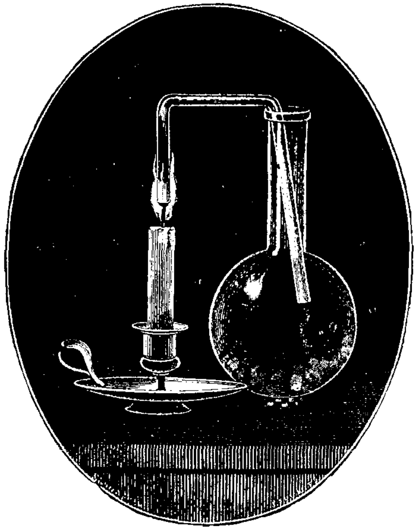

FIG. 39.—Faraday's experiment for investigating the different parts of a candle flame.

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[45] If hydrogen gas be passed through a volatile liquid hydrocarbon—for instance, through benzine (the benzine may be poured directly into the vessel in which the hydrogen is generated)—its vapour then burns with the hydrogen and gives a very bright flame, because the resultant particles of carbon (soot) become incandescent. Benzine or platinum gauze, introduced into a hydrogen flame, may be employed for illuminating purposes. The smoke of stoves, owing to imperfect combustion (due to various causes, especially to the imperfect mixture of the products of combustion with air and a local fall of temperature) of the fuel, frequently contains soot. This could not occur unless the soot had been previously formed in the flame.

unconsumed particles of charcoal are carried off by the current of air.[46]

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[46] In **flames**, the separate parts may be distinguished with more or less distinctness. That portion of the flame to which the combustible vapours or gases flow is not luminous because its temperature is still too low for the process of combustion to take place in it. This is the space which in a candle surrounds the wick, or in a gas jet is immediately *above the orifice from which the gas escapes*. In a candle, the combustible vapours and gases formed by the action of heat on the melted tallow or stearin, rise in the wick and are heated by the high temperature of the flame. By the action of the heat, the solid or liquid substance is here, as in other cases, decomposed, forming products of dry distillation, and these products occur in the central portion of the flame of a candle. The air travels to it from the outside, and is not able to intermix equally with the vapours and gases in all parts of the flame at once; consequently in the outer portion of the flame the amount of oxygen will be greater than in the interior portions. But, owing to diffusion, the oxygen, of course mixed with nitrogen, flowing towards the combustible substance, does finally penetrate to the interior of the flame (when the combustion takes place in ordinary air). The combustible vapours and gases combine with this oxygen, evolve a considerable amount of heat, and bring about that state of incandescence which is so necessary both for keeping up the combustion and also for the uses to which the flame is applied. Passing from the colder envelope of air through the interior of the flame to the source of the combustible vapours (for instance, the wick), we evidently first traverse layers of higher and higher temperature, and then portions which are less and less hot, in which the combustion is less complete, owing to the limited supply of oxygen.

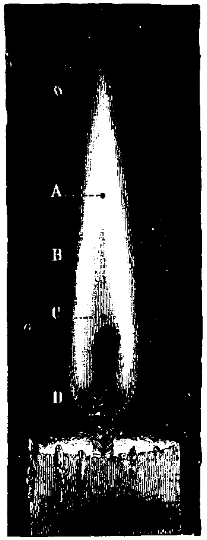

FIG. 40.—In the candle flame the portion C contains the vapours and products of decomposition; in the bright zone A the combustion has commenced, and particles of carbon are emitted; and in the pale zone B the combustion is completed.

Thus, unburnt products of the decomposition of organic substances occur in the interior of the flame. But there is always free hydrogen in the interior of the flame, even when oxygen is introduced there, or when a mixture of hydrogen and oxygen burns, because the temperature evolved in the combustion of hydrogen or the carbon of organic matter is so high that the products of combustion are themselves partially decomposed—that is, dissociated—at this temperature. Hence, in a flame a portion of the hydrogen and of the oxygen which might combine with the combustible substances must always be present in a free state. If a hydrocarbon burns, and we imagine that a portion of the hydrogen is in a free state, then a portion of the carbon must also occur in the same form in the flame, because, other conditions being unchanged, carbon burns after hydrogen, and this is actually observed in the combustion of various hydrocarbons. Charcoal, or the soot of a common flame, arises from the dissociation of organic substances contained in the flame. The majority of hydrocarbons, especially those containing much carbon—for instance, naphthalene—burn, even in oxygen, with separation of soot. In that portion of the flame where the hydrogen burns, the carbon remains unburnt, or at least partly so. That the interior of the flame contains a mixture which is still capable of combustion may be proved by the following experiment. A portion of the gases may be withdrawn by an aspirator from the central portion of the flame of carbonic oxide, which is combustible in air. For this purpose Deville passed water through a metallic tube, having a fine lateral orifice, placed in the flame. As the water flows along the tube, portions of the gases of

The combination of various substances with oxygen may not present any signs of combustion—that is, the temperature may rise but inconsiderably. This may proceed from the fact that either the reaction of the substance (for example, tin, mercury, lead at a high temperature, or a mixture of pyrogallol with caustic potash at the ordinary temperature) evolves but little heat, or the heat evolved is transmitted to good conductors of heat, like metals, and so dispersed, or combination with oxygen takes place so slowly that the heat evolved succeeds in gradually passing to the surrounding objects. Combustion is only a particular, intense, and evident case of combination with oxygen. Respiration is also an act of combination with oxygen: it also serves, like combustion, for the development of heat by those chemical processes which accompany it (the transformation of

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the flame enter, and, passing along the tube alternately with small cylinders of water, are carried away into an apparatus where they can be investigated. It appears that all portions of the flame obtained by the combustion of a mixture of carbonic oxide and oxygen contain a portion of this mixture still unburnt. The researches of Deville and Bunsen showed that in the explosion of a mixture of hydrogen or of carbonic oxide with oxygen in a closed space, complete combustion never takes place immediately. If two volumes of hydrogen and one volume of oxygen be confined in a closed space and exploded, the pressure will not attain that magnitude which it would do, were there immediate and complete combustion. It may be calculated that the pressure should attain 20–30 atmospheres; but in reality it does not exceed $9\frac{1}{2}$ atmospheres.

Hence the admixture of the products of combustion with an explosive mixture prevents the combustion of the remaining mass, although this is capable of burning. Admixture of carbonic anhydride prevents carbonic oxide from burning. The presence of any other foreign gas interferes in the same manner. This indicates that every portion of a flame must contain combustible, burning, and already burnt substances—i.e., oxygen, carbon, carbonic oxide, hydrogen, hydrocarbons, carbonic anhydride, and water—in one place. Consequently **it is impossible to attain instantaneous complete combustion**, and this is one of the reasons of the phenomenon of flame. A certain space is required, and the temperature must be unequal in different parts of it. In this space different quantities of the component parts are successively subjected to combustion, and to partial cooling under the influence of adjacent objects. If the combustion could be concentrated at one spot, the temperature would be incomparably higher than it is under the actual circumstances.

The various regions of the flame have frequently formed the subject of experimental research, and the experiments conducted by Smithells and Ingle (1892) are particularly instructive: they show that the reducing (inner) and oxidising (outer) portions of the flame of a burning gas may be separated by taking a Bunsen burner and surrounding the flame of the gas burnt in it by another wider tube (either without the access of air to the annular space or allowing only a small current of air to pass), when a gaseous mixture, containing oxide of carbon and capable of further combustion, will issue from this enveloping tube, so that a second flame, corresponding to the exterior (oxidising) portion of an ordinary flame, may be obtained above the enveloping tube. This division of the flame into two portions is particularly clear when cyanogen, C_2N_2, is burnt, because the interior portion (where CO is chiefly formed, according to the equation, $C_2N_2 + O_2 = 2CO + N_2$, but a portion of the nitrogen is oxidised) is of a rose colour, while the exterior portion (where the CO burns into CO_2 at the expense of a fresh quantity of oxygen and of the oxides of nitrogen proceeding from the interior portions) is of a bluish-grey colour.

oxygen into carbonic anhydride). Lavoisier enunciated this in the lucid expression, 'Respiration is slow combustion.'

Reactions involving slow combination of substances with oxygen are termed **oxidations.** Combination of this kind (and also combustion) often results in the formation of acid substances, and hence the name **oxygen** (*Sauerstoff*). Combustion is only rapid oxidation. Phosphorus, iron, and wine may be taken as examples of substances which oxidise slowly in air at the ordinary temperature. If such a substance is left in contact with a definite volume of air or oxygen, it will absorb the oxygen little by little. This slow oxidation is not often accompanied by a sensible evolution of heat; an evolution of heat really does occur, but is not apparent to our senses owing to the small rise in temperature which takes place; this is due to the slow rate of the reaction and to the dispersion of the heat formed as radiant heat, &c. Thus, in the oxidation of wine and its transformation into vinegar by the usual method of preparation of the latter, the heat evolved cannot be observed, because the process extends over several weeks; but in the so-called rapid process of the manufacture of vinegar, when a large quantity of wine is comparatively rapidly oxidised, the evolution of heat is quite apparent.

Such slow processes of oxidation are always taking place in nature by the action of the atmosphere. Dead organisms and the substances obtained from them—such as bodies of animals, wood, wool, grass, &c.—are especially subject to this action. They **rot** and **decompose**—that is, their solid matter is gradually transformed, completely or partially, into gases, under the influence of moisture and atmospheric oxygen, and generally under the influence of other organisms, such as moulds, worms, micro-organisms (bacteria), and the like. These are processes of slow combustion, of slow combination with oxygen. It is well known that manure rots and develops heat and that stacks of damp hay, damp flour, straw, &c., become heated and are changed in the process.[47] In all these transformations the same chief products of combustion are formed as those which are contained in smoke: the carbon gives carbonic anhydride, and the hydrogen, water. Hence these processes require oxygen just like combustion. This is the reason why the entire prevention of access of air hinders these transformations[48] and an

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[47] Cotton waste (used in factories for cleaning machines from lubricating oil), soaked in oil and lying in heaps, is self-combustible, being oxidised by the air. In general, the oxidation of combustible bodies (for instance, of coal containing pyrites undergoing oxidation) may produce spontaneous combustion.

[48] When it is desired to preserve a supply of vegetable and animal food, the access of the oxygen of the atmosphere (and also of the germs of organisms present in the air) is often prevented. With this object, articles of food are often kept in hermetically closed

increased supply of air accelerates them. The mechanical treatment of arable lands by the plough, harrow, and other similar means has not only the object of facilitating the spread of roots in the ground, and of making the soil more permeable to water, but it also serves to facilitate the access of the air to the component parts of the soil, as a consequence of which the organic remains of soil rot—as it were, breathe air and evolve carbonic anhydride. One acre of good garden land, in the course of a summer, evolves more than sixteen tons of carbonic anhydride.

It is not only vegetable and animal substances which are subject to slow oxidation in the presence of water and air. Some metals rust under these conditions. Many metallic sulphides (for example, pyrites) are very easily oxidised with access of air and moisture. So that processes of slow oxidation proceed throughout nature. However, there are many elements which do not, under any circumstances, combine directly with gaseous oxygen; nevertheless, their compounds with oxygen may be obtained. Platinum, gold, iridium, chlorine, and iodine are examples of such elements. In this case recourse is had to a so-called **indirect method of oxidation**—i.e., the given substance is combined with another element, and by a method of double decomposition, this element is replaced by oxygen. The oxides so formed often readily lose their oxygen. Such, for example, are the compounds of oxygen with chlorine, nitrogen, and platinum, which evolve oxygen on heating, so that they may be used as oxidising agents. In this respect **oxidising agents,** or those compounds of oxygen which are employed in chemical and technical practice for transferring oxygen to other substances, are especially noteworthy. The most important among these is nitric acid or **aqua fortis,** which is rich in oxygen and capable of evolving it when heated, and easily oxidises a great number of substances. Thus, nearly all metals and organic substances containing carbon and hydrogen are more or less oxidised when heated with nitric acid. If strong nitric acid be taken, and a piece of burning charcoal be immersed in the acid, it continues to burn. Chromic acid acts like nitric acid, alcohol burning when mixed with it. Although the action is not so marked, even water may oxidise with its oxygen. Sodium is not oxidised in perfectly dry oxygen at the ordinary temperature, but it burns very easily in water and aqueous vapour. Charcoal can burn in carbonic anhydride—a product of combustion—forming carbonic oxide. Magnesium burns in the same gas, separating carbon from it. Speaking generally, combined oxygen can pass from one compound to another.

The products of combustion or oxidation—and in general the definite compounds of oxygen—are termed **oxides.** Some oxides are not capable of combining with other oxides—or combine with only a few, and then with the evolution of very little heat; others, on the contrary, easily enter into combination with many other oxides, and in general possess remarkable chemical activity. This difference, however, is not well defined, and will become clearer as we become acquainted with the various oxides.

The class of oxides capable of entering into mutual combination we will term **saline oxides.** They fall into two chief groups—at least as regards the most extreme members. The members of one group combine with the members of the other group with particular ease. As representative of one group may be taken the oxides of the metals, magnesium, sodium, calcium, &c. Representatives of the other group are the oxides formed by the non-metals, sulphur, phosphorus, carbon. Thus, if we take the oxide of calcium, or lime, and bring it into contact with oxides of the second group, combination very readily ensues with the evolution of heat. For instance, if we mix calcium oxide with oxide of phosphorus they form phosphate of lime. If we pass the vapour of sulphuric anhydride, obtained by the combination of sulphurous oxide with oxygen, over pieces of lime heated to redness, the sulphuric anhydride is absorbed by the lime with the formation of a substance called 'calcium sulphate.' The oxides of the first kind, which contain metals, are termed **basic oxides** or **bases.** Lime is a familiar example of this class. The oxides of the second group, which are capable of combining with the bases, are termed **anhydrides of the acids** or **acid oxides.** Sulphuric anhydride, SO_3, may be taken as a type of the latter group. It is a compound of sulphur with oxygen, formed not directly, but by the addition of a fresh quantity of oxygen to sulphurous anhydride, SO_2, by passing it together with oxygen over incandescent spongy platinum. Carbonic anhydride, phosphoric anhydride, sulphurous anhydride, are all acid oxides.

If a given element forms but one basic oxide, it is termed the **oxide**; for example, calcium oxide, magnesium oxide, potassium oxide. Some indifferent oxides are also called 'oxides,' if they have not the properties of peroxides and at the same time do not show the properties of acid anhydrides; for example, carbonic oxide, of which mention has already

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vessels, from which the air has been withdrawn; vegetables are dried and soldered up, while hot, in tin boxes; sardines are immersed in oil, &c. The removal of water from substances is also sometimes resorted to with the same object (the drying of hay, corn, fruits), as also is saturation with substances which absorb oxygen (such as sulphurous anhydride) or which hinder the growth of organisms forming the first cause of putrefaction, as in processes of smoking, embalming, and in the keeping of fishes and other animal specimens in spirit, &c.

been made. If an element forms two basic oxides (or two indifferent oxides not having the characteristics of a peroxide), that of the lower degree of oxidation is called a **suboxide**—that is, suboxides contain less oxygen than oxides. Thus, when copper is heated to redness in a furnace, it increases in weight and absorbs oxygen, until for 63 parts of copper there is absorbed not more than 8 parts of oxygen by weight, forming a red mass, which is suboxide of copper, Cu_2O; but if the roasting be prolonged, and the draught of air increased, 63 parts of copper absorb 16 parts of oxygen, and form black oxide of copper, CuO. Sometimes, to distinguish between the degrees of oxidation, a change of suffix is made in the oxidised element, **-ic** oxide denoting the higher degree of oxidation, and **-ous** oxide the lower degree. Thus ferrous oxide, FeO, and ferric oxide, Fe_2O_3, are the same as suboxide of iron and oxide of iron. If an element forms one acid anhydride only, it is then named by an adjective formed from the name of the element made to end in **-ic** and the word **anhydride**. When an element forms two anhydrides, then the suffixes **-ous** and **-ic** are used to distinguish them, **-ous** signifying less oxygen than **-ic**; for example, sulphurous and sulphuric anhydrides.[49] When several oxides are formed from the same

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[49] It must be remarked that certain elements form oxides of both chief kinds—i.e., basic and acid; for example, manganese forms the basic oxides: manganous oxide and manganic oxide, and the acid oxides: red oxide of manganese and manganic anhydride. Between them stands the dioxide (or peroxide) which was mentioned above and is a feeble base and a feeble acid anhydride. The basic oxides contain less oxygen than the peroxides, and the peroxides less than the acid anhydrides. The majority of elements, however, do not give all three kinds of oxides, some giving only one degree of oxidation. It must further be remarked that there are oxides formed by the combination of acid anhydrides with basic oxides, or, in general, of oxides with oxides. For every oxide having a higher and a lower degree of oxidation, it might be said that the intermediate oxide was formed by the combination of the higher with the lower oxide. But this is not true in all cases—for instance, when the oxide under consideration forms a whole series of independent compounds—for oxides which are really formed by the combination of two other oxides do not give such independent compounds, but in many cases decompose into the higher and lower oxides. As the intensity of the basic and acid properties varies considerably in different oxides, and some oxides combine (form salts) both with powerful bases and with strong acids, the nomenclature of the oxides, based on their salt-forming capacity, is more or less conventional and founded on historical tradition. Therefore, it is now often customary to name the oxides after the number of atoms of oxygen they contain; for instance, SO_2, dioxide of sulphur; SO_3, trioxide of sulphur; MnO, monoxide of manganese; Mn_2O_3, sesquioxide of manganese; MnO_2, dioxide of manganese, &c. But this method has the disadvantage of ignoring the qualities of the oxides, which are historically of primary importance in chemistry. Therefore (for science not founded on history is absurd), in this work, the *quantitative* nomenclature is only had recourse to where the oxides do not possess distinctly basic, acid, or peroxide properties; for example, MnO_2 and PbO_2 are better named dioxides than peroxides, as the latter (see Chapter IV.) are assumed to possess a special series of particular properties. A nomenclature, like a language, must always be a matter of conventional agreement. The propagation of knowledge depends largely upon it; but the substance and essence of knowledge do not, for language is a means and not an end

element, the prefixes **mono-**, **di-**, **tri-**, **tetra-**, are used, thus; chlorine monoxide, chlorine dioxide, chlorine trioxide, and chlorine tetroxide or chloric anhydride.

The majority of, if not all, basic and acid oxides combine with water, either by a direct or an indirect method, forming **hydrates**, that is, compounds which split up only into water and an oxide. It is well known that many substances are capable of combining with water. Oxides possess this property in the highest degree. We have already seen examples of this (Chapter I.) in the combination of lime, and of sulphuric and phosphoric anhydrides, with water. The resulting combinations are basic and acid hydrates. Acid hydrates are called **acids** because they have an acid taste when dissolved in water (or saliva), for then only can they act on the palate. Vinegar, for example, has an acid taste because it contains acetic acid dissolved in water. Sulphuric acid, H_2SO_4, to which we have frequently referred, because it is the acid of the greatest importance both in practical chemistry and for its technical applications, is really a hydrate formed by the combination of sulphuric anhydride, SO_3, with water, H_2O. Besides their acid taste, dissolved acids or acid hydrates have the property of changing the blue colour of certain vegetable dyes to red. Of these dyes **litmus** is especially noticeable and is much used. It is the blue substance extracted from certain lichens, and is used for dyeing tissues blue: it gives a blue infusion with water. This infusion, on the addition of an acid, **changes from blue to red**.[50]

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[50] Blotting or unsized paper, soaked in a solution of litmus, is usually employed for detecting the presence of acids. This paper is cut into strips, and is called *test paper*; when dipped into acid it turns red. This is a most sensitive reaction, and may be employed for testing for the smallest traces of acids. If 10,000 parts by weight of water be mixed with 1 part of sulphuric acid, the coloration is distinct, and it is even perceptible on the addition of ten times more water. Certain precautions must, however, be taken in the preparation of such very sensitive litmus paper. Litmus is sold in lumps. Take, say, 100 grams of it; powder it, and add it to pure cold water in a flask; shake and decant the water. Repeat this three times. This is done to wash away easily soluble impurities, especially alkalies. Transfer the washed litmus (it is washed with absolute alcohol to remove the non-sensitive reddish colouring matter) to a flask, and pour in 600 c.c. of water, heat, and allow the hot infusion to remain for some hours in a warm place. Then filter, and divide the filtrate into two parts. Add a few drops of nitric acid to one portion, so that a faint red tinge is obtained, and then mix the two portions. Add spirit to the mixture, and keep it in a stoppered bottle (it soon spoils if left open to the air). This infusion may be employed directly; it reddens in the presence of acids, and turns blue in the presence of alkalis. If evaporated, a solid mass is obtained which is soluble in water, and may be kept unchanged for any length of time. The test paper may be prepared as follows:—Take a strong infusion of litmus and soak blotting-paper with it; dry the latter and cut it into strips, and use it as test paper for acids. For the detection of alkalis, the paper must be soaked in a solution of litmus just reddened by a few drops of acid; if too much acid be taken, the paper will not be sensitive. Such acids as sulphuric acid colour litmus, and especially its infusion, a brick-red colour, whilst more feeble acids,

Basic oxides, in combining with water, form hydrates, of which, however, very few are soluble in water. Those which are soluble in water have an alkaline taste like that of soap or of water in which wood ashes have been boiled, and are called **alkalies.** Alkalies have the property of restoring the blue colour to litmus which has been reddened by the action of acids. The hydrates of the oxides of sodium and potassium, NaHO and KHO, are examples of basic hydrates easily soluble in water. They are true alkalis, and are termed **caustic,** because they act very powerfully on the tissues of animals and plants. Thus NaHO is called 'caustic' soda.

The saline oxides are capable of combining together and with water. Water itself is an oxide, and not an indifferent one, for it can, as we have seen, combine with basic and acid oxides: it is a representative of a whole series of saline oxides, **intermediate oxides,** capable of combining with both basic and acid oxides. There are many such oxides, which, like water, combine with basic and acid anhydrides; for

instance, the oxides of aluminium and tin, &c. From this it may be concluded that all oxides might be placed, in respect to their capacity for combining with one another, in one uninterrupted series, at one extremity of which would stand those oxides which do not combine with the bases—that is, the alkalis—while at the other end would be the acid oxides, and in between, those oxides which combine with one another and with both the acid and basic oxides. The further apart the members of this series are, the more stable are the compounds they form together, the more energetically do they act on each other, the greater as a rule the quantity of heat evolved in their reaction, and the more marked is their saline chemical character.

Although basic and acid oxides combine together, they rarely react on each other; this depends on the fact that the majority of them are solids or gases—that is, they occur in the state least prone to chemical reaction. The gaseo-elastic state is with difficulty destroyed, because it necessitates overcoming the elasticity proper to the gaseous particles. But the solid state is characterised by the immobility of its particles, whilst chemical action requires contact and hence a displacement and mobility. If solid oxides be heated, and especially if they be melted, reaction proceeds with great ease. But such a change of state rarely occurs in nature or in practice. For example, in the manufacture of glass, the oxides contained in it are combined together in a molten mass. But when oxides combine with water, and especially when they form hydrates soluble in water, the mobility of their particles increases to a considerable extent, and their interaction is greatly facilitated. Reaction then often takes place at the ordinary temperature—easily and rapidly; so that this kind of reaction belongs to the class of those which take place with unusual facility, and are, therefore, very often taken advantage of in practice, and are going on in nature at every step. We will now consider the reactions of oxides in the state of hydrates, not losing sight of the fact that water is itself an oxide with definite properties, and has, therefore, no little influence on the course of those changes in which it takes part.

If we take a definite quantity of an acid, and add an infusion of litmus to it, it turns red; the addition of an alkaline solution does not immediately alter the red colour of the litmus, but on adding more and more of the alkaline solution a point is reached when the red colour changes to violet, and then the further addition of a fresh quantity of the alkaline solution changes the colour to blue. This change of the colour of the litmus is a consequence of the formation of a new compound. This reaction is termed the **saturation** or **neutralisation** of the acid by the base, or *vice versâ.* The solution in which the acid

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such as carbonic, give a faint wine-red tinge. Test paper of a yellow colour is also employed: it is dyed by an infusion of turmeric roots in spirit. In alkalis it turns brown, but regains its original hue in acids. Many blue and other vegetable colouring matters may be used for the detection of acids and alkalis; for example, infusions of cochineal, violets, logwood, &c. Certain artificially prepared substances and dyes may also be employed. Thus rosolic acid, $C_{20}H_{16}O_3$, and phenolphthaleïn, $C_{20}H_{14}O_4$ (which is used in an alcoholic solution, and is not suitable for the detection of ammonia), are colourless in an acid, and red in an alkaline, solution. Cyanine is also colourless in the presence of acids, and gives a blue coloration with alkalis. Methyl-orange (yellow in an aqueous solution) is not altered by alkalis, but becomes pink with acids (weak acids have no action), &c. These are very sensitive tests. Their behaviour in respect to various acids, alkalis, and salts sometimes gives the means of distinguishing substances from each other, and even for distinguishing different stages of combination between bases and acids; but we will not enter upon the details of this subject, because it chiefly concerns certain portions of analytical chemistry.

However certain peculiarities of these two reagents, phenolphthaleïn and methyl-orange, deserve our attention, all the more as they may both be obtained in a perfectly chemically pure form exhibiting their peculiarities, and they were recommended by a special committee of the Paris Congress of Chemists in 1900. The former (phenolphthaleïn) reacts equally well with feeble and strong acids; whilst methyl-orange (otherwise known as helianthine) only reacts with strong mineral acids (H_2SO_4, HCl, &c.), and is not acted upon by such feeble acids as carbonic, salicylic, &c. (which is often very convenient). The transition from the reddish acid solution to the colourless (from the addition of alkalis) and back is so distinct with phenolphthaleïn that it forms one of the most sensitive reagents. Methyl-orange is less sensitive, especially under artificial (yellow) illumination.

Attention must also be drawn to the fact that in calling a solution neutral, acid, or basic, according to the change of colour of litmus paper, it is necessary to add (or understand) 'with regard to litmus,' as other reagents may give other results. Here, again, as in the case of distinguishing bases from acids, or neutral salts from acid salts, &c., there is a certain conventionalism of speech or expression which it is very difficult to avoid, but which has very little significance to the science itself, although apparently important to the beginner. In such cases the student is advised, like Arago, to go on further, and the details will become gradually clear of themselves.

properties of the acid are saturated by the alkaline properties of the base is termed a **neutral** solution. Such a solution, although derived from the mixture of a base with an acid, does not exhibit either an acid or basic reaction towards litmus; yet it preserves many other signs of the acid and alkali. What takes place is essentially the same as in the formation of water from hydrogen and oxygen. It is observed that in such a definite admixture of an acid with an alkali, besides the changes in the colour of litmus there is a heating effect—i.e., an evolution of heat—which is alone sufficient to prove that there was chemical action. And, indeed, if the resultant violet solution be evaporated, there separates out, not the acid or the alkali originally taken, but a substance which has neither acid nor alkaline properties, but is usually solid and crystalline, having a saline appearance: this is a **salt** in the chemical sense of the word. Hence a salt is derived from the reaction of an acid on an alkali, in a certain definite proportion. The water here taken for solution plays no part other than that of a medium, facilitating the progress of the reaction. This is seen from the fact that the anhydrides of the acids are able to combine with basic oxides, and give the same salts as do the acids with the alkalis or hydrates. Hence, a salt is a compound of definite quantities of an acid and an alkali. In the latter reaction, water is separated out if the substance formed is the same as is produced by the combination of anhydrous oxides together.[51] Examples of the formation of salts from acids and bases are easily observed, and are very often applied in practice. If we take, for instance, insoluble magnesium oxide (magnesia), it is easily dissolved in sulphuric acid, and on evaporation gives a saline substance, bitter, like all the salts of magnesium, and familiar to all under the name of Epsom salts, which is used as a purgative. If a solution of caustic soda—which is obtained, as we saw, by the action of water on sodium oxide—be poured into a flask in which charcoal has been burnt; or if carbonic anhydride, which is produced under so many circumstances, be passed through a solution of caustic soda, sodium carbonate or soda, Na_2CO_3, of which we have spoken several times, and which is prepared on a large scale and often used in manufactures, is obtained. This reaction

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[51] That water really is separated in the reaction of acid on alkaline hydrates may be shown by taking some other intermediate hydrate—for example, alumina—instead of water. Thus, if a solution of alumina in sulphuric acid be taken, it will have, like the acid, an acid reaction, and will therefore colour litmus red. If, on the other hand, a solution of alumina in an alkali—say potash—be taken, it will have an alkaline reaction, and will turn red litmus blue. On adding the alkaline to the acid solution until neither an alkaline nor an acid reaction is produced, a salt is formed, consisting of sulphuric anhydride and potassium oxide. In this, as in the reaction of hydrates, an intermediate oxide is separated out—namely, alumina. Its separation will be very evident in this case, as alumina is insoluble in water.

is expressed by the equation, $2NaHO+CO_2=Na_2CO_3+H_2O$. Thus, the various bases and acids form an innumerable number of different salts.[52] Salts constitute an example of definite chemical compounds, and both in the history and practice of science are most often cited as confirming the conception of definite chemical compounds. Indeed, all the indications of a definite chemical combination are clearly seen in the formation and properties of salts. Thus, they are produced from definite proportions of oxides, heat is evolved in their formation,[53] and

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[52] The mutual interaction of hydrates, and their capacity of forming salts, may be taken advantage of for determining the character of those hydrates which are insoluble in water. Let us imagine that a given hydrate, whose chemical character is unknown, is insoluble in water, so that it is impossible to test its reaction on litmus. It is then mixed with water, and an acid—for instance, sulphuric acid—is added to the mixture. If the hydrate taken be basic, reaction will take place, either directly or on heating, with the formation of a salt. In certain cases, the resultant salt is soluble in water, and this will at once show that combination has taken place between the insoluble basic hydrate and the acid, with the formation of a soluble salt. In those cases where the resultant salt is insoluble, the water still loses its acid reaction, and therefore it may be ascertained, by the addition of an acid, whether a given hydrate has a basic character, like the hydrates of oxide of copper, lead, &c. If the acid does not act on the given insoluble hydrate (at any temperature), then it has not a basic character, and it should be tested as to whether it has an acid character. This is done by taking an alkali, instead of the acid, and by observing whether the unknown hydrate then dissolves, or whether the alkaline reaction (entirely or partially) disappears. Thus it may be proved that hydrate of silica is acid, because it dissolves in alkalis and not in acids. If it be a case of an insoluble intermediate hydrate, then it will be observed to react on both the acid and alkali. An instance of this is hydrate of alumina, which is soluble both in caustic potash and in sulphuric acid.

The **degree of affinity** or chemical **energy** proper to oxides and their hydrates is very variable; some extreme members of the series possess it to a great extent. When acting on each other they evolve a large quantity of heat, and when acting on intermediate hydrates they also evolve heat to a considerable degree, as we saw in the combinations of lime and sulphuric anhydride with water. When extreme oxides combine they form stable salts, which are decomposed with difficulty, and often show characteristic properties. The compounds of the intermediate oxides with each other, or even with basic and acid oxides, present a very different case. However much alumina we may dissolve in sulphuric acid, we cannot saturate the acid properties of the sulphuric acid, and the resulting solution will always have an acid reaction towards litmus. So also, whatever quantity of alumina is dissolved in an alkali, the resulting solution will always present an alkaline reaction.

[53] In order to give an idea of the quantity of heat evolved in the formation of salts, I append a table of data for *very dilute aqueous solutions* of acids and alkalis, according to the determinations of Berthelot and Thomsen. The figures are given in major calories—that is, in thousands of units of heat. For example, 49 grams of sulphuric acid, H_2SO_4, taken in dilute aqueous solution, when mixed with such an amount of a weak solution of caustic soda, NaHO, that a neutral salt is formed (when all the hydrogen of the acid is replaced by the sodium), evolves 15,800 units of heat.

	49 parts of H_2SO_4	63 parts of HNO_3		49 parts of H_2SO_4	63 parts of HNO_3
NaHO	15·8	13·7	MgO	15·6	13·8
KHO	15·7	13·8	FeO	12·5	10·7 (?)
NH_3	14·5	12·5	ZnO	11·7	9·8
CaO	15·6	13·9	Fe_2O_3	5·7	5·9
BaO	18·4	13·9			

the chemical character of the oxides and many of the physical properties become hidden in their salts. For example, when gaseous carbonic anhydride combines with a base to form a solid salt, the elasticity of the gas quite disappears in its passage into the salt,[54] just as the elasticity of hydrogen and oxygen does in the formation of water.

Judging from the above, a salt is a compound of basic and acid oxides, or the result of the action of hydrates of these classes on each other, with separation of water. But salts may be obtained by other methods. It must not be forgotten that basic oxides are formed by metals, and acid oxides usually by non-metals. But metals and non-metals are capable of combining together, and a salt is frequently formed by the oxidation of such a compound. For example, iron very easily combines with sulphur, forming iron sulphide, FeS (as we saw in the Introduction); in air, and especially moist air, this absorbs oxygen, with the formation of the same salt, $FeSO_4$, as may be obtained by the combination of the oxides of iron and sulphur ($FeO + SO_3$) or of the hydrates of these oxides ($FeH_2O_2 + H_2SO_4 = FeSO_4 + 2H_2O$). In general, salts are formed in most diverse reactions.[54a] Hence, it cannot be said or supposed that a salt has the properties of the oxides, or must necessarily contain two kinds of oxides in itself. The derivation of

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These figures cannot be considered as the heats of neutralisation, because the water here plays its part. Thus, for instance, sulphuric acid and caustic soda, in dissolving in water, evolve very much heat, and the resultant sodium sulphate, in dissolving in water, very little; consequently, the amount of heat evolved in an anhydrous combination will be different from that evolved in a hydrated combination. Those acids which are not energetic in combining with the quantities of alkalis required for the formation of normal salts of sulphuric or nitric acids always, however, give less heat. For instance, with caustic soda: carbonic acid gives 10·2, hydrocyanic 2·9, and hydrogen sulphide 3·9, major calories. And as feeble bases (for example, Fe_2O_3) also evolve less heat than those which are more powerful, so a certain general correlation between thermochemical data and the degree of affinity shows itself here, as in other cases (see Chapter II., note 7). This does not, however, give any reason for measuring the affinity which binds the elements of salts by the heat of their formation in dilute solutions. This is very clearly demonstrated by the fact that water is able to decompose many salts, and is separated in their formation.

[54] Carbonic anhydride evolves heat in dissolving in water. The solution easily dissociates and evolves carbonic anhydride, according to the law of Henry and Dalton (see Chapter I.). In dissolving in caustic soda, it either gives a normal salt, Na_2CO_3, which does not evolve carbonic anhydride, or an acid salt, $NaHCO_3$, which easily evolves carbonic anhydride when heated. The same gas, when dissolved in solutions of salts, acts in one or the other manner (see Chapter II., note 38). Here it is seen what a successive series of relations exists between compounds of a different order, between substances of different degrees of stability. By making a distinction between solutions and chemical compounds, we overlook those neutral transitions which in reality exist.

[54a] For example, the sodium salt of formic acid, $CHNaO_2$, is formed by the direct absorption of carbonic acid gas, CO_2, by sodium hydride, NaH; ammonium nitrite is formed directly from the nitrogen of the air, N_2, and water, as a by-product in many cases of oxidation taking place in the air; calcium sulphite is obtained from the oxidation of calcium sulphide and polysulphides, and so on.

salts from oxides is merely one of the methods of their preparation. We saw, for instance, that in sulphuric acid it was possible to replace the hydrogen by zinc, and that by this means zinc sulphate was formed; so likewise the hydrogen in many other acids may be replaced by zinc, iron, potassium, sodium, and a whole series of similar metals, corresponding salts being obtained. The hydrogen of the acid, in all these cases, is exchanged for a metal, and a salt is obtained from the hydrate. Regarding a salt from this point of view, it may be said that **a salt is an acid in which hydrogen is replaced by a metal.** This definition shows that a salt and an acid are essentially compounds of the same series, with the difference that the latter contains hydrogen and the former a metal. Such a definition is more exact than the first definition of salts, inasmuch as it likewise includes those acids which do not contain oxygen, and, as we shall afterwards learn, there is a series of such acids. Such an element as chlorine gives compounds with hydrogen in which the hydrogen may be replaced by a metal, forming substances which in their reactions and external characters resemble the salts formed from oxides. Table salt, NaCl, is an example of this. It may be obtained by the replacement of hydrogen in hydrochloric acid, HCl, by the metal sodium, just as sulphate of sodium, Na_2SO_4, may be obtained by the replacement of hydrogen in sulphuric acid, H_2SO_4, by sodium. The external appearance of the resulting products, their neutral reaction, and even their saline taste, show their resemblance to one another.

To the fundamental properties of salts yet another must be added—namely, that they are more or less **decomposed by the action of a galvanic current.** The results of this decomposition are very different according to whether the salt is taken in a fused or dissolved state. But the decomposition may generally be so represented that the metal or cation appears at the electro-negative pole or cathode (like hydrogen in the decomposition of water, or its mixture with sulphuric acid), and the remaining parts of the salt, the anion, appear at the electro-positive pole or anode (where the oxygen of water appears). If, for instance, an electric current acts on an aqueous solution of sodium sulphate, Na_2SO_4, we may assume that the sodium appears at the negative pole, and oxygen and the anhydride of sulphuric acid, i.e., the anion SO_4, at the positive pole. But in the solution itself the result is different, for sodium decomposes water with evolution of hydrogen, forming caustic soda; consequently hydrogen will be evolved and caustic soda appear at the negative pole, while at the positive pole the sulphuric anhydride combines with water and forms sulphuric acid, and therefore oxygen will be evolved and sulphuric acid formed round this pole.[55] In other cases, when the metal separated is not able to decompose water, it will be deposited in a free state. Thus, for example, in the decomposition of copper sulphate, copper separates out at the cathode, and oxygen and sulphuric acid appear at the anode; and if a copper plate be attached to the positive pole, then the oxygen evolved will oxidise the copper, and the oxide of copper will dissolve and be deposited at the negative pole—that is, a transference of copper from the positive to the negative pole ensues. The galvanoplastic art (electrotyping) is based on this principle.[56] The most radical and general properties of salts (including also such salts as table salt, which contain no oxygen) may therefore be expressed by representing the salt as composed of a metal M and a haloid X—that is, by expressing the salt by MX. In common table salt the metal is sodium, and the haloid, an elementary body, chlorine. In sodium sulphate, Na_2SO_4, sodium is again the metal, but the complex group, SO_4, is the haloid. In sulphate of copper, $CuSO_4$, the metal is copper and the haloid the same as in the preceding salt. Such a representation of salts expresses with great simplicity the **capacity of every salt to enter into saline double decompositions with other salts**, this consisting in a mutual replacement of the metals in the salts. This exchange of their metals is the fundamental property of salts.[56a] In the case of two salts with different metals

and haloids, which are in solution or fused, or in any other manner brought into contact, the metals of these salts will always partially or wholly exchange places. If we designate one salt by MX, and the other by NY, then we either partially or wholly obtain from them new salts, MY and NX. Thus we saw, in the Introduction, that on mixing solutions of table salt, NaCl, and silver nitrate, $AgNO_3$, a white insoluble precipitate of silver chloride, AgCl, is formed and a new salt, sodium nitrate, $NaNO_3$, obtained in solution. If the metals of salts exchange places in reactions of double decomposition, it is clear that metals themselves, taken in a separate state, are able to act on salts, as zinc evolves hydrogen from acids, and as iron separates copper from copper sulphate. When, to what extent, and which metals displace each other, and how the metals are distributed between the haloids, will be discussed in Chapter X., where we shall be guided by those reflections and deductions which Berthollet introduced into the science at the beginning of the last century.

According to the above observations, an acid is nothing more than a salt of hydrogen. Water itself may be looked upon as a salt in which the hydrogen is combined with either oxygen or the aqueous radicle, OH; water will then be HOH, and alkalis or basic hydrates, MOH. The group OH, or the **aqueous radicle**, otherwise called **hydroxyl**, may be looked on as a haloid (a special X), like the chlorine in table salt, not only because the element Cl and the group OH very often change places, and combine with one and the same element, but also because free chlorine is very similar in many properties and reactions to peroxide of hydrogen, which has the same composition as the aqueous radicle, as we shall afterwards see in Chapter IV. Alkalis and basic hydrates are also salts consisting of a metal and hydroxyl; for instance,

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[55] This kind of decomposition may be easily observed by pouring a solution of sodium sulphate into a U-shaped tube and inserting electrodes in the two branches. If the solution be coloured with an infusion of litmus, it will easily be seen that it turns blue at the cathode, owing to the formation of sodium hydroxide, and red at the electro-positive pole, from the formation of sulphuric acid.

[56] In other cases the decomposition of salts by the electric current may be accompanied by much more complex results. Thus, when the metal of the salt is capable of a higher degree of oxidation, such a higher oxide may be formed at the positive pole by the oxygen which is evolved there. This takes place, for instance, in the decomposition of salts of silver and manganese by the galvanic current, peroxides of these metals being formed. Thus in the electrolysis of a solution of KCl, KClO is formed, while with sulphuric acid (corresponding to SO_3) persulphuric acid, corresponding to S_2O_7, is formed. But all the phenomena as yet known may be expressed by the above hypothesis, that the current decomposes salts into metals, which appear at the negative pole, and the remaining component parts, which appear at the positive pole. Many physico-chemical researches, starting with those of Faraday, Hittorf, and Kohlrausch, have been made on the mechanism of the transference of the ions, the velocity of their motion and their condition in solutions, especially during the last ten years Further details on this complex subject and a criticism of the existing theories must be looked for in works on physical chemistry. Here it would be out of place to enlarge upon this subject, all the more so, as it has not yet had any direct influence upon purely chemical knowledge.

[56a] The presence in salts MX of a metallic element M (in acids it is equivalent to hydrogen, in ammonium salts to ammonium, &c.) capable of easily entering into double decomposition with metals, taken either in the form of other salts, or in general of saline compounds, or else in the form of the metals themselves (especially Na, K, Zn, &c.), forms the fundamental characteristic of the saline substances or primary compound bodies formed by the elements. These primary compounds form the first step in the study of chemistry. The further development of chemistry proved the existence of a vast series of more complex compounds, especially hydrocarbons, which do not evince the clearly expressed peculiarities of salts. Such are chiefly the 'organic' or complex carbon compounds studied by 'organic chemistry.' Although they include their acids, bases, and salts, the primary grouping of the elements of which they are made up is evidently different from that in salts, acids, &c., as the hydrogen in the hydrocarbons from which they proceed has not, or but rarely has (for instance, in acetylene, C_2H_2) the property possessed by 'metallic' hydrogen (as in HCl, H_2SO_4, NaHO, &c.) of being replaced by metals. The cause of this must evidently be looked for in the fundamental properties of the carbon, which enters into the composition of these compounds; but it must be confessed that at present there is no satisfactory or legitimate explanation for these peculiarities (the recognition of 'complex radicles' and such like concessions only presents a scheme or generalisation of the phenomenon, but not an explanation), or of the fundamental difference between the saline compounds of the elements and those organic compounds which do not evince saline properties. This is one of the great problems awaiting solution in chemistry, a science which is, strictly speaking, still young and new.

caustic soda, NaOH, which is therefore termed sodium hydroxide. According to this view, **acid salts** are those in which only a portion of the hydrogen is replaced by a metal, and a portion of the hydrogen of the acid remains. Thus sulphuric acid, H_2SO_4, not only gives the normal salt Na_2SO_4, with sodium, but also an acid salt, $NaHSO_4$. A **basic salt** is one in which the metal is combined, not only with the haloids of acids, but also with the aqueous radicle of basic hydrates—for example, bismuth gives, not only a normal salt of nitric acid, $Bi(NO_3)_3$, but also basic salts, like $Bi(OH)_2(NO_3)$.

As basic and acid salts of the oxygen acids contain hydrogen and oxygen, they are able to part with these as water and to give anhydro-salts, which it is evident will be compounds of normal salts with anhydrides of the acids or with bases. Thus the above-mentioned acid sodium sulphate corresponds with the anhydro-salt, $Na_2S_2O_7$, equal to $2NaHSO_4$, less H_2O. The loss of water is here, and frequently in other cases, brought about by heat alone, and therefore such salts are frequently termed **pyro-salts**; for instance, the preceding is sodium pyrosulphate ($Na_2S_2O_7$), or it may be regarded as the normal salt Na_2SO_4 + sulphuric anhydride, SO_3. **Double salts** are those which contain either two metals, $KAl(SO_4)_2$, or two haloids.[57]

Inasmuch as oxygen compounds predominate in nature, it should be expected from what has been said above that salts, rather than acids or bases, would occur most frequently in nature, for these latter would

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[57] The above-enunciated generalisation of the conception of salts as compounds of the metals (simple, or compound, like ammonium, NH_4), with the haloids (simple, like chlorine, or compound, like cyanogen, CN, or the radicle of sulphuric acid, SO_4), capable of entering into double saline decomposition, which is in accordance with the general data respecting salts, was only gradually arrived at after a succession of most varied *propositions as to the chemical structure of salts.*

Salts belong to the class of substances which have been known since very early times, and have long been investigated in many directions. At first, however, no distinction was made between salts, acids, and bases. Glauber prepared many artificial salts during the latter half of the seventeenth century. Up to that time the majority of salts were obtained from natural sources, and that salt which we have referred to several times—namely, sodium sulphate—was named Glauber's salt, after this chemist. Rouelle distinguished *normal*, *acid*, and *basic* salts, and showed their action on vegetable dyes; but he also confounded many salts with acids (even now every acid salt ought to be regarded as an acid, because it contains hydrogen, which may be replaced by metals, and is hence the hydrogen of an acid). Baumé disputed Rouelle's opinion concerning the subdivision of salts, *contending that only normal salts are true salts*, and that basic salts are simple mixtures of normal salts with bases, and acid salts, mixtures with acids, since washing alone could remove the base or acid from them. Rouelle, in the middle of the last century, however, rendered a great service to the study of salts and the diffusion of knowledge respecting *this class of compounds* by his *attractive lectures.* Like the majority of the chemists of that period, he did not employ the balance in his researches, but satisfied himself with purely qualitative data. The first quantitative researches on salts were carried on about this time by **Wenzel**, who was the director of the Freiberg mines, in Saxony. Wenzel studied the double decomposition of salts, *and observed that, in the double decomposition of neutral salts, a neutral salt was always obtained.* He proved, by a method of weighing, that this is due to the fact that the saturation of a given quantity of a base requires equal relative quantities of different acids. Having taken two neutral salts—for example, sodium sulphate and calcium *nitrate—let us mix their* solutions together. Double decomposition takes place, because calcium sulphate is formed, which is almost insoluble. However much we might add of each of the salts, the neutral reaction will still be preserved; consequently the neutral character of the salts is not destroyed by the *interchange of metals*; *that is to say,* that quantity of sulphuric acid which saturated the sodium is sufficient for the saturation of the calcium, and that amount of nitric acid which saturated the calcium is enough to saturate the sodium contained in combination with sulphuric acid in sodium sulphate. Wenzel was even convinced that matter does not disappear in nature, *and on this principle he corrects,* in his *Doctrine of Affinity*, the results of his experiments when he found that he obtained less than he had originally taken. Although Wenzel deduced the law of the double decomposition of salts quite correctly, he did not determine those quantities in which acids and bases act on each other. This was carried out at the end of the eighteenth century by **Richter**. He determined the quantities by weight of the bases which saturate acids, and of the acids which saturate bases, and obtained comparatively accurate results, although his conclusions were not correct, for he states that the quantity of a base saturating a given acid varies in arithmetical progression, and the quantity of an acid saturating a given base in geometrical progression. Richter studied the deposition of metals from their salts by other metals, and observed that the neutral reaction of the solution is not destroyed by this exchange. He also determined the quantities by weight of the metals replacing one another in salts. He showed that copper displaces silver from its salts, and that zinc displaces copper and a whole series of other metals. Those quantities of metals which were capable of replacing one another were termed **equivalents**.

Richter's teaching found no followers, because, although he fully believed in the discoveries of Lavoisier, yet he still held to the phlogistic reasonings which rendered his expositions very obscure. The work of the Swedish savant **Berzelius** in the beginning of the nineteenth century freed the facts discovered by Wenzel and Richter from the obscurity of former conceptions and led to their being explained in accordance with Lavoisier's views, and in the sense of the law of multiple proportions which had already been discovered by Dalton. On applying to salts those conclusions which Berzelius arrived at by a whole series of researches of remarkable accuracy, we arrive at the following law of equivalents—*one part by weight of hydrogen in an acid is replaced by the corresponding equivalent weight of any metal*; and, therefore, when metals replace each other, their respective weights are in the same ratio as their equivalents. Thus, for *instance,* one part by weight of hydrogen is replaced by 23 parts of sodium, 39 parts of potassium, 12 parts of magnesium, 20 parts of calcium, 28 parts of iron, 108 parts of silver, 33 parts of zinc, &c.; and, therefore, if zinc replaces silver, 33 parts of the zinc will take the place of 108 parts of silver, or 33 parts of zinc will be substituted by 23 parts *of sodium, &c.*

The doctrine of equivalents would be precise and simple did every metal only give one oxide or one salt. It is rendered complicated from the fact that many metals form several oxides, and consequently offer different equivalents in their different degrees of oxidation. For example, there are oxides containing iron in which its equivalent is 28—this is in the salts formed by the suboxide; and there is another series of salts in which the equivalent of iron equals 18⅔—which contain less iron, and consequently more oxygen, and correspond with a higher degree of oxidation—ferric oxide. It is true that the former salts are *easily formed by the direct action* of metallic iron on acids, and the latter only by a further oxidation of the compound formed already; but this is not always so. In the cases of copper, mercury, and tin, under different circumstances, salts are formed which correspond with different degrees of oxidation of these metals, and many metals have two equivalents *in their different* salts—that is, in salts corresponding with the always tend to combine forming salts, especially through the medium of the all-pervading water. And, as a matter of fact, salts are found everywhere in nature. They occur in animals and plants, although in but

small quantity, because, as forming the last stage of chemical reaction, they are capable of only a few simple chemical transformations. And organisms are bodies in which a series of uninterrupted, varied, and active chemical transformations proceed, whilst salts, which only enter into double decompositions between each other, are little prone to such changes. But organisms always contain salts. Thus, for instance, bones contain calcium phosphate, the juice of grapes potassium tartrate (cream of tartar), certain lichens calcium oxalate, and the shells of mollusca calcium carbonate, &c. As regards water and soil, portions of the earth in which the chemical processes are less active, these are full of salts. Thus the waters of the oceans, and all others (Chap. I.), abound in salts, and in the soil, in the rocks of the earth's crust, in the upheaved lavas, and in the falling meteorites the salts of silicic acid, and especially its double salts, predominate. Saline substances also make up the composition of those limestones which often form mountain chains and whole thicknesses of the earth's strata, these consisting of calcium carbonate, $CaCO_3$.

Thus we have seen oxygen in a free state and in various compounds of different degrees of stability, from unstable and slightly stable compounds (like Berthollet's salt and nitre) to the most stable silicon compounds, such as exist in granite. We saw an entirely similar gradation of stability in the compounds of water and of hydrogen. In all its aspects oxygen, as an element, or single substance, remains the same, however varied its chemical states, just as a substance may appear in many different physical states of aggregation. But our notion of the immense variety of the chemical states in which oxygen can occur would not be completely understood if we did not make ourselves acquainted with it in the form in which it occurs in ozone and peroxide.

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different degrees of oxidation. Thus it is impossible to endow every metal with one definite equivalent weight. Hence the conception of equivalents, while playing an important part from an historical point of view, appears, with a fuller study of chemistry, to be but subordinate to a higher conception, with which we shall afterwards become acquainted.

The fate of the theoretical views of chemistry was for a long time bound up with the history of salts. The clearest representation of this subject dates back to Lavoisier, and was systematically developed by Berzelius. This representation is called the **binary** theory. All compounds, and especially salts, are represented as consisting of two parts. Salts are represented as compounds of a basic oxide (a base) and an acid (that is, an anhydride of an acid, then termed an acid), whilst hydrates are represented as compounds of anhydrous oxides with water. Such an expression was employed not only to denote the most usual method of formation of these substances (where it would be quite true), but also to express that internal distribution of the elements by which it was proposed to explain all the properties of these substances. Copper sulphate was supposed to contain two most intimate component parts—copper oxide and sulphuric anhydride. This is an hypothesis. It arose from the so-called **electro-chemical hypothesis**, which supposed the two component parts to be held in mutual union, because one component (the anhydride of the acid) has electro-negative properties, and the other (the base in salts) electro-positive. The two parts are attracted together, like substances having opposite electrical charges. But as the decomposition of salts in a state of fusion by an electric current always gives a metal, that representation of the constitution and decomposition of salts called the **hydrogen theory of acids** is nearer the truth than that which considers salts as made up of a base and an anhydride of an acid. But the hydrogen theory of acids is also a binary hypothesis, and does not contradict the electro-chemical hypothesis, but is rather a modification of it. The binary theory dates from Rouelle and Lavoisier, the electro-chemical aspect was zealously developed by Berzelius, and the hydrogen theory of acids is due to Davy and Liebig.

These hypothetical views simplified and generalised the study of a complicated subject, and served to support further arguments; but when salts were in question it was equally convenient to follow one or the other of these hypotheses. But these theories were brought to bear on all other substances, on all compound substances. Those upholding the binary and electro-chemical hypotheses searched for two anti-polar component parts, and endeavoured to express the process of chemical reactions by electro-chemical and similar differences. As zinc replaces hydrogen, they concluded that it is more electro-positive than hydrogen, whilst they forgot that hydrogen may, under different circumstances, displace zinc – for instance, at a red heat. Chlorine and oxygen were considered as being of opposite polarity to hydrogen, because they easily combine with it; nevertheless both are capable of replacing hydrogen, and, what is very characteristic, in the replacement of hydrogen by chlorine in carbon compounds, not only does the chemical character often remain unaltered, but even the external form may remain unchanged, as was shown by Laurent and Dumas. These considerations undermine the binary, and more especially the electro-chemical, theory. An explanation of known reactions then began to be sought for, not in the difference of the polarity of the different substances, but in the joint influences of all the elements on the properties of the compound formed. This is the reverse of the preceding hypothesis.

This reversal was not, however, limited to the destruction of the tottering foundations of the preceding theory: it proposed a new doctrine, and laid the foundation for the modern progress of our science. This doctrine may be termed the **unitary theory**—that is, it strictly acknowledges the joint influences of the elements in a compound substance, denies the existence of separate and contrary components in them, regards copper sulphate, for instance, as a strictly definite compound of copper, sulphur, and oxygen; then seeks for compounds which are analogous in their properties, and, placing them side by side, endeavours to express the influence of each element in determining the united properties of its compound. In the majority of cases it arrives at conclusions similar to those which are obtained by the above-mentioned hypotheses, but in certain special cases the conclusions of the unitary theory are in entire opposition to those of the binary theory and its corollaries. Cases of this kind are most often met with in the consideration of compounds of a more complex nature than salts, especially organic compounds containing hydrogen. But it is not in this change from an artificial to a natural system, important as it is, that the chief service and strength of the unitary doctrine lies. By a simple review of the vast store of data regarding the reactions of typical substances, it succeeded from its first appearance in establishing a new and important law; it introduced a new conception into science—namely, the conception of *molecules*, with which we shall soon become acquainted. The deduction of the law and of the conception of molecules has been verified by facts in a number of cases, and was the cause of the majority of chemists of our times deserting the binary theory and accepting the unitary theory, which forms the basis of the present work. **Laurent** and **Gerhardt** must be considered as the founders of this doctrine.

of hydrogen. In these it is most unstable and active, its energy having apparently increased. They illustrate fresh aspects of chemical correlations, and the variety of the forms in which matter can appear stand out clearly. We will therefore consider these two substances somewhat in detail.[58]

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[58] This consignment of ozone and peroxide of hydrogen to a separate chapter is all the more necessary, as the difference between saline oxides (capable of forming acids, bases, and salts) and peroxides, is held to all through this work. The former, which have been cursorily considered in the present chapter, correspond with water, the latter with peroxide of hydrogen and ozone. The peroxides always contain more oxygen than the saline oxides, and easily part with their excess of oxygen, which oxidises and in general reacts like the excess of oxygen in ozone and peroxide of hydrogen. Although in an arithmetical sense peroxide of hydrogen, H_2O_2, is related to water in the same way as SO_3 to SO_2, or Cu_2O_2, to Cu_2O or in general a higher degree of oxidation to a lower, yet in its reactions the difference appears to be far deeper, as I trust the reader will gradually recognise. Moreover water and the saline oxides corresponding with it have been studied far more than the peroxides, which play a more modest part in nature and the industries. The peroxides have their own special and important interest, which is not, however, so general a one as that presented by water and salts.

CHAPTER IV

OZONE AND HYDROGEN PEROXIDE—DALTON'S LAW

VAN MARUM, during the eighteenth century, observed that air, when subjected to the action of a series of electric sparks, acquired a peculiar smell and the property of combining with mercury at the ordinary temperature. This was afterwards confirmed by a number of fresh experiments. Even in the simple revolution of an electrical machine, when electricity diffuses into the air or passes through it, the peculiar and characteristic smell of ozone, proceeding from the action of the electricity on the oxygen of the atmosphere, is recognised. In 1840 Professor Schönbein, of Basle, turned his attention to this odoriferous substance, and showed that it is also formed, with the oxygen evolved at the positive pole, in the decomposition of water by the action of a galvanic current; also in the oxidation of phosphorus in damp air, and in the oxidation of a number of other substances (especially turpentine), although it is distinguished for its instability and capacity for oxidising other substances. The same gas is also formed in many cases where oxygen is formed at the ordinary (or a lower) temperature; for instance, in the decomposition of acidulated water by the galvanic current, by the action of gaseous fluorine on water ($3H_2O+3F_2=6HF+O_3$), or by the action of sulphuric acid on permanganate of potassium,[1] &c. The characteristic smell of this substance gave it its name, from the Greek ὄζω, 'I emit an odour.' Schönbein pointed out that **ozone** is capable of oxidising many substances on which oxygen does not act at the ordinary temperature. For instance, that it oxidises silver, mercury, charcoal, and iron with great energy at the ordinary

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[1] This experiment must be made with small quantities and with caution, as an explosion may easily take place.

Jörissen (1897) found that ozone is formed whenever oxygen oxidises at the ordinary temperature (in the slow oxidation of zinc, of $P(C_2H_5)_3$, of lead in the presence of sulphuric acid, the potassium in KCN in acting on gold, &c.). The molecules of oxygen then, as it were, always split up into two portions, one going to oxidise and the other forming ozone. This coincides with what is said later respecting the difference between oxygen gas, O_2, and ozone, O_3, in which only $\frac{1}{3}$ of the oxygen acts.

temperature, decolorises (oxidises) blue indigo and many other organic colouring matters, &c. It might be thought that ozone was some new compound substance, as it was at first supposed to be; but careful observations made in this direction have long since led to the conclusion that ozone is nothing but oxygen altered in its properties. This is most strikingly proved by the complete transformation of oxygen containing ozone into ordinary oxygen when it is passed through a tube heated to 250°. Further, at a low temperature pure oxygen gives ozone when electric sparks are passed through it (Marignac and De la Rive). Hence it is proved, both by synthesis and analysis, that ozone is that same oxygen with which we are already acquainted, only endowed with particular properties and in a particular state. By whatever method it be obtained, the amount of it contained in the oxygen is inconsiderable, generally only a small fraction per cent., rarely 2 per cent., and only under low temperatures as much as 20 per cent. The reason of this must be looked for first in the fact that *ozone in its formation from oxygen absorbs heat*, i.e., evolves heat, in its conversion into ordinary oxygen. If any substance be burnt in a calorimeter at the expense of ozonised oxygen, more heat is evolved than when it is burnt in ordinary oxygen, and Berthelot showed that this difference is very large—namely, 29,600 heat units correspond with every forty-eight parts by weight of ozone. This signifies that the transformation of forty-eight parts of oxygen into ozone is accompanied by the absorption of this quantity of heat, and that the reverse process evolves this quantity of heat. Therefore the *passage of ozone into oxygen* should take place easily and completely (as an exothermal reaction), like combustion. At 250° ozone entirely disappears, forming oxygen. Any rise of temperature may thus bring about the breaking up of ozone, and as a rise of temperature takes place in the action of an electrical discharge, there are, in an electric discharge, the conditions both for the preparation of ozone and for its destruction. Hence it is clear that the transformation of oxygen into ozone *as a reversible reaction* has a limit when a state of equilibrium is arrived at between the products of the two opposite reactions, that the phenomena of this transformation accord with the phenomena of *dissociation*, and that a fall of temperature should aid the formation of a large quantity of ozone.[1a] Further, it is evident, from what has been said, that the best way of preparing ozone is not by electric sparks,[2] which raise the temperature, but by the employment of a continual discharge or flow of electricity—that is, by the action of a **silent discharge.**[3] For this reason all **ozonisers** (which are of most varied construction), or forms of apparatus for the preparation of ozone from oxygen (or air) by the action of electricity, now usually consist of sheets of metal—for instance, tinfoil—or a solution of sulphuric acid mixed with chromic acid, &c., separated by thin glass surfaces placed at short distances from each other, and between which the oxygen or air to be ozonised is introduced and subjected to the action of the silent discharge.[4] Thus in Berthelot's

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[1a] This conclusion, deduced by me as far back as 1878 (*Moniteur Scientifique*) by conceiving the molecules of ozone (see later) as more complex than those of oxygen, and ozone as containing a greater quantity of heat than oxygen, has been proved experimentally by the researches of Mailfert (1880), who showed that the passage of a silent discharge through a litre of oxygen at 0° may form up to 14 milligrams of ozone, and at -80° up to 60 milligrams; but best of all in the determinations of Chappuis and Hautefeuille (1880), who found that at a temperature of -25° a silent discharge converted 20 per cent. of oxygen into ozone, whilst at 20° it was impossible to obtain more than 12 per cent., and at 100° less than 2 per cent. of ozone was obtained.

[2] A series of electric sparks may be obtained by an ordinary electrical machine, the electrophorus machines of Holtz and Teploff, &c., Leyden jars, Ruhmkorff coils, or similar means, when the opposite electricities are able to accumulate at the terminals of conductors, and a discharge of sufficient electrical intensity passes through the non-conducting air or oxygen.

[3] A silent discharge is such a combination of opposite statical (potential) electricities as takes place (generally between large surfaces) regularly, without sparks, slowly, and quietly (as in the dispersion of electricity). The discharge is only luminous in the dark; there is no observable rise of temperature, and therefore a larger amount of ozone is formed. But nevertheless, on continuing the passage of a silent discharge through ozone it is destroyed. For the action to proceed well a large surface is necessary, and consequently a source of electricity at a high potential. For this reason the silent discharge is best produced by a Ruhmkorff coil, this being the most convenient means of obtaining statical electricity at a considerable potential when the comparatively feeble current of a galvanic battery is employed.

[4] *v. Babo's apparatus* was one of the first constructed for ozonising oxygen by means of a silent discharge (and is still one of the best). It is composed of a number (twenty or more) of long, thin, capillary glass tubes closed at one end. A platinum wire, extending along their whole length, is introduced into the other end of each tube, and this end is then fused up round the wire, the end of which protrudes outside the tube. The protruding ends of the wires are arranged alternately on two sides in such a manner that on each side there is an equal number of closed ends and wires. A bunch of such tubes (forty should make a bunch of not more than 1 cm. diameter) is placed in a glass tube, and the ends of the wires are connected with two conductors, and are fused to the ends of the surrounding tube. The discharge of a Ruhmkorff coil is passed through these ends of the wires, and the dry air or oxygen to be ozonised is passed through the tube. If oxygen be passed through, ozone is obtained in large quantities and free from oxides of nitrogen, which are formed to some extent when air is acted on. At low temperatures ozone is formed in *large quantities*. As ozone acts on corks and indiarubber, the apparatus should be made entirely of glass. With a powerful Ruhmkorff coil and forty tubes the ozonation is so powerful that the gas when passed through a solution of iodide of potassium not only sets the iodine free, but even oxidises it to potassium iodate, so that in five minutes the gas-conducting tube is choked up with crystals of the insoluble iodate. In the majority of ozonisers the two tubes are lined with sheet tin or other metal and oxygen is passed through the annular space through which the silent discharge takes place. This kind of ozoniser may be used for ozonising the air of hospitals, &c., for the purpose of disinfection (Chap. V.). Ozone is employed for bleaching, &c., but its application in general requires perfecting.

apparatus (fig. 41), the glass F and the tube A contain sulphuric acid, connected with the poles of a source of electricity, e.g., with the terminals of a Ruhmkorff's coil. A silent discharge passes through the thin walls of the glass cylinders A and B, over all their surfaces, and consequently, if oxygen be passed through the apparatus by the tube C, it will be ozonised in the annular space between A and B. The ozonised oxygen escapes by the tube D, and may be introduced into any other apparatus.[5]

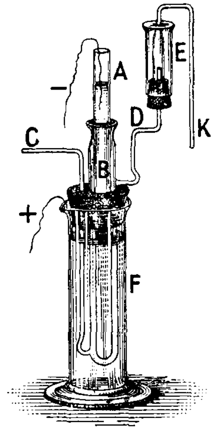

FIG. 41.—Berthelot's apparatus for the production of ozone by the silent discharge.

The properties of ozone[6] distinguish it in many respects from oxygen. Ozone very rapidly decolorises indigo, litmus, and many other dyes by *oxidising them*. Silver is oxidised by it at the ordinary temperature, whilst oxygen is not able to oxidise silver even at high temperatures; a bright silver plate rapidly turns black (from oxidation) in ozonised oxygen. It is rapidly absorbed by mercury, forming the oxide; it transforms the lower oxides into higher—for instance, sulphurous anhydride into sulphuric, nitrous oxide into nitric, arsenious anhydride (As_2O_3) into arsenic anhydride

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[5] In order to connect the ozoniser with any other apparatus it is impossible to make use of indiarubber, mercury, or cements, &c., *because they are themselves acted on by*, and act on, ozone. All connections must, as was first proposed by Brodie, be hermetically closed by sulphuric acid, which is not acted on by ozone. Thus, a cork is passed over the vertical end of a tube, over which a wide tube passes, so that the end of the first tube protrudes above the cork; mercury is first poured over the cork (to prevent its being acted on by the sulphuric acid), and then sulphuric acid is poured over the mercury. The protruding end of the first tube is covered by the lower end of a third tube immersed in the sulphuric acid.

[6] The method above described is the only one which has been well investigated. The admixture of nitrogen, or even of hydrogen, and especially of silicon fluoride, appears to aid the formation and preservation of ozone. Amongst other methods for preparing ozone we may mention the following:—1. In the action of oxygen on phosphorus at the ordinary temperature, a portion of the oxygen is converted into ozone. At the ordinary temperature a stick of phosphorus, partially immersed in water and partially in air in a large glass vessel, causes the air to acquire the odour of ozone. It must further be remarked that if the air be left for long in contact with the phosphorus, or without the presence of water, the ozone formed is destroyed by the phosphorus. 2. By the action of sulphuric acid on peroxide of barium. If the latter be covered with strong sulphuric acid (the acid, if diluted with only one-tenth of water, does not give ozone), then at a low temperature the oxygen evolved contains ozone, and in much greater quantities than is obtained by the action of electric sparks or phosphorus. 3. Ozone may also be obtained by decomposing strong sulphuric acid by potassium manganate, especially with the addition of barium peroxide.

(As_2O_5), &c.[7] But what is especially characteristic in ozone is the decomposing action it exerts on potassium iodide. Oxygen does not act on this salt, but ozone passed into a solution of potassium iodide **liberates iodine**, whilst the potassium is obtained as caustic potash, which remains in solution: $2KI+H_2O+O=2KHO+I_2$. As the presence of minute traces of free iodine may be discovered by means of starch, with which it forms a very dark blue-coloured substance, a mixture of potassium iodide with starch paste will detect the presence of very small traces of ozone.[8] Ozone is destroyed or converted into ordinary oxygen not only by heat, but also by long keeping, especially in the presence of alkalis, peroxide of manganese, chlorine, &c., and also when it acts by oxidation (see later).

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[7] It is said that ozone oxidises water and converts it into peroxide of hydrogen. Ozone takes up the hydrogen from hydrochloric acid; chlorine is liberated, and can dissolve gold. Iodine is directly oxidised by *ozone*, but not by oxygen. Ammonia, NH_3, is oxidised by ozone into ammonium nitrite (and nitrate), $2NH_3+O = NH_4NO_2+H_2O$, and therefore a drop of ammonia, on falling into the gas, gives a thick cloud of the salts formed. Ozone converts colourless lead oxide into brown dioxide, and suboxide of thallium (which is colourless) into oxide (which is brown), so that this reaction is made use of for detecting the presence of ozone. Lead sulphide, PbS (black), is converted into sulphate, $PbSO_4$ (colourless), by ozone. A neutral solution of manganese sulphate gives a precipitate of manganese peroxide, and an acid solution may be oxidised into permanganic acid, $HMnO_4$. With respect to the oxidising action of ozone on organic substances, it may be mentioned that with ether, $C_4H_{10}O$, ozone gives ethyl peroxide, which is capable of decomposing with explosion (according to Berthelot), and is decomposed by water into alcohol, $2C_2H_6O$, and hydrogen peroxide, H_2O_2.

[8] This reaction is the one usually made use of for detecting the presence of ozone. In the majority of cases paper is soaked in solutions of potassium iodide and starch. Such **ozonometrical** or iodised starch-paper, when damp, turns blue in the presence of ozone, and the tint obtained varies considerably (to black), according to the length of time it is exposed and to the amount of ozone present. Even the amount of ozone in a given gas may to a certain degree be judged by the shade of colour acquired by the paper if preliminary tests be made.

Test-paper for ozone is prepared in the following manner:—One gram of neutral potassium iodide is dissolved in 100 grams of distilled water; 10 grams of starch are then shaken up in the solution, and the mixture is boiled until the starch is converted into a jelly. This jelly is then smeared over blotting-paper and left to dry. It must be remarked, however, that *the colour of iodised starch-paper is changed, not only by the action of ozone, but by that of many other oxidisers*, the oxides of nitrogen (especially N_2O_3) and hydrogen peroxide. *Houzeau proposed soaking common litmus-paper with a* solution of potassium iodide, which in the presence of ozone would turn blue, owing to the formation of KHO. In order to determine if the blue colour is not produced by an alkali (ammonia) in the gas, a portion of the paper is *not* soaked in the potassium iodide, but moistened with water: this portion will then also turn blue if ammonia be present. A reagent for distinguishing ozone from hydrogen peroxide with certainty is not known, and therefore these substances in very small quantities (for instance, in the atmosphere) may easily be confounded. Formerly the mistake has frequently been made of ascribing the alteration of iodised starch-paper in the air to the presence of ozone (note 13a); at the present time there is reason to believe that it is most often due to the presence of nitrous acid (Ilosvay, 1889).

Hence **ozone**, although it has the same **composition as oxygen**, differs from it in stability, and by the fact that it **oxidises** a number of substances very **energetically** at the ordinary temperature. In this respect ozone resembles the oxygen of certain unstable compounds, or oxygen at the moment of its liberation.

In ordinary oxygen and ozone we see an example of one and the same substance, in this case an element, appearing in two states. This indicates that the properties of a substance, and even of an element, may vary without its composition varying. Very many such cases are known. Such cases of a chemical transformation which determines a difference in the properties of one and the same element are termed cases of **isomerism**. The isomerism of elements is termed **allotropy**. The cause of isomerism evidently lies deep within the essential nature of a substance, and its investigation has already led to a number of results of unexpected importance and of immense scientific significance. It is easy to understand the difference between substances containing different elements or the same elements in different proportions. That a difference should exist in these cases necessarily follows, if, as our knowledge compels us, we admit that there is a radical difference between the various simple bodies or elements. But when the composition—i.e., the quality and quantity—of the elements in two substances is the same and yet their properties are different, it is clear that the conceptions of diverse elements and of the varying composition of compounds alone are insufficient for the expression of all the diversity of properties of matter in nature. Something else, still more profound and internal than the composition by weight of substances, must, judging from isomerism, determine the properties and transformation of substances.[8a]

On what are the isomerism of ozone and oxygen, and the peculiarities of ozone, dependent? On what, besides the extra store of energy, which clearly expresses the peculiarities of ozone, rests the cause of its difference from oxygen? These questions for long occupied the minds of investigators, and were the motive for the most varied, exact, and accurate researches, which were chiefly directed to the study of the volumetric relations exhibited by ozone. In order to acquaint the reader with the previous researches of this kind, I cite the following from a memoir by Soret, in the 'Transactions of the French Academy of Sciences' for 1866:

'Our present knowledge of the volumetric relations of ozone may be expressed in the following manner:

'1. "Ordinary oxygen in changing into ozone under the action of electricity shows a diminution in volume." This was discovered by Andrews and Tait.

'2. "In acting on ozonised oxygen with potassium iodide and other substances capable of being oxidised, we destroy the ozone, but the volume of the gas remains unchanged." For the researches of Andrews, Soret, von Babo, and others showed that the proportion of ozonised oxygen absorbed by the potassium iodide is equal to the original contraction of volume of the oxygen—that is, in the absorption of the ozone the volume of the gas remains unchanged. From this it might be imagined that ozone, so to speak, occupies no space—is indefinitely dense.

'3. "By the action of heat ozonised oxygen increases in volume, and is transformed into ordinary oxygen. This increase in volume corresponds with the quantity of ozonised oxygen which is given up to the potassium iodide in its decomposition" (the same observers).

'4. These unquestionable experimental results lead to the conclusion that ozone is denser than oxygen, and that in its oxidising action it gives off that portion of its substance to which is due the increased density distinguishing it from ordinary oxygen.'

If we imagine (says Weltzien) that n volumes of ozone consist of n volumes of oxygen combined with m volumes of the same substance, and that ozone in oxidising gives up m volumes of oxygen and leaves n volumes of ordinary oxygen gas, then all the above facts can be explained; otherwise it must be supposed that ozone is infinitely dense. 'In order to determine the density of ozone' (we again cite Soret) 'recourse cannot be had to the direct determination of the weight of a given

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[8a] Under that atomic (Chap. VII.) conception of matter which is recognised by modern science, isomerism cannot be regarded otherwise than as a modification in the distribution of similar atoms in space, that is, with respect to each other. Hence, among isomerides, we distinguish polymerides, which differ from each other chiefly in the number of atoms forming the individual system or molecule of the substance. Thus ozone, O_3, by its density, is regarded as the polymeride of oxygen, O_2. But isomerism may also occur with an equal number of atoms in the molecules, if their mutual distribution or *structure* (constitution) be different. In organic chemistry, where polymerides and other isomerides are very frequent, it is especially important to have in view not only the composition but also the structure of compounds. But this is a matter of secondary importance in the study of the elements, which forms the main object of the present work, because the properties of substances are chiefly determined by the properties of the elements they contain, and the main problem of study should be deducing the properties of substances from those of the elements, and therefore I consider the chief object of this work to be an expression of the properties of the chemical elements. And as the chemical elements can only be conceived from the simple and compound substances they form, they compose the chief subject of our work. It does not aim at embracing the whole province of chemistry, but only at acquainting the reader with that portion which concerns the doctrine of the chemical elements. In this respect it forms an introduction to chemistry as a science, but even then it is impossible to avoid mentioning the fundamental conceptions of structure and isomerism.

volume of the gas, because ozone cannot be obtained in a pure state. It is always mixed with a very large quantity of oxygen. It was necessary, therefore, to have recourse to such substances as would absorb ozone without absorbing oxygen and without destroying the ozone. Then the density might be deduced from the decrease of volume produced in the gas by the action of such solvents in comparison with the quantity of oxygen given up to potassium iodide. Advantage must also be taken of the determination of the increase of volume produced by the action of heat on ozone, if the volume occupied by the ozone before heating be known.' Soret found two such substances, turpentine and oil of cinnamon. 'Ozone disappears in the presence of turpentine. This is accompanied by the appearance of a dense vapour, which fills a vessel of small capacity (0·14 litre) to such an extent that it is impenetrable to direct solar rays.' On measuring the gaseous volume before and after the action of both volatile oils, a considerable decrease is remarked. On applying all the necessary corrections (for the solubility of oxygen in the oily liquids named above, for the pressures of their vapour, for the change of pressure, &c.) and making a series of comparative determinations, Soret obtained the following result: two volumes of ozone capable of being dissolved, when changed to ordinary oxygen (by heating with a wire brought to a red heat by a galvanic current) increase by one volume. Hence it is evident that in the formation of ozone three volumes of oxygen give two volumes of ozone—that is, its density (referred to hydrogen) is 24 if the density of oxygen is 16. Ladenburg (1900) verified and confirmed Soret's conclusion by a modified method and direct weighings.

The observations and determinations of Soret showed, therefore, that ozone is heavier than oxygen, and even than carbonic anhydride (because ozonised oxygen passes through fine orifices more slowly than either pure oxygen or its mixtures with carbonic anhydride), although lighter than chlorine (it flows more rapidly through such orifices than chlorine), and they indicated that **ozone is one and a half times denser than oxygen**, which may be expressed by designating a molecule of oxygen by O_2 and of ozone by O_3, and hence ozone, OO_2, is comparable with compound substances[9] formed by oxygen, as, for instance, CO_2,

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[9] Ozone is, as it were, an oxide of oxygen, just as water is an oxide of hydrogen. Just as aqueous vapour is composed of two volumes of hydrogen and one volume of oxygen, which on combining condense into two volumes of aqueous vapour, so also two volumes of oxygen are combined with one volume of oxygen to give two volumes of ozone. In the action of ozone on different substances it is only that additional portion of the molecule, by which it differs from ordinary oxygen, that combines with other bodies, and that is why, under these circumstances, the volume of the ozonised oxygen does not change. Starting with two volumes of ozone, one-third of its weight is parted with, and two *volumes of oxygen remain.*

SO_2, NO_2, &c. This explains the chief differences between ozone and oxygen, and the cause of the isomerism, and at the same time leads one to expect[10] that ozone, being a gas which is denser than oxygen, would be liquefied much more easily. This was actually shown to be the case by Chappuis and Hautefeuille in 1880, in their researches on the **physical properties of ozone**, and therefore if ozonised air or oxygen be passed through a tube cooled by liquid air, the ozone is converted into a blue liquid of sp. gr. 1·46, which must be manipulated with extreme caution, as it passes into ordinary oxygen at the ordinary temperature, with the evolution of heat and violent explosion (owing to the rapid increase in volume). Its boiling-point under a pressure of 760 mm. is about −106° *according to* Olzewsky, and −125° according to Ladenburg. Liquid and compressed[11] ozone is **sky-blue**. It explodes violently when suddenly compressed and heated, changing into ordinary oxygen and evolving, like all explosive substances,[12] that excess of heat which distinguishes it from oxygen.

Thus, judging by what has been said above, ozone should be formed in nature, not only in the many processes of oxidation which go on, but also by the condensation of atmospheric oxygen. The significance of

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The above observations of Soret on the capacity of turpentine for dissolving ozone, together with Schönbein's researches on the formation of ozone in the oxidation of turpentine and of similar volatile vegetable oils (entering into the composition of *perfumes*), also explain the action of this ethereal oil on a great many substances. It is known that turpentine oil, when mixed with many substances, promotes their oxidation. In this case it probably not only itself promotes the formation of ozone, but also dissolves ozone from the atmosphere, and thus acquires the property of oxidising many substances. It bleaches linen and cork, decolorises indigo, promotes the oxidation and hardening of boiled linseed oil, &c. These properties of turpentine oil are made use of in practice. Dirty linen and many stained materials are easily cleaned by turpentine, not only because it dissolves the grease, but also because it oxidises it. The admixture of turpentine with drying (boiled) oil, oil-colours, and lacs aids their rapid drying because it attracts ozone. Ozonisation perhaps explains the refreshing influence ethereal oils have in scents and other similar preparations, and also the salubrity of the air of pine forests. Water upon which a layer of turpentine oil has been poured acquires, when left standing in the light, the disinfecting and oxidising properties of ozonised turpentine (is this due to the formation of H_2O_2?).

[10] The densest, most complex, and heaviest particles of matter, under similar conditions, should evidently be less capable of passing into a state of gaseous motion, should sooner attain a liquid state, and have a greater cohesive force. These theoretical premises, having been verified, do much to confirm the modern (Avogadro-Gerhardt's) theory of chemical molecules.

[11] The blue colour proper to ozone may be seen through a tube one metre long, filled with oxygen, containing 10 per cent. of ozone.

[12] All explosive bodies and mixtures (gunpowder, detonating gas, &c.) evolve heat in exploding—that is, the reactions which accompany explosions are exothermal. In this manner ozone in decomposing evolves latent heat, although generally heat is absorbed in decomposition. This shows the meaning and cause of explosion.

ozone in nature has often arrested the attention of observers. There is a series of ozonometrical observations which show the different amounts of ozone in the air at different localities, at different times of the year, and under different circumstances. But the observations made in this direction cannot be considered as sufficiently exact, because the methods in use for determining ozone were not quite accurate. It is, however, indisputable[13] that the amount of ozone in the atmosphere is subject to variation; that the air of dwellings contains no ozone (it disappears in oxidising organic matter); that the air of fields and forests always contains ozone, or substances (peroxide of hydrogen) which act like it (on iodised starch paper, &c.)[13a], that the amount of ozone increases after storms; and that miasmata, &c., are destroyed by ozonising the atmosphere. It readily oxidises organic substances, and miasmata are produced by organic substances and the germs of organisms, all of which are easily changed and oxidised. Indeed, many miasmata—for instance, the volatile substance of decomposing organisms—are clearly destroyed or changed, not only by ozone, but also by many other powerfully oxidising substances, such as peroxide of hydrogen, chlorine water, potassium permanganate, and the like.[14] All that is now known respecting the presence of ozone in the air may be summed up in the following words: A small quantity of an oxidising substance, resembling ozone in its reactions, has undoubtedly been observed and determined in the atmosphere, especially in fresh air, for instance after a storm; and it is very likely that this substance contains a mixture of such oxidising substances as ozone, peroxide of hydrogen, and the lower oxides of nitrogen (especially nitrous acid and its ammonium salt)

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[13] In Paris it has been found that the further one goes from the centre of the town the greater becomes the amount of ozone in the air. The reason of this is evident: in a city there are many conditions for the destruction of ozone. This is why we distinguish country air from that of cities by its freshness. In spring the air contains more ozone than in autumn; the air of fields more than the air of towns.

[13a] The question of the presence of ozone in the air has not yet been fully elucidated, as those reactions by which ozone is generally detected are also common to nitrous acid (and its ammonium salt). Ilosvay de Ilosva (1889), in order to exclude the influence of such bodies, passed air through a 40 per cent. solution of caustic soda, and then through a 20 per cent. solution of sulphuric acid (these solutions, according to this author, do not destroy ozone), and tested the air thus purified for the presence of ozone. As no ozone was then detected, the author concludes that all the effects which were formerly ascribed to ozone should be referred to nitrous acid. But this conclusion requires more careful verification since the researches of Professor Schönbein on the presence of peroxide of hydrogen in the atmosphere.

[14] The oxidising action of ozone may be taken advantage of for technical purposes; for instance, for destroying colouring matters. It has even been employed for bleaching tissues and for the rapid preparation of vinegar, although these methods have not yet received wide application.

produced from the elements of the atmosphere by oxidation and by the action of electrical discharges.[15]

Thus in ozone we see (1) the capacity of elements (and it must be all the more marked in compounds) of changing in properties without altering in composition; this is termed **isomerism**; (2) the capacity of certain elements for condensing themselves into molecules of different densities; this forms a special case of isomerism called **polymerism**; (3) the capacity of oxygen for appearing in a still more active and energetic chemical state than that in which it occurs in ordinary gaseous oxygen; and (4) the formation of unstable equilibria or chemical states, which are illustrated both by the ease with which ozone acts as an oxidiser and by its capacity for decomposing with explosion.[16]

Hydrogen peroxide.—Many of those properties which we have seen in ozone belong also to a peculiar substance containing oxygen and hydrogen and called hydrogen peroxide or oxygenated water. This substance was discovered in 1818 by Thénard. When heated it is decomposed into water and oxygen, evolving as much oxygen as is contained in the water remaining after the decomposition. That portion of oxygen by which hydrogen peroxide differs from water behaves in a number of cases just like the active oxygen in ozone, which distinguishes it from ordinary oxygen. In H_2O_2, and in O_3, one atom of oxygen acts as a powerful oxidiser, and on separating out it leaves H_2O or O_2, which do not act so energetically, although they still contain oxygen.[17] Both H_2O_2 and O_3 contain the oxygen, as it were, in a condensed state, and when freed from pressure by the forces (internal) of the elements in another substance, this oxygen is easily evolved, and therefore acts as oxygen does at the moment of its liberation. Both substances in decomposing, with the separation of a portion of their oxygen, *evolve* heat, whilst decomposition is usually accompanied by an absorption of heat.

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[15] The connection between ozone and peroxide of hydrogen, presently to be described, is so great that wherever one of them occurs, the other is sure to be found if the reaction proceeds in the presence of water; for instance, in the preparation of ozone by phosphorus, in flames, or by the action of BaO_2 on H_2SO_4, &c. But this is readily understood if ozone and water form peroxide of hydrogen, as is now supposed. This reaction is probably expressed by the equation, $O_3 + H_2O = O_2 + H_2O_2$, although experimental proofs are yet wanting to confirm this.

[16] A number of substances resemble ozone in one or other of these respects. Thus cyanogen, C_2N_2, nitrogen chloride, &c., decompose with explosion and evolution of heat. Nitrous anhydride, N_2O_3, forms a blue liquid like ozone, and in a number of cases oxidises like ozone.

[17] It is evident that there is a want of words here for distinguishing oxygen, O, as an ultimate **element** from oxygen, O_2, as a **free element**. The latter should be termed oxygen gas did not custom and the length of the expression render it inconvenient.

Hydrogen peroxide is formed under many circumstances by combustion and oxidation, but in very limited quantities; thus, for instance, it is sufficient to shake up zinc with sulphuric acid, or even with water, to observe the formation of a certain quantity of hydrogen peroxide in the water.[18] From this cause, probably, a series of different oxidation processes are accomplished in nature, and according to Professor Schöne, of Moscow, hydrogen peroxide occurs in the atmosphere, although in variable and small quantities, and probably its formation is connected with ozone, with which it has much in common. There is reason to think (but it has not been proved) that peroxide of hydrogen is directly formed by the action of ozone on water. The usual mode of formation of hydrogen peroxide, and the method by which it may be indirectly obtained,[19] is by the double decomposition of an acid and the peroxides of certain metals, especially those of potassium, calcium, and barium.[20] We saw, when speaking of oxygen (Chap. III.), that it is only necessary to heat the anhydrous oxide of barium to a red heat in a current of air or oxygen (or, better still, to heat it with potassium chlorate, and then to wash away the potassium chloride formed) to obtain peroxide of barium.[21] Barium peroxide gives hydrogen peroxide by the action of dilute acids in the cold.[22] The process of decomposition is very clear in this case: the hydrogen of the acid replaces the barium of the peroxide, a barium salt of the acid being formed, while the hydrogen peroxide formed in the reaction remains in solution.[23]

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[18] Schönbein states that the formation of hydrogen peroxide is to be remarked in every oxidation in water or in the presence of aqueous vapour. According to Struve, hydrogen peroxide is contained in snow and in rain water, and its formation, together with that of ozone and ammonium nitrate, is even probable in the processes of respiration and combustion. A solution of tin in mercury, or liquid tin amalgam, when shaken up in water containing sulphuric acid, produces hydrogen peroxide, whilst iron under the same circumstances does not give rise to its formation. The presence of small quantities of hydrogen peroxide in these and similar cases is recognised by many reactions. Among them, the action **on chromic acid** in the presence of ether is very characteristic. Hydrogen peroxide converts the chromic acid into a higher oxide, Cr_2O_7, which is of a dark-blue colour and dissolves in ether. This ethereal solution is to a certain extent stable, and therefore the presence of hydrogen peroxide may be recognised by mixing the liquid to be tested with ether and adding a few drops of a solution of chromic acid. On shaking the mixture, the ether dissolves the higher oxide of chromium which is formed, and on rising to the top acquires a blue colour. The formation of hydrogen peroxide in the combustion and oxidation of substances containing or evolving hydrogen must be understood in the light of the conception, to be considered later, of molecules occupying equal volumes in a gaseous state. At the moment of its evolution a molecule H_2 combines with a molecule O_2, and gives H_2O_2. As this substance is unstable, a large proportion of it is decomposed, a small amount only remaining unchanged. If it is obtained, water is easily formed from it: this reaction evolves heat, and the reverse action is not very probable. Direct determinations show that the reaction, $H_2O_2 = H_2O + O$, evolves 22,000 heat units. From this it will be understood how easy is the decomposition of hydrogen peroxide, as well as the fact that a number of substances which are not directly oxidised by oxygen are oxidised by hydrogen peroxide or by ozone, which also evolves heat on decomposition. Such a representation of the origin of hydrogen peroxide was developed by me about 1870. Subsequently (1890) Traube has pronounced a similar opinion, stating that Zn under the action of water and air gives, besides ZnH_2O_2, also H_2O_2.

[19] The formation of hydrogen peroxide from barium peroxide by a method of double decomposition is an instance of a number of **indirect methods of preparation**. A substance A does not combine with B, but A B is obtained from A C in its action on B D (see Introduction) when C D is formed. Water does not combine with oxygen, but when present in an acid it acts on the compound of oxygen with barium oxide, because this oxide gives a salt with an acid anhydride. It is to be remarked that the passage of barium oxide, BaO, into the peroxide, BaO_2, is accompanied by the **evolution** of 12,100 heat units per 16 parts of oxygen by weight combined, but the passage of H_2O into the peroxide H_2O_2 does not proceed directly, because it would be accompanied by the **absorption** of 22,000 units of heat per 16 parts by weight of oxygen combined. Barium peroxide, in acting on an acid, evidently evolves less heat than the oxide, and it is this difference of heat that is absorbed in the hydrogen peroxide.

[20] Dioxides of lead and manganese, and other analogous peroxides (see Chap. III., note 9), do not give hydrogen peroxide under these conditions, but yield chlorine with hydrochloric acid.

[21] The impure barium peroxide obtained in this manner may be easily purified. For this purpose it is dissolved in a dilute solution of nitric acid. A certain quantity of an insoluble residue always remains, from which the solution is separated by filtration. The solution will contain not only the compound of the barium peroxide, but also a compound of the barium oxide itself, a certain quantity of which always remains uncombined with oxygen. The acid compounds of the peroxide and oxide of barium are easily distinguishable by their different stability. The peroxide gives an unstable compound, and the oxide a stable salt. By adding an aqueous solution of barium oxide to the resultant solution, the whole of the peroxide contained in the solution may be precipitated as a pure aqueous compound (Kouriloff, 1889, obtained the same result by adding an excess of BaO_2). The first portions of the precipitate will consist of impurities—for instance, oxide of iron—which are rejected. The barium peroxide then separates out, and is collected on a filter and washed; it forms a substance having a definite composition, $BaO_2,8H_2O$. Pure hydrogen peroxide should always be prepared from such purified barium peroxide.

[22] In the cold, strong sulphuric acid with barium peroxide gives ozone; when diluted with a certain amount of water it gives oxygen (see note 6), whilst hydrogen peroxide is only obtained by the action of very weak sulphuric acid. Hydrochloric, hydrofluoric, carbonic, hydrofluosilicic, and other acids, when diluted with water, also give hydrogen peroxide with barium peroxide. Schöne, who very carefully investigated hydrogen peroxide, showed that it is formed by the action of many of the above-mentioned acids on barium peroxide. In preparing peroxide of hydrogen by means of sulphuric acid, the solution must be kept cold. A solution of maximum concentration may be obtained by successive treatments with sulphuric acid of increasing strength. In this manner a solution containing from 2 to 3 grams of pure peroxide in 100 c.c. of water may be obtained.

[23] With the majority of acids, the salt of barium which is formed remains in solution; thus, for instance, by employing hydrochloric acid, hydrogen peroxide and barium chloride remain in solution. Complicated processes would be required to obtain pure hydrogen peroxide from such a solution. It is much more convenient to take advantage of the action of carbonic anhydride on the pure hydrate of barium peroxide (note 21). For this purpose the hydrate is stirred up in water, and a rapid stream of carbonic anhydride is passed through the water. Barium carbonate, insoluble in water, is formed, and the hydrogen peroxide remains in solution, so that it may be separated from the carbonate by filtering. Sometimes hydrofluosilicic acid is employed, its barium salt being also insoluble in water. The purest H_2O_2 is obtained by distilling *in vacuo*. But in the absence of water it easily decomposes, and cannot be kept for long. It keeps better if a small amount of acid be added to it.

The reaction is expressed by the equation, $BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$. It is best to take a cold dilute solution of sulphuric acid and to almost saturate (testing with litmus) it with barium peroxide, so that a small excess of acid remains; insoluble barium sulphate is formed. A more or less dilute (3–4 per cent.) aqueous solution of hydrogen peroxide is obtained. This solution may be concentrated, that is to say, evaporated in a vacuum over sulphuric acid. In this way the water may even be entirely evaporated from the solution of the hydrogen peroxide; but in this case it is necessary to work at a low temperature, and not keep the peroxide long in the rarefied atmosphere, as otherwise it decomposes.[23a] A solution of peroxide of hydrogen (mixed with the solution of a salt of sodium, NaX) *is used for bleaching* (especially silk and wool) on a large scale, and is now usually prepared from peroxide of sodium, Na_2O_2, by the action of dilute acids: $Na_2O_2 + 2HX = 2NaX + H_2O_2$.[24]

When pure, hydrogen peroxide is a colourless liquid, without smell, and having a very unpleasant taste—such as belongs to the salts of many metals—the so-called 'metallic' taste. Water stored in zinc vessels has this taste, which is probably due to its containing hydrogen peroxide. The pressure of the vapour of hydrogen peroxide is less than that of aqueous vapour; this enables its solutions to be concentrated in a vacuum. The *specific gravity* of anhydrous hydrogen peroxide is 1·455–1·5. It has a bluish tint and decomposes, with the evolution of oxygen, when heated, especially if it is not perfectly pure. But if no solid powdery matter be present it evaporates without decomposition when heated under a low pressure (10–50 mm. of mercury). This is taken advantage of to obtain it pure. The water then passes over first, because it boils at a lower temperature. The more dilute the aqueous solution, the more stable it is. Very weak solutions may be distilled without decomposing the hydrogen peroxide. It decolorises solutions of litmus and turmeric, and acts in a similar oxidising manner on many colouring matters of organic origin (for which reason it is employed for bleaching tissues).[24a]

[23a] Hydrogen peroxide may be extracted from very dilute solutions by means of ether, which dissolves it. A solution of hydrogen peroxide in water may be concentrated by cooling it to a low temperature, when the water crystallises out—that is, is converted into ice—whilst the hydrogen peroxide remains in solution, as it only freezes at very low temperatures (in liquid air). It must be observed that hydrogen peroxide, in a strong solution in a pure state, is exceedingly unstable even at the ordinary temperature, and it must therefore be preserved in vessels always kept cold, as otherwise it evolves oxygen and forms water.

[24] Peroxide of sodium (Chap. XII., note 49) is prepared by burning sodium in dry air.

[24a] Peroxide of hydrogen has an industrial application in the arts; for instance, (1) as a bleaching agent, it having the important advantage over chloride of lime, SO_2, &c., of not acting upon the material under treatment: it may be used for bleaching feathers, hair, silk, wool, wood, &c., and it also removes stains of all kinds, such as wine, ink, and fruit-stains; (2) it destroys bacteria, as does ozone, without having any injurious effect upon the human body. It can also be used for washing all kinds of wounds, for purifying the air in the sick-room, &c.; and (3) as a preserving agent for potted meats, &c. A small amount of sulphuric acid is often added to the aqueous (3 per cent.) solution in order to store it for industrial purposes.

Many substances decompose hydrogen peroxide, forming water and oxygen, without apparently suffering any change. In this case, substances in a state of fine division show a much quicker action than compact masses, from which it is evident that the action is here based on contact (see Introduction). It is sufficient to bring hydrogen peroxide into contact with charcoal, gold, dioxide of manganese, the alkalis, metallic silver, or platinum, to bring about the above decomposition,[25] which, if proceeding very rapidly with pure peroxide or strong solutions, may lead to an explosion. Besides which, hydrogen peroxide forms water and parts with its oxygen with great ease to a number of substances which are capable of being oxidised or of combining with oxygen, and in this respect is very like ozone and other **powerful oxidisers.**[26] To the class of contact phenomena, which

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[25] As the result of careful research, certain of the *catalytic* or contact phenomena have been subjected to exact explanation, which shows that some substance present participates in these reactions, but does not affect the series of changes proceeding from mechanical actions alone. Thus, *for instance*, Schöne showed that with hydrogen peroxide, alkalies give peroxides of the alkaline metals, which combine with the remaining hydrogen peroxide, forming unstable compounds which are easily decomposed, and therefore alkalies evince a decomposing (catalytic) influence on solutions of hydrogen peroxide. Only acid solutions of hydrogen peroxide, and then only dilute ones, can be preserved well.

[26] **Hydrogen peroxide**, as a substance containing much oxygen (namely, 16 parts to one part by weight of hydrogen), exhibits many **oxidising reactions**. Thus, it oxidises arsenic, converts lime into calcium peroxide and the oxides of zinc and copper into peroxides. It parts with its oxygen to many sulphides, converting them into sulphates, &c.; thus, it converts black lead sulphide, PbS, into white lead sulphate, $PbSO_4$, copper sulphide into copper sulphate, and so on. The restoration of old oil paintings by hydrogen peroxide is based on this action. Oil colours are usually admixed with white lead, and in many cases the colour of oil-paints becomes darker in process of time. This is partly due to the sulphuretted hydrogen contained in the air, which acts on *white lead, forming* lead sulphide, which is black. The intermixture of the black colour darkens the rest. In cleaning a picture with a solution of hydrogen peroxide, the black lead sulphide is converted into white sulphate, and the colours brighten owing to the disappearance of the black substance which previously darkened them. Hydrogen peroxide oxidises with particular energy substances containing hydrogen and capable of easily parting with it to oxidising substances. Thus it decomposes hydriodic acid, setting the iodine free and converting the hydrogen it contains into water; it also decomposes sulphuretted hydrogen in exactly the same manner, setting the sulphur free. Starch paste with potassium iodide is not, however, directly coloured by peroxide of hydrogen in the entire absence of free acids; but the addition of a small quantity of ferrous sulphate (green vitriol) or of lead acetate to the mixture is enough to entirely blacken the paste. This is, like chromic acid and ether (see note 8), a very sensitive reagent (test) for peroxide of hydrogen.

are so characteristic of hydrogen peroxide as a substance which is unstable and easily decomposable with the evolution of heat, must be referred the following: in the presence of many substances containing oxygen it evolves not only its own oxygen, but also that of the substances which are brought into contact with it—that is, **it acts in a reducing manner**. It behaves thus with the oxides of silver, mercury, gold, and platinum, lead dioxide, &c. The oxygen in these substances is not stable, and therefore the feeble influence of contact is enough to destroy its position. Hydrogen peroxide, especially in a concentrated form, in contact with these substances, evolves an immense quantity of oxygen, so that an explosion takes place, and an exceedingly powerful evolution of heat is observed if hydrogen peroxide in a concentrated form be made to drop upon these substances in the form of dry powder. The decomposition also proceeds with dilute solutions,[27] but more slowly.

Just as a whole series of saltlike compounds, especially the oxides, hydrates, and salts, correspond with water, so also there are many substances analogous to hydrogen peroxide. Thus, for instance, calcium peroxide is related to hydrogen peroxide in exactly the same way as calcium oxide or lime is related to water. In both cases the hydrogen is replaced by calcium.[27a] But it is particularly instructive

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[27] To explain the phenomenon, Brodie, Clausius, and Schönbein suppose ordinary oxygen to be an electrically neutral substance, composed, so to speak, of two oppositely electrified kinds of oxygen—positive and negative. It is supposed that hydrogen peroxide contains one kind of such polar oxygen, whilst in the oxides of the above-named metals the oxygen is of opposite polarity. It is further supposed that in the oxides of the metals the oxygen is electro-negative, and in hydrogen peroxide electro-positive, and that on the mutual contact of these substances ordinary neutral oxygen is evolved as a consequence of the mutual attraction of the oxygens of opposite polarity. Brodie admitted the polarity of oxygen in combination, but not in an uncombined state, whilst Schönbein supposes uncombined oxygen to be polar also and regards ozone as electro-negative oxygen. The supposition that the oxygen of ozone is different from that of hydrogen peroxide is contradicted by the fact that in acting on barium peroxide strong sulphuric acid forms ozone, and dilute acid forms hydrogen peroxide.

[27a] It should be mentioned that Schiloff (1893) on taking a 3 per cent. solution of H_2O_2, adding soda to it, and then extracting the peroxide of hydrogen from the mixture by shaking it with ether, obtained a 50 per cent. solution of H_2O_2, which, although perfectly free from other acids, gave a **distinctly acid reaction** with litmus. And here attention should first of all be turned to the fact that the peroxides of the metals correspond with H_2O_2, like salts with an acid, for instance, Na_2O_2 and BaO_2, &c. Furthermore, it must be remembered that O is an analogue of S (Chaps. XV. and XX.), and sulphur gives H_2S, H_2SO_3, and H_2SO_4. And sulphurous acid, H_2SO_3, is unstable as a hydrate, and forms water and the anhydride SO_2. If the sulphur be replaced by oxygen, then instead of H_2SO_3 and SO_2, we have H_2OO_3 and OO_2. The latter is ozone, while K_2O_4 (peroxide of potassium) corresponds with the hydrate H_2O_4 as with an acid. And between H_2O and H_2O_4 there may exist intermediate compounds, the first of which would be H_2O_2, in which, from analogy to the sulphur compounds, one would expect acid properties. Besides which we may mention that for sulphur, besides H_2S (which is a

to remark that the nearest approach to the properties of hydrogen peroxide is afforded by a non-metallic element, chlorine, which, in its action on colouring matters, its capacity for oxidising and for evolving oxygen from many oxides, exhibits behaviour analogous to that of hydrogen peroxide. Even the very formation of chlorine is closely analogous to the formation of peroxide of hydrogen; chlorine is obtained from manganese peroxide (dioxide), MnO_2, and hydrochloric acid, HCl, and hydrogen peroxide from barium peroxide (dioxide), BaO_2, and the same acid. The result in one case is essentially water, chlorine, and manganese chloride; and in the other case, barium chloride and hydrogen peroxide are produced. Hence water + chlorine corresponds with hydrogen peroxide, and the action of chlorine in presence of water is analogous to the action of hydrogen peroxide. This analogy between chlorine and hydrogen peroxide is expressed in the conception of an aqueous radicle, which (Chapter III.) has already been mentioned. **This aqueous radicle** (or hydroxyl, HO) is that which is left if water be imagined to be deprived of half of its hydrogen. According to this method of expression, caustic soda will be a compound of sodium with the aqueous radicle, because it is formed from water with the evolution of half the hydrogen. This is expressed by the following formulæ: water, H_2O or HHO and caustic soda, NaHO, just as hydrochloric acid is HCl and sodium chloride NaCl. Hence the aqueous radicle HO is a compound radicle, just as chlorine, Cl, is a simple radicle. They both

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feeble acid), H_2S_2, H_2S_3, H_2S_5 are known. Thus, in many respects, H_2O_2 offers points of resemblance to acid compounds, and, as regards its qualitative (reactive) analogies, it not only resembles Na_2O_2, BaO_2, &c., but also persulphuric acid HSO_4 (to which the anhydride S_2O_7 corresponds), &c., which will be subsequently described. And here we may add, respecting the now vast class of per-compounds, (*a*) that they are formed under the same conditions as peroxide of hydrogen (for instance, by electrolysis, at the anode) or by its double decomposition or combination; (*b*) that elements like S, C, &c., which give acids, are able to form per-compounds or per-acids, which in their turn form salts with the alkalis; for instance, per-sulphuric acid; (*c*) that metals like molybdenum, vanadium, &c., which give higher acid oxides, R_2O_n, are usually able also to form per-acids corresponding with the higher oxides and oxygen; (*d*) that metals giving bases R_2O_n are often able also to form peroxides, containing a further amount of oxygen; for instance, sodium, barium, &c.; but these peroxides, while able to combine with other peroxides and per-acids, are apparently unable to give salts with ordinary acids; and (*e*) all such per-compounds are able to give peroxide of hydrogen, to the reactions of which their own are similar. Prof. P. G. Melikoff (Odessa) has done much work on the per-compounds of different elements, and has arrived at the following conclusions (1902): 1. The elements of high atomic weights belonging to the even series form per-acids by the action of H_2O_2. 2 Among the typical elements (see Chap. XV.), only boron forms a per-acid by the action of H_2O_2. 3. The typical elements, having acid properties (for instance, C, N), only form salts of the per-acids by electrolysis. Per-compounds are formed by the action of H_2O_2 on salts as well as on bases and acids. For instance, Kazanetsky showed that potash, K_2CO_3, is able to form with H_2O_2 a saline compound, in which the excess of oxygen must be regarded as united, not to the basic or acid oxide, but to the salt formed by them, or else that H_2O_2 is able to attach itself to entire molecules like water of crystallisation.

give hydrogen compounds, HHO, water, and HCl, hydrochloric acid; sodium compounds, NaHO and NaCl, and a whole series of analogous compounds. Free chlorine in this sense will be ClCl, and hydrogen peroxide HOHO, which indeed expresses its composition, because it contains twice as much oxygen as water does.[28]

Thus in ozone and hydrogen peroxide we see examples of very unstable, easily decomposable (in time spontaneously, and on contact) substances, full of the energy necessary for change,[28a] capable of being easily reconstituted (in this case decomposing with the evolution of heat); they are therefore examples **of unstable chemical equilibria.** If a substance exists, it signifies that it already presents a certain form of equilibrium between those elements of which it is built up. But chemical, like mechanical, equilibria exhibit different degrees of stability or solidity.[29]

Besides this, hydrogen peroxide presents another side of the subject which is none the less clear and of general importance.

Hydrogen unites with oxygen in two degrees of oxidation: water

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[28] Tamman and Carrara showed, by determining the depression (fall of the temperature of the formation of ice, Chapters I. and VII.), that the molecule of peroxide of hydrogen contains H_2O_2, and not HO or H_3O_3.

[28a] The lower oxides of nitrogen and chlorine and the higher oxides of manganese are also formed with the absorption of heat, and therefore, like hydrogen peroxide, act in a powerfully oxidising manner, and are not formed by the same methods as the majority of other oxides. It is evident that, being endowed with a richer store of energy (acquired in combination or by absorption of heat), such substances, compared with others poorer in energy, will exhibit a greater diversity of chemical action with other substances.

[29] If the point of support of a body lies in a vertical line below the centre of gravity, it is in unstable equilibrium. If the centre of gravity lies below the point of support, the state of equilibrium is very stable, and a vibration may take place about this position of stable equilibrium, as in a pendulum or balance, where the body finally assumes a position of stable equilibrium. But if, keeping to the same mechanical example, the body be supported, not on a point, in the geometrical sense of the word, but on a small plane, then the state of unstable equilibrium may be preserved, unless destroyed by external influences. Thus a man stands upright supported on a plane, or on several points of the surfaces of his feet, having the centre of gravity above the points of support. Vibration is then possible, but it is limited, otherwise on passing outside the limit of possible equilibrium another more stable position is obtained, about which vibration becomes more possible. A prism immersed in water may have several more or less stable positions of equilibrium. The same is also true with the atoms in molecules. Some molecules present a state of more stable equilibrium than others. Hence, from this simple comparison, it will be at once evident that the stability of molecules may vary considerably; that one and the same elements, taken in the same number, may give isomerides of different stability; and, lastly, that there may exist states of equilibria which are so unstable, so ephemeral, that they will only arise under particularly special conditions—such, for example, as certain hydrates mentioned in the first chapter (see notes 57, 67, and others). And if in one case the instability of a given state of equilibrium is expressed by its instability with a change of temperature or physical state, it is in other cases expressed by the facility with which it decomposes under the influence either of contact or of the chemical influence of other substances.

or hydrogen oxide, and oxygenated water or hydrogen peroxide; for a given quantity of hydrogen, the peroxide contains twice as much oxygen as does water. This is a fresh example confirming the correctness of the law of multiple proportions, to which we have already referred in speaking of the water of crystallisation of salts. We can now formulate this law—**the law of multiple proportions.** *If two substances A and B (either simple or compound) unite together to form several compounds,* A_nB_m, A_qB_r . . ., *then, having expressed the compositions of all these compounds in such a way that the quantity (by weight or volume) of one of the component parts is a constant quantity* A, *it will be observed that in all the compounds* AB_a, AB_b . . . *the quantities of the other component part,* B, *will always be in commensurable relations, generally in simple multiple proportion—that is, that* $a : b$ . . . *(or m/n is to r/q) can be expressed as the ratio of simple whole numbers; for instance, as* 1 : 2, 2 : 3, *or* 3 : 4. . . .

The analysis of water shows that in 100 parts by weight it contains 11·19 parts by weight of hydrogen and 88·81 of oxygen, and the analysis of peroxide of hydrogen shows that it contains 94·07 parts of oxygen to 5·93 parts of hydrogen. Here the analyses are expressed, as they generally are, in percentages; that is, they give the amounts of the elements in a hundred parts by weight of the substance. The direct comparison of the percentage compositions of water and hydrogen peroxide does not reveal any simple relation. But such a relation is immediately apparent if we calculate the compositions of water and hydrogen peroxide, taking either the quantity of oxygen or the quantity of hydrogen as a constant quantity—for instance, unity. The proportions show that in water there are contained eight parts of oxygen to one part of hydrogen, and in hydrogen peroxide sixteen parts of oxygen to one part of hydrogen; or one-eighth part of hydrogen in water and one-sixteenth part of hydrogen in hydrogen peroxide to one part of oxygen. Naturally, the analysis does not give these figures with absolute exactness—it gives them within a certain degree of error—but they approximate, as the error diminishes, to the limit 1 : 2 here given.

An exactly similar multiple proportion is observed in the composition of all other well-investigated definite chemical compounds,[30]

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[30] When, for example, any element forms several oxides, these are subject to the law of multiple proportions. For a given quantity of the non-metal or metal the quantities of oxygen in the different degrees of oxidation will stand as 1 : 2, or as 1 : 3, or as 2 : 3, or as 2 : 7, and so on. Thus, for instance, copper combines with oxygen in at least two proportions, forming the oxides found in nature, and called the suboxide and the oxide of copper, Cu_2O and CuO; the oxide contains twice as much oxygen as the suboxide. Lead also presents two degrees of oxidation, the oxide and dioxide, and in the latter

and therefore the law of multiple proportions is accepted in chemistry as the starting-point from which other considerations proceed.

The law of multiple proportions was discovered at the beginning of the *last* century by **John Dalton**, of Manchester, *in investigating* the compounds of carbon with hydrogen. It appeared that two gaseous compounds of these substances—marsh gas, CH_4, and olefiant gas, C_2H_4, contain, for one and the same quantity of hydrogen, quantities of carbon which stand in multiple proportion, marsh gas containing relatively half as much carbon as olefiant gas. Although the analysis of that time was not exact, still the accuracy of this law, recognised by Dalton, was confirmed by later and more accurate investigations. On establishing the law of multiple proportions, Dalton gave a hypothetical explanation for it. This explanation is based on the atomic theory of matter. In fact, the law of multiple proportions may be very easily understood by admitting the atomic structure of matter.

The **essence of the atomic theory** is that matter is supposed to consist of an agglomeration of small and indivisible (by natural forces) parts—atoms—which do not fill up the whole space occupied by a substance, but stand apart from each other, as the sun, planets, and stars do not fill up the whole space of the universe, but are at a distance from each other.[30a] The form and properties of substances are deter-

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there is twice as much oxygen as in the former, the formulæ being PbO and PbO_2. When a base and an acid are capable of forming several kinds of salts, normal, acid, basic, and anhydro-, it is found that these also clearly exemplify the law of multiple proportions. This was demonstrated by Wollaston soon after the discovery of the law in question. We saw in the first chapter that salts show different degrees of combination with water of crystallisation, and that these obey the law of multiple proportions. By endeavouring in Chap. I. to prove hypothetically that in solutions we have nothing else but the liquid products of the dissociation of definite hydrates which are subject to the law of multiple proportions, it is my aim to bring also this class of indefinite compounds under the general principle enunciated by Dalton; just as astronomers have discovered a proof and not a negation of the laws of Newton in the phenomena known as perturbations.

[30a] I have no doubt that the atomic theory, so steadfastly applied, after its adoption in chemistry, to all natural science in the nineteenth century, has its philosophical *defects proper to materialism.* Yet it cannot be denied that atomism presents a sublime generalisation in harmony with the fundamental principles of philosophy, for it directly assimilates the structure of the universe (in the form in which it has been revealed by the conquests of astronomy—consisting of solitary suns and planets separated by space but *united by reacting forces*) to the structure of matter out of atoms, and by so doing greatly facilitates the comprehension of things and phenomena. According to this view, a molecule of matter is as complex as an entire universe, and it contains its solitary bodies—atoms—maintained, like the suns and planets, by their proper forces in *mobile but stable equilibrium, its systems, &c.* One of the merits of atomism is that it has brought the infinitely small into harmony with the infinitely great, and by so doing has gained new life. The natural philosophy of modern times has the further merit over that of former ages, that it no longer regards man as the pivot of the universe, but *consciously submits itself to harmonious, coherent,* and logical laws embracing all time

mined by the positions of their atoms in space and by their state of motion, whilst the reactions accomplished by substances are regarded as redistributions of the relative positions of atoms and as changes in their motion. The atomic representation of matter arose in very ancient times,[31] and until recently was at variance with the dynamical

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and space and extending alike over the immensity of the heavens and the infinitesimal atom. The radical defect of modern atomism, I think, lies in the vagueness of the conception of the 'ether' filling both interplanetary and interatomic space, but in directing its chief attention to the investigation of phenomena which take place in 'ether' (electric, luminiferous, &c.), modern science is, I think, following the right direction for revealing the hidden mysteries of nature. Modern science endeavours to, but cannot yet clearly, interpret by means of ether, as a substance material, though imponderable and chemically active, yet not giving chemically ponderable bodies. This is one of the problems of science which have been bequeathed to us by the nineteenth century.

[31] Leucippus, Democritus, and especially Lucretius, in the classical ages, represented matter as made up of atoms—that is, of parts incapable of further division. The geometrical impossibility of such an admission, as well as the conclusions which were deduced by the ancient atomists from their fundamental propositions, prevented other philosophers from following them, and the atomic doctrine, like very many others, lived in the imaginations of its followers without being ratified by fact. Between the present atomic theory and the doctrine of the above-named ancient philosophers there is naturally a remote historical connection, as between the doctrines of Pythagoras and *Copernicus*, but they are essentially different. For us the atom is indivisible, not in the geometrical abstract sense, but only in a physical and chemical sense. It would be better to call the atoms indivisible **individuals**. The Greek 'atom' corresponds with the Latin 'individual,' both according to the etymology and original sense of the words, but in course *of time these two words have acquired a different meaning.* The 'individual' *is mechanically* and geometrically divisible, and only indivisible in a special sense. The earth, the sun, a man, and a fly are individuals, although geometrically divisible. Thus the 'atoms' of contemporary science, indivisible in a chemical sense, form those units with which we *are concerned in the investigation of the natural phenomena of matter,* just as a *man* is an indivisible unit in the investigation of social relations, or as the stars, planets, and luminaries serve as units in astronomy. The formation of the vortex hypothesis, in which, as we shall afterwards see, atoms are entire whirls, mechanically complex, although physico-chemically *indivisible, clearly shows that the scientific men of our time, in* holding to the atomic theory, have only borrowed the word and form of expression from the ancient philosophers, and not the essence of their atomic doctrine. It is erroneous to imagine that the contemporary conceptions of the atomists are nothing but the repetition of the metaphysical reasonings of the ancients. To show the true *meaning* of the atomism of the ancient philosophers, and the profound difference between their points of argument and those of contemporary men of science, I cite the following fundamental propositions of Democritus (B.C. 470–380) as the best expounder of the atomic doctrine of the ancients:—(1) Nothing can proceed from nothing, nothing that exists (and hence matter) can disappear or be destroyed, and every change consists only of a combination or separation. (2) Nothing is accidental, there is a reason and necessity for everything. (3) All except atoms and vacua is reason and not existence. (4) The atoms, which are infinite in number and form, constitute the visible universe by their motion, impact, and consequent revolving motion. (5) The variety of objects depends only upon a difference in the number, form, and order of the atoms of which they are formed, and not upon a qualitative difference of their atoms, which only act upon each other by pressure and impact. (6) The spirit, like fire, consists of minute spherical, smooth, and very mobile and all-penetrating atoms, whose motion forms the phenomenon of life. These Democritan, chiefly metaphysical, principles of atomism are so essentially different from the principles of the present atomic doctrine, which is exclusively applied to explaining the

hypothesis, which considers matter as only a manifestation of forces. At the present time, however, the great majority of scientific men uphold the atomic hypothesis, but the present conception of an atom is quite different from that of the ancient philosophers. An atom at the present day is regarded rather as an ultimate, measurable individual or unit, which is indivisible by physical[32] and chemical forces, whilst the atom of the ancients was indivisible even in a geometrical sense, that is, infinitely small. When **Dalton** (1804) discovered the law of multiple proportions, he pronounced himself in favour of the atomic doctrine, because it enables this law to be very easily understood. If the divisibility of every element has a limit, namely, the atom, then the atoms of elements are the extreme limits of all divisibility, and if they differ from each other in their nature, the formation of a compound from elementary matter must consist in the aggregation of several different atoms into one whole or system of atoms, now termed **particles or molecules.** As atoms can only combine in a system in their entire masses, it is evident that not only the law of definite composition, but also that of multiple proportions, must apply to the combination of atoms with one another; for one atom of a substance can combine with one, two, or three atoms of another substance, or in general one, two, or three atoms of one element are able to combine with one, two, or three atoms of another, this being the essence of the law of multiple proportions. Many chemical and physical data are well explained by the aid of the atomic theory. The displacement of one element by another follows the law of equivalence. In this case one or several atoms of a given element take the place of one or several atoms of another element in its compounds. The atoms of different substances can be mixed together in the same sense as sand can be mixed with clay. They do not unite into one whole—i.e., there is not a perfect blending in the one or the other case, but only a juxtaposition, a homogeneous whole being formed from individual parts. This is the first and most simple method of applying the atomic theory to the explanation of chemical phenomena.[33]

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phenomena of the external world, that it may be useful to mention the essence of the atomic propositions of Boscovitch, a Slav who lived in the middle of the eighteenth century, and who is regarded as the founder of the modern atomic doctrines, which, however, did not take hold upon the minds of scientific men, and were rarely applied, prior to the time of Dalton—i.e., until the beginning of the nineteenth century. The **doctrine of Boscovitch** was enunciated by him in 1758–1764 in his *Philosophiæ naturalis theoria reducta ad unicam legem virium in natura existentium.* Boscovitch considers matter to be composed of atoms, and the atoms to be the points or centres of forces (just as the stars and planets may be considered as points of space), acting between bodies and their parts. These forces vary with the distance, so that beyond a certain very small distance all atoms, and hence also their aggregates, are attracted according to Newton's law, but at less distances, wavelike spheres of gradually decreasing attraction and *increasing (as the distance decreases)* repulsion alternate, until at last at a minimum distance only the repellent action remains. Atoms, therefore, cannot merge into each other. Consequently, the atoms are held at a certain distance from each other, and therefore occupy space. Boscovitch compares the spheres of repulsion surrounding the atoms to the spheres of action of firing of a detachment of soldiers. According to his doctrine, atoms are indestructible, do not merge into each other, have mass, and are everlasting and mobile under the action of the forces proper to them. Maxwell rightly calls this hypothesis the 'extreme' among those existing to explain matter, but many aspects of Boscovitch's doctrine repeat themselves in the views of our day, with this essential difference, that instead of a mathematical point furnished with the properties of mass, the atoms are endowed with a corporality, just as the stars and planets are corporal, although in certain aspects of their interaction they may be regarded as mathematical points. In my opinion, the atomism of our day must first of all be regarded merely as a convenient method for the investigation of ponderable matter, a working hypothesis. As a geometrician in reasoning about curves represents them as formed of a succession of straight lines, because such a method enables him to analyse the subject under investigation, so the scientific man applies the atomic theory as a means of analysing the phenomena of nature. Naturally there are people now, as in ancient times, and as there always will be, who apply reality to imagination, and therefore there are to be found atomists of extreme views; but it is not in their spirit that we should acknowledge the great services rendered to all science by the atomic doctrine, which, while it has been essentially independently developed, is, if it be desired to reduce all ideas to the teachings of the ancients, a union of the ancient dynamical and atomic doctrines.

[32] Dalton and many of his successors distinguished the atoms of elements and compounds, in which they clearly symbolised the difference between their opinion and the representations of the ancients. At the present time, only the individual particles of the elements, indivisible by physical and chemical forces, are termed atoms, while those of compounds indivisible under physical changes are termed molecules: these latter are divisible into atoms by chemical forces. But the atoms of simple bodies according to many contemporary men of science (Crookes, J. Thomson, Lord Kelvin, and others, especially among the English) split up, under certain circumstances, into primary infinitesimal parts (electrons, radiant matter, &c.), which clearly proves that many now consider the atom to be divisible. But here we stand evidently on the very limits of contemporary knowledge, and I therefore think it my duty to advise the beginner to refrain from this province of thought, for there is here much that is possible, but nothing certain.

[33] In the present condition of science, either the atomic or the dynamical hypothesis is inevitably *obliged to* admit the existence of an invisible and imperceptible motion in matter, without which it is impossible to understand either light or heat, gaseous pressure, or any of the mechanical, physical, or chemical phenomena. The ancients saw vital motion in animals only, but to us the smallest particle of matter, endowed with *vis viva*, or energy in some degree or other, is incomprehensible without self-existent motion. Thus motion has become a conception inseparably knit with the conception of matter, and this has prepared the ground for the revival of the dynamical hypothesis of the constitution of matter. In the atomic theory there has arisen that generalising idea by which the world of atoms is constructed, like the universe of heavenly bodies, of its suns, planets, and meteors, endowed with everlasting force of motion and forming molecules, just as the heavenly bodies form systems like the solar system; and these molecules are only relatively indivisible in the same way as the planets of the solar system are inseparable, and are stable and lasting like the solar system. Such a representation, without necessitating the absolute indivisibility of atoms, expresses all that science can require for a hypothetical representation of the constitution of matter. In closer proximity to the dynamical hypothesis of the constitution of matter is the ofttimes revived **vortex**

A certain number of atoms n of an element A in combining with several atoms m of another element B give a compound A_nB_m, each

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hypothesis. Descartes first endeavoured to develop it, while Helmholtz and Thomson (Lord Kelvin) gave it a fuller and more modern form and many scientific men applied it to physics and chemistry. The idea of vortex rings serves as the starting-point of this hypothesis; these are familiar to all in the rings of tobacco smoke, and may be artificially obtained by giving a sharp blow to the sides of a cardboard box having a circular orifice and filled with smoke. Phosphoretted hydrogen, as we shall see later on, when bubbling from water always gives very perfect vortex rings in a still atmosphere. In such rings it is easy to observe a constant circular motion about their axes, and to notice the stability the rings possess in their motion of translation. This unchangeable mass, endowed with a rapid internal motion, is likened to the atom. In a medium deprived of friction, such a ring, as is shown by a theoretical consideration of the subject from a mechanical point of view, would be perpetual and unchangeable. The rings are capable of grouping together, and in combining, without being absolutely indivisible, they do not break up into parts. The vortex hypothesis has been established in our times, but it has not been fully developed; it can be applied to the explanation of chemical phenomena, although not readily; it tells us nothing of the nature of the space existing between the rings (just as it is not clear what exists between atoms and between the planets), neither does it tell us what is the nature of the moving substance of the ring, and therefore for the present it only presents the germ of a hypothetical conception of the constitution of matter; consequently I consider that it would be superfluous to speak of it in greater detail.

However, the thoughts of investigators are now (and naturally will be in the future), as they were in the time of Dalton, often turned to the question of the limitation of the mechanical division of matter, and the atomists have searched for an answer in the most diverse spheres of nature. In order to show how closely all the provinces of natural science are bound together, I select one of the methods of attacking this problem which does not in any way refer to chemistry.

Wollaston suggested investigating the **atmosphere of the heavenly bodies** as a means for confirming the existence of atoms. If the divisibility of matter be infinite, then air must extend throughout the entire space of the heavens, just as it extends all over the earth by virtue of its elasticity and diffusion. If the infinite divisibility of matter be admitted, it is impossible that any portion of the whole space of the universe can be entirely void of the component parts of our atmosphere. But if matter be divisible down to a certain limit only—namely, down to the atom—then there *can exist* a heavenly body void of an atmosphere; and if such a body be discovered, it would serve as an important factor in determining the validity of the atomic doctrine. The moon has long been regarded as such a luminary, and on this account, and especially because of its proximity to the earth, has been cited as the best proof of the validity of the atomic doctrine. This proof is apparently (Poisson) deprived of some of its force by the possibility of the transformation of the component parts of our atmosphere into a solid or liquid state at immense heights above the earth's surface, where the temperature is exceedingly low; but a series of researches (Pouillet) has shown that the temperature of the heavenly space is comparatively not so very low, and is attainable by experimental means, so that at the low existing pressure the liquefaction of the gases of the atmosphere cannot be expected even on the moon. Hence the absence of an atmosphere about the moon, if it were not subject to doubt, would be counted a forcible proof of the atomic theory. As a proof of the absence of a lunar atmosphere, it is cited that the moon, in its independent motion between the stars, when eclipsing a star—that is, when passing between the eye and the star—does not show any signs of refraction at its edge; the image of the star does not alter its position in the heavens on approaching the moon's surface; consequently there is no atmosphere on the moon's surface capable of refracting light rays. It is on this that the proof of the absence of a lunar atmosphere is based. But this is a very weak proof, and there are even facts which are in exact contradiction to it, and by

molecule of which will contain the atoms of the elements A and B in this ratio, and therefore the compound will present a **definite composition,** expressed by the formula A_nB_m, where A and B are the weights of the atoms, and n and m their relative numbers. If the same elements A and B, in addition to A_nB_m, also yield another compound A_rB_q, then by expressing the composition of the first compound by $A_{nr}B_{mr}$ (and

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means of which the existence of a lunar atmosphere may be proved. The entire surface of the moon is covered with a number of mountains, having, in the majority of cases, the conical form natural to volcanoes. The volcanic character of the lunar mountains was confirmed in October 1866, when a change was observed in the form of one of them (the crater Linnea). These mountains must be on the edge of the lunar disc. Seen in profile they screen one another and interfere with observations on the surface of the moon, so that when looking at the edge of the lunar disc we are obliged to make our observations not on the moon's surface, but at the summits of the lunar mountains. These mountains are higher than those on our earth, and consequently at their summits the lunar atmosphere must be exceedingly rarefied, even if it possess an observable density at the surface. Knowing the mass of the moon to be eighty-two times less than that of the earth, we are able to show that our atmosphere at the moon's surface would be about twenty-eight times lighter than it is on the earth, and consequently at the very surface of the moon the refraction of light by the lunar atmosphere must be very slight, whilst at the heights of the lunar mountains it must be imperceptible, and would be lost within the limits of experimental error. So that the absence of refraction of light at the edge of the moon's disc cannot as yet be urged in proof of the absence of a lunar atmosphere. There is even a series of observations obliging us to admit the existence of such an atmosphere. These researches are due to Sir John Herschel. This is what he writes: 'It has often been remarked that during the eclipse of a star by the moon there occurs a peculiar optical illusion; it seems as if the star before disappearing passed over the edge of the moon and is seen through the lunar disc, sometimes for a fairly long period of time. I myself have observed this phenomenon, for the occurrence of which there is perfectly trustworthy evidence. I ascribe it to optical illusion; but it must be admitted that the star might have been seen on the lunar disc through some deep ravine on the moon.' Geniller, in Belgium (1856), following the opinion of Cassini, Euler, and others, gave an explanation of this phenomenon: he considers it due to the refraction of light in the valleys of the lunar mountains which occur on the edge of the lunar disc. In fact, although these valleys do not probably present the form of straight ravines, yet it may sometimes happen that the light of a star is so refracted that its image might be seen, notwithstanding the absence of a direct path for the light-rays. He then goes on to remark that the density of the lunar atmosphere must be variable in different parts owing to the very long nights on the moon. On the dark, or non-illuminated portion, owing to the long nights, which last thirteen of our days and nights, there must be excessive cold, and hence a denser atmosphere, whilst, on the contrary, on the illuminated portion the atmosphere must be much more rarefied. This variation in the temperature of the different parts of the moon's surface explains also the absence of clouds, notwithstanding the possible presence of air and aqueous vapour, on the visible portion of the moon. The presence of atmospheres round the sun and planets, judging from astronomical observations, may be considered as fully proved. On Jupiter and Mars bands of clouds may even be distinguished.

Thus the atomic doctrine, admitting only a finite mechanical divisibility, must be, as yet at least, accepted merely as a means, similar to that which a mathematician employs when he breaks up a continuous curvilinear line into a number of straight lines. There is a simplicity of representation in atoms, but there is no absolute necessity to have recourse to them. The conception of the individuality of the parts of matter exhibited in chemical elements is alone necessary and certain.

this is the same composition as A_nB_m), and that of the second compound by $A_{rn}B_{qm}$, we have the law of multiple proportions, because for a given quantity of the first element, A_{rn}, there occur quantities of the second element bearing the same ratio to each other as *mr* bears to *qn*; and as *m*, *r*, *q*, and *n* are whole numbers, their products are also whole numbers, and it is this that is expressed by the law of multiple proportions. Consequently the atomic theory is in accordance with and evokes the first laws of definite chemical compounds: the law of definite composition and the law of *multiple proportions*.

The same thing is seen in the relation of the atomic theory to the third law of definite chemical compounds—the **law of reciprocal combining weights**—which is as follows:—If a certain weight of a substance C combine with a weight *a* of a substance A, and with a weight *b* of a substance B, then, also, the substances A and B will combine together in quantities *a* and *b* (or in multiples of them). This follows at once from our conception of atoms. Let A, B, *and* C be the weights of the atoms of the three elements, and for simplicity of reasoning let us suppose that combination takes place between single atoms. It is evident that if the element C gives AC and BC, then the elements A and B will give a compound AB, or A_nB_m. And this is what we really find in nature. Sulphur combines with hydrogen and with oxygen. Sulphuretted hydrogen contains thirty-two parts by weight of sulphur to every two parts by weight of hydrogen; this is expressed by the formula H_2S. Sulphur dioxide, SO_2, contains thirty-two parts of sulphur and thirty-two parts of oxygen, and therefore we conclude, from the law of combining weights, that oxygen and hydrogen will combine in the proportion of two parts of hydrogen and thirty-two parts of oxygen, or in some multiples of these numbers. And we have seen this to be the case. Hydrogen peroxide contains thirty-two parts of oxygen, and water sixteen parts, to every two parts of hydrogen; and so it is in all other cases. This consequence of the atomic theory is in accordance with nature and with the results of analysis, and is one of the most important laws of chemistry. It is a law, because it indicates the *relation between* the weights of substances entering into chemical combination. Further, it is an eminently exact law, and not an approximate one. The law of combining weights is a law of nature, and by no means an hypothesis, for even if the entire theory of atoms be refuted, the laws of multiple proportions and of combining weights will still remain, inasmuch as they are the expression of facts. They may be foreseen from the atomic theory, and historically the law of combining weights is intimately connected with this theory; they are, however, not identical, but only connected, with it. The law of combining weights is formulated with great ease, and is an immediate consequence of the atomic theory, without which it would be difficult to understand. Data for its evolution existed previously, but it was not formulated until those data were interpreted by the atomic theory, an hypothesis which up to the present time has contradicted neither experiment nor fact, and is useful and of general application. Such is the nature of hypotheses. They are indispensable to science; they bestow an order and simplicity which are only attainable with difficulty without their aid. The whole history of science is a proof of this. And it may therefore be truly said that it is better to hold to an hypothesis which may afterwards prove untrue than to have none at all. Hypotheses facilitate scientific work and render it consistent. Like the plough of the husbandman, they help forward the work of the labourer in the search for truth.

CHAPTER V

NITROGEN AND AIR

Although oxygen is chemically the most active component of the atmosphere surrounding us, nitrogen forms the greater part of it by weight and by volume, and indeed constitutes over three-quarters (by volume) of the atmosphere; and as **nitrogen** is only slightly lighter than oxygen, it forms about three-quarters of the air by weight also. While entering in so considerable a quantity into the composition of air, nitrogen does not seem to play any active part in the atmosphere, the chemical action of which is mainly dependent on the oxygen it contains. But a correct idea of the part played by the nitrogen in the air can only be formed when we have learnt that animals cannot exist in pure oxygen, but pass into an abnormal state, and even die; and that the nitrogen of the air, although slowly, forms numerous compounds, many of which play a most important part in nature, especially in the life of organisms. Plants, and especially animals, besides requiring free oxygen, are absolutely dependent upon nitrogenous compounds for their nutrition, because these form their most chemically active components. However, neither plants[1] nor animals directly absorb the gaseous nitrogen of the air, but take it up from ready-formed nitrogenous compounds; further, plants are nourished by the nitrogenous substances contained in the soil and water, and animals by the nitrogenous substances contained in plants and in other animals. Atmospheric electricity is capable of aiding the passage of gaseous nitrogen into nitrogenous compounds, as we shall afterwards see, and the resultant substances are carried to the soil by rain, and there serve for the nourishment of plants. Plentiful harvests, fine crops of hay, vigorous growth of trees—other conditions being equal—are only obtained when the soil contains **ready-formed nitrogenous compounds**, consisting either of those which occur in air and water, or of the residues of the decomposition of other plants or animals (as in manure). The nitrogenous substances contained in animals have their

origin in those substances which are formed in plants. Thus the nitrogen of the atmosphere is the origin of all the nitrogenous substances occurring in animals and plants, although not directly so, but only after first combining with the other elements of air.

The nitrogenous compounds which enter into the composition of plants and animals are of primary importance; no vegetable or animal cell—that is, the elementary form of organism—exists without containing a nitrogenous substance, and, moreover, the life of the organism manifests itself primarily in these nitrogenous substances. The germs, seeds, and those parts by which cells multiply abound in nitrogenous substances; the sum total of the phenomena which are proper to organisms depends primarily on the chemical properties of the readily changeable complex (albuminous) nitrogenous substances which enter into their composition. It will be sufficient, for instance, to point out the fact that vegetable and animal organisms, clearly distinguishable as such, are characterised by the different degrees of energy they manifest, and at the same time by a difference in the amounts of nitrogenous substances they contain. In plants, which compared with animals possess but little activity, being incapable of independent movement, &c., the proportion of nitrogen is very much less than in animals, whose tissues are almost exclusively formed of nitrogenous substances. It is remarkable that the nitrogenous parts of plants, chiefly of the lower orders, sometimes present both forms and properties resembling those of animal organisms; this is seen, for example, in the zoospores of seaweeds, or those parts by means of which the latter multiply themselves. On leaving the seaweed these zoospores resemble in many respects the lower orders of animal life, having, like the latter, the property of motion. They also approach the animal kingdom in their composition, their outer coating containing nitrogenous matter. Directly the zoospore becomes covered with that non-nitrogenous or cellular coating which is proper to all the ordinary cells of plants, it loses all resemblance to an animal organism and becomes a small plant. It may be thought from this that the cause of the difference between the vital processes of animals and those of plants lies in the different amounts of nitrogenous substances they contain. The nitrogenous substances which occur in plants and predominate in animals belong to a series of exceedingly complex and very changeable chemical compounds; their elementary composition alone shows this, for besides nitrogen they contain carbon, hydrogen, oxygen, and sulphur. Being distinguished by a very great instability under many conditions in which other compounds remain unchanged, these substances are fitted for those perpetual and regular changes which form the first condition

[1] See note 15^{a}.

of vital activity. These complex and changeable nitrogenous substances of the organism are called **proteïd substances.** The white of eggs is a familiar example of such substances. They are also contained in the tissues of the flesh of animals, the curdy elements of milk, the glutinous matter of wheaten flour, or so-called gluten, which forms the chief component of macaroni, &c.

Nitrogen occurs in the earth's crust, in compounds either forming the remains of plants and animals, or derived from the nitrogen of the atmosphere as a consequence of its combination with the other component parts of the air. It is not found in other forms in the earth's crust; so that nitrogen must be considered, in contradistinction to oxygen, as an element which is purely superficial, and extends hardly at all to the depths of the earth.[1a]

Nitrogen is liberated in a free state in the decomposition—for example, by combustion—of the **nitrogenous organic substances** entering into the composition of organisms. All organic substances burn when heated to redness with oxygen (or substances readily yielding it, such as oxide of copper); the oxygen combines with the carbon, sulphur, and hydrogen, and the nitrogen is evolved in a free state, because at a high temperature it forms no stable compound, but remains uncombined. Carbonic anhydride and water are formed from the carbon and hydrogen respectively, and therefore to obtain pure nitrogen it is necessary to remove the carbonic anhydride from the gaseous products obtained (after drying). This may be done very easily by the action of alkalies—for instance, caustic soda. The amount of nitrogen in organic substances is determined by a method founded on this.

It is also very easy to obtain **nitrogen from air,** because oxygen combines with many substances. Either phosphorus or metallic copper is usually employed for removing the oxygen from air, but, naturally, a number of other substances may also be used. If a small

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[1a] The reason why there are no nitrogenous substances within the earth's mass other than those which have come there with the remains of organisms, or from the air with rain-water, must be looked for in two circumstances. In the first place, in the instability of many nitrogenous compounds, which are liable to break up with the formation of gaseous nitrogen; and in the second place in the fact that the salts of nitric acid, forming the product of the action of air on many nitrogenous and especially organic compounds, are very soluble in water, and on penetrating into the depths of the earth (with water) give up their oxygen. The result of the changes of the nitrogenous organic substances which fall into the earth is without doubt frequently, if not invariably, the formation of gaseous nitrogen. Thus the gas evolved from coal always contains much nitrogen (together with marsh gas, carbonic anhydride, and other gases). The statement that a small amount of nitrogen is evolved during volcanic eruptions cannot be taken as proved, because air easily penetrates into the depths of the earth, whence it is ejected in volcanic disturbances.

saucer on which a piece of phosphorus is laid be placed on a cork floating on water, and the phosphorus be lighted, and the whole covered with a glass bell jar, the air under the jar will be deprived of its oxygen, and nitrogen alone remain; hence, on cooling, the water will rise to a certain extent in the bell jar. The same object (obtaining nitrogen from the air) is attained much more conveniently and perfectly by passing air through a red-hot tube containing copper filings. At a red heat, metallic copper combines with oxygen and gives a black powdery copper oxide. If the layer of copper be sufficiently long and the current of air slow, all the oxygen will be absorbed, and nitrogen alone will pass from the tube.[2]

Nitrogen may also be procured from many of its **compounds with oxygen**[3] **and hydrogen,**[4] but the best fitted for this purpose is a saline mixture containing, on the one hand, a compound of nitrogen with oxygen, termed nitrous anhydride, N_2O_3, and, on the other hand, ammonia (taken as a salt, Chap. VI.), NH_3—that is, a compound of nitrogen with hydrogen. By heating such a mixture, the oxygen of the nitrous anhydride combines with the hydrogen of the ammonia, forming water, and gaseous nitrogen is evolved, $2NH_3+N_2O_3=3H_2O+N_4$. Nitrogen is obtained by this method in the following manner:—A solution of caustic potash is saturated with nitrous anhydride, by which means potassium nitrite is formed, while a solution of hydrochloric acid is saturated with ammonia, by which means a saline substance called sal-ammoniac, NH_4Cl, is formed. The two solutions thus prepared are mixed together and heated. Reaction takes place according to the equation: $KNO_2+NH_4Cl=KCl+2H_2O+N_2$. This reaction proceeds in virtue of the fact that potassium nitrite and ammonium chloride are salts which, on interchanging their metals, give potassium chloride and ammonium nitrite, NH_4NO_2, which breaks up into water

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[2] In the presence of solutions of acids, copper (best as turnings, which present a large surface) absorbs oxygen at the ordinary temperature, forming CuO; or, better still, in the presence of a solution of ammonia, when it forms a bluish-violet solution of oxide of copper in ammonia. Nitrogen is very easily procured by this method. A flask filled with copper turnings is closed with a cork furnished with a funnel and stopcock. A solution of ammonia is poured into the funnel, and caused to drop slowly upon the copper. If at the same time a current of air be passed slowly through the flask (from a gasholder), then all the oxygen will be absorbed from it and the nitrogen will pass from the flask. The gas should be washed with water to retain any ammonia that may be carried off with it.

[3] The oxygen compounds of nitrogen (for example, N_2O, NO, NO_2) are decomposed at a red heat by themselves, and under the action of red-hot copper, iron, sodium, &c., they give up their oxygen to the metals, leaving the nitrogen free. According to Meyer and Langer (1885), nitrous oxide, N_2O, decomposes below 900°, although not completely.

[4] Chlorine and bromine (in excess), as well as bleaching powder (hypochlorites), take up the hydrogen from ammonia, NH_3, leaving nitrogen. Nitrogen is best procured from ammonia by the action of a solution of sodium hypobromite on solid sal-ammoniac.

and nitrogen. This reaction does not take place without the aid of heat, but it proceeds very readily at a moderate temperature. Of the resultant substances, the nitrogen alone is gaseous. Pure nitrogen may be obtained by drying the resultant gas and passing it through a solution of sulphuric acid (to absorb a certain quantity of ammonia which is evolved in the reaction).[4a] Before 1894, it was generally thought that nitrogen obtained from air did not differ in any way from that prepared from its compounds (after being purified); but Lord Rayleigh, in determining the weight of a known volume of nitrogen obtained by different methods, found that the nitrogen of air is almost $\frac{1}{200}$ heavier than that extracted from its compounds. Subsequently Lord Rayleigh, together with W. Ramsay, showed that the difference in density was due to the presence in the atmospheric nitrogen of a small amount of an inactive gas resembling nitrogen, which they named **argon**, and of certain other gases of which mention is made at the end of this chapter.[5]

Nitrogen is a gaseous substance which does not differ much in physical properties from air: its density, referred to that of hydrogen, is equal to 13·9—that is, it is slightly lighter than air; one litre of nitrogen weighs 1·251 gram (at 0° and 760 mm.). Nitrogen mixed with oxygen, which is slightly heavier than air, forms air. It is a gas which, like oxygen and hydrogen, is liquefied with difficulty, and is but slightly soluble in water and other liquids. Its absolute boiling-point[5] is about $-146°$. Liquid nitrogen boils at $-193°$, its specific gravity at this temperature being about 0·89. At about $-213°$, in vaporising under diminished pressure, nitrogen solidifies into a colourless snow-like mass. Nitrogen does not burn,[5a] does not support combustion, is not absorbed chemically by any of the reagents used in gas analysis, at least at the ordinary temperature—in a word, it presents a whole series of negative chemical properties. This is expressed by saying that this element has no energy for forming compounds. Although it is capable of forming compounds both with oxygen and hydrogen as well as with carbon, yet these compounds are only formed under special conditions, to which we shall turn our attention directly. At a red heat nitrogen combines with boron, titanium, silicon, barium, magnesium, and lithium,

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[4a] Ammonium nitrite may be prepared separately, only it decomposes with an explosion, and is difficult to deal with (Chap. VI. note 56).

[5] Owing to this, nitrogen obtained from air differs slightly in some of its properties from pure nitrogen, as will be presently explained. There is no need to say that Rayleigh's and Ramsay's discoveries are among the most remarkable ever made in science, and prove to what a high degree of perfection the exact comparative investigation of substances may be brought.

[5a] See note 11a.

forming very stable nitrogenous compounds,[6] whose properties are entirely different from those of nitrogen compounds of hydrogen, oxygen, and carbon. However, the combination of nitrogen with carbon, although it does not take place directly between the elements at a red heat, yet proceeds with comparative ease when a mixture of charcoal with an alkaline carbonate, especially potassium carbonate or barium carbonate, is heated to redness, carbo-nitrides or cyanides of the metals being formed; for instance, $K_2CO_3 + 4C + N_2 = 2KCN + 3CO$.[7]

Nitrogen is found with oxygen in the air, but these two elements do not readily combine. Cavendish, however, in the eighteenth century, showed that **nitrogen combines with oxygen under the influence of a series of electric sparks.** Electric sparks in passing through a moist[8] mixture of nitrogen and oxygen cause these elements to combine, forming reddish-brown fumes of oxides of nitrogen,[9] which with water

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[6] The combination of boron with nitrogen, for instance, is accompanied by the evolution of sufficient heat to raise the mass to redness; titanium combines so easily with nitrogen that it is difficult to obtain it free from that element; lithium and magnesium easily absorb nitrogen at a red heat. It is a remarkable and instructive fact that these compounds of nitrogen are very stable and non-volatile. Carbon (C = 12) with nitrogen gives cyanogen, C_2N_2, which is gaseous and very unstable, and the molecule of which is not large, whilst boron (B = 11) forms a nitrogenous compound which is solid, non-volatile, and very stable. Its composition, BN, is similar to that of cyanogen, but its molecular formula, B_nN_n, is probably greater. Its composition, like those of N_2Mg_3, NNa_3, N_2Hg_3, and of many of the metallic nitrides, corresponds with ammonia in which all the hydrogen is replaced by a metal. A detailed study of the transformations of the nitrides now known may lead to the discovery of many facts in the history of nitrogen.

[7] This reaction, so far as is known, does not proceed beyond a certain limit, probably because cyanogen, CN, itself breaks up into carbon and nitrogen.

[8] Frémy and Becquerel took dry air, and observed the formation of brown vapours of oxides of nitrogen when sparks are passed.

[9] If a mixture of one volume of nitrogen and fourteen volumes of hydrogen be burnt, water and a considerable quantity of nitric acid are formed. It may be partly due to this that a certain quantity of nitric acid is produced in the slow oxidation of nitrogenous substances in an excess of air. This is especially facilitated by the presence of an alkali, with which the nitric acid formed can combine. If a galvanic current be passed through water containing the nitrogen and oxygen of the air in solution, then the hydrogen and oxygen set free combine with the nitrogen, forming ammonia and nitric acid.

When copper is oxidised at the expense of the air at the ordinary temperature in the presence of ammonia, oxygen is absorbed, not only for combination with the copper, but also for the formation of nitric acid.

The combination of nitrogen with oxygen, even, for example, by the action of electric sparks, is not accompanied by an explosion or rapid combination, as in the action of a spark on a mixture of oxygen and hydrogen. This is explained by the fact that heat is not evolved in the combination of nitrogen with oxygen, but is absorbed—an expenditure of energy is required, there being no evolution of energy. In other words, the combination of hydrogen with oxygen is an exothermal reaction, and the combination of nitrogen with oxygen an endothermal reaction.

A condition particularly favourable to the oxidation of nitrogen is the explosion of detonating gas and air if the former be *in excess*. If a mixture of two volumes of detonating gas and one volume of air be exploded, one-tenth of the air is converted form nitric acid,[10] NHO_3. The presence of the latter is easily recognised, not only from its reddening of litmus paper, but also from its acting as a powerful oxidiser, even of mercury. Conditions similar to these occur in nature, during a thunderstorm or in other electric discharges which take place in the atmosphere; whence it may be taken for granted that air and rain-water always contain a certain amount of nitric and nitrous acids.[11] Besides which, Crookes (1892) showed that under certain circumstances, and when electricity of high potential[11a] passes through the air, the combination of nitrogen with oxygen is accompanied by the formation of a true flame. This was also observed previously during the passage of electric discharges through the air.

Further observations showed that under the influence of electric discharges,[12] silent as well as with sparks, nitrogen is able to enter into

into nitric acid, and consequently after the explosion has taken place there remain only nine-tenths of the volume of air originally taken. If a larger proportion of air be taken—for instance, four volumes to two of detonating gas—then the temperature of the explosion is lowered, the volume of air taken remains unchanged, and no nitric acid is formed. This gives a rule to be observed in making use of the eudiometer—namely, that to diminish the force of the explosion not less than an equal volume of air should be added to the explosive mixture. On the other hand a large excess must not be taken, as no explosion would then ensue (see Chapter III., note 34). Probably, in the future, means will be found for obtaining compounds of nitrogen on a large industrial scale by the aid of electric discharges, and by making use of the inexhaustible mass of nitrogen in the atmosphere.

[10] In reality, nitric oxide, NO, is first formed, but with oxygen and water it gives (brown fumes) nitrogen peroxide, which, as we shall afterwards learn, in the presence of water and oxygen gives nitric acid.

[11] The nitric acid contained in soil, river water (Chapter I., note 2), wells, &c., proceeds (like carbonic anhydride) from the oxidation of organic compounds which have fallen into the water, soil, &c.

[11a] Crookes employed a current of 15 ampères at 65 volts, and passed it through an induction coil with 330 vibrations per second, and obtained a flame between the poles placed at a distance of 46 mm., which after the appearance of the arc and flame could be increased to 200 mm. A platinum wire was fused in the flame of the burning nitrogen.

[12] This property of nitrogen, which under normal conditions is inactive, leads to the idea that, under the influence of an electric discharge, gaseous nitrogen changes in its properties, if not permanently like oxygen (electrolysed oxygen or ozone does not react on nitrogen, according to Berthelot), it may be temporarily at the moment of the action of the discharge, just as some substances under the action of heat are permanently affected (that is, when once changed remain so—for instance, white phosphorus passes into red, &c.), whilst others are only temporarily altered (the dissociation of S_6 into S_2 or of sal-ammoniac into ammonia and hydrochloric acid). Such a proposition is favoured by the fact that nitrogen gives two kinds of spectra, with which we shall afterwards become acquainted. It may be that the molecules of gaseous nitrogen, N_2, then give less complex molecules, N, containing one atom, or that the bond between the atoms in the molecules is weakened. Probably under a silent discharge the molecules of oxygen, O_2, are partly decomposed and the individual atoms O combine with O_2, forming ozone O_3.

many reactions with hydrogen and with many hydrocarbons, although these reactions cannot be effected by exposure to a red heat. Thus, for instance, a series of electric sparks passed through a mixture of nitrogen and hydrogen causes these gases to combine and **form ammonia**[13] or nitrogen hydride, NH_3, composed of one volume of nitrogen and three volumes of hydrogen. This combination is limited to the formation of 6 per cent. of ammonia, because ammonia is decomposed, although not entirely ($\frac{24}{100}$), by electric sparks. This signifies that, under the influence of an electric discharge, the reaction, $NH_3 = N + 3H$, is reversible; consequently it is a dissociation, and in it a state of equilibrium is arrived at. The equilibrium may be destroyed by the addition of gaseous hydrochloric acid, HCl, because with ammonia this forms a solid saline compound, sal-ammoniac, NH_4Cl, which (being formed from a gaseous mixture of 3H, N, and HCl) fixes the ammonia. The remaining mass of nitrogen and hydrogen, under the action of the sparks, again forms ammonia, and in this manner *solid sal-ammoniac is obtained to the end by the action of a series of electric sparks on a mixture of gaseous nitrogen, hydrogen, and hydrogen chloride.* This is also, like the production of nitric acid,[14] an instance of the synthesis of nitrogenous compounds from gaseous nitrogen. Berthelot (1876) showed that, under the action of a silent discharge, many non-nitrogenous organic substances (benzene, C_6H_6, cellulose in the form of paper, gum, $C_6H_{10}O_5$, &c.) absorb nitrogen and form complex nitrogenous compounds, which are capable, like albuminous substances, of evolving their nitrogen as ammonia when heated with alkalies.[15]

[13] This reaction, discovered by Chabrié and investigated by Thénard, was only rightly understood when Deville applied the principles of dissociation to it.

[14] The action of nitrogen on acetylene (Berthelot) resembles this reaction. A mixture of these gases under the influence of a silent discharge gives hydrocyanic acid, $C_2H_2 + N_2 = 2CNH$. This reaction cannot proceed beyond a certain limit because it is reversible.

[15] Berthelot successfully employed electricity of even feeble potential in these experiments, which fact led him to think that in nature, where the action of electricity takes place very frequently, a part of the complex nitrogenous substances may be formed in this way from the gaseous nitrogen of the air.

As the nitrogenous substances of organisms play a very important part in them (organic life cannot exist without them), and as the nitrogenous substances introduced into the soil are capable of invigorating its crops (of course in the presence of the other nourishing principles required by plants), the question of the means of converting the atmospheric nitrogen into the nitrogenous compounds of the soil, or into **assimilable nitrogen** capable of being absorbed by plants and of forming complex (albuminous) substances in them, is one of great theoretical and practical interest.

One thousand tons of farmyard manure do not generally contain more than four tons of nitrogen in the form of complex nitrogenous substances, and this amount of nitrogen is contained in twenty tons of ammonium sulphate, so that the effect of a large mass of farmyard manure may, as regards the introduction of nitrogen, be produced by small quantities of artificial nitrogenous fertilisers (see note 15a).

By such indirect methods does the gaseous nitrogen of the atmosphere yield its primary compounds, in which form it enters into plants, and is elaborated in them into complex albuminous substances.[15a] But, starting from a given compound of nitrogen with hydrogen or oxygen, we may, without the aid of organisms, obtain, as will afterwards be partially indicated, most varied and complex nitrogenous substances, which cannot by any means be formed directly from gaseous nitrogen. In this we see an example, not only of the difference between an element in the free state and an intrinsic element (as a simple body nitrogen is an indifferent gas, but as an element it forms many very active compounds and determines their individual peculiarities; see following chapter), but also of those circuitous or *indirect methods* by which substances are formed in nature. The discovery, prognostication, and, in general, the study of such indirect methods of the preparation and formation of substances form one of the essential problems of chemistry. From the fact that A does not act at all on B, it must not be concluded that a compound AB is not to be formed. The substances A and B contain elementary atoms which occur in AB, but their state or the nature of their motion may not be at all that which is required for the formation of AB, and in this substance the chemical state of the elements may be as different as the states of the atoms of oxygen in ozone and in water. Thus free nitrogen is inactive; but in its compounds it very easily enters into changes and is distinguished by great activity. An acquaintance with the compounds of nitrogen confirms this. But, before entering on this subject (Chap. VI.), let us consider air as a mass containing free nitrogen, and as the medium in which the majority of natural phenomena take place.

Judging from what has been already stated, it will be evident that **atmospheric air**[16] consists of a mixture of several gases and vapours.

[15a] Although the numerous, and as far as possible accurate and varied researches made in the physiology of plants have proved that the higher forms of plants are not capable of directly absorbing the nitrogen of the atmosphere and converting it into complex albuminous substances, still it has been long and repeatedly observed that the amount of nitrogenous substances in the soil is increased by the cultivation of plants of the bean (leguminous) family, such as the pea, acacia, &c. A closer study of these plants has shown (Hellriegel) that this is connected with the formation of peculiar nodular swellings in their roots caused by the growth of peculiar micro-organisms (bacteria) which live in the soil with the roots, and are capable of absorbing nitrogen from the air, i.e., of converting it into assimilated nitrogen. This branch of plant physiology, which forms another proof of the important part played by micro-organisms in nature, cannot be discussed in this work, but it should be mentioned, since it is of great theoretical and practical interest.

[16] Under the name of atmospheric air the chemist and physicist understand ordinary air containing nitrogen and oxygen, argon, and similar elementary gases, not absorbed

Some of them are met with in it in nearly constant proportions, whilst others, on the contrary, are very variable in their amount. The chief component parts of air, placed in the order of their relative amounts, are the following: nitrogen, oxygen, aqueous vapour, carbonic anhydride, argon, krypton, xenon, neon, nitric acid, salts of ammonia, hydrogen, helium, oxides of nitrogen, and also ozone, hydrogen peroxide, and complex organic nitrogenous substances. Besides these, air generally contains water, as spray, drops, and snow, and particles of solids, perhaps of cosmic origin in certain instances, but in the majority of cases proceeding from the mechanical translation of solid particles from one locality to another by the wind. These small solid and liquid particles (having a large surface in proportion to their weight) are suspended in air just as solid matter is suspended in turbid water: they often settle on the surface of the earth, but the air is never entirely free from them because they are never in a state of complete rest. Then, again, as everyone knows by experience, air not infrequently contains incidental traces of various substances. These incidental substances sometimes act injuriously and sometimes act as carriers of infectious diseases.

In the air of the various countries of the earth, at different latitudes and at different altitudes above its surface, on the ocean or on the dry land—in a word, in the air of the most diverse localities of the earth—the oxygen and nitrogen are found everywhere to be in a constant ratio, and are accompanied by small amounts of argon, krypton, and other gases exhibiting an inactivity similar to that of nitrogen (see later portion of this chapter). This is, moreover, self-evident from the fact that the air is constantly diffusing (intermixing by virtue of the internal motion of the gaseous particles), and is also put into motion and mixed by the

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(like H_2O and CO_2) by sulphuric acid or alkalies at the ordinary temperature, although these latter component parts of air have a very important influence on the living matter of the earth's surface. That air is so represented in science is based on the fact that the elementary components are met with in air in a constant quantity, whilst the H_2O and CO_2 are variable. The solid impurities may be separated from air required for chemical or physical research by simple filtration through a long layer of cotton-wool placed in a tube. Organic impurities are removed by passing the air through a solution of potassium permanganate. The carbonic anhydride contained in air is absorbed by alkalies—best of all, soda-lime, which in a dry state in porous lumps absorbs it with exceeding rapidity and completeness. Aqueous vapour is removed by passing the air over calcium chloride, strong sulphuric acid, or phosphoric anhydride. Air thus purified is accepted as containing only nitrogen and oxygen, argon, &c., although in reality it still contains a certain quantity of hydrogen and hydrocarbons, from which it may be purified by passing over copper oxide heated to redness. The copper oxide then oxidises the hydrogen and hydrocarbons—it burns them, forming water and carbonic anhydride, which may be removed as above described. When it is said that, in the determination of the density of gases, the weight of air is taken as unity, it is understood to be air purified in this manner.

wind, so that it becomes equalised in its composition over the entire surface of the earth. In those localities where the air is subject to change, and is in a more or less enclosed space, or, at any rate, in an unventilated space, it may alter very considerably in its composition. For this reason the air in dwellings, cellars, and wells, in which there are substances absorbing oxygen, contains less of this gas, whilst the air on the surface of standing water, which abounds in the lower orders of plant life evolving oxygen, contains an excess of this gas.[17] The constant composition of air—over the whole surface of the earth—has been proved by a number of most careful researches.[18]

[17] The air held in the fissures of glaciers contains only 10 per cent. by volume of oxygen. This is owing to the fact that oxygen is much more soluble than nitrogen in snow-water and snow at a low temperature.

[18] The analysis of air by weight conducted by Dumas and Boussingault in Paris, which they repeated many times between April 27 and September 22, 1841, under various conditions of weather, showed that the amount by weight of oxygen only varies between 22·89 per cent. and 23·08 per cent., the average amount being 23·07 per cent. Brunner in Berlin, Bravais at Faulhorn in the Bernese Alps, at a height of two kilometres above the level of the sea, Marignac at Geneva, Lewy at Copenhagen, and Stas at Brussels, have analysed the air by the same methods, and found that its variation in composition does not exceed the limits determined for Paris. The most recent determinations (with an accuracy of ±0·05 per cent.) confirm the conclusion that the composition of pure air is comparatively constant.

There are some grounds (which will be mentioned shortly) for considering that the composition of the air at great altitudes is slightly different from that at attainable heights—namely, that it is richer in the lighter nitrogen—and several fragmentary observations made at Munich (Jolly, 1880) gave reason for thinking that in the upward currents (that is, in the regions of minimum barometric pressure or at the centres of meteorological cyclones) the air is richer in oxygen than in the descending currents of air (in the regions of anticyclones or of barometric maxima); but more carefully conducted observations showed this supposition to be incorrect. Improved methods for the analysis of air have shown that certain slight variations in its composition do actually occur; but in the first place these depend on incidental local influences (on the passage of the air over mountains and large surfaces of water, regions of forest and herbage, and the like), and are also limited to quantities scarcely distinguishable from possible errors in the analyses. The researches made by Kreisler in Germany (1885) are particularly convincing.

The considerations which lead to the supposition that the atmosphere at great altitudes contains less oxygen than that at the surface of the earth are based on the law of partial pressures (Chap. I.). According to this law, the equilibrium of the oxygen in the strata of the atmosphere is not dependent on the equilibrium of the nitrogen, and the variations in the densities of the two gases with the height are determined by the pressures of separate gases. Details of the calculations and considerations involved therein are contained in my work: *On Barometric Levellings*, 1876, p. 48. On the basis of the law of partial pressures and of hypsometrical formulæ, expressing the laws of the variation of pressures at different altitudes, the conclusion may be deduced that in the upper strata of the atmosphere the proportion of nitrogen with respect to oxygen increases, but the increase will not exceed a fraction per cent., even at altitudes of four and a half to six miles, the greatest height within the reach of man either by climbing mountains or by means of balloons. This conclusion is confirmed by the analysis of air collected by Welch in England during his aëronautic ascents.

The analysis of air is effected by converting the oxygen into a non-gaseous compound, so as to separate it from the air. The original volume of the air is first measured, and then the volume of the remaining nitrogen. The quantity of oxygen is calculated either from the difference between these volumes or by the weight of the oxygen compound formed. All the volumetric measurements have to be corrected for pressure, temperature, and moisture (Chapters I. and II.) The medium employed for converting the oxygen into a non-gaseous substance should enable it to be completely taken away from the nitrogen without evolving any gaseous substance. Thus, for instance,[19] a mixture of pyrogallol, $C_6H_6O_3$, with a solution of a caustic alkali absorbs oxygen with great ease at the ordinary temperature (the solution turns black), but it is unsuited for accurate analysis, because it requires an aqueous solution of an alkali, and it alters the composition of the air by acting on it as a solvent. However, for approximate determinations this simple method gives results which are entirely satisfactory.[20]

The determinations in a eudiometer (Chapter III.) give more exact results, if all the necessary corrections for changes of pressure, temperature, and moisture are taken into account. This determination is carried out essentially as follows:—A certain amount of air is introduced into the eudiometer, and its volume is determined. About an equal volume of dry hydrogen is then passed into the eudiometer, and the volume again determined. The mixture is then exploded by a spark from a Leyden jar or Ruhmkorff coil. The remaining volume of the gaseous mixture is again measured: it will be less than the second of the previously measured volumes. Of three volumes which have disappeared, one belonged to the oxygen and two to the hydrogen; consequently one-third of the loss of volume indicates the amount of oxygen contained in the air.[21]

[19] The complete absorption of the oxygen may be attained by introducing moist phosphorus into a definite volume of air: this is shown by the fact that the phosphorus becomes non-luminous in the dark. The amount of oxygen may be determined by measuring the volume of nitrogen remaining. This method, however, cannot give accurate results, owing to a portion of the air being dissolved in the water, to the combination of some of the nitrogen with oxygen, and to the necessity for introducing and withdrawing the phosphorus, which cannot be accomplished without admitting bubbles of air.

[20] For rapid and approximate analyses (technical and hygienic), such a mixture is very suitable for determining the amount of oxygen in mixtures of gases from which the substances absorbed by alkalies have first been removed. According to some observers, this mixture evolves a certain (small) quantity of carbonic oxide after absorbing oxygen.

[21] Details of eudiometrical analysis must, as was pointed out in Chap. III., note 32, be looked for in works on analytical chemistry. The same remark applies to the other analytical methods mentioned in this work. They are only described for the purpose of showing the diversity of the methods of chemical research.

The most exact method for the analysis of air, and one which is accompanied by the smallest error, consists in the direct weighing, as far as is possible, of the oxygen, nitrogen, water, and carbonic anhydride contained in it. For this purpose the air is first passed through a weighed apparatus (which will be considered presently) for retaining the moisture and carbonic anhydride, and is then led through a tube which contains shavings of metallic copper and has been previously weighed, the remaining nitrogen being afterwards collected and weighed. A long layer of such copper heated to redness absorbs all the oxygen from the air, but does not act on the nitrogen. The nitrogen is determined in a weighed and exhausted globe by ascertaining the increase in weight, while the amount by weight of oxygen is shown by the increase in weight of the tube with the copper.

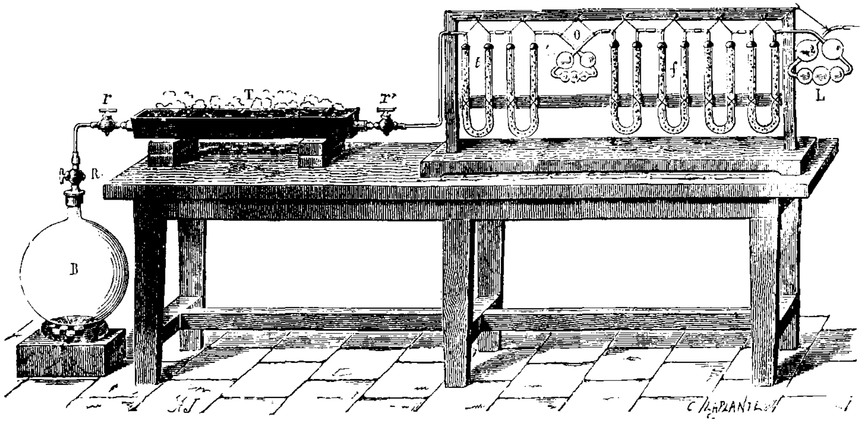

FIG. 42.—Dumas and Boussingault's apparatus for the analysis of air by weight. The globe B contains 10–15 litres. The air is first pumped out of it, and it is weighed empty. The tube T connected with it is filled with copper, and is weighed empty of air. It is heated in a charcoal furnace. When the copper has become red-hot, the stopcock *r* (near R) is slightly opened, and the air passes through the vessels L, containing a solution of potash, and *f*, containing solutions and pieces of caustic potash, which remove the carbonic anhydride from the air, and then through *o* and *t*, containing sulphuric acid (which has been previously boiled to expel dissolved air) and pumice-stone, which removes the moisture from the air. The pure air then gives up its oxygen to the copper in T. When the air passes into T the stopcock R of the globe B is opened, and it becomes filled with nitrogen. When the air ceases to flow in, the stopcocks are closed, and the globe B and tube T weighed. The nitrogen is then pumped out of the tube and it is weighed again. The increase in weight of the tube shows the amount of oxygen, and the difference between the second and third weighings of the tube, with the increase in weight of the globe, gives the weight of the nitrogen.

Air free from moisture and carbonic anhydride[22] contains 23·17 to

23·03 per cent.[23] by weight of oxygen; the mean amount of oxygen will therefore be 23·12±0·05 per cent. by weight, and 20·91 by volume.[24]

The possibility of the composition of air being altered by the mere action of a solvent very clearly shows that the component parts of air are in a state of mixture, in which any gases may occur; they do not in this case form a definite compound, although the composition of the atmosphere does appear constant under ordinary conditions. The fact that its composition varies under different conditions confirms the truth of this conclusion, and therefore the constancy of the composition of air must not be considered as in any way dependent on the nature of the gases entering into its composition, but only as proceeding from cosmic phenomena co-operating towards this constancy. It must be admitted, therefore, that over the entire surface of the earth,[25] the

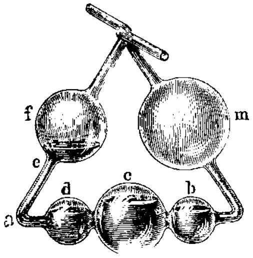

FIG. 43.—Apparatus for the absorption and washing of gases, known as Liebig's bulbs. The gas enters *m*, presses on the absorptive liquid, and passes from *m* into *b*, *c*, *d*, and *e* consecutively, and escapes through *f*.

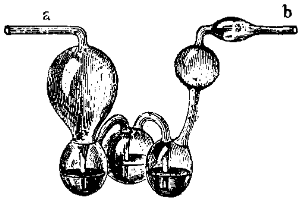

FIG. 44.—Geissler's potash bulbs. The gas enters at *a*, passes through a solution of potash in the lower bulbs, where the carbonic anhydride is absorbed, and then escapes from *b*. The lower bulbs are arranged in a triangle, so that the apparatus can stand without support.

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[22] De Saussure observed that air freed from carbonic anhydride and submitted to the action of a series of electric sparks again shows the presence of a small quantity of carbonic anhydride, and Boussingault found that air free from moisture, after being passed over red-hot copper oxide, invariably appears to contain a small quantity of water. These observations lead to the assumption that air always contains a certain quantity of gaseous hydrocarbons, like marsh gas, which, as we shall afterwards learn, is evolved from the earth, marshes, &c. Its amount, however, does not exceed a few hundredths per cent. A. Gauthier's careful researches (1898–1901) proved this beyond doubt, as will be explained presently; but it appeared that the amount of hydrocarbons is variable and in some cases zero, while hydrogen is always present to the amount of about 0·02 per cent. (see note 29).

[23] The analyses of air are accompanied by errors, variations of composition of a few hundredths per cent. being found; the average normal composition of air is therefore only correct to the first decimal place.

[24] These figures express the mean composition of pure air as given by the most accurate determinations; they are accurate within ±0·05 per cent.

[25] In Chap. III., note 4, an approximate calculation is made for the determination of the balance of oxygen in the entire atmosphere; it may therefore be supposed that the composition of air will vary from time to time, the relation between vegetation and the oxygen-absorbing processes changing; but as the atmosphere of the earth can hardly have a definite limit and we have already seen (Chap. IV., note 33) that there are observations confirming this, it follows that variations in the composition of our atmosphere are distributed throughout celestial space, and therefore it must be supposed that any variation in the composition of the air in the course of ages can only take place

processes evolving oxygen, and chiefly the processes of the respiration of plants, have an influence equal and opposite to that exerted by those processes which absorb oxygen.

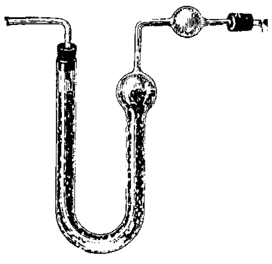

FIG. 45.—Tube for the absorption of carbonic acid. A plug of cotton-wool is placed in the bulb to prevent the powder of soda-lime being carried off by the gas. The tube contains soda-lime and chloride of calcium.

Air always contains more or less moisture [26] and **carbonic anhydride**, which are produced by the respiration of animals and the combustion of carbon and carboniferous compounds. The latter gas shows the properties of an acid anhydride. In order to determine the amount of carbonic anhydride in air, substances which absorb it—namely, alkalies—are employed, either in solution or in the solid state. A solution of caustic potash, KHO, is poured into light glass vessels, through which the air is passed, and the amount of carbonic anhydride is determined by the increase in weight of the vessel. But it is best to take a porous alkaline solid such as soda-lime.[27] With a slow current of air, a layer of soda-lime 20 cm. in length is sufficient to completely deprive 1 cubic metre of air of the carbonic anhydride it contains. A series of tubes containing calcium chloride for absorbing the moisture [28] is placed before the apparatus for the absorption of the carbonic anhydride, and a measured mass of air is passed through the whole apparatus by means of an aspirator. In this manner the determination of the moisture is combined with the absorption of the carbonic anhydride. The arrangement shown in fig. 42 is such a combination.

The amount of carbonic anhydride [29] in free air is incomparably more constant than the amount of moisture. The average amount in 100 volumes of dry air is approximately 0·03 volume—that is, 10,000 volumes of air contain about three volumes of carbonic anhydride, most frequently about 2·95 volumes. As the specific gravity of

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exceedingly slowly, and in a manner imperceptible by direct experiment. The composition of the atmosphere must, however, have undergone considerable changes during the course of the geological history of the earth (i.e., during millions of years). This is particularly true concerning the amount of carbonic anhydride, as it has been largely absorbed by the earth's crust and soil in the sedimentary formations composed of salts of carbonic acid (for instance, limestones, $CaCO_3$) and in coal. The temperature of the earth's surface must depend greatly upon the amount of CO_2 in the air, because this affects the diathermancy of the atmosphere (just as the glass of a hothouse hinders it from cooling and collects the heat of the sun's rays). The undoubted difference of climate in different geological periods is now accounted for in this manner. Thus the climate of Central Europe was colder during the glacial period and much warmer during the mammoth period. The researches of Brown and Escombe (1902), strange to say, showed that dicotyledons strike not better but far worse when the amount of carbonic anhydride in the air increases (how is it with gymnosperms ?).

[26] The amount of moisture contained in the air is considered in greater detail in the study of physics and meteorology, and the subject has been mentioned above in Chapter I., note 1, where the methods of absorbing moisture from gases were pointed out.

[27] Soda-lime is prepared in the following manner:—Unslaked lime is finely powdered and mixed with a slightly warmed and very strong solution of caustic soda. The mixing should be done in an iron dish, and the materials should be well stirred together until the lime begins to slake. When the mass becomes hot, it boils, swells up, and solidifies, forming a porous mass very rich in alkali and capable of rapidly absorbing carbonic anhydride. A lump of caustic soda or potash presents a much smaller surface for absorption, and therefore acts much less rapidly. It is necessary to place an apparatus for absorbing water after the apparatus for absorbing the carbonic anhydride, because the alkali in absorbing the latter gives off water.

[28] It is evident that the calcium chloride employed for absorbing the water should be free from lime or other alkalies in order that it may not retain carbonic anhydride. Such calcium chloride may be prepared in the following manner: A perfectly neutral solution of calcium chloride is prepared from lime and hydrochloric acid; it is then carefully evaporated, first on a water-bath and then on a sand-bath. When the solution attains a certain strength a scum is formed, which solidifies at the surface. This scum is collected, and will be found to be free from caustic alkalies. It is necessary in any case to test it before use, as otherwise a large error may be introduced into the results owing to the presence of free alkali (lime). It is best to pass carbonic anhydride through the tube containing the calcium chloride for some time before the experiment in order to saturate any free alkali that may remain from the decomposition of a portion of the calcium chloride by water, $CaCl_2 + 2H_2O = CaOH_2O + 2HCl$.

[29] Recourse is had to special methods when the determination only takes note of the carbonic anhydride of the air. For instance, it is absorbed by an alkali which does not contain carbonates (by a solution of baryta or caustic soda mixed with baryta), and then the carbonic anhydride is expelled by an excess of an acid, and its amount determined by the volume given off. A rapid method of determining CO_2 (for hygienic purposes) is given by the fall of pressure produced by the introduction of an alkali (the air having been either brought to dryness or saturated with moisture). Dr. Schidloffsky's apparatus is based upon this principle. The question as to the amount of carbonic anhydride present in the air has been submitted to many voluminous and exact researches, especially those of Reiset, Schloesing, Müntz, and Aubin, who showed that the amount is not subject to such variations as at first stated. The existing data concerning the amount of CO_2 in the air have been supplemented (1902) by observations made by A. Levy and Henriet, who found that, after leaving air in contact with an alkali for several days so that all the CO_2 was absorbed, they obtained a further quantity of CO_2 which varied in different cases, but sometimes approached the normal amount. A commission deputed by the Paris Academy of Sciences to verify this unexpected discovery convinced themselves of its reality, and in one experiment (July 27, 1902) obtained a further 0·0216 per cent. of CO_2 (by volume) after having absorbed all the original CO_2 (about 0·03 per cent. vol.) with baryta. Henriet showed that this second portion of CO_2 originates in the subsequent oxidation of an organic substance which is present in the air and occurs in solution in the water obtained by the condensation of its moisture, and he supposes this body to be an amide of formic acid. These observations were made in Paris and also at Mont Sourie, near Paris. They are, however, too recent to allow of their being regarded as perfectly trustworthy; and what is, in my opinion, still more important, there is no proof either that the air of all localities would exhibit this peculiarity or that it is not a consequence of urban conditions, and hence due to a change produced in the air by the crowded life of cities. Further, it is not known whether it would be observable in air containing such oxidising agents as ozone, peroxide of hydrogen, and oxides of nitrogen. But in any case it is a matter of great interest.

carbonic anhydride referred to air is 1·52, it follows that 100 parts by weight of air contain about 0·045 part by weight of carbonic anhydride. This quantity varies according to the time of year (more in winter), the altitude above the level of the sea (less at high altitudes), the proximity to forests and fields (less) or cities (greater), &c. But the variation is small and rarely exceeds the limits of $2\frac{1}{2}$ to 4 ten-thousandths by volume.[30] As there are many natural local influences which either increase the amount of carbonic anhydride in the air (respiration, combustion, decomposition, volcanic eruptions, &c.), or diminish it (absorption by plants and water), the reason of the great constancy in the amount of this gas in the air must be looked for, in the first place, in the fact that the wind mixes the air of various localities together, and, in the second place, in the fact that the waters of the ocean, holding carbonic acid in solution,[31] form an immense reservoir for regulating the amount of this gas in the atmosphere. Immediately the partial pressure of the carbonic anhydride in the air decreases, the water evolves more of the gas, whilst when its partial pressure increases, some of it is absorbed in this, as in so many other instances.[32] Hence nature supplies the conditions for a state of equilibrium.

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[30] In enclosed spaces, in dwellings, cellars, wells, caves, and mines, where the renewal of air is impeded, the case is different. Under these circumstances large quantities of carbonic anhydride may accumulate. In cities, where many conditions (respiration, decomposition, combustion) for the evolution of carbonic anhydride exist, its amount is greater than in free air; yet even in still weather the difference does not often exceed one ten-thousandth (that is, rarely attains 4 instead of 2·9 vols. in 10,000 vols. of air).

[31] In the sea, as well as in fresh water, carbonic acid occurs in two forms, being both directly dissolved in the water, and combined with lime as calcium bicarbonate (hard waters sometimes contain very much carbonic acid in this form). The pressure of the carbonic anhydride in the first form varies with the temperature, and its amount with the partial pressure; and the same is the case with that existing in the form of acid salts, for direct experiments show a similar dependence here, although the quantitative relations are different in the two cases.

[32] In studying the phenomena of nature the conclusion is arrived at that the universally reigning state of mobile equilibrium forms the chief reason for that harmonious order which impresses all observers. It not unfrequently happens that we do not see the causes regulating the order and harmony; in the particular instance of carbonic anhydride, it is a striking circumstance that in the first instance a search was made for an harmonious and strict uniformity, and in incidental (insufficiently accurate and fragmentary) observations, conditions were even found for concluding it to be absent. When, later, the existence of this uniformity was confirmed, the causes regulating such order were also discovered. The researches of Schloesing were of this character. Deville's idea of the dissociation of the acid carbonates of sea-water is suggested in them. In many other cases also a correct interpretation can only follow from a detailed investigation. It is the function of science to discover the existence of a general reign of order in nature and to find the causes governing this order. And this refers in equal measure to the relations of man (social and political) and to the entire universe as a whole, and also to the world of material inanimate substances, in which natural science is gradually discovering an equilibrated order of things wherever it pursues the requisite research.

Besides nitrogen, oxygen, moisture, and carbonic acid, all the other substances occurring in air are found in infinitesimally small proportions by weight, and therefore the **weight of any volume of air** (at a given temperature and pressure) depends mainly on the above-named components. The weight of a litre of pure air (that of a litre of water at 4° and 760 mm. being 1,000 grams), free from dust, moisture, and carbonic anhydride, at 0° and 760 mm., has been determined as follows:[33]

	Average weight of litre gramme	Under acceleration of gravity, g= metres
Regnault (1847)	1·29347	9·8100
Jolly (1880)	1·29316	9·8073
Leduc (1892)	1·29330	9·8100
Rayleigh (1893)	1·29362	9·8126

The last column gives the acceleration due to gravity in metres. It has an effect upon the value of the barometric column, for 760 mm. of mercury presents a greater pressure, the greater the acceleration due to gravity. The average weight of a litre of pure air under an acceleration g is:

$$e_0 = g \times 0{\cdot}131844 \text{ gram.}$$

Defarges gives an average of $g=9{\cdot}80665$[34] for latitude 45° and therefore $e_0=1{\cdot}2929$ gram (the density being about 14·4 with respect to hydrogen). The weight of air containing 0·03 per cent. by volume of CO_2 will be greater by 0·0006 gram. Hence if at a given locality the observed barometric pressure reduced to 0° be P mm., the vapour pressure of water p mm., the temperature t (according to the Centigrade thermometer, and corrected to the hydrogen scale) and the acceleration of gravity g metres, then the weight of a litre of air (with an error not greater than about 0·0002 gram) will be:

$$e = \frac{g}{9{\cdot}80665} \times 1{\cdot}2935 \times \frac{P - 0{\cdot}38p}{760} \times \frac{273}{273+t} \text{ gram.}^{35}$$

A knowledge of the exact weight of a litre of air is of great

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[33] See 'The Publications of the Weights and Measures Department,' 1894, part i., p. 85.

[34] The acceleration of gravity for a given latitude L° and elevation above the sea level, H metres, will then (if the terrestrial globe be assumed to be a regular ellipsoid at the level of the sea, which, strictly speaking, is not the case) be given by:

$$g = \frac{9{\cdot}80665\ (1 - 0{\cdot}0026 \cos 2L)}{1 + 0{\cdot}000000196\ H}.$$

But the most accurate results are obtained by direct experiment, because the proximity of the sea or mountains, the nature of the geological formations of a given locality, and irregularities in the ellipsoidal form of the earth also affect the value of g.

[35] The effect of the local acceleration of gravity on the weight of a litre of air is determined exclusively by the dependence of this weight on the pressure and the

importance in determining the exact weight of objects and weights, where it is necessary to introduce corrections for the weight of air displaced,[36] and also in investigating many meteorological phenomena, the movements of the atmosphere being determined chiefly by the different densities of different volumes of air which are at the same level and are moving freely.[37]

Although **liquid air**, as mentioned in Chapter II., was already known in 1877 (Pictet and Cailletet), it was not until much later, in the nineties, that the means were discovered, thanks to the labours of Olzewsky, Wroblewsky, Dewar, Linde, and others, for obtaining it easily in considerable quantities, and even for using it for scientific and industrial purposes, for obtaining low temperatures and for concentrating the oxygen (boiling at −181°) from the more volatile nitrogen (boiling at −193°)[38] by evaporating the liquid mixture. Linde's apparatus for liquefying air is the most widely known.[39] It consists of two pumps B_1 and B_2, which compress the indrawn air to 15–20 and 200 atmospheres respectively. As the compression of air to such an extent as 200 atmospheres evolves considerable heat, and as the liquefaction of air requires a low temperature, the pumps and compressed air are cooled to a low temperature[40] (a small amount of water is introduced into the cylinder B_1 for this purpose) by three refrigerators D_1, D_2, and G after the preliminary compression to 15–20 atmospheres and after the compression to 200 atmospheres. And as the refrigeration and

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measurement of this pressure by the barometric column. At first it might appear to be a question of the *difference* (see 'Mechanics and Physics') which exists between the conceptions of mass and weight, as the latter is determined by the acceleration of gravity, or weight is pressure. But the weights, expressing a definite mass, remain the same, and consequently when a weight is expressed by them (as is customary both in chemistry and in ordinary practice) they vary in the pressure they produce according to the locality in which they are situated. In other words, weights, for instance, the gram, as a matter of fact express units of mass; but they are also measures of weight in the generally accepted sense of the word. This is all only a question of nomenclature and of the conditional expression of conceptions, over which I think it is unnecessary to linger, for science should give clear conceptions and not temporise with words, although unfortunately we cannot express our ideas without them; and if the term 'weight' is frequently used in chemistry in the sense of mass (for instance, the weight of an atom or of a gram), still this does not introduce any inexactitude into the science, particularly as words often have more meanings than one. Thus the word 'mass' expresses the conception of a multitude of substances besides the mechanical notion of the amount of ponderable matter, and the word 'weight' not only signifies the amount of a substance in units of weight, but also the counterpoises themselves. I think it only complicates matters to introduce any changes in words or to invent special ones for every conception.

[36] For rapid calculation the weight of a litre of air (in a room) in St. Petersburg may under these conditions (P, t, and p) be obtained by the formula, $e = 1{\cdot}20671 + 0{\cdot}0016\,[P_1 - 755 + 2{\cdot}6\,(18 - t)]$, where $P_1 = P - 0{\cdot}38p$. In determining the weight of small and heavy objects (crucibles, &c., in analysis, and in determining the specific gravities of liquids, &c.) **a correction may be introduced for the loss of weight** in the air of the room, by taking the weight of a litre of air displaced as 1·2 gram, and consequently allowing 0·0012 gram for every cubic centimetre. But if gases or, in general, large vessels are weighed, and the weighings require to be accurate, it is necessary to take into account all the data (t, P, and p), because sensitive balances can determine the possible variations of the weight of air, as in the case of a litre of air the weight varies in centigrams, even at a constant temperature, with variations of P and p. Some time ago (1859), I proposed the following method and applied it for this purpose. A large light and closed vessel is taken, and its volume and weight in a vacuum accurately determined and verified from time to time. On weighing it we obtain the weight in air of a given density, and by subtracting this weight from its absolute weight and dividing by its volume we obtain the density of the air.

[37] At about the normal pressure and within the limits of 0° and 25°, an increase of pressure of about 3 mm. produces the same variation in the density of air, as a fall in temperature of 1°. It appears to me therefore that an investigation of the variation in the distribution of the densities of air at various periods over the surface of the earth (which may be easily accomplished now with kites and self-registering apparatus) might give most important and instructive meteorological data. The following table, which I have compiled from Glaisher's observations, assuming the temperature at the surface of the earth to be +15°, pressure 760 mm., and relative moisture 60 per cent., gives an idea of the variation of the density of the air during fine weather:—

Pressure	t° Centigrade	Moisture	Elevation	Weight of a litre of air
mm.		per cent.	m.	gram
760	+ 15·0	60	0	1·222
700	11·0	64	690	1·141
650	7·6	64	1,300	1·073
600	4·3	63	1,960	1·003
550	+ 1·0	62	2,660	0·931
500	− 2·4	58	3,420	0·857
450	− 5·8	52	4,250	0·781
400	− 9·1	44	5,170	0·703
350	− 12·5	36	6,190	0·624
300	− 15·9	27	7,360	0·542

As a matter of fact, *especially in cloudy weather*, the distribution of the density with the altitude is often much less regular, owing chiefly to the want of uniformity of the fall of temperature with increase of height.

[38] Liquid air floats on water, because its density, owing to the larger amount of nitrogen, is less than that of water; but when much of the nitrogen evaporates and the proportion of oxygen becomes greater it sinks under water, because liquid oxygen is *slightly heavier than water* at the temperature of liquid air. The colourless liquid air acquires a bluish tint as it becomes richer in oxygen.

[39] It may be obtained in different sizes. The large Linde machine which E. L. Nobel supplied to the St. Petersburg Weights and Measures Department requires a motive power of 12-horse power, and according to F. T. Blumbach can, when in good working order, supply 5 litres of liquid air per hour.

[40] The cooling in the refrigerators (D_1, D_2, and G) is carried on by cold water or ice, or, better still, by a mixture of salt and snow (about −20°, according to the method used in the Department of Weights and Measures of St. Petersburg) or by a mixture of snow (pounded ice) and crystals of chloride of calcium, or some other freezing mixture (Chap. I., note 26, and Chap. II., note 27). It must be remembered that in general the liquefaction of air (Chap. II., note 29) cannot take place at a temperature above −150° (the critical temperature of oxygen), and therefore expansion (to 1·5 atmosphere) of compressed (to 200 atmospheres) gas will give more liquid air, the lower the original temperature of the compressed gas (i.e., when under a pressure of 200 atmospheres).

compression of the air cause the moisture in it to precipitate partly as water (which is collected in F)[41] and partly as ice, which might close the pipes conveying the compressed air, it is necessary to have a separator F[42] through which the compressed air is made to pass after leaving the pumps. It then travels through a long copper spiral H,[43] situated in three high prism-shaped boxes in which the further refrigeration of the compressed gas takes place. These boxes are lined with bad conductors of heat (wool, down, felt) to prevent the warmth of the external air passing through. Besides which, the internal copper spiral, conveying the compressed air, is surrounded along its entire length by two similar but wider metallic spirals along which the refrigerated air which remains unliquefied is carried back to the pumps or escapes into the room, as will be presently explained.[44] This facilitates (naturally after the lapse of some time) the further refrigeration of the compressed air, which cannot of course liquefy spontaneously under a pressure of 200 atmospheres and at a temperature of −20° or even −50° (when cooled by a mixture of snow and crystals of calcium chloride), because the critical temperature (absolute boiling-point) of nitrogen lies much lower, namely, at about −146°. To obtain the requisite fall of temperature, the end of the internal copper spiral is furnished with a conical cock, K_2, by means of which the compressed air is made to expand from a pressure of 200 to 15–20 atmospheres.[45] And as the increase in volume so produced causes the temperature of the air to fall by about 50°, the air will, on expansion, fall from a temperature t of between −15° and −20° to about −60°. This refrigerated air passes from the expansion box along the annular space surrounding the copper spiral into the pump B_2, and in so doing cools the air compressed under 200 atmospheres to −50° or −60°, and after this again expands; the

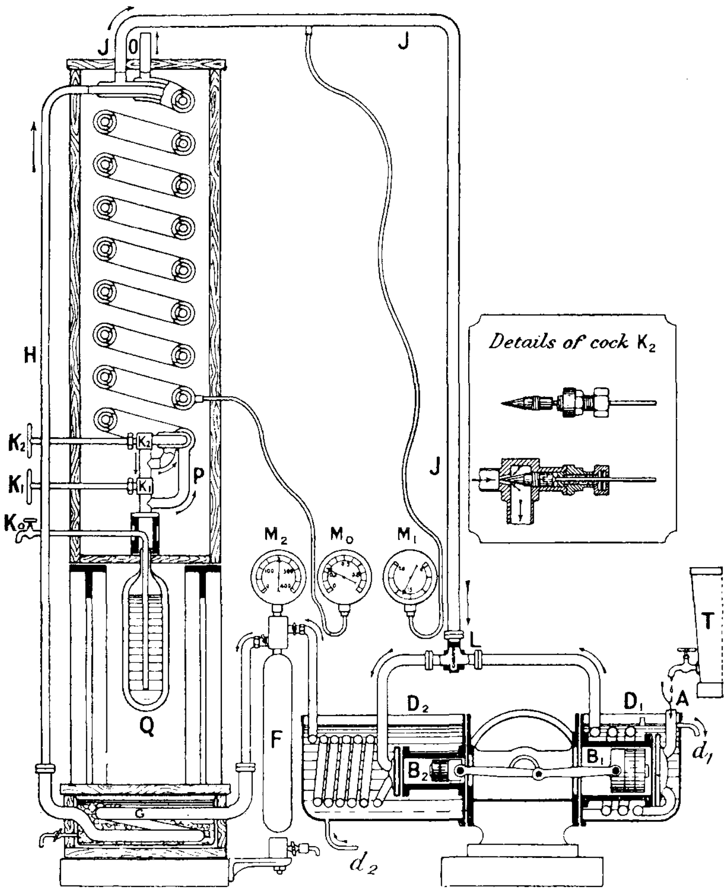

FIG. 46.—Linde's apparatus for the liquefaction of air. A, the entrance for the air (with a small quantity of water from T) into the double-acting pump. B_1, the low-pressure (20 atms.), and B_2, the high-pressure (200 atms.), cylinders D_2 and D_1, vessels through which runs cold water (d_2-d_1) for cooling the warm compressed air passing to the copper spiral. F, water-separator made of steel. G, steel spiral surrounded by a mixture of ice and salt (−15°). H, the inner tube of a triple copper spiral (the compressed and expanded air take opposite courses) surrounded by wool. K_2, conical cock for the expansion of the compressed air from 200 to 18 atmospheres pressure. J, tube through which the cooled gas returns through the valve L to the piston B_2. K_1, cock for expanding from 18 atms. to the ordinary pressure. The liquid air collects in the Dewar's vessel Q, and that which evaporates escapes from the apparatus through the third exterior spiral P–O. K_0, syphon cock for pouring out the liquid air after closing the aperture O. M_2, M_1, and M_0, manometers for the systems of tubes at pressures of 200, 20, and 1 atm. respectively.

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[41] It is evident that the water must be got rid of before letting the compressed air into the refrigerators (which are often spiral in form) where the temperature is below 0°, so that the water should not freeze in them and hinder the passage of the compressed air. This must be kept in view in constructing refrigerators of this type.

[42] The drops of water are collected by a metallic funnel as they enter the separator, and form a stream of water which remains in the separator. As any remaining water and the carbonic anhydride in the air solidify at the temperature of liquid air (about −190°), the liquid air obtained in the apparatus has the appearance of a turbid liquid, which is purified by simply filtering through unsized paper. A double-walled funnel, like the vessels described in Chap. II., note 32, for preserving liquid gases, should be taken for this purpose.

[43] In the apparatus at the St. Petersburg Weights and Measures Department it is 25 metres long.

[44] It is evident that the cold air obtained by expansion travels upwards in the annular space surrounding the inner spiral if the air travels downwards in the internal tube. This facilitates the refrigeration of the air passing through the inner spiral.

[45] The variation of the pressure in the apparatus is determined by means of pressure gauges. The first, M_2, indicates about 200 atmospheres and is situated before the entrance for the compressed air into the spiral. The gauge M_1 indicates about 15–20 atmospheres and gives the pressures in the box where the expansion goes on. The third gauge, M_0, gives the ultimate expansion, about $1\frac{1}{10}$ atmosphere.

temperature falls still further, and so on. In other words, when the apparatus continues working the gas compressed under 200 atmospheres is cooled more and more by expanding to 15–20 atmospheres. If the cock K_1 be now opened sufficiently to allow this refrigerated air to expand once more to a pressure of about one atmosphere,[46] its rapid expansion will be accompanied by a correspondingly rapid fall of temperature.[47] Then a portion of the air remains in the form of an exceedingly cold gas and escapes into the atmosphere through a third (external) copper tube which surrounds the whole of the upper portion of the spiral in the box, while the rest of the air passes into a liquid state, having a temperature of about − 190°. The stream of liquid air so formed is collected in a double-walled vessel, like that described in Chapter II., note 32. This liquid air can be kept in this state for many days (for even fourteen days if about 2 litres be taken, and there be a perfect vacuum between the walls of the vessel). At first it is chiefly the nitrogen that evaporates, so that in the end a liquid very rich in oxygen is obtained.

As liquid air possesses and preserves (in evaporating) a very low temperature (between −190° and −185°, according to the amount of oxygen it contains), it makes possible many interesting experiments, especially of a physical nature. For instance, when mercury is poured into liquid air it freezes and becomes so cold that it can be hammered and rolled like lead. Alcohol and many other liquids which do not freeze in the most severe frosts are easily converted into solid matter by liquid air. When cooled by liquid air, indiarubber becomes exceedingly brittle, hard, and fragile, and lead sonorous. If an exhausted glass globe be filled with the vapour of mercury (by means of a Sprengel air pump), and any portion of it be cooled by liquid air (by moistening a piece of wadding on a stick with it and then rubbing the exterior of the globe), the mercury is immediately precipitated as a mirror on the spot cooled. If a glass globe be filled with the reddish-brown vapour of bromine (by boiling liquid bromine in the globe and so expelling the air, and then sealing up the globe), and any portion of its surface be cooled by liquid air, the bromine collects so completely about the cold spot in a solid form that the inside of the globe becomes quite colourless.

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[46] The cock K_1 is opened just enough to reduce the pressure to about 1·1 atmosphere. A slight excess of pressure is given to make the cold expanded gas pass into the external annular space surrounding the spiral.

[47] When the temperature of the compressed air is between 0° and − 50°, a fall in pressure of 1 atmosphere only produces a cooling effect of 0·2–0·3°; but when the gas has been cooled to − 190° or − 200°, the same fall of pressure (1 atmosphere) lowers the temperature of the air by almost 2°, that is, the colder the air is, the more it is chilled by the same fall of pressure.

Those physical properties of the metals which vary to any considerable extent with the temperature are greatly affected by liquid air.[48] Thus the resistance offered by metals to an electric current, although not completely destroyed, is very greatly diminished in liquid air, and becomes infinitely small at about − 273° (absolute zero)[49] for all metals. A finger may be plunged for a moment into liquid air with impunity, notwithstanding its low temperature, this being due to the formation of a non-conducting layer of gas between the skin and the liquid, which passes into a spheroidal state, similar to that of a drop of water poured on to a red-hot iron. Many chemical reactions which proceed at the ordinary temperature do not take place at the temperature of liquid air (see Introduction, p. 34).[49a]

Turning to the other components of air (besides N_2, O_2, H_2O, and CO_2) the first to be mentioned is **Argon**, Ar (or sometimes A), whose discovery (1894) by Rayleigh and Ramsay has already been described. When Rayleigh discovered that the nitrogen remaining from air after the removal of O_2, H_2O, and CO_2 was heavier (by $\frac{1}{200}$) than nitrogen prepared from any of its compounds (with oxygen, hydrogen, metals, or carbon), no doubt remained that the nitrogen of the air contained some other gas heavier than nitrogen. To separate this gas it was necessary to convert the nitrogen into some of its non-gaseous compounds, as the new gas evidently did not enter into the composition of any of the compounds formed by nitrogen.[50] The following two methods were adopted for this purpose: (1) oxidation of the nitrogen and (2) absorption of the nitrogen by metallic magnesium.

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[48] At low temperatures chemical reaction often becomes so feeble (or even ceases altogether) that only the negative side of the question is evident; but this aspect of the subject cannot explain much, because the substances become so hard that they lose the mobility of parts necessary for chemical reaction. But as the oxygen in liquid air is compressed it supports combustion with particular energy (for instance, a smouldering cigarette bursts into flame). This has even been taken advantage of for causing explosions, as a piece of wadding or charcoal moistened with liquid air (especially if it be rich in oxygen) gives a violent explosion if it is set fire to by a spark or pistol-shot. Owing to the cheapness of liquid air this method has its economical advantages.

[49] The increase in intensity of phosphorescence at low temperatures (paraffin, bone, &c.) is mentioned in Chap. II., note 32.

[49a] There can be no doubt that the preparation of liquid air on a large scale may prove most valuable for many purposes, and especially for obtaining air rich in oxygen at a low price and for producing extreme cold.

[50] Rayleigh and Ramsay made many most interesting experiments before they succeeded in isolating argon, proving the substance they were seeking to be heavier than nitrogen and quite distinct from it in its properties. Thus they divided air by diffusion (through a porous clay tube) into a lighter (diffusive) portion and a heavier residue, and obtained nitrogen from both (by absorbing the oxygen with copper). It was found that the nitrogen which diffused through the tube was lighter than the residue, which had therefore accumulated the heavier unknown substance.

Cavendish (1786) knew that the nitrogen of the air, under certain conditions and especially by the action of an electric discharge in the presence of alkalies or in the explosion of detonating gas,[51] can be converted into nitric acid if a sufficient amount of oxygen (and moisture) be added to it; and he also observed that a portion of the nitrogen is not converted into nitric acid.[52] After conversion into nitric acid, that is, after oxidation, the nitrogen can be easily removed (by means of alkalies, which form salts of nitric acid); and if excess of oxygen was taken, this also can be easily removed by passing it over red-hot copper.[53] Still this method is complicated, and it was therefore abandoned in favour of the method of absorption by finely powdered magnesium.[54] When heated, this powdered magnesium converts all the

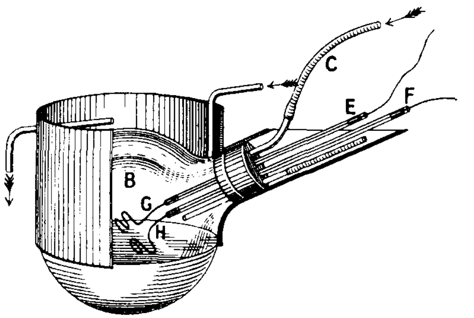

FIG. 47.—Apparatus for converting the nitrogen of the air (by the help of added oxygen) into nitric acid. Through C passes air mixed with oxygen. E G and F H are conductors from a Ruhmkorff's coil. The flask B contains a solution of caustic soda, which absorbs the nitric acid formed by the sparks; it is cooled by means of water.

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[51] See note 9.

[52] Cavendish evidently had argon and its associates in this portion, but the small quantity of the residue probably prevented him from investigating the residual gas more closely.

[53] It is most important to note that Rayleigh and Ramsay obtained argon not only from the nitrogen of the air but also from nitrogen obtained from its compounds, although in the first case more than 1 vol. of argon (and its associates; see further) was given by 100 vols. of nitrogen, whilst in the second they only obtained 0·1 vol. The authors explain the presence of argon in the second instance by the fact that they collected the gas over water which might have contained argon in solution. Until this is verified it may be assumed that argon is capable of being formed from nitrogen in some way or another. This view is mentioned in the succeeding notes.

[54] Magnesium in the form of powder may be bought. Hempel advises mixing it with unslaked lime. Small pieces (thin leaves) of metallic sodium are also sometimes mixed with the magnesium, but the best plan is to add metallic lithium, which absorbs nitrogen *with avidity. The magnesium in one of these forms is placed in an iron tube* (unsoldered) and heated, and dry air (without CO_2) is then passed over it. The oxygen of the air is absorbed by the magnesium before the nitrogen. In order to absorb all the nitrogen, the gaseous residue (impure argon) must be passed over the magnesium several times until the spectrum (obtained by electric sparks of high intensity) no longer exhibits the characteristic lines of nitrogen. And as the residue of argon is small, and the intricate apparatus employed in its preparation must necessarily embrace a considerable gaseous *volume which increases with the number of tubes of magnesium employed*, the apparatus is constructed in such a manner as to cause the residue of gas to repeatedly pass over one and the same tube containing magnesium. This may be done in several

nitrogen into solid non-volatile nitride of magnesium, N_2Mg_3, without absorbing the argon.[55] The residue, which is left unabsorbed by the magnesium, is a gas having a density of about 20 compared with that of hydrogen, whilst the densities of nitrogen and oxygen are 14 and 16 respectively. A similar gaseous residue, which is not absorbed either by ordinary solutions of reagents (alkalies, acids, salts), or by copper, magnesium, lithium, or other incandescent metals, is obtained from the air (formerly in solution) expelled by boiling from ordinary and sea water and from the water of many mineral springs (in the Pyrenees, Iceland, Germany, &c.); and here the *amount of this gaseous residue* is even greater than in ordinary air, which gives about 7 litres of residue per 1,000 litres. This residue,[56] when cooled by liquid air and evaporated under a low pressure (i.e., at about −200°), is entirely converted into a liquid (a portion, however, crystallising, especially at the *temperature* of liquid hydrogen). If this liquid is evaporated under the ordinary pressure (760 mm.) a portion of it comes over below −186°, and this portion contains helium and neon, of which mention will be made later on, while a portion which remains liquid at temperatures considerably above −186° contains krypton and xenon (see below). The main portion of the residue, however, distils over at about this temperature, and that portion which boils between −185° and −187° (under a pressure of 760 mm.) is true argon.[57] Air contains about 0·7 per cent. of argon by volume, and somewhat less than 0·2 per cent. of its associates, helium, neon, krypton, and xenon. Argon readily solidifies into a colourless mass, like ice, at about −190° under the atmospheric pressure.[58] In a gaseous state, argon is 19·8 times

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ways, but it is best to make the residual gas return to the point from which it originally entered the tube with magnesium. For this purpose a small mercury aspirator (Chap. II., note 16) is placed at the end of the tube and draws the gas through a glass tube back to that containing the magnesium. As it travels along this path the gas meets two platinum wires soldered into the glass tube, through which electric sparks are passed for exhibiting the spectrum. The mercury falling into the funnel of the aspirator compels the gas to pass once more along the magnesium tube which is furnished with a metallic mixer, worked from time to time by hand, to stir the magnesium and bring fresh surfaces into contact with the gas.

[55] Professor A. P. Lidoff (1902) showed that this method of absorbing nitrogen may even be employed for the analytical determination of nitrogen by weight.

[56] This residue was at first considered to be pure argon (1894–1895), but it was afterwards (chiefly owing to the researches of Ramsay and Travers) found to be a mixture of at least five gases—helium, neon, argon, krypton, and xenon.

[57] As argon has not yet been brought into a state of combination, its further purification is impossible. It is proved, however, to be a uniform substance by the fact that its boiling-point is constant and that diffusion (through porous diaphragms) gives portions *of similar density.*

[58] The critical temperature of argon is about −117° and the critical pressure about 53 atmospheres.

heavier than hydrogen,[59] and in a liquid state (at −186°) 1·5 times heavier than water.[60] Although so well characterised in its physical properties, argon is distinguished in a chemical sense by such inactivity and immutability that in this respect it stands alone. All endeavours to bring it into chemical reaction have as yet been fruitless.[61] This is all the more remarkable because argon (and its associates) is contained, together with nitrogen,[62] in a fairly stable condition in certain (especially Scandinavian) minerals containing uranium, tantalum, yttrium, and other rare metals; for instance, in uranite, cleveite, monazite, eshenite, fergusonite, &c. If these minerals are slightly heated, they give off water and carbonic anhydride, but no nitrogen or argon, or their associates. These are only given off by strongly heating (to the temperature at which ordinary glass becomes soft) the minerals with sulphuric acid, or, better still, with acid sulphate of potassium ($KHSO_4$) or bichromate of potassium ($K_2Cr_2O_7$). If all the air be first exhausted by a Sprengel pump, the gases may be easily collected as they pass over. These gases generally consist of nitrogen, argon, and helium. Previous to Ramsay's discovery they were considered to be nitrogen. It is evident that the gases are held in the minerals in the form of somewhat stable compounds (decomposed, however, by sulphuric acid, &c.), and not simply in a state of absorption, for absorbed gases pass over of themselves when heated *in vacuo*; but neither argon, nor helium, nor their associates can be driven off in this manner. The absorption of argon by water, on the other hand, takes place with greater facility than that of nitrogen, about four volumes of argon being dissolved by 100 volumes of water at the ordinary temperature and pressure (almost the same as oxygen).

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[59] In Chap. XIV., note 7, it is shown that k, or the ratio of the two specific heats (at constant volume and at constant pressure), decreases as the complexity of the molecules of a gas, that is, as the number of atoms in the molecule increases. For gases containing 1 atom in the molecule the ratio is about 1·6–1·8; for 2 atoms, about 1·4; for 3, 1·3, and so on. This ratio was determined for argon (Rayleigh, Dorn) and found to be =1·67; from which it is concluded that its molecule is composed of one atom, like that of mercury, i.e., that argon is an element and that its molecule contains 1 atom. However, this cannot be considered as proved, because the value of k varies considerably for gases having the same number of atoms in the molecule, and greatly depends upon the range of temperature and apparently on the store of chemical energy (for instance, for chlorine, Cl_2, k is less than for N_2, CO, &c.), which we need not consider further here.

[60] The luminous spectrum given by the gas when an electric discharge of high intensity is passed through it (between two platinum wires in a Geissler or Plucker tube; see Chap. XIII.) is very important for characterising and determining the individuality of argon and its associates, helium, neon, krypton, and xenon. The spectra of argon and its associates (and also of some other gases) vary with the intensity of the electricity and with the pressure of the gas in which the discharge takes place. The characteristic lines for argon (Crookes, Dorn, &c.) are two red ones with wave lengths of 707 and 696 millionths of a millimetre (thousandths of a micron).

[61] However, Berthelot obtained some argon from Ramsay in 1895, and subjected it to a silent discharge in a vessel together with benzene, C_6H_6, and observed that the argon was absorbed and gave a substance similar to that given by nitrogen under like conditions. It is not known if the argon was perfectly pure, and no further explanations have been published on this subject.

[62] It is not known in what form of combination or state the argon, helium, and other gases are present in cleveite, eshenite, and other minerals. It is not even known if they form an essential component of these minerals or if their presence is due to some impurity. Owing to the rarity of these minerals and the small amounts of argon, &c. obtained from them, there yet remains much to be done in this province of research, and many interesting data are yet to be looked for.

Thus argon must be regarded as a peculiar gas distinguished by its great chemical inactivity, but possessing perfectly defined physical properties, among which a typical spectrum must also be noted (see note 60). And as typical spectra chiefly belong to simple bodies,[63] argon is placed among their number, although the chief characteristics of simple bodies, namely, the independence and individuality of their corresponding compounds, are not exhibited by argon.[64] However, it is quite possible to imagine a class of elements which do not combine with hydrogen or oxygen to form acids or bases, just as many elements are known which do not combine with hydrogen, while fluorine does not combine with oxygen to form saline substances. If such be the case, we have the right to form a special **group of the argon elements,** including helium, He, neon, Ne, argon, Ar, krypton, Kr, and xenon Xe; not only because they accompany each other in the nitrogen of the atmosphere, and are perfectly analogous to each other in their inertness and incapacity for entering into combination in the ordinary way, or for forming compounds more or less resembling bases, acids, or salts, but

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[63] In Chap. XIII. we shall see, however, that compound bodies have also their spectra, if they can be subjected to the necessary degree of incandescence.

[64] Neither are there any reasons for considering argon as a compound substance, although when it was first discovered (1894) I had my reasons for considering it a polymeride of nitrogen, N_3, standing in the same relation to nitrogen, N_2, as ozone, O_3, does to oxygen, O_2 (see last edition of *Principles of Chemistry*), but formed with the evolution of heat (ozone is formed with the absorption of heat). If argon and its associates (helium, &c.) be regarded as individual chemical elements, then, owing to their incapacity to form saline compounds of the type RX_n (see Chap. XV.), they must be placed in a special, so to speak, zero group preceding the first group, the elements of which give RX, and forming a transition stage towards the halogens (group VII. giving hydrogen compounds of the type RX and oxygen compounds of the type RX_7). This view, which answers to what Ramsay stated to me personally (March 19, 1900) is in accordance with the fact that argon and its analogues contain one atom in their molecule, which gives the possibility of determining the atomic weight from the density, for the atomic weights of such elements referred to that of hydrogen (Chap. VII.) are approximately equal to twice the densities of the gases also referred to that of hydrogen. Thus if the density of argon is 19·8, its atomic weight must be near to 39·6. And the periodic law (Chap. XV.) requires that the order in which the elements stand according to their atomic weights should correspond with their properties, and therefore the atomic weights of argon and its analogues should be greater than the atomic weights of the halogens of

also because [65] this group of argon elements is exactly similar (even in the values of the atomic weights) to the other most characteristic groups of the elements spoken of more fully in Chap. XV.

The analogues of argon have all been found, as already mentioned, in air; that is, in its nitrogen; but they also accompany nitrogen and argon in the above-named minerals, such as cleveite, and **Helium**, He=4·0, was first obtained by Ramsay in 1895 by heating cleveite with sulphuric acid. The history of helium, however, begins before its discovery was an accomplished fact, and it had even been named, for Lockyer, from observations on the spectrum of the solar protuberances (Chap. XIII.), foretold the existence of an element giving a bright pale yellow line (wave length 587·0 thousandths of a micron), and a feebler green line (wave length 508). Helium may be separated from argon, nitrogen, and the other argon gases, owing to its being lighter than any of them, and therefore passing through porous partitions in larger quantity. Moreover it does not pass into a liquid state under the action of cold, even at the temperature produced by liquid hydrogen,[66] and if helium is present in admixture with the other argon gases it dissolves in them when they liquefy, but the solution parts with almost pure helium at $-250°$ (in liquid hydrogen) in a vacuum. The density of helium is only twice that of hydrogen, so that it is the lightest of all gases except hydrogen. In other respects helium is exactly like argon.[67] **Neon**, Ne=19·9, which accompanies helium in air and has the density 9·95, differs in the free state from helium in the fact that it liquefies in the cold produced by liquid air, and remains liquid at the temperature of liquid hydrogen under a low pressure; it boils below $-186°$ (that is, is more volatile than argon) and gives a spectrum with brilliant reddish-orange lines (650, 641). Among the liquefiable argon gases, two more gases occur in those portions of liquid air which evaporate with the greatest difficulty, namely, **Krypton**, Kr=81·8, and **Xenon**, X=128, discovered by Ramsay and Travers. They are also looked upon as simple bodies, but they boil at a higher temperature than argon. The spectrum of the former is greenish yellow (wave lengths of the most brilliant lines,[68] 558, 477, 474, and 450 thousandths of a micron), while that of the latter is blue (wave lengths 492, 481, 474, 467, 463). The density of krypton is 40·6 and that of xenon, 63·5; so that these gases are much heavier than all the other gases in the atmosphere (the density of CO_2 being, for example, 22). However, they are present in such minute quantities in the atmosphere that it requires great perseverance to extract even the smallest amount of such a gas as xenon, for only four volumes of it have been procured from 600 million volumes of air. The amount of krypton in air is much greater, but still far less than that of argon.

If these five argon gases be compared, they are all seen to be of very rare occurrence on the earth, to be chemically inactive, and to present a distinct sequence in the variation of their properties.

	He	Ne	Ar	Kr	Xe
Density	1·98	9·95	19·96	40·88	64
Boiling-point: below	$-262°$	$-239°$	$-187°$	$-152°$	$-109°$ [68a]

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group VII., but less than those of the alkali metals of group I. This is, if not quite, at all events very nearly confirmed by their *observed* densities.

	He	Ne	Ar	Kr	Xe
Density (H=1)	2·0	9·95	19·8	40·6	63·5

Therefore taking hydrogen = 1 (and we take it = 1·008) the atomic weights of these elements will be:

He = 4:	Ne = 19·9:	Ar = 39·6:	Kr = 81·2:	Xe = 127·0
helium	neon	argon	krypton	xenon

These values of the atomic weights of the halogens of group VII. and those of the alkali metals of group I. (taking H = 1) are:

Group VII.		F	Cl	Br	I
		18·9	35·2	79·4	125·9
„ I.	Li	Na	K	Rb	Cs
	7·0	22·9	38·9	84·8	132·0

All the analogues of argon (judging by their densities) have, therefore, greater atomic weights than the corresponding elements of group VII., and smaller atomic weights than those of the alkali metals (argon presents a slight discrepancy, as, judging from Cl and K, its atomic weight should be about 37, that is, its density should be 18·5 instead of 19·8. This leads one to think that argon still includes some other gas of high density in admixture with it). Moreover, we find that F, Cl, Br, and I exhibit a resemblance to each other similar to that shown by Li, Na, K, Rb, and Cs, or He, Ne, Ar, Kr, and Xe. The parallel goes still further, for the first members of all three groups have certain peculiarities, as we shall see later. These considerations support the idea of the elementary character of the analogues of argon, and indicate to us their position in regard to the other elements. *Still*, it is impossible to be quite sure of the true nature of these gases until some of their compounds (for instance, of the kind present in cleveite, fergusonite, &c.) have been obtained. Professor Ramsay himself first informed me (1900, see above) of the position occupied by the analogues of argon in the periodic system between the halogens and the metals of the alkalies; later Professor Ramsay published a paper on the subject, and in 1902 communications on the same subject were published by N. N. Beketoff, Piccini, and others. For my part, when I saw the above regularity, I became more inclined than before to regard argon and its analogues with their peculiar combination of properties as elementary substances standing, not in group VIII., as some think, but forming a special (zero) group.

[65] As explained in the preceding note

[66] At first it was thought that helium could be converted into a liquid at low temperatures, but now it appears that this is only true for impure helium.

[67] The ratio of the specific heats is about 1·66, as with argon. Helium, as an unliquefiable gas, is used in thermometers for determining the lowest possible temperatures.

[68] Similar green spectrum lines are observed in the spectrum of the aurora borealis.

[68a] Since the spectrum lines of helium have been observed in the sun and in certain stars, and those of krypton and the others in the corona, zodiacal light, and aurora borealis, these gases may be assumed to enter into the composition of interplanetary space and to have some connection with the substance which forms 'ether.'

We will now consider the few remaining gases and vapours occurring in ordinary air.[69]

The researches of Saussure (1806), Boussingault (1833), and especially of A. Gauthier (1899–1900) showed that the air, even at high altitudes, always contains about 0·02 per cent. (by volume) of **hydrogen** and a variable amount (more in cities and forests, less on mountains) of hydrocarbons, such as marsh gas, evolved in the decay of plants (Chapter VIII.).[69a] Their presence is shown by the fact that when air, which has been quite freed from water and carbonic anhydride, is passed over a long layer of red-hot copper oxide it again gives these substances (see note 22) in the proportion of 1 part by weight of hydrogen to generally less than 3 parts by weight of carbon, or with mountain air even ten times less; while marsh gas, CH_4, which contains more hydrogen than any other known compound of carbon, contains 3 parts by weight of hydrogen to 1 part of carbon. As the hydrogen of the atmosphere may partly oxidise to form water, and must partly pass into the interplanetary space, owing to its diffusive properties (Chap. I., notes 34 and 35), it is evident that its presence in air cannot be explained unless constant sources for its formation exist in nature. According to A. Gauthier, such a source is found in rocks, like the granites, as these evolve hydrogen (in small quantity) when acted upon by aqueous vapour in a vacuum and when heated to redness with phosphoric anhydride. Therefore there is reason to think that the rock formations of the earth cause a constant flow of hydrogen to the atmosphere.[70]

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[69] Of course in special cases, when particular gases or vapours, for instance, SO_2, H_2S, &c., are evolved, they may pass into the surrounding air, but they either undergo change or disperse.

[69a] Besides the ten-thousandths (by volume) of hydrogen and hydrocarbons, Gauthier found small traces (especially in the air of towns), or some millionths by volume, of carbon monoxide, CO, as a product of imperfect combustion. It was determined by its reaction (at 60°–80°) with iodic anhydride, I_2O_5 (previously calcined to drive off all moisture), which, as Ditte showed, gives iodine and carbonic anhydride, $I_2O_5 + 5CO = I_2 + 5CO_2$. The resultant iodine and carbonic anhydride are easily collected, the former by powdered copper and the latter by washing with caustic baryta, which absorbs the slightest traces of CO_2 from any gaseous mixture.

[70] The investigation of liquid air and the discovery of small amounts of hydrogen, argon, helium, &c., in it have been accomplished during the last few years by means of extensive and very careful researches, thus proving in a most instructive manner that more and more new objects may be found in all that surround us if we follow a method of careful research based upon the logical study of facts already known. I make this remark for the benefit of those beginners who may be discouraged by the vast stores of scientific research, and may imagine that there is nothing left for them to discover. But as a matter of fact there remains to be discovered far more than has as yet been made known. Newton rightly said that we have only become acquainted with the grains of sand on the shores of the infinite ocean of nature. These words of the great investigator are, I think, as true now after 200 years of indefatigable labour as they were then, for

The presence of **ammonia**, a compound of nitrogen and hydrogen, in the air is indicated by the fact that all acids exposed to the air absorb ammonia from it after a time. De Saussure observed that aluminium sulphate is partially converted by air into a double sulphate of ammonium and aluminium, the so-called ammonia alum. Quantitative determinations have shown that the amount of ammonia[71] contained in air varies at different periods. However, it may be accepted that 100 cubic metres of air do not contain less than 1 or more than 5 milligrams of ammonia.[72] The air in those places where animal substances undergoing change are accumulated, and especially that of stables, generally contains a much greater quantity of this gas. This is the reason of the peculiar pungent smell noticed in such places. Moreover, as we shall learn in the following chapter, ammonia combines with acids, and should therefore be found in air in the form of such combinations, since air contains carbonic and nitric acids.

The presence of **nitric acid** in air is proved without doubt by the fact that rain-water contains an appreciable amount of it.

Further (as already mentioned in Chap. IV.), air contains a small and variable amount of ozone and hydrogen peroxide and nitrous acid (and its ammonia salt), i.e., substances having a direct oxidising action (for instance, upon iodised starch-paper), but these are present in very small quantities[73] (Chap. IV.).

Besides substances in a gaseous or vaporous state,[74] there is always found a more or less considerable quantity of solid substances as **dust**, and also salts and organic matter not enumerated above. If a linen surface, moistened with an acid, be placed in perfectly pure air, the washings are found to contain sodium, calcium, iron, and potassium.[75]

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the few grains, or even stones, we have gathered have only revealed fresh depths in the unknown.

[71] Schloesing studied the equilibrium of the ammonia of the atmosphere and of the rivers, seas, &c., and showed that the amount of the gas is interchangeable between them. The ratio between the amount of ammonia in a cubic metre of air and in a litre of water at 0° = 0·004, at 10° = 0·010, at 25° = 0·040 to 1, and therefore in nature there is a state of equilibrium in the amount of ammonia in the atmosphere and waters.

[72] It is remarkable that it occurs in greater quantity on mountains than in valleys (the same thing is observed with ozone and even CO_2).

[73] Though being formed in the air, these oxidising substances (N_2O_3, ozone, and hydrogen peroxide) at the same time rapidly disappear from it by causing the oxidation of substances capable of being oxidised. Owing to this instability their amounts vary considerably, and, as would be expected, they are met with to an appreciable extent in pure air, whilst their amount decreases to zero in the air of cities and especially of dwellings, where there is a maximum of substances capable of oxidation and a minimum of conditions favouring the formation of such bodies.

[74] Amongst them we may mention iodine and alcohol, C_2H_6O, which Müntz found to be always present in air, soil, and water, although in minute traces only.

[75] A portion of the atmospheric dust is of cosmic origin: this is indisputably proved by the fact that it contains metallic iron, as do meteorites. Nordenskiöld found iron in

Linen moistened with an alkali absorbs carbonic, sulphuric, phosphoric, and hydrochloric acids. Further, the presence of organic substances in air has been proved by a similar experiment. If a glass globe be filled with ice and placed in a room where are a number of people, the presence of organic substances, such as albuminous bodies, may be detected in the water which condenses on the surface of the globe. It may be that the miasmata causing infection in marshy localities, hospitals, and in certain epidemic diseases, proceed from the presence of such substances in the air (and especially in water, which contains many micro-organisms), as well as from the presence of germs of lower organisms in the air in the form of a minute dust. Pasteur proved the existence of such germs in the air by the following experiment: He placed in a glass tube some gun-cotton (pyroxylin), which has the appearance of ordinary cotton and is soluble in a mixture of ether and alcohol, forming the so-called collodion. A current of air was passed through the tube for a long time, after which the gun-cotton was dissolved in a mixture of ether and alcohol. An insoluble residue was thus obtained which actually contained the germs of organisms, as was shown by microscopical observations, and by their capacity of developing under favourable conditions into organisms (mould, &c.). The presence of these germs determines the property possessed by air of bringing about the processes of putrefaction and fermentation—that is, the fundamental alteration of organic substances accompanied by an entire change in their properties. The appearance of lower organisms, both vegetable and animal, is always to be observed in these processes. Thus, for instance, in the process of fermentation, when, for example, wine is procured from the sweet juice of grapes, a sediment separates out which is known under the name of lees, and contains peculiar yeast organisms. Germs are required before these organisms can appear.[76] These germs are floating in the air, and fall therefrom into the sweet fermentable liquid. Finding themselves under favourable conditions, the germs develop into organisms, they are nourished at the expense of the organic substances present, and during their growth change and destroy these substances and bring about fermentation and putrefaction. This explains why, for instance, the juice of the grape when contained in the skin of the fruit, which allows access of the air but is impenetrable to the germs, does not ferment or change so long as the skin remains intact. It is for this reason also that animal substances when kept out of contact of air may be preserved for a great length of time. Preserved foods for long sea voyages are kept in this way.[77] It is hence evident that, however infinitesimal the quantity of germs carried in the atmosphere may be, they have an immense significance in nature.[78]

Thus we see that air contains a great variety of substances. The nitrogen, which is found in it in the largest quantity, has the least influence on those processes which are accomplished by the action of air. The oxygen, which is met with in a lesser quantity than the nitrogen, takes, on the contrary, a very important part in a number of reactions: it supports combustion and respiration, it brings about decomposition and every process of slow oxidation. The part played by the moisture of air is well known; without it and its precipitations the earth would be a desert. The carbonic anhydride, which is met with in still smaller quantities, has an immense significance in nature, inasmuch as it serves for the nourishment of plants. The importance of the ammonia and nitric acid is very great, because they are the sources of the nitrogenous substances constituting an indispensable element in all living organisms. And, lastly, the infinitesimal quantity of germs also has a great significance in a number of processes. Thus it is not the quantitative but the qualitative relations of the component parts of the atmosphere which determine its importance in nature.[79]

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the dust covering snow, and Tissandier detected it in every kind of air, although naturally in very small quantities.

[76] The idea of the spontaneous growth of organisms in a suitable medium, although still upheld by many, has been discarded since the work of Pasteur and his followers (and to a certain extent of his predecessors), because it has been proved how, when, and whence (from the air, water, &c.) the germs appear, and that neither fermentation nor infectious diseases can take place without them; and chiefly because it has been shown that any change accompanied by the development of the organisms introduced may be brought about at will by the introduction of the germs into a suitable medium.

[77] In confirmation of the fact that putrefaction and fermentation depend on germs carried in the air, we may cite the circumstance that poisonous substances destroying the life of organisms prevent or hinder the appearance of the above processes. Air which has been heated to redness or passed through sulphuric acid no longer contains the germs of organisms (sterilisation), and loses the power of producing fermentation and putrefaction.

[78] Their presence in the air is naturally due to the diffusion of germs into the atmosphere, and owing to their microscopical dimensions; they hang, as it were, in the air by virtue of the large surface they possess compared with their weight. In Paris the amount of dust suspended in the air amounts to from 6 (after rain) to 23 grams per 1,000 cm. of air.

[79] We see similar cases everywhere. For example, the predominating mass of sand and clay in the soil takes scarcely any chemical part in the economy of the soil in respect to the nourishment of plants. The plants by their roots search for substances which are diffused in comparatively small quantities in the soil. If a large proportion of these nourishing substances is removed, then the plants will not develop in the soil, just as animals die in oxygen. There exists everywhere a medium in things, determined by equilibrium. The Russian proverb says, 'Too much salt or too little salt is alike an evil.' It is the same in political and social relations.

Air, being a mixture of various substances, may suffer considerable **changes** in consequence of incidental circumstances. It is particularly necessary to remark those changes in the composition of air which take place in dwellings and in various localities where human beings have to remain during a lengthy period of time. The respiration of human beings and animals alters the air.[80] A similar deterioration of air is produced by the influence of decomposing organic substances, and especially of substances burning in it, and then the amount of oxygen decreases while the proportion of noxious impurities increases.[81] Hence it is necessary to have regard to the purification of the air of dwellings. The renewal of air, the replacing of respired by fresh air, is termed 'ventilation,'[82] and the removal of foreign and injurious admixtures from the air is called 'disinfection.'[83] The accumulation of all kinds

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[80] A man in breathing burns about 10 grams of carbon per hour—that is, he produces about 880 grams, or (as 1 cub.m. of carbonic anhydride weighs about 2,000 grams) about $\frac{5}{12}$ c.m. of carbonic anhydride. The air coming from the lungs contains 4 per cent. of carbonic anhydride by volume. The exhaled air acts as a direct poison, owing to the presence of this gas and other impurities.

[81] For this reason candles, lamps, and gas change the composition of air almost in the same way as respiration. In the burning of 1 kilogram of stearin candles, 50 cubic metres of air are changed as by respiration—that is, 4 per cent. of carbonic anhydride will be formed in this volume of air. The respiration of animals and the exhalations from their skins and especially from their intestines and the transformations taking place in these bodies contaminate the air to a still greater extent, because they introduce into it other volatile substances besides carbonic anhydride. At the same time that carbonic anhydride is formed the amount of oxygen in the air decreases, and there is noticed the appearance of miasmata which occur in but small quantity, but which are noticeable in passing from fresh air into a confined space full of such adulterated air. The researches of Schmidt and Leblanc and others show that even when the percentage of oxygen in air is reduced, as a result of respiration, merely from 20·9 to 20·6, the air becomes noticeably less fit for respiration, and that the heavy feeling experienced in such air increases with a further diminution in the percentage of oxygen. It is difficult to remain for a few minutes in air containing only 17·2 per cent. of oxygen. These observations were chiefly obtained by observations on the air of mines at different depths below the surface. The air of theatres and buildings full of people also proves to contain a deficiency of oxygen: it was found on one occasion that at the end of a theatrical representation the air in the stalls contained 20·75 per cent. of oxygen, whilst that in the upper part of the theatre contained only 20·36 per cent. The amount of carbonic anhydride in the air may be taken as a measure of its purity (Pettenkofer). When it reaches 1 per cent. it is very difficult for human beings to remain long in such air, and it is necessary to set up a vigorous ventilation for the removal of the adulterated air. In order to keep the air in dwellings in a uniformly good state, it is necessary to introduce *at least* 10 cubic metres of fresh air per hour per person. We saw that a man exhales about five-twelfths of a cubic metre of carbonic anhydride per day. Accurate observations have shown that air containing 0·1 per cent. of exhaled carbonic anhydride (and consequently also a corresponding amount of the other substances evolved together with it) is not felt to be oppressive; and therefore the five-twelfths of a cubic metre of carbonic anhydride should be diluted with 420 cubic metres of fresh air if it be desired to have not more than 0·1 per cent. (by volume) of carbonic anhydride present. Hence a man requires 420 cubic metres of air per day, or 18 cubic metres per hour. With the introduction of only 10 cubic metres of fresh air per hour per person, the proportion of carbonic anhydride may reach 0·2 per cent., and the air will not then be of the requisite freshness.

[82] The **ventilation** of inhabited buildings is most necessary, and is even indispensable in hospitals, schools, and similar buildings. In winter it is carried on by the so-called calorifiers or stoves heating the air before it enters. The best kind of calorifiers in this respect are those in which the fresh cold air is led through a series of flues heated by the hot gases coming from a stove. In ventilation, particularly during winter, care is taken that the incoming air shall be moist, because in winter the amount of moisture in the air is very small. Ventilation, besides introducing fresh air into a dwelling-place, must also withdraw the air already spoilt both by respiration and from other causes—that is, it is necessary to construct channels for the escape of the bad air, besides those for the introduction of fresh air. In ordinary dwelling-places, where not many people are congregated, the ventilation is maintained by natural means—by fires, crevices, windows, and various orifices in walls, doors, and windows. In mines, factories, and workrooms ventilation is of the greatest importance.

Animal vitality may, however, continue for a period of several minutes in air containing as much as 30 per cent. of carbonic anhydride if the remaining 70 per cent. consist of ordinary air; but respiration ceases after a certain time, and death may even ensue. The flame of a candle is very rapidly extinguished in an atmosphere containing from 5 to 6 per cent. of carbonic anhydride; but animal vitality can be sustained in it for a somewhat long time, although the effect of such air is exceedingly painful even to the lower animals. The presence of 1 per cent. of carbonic oxide is fatal even to cold-blooded animals. The air in the galleries of a mine where blasting has taken place is known to produce a state of insensibility resembling that produced by charcoal fumes. Deep wells and vaults not infrequently contain similar substances, and their atmosphere often causes suffocation. The atmosphere of such places cannot be tested by lowering a lighted candle into it, as these poisonous gases would not extinguish the flame. This method only suffices to indicate the amount of carbonic anhydride. If a candle keeps alight, it signifies that there is less than 6 per cent. of this gas. In doubtful cases it is best to lower a dog or other animal into the air to be tested. If CO_2 be very carefully added to air, the flame of a candle is not extinguished (although it becomes very much smaller) even when the gas is present to the extent of 12 per cent. Researches made by F. Clowes (1894) show that the flames (¾ in. long) of different combustible substances are extinguished by the gradual addition of different percentages of nitrogen and carbonic acid to the air; the percentages sufficient to extinguish the flame being as follows (the percentage of oxygen present being given in parenthesis):

	per cent. of CO_2	per cent. of N_2
Absolute alcohol	14 (18·1)	21 (16·6)
Candle	14 (18·1)	22 (16·4)
Hydrogen	58 (8·8)	70 (6·3)
Coal gas	33 (14·1)	46 (11·3)
Carbonic oxide	24 (16·0)	28 (15·1)
Methane	10 (18·9)	17 (17·4)

The flames of all solid and liquid substances are extinguished by about the same percentage of CO_2 or N_2, but the flames of different gases vary in this respect, and hydrogen continues to burn in mixtures which are far poorer in oxygen than those in which the flames of other combustible gases are extinguished; the flame of methane is the most easily extinguished. The percentage of nitrogen may be greater than that of carbonic anhydride. This, together with the fact that under the above circumstances the flame of a gas, before going out, becomes fainter and increases in size, indicates that the chief reason for the extinction of the flame is the fall in its temperature.

[83] Different so-called **disinfectants** purify the air and prevent the injurious action of

of impurities in the air of dwellings and cities is the reason why the air of mountains, forests, seas, and non-marshy localities covered with vegetation or snow is distinguished for its freshness and for its beneficial action.[84]

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certain of its components by changing or destroying them. Disinfection is especially necessary in those places where volatile substances are evolved into the air in considerable quantity, and where organic substances are decomposed; for instance, in hospitals, closets, &c. The numerous disinfectants employed are of the most varied nature. They may be divided into oxidising, antiseptic, and absorbent substances. To the oxidising substances used for disinfection belong chlorine and also various substances evolving it, because chlorine in the presence of water oxidises the majority of organic substances. This is why chlorine is used as a disinfectant for Siberian plagues. Further, to this class belong the permanganates of the alkalies and peroxide of hydrogen, substances readily oxidising matters dissolved in water. These salts are not volatile like chlorine, and therefore act much more slowly, and have a much more limited sphere of action. Antiseptic substances are those which convert organic substances into such as are little prone to change, and prevent putrefaction and fermentation. They most probably kill the germs of organisms occurring in miasmata. The most important of these substances are creosote and phenol (carbolic acid), which occur in tar and are used for preserving smoked meat. Phenol is a substance little soluble in water, volatile, oily, and having the characteristic smell of smoked objects. Its action on animals in considerable quantities is injurious, but in small quantities, used in the form of a weak solution, it prevents change in animal matter. The smell of urinals, which depends on the change of excremental matter, may be easily removed by means of chlorine or phenol. Salicylic acid, thymol, common tar and especially its solution in alkalies as proposed by Nensky, &c., have the same property. Absorbent substances are of no less importance, especially as preventives, than the preceding two classes of disinfectants, inasmuch as they are innocuous. They are those substances which absorb the odoriferous gases and vapours which are emitted during putrefaction, and which are chiefly ammonia, sulphuretted hydrogen, &c. To this class of disinfectants belong charcoal, certain salts of iron, gypsum, salts of magnesia, and similar substances, as well as peat, mould, and clay. Questions of disinfection and ventilation are among the most serious problems of every-day life and hygiene. These questions are so vast that we are here able to give only a short outline of their nature.

[84] As it is often necessary in making researches of different kinds (especially such as concern combustion, respiration, &c.) to make detailed calculations based on a knowledge of the composition of ordinary air by weight and volume, I think it well to sum up here the existing data on the composition of air. First of all the component parts of air must be divided into those which are constant and those which are variable or incidental (such as the products of smoke or respiration). Among the latter, moisture must be included, because its absolute quantity (for instance, the number of grams per cubic metre) varies considerably with the temperature and degree of dryness of the air. The following calculation relates to the constant components of the air, on the assumption that dry air contains about 23·12 per cent. of oxygen by weight (with a possible variation of not more than ± 0·05 per cent.), and that a litre of such air (under normal conditions, i.e., at 0° and 760 mm. and at latitude 45°) weighs about 1·293 grm. Then it must be remembered that although hydrogen, ammonia, &c., always enter into the composition of air, they occur in but small proportions (for instance, 0·02 per cent. by vol. or 0·0018 per cent. by weight of hydrogen), and act so slightly upon the weight of a given volume of air, and on all the calculations appertaining to it, that their influence may be neglected in comparison with that of the variations in the amounts of oxygen and nitrogen. These component parts should be included under the category of 'various other components,' just as the category 'argon' also includes its associates krypton, neon, xenon, and helium. Thus the composition of dry air is:

By volume per cent.		Weight of litre at 0° and 760 mm.	Per cubic metre at 0° and 760 mm.	By weight per cent.
Oxygen—20·91		1·429	129·8	23·12
Nitrogen—78·23		1·251	978·7	75·7
Argon—(&c.)—0·80		1·78	14·2	1·10
Carbonic anhydride—0·03		1·98	0·6	0·95
Various other components—0·03		0·32	0·1	0·01
Dry air	100·000	—	1292·4	100·00

The last cipher in each of the above numbers is of doubtful accuracy, as the observations are subject to possible errors and the composition of air varies (for argon Schloesing gives 0·935 per cent. by vol.). The amount of each component part and the weight of a cubic metre of air in different cases are easily calculated from what has been said in Chap. I., note 1, that is if we know the vapour pressure p mm. of the water vapour in the air, the barometric pressure P mm. and the temperature $t°$; for instance if $P = 740$, $t = 20°$ and $p = 10$ mm. (relative moisture 57·4 per cent.), then taking the weight of a litre of aqueous vapour (under normal conditions) as 0·8 gram, we find that the volume of the aqueous vapour stands to the volume of dry air in the ratio $p : P - p$ or $10 : 740 - 10$; i.e., that a litre of air will contain 13·5 c.c. of aqueous vapour and 986·5 c.c. (or millilitres) of dry air, and as the composition by volume of the latter is known we can find the amount by volume of all the remaining components. Knowing also that a litre of aqueous vapour under normal conditions weighs 0·8 gram, and that the coefficient of expansion of gases and vapours is 0·00367, it is easy to calculate the composition by weight and also the weight of a litre, recollecting, however, that the laws of gases and vapours (Boyle's, Dalton's, &c.) are only approximate, and cannot give absolutely accurate results.

CHAPTER VI

THE COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN

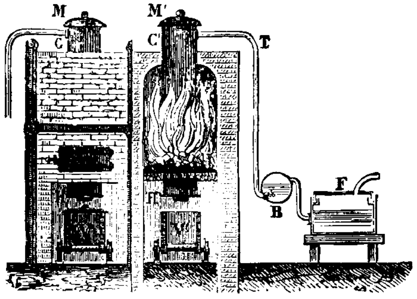

Fig. 48.—The dry distillation of bones on a large scale. The bones are heated in the vertical cylinders C (about 1½ metre high and 30 centimetres in diameter). The products of distillation pass through the tubes T into the condenser B and receiver F. When the distillation is completed the trap H is opened, and the burnt bones are loaded into trucks V. The roof M is then opened and the cylinders are charged with a fresh quantity of bones. The ammonia water is preserved, and is used for the preparation of ammoniacal salts, as is shown in the following drawing.

In the last chapter we saw that nitrogen does not directly (i.e., under ordinary conditions) combine with hydrogen or oxygen, but hydrogen and oxygen compounds of nitrogen are formed indirectly, and are even present in the atmosphere, water, and soil. Thus a mixture of nitrogen and hydrogen, in presence of hydrochloric acid gas, HCl, forms ammonium chloride, NH_4Cl, under the action of a series of electric sparks.[1] In ammonium chloride, HCl is combined with NH_3; consequently here we find nitrogen and hydrogen directly forming **ammonia.**[2] This is the simplest typical compound of nitrogen, and therefore we shall begin with it. Almost all the **nitrogenous constituents of plants and**

animals when heated with an alkali evolve their nitrogen as ammonia. But even without the presence of an alkali the majority of nitrogenous substances, when decomposed or heated with a limited supply of air, evolve their nitrogen, if not entirely, at all events partially, in the form of ammonia. When animal substances such as skins, bones, flesh, hair, horns, &c., are heated without access of air in iron retorts, they undergo what is termed dry distillation. A portion of the resultant substances remains in the retort and forms a carbonaceous residue, whilst the other portion, in virtue of its volatility, escapes through the tube leading from the retort. The vapours given off, on cooling, form a liquid which separates into two layers: the one, which is oily, is composed of the so-called animal oils (*oleum animale*): the other, an aqueous layer, contains a solution of ammonium salts. If this solution be mixed with lime and heated, the lime takes up the elements of carbonic acid from the ammonium salts, and ammonia is evolved as a gas.[3] In ancient times ammonium compounds were imported into

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[1] The ammonia in the air, water, and soil proceeds from the decomposition of the nitrogenous substances of plants and animals, and also probably from the reduction of nitrates. Ammonia is always formed in the rusting of iron. Its formation in this case depends in all probability either on the decomposition of water and on the action of the hydrogen, at the moment of its evolution, on the nitric acid contained in the air (Cloez) or on the formation of ammonium nitrite, which takes place under many circumstances, and in its composition, NH_4NO_2, is equal to nitrogen, N_2 + water, $2H_2O$. The evolution of vapours of ammonia compounds is sometimes observed in the vicinity of volcanoes. At a red heat nitrogen combines directly with boron, calcium, magnesium, and many other metals, and the compounds thus formed, when heated with a caustic alkali, or in the presence of water, give ammonia. These are examples of the indirect combination of nitrogen with hydrogen.

[2] If a silent discharge or a series of electric sparks is passed through ammonia gas, the latter is decomposed into nitrogen and hydrogen. This is a phenomenon of dissociation; that is, a series of sparks do not totally decompose the ammonia, but leave a certain portion undecomposed. One volume of nitrogen and three volumes of hydrogen are obtained by the decomposition of two volumes of ammonia. Ramsay and Young (1884) investigated the decomposition of NH_3 under the action of heat, and showed that at 500°, 1½ per cent. is decomposed; at 600°, about 18 per cent.; and at 800°, 65 per cent.; but these results were hardly free from the influence of 'contact.' The action of a silent discharge on a mixture of nitrogen and hydrogen also gives ammonia, but not to completion.

The presence of free ammonia—that is, ammonia not combined with acids—in a gas or aqueous solution may be recognised by its characteristic smell. But many ammonia salts do not possess this smell. However, on the addition of an alkali (for instance, caustic lime, potash, or soda), they evolve ammonia gas, especially when heated. The presence of ammonia may be made visible by introducing a substance moistened with strong hydrochloric acid into its neighbourhood. A white cloud, or visible white vapour, then makes its appearance. This depends on the fact that both ammonia and hydrochloric acid are volatile, and on coming into contact with each other produce solid sal-ammoniac, NH_4Cl, which forms a cloud. This test is usually made by dipping a glass rod into hydrochloric acid and holding it over the vessel from which the ammonia is evolved. With small amounts of ammonia this test is, however, untrustworthy, as the white vapour is scarcely observable. In this case it is best to take paper moistened with mercurous nitrate, $HgNO_3$. This paper turns black in the presence of ammonia owing to the formation of a black compound of ammonia with mercurous oxide. The smallest traces of ammonia (for instance, in river water) may be detected by means of the so-called *Nessler's reagent*, containing an alkaline solution of mercury in potassium iodide, which forms a brown precipitate (Hg_2NIH_2O) with the smallest quantities of ammonia. It will be useful here to give the thermo-chemical data (in thousands of heat units, according to Thomsen), or the quantities of heat *evolved* in the formation of ammonia and its compounds in quantities expressed by their formulæ. Thus, for instance, $(N + H_3)$ 26·7 indicates that 14 grams of nitrogen in combining with 3 grams of hydrogen develop sufficient heat to raise the temperature of 26·7 kilograms of water 1°. $(NH_3 + nH_2O)$ 8·4 (heat of solution); $(NH_3,nH_2O + HCl,nH_2O)$ 12·3; $(N + H_4 + Cl)$ 90·6; $(NH_3 + HCl)$ 41·9.

[3] The same ammonia water is obtained, although in smaller quantities in proportion to the weight taken, in the dry distillation of plants and of coal, which consists of the remains of fossil plants. In all these cases the ammonia proceeds from the destruction

Europe from Egypt, where they were prepared from the soot obtained in the employment of camel's dung as fuel in the locality of the temple of Jupiter Ammon (in Libya), and therefore the salt obtained was called 'sal-ammoniacum,' from which the name of 'ammonia' is derived. At the present time ammonia is obtained almost exclusively, on a large scale, from the products of the dry distillation of coal. The ammoniacal liquor obtained in the preparation of coal gas and coke (which contains ammonium salts, chiefly the carbonate in solution) is placed in a retort with lime and heated; the ammonia is then evolved together with steam.[4] In the arts, only a small amount of ammonia is used in a free state, that is, in aqueous solution; the greater portion of it is converted into different salts having technical uses, especially

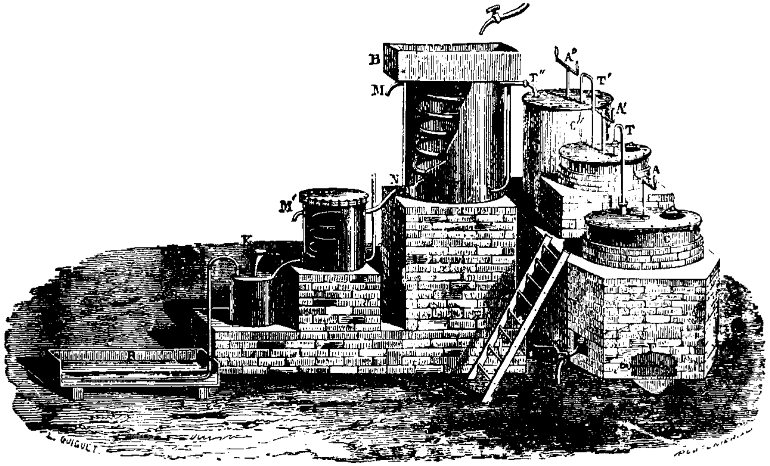

FIG. 49.—Method of abstracting ammonia, on a large scale, from ammonia water obtained at gas-works by the dry distillation of coal, or by the fermentation of urine, &c. This water is mixed with lime and poured into the boiler C″, and thence into C′ and C consecutively. The last boiler is heated directly over a furnace, and hence no ammonia remains in solution after the liquid has been boiled in it. The liquid is therefore then thrown away. The ammonia vapour and steam pass from the boiler C, through the tube T, into the boiler C′, and then into C″, so that in C′ the solution becomes stronger than in C, and still stronger in C″. The boilers are furnished with stirrers A, A′, and A″ to prevent the lime from settling. From C″ the ammonia and steam pass through the tube T″ into worm condensers surrounded with cold water, thence into the Woulfe's bottle P, where the solution of ammonia is collected, and finally the still uncondensed ammonia vapour is led into the flat vessel R, containing acid which absorbs the last traces of ammonia.

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of the complex nitrogenous substances occurring in plants and animals. The ammonium salts employed in the arts are prepared by this method. The greater part of the ammonium salts are now prepared from the ammonia water obtained as a by-product in the dry distillation of coal in the manufacture of coke and illuminating gas.

[4] The technical methods for the preparation of ammonia water, and for the extraction of ammonia from it, are to a certain extent explained in the figures accompanying the text.

sal-ammoniac, NH_4Cl, and ammonium sulphate, $(NH_4)_2SO_4$. They are saline substances which are formed on account of the capability of ammonia, NH_3, of combining with all acids, HX, forming ammonium salts, NH_4X. Sal-ammoniac, NH_4Cl, is a compound of ammonia with hydrochloric acid. It is prepared by passing the vapours of ammonia and water, evolved, as above described, from ammoniacal liquor, into an aqueous solution of hydrochloric acid; on evaporating the solution, sal-ammoniac is obtained in the form of soluble crystals[5] resembling common salt in appearance and properties. **Ammonia** may be very easily prepared **from** this **sal-ammoniac**, NH_4Cl, as from any other ammoniacal salt, by heating it with lime. Calcium hydroxide, CaH_2O_2, being an alkali, takes up the acid forming calcium chloride and sets free the ammonia, according to the equation: $2NH_4Cl + CaH_2O_2 = 2H_2O + CaCl_2 + 2NH_3$. In this reaction the ammonia is evolved as a gas.[6]

It must be observed that all the complex nitrogenous substances of plants, animals, and soils are decomposed when heated with an excess of sulphuric acid, the whole of their nitrogen being converted into ammonium sulphate, from which it may be liberated by treatment with an excess of alkali. This reaction is so complete that it forms the basis of Kjeldahl's method for estimating the amount of nitrogen in its compounds.

Ammonia is a colourless **gas**, resembling, in its outward appearance, those with which we are already acquainted, but clearly distinguishable from any other gas by its very characteristic and pungent smell. It irritates the eyes, and it is positively impossible to inhale it. Animals die in it. Its density, referred to that of hydrogen, is 8·5; hence it is lighter than air. It belongs to the class of gases which are easily liquefied.[7]

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[5] Usually these crystals are sublimed by heating them in crucibles or pots, when the vapours of sal-ammoniac condense on the cold covers as a crust, in which form the salt is placed on the market.

[6] In the laboratory ammonia may be prepared in a glass flask by mixing equal parts by weight of slaked lime and finely powdered sal-ammoniac, the neck of the flask being connected with an arrangement for drying the gas obtained. In this instance neither calcium chloride nor sulphuric acid can be used for drying the gas, since both these substances absorb ammonia, and therefore solid caustic potash, which is capable also of retaining the water, is employed. The gas-conducting tube leading from the desiccating apparatus is introduced into a mercury bath, if dry gaseous ammonia is required, because water cannot be employed in collecting ammonia gas. Ammonia was first obtained in this dry state by Priestley, and its composition was investigated by Berthollet at the end of the eighteenth century. Oxide of lead mixed with sal-ammoniac (Isambert) evolves ammonia with still greater ease than lime. The cause and process of the decomposition are almost the same: $2PbO + 2NH_4Cl = Pb_2OCl_2 + H_2O + 2NH_3$, lead oxychloride being (probably) formed.

[7] This is evident from the fact that its absolute boiling-point lies at about +130° (Chap. II., note 29). It may therefore be liquefied by pressure alone at the ordinary, and

Faraday employed the following method for liquefying ammonia. Ammonia when passed over dry silver chloride, AgCl, is absorbed by it to a considerable extent, especially at low temperatures.[8] The solid compound, $AgCl,3NH_3$, thus obtained is introduced into a thick bent tube (fig. 51), whose open end *c* is then fused up. The compound is then slightly heated at *a*, and the ammonia comes off, owing to the easy dissociation of the compound. The other end of the tube is immersed in a freezing mixture. The pressure of the gas coming off combined with the low temperature at one end of the tube, causes the ammonia evolved to condense into a liquid, in which form it collects at the cold end of the tube. If the heating be stopped, the silver chloride will again absorb the ammonia. In this manner one tube may serve for repeated experiments. Ammonia may always be liquefied by the ordinary methods—that is, by pumping dry ammonia gas into a refrigerated space. Liquefied ammonia is a colourless and very mobile liquid,[9] whose specific gravity at 0° is 0·63 (E. Andréeff). At the temperature given by a mixture of liquid carbonic anhydride and ether, liquid ammonia crystallises, and in this form its odour is feeble, because at so low a temperature its vapour pressure is very inconsiderable. The boiling-point (at 760 mm.) of liquid ammonia is about 34°, the melting-point about −78°, and the absolute (critical) boiling-point about +130°.

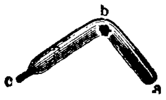

FIG. 51.—The liquefaction of ammonia in a thick bent glass tube. A compound of chloride of silver and ammonia is placed in the end *a*, and the end *c* is then sealed up.

Ammonia, containing, as it does, a large proportion of hydrogen, is

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even at much higher temperatures. The latent heat of evaporation of ammonia is about 300 units of heat; and hence liquid ammonia may be employed for the production of cold. Strong aqueous solutions of ammonia, which in parting with their ammonia act in a similar manner, are not infrequently employed for this purpose. Suppose a saturated solution of ammonia to be contained in a closed vessel furnished with a receiver. If the ammoniacal solution be heated, the ammonia, with a small quantity of water, will pass off from the solution, and in accumulating in the apparatus will produce a considerable pressure, and will therefore liquefy in the cooler portions of the apparatus. Hence liquid ammonia will be obtained in the receiver. The heating of the vessel containing the aqueous solution of ammonia is then stopped. After having been heated it contains only water, or a solution poor in ammonia. When once it begins to cool, the ammonia vapours commence dissolving in it, the space becomes rarefied, and a rapid vaporisation of the liquefied ammonia left in the receiver takes place. In evaporating in the receiver it will cause the temperature therein to fall considerably, and will itself pass into the aqueous solution. In the end, the same ammoniacal solution as was originally taken is re-obtained. Thus, in this case, on heating one portion of the closed vessel, compression of the ammonia takes place, and on cooling, the liquid evaporates and so generates great cold. This is the principle of the simplest form of *Carré's ice-making machine*, shown in fig. 50. C is a vessel made of boiler plates into which the saturated solution of ammonia is poured; *m* is a tube conducting the ammonia vapour to the receiver A. All parts of the apparatus should be hermetically joined together, and should be able to withstand a pressure of ten atmospheres. The apparatus should be freed from air, which would otherwise hinder the liquefaction of the ammonia. The process is carried on as follows:—The apparatus is first so inclined that any liquid remaining in A may flow into C. The vessel C is then placed upon a stove F, and heated until the thermometer *t* indicates a temperature of 130° C. During this time the ammonia has been expelled from C, and has liquefied in A. In order to facilitate the liquefaction, the receiver A should be immersed in a tank of water R (see the left-hand drawing in fig. 50). When it may be supposed that the ammonia has been expelled, the fire is removed from under C, which in its turn is immersed in the tank of water R, as is represented in the right-hand drawing of fig. 50. The liquefied ammonia then evaporates, and passes over into the water in C. This causes the temperature of A to fall considerably. The substance to be refrigerated is placed in a vessel G, in the cylindrical space inside the receiver A. The heating and also the refrigeration are kept on for about half an hour, and with an apparatus of ordinary dimensions (containing about two litres of ammonia solution), five kilograms of ice are produced by the consumption of one kilogram of coal. In industrial works larger and more complicated types of Carré's machines are employed.

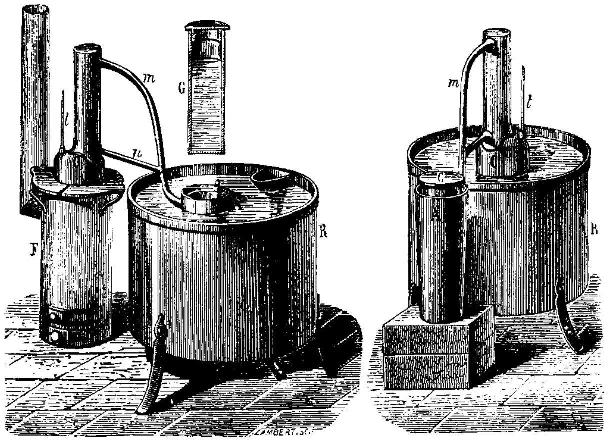

FIG. 50—Carré's apparatus. Described in text.

[8] Below 15° (according to Isambert), the compound $AgCl,3NH_3$ is formed, and above 20° the compound $2AgCl,3NH_3$. The pressure of the ammonia evolved from the latter substance is equal to the atmospheric pressure at 68°, whilst for $AgCl,3NH_3$ the same happens at about 20°; hence, at higher temperatures, the pressure is greater than that of the atmosphere, whilst at lower temperatures the ammonia is absorbed and forms this compound. Consequently, all the phenomena of dissociation are here clearly to be observed. Joannis and Croisier (1894) made investigations with AgBr, AgI, AgCN, and $AgNO_3$, and found that they all give definite compounds with NH_3; for instance, $AgBr,3NH_3$; $2AgBr,3NH_3$ and $AgBr,2NH_3$; they are all colourless solid substances which decompose under the atmospheric pressure at +3·5°, +34°, and +51° respectively.

[9] The liquefaction of ammonia may be accomplished without increase of pressure by means of freezing mixtures producing temperatures below −35°. It may even take place in the severe frosts of a Russian winter. The application of liquid ammonia as a motive power for engines forms a problem which has to a certain extent been solved by the French engineer Tellier and others. Liquid ammonia resembles water in many respects; its specific heat is 1·02 (Ellean); the latent heat of evaporation at −30° is 330 cals. (pressure 1·15 atmosphere), at 0° = 316 (pressure 4·21 atmospheres), at +30° = 300 cals. (pressure 11·62 atmospheres).

capable of combustion; it does not, however, burn steadily, and sometimes not at all, in ordinary atmospheric air (the temperature not being sufficiently high). In pure oxygen it burns with a greenish-yellow flame,[10] forming water, whilst the nitrogen set free gives partly oxygen compounds, that is, oxides of nitrogen, and partly escapes in an uncombined form. The decomposition of ammonia into hydrogen and nitrogen not only takes place at a red heat and under the action of electric sparks, but also under the influence of many oxidising substances; for instance, by passing ammonia through a tube containing red-hot copper oxide. The water thus formed may be collected by substances absorbing it, and the nitrogen may be measured in the gaseous state, and thus the composition of ammonia determined. In this manner it is found that ammonia contains very nearly 3 parts by weight of hydrogen to 14 parts by weight of nitrogen; whilst 3 vols. of hydrogen and 1 vol. of nitrogen form 2 vols of ammonia.[11]

Ammonia is capable of combining with a number of substances, forming, like water, compounds of various degrees of stability. It is more **soluble** than any of the gases yet described, both in water and in many aqueous solutions. We have already seen, in the first chapter, that one volume of water, at the ordinary temperature, dissolves about 700 vols. of ammonia gas. If a piece of ice be placed in ammonia gas it melts and absorbs the gas with great rapidity. The great solubility of ammonia enables it to be kept ready for use in the form of an aqueous solution,[12] which is known commercially as **spirits of hartshorn.**

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[10] The combustion of ammonia in oxygen may be easily demonstrated by means of incandescent platinum. A small quantity of an aqueous solution of ammonia, containing about 20 per cent. of the gas, is poured into a wide-mouthed beaker of about one litre capacity. A gas-conducting tube about 10 mm. in diameter, and supplying oxygen, is immersed in the aqueous solution of ammonia. But before introducing the gas, an incandescent platinum spiral is placed in the beaker; in the presence of the platinum the ammonia is oxidised and burns, whilst the platinum wire becomes still more incandescent. The solution of ammonia is heated and oxygen passed through the solution. The oxygen, as it bubbles off from the ammonia solution, carries with it a part of the ammonia, and this mixture explodes on coming into contact with the incandescent platinum. This is followed by a certain cooling effect owing to the combustion ceasing; but after a short interval this is renewed, so that one feeble explosion follows another. During the period of oxidation without explosion, white vapours of ammonium nitrite and red-brown vapours of oxides of nitrogen make their appearance, while during the explosion there is complete combustion, and consequently water and nitrogen are formed.

[11] This may be verified by their densities. Nitrogen is 14 times denser than hydrogen, and ammonia, 8½ times. If 3 volumes of hydrogen with 1 volume of nitrogen gave 4 volumes of ammonia, then these 4 volumes would weigh 17 times as much as 1 volume of hydrogen; consequently 1 volume of ammonia would be 4¼ times heavier than the same volume of hydrogen. But if these 4 volumes only give 2 volumes of ammonia, the latter will be 8½ times as dense as hydrogen, which is found to be actually the case.

[12] Aqueous solutions of ammonia are lighter than water, and at 15° (taking water at 4° as 10,000) their specific gravity, s, as dependent on p, the percentage amount (by weight)

Ammonia water is continually evolving ammoniacal vapour, and so has the characteristic smell of ammonia itself, and is therefore employed for making smelling salts. It is a very characteristic and important

of ammonia, is given by the expression: $s = 9{,}992 - 42{\cdot}5p + 0{\cdot}21p^2$; for instance, with 10 per cent., $s = 9{,}588$. If t represents the temperature between the limits of +10° and +20°, then the expression $(15 - t)\,(1{\cdot}5 + 0{\cdot}14p)$ must be added to the above formula for the specific gravity. Solutions containing more than 24 per cent. of the gas have not been sufficiently investigated with respect to the variation of their specific gravity. It is, however, easy to obtain more concentrated solutions, and at 0° solutions approaching NH_3,H_2O (48·6 per cent. NH_3) in their composition, and of sp. gr. 0·85, may be prepared. But such solutions give up much of their ammonia at the ordinary temperature, so that more than 24 per cent. of NH_3 is rarely contained in solution. Ammonia solutions containing a considerable amount of ammonia give at temperatures far below 0° (for instance, an 8 per cent. solution at −14° and the strongest solutions at −48°) ice-like crystals which seem to contain ammonia. The whole of the ammonia may be expelled from a solution by heating, even at a comparatively low temperature; hence on heating aqueous solutions containing ammonia, a very strong solution of ammonia is obtained in the distillate. Alcohol, ether, and many other liquids are also capable of dissolving ammonia. Solutions of ammonia, when exposed to the atmosphere, give off a part of their ammonia in accordance with the laws of the solutions of gases in liquids, which we have already considered. But the ammoniacal solutions at the same time absorb carbonic anhydride from the air, and ammonium carbonate remains in the solution.

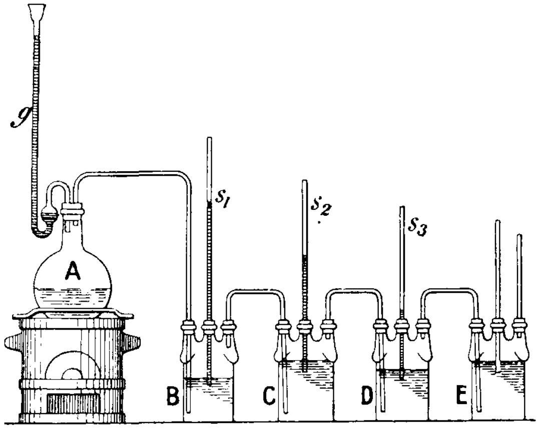

FIG. 52.—Apparatus for preparing solutions of ammonia.

Solutions of ammonia are required both for laboratory and factory operations, and have therefore to be frequently prepared. For this purpose the arrangement shown in fig. 52 is employed in the laboratory. In works the same arrangement is used, only on a larger scale (with earthenware or metallic vessels). The gas is prepared in a flask A, whence it is led through a series of Woulfe's bottles, B, C, D, E. The gas is dissolved in B, but the solution soon becomes saturated, and a purer (washed) ammonia passes over into the following vessels, in the last of which only a pure solution is obtained. The bent funnel tube G in the flask preserves the apparatus from the possibility both of the pressure of the gas evolved in it becoming too great (when the gas escapes through it into fact that ammonia has an alkaline reaction, and colours litmus paper blue, just like caustic potash or lime; it is therefore sometimes called **caustic ammonia** (volatile alkali). Acids may be saturated by ammonia water or gas in exactly the same way as by any other alkali. In this process **ammonia combines directly with acids,** and this forms the most characteristic chemical reaction of this substance. If sulphuric, nitric, acetic, or any other acid is brought into contact with ammonia, it absorbs it, and in so doing evolves a large amount of heat and forms a compound having all the properties of a salt. Thus, for example, sulphuric acid, H_2SO_4, in absorbing ammonia, forms (on evaporating the solution) one or both of two salts, according to the relative quantities of ammonia and acid. One salt is formed from $NH_3+H_2SO_4$, and consequently has the composition NH_5SO_4, and the other is formed from $2NH_3+H_2SO_4$, and its composition is therefore $N_2H_8SO_4$. The former has an acid

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the air), and also from the pressure accidentally falling too low (for instance, owing to a cooling effect, or from the reaction stopping). If this takes place, the air passes into the retort, otherwise the liquid from B would be drawn into A. The safety tubes s_1, s_2, &c., in each Woulfe's bottle, open at both ends and immersed in the liquid, serve for the same purpose. Without them, in case of an accidental stoppage in the evolution of so soluble a gas as ammonia, the solution would be sucked from one vessel to another; for instance, from into D, &c. In order to see clearly the necessity for *safety tubes* in a gas apparatus, it must be remembered that the *gaseous pressure* in the interior of the arrangement must exceed the atmospheric pressure by the sum of the heights of the columns of liquid through which the gas has to pass.

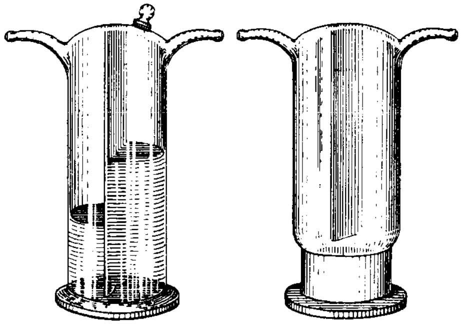

FIG. 53.—Tischenko's apparatus for washing or absorbing gases. In the form shown in the right-hand figure, solids such as fused calcium chloride, potash, &c. may be employed.

Instead of setting up each time such a cumbersome and breakable apparatus as the above, various ready-made forms are now employed which greatly simplify the matter. Among such, Prof. Tischenko's apparatus, shown in fig. 53, is distinguished for its simplicity and regular action. It is composed of a glass jar furnished with a glass partition passing down the middle and having one or more holes at the bottom. A gas-conducting tube extends from the upper portion of each side of the jar, and the top is provided with a stoppered opening for pouring in the liquid used for washing the gas. If the liquid be introduced in such quantity as not quite to fill either half of the jar, but sufficient to cover the holes at the bottom of the partition, then the gas will be able to pass in either direction without forcing the liquid out of the jar. If, for instance, the pressure be greater on the right-hand side than the left, then the liquid will pass from the right to the left, and the gas will rise in bubbles through the column of liquid. If the pressure be reversed the same thing takes place in the opposite direction. A series of such jars may be advantageously used in the preparation of saturated solutions of ammonia.

reaction and the latter a neutral reaction, and they are called respectively acid ammonium sulphate (ammonium hydrogen sulphate) and normal ammonium sulphate or simply ammonium sulphate. Similar salts are formed by the action of all other acids; but certain of them are able to form normal ammonium salts only, whilst others give both acid and normal ammonium salts. This depends on the nature of the acid and not on the ammonia, as we shall afterwards see. Ammonium salts are very similar in appearance and in many of their properties to metallic salts; for instance, sodium chloride or table salt, NaCl, resembles sal-ammoniac, or ammonium chloride, NH_4Cl, not only in its outward appearance but even in crystalline form, in its property of giving precipitates with silver salts, in its solubility in water, and in its power of evolving hydrochloric acid when heated with sulphuric acid—in a word, a most perfect analogy is to be remarked in an entire series of reactions. An analogy in composition is seen if sal-ammoniac, NH_4Cl, be compared with table salt, NaCl; or ammonium hydrogen sulphate, NH_4HSO_4, with sodium hydrogen sulphate, $NaHSO_4$; or ammonium nitrate, NH_4NO_3, with sodium nitrate, $NaNO_3$, &c.[13] It is seen, on comparing the above compounds, that the part which sodium takes in the sodium salts is played in ammonium salts by a group, NH_4, which is called **ammonium.** If table salt be called 'sodium chloride,' then sal-ammoniac should be and is called 'ammonium chloride.'

The hypothesis that ammoniacal salts correspond with a complex metal ammonium was enunciated by the famous Swedish chemist Berzelius, after a proposition put forward by Ampère. The analogy

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[13] The analogy between the ammonium and sodium salts might seem to be destroyed by the fact that the latter are formed from the alkali or oxide and an acid, with the separation of water, whilst the ammonium salts are directly formed from ammonia and an acid without the separation of water; but the analogy is restored if we compare soda to ammonia water, and liken caustic soda to a compound of ammonia with water. Then the very preparation of ammonium salts from such a hydrate of ammonia will completely resemble the preparation of sodium salts from soda. We may cite as an example the action of hydrochloric acid on both substances.

$NaHO$	+	HCl	=	H_2O	+	$NaCl$
Sodium hydroxide		Hydrochloric acid		Water		Table salt
NH_4HO	+	HCl	=	H_2O	+	NH_4Cl
Ammonium hydroxide		Hydrochloric acid		Water		Sal-ammoniac

Just as in soda, so also in ammonia hydrate, the hydroxyl or aqueous radicle OH is replaced by chlorine. The analogy between NH_4 and Na and H is moreover exhibited by the fact that anhydrous peroxide of hydrogen directly absorbs ammonia gas (H_2O_2 is taken in the form of an ethereal solution) and forms a peroxide compound, NH_4HO_2 (cubical crystals insoluble in ether) like H_2O_2 or Na_2O_2. Moissan in his researches on Weyl's compounds (see following note), for instance, NH_3Na, considers that free ammonium may be regarded as ammonia hydride, NH_3H, that is, as an analogue of these compounds.

between ammonium and metals is probable, owing to the fact that mercury is able to form an amalgam with ammonium similar to those which it forms with sodium and many other metals. The only difference between **ammonium amalgam** and sodium amalgam consists in the instability of the ammonium, which easily decomposes into ammonia and hydrogen.[14] Ammonium amalgam may be prepared from sodium amalgam. If the latter be shaken up with a strong solution of sal-ammoniac the mercury swells up violently and loses its mobility whilst preserving its metallic appearance. In so doing the mercury dissolves ammonium—that is, the sodium in the mercury is replaced by the ammonium, which it replaces in the sal-ammoniac, forming sodium chloride, $NH_4Cl+HgNa=NaCl+HgNH_4$. Naturally the formation of ammonium amalgam does not absolutely prove the existence of ammonium itself in a separate state; but it shows the possibility of this substance existing, and its analogy with the metals,

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[14] By subjecting sodium to the action of ammonia at the ordinary temperature and under considerable pressures, Weyl (1864) obtained a liquid which was subsequently investigated by Joannis (1889), who confirmed Weyl's results. At 0° and the atmospheric pressure the composition of this substance is $Na+5{\cdot}3NH_3$. The removal (at 0°) of ammonia from the liquid gives a solid copper-red body having the composition NH_3Na. The determination of the molecular weight of this substance by the fall of the pressure of liquid ammonia gave the composition $N_2H_6Na_2$. It is therefore free ammonium in which one H is replaced by Na. Compounds with potassium, lithium, calcium, &c. proved to have analogous compositions. Dry NH_3 is absorbed by lithium at +70°, forming a blue liquid, and it also gives similar liquids with sodium and potassium at −20°, whilst with metallic calcium at +20° it forms a solid compound, $Ca,4NH_3$. When heated, all these compounds decompose into ammonia and the metal, or into an amide NH_2R and H_2 (Moissan, Chap. XIV., note 62). By the decomposition of NH_3Na at the ordinary temperature, Joannis (1891) obtained hydrogen and sodium amide, NH_2Na, in small colourless crystals soluble in water. The addition of liquid ammonia to metallic sodium and a saturated solution of sodium chloride gives NH_4Na_2Cl, that is, sal-ammoniac in which H_2 is replaced by Na_2.

Ammonium amalgam was originally obtained in exactly the same way as sodium amalgam (Davy); namely, a piece of sal-ammoniac was taken and moistened with water (in order to render it a conductor of electricity). A cavity was made in it, into which mercury was poured, and it was laid on a sheet of platinum connected with the positive pole of a galvanic battery, the negative pole of which was put into connection with the mercury. On passing a current the mercury increased considerably in volume, and became plastic, while preserving its metallic appearance, just as would be the case were the sal-ammoniac replaced by a lump of a salt of sodium or of one of a number of other metals. Moissan (1901) prepared amalgams with the aid of liquid ammonia and low temperatures. The amalgam of sodium does not act upon liquid ammonia, but dry iodide of ammonium reacts, forming—without the evolution of gas—a liquid amalgam of ammonium which solidifies into a compact mass when cooled to −80°. If it be warmed (after washing and drying) it becomes liquid at −40°, and then effervesces and swells up owing to the formation of gases, which were found to contain hydrogen and ammonia, $2NH_3+H_2$. All efforts to obtain the ammonium itself, for instance, by the reaction $2NH_3Li+H_2S=Li_2S+2NH_4$ at low temperatures (to −70°) were unsuccessful, and only gave a mixture of NH_3 and H_2.

because only metals dissolve in mercury.[15] Ammonium amalgam crystallises in cubes, three times heavier than water; it is stable only in the cold, and particularly so at very low temperatures. It begins to decompose at the ordinary temperature, evolving ammonia and hydrogen in the proportion of two volumes of ammonia to one volume of hydrogen, $NH_4=NH_3+H$. Under the action of water, ammonium amalgam gives hydrogen and ammonia water, just as sodium amalgam gives hydrogen and sodium hydroxide; and therefore, in accordance with the ammonium theory, ammonia water or caustic ammonia must be looked on as containing ammonium hydroxide, NH_4OH,[16] just as an aqueous solution of caustic soda contains NaOH. The ammonium hydroxide, like ammonium itself, is an unstable substance, which readily dissociates and can only exist in a free state at low temperatures.[17] Ordinary solutions of ammonia may be looked upon as the products of the dissociation of this hydroxide, inasmuch as $NH_4OH=NH_3+H_2O$. In its chemical reactions caustic ammonia (and in general, solutions of NH_3 in water) is exactly similar to caustic soda, NaHO; thus it neutralises acids, enters into double saline decompositions (for instance, a salt MX gives the reaction, $NH_4OH+MX=NH_4X+MOH$), &c., only with this difference, that this alkali can be entirely and readily volatilised.

All ammoniacal salts **decompose at a red heat** into ammonia and an acid, which, on cooling in contact with each other, recombine. If the acid be non-volatile, the ammoniacal salt, when heated, evolves the ammonia, leaving the non-volatile acid behind; if the acid be volatile, then, on heating, both the acid and ammonia volatilise together, and on cooling recombine into the salt which originally served for the formation of their vapours.[18]

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[15] We may mention, however, that under certain conditions hydrogen is also capable of forming an amalgam resembling the amalgam of ammonium. If an amalgam of zinc is shaken up with an aqueous solution of platinum chloride, without access of air, a spongy mass is formed which easily decomposes, with evolution of hydrogen.

[16] We saw above (note 12) that the solubility of ammonia in water at low temperatures attains to the molecular ratio, NH_3+H_2O, in which these substances are contained in caustic ammonia; and it may perhaps be possible, at exceedingly low temperatures, to obtain ammonium hydroxide, NH_4HO, in a solid form. Regarding solutions as dissociated definite compounds, we should see a confirmation of this view in the property shown by ammonia of being extremely soluble in water, and in so doing of approaching to the limit NH_4HO.

[17] In confirmation of the truth of this conclusion we may cite the fact that there exist, in a free state and as comparatively stable compounds, a series of alkaline hydroxides, NR_4HO, which are perfectly analogous to ammonium hydroxide, and present a striking resemblance to it and to sodium hydroxide, with the only difference that the hydrogen in NH_4HO is replaced by complex groups, $R=CH_3$, C_2H_5, &c., for instance $N(CH_3)_4HO$. Details will be found in works on organic chemistry.

[18] The fact that ammoniacal salts are decomposed when ignited, and not simply sublimed, may be proved by a direct experiment with sal-ammoniac, NH_4Cl, which in a

Ammonia is capable of combining not only with acids, but also with many salts, as was seen from its forming definite compounds, $AgCl,3NH_3$ and $2AgCl,3NH_3$ (mentioned above), with silver chloride. Ammonia is absorbed with evolution of heat by various oxygen salts of the metals, and also by the chlorine, iodine, and bromine compounds of many metals. Certain of these compounds part with their ammonia when left exposed to the air, but others only do so at a red heat; many give up their ammonia when dissolved, whilst others dissolve without decomposition, and when their solutions are evaporated, separate unchanged All these facts merely indicate that ammoniacal, like aqueous, compounds dissociate with greater or less facility.[19] Certain metallic oxides also absorb ammonia and are dissolved by ammonia water. This is the case, for instance, with the oxides of zinc, nickel, copper, and many others, the majority of the compounds thus formed being unstable. The property of ammonia of combining with various oxides explains its action on certain metals, for instance, on copper in the presence of air.[19a]

The similarity between the relations of ammonia and of water to salts and other substances is more especially marked in those cases in which the salt is capable of combining with both ammonia and water. Take, for example, copper sulphate, $CuSO_4$, which, as we saw in Chapter I., gives with water blue crystals, $CuSO_4,5H_2O$; but the anhydrous salt also absorbs dry ammonia in the same molecular proportions, forming a blue substance, $CuSO_4,5NH_3$, and therefore the ammonia combining with salts may be termed **ammonia of crystallisation.**

Many **products** of direct or indirect **substitution** correspond to ammonia, its compounds with water and the ammonium salts. Certain

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state of vapour is decomposed into ammonia, NH_3, and hydrochloric acid, HCl, as will be explained in the following chapter. The readiness with which ammonium salts decompose is seen from the fact that a solution of ammonium oxalate is decomposed with evolution of ammonia even at − 1°. Dilute solutions of ammonium salts, when boiled, give aqueous vapour having an alkaline reaction owing to the presence of free ammonia given off from the salt.

[19] As we have seen in note 8, Isambert studied the dissociation of ammoniacal compounds, and showed that at low temperatures many salts are able to combine with a still greater amount of ammonia, which proves an entire analogy with hydrates; and as in this case it is easy to isolate the definite compounds, and as also the least possible pressure of ammonia is greater than that of water, the ammoniacal compounds present a great and peculiar interest, as a means of explaining the nature of aqueous solutions and as a confirmation of the hypothesis of the formation of definite compounds in them. For these reasons we shall frequently refer to these compounds in the further exposition of this work.

[19a] Chap. V., note 2. This is the reason why copper vessels cannot be used for holding ammonia. Iron is not acted on by it. As zinc evolves hydrogen from ammonia (in aqueous solution) it may act like copper; but the affinity is small in this case, so that the oxygen affinity must also be taken into account. Copper alloys may be cleaned (the superficial coating of oxides removed) with a solution of ammonia.

of the elements, for instance, sodium, zinc, chlorine, &c., directly displace a portion of the hydrogen from NH_3 and take its place. The displaced hydrogen then appears either in the free state or combined with the simple body. If metallic sodium be heated in an atmosphere of dry ammonia it will displace a portion of the hydrogen in the ammonia and form sodium amide, $NaNH_2$, according to the equation: $NH_3 + Na = NaNH_2 + H$. Chlorine acts in essentially the same way, forming $ClNH_2$, but the hydrogen evolved, owing to its great affinity for chlorine, gives HCl, and in general the reaction is more complicated (see Chap. XI.), although fundamentally it is the same as in the case of sodium. Certain metallic compounds resembling ammonia in their composition and reactions, and in which the hydrogen is replaced by the metal, are formed directly by heating the metal in nitrogen. Thus lithium and magnesium readily absorb nitrogen when heated, forming nitrides, NLi_3 and N_2Mg_3, which give ammonia with water (for instance, $N_2Mg_3 + 6H_2O = 3MgH_2O_2 + 2NH_3$). This shows that they, like sodium amide, are analogous to ammonia, and have the same composition and structure, with the difference that all the hydrogen is replaced by a metal, just as the metallic oxides correspond to water and may be regarded as products of substitution of the hydrogen in water by metals. But the hydrocarbon products of substitution of the hydrogen in ammonia present even greater interest. They have the composition NH_2R, NHR_2, and NR_3, where R is a hydrocarbon group (or residue), such as CH_3, C_2H_5, C_6H_5, &c. These compounds, which are described fully in organic chemistry, are especially instructive because they preserve in themselves the faculty of ammonia for combining with acids and forming salts, and thus resemble ammonia completely in their chemical characters also. In nature such nitrogenous hydrocarbon derivatives of ammonia are met with in plants and animals, and are known as alkaloids owing to their capacity of combining with acids like ammonia; such, for instance, are quinine, nicotine, &c.[20]

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[20] The practical applications of ammonia are very varied. The use of ammonia as a stimulant, in the form of the so-called 'smelling salts' or of spirits of hartshorn, in cases of faintness, &c., is known to everyone. The volatile carbonate of ammonium, or a mixture of an ammonium salt with an alkali, is also employed for this purpose. Ammonia also produces a well-known stimulating effect when rubbed on the skin, for which reason it is sometimes employed for external applications. Thus, for instance, the well-known volatile salve is prepared from any liquid oil by shaking up with a solution of ammonia. A portion of the oil is thus transformed into a soapy substance. The solubility of greasy substances in ammonia, which proceeds from the formation both of emulsions and soaps, explains its use in extracting grease-spots. It is also employed as an external application for stings from insects and for poisonous snake-bites, and in general in medicine. It is also remarkable that in cases of drunkenness a few drops of ammonia in water taken internally rapidly renders a person sober. A large quantity of ammonia is used in dyeing, either for the solution of certain dyes—for example, carmine—or for

We shall now pass on to the consideration of the other compounds of nitrogen with hydrogen, and also of those with oxygen.

But in order to grasp the relation between ammonia and the other compounds of nitrogen it is necessary to recognise the general **law of substitution**, which is applicable to all cases of substitution between elements,[20a] and to show therefore what may be the conditions of substitution between oxygen and hydrogen as component parts of water. The law of substitution may be deduced from mechanical principles, if the molecule be conceived as a system of elementary atoms occurring in a certain chemical and mechanical equilibrium. By likening the molecule to a system of bodies in a state of motion—for instance, to the sum total of the sun, planets, and satellites, existing in conditions of mobile equilibrium—we should expect the action of one part in this system to be equal and opposite to the other, according to Newton's third law of mechanics. Hence, given a molecule of a compound, for instance, H_2O, NH_3, NaCl, HCl, &c., its two parts must, in a chemical sense, represent two things somewhat alike in force and properties, and therefore *every two parts into which a molecule of a compound may be divided* **are capable of replacing each other.**[21] In order that the application of the law should become clear it is evident that among compounds the most stable should be chosen. We shall therefore take hydrochloric acid and water as the most stable compounds of hydrogen.[21a] According to the above law of substitution, if the elements H and Cl are able to form a molecule, HCl, and a stable one, they are able to replace each other. And, indeed, we shall afterwards see (Chap. XI.) that in a number of instances substitution between hydrogen and chlorine can take place. Given RH, then RCl is possible, because HCl exists and is stable. The molecule of water, H_2O, may be divided in two ways, because it contains three atoms: into H and (HO) on the one hand, and into H_2 and O on the other. Consequently, being given RH, its substitution products will be R(HO) according to the first form, and R_2O according to the second; being given RH_2, its corresponding substitution products will be RH(OH), $R(OH)_2$, RO, $(RH)_2O$, &c. The group (OH) is the same **hydroxyl or aqueous radicle** which we have already mentioned in the third chapter as a component part of hydroxides and alkalies—for instance, Na(OH), $Ca(OH)_2$, &c. It is evident, judging from H(HO) and HCl, that (OH) can be substituted by Cl, because both are replaceable by H; and this is of common occurrence in chemistry, because metallic chlorides—for example, NaCl and NH_4Cl—correspond with hydroxides of the alkalis, Na(OH) or $NH_4(OH)$. In hydrocarbons—for instance, C_2H_6—the hydrogen is replaceable by chlorine and by hydroxyl. Thus ordinary alcohol is C_2H_6, in which one atom of H is replaced by (OH), that is, $C_2H_5(OH)$. It is evident that the replacement of hydrogen by hydroxyl forms essentially the phenomenon of oxidation, because RH gives R(OH), or RHO. Hydrogen peroxide may

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changing the tints of others, or else for neutralising the action of acids. It is also employed in the manufacture of artificial pearls. For this purpose the small scales of a peculiar small fish are mixed with ammonia, and the liquid so obtained is blown into small hollow glass beads shaped like pearls.

In nature and the arts, however, ammonium salts, and not free ammonia, are most frequently employed. It is in this form that a portion of that **nitrogen** which is necessary for the formation of albuminous substances **is supplied to plants**. In this way a large quantity of ammonium sulphate is now employed as a fertilising substance. But the same effect may be produced by nitre or by animal refuse, which in decomposing gives ammonia. For this reason an ammoniacal (hydrogen) compound which may be introduced into the soil in the spring will be converted into a nitrate (oxygen salt) in the summer.

[20a] When the element chlorine, as we shall afterwards more fully learn, replaces hydrogen, the reaction by which such an exchange is accomplished proceeds as a substitution, $AH + Cl_2 = ACl + HCl$, so that two substances, AH and chlorine, react on each other and two substances, ACl and HCl, are formed; and, further, two molecules react on each other, and two others are formed. Such reactions proceed very easily, but the substitution of one element, *A*, by another, *X*, does not always proceed with such ease, clearness or simplicity. The substitution between oxygen and hydrogen is very rarely accomplished by the direct action of the free elements, but the substitution between these elements, one for another, forms the most common case of oxidation or reduction. In speaking of the law of substitution, I have in view the substitution of the elements one by another, and not the direct reaction of substitution. The law of substitution determines the cycle of the combinations of a given element if a few of its compounds (for instance, the hydrogen compounds) be known. A development of the conceptions of the law of substitution may be found in my lecture given at the Royal Institution in London, 1889 (two lectures read in London. See 2nd edition of *Principles of Chemistry*).

[21] It is evident from the essence of the matter that affinity must play a certain part in substitution, that is to say, that although chlorine, for instance, forms NaCl with sodium, and therefore Cl can replace Na, yet this does not take place in every case. The law indicates the possibility of such a substitution taking place, and, what is still more important, it foretells the relative amounts of the substituting groups. Two atoms of hydrogen are replaced, judging from the composition of water, not by two atoms, but by one atom, of oxygen. The greater the complexity of the molecule the more difficult will it naturally be to obtain the products of substitution of all its subdivisions. It should further be remarked that in its above form the law of substitution simultaneously generalises the principles of such phenomena as metalepsis (see, in Chap. XI., the substitution of hydrogen by chlorine), oxidation, and homology (Chap. VIII.), which are as a rule (especially under the influence of the electrical and the dualistic conceptions) considered separately and independently of each other. The ordinary common instances of substitution of like by like are that quantities separately equal to some third are equal to each other; from which it is evident that if MX and RX exist then M can replace R, and *vice versa*.

[21a] If hydrogen peroxide be taken as a starting-point, then still higher forms of oxidation than those corresponding with water should be looked for. They should possess the properties of hydrogen peroxide, especially that of parting with their oxygen with extreme ease (even by contact). Such compounds are known. Pernitric, persulphuric, and similar acids present these properties, as we shall see when describing them.

in this sense be regarded as water in which the hydrogen is replaced by hydroxyl; H(OH) gives $(OH)_2$ or H_2O_2. The other form of substitution—namely, that of O in the place of H_2—is also a common chemical phenomenon. Thus alcohol, C_2H_6O, or $C_2H_5(OH)$, when oxidising in the air, gives acetic acid, $C_2H_4O_2$, or $C_2H_3O(OH)$, in which H_2 is replaced by O.

In the further course of this work we shall have frequent occasion to refer to the law of substitution for explaining many chemical phenomena and relations.

We shall now apply these conceptions to ammonia in order to see its relation to other compounds of nitrogen. It is evident that many substances should be obtainable from ammonia, NH_3, or aqueous ammonia, $NH_4(OH)$, by replacing their hydrogen by hydroxyl, or H_2 by oxygen. And such is the case. The extreme cases of substitution will be obtained on the one hand when we imagine the substitution of hydrogen in ammonia, NH_3, by hydroxyl, so that $NH_2(OH)$ is obtained, and on the other hand when we imagine that all the hydrogen in $NH_4(OH)$ is replaced by oxygen, so that $NO_2(OH)$ is formed. Both these possible extreme cases of the application of the law of substitution are evidently products of oxidation, for $NH_2(OH) = NH_3 + O$ and $2NO_2(OH) = 2\ NH_3 + 4O_2 + 2H_2O$, and they are both known as independent substances. The first, $NH_2(OH)$, is called **hydroxylamine,** because substances containing the ammonia residue, NH_2, are called amides or amines, and the residue itself amide, and the aqueous residue OH, as we already know, is called hydroxyl, and here these two are combined together. The second of the above substitution products, the highest oxidation compound, $NO_2(OH)$, is nothing else but nitric acid, which corresponds to the anhydride, N_2O_5, and salts NMO_3. And as intermediate substitution products can be placed between these two extreme cases, we see that, starting from ammonia and its compound with water, we are enabled by the law of substitution to understand the relations of all the known compounds of nitrogen, hydrogen, and oxygen. It is simplest to start with caustic ammonia and substitution by hydroxyl.

The *first* product of this substitution will be $NH_3(OH)_2 = NH_5O_2$. The separation of H_2O from it will give the above **hydroxylamine,** $NH_2(OH)$. This substance was obtained as a salt, i.e., combined with an acid, in 1865 by Lossen as a product of the deoxidation (by the action of nascent hydrogen, SO_2, and other reducing agents) of nitric acid. The salt formation is determined by the fact that hydroxylamine still contains a large proportion of hydrogen in combination with the nitrogen, so that the substance obtained is able, like ammonia, to

form salts with acids.[22] But the formation of hydroxylamine, $NH_2(OH) = NH_3O$, indicates the possibility of the formation of two other compounds of nitrogen: N_2H_4 and NH, that is, of free amide $(NH_2)\ (NH_2) = N_2H_4$ and free imide NH (equivalent to $NH_3O - H_2O$), in which, as hydrogen compounds similar to ammonia, one would also expect to find a faculty for combining with acids. The possibility of the existence of free amide

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[22] The compound of hydroxylamine with hydrochloric acid has the composition $NH_2(OH)HCl = NH_4ClO$, being, as it were, oxidised sal-ammoniac. It was prepared by Lossen in 1866 by the action of tin and hydrochloric acid in the presence of water on a substance called ethyl nitrate, the hydrogen liberated from the hydrochloric acid by the tin acting upon the elements of nitric acid—

$$\underset{\text{Ethyl nitrate}}{C_2H_5{\cdot}NO_3} + \underset{\substack{\text{Hydrogen from}\\ \text{HCl and Sn}}}{6H + HCl} = \underset{\text{Hydroxylamine + HCl}}{NH_4OCl} + \underset{\text{Water}}{H_2O} + \underset{\text{Alcohol}}{C_2H_5{\cdot}OH}$$

Thus in this case the nitric acid is deoxidised, not directly into nitrogen, but into hydroxylamine. On mixing nitric acid with water and either sulphuric or hydrochloric acid, cooling the solution and subjecting it to the action of an electric current, using a mercury or amalgamated lead cathode, the nitric acid is almost completely reduced to hydroxylamine (Tafel, 1902). Hydroxylamine is also formed by passing nitric oxide, NO, into a mixture of tin and hydrochloric acid—that is, by the action of the hydrogen evolved on the nitric oxide, $NO + 3H + HCl = NH_4OCl$—and in many other reactions. According to Lossen's method, a mixture of 30 parts of ethyl nitrate, 120 parts of tin, and 40 parts of a solution of hydrochloric acid of sp. gr. 1·06 is made, and after a certain time the reaction commences spontaneously. When the reaction has ceased the tin is separated by means of hydrogen sulphide and the solution evaporated, a large amount of sal-ammoniac being thus obtained (owing to the further action of hydrogen on the hydroxylamine compound, from which it takes up oxygen and forms water); a solution ultimately remains containing the hydroxylamine salt, which is dissolved in anhydrous alcohol and purified by the addition of platinum chloride, which precipitates any ammonium salt still remaining in the solution. After concentrating the alcoholic solution, the hydroxylamine hydrochloride separates in crystals. This substance melts at about 150°, and in so doing decomposes into nitrogen, hydrogen chloride, water, and sal-ammoniac. A sulphuric acid compound of hydroxylamine may be obtained by mixing a solution of the above salt with sulphuric acid; like the hydrochloride, it is soluble in water. Hydroxylamine, then, like ammonia itself, forms a series of salts in which one acid may be substituted for another. It might be expected that, by mixing a strong solution of a hydroxylamine salt with a solution of a caustic alkali, hydroxylamine itself would be liberated, just as an ammonium salt under these circumstances evolves ammonia; but the liberated hydroxylamine is immediately decomposed with the formation of nitrogen and ammonia (and probably nitrous oxide), $3NH_3O = NH_3 + 3H_2O + N_2$. Dilute solutions give the same reaction, although very slowly, but by decomposing a solution of the sulphate with barium hydroxide a certain amount of hydroxylamine is obtained in solution (it is partly decomposed). Like ammonia, hydroxylamine in aqueous solution precipitates basic hydrates, and it deoxidises the oxides of copper, silver, and other metals. Free hydroxylamine was obtained by Lobry de Bruyn (1891) and is a solid, colourless, crystalline substance (sp. gr. 1·935), without odour, and melting at +33°. It is highly hygroscopic and readily distils under a low pressure (it is purified in this way), but decomposes with explosion when heated at the ordinary pressure. It is almost insoluble in ordinary solvents like chloroform, benzene, acetic ether, and carbon bisulphide. Its aqueous solutions, containing up to 60 per cent. (sp. gr. 1·15 at 20°), are tolerably stable, and may be kept for many weeks without undergoing any change. Lobry de Bruyn used the hydrochloric acid salt to prepare pure hydroxylamine. The salt was first is in accordance with the law of substitution, because if ammonia be expressed as $(NH_2)H$, the group NH_2 should be able to replace hydrogen, and this exchange would result in the formation of amide $(NH_2)NH_2 = N_2H_4$. This substance was obtained by Curtius (1887), and was named **hydrazine**, N_2H_4.[22a] It forms a liquid boiling at about 113°, and capable of giving a stable hydrate N_2H_4,H_2O, which may be regarded as caustic ammonia, NH_4OH, in which H is replaced by NH_2. This hydrate is distinctly alkaline. Hydrazine is also formed by reducing hyponitrous acid, $N_2(OH)_2$, with ammonium sulphide, $N_2H_2O_2+3H_2 = N_2H_4+2H_2O$. We shall afterwards become acquainted with this acid, because, like amide, it forms one of the intermediate substances between ammonia and nitric acid, and so far such intermediary products have been almost exclusively obtained from more highly oxidised products by a method of reduction, and not by the oxidation of more highly hydrogenated compounds. The free amide NH (or maybe N_nH_n), equivalent to hydroxylamine less water, has not yet been obtained separately, and if it be at any time prepared, it will be as a substance which easily decomposes into nitrogen and hydrogen.[23]

The *second* product of the substitution of hydrogen by hydroxyl, in caustic (aqueous) ammonia, $NH_2(OH)_3 = NH_5O_3$, should by the abstraction of water give NH_3O_2 and NHO. This latter is hyponitrous acid, which appears, however, in the form of a polymeride, $N_2H_2O_2$, described further on. But as it still contains hydrogen and oxygen, it is to be expected that it should part with water, and give the nitrous oxide described later.

$$NHO+NHO=H_2O+N_2O.$$

The *third* product of substitution, $NH(HO)_4 = NH_5O_4$, when deprived

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treated with sodium methylate, (CH_3NaO), after which methyl alcohol was added to the mixture. The precipitated sodium chloride was separated from the solution by filtration. (The methyl alcohol is added to prevent the precipitated chloride of sodium from coating the insoluble hydrochloride of hydroxylamine.) Under the action of NaHO, hydroxylamine gives NH_3 and NHO_2 or N_2O, while it forms nitric acid (Kolotoff, 1893) under the action of oxidising agents. It is obtained in a great number of reactions; for instance, by the action of tin on dilute nitric acid and by the action of zinc on ethyl nitrate and dilute hydrochloric acid. The relation between hydroxylamine, $NH_2(OH)$, and nitrous acid, $NO(OH)$, which is so clear in the sense of the law of substitutions, becomes a reality in those cases in which reducing agents act on salts of nitrous acid. Thus Raschig (1888) proposed the following method for the preparation of hydroxylamine sulphate. A mixture of strong solutions of potassium nitrite, KNO_2, and hydroxide, KHO, in molecular proportions, is prepared and cooled. An excess of sulphurous anhydride is then passed into the mixture and the solution boiled for a long time. A mixture of the sulphates of potassium and hydroxylamine is thus obtained: $KNO_2 + KHO + 2SO_2 + 2H_2O = NH_2(OH),H_2SO_4 + K_2SO_4$, and these may be separated from each other by crystallisation.

[22a] Free **amidogen** or **hydrazine**, N_2H_4, or $2NH_2$, was prepared by Curtius (1887) by means of ethyl diazoacetate, or triazoacetic acid. Curtius and Jay (1889) showed that triazoacetic acid, $CHN_2.COOH$ (the formula should be tripled), when heated with water or a mineral acid, gives (quantitatively) oxalic acid and amidogen (hydrazine), $CHN_2.COOH + 2H_2O = C_2O_2(OH)_2 + N_2H_4$—i.e., expressed empirically, the oxygen of the water replaces the nitrogen of the azoacetic acid. The amidogen is thus obtained in the form of a salt. With acids, amidogen forms very stable salts of the two types N_2H_4,HX and N_2H_4,H_2X_2; as, for example, with HCl, H_2SO_4, &c. These salts are easily crystallised; in acid solutions they act as powerful reducing agents, evolving nitrogen; when ignited they are decomposed into ammoniacal salts, nitrogen, and hydrogen; with nitrites they evolve nitrogen. The sulphate N_2H_4,H_2SO_4 is sparingly soluble in cold water (3 parts in 100 of water), but is very soluble in hot; its specific gravity is 1·378 and it fuses at 254° with decomposition. The hydrochloride $N_2H_4,2HCl$ crystallises in octahedra, is very soluble in water, but not in alcohol; it fuses at 198°, evolving hydrogen chloride and forming the salt N_2H_4,HCl; when rapidly heated it decomposes with an explosion; with platinic chloride it immediately evolves nitrogen, forming platinous chloride. By the action of alkalies the salts $N_2H_4,2HX$ give **hydrate of amidogen**, N_2H_4,H_2O, which is a fuming liquid (specific gravity 1·03), solidifying at about 10° and boiling at 199°, almost without odour, and whose aqueous solution corrodes glass and indiarubber, has an alkaline taste and poisonous properties. With oxide of barium the hydrate gives anhydrous hydrazine as a liquid (sp. gr. 1·01) boiling at 113° (but it is best to distil it under a low pressure because it readily decomposes), and solidifying at about +1°. The reducing properties of the hydrate are clearly seen from the fact that it reduces the metals platinum and silver from their solutions. With mercuric oxide it explodes. Iodic acid HIO_3 (and also its salts, even the insoluble barium salt BaI_2O_6) oxidises the salts of hydrazine at the ordinary temperature, and is entirely converted into hydriodic acid, with the evolution of free nitrogen (Ditte); for instance, $BaI_2O_6 + 3N_2H_4,H_2SO_4 = 2HI + 2H_2SO_4 + BaSO_4 + 6H_2O + 3N_2$ (this reaction is so complete that the amount of barium may be determined by the volume of nitrogen evolved; it was proposed by Rigler as an analytical method). It reacts directly with the aldehydes RO, forming N_2R_2 and water; for example, with benzaldehydes it gives the very stable insoluble *benzalazine*, $(C_6H_5CHN)_2$, of a yellow colour. We may add that hydrazine often forms double salts; for example, $MgSO_4,N_2H_4,H_2SO_4$ or KCl,N_2H_4,HCl, and that it is also formed by the action of nitrous acid upon aldehyde ammonia. The products of the substitution of the hydrogen in hydrazine by hydrocarbon groups R ($R = CH_3$, C_2H_5, C_6H_5, &c.) were obtained before hydrazine itself; for example, $NHRNH_2$, NR_2NH_2, and $(NRH)_2$.

The heat of formation of hydrated hydrazine, −9·5 cals., from its elements was deduced from the heat of combustion, +127·7 cals., determined by burning N_2H_4,H_2SO_4 in a calorimetric bomb. Thus hydrazine is an endothermal compound: its passage into ammonia by combination with hydrogen is accompanied by the evolution of 51·5 cals. In the presence of an acid these figures become greater by +14·4 cals. Hence the direct converse transformation of ammonia into hydrazine is impossible. As regards the passage of hydroxylamine into hydrazine, it would be accompanied in aqueous solution by an evolution of heat (+21·5 cals.).

Amidogen must be regarded as a compound which stands in the same relation to ammonia as hydrogen peroxide to water. As was clearly to be expected, water, H(OH), gives, according to the law of substitution, (OH)(OH)—that is, peroxide of hydrogen. So also ammonia, $H(NH_2)$, forms hydrazine, $(NH_2)(NH_2)$—that is, the free radicle of ammonia, NH_2, or amidogen. In the case of phosphorus a similar substance, as we shall afterwards see, has long been known under the name of liquid phosphoretted hydrogen, P_2H_4.

[23] **Imide**, NH, has not been obtained in a free state, but its hydrochloric acid salt, NH,HCl, has apparently been obtained (1890) by Maumené by igniting the double bichloride of platinum and ammonium chloride, $PtCl_2,NH_4Cl = Pt + 2HCl + NH,HCl$. It is soluble in water, and crystallises from its solution in hexagonal rhombic prisms. It gives a double salt with $FeCl_3$ of the composition $FeCl_3,3NHHCl$. The salt NH,HCl is similar (isomeric) to the first possible product of the metalepsis of ammonia, NH_2Cl, although it can hardly resemble it in any of its properties.

of water, should yield nitrous acid (treated of later), NHO_2, and its orthohydrate, $N(OH)_3$, and by the total abstraction of the elements of water,

$$NHO_2 + NHO_2 = H_2O + N_2O_3,$$

nitrous anhydride, N_2O_3, which is also described in the following pages.

The *fourth* and last product of substitution, $N(HO)_5$, less water, gives orthonitric acid, NH_3O_4,[24] and the most highly oxidised product of nitrogen, nitric acid, NHO_3, and its anhydride, N_2O_5:[25] $NHO_3 + NHO_3 = H_2O + N_2O_5$. And as it is supposed in the above equations that two molecules of hydrate are taken, it follows that intermediate oxides of nitrogen, N_2O_2 and N_2O_4, or their polymerides, NO and NO_2, may also be looked for. All these bodies are known and are described in what follows.

We shall, however, first show by two examples that in the first place the passage of ammonia into the oxygen compounds of nitrogen up to nitric acid, as well as the converse preparation of ammonia (and consequently of the intermediate compounds also) from nitric acid, are reactions which proceed directly and easily under many circumstances,[26] and in the second place that the above general principle of substitution gives the possibility of understanding many, at first sight, unexpected and complex relations and transformations, such as the preparation of hydrazoic acid, HN_3. In nature the matter is complicated by a number of influences and circumstances, but in the law the relations are presented in their simplest aspect.

It is easy to prove the possibility of the oxidation of ammonia into nitric acid by passing a mixture of ammonia and air over heated spongy platinum. This causes the oxidation of the ammonia, giving nitric acid, which partially combines with the excess of ammonia.

The converse transformation of nitric acid into ammonia is effected by the action of hydrogen at the moment of its evolution.[27] Thus metallic aluminium, evolving hydrogen from a solution of caustic soda, is able to completely convert nitric acid added to the mixture (as a salt, because the alkali gives a salt with the nitric acid) into ammonia, $NHO_3 + 8H = NH_3 + 3H_2O$. And as, judging from what was said above, ammonia and nitric acid are the extreme compounds of nitrogen with hydrogen and oxygen, and all the other compounds of these elements may be regarded as intermediate compounds, so the passage of NH_3 to HNO_3, and the reverse, clearly show that all the hydrogen and oxygen

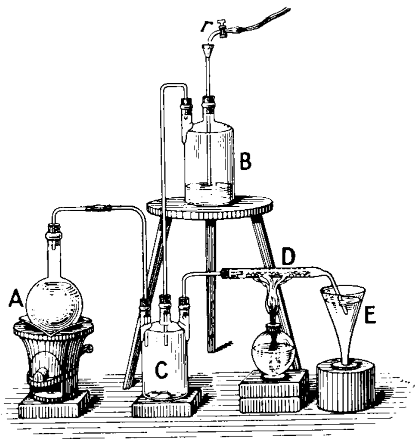

FIG. 54.—Conversion of ammonia into nitric acid. Air is driven out of the bottle B (by the stream of water from r) into C, where it mixes with the ammonia evolved from an aqueous solution in A. The mixed gases pass from C through the heated tube D containing spongy platinum. The nitric acid formed is collected in water in the vessel E.

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[24] Phosphorus (Chap. XIX.) gives the hydride PH_3, corresponding with ammonia, NH_3, and forms phosphorous acid, PH_3O_3, which is analogous to nitrous acid, just as phosphoric acid is to nitric acid; but phosphoric (or, better, orthophosphoric) acid, PH_3O_4, is capable of giving up water yielding pyro- and meta-phosphoric acids. The latter is equal to the ortho-acid minus water $= PHO_3$, and therefore nitric acid, NHO_3, is really meta-nitric acid. So also nitrous acid, HNO_2, is meta-nitrous (anhydrous) acid, and thus the ortho-acid is $NH_3O_3 = N(OH)_3$. Hence for nitric acid we should expect to find, besides the ordinary or meta-nitric acid, $HNO_3(=\frac{1}{2}N_2O_5H_2O)$, and ortho-nitric acid, $H_3NO_4(=\frac{1}{2}N_2O_5,3H_2O)$, an intermediate pyro-nitric acid, $N_2H_4O_7$, corresponding with pyrophosphoric acid, $P_2H_4O_7$. We shall see (for instance, in Chap. XVI., note 21) that in nitric acid there is indeed an inclination of the ordinary salts (of the meta-acid) MNO_3, to combine with bases M_2O, and to approximate to the composition of ortho-compounds which are equivalent to the meta-compound plus a base ($MNO_3 + M_2O = M_3NO_4$).

[25] Nitric acid corresponds with the anhydride N_2O_5, which will afterwards be described, and which must be regarded as the highest saline oxide of nitrogen, just as is Na_2O (and the hydroxide NaHO) in the case of sodium, although sodium forms a peroxide, possessing the property of parting with its oxygen with the same ease as hydrogen peroxide, if not on heating, at all events in reactions—for instance, with acids. So also nitric acid has its corresponding peroxide, which may be called **pernitric acid.** Its composition is not well known, but is probably NHO_4, so that its corresponding anhydride would be N_2O_7. It is formed by the action of a silent discharge on a mixture of nitrogen and oxygen, a portion of its oxygen being hence similar to that in ozone. The instability of this substance (obtained by Hautefeuille, Chappuis, and Berthelot), which readily splits up with formation of nitric peroxide, and its resemblance to persulphuric acid, which we shall afterwards describe, will permit our passing over the consideration of the little that is further known concerning it.

[26] In reality it appears up to the present that the process of oxidation leads to the formation of nitric and nitrous acids, but not to the formation of the intermediate hydrogen compounds which so far have only been obtained by a method of reduction from higher degrees of oxidation. The action of a galvanic current on solutions of nitric acid, in the presence of H_2SO_4 or HCl at the cathode, especially if the latter consist of mercury or an amalgamated metal, leads entirely to the formation of the hydroxylamine salt (Tafel, 1902); but as a rule reduction leads to the formation of ammonia, especially if the cathode be of copper.

[27] The formation of ammonia is observed in many cases of oxidation by means of nitric acid. This substance is even formed in the action of nitric acid on tin, especially if dilute acid be employed in the cold. A still more considerable amount of ammonia is obtained if, in the action of nitric acid, there are conditions directly tending to the evolution of hydrogen, which then reduces the acid to ammonia; for instance, in the action of zinc on a mixture of nitric and sulphuric acids. But hydrogen gas itself can in presence of platinum and by the aid of heat convert the oxide of nitrogen, for instance, NO, into ammonia:

$$2NO + 5H_2 = 2NH_3 + 2H_2O.$$

compounds of nitrogen form one natural series. This sequence of compounds becomes particularly distinct when considered under the light of the law of substitutions.

The same law gives the possibility of foreseeing the relations of trinitride of hydrogen, HN_3, to the members of this series.

In **1890**, Curtius, in Germany, obtained this substance as a very volatile (at $+37°$), soluble, and very explosive liquid having the distinctive properties of an acid, dissolving zinc, aluminium, &c., with the evolution of hydrogen, and giving, like hydrochloric acid, salts; for example, a sodium salt, NaN_3; an ammonium salt, $NH_4N_3=N_4H_4$; a barium salt, $Ba(N_3)_2$, &c. He therefore named it **hydrazoic acid**, HN_3.[27a] The extraordinary composition of the compound (ammonia,

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[27a] Curtius started with benzoylhydrazine, $C_6H_5CONHNH_2$ (hydrazine; see note 20a) (this substance is obtained by the action of hydrated hydrazine on the compound ether of benzoic acid). Benzoylhydrazine, under the action of nitrous acid, gives benzoylazoimide and water:

$$C_6H_5CONHNH_2+NO_2H=C_6H_5CON_3+2H_2O.$$

Benzoylazoimide when treated with sodium alcoholate gives the sodium salt of hydrazoic acid:

$$C_6H_5CON_3+C_2H_5ONa=C_6H_5CO_2C_2H_5+NaN_3.$$

The addition of ether to the resultant solution precipitates the NaN_3, and this salt, when treated with sulphuric acid, gives gaseous hydrazoic acid, HN_3. It has an acrid smell, and is easily soluble in water. The aqueous solution exhibits a strongly acid reaction and dissolves metals, giving the corresponding salts. With hydrazoic acid, gaseous ammonia forms a white cloud, consisting of the ammonium salt, NH_4N_3, which separates out from an alcoholic solution in the form of white lustrous scales. The salts of hydrazoic acid are obtained by reactions of substitution with the sodium or ammonium salts. In this manner Curtius obtained and studied the salts of silver (AgN_3), lead (PbN_6), and barium (BaN_6). With hydrazine, N_2H_4, hydrazoic acid forms saline compounds in the composition of which there are one or two molecules of N_3H per one of hydrazine; e.g., N_5H_5 and N_8H_6. The first, which was obtained in an almost pure form, crystallises from an aqueous solution in dense, volatile, lustrous prisms (up to 1 in. long), melting at 50°, and deliquescing in the air; from a solution in boiling alcohol it separates out in bright crystalline plates. This salt, N_5H_5, has the same empirical composition, N_4H_4, as imide, but its molecular weight and structure are different. Curtius also obtained (1893) hydrazoic acid by passing the vapour of N_2O_3 (evolved by the action of HNO_3 on As_2O_3) into a solution of hydrazine, N_2H_4. Similarly Angeli, by acting upon a saturated solution of silver nitrite with a strong solution of hydrazine, obtained the explosive, AgN_3, in the form of a precipitate, and this reaction, which is based upon the equation: $N_2H_4+NHO_2=HN_3+2H_2O$, proceeds so easily that it forms an experiment for the lecture table. The amide of potassium, NH_2K (obtained by the action of dry NH_3 on heated potassium), gives the potassium salt when acted upon by nitrous oxide, $NH_2K+N_2O=N_3K+H_2O$. This is the most convenient method for obtaining the potassium salt of hydrazoic acid, and therefore the acid itself. A thermal investigation of hydrazoic acid by Berthelot and Matignon gave for the heat of solution of the ammonium salt, N_3HNH_3 (1 grm. in 100 parts of water) the value -708 cals. and for the heat of neutralisation by barium hydrate $+10{\cdot}0$ cals. and by ammonia $+8{\cdot}2$ cals. The heat of combustion of N_4H_4 ($+163{\cdot}8$ cals. at a constant vol.) gives the heat of formation of the salt N_4H_4 (solid) as $-25{\cdot}3$ cals. and (solution) $-32{\cdot}3$ cals.; this explains the explosive nature of this compound. In its heat of forma-

NH_3, contains one N atom and three H atoms; in HN_3, on the contrary, there are three N atoms and one H atom), the ready decomposition of its salts with explosion, and above all its distinctly acid character (an aqueous solution shows a strong acid reaction to litmus), not only indicated the importance of this unexpected discovery, but at first gave rise to some perplexity as to the nature of the substance obtained, for the relations in which HN_3 stood to other simple compounds of nitrogen which had long been known was not at all evident, and the scientific spirit requires that there should be a distinct bond between every innovation, every fresh discovery, and that which is already firmly established and known; for upon this basis is founded that apparently paradoxical union in science of a conservative stability with an irresistible and never-ceasing improvement. This missing connection between the newly discovered hydrazoic acid, HN_3, and the long known ammonia, NH_3, and nitric acid, HNO_3, may be found in the law of substitution, starting from the well-known properties and composition of nitric acid and ammonia, as I mentioned in the 'Journal of the Russian Physico-Chemical Society' (1890). The essence of the matter lies in the fact that to the hydrate of ammonium, or caustic ammonia, NH_4OH, there should correspond, according to the law of substitution, an ortho-nitric acid, $H_3NO_4=NO(OH)_3$, which equals $NH_4(OH)$ with the substitution in it of (*a*) two atoms of hydrogen by oxygen ($O-H_2$) and (*b*) two atoms of hydrogen by the aqueous radicle ($H-OH$). The analogue of nitric acid, phosphoric acid, gives corresponding ortho- and meta-acids, PH_3O_4 and PHO_3, with great ease, as we shall afterwards see (Chap. XIX.). The existence of an ortho-nitric acid, NH_3O_4, is to be expected also from other analogies (Chapter XV.). Ordinary or meta-nitric acid is merely this ortho-nitric acid minus water. To ortho-nitric acid there should correspond the ammoniacal salts: mono-substituted, $H_2NH_4NO_4$; bi-substituted, $H(NH_4)_2NO_4$; and tri-substituted, $(NH_4)_3NO_4$. These salts, containing as they do hydrogen and oxygen, like many similar ammoniacal salts (see, for instance, Chapter IX.—Cyanides), are able to part with them in the form of water. Then from the first salt we have: $H_2NH_4NO_4-4H_2O=N_2O$—nitrous oxide, and from the second, $H(NH_4)_2NO_4-4H_2O=HN_3$—hydronitrous acid, and from the third, $(NH_4)_3NO-4H_2O=N_4H_4$—the ammonium salt of the same acid. The composition of HN_3 should be thus understood, whilst its acid properties are explained by the fact that the water ($4H_2O$) from

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tion from its elements, $N_3H=-62{\cdot}6$ cals., this compound differs from all the hydrogen compounds of nitrogen in having a maximum absorption of heat, which explains its instability.

$H(NH_4)_2NO_4$ is formed at the expense of the hydrogen of the ammonium and the oxygen of the nitric acid, so that there remains the hydrogen of nitric acid, which may be replaced by metals and so give salts. Moreover, nitrogen undoubtedly belongs to the category of metalloids which give acids, like S, Cl, C, P, and therefore, under the influence of three of its atoms, one atom of hydrogen acquires those properties which it has in acids, just as in HCN (hydrocyanic acid) the hydrogen has received these properties under the influence of the carbon and nitrogen (and HN_3 may be regarded as HCN, where C has been replaced by N_2). Moreover, besides explaining the composition and acid properties of HN_3, the above method gives the possibility of foretelling the closeness of the bond between hydrazoic acid and nitrous oxide, for $N_2O+NH_3=HN_3+H_2O$. This reaction, which was foreseen from the above considerations, was accomplished by Wislicenus (1892), who synthesised the sodium salt by taking the amide of sodium, NH_2Na (obtained by heating Na in a current of NH_3), and acting upon it (when heated) with nitrous oxide, N_2O, the reaction being: $2NH_2Na+N_2O=NaN_3+NaHO+NH_3$. The resultant salt, NaN_3, gives hydrazoic acid when acted upon by sulphuric acid, $NaN_3+H_2SO_4=NaHSO_4+HN_3$. The latter gives, with the corresponding solutions of their salts, the insoluble (and readily explosive) salts of silver, AgN_3 (insoluble, like AgCl or AgCN), and lead, $Pb(N_3)_2$.

Thus the law of substitution in the above form renders it possible to connect the various compounds of nitrogen with hydrogen and oxygen by a more intimate bond.

The compounds of nitrogen with oxygen also present an excellent example of the law of multiple proportions, because they contain, for every 14 parts by weight of nitrogen, 8, 16, 24, 32, and 40 parts by weight respectively of oxygen. The compositions of these compounds are as follows:—

N_2O, nitrous oxide; hydrate NHO.
N_2O_2, nitric oxide, NO.
N_2O_3, nitrous anhydride; hydrate NHO_2.
N_2O_4, peroxide of nitrogen, NO_2.
N_2O_5, nitric anhydride; hydrate NHO_3.

Of these compounds,[28] nitrous and nitric oxides, peroxide of nitrogen, and nitric acid, NHO_3 are characterised as being the most stable. *The lower oxides, when coming into contact with the higher, may give the intermediate forms*, for instance, NO and NO_2 form N_2O_3; **and the** *intermediate oxides may, in splitting up, give a higher and lower oxide*, e.g., N_2O_4 gives N_2O_3 and N_2O_5, or, in the presence of water, their hydrates.

We have already seen that, under certain conditions, nitrogen combines with oxygen, and we know also that ammonia may be oxidised. In these cases various oxidation products of nitrogen are formed, but in the presence of water and an excess of oxygen they always give nitric acid. Nitric acid, as corresponding with the highest oxide, is able, on deoxidation, to give the lower oxides; it is the only nitrogen acid whose salts occur somewhat widely distributed in nature, and it has many technical uses, for which reason we shall begin with it.

Nitric acid, NHO_3, is likewise known as aqua fortis. In a free state it is only met with in small quantities in nature, in the air and in rain-water after storms; but even in the atmosphere nitric acid does not long remain free, but combines with ammonia, traces of which are always found in air. On falling on the soil and into running water, &c., the nitric acid comes everywhere into contact with bases (or their salts), which readily act on it, so that it is converted into the nitrates of these bases. Hence nitric acid is always met with in nature in the form of salts. The soluble salts of nitric acid are called **nitres**. This name is derived from the Latin *sal nitri*. The potassium salt, KNO_3, is common or prismatic nitre, and the sodium salt, $NaNO_3$, Chili saltpetre, or cubic nitre. Nitres are formed in the soil when a nitrogenous substance is slowly oxidised, in the presence of an alkali, by means of the oxygen of the atmosphere. In nature there are very frequent

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[28] According to the thermochemical determinations of Favre, Thomsen, and more especially of Berthelot, it follows that, in the formation of quantities of the oxides of nitrogen expressed by their formulæ, if gaseous nitrogen and oxygen be taken as the starting-points, and if the compounds formed be also gaseous, the following amounts of heat, expressed in thousands of heat units, are *absorbed* (hence a minus sign):—

N_2O		N_2O_2		N_2O_3		N_2O_4		N_2O_5
−21		−43		−22		−5		−1
	−22		+21		+17		+4	

The differences are given in the lower line. For example, if N_2, or 28 grams of nitrogen, combine with O—that is, with 16 grams of oxygen—21,000 units of heat will be absorbed, that is, sufficient heat to raise 21,000 grams of water through 1°. Naturally, direct observations are impossible in this case; but if charcoal, phosphorus, or similar substances are burned both in nitrous oxide and in oxygen, and the heat evolved observed in both cases, then the difference (more heat will be evolved in burning in nitrous oxide) gives the figures required. If N_2O_2, by combining with O_2, gives N_2O_4, then, as is seen from the table, heat should be *developed* to the extent of 38,000 units, i.e., NO + O = 19,000 units of heat. The differences given in the table show that the maximum absorption of heat corresponds with nitric oxide, from which the higher oxides are formed with evolution of heat. If liquid nitric acid, NHO_3, is to be decomposed into $N+O_3+H$, 41,000 heat units will be required; that is, an evolution of heat takes place in its formation from the gases. It should be observed that the formation of ammonia, NH_3, from the gases $N+H_3$ evolves 12·2 thousand heat units, so that free nitrogen has a greater tendency to combine with hydrogen than with oxygen.

instances of such oxidation. For this reason certain soils and rubbish heaps—for instance, lime rubbish (in the presence of a base—lime)—contain a more or less considerable amount of nitre. One of these nitres—sodium nitrate—is extracted from the earth in large quantities in Chili, where it was probably formed by the oxidation of animal refuse. This kind of nitre is employed in practice for the manufacture of nitric acid and the other oxygen compounds of nitrogen. Nitric acid is obtained from **Chili saltpetre** *by heating* it with **sulphuric acid.** The hydrogen of the sulphuric acid replaces the sodium in the nitre. The sulphuric acid then forms either an acid salt, $NaHSO_4$, or a normal salt, Na_2SO_4, whilst nitric acid is formed from the nitre and volatilised. The decomposition is expressed by the equation: (1) $NaNO_3+H_2SO_4=HNO_3+NaHSO_4$, if the acid salt is formed, or by (2) $2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$, if the normal sodium sulphate is formed. With an excess of sulphuric acid, at a moderate heat (up to 200°), and at the commencement of the reaction, the decomposition proceeds according to the first equation; and on further heating (to 230°) with a sufficient amount of nitre, according to the second, because the acid salt $NaHSO_4$ itself acts like an acid (its hydrogen being replaceable as in acids), according to the equation: $NaNO_3+NaHSO_4=Na_2SO_4+HNO_3$.

The sulphuric acid, as it is said, here displaces the nitric acid from its compound with the base.[29] Thus, in the reaction of sulphuric acid on nitre there is formed a non-volatile salt of sulphuric acid, which remains together with an excess of this acid in the distilling apparatus,

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[29] This often gives rise to the supposition that sulphuric acid possesses a considerable degree of affinity or energy compared with that of nitric acid, but we shall afterwards see that the conception of the relative degree of affinity of acids and bases is, in many cases, exceedingly inaccurate and need not be accepted so long as it is possible to explain the observed phenomena without admitting any supposition whatsoever of the degree of the force of affinity, because the latter cannot be measured. The action of sulphuric acid upon nitre may be explained by the simple fact that the resultant nitric acid is volatile. The nitric acid is the only one of all the substances partaking in the reaction which is able to pass into vapour, the others being non-volatile, or, more strictly speaking, exceedingly difficultly volatile substances. Let us imagine that the sulphuric acid is only able to set free a small quantity of nitric acid from its salt, and this will suffice to explain the decomposition of the whole of the nitre by the sulphuric acid, because when the nitric acid is separated it is formed into vapour on heating, and passes away from the sphere of action of the remaining substances; then the free sulphuric acid will liberate a further small quantity of nitric acid, and so on until it drives off the entire quantity. It is evident from this explanation that it is essential that the sulphuric acid should be in excess (although not greatly) throughout the reaction; according to the equation expressing the reaction, 98 parts of sulphuric acid are required per 85 parts of Chili saltpetre; but if this proportion be maintained in practice the nitric acid will not all be disengaged by the sulphuric acid; an excess of the latter must be taken, and as a rule 80 parts of Chili saltpetre are taken per 98 parts of acid, so that a portion of the latter remains free to the very end of the reaction.

and nitric acid, which is converted into vapour, and may be condensed, because it is a liquid and volatile substance. On a small scale, this reaction may be carried on in a glass retort with a glass condenser. On a large scale, in chemical works, the process is exactly similar, but

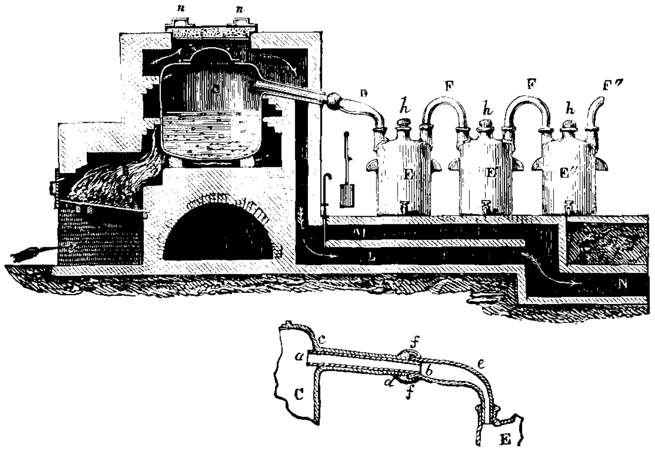

FIG. 55.—Method of preparing nitric acid on a large scale. A cast-iron retort, C, is fixed in the furnace, and heated by the fire, B. The flame and products of combustion are at first led along the flue, M (in order to heat the receivers), and afterwards into L. The retort is charged with Chili saltpetre and sulphuric acid, and the cover luted on with clay and gypsum. A clay tube *a*, is fixed into the neck of the retort (in order to prevent the nitric acid from corroding the cast iron), and a bent glass tube, D, luted on to it. This tube carries the vapours into a series of earthenware receivers, E. Nitric acid mixed with sulphuric acid collects in the first. The purest nitric acid is procured from the second, whilst that which condenses in the third receiver contains hydrochloric acid, and that in the fourth nitrous oxide. Water is poured into the last receiver in order to condense the residual vapours.

iron retorts are employed for holding the mixture of nitre and sulphuric acid, and earthenware three-necked bottles are used instead of a condenser,[30] as shown in fig. 55.

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[30] It must be observed that sulphuric acid, at least when undiluted (60° Baumé), corrodes cast iron with difficulty, so that it may be heated in cast-iron retorts. Nevertheless, both sulphuric and nitric acids have a certain action on cast iron, so that the acid obtained will contain traces of iron. In practice sodium nitrate (Chili saltpetre) is usually employed, as it is cheaper, but in the laboratory it is best to take potassium nitrate, because it is purer and does not froth up so much as sodium nitrate when heated with sulphuric acid. In the action of an excess of sulphuric acid on nitre and nitric acid a portion of the latter is decomposed, forming lower oxides of nitrogen, which are dissolved in the nitric acid. A portion of the sulphuric acid itself is also carried over as spray by the vapours of the nitric acid. Hence sulphuric acid occurs as an impurity in commercial nitric acid. A certain amount of hydrochloric acid will also be found to be present in it, because sodium chloride is generally found as an impurity in nitre, and under the action of sulphuric acid it forms hydrochloric acid. Commercial acid further contains a considerable excess of water above that necessary for the formation of the hydrate, because water is first poured into the earthenware vessels employed for condensing the nitric acid in order to facilitate its cooling and condensation. Further, the

The nitric acid obtained generally contains water. It is extremely difficult to deprive it of all the admixed water without destroying a portion of the acid itself and partially converting it into lower oxides, because in the absence of excess of water it is very unstable. When rapidly distilled a portion is decomposed, giving free oxygen and lower oxides of nitrogen, which, together with the water, remain in solution with the nitric acid. It is therefore necessary to work with great care in order to obtain a pure hydrate of nitric acid, HNO_3, and to mix the nitric acid obtained from nitre, as above described, with sulphuric acid, which takes up the water, and to distil it at the lowest possible temperature—that is, by lowering the pressure and by placing the retort holding the mixture in a water or oil bath and carefully heating it. The first portion of the nitric acid thus distilled boils at 86°, has a specific gravity at 15° of 1·526, and solidifies at $-50°$; it is very unstable at higher temperatures. This is the normal hydrate, HNO_3, which corresponds with the salts, NMO_3, of nitric acid. When diluted with water, nitric acid presents a higher boiling-point, not only as compared with that of the nitric acid itself, but also with that of water; so that if very dilute nitric acid be distilled, the first portions passing over will consist of almost pure water, until the boiling-point in the vapours reaches 121°. At this temperature a compound of nitric acid with water, containing about 70 per cent. of nitric acid,[31] distils over; its specific gravity at 15° is 1·421. If the solution contain less than 25 per cent. of water, then, the specific gravity of the solution being above 1·44, HNO_3 evaporates off and fumes in the air, forming the above hydrate, whose vapour pressure is less than that of water. Such solutions form *fuming nitric acid.* On distillation this gives monohydrated acid,[32] HNO_3, which is a hydrate boiling at 121°, so that it is obtained from both weak and strong solutions. Fuming nitric acid, under the action not only of organic substances, but even of heat, loses a portion of its oxygen, forming lower oxides of nitrogen, which impart a *reddish-brown colour* to it;[33] the pure acid is colourless.

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acid of composition HNO_3 decomposes with great ease, with the evolution of oxides of nitrogen. Thus the commercial acid contains a large number of impurities, and is frequently purified in the following manner:—Lead nitrate is first added to the acid as it forms non-volatile and almost insoluble (precipitated) substances with the free sulphuric and hydrochloric acids, according to the equations: $Pb(NO_3)_2+2HCl=PbCl_2+2NHO_3$ and $Pb(NO_3)_2+H_2SO_4=PbSO_4+2NHO_3$. Potassium chromate is then added to the impure nitric acid, by which means oxygen is liberated from the chromic acid, and this oxygen, at the moment of its evolution, oxidises the lower oxides of nitrogen and converts them into nitric acid. A pure nitric acid, containing no impurities other than water, may then be obtained by carefully distilling (under a low pressure) the acid, treated as above described, and particularly if only the middle portions of the distillate are collected. Such acid should give no precipitate, either with a solution of barium chloride (a precipitate shows the presence of sulphuric acid) or with a solution of silver nitrate (a precipitate shows the presence of hydrochloric acid), nor should it, after being diluted with water, give a coloration with starch containing potassium iodide (a coloration shows the admixture of other oxides of nitrogen). The oxides of nitrogen may be most easily removed from impure nitric acid by heating it for some time with a small quantity of pure charcoal. By the action of nitric acid on the charcoal carbonic anhydride is evolved, and this carries off the lower oxides of nitrogen. On re-distilling, pure acid is obtained. The oxides of nitrogen occurring in solution may also be removed by passing air through the nitric acid.

[31] Dalton, Smith, Bineau, and others considered that the hydrate of nitric acid of constant boiling-point (see Chap. I., note 60) was the compound $2HNO_3,3H_2O$, but Roscoe showed that its composition changes with a variation of the pressure and temperature under which the distillation proceeds. Thus, at a pressure of 1 atmosphere the solution of constant boiling-point contains 68·6 per cent., and at one-tenth of an atmosphere 66·8 per cent. of the acid. Judging from what has been said concerning solutions of hydrochloric acid, and from the variation of specific gravity, I think that the comparatively large decrease in the pressure of the vapours depends on the formation of a hydrate, $NHO_3,2H_2O$ (=53·6 per cent.) Such a hydrate may be expressed by $N(HO)_5$, that is, as $NH_4(HO)$, in which all the equivalents of hydrogen are replaced by hydroxyl. The constant boiling-point will then be the temperature of decomposition of this hydrate.

The variation of the specific gravity at 15° from water ($p=0$) to the hydrate $NHO_3,5H_2O$ (41·2 per cent. HNO_3) is expressed by $s=9992+57{\cdot}4p+0{\cdot}16p^2$, if water=10,000 at 4°. For example, when $p=30$ per cent., $s=11{,}860$. For more concentrated solutions, the presence must be assumed of at least the above-mentioned hydrate, $HNO_3,2H_2O$, of which the specific gravity $s=9570+84{\cdot}18p-0{\cdot}240p^2$; but perhaps (the results of observations of the specific gravity of the solutions not being in sufficient agreement to warrant a conclusion) the hydrate $HNO_3,3H_2O$ should be recognised, as is indicated by many nitrates (Al, Mg, Co, &c.), which crystallise with this amount of water of crystallisation. From $HNO_3,2H_2O$ to HNO_3 the specific gravity of the solutions (at 15°) is given by: $s=10{,}652+62{\cdot}08p-0{\cdot}160p^2$. The hydrate $HNO_3,2H_2O$ is recognised by Berthelot on the basis of the thermo-chemical data for solutions of nitric acid, because on approaching to this composition there is a rapid change in the amount of heat evolved by mixing nitric acid with water. Pickering (1892) by refrigeration obtained the crystalline hydrates: HNO_3,H_2O, melting at $-37°$ and $HNO_3,3H_2O$, melting at $-18°$. A more detailed study of the reactions of hydrated nitric acid would no doubt show, on approaching these hydrates, the existence of change in the process and rapidity of reaction.

[32] The normal hydrate HNO_3, corresponding with the ordinary salts, may be termed the monohydrated acid, because the anhydride N_2O_5 forms with water this normal nitric acid. In this sense the hydrate $HNO_3,2H_2O$ is the pentahydrated acid: $N_2O_5+5H_2O$.

[33] For technical and laboratory purposes recourse is frequently had to *red fuming nitric acid*—that is, the normal nitric acid, HNO_3, or strong solutions of it (containing less than $1\frac{1}{2}H_2O$), containing lower oxides of nitrogen, NO_2 and N_2O_3, in solution. This acid is prepared by decomposing nitre with half its weight of strong sulphuric acid, or by distilling nitric acid with an excess of sulphuric acid. The normal nitric acid is first obtained, but partially decomposes, and gives the lower oxidation products of nitrogen, which are dissolved by the nitric acid, to which they impart its usual brown or reddish colour. This acid fumes in the air, from which it attracts moisture, forming a less volatile hydrate. If carbonic anhydride be passed through the reddish-brown fuming nitric acid for a long period of time, especially if assisted by a moderate heat, it expels all the lower oxides, and leaves a colourless acid free from these oxides. It is necessary, in the preparation of the red acid, that the receivers should be kept quite cool, because it is only when cold that nitric acid is able to dissolve a large proportion of the oxides of nitrogen. The strong red fuming acid has a specific gravity 1·56 at 20°, and

Nitric acid, as an **acid hydrate**, enters into reactions of double decomposition with bases, basic hydrates (alkalies), and salts. In these cases salts of nitric acid are obtained. An alkali and nitric acid give water and a salt; for instance, with lime, $CaO+2HNO_3=Ca(NO_3)_2+H_2O$.[34] The composition of the ordinary salts of nitric acid may be expressed by the general formula $M(NO_3)_n$, where M indicates a metal replacing the hydrogen in one or several (n) molecules of nitric acid. We shall find afterwards that the atoms M of metals are equivalent to one (K, Na, Ag) atom of hydrogen, or two (Ca, Mg, Ba), or three (Al, In), or, in general, n atoms of hydrogen. **The salts of nitric acid** are especially characterised by being all **soluble in water**.[35] Owing to the property common to all these salts of entering into double decompositions and also to the volatility of nitric acid, they evolve nitric acid when heated with sulphuric acid. They are all, like the acid itself, capable of evolving oxygen when heated, and consequently of acting as oxidising substances; thus, for instance, they deflagrate with ignited carbon, which burns at the expense of the oxygen of the salt, and forms gaseous products of combustion.[36]

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has a suffocating smell of the oxides of nitrogen. When the red acid is mixed with water it turns green, and then bluish, and with an excess of water ultimately becomes colourless. This is owing to the fact that the oxides of nitrogen in the presence of water and nitric acid undergo change, and give coloured solutions.

Marchlewsky (1892) showed that the green solutions contain (besides HNO_3) HNO_2 and N_2O_4, whilst the blue solutions contain only HNO_2 (see note 48).

The action of red fuming nitric acid (or a mixture of it with sulphuric acid) is in many cases very powerful and rapid, and sometimes quite different from that of pure nitric acid. Thus iron becomes covered with a coating of oxides, and is insoluble in acids; it becomes, as it is said, passive. Also chromic acid (and potassium dichromate) gives oxide of chromium with this red acid, which is thus deoxidised. This is owing to the presence of the lower oxides of nitrogen, which are capable of being oxidised—that is, of passing into nitric acid like the higher oxides. But, generally, the action of fuming nitric acid, both red and colourless, is powerfully oxidising.

[34] Hydrogen is not evolved in the action of nitric acid (especially strong) on metals, even with those metals which evolve hydrogen under the action of other acids. This is because at the moment of its separation the hydrogen reduces the nitric acid, with formation of the lower oxides of nitrogen, as we shall see later.

[35] Certain basic salts of nitric acid, however (for example, the basic salt of bismuth), are insoluble in water, but, on the other hand, all the normal salts are soluble; this is an exceptional phenomenon among acids, all the ordinary acids forming insoluble salts with one or another base. Thus, of sulphuric acid the salts of barium, lead, &c., of hydrochloric acid the salts of silver, &c., are insoluble in water. However, the normal salts of acetic and certain other acids are all soluble.

[36] **Ammonium nitrate**, NH_4NO_3, is easily obtained by adding a solution of ammonia or of ammonium carbonate to nitric acid until it becomes neutral. On evaporating this solution, crystals of the salt are formed which contain no water of crystallisation. It crystallises in prisms like those formed by common nitre, and has a refreshing taste; 100 parts of water at $t°$ dissolve $54+0{\cdot}61\,t$ parts by weight of the salt. It is soluble in alcohol, melts at 160°, and is decomposed at about 180°, forming water and nitrous oxide, $NH_4NO_3=2H_2O+N_2O$. If ammonium nitrate is mixed with sulphuric acid, and the mixture heated to about the boiling-point of water, nitric acid is evolved, and ammonium hydrogen sulphate remains in solution; but if the mixture be heated rapidly to 160°, nitrous oxide will be evolved. In the first case the sulphuric acid takes up ammonia, and in the second place water. Ammonium nitrate is employed in practice for the artificial production of cold, because in dissolving in water it lowers the temperature very considerably. For this purpose it is best to take equal parts by weight of the salt and water. The salt must first be reduced to a powder and then rapidly stirred up in the water, when the temperature will fall from +15° to −10°, so that the water freezes.

Ammonium nitrate absorbs ammonia, with which it forms unstable compounds resembling compounds containing water of crystallisation [Divers (1872), Raoult (1873)]. At −10°, $NH_4NO_3,2NH_3$ is formed; it is a liquid of sp. gr. 1·15, which loses all its ammonia under the influence of heat. At +28°, NH_4NO_3,NH_3 is formed as a solid which easily parts with its ammonia when heated, especially in solution.

Troost (1882) investigated the dissociation pressures of the compounds formed, and came to the conclusion that a definite compound corresponding to the formula $2NH_4NO_3,3NH_3$ is formed, because the pressure of dissociation remains constant in the decomposition of such a compound at 0°. V. Kouriloff (1893), however, considers that the constancy of the pressure of the ammonia evolved is due to the decomposition of a saturated solution, and not of a definite compound. During decomposition the system is composed of a liquid and a solid, and the pressure only becomes constant from the moment the solid begins to precipitate. The composition $2NH_4NO_3,3NH_3$ corresponds with a saturated solution at 0°, and the solubility of NH_4NO_3 in NH_3 increases with a rise of temperature.

Nitric acid also enters into double decompositions with a number of hydrocarbons, which possess no alkaline characters and do not react with other acids. Under these circumstances the nitric acid gives water and a new substance termed a **nitro-compound.** The chemical character of the nitro-compound is the same as that of the original substance; for example, if an indifferent substance be taken, the nitro-compound obtained from it will also be indifferent; whilst if an acid be taken, an acid will be obtained.[36a] Benzene, C_6H_6, for instance, acts according to the equation: $C_6H_6+HNO_3=H_2O+C_6H_5NO_2$, nitrobenzene being produced. The substance taken, C_6H_6, is a liquid hydrocarbon which has a faint tarry smell, boils at 80°, and is lighter than water; the action of nitric acid yields nitrobenzene, which is a substance boiling at about 210°, heavier than water, and having an almond-like odour: it is employed in large quantities for the preparation of aniline and aniline dyes.[37] As the

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[36a] This is explained by saying that in true nitro-compounds the residue of nitric acid NO_2 takes the place of the hydrogen in the hydrocarbon group. For example, if C_6H_5OH be given, then $C_6H_4(NO_2)OH$ will be a true nitro-compound having the radical properties of C_6H_5OH. If, on the other hand, the NO_2 replace the hydrogen of the aqueous radicle ($C_6H_5ONO_2$), the chemical character is changed, as in the passage of KOH into $KONO_2$ (nitre) (see note 37 and Organic Chemistry).

[37] The compound ethers of nitric acid in which the hydrogen of the aqueous radicle (OH) is replaced by the residue of nitric acid (NO_2) are frequently called nitro-compounds. But in their chemical character they differ from true nitro-compounds (for details see Organic Chemistry) and do not burn like them. The action of nitric acid on cellulose, $C_6H_{10}O_5$, is an example. This substance, which forms the outer coating of all plant cells, occurs in an almost pure state in cotton, in common writing

nitro-compounds contain both combustible elements (hydrogen and carbon), as well as oxygen in unstable conbination with nitrogen, in the form of the radicle NO_2 of nitric acid, they decompose, when ignited or even when struck, with an explosion, owing to the pressure of the vapours and gases formed—free nitrogen, carbonic anhydride, CO_2, carbonic oxide CO, and aqueous vapour. In the explosion of nitro-compounds [37a] much heat is evolved, as in the combustion of gunpowder or detonating gas, and the force of explosion in a closed space is great, because from a solid or liquid nitro-compound occupying a small space there are formed only vapours and gases, the pressure of which is great, not merely on account of the small space in which they are formed, but

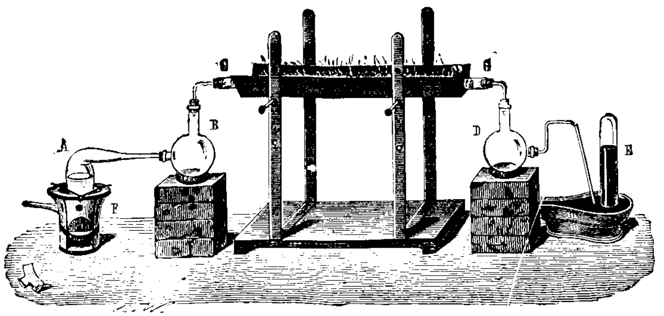

FIG. 56.—The method of decomposition of nitrous anhydride, also applicable to the other oxides of nitrogen, and to their analysis. NO_2 is generated from nitrate of lead in the retort A. Nitric acid and other less volatile products are condensed in B. The tube CC contains copper, and is heated from below. Undecomposed volatile products (if any are formed) are condensed in D, which is cooled. If the decomposition is incomplete, brown fumes make their appearance in this receiver. The gaseous nitrogen is collected in the cylinder E.

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paper, and in flax, &c.; under the action of nitric acid it yields water and nitrocellulose (like water and KNO_3 from KHO), which, although it has the same appearance as the cotton originally taken, differs from it entirely in properties. It explodes when struck, bursts into flame very easily under the action of sparks, and acts like gunpowder, whence its name of pyroxylin, or gun-cotton. The composition of gun-cotton is $C_6H_7N_3O_{11} = C_6H_{10}O_5 + 3NHO_3 - 3H_2O$. The proportion of the group NO_2 in nitrocellulose may be decreased by limiting the action of the nitric acid, compounds being then obtained with different properties; for instance the (impure) well-known *collodion cotton*, containing from 11 to 12 per cent. of nitrogen, and *pyro-collodion* (Mendeléeff, 1890), containing from 12·5 to 12·4 per cent. of nitrogen. Both these products are soluble in a mixture of alcohol and ether (in collodion a portion of the substance is soluble in alcohol), and the solution when evaporated gives a transparent film, which is insoluble in water. A solution of collodion is employed in medicine for covering wounds, and in wet-plate photography for giving on glass an even coating of a substance into which the various reagents employed in the process are introduced. The composition of pyro-collodion, $C_{30}H_{38}(NO_2)_{12}O_{25}$ (i.e. a product of the substitution of 12 atoms of hydrogen by the residue of nitric acid NO_2 in $5C_6H_{10}O_5$), is such that when exploded the whole of its hydrogen is capable of forming water and all its carbon, carbon monoxide, CO, occupying a larger volume than would be occupied by the CO_2 formed from the same amount of oxygen (because $CO_2 = 2$ vols. and $CO = 2$ vols., and consequently $2CO = 4$ vols.). Therefore the normal (in the absence of subsidiary reactions) decomposition of pyro-collodion is expressed by the equation: $C_{30}H_{38}(NO_2)_{12}O_{25} = 30CO + 19H_2O + 6N_2$. As the form of nitrocellulose which evolves the greatest quantity (by volume) of vapours and gases (from a given weight of nitrocellulose), pyro-collodion presents one of the most convenient smokeless powders for artillery, all the more so because experiments made at the Russian Admiralty Research Laboratory (see the Admiralty Magazine for 1895) show that properly prepared ribbons of this powder burn when exploded in successive layers (which is required in firing guns to prevent them from bursting), and that it may be kept for an indefinite period if well washed in water, notwithstanding that it contains 58 per cent. of oxygen.

[37a] The property possessed by nitroglycerin (occurring in dynamite), nitrocellulose, and the other nitro-compounds, of burning with an explosion, and their employment for smokeless powder and as explosives in general, is explained in the same way as the deflagration and explosion of a mixture of nitre and charcoal; in both cases the elements of the nitric acid occurring in the compound are decomposed, the oxygen in burning uniting with the carbon, and the nitrogen being set free; thus a very large volume of gaseous substances (nitrogen and oxides of carbon) is rapidly formed from the solid substances originally taken. These gases occupy an incomparably larger volume than the original substance, and therefore produce a powerful pressure and explosion. It is evident from their power of exploding with the development of heat (that is, in decomposing, not with the absorption of energy, as is generally the case, but with the evolution of energy), that the nitro-compounds form stores of energy which are readily set free, and that consequently their elements occur in a state of particularly energetic motion, which is especially strong in the group NO_2; this group is common to all nitro-compounds, and all the oxygen compounds of nitrogen are unstable, easily decomposable, and (note 28) absorb heat in their formation. On the other hand, the nitro-compounds are instructive as an example and proof of the fact that the elements and groups forming compounds are united in definite order in the molecules of a compound. A blow, concussion, or rise of temperature is necessary to bring the combustible elements C and H into the most intimate contact with NO_2, and to distribute the elements in a new order in new compounds.

As regards the composition of the nitro-compounds, it will be seen that the hydrogen of a given substance is replaced by the complex group NO_2 of the nitric acid. The same is observed in the passage of alkalies into nitrates, so that the reactions of substitution of nitric acid—that is, the formation of salts and nitro-compounds—may be expressed in the following manner. In these cases the hydrogen is replaced by the so-called **radicle of nitric acid** NO_2, as is evident from the following table:—

Caustic potash . . .	KHO.	Glycerin	$C_3H_5H_3O_3$.
Nitre	$K(NO_2)O$.	Nitroglycerin	$C_3H_5(NO_2)_3O_3$.
Hydrate of lime . . .	CaH_2O_2.	Phenol	C_6H_5OH.
Calcium nitrate . . .	$Ca(NO_2)_2O_2$.	Picric acid	$C_6H_2(NO_2)_3OH$, &c.

The difference between the salts formed by nitric acid and the nitro-compounds consists in the fact that nitric acid is very easily separated from the salts of nitric acid by means of sulphuric acid (that is, by a method of double saline decomposition), whilst nitric acid is not displaced by sulphuric acid from true nitro-compounds; for instance, nitrobenzene, $C_6H_5NO_2$. As nitro-compounds are formed exclusively from hydrocarbons, they are described with them in organic chemistry.

The group NO_2 of nitro-compounds in many cases (like all the oxidised compounds of nitrogen) passes into the ammonia group or the ammonia radicle NH_2. This requires the action of reducing substances evolving hydrogen: $RNO_2 + 6H = RNH_2 + 2H_2O$. Thus Zinin converted nitrobenzene, $C_6H_5{\cdot}NO_2$, into aniline, $C_6H_5{\cdot}NH_2$, by the action of hydrogen sulphide.

Admitting the existence of the group NO_2, as replacing hydrogen in various compounds, nitric acid may be considered as water in which half the hydrogen is replaced by the radicle of nitric acid. In this sense nitric acid is nitro-water, $(NO_2)OH$, and its anhydride dinitro-water, $(NO_2)_2O$. In nitric acid the radicle of nitric acid is owing also to the high temperature corresponding to the decomposition (explosive combustion) of the nitro-compound.[38]

If the vapour of nitric acid is passed through an even moderately heated glass tube, the formation of dark-brown fumes of the lower oxides of nitrogen and the separation of free oxygen may be observed, $2NHO_3 = H_2O + 2NO_2 + O$. Even light produces a similar decomposition, but not a complete one. The decomposition is complete at a white heat, when nitrogen is formed: $2NHO_3 = H_2O + N_2 + O_5$. Hence it is easily understood that nitric acid may part with its oxygen to a number of substances capable of being oxidised.[39] It is consequently an **oxidising agent.** Charcoal, as we have already seen, burns in nitric acid; phosphorus, sulphur, iodine, and the majority of metals also decompose nitric acid, some on heating and others even at the ordinary temperature: the substances taken are oxidised and the nitric acid is deoxidised, yielding compounds containing less oxygen.

A few metals, such as gold and platinum, do not act on nitric acid, but the majority decompose it; in so doing, an oxide of the metal is formed, which, if it has the character of a base, acts on the remaining nitric acid; hence, with the majority of metals, the result of the reaction is usually not an oxide of the metal, but the corresponding salt of nitric acid, and, at the same time, one of the lower oxides of nitrogen. The resulting salts of the metals are soluble, and hence it is said that nitric acid *dissolves* nearly all metals.[40] This is termed the *solution* of metals by acids, although it is not a case of simple solution, but a complex chemical change of the substances taken. When treated with this acid, those metals whose oxides do not combine with nitric acid yield the oxide itself, and not a salt; for example, tin acts in this manner on nitric acid, forming a hydrated oxide, SnH_2O_3, which is obtained in the form of a white powder: $Sn + 4NHO_3 = H_2SnO_3 + 4NO_2 + H_2O$. Silver is able to take up still more oxygen, and to convert a large proportion of nitric acid into nitrous anhydride: $4Ag + 6HNO_3 = 4AgNO_3 + N_2O_3 + 3H_2O$. Copper takes up still more oxygen from nitric acid, converting it into nitric oxide, and, by the action of zinc, nitric acid is able to give up a still further quantity of oxygen, forming nitrous oxide: $4Zn + 10NHO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$.[41] Sometimes, and especially

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combined with hydroxyl, just as in nitrobenzene it is combined with the radicle of benzene.

It should here be remarked that the group NO_3 may be recognised in the salts of nitric acid, because the salts have the composition $M(NO_3)_n$, just as the metallic chlorides have the composition MCl_n. But the group NO_3 does not form any other compounds beyond the salts, and therefore it should be considered as hydroxyl, HO, in which H is replaced by NO_2.

[38] The nitro-compounds play a very important part in mining and artillery. Detailed accounts of them must be looked for in special works, among which the works of A. R. Shuliachenko and T. M. Chelltsoff occupy an important place in the Russian literature on this subject, although historically the scientific works of Abel in England and Berthelot in France stand pre-eminent. The latter elucidated much in connection with explosive compounds by a series of both experimental and theoretical researches. Among explosives particularly important places from a practical point of view are occupied by ordinary or black gunpowder (Chap. XIII., note 16), fulminating mercury (Chap. XVI., note 26), the different forms of gun-cotton (Chap. VI., note 37), and nitro-glycerin (Chap. VIII., note 45, and Chap. XII., note 33). The latter when mixed with solid pulverulent substances, like magnesia, tripoli, &c., forms dynamite, which is so largely used in quarries and mines, in driving tunnels, &c. We may add that the simplest true nitro-compound, that is, marsh gas, CH_4, in which all the hydrogens are replaced by NO_2 groups, $C(NO_2)_4$ has been obtained by L. N. Shishkoff, as well as nitroform, $CH(NO_2)_3$.

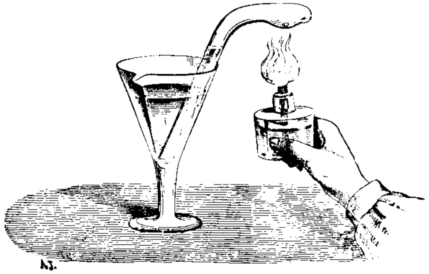

FIG. 57.—Decomposition of nitrous oxide by sodium.

[39] Nitric acid may be completely decomposed by passing its vapour over highly incandescent copper, because the oxides of nitrogen first formed give up their oxygen to the red-hot metallic copper, so that water and nitrogen gas alone are obtained. This forms a means for determining the composition both of nitric acid and of all the other compounds of nitrogen with oxygen, because by collecting the gaseous nitrogen formed it is possible from its volume to calculate its weight, and consequently its amount in a given quantity of a nitrogenous substance; and by weighing the copper before and after the decomposition it is possible to determine the amount of oxygen by the increase in weight. The complete decomposition of nitric acid is also accomplished by passing a mixture of hydrogen and nitric acid vapours through a red-hot tube. Sodium also decomposes the oxides of nitrogen at a red heat, taking up all the oxygen. This method is sometimes used for determining the composition of the oxides of nitrogen.

[40] The application of this acid for etching copper or steel in engraving is based on this fact. The copper is covered with a coating of wax, resin, &c. (etching ground), on which nitric acid does not act, and which is afterwards removed in certain parts with a needle, and the whole then washed in nitric acid. The parts coated remain untouched whilst the uncovered portions are eaten into by the acid. Copper plates for etchings, aquatints, &c., are prepared in this manner.

[41] The formation of such complex equations as the above often presents some difficulty to the beginner. It should be observed that if the reacting and resultant substances be known, it is easy to form an equation for the reaction. Thus, if we wish to form an equation expressing the fact that nitric acid acting on zinc gives nitrous oxide, N_2O, and zinc nitrate, $Zn(NO_3)_2$, we must reason as follows:—Nitric acid contains hydrogen, whilst the salt and nitrous oxide do not; hence water is formed, and therefore it is as though anhydrous nitric acid, N_2O_5, were acting. For its conversion into nitrous oxide it parts with four equivalents of oxygen, and hence it is able to oxidise four equivalents of zinc and thus convert them into zinc oxide, ZnO. These four equivalents of zinc oxide require for their conversion into the salt four more equivalents of nitric anhydride; consequently five equivalents in all of the latter are required, or ten equivalents of nitric acid. Thus in order to express the reaction in whole numbers of equivalents ten equivalents of nitric acid are necessary and four equivalents of zinc. It must not be forgotten, however, that there are very few such reactions which can be entirely expressed

with dilute solutions of nitric acid, the deoxidation proceeds as far as the formation of hydroxylamine and ammonia, and in some cases it leads to the formation of nitrogen itself. The formation of one or other nitrogenous substance from nitric acid is determined not only by the nature of the reacting substances, but also by the relative masses of water and nitric acid, and also by the temperature and pressure, that is, by the sum total of the conditions of reaction; and as in a given mixture even these conditions vary (the temperature and the relative masses vary), it not unfrequently happens that a mixture of different deoxidation products of nitric acid is formed.

Thus the action of nitric acid on metals consists in their being oxidised, whilst the acid itself is converted, according to the temperature, the concentration in which it is taken, the nature of the metal, &c., into lower oxides, ammonia, or even into nitrogen.[42] Many compounds are oxidised by nitric acid like metals and other elements; for instance, lower oxides are converted into higher oxides. Thus, arsenious acid is converted into arsenic acid, suboxide of iron into oxide, sulphurous acid into sulphuric acid, the sulphides of the metals, M_2S, into sulphates, M_2SO_4, &c.; in a word, nitric acid brings about oxidation, its oxygen being taken up and transferred to many other substances. Certain substances are oxidised by strong nitric acid so rapidly and with so great an evolution of heat that they deflagrate and burst into flame. Thus turpentine, $C_{10}H_{16}$, bursts into flame when poured into fuming nitric acid. In virtue of its oxidising property, nitric acid *removes the hydrogen* from many substances. Thus it decomposes hydriodic acid, separating the iodine and forming water; and if fuming nitric acid be poured into a flask containing gaseous hydriodic acid, a rapid reaction takes place, accompanied by flame and the separation of violet vapours of iodine and brown fumes of oxides of nitrogen.[43]

As nitric acid is very easily decomposed with the separation of oxygen, it was for a long time supposed that it was not capable of forming the corresponding **nitric anhydride,** N_2O_5; but first of all, Deville, and subsequently Weber and others, discovered the methods of its formation. Deville obtained nitric anhydride by decomposing silver nitrate by chlorine at a moderate heat. Chlorine acts on the above salt at a temperature of 95° ($2AgNO_3+Cl_2=2AgCl+N_2O_5+O$), and when once the reaction is started, it continues by itself without further heating. Brown fumes are given off, which are condensed in a tube surrounded by a freezing-mixture. A portion condenses in this tube and a portion remains in the gaseous state; the latter contains free oxygen. A crystalline mass and a liquid substance are obtained in the tube; the liquid is poured off, and a current of dry carbonic acid gas passed through the apparatus in order to remove all traces of volatile substances (liquid oxides of nitrogen) adhering to the crystals of nitric anhydride. These form a voluminous mass of rhombic crystals (density 1·64), which are sometimes of rather large size; they melt at about 30° and distil at about 47°. In distilling, a portion of the substance is

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by simple equations. The majority of equations of reactions only express the chief and ultimate products of reaction, and thus none of the three preceding equations express all that actually occurs in the action of metals on nitric acid. In no one of them is one oxide of nitrogen alone formed, but always several, either together or consecutively—according to the temperature and strength of the acid. And this is easily intelligible. The resulting oxide is itself capable of acting on metals and of being deoxidised, and in the presence of the nitric acid it may change the acid and be itself changed. The equations given must be looked on as a systematic expression of the main features of the reactions, or as a limit towards which they tend, but to which they only attain in the absence of disturbing influences.

[42] Montemartini endeavours to show that the products evolved in the action of nitric acid upon metals (and their amount) are in direct connection with both the concentration of the acid and the capacity of the metals to decompose water. Those metals which only decompose water at a high temperature give, under the action of nitric acid, NO_2, N_2O_4, and NO; whilst those metals which decompose water at a lower temperature give, besides the above products, N_2O, N, and NH_3; and, lastly, the metals which decompose water at the ordinary temperature also evolve hydrogen. Nitric acid diluted with a large quantity of water does not oxidise copper, but it oxidises tin; dilute nitric acid also does not oxidise either silver or mercury; but, on the addition of nitrous acid, even dilute acid acts on the above metals. This naturally depends on the less stability of nitrous acid, and on the fact that after the commencement of the action the nitric acid is itself converted into nitrous acid, which continues to act on the silver and mercury. Veley (Oxford, 1891) made detailed researches on the action of nitric acid upon Cu, Hg, and Bi, and showed that nitric acid of 30 per cent. strength does not act upon these metals at the ordinary temperature if nitrous acid (traces of which are destroyed by urea) and oxidising agents such as H_2O_2, $KClO_3$, &c. are entirely absent; but in the presence of even a small amount of nitrous acid the metals form nitrites, which, with HNO_3, form nitrates and the oxides of nitrogen, which re-form the nitrous acid necessary for starting the reaction, because the reaction, $2NO+HNO_3+H_2O=3HNO_2$, is reversible. The above metals are quickly dissolved in a 1 per cent. solution of nitrous acid. Moreover, Veley observed that nitric acid is partially converted into nitrous acid by gaseous hydrogen in the presence of the nitrates of Cu and Pb.

[43] When nitric acid acts on many organic substances it often happens that not only is hydrogen removed from them, but also oxygen introduced; thus, for example, nitric acid converts toluene, C_7H_8, into benzoic acid, $C_7H_6O_2$. In certain cases, also, a portion of the carbon contained in an organic substance burns at the expense of the oxygen of the nitric acid. So, for instance, phthalic acid, $C_8H_6O_4$, is obtained from naphthalene, $C_{10}H_8$. Thus the action of nitric acid on the hydrocarbons is often most complex; not only does nitration take place, but also separation of carbon, displacement of hydrogen, and combination of oxygen. There are few organic substances which can withstand the action of nitric acid, and it causes fundamental changes in a number of them. It leaves a yellow stain on the skin, and in large quantity causes a wound and entirely eats away the membranes of the body. The tissues of plants are eaten into with the greatest ease by strong nitric acid in just the same manner. One of the most durable blue vegetable dyes employed in dyeing tissues is *indigo*; yet it is readily *converted into a yellow substance* by the action of nitric acid, and small traces of free nitric acid may be recognised by this means.

decomposed. With water these crystals give nitric acid. Nitric anhydride is also obtained by the action of phosphoric anhydride, P_2O_5, on cold pure nitric acid (below 0°). During the very careful distillation of equal parts by weight of these two substances a portion of the acid decomposes, giving a liquid compound, $H_2O,2N_2O_5=N_2O_5,2HNO_3$, whilst the greater part of the nitric acid gives the anhydride according to the equation: $2NHO_3+P_2O_5=2PHO_3+N_2O_5$. On heating, nitric anhydride decomposes either with an explosion, or gradually, into nitric peroxide and oxygen: $N_2O_5=N_2O_4+O$.

Nitrogen peroxide, N_2O_4, and **nitrogen dioxide**, NO_2, express one and the same composition, but they should be distinguished like ordinary oxygen and ozone, although in this case their mutual conversion is more easily effected and takes place on vaporisation; also, O_3 loses heat on passing into O_2, whilst N_2O_4 absorbs heat in forming NO_2.

Nitric acid in acting on tin and on many organic substances (for example starch) yields brown vapours, consisting of a mixture of N_2O_3 and NO_2. A purer product is obtained by the decomposition of lead nitrate by heat, $Pb(NO_3)_2=2NO_2+O+PbO$, when non-volatile lead oxide, *oxygen gas, and nitrogen dioxide are formed.* The latter condenses, in a well-cooled vessel, to a brown liquid, which boils at about 22°. The purest peroxide of nitrogen, solidifying at −9°, is obtained by mixing dry oxygen in a freezing-mixture with twice its volume of dry nitric oxide, NO, when transparent prisms of nitrogen peroxide are formed in the receiver: they melt into a colourless *liquid at about* −10°. When the temperature of the receiver is above −9°, the crystals melt,[44] and at 0° give a reddish-yellow liquid, like that obtained in the decomposition of lead nitrate. The vapours of nitrogen peroxide have a characteristic odour, and at the ordinary temperature are of a dark-brown colour, but at lower temperatures the colour of the vapour is much fainter. When heated, especially above 50°, the colour becomes a very dark brown, so that the vapours almost lose their transparency.

The causes of these peculiarities of nitrogen peroxide were not clearly understood until Deville and Troost determined the density and dissociation of the vapour of this substance at different temperatures, and showed that the density varies. If the density is referred to that of hydrogen at the same temperature and pressure, it is found to vary from 38 at the boiling-point, or about 27°, to 23 at 135°, after which the density remains constant up to those high temperatures at which the oxides of nitrogen are decomposed. As on the basis of the laws enunciated in the following chapter, the density 23 corresponds with the compound NO_2 (because the weight corresponding with this molecular formula is 46, and the density referred to hydrogen as unity is equal, as we shall presently see, to half the molecular weight); at temperatures above 135° the existence of nitrogen dioxide only must be recognised. It is this gas which is of a brown colour. At a lower temperature it forms nitrogen peroxide, N_2O_4, whose molecular weight, and therefore density, is twice that of the dioxide. This substance, which is polymeric with nitrogen dioxide, as ozone is polymeric with oxygen, and has twice as great a vapour density (46 referred to hydrogen), is formed in greater quantity the lower the temperature, and crystallises at −10°. The reasons both of the variation of the colour of the gas (N_2O_4 gives colourless and transparent vapours, whilst those of NO_2 are brown and opaque) and the variation of the vapour density with the variation of temperature are thus made quite clear; and as at the boiling-point a density 38 was obtained, at that temperature the vapours consist of a mixture of 79 parts by weight of N_2O_4 with 21 parts by weight of NO_2.[45] It is evident that a decomposition here takes place, the peculiarity of which consists in the fact that the product of decomposition, NO_2, is polymerised (i.e. becomes denser, combines with itself) at a lower temperature; that is, the reaction

$$N_2O_4=NO_2+NO_2$$

is a reversible reaction, and consequently the whole phenomenon represents a **dissociation** in a homogeneous gaseous medium, where the original substance, N_2O_4, and the resultant, NO_2, are both gases. The *measure of dissociation* will be expressed if we find the proportion of the quantity of the substance decomposed to the whole amount of the substance. At the boiling-point, therefore, the measure of the decomposition of nitrogen peroxide will be 21 per cent.; at 135° it = 1, *and at 10° it = 0, the N_2O_4 then* being not decomposable. Consequently the limits of dissociation at the atmospheric pressure are −10° and 135°.[46] Within the limits of these temperatures the

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[44] According to certain investigations, if a brown liquid is formed from the melted crystals by heating above −9°, then they no longer solidify at −10°, probably because a certain amount of N_2O_3 (and oxygen) is formed, and the liquid does not solidify, even at −30°, *or it may be that the* passage from $2NO_2$ into N_2O_4 is not so easily accomplished as the passage from N_2O_4 into $2NO_2$.

Liquid nitrogen peroxide (that is, a mixture of NO_2 and N_2O_4) is employed in admixture with hydrocarbons as an explosive.

[45] Because if x equal the amount by weight of N_2O_4, its volume will $=x/46$, and the amount of NO_2 will $=100-x$, and consequently its volume will $=(100-x)/23$. But the mixture, having a density 38, will weigh 100; consequently its volume will $=100/38$. Hence $x/46+(100-x)/23=100/38$, or $x=79{\cdot}0$.

[46] The phenomena and laws of dissociation, which we shall consider only in particular instances, are discussed in detail in works on theoretical chemistry. Nevertheless, in

vapours of nitrogen peroxide have not a constant density; but, on the other hand, above and below these limits, definite substances exist. Thus, above 135°, N_2O_4 has ceased to exist and NO_2 alone remains. It is evident that at the ordinary temperature there is a partially dissociated system or a mixture of nitrogen peroxide, N_2O_4, and nitrogen dioxide, NO_2. In the brown liquid boiling at 22° probably a portion of the N_2O_4 has already passed into NO_2, and it is only the colourless liquid and crystalline substance at $-10°$ that can be considered as pure nitrogen peroxide.[47]

The above explains the action of nitrogen peroxide on water at low temperatures. N_2O_4 then acts on water like a mixture of the anhydrides of nitrous and nitric acids. The first, N_2O_3, may be looked upon as water in which each of the two atoms of hydrogen is replaced by the radicle NO, while in the second each hydrogen is replaced by the radicle NO_2, belonging to nitric acid; and in nitrogen peroxide one atom of the hydrogen of water is replaced by NO and the other by NO_2, as is seen from the formulæ—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O;\quad \left.\begin{matrix}NO\\NO\end{matrix}\right\}O;\quad \left.\begin{matrix}NO\\NO_2\end{matrix}\right\}O;\quad \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O;$$

or

$$H_2O;\quad N_2O_3;\quad N_2O_4;\quad N_2O_5.$$

In fact, nitrogen peroxide at low temperatures gives with water (ice) both nitric, HNO_3, and nitrous, HNO_2, acids. The latter, as we shall

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respect to nitrogen peroxide, as an historically important example of dissociation in a homogeneous gaseous medium, we will cite the results of the careful investigations (1885–1886) of E. and L. Natanson, who determined the densities under various conditions of temperature and pressure. The degree of dissociation, expressed as above (it may also be expressed otherwise—for example, by the ratio of the quantity of substance decomposed to that unaltered), proves to increase at all temperatures as the pressure diminishes, which would be expected for a homogeneous gaseous medium, as a decreasing pressure aids the formation of the lightest product of dissociation (that having the least density or largest volume). Thus in the Natansons' experiments the degree of dissociation at 0° increases from 10 per cent. to 30 per cent., with a decrease of pressure of from 251 to 38 mm.; at 49·7° it increases from 49 per cent. to 93 per cent. with a fall of pressure of from 498 to 27 mm., and at 100° it increases from 89·2 per cent. to 99·7 per cent. with a fall of pressure from 732·5 to 11·7 mm. At 130° and 150° the decomposition is complete—that is, only NO_2 remains at the low pressures (less than the atmospheric) at which the Natansons made their determinations; but it is probable that at higher pressures (of several atmospheres) molecules of N_2O_4 would still be formed, and it would be exceedingly interesting to trace the phenomena under the conditions both of very considerable pressures and of relatively large volumes.

[47] Liquid nitrogen peroxide is said by Geuther to boil at 22°–26°, and to have a sp. gr. $=1·494$ at 0° and 1·474 at 15°. It is evident that, in the liquid as in the gaseous state, the variation of density with the temperature depends not only on physical, but also on chemical changes, as the amount of N_2O_4 decreases and the amount of NO_2 increases as the temperature rises, and they (as polymeric substances) should have different densities, just as is the case, for instance, with the hydrocarbons C_5H_{10} and $C_{10}H_{20}$.

It may not be superfluous to mention here that the measurement of the specific heat

afterwards see, splits up into water and the anhydride, N_2O_3. If, however, warm water acts on nitrogen peroxide, only nitric acid and monoxide of nitrogen are formed: $3NO_2+H_2O=NO+2NHO_3$.

Although NO_2 is not decomposed into N and O even at 500°, still in many cases it acts as an oxidising agent. Thus, for instance, it oxidises mercury, converting it into mercurous nitrate, $2NO_2+Hg=HgNO_3+NO$, being itself deoxidised into nitric oxide, into which the dioxide passes in many other instances, and from which it is easily formed.[48]

Nitrous anhydride, N_2O_3, corresponds [49] with nitrous acid, NHO_2, which forms a series of salts, the nitrites—for example, the sodium salt $NaNO_2$,[49a] the ammonium salt $(NH_4)NO_2$,[50] the silver salt $AgNO_2$,[51] &c. Neither the anhydride nor the hydrate of the acid is

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of a mixture of the vapours of N_2O_4 and NO_2 enabled Berthelot to determine that the transformation of $2NO_2$ into N_2O_4 is accompanied by the evolution of about 13,000 units of heat, and as the reaction proceeds with equal facility in either direction, it will be exothermal in the one direction and endothermal in the other; and this clearly demonstrates the possibility of reactions taking place in either direction, although, as a rule, reactions evolving heat proceed with the greater ease.

[48] Nitric acid of sp. gr. 1·51 in dissolving nitrogen peroxide becomes brown, whilst nitric acid of sp. gr. 1·32 is coloured greenish blue, and acid of sp. gr. less than 1·15 remains colourless after absorbing nitrogen peroxide (note 33).

[49] Nitrogen peroxide as a mixed substance has no corresponding independent salts, but Sabatier and Senderens (1892) showed that, under certain conditions, NO_2 combines directly with some metals—for instance, copper and cobalt—forming Cu_2NO_2 and $CoNO_2$ as dark brown powders, which do not, however, exhibit the reactions of salts. Thus by passing gaseous nitrogen dioxide over freshly reduced (from the oxidised compounds by heating with hydrogen) copper at 25°–30°, Cu_2NO_2 is directly formed. With water it partly gives off NO_2 and partly forms nitrite of copper, leaving metallic copper and its suboxide. The nature of these compounds has not yet been sufficiently investigated.

[49a] This sodium salt, $NaNO_2$, is the most largely used in the arts, as it reacts with the amides of certain colouring matters forming dyes for tissues. It is called 'nitrite,' and is prepared in the same way as KNO_2 (see further on).

[50] Ammonium nitrite may be easily obtained in solution by a method of double decomposition (for instance, of the barium salt with ammonium sulphate) similar to that employed for the other salts of nitrous acid, but it decomposes with great ease when evaporated, with evolution of gaseous nitrogen, as already mentioned (Chap. V.). If the solution, however, is evaporated at the ordinary temperature under the receiver of an air-pump, a solid saline mass is obtained, which is easily decomposed when heated. The dry salt even decomposes with an explosion when struck, or when heated to about 70°: $NH_4NO_2=2H_2O+N_2$. It is also formed by the action of aqueous ammonia on a mixture of nitric oxide and oxygen, or by the action of ozone on ammonia, and in many other instances. Sörensen (1894) prepared NH_4NO_2 by the action of a mixture of N_2O_3 and other oxides of nitrogen on lumps of ammonium carbonate, extracting the nitrite of ammonium formed with absolute alcohol, and precipitating it from this solution by ether. This salt is crystalline, dissolves in water with absorption of heat, and attracts moisture from the air. In order to preserve the salt it should be covered with a layer of pure dry ether.

[51] Silver nitrite, $AgNO_2$, is obtained as a very slightly soluble substance, which is precipitated, on mixing solutions of silver nitrate, $AgNO_3$, and potassium nitrite, KNO_2. It

known in a perfectly pure state. The anhydride has only been obtained as a very unstable substance, and has not yet been fully investigated; and on attempting to obtain the acid NHO_2 from its salts, it always gives water and the anhydride, whilst the latter, as an intermediate oxide, partially or wholly splits up into $NO+NO_2$. But the salts of nitrous acid are distinguished for their great stability. Potassium nitrate, KNO_3, may be converted into potassium nitrite by depriving it of a portion of its oxygen; for instance, by fusing it (at not too high a temperature) with metals such as lead, $KNO_3+Pb=KNO_2+PbO$.[51a] The resultant salt is soluble in water, whilst the oxide of lead is insoluble. With sulphuric and other acids the solution of potassium nitrite[52] immediately evolves a brown gas, nitrous anhydride: $2KNO_2+H_2SO_4=K_2SO_4+N_2O_3+H_2O$. The same gas ($N_2O_3$) is obtained by passing nitric oxide at 0° through liquid nitrogen tetroxide,[53] or by heating starch with nitric acid of sp. gr. 1·3. At a very low temperature it condenses into a blue liquid boiling at about 0°,[54] but then partially decomposing into $NO+NO_2$. Nitrous anhydride possesses a remarkable capacity for oxidising. Ignited bodies burn in it; nitric acid absorbs it, and then acquires the property of acting on silver and other metals, even when diluted (see note 42). **Potassium iodide** is oxidised by this gas just as it is by ozone (and by peroxide of hydrogen, chromic and other acids, but not by dilute nitric acid or sulphuric acid), with the **separation of iodine.** This iodine may be recognised (Chapter IV.) by its turning starch blue. Very small traces of nitrites may be easily detected by this method. If, for example, starch and potassium iodide are added to a solution of potassium nitrite (at first there will be no change, there being no free nitrous acid), and then sulphuric acid, the nitrous acid (or its anhydride) set free liberates iodine, which produces a blue colour with the starch. Nitric acid does not act in this manner, but in the presence of zinc the coloration takes place, which proves the formation of nitrous acid in the deoxidation of nitric acid.[55] Nitrous acid acts directly on ammonia, forming nitrogen and water, $HNO_2+NH_3=N_2+2H_2O$.[56]

As nitrous anhydride easily splits up into NO_2+NO, so, like NO_2, with warm water it gives nitric acid and nitric oxide, according to the equation: $3N_2O_3+H_2O=4NO+2NHO_3$.

Being in a lower degree of oxidation than nitric acid, nitrous acid and its anhydride are oxidised in solution by many oxidising substances —for example, by potassium permanganate—into nitric acid.[57]

Nitric oxide, NO.—This permanent gas[58] (that is unliquefiable by pressure without the aid of cold) may be obtained by the deoxidation of any of the above-described compounds of nitrogen with oxygen. The deoxidation of nitric acid by metals is the usual method employed for its preparation. Dilute nitric acid (sp. gr. 1·18 but not stronger, as then N_2O_3 and NO_2 are produced) is poured into a flask containing

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is soluble in a large volume of water, and this is taken advantage of to free it from silver oxide, which is also present in the precipitate, owing to the fact that potassium nitrite always contains a certain amount of oxide, which with water gives the hydroxide, forming oxide of silver with silver nitrate. The solution of silver nitrite gives, by double decomposition with metallic chlorides (for instance, barium chloride), insoluble silver chloride and the nitrite of the metal taken (in this case, barium nitrite, $Ba(NO_2)_2$).

[51a] Leroy (1889) obtained KNO_2 by mixing powdered KNO_3 with BaS, igniting the mixture in a crucible and washing the fused salts; $BaSO_4$ is then left as an insoluble residue, and KNO_2 passes into solution: $4KNO_3+BaS=4KNO_2+BaSO_4$.

[52] Probably potassium nitrite, KNO_2, when strongly heated, especially with metallic oxides, evolves N and O, and yields potassium oxide, K_2O, because nitre is liable to such a decomposition; but it has, as yet, been but little investigated.

[53] The reaction $N_2O_3=NO_2+NO$ is probably reversible, i.e. resembles the conversion of N_2O_4 into NO_2. The brown colour of the fumes of N_2O_3 is due to the formation of NO_2.

If nitrogen peroxide is cooled to −20°, and half its weight of water added to it drop by drop, the tetroxide is decomposed, as we have already stated, into nitrous and nitric acids; the former does not then remain as a hydrate, but straightway passes into the anhydride, and hence if the resultant liquid be slightly warmed vapours of nitrous anhydride, N_2O_3, are evolved, and condense into a blue liquid, as was shown by Fritzsche. This method of preparing nitrous anhydride apparently gives the purest product, but it easily dissociates, forming NO and NO_2 (and therefore also nitric acid, if water is present).

[54] According to Thorpe, N_2O_3 boils at + 18°. Geuther gives the boiling-point as + 3·5°, and the sp. gr. at 0° as 1·449.

[55] In its oxidising action nitrous anhydride gives nitric oxide, $N_2O_3=2NO+O$. Thus its analogy to ozone becomes still more marked, because in ozone it is only one-third of the oxygen that acts in oxidising; from O_3 there is obtained O, which acts as an oxidiser, and common oxygen O_2. In a physical aspect the relation between N_2O_3 and O_3 is revealed in the fact that both substances are of a blue colour when in the liquid state.

[56] This reaction is taken advantage of for converting the amides, NH_2R (where R is an element or a complex group), into hydroxides, RHO. In this case NH_2R+NHO_2 forms $2N+H_2O+RHO$; H_2N is replaced by HO, the radicle of ammonia by the radicle of water. This reaction is employed for transforming many nitrogenous organic substances having the properties of amides into their corresponding hydroxides. Thus aniline, $C_6H_5{\cdot}NH_2$, which is obtained from nitrobenzene, $C_6H_5{\cdot}NO_2$ (note 37), is converted by nitrous anhydride into phenol, $C_6H_5{\cdot}OH$, which occurs in the creosote extracted from coal tar. Thus the H of the benzene is successively replaced by NO_2, NH_2, and HO; this method is suitable for other cases also. With the acid amides of the aromatic series of hydrocarbons, nitrous acid gives highly coloured diazo-compounds.

[57] The action of a solution of potassium permanganate, $KMnO_4$, on nitrous acid in the presence of sulphuric acid is determined by the fact that the higher oxide of manganese, Mn_2O_7, contained in the permanganate is converted into the lower oxide, MnO, which as a base forms manganese sulphate, $MnSO_4$, while the oxygen serves for the oxidation of HNO_2 into HNO_3. As the solution of the permanganate is of a red colour, whilst that of manganese sulphate is almost colourless, this reaction is clearly seen, and may be employed for the detection and determination of nitrous acid and its salts.

[58] The absolute boiling-point = −93° (see Chap. II., note 29). The liquefied gas boils at −142°, and the melting-point is −152°.

metallic copper.[59] The reaction commences at the ordinary temperature. Mercury and silver also give nitric oxide with nitric acid. In these reactions with metals one portion of the nitric acid is employed in the oxidation of the metal, whilst the other, and by far the greater, portion combines with the metallic oxide so obtained, with formation of the nitrate corresponding with the metal taken. The first action of the copper on the nitric acid is thus expressed by the equation :

$$2NHO_3+3Cu=H_2O+3CuO+2NO.$$

The second reaction consists in the formation of copper nitrate—

$$6NHO_3+3CuO=3H_2O+3Cu(NO_3)_2.$$

Adding these two equations together we obtain :

$$8NHO_3+3Cu=3Cu(NO_3)_2+2NO+4H_2O.$$

Nitric oxide is a colourless gas which is only slightly soluble in water ($\frac{1}{20}$ of a volume at the ordinary temperature). Reactions of double decomposition in which nitric oxide readily takes part are not known—that is to say, it is an indifferent, not a saline, oxide. Like *the other oxides of nitrogen, it is decomposed into its elements at a red* heat (starting from 900°, 60 per cent. of it forms N_2 and $2N_2O_3$ at 1200°, but complete decomposition into N_2 and O_2 only takes place at the melting-point of platinum ; Emich, 1892). The most characteristic property of nitric oxide is its capacity for directly and easily combining with oxygen (with evolution of heat). With **oxygen** it forms **nitrous anhydride** and **nitrogen peroxide** : $2NO+O=N_2O_3$; $2NO+O_2=2NO_2$.

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[59] Kammerer proposed preparing nitric oxide, NO, by pouring a solution of sodium nitrate over copper shavings and adding sulphuric acid drop by drop. The oxidation of ferrous salts by nitric acid also gives NO. One part of strong hydrochloric acid is taken and iron is dissolved in it ($FeCl_2$), and then an equal quantity of hydrochloric acid and also nitre are added to the solution. On heating, nitric oxide is evolved. In the presence of an excess of sulphuric acid and mercury the conversion of nitric acid into nitric oxide is complete (that is, the reaction proceeds to the end, and the nitric oxide is obtained without other products), and upon this is founded one of the methods for determining *nitric acid (in nitrometers of various kinds, described in text-books of analytical* chemistry), as the amount of NO can be easily and accurately measured volumetrically. The amount of nitrogen in gun-cotton, for instance, is determined by dissolving it in sulphuric acid. Nitrous acid acts in the same manner. Upon this property Emich (1892) founds his method for preparing pure NO. He pours mercury into a flask, and then covers it with sulphuric acid, in which a certain amount of $NaNO_2$ or other substance corresponding to HNO_2 or HNO_3 has been dissolved. The evolution of NO proceeds at the ordinary temperature, becoming more rapid as the surface of the mercury is increased (if the flask is shaken, the reaction proceeds very rapidly). If the gas is passed over KHO, it is obtained quite pure, because KHO does not act upon NO at the ordinary temperature (if heated, KNO_2 and N_2O or N_2 are formed).

If nitric oxide is mixed with oxygen and immediately shaken up with caustic potash, it is almost entirely converted into potassium nitrite ; whilst after a certain time, when the formation of N_2O_4 has already commenced, a mixture of potassium nitrite and nitrate is obtained. If oxygen is passed into a bell-jar filled with nitric oxide, brown fumes of N_2O_3 and NO_2 are formed, even in the absence of moisture ; in presence of water these give, as we already know, nitric acid and nitric oxide, so that with excess of water and oxygen the whole of the nitric oxide is easily and directly converted into nitric acid. This reaction of the re-formation of nitric acid from nitric oxide, air, and water, $2NO+H_2O+O_3=2HNO_3$, is frequently made use of in practice. The experiment showing the conversion of nitric oxide into nitric acid is very striking and instructive. As the intermixture of the oxygen with the oxide of nitrogen proceeds, the nitric acid formed dissolves in water, and if an excess of oxygen has not been added, the whole of the gas (nitric oxide), being converted into HNO_3, is absorbed, and the water entirely fills the bell-jar previously containing the gas.[60] It is evident that nitric oxide[61] in combining with oxygen has a strong tendency to give the higher types of nitrogen compounds, which we see in nitric acid, HNO_3 or $NO_2(OH)$, in nitric anhydride, N_2O_5 or $(NO_2)_2O$, and in ammonium chloride, NH_4Cl. If X stand for an atom of hydrogen, or its equivalents, chlorine, hydroxyl, &c., and if O, which is, according to the law of substitution, equivalent to H_2, be indicated by X_2, then the three compounds of nitrogen above named should be considered as compounds of the type or form NX_5. For example, in nitric acid

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[60] This transformation of the permanent gases, nitric oxide and oxygen, into liquid nitric acid in the presence of water, and with the evolution of heat, presents a most striking instance of liquefaction produced by the action of chemical forces. The latter perform with ease the work which physical (cooling) and mechanical (pressure) forces effect only with difficulty. In this the motion, which is so distinctively the property of the gaseous molecules, is apparently destroyed.

[61] Nitric oxide is capable of entering into many characteristic combinations; it is absorbed by the solutions of many acids—for instance, tartaric, acetic, phosphoric, sulphuric—and metallic chlorides (for example, $SbCl_5$, $BiCl_3$, &c., with which it forms definite compounds; Besson 1889), and also by the solutions of many salts, especially those formed by suboxide of iron (for instance, ferrous sulphate). In this case a brown compound is formed which is exceedingly unstable, like all the analogous compounds of nitric oxide. Ammonia is obtained by the action of a caustic alkali on the resultant compound, because the oxygen of the nitric oxide and water are transferred to the ferrous oxide, forming ferric oxide, whilst the nitrogen combines with the hydrogen of the water. According to the investigations of Gay (1885), the compound is formed with the evolution of a large quantity of heat, and is easily dissociated, like a solution of ammonia in water. If the presence of a radicle NO_2, of the composition of nitrogen peroxide, must be recognised in the compounds of nitric acid, then a radicle NO, having the composition of nitric oxide, may be admitted in compounds of nitrous acid. The compounds in which the radicle NO is recognised are called *nitroso-compounds*. These substances are described in Prof. Bunge's work (Kief, 1868).

$X_5=O_2+(OH)$, where $O_2=X_4$, and $OH=X$; whilst nitric oxide is a compound of the form NX_2. Hence this lower form, like lower forms in general, strives by combination to attain to the higher forms proper to the compounds of a given element. NX_2 passes consecutively into NX_3—namely, into N_2O_3 and NHO_2—NX_4 (for instance, NO_2) and NX_5.[61a]

As the decomposition of nitric oxide begins at temperatures above 900°, **many substances burn in it**; thus, ignited phosphorus continues to burn in nitric oxide, but sulphur and charcoal are extinguished in it. This is due to the fact that the heat evolved in the combustion of these two substances is insufficient for the decomposition of the nitric oxide, whilst the heat developed by burning phosphorus suffices to produce this decomposition. That nitric oxide really supports combustion, owing to its being decomposed by the action of heat, is proved by the fact that strongly ignited charcoal continues to burn in the same nitric oxide[62] in which a feebly incandescent piece of charcoal is extinguished.

The compounds of nitrogen with oxygen, which we have so far considered, may all be prepared from nitric oxide, and may themselves be converted into it. Thus nitric oxide stands in intimate connection with them.[63] The passage of nitric oxide into the higher degrees of

oxidation and the converse reaction is employed in practice as a means for **transferring the oxygen of the air** to substances capable of being oxidised. Starting with nitric oxide, it may easily be converted, with the aid of the oxygen of the atmosphere and water, into nitric acid, N_2O_3, and NO_2, and by their means employed to oxidise other substances. In this oxidising action nitric oxide is again formed, and it may again be converted into nitric acid, and so on continuously, if only oxygen and water be present. Hence the fact, which at first appears to be a paradox, that by means of a small quantity of nitric oxide in the presence of oxygen and water it is possible to oxidise an indefinitely large quantity of substances which cannot be directly oxidised, either by the action of the atmospheric oxygen or by the action of nitric oxide itself. The sulphurous anhydride, SO_2, which is obtained in the combustion of sulphur and in roasting many metallic sulphides in the air, is an example of this kind. In practice this gas is obtained by burning sulphur or iron pyrites, FeS_2, the latter being thereby converted into oxide of iron and sulphurous anhydride, SO_2. In contact with the oxygen of the atmosphere this gas does not pass into the higher degree of oxidation, sulphuric anhydride, SO_3,[63a] and if it does form sulphuric acid with water and the oxygen of the atmosphere, $SO_2+H_2O+O=H_2SO_4$, it does so very slowly. With nitric acid (and especially with nitrous acid, but not with nitrogen tetroxide) and water, sulphurous anhydride, on the contrary, very easily forms sulphuric acid, and especially so when slightly heated (about 40°), the nitric acid (or, better still, nitrous acid) being converted into nitric oxide—

$$3SO_2+2NHO_3+2H_2O=3H_2SO_4+2NO.$$

The presence of water is absolutely indispensable here, otherwise sulphuric anhydride is formed, which combines with the oxides of nitrogen (nitrous anhydride), forming a crystalline substance containing oxides of nitrogen (*chamber crystals*, which will be described in Chapter XX). Water destroys this compound, forming sulphuric acid and separating the oxides of nitrogen. The water must be taken in a greater quantity than that required for the formation of the hydrate H_2SO_4, because the latter absorbs oxides of nitrogen. With an excess of water, however, solution does not take place. If, in the above reaction, only water, sulphurous anhydride, and nitric or nitrous

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[61a] In this example we see an instance of variable atomicity, of which we shall have further occasion to speak, especially in Chap. X., note 1.

[62] A mixture of nitric oxide and hydrogen is inflammable. If a mixture of the two gases be passed over spongy platinum the nitrogen and hydrogen even combine, forming ammonia. A mixture of nitric oxide with many combustible vapours and gases is very inflammable. A very characteristic flame is obtained on burning a mixture of nitric oxide and the vapour of the combustible carbon bisulphide, CS_2. The latter substance is very volatile, so that it is sufficient to pass the nitric oxide through a layer of the carbon bisulphide (for instance, in a Woulfe's bottle) in order that the gas escaping should contain a considerable amount of the vapours of this substance. This mixture continues to burn when ignited, and the flame emits a large quantity of the so-called ultra-violet rays, which are capable of inducing chemical combinations and decompositions, and therefore the flame may be employed in photography in the absence of sufficient daylight (magnesium light and electric light have the same property). There are many gases (for instance, ammonia) which when mixed with nitric oxide explode in a eudiometer.

[63] The oxides of nitrogen naturally do not proceed directly from oxygen and nitrogen by contact alone, because their formation is accompanied by the absorption of a large quantity of heat, for (see note 29) about 21,500 heat units are absorbed when 16 parts of oxygen and 14 parts of nitrogen combine; consequently the decomposition of nitric oxide into oxygen and nitrogen is accompanied by the evolution of this amount of heat; and therefore with nitric oxide, as with all explosive substances and mixtures, the reaction once started is able to proceed by itself. In fact, Berthelot remarked the decomposition of nitric oxide in the explosion of fulminate of mercury. This decomposition does not take place spontaneously; substances even burn with difficulty in nitric oxide, probably because a certain portion of the nitric oxide in decomposing gives oxygen, which combines with another portion of nitric oxide, and forms nitric peroxide, a somewhat more stable compound of nitrogen and oxygen. The further combinations of nitric oxide with oxygen all proceed with the evolution of heat, and take place spontaneously by contact with air alone. It is evident from these examples that the application of thermochemical data is limited.

[63a] But in the presence of spongy platinum (and other contact agents), and when heated, SO_2 does form SO_3 with the oxygen of air. This is now taken advantage of for the manufacture of sulphuric acid. See Chap. XX. (the contact process).

acid be taken in a definite quantity, then a definite quantity of sulphuric acid and nitric oxide will be formed, according to the preceding equation; but there the reaction ends, and the excess of sulphurous anhydride, if there be any, will remain unchanged. But if we add air and water, then the nitric oxide will unite with the oxygen to form nitrogen peroxide, and the latter with water to form nitric and nitrous acids, which again give sulphuric acid from a fresh quantity of sulphurous anhydride. Nitric oxide is again formed, which is able to start the oxidation afresh if there be sufficient air. Thus it is possible with a definite quantity of nitric oxide to convert an indefinitely large quantity of sulphurous anhydride into sulphuric acid, water and oxygen only being required.[64] This may be easily demonstrated by an experiment on a smaller scale, if a certain quantity of nitric oxide be first introduced into a flask, and sulphurous anhydride, steam, and oxygen be then continually passed in. Thus the above-described reaction may be expressed in the following manner:

$$nSO_2+nO+(n+m)H_2O+NO=nH_2SO_4,mH_2O+NO,$$

if we consider only the original substances and those finally formed. In this way a definite quantity of nitric oxide may serve for the conversion of an indefinite quantity of sulphurous anhydride, oxygen, and water into sulphuric acid. In reality, however, there is a limit to this, because air, and not pure oxygen, is employed for the oxidation, so that it is necessary to remove the nitrogen of the air and to introduce a fresh quantity of air. A certain quantity of nitric oxide will pass away with this nitrogen, and will in this way be lost.[65]

The preceding series of changes serves as the basis of the **manufacture of sulphuric acid** or so-called **chamber acid.** This acid is prepared on a very large scale in chemical works, because it is the cheapest acid whose action can be applied in a great number of cases. It is therefore used in immense quantities.

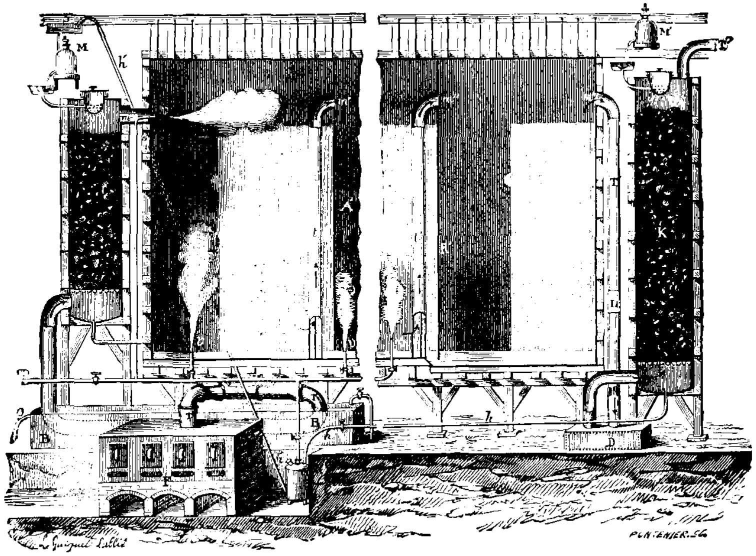

Fig. 58.—Section of sulphuric acid chambers, the first and last chambers only being represented. The tower to the left is called the Glover's tower, and that on the right the Gay-Lussac's tower. Less than $\frac{1}{100}$th of the natural size.

The process is carried on in a series of chambers (or in one divided by partitions as in fig. 58, which shows the beginning and end of a

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[64] The instance of the action of a small quantity of NO in inducing a definite chemical reaction between large masses ($SO_2+O+H_2O=H_2SO_4$) is very instructive, because the details relating to it have been studied, and show that intermediate forms of reaction may be discovered in the so-called contact or catalytic phenomena. The essence of the matter here is that A ($=SO_2$) reacts upon B ($=O$ and H_2O) in the presence of C, because it gives BC, a substance which forms AB with A, and again liberates C. *Consequently C is a medium, a transferring substance, without which the* reaction does not proceed. Many similar phenomena may be found in other departments of life. Thus the merchant is an indispensable medium between the producer and the consumer; experiment is a medium between the phenomena of nature and the cognisant faculties, and language, customs, and laws are media which are as necessary for the exchanges of social intercourse as nitric oxide for those between sulphurous anhydride and oxygen and water.

[65] If the sulphurous anhydride be prepared by roasting iron pyrites, FeS_2, then each equivalent of pyrites (equivalent of iron, 56, of sulphur 32, of pyrites 120) requires six equivalents of oxygen (that is, 96 parts) for the conversion of its sulphur into sulphuric acid (for forming $2H_2SO_4$ with water), besides $1\frac{1}{2}$ equivalent (24 parts) for converting the iron into oxide, Fe_2O_3; hence the combustion of the pyrites for the formation of sulphuric acid and ferric oxide requires the introduction of an equal weight of oxygen (120 parts of oxygen to 120 parts of pyrites), or five times its weight of air, of which four (the four-fifths of nitrogen) will remain inactive, and in the removal of the exhausted air will carry off the remaining nitric oxide. If not all, at least a large portion of the nitric oxide may be collected by passing the escaping air, still containing some oxygen, through substances which absorb oxides of nitrogen. Sulphuric acid itself may be employed for this purpose if it be used in the form of the hydrate H_2SO_4, or containing only a small amount of water, because such sulphuric acid dissolves the oxides of nitrogen. They may be easily expelled from this solution by heating or by dilution with water, as *they are only slightly soluble in aqueous sulphuric acid.* Besides which, sulphurous anhydride acts on such sulphuric acid, being oxidised at the expense of the nitrous anhydride, and forming nitric oxide from it, which again enters into the cycle of action. For this reason, the sulphuric acid which has absorbed the oxides of nitrogen escaping from the chambers in the tower K (see fig. 58) is led back into the first chamber, where it comes into contact with sulphurous anhydride, by which means the oxides of nitrogen are re-introduced into th reaction which proceeds in the chambers. This is the use of the towers (Gay-Lussac's and Glover's) which are erected at either end of the chambers.

chamber) constructed of sheet lead. These chambers are placed one against the other, and communicate by tubes or special orifices so placed that the inlet tubes are in the upper portion of the chamber, and the outlet in the lower and opposite end. The current of steam and gases necessary for the preparation of the sulphuric acid passes through these chambers and tubes. The acid as it is formed falls to the bottom of the chambers or runs down their walls, and flows from chamber to chamber (from the last towards the first), to permit of which the partitions do not reach to the bottom. The floor and walls of the chambers should therefore be made of a material on which the sulphuric acid will not act. Among the ordinary metals lead is the only one suitable.[65a]

For the formation of the sulphuric acid it is necessary to introduce sulphurous anhydride, steam, air, and nitric acid, or some oxide of nitrogen, into the chambers. The sulphurous anhydride is produced by burning sulphur or iron pyrites. This is carried on in the furnace with four hearths to the left of the drawing. Air is led into the chambers and furnace through orifices in the furnace doors. The current of air and oxygen is regulated by opening or closing these orifices to a greater or less extent. The ingoing draught in the chambers is brought about owing to heated gases and vapours passing into the chambers, whose temperature is further raised by the reaction itself, and also by the remaining nitrogen being continually withdrawn from the outlet (above the tower K) by a tall chimney situated near the chambers. Nitric acid is prepared from a mixture of sulphuric acid and Chili saltpetre, in the furnaces in which the sulphurous anhydride is evolved (or in special furnaces). Not more than eight parts of nitre are taken to every 100 parts of sulphur burnt. On leaving the furnace the vapours of nitric acid and oxides of *nitrogen mixed with air and sulphurous* anhydride first pass along the horizontal tubes T into the receiver B B, which is partially cooled by water flowing in on the right-hand side and running out on the left by *o*, in order to reduce the temperature of the gases entering the chamber. The gases then pass up a tower filled with coke, shown to the left of the drawing. In this tower are placed lumps of coke (*the residue from the dry distillation* of coal), over which sulphuric acid trickles from the reservoir M. This acid has absorbed in the end tower K the oxides of nitrogen escaping from the chamber. This end tower is also filled with coke, over which a stream of strong sulphuric acid trickles from

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[65a] Other metals, such as iron, copper, zinc, are corroded by it; glass and china are not acted upon, but they crack from the variations of temperature taking place in the chambers, besides which they are more difficult to join properly than lead; wood, &c., becomes charred.

the reservoir M′. The acid spreads over the coke, and, owing to the large surface offered by the latter, absorbs the greater part of the oxides of nitrogen escaping from the chambers. The sulphuric acid in passing down the tower becomes saturated with the oxides of nitrogen, and flows out at *h* into a special receiver (in the drawing situated by the side of the furnaces), from which it is forced by steam pressure up the tubes *h′ h′* into the reservoir M, situated above the first tower. The gases passing through this tower (hot) from the furnace, on coming into contact with the sulphuric acid, take up the oxides of nitrogen contained in it, and these are thus returned to the chamber and again participate in the reaction. The sulphuric acid left after the extraction of these oxides flows into the chambers. Thus, on leaving the first coke tower the sulphurous anhydride, air, and vapours of nitric acid and of the oxides of nitrogen pass through the upper tube *m* into the chamber. Here they come into contact with steam introduced by lead tubes into various parts of the chamber. The reaction takes place in the presence of water, the sulphuric acid falls to the bottom of the chamber, and the same process takes place in the following chambers until the whole of the sulphurous anhydride is consumed. A somewhat greater proportion of air than is strictly necessary is passed in, in order that no sulphurous anhydride should be left unaltered for want of sufficient oxygen. The presence of an excess of oxygen is shown by the colour of the gases escaping from the last chamber. If they be of a pale colour it indicates an insufficiency of air (and the presence of sulphurous anhydride), as otherwise peroxide of nitrogen would be formed. A very dark colour shows a large excess of air, which is also disadvantageous, because it increases the inevitable loss of nitric oxide by increasing the mass of the escaping gases.[66]

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[66] By this means as much as 2,500,000 kilograms of chamber acid, containing about 60 per cent. of the hydrate H_2SO_4 and about 40 per cent. of water, may be manufactured per year in one plant of 5,000 cubic metres capacity (without stoppages). This process has been brought to such a degree of perfection that as much as 300 parts of the hydrate H_2SO_4 are obtained from 100 parts of sulphur, the theoretical amount being not greater than 306 parts. The acid parts with its excess of water on heating. For this purpose it is heated in lead vessels. However, the acid containing about 75 per cent. of the hydrate (60° Baumé) already begins to act on the lead when heated, and therefore the further removal of water is conducted by evaporating in glass or platinum vessels, as will be described in Chap. XX. The aqueous acid (50° Baumé) obtained in the chambers is termed chamber acid. The acid concentrated to 60° Baumé is more generally employed, and sometimes the hydrate (66° Baumé) termed vitriol acid is also used. In England alone more than 1,000 million kilograms of chamber acid are produced by this method. The formation of sulphuric acid by the action of nitric acid was discovered by Drebbel, and the first lead chamber was erected by Roebuck, in Scotland, in the middle of the eighteenth century. The essence of the process was only brought to light at the beginning of the last century, when many improvements were introduced into practice.

Nitrous oxide, N_2O,[67] is similar to water in its volumetric composition. Two volumes of nitrous oxide are formed from two volumes of nitrogen and one volume of oxygen, as may be shown by the ordinary method for the analysis of the oxides of nitrogen (by passing them over red-hot copper or sodium). In contradistinction to the other oxides of nitrogen, it is not directly oxidised by oxygen, but it may be obtained from the higher oxides of nitrogen by the action of certain deoxidising substances; thus, for example, a mixture of two volumes of nitric oxide and one volume of sulphurous anhydride, if left in contact with water and spongy platinum, is converted into sulphuric acid and nitrous oxide, $2NO + SO_2 + H_2O = H_2SO_4 + N_2O$. Nitric acid, also, under the action of certain metals—for instance, of zinc [68]—gives nitrous oxide, although in this case mixed with nitric oxide. The usual method of preparing nitrous oxide consists in the decomposition of ammonium nitrate by the aid of heat, because in this case only water and nitrous oxide are formed, $NH_4NO_3 = 2H_2O + N_2O$ (a mixture of NH_4Cl and KNO_3 is sometimes taken). The decomposition [69] proceeds very easily in an apparatus like that used for the preparation of ammonia or oxygen—that is, in a retort or flask with a gas-conducting tube. The decomposition must, however, be carried on carefully, as otherwise nitrogen is formed from the decomposition of the nitrous oxide.[70]

Nitrous oxide is a colourless gas with a faint but characteristic smell. It is somewhat soluble in cold water, but only slightly soluble in warm water (and is therefore collected over warm water). It is not a permanent gas (absolute boiling-point +39°), that is, it is easily liquefied by the action of cold under a high pressure; at 15° it may be liquefied by a pressure of about 40 atmospheres. The gas is usually liquefied by means of the force pump [71] shown in fig. 59. As it is liquefied with comparative ease, and as the cold produced by its vaporisation is very considerable,[72] it is often employed (as also is liquid carbonic anhydride) in investigations requiring a low temperature.

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[67] If the hydrate HNO_3 corresponds to N_2O_5, the hydrate HNO, **hyponitrous acid**, corresponds to N_2O, and in this sense N_2O is **hyponitrous anhydride**. Hyponitrous acid, NHO, was obtained in the form of its corresponding salts RNO, or $R_2N_2O_2$, by Divers. They are prepared by the reduction of nitrous (and consequently of nitric) salts by sodium amalgam. If this amalgam be added to a cold solution of an alkaline nitrite until the evolution of gas ceases, and the excess of alkali be saturated with acetic acid, an insoluble yellow precipitate of silver hyponitrite, NAgO, will be obtained on adding a solution of silver nitrate. This hyponitrite is insoluble in cold acetic acid, and decomposes when heated, with evolution of nitrous oxide. If rapidly heated it decomposes with an explosion. It is dissolved unchanged by weak mineral acids, whilst the stronger acids (for example, sulphuric and hydrochloric acids) decompose it with the evolution of nitrogen, nitric and nitrous acids remaining in solution. Among the other salts of hyponitrous acid, HNO, those of lead, copper, and mercury are insoluble in water. Judging by the bond existing between hyponitrous acid and the other compounds of nitrogen, there is reason for thinking that its formula should be doubled, $N_2H_2O_2$. For instance, Thum (1893) on gradually oxidising hydroxylamine, $NH_2(OH)$, into nitrous acid, NO(OH) (note 25), by means of an alkaline solution of $KMnO_4$, first obtained hyponitrous acid, $N_2H_2O_2$, and then a peculiar intermediate acid, $N_2H_2O_3$, which, by further oxidation, gave nitrous acid. On the other hand, Wislicenus (1893) showed that in the action of the sulphuric acid salt of hydroxylamine upon nitrite of sodium, there is formed, besides nitrous oxide (according to V. Meyer, $NH_3O, H_2SO_4 + NaNO_2 = NaHSO_4 + 2H_2O + N_2O$), a small amount of hyponitrous acid which may be precipitated in the form of the silver salt; and this reaction is most simply expressed by taking the doubled formula of hyponitrous acid, $NH_2(OH) + NO(OH) = H_2O + N_2H_2O_2$. The best argument in favour of the doubled formula is the property possessed by hyponitrous acid of forming acid salts, $HNaN_2O_2$ (Zorn), and also the determination of its molecular weight in solution by the method described in the following chapter.

According to Thum, the following are the properties of hyponitrous acid. When liberated from the dry silver salt by the action of dry sulphuretted hydrogen, hyponitrous acid is unstable, and easily explodes even at low temperatures. But when dissolved in water (having been formed by the action of hydrochloric acid upon the silver salt), it is stable even when boiled with dilute acids or alkalies. The solution is colourless and has a strongly acid reaction. In the course of time, however, the aqueous solution also decomposes into nitrous oxide and water. The complete oxidation by permanganate of potash proceeds according to the following equation: $5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 = 10HNO_3 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$. In alkaline solution, $KMnO_4$ only oxidises hyponitrous acid into nitrous and not into nitric acid. Nitrous acid has a decomposing action upon hyponitrous acid, and if the aqueous solutions of the two acids be mixed together they immediately give off oxides of nitrogen. Hyponitrous acid does not liberate CO_2 from its salts, but, on the other hand, it is not displaced by CO_2.

[68] It is remarkable that electro-deposited copper powder gives nitrous oxide with a 10 per cent. solution of nitric acid, whilst ordinary copper gives nitric oxide. It is here evident that the physical and mechanical structure of the substance affects the course of the reaction—that is to say, it is a case of contact or surface action.

[69] This decomposition is accompanied by the evolution of about 25,000 calories per gram-molecule, NH_4NO_3, and therefore takes place with ease, and sometimes with an explosion.

[70] In order to remove any nitric oxide that might be present, the gas obtained is passed through a solution of ferrous sulphate. As nitrous oxide is very soluble in cold water (at 0°, 100 volumes of water dissolve 130 volumes of N_2O; at 20°, 67 volumes), it must be collected over warm water. The nitrous oxide is much more soluble than nitric oxide, which is in agreement with the fact that nitrous oxide is much more easily liquefied than nitric oxide. Villard obtained a crystallohydrate, $N_2O,6H_2O$, which was tolerably stable at 0°.

[71] Faraday obtained liquid nitrous oxide by the same method as he employed for liquid ammonia, by heating dry ammonium nitrate in a closed bent tube, one arm of which was immersed in a freezing mixture. In this case two layers of liquid are obtained at the cooled end, a lower layer of water and an upper layer of nitrous oxide. This experiment should be conducted with great care, as the pressure of the nitrous oxide in a liquid state is considerable, namely (according to Regnault), at +10°, 45 atmospheres, at 0°, 36 atmospheres, at −10°, 29 atmospheres, and at −20°, 23 atmospheres. It boils at about −90°, and the pressure is then of course 1 atmosphere.

[72] Liquid nitrous oxide, in vapourising at the same pressures as liquid carbonic anhydride, gives rises to almost equal or even slightly lower temperatures. Thus at a pressure of 25 mm. carbonic anhydride gives a temperature as low as −115°, and nitrous oxide −125° (Dewar). The similarity of these properties and even of the absolute boiling-point ($CO_2 + 32^\circ$, $N_2O + 86^\circ$) is all the more remarkable because these gases have the same molecular weight, namely, 44.

Liquid nitrous oxide is a very mobile, colourless liquid, which boils at − 89·8°, acts on the skin, and is incapable of oxidising potassium, phosphorus, or carbon; its specific gravity is slightly less than that of water (0·910 at 0°, 0·856 at 10°, 0·60 at 35°, and 0·45 at 39°; Villard, 1894). When it is evaporated under the receiver of an air-pump, its temperature falls to −100°, and the liquid solidifies into a snowlike mass, and partially forms transparent crystals. Both these substances are solid nitrous oxide. It melts at about −102°.[73]

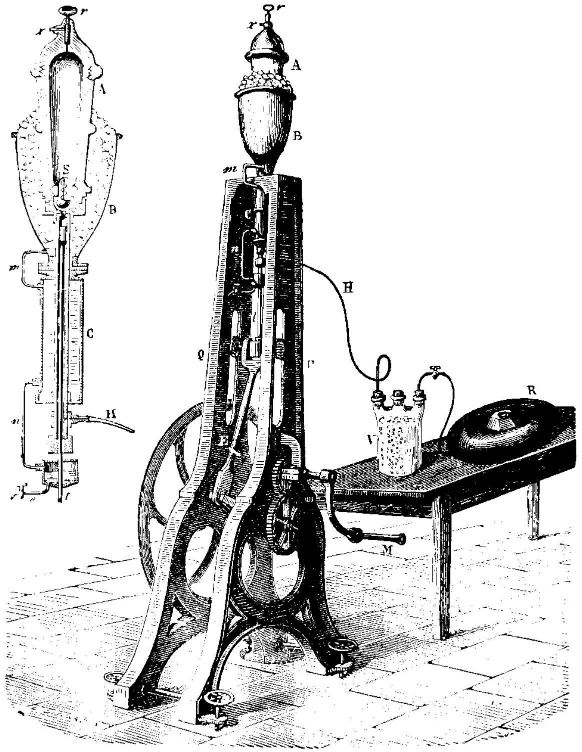

Fig. 59.—Natterer's apparatus for the preparation of liquid nitrous oxide and carbonic anhydride. The gas first passes through the vessel V, for drying, and then into the pump (a section of the upper part of the apparatus is given on the left). The piston *t* of the force pump is moved by the crank E and fly-wheel turned by hand. The gas is pumped into the iron chamber A, where it is liquefied. The valve S allows the gas to enter A, but not to escape from it. The chamber and pump are cooled by the jacket B, filled with ice. When the gas is liquefied the vessel A is unscrewed from the pump, and the liquid may be poured from it by inverting it and unscrewing the valve *r*, when the liquid runs out of the tube *x*.

When introduced into the respiratory organs (and consequently, owing also to its solubility, in the blood) nitrous oxide produces a peculiar kind of intoxication accompanied by spasmodic movements, and hence this gas, discovered by Priestley in 1776, received the name of *laughing gas*. On prolonged respiration it produces a state of insensibility (it is an anæsthetic like chloroform), and is therefore employed in dental and surgical operations, but too prolonged respiration causes death.

Nitrous oxide is easily decomposed into nitrogen and oxygen by the action either of heat, or of a series of electric sparks; and this explains why a number of substances which cannot burn in nitric oxide do so with great ease in nitrous oxide. In fact, when nitric oxide yields oxygen on decomposition, it immediately absorbs it, forming NO_2; whilst nitrous oxide does not possess this capacity for further combination with oxygen.[74] A mixture of nitrous oxide with hydrogen explodes like detonating gas, gaseous nitrogen being formed, $N_2O+H_2=H_2O+N_2$. The volume of the remaining nitrogen is equal to that of the original nitrous oxide, and also to that of the hydrogen entering into combination with the oxygen; hence in this reaction equal volumes of nitrogen and hydrogen replace each other. Nitrous oxide is also very easily decomposed by red-hot metals; also sulphur, phosphorus, and charcoal burn in it, although not so brilliantly as in oxygen. A substance in burning in nitrous oxide evolves more heat than an equal quantity burning in oxygen; which clearly shows that in the formation of nitrous oxide by the combination of nitrogen with oxygen there is not an evolution but an absorption of heat, there being no other source for the excess of heat in the combustion of substances in nitrous oxide (see note 28). If a given volume of nitrous oxide be decomposed by a metal—for instance sodium—there remains, after cooling, a volume of nitrogen exactly equal to that of the nitrous oxide taken; consequently the oxygen is, as it were, distributed between the atoms of nitrogen without producing an increase in the volume of the nitrogen.

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[73] A very characteristic experiment of simultaneous combustion and intense cold may be performed by means of liquid nitrous oxide; if liquid nitrous oxide be poured into a test tube containing mercury the latter will solidify, and if a piece of red-hot charcoal be thrown upon the surface of the nitrous oxide it will continue to burn very brilliantly, giving rise to a high temperature.

[74] In the following chapter we shall consider the volumetric composition of the oxides of nitrogen, which will explain the difference between nitric and nitrous oxides. Nitrous oxide is formed with a diminution of volume (contraction), but nitric oxide without contraction, its volume being equal to the sum of the volumes of the nitrogen and oxygen of which it is composed. By oxidation, if this could be directly accomplished, two volumes of nitrous oxide and one volume of oxygen would not give three but four volumes of nitric oxide. These facts must be taken into consideration in comparing the heats of formation, the capacities for supporting combustion, and other properties of nitrous and nitric oxides, N_2O and NO.

Although nitrous oxide, N_2O, is not absorbed by caustic alkalies, for instance, NaHO, nor by basic oxides, for instance, PbH_2O_2, yet saline compounds such as N_2NaHO_2 or PbN_2O_2 and their corresponding **hyponitrous acid**, $N_2H_2O_2$, forming as it were the hydrate of nitrous oxide, are known and are formed in the decomposition of nitrous oxide (see note 67). The salts of hyponitrous acid are best formed by the reduction (by sodium amalgam, hydrated ferrous oxide, &c.) of the salts of nitrous acid, or by their double decomposition with the salts of hydroxylamine.

$$NH_2OH+NHO_2=N_2H_2O_2+H_2O.$$[75]

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[75] It is said that a peculiar isomeride of hyponitrous acid—$N_2H_2O_2$—is obtained from nitrourethane, $C_3H_6N_2O_4$, but this question is not sufficiently certain to be treated of in an elementary text-book.

CHAPTER VII

MOLECULES AND ATOMS. THE LAWS OF GAY-LUSSAC AND AVOGADRO-GERHARDT.

HYDROGEN combines with oxygen in the proportion of two volumes to one. The composition by volume of nitrous oxide is exactly similar—this gas being composed of two volumes of nitrogen and one volume of oxygen. By decomposing ammonia by the action of an electric spark it is easy to prove that it contains one volume of nitrogen to three volumes of hydrogen. So, similarly, whenever a compound is decomposed and the **volumes of the gases** proceeding from it are measured, it is found that the volumes of the gases or vapours entering into combination stand in very simple relations to one another. With water, nitrous oxide, &c., this may be proved by direct observation; but in the majority of cases, and especially with substances which, although volatile—that is, capable of passing into a gaseous (or vaporous) state—are liquid at the ordinary temperature, such a direct method of observation presents many difficulties. But, then, if the densities of the vapours and gases be known, the same simplicity in their ratio is shown by calculation. The volume of a substance is proportional to its weight, and inversely proportional to its density, and therefore by dividing the amount by weight of each substance entering into the composition of a compound by its density in the gaseous or vaporous state we shall obtain factors which will be in the same proportion as the volumes of the substances entering into the composition of the compound.[1] Thus, for example, water contains eight parts by weight of oxygen to one part by weight of hydrogen, and their densities are 16

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[1] If the weight be indicated by P, the density by D, and the volume by V, then

$$\frac{P}{D}=KV$$

where K is a coefficient depending on the method of expressing P, D, and V. But, whatever it be, K is cancelled in dealing with the comparison of volumes, because comparative and not absolute measures of volumes are taken. In this chapter, as throughout the book, the weight P is given in grams in dealing with absolute weights; and if comparative, as in the expression of chemical composition, then the weight of an atom of oxygen is taken as 16, and that of an atom of hydrogen as 1·008.