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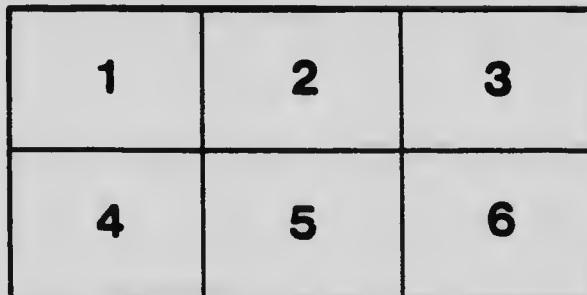
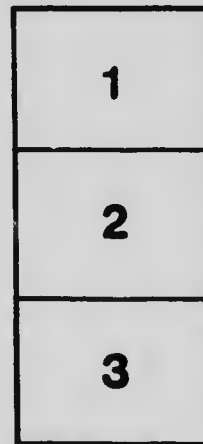
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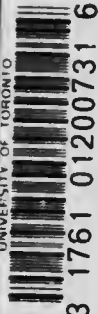
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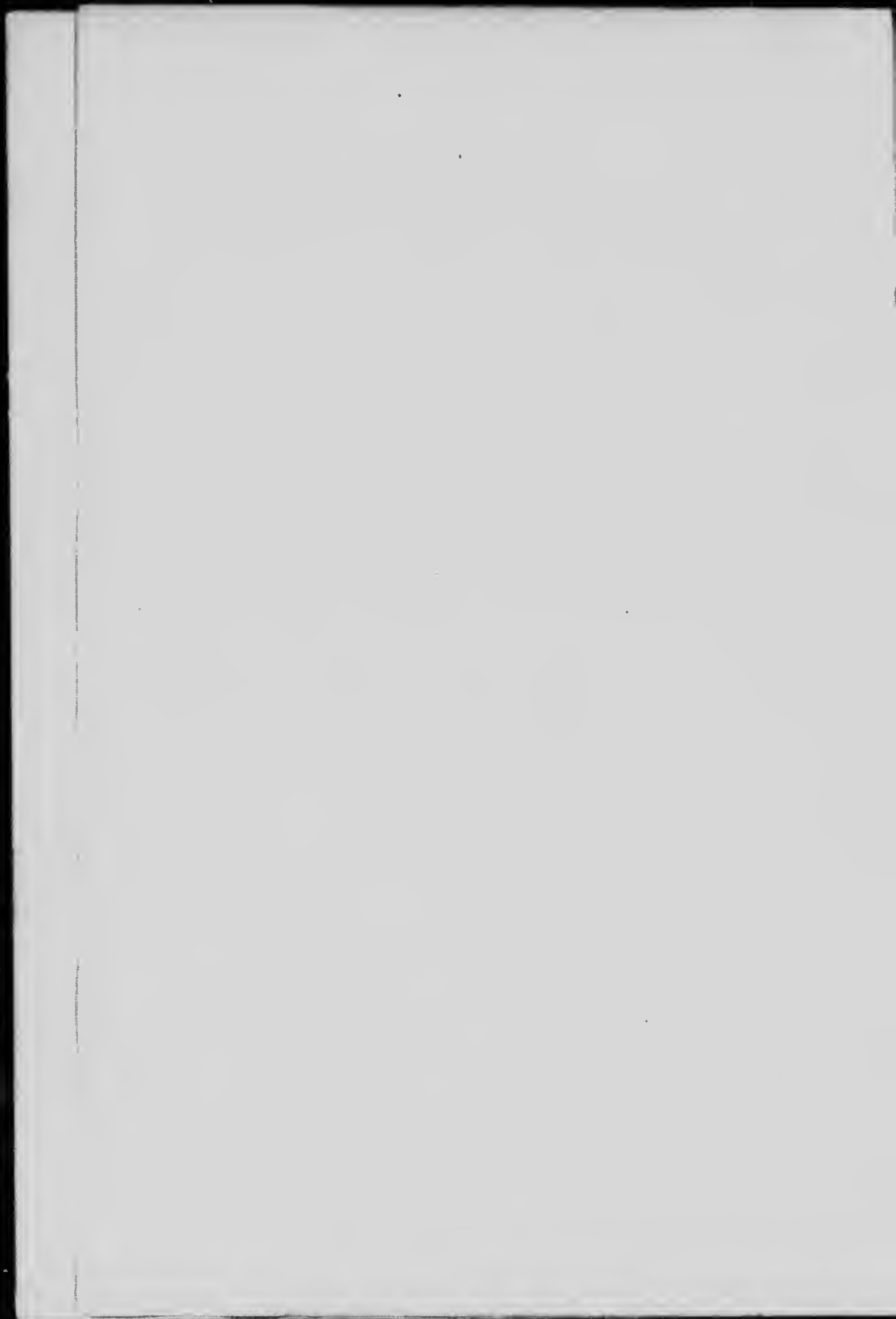


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THE NEW REQUIREMENTS IN CHEMISTRY
FOR JUNIOR MATRICULATION

W. LASH MILLER



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THE NEW REQUIREMENTS IN CHEMISTRY

FOR JUNIOR MATRICULATION AND FOR THE
DEPARTMENTAL EXAMINATIONS OF
THE PROVINCE OF ONTARIO

BY

W. Lash
W. LASH MILLER, Ph.D., F.R.S.C.

MEMBER OF THE WASHINGTON ACADEMY OF SCIENCES
ASSOCIATE-PROFESSOR OF PHYSICAL CHEMISTRY IN THE UNIVERSITY
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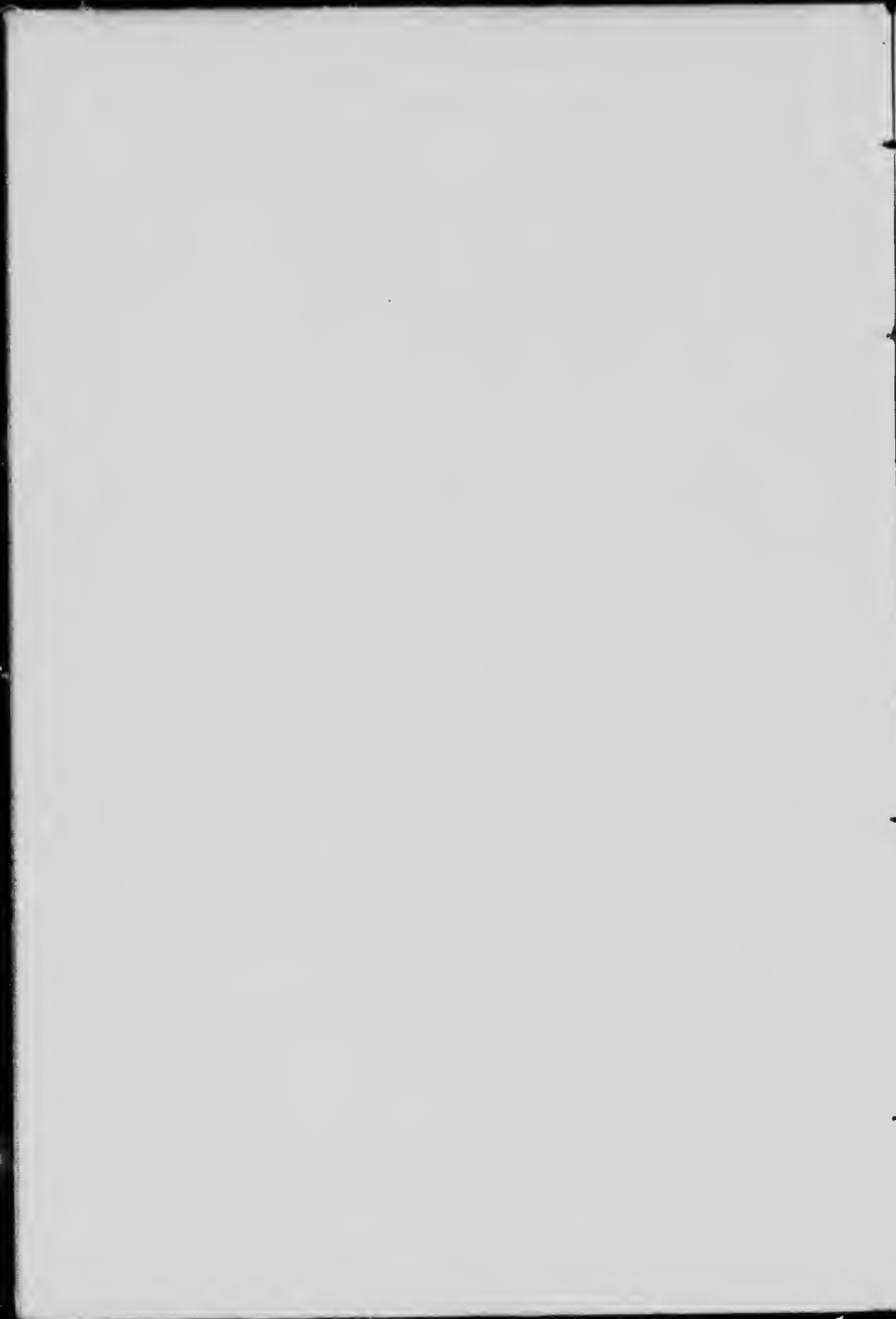
PREFACE

In the new "Regulations of the Education Department of the Province of Ontario" the work formerly prescribed under "Chemistry of the Lower School" has been changed by the omission of "The Atomic Theory and Molecular Theory" and the insertion of "Mixtures, solutions, chemical compounds, elements, combining weights, chemical formulæ and equations, with easy numerical examples"; while to the "Chemistry of the Upper School" there has been added "Chemical and physical reactions, rates of reactions, reversible reactions, chemical equilibrium," and the paragraph requiring a practical examination has been removed. These changes have been adopted by the University in defining the work for Junior Matriculation.

Some of these subjects—chemical equilibrium, for instance—are new, and are introduced to bring the teaching up to date; others, such as mixture, element, etc., were implicitly prescribed in the old curriculum, but by printing them among the Requirements their importance has been emphasized.

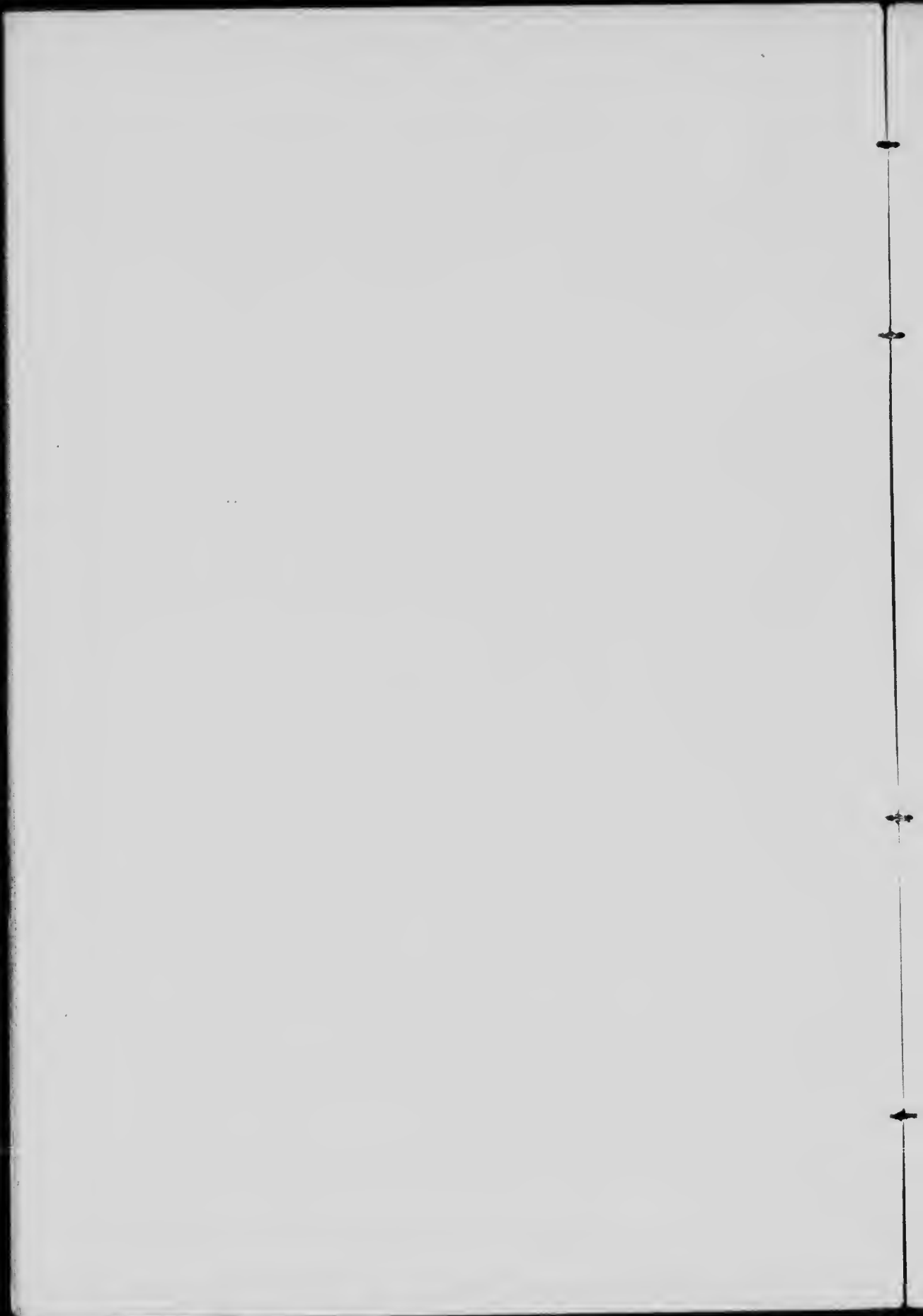
It is hoped that this little book may prove of service to the Teachers of Chemistry throughout the Province by supplying them with concrete examples for use in their lessons and in the school laboratories, and by attracting their attention to some loose ways of speaking and thinking that ought to be avoided. Many of the experiments were worked out with Dr. F. B. Kenrick for a course of lectures delivered in 1898-1900; and Dr. F. B. Allan's experience as Departmental Examiner has helped very much in deciding what to include and what to leave out—the author is glad of this opportunity of thanking his colleagues for their assistance.

The University of Toronto
Christmas, 1904



CONTENTS.

	PAGE
I. DEFINITIONS, LAW OF CONSERVATION OF MASS. Plain language: "mixture," "properties," "new substance." Conservation of mass: experiments, balance, mass and weight. "Compounds": "contain," "physical and chemical compounds," the difference exaggerated	1
II. PHYSICAL COMPOUNDS. Brine: graphic representation, interpolation, extrapolation, saturated unsaturated and supersaturated solutions, advantages of graphic method. Other liquid solutions: plain soda, vinegar. Solid solutions: glass, isomorphous mixtures. Mixtures of gases: air	9
III. MECHANICAL MIXTURES. Obvious case: Gunpowder, a fallacious argument exposed. A more complicated case	15
IV. ANALYSIS AND SYNTHESIS. THE CHEMICAL ELEMENTS. Direct synthesis. Direct analysis. Indirect analysis and synthesis: a <i>petitio principii</i> . Elements: allotropic forms; a misleading phrase	17
V. CHEMICAL COMPOUNDS. LAWS OF CHEMICAL COMBINATION. Definite proportions. Reciprocal proportions, cards. Multiple proportions, cards. Combination of gases by volume. THEORIES AND EXPLANATIONS: Atomic and Molecular theories, a modern view, Descartes' Golden Rule. Why an "explanation" is needed; Lemery's hypothesis, Ehrlich's diagrams. Why the Atomic hypothesis was generally accepted; why its influence has waned; advantages of the modern view	20
VI. CHEMICAL FORMULÆ. THE INTERNATIONAL ATOMIC WEIGHTS. Card Formulæ. International weights, symbols, O = 16 the basis. Advantages of teaching by cards; example	26
VII. CHEMICAL AND PHYSICAL REACTIONS. History of the distinction, analogous cases. Injury done by hypothetical explanations, false law of Maximum Work. Equilibrium: Le Chatelier's law; reactions analogous to those between ice and water, water and steam, salt and brine; chemical equilibria in gases and in solutions; further examples. Non-reversible reactions, continuity	33
VIII. RATES OF REACTION. Factors on which rates depend, catalytic agents. Delayed reactions. Action of light	41
IX. SUGGESTIONS FOR A LABORATORY COURSE	45



CHAPTER I.

DEFINITIONS : LAW OF THE CONSERVATION OF MASS

One of the most marked peculiarities of Chemistry as a science is its use of plain language, and the almost total absence of technical terms. Analysis, synthesis, isomorphous, allotropic, valency with its derivatives, and a few others not in common use such as metathesis, artiad, perissad—these are all the foreign words to be found in the index to the "High School Chemistry"—what a contrast to the corresponding volumes on Botany and Zoology!

The custom is international, and the reason commonly given is that Chemists are the spiritual descendants of ignorant metal workers and Alchemists, while Biologists represent the Doctors of Medicine, with their gold-headed canes and classical education. Be that as it may, a new term derived from the Latin or Greek has next to no chance of success in Chemistry, it is almost certain to be ousted by some common word or phrase taken from everyday language.

At first sight it might seem a matter for congratulation that one science, at least, has found it possible to get on without the invention of a new vocabulary, but on closer examination it is apparent that there are very decided disadvantages entailed by the unsystematic use of "plain" language. A new word from the Greek is defined when coined, and its meaning need not be uncertain; but if an English word be adopted and given a scientific signification, its new meaning is apt to be confounded with the loose use of the word in everyday life.

The terms "mixture," "compound," "contain," and many others are instances of such words with a double meaning—restricted in Chemistry, wider in common use—and before they can be employed with advantage it is necessary to define them.

When two substances are brought together, their properties may remain altogether unchanged, in which case the two are said to form a "mechanical mixture" containing both of them; this somewhat clumsy term being adopted instead of the shorter "mixture" because the latter word is universally employed in speaking of "mixtures of gases," "mixtures of alcohol and water," etc., which are not "mechanical mixtures" at all. If on the other hand the properties change, as when water is poured on salt, or hydrogen is burned in oxygen, a "reaction" is said to take place, and a "new substance" is said to be formed,—brine in the first case, and steam in the second. Very often the product is a mechanical mixture of one or more new substances with more or less of the old ones unaltered; as for example when a little water is poured on a lot of salt, when silver nitrate is added to sea water, or when a silver coin is rubbed with sulphur.

The word "properties" itself has a restricted meaning in chemistry. Position, form, and size, are passed over as of no moment; the "physical properties," viz.: density, colour (except in so far as it depends on size or position), refractive index, fluidity, electrical conductivity, etc., are not disregarded; but the most important, naturally, are the "chemical" properties, in particular the ability to combine with other substances.

When properties change, it is usual to say that a new or different substance has been formed—indeed in defining the various substances there is nothing but their properties to go by. An important exception to this usage, however, is met with in the case of substances whose properties change continuously on heating. Hot and cold iron, for instance, are not spoken of as different substances, although they differ both physically and chemically (see pg. 40). Ice, water, steam, on the other hand, are "different"; and when salt is dissolved in water, a "new substance"—brine—is formed. That the distinction cannot be carried through to its logical conclusion will be shewn in the sequel; in the meantime the exception must be noted.

The new substance need not differ in *all* properties from the old. When copper and sulphur are ground together and form sulphide of copper, there is no change of volume; and in every case the weight of the new substances is the same as that of the substances from which they have been formed. This latter fact has been known for little longer than a century, and is included in the

LAW OF THE CONSERVATION OF MASS,

a "law," in the scientific sense, being the statement of some generalization from experience.

The use of the balance dates back to the time of the Egyptians at least, and the fact that the weight of a mixture is the sum of the weights of its components is too familiar to need demonstration—it is tacitly assumed by every grocer who mixes tea, biscuits or candies for his customers on the scales. That the weight of a lump of salt is not lost when it disappears in water is perhaps not so obvious, and there are lots of people who are hardly ready to believe that the weight of a man plus his dinner is the same before and after eating. Very simple experiments however are sufficient to set doubt on these points at rest.

It is otherwise with the phenomena of combustion; only when the study of gases was taken up in earnest and the methods of collecting and weighing them were developed (at the end of the eighteenth century) was it discovered that the law of conservation of mass applies to all chemical reactions without exception.

When finely divided iron—*ferrum redactum*—is heated in air it burns; and that the product of combustion weighs more than the iron consumed may be shewn by dipping the poles of a horse-shoe magnet in the iron powder, hanging it on a balance, and setting fire to the iron with a spirit lamp—a dish should be placed in the pan to catch any particles that may drop off.

If however the combustion be carried out in a closed bottle of oxygen,¹ no change of weight occurs. The iron may be held in a small cylinder two inches long, closed at the bottom and attached to a stout wire passing through the cork; it may be ignited electrically by means of a second wire which also passes through the cork and touches the surface of the powder near the cylinder. After shewing that the weight is unaffected by the reaction, the ignition wire may be pulled out, air will rush in, and the balance will shew an increase of weight.

The explanation of the gain in weight in the first experiment, then, is that the product of combustion contains one of the constituents of the air. That air itself has weight may be shewn in a very convincing manner by pumping it with a bicycle pump or rubber syringe into a common round quart bottle provided with a cork and tap,² well tied in, and weighing before and after.

If hydrochloric acid be poured on baking soda there is violent effervescence and a loss of weight; the soda may be placed in a beaker on the pan of the balance, and the acid in a test-tube standing in the beaker; after balancing, mix. If the same reaction be carried out in the bottle which served for weighing the air (the acid in a test-tube as before, and the mixing effected by tilting the bottle) the weight remains unchanged, but when the tap is opened carbon dioxide escapes and the pan rises. Four grammes of sodium bicarbonate is a safe amount to take if the bottle holds a quart; rocc of concentrated hydrochloric acid is sufficient.

The well known experiment to demonstrate that the products of combustion of a candle weigh more than the candle itself may also be shewn in this connection. The flame must be protected by a piece of tin or brass fixed a little below the gauze, or drops of liquid falling from the potash may extinguish it.

¹ A common round bottle holding about a quart will serve very well; the cork should fit tight and be well vaselined; the holes for the wire (telegraph wire) may be made with an awl, if the wires be sharpened at the end and vaselined they will pass through air-tight. The cylinder to hold the iron powder may be made by wrapping fine wire gauze round the rod of a retort-stand and hammering in the end. If the 110 volt circuit be used for firing, four 16 c.p. lamps in parallel may be used as a rheostat; a bend in the ignition wire outside the cork helps to pull it out.

² A glass-tap will do, or one of the small brass "petcocks" used on the gauges of steam boilers.

As the matter is important, it might be well to shew that addition of the solution of a sulphocyanate to one of a ferric salt, or of dilute sulphuric acid to lead acetate solution, although obviously leading to the formation of new substances, does not entail change of weight.

A HOME-MADE BALANCE¹

A balance with which to carry out the experiments described above may easily be made as follows, at a cost of less than a dollar; when carrying a kilogramme on each arm, one gramme additional is enough to move the pans through three inches.

In fig. 1. *i* shews the balance in perspective, *ii* is a view of the beam from above, *iii* is the stiffening piece, *iv* is a transverse section through the beam, column, and screws which serve as "knife edges" and *v* is a section through the beam near the end, to shew how the pans are supported.

The base is a piece of board 8x30 inches; the column is of wood 3 in. from front to back of *i*, one in. from right to left, and 18 in. high, screwed to the base and supported by two triangular pieces *E*. A notch $\frac{3}{8}$ in. deep \times $1\frac{3}{4}$ in. is cut out of the top as shewn in *ii* and two small pieces of brass are screwed on at *D*. The beam is a lath *A* 25 in. long, $\frac{1}{4}$ thick and $1\frac{1}{2}$ wide, with a notch at each end $\frac{3}{8}$ in. wide and 1 in. long; it is stiffened by a vertical piece *B* of the same thickness, 23 in. long and 1 in. high in the centre, tapering to both ends, and fastened to *A* by screws. A transverse piece *C* of the shape shewn in *ii* and *iv* carries two screws *X* (flat head bright, 1 in. No. 6) whose points are filed sharp and rock on the brass plates *D*. Four more screws *Y* ($\frac{3}{4}$ in. No. 4), two at each end of the beam, carry small pieces of sheet brass *G* ($1\frac{1}{2}$ by $\frac{3}{8}$ in.) to each of which is soldered a wire loop; the pans, of galvanized iron $6\frac{1}{2}$ in. diameter, are hung from the loops by three strings each, so as to come about 3 in. above the base.

The points of the six screws *X*, *Y*, and the centre of gravity of the beam should be nearly in the same plane; the delicacy of the balance is increased by screwing down the two screws *X*, if they are too low, however, the beam will overbalance on either side and will not rise. The balance should be adjusted once for all, best when carrying bottle and counterbalance. A pointer with small adjustable weight may be added if desired.

A round piece of 4 lb. lead, turned up at the edge to form a saucer, makes a good counterbalance for the bottle used in the experiments of page 3; it should be made a little so light, and sand added to balance.

¹ The Central Electric and School Supply Co., 36 Adelaide St. W., Toronto, offers these balances at four dollars each.

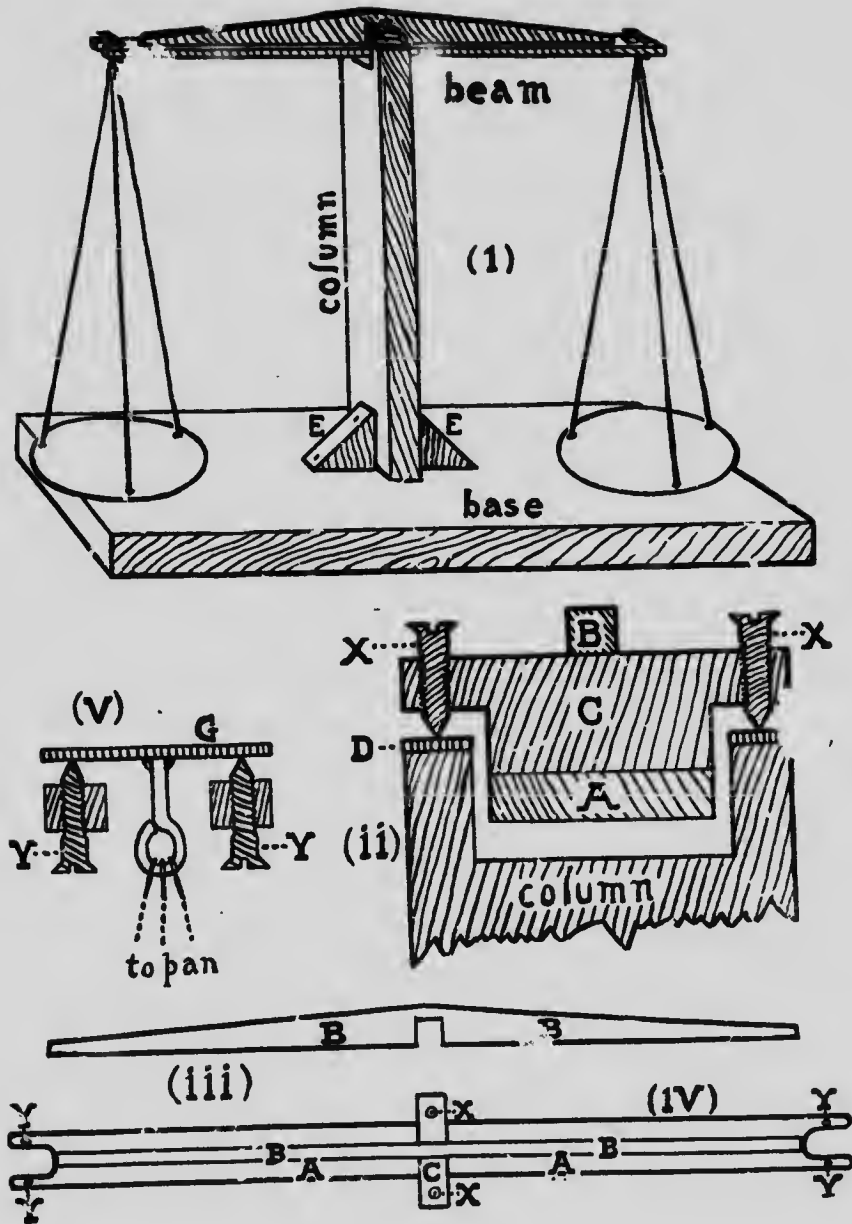


FIG. I.

MASS AND WEIGHT

The experiments described in the preceding paragraphs shew that the weight of the products of a reaction is the same as that of the original substances; and as in any given place the weight of a body is proportional to its mass, the mass of the products of a reaction must be equal to the mass of the original substances.

A discussion of the relations between weight and mass belongs properly to the subject of mechanics; it is sufficient for the present purpose to say that while the weight of a body is proportional to the force required to lift it perpendicularly, its mass is proportional to the force required to throw it horizontally at a given rate. The mass of any article is independent of its position, but the weight decreases as the equator is approached, and is less at high levels than at low. A piece of brass for example that weighed 50 grammes at the top of the University tower, would weigh half a milligramme more if suspended from the pan of the balance by a thread 100 feet long; and a consignment of diamonds from South Africa weighs more in London than in Johannesburg—however, as the weights against which the stones are balanced are likewise heavier in London, the Consignee profits nothing.

It is impossible, consequently, to speak of a "law of the conservation of weight," but the chemical experiments just discussed, together with evidence that mass is unaffected by position, establish the law of the conservation of mass.

The expression "conservation of matter" is often used in this connection; but as "matter" is a metaphysical conception, very difficult to define, it is better to stick to a name that has direct reference to the experiments.

COMPOUNDS

When two or more substances react and form but one product, the latter is called a "compound" and is often said to "contain" the others; 100 g of water and 10 g of salt for instance react to form 110 g of brine, "which contains 100 g of water and 10 g of salt," and one gramme of hydrogen reacts with 8 g of oxygen forming 9 g of steam, each gramme of which "contains" $\frac{1}{9}$ g of hydrogen and $\frac{8}{9}$ g of oxygen. Further, when a single substance (as distinguished from a mechanical mixture of several) turns into two or more others—when marble is heated, for instance, or water is electrolysed—it is likewise said to be a compound, and to contain the others.

Except in a few recent publications, only chemical compounds and elements are spoken of as "contained"; brine contains water and salt, but not water and a more concentrated brine; moreover, chemical

compounds are generally said to contain their elements only, although it is customary to speak of the ammonium salts as containing ammonia, hydrated salts as containing water, and marble as containing lime and carbonic acid. The usage in both respects has changed from time to time.

It is obvious that when used in this connection the meaning of the word "contain" is very different from that attached to it when speaking of mechanical mixtures. When powdered with glass, sulphur with all its properties is as truly present in the mixture as when it was contained in the bottle when burned in oxygen, both sulphur and oxygen disappear, and their place is taken by a new substance differing in properties from both. This double use is confusing but cannot be helped, and it is best to regard the word as meaning only that the substances "contained" can be turned into, or made out of, the substance that "contains" them.

PHYSICAL AND CHEMICAL COMPOUNDS

Salt and water can unite to form a series of brines varying continuously in composition, and in this respect differ from sodium and chlorine which can unite in but one proportion, forming common salt; if more than 153.7 g of chlorine be taken for every 100 g of sodium the excess of chlorine remains unaltered, and *vice versa*.

This distinction can be expressed in words by saying that salt and water combine in *variable* proportions, while sodium and chlorine combine in *definite* proportions. The products of combination in variable proportions will be called "Physical Compounds," while those of combination in definite proportions are "Chemical Compounds."

These two classes have long been distinguished, and attempts have been made to show that they are more different than is in fact the case. Great stress is laid on the fact that aqueous solutions differ from water in degree only—this is obviously true, very dilute solutions are almost identical with water in every respect; but how do they resemble salt? Certainly not in appearance. In taste? The man must have a dry tongue who can satisfy himself of that.

In chemical properties, too, brine resembles water; both give off steam on heating—but so does blue vitriol, a "chemical" compound of copper sulphate and water. And is it not generally true that chemical compounds differ from their components in degree only? Oxygen and hot iron give the magnetic oxide, steam and hot iron do the same thing. Hydrogen unites with oxygen and mercury with chlorine; do they lose these properties by entering into chemical combination, the hydrogen with the chlorine, and the mercury with the oxygen?

As the proportion of water decreases, the solution resembles pure water less and less; chemically as well as otherwise. If water be dropped

on sodium carbonate¹ the hydrated salt is formed; and if a little alcohol be dissolved in the water, it seems to make no difference. But if strong alcohol be used, i.e. a solution of water and alcohol containing only a few percent of water, no hydrate is formed; indeed if a clear crystal of the latter substance be covered with the alcohol it becomes opaque and falls to a powder of sodium carbonate. In this instance the "chemically" combined water resembles pure water in combining with alcohol, and the "physically" combined water (in the "strong alcohol") differs from pure water in not combining with sodium carbonate.

It is natural to ask why there should be a general tendency to exaggerate the difference between these two classes of compounds. An answer is given in the opening paragraphs of the chapter on Reactions.

¹ Prepared by heating washing soda in an evaporating dish over a Bunsen burner.

CHAPTER II.

PHYSICAL COMPOUNDS

These are also known as "Compounds of variable composition," and sometimes as "Solutions." After a page or two on brine, which is typical of the whole group, some solid and gaseous "solutions" will be dealt with shortly.

Brine. The members of the series of brines that can be formed by dissolving more or less salt in a given quantity of water are usually identified by the "percent" of salt which they contain. This method, however, is not free from ambiguity, as a "five percent salt solution" may mean either a solution containing 100 parts (by weight) of water and five of salt, or one containing 5 of salt and 95 of water, making 100 in all;¹ and although for many purposes the difference is of no moment, when speaking accurately the distinction must be borne in mind.

When the percentage of salt is large the solution is said to be concentrated, when it is small, dilute.

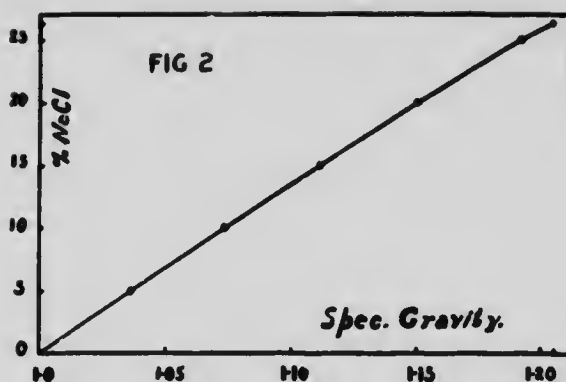
The properties of the brines vary continuously with their concentration, that is, with the percent of salt they contain. All are liquid, and will boil when heated sufficiently, but the fluidity (as measured by the rate at which they flow through a narrow tube under standard conditions) decreases, the boiling-point rises, and the freezing-point falls as the concentration increases in the series; the density (specific gravity), optical properties (refraction and absorption of light), and electrical conductivity also change with the concentration. The following table of the specific gravities of solutions of common salt in water may serve as an example :

grammes salt in 100 g water	sp. gr. at 15°C
5	1.036
10	1.070
15	1.111
20	1.151
25	1.192
26.4	1.204

GRAPHIC REPRESENTATION

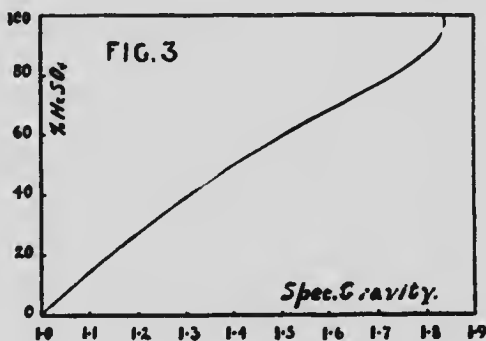
The information contained in this table is repeated in another form in the accompanying figure. The result of each specific gravity determination, and the composition of the solution with which it was carried out, are

¹ This would be a 5.26 per cent. solution, using the word in its first meaning.



given in the table by means of two numbers in the same horizontal line; while in the figure they are indicated by the position of a dot, the distance of the dot to the right of the perpendicular line giving the specific gravity, while its distance from the bottom of the figure gives the per cent of salt, according to scales drawn on the horizontal and perpendicular lines respectively.

In the figure the dots representing the experiments are joined by a smooth line, and the specific gravities of solutions other than those experimented with may be determined by inserting dots in the line at points corresponding to their compositions, and measuring the distances of these dots from the side of the figure; if it were sought to determine the specific gravity of a 25% solution from those of solutions containing less salt, by extending the line free-hand to the right, the result would be obtained by "extrapolation"—this method is obviously less reliable than the other. In order to facilitate the process of measurement, the curves are generally drawn on specially ruled paper. The curve (or the table) may also be used to find the composition of a

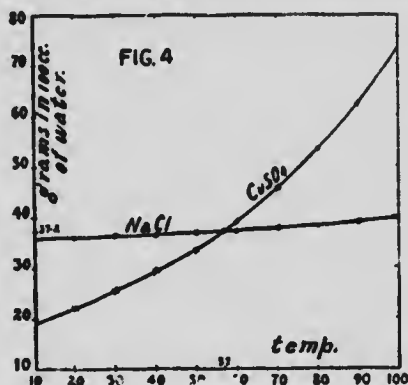


salt solution from its specific gravity; indeed, this is the method usually employed in commerce for ascertaining the concentrations of acids, lyes, and solutions of all kinds.

The sp. gr. curve for common salt is almost a straight line; this is not the case with sulphuric acid. In fig. 3 " $\%H_2SO_4$ " signifies the weight of acid in 100 parts of the solution.

SATURATED, UNSATURATED, AND SUPERSATURATED SOLUTIONS

It will be observed that the table (and the curve) stop at the solution which contains 26.4 grammes of salt to 100 grammes of water; this solution is "saturated," or better "saturated with salt at $15^\circ C$ " which means that it can be stirred with salt at that temperature without changing its composition. The composition of the saturated solution depends on the temperature, and it is a general rule—though not without exceptions—that the higher the temperature the greater the concentration of the saturated solution. This is usually expressed by saying that "salts are more soluble in hot water than in cold." In the case of common salt the difference is slight, with blue vitriol it is very marked. In fig. 4 the position of the dots give the compositions of the saturated



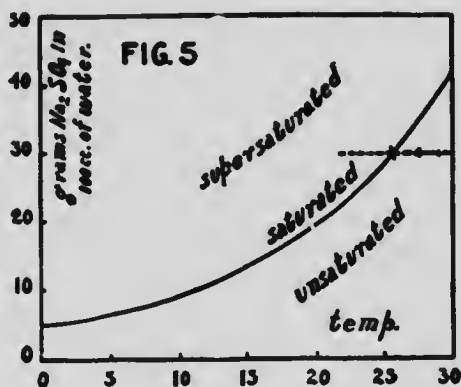
solutions of common salt in water at various temperatures from $0^\circ C$ to $100^\circ C$, while the crosses give the compositions of the solutions saturated with the vitriol. It will be observed that both curves rise to the right, that is, in both cases the concentrations of the saturated solutions are greater at high temperatures than at low, while the steepness of the vitriol curve as compared with the flatness of the solubility curve for salt shews that in the former case the temperature has much more effect on the solubility than in the latter. At $57^\circ C$ where the two curves cross, 100 grammes of water can dissolve 37.2 grammes of either salt, while above that temperature the blue vitriol is the more soluble and below it the less. It is because so much information can be obtained from

a mere glance at the figure, that in many cases the graphical method is preferable to the use of tables.

In certain cases—notably sodium sulphate, sodium acetate, alum, sodium thiosulphate—it is possible to prepare solutions containing much more salt than the saturated solution at the same temperature; these are called "supersaturated solutions," and if one of them is brought into contact with a crystal of the salt which it contains or of a salt isomorphous with it, the crystal grows, and the solution becomes more and more dilute, until it becomes saturated—from the other side, as it were.

Thus, the saturated solution of any solid substance at any given temperature is the solution which may be brought into contact with that solid without change while unsaturated solutions would dissolve the solid, and supersaturated solutions would deposit it.

In the case of the substances named above, all of which are more soluble in hot water than in cold, supersaturated solutions may be made by cooling a concentrated solution prepared at a high temperature; the process is illustrated by fig. 5 in which the dots represent a 30 per-



cent solution of sodium sulphate being cooled from 30°C to 20°C. At 26° it is saturated, when warmer it is unsaturated, and when cooler supersaturated. As a mere speck of the salt (in the case of alum, one hundred-millionth of a milligramme) causes the deposition of crystals, the cooling should be carried out in a flask whose neck is closed with cotton wool; if the solution be boiled for a moment any crystals adhering to the neck will be washed down and dissolved.¹

¹ A supersaturated solution may be prepared from 100g of crystallized sodium sulphate (Glauber's salt) and 60g water, as directed above. Others by "melting" crystallized sodium acetate, sodium thiosulphate, or calcium chloride in a test tube closed with cotton batting. To destroy crystals in the upper part of the tube, let it stand in boiling water.

OTHER LIQUID SOLUTIONS

Plain soda is a solution of a gas in water; the effect of pressure on the solubility may be seen by turning a soda syphon upside down and letting the gas out in portions, shaking each time to restore equilibrium. When poured in a glass the soda water remains supersaturated for some time, a bubble of air in a capillary tube, a lump of sugar, or a piece of unglazed earthenware with air in the pores, causes an evolution of gas. Unlike the salts, most gases are more soluble in cold water than in hot. (Heat the soda water).

Vinegar is a solution of two liquids; whether of acetic acid in water or of water in acetic acid, is merely a matter of words. Below the melting points of the constituents (17° and 0°C respectively) solutions saturated with ice and with solid acetic acid may be obtained. Solutions containing two liquids are often spoken of as "mixtures"; they are obviously not mechanical mixtures however—their formation is attended by change of volume, etc., and also of chemical properties (see page 8, alcohol and water).

SOLID SOLUTIONS

The constituents of glass may be combined to form a clear melt in all proportions within certain limits; the melted glass is thus a compound of variable composition, and so is the homogeneous solid formed on cooling it.

Isomorphous mixtures, are physical compounds, not mechanical mixtures. If a cold saturated solution of alum be mixed with a cold saturated solution of one-tenth its weight of chrome alum¹ and let stand in a flat dish, purplish crystals will be deposited "containing" both alums. Their colour and their composition depend on the relative quantities of alum and chrome alum taken. By grinding a portion with water a saturated solution may be formed, which does not change in composition when shaken with the purple crystal powder; but if poured on a little powdered chrome alum, dissolves it readily, turning much darker. This is proof that there was no chrome alum mechanically mixed in the purple crystals.

Similar experiments can be carried out with the light blue crystals deposited from a hot solution of copper and zinc sulphates, or with the yellow crystals from a boiling solution of ammonium chloride to which ferric chloride has been added (this solution must be filtered before cooling).

¹ Solutions of chrome alum must not be heated.

MIXTURES OF GASES

Air. When a litre of oxygen and one of nitrogen are brought together, it is customary to speak of the resulting two litres of gas as a "mixture"; these gaseous mixtures, however, like the "mixtures of liquids," come under the definition of Physical Compounds. If the "mixture" be shaken with water, the amount of each gas dissolved is less than if the gases had each been shaken separately with the same volume of water; thus by "mixing" the oxygen with another gas its solubility has been reduced, while in the case of mechanical mixtures the solubility and all other properties are unaffected.

CHAPTER III.

MECHANICAL MIXTURES

It is not always easy to decide whether a substance submitted for examination is a mechanical mixture or not. Sometimes however mere inspection will suffice, as in the following cases—most of them “of commercial or industrial importance.”

Solids :—pepper and salt, granite.

Solids and liquids :—mud, slush, dregs.

Solids and gases :—smoke, dust.

Liquids :—milk, emulsions.

Liquids and gases :—fog, foam, lather.

With very fine powders it is sometimes not possible to distinguish the individual particles, even under a microscope. *Gunpowder* is a case in point; it is made from sulphur, nitre, and charcoal—are these substances mixed or combined? If the powder be a mechanical mixture, the properties of all three constituents must be retained unchanged.

First, the volume; 100 grammes of a sample of gunpowder contained

9.72 g Sulphur, of sp. gr. 2.069	occupying 4.70cc
74.49 g Nitre, “ “ 2.105	35.39
15.79 g Charcoal, “ “ 1.450	10.89

100.00 g of the constituents thus occupy 50.98cc

while 100 g of gunpowder (sp. gr. 1.958) occupy 51.07cc, practically the same volume. This result is in accordance with the supposition that gunpowder is a mechanical mixture, but does not prove it to be one, for cases of combination are known which do not involve a change of volume; the formation of cuprous sulphide from copper and sulphur for instance, or of hydrogen chloride from hydrogen and chlorine.

Second, the sublimation of sulphur. If gunpowder be heated carefully, the vapour of sulphur is given off. But as the vapour of water is given off by many crystallized salts when heated, and as carbon dioxide is given off by marble in the lime-kiln, this experiment is no proof that the sulphur is only mixed with the nitre and carbon and not combined with them.

Third, the solubilities. Nitre dissolves in water, and sulphur in carbon bisulphide; if gunpowder be shaken with water a solution of nitre is obtained, while from the residue sulphur may be removed by carbon bisulphide, leaving carbon behind. *These facts, like the specific gravity determinations and the sublimation of sulphur, are no proof that the nitre and sulphur were not combined, as may be seen from the following*

analogous case :—Bismuth oxide, nitric acid and water brought together in the proper proportions, unite to form the chemical compound crystallized bismuth nitrate.¹ If the nitrate however be shaken with water a solution of nitric acid is formed and bismuth oxide remains undissolved. The bismuth salt is said to be "decomposed by water"—why not say the same of the gunpowder ?

A quantitative experiment, however, settles the question. When 100 grammes of gunpowder are shaken with water, the composition of the solution of nitre obtained is the same as if 74.49 grammes of nitre had been shaken with the same amount of water at the same temperature; the solubility of the nitre has not been affected by adding sulphur and carbon. This shews that the nitre in gunpowder has quantitatively the same power of entering into combination (with water) as the same weight of nitre in the pure state; and may be regarded as conclusive proof that the nitre is not combined with the sulphur or carbon. In a mechanical mixture the properties remain unchanged, and in gunpowder the property of the nitre that the Chemist cares most about, viz., the ability to react, is quite unaffected by the presence of the other ingredients. With bismuth nitrate the reverse is true; the nitric acid sticks tight to the bismuth oxide, and it takes a great deal of water to wash it all away; pure nitric acid is miscible with water in all proportions.

A more complicated case. The same method may be employed in the case of a mixture of common salt and sal-ammoniac; the amount of sal-ammoniac dissolved when an excess of the mixture is shaken with 100 grammes of water is the same as when pure sal-ammoniac is shaken with a solution containing 100 grammes of water and as much salt as is found in the solution prepared from the mixture. This addition of salt must not be overlooked, because sal-ammoniac is less soluble in brine than in pure water; moreover, as the solubility depends on the temperature, this factor must be kept the same in the experiments to be compared.

¹ $\text{Bi}_2\text{O}_3 + 6 \text{HNO}_3 + 2 \text{H}_2\text{O} = 2 \text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

CHAPTER IV.

ANALYSIS AND SYNTHESIS. THE CHEMICAL ELEMENTS

In the last two examples it has been assumed that the constituents were known; the point to be decided was whether they were mixed or combined. To discover what the constituents are is in itself often a difficult matter; the means employed may be grouped into four classes

(i) *Direct Synthesis*. Gunpowder, for instance, may be "synthesized" or "put together" from carbon, nitre, and sulphur; brine from water and salt; and limestone from quicklime and carbon dioxide. It is clear that a synthesis, if carried out quantitatively, tells not only what the constituents are, but also the proportions in which they are contained in the substance synthesized; the compositions of a number of the commoner chemical compounds have been determined in this manner, for example :—water, hydrogen chloride, carbon dioxide, cupric oxide and silver chloride.

(ii) *Direct Analysis*. When limestone is heated so as to drive off carbon dioxide and leave quicklime, it is said to be "broken up" or "analysed"; the experiment when carried out quantitatively shews that 100 parts of limestone contain 56 parts of quicklime and 44 parts of the dioxide. Examples of other common substances whose composition has been ascertained in the same way are :—ammonia, baking soda, blue vitriol, and mercuric oxide.

Instead of heating the substance it may be cooled—brine for instance will deposit ice or salt, depending on its composition, and thus one at least of the constituents may be determined.

In some cases direct analysis may be effected by means of the electric current; water, and many metallic salts—fused lead chloride, for instance—may be analysed in this way.

In a few instances it is sufficient to change the pressure in order to bring about decomposition; lowering the pressure over soda water, for instance, or bringing brine into a vacuum.

These "direct" methods of synthesis and analysis, though simple theoretically, are applicable in comparatively few cases; and the ordinary processes of chemical analysis come almost without exception under the heads of

(iii) and (iv) *Indirect Analysis and Synthesis*. These methods are separated from the first two because they involve the use of chemicals other than the substance under investigation. In order to draw any safe conclusion from the behaviour of the unknown substance with

these "reagents" however, it is necessary that the reaction should be studied quantitatively. For example, the fact that when sodium acts on water hydrogen is evolved, is sometimes quoted as evidence that water contains hydrogen; it is obvious that with equal propriety the conclusion might be drawn that *sodium* contains hydrogen, while there is nothing in the experiment that conflicts with the view that hydrogen is a compound, some of whose constituents are contained in the sodium and the others in the water.

To say that sodium is an element, and that the hydrogen must therefore have come from the water, is to beg the question; there is no sign by which an element may be recognized as such; sodium is an element only so long as it has not been analyzed or synthesized, and without further information it is allowable to suppose that the reaction with water furnishes the long-sought-for analysis. As a matter of history, metals were long thought to contain hydrogen, and their striking family resemblances were ascribed to the influence of this common constituent.

If the reaction be studied quantitatively, however, the interpretation is plain. Ten grammes of sodium with 100 g water give 0.43 g hydrogen and 109.57 g of a lye that can be prepared from, and consequently "contains," 13.48 g of sodium oxide and 96.09 g of water. Sodium oxide has been prepared by direct synthesis; 13.48 g of it contain 10 g of sodium and 3.48 g of oxygen. Thus all the sodium and 96.09 g of the water are contained in the lye, together with 3.48 g of oxygen, which with the 0.43 g of hydrogen appears in place of the remaining 3.91 g of water. The quantitative experiment thus shews not only that water contains hydrogen but also that it contains oxygen, and gives the proportions in which they are united. It will be observed that in the argument neither the sodium nor the hydrogen is assumed to be an element; but no logical conclusion could be arrived at without full information as to the ultimate whereabouts of the reagent—in this case sodium—or its components.

ELEMENTS

There are a few substances which, in spite of many attempts, have neither been synthesized nor analyzed; they are placed in a class by themselves, and are known as the "Chemical Elements." The number of substances in this group changes from time to time; one hundred and twenty years ago, for instance, water was very properly regarded as an element; and more recently a compound of vanadium and oxygen was thought to be undecomposable. On the other hand, bromine was at first taken for a compound of chlorine with iodine, and chlorine itself was long regarded as an oxide. There is no sure sign by which an ele-

ment may be recognized; and even now there is much uncertainty as to the nature of some of the generally accepted elements, in particular some of those derived from the rare earths; it is quite likely that further investigation may remove several of them from the list.

Many of the elements exist in more than one "form" or "allotropic modification." Yellow phosphorus, for instance, on standing in the sunlight turns red, and loses much of its inflammability; as this change occurs without addition of any foreign substance, as the red phosphorus can be reconverted into yellow by heating, and as both give the same products when acted on by oxygen, chlorine, etc., these two very different substances are often spoken of as "the same thing." Even from a strictly chemical point of view, however, this curious misuse of the English language is indefensible; the products of oxidation are the same, but the conditions under which they arise are very different; and now that more attention is being paid to the conditions under which reactions occur, it is better to let the old phrase drop.

CHAPTER V.

CHEMICAL COMPOUNDS. LAWS OF CHEMICAL COMBINATION

1. *Law of combination in definite proportions.*

Chemical compounds and elements combine in definite proportions to form new chemical compounds.—

Proust, 1799.

They combine in "indefinite" proportions also; the product being then called a "Physical Compound" or solution; the "law" of combination in definite proportions is thus only the definition of the group of "Chemical Compounds." The word "definite" as used above has a special meaning; by act of parliament, proof spirit has the definite composition 97.23 grammes of alcohol to 100 grammes of water, it is none the less but one of an infinite series of solutions containing alcohol and water; and although the composition of Dover's powder is fixed by the British Pharmacopœa, that does not prevent its being a "mechanical mixture." Many cases are known of substances which combine in two or more proportions, mercury and oxygen for instance; in the absence of a continuous series of other compounds approaching them closely in composition they must be regarded as chemical compounds.

The question whether chemical compounds as defined above actually exist or not, was the subject of a long discussion in the beginning of the nineteenth century; the French Chemist Proust, who took the affirmative, being in the end successful. The same question was subsequently taken up by Stas (1867) who devoted to it some of the most careful experimental work ever carried out by a Chemist; he shewed for instance, that silver chloride prepared by three different methods and under the most diverse conditions does not differ in composition by as much as one part in ten thousand. It is, no doubt, this constancy of composition, which early attracted attention, that caused these substances to be regarded as peculiarly "pure," and earned them the title of "chemical" compounds *par excellence*.

2. *Law of combination in reciprocal proportions.*

The ratios between the weights of A, B, C, etc., which unite with a given weight of W are equal to or some simple multiple of the ratios in which they unite with fixed weights of X, Y, Z, etc. (A, B, C, W, X, Y, Z, and the products of their union must all be either chemical compounds or elements).....Richter, 1791.

When hydrogen chloride and red oxide of mercury are brought together under proper conditions, in quantities such that the hydrogen of the acid and the oxygen of the oxide are present in the proportions in which they unite to form water, a reaction takes place, the oxide and acid disappear, while water and corrosive sublimate are formed *and nothing else*.

From the composition of three of these substances, therefore, that of the fourth can be calculated. For example —100 grammes of the red oxide contain 92.59 g of mercury and 7.41 g of oxygen, which latter needs 0.933 g of hydrogen to form water. This weight of hydrogen is combined with 32.82 g chlorine in 33.75 g of hydrogen chloride. As *nothing but water and corrosive sublimate* are formed by the reaction, 125.41 g of the latter substance must be produced, containing 92.59 g of mercury, and 32.82 g of chlorine.

The occurrence of reactions of the type known as "double decomposition" or "metathesis" thus establishes the existence of relationships between the compositions of the chemical compounds, which have been made use of since 1791 to supplement the ordinary methods of analysis. Richter, who was the first to call attention to this matter, spoke of it as the "touchstone of analysis."

The fact that the weights of oxygen and chlorine which unite with a certain given weight of mercury will also unite with another fixed weight of hydrogen, may be familiarized by the use of cards, on which names and numbers are written as follows :—

mercury 92.59	oxygen 7.41	hydrogen 0.933	chlorine 32.82
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Four cards are sufficient, by interchanging them the symbols of the products of the reaction can be formed from those of the original substances.

3. Law of combination in multiple proportions.

If two bodies, A and B, form several chemical compounds with each other, the different weights of B which combine with a fixed weight of A bear a simple ratio to each other. . . . Dalton, 1803.

It has already been pointed out that two substances may unite in more than one proportion to form several chemical compounds. Oxygen and mercury, for instance, form a black oxide containing 96.15 percent of mercury as well as the red one containing 92.59 percent.

Expressed in this manner, no simple relation between the compositions of these two substances is apparent; if however quantities

containing the same weight of oxygen be compared, it will be seen that the latter contains twice as much mercury as the former.

	Red Oxide	Black Oxide	
Oxygen	7.41	3.85	7.41
Mercury	92.59	96.15	185.18
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100.00	100.00	192.59

The composition of the black oxide can therefore be expressed by the tickets used on page 21 to represent that of the red oxide

mercury 92.59	mercury 92.59	oxygen 7.41
------------------	------------------	----------------

using two mercury tickets instead of one.

These multiple proportions are met with not only when the substances combining are elements, but also when they are chemical compounds—indeed if it were otherwise we should have an infallible means of recognizing the elements as such, which is far from being the case—for example :—

	Washing Soda	Baking Soda	
Sodium oxide	21.69	36.94	21.69
Carbon dioxide	15.37	52.35	30.74
Water	62.94	10.71	6.29
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100.00	100.00	58.72

By "simple ratio" Dalton understood 1 : 1, 1 : 2, 1 : 3, 2 : 3; even 3 : 4 was at first hardly regarded as "simple". Later work with the compounds of carbon and hydrogen, however, has brought to light such ratios as 360 : 361, so that the law of multiple proportions in its original form is not of general applicability. It holds very well for the compounds usually dealt with in first lessons on Chemistry.

4. Law of combination of gases by volume.

There is a simple relation between the volumes¹ of the gases which disappear or are formed in any reaction involving only chemical compounds and elements.—

Gay-Lussac, 1809.

For instance, two volumes of steam are formed by the combination of two volumes of hydrogen and one of oxygen; two volumes of carbon monoxide combine with one of oxygen to give two of carbon dioxide; one volume of steam on reacting with hot iron, gives an oxide of iron and one volume of hydrogen.

Later experiments have shewn that the ratios cannot be represented exactly by small numbers, and that they depend on the temper.

¹ As the volume of a gas depends on its temperature and pressure, all comparisons must be made under the same conditions.

ature and pressure; for instance, at room temperature and atmospheric pressure one vol. oxygen unites with 2.0003 vols. carbon monoxide to form 1.9879 vols. carbon dioxide; while at 10 atmospheres pressure, one vol. oxygen gives 1.8289 vols. carbon dioxide. This change is observed not because the proportions by weight in which the gases react are affected by the pressure, but because on increasing the pressure the volume of the dioxide is decreased more than is that of the oxygen. Guy-Lussac's law unlike the "law" of combination in definite proportions, is thus not *exact*, but only approximately true; the lower the pressure the better it holds.

THEORIES AND EXPLANATIONS

When striking and unfamiliar facts force themselves on the attention, there is a natural desire to "explain" them in some way or other; an explanation of the laws of combination in reciprocal and multiple proportions is offered by the Atomic and Molecular theories. These theories assume that all substances are composed of small indivisible particles, the atoms, which unite by twos or threes or larger groups—molecules, *i.e.*, "little heaps"—to constitute the "ultimate particles" of various chemical compounds. As no microscope has shewn any trace of these atoms or molecules, it is necessary to assume that they are very small indeed.

The molecules thus take the place of the groups of tickets of pages 21 and 22, while the atoms correspond to the individual cards. It is further assumed that each atom has a definite weight, just as each ticket represents a definite number of grammes, so that the analogy between the atoms and the tickets is complete.

The view of the Atomic Theory which is now gaining ground is, that the world of atoms stands in the same relation to the facts of chemistry that Lilliput and Brobdingnag did to the England of Swift's time, or that the diagram of page 11 does to the solubility experiments;—in fact, that the atoms are exactly on a par with the tickets. But for nearly a century atoms and molecules have been taken very seriously indeed; so difficult is it to follow the

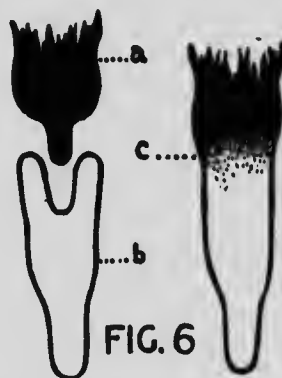
Golden Rule for discovering scientific truth

Give unqualified assent to no propositions but those the truth of which is so clear and distinct that they cannot be doubted René Descartes, 1637.

In this connection it is proper to ask why an explanation of the laws of chemical combination seems necessary, and why this particular hypothesis has proved so satisfactory.

When a stone falls to the ground, no one wonders; and to the present day no "explanation" of that very common occurrence has been forthcoming. Everyone knows that stones are heavy—and so they "naturally" fall when they get a chance. To say that the motion is due to the attraction of gravity is to play with words, like the physician who ascribed the anæsthetic action of chloroform to its "soporific qualities". The laws of chemical combination however are unexpected, unfamiliar, wonderful—that is why they "need" an explanation.

The wonder, of course, and the need, are in the Chemist, not in the chemicals; and the nature of the explanation that will satisfy him depends upon his experience and education. In Lemery's "Cours de Chimie," a book which passed through thirteen editions between 1707 and 1715, was translated into all the chief languages of Europe, and was universally regarded as the best text-book of its day, the Author ascribes the properties of acids to their "smallest particles" being finely pointed, "one can detect the sharpness by the tongue,"—while alkalis he explained, were porous, like unglazed pottery. When acids and alkalis are brought together, the fine points of the former enter the pores of the latter, and break off there, so that the resulting body has neither points nor pores, and the formation of neutral salts by the action of acids on alkalis is explained! This explanation, now-a-days, may seem a trifle naïve; but the celebrated Physiologist, Prof. Ehrlich, in



a and b, components : c, compound.

representing the "ultimate particles" of the constituents of blood serum, makes use of diagrams which resemble nothing so much as the micro-organisms and animal cells with which his training as a Biologist has made him familiar!

The general acceptance of the hypothesis of atoms must be ascribed to the powerful impression produced on men's minds by the astronomical

discoveries of the seventeenth century. Leibnitz pictured the universe as formed of a finite number of particles each with its own velocity and direction; Laplace imagined a world-formula enabling all events past and future to be calculated from the motions of the atoms by the laws of mechanics; and Dalton's "discovery of the means of weighing the atoms" seemed but a prelude to the advent of that younger Newton who would reduce all science to "the mechanics of the atoms."

But the "younger Newton" has been long in coming; and the waiting world has had time to reflect on his great predecessor's motto *hypotheses non fingo*, and to realize that from the days of Galileo none of the founders of mechanics and astronomy made their reputations by inventing "explanations" of the motions of the planets or the fall of apples, but by observing facts, describing them accurately and simply in mathematical language, and collecting the results of their work in the form of a few unexplained generalizations, or "laws". As moreover, the atomic hypothesis (unlike the otherwise analogous hypothesis of a luminiferous ether) has not been as fruitful as was expected in opening up new fields for research, while in certain branches of chemistry it has proved a hindrance rather than a help, it is not surprising that much of the early enthusiasm for it has cooled, and that the present tendency is to keep the facts of the science sharply distinguished from the hypothetical explanation, with great resultant gain in clearness of thought and expression.

Who now-a-days would define an element as "a substance whose molecules consist of like atoms," and who cannot see that to explain the action of hydrogen on chlorine as due to "the attraction of the hydrogen atom for the atom of chlorine" is but to put oneself on a level with the Physician of soporific memory? Not so long ago, such definitions and explanations were to be found in every text-book, and did much to confuse the beginners whom they purported to instruct.

CHAPTER VI.

CHEMICAL FORMULÆ. THE INTERNATIONAL ATOMIC WEIGHTS.

1. Because of the law of combination in reciprocal proportions, the composition of chemical compounds can be represented by cards.

On page 21 the reaction between red oxide of mercury and hydrochloric acid was represented by tickets¹ as follows :—

Merc	Ox	and	Hy	Chl	give	Merc	Chl	and	Hy	Ox
92.59	7.41		0.933	32.82		92.59	32.82		0.933	7.41

The reaction between red oxide of mercury and sulphuretted hydrogen can be similarly represented if one more card be added to the pack.² As before, 100 g of the oxide react with just as much sulphuretted hydrogen as is necessary to form water, in addition to which there is formed mercuric sulphide, and nothing more; the 14.85 g of sulphur that was formerly combined with the 0.933 g of hydrogen is now "contained" in the mercuric sulphide. "Sulphur 14.85" is evidently the inscription for the new ticket.

As corrosive sublimate and sulphuretted hydrogen give mercuric sulphide, hydrochloric acid, and nothing else, the reaction between them can evidently be represented by the same cards; and so can the reaction between chlorine and sulphuretted hydrogen, giving hydrochloric acid and sulphur.

2. For this purpose the actual numbers on the cards are immaterial, only their ratios are of importance.

The numbers on the cards were chosen because of the chance use of 100 g of red oxide of mercury in the first experiment. If fifty grammes had been taken, all the numbers would have been divided by two; and it is thus obvious that only the ratios between the numbers, not their actual values, are of importance. The number on the hydrogen card is less than any other of the four; if it be replaced by 1, and the others be reduced in like proportion (by dividing by 0.933) the numbers so obtained are called the "equivalent weights" or "equivalents" of mercury, oxygen, etc. A set of five "equivalent" cards³ should be prepared, preferably of a different colour to those first used.

¹ For economy in printing, the outlines of the cards are omitted and the names abbreviated.

² First pack.

³ Second pack.

3. The existence of compounds in multiple proportions raises the question, "Which multiple shall be written on the card?"

On page 22 it was pointed out that the composition of the black oxide of mercury can be represented by using two mercury cards and one oxygen card, three in all, while two suffice for the red oxide. A little consideration shews that if 3.97 be written on the oxygen card¹ instead of 7.94, the red oxide will be represented by three cards and the black by two; the same result would be reached if 99.24 on the mercury card were replaced by 198.48, leaving the oxygen with 7.94.

Which shall be adopted—7.94 or 3.97, 99.24 or 198.48?

4. This has been answered by making the cards express more than the composition of the chemical compounds.

Of the four substances involved in the reaction

Merc	Ox	and	Hy	Chl	giving	Merc	Chl	and	Hy	Ox
99.24	7.94		1	35.18		99.24	35.18		1	7.94

three are gases at high temperatures; at 500°C and one atmosphere pressure, for instance, the 8.94 g steam occupy 31.5 litres, the 36.18 g hydrogen chloride occupy 62.9 litres, and the 134.42 g corrosive sublimate occupy 30 litres. The volume of hydrogen chloride represented by the second group of tickets is thus about twice that of the sublimate represented by the third group, or that of the steam represented by the last.

If the 36.18 g of hydrogen chloride could be represented by two groups, leaving the others as before, the volumes of each of the three gases represented by a group of tickets would obviously be the same. This result might be accomplished, for instance, by writing $\frac{1}{2}$ instead of 1 on the hydrogen ticket, and 17.59 instead of 35.18 on the chlorine card, thus

Merc	Ox	Hy	Chl	Hy	Chl	give	Merc	Chl	Chl	Hy	Hy	Ox
99.24	7.94	0.5	17.59	0.5	17.59		99.24	17.59	17.59	0.5	0.5	7.94

Or if it be decided to stick to 1 on the hydrogen card²

Merc	Ox	Hy	Chl	Hy	Chl	give	Merc	Chl	Chl	Hy	Hy	Ox
198.48	15.88	1	35.18	1	35.18		198.48	35.18	35.18	1	1	15.88

In all three methods of representation, the proportions between the weights of the chemicals are the same; but in the second and third each group of tickets stands for the same volume of gas, and in every case the number of tickets has been kept as small as possible.

¹ Third pack.

² Fourth pack.

Advantage has thus been taken of the power to double, halve, etc., the numbers on the various tickets in order to make the resultant symbols or "formulae" represent *more* than the relative weights of the substances reacting. In the examples just given, the relative volumes of the gases involved in the reaction are indicated; and attempts have been made to include information as to the specific heat, crystalline form, etc., as well.

This additional comprehensiveness is often gained by a corresponding sacrifice of simplicity, as when the symbol $\begin{matrix} \text{Hy} & \text{Ox} \\ 1 & 7.94 \end{matrix}$ for water is replaced by $\begin{matrix} \text{Hy} & \text{Hy} & \text{Ox} \\ 1 & 1 & 15.88 \end{matrix}$. It is even necessary, if the latter formula be adopted, to represent hydrogen and oxygen gases by two tickets each, because 2×1 g of hydrogen or 2×15.88 g of oxygen occupy the same volume as 17.88 g of steam.

5. Standard cards.¹ The "International Atomic Weights."

More than eighty years elapsed since the discovery of the law of combination in multiple proportions, before a standard set of numbers was generally agreed upon—as late as 1890 the formula HO for water (corresponding to our $\begin{matrix} \text{Hy} & \text{Ox} \\ 1 & 7.94 \end{matrix}$) was in common use in France, while in England and Germany it was given up for H₂O in 1860-70. Unanimity has been secured at length, however, and the numbers finally adopted are known as "The International Atomic Weights"²; they are revised annually by a small Committee representing the principal Chemical Societies of the world.

After much discussion the Committee selected oxygen as the element with which the others are to be compared, set its "international weight" arbitrarily 16.000, and adopted the volume of 32 g of oxygen gas as the "standard volume" to be represented by the formulas of all gaseous chemical compounds.

The "oxygen equivalent" of each element, that is, the weight that will combine with 16.000 g of oxygen, or with the oxygen equivalent of some other element (determined in its turn against oxygen), was ascertained as accurately as possible by a critical examination of the published analyses. Many elements, mercury for instance, have

¹ Fifth pack.

² As the formulae represent facts, and are therefore quite independent of any hypothetical "explanations" that may be adopted from time to time, it is well to avoid as far as possible the language of a special theory. From this point of view it is better to use "International Weight" rather than "Atomic Weight" as an abbreviation of the official name "International Atomic Weight"; the term suggested has the further advantage of being unambiguous—there are several sets of "atomic weights" in use, but only one "international."

more than one oxygen equivalent, but these are connected by the law of multiple proportions.

The weights of the "standard volume" of as many gaseous compounds as possible of each element were collected; and that multiple or "simple" fraction— $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, $\frac{4}{5}$ —of the oxygen equivalent was chosen as "international weight" which came nearest the G.C.M. of the weights of the element in the standard volumes of its gaseous compounds. For instance, the oxygen equivalents of mercury are 200.0 and 400.0, the standard volume of mercuric chloride (a gas at high temperatures) contains 210 g mercury, and that of mercuric bromide 196 g mercury, 200.0 was chosen as international weight; the oxygen equivalents of bismuth are 83.4 and 139.0, the standard volume of the vapour of bismuth chloride contains 217 g bismuth, 208.5 was adopted as the international weight.

This method of selection has made it possible to write formulæ for these gaseous compounds which besides giving their compositions accurately, furnish a close approximation to the weights of the standard volume.

In the case of elements whose gaseous compounds—where they have any—had not been studied from this point of view, it was necessary to adopt other principles of selection. Nearly half of the known elements fall into this class, which includes seven of those prescribed for study in the Ontario High Schools, viz.: sodium, potassium, magnesium, calcium, strontium, barium, and manganese. The specific heats of five of these were known, and that "simple fraction" of the oxygen equivalent was chosen as international weight which, when multiplied by the specific heat gave a number between 6 and 7 as product.¹ The oxygen equivalent of sodium, for instance, is 11.525, its specific heat 0.293, and 23.05 was chosen as international weight.

For the other two, barium and strontium, the weight was selected so that the formulæ of their compounds might resemble those of calcium:—CaO, SrO, BaO; CaCl₂, SrCl₂, BaCl₂. Chemical similarity was thus paralleled by similarity in formulæ.

The case of copper perhaps deserves a word to itself. The only compound of that element that has been gasified and measured is cuprous chloride, its standard volume contains 131 g of copper. The oxygen equivalents are 63.6 and 127.2. Instead of taking 127.2 as international weight, however, 63.6 has been selected, partly because of the specific heat (0.094), and partly in order that the formulæ of the copper compounds might resemble those of the compounds of zinc, etc., with which they are isomorphous.

¹ The product sp. ht. \times int. wt. for 41 of the solid elements lies between 6 and 7, for 9 between 5 and 6, and for 1 below 5.

The weights and formulæ thus arrived at constitute a "natural" system, in the sense in which one speaks of natural systems in Zoology or Botany, as distinguished from an artificial system like the Linnean. Formulæ primarily invented to record compositions, specific heat determinations, or experiments with gases, shew analogies in many other respects; the Periodic Law is a striking illustration of relationships which were totally unsuspected by the original founders of the system. Up to the present, however, no explanation of these regularities has been advanced; and the place which the theory of evolution holds in Biology, is, in Chemistry, still unfilled.

6. Chemical Symbols.

The Committee further adopted¹ a letter or letters as the symbol for each element, which take the place of both name and number (international weight) on the "standard tickets". O, for instance, stands for 16.000 g of oxygen, H₂ for 2 × 1.008 g of hydrogen, 2H₂O for 36.032 g of water, that is for two groups of three cards each.

By adding up the weights corresponding to the various symbols in the chemical formula, the "formula weight," "gramme molecular weight," or weight of one "mole" of the compound is obtained. In the case of gases or vapours this weight occupies (approximately, see page 23) the same volume as 32 g of oxygen at the same temperature and pressure—at 0°C and 760mm for instance, 22.4 litres.

7. Why was O=16.000 made the basis of the International Atomic Weights?

Two points only remain to be cleared up. Why was 16.000 taken for the International Weight of oxygen? and why is the volume of 32.000 g of the same gas adopted as the standard volume in writing chemical formulæ?

The decisions of the Committee were based on eminently practical grounds. Most of the equivalent weights have been determined, directly or indirectly, by comparison with oxygen, and in many cases the quantity of an element that combines with one gramme of oxygen can be determined with greater accuracy than the weight of oxygen that combines with one gramme of hydrogen; so that, if hydrogen were taken as the standard, the combining weights of these latter would be affected not only by the error or uncertainty in the analysis of the oxide, but also by the greater error in the determination of the ratio H/O. Oxygen, therefore, has been selected as the standard of comparison; but instead of assigning it the weight 1, or 100, (as was commonly done between 1820 and 1850) the number 16.000 was chosen in order to make

¹ Adopted, not originated; the Committee was formed to secure uniformity, and introduced as little change in the prevalent customs as possible.

the International table differ as little as possible from those in general use at the time of its first publication (in 1900).

With regard to the volume. One litre of carbon monoxide contains very nearly the same amount of oxygen as a litre of steam measured at the same temperature and pressure; a litre of oxygen gas or carbon dioxide twice as much; a litre of the vapour of glycerine three times, and a litre of nickel carbonyl four times as much; in fact, so far as is known, all the gaseous compounds of oxygen contain either the same amount of oxygen per litre as steam does, or some whole multiple of that amount. There is therefore no necessity to write the formula for steam with more than one O, that of oxygen gas would then have two, glycerine three, etc. But O_2 stands for 32.000 g of oxygen; and therefore the volume of 32 g of oxygen is the volume which the formula of any chemical compound in the gaseous state must be constructed to represent.

To some of those who are accustomed to teach chemistry "by atoms" the question may suggest itself—"What is gained by all this talk about laws of combination, tickets, formula weights, international weights, and the rest of it, if nothing but the ordinary chemical formulæ are to be used after all? Would it not be much easier to stick to the familiar atoms and molecules?"

The gain is primarily to the pupil, and loss of ease primarily to the teacher. If a boy asks "Why is H_2O written for water?" the Teacher-by-Atoms may reply, "Because its molecule contains one atom of oxygen and two of hydrogen"; but the Teacher-By-Tickets has no such refuge—he must tell the whole truth or be found out. If, parodying his colleague's answer, he replies "Because the group of tickets representing water is made up of one oxygen and two hydrogen tickets" he will promptly be met with the further question "Why is that?" To the corresponding question the Teacher-By-Atoms might retort, "That has been found out by very delicate measurements, which are quite beyond your comprehension at this stage"; but as the Teacher-By-Tickets has introduced his symbols with the avowed object of assisting the class to comprehend the laws of combination, he cannot dodge the issue, but must go into the whole matter again and again, until both he and his pupils are thoroughly familiar with the meaning of the chemical formulæ, and of the laws on which their use is based.

Nothing less should satisfy him.

In teaching this subject I have found it a good plan to weigh out and have on the table about 100 g of the red oxide of mercury, 125 g corrosive sublimate, 8 g water, and a 5-gallon bottle or box to represent the 33.75 g of hydrochloric acid gas. Beside the red oxide may be placed the two tickets "Mercury 92.59" and "Oxygen 7.41" of page 21, and the meaning of the statement "100 g of the red oxide contain 92.59 g mercury and 7.41 g oxygen" explained at length. Similarly with the hydrochloric acid. The reason why 33.75 g acid were taken is then explained, the hydrogen and oxygen tickets moved over to the sample of water, and great emphasis laid on the fact that the mercury and chlorine left over are present in exactly the proportions in which they unite to form corrosive sublimate. The pupils should be asked how it might be shown that the sublimate is a chemical compound; for if it were a solution, or a mechanical mixture, the law of combination in reciprocal proportions would not amount to much. It is better when possible to use names like "red oxide," "sublimate," "water," instead of the modern chemical terms, which were made up after the law of reciprocal proportions was discovered, and might sometimes almost seem to beg the question.

Each pupil should make his own cards, five packs in all. If at the close of the instruction (which, of course, cannot possibly be crammed into one lesson) he can explain intelligently the reasons for the different numbers on the corresponding cards of the different packs, it is safe to assume that he understands the laws of combination and the use of formulae.

Only one reaction has been discussed in the text, but a number of others should be used in teaching.

CHAPTER VII.

CHEMICAL AND PHYSICAL REACTIONS. CHEMICAL EQUILIBRIUM.

The distinction between chemical and physical reactions originated in the very obvious contrast between the quantitative and almost instantaneous reactions of the analytical laboratory on the one hand, and the slow, incomplete and reversible phenomena of melting, boiling and solution on the other. A few connecting links between the two classes presented themselves, then others were sought out and studied, until finally general laws have been discovered and methods of calculation introduced which treat the physical reactions as but simple instances of the chemical.

The history of the present case can be paralleled by examples from every "natural" system of classification; for distinctions of this kind, based on striking differences between extreme cases taken as types, seem to be a necessary feature in the development of every inductive science. From every science moreover illustrations can be drawn of the difficulty with which such conceptions, once introduced, are given up; more particularly when hypothetical explanations of them have been put forward, which are apt to cloud the judgment with the fogs of belief. The present views of the nature of combustion for instance, were generally adopted only after a protracted struggle with the belief in Phlogiston; Linnæus' explanation of the existence of species "*Species tot sunt diversæ, quot diversæ formæ ab initio sunt creatæ*" hindered the progress of science for a hundred years; and the persistent endeavour to keep the physical reactions separate from the chemical has been much helped by, if it is not altogether due to, arguments drawn from the hypothesis of the atoms.

As the Atomic and Molecular theories were invented to explain the laws of chemical combination, it was necessary to assume that the atoms combine in definite and multiple proportions; and as the constituents of solutions do not combine according to these laws, it must further be assumed that solutions are not formed "by the union of atoms," and they have been regarded in consequence as mere "mixtures of molecules" not held together by "chemism"¹ at all. Hence exaggeration of the differences between chemical and physical compounds (page 7).

¹ As this word is associated with a false view of nature it ought to be dropped.

A natural corollary of this view is that the phenomena attending the formation of solutions must be different in kind to those accompanying the exertion of "chemism" in the formation of a chemical compound; and the evolution of heat in the latter case has come to be regarded as a necessary consequence of the collision of the atoms, and indeed finally as a direct measure of the force exerted by "chemism" in the reaction. Thus originated

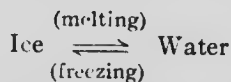
The false law of Maximum Work.

"Every chemical reaction which occurs without the assistance of foreign energy gives off heat."

"Physical" reactions are obviously exempt from the application of this law—when water freezes heat is given out, and when ice melts it is absorbed; and it was the discovery that numerous "genuine chemical" reactions are reversible, in the sense that the reaction between water and ice is reversible, absorbing heat when taking place in one direction and giving it off in the other, that led to the repeal of the false law, and to the final abandonment of the distinction between the two classes of reactions.

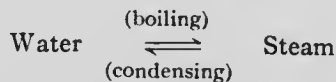
EQUILIBRIUM.

When ice and water are brought together below 0°C , the water freezes; if the temperature be raised above 0° the ice melts; at 0° neither change takes place. The two reactions may be represented by the symbol



and are said to be "in equilibrium" at 0°C . They are often spoken of as one reaction which may take place "in two directions," viz., from the right to the left of the symbol, or *vice versa*.

The reactions



are in equilibrium at 100°C and one atmosphere pressure; if the pressure be changed the temperature at which water and steam can remain in contact changes also (see the tables of the vapour tensions of water, or of the boiling-points of water at different pressures). In this respect the present case seems to differ from the equilibrium between water and ice; the difference is only one of degree, however, for careful experiments have shewn that the freezing-point of water is lowered 0.0076°C for every additional atmosphere of pressure.

Le Chatelier's Law.

The direction of the reaction which takes place in this and other cases when equilibrium is disturbed, is given in the following Law :

In a system at equilibrium, raising the temperature causes the reaction to take place in the direction that absorbs heat, raising the pressure causes the reaction to take place in the direction that decreases the volume, and increasing the concentration of one of the reagents causes the reaction to take place in the direction that reduces the concentration of that reagent; while the opposite changes produce the opposite effects.

The meaning of the law is best made clear by an example. Imagine a closed vessel containing steam and water at 100° and one atmosphere pressure, and suppose that increase of pressure instead of causing the formation of water caused that of steam—the result of this reaction would be further increase of pressure followed by formation of more steam, and so on, ending in an explosion; all brought about by the first small, perhaps accidental, increase in the temperature; so that Le Chatelier's law may be regarded as a *definition* of equilibrium, distinguishing it on the one hand from explosive reactions, and on the other from what are often called, for the want of a better name "false equilibria".

An example of the latter is afforded by the reaction between hydrogen and oxygen. At ordinary temperatures these gases may be brought together with water without the occurrence of either of the reactions



there is however no "equilibrium," small changes of temperature or pressure not "causing the reaction to take place".

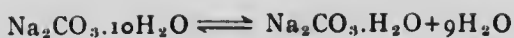
An account of the methods employed in studying and classifying the chemical equilibria may be found in works on the "Phase Rule"; in the present chapter a few examples are given to illustrate some of the chief types.

(i) Reactions analogous to that between ice and water.

Reaction between allotropic forms of the same element. Above 95.5°C rhombic sulphur turns into monoclinic, below that temperature the reverse takes place, at 95.5°C there is equilibrium (See Roscoe and Schorlemmer's Treatise on Chemistry).

"Melting" of washing soda, crystallized sodium sulphate, etc. If a crystal of washing soda be heated to 34°C it "melts" forming a solution mixed with a powder of the monohydrate. The reaction, which is not very accurately¹ represented by the equation

¹ A solution is formed, and not water (H_2O) as stated in the equation; inaccuracies of this nature, however, are usually considered allowable in chemical equations. The same equation can be used to represent the efflorescence of the washing soda (see page 36).

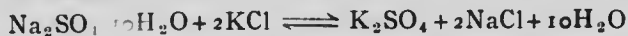


is in equilibrium at 34° .

Reaction between two double salts. If a few grammes of crystallized cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, be ground with about its own volume of potassium chloride, and the mixture heated in a test tube by immersing in boiling water, the brown cupric potassium chloride $\text{CuCl}_2 \cdot \text{KCl}$ is formed, and on cooling again disappears. The equilibrium temperature of the reaction

$\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ (blue) $\rightleftharpoons \text{KCl} + 2\text{H}_2\text{O} + \text{CuCl}_2 \cdot \text{KCl}$ (brown) is 92°C . To ensure the reverse reaction, it is well to stir the mixture on cooling, so that the three substances on the right may be brought into contact.

A case of double decomposition. If potassium chloride and crystallized sodium sulphate be ground together in a mortar, the mass becomes moist, and crystals of potassium sulphate and sodium chloride are deposited. The reaction, which may be represented by the equation



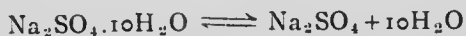
is in equilibrium at 3.5 degrees C ; if cooled below that temperature the original substances are formed again and the mass solidifies.

(ii) Reactions analogous to that between water and steam.

These examples differ from the preceding only because a gas takes part in the reaction, which is consequently accompanied by a great change of volume. In both cases the reactions are in equilibrium at one temperature only for each pressure; but change of pressure has much more effect on the temperature of equilibrium here than in the others. *Sublimation.* If a little iodine be placed between a pair of watch-glasses, and the under glass be heated, the iodine gives off vapour which condenses on the upper (cool) glass. Sublimation of solids is thus analogous to distillation of liquids.

Solid iodine \rightleftharpoons Iodine vapour

Efflorescence. When crystals of washing soda, hydrated sodium sulphate, etc., are left in an open vessel in a dry room, they fall to a powder of the anhydrous salt; and if this powder be placed under a bell-jar with a dish of water beside it, it cakes together and the hydrate is formed again.



Decomposition of carbonates by heating. $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$

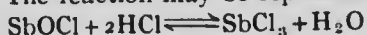
In a lime kiln the reaction takes place in one direction, and at ordinary temperatures in the other. Sodium bicarbonate behaves in much the same manner. (Heat some in a test-tube).



(iii) Reactions analogous to that between salt and brine.

In these reactions there is a solid in equilibrium with a liquid whose composition changes with the temperature. (See "saturated solutions" page 11.)

Antimony chloride and hydrochloric acid. To a boiling dilute solution of tartar emetic add hydrochloric acid drop by drop until the precipitate of oxychloride is just redissolved. On cooling the precipitate reappears, and is again dissolved on heating. If too much acid has been used, add a little water. The reaction may be represented thus:—



Antimony chloride and hydrogen sulphide. See page 39, d and e. Similar examples are easy to find.

(iv) Chemical equilibrium in gases and in solutions.

Nitrogen peroxide. At high temperatures and low pressures this gas is dark red in colour, and its "standard volume" weighs about 46 g, corresponding to the formula NO_2 ; but at low temperatures and high pressures it is almost colourless, and the weight of its standard volume approaches that required by the formula N_2O_4 . At ordinary temperatures and pressures the gas may be regarded as containing both substances in equilibrium



Ferric sulphocyanate. Approximately equivalent solutions of ammonium sulphocyanate and ferric chloride may be prepared as follows: (a) Ammonium sulphocyanate 7.5 grammes, water to make 200cc. (b) Commercial (basic) ferric chloride 6 g, conc. hydrochloric acid 25cc, water to make 200cc. Five cc of each are mixed in a large vessel, about two litres of tap water added, and the orange-coloured solution poured in equal quantities into four glasses.

To the	is added	The colour becomes	Reac'n
1st	5cc sulpho. sol'n.	dark red	→
2nd	5cc ferric sol'n.	dark red	→
3rd	50cc am. chlor.	almost colourless	←
While the 4th is kept for comparison. Orange.			

(By "am. chlor." is meant a saturated solution of ammonium chloride).

If the reaction be represented¹ by the equation

¹The use of chemical formulæ to represent the reactions of solutions is based on a number of conventions which cannot be discussed here. The experiments shew changes of colour, etc., when solutions are mixed (or let stand, see page 42), while the symbols in the equations represent compositions and quantities of solid chemical compounds. The employment of chemical formulæ to represent physical compounds is somewhat analogous to the use of structural formulæ in organic chemistry, as in both cases an attempt is made to include in a symbol an epitome of the reactions of the substance represented; but at best the representation is incomplete, for the direction and rate of the reaction depend on the concentrations of the solutions, which are ignored in the ordinary chemical equations. The most successful system of "structural formulæ" for aqueous solutions is founded mainly on electrochemical experiments, and is used throughout Ostwald's "Principles of Inorganic Chemistry," one of the books recommended for High School libraries.



and the amount of ferric sulphocyanate be judged from the depth of colour of the solution, the reaction between equivalent quantities must be regarded as incomplete. The changes of colour are interpreted by the arrows in the last column, (indicating the direction of the reaction). —Note the agreement with Le Chatelier's law.

v. Further examples.

Bismuth chloride water. A bismuth solution is prepared as follows:—Commercial "bismuth trisnit." 40 g, hydrochloric acid (sp. gr. 1.175) 40cc; rub together in a mortar, as the powder cakes; a trifling residue may be filtered off. The reaction with water may be represented by the equation



To 50cc water add 5cc bismuth solution.....	→
Add 5cc hydrochloric acid (sp. gr. 1.175).....	←
" 75cc water.....	→
" 5cc acid.....	←
" 200cc water.....	→
" 10cc acid.....	←
" 500cc water.....	→
Pour in acid from the bottle.....	←

Sulphuric acid and sodium chloride. (i) Concentrated sulphuric acid is poured into its own volume of a saturated solution of common salt in a test tube. The solution may be cooled under the tap and shaken, but usually a crystal of Glauber's salt must be added before crystallization will occur. The liquid is then poured off, and the crystals dried on a piece of unglazed pottery (flower-pot). (ii) If some of the sodium sulphate so prepared be covered with concentrated hydrochloric acid on a watch-glass it is at once changed to a fine powder of sodium chloride, which in turn may be freed from acid on the porous plate.

To demonstrate the change from chloride to sulphate and back again, mix a drop of the original salt solution with a little water on a piece of glass and warm till crystallization sets in; do the same with small portions of the sulphate and chloride formed in the experiment; the crystals of the two salts are very different in appearance. The equation is



Antimony chloride and hydrogen sulphide. An antimony solution is prepared by dissolving 2 g of tartar emetic in 15cc of hydrochloric acid (sp. gr. 1.175) and adding 85cc of water. This solution cannot be kept more than two or three hours as a precipitate of oxychloride is slowly formed.



- (a) Pass a little H_2S into 5cc antimony solution \rightarrow
 (b) Add 8cc hydrochloric acid (sp. gr. 1.175) \leftarrow
 (c) Add 5cc antimony solution \rightarrow
 (d) Heat, not to boiling \leftarrow
 (e) Cool again, in a dish of water \rightarrow
 (f) Add 6cc of the acid \leftarrow
 (g) Pass in H_2S under pressure \rightarrow
 (h) Reduce pressure by filter-pump \leftarrow

Notes. (c) If the addition of antimony does not bring down a fairly heavy precipitate, hydrogen sulphide should be passed in again, or there will be no precipitate in (e). (e) Cool only until a precipitate appears, then add the acid (f) and finish cooling; if too much precipitate is formed it dissolves very slowly in the acid. (g) With a rubber "syringe" (bulb and two valves) a pressure of about one metre of mercury above the atmospheric pressure may be maintained; if (g) and (h) be attempted, a small round bottomed flask with a perforated rubber stopper and tap should be used. It should be well tested for leaks before the experiment.

Steam and hot iron. Steam passed over hot iron converts it into the magnetic oxide with liberation of hydrogen; hydrogen, on the other hand reduces the magnetic oxide to iron with formation of steam. The reaction



is in equilibrium when the gaseous solution reaches a certain composition, which depends on the temperature.

"NON-REVERSIBLE" REACTIONS. CONTINUITY.

When zinc dissolves in sulphuric acid, hydrogen gas is given off and a solution of zinc sulphate is formed. In view of the numerous reactions discussed in the preceding paragraphs it might be thought possible to get the zinc and acid back again by the action of hydrogen under high pressure on the solution; this has not proved possible, however, and as the original substances cannot be recovered from the products of the reaction by change of temperature, pressure, or the concentration of the solution, the reaction is usually spoken of as "non-reversible."

It is non-reversible, however, only in a narrow technical sense; for if a current of electricity be passed from a platinum plate charged with hydrogen, through a solution of zinc sulphate to another platinum plate, the hydrogen and the sulphate turn into sulphuric acid and zinc—the reaction is thus reversible by electrical means, though not by change of temperature, pressure, or concentration.

When sugar is burned it is converted into water and carbon dioxide, which cannot be induced to turn back into sugar again by any amount of variation in temperature, pressure, concentration or electrical conditions. But, in a wider sense, this reaction is just as little "non-reversible" as the others—how was the sugar formed in the first place, if not from carbon dioxide and water in a plant?

The non-reversible chemical reactions are merely the last terms in a series of which the physical reactions are the simplest members, and the reversible chemical reactions the intermediate terms. And just as the physical reactions are connected with the chemical on the one hand, so they are on the other with changes which nobody calls "reactions" at all. Hot and cold iron are "the same thing," and so are, compressed and rarefied air; yet the change from one to the other involves the absorption or evolution of heat, change in density and colour, and change in chemical properties as well:—hot iron with oxygen and water gives the magnetic oxide, cold iron the sesquioxide; compressed air is more soluble in water than air at ordinary pressure.

Thus, though for practical purposes distinctions are introduced, it is important to remember that they are distinctions of degree only, not of kind; and that between the simplest physical experiments and the most complicated chemical reactions there is a complete series of connecting links.

CHAPTER VIII.

RATES OF REACTIONS.

A few simple experiments with zinc and sulphuric acid shew how the rate of evolution of hydrogen gas depends on the area of the zinc, the concentration of the acid, and the temperature. If a drop of copper sulphate solution be added the zinc turns black from deposition of copper and the rate is increased; if a little mercuric chloride solution be added it turns silvery and the rate is diminished.

In the hydrogen generator the heat liberated as the reaction proceeds raises the temperature and tends to increase the rate, while the fall in concentration of the acid, and the diminution of the area of the zinc tend to decrease it; the net result being that the rate at first increases, reaches a maximum, and then falls off to zero.

This reaction may be regarded, in a sense, as typical; for the area of the surface of solids, the concentrations of solutions, the temperature, and the presence of "catalysers" (see page 42) are the factors on which the rates of reactions in general depend. Light has an effect in certain cases, and so have electrical conditions when the reaction is accomplished by electrolysis.

Most of the reactions used in analysis are extremely rapid—indeed they are selected partly for that very reason—but even in the text-books of analysis a few cases can be found where "the mixture must be let stand for a few hours" to complete the reaction. Examples are: the precipitation of phosphates by magnesia mixture or molybdic acid, and the determination of potassium by platinum chloride.

One of the analytical reactions may be selected for a somewhat closer study.

Potassium permanganate and Oxalic acid. Three solutions are necessary:—*Pm* potassium permanganate 3.2 g, water to make 1 litre; *Ox* crystallized oxalic acid 3.2 g, water to 50cc; *Ac* sulphuric acid 100cc, water 90cc, this must be cooled to room temperature before using. Equal volumes of these solutions contain the permanganate and oxalic acid in the proportions required by the equation

$$2\text{KMnO}_4 + 5\text{C}_2\text{H}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2$$

but sixty times as much as sulphuric acid.

Comparison of the time required to decolourize the following solutions (mix in the order given, and count the time from adding the *Pm*)

- (i) Water 5cc, *Ox* 50cc, *Ac* 100cc, *Pm* 5cc, (total volume 160cc)
- (ii) Water 80cc, *Ox* 50cc, *Ac* 25cc, *Pm* 5cc, (total volume 160cc)

shews that increasing the concentration of the acid increases the rate of the reaction, although even in (ii) there is 300 times as much acid as is required by the equation.

The great influence of the temperature may be shewn by using the quantities of (i) but heating nearly to boiling before adding the *Pm*.

The solution

(iii) Ox 50cc, Ac 100cc, Pm 10cc, (total volume 160cc) in which the concentration of the permanganate is twice as great as in (i), is decolourized in nearly the same time, so that doubling the concentration (weight in a fixed volume) of the permanganate, has doubled the amount reduced in a fixed time, or has doubled the rate of the reaction. The rate is (nearly) proportional to the concentration of the potassium permanganate.

CATALYTIC AGENTS

If a second 5cc of *Pm* be added to solution (i) after the first portion has been reduced, the reduction takes place much more quickly than before; and a third portion is still more quickly decolourized. This is due to the manganous sulphate formed in the previous experiments; which, in some manner not completely understood, accelerates the reaction.

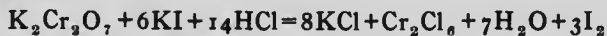
Substances like this which affect the rate without, apparently, taking part in the reaction, are termed "catalytic agents" or catalysers; the action of platinum in accelerating the union of hydrogen and oxygen, or of sulphur dioxide and oxygen, is a well known example of catalysis which has recently been turned to account in the "contact process" for the manufacture of sulphuric acid, and has long served as basis for innumerable "matchless" gas lighters. Copper in the hydrogen generator, and manganese dioxide in the preparation of oxygen from potassium chlorate also act "catalytically."

The enzymes, or unorganized ferments—rennet, for example—which play such a part in the chemistry of life, are catalytic agents; and many reactions which were formerly thought to be due to the life processes of micro-organisms are now referred to the catalytic action of chemicals generated by them. The fermentation of sugar, for instance, is caused by a "zymase" which can be obtained from yeast by killing the cells, grinding with sand, adding water, and filtering.

"Negative catalysers" retard instead of accelerating; some of the poisons seem to act in this manner.

The effect of concentrations, temperature, and catalysers may be illustrated by one more reaction, namely that between *Potassium iodide and chromic acid*. The following solutions are convenient:—Potassium bichromate 2½ g, water to make 1 litre; potassium iodide 8½ g, water

to make 1 litre; sulphuric acid 3cc, water to 1 litre; crystallized ferrous sulphate 7 g, water to 500cc; iron alum 10 g, water to 100cc; starch $\frac{1}{2}$ g mixed with a little cold water and poured into 500cc of boiling water, cool before use.



The rate is increased when the concentration of bichromate, iodide, or acid is increased; ferrous sulphate acts as a positive catalyser, ferric alum by itself has very little effect, but much reduces the acceleration caused by the ferrous salt.

DELAYED REACTIONS

The great effect of temperature on the rates of reactions has already been illustrated; as a general rule every rise of 10°C about doubles the rate— 100° would thus multiply it by 1000. This accounts for the fact that many substances which combine vigorously at a red heat appear to be without action on each other at ordinary temperatures; thus the catalytic action of platinum on mixtures of hydrogen and oxygen may be regarded as acceleration of a reaction already taking place, and the spontaneous combustion of coal heaps may be traced to the heat given off by slow oxidation, which raises the temperature of the interior of the heap and increases the rate of the reaction, until finally the whole mass is red hot.

There are however some cases of "delayed" or "retarded" reactions to which this explanation is not applicable; supersaturated solutions for instance have been kept for years without the deposition of crystals; and as the first speck of the solid salt is enough to bring about a quick reaction, it is not possible to assume that crystallization is going on "very slowly" all the while.

The rate at which the crystallization proceeds may be studied if the solution while still hot be sucked up into a narrow glass tube, which is then closed at both ends by small caps made from an inch of rubber tube and a scrap of glass rod. After cooling, one of the caps may be removed and a crystal of the salt introduced. If tube and caps be wet just before filling, and if the outside be washed off as soon as possible after putting on the caps, there is very little danger of premature crystallization.

THE ACTION OF LIGHT

The action of light in accelerating the reduction of silver salts by organic matter (gelatine), or the reduction of ferric salts by ferricyanides (blue print) is familiar to all; the warning that accompanies each film "to be developed not later than . . ." is a reminder that the reaction takes place even in the dark, and that light only hurries it up. The decomposition of chlorine water in the light is also a familiar experiment;

and the browning of acidified solutions of potassium iodide is due to the action of light in accelerating the oxidation of hydriodic acid by oxygen dissolved from the air.

In some cases the light does not merely change the rate of a reaction that would have taken place in any event, but actually reverses its direction; as in the formation of sugar and starch from carbonic acid and water in plants, where light is absorbed by the leaves and its energy stored up in the products of the reaction. Numerous attempts have recently been made—some with a measure of success—to imitate this action of the plants by inventing reactions which take place in one direction in the light and in the other in the dark. If it should prove possible to store any large fraction of the sun's energy by such means, the wastes of the Sahara might well become the seat of important industries.

CHAPTER IX.

SUGGESTIONS FOR A LABORATORY COURSE

The matters dealt with in this pamphlet are at the very root of chemical science; they should not be put off until a few weeks before the end of the term and crammed for examination. On the other hand to begin a course on Chemistry with a disquisition on the use of plain language, followed by a lot of definitions, when the boys are all waiting to prepare hydrogen and burn phosphorus in oxygen, might very well disgust them with the whole subject; it is better to begin with the attractive experiments and work in conceptions and definitions as opportunity offers.

This may be done in an infinite number of ways, all good; the following may serve as an example.

HYDROGEN

The course might begin with the preparation of hydrogen from sodium and water, and from zinc and sulphuric acid, in connection with which the circumstances modifying the rate of the reaction should be taken up.

Its properties, (lightness, inflammability) distinguish it from air, which in some respects it resembles very closely; as it differs from zinc, acid, water, and sodium, it is a "new substance." Granulated zinc and stick zinc, on the other hand, which differ only in form and size, are "the same thing."

Attention may then be directed to the other new substances, viz., lye (some should be put away in a bottle), and the liquor remaining on the zinc; if the contents of the generator have been let stand with excess of zinc since the last lesson most of the acid will be gone, and the "mechanical mixture" may be separated by filtration. The lye and the liquor resemble water in some respects, but are at least as different from it as lemonade or tea is.

The clear liquor may then be evaporated and the crystals dried on filter paper. Part of the solution should be distilled and the vapour condensed to shew that pure steam is given off; and the meaning of the expression "the liquor contains water and the crystals" should be explained. Some of the crystals should then be heated in a test tube, to shew that they also "contain" water.

The meaning of concentrated, dilute, saturated, and unsaturated solutions may be explained, and it may be shewn that the white vitriol¹

¹ It wont hurt to call it "zinc sulphate" if nothing is said about a formula, or atoms.

is more soluble in hot water than in cold. Supersaturated solutions of zinc sulphate are difficult to prepare, and each teacher must decide for himself whether it is advisable to make them from sodium sulphate (or alum) at this stage, or to postpone that part of the subject. It is easy to shew that concentrated solutions boil at higher temperatures than dilute. (Do the boys know that water has a boiling-point? that turning up the gas under boiling water only makes it boil faster, and does not raise the temperature?) If the school has a few specific gravity spindles, solutions containing different percentages of vitriol may be made by adding 1, 2, 3, volumes of water to a solution of known composition furnished by the teacher, their densities may be determined and the results plotted on squared paper.

OXYGEN

The action of heat on red oxide of mercury proves that substance to contain mercury and oxygen.

The catalytic action of manganese dioxide in the preparation of oxygen from potassium chlorate may be illustrated by heating a little of the salt in a test tube until oxygen begins to come off, and then adding a pinch of the dioxide. After cooling, the mass may be ground and dissolved in water when the dioxide is found unchanged.

After shewing the combustion of iron, sodium, etc., in oxygen, the experiments on the conservation of mass (page 3) may be introduced. When burned in air, 5 g of *ferrum redactum*¹ gains nearly 2 g in weight, and loses the power of effervescing with dilute sulphuric acid; if proportionally less oxygen be available (as in the bottle experiment of page 3) some of the iron remains unaltered, and gives off gas with acid. These experiments may be used to introduce the conception of combination in definite proportions and the definition of chemical compounds as distinguished from solutions.

Having been shewn experimentally that the magnetic oxide is a chemical compound, and that one gramme of it contains $\frac{7}{8}$ g of oxygen and $\frac{1}{8}$ g of iron, the boys may be informed that the products of combustion of zinc, magnesium, etc., are also chemical compounds, oxides. When sodium is burned a mixture of oxide and peroxide is formed, but on dissolving in water and boiling, oxygen is given off, and the solution obtained is the same as if pure oxide had been used. It should be compared with the lye kept from the first day's experiment.

¹ If an analytical balance is available, half a gramme may be heated in an open crucible until the weight becomes constant, noting the increase. If not, 5 g may be spread on an upturned crucible lid, heated for five minutes, cooled a little and weighed; the lumps should be powdered, and the whole heated for another five minutes by which time the iron is practically all oxidized, and the balance shows a gain of nearly two grammes.

The pupils are now in a position to understand the argument of page 18 on the indirect analysis of water; and as they have seen several syntheses (sodium oxide, zinc oxide, magnetic oxide of iron, etc.) and analyses (red oxide of mercury, white vitriol into water and zinc sulphate, water indirectly) the conception of a chemical element may be explained.

WATER

The composition of water (electrolysis, eudiometer) may now be taken up, affording a new illustration of combination in definite proportions, and introducing the law of combination of gases by volume.

Then the action of steam on hot magnesium (which does not need such a high temperature as iron) may be compared with the action of water on sodium. The respects in which water and aqueous solutions resemble one another have already been spoken of under hydrogen; here is the opportunity to point out that both oxygen and steam are gases, and that both form oxides with magnesium, iron, etc.; the oxygen has not lost *all* its properties by uniting with hydrogen.

The action of steam on hot iron requires a fairly high temperature, it is well to use as many burners as can be got under the tube (gas pipe), and to concentrate the heat by pieces of asbestos paste-board, or tiles; the experiment is only worth bothering with because the reduction of the magnetic oxide by hydrogen furnishes the first example of a chemical reaction reversed; but if the experiments are too troublesome it might be better to postpone all discussion of this subject until "acids, bases, and salts" are taken up, when the reversible reaction between hydrochloric acid and sodium sulphate should be studied.

CHLORINE

Among other experiments, sodium should be burned in chlorine, and the composition (in parts per hundred) of the resulting salt given. The composition of hydrochloric acid should be demonstrated by experiments, and its properties as an "acid" illustrated.

The reaction between sodium oxide and hydrochloric acid giving water and common salt may then be discussed after the manner of page 21 introducing the law of reciprocal proportions, and the use of tickets. "Sodium 74.24" and "oxygen 25.76" may be taken to represent 100 g of sodium oxide, and "hydrogen 3.238" "chlorine 114.1" to represent the hydrochloric acid containing hydrogen enough to form water with the oxygen of the 100 g of sodium oxide. After shewing that the actual numbers chosen for the tickets are arbitrary, and that their ratios only are of importance for the present purpose (page 26) introduce the international weights, as an established convention, reserving the intermediate steps of the argument until the use of formulæ is more familiar.

