MAGNESIUM.

Symbol Mg.   Atomic weight 24.

Source.—Magnesium is abundant in nature in the form of magnesian or mountain limestone, or *dolomite*, a double carbonate of magnesium and calcium in common use as a building-stone (*e. g.*, the Houses of Parliament and the School of Mines in London), and *magnesite*, a tolerably pure carbonate of magnesium, though too "stony" for direct use in medicine, even if very finely powdered. Chloride of magnesium and sulphate of magnesium (Epsom salt) also occur in sea-water and in the water of many springs. A monohydrous sulphate ($MgSO_4,H_2O$) termed *kieserite* occurs near Stassfurt in Prussia. Metallic magnesium may be obtained from the chloride by the action of sodium. It burns readily in the air, emitting a dazzling light, due to the white heat to which the resulting particles of magnesia (MgO) are exposed. The chloride employed as a source of the metal is obtained by dissolving the carbonate in hydrochloric acid, adding some chloride of ammonium, evaporating to dryness, heating the residue in a flask (on the small scale a large test-tube or Florence flask) until the chloride of ammonium is all volatilized and the chloride of magnesium remains as a clear fused liquid. The latter is poured on to a clean earthenware slab. The chloride of ammonium prevents reaction between chloride of magnesium and water in the last stages of the operation and consequent formation of oxide (or oxychloride) of magnesium and hydrochloric acid gas.
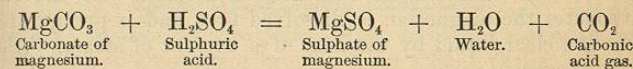
Quantivalence.—The atom of magnesium is bivalent, Mg''.

Reactions having Synthetical Interest.

Sulphate of Magnesium.

First Synthetical Reaction.—To a few drops of sulphuric acid and a little water in a test-tube, made hot (or to larger quantities in larger vessels), add powdered native carbonate of magnesium, *magnesite*, $MgCO_3$, until effervescence ceases, subsequently boiling to aid in the expulsion of the carbonic acid gas. The filtered liquid is a solution of sulphate of magnesium ($MgSO_4$), crystals of which, *Epsom salt* ($MgSO_4,7H_2O$) (*Magnesii Sulphas*, U. S. P.), may be obtained on evaporating most of the water and setting the concentrated solution aside to cool. This is an ordinary manufacturing process. Instead of magnesite, *dolomite*, the common magnesian limestone (carbonate of magnesium and calcium, $CaCO_3,MgCO_3$), may be employed, any iron being removed by evaporating the solution (filtered from the sulphate of calcium produced) to dryness, gently igniting to decompose sulphate of iron, dissolving in water, filtering from oxide of iron, and crystallizing. (If neither mineral be at hand, the practical student may use a

little of the ordinary manufactured carbonate of pharmacy, for the chemical action is almost identical, and it is the chemistry and not, just now, the commercial economy of the matter that he is studying. The manufacturer must, of course, commence with one of the above mineral carbonates furnished by nature, from that make his sulphate, and from the latter, as will be seen directly, make the pure pulverulent carbonate of pharmacy.)

$$MgCO_3 \;+\; H_2SO_4 \;=\; MgSO_4 \;+\; H_2O \;+\; CO_2$$

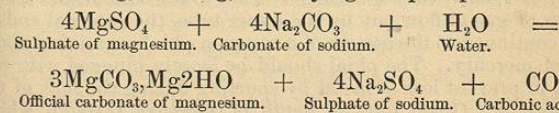Carbonate of magnesium. Sulphuric acid. Sulphate of magnesium. Water. Carbonic acid gas.

Sulphate of magnesium readily crystallizes in large, colorless, transparent, rhombic prisms; but, from concentrated solutions, the crystals are deposited in short thin needles, a form more convenient for manipulation, solution, and general use in medicine.

Iron may be detected in sulphate of magnesium by adding the common alkaline solution of chlorinated lime or chlorinated soda to some aqueous solution of the salt; brown hydrate of iron ($Fe_2 6HO$) is then precipitated. Sulphydrate ammonium will also give a black precipitate if iron be present.

Carbonates of Magnesium.

Second Synthetical Reaction.—To solution of sulphate of magnesium add solution of carbonate of sodium, and boil; the resulting precipitate is *light* carbonate of magnesium (*Magnesiæ Carbonas Levis*, B. P.; *Magnesii Carbonas*, U. S. P.), the old light carbonate of magnesia, a white, partly amorphous, partly minutely crystalline mixture of carbonate and hydrate of magnesium ($3MgCO_3,Mg2HO,4H_2O$, B. P.; $4MgCO_3,Mg2HO,5H_2O$, U. S. P.). A denser, slightly granular precipitate of similar chemical composition (*Magnesiæ Carbonas*, B. P.), the old heavy carbonate of magnesia, is obtained on mixing strong solutions of the above salts, evaporating to dryness, then removing the sulphate of sodium by digesting the residue in hot water, filtering, washing, and drying the precipitate.

$$4MgSO_4 \;+\; 4Na_2CO_3 \;+\; H_2O \;=$$

Sulphate of magnesium. Carbonate of sodium. Water.

$$3MgCO_3,Mg2HO \;+\; 4Na_2SO_4 \;+\; CO_2$$

Official carbonate of magnesium. Sulphate of sodium. Carbonic acid gas.

The official (B. P.) proportions for the light carbonate are 10 of sulphate of magnesium and 12 of crystals of carbonate of sodium, each dissolved in 80 of cold water, the solutions mixed, boiled for 15 minutes, the precipitate collected on a filter, well washed, drained, and dried over a water-bath. The heavier carbonate is made with the same proportions of salts, each dissolved in 20 instead of 80 of

water, the mixture evaporated quite to dryness, and the residue washed by decantation or filtration until all sulphate of sodium is removed (shown by a white precipitate—sulphate of barium—ceasing to form on the addition of solution of chloride or nitrate of barium to a little of the filtrate).

Another (Pattinson's) Process.—Considerable quantities of carbonate of magnesium are now prepared by treating dolomite (see p. 115) with carbonic acid under pressure. Of the two carbonates the magnesian is dissolved first, and is precipitated from the clear liquid by the heat of a current of steam. (See next reaction.)

Third Synthetical Reaction.—Pass carbonic acid gas, generated as described on page 71, into a mixture of water and carbonate of magnesium contained in a test-tube. After some time, separate undissolved carbonate by filtration; the filtrate contains normal carbonate of magnesium ($MgCO_3 3H_2O$) dissolved by carbonic acid. When of a strength of about 10 grains of official carbonate in one ounce, such a solution constitutes "*Fluid Magnesia*" (*Liquor Magnesiæ Carbonatis*, B. P.). It is impossible to obtain a strength of over 3 per cent. at about 55° F. is reduced to $2\frac{1}{2}$ per cent. at 70° and to about 2 per cent. at 80° F.

Officially, 1 pint is directed to be made from freshly prepared carbonate. The latter is obtained by adding a hot solution of 2 ounces of sulphate of magnesium in half a pint of water to one of $2\frac{1}{2}$ ounces of crystals of carbonate of sodium in another half pint of water, boiling the mixture for a short time (to complete decomposition), filtering, thoroughly washing the precipitate, placing the latter in 1 pint of distilled water, and transmitting carbonate acid gas through the liquid (say, at the rate of three or four bubbles per second) for an hour or two, then leaving the solution in contact with the gas under pressure of about 3 atmospheres for twenty-four hours, and, finally, filtering from undissolved carbonate, and, after passing in a little more gas, keeping in a well-corked bottle. Slight pressure is best produced by placing the carbonate and water in a bottle fitted with a cork and tubes as for a wash-bottle (p. 97 or 108), conveying the gas by the tube which reaches to the bottom, and allowing excess of gas to flow out by the upper tube, the external end of which is continued to the bottom of a common phial containing about an inch of mercury. The phial should be loosely plugged with cotton-wool, to prevent loss of metal by spurting during the flow of the gas through it. (Each inch in depth of mercury through which the gas escapes corresponds to about half a pound pressure on every square inch of surface within the apparatus.)

Heat a portion of the solution; true carbonate of magnesium containing combined water ($MgCO_3,3H_2O$) is precipitated. The water in this compound is probably in the state of water of crystallization, for a salt having the same composition is deposited in crystals by the

spontaneous evaporation of the solution of carbonate of magnesium. The official "carbonate" ($3MgCO_3.Mg2HO,4H_2O$) is another of these very common *hydrous* compounds.

Exposed to cold, the solution of "fluid magnesia" sometimes affords large thick crystals ($MgCO_3,5H_2O$), which, in contact with the air, lose water, become opaque, and then have the composition of those deposited by evaporation ($MgCO_3,3H_2O$).

Oxide of Magnesium (Magnesia).

Fourth Synthetical Reaction.—Heat light dry carbonate of magnesium in a porcelain crucible over a lamp (or in a larger earthen crucible in a furnace) till it ceases to effervesce on adding, to a small portion, water and acid; the residue is light magnesia (MgO) (*Magnesia Levis*, B. P.; *Magnesia*, U. S. P.). The same operation on the heavy carbonate yields heavy magnesia (MgO) (*Magnesia Ponderosa*, U. S. P.). Both are sometimes spoken of as "calcined magnesia." A given weight of the official light magnesia occupies three and a half times the bulk of the weight of heavy magnesia.

$$3MgCO_3,Mg2HO \ = \ 4MgO \ + \ H_2O \ + \ 3CO_2$$
Official carbonate of magnesium.   Oxide of magnesium.   Water.   Carbonic acid gas.
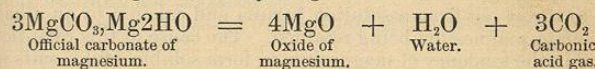
A trace only of magnesia is dissolved by water. Moisten a grain or two of magnesia with water, and place the paste on a piece of red litmus-paper; the wet spot, after a time, becomes blue, showing that the magnesia is slightly soluble.

"*Effervescing Citrate of Magnesia*," so called, is generally a mixture of bicarbonate of sodium, citric acid, tartaric acid, sugar, either carbonate or sulphate of magnesium, or both, and flavoring essences. True citrate of magnesium is easily made by heating together calcined magnesia and citric acid; it is frequently prescribed in France in doses of two ounces.

The official "Granulated Citrate of Magnesium" (*Magnesii Citras Granulatus*, U. S. P.) is made as follows: Mix 11 parts of carbonate of magnesium intimately with 33 of citric acid, and enough distilled water to make a thick paste; dry this at a temperature not exceeding 30° C (86° F.), and reduce it to a fine powder. Then mix it intimately with 8 of sugar (No. 60 powder), 37 of bicarbonate of sodium, and 15 of citric acid previously reduced to a very fine powder. Dampen the mass with a sufficient quantity of alcohol, and rub it through a No. 20 tinned-iron sieve, to form a coarse, granular powder. Lastly, dry it in a moderately warm place.

The official Effervescing "Solution of Citrate of Magnesium" (*Liquor Magnesii Citratis*, U. S. P.) is made by dissolv-

ing carbonate of magnesium in slight excess of solution of citric acid, adding syrup of citric acid, placing the diluted liquid in an aërated-water bottle, dropping in crystals of bicarbonate of potassium, corking, "wiring," and shaking till the crystals are dissolved.

The formula of citrate of magnesium deposited from solution is $Mg_3 2C_6H_5O_7, 14H_2O$.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Add solution of hydrate or carbonate of ammonium to a magnesian solution (sulphate, for example) and warm the mixture in a test-tube; the precipitation of part only of the magnesium as hydrate ($Mg2HO$) or carbonate ($MgCO_3$) occurs. Add now to a small portion of the mixture of precipitate and liquid a considerable excess of solution of chloride of ammonium; the precipitate is dissolved.

This is an important reaction, especially as regards carbonate of magnesium, the presence of chloride of ammonium enabling the analyst to throw out from a solution barium and calcium by an alkaline carbonate, magnesium being retained. The cause of this retention is found in the tendency of magnesium to form soluble double salts with potassium, sodium, or ammonium. In analysis, the chloride of ammonium should be added before the carbonate, as it is easier to prevent precipitation than to redissolve a precipitate once formed.

Second Analytical Reaction.—To some of the solution resulting from the last reaction, add solution of phosphate of sodium or ammonium; phosphate of magnesium and ammonium ($MgNH_4PO_4$) is precipitated.——3*d*. To another portion add arseniate of ammonium; arseniate of magnesium and ammonium ($MgNH_4AsO_4$) is precipitated.

Note.—Barium and calcium are also precipitated by alkaline phosphates and arseniates. The other precipitants of magnesium are also precipitants of barium and calcium. In other words, there is no *direct* test for magnesium. Hence the analyst always removes any barium or calcium by an alkaline carbonate, as above indicated; the phosphate of sodium, or arseniate or phosphate of ammonium, then becomes a very delicate test of the presence of magnesium. In speaking of magnesium tests, the absence of barium and calcium salts is to be understood.

QUESTIONS AND EXERCISES.

168. Name the natural sources of the various salts of magnesium.

169. Give a process for the preparation of Epsom salt.
170. Draw diagrams illustrative of the formation of sulphate of magnesium from *magnesite* and from *dolomite*.
171. Show by an equation the process for the preparation of the official Carbonate of Magnesium.
172. What circumstances determine the two different states of aggregation of the *Magnesiæ Carbonas* and *Magnesiæ Carbonas Levis*?
173. What are the relations of *Magnesia* and *Magnesia Levis* to the British official Carbonates of Magnesium?
174. How much denser is the one than the other?
175. Is magnesia soluble in water?
176. How is "Fluid Magnesia" prepared?
177. Mention the effects of heat and cold on "Fluid Magnesia."
178. How much magnesia (MgO) can be obtained from 100 grains of Epsom salt?
179. Calculate the amount of official Carbonate of Magnesium which will yield 100 grains of magnesia.
180. Can magnesium be detected in presence of barium and calcium?
181. Describe the analysis of an aqueous liquid containing salts of barium, calcium, and magnesium.
182. How may magnesium be precipitated from solutions containing ammoniacal salts?

Quantivalence.

On reviewing the foregoing statements regarding compounds of the three univalent radicals, potassium, sodium, and ammonium, and the three bivalent elements, barium, calcium, and magnesium, the doctrine of quantivalence will be more clearly understood, and its usefulness more apparent. Quantivalence, or the value of atoms, is, in short, in chemistry, closely allied to value in commercial barter. A number of articles, differing much in weight, appearance, and general characters, may be of equal money value; and if these be regarded, for convenience, as having a sort of unit of value, others worth double as much might be termed bivalent, three times as much trivalent, and so on. In like manner, chemical radicals, no matter whether elementary, like potassium (K), iodine (I), or sulphur (S), or compound, like those of nitrates (NO_3), sulphates (SO_4), or acetates ($C_2H_3O_2$), have a given chemical value in relation to each other, and are exchangeable for, and will unite with, each other to an extent determined by that value.

Most chemical salts apparently, though probably not really, have two parts, a basylous and acidulous, the one quantivalently balancing the other. The formulæ of the chief of these radicals and their quantivalence are given on the following page. Examples of formulæ of salts containing univalent, bivalent, and trivalent radicals are also appended.

6

QUANTIVALENCE OF COMMON RADICALS.

Univalent Radicals, or *Monads*.		Bivalent Radicals, or *Dyads*.		Trivalent Radicals, or *Triads*.	
Acidulous.	Basylous.	Acidulous.	Basylous.	Acidulous.	Basylous.
H	H	O	Ca	PO_4	As
Cl	K	SO_4	Mg	BO_3	Sb
I	Na	CO_3	Zn	$C_6H_5O_7$	Bi
HO	NH_4	C_2O_4	Cu	AsO_3	$\{Fe^{iii}(ic)$
NO_3	Ag	$C_4H_4O_6$	Hg(ic)	AsO_4	or
$C_2H_3O_2$	Hg(ous)	S	Fe(ous)	$C_4H_3O_5$	$\{Fe^{vi}{}_2(ic)$

Note 1.—The hydrogen (H) in the basylous parts of salts has entirely different functions from the hydrogen (H) in the acidulous part. The latter gives compounds commonly termed *hydrides* (*e. g.*, AsH_3); in the former the element is the basylous radical of acids (*e. g.*, HCl, H_2SO_4). In compound radicals (*e. g.*, $C_2H_3O_2$ or NH_4) the properties of hydrogen are no longer apparent; the chemical force resident in the atoms of such radicals seems to be mainly exerted in binding those atoms together.

Note 2.—The name, symbol, and quantivalence of all the important elements are given in a Table immediately preceding the Index.

Examples of Formulæ of Salts containing Univalent, Bivalent, and Trivalent Radicals.

The reader will find instructive practice in writing twenty or thirty imaginary formulæ of salts by placing in juxtaposition acidulous and basylous radicals, as in the following table of examples. Just as in a pair of scales a 2-lb. weight must be balanced by two 1-lb. weights, or a 4-lb. weight by two 2-lb. weights, or by one 3-lb. and one 1-lb. weight, so a bivalent radical unites with a bivalent radical or with two univalent radicals, a quadrivalent radical with two bivalent radicals, or with one trivalent and one univalent radical, and so on.

(R = any basylous Radical.)   (*R* = any acidulous Radical.)

General formula.	Examples.
$R'R'$	KI, NaCl, $NH_4C_2H_3O_2$, $AgNO_3$.
$R''R'_2$ . . .	$CaCl_2$, $Zn2C_2H_3O_2$, $Pb2NO_3(BaNO_3C_2H_3O_2)$.
$R'''R'_3$ . . .	$Bi3NO_3$, AsH_3, $SbCl_3$.
R'_2R'' . . . $\}$	$\{$ K_2CO_3, Na_2SO_4, $H_2C_4H_4O_6$.
$R'R'R''$ . . . $\}$	$\{$ $KHCO_3$, $NaHSO_4$ $KNaC_4H_4O_6$.
R'_3R''' . . . $\}$	$\{$ Am_3PO_4, $K_3C_6H_5O_7$, H_3AsO_3.
$R'_2R'R'''$ . . $\}$	$\{$ Na_2HPO_4, Na_2HAsO_4.
$R''R''$	$CaCO_3$,MgO, $CuSO_4$, HgO, $FeSO_4$.
$R''_3R'''_2$ . .	Ca_32PO_4, $Ca_32C_6H_5O_7$.
$R''R'R'''$ . .	$MgAmPO_4$, $CuHAsO_3$.
$R'''R''R'$ . .	$BiONO_3$.
$R''_2R'''_2R''$.	$Bi_2O_2CO_3$.
$R'''_2R''_3$ . .	As_2O_3, Sb_2O_3, Fe_2O_3, Fe_23SO_4.
$R'''R'''$ . . .	$BiC_6H_5O_7$.
$R'''_2R'_6$ . . .	Fe_2Cl_6, Fe_26NO_3, $Fe_26C_2H_3O_2$.

Quadrivalent Radicals or *Tetrads*, Quinquivalent Radicals or *Pentads*, and Sexivalent Radicals or *Hexads*, are known.

EXERCISE.

183. Write an exposition of the doctrine of Quantivalence within the limits of a sheet of note paper.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION* OF A SALT OF **ONE** OF THE METALS, BARIUM, CALCIUM, MAGNESIUM.

Add yellow chromate of potassium to a portion of the solution to be examined; a precipitate indicates barium.

If no barium is present, add chloride and carbonate of ammonium, and boil; a precipitate indicates calcium.

If barium and calcium are proved to be absent, add chloride of ammonium, ammonia, and then either phosphate of sodium or arseniate of ammonium; a white granular precipitate indicates magnesium.

Ammonia is here added to yield the necessary elements to ammonio-magnesian phosphate or ammonio-magnesian arseniate, both of which are highly characteristic precipitates; and chloride of ammonium is added to prevent a mere partial precipitate of the magnesium by the ammonia.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF **ONE, TWO, OR ALL THREE** OF THE METALS, BARIUM, CALCIUM, MAGNESIUM.

Add chromate of potassium to the solution; barium, if present, is precipitated. Filter, if necessary, and add to the *filtrate* (that is, the liquid which has run through the filter) chloride, hydrate, and carbonate of ammonium, and boil; calcium, if present, is precipitated. Filter, if requisite, and add phosphate of sodium; magnesium, if present, is precipitated.

Note.—Red chromate of potassium must not be used in these operations, or a portion of the barium will remain in the liquid and be thrown down with, or in place of, the carbonate of calcium (*vide* p. 103). The yellow chromate must not contain carbonate of potassium, or calcium will be precipitated with, or in place of, barium.

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* In preparing such solutions for analysis, salts should be selected which do not decompose each other. Chlorides will serve in most cases, but nitrates and acetates are still more convenient.

The absence of carbonate is proved by the non-occurrence of effervescence on the addition of hydrochloric acid to a little of the solution of the chromate, previously made hot in a test-tube. If the yellow chromate has been prepared by adding excess of ammonia to solution of red chromate of potassium, its addition to the liquid to be analyzed must be preceded by that of solution of chloride of ammonium, the precipitation of a portion of the magnesium (by the free ammonia in the yellow chromate) is thus prevented, for chloride of ammonium solution is a good solvent of hydrate (and carbonate) of magnesium, as already stated on page 120.

Note 1.—The analysis of solutions containing the foregoing metals is commenced by the addition of chloride of ammonium (NH_4Cl) and ammonia (NH_4HO), simply as a precautionary measure, the former compound preventing partial precipitation of magnesium, the latter neutralizing acids. The carbonate of ammonium ($(NH_4)_2CO_3$) is the important group reagent—the precipitant of barium and calcium.

Note 2.—In the following, and in subsequent charts of analytical processes, the leading precipitants will be found to be ammonium salts. These, being volatile, can be got rid of towards the end of the operations, and thus the detection of potassium and sodium be in no way prevented—an advantage which could not be had if such salts as chromate of potassium or phosphate of sodium were the group-precipitants employed.

Note 3.—Acetic, and not hydrochloric or nitric, acid is used in dissolving the barium and calcium carbonates, because chromate of barium, on the precipitation of which the detection of barium depends, is soluble in the stronger acids, and therefore could not be thrown down in their presence.

TABLE OF SHORT DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

To the solution add NH_4Cl, NH_4HO, $(NH_4)_2CO_3$; boil and filter.

Precipitate Ba Ca. Wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4, and filter.		Filtrate Mg Am Na K. Add Am_2HPO_4, shake, filter.	
Precipitate Ba.*	Filtrate Ca. Test by $(NH_4)C_2O_4$.	Precipitate Mg.	Filtrate NH_4 Na K. Evap. to dryness, ignite, dissolve residue in water. Test for K by $PtCl_4$. Test for Na by flame. Test orig. sol. for NH_4

* It is perhaps scarcely necessary to state that this precipitate is

Note on Classification.—The compounds of barium, calcium, and magnesium, like those of the alkali metals, have many analogies; the carbonate, phosphate, and arseniate of each is insoluble in water, which sufficiently distinguishes them from the members of the class first studied. They possess, however, well-marked differences, so that their separation from each other is easy. The solubility of their hydrates in water marks their connection with the alkali metals; the slightness of that solubility, diminishing as we advance further and further from the alkalies, baryta being most and magnesia least soluble in water, points to their connection with the next class of metals, the hydrates of which are insoluble in water. These considerations must not, however, be over-valued. Though the solubility of their hydrates places barium nearest and magnesium farthest from the alkali metals, the solubility of their sulphates gives them the opposite order, magnesium-sulphate being most soluble, calcium-sulphate next, strontium-sulphate third (strontium is a rarer element, which will be mentioned subsequently), and barium-sulphate insoluble in water. These elements are sometimes spoken of as the metals of the alkaline earths.

Note.—In connection with the bivalence of the metals Barium, Calcium, and Magnesium, it is interesting to note that just as bivalent acidulous radicals give salts containing two atoms of univalent basylous radicals (K_2SO_4, $NaHSO_4$, H_2CO_3, $KNaC_4H_4O_6$), so bivalent basylous radicals yield salts containing two atoms of univalent acidulous radicals, as seen in acetonitrate of barium, $BaC_2H_3O_2NO_3$, a salt which is a definite compound, and not a mere mixture of acetate with nitrate of barium. A very large number of such salts is known.

Distillation.

The water with which, in analysis, solution of a salt or dilution of a liquid is effected should be pure. Well- or river-water is unfit for the purpose, because containing alkaline and earthy salts (about 20 to 60 grains per gallon), derived from the soil through which the water percolates, and rain-water is not unfrequently contaminated with the dust and débris which fall on the roofs whence it is usually collected. Such water is purified by *distillation*, an operation in which the water is by ebullition converted into steam, and the steam condensed again to water in a separate vessel, the fixed earthy and other salts remaining in the vessel in which the water is boiled.

of course not barium (Ba) itself, but chromate of barium ($BaCrO_4$), as any reader who has carefully gone through the "foregoing analytical reactions" will know. The occurrence of chromate of barium at this particular place, however, and under the circumstances described, is abundant evidence of the presence of barium (Ba, in some form or other) in the liquid analyzed—which was a part of the problem to be solved by the operator. Similar remarks apply, of course, to the Ca, which is finally precipitated as oxalate (CaC_2O_4), to Mg, which is thrown out as ammonio-phosphate ($MgNH_4PO_4$), to NH_4, Na, and K, and to the elements similarly alluded to in the other subsequent tables for "short" directions for analysis.

On the large scale, ebullition is effected in metal boilers having a hood or head in which is a lateral opening through which passes the steam ; on the small scale, either a common glass flask is employed, into the neck of which, by a cork, is inserted a glass tube

Fig. 28.
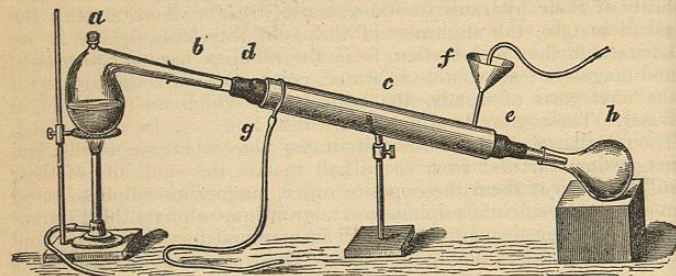
bent to an acute angle, or a *retort* is used (*a*, Fig. 28) a sort of long-necked Florence flask, dextrously bent near the body by the glass-worker to an appropriate angle (hence the name *retort*, from *retorqueo*, to bend back). *Condensation* is effected by surrounding the lateral steam-tube with cold water. In large stills the steam-tube, or *condensing-worm*, is usually a metal (tin) pipe, twisted into a spiral form for the sake of compactness, and so fixed in a tub that a few inches of one end of the pipe may pass through and closely fit a hole bored near the bottom of the tub. Cold water is kept in contact with the exterior of the pipe, provision being made for a continuous supply to the bottom, while the lighter water heated by the condensing steam runs off from the top of the column. The condenser for a flask or retort may be a simple glass tube of any size, placed within a second much wider tube (a common long, narrow lamp-glass answers very well for experimental operations), the inner tube being connected at the extremities of the wider by bored corks ; a stream of water passes into one end of the inclosed space (the end furthest from the retort) through a small glass tube inserted in the cork, and out at the other through a similar tube. The common (Liebig's) form of laboratory condenser is a glass tube three-fourths of an inch wide and a yard long (*b*, Fig. 28), surrounded by a shorter tin or zinc tube (*c*, Fig. 28) two inches in diameter, and having at each extremity a neck, through which the glass tube passes. The ends of the necks of the tin tube, and small portions of glass tube near them, are connected by means of a strip of sheet caoutchouc carefully bound round, or by short, wide India-rubber tubes (*d* and *e*, Fig. 28). An aperture near the lower part of the tin tube provides for the admission of a current of cold water, and a similar aperture near the top (*g*, Fig. 28) allows the escape of heated water. The inner tube may thus constantly be surrounded by cold water, and heated vapors passing through it be perfectly cooled and condensed in any receiver (*h*, Fig. 28).

The official Water (*Aqua*, U. S. P.) is to contain "not more than 1 part of fixed impurities in 10,000 parts," and to be so free from organic matter that when tinted rose-red with permanganate of potassium the color should not be destroyed after boiling the fluid for 5 minutes, or, in the case of Distilled Water, after setting the vessel aside, well covered, for ten hours.

In distilling several gallons of water for analytical or medicinal purposes (*Aqua Destillata*, U. S. P.) the first two or three pints should be rejected, because likely to contain ammoniacal and other volatile impurities.

Rectification is the process of redistilling a distilled liquid. *Rectified spirit* is spirit of wine thus treated.

Dry or *destructive distillation* is distillation in which the condensed products are directly formed by the decomposing influence of the heat applied to the dry or non-volatile substances in the retort or still.

EXERCISE.

184. Write from memory two or three paragraphs descriptive of *distillation*.

RECAPITULATION.

The subject just alluded to (distillation) naturally excites wonder respecting the cause of the physical difference between solid, liquid, and gaseous water. (Common observation will have suggested to the student that the force of heat has much to do with the difference, and if he will turn to the chapter on *latent heat* in any book on Physics he will find that, as already indicated (p. 85), when ice liquefies by heat a very large amount of heat must be used before the slightest rise of temperature occurs. Afterwards the addition of heat makes the water hotter and hotter until one other point is reached (the boiling-point), when here again a great amount of heat is absorbed without causing the slightest rise in temperature. Afterwards more heat makes the gaseous water hotter and hotter, until, like a bar of iron, the steam, under special conditions, is made red hot or white hot.) Different bodies absorb different amounts of heat in changing their physical condition from solid to liquid or liquid to gas (or vapor). The amount is constant for any one body, hence definite comparative numbers may be used for expressing the latent heats of substances.
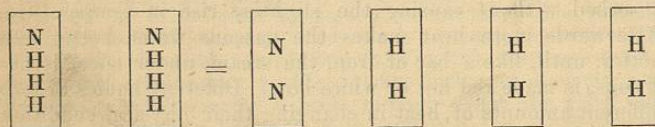
The absorption of heat at particular (liquefying and vaporizing) points must not be confounded with an analogous physical action, namely, the absorption of heat which goes on when a body is rising in temperature. The amount of this

absorption differs with different substances. That is to say, if equal weights of several substances, all at the same temperature, be all heated to a stated higher temperature, very different amounts of fuel will be required. The particular or specific amount in each case is always the same, hence the *specific heats* of substances may be expressed by numbers. See the chapter on "Specific Heat" in any manual of Physics.

But after reading what has been stated respecting the constitution of matter (pp. 42 to 45), the chemical student will, in connection with the subject of distillation, be led, once more, to think over the subject of the molecular constitution of solid, liquid, and gaseous water, and of the molecular condition of bodies generally. As previously stated, little can be told him respecting the molecular condition of solids and liquids, for temperature and pressure affect them unequally, whence we conclude that, though the relation to each other of the molecules of any one substance is constant, this relation is different in different bodies. Different *gases*, however, are not differently affected, but similarly affected by temperature and pressure, whence we conclude that their molecular constitution—the relations of their molecules to one another—is similar.

Another gas, ammonia, has been brought before the reader since the molecular constitution of gases was considered.

A small quantity of ammonia gas inclosed in the upper part of a roughly graduated test-tube over *mercury* (*water* would dissolve it) and exposed to the continuous action of the electric spark by means of wires of platinum fused in the sides of the tube, is decomposed into its elements nitrogen and hydrogen, the bulk of gas operated on being exactly doubled. This expansion is not due to the gaseous molecules receding from each other, but to every two molecules becoming four similar-sized molecules:—

$$
\begin{array}{|c|}\hline N \\ H \\ H \\ H \\\hline\end{array}
\begin{array}{|c|}\hline N \\ H \\ H \\ H \\\hline\end{array}
=
\begin{array}{|c|}\hline N \\ N \\\hline\end{array}
\begin{array}{|c|}\hline H \\ H \\\hline\end{array}
\begin{array}{|c|}\hline H \\ H \\\hline\end{array}
\begin{array}{|c|}\hline H \\ H \\\hline\end{array}
$$

Here each space (rectangular, chiefly for convenience in printing) represents a molecule, and each letter one atom. Each space, if regarded as the side of a double cube, may also, for the moment, represent two volumes—such two volumes yielding, in the decomposition, one volume of nitrogen and three volumes of hydrogen, or the four such volumes of ammo-

nia shown in the diagram yielding two volumes of nitrogen and six volumes of hydrogen.

Remembering that a symbol (of a gas) represents one volume, that *a formula (of a gas) always represents two volumes*, the pupil will now see how full of meaning is such an equation as the following, including, as it does, names of the elements, number of the atoms, nature of the molecules, number of the molecules, weights of atoms of the molecules, and therefore weights of bulks of the bodies, and extent of expansion in the disunion of the elements, and therefore their extent of contraction in the act of union:—

$$2NH_3 = N_2 + 3H_2.$$
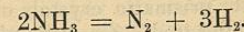
AT THIS STAGE THE LEARNER IS AGAIN RECOMMENDED TO READ THE PARAGRAPHS ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY, AND TO RETURN TO THEM FROM TIME TO TIME UNTIL THEY ARE THOROUGHLY COMPREHENDED.

ZINC, ALUMINIUM, IRON.

These three elements are classed together for analytical convenience rather than for more general analogies.

ZINC.

Symbol Zn.   Atomic weight 64.9.

Source.—Zinc is tolerably abundant in nature as sulphide (Zn''), or *blende*, and carbonate (ZnCO$_3$), or *calamine* (from *calamus*, a reed, in allusion to the appearance of the mineral). The ores are roasted to expel sulphur, carbonic acid gas, and some impurities, and the resulting oxide distilled with charcoal, when the metal vaporizes and readily condenses. Zinc is a brittle metal, but at a temperature somewhat below 300° F. is malleable, and may be rolled into thin sheets. Above 400° it is again brittle, and may then be pulverized. At 773° F. it melts, and at a bright red heat is volatile. Zinc in exceptionally fine powder ignites spontaneously, especially if damp or if stored in a warm place.

Uses.—Its use as a metal is familiar; alloyed with nickel and copper it yields german silver, with twice its weight of copper forms common brass, and as a coating on iron (the so-called *galvanized* iron) greatly retards the formation of rust. Most of the salts of zinc are prepared directly or indirectly from the metal (*Zincum*, U. S. P.).
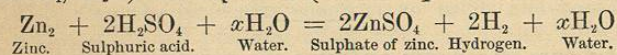
Quantivalence.—The atom of zinc is bivalent, Zn''.

Molecular Weight.—Some remarks on this point will be made under Mercury.

6*

REACTIONS HAVING (a) SYNTHETICAL AND (b) ANALYTICAL INTEREST.

(a) Synthetical Reactions.

Sulphate of Zinc.

First Synthetical Reaction.—Heat zinc (4 parts) with water (20 parts) and sulphuric acid (3 fl. parts) in a test-tube (or larger vessel) until gas ceases to be evolved; solution of sulphate of zinc ($ZnSO_4$) results. Filter (to separate the particles of lead, carbon, etc., commonly contained in sheet zinc), and concentrate the solution in an evaporating-dish; on cooling, colorless, transparent, prismatic crystals of Sulphate of Zinc ($ZnSO_4,7H_2O$) are deposited (*Zinci Sulphas*, U. S. P.).

$$Zn_2 + 2H_2SO_4 + xH_2O = 2ZnSO_4 + 2H_2 + xH_2O$$

Zinc.　Sulphuric acid.　Water.　Sulphate of zinc. Hydrogen.　Water.

Zinc does not displace hydrogen from the sulphuric acid alone, nor from the water alone, yet it does from the mixture. The possible explanation is that as sulphuric acid combines with several different quantities of water to form definite hydrous compounds (H_2SO_4,H_2O; $H_2SO_4,2H_2O$; etc.), it is one or more of these that is decomposed with elimination of hydrogen. At present we can only say that an unknown (x) amount of water is required in the reaction.

Note.—This reaction affords hydrogen and sulphate of zinc; it also develops electricity. Of several methods of evolving hydrogen, it is the most convenient; of the two or three means of preparing sulphate of zinc, it is the most commonly employed; and of the many reactions which may be utilized in the development of dynamic electricity, it is one of the most convenient. The apparatus in which the reaction is effected differs according to the requirements of the operator: if the sulphate of zinc alone is wanted, an open dish is all that is necessary, the action being, perhaps, accelerated by heat; if hydrogen, a closed vessel and delivery-tube; if electricity, square vessels called cells, and certain complementary materials, forming altogether what is termed a battery. In each operation for one product, the other two are commonly wasted. It would not be difficult for the operator, as a matter of amusement, to construct an apparatus from which all three products should be collected.

Purification.—Impure sulphate of zinc may be purified in the same manner as impure chloride (see next reaction).

Sulphate of zinc is isomorphous with sulphate of magnesium, and like that salt, loses six-sevenths of its water of crystallization at 212° F.

Chloride of Zinc.

Second Synthetical Reaction.—Dissolve zinc in hydrochloric acid mixed with half its bulk of water; the resulting solution
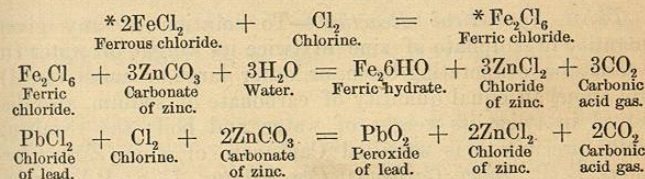
contains chloride of zinc. Evaporate the liquid till no more steam escapes; Chloride of Zinc ($ZnCl_2$) in a state of fusion remains, and on cooling is obtained as an opaque white solid (*Zinci Chloridum*, U. S. P.).

It is soluble in water, alcohol, or ether.

$$Zn_2 + 4HCl = 2ZnCl_2 + 2H_2$$

Zinc.　Hydrochloric acid. Chloride of zinc.　Hydrogen.
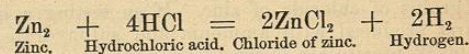
This reaction is analogous to that previously prescribed. The Burnett deodorizing or disinfecting liquid is solution of chloride of zinc.

Purification of Chloride or Sulphate of Zinc.—Zinc sometimes contains traces of iron or lead; and these, like zinc, are dissolved by most acids, with formation of soluble salts; they may be recognized in the liquids by applying the tests described hereafter to a little of the solution in a test-tube. Should either be present in the above solution, a little chlorine-water is added to the liquid till the odor of chlorine is permanent, and then the whole well shaken with some hydrate of zinc or the common official "carbonate" of zinc (really hydrato-carbonate—see p. 132). In this way iron is precipitated as ferric hydrate, and lead as peroxide :—

$$*2FeCl_2 + Cl_2 = *Fe_2Cl_6$$

Ferrous chloride.　Chlorine.　Ferric chloride.

$$Fe_2Cl_6 + 3ZnCO_3 + 3H_2O = Fe_26HO + 3ZnCl_2 + 3CO_2$$

Ferric chloride.　Carbonate of zinc.　Water.　Ferric hydrate.　Chloride of zinc.　Carbonic acid gas.

$$PbCl_2 + Cl_2 + 2ZnCO_3 = PbO_2 + 2ZnCl_2 + 2CO_2$$

Chloride of lead.　Chlorine.　Carbonate of zinc.　Peroxide of lead.　Chloride of zinc.　Carbonic acid gas.

In the British Pharmacopœia the possible presence of impurities in the zinc is recognized, and the process of purification just described incorporated with the process of preparation of *Zinci Chloridum*, *Liquor Zinci Chloridi*, and *Zinci Sulphas*. In the purification of the sulphate of zinc the action of chlorine on any ferrous sulphate will result in the formation of ferric sulphate as well as ferric chloride :—

$$6FeSO_4 + Cl_6 = 2(Fe_23SO_4) + Fe_2Cl_6;$$
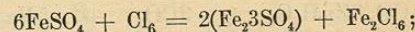
carbonate of zinc will then give chloride as well as sulphate of zinc, and thus the whole quantity of sulphate of zinc be slightly contaminated by chloride. On evaporating and crystallizing, however, the chloride of zinc will be retained in the mother-liquor. This process admits of *general* application.

For *Liquor Zinci Chloridi*, B. P., 1 pound of zinc is placed in a mixture of 44 fluidounces of hydrochloric acid and 20 of water, the

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* It will be noticed that the atom of iron is represented, in these equations, as exerting both bivalent and trivalent activity; this will be alluded to when iron comes under consideration.