

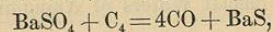
BARIUM, CALCIUM, MAGNESIUM.

These three elements have many analogies. Their atoms are bivalent.

BARIUM.

Symbol Ba. Atomic weight 136.8.

The analytical reactions only of this metal are of interest to the general student of pharmacy. The nitrate (Ba_2NO_3) and the chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) are the soluble salts in common use in analysis ("Test-Solution of Chloride of Barium," 1 in 10 of water, U. S. P.); and these and others are made by dissolving the native carbonate (BaCO_3), the mineral *witherite*, in acids, or by heating the other common natural compound of barium, the sulphate, *heavy white* or *heavy spar* (BaSO_4), with coal, which yields sulphide of barium (BaS),



and dissolving the sulphide in appropriate acids. When the nitrate is strongly heated, it is decomposed, the oxide of barium or *baryta* (BaO) remaining. Baryta, on being moistened, assimilates the elements of water with great avidity, and yields hydrate of barium (Ba_2HO). The latter is tolerably soluble, giving *baryta-water*; and from this solution crystals of hydrate of barium are obtained on evaporation.

The operations above described may all be performed in test-tubes and small porcelain crucibles heated by the gas-flame. Quantities of 1 oz. to 1 lb. require a coke-furnace.

Peroxide of barium (BaO_2) is formed on passing air over baryta heated to about 600°F . On raising the temperature, oxygen is evolved and baryta remains. This is Boussingault's old process. But the baryta loses its absorbing power after a time. If the air be freed from carbonic acid gas and the peroxide be not exposed to a much higher temperature than 800°F . (by heating in a vacuum), the baryta can be used over and over again. This improvement is by Messrs. Brin, who sell the oxygen compressed within strong metal cylinders. By the action of dilute hydrochloric acid it yields solution of *peroxide of hydrogen* (H_2O_2), the old *oxygenated water*. On neutralizing solution of peroxide of hydrogen with ammonia and adding permanganate of potassium, oxygen gas is evolved, its volume indicating the oxygen-strength of the original solution.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

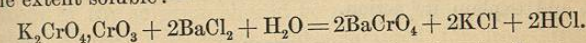
First Analytical Reaction.—To the aqueous solution of any soluble salt of barium (nitrate or chloride, for example) add dilute sulphuric acid; a white precipitate is obtained. Set the test-tube aside for two or three minutes, and when some of the precipitate has fallen to the bottom pour away the supernatant liquid; wash the precipitate by adding water, shaking, setting aside, and again decanting; then add strong nitric acid, and boil; the precipitate is insoluble.

The production of a white precipitate by sulphuric acid, insoluble even in hot nitric acid, is highly characteristic of barium. The name of this precipitate is sulphate of barium; its formula is BaSO_4 .

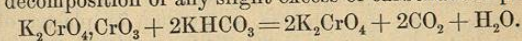
Antidotes.—In cases of poisoning by soluble barium salts, obvious antidotes would be solutions of alum or of any sulphates, such as those of magnesium and sodium (Epsom salt, Glauber's salt).

Second Analytical Reaction.—To a barium solution add solution of the yellow chromate of potassium (K_2CrO_4); a pale yellow precipitate (BaCrO_4) falls. Add acetic acid to a portion of the chromate of barium; it is insoluble. Add hydrochloric or nitric acid to another portion; it is soluble.

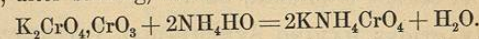
"Neutral Chromate."—The red chromate (or bichromate) of potassium ($\text{K}_2\text{CrO}_4, \text{CrO}_3$) must not be used in this reaction, or the barium will be only imperfectly precipitated; for the red salt gives rise to the formation of free acid, in which chromate of barium is to some extent soluble:—



Yellow chromate is obtained on adding bicarbonate of potassium, in small quantities at a time, to a hot solution of the red chromate until effervescence ceases; a little more red chromate is then added to ensure decomposition of any slight excess of carbonate of potassium.



For analytical purposes, solution of a neutral chromate is still more readily prepared by simply adding solution of ammonia to solution of red chromate of potassium, until the liquid turns yellow, and, after stirring, smells of ammonia.



Other Analytical Reactions.—To a barium solution add a soluble carbonate (carbonate of ammonium ($(\text{NH}_4)_2\text{CO}_3$) will generally be rather more useful than others); a white precipitate of carbonate of barium (BaCO_3) results.—To more of the solution add an alkaline phosphate or arseniate (phosphate of sodium (Na_2HPO_4) is the most common of these chemically analogous salts, but phosphate of ammonium (Am_2HPO_4) or arseniate (NH_4HAsO_4) will subsequently have the preference); white phosphate of barium (BaHPO_4), insoluble in pure water, but slightly soluble in aqueous solutions of some salts, or arseniate of barium (BaHAsO_4), both soluble even in acetic and other weak acids, are precipitated.—To another portion add oxalate of ammonium ($(\text{NH}_4)_2\text{C}_2\text{O}_4$); white oxalate of barium (BaC_2O_4) is precipitated, soluble in the diluted mineral acids, and sparingly so in acetic acid.—The silico-fluoride of barium (BaSiF_6) is insoluble, and falls readily if an equal volume of spirit of wine be added to the solution under examination after

the addition of hydrofluosilicic acid (H_2SiF_6).—Barium salts, moistened with hydrochloric acid, impart a greenish color to flame.

Mem.—Good practice will be found in writing out equations descriptive of each of the foregoing reactions.

QUESTIONS AND EXERCISES.

138. What is the quantivalence of barium?
139. Write down the formulæ of oxide, hydrate, chloride, nitrate, carbonate, and sulphate of barium; and state how these salts are prepared.
140. Describe the preparation of peroxide of hydrogen.
141. Which of the tests for barium are most characteristic? Give an equation of the reactions.
142. Name the antidote in cases of poisoning by soluble barium salts, and explain its action.

CALCIUM.

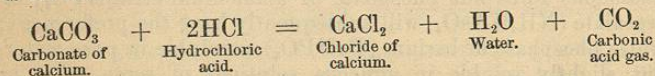
Symbol Ca. Atomic weight 40.

Calcium compounds form a large proportion of the crust of our earth. Carbonate of calcium is met with as chalk, marble, limestone, calc-spar, etc.; the sulphate, as gypsum or plaster of Paris (native sulphate of calcium— $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ —rendered nearly anhydrous by heat), and alabaster; the silicate in many minerals; the fluoride of calcium as fluor-spar. The phosphate is also a common mineral. The element itself is only isolated with great difficulty. The atom of calcium is bivalent, Ca^{++} .

REACTIONS HAVING SYNTHETICAL INTEREST.

Chloride of Calcium.

First Synthetical Reaction.—To some hydrochloric acid add carbonate of calcium (chalk, or, the purer form, white marble) (CaCO_3) until effervescence ceases, filter; solution of chloride of calcium (CaCl_2), the most common soluble salt of calcium, is formed.



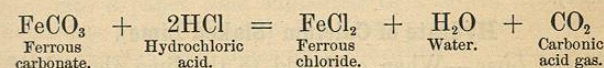
This solution contains carbonic acid, and will give a precipitate of carbonate of calcium on the addition of lime-water. It may be obtained quite neutral by well boiling before filtering off the excess of marble. It is a serviceable test-liquid in analytical operations.

Solution of chloride of calcium evaporated to a syrupy consistence readily yields crystals ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$). These are extremely deliquescent. The solution, evaporated to dryness, and the white residue heated to about 200°C ., gives solid chloride of calcium

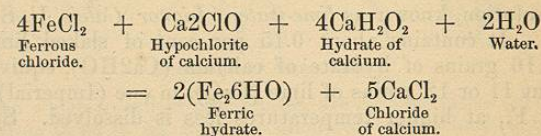
($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in a porous form. The resulting agglutinated lumps (*Calcii Chloridum*, U. S. P.) are much used for drying gases and for freeing certain liquids from water. The salt is soluble in alcohol. One part of the salt in ten of water constitutes a useful test-liquid, "Test-solution of Chloride of Calcium," U. S. P.

Mem.—The practical student has already met with solution of chloride of calcium as a by-product or secondary product in the preparation of carbonic acid gas.

Marble often contains ferrous carbonate (FeCO_3), which in the above process becomes converted into ferrous chloride, rendering the chloride of calcium impure:—



If absolutely pure chloride of calcium be required, a few drops of the solution should be poured into a test-tube or test-glass, diluted with water, and examined for iron (by adding sulphhydrate of ammonium, which gives a black precipitate with salts of iron), and, if the latter is present, hypochlorite of calcium (in the form of chlorinated lime) and slaked lime should be added to the remaining bulk of the liquid, and the whole boiled for a few minutes, whereby iron (as ferric hydrate) is thus precipitated; on filtering, a pure solution of chloride of calcium is obtained:—

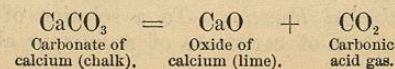


This is the official process, and may be imitated on the small scale after adding a minute piece of iron to a fragment of the marble before dissolving in acid.

The names, formulæ, and reactions of these compounds of iron will be best understood when that metal comes under treatment.

Oxide of Calcium (Quick Lime).

Second Synthetical Reaction.—Place a small piece of chalk in a strong grate-fire or furnace and heat until a trial fragment, chipped off from time to time and cooled, no longer effervesces on the addition of acid; caustic lime, CaO (*Calc.*, U. S. P.), remains.

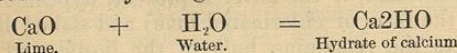


Note.—Etymologically considered, this action is analytical (*ἀναλυσ*, *analuo*, I resolve) and not synthetical (*συνθεσις*, *synthesis*, a putting together); but conventionally it is synthetical, and not analytical; for in this, the usual sense, synthesis is the application of chemical action with the view of producing something, analysis the application of chemical action with the view of finding out the composition of a substance. In the etymological view of the matter, there is scarcely an operation performed either by the analyst or by the manufacturer but includes both analysis and synthesis—that is, includes interchange, or *metathesis*.

Lime-kilns.—On the large scale the above operation is carried on in what are termed *lime-kilns* (*Kiln*, Saxon, *cyln*, from *cylene*, a furnace).

Hydrate of Calcium (Slaked Lime).

Slaked Lime.—When cold, add to the lime about half its weight of water, and notice the evolution of steam and other evidence of strong action; the product is *slaked* lime or hydrate of calcium (Ca_2HO), with whatever slight natural impurities the lime may contain. The slaking of hard or “stony” lime may be accelerated by using hot water.



Lime-water.—Place the hydrate of calcium (washed with a little water to remove traces of soluble salts) in about a hundred times its weight of water; in a short time a saturated solution, known as *lime-water* (*Liquor Calcis*, U. S. P.), results. It contains about 0.15 per cent of slaked lime, or about 16 grains of hydrate of calcium (Ca_2HO), equivalent to about 11 or 12 grains of lime (CaO), in one (Imperial) pint at 60° F., at higher temperatures less is dissolved. Sp. gr. 1.0015.

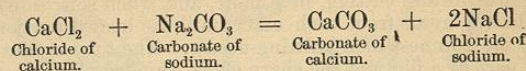
Strong Solution of Lime.—Slaked lime is more soluble in aqueous solution of glycerin and much more soluble in aqueous solution of sugar than in pure water. The *Syrupus Calcis*, U. S. P., is such a solution, containing 5 parts of lime and 30 of sugar in 100 parts, by weight, of fluid.

Solutions of hydrate of calcium absorb carbonic acid gas on exposure to air, a semi-crystalline precipitate of carbonate being deposited. When the saccharated solution is heated, there is precipitated a compound consisting of three molecules of lime with one of sugar. When it is freely exposed to air, oxygen is absorbed and the solution becomes colored.

Carbonate of Calcium.

Third Synthetical Reaction.—To a solution of chloride of calcium add excess of carbonate of sodium, or about 5 parts

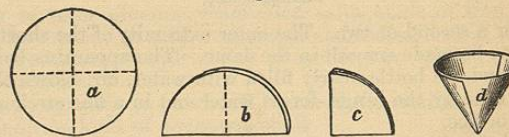
of dry chloride to 13 of carbonate; a white precipitate of carbonate of calcium (*Calcii Carbonas Præcipitatus*, U. S. P.) (CaCO_3) results. If the solutions of the salts be made hot before admixture, and the whole set aside for a short time, the particles aggregate to a greater extent than when cold water is used, and the product is finely granular or slightly crystalline.



Collect and purify this *Precipitated Chalk* by pouring the mixture into a paper cone supported by a funnel, and, when the liquid has passed through the filter, pour water over the precipitate three or four times until the whole of the chloride of sodium is washed away. This operation is termed *washing a precipitate*. When dried by aid of a water-bath (p. 110) or other means, the precipitate is fit for use.

Filtering-paper, or *bibulous-paper* (from *bibo*, to drink), is simply good unsized paper made from the best white rags—white blotting-paper, in fact, of unusually good quality. Students' or analysts'

Fig. 22.



Construction of Paper Filters.

filters, on which to collect precipitates, are circular pieces (*a*) of this paper, from three to six inches in diameter, twice folded (*b*, *c*), and then opened out so as to form a lollow cone (*d*). Square pieces of filter paper are rounded by scissors after twice folding. The cone is supported by a glass or earthenware funnel.

Filters should *always* be cut round so as to form a cone. If the square piece of paper is folded and used without being so cut or trimmed, an ugly angular filter results, from which it is difficult to wash all “mother-liquor” (the solution of chloride of sodium is the “mother-liquor” in the previous reaction). Moreover, if a spirituous or other volatile liquor is being passed through such an angular filter, much of the liquid will also be wasted by evaporation from the unnecessarily large surface exposed.

Paper filters of large size are apt to break at the point of the cone. This may be prevented, and the rate of filtration be much accelerated, by supporting the paper cone in a cone of muslin.

Washing-bottle.—Precipitates are best washed by a fine jet of water directed on to the different parts of the filter. A common narrow-necked bottle of about half-pint capacity (Fig. 23) is fitted

with a cork; two holes are bored through the cork, the one for a glass tube reaching to the bottom of the bottle within, and externally bent to a slightly acute angle, the other for a tube bent to a slightly obtuse angle, the inner arm terminating just within the bottle. The outer arms may be about 3 inches in length. The extremity of the outer arm continuous with the long tube should be previously drawn out to a fine capillary opening by holding the original tube, before cutting, in a flame, and, when soft, slowly pulling the halves away from each other until the heated portion is reduced to the thinness of a knitting-needle. The tube is now cut at the thin part by a file, and the sharp edges rounded off by placing in

Fig. 23.



Washing-bottles.

Fig. 24.



a flame for a second or two. The outer extremity of the shorter tube should also be made smooth in the flame. The apparatus being put together, and the bottle nearly filled with water, air, blown through the short tube by the lungs, forces water out in a fine stream at the capillary orifice.

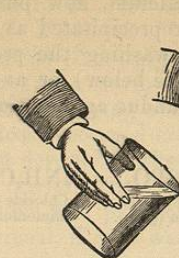
For a *hot-water washing flask* (Fig. 24) the tubes and cork are fitted to a flask which may be heated. A strip of leather tied round the neck will protect the fingers.

Decantation.—Precipitates may also be washed by allowing them to settle, pouring off the supernatant liquid (Fig. 25), agitating with water, again allowing to settle, and so on. This is washing by *decantation* (*de*, from, *canthus*, an edge). If a stream of liquid flowing from a basin or other vessel exhibits any tendency to run down the outer side of the vessel, it should be guided by a glass rod placed against the point whence the stream emerges (Fig. 26).

If the vessel be too large to handle with convenience, the wash water may be drawn off by a *siphon*, as shown in miniature in Fig. 27. A siphon is a tube of glass, metal, gutta-percha, or India-rubber bent into the form of a V or U, filled with water, and inverted; one end immersed in the wash-water, and the other allowed to hang over the side of the vessel. So long as the outer orifice of the instrument is below the level of any liquid in the vessel, so long will that liquid flow from within outwards.*

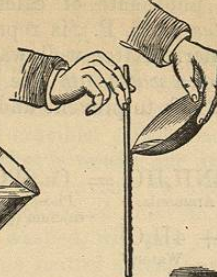
* The nature of the action of a siphon is simple. The column of water in the outer limb is longer, and therefore heavier than the column of

Fig. 25.



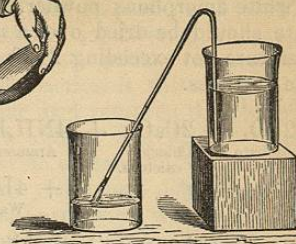
Decantation.

Fig. 26.



Decantation.

Fig. 27.



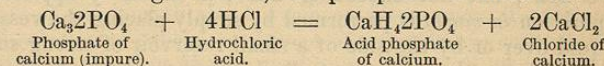
Siphon in action.

Prepared carbonate of calcium (*Creta Præparata*, U. S. P.) is merely washed chalk or *whiting*, only that in pharmacy fashion demands that the chalk be in little conical lumps, about the size of thimbles, instead of the larger rolls characteristic of "whiting." Wet whiting pushed, portion by portion, through a funnel, and each separately dried, gives the conventional *Creta Præparata*. Its powder is amorphous. If either the precipitated or prepared carbonate of calcium contains alumina, magnesian salts, oxide of iron, or phosphates, its solution in acid, evaporated and redissolved in water, will yield a precipitate of hydrates or phosphates on addition of saccharated solution of lime.

Testa Præparata is powdered oyster-shell, similarly treated. It is an inferior kind of prepared chalk.

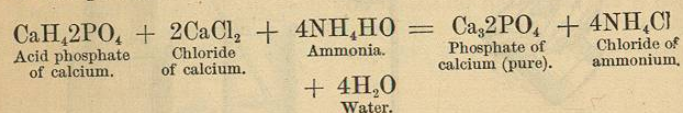
Phosphate of Calcium.

Fourth Synthetical Reaction.—Digest bone-ash (bones burnt in an open crucible with free access of air until all animal and carbonaceous matter has been removed—impure phosphate of calcium (*Os Ustum*, B. P.)) with twice its weight of hydrochloric acid diluted with four times its bulk of water, in a test-tube or larger vessel; the phosphate is dissolved.



similar area in the inner limb. (The length of the inner limb must be reckoned from the surface of the liquid, the portion below the surface playing no part in the operation.) Being heavier, it naturally falls by gravitation, the liquor in the shorter limb instantly following, because pressed upwards by the air. The air, be it observed, exerts a similar amount of pressure on the liquid in the outer limb: in short, atmospheric pressure causes the retention of liquid in the instrument, while gravitation determines the direction of the flow.

Dilute with water, filter, boil, and when cold add excess of solution of ammonia; the phosphate of calcium, now pure (*Calcii Phosphas Præcipitatus*, U. S. P.), is reprecipitated as a light white amorphous powder. After well washing the precipitate should be dried over a *water-bath* (see below), or at a temperature not exceeding 212°, to prevent undue aggregation of the particles.



Bone-ash or bone-earth contains small quantities of carbonate and sulphide of calcium. These are decomposed in the above process by the acid, chloride of calcium being formed; on boiling the mixture, carbonic acid gas and sulphuretted hydrogen gas are evolved. Any carbonaceous or siliceous matter, etc. is removed by filtration. In bones the phosphate of calcium is always accompanied by a small quantity of an allied substance, phosphate of magnesium; a trace of fluoride of calcium (CaF_2) is also present.

A *Water-bath* for the evaporation of liquids or for drying moist solids at temperatures below 212° F. is an iron, tin, or earthenware pan, the mouth of which can be narrowed by iron or tin diaphragms of various sizes, and having orifices adapted to the diameters of evaporating dishes or plates. In the British Pharmacopœia, "when a *water-bath* is directed to be used, it is to be understood that this term refers to an apparatus by means of which water or its vapor, at a temperature not exceeding 212°, is applied to the outer surface of a vessel containing the substance to be heated, which substance may thus be subjected to a heat near to, but necessarily below, that of 212°. In the *steam-bath* the vapor of water at a temperature above 212°, but not exceeding 230°, is similarly applied." Evaporation *in vacuo* is performed by simply placing the vessel of liquid over or by the side of a small reservoir of strong sulphuric acid, or other absorbent of moisture, on the plate of an air-pump, covering with a capacious glass hood or "receiver," and exhausting.

Bone-black, or *Animal Charcoal* (*Carbo Animalis*, U. S. P.), is the residue obtained on subjecting dried bones to a red heat without access of air. It is a mixture of about 9 parts of mineral matter with 1 of carbonaceous matter. The operation may be imitated by heating a few fragments of bone in a covered

porcelain crucible in a fume chamber until smoke and vapor cease to be evolved. Purified Animal Charcoal (*Carbo Animalis Purificatus*, U. S. P.) is obtained by digesting animal charcoal (2 parts) in hydrochloric acid (3 parts) and water (30 parts) in a warm place for a day or so, filtering, thoroughly washing, drying over a *water-bath*, and igniting the product in a closely covered crucible. The reaction is the same as that just described; that is to say, the acid removes the phosphate of calcium from the carbon of animal charcoal by forming soluble acid phosphate and chloride of calcium. The residual charcoal, if well washed, will not yield more than about 2 per cent. of calcareous matter when burnt with free access of air or with the aid of the oxygen of a little red oxide of mercury.

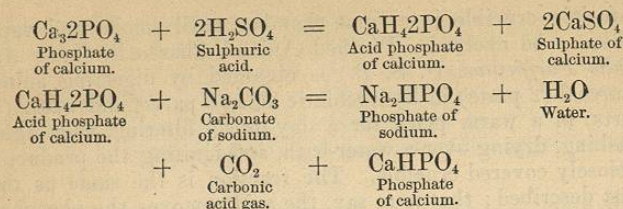
Wood Charcoal (*Carbo Ligni*, U. S. P.) is wood similarly ignited without access of air.

Decolorizing Power of Animal Charcoal.—Animal charcoal, in small fragments, is the material employed in decolorizing solutions of common brown sugar with the view of producing white lump sugar. Its power and the nearly equal power of an equivalent quantity of the purified variety may be demonstrated on solution of litmus or logwood.

Syrupus Calcii Lacto-phosphatis, U. S. P., is a flavored solution of precipitated phosphate of calcium in lactic acid.

Phosphate of Sodium.—Phosphate of calcium is converted into phosphate of sodium (*Sodii Phosphas*, U. S. P.) ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) as follows: Mix, in a mortar, 3 ounces of ground bone-earth with one fluidounce of sulphuric acid; set aside for twenty-four hours to promote reaction; mix in about 3 ounces of water, and put in a warm place for two days, a little water being added to make up for that lost by evaporation; stir in another 3 ounces of water, warm the whole for a short time, filter, and wash the residual sulphate of calcium on the filter to remove adhering acid phosphate of calcium; concentrate the filtrate (the liquid portion), which is a solution of acid phosphate of calcium, to about 3 ounces, filter again, if necessary, add solution of (about 4½ ounces of crystals of) carbonate of sodium to the hot filtrate until a precipitate (a phosphate of calcium, CaHPO_4) ceases to form, and the fluid is faintly alkaline; filter, evaporate, and set aside to crystallize.

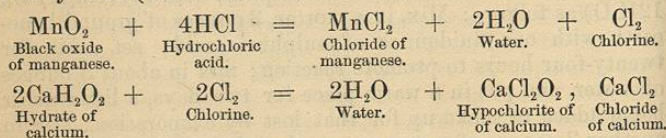
Phosphate of sodium occurs "in transparent colorless rhombic prisms, terminated by four converging planes, efflorescent, tasting like common salt." One part to ten of water constitutes "Solution of Phosphate of Sodium," B. P. The following equations show the two decompositions which occur during the operation:—



Ordinary phosphate of sodium ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) effloresces rapidly in the air until nearly half its water has escaped, when it has a permanent composition represented by the formula $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$. Phosphate of sodium has an alkaline reaction; neutralization by acid results in the removal of half its sodium and formation of the salt $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$.

Hypochlorite of Calcium.

Fifth Synthetical Reaction.—Pass chlorine, generated as already described, into damp slaked lime contained in a piece of wide tubing, open at the opposite end to that in which the delivery-tube is fixed. (A test-tube, the bottom of which has been accidentally broken, is very convenient for such operations.) The product is ordinary *bleaching-powder*, a compound of hypochlorite and chloride of calcium, commonly called *chloride of lime* (*Calx Chlorata*, U. S. P.).



Chlorinated lime, exposed to air and moisture, as in disinfecting the air of sick-rooms, slowly yields hypochlorous acid (HClO). Free hypochlorous acid soon breaks up into water, chloric acid (HClO_3), and free chlorine. Chloric acid is also unstable, decomposing into oxygen, water, chlorine, and perchloric acid (HClO_4). The small quantity of hypochlorous acid diffused through an apartment when bleaching-powder is exposed thus, yields fourteen-fifteenths of its chlorine in the form of chlorine gas—one of the most efficient of known disinfectants.

Constitution of Bleaching-powder.—Treated with alcohol, bleaching-powder does not yield its chloride of calcium to the solvent, hence the powder is not a mere mixture of chloride and hypochlorite of calcium: water, also, does not dissolve out first one salt, and then the other, but both together, in the molecular proportions of the above formula. On the other

hand, when the aqueous solution is cooled, or evaporated *in vacuo*, crystals are obtained which Kingzett has shown to be nearly pure hypochlorite of calcium, the solution containing chloride of calcium. While the former fact indicates that the powder is a compound, and not a mere mixture, the latter indicates that it is a feeble compound; an adhesion of molecules of hypochlorite and chloride, as shown in the equation, rather than any more intimate or closer combination of atoms. If it be regarded as a single rather than a double salt, then the

following formula may be employed, CaOCl_2 or $\text{Ca} \begin{Bmatrix} \text{Cl} \\ \text{ClO} \end{Bmatrix}$.

Bleaching-liquor.—Digest chlorinated lime in water, in which the bleaching compound is soluble, filter from the undissolved lime, and test the bleaching powers of the clear liquid by adding a few drops to a decoction of logwood slightly acidulated. One pound of this bleaching-powder, shaken several times during three hours with 1 gallon of water, forms Solution of Chlorinated Lime (*Liquor Calcis Chlorinatæ*, B. P.).

Sixth Synthetical Reaction.—Heat a mixture of 10 parts of powdered lime and 9 of sulphur in a crucible having a luted cover for an hour. The product, when cold, rubbed to powder, constitutes Sulphurated Lime (*Calx Sulphurata*, U. S. P.). It should contain not less than 36 per cent. of sulphide of calcium (CaS); the remainder is sulphate, with, probably, sulphite and hyposulphite of calcium.

Gummate of Calcium.

Gummate of Calcium is the only official calcium salt that remains to be noticed. This compound is, in short, *arabin*, the ordinary Gum Acacia, or Gum Arabic (*Acacia*, U. S. P.), a substance too well known to need description. A solution of gum arabic in water (*Mucilago Acaciæ*, U. S. P.) yields a white precipitate of oxalate of calcium on the addition of solution of oxalate of ammonium. Or a piece of gum burnt to an ash in a porcelain crucible yields a calcareous residue, which, dissolved in dilute acids, affords characteristic reactions with any of the following analytical reagents for calcium. In some specimens of gum arabic a portion of the calcium is displaced by an equivalent quantity of potassium or magnesium. The gummie or arabic radical may be precipitated as opaque gelatinous gummate of lead by the addition of solution of oxy-acetate of lead (*Liquor Plumbi Subacetatis*, U. S. P.) to an aqueous solution of gum. These statements may be experimentally verified by the practical student.

Tragacanth (*Tragacantha*, U. S. P.) is a mixture of soluble arabinoid gum and a variety of calcium gum insoluble in water, termed *bassorin*. With water a gelatinous mucilage is formed (*Mucilago Tragacanthæ*, U. S. P., contains 6 parts of tragacanth, 18 of glycerin, and 76 of water).

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Add sulphuric acid, very highly diluted, to a calcium solution contained in a test-tube or small test-glass; sulphate of calcium ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is formed, but is not precipitated, it being, unlike sulphate of barium, slightly soluble in water.

Solution of Sulphate of Calcium.—A quarter of an ounce of that (dried) form of sulphate of calcium known as plaster of Paris (CaSO_4) digested in one pint of water for a short time, with occasional shaking, and the mixture filtered, yields the official test-liquid termed "Solution of Sulphate of Calcium," B. P. About 400 parts of the solution contain 1 of calcium.

Second Analytical Reaction.—Add yellow chromate of potassium (K_2CrO_4) or other neutral chromate (KNH_4CrO_4), to a calcium solution slightly acidified with acetic acid; chromate of calcium (CaCrO_4) is probably formed, but it is not precipitated. Barium is precipitated by the chromic radical.

These two negative reactions are most valuable in analysis, as every precipitant of calcium is also a precipitant of barium; but the above two reagents are precipitants of barium only. Hence calcium, which when alone can be readily detected by the following reactions, cannot by any reaction be detected in the presence of barium. But by the sulphuric or chromic test barium is easily removed, and then either of the following reagents will throw down the calcium.

Other Analytical Reactions.—Add carbonate of ammonium, phosphate of sodium, arseniate of ammonium, and oxalate of ammonium to calcium solutions as described under the analytical reactions of barium, and write out descriptive equations. The precipitates correspond in appearance to those of barium; their constitution is also similar, hence their correct formulæ can easily be deduced. Of these precipitants oxalate of ammonium is that most commonly used as a reagent for calcium salts, barium being absent. The oxalate of calcium is insoluble in acetic, but soluble in hydrochloric or nitric acid.—Calcium compounds impart a reddish color to the flame.

QUESTIONS AND EXERCISES.

143. Enumerate some of the common neutral compounds of calcium. *Chalk, marble, lime, &c.*

144. Explain, by an equation, the action of hydrochloric acid on marble. What official compounds result? *But $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$*

145. Why is chloride of calcium used as a desiccator for gases? *It absorbs oxygen.*

146. How would you purify Chloride of Calcium which has been made from ferruginous marble? Give diagrams. *$\text{Ca}_2\text{Cl}_2\text{O} + 4\text{CaH}_2\text{O}_2 + 2\text{H}_2\text{O} =$*

147. Write a few lines on the chemistry of the lime-kiln. *$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$*

148. In what sense is the conversion of chalk into lime an analytical action? *$\text{Ca} + \text{heat} = \text{CaO} + \text{H}_2\text{O} = \text{Ca}_2\text{HO}$*

149. What occurs when lime is "slaked"? *$\text{CaO} + \text{H}_2\text{O} = \text{heat}$*

150. To what extent is lime soluble in water? to what in syrup? *$5\text{Pt} \text{ CaO} + 30\text{Pt} \text{ Si}$*

151. Describe the preparation of the official Precipitate of Carbonate of Calcium; in what does it differ from Prepared Chalk? *It is made from the best white*

152. In what does filtering-paper differ from other kinds of paper? *It is made from the best white*

153. Explain the construction of a "washing-bottle" for cleansing precipitates by water. *It holds a liquid with two holes through the*

154. Describe decantation. *It is done by pouring the liquid from one vessel into another, leaving the solid behind.*

155. Describe the construction and manner of employment of a siphon. *A siphon is a glass or rubber tube, bent at the other end, and used for drawing liquid from one vessel into another.*

156. Explain the mode of action of a siphon. *It is based on the difference in the level of the liquid in the two vessels.*

157. What is the difference between Bone, Bone-earth, and Precipitated Phosphate of Calcium?

158. How is "Bone-earth" purified for use in medicine?

159. Explain the action of hydrochloric acid on Animal Charcoal in the conversion of *Carbo Animalis* into *Carbo Animalis Purificatus*.

160. What is the chemical difference between *Carbo Animalis* and *Carbo Ligni*?

161. Give equations showing the conversion of Phosphate of Calcium into Phosphate of Sodium.

162. Write a short article on the manufacture, composition, and uses of "bleaching-powder."

163. How may calcium be detected in Gum Arabic?

164. State the chemical nature of Tragacanth.

165. To what extent is sulphate of calcium soluble in water?

166. Can calcium be precipitated from an aqueous solution containing barium?

167. Barium being absent, what reagents may be used for the detection of calcium? Which is the chief test?

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 ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) 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.

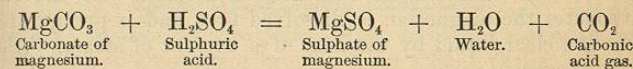
Quantivalence.—The atom of magnesium is bivalent, Mg'' .

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* ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) (*Magnesium Sulphate*, 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, $\text{CaCO}_3 \cdot \text{MgCO}_3$), 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.)

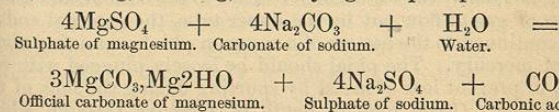


Sulphate of magnesium readily crystallizes in large, colorless, transparent, rhombic prisms; but, from concentrated solutions, the crystals are deposited in short thin needles, a form more convenient for manipulation, solution, and general use in medicine.

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_2OH) 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 (*Magnesia Carbonas Levis*, B. P.; *Magnesium Carbonas*, U. S. P.), the old *light* carbonate of magnesia, a white, partly amorphous, partly minutely crystalline mixture of carbonate and hydrate of magnesium ($3\text{MgCO}_3 \cdot \text{Mg}_2\text{HO} \cdot 4\text{H}_2\text{O}$, B. P.; $4\text{MgCO}_3 \cdot \text{Mg}_2\text{HO} \cdot 5\text{H}_2\text{O}$, U. S. P.). A denser, slightly granular precipitate of similar chemical composition (*Magnesia 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.



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