

The practical student should examine solutions containing the common metals until he is able to analyze with facility and accuracy. In this way he will best perceive the peculiarities of each element and their general relations to each other. As the rarer metals are not included here, the tables are not complete analytical schemes; only general memoranda respecting them will therefore now be given.

MEMORANDA RELATING TO THE GENERAL ANALYTICAL
TABLE (PAGE 220).

The *group-tests* adopted in the Table are, obviously, *hydrochloric acid*, *sulphuretted hydrogen*, *sulphydrate of ammonium*, *carbonate of ammonium*, and *arsenate of ammonium*. If a group-test produces no precipitate, it is self-evident that there can be no member of the group present. At first, therefore, add only a small quantity of a group-test, and if it produces no effect add no more; for it is not advisable to overload a solution with useless reagents; substances expected to come down as precipitates are not unfrequently held in the liquid by excess of acid, alkali, or strong aqueous solution of some group-reagent, thoughtlessly added. Indeed, experienced manipulators not unfrequently make preliminary trials with group-reagents on a few drops only of the liquid under examination; if a precipitate is produced, it is added to the bulk of the original liquid and the addition of the group-reagent continued; if a precipitate is not produced, the few drops are thrown away, and the unnecessary addition of a group-reagent thus avoided altogether, an advantage fully making up for the extra trouble of making a preliminary trial.—While shunning excess, however, care must be taken to avoid deficiency; a substance only partially removed from solution through the addition of an insufficient amount of a reagent will appear where not expected, be consequently mistaken for something else, and cause much trouble; this will not occur if the appearance, odor, or reaction of the liquid on test-paper be duly observed. It is also a good plan, when a group-reagent has produced a precipitate and the latter has been filtered out, to add a little more of the reagent to the clear filtrate; if more precipitate is produced, an insufficient amount of the group-test was introduced in the first instance; but the error is corrected by simply refiltering; if no precipitate occurs, the mind is satisfied and the way cleared for further operations.

Group-precipitates, or any precipitates still requiring examination, should, as a rule, be well washed before further testing; this is to remove the aqueous solution of other substances ad-

hering to the precipitate (the mother liquor, as it is termed), so that subsequent reaction may take place fairly between the reagent used and the precipitate only.—A precipitate is sometimes in so fine a state of division as to retard filtration by clogging the pores of the paper, or even to pass through the filter altogether; in these cases the mixture may be warmed or boiled (or a fresh quantity of the original solution may be warmed *before* the group-test is added), which usually causes aggregation of the particles of a precipitate, and hence facilitates the passage of liquids.

Division of Work.—It is immaterial whether a solution be first divided into group-precipitates or each precipitate be examined as soon as produced; if the former method be adopted, confusion will be avoided by labelling or marking the funnels or papers holding the precipitate, "the HCl ppt.," "the H₂S ppt.," and so on.

The colors and general appearance of the various sulphides and hydrates precipitated should be borne in mind, as the absence of other bodies, as well as the presence of those thrown down, is often at once thus indicated.

Application of confirmatory tests must be frequent.

Results of analysis should be recorded neatly in a memorandum-book.

The various reactions which occur in an analysis have already come before the reader in going through the tests for the individual metals or in other analytical operations; it is unnecessary, therefore, again to draw out equations or diagrams. But the reactions should be thought over, and if not perfectly clear to the mind, be written out again and again till thoroughly understood.

QUESTIONS AND EXERCISES.

339. Give processes for the qualitative analysis of liquids containing the following substances:—*a.* Antimony and Mercurous salt; *b.* Lead and Calcium; *c.* Silver and Mercurous salt; *d.* Lead and Mercuric salt; *e.* Copper and Arsenicum; *f.* Arsenicum and Antimony; *g.* Aluminium and Zinc; *h.* Iron and Copper; *i.* Magnesium, Calcium, and Potassium; *j.* Silver, Antimony, Zinc, Barium, and Ammonium.

340. Enumerate the so-called group-tests.

341. Give a general sketch of the method of analyzing a solution suspected to contain two or more salts of common metals.

342. Classify the common metals according to their analytical relations.

METALS OF MINOR PHARMACEUTICAL IMPORTANCE.

Thus far has been considered, somewhat in detail, the chemistry of the common metals, salts of which are frequently used in medicine or in testing medical substances. These are—

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|---------------|------------|------------|------------|----------|
| Potassium, | Barium, | Zinc, | Arsenicum, | Mercury, |
| Sodium, | Calcium, | Aluminium, | Antimony, | Lead, |
| Ammonium (?), | Magnesium, | Iron. | Copper, | Silver. |

Of the remaining metals, eight have considerable interest for the student of medicine or of pharmacy, namely :—

| | | | | |
|----------|------------|-------|-----------|----------|
| Lithium, | Manganese, | Tin, | Platinum, | Bismuth. |
| Cerium, | Chromium, | Gold, | | |

Compounds of four more occasionally come under notice :—

| | | | |
|------------|---------|---------|----------|
| Strontium, | Cobalt, | Nickel, | Cadmium. |
|------------|---------|---------|----------|

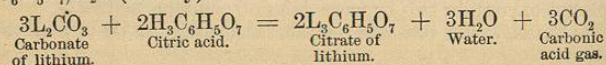
These twelve metals of minor pharmaceutical interest may be shortly studied, a few only of the reactions of each (just those mentioned in the following pages) being performed. When all have been thus treated, their respective positions in the analytical groups will be indicated, and a tabular scheme by which an analysis of a solution containing any metal may be effected. Thus, step by step, we may learn how to analyze almost any substance that may occur, and know to what extent the presence of a rarer will interfere with the ordinary tests for a common element; additional illustrations of the working of chemical laws will be acquired, and the store of chemical and pharmaceutical facts increased. The opportunity thus afforded for improvement in habits of neatness in manipulation, precision, and classification furnishes another and no mean reason why such experiments should be prosecuted, the direct value of which may not be considerable to medical and pharmaceutical learners.

LITHIUM.

Symbol L. Atomic weight 7.

Lithium is widely distributed in nature, but usually in minute proportions compared with other elements. A trace of it may be found in most soils and waters, a Cornish spring containing considerable quantities as chloride.

One salt used in medicine is the *Citrate* ($\text{L}_3\text{C}_6\text{H}_5\text{O}_7$) (*Lithii Citras*, U. S. P.), occurring in white deliquescent crystals or powder, prepared by dissolving 50 grains of the Carbonate (L_2CO_3) and 95 of citric acid (50 to 95 if both are quite pure) in 1 ounce of water, evaporating to a low bulk, and setting aside in a dry place to crystallize, or at once evaporating to dryness and powdering the residue. The crystals have the formula $\text{L}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 4\text{H}_2\text{O}$; dried at 212°F , $\text{L}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ (Umney).



The benzoate (*Lithii Benzoas*, $\text{LC}_7\text{H}_5\text{O}_2$, U. S. P.), bromide (*Lithii Bromidum*, LBr, U. S. P.), and salicylate (*Lithii Salicylas*, $2\text{LC}_7\text{H}_5\text{O}_3 \cdot \text{H}_2\text{O}$, U. S. P.) may be similarly prepared from the respective acids.

The above-named lithium salts are officially tested as follows, the Bromide being acted upon directly without ignition :—

"On dissolving the residue, left on ignition [of either salt] in diluted hydrochloric acid, and evaporating the filtered solution to dryness, 1 part of the residue should be completely soluble in 3 parts of absolute alcohol, which, when ignited, should burn with a crimson flame, and the addition of an equal volume of stronger ether to the alcoholic solution should produce no precipitate (salts of alkalies). On dissolving another portion of the residue in a small quantity of water, the solution should produce no precipitate with test-solution of oxalate of ammonium (salts of alkaline earths). The aqueous solution should remain unaffected by hydrosulphuric acid or sulphide of ammonium (abs. of metals)."—U. S. P.

The carbonate (*Lithii Carbonas*, U. S. P.) is a white granular powder obtained from the minerals which contain lithium; namely, lepidolite (from *λεπίς*, *lepis*, a scale, and *λίθος*, *lithos*, a stone; it has a scaly appearance), triphane (from *τρεῖς*, *treis*, three, and *φαῖνω*, *phainō*, I shine), or spodumene (from *σποδών*, *spodōn*, I reduce to ashes, in allusion to its exfoliation in the blowpipe-flame), and petalite (from *πέταλον*, *petalon*, a leaf; its character is leafy and laminated). Each contains silicate of aluminium, with fluoride of potassium and lithium in the case of Austrian lepidolite, which is the most abundant source, and silicate of sodium and lithium in the others. The lepidolite is decomposed by sulphuric acid; alumina, etc., precipitated by ammonia; the filtrate evaporated and the residue ignited; the resulting sulphates dissolved in water and the lithium precipitated by a carbonate. The preparation of alum is sometimes made a part of the process, and other obvious modifications may be introduced. *Liquor Lithiæ Effervescens*, B. P., is a solution of 10 grains of carbonate of lithium in 1 pint of water charged with 5 times its volume of carbonic acid gas and kept in ordinary aerated-water bottles. "Half a pint, evaporated to dryness, yields 5 grains of a white solid residue, answering to the tests for carbonate of lithium. . . . Ten grains of the latter salt neutralized with sulphuric acid, and afterwards heated to redness, leave 14.86 grains of dry sulphate of lithium, which, when redissolved in distilled water, yields no precipitate with oxalate of ammonium or solution of lime," indicating absence of salts of calcium and aluminium. Citrate of lithium should yield by incineration 52.8 per cent. of white carbonate of lithium. According to C. N. Draper, carbonate of lithium is soluble in 68 parts of water at 15°C ., and 131 at 100° .

*Urate of lithium** is more soluble than urate of sodium; hence

* Urates will be considered subsequently in connection with uric acid.

lithium preparations are administered to gouty patients in the hope that urate of sodium, with which such systems are loaded, may be converted into urate of lithium and removed.

In chemical position lithium stands between the alkaline and the alkaline-earth metals, its hydrate, carbonate, and phosphate being slightly soluble in water. The double chloride of platinum and lithium also is soluble in water. Its atom is univalent, L' .

Analytical Reaction.—Moisten the end of a platinum wire with solution of a minute particle of solid lithium salt, and introduce it into the flame of a Bunsen burner or other slightly colored flame (spirit-lamp or blowpipe-flame); a magnificent crimson tinge is imparted.

The light thus emitted by ignited lithium vapor is of a purer scarlet than that given by strontium, the next element. When the flames are examined by spectral analysis (physically analyzed by a prism), the red rays are, in the case of strontium, found to be associated with blue and yellow, neither of which is present in the lithium light, blue lithium rays only appearing at temperatures much higher than those of ordinary air-gas flames.

STRONTIUM.

Symbol Sr. Atomic weight 87.4.

Source.—Strontium is not widely distributed in nature, but the carbonate ($SrCO_3$) known as *strontianite*, and the sulphate ($SrSO_4$), known as *celestine* (from *cælum*, the sky, in allusion to its occasional bluish color), are by no means rare minerals.

Salts of strontium are not employed in medicine. They are chiefly used by firework-manufacturers in preparing red fire. The color they impart to flame is a beautiful crimson—ignited strontium vapor emitting red rays, as already explained. Nitrate of strontium (Sr_2NO_3) is best for pyrotechnic compositions, its oxygen enabling it to burn freely when mixed with charcoal, sulphur, etc. It, or any salts, may be obtained by dissolving the carbonate in the appropriate acid, or by igniting the cheaper sulphate with coal, whereby sulphide (SrS) is produced, and dissolving this in acid.

The position of strontium among the chemical elements is between barium and calcium; its sulphate is very sparingly soluble in water. Its atom, like those of barium and calcium, is bivalent (Sr'').

Analytical Reactions (Tests).

First Analytical Reaction.—To a solution of a strontium salt (Sr_2NO_3 or $SrCl_2$) add carbonate of ammonium; a white precipitate of carbonate of strontium ($SrCO_3$) falls.

Second Analytical Reaction.—To a solution of a strontium salt add sulphuric acid previously so diluted that it will not precipitate calcium salts, or add an equally dilute solution of any sulphate (e. g., that of calcium itself); a white precipitate of sulphate of strontium ($SrSO_4$) falls. The formation of this

precipitate is promoted by stirring and setting the liquid aside for some time.

Barium is precipitated immediately under similar circumstances.

Third Analytical Reaction.—To a dilute solution of a strontium salt add yellow chromate of potassium; no precipitate falls.

Barium may be separated from strontium by chromate of potassium, that reagent at once precipitating barium from aqueous or acetic solutions. The value of the reaction is enhanced if the solutions be dilute and if acetic acid or acetate of ammonium be present, chromate of strontium being far more soluble in such fluids than in water (Ransom). It is also more soluble in cold than in hot fluids.

Fourth Analytical Reaction.—Insert a fragment of a strontium salt in the blowpipe-flame, or other equally colorless flame, or hold the end of a platinum wire dipped into a strontium solution in the flame; a crimson color is imparted.

Other Analytical Reactions.—Alkali-metal phosphates, arseniates, and oxalates give white insoluble precipitates with strontium as with barium and calcium.—Strontium, like calcium, but unlike barium, is not precipitated by hydrofluosilicic acid.

CERIUM. Ce. At. wt. 138.—This element occurs in the mineral cerite (a silicate of iron, calcium, and the three rare metals, cerium, lanthanum, and didymium); also occasionally as impure fluoride, carbonate, and phosphate. The oxalate of cerium, a white granular powder, is the only official salt; it may be obtained from cerite by boiling the powdered mineral in strong hydrochloric acid for several hours, evaporating, diluting, and filtering to separate silica; adding ammonia to precipitate hydrates of all the metals except calcium; filtering off, washing, redissolving in hydrochloric acid, and adding oxalic acid to precipitate oxalate of cerium. The preparation will still contain oxalates of lanthanum and didymium; it is therefore strongly calcined, the resulting oxides of lanthanum and didymium dissolved out to some extent by boiling with a concentrated solution of chloride of ammonium, the residual oxide of cerium dissolved in boiling hydrochloric acid, and oxalate of ammonium added to precipitate white, granular oxalate of cerium ($Ce_2'''3C_2O_4 \cdot 9H_2O$). According to Hartley the precipitated hydrates are treated with chlorine, by which ceric hydrate is left insoluble and the other hydrates converted into soluble hypochlorites.

Oxalate of cerium (*Cerii Oxalas*, U. S. P.) is decomposed at a dull red heat, 48 per cent. of a yellow, or, more generally, a salmon-colored, mixture of oxides remaining; usually the didymium present gives the ignited residue a reddish or reddish-brown color; it is then soluble in boiling hydrochloric acid (without effervescence; indicating, indirectly, absence of earthy and other carbonates or oxalates),

and the solution gives, with excess of a saturated solution of sulphate of potassium, a crystalline precipitate of double sulphate of cerium and potassium. Alumina mixed with oxalate of cerium may be detected by boiling with solution of potash, filtering, and adding excess of solution of chloride of ammonium, when a white flocculent precipitate of hydrate of aluminium will be obtained. Oxide of zinc is revealed on boiling in potash and adding sulphide of ammonium, when white sulphide of zinc falls. The oxalic radical is recognized by neutralizing the potash solution by acetic acid and adding chloride of calcium; white oxalate of calcium is then precipitated; this precipitate, though insoluble in acetic, should be wholly dissolved by hydrochloric acid. Acid or neutral cerium solutions give with acetate of sodium and peroxide of hydrogen a brownish-red color (Hartley).

According to H. G. Greenish, most samples of oxalate of cerium have as impurities traces of lead, iron, and magnesium.

MANGANESE.

Symbol Mn. Atomic weight 54.8.

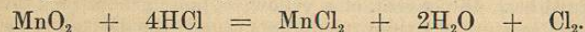
Source.—Manganese is a constituent of many minerals, and as black oxide, or dioxide, or binoxide (MnO_2) (*Mangan Oxidum Nigrum*, U. S. P., "containing not less than 66 per cent. of pure oxide, MnO_2 "), or *pyrolusite* (from *πῦρ*, *pur*, fire, and *λίσις*, *lusis*, a loosing or resolving, in allusion to the readiness with which it is split up by heat into a lower oxide and oxygen), occurs frequently in abundance in the south-west of England, Aberdeenshire, and most of the countries of Europe. It is met with as a steel-gray mass of prismatic crystals or in black shapeless lumps.

The chemical position of manganese is close to iron and three other metals still to be considered—cobalt, nickel, and chromium. Its atom apparently has sexivalent affinities, as seen in manganate of potassium, (K_2MnO_4); but commonly it is quadrivalent (Mn^{IV}) or bivalent (Mn^{II}).

Uses.—Metallic manganese, which may be isolated by aid of sodium, is used in alloy with iron in the manufacture of some varieties of steel. The black oxide is an important agent in the production of chlorine, the preparation of green and red disinfecting manganates, purple glass, and black glazes for earthenware.

Reactions having both Synthetical and Analytical Interest.

First Reaction.—Boil a few grains of black oxide of manganese with some drops of hydrochloric acid until chlorine ceases to be evolved; add water, and filter; the filtrate is a solution of manganous chloride (MnCl_2).



This is the reaction commonly applied in the preparation of chlorine gas. It is also a ready method of preparing a manganous salt for analytical experiments. Coupled with the application of re-

agents to the filtrate, the reaction is that by which a black powder or mineral would be recognized as black oxide of manganese. Black oxide of manganese dissolves in cold hydrochloric acid, forming a dark-brown solution of a higher chloride or chlorides, MnCl_3 , Mn_2Cl_7 , or, possibly, MnCl_4 .

Second Reaction.—Heat a particle of a manganese compound with a grain or two of carbonate and hydrate of potassium and a fragment of nitrate or chlorate of potassium on platinum foil in the blowpipe-flame; a green mass containing *manganate of potassium* (K_2MnO_4) results. Boil the foil in a little water; the green manganate dissolves and soon changes to solution of the purple *permanganate of potassium* ($\text{K}_2\text{Mn}_2\text{O}_8$).

This is a delicate analytical test for manganese.

The reaction is similar to that by which permanganate of potassium (*Potassii Permanganas*, U. S. P.) is prepared for use in volumetric analysis. Equations showing the exact action which occurs in making the salt according to the process of the British Pharmacopœia have already been given in connection with the compounds of potassium (*vide* p. 76). The proportions of ingredients and details of the operation are as follows:—

Reduce $3\frac{1}{2}$ parts (for experiment each "part" may be $\frac{1}{4}$ th oz.) of chlorate of potassium to fine powder, and mix it with 4 of black oxide of manganese; put the mixture into a porcelain basin, and add to it 5 parts of solid caustic potash, previously dissolved in 4 parts of water. Evaporate to dryness, stirring diligently to prevent spitting. Pulverize the mass, put it into a covered Hessian or Cornish crucible, and expose it to a dull red heat (not higher) for an hour (20 or 30 minutes for quantities of 1 or 2 oz.), or till it has assumed the condition of a semi-fused mass. Allow to cool, pulverize, and boil with about 30 parts of water. Let the insoluble matter subside, decant the fluid, boil again with about 10 parts of water, again decant, neutralize the united liquors accurately with diluted sulphuric acid (or, better, carbonic acid gas), and evaporate till a pellicle forms. Set aside to cool and crystallize. Drain the crystalline mass, boil it in 6 parts of water, and strain through a funnel the throat of which is slightly obstructed by a little asbestos or gun-cotton. Let the fluid cool and crystallize, drain the dark purple slender prismatic crystals, and dry them by placing under a bell-jar over a vessel containing sulphuric acid.

Instead of converting the manganate into permanganate by ebullition, by which one-third of the manganate is lost, Städeler recommends chlorine to be passed through the cold solution until the green color is entirely changed to purple.

Solutions of the manganates of potassium and sodium are in common use as disinfectants under the name of Condyl's Fluid. They act by oxidizing organic matter, the manganic or permanganic radical being reduced to black manganic oxide, or even a lower oxide. The reason for using asbestos instead of paper in filtering the solutions will now be understood.

The changes in color which the green mass of the above process undergoes when dropped into warm water procured for it the old name of *mineral chameleon*.

Third Reaction.—Make a borax bead by heating a fragment of the salt on the looped end of a platinum wire in the blow-pipe-flame until a clear transparent globule is obtained. Place on the bead a minute portion of a manganese compound, or touch it with a drop of solution. Again fuse the borax, using the point of the flame; a bead of a violet or amethystine tint is produced.

This is a good analytical reaction. It has also synthetical interest, illustrating the use of black oxide of manganese in producing common purple-tinted glass.

Expose the bead to the reducing part of the flame, the part nearer to the blowpipe, where there are highly heated hydrocarbon gases greedy of oxygen; the color disappears.

This is owing to the reduction of the manganic compound to a manganous condition, in which it no longer possesses peculiar coloring-power. This action also illustrates the use of black oxide of manganese in glass-manufacture. Glass when first made is usually of a green tint, owing to the presence of ferrous impurities; the addition of manganic oxide to the materials converts the ferrous into ferric compounds, which have comparatively little colorific power, it itself being thereby reduced to manganous oxide, which also gives but little color. If excess of manganic oxide be added, a purple tint is produced.

Reactions having Analytical Interest (Tests).

Fourth Reaction.—Through a solution of a manganous salt acidified by hydrochloric acid pass sulphuretted hydrogen; no decomposition occurs. Add ammonia; the sulphhydrate of ammonium thus formed causes the precipitation of a yellowish-pink or flesh-tinted precipitate of manganous sulphide (MnS) in a hydrous state.

This reaction is characteristic, sulphide of manganese being the only flesh-colored sulphide known. The salt used may be the manganous chloride obtained in the first reaction; but such crude solutions usually give a black precipitate with sulphhydrate of ammonium, owing to the presence of iron. The latter element may be precipitated, however, on adding excess of ammonia (and rapidly filtering, or oxygen will be absorbed and most of the manganese also precipitated (or on boiling the manganous solution with a very little carbonate of sodium, which attacks the ferric salt in preference to the manganous. Pure manganous chloride may be similarly obtained on boiling the impure solution with manganous carbonate; the latter decomposes the ferric chloride with production of ferric

hydrate and more manganous chloride, and evolution of carbonic acid gas.

To the recently precipitated manganous sulphide add acetic acid; it is dissolved.

This solubility enables manganese to be separated from nickel, cobalt, and zinc, whose sulphides are insoluble in weak acetic acid. To express the fact in another way—manganese is not precipitated by sulphuretted hydrogen from a solution containing free acetic acid only.

Fifth Reaction.—To solution of manganous salt add ammonia; a white precipitate of manganous hydrate (Mn_2HO) falls. Add excess of ammonia; some of the precipitate is dissolved, and may be detected in the quickly filtered solution by sulphhydrate of ammonium. But both precipitate and solution rapidly absorb oxygen, the manganese passing into a more highly oxidized condition in which it is insoluble in ammonia.

The fixed alkalis give a similar precipitate *insoluble* in excess. The precipitate rapidly absorbs oxygen, becomes brown, and gradually passes into a higher oxide.

Sixth Reaction.—Heat a little black oxide of manganese in a test-tube with sulphuric acid; oxygen is evolved and sulphate of manganese formed (*Mangan Sulphas*, $MnSO_4 \cdot 4H_2O$, U. S. P.); add water, boil, filter, evaporate, and set aside to crystallize. Larger quantities are made in a similar manner.

Sulphate of manganese ($MnSO_4 \cdot 5H_2O$) occurs in colorless or pale rose-colored, transparent crystals, which, when deposited from a solution at a temperature between 68° and 86° , have the form of right rhombic prisms, and contain four molecules of water (U. S. P.). This salt is very soluble in water. Other sulphates containing 1, 2, 3, and 9 of water are known. The solution is not colored by tincture of nutgall (a black shows iron), but affords with caustic alkalis a white precipitate (Mn_2HO), which, by exposure to the air, soon absorbs oxygen, and becomes brown. Sulphhydrate of ammonium throws down a flesh-colored precipitate (MnS), and ferrocyanide of potassium a white one (Mn_2Fcy).

Many other reactions occur between manganese salts and various reagents, but are of no particular synthetical or analytical interest.

A good method proposed by Crum, for detecting minute quantities of manganese, consists in adding dilute nitric acid and either red lead or the puce-colored oxide or peroxide of lead to the solution, and then boiling; a red tint, said to be due to permanganic acid, is imparted to the liquid.

COBALT AND NICKEL.

Krüss and Schmidt state (1889) that these very closely-allied metals, as hitherto known, are not true elements, but contain a third element, the oxide of which resembles, yet distinctly differs from, alumina and oxide of zinc.

COBALT.

Symbol Co. Atomic weight 58.6.

Source.—Cobalt occurs sparingly in nature as the arsenide (CoAs_2), or *tin-white cobalt*, and occasionally as a double arsenide and sulphide ($\text{CoAs}_2, \text{CoS}_2$), or *cobalt glance* (from *glanz*, brightness, in allusion to its lustre).

Uses.—Its chief use is in the manufacture of blue glass, the color of which is due to a compound of cobalt. Cobalt is also the coloring constituent of *smalt* (from *smelt*, a corruption of *mel*), a finely-ground sort of glass, used as a blue pigment by paper-stainers and others, and employed also by laundresses to neutralize the yellowish appearance of washed linen.

The salts of cobalt may be obtained from the oxide (CoO), and the oxide from *zaffre*, a mixture of sand and roasted ore.

Quantivalence.—The atom of cobalt often exhibits quadrivalent affinities, but still more often exerts only bivalent powers (Co''). Cobalt has analytical relations with zinc, nickel, and manganese, and may be regarded as a member of the iron group.

Analytical Reactions (Tests).

First Analytical Reaction.—Pass sulphuretted hydrogen through an acidified solution of a salt of cobalt—the chloride (CoCl_2) or nitrate (Co_2NO_3), for example; no decomposition occurs. Add ammonia; the sulphhydrate of ammonium thus formed causes the precipitation of black sulphide of cobalt (CoS).

The moist precipitate slowly absorbs oxygen from the air, becoming converted into sulphate of cobalt (CoSO_4).

Second Analytical Reaction.—Add ammonia gradually to a cobalt solution; a blue precipitate of impure hydrate of cobalt (Co_2HO) falls. Add excess of ammonia; the precipitate is dissolved, yielding a liquid somewhat more reddish-brown than the original solution.

A similar precipitate is given by the fixed alkalis. *insoluble* in excess.

Third Analytical Reaction.—Make a borax bead by heating a fragment of the salt on the looped end of a platinum wire in a blowpipe-flame until a clear transparent globule is obtained. Place on the bead a minute portion of a cobalt compound, or

touch it with a drop of solution. Again fuse the borax; a blue bead results.

This is a delicate test for cobalt. From what has previously been said, it will be seen that this experiment has also considerable synthetic interest.

Fourth Analytical Reaction.—To a solution of a salt of cobalt add two or three drops of hydrochloric acid, then excess of solution of cyanide of potassium, and boil for ten minutes; oxygen is absorbed, and cobalticyanide of potassium ($\text{K}_6\text{Co}_2\text{Cy}_{12}$) formed. Add hydrochloric acid, and boil the mixture (in a fume-cupboard, to avoid inhalation of any hydrocyanic acid); the excess of cyanide of potassium is thus decomposed, but the cobalticyanide is unaffected. Now add excess of solution of potash; the cobalticyanide of potassium probably is decomposed, but the cobalt remains dissolved in the alkaline liquid.

Nickel under similar circumstances is precipitated, the reaction thus affording means of separating these closely allied metals from each other.

Other Reactions between a cobalt solution and different reagents may be performed, and various precipitates obtained; but these have no special analytical interest.

Invisible Ink.—Many salts of cobalt containing water of crystallization are light red, the anhydrous more or less blue. Prove this by writing some words on paper with a solution of chloride of cobalt sufficiently dilute for the characters to be invisible when dry; hold the sheet before a fire or over a flame; the letters at once become visible, distinct, and of a blue color. Breathe on the words, or set the sheet aside for a while; the characters are once more invisible, owing to absorption of moisture. Hence solution of chloride of cobalt forms one of the so-called *sympathetic inks*.

NICKEL.

Symbol Ni. Atomic weight 58.6.

The ores of these metals are commonly associated in nature. Indeed, it is from *speiss*, an arsenio-sulphide of nickel obtained in the manufacture of smalt, a pigment of cobalt already mentioned, that most of the nickel met with in commerce is obtained. It is much used in the preparation of the white alloy known as German or nickel silver, and for plating iron.

Quantivalence.—Nickel exerts bivalent activity (Ni'') in its ordinary compounds. Its salts and their solutions are usually green. They are chiefly made, directly or indirectly, from the metal itself.

Analytical Reactions (tests).

First Analytical Reaction.—Pass sulphuretted hydrogen through an acidified solution of a salt of nickel—chloride (NiCl_2), nitrate (Ni_2NO_3), or sulphate (NiSO_4); no decomposition occurs. Add ammonia; the sulphhydrate of ammonium thus formed causes the precipitation of black sulphide of nickel (NiS).

Note.—When sulphate of nickel is precipitated by the direct addition of the common yellow solution of sulphhydrate of ammonium, which always contains free sulphur, there is much difficulty in filtering the mixture, owing to the slight solubility of sulphide of nickel in the reagent and the formation of some sulphate of nickel (NiSO_4), oxygen being absorbed from the air by the sulphide. This may be avoided by warming the mixture and using freshly-made sulphhydrate of ammonium, in which the sulphide of nickel is insoluble; or, where practicable, the salt of nickel may be precipitated from an ammoniacal solution by sulphuretted hydrogen.

Second Analytical Reaction.—Add ammonia drop by drop to a nickel solution; a pale-green precipitate of hydrate of nickel (Ni_2HO) falls, especially on boiling the mixture. Add excess of ammonia; the precipitate dissolves, yielding a bluish rather than the original green-colored solution.

A similar precipitate is given by the fixed alkalies, *insoluble* in excess.

Third Analytical Reaction.—Nickel salts color a borax bead, when hot, a reddish-yellow tint; the reaction is not very serviceable analytically.

Fourth Analytical Reaction.—To a solution of a salt of nickel add solution of cyanide of potassium; cyanide of nickel (NiCy_2) is precipitated. Add excess of solution of cyanide of potassium; the precipitate is dissolved with formation of double cyanide of nickel and potassium ($\text{NiCy}_2 \cdot 2\text{KC}_y$). Next add hydrochloric acid, and boil the mixture (in a fume-cup-board), adding a little hydrochloric acid from time to time until all smell of hydrocyanic acid has disappeared. Lastly, add excess of solution of potash; hydrate of nickel is precipitated.

Qualitative Separation of Cobalt and Nickel.

The foregoing reaction serves for the separation of nickel from cobalt. On adding excess of hydrochloric acid to a solution containing the two metals, together with cyanide of potassium, a precipitate of cyanide of nickel and cobaltocyanide of nickel occurs. By ebullition with excess of hydrochloric acid the cyanide of nickel is decomposed, chloride of nickel going into solution. On then adding excess of potash, hydrate of nickel is precipitated. The cobaltocyanide of nickel is not decomposed by the acid; but is by the alkali,

its cobalt going into solution and its nickel remaining insoluble as hydrate. After filtering off the nickel, cobalt is detected in the filtrate by evaporating to dryness and testing the residue with borax in the blowpipe-flame.

(*This process requires much practice for its successful performance, and need not be attempted by pupils whose studies are restricted to medicine and pharmacy.*)

The value of this method (Skey and Davies) turns on the facts that ferridecyanide of nickel is not a colored body, while ferridecyanide of cobalt is reddish-brown, and that ferridecyanogen has apparently, *in ammoniacal solution*, greater affinity for cobalt than for nickel, while ferrocyanogen has, apparently, greater affinity for nickel than for cobalt. The formulæ of these so-called ferrocyanides and ferridecyanides of cobalt and nickel have not been definitely ascertained.

Other reactions between a nickel solution and various reagents give, in many cases, insoluble precipitates which, from their green color, are occasionally useful in distinguishing nickel from allied elements.

CHROMIUM.

Symbol Cr. Atomic weight 52.4.

Source.—The chief ore of chromium is chrome ironstone, a mixture of the oxides of the metals ($\text{FeO}, \text{Cr}_2\text{O}_3$), occurring chiefly in the United States and Sweden. In constitution it seems to resemble magnetic iron ore ($\text{FeO}, \text{Fe}_2\text{O}_3$). The metal may be isolated by aid of sodium.

Preparation of Red Chromate of Potassium.—On roasting the powdered ore with carbonate of potassium and nitre, yellow chromate of potassium (K_2CrO_4) is obtained; the mass, treated with acid, yields red or bichromate ($\text{K}_2\text{CrO}_4, \text{CrO}_3$) (*Potassii Bichromas*, U. S. P.); from this salt other chromates are prepared, and by reduction, as presently explained, the salts of chromium itself. The yellow and orange chromates of lead are largely used as pigments.

Note on Constitution.—Red chromate of potassium is a somewhat abnormal salt, containing, probably, neutral chromate associated with chromic anhydride, and hence termed *anhydrochromate of potassium*. The value of chromates as chemical reagents is alluded to in connection with chromate of barium (p. 103). Heated strongly in a crucible, red chromate of potassium splits up into yellow chromate, glistening oxide of chromium, and oxygen; red chromate of ammonium into oxide of chromium, water, and nitrogen $(\text{NH}_4)_2\text{CrO}_4, \text{CrO}_3 = \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{N}_2$.

Quantivalence.—Chromium stands in close chemical relation to iron, aluminium, and manganese. Its atom is sexivalent if the formula of the fluoride (CrF_6) be correct. Like iron and aluminium, it is trivalent, as seen in chromic chloride (Cr_2Cl_6), but sometimes exerts only bivalent activity, as in chromous chloride (CrCl_2).