

*Analytical Reactions (tests).*

*First Analytical Reaction.*—Pass sulphuretted hydrogen through an acidified solution of a salt of nickel—chloride ( $\text{NiCl}_2$ ), nitrate ( $\text{Ni}_2\text{NO}_3$ ), or sulphate ( $\text{NiSO}_4$ ); no decomposition occurs. Add ammonia; the sulphhydrate of ammonium thus formed causes the precipitation of black sulphide of nickel ( $\text{NiS}$ ).

*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 ( $\text{NiSO}_4$ ), 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 ( $\text{Ni}_2\text{HO}$ ) 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 ( $\text{NiCy}_2$ ) 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 ( $\text{K}_2\text{CrO}_4$ ) 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

$$(\text{NH}_4)_2\text{CrO}_4 \cdot \text{CrO}_3 = \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{N}_2.$$

*Quantivalence.*—Chromium stands in close chemical relation to iron, aluminium, and manganese. Its atom is sexivalent if the formula of the fluoride ( $\text{CrF}_6$ ) be correct. Like iron and aluminium, it is trivalent, as seen in chromic chloride ( $\text{Cr}_2\text{Cl}_6$ ), but sometimes exerts only bivalent activity, as in chromous chloride ( $\text{CrCl}_2$ ).



*Passage of Chromium from the Acidulous to the Basylous Side of Salts.*—Through an acidified solution of red chromate of potassium pass sulphuretted hydrogen; sulphur is deposited, and a green salt of chromium remains in solution, chloride ( $\text{Cr}_2\text{Cl}_6$ ) if hydrochloric acid be used, and sulphate ( $\text{Cr}_2\text{SO}_4$ ) if sulphuric be the acid employed. Boil the liquid to expel excess of sulphuretted hydrogen, filter, and reserve the solution for subsequent experiments. (For an equation of this reaction, see p. 237.)

Alcohol, sugar, or almost any substance which is tolerably liable to oxidation, will answer as well as sulphuretted hydrogen.

*Sulphate of chromium* ( $\text{Cr}_2\text{SO}_4$ ), like sulphate of aluminium ( $\text{Al}_2\text{SO}_4$ ), unites with alkali-metal sulphates to form *alums*, which resemble common alum both in crystalline form, and, as far as we know, in internal structure: they are of purple color.

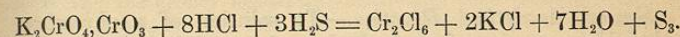
#### REACTIONS.

*Chromium as Chromic Acid, or other Chromate.*—This is the state in which chromium will usually be met with, the most common salt being the red chromate or bichromate of potassium. Mix four volumes of a cold, saturated aqueous solution of red chromate of potassium with five of oil of vitrol; on cooling, *chromic anhydride* ( $\text{CrO}_3$ ), *Acidum Chromicum*, U. S. P., or *anhydrous chromic acid*, separates in crimson needles. After well draining, the crystals may be freed from adhering sulphuric acid by washing once or twice with nitric acid: the latter may be removed by passing dried and slightly warmed air through a tube containing the crystals. It may be quite freed from sulphuric acid by one or two recrystallizations. In contact with moisture chromic anhydride takes up water and forms solution of true chromic acid ( $\text{H}_2\text{CrO}_4$ ), 1 part of the anhydride and 3 parts of water forming the *Liquor Acid Chromici*, B. P. Chromic anhydride is a powerfully corrosive oxidizing agent. It melts between  $356^\circ$  and  $374^\circ \text{F.}$ , and at a high temperature decomposes, yielding oxide of chromium and oxygen; it oxidizes organic substances with great violence.

The oxygen in chromic acid and other chromates, and in manganates, permanganates, black oxide of manganese, and puce-colored oxide of lead, is in a physically different state from that in peroxide of hydrogen, peroxide of barium, and similar compounds. On bringing chromic acid or the above acidified solution of red chromate of potassium into contact with solution of peroxide of hydrogen, a strong effervescence of oxygen ensues. According to Schönbein and Brodie the oxygen of chromic acid is in the negative or ozonic state, while that of peroxide of hydrogen is in the positive or

so-called antozonic condition. Both are equally active, but neutralize each other, forming neutral or ordinary oxygen.

In the analytical examination of solutions containing chromates, the chromium will always come out in the state of green chromic hydrate, along with ferric hydrate and alumina, the prior treatment by sulphuretted hydrogen reducing the chromium in the molecule to the lower state, thus:—



Chromium having been found in a solution, its condition as chromate may be ascertained by applying to the original solution salts of barium, mercury, lead, and silver. (See the various paragraphs relating to those metals.)

$\text{BaNO}_3$	gives yellow	$\text{BaCrO}_4$	with chromates.
$\text{Hg}_2\text{NO}_3$	" red	$\text{Hg}_2\text{CrO}_4$	"
$\text{AgNO}_3$	" "	$\text{Ag}_2\text{CrO}_4$	"
"	" "	$\text{Ag}_2\text{CrO}_4, \text{CrO}_3$	with bichromates.
$\text{Pb}_2\text{C}_2\text{H}_3\text{O}_2$	yellow	$\text{PbCrO}_4$	with both.

Nitrate of barium does not completely precipitate bichromates, bichromate of barium being soluble in water; the chromate of barium is insoluble in water or acetic acid, but soluble in hydrochloric or nitric acid. Mercurous nitrate does not wholly precipitate bichromates: mercuric nitrate or chloride only partially precipitates chromates, and does not precipitate bichromates. The mercurous chromate is insoluble, or nearly so, in diluted nitric acid. The silver chromates are soluble in acids and alkalies. Acetate of lead precipitates chromates and bichromates, acetic acid being set free in the latter case.

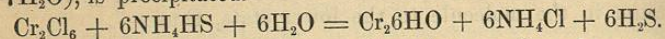
A delicate reaction for dry chromates will be found in the formation of *chlorochromic anhydride* ( $\text{CrO}_2\text{Cl}_2$ ). A small portion of the chromate is placed in a test-tube with a fragment of dry chloride of sodium and a drop or two of oil of vitrol, and the mixture heated; red irritating fumes of chlorochromic anhydride are evolved, and condense in dark-red drops on the side of the tube.

Large quantities of pure distilled chlorochromic anhydride are obtained by the same reaction, the operation being conducted in a retort, with thoroughly dry materials, for the compound is decomposed by water. It may be regarded as chromic anhydride in which an atom of oxygen is displaced by an equivalent quantity (two atoms) of chlorine. It is not used in medicine, but is of interest to the chemical student as being an illustration of a class of similar bodies—*chloro-acidulous* or *chloro-anhydrous compounds*. The reaction is also occasionally serviceable for the detection of chlorides.



*Analytical Reactions of Chromium Salts (Tests).*

*First Analytical Reaction.*—To solution of a salt of chromium (chloride, sulphate, or chrome alum) add sulphhydrate of ammonium; a bulky green precipitate of chromic hydrate ( $\text{Cr}_2\text{6HO}$ ), containing a large quantity of water (7 molecules,  $7\text{H}_2\text{O}$ ), is precipitated.



*Second Analytical Reaction.*—To solution of a chromium salt add ammonia; chromic hydrate is precipitated, insoluble in excess.

*Third Analytical Reaction.*—To solution of a chromium salt add solution of potash or soda, drop by drop; chromic hydrate is precipitated. Add excess of the fixed alkali; the precipitate is dissolved. Boil well the solution; the chromic hydrate is reprecipitated.

*Iron, Chromium, and Aluminium Salts*, chemically so alike, may be separated by this reaction. Ferric hydrate is insoluble in solutions of the fixed alkalies, cold or hot; chromium hydrate, soluble in cold but not in hot; hydrate of aluminium, in both. To a solution containing all three metals, therefore, add potash or soda, stir, and filter; the iron is thrown out: boil the filtrate, and filter; the chromium is thrown out: neutralize the filtrate by acid, and then add ammonia; the aluminium is thrown out. Note, however, that ferric hydrate will prevent hydrate of chromium being dissolved by potash or soda if the ferric hydrate is in considerable excess. Before concluding that chromium is entirely absent, the 4th reaction should be performed. The hydrates of iron, chromium, and aluminium are insoluble in ammonia, and may therefore be easily separated from the hydrates of the somewhat analogous metals zinc, cobalt, nickel, and manganese.

*Fourth Analytical Reaction.*—Add a salt of chromium (either of the above precipitates of chromic oxide or the dry residue of the evaporation of a few drops of a solution of a chromium salt) to a few grains of nitre and carbonate of sodium on platinum foil, and fuse the mixture in the blowpipe-flame; a yellow mass of chromate of potassium and sodium ( $\text{KNaCrO}_4$ ) is formed. Dissolve the mass in water, add acetic acid to decompose excess of carbonate, and apply the reagents for chromates.

This is a delicate and useful reaction if carefully performed.

**TIN.**

Symbol Sn. Atomic weight 117.7.

*Source.*—The chief ore of tin is stannic oxide ( $\text{SnO}_2$ ), occurring

in veins under the name of *tinstone*, or in alluvial deposits as *stream-tin*. The oldest mines are those of Cornwall. Much tin is now imported from Australia.

*Preparation.*—The metal is obtained by reducing the roasted and washed ore by charcoal or anthracite\* coal at a high temperature, and is purified by slowly heating, when the pure tin, fusing first, is run off, a somewhat less fusible alloy of tin with small quantities of arsenicum, copper, iron, or lead remaining. The latter is known as *block tin*; the former heated till brittle and then hammered or let fall from a height splits into prismatic fragments, resembling starch or columnar basalt, and is named *dropped* or *grain tin*. Good tin emits a crackling noise in bending, termed the cry of tin, caused by the friction of its crystalline particles on each other.

*Uses.*—Tin is an important constituent of such alloys as pewter, Britannia metal, solder, speculum-metal, bell-metal, gun-metal, and bronze. It is very ductile, and may be rolled into plates or leaves, known as *tin foil*, varying from  $\frac{1}{320}$  to  $\frac{1}{1000}$  of an inch in thickness. Common tin foil, however, usually contains a large proportion of lead. The reflecting surface of *looking-glasses* was, formerly, always an amalgam of tin and mercury, produced by carefully sliding a plate of glass over a sheet of tin foil on which mercury had been rubbed, and then excess of mercury poured; but pure silver, deposited from a solution, is now largely employed. *Pins* are made of brass wire, on which tin is deposited. *Tin plate*, of which common utensils are made, is iron alloyed with tin by dipping the acid-cleaned sheet into melted tin covered with oil, which, by dissolving any trace of oxide, or, perhaps, by preventing oxidation, enables the tin more completely to alloy with the iron. *Tin tacks* are in reality tinned iron tacks; a tin nail would be too soft to drive into wood. Tin may be granulated by melting and triturating briskly in a hot mortar, by shaking melted tin in a box on the inner sides of which chalk has been rubbed, or, in thin little bells or corrugated fragments (Granulated Tin, B. P.), by melting in a ladle, and immediately it is fluid, pouring from the height of a few feet into water. Powdered tin has been used medicinally as a mechanical irritant to promote expulsion of worms. The hair of the pods of *Kiwach* or *Cowhage* (Hindustani) (*Mucuna pruriens*, P. I.) is almost the only medicine (excluding diluents and dentifrices) which acts in such a directly mechanical manner.

*The chemical position of tin* among the metals is close to that of arsenicum and antimony. Its atom is quadrivalent and bivalent. The two classes of salts are termed stannic and stannous respectively. They are all made directly or indirectly from the metal itself.

\* *Anthracite* (from *ἀνθραξ*, *anthrax*, a burning coal) or *stone coal* differs from the ordinary *bituminous* or *caking coal* in containing less volatile matter, and, therefore, in burning without flame. It gives a higher temperature, and from its non-caking properties is, in furnace operations, more manageable than bituminous coal.



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

(a) *Synthetic Reactions.*

**Chloride of Tin. Stannous Chloride.**

*First Synthetic Reaction.*—Warm a fragment of tin with hydrochlorous acid; hydrogen escapes and solution of stannous chloride ( $\text{SnCl}_2$ , perhaps  $\text{Sn}_2\text{Cl}_4$ ) is formed. It may be retained for future experiments.

One ounce of tin dissolved in three fluidounces of hydrochloric acid and one of water, and the resulting solution diluted to five fluidounces, constitutes the "Solution of Stannous Chloride," B. P.

*Solid Stannous Chloride.*—By evaporation of the above solution stannous chloride is obtainable in crystals ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ). It is a powerful reducing agent, even a dilute solution precipitating gold, silver, and mercury from their solutions, converting ferric and cupric into ferrous and cuprous salts, and partially deoxidizing arsenic, manganic, and chromic acids. It absorbs oxygen from the air, and is decomposed when added to a large quantity of water unless some acid be present. It is used as a mordant in dyeing and calico-printing.

**Perchloride of Tin. Stannic Chloride.**

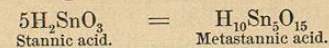
*Second Synthetic Reaction.*—Through a portion of the solution of the stannous chloride of the previous reaction pass chlorine gas; solution of stannic chloride ( $\text{SnCl}_4$ ) is formed. Or add hydrochloric acid to the stannous solution, boil, and slowly drop in nitric acid until no more fumes are evolved; again stannic chloride results. Reserve the solutions for subsequent experiments.

**Stannic Oxide, or Anhydride, and Stannates.**

*Third Synthetic Reaction.*—Boil a fragment of tin with nitric acid, evaporate to dryness, and strongly calcine the residue; light buff-tinted stannic anhydride ( $\text{SnO}_2$ ) is produced. Heat the stannic anhydride with excess of solid caustic potash or soda; stannate of the alkali metal ( $\text{K}_2\text{SnO}_3$  or  $\text{Na}_2\text{SnO}_3$ ) results. Dissolve the stannate in water, and add hydrochloric acid; white, gelatinous stannic acid ( $\text{H}_2\text{SnO}_3$ ) is precipitated. Stannic acid is also obtained on adding an alkali to solution of stannic chloride; it is soluble in excess of acid or alkali.

The product of the action of nitric acid on tin is also an acid, but from its insolubility in hydrochloric and other acids is different from ordinary stannic acid. It is termed *metastannic acid* (from *meta*, beyond), and probably has a composition expressed by the

formula  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ . (*Vide* Index, "Isomerism.") It is also produced on gently heating stannic acid:—



Metastannates have the general formula  $\text{M}_2\text{H}_8\text{Sn}_5\text{O}_{15}$ . Both acids yield buff-colored stannic oxide or anhydride ( $\text{SnO}_2$ ) when strongly heated. The latter is employed in polishing plate under the name of *putty powder*. Stannate of sodium ( $\text{Na}_2\text{SnO}_3 \cdot 4\text{H}_2\text{O}$ ) is used as a mordant by dyers and calico-printers under the name of *tin prepare-liquor*.

(b) *Reactions having Analytical Interest (Tests).*

*Stannous or Stannic Salts.*—Heat any solid tin compound with a mixture of cyanide of potassium and carbonate of sodium on charcoal by the inner flame of the blowpipe. Globules of tin separate, having, when cut by a knife, characteristic brightness and hardness.

STANNOUS SALTS.

*First Analytical Reaction.*—Through a dilute solution of a stannous salt (stannous chloride, for example; see previous page) pass sulphuretted hydrogen gas; brown stannous sulphide ( $\text{SnS}$ ) is precipitated. Pour off the supernatant liquid, add ammonia to the moist precipitate (to neutralize acid), and lastly yellow sulphhydrate of ammonium solution; the precipitate is dissolved.

Aqueous solution of sulphhydrate of ammonium becomes yellow when a day or two old, and then contains excess of sulphur, that element having become displaced by oxygen absorbed from the air; hence, in the above reaction, the stannous sulphide ( $\text{SnS}$ ), in dissolving, becomes stannic sulphide ( $\text{SnS}_2$ ); for the latter is precipitated on decomposing the alkaline liquid by an acid.

*Second Analytical Reaction.*—To solution of a stannous salt add solution of potash or soda; white stannous hydrate falls ( $\text{Sn}2\text{HO}$ ). Add excess of the alkali; the precipitate dissolves. Boil the solution; some of the tin is precipitated as blackish stannous oxide ( $\text{SnO}$ ).

Ammonia gives a similar precipitate, insoluble in excess. The alkaline carbonates do the same, carbonic acid gas escaping.

STANNIC SALTS.

*Third Analytical Reaction.*—Through a solution of a stannic salt (stannic chloride, for example; see page 239) pass sulphuretted hydrogen gas; yellow stannic sulphide ( $\text{SnS}_2$ ) is precipi-



tated. Pour off the supernatant liquid, and to the moist precipitate add ammonia (to neutralize acid), and then sulphhydrate of ammonium; the precipitate dissolves.

*Note.*—In precipitating stannic sulphide the presence of too much hydrochloric acid must be avoided; the formation of the precipitate is also facilitated if the solution be warmed. Stannic sulphide, like the sulphide of arsenicum and antimony, dissolves in a solution of alkaline sulphide or sulphhydrate, with formation of definite crystallizable sulphostannates ( $M_2SnS_3$ ).

*Anhydrous stannic sulphide*, prepared by sublimation, has a yellow or orange lustrous appearance, and is used by decorators as *bronzing-powder*. It is sometimes termed *mosaic gold*.

*Fourth Analytical Reaction.*—To solution of a stannic salt add potash or soda; white stannic acid falls ( $H_2SnO_3$ ). Add excess of the alkali; the precipitate dissolves. Boil the mixture; no reprecipitation occurs—a fact enabling stannic to be distinguished from stannous salts.

Ammonia gives a similar precipitate, soluble, but not readily, in excess. The fixed alkali-metal carbonates do the same, carbonic acid gas escaping; after a time the stannic salt is again deposited, probably as stannate of the alkali metal. Carbonate of ammonium and acid carbonates of alkali metals give a precipitate of stannic acid insoluble in excess.

*Antidotes.*—In cases of poisoning by tin salts (dyer's tin liquor, *e. g.*), solution of carbonate of ammonium should be given. White of egg is also said to form an insoluble precipitate with compounds of tin. Vomiting should be speedily induced, and the stomach-pump quickly applied.

### GOLD.

Symbol Au. Atomic weight 196.85.

*Source.*—Gold occurs in the free state in nature, occasionally in nodules or *nuggets*, but commonly in a finer state of division termed *gold dust*.

*Preparation.*—Gold is separated from the sand, crushed quartz, or other earthy matter with which it may be associated, by agitation with water, when the gold, from its relatively greater specific gravity, falls to the bottom of the vessel first, the lighter mineral matter being allowed to run off with the water. From this rich sand the gold is dissolved out by mercury, the amalgam filtered, and afterwards distilled, when the mercury volatilizes and gold remains. The amalgamation may be much facilitated by the use of a small proportion of sodium, as already described in treating of silver.

*Pure gold* is too soft for general use as a circulating medium. *Gold coin* is an alloy of copper and gold, that of Great Britain containing 1 of the former to 11 of the latter, or  $8\frac{1}{3}$  per cent. of copper, that of France, Germany, and the United States about 10

per cent. *Jeweller's gold* varies in quality, every 24 parts containing 18, 15, 12, or 9 parts of gold, the alloys being technically termed 18, 15, 12, or 9 *carat fine*. Articles made of the better qualities are usually stamped by authority. Trinkets of inferior intrinsic worth are commonly thinly coated with pure gold by electro-deposition or otherwise. The so-called *Mystery gold* is an alloy of about 1 part platinum and 2 parts copper with a little silver. It resists the action of strong nitric acid. The action of aqua regia, and then ammonia, reveals its cupric character. *Gold leaf* (U. S. P.) is nearly pure gold passed between rollers till it is about  $\frac{1}{800}$  of an inch in thickness, and then hammered between sheets of animal membrane termed gold-beater's skin and calf-skin vellum till it is  $\frac{1}{160000}$  or  $\frac{1}{200000}$  of an inch in thickness. It may even be hammered till 280,000 leaves would be required to form a pile an inch thick.

*Gold Coinage.*—The weight of gold is expressed in Great Britain in ounces troy and decimal parts of an ounce, and the metal is always taken to be of standard fineness (11 gold and 1 alloy) unless otherwise described. The degree of fineness of gold, as ascertained by assay, is expressed decimally, fine pure gold ("gold free from metallic impurities," B. P.) being taken as unity, or 1.000. Thus gold of British standard is said to be 0.9166 fine, of French standard 0.900 fine. The legal weight of the sovereign is 0.2568 ounce of standard gold, or 123.274 grains. The weight came from one pound of standard gold (5760 grains) being coined into 44½ guineas. Gold coins are legal tender to any amount, provided that the weight of each sovereign does not fall below 122.5 grains, or in the case of a half sovereign 61.125 grains; these are the "least current" weights of the coins.

*Note.*—In chemical analysis gold comes out among the sulphides of the metals precipitated by sulphuretted hydrogen; and of those sulphides, it, like the sulphides of tin, antimony, and arsenicum, is soluble in sulphhydrate of ammonium.

*Quantivalence.*—Gold is trivalent ( $Au'''$ ), but in some compounds univalent ( $Au'$ ).

### REACTIONS.

*Synthetical Reactions.*—Place a fragment of gold (*e. g.*, gold leaf) in ten or twenty drops of aqua regia (a mixture of three parts of nitric and four or five of hydrochloric acid), and set the test-tube aside in a warm place; solution of perchloride of gold or auric chloride ( $AuCl_3$ ) results. When the metal is dissolved, evaporate nearly to dryness to remove most of the excess of fluid, dilute with water, and retain the solution for subsequent experiments. Sixty grains of gold treated thus, and the resulting chloride dissolved in five ounces of distilled water, constitute "Solution of Perchloride of Gold," B. P. The persalt itself is very deliquescent. A compound of the chloride of gold and sodium, in molecular proportions, crystallizes readily and is more stable.





This reaction has analytical interest also; for in examining a substance suspected to be or contain metallic gold, solution would have to be effected in the above way before reagents could be applied. Gold is insoluble in hydrochloric, nitric, and the weaker acids.

*Chloride of Gold and Sodium* (*Auri et Sodii Chloridum*, U. S. P.) is "a mixture composed of equal parts of dry chloride of gold and chloride of sodium."

#### *Analytical Reactions (Tests).*

*First Analytical Reaction.*—Through a few drops of solution of an auric salt (the chloride,  $\text{AuCl}_3$ , is the only convenient one) pass sulphuretted hydrogen; brown auric sulphide ( $\text{Au}_2\text{S}_3$ ) is precipitated. Filter, wash, and add yellow sulphhydrate of ammonium solution; the precipitate dissolves.

*Second Analytical Reaction.*—To solution of a salt of gold add ferrous salt, and set the tube aside; metallic gold is precipitated, a ferric salt remaining in solution.

This is a convenient way of preparing pure gold, or *fine gold* as it is termed, or of working up the gold residues of laboratory operations. The precipitate, after boiling with hydrochloric acid, washing and drying, may be obtained in a button by mixing with an equal weight of borax or acid sulphate of potassium and fusing in a good furnace.

*Third Analytical Reaction.*—Add a few drops of dilute solutions of stannous and stannic chloride to a considerable quantity of distilled water; pour the liquid, a small quantity at a time, in a very dilute solution of auric chloride ( $\text{AuCl}_3$ ), well stirring; the mixture assumes a purple tint, and flocks of a precipitate known as the *Purple of Cassius* (from the name of the discoverer, M. Cassius) are produced.

The same compound is formed on immersing a piece of tin foil in solution of auric chloride; it is said to be a mixture of auric, aurous, stannic, and stannous oxides. It is the coloring agent in the finer varieties of ruby glass.

### PLATINUM.

Symbol Pt. Atomic weight 195.

*Source.*—Platinum, like gold, usually occurs in nature in the free state, the chief sources of supply being Mexico, Brazil, and Siberia. It is separated from the alluvial soil by washing.

*Uses.*—The chief use of platinum is in the construction of foil, wire, crucibles, spatulas, capsules, evaporating-dishes, and stills for the use of the chemical analyst or manufacturer. It is tolerably hard, fusible with very great difficulty, not dissolved by hydrochloric, nitric,

or sulphuric acid, and only slightly affected by alkaline substances. It is attacked by aqua regia, with production of perchloride of platinum or platonic chloride ( $\text{PtCl}_4, 5\text{H}_2\text{O}$ ). It forms fusible alloys with lead and other metals, and with phosphorus a phosphide, which easily melts. Neither of these substances, therefore, nor mixtures which may yield a metal, should be heated in platinum vessels.

The chemical position of platinum among the elements is close to that of gold. Its atom is quadrivalent in some compounds, in others apparently bivalent ( $\text{Pt}'$ ). The higher salts are termed *platonic*, the lower *platinous*.

The specific gravity of platinum is 21.5; and that of iridium, an allied metal, 22.4.

#### REACTIONS.

##### Perchloride of Platinum. Platonic Chloride.

*Synthetical Reaction.*—Place a fragment of platinum in a little aqua regia and set the vessel aside in a warm place, adding more acid from time to time if necessary; solution of perchloride of platinum ( $\text{PtCl}_4$ ) results. Evaporate the solution to remove excess of acid, and complete the desiccation over a water-bath. Dissolve the residue in water, and retain the solution for subsequent experiments, and as a reagent for the precipitation of salts of potassium and ammonium.

A quarter of an ounce of platinum treated in the above manner, and the resulting chloride dissolved in five ounces of water, constitutes "Solution of Perchloride of Platinum," B. P., or 1 part of pure platonic chloride ( $\text{PtCl}_4, 5\text{H}_2\text{O}$ ) dissolved in 20 of distilled water gives "Test Solution of Platonic Chloride," U. S. P.

This reaction has analytical interest also; for in examining a substance suspected to be or to contain metallic platinum, solution would have to be thus effected before reagents could be applied.

#### *Analytical Reactions (Tests).*

*First Analytical Reaction.*—Through a few drops of a solution of a platonic salt ( $\text{PtCl}_4$  is the only convenient one), to which an equal quantity of solution of chloride of sodium has been added, pass sulphuretted hydrogen; dark-brown platonic sulphide ( $\text{PtS}_2$ ) is precipitated. Filter, wash, and add sulphhydrate of ammonium; the precipitate dissolves.

If chloride of sodium be not present in the above reaction, the precipitated sulphide will contain platinous chloride, and may detonate if heated.

*Second Analytical Reaction.*—Add excess of solution of carbonate of sodium and some sugar to solution of perchloride of platinum and boil; a precipitate of metallic platinum falls.

*Platinum Black* is the name of this precipitate. It possesses in

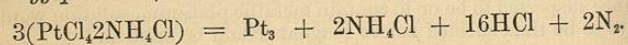


a high degree a quality common to many substances, but largely possessed by platinum, namely, that of absorbing or *occluding* gases. In its ordinary state, after well washing and drying, it absorbs from the air and retains many times its bulk of oxygen. A drop of ether or alcohol placed on it is rapidly oxidized, the platinum becoming hot. This action may be prettily shown by pouring a few drops of ether into a beaker (one having portions of the top and sides broken off answers best), loosely covering the vessel with a card, and suspending within the beaker a platinum wire, one end being attached to the card by passing through its centre, the other terminating in a short coil or helix near the surface of the ether; on now warming the helix in a flame and then rapidly introducing it into the beaker, it will become red hot, and continue to glow so long as there is ether in the vessel. In this experiment real combustion goes on between the ether vapor and the concentrated oxygen of the air, the products of the oxidation revealing themselves by their odor.

*Third Analytical Reaction.*—To solution of perchloride of platinum add solution of chloride of ammonium; a yellow granular precipitate of double chloride of platinum and ammonium ( $\text{PtCl}_4 \cdot 2\text{AmCl}$ ) falls. When slowly formed in dilute solutions, the precipitate is obtained in minute orange prisms.

Chloride of potassium (KCl) gives a similar precipitate ( $\text{PtCl}_4 \cdot 2\text{KCl}$ ). Platinic chloride having been stated to be a test for potassium and ammonium salts, the reader is prepared to find that potassium and ammonium salts are tests for platinic salts. The double sodium compound ( $\text{PtCl}_4 \cdot 2\text{NaCl}$ ) is soluble in water.

Collect the precipitate, dry, and heat in a small crucible; it is decomposed, and metal, in the finely divided state of *spongy platinum*, remains.



Heat decomposes the potassium salt into  $\text{Pt} + 2\text{KCl} + \text{Cl}_2$ , the chlorine escaping and the chloride of potassium remaining with the platinum.

*In working up the platinum residues of laboratory operations*, the mixture should be dried, burnt, boiled successively with hydrochloric acid, water, nitric acid, water, then dissolved in aqua regia, excess of acid removed by evaporation, chloride of ammonium added, the precipitate washed with water, dried, ignited, and the resulting spongy platinum retained or converted into perchloride for use as a reagent for alkali metals. It is by this process that the native platinum is treated to free it from the rare metals palladium, rhodium, osmium, ruthenium, and iridium. The spongy platinum is converted into the massive condition by a refinement on the blacksmith's process of *welding* (German *wellen*, to join), or by fusing in a flame of pure oxygen and hydrogen gases, the oxyhydrogen blowpipe.

*Occlusion by Spongy Platinum.*—Spongy platinum has great power of occlusion. A small piece held in a jet of hydrogen causes

ignition of the gas, owing to the close approximation of particles of oxygen (from the air) and hydrogen. Döbereiner's lamp is constructed on this principle—the apparatus being essentially a vessel in which hydrogen is generated by the action of diluted sulphuric acid on zinc, and a cage for holding the spongy platinum.

### CADMIUM.

Symbol Cd. Atomic weight 111.8.

In most of its chemical relations cadmium (*Cadmium*, U. S. P.) resembles zinc. In nature it occurs chiefly as an occasional constituent of the ores of that metal. In distilling zinc containing cadmium, the latter, being the more volatile, passes over first. In analytical operations, cadmium, unlike zinc, comes down among the metals precipitated by sulphuretted hydrogen; that is, its sulphide is insoluble in dilute hydrochloric acid, while sulphide of zinc is soluble. It is a white malleable metal nearly as volatile as mercury. Sp. gr. 8.7.

Beyond the occasional employment of the sulphide as a pigment (*jaune brillant*), and the iodide in photography, cadmium and its salts are but little used. The atom of cadmium is bivalent ( $\text{Cd}''$ ).

### REACTIONS.

#### Iodide of Cadmium.

*First Synthetical Reaction.*—Digest together in a flask metallic cadmium, water, and iodine until the color of the iodine disappears; solution of iodide of cadmium ( $\text{CdI}_2$ ) remains. Pearly micaceous crystals may be obtained on evaporating the solution.

This salt is employed, with other iodides, in iodizing collodion for photographic purposes. It melts when heated, and is soluble in water or spirit, the solution reddening litmus-paper.

#### Sulphate of Cadmium.

*Second Synthetical Reaction.*—Dissolve cadmium in nitric acid; pour the resulting solution of nitrate of cadmium ( $\text{Cd}(\text{NO}_3)_2$ ) into a solution of carbonate of sodium; dissolve the precipitate of carbonate of cadmium ( $\text{CdCO}_3$ ) in dilute sulphuric acid, separate and crystallize. Sulphate of cadmium ( $\text{CdSO}_4$ ) is a white crystalline salt soluble in water.

*First Analytical Reaction.*—Through solution of a cadmium salt ( $\text{CdI}_2$  or  $\text{CdCl}_2$ ) pass sulphuretted hydrogen; a yellow precipitate of sulphide of cadmium ( $\text{CdS}$ ) falls, resembling in appearance arsenious, arsenic, and stannic sulphides. Add sulphhydrate of ammonium; the precipitate, unlike the sulphides just mentioned, does not dissolve.