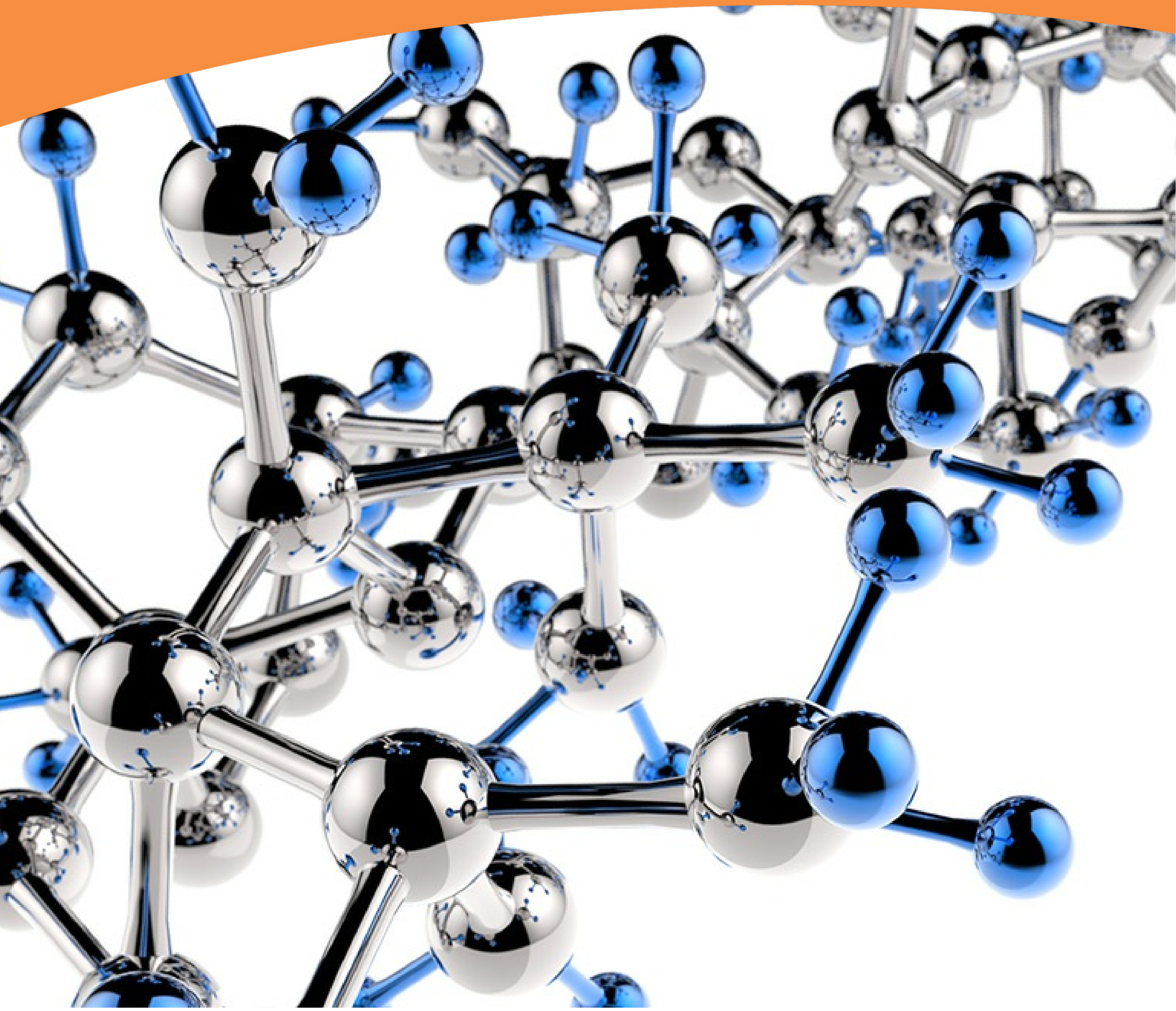
Essential Descriptive Inorganic Chemistry

What every chemistry student should know

Peter G. Nelson



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PETER G. NELSON

ESSENTIAL DESCRIPTIVE INORGANIC CHEMISTRY

WHAT EVERY CHEMISTRY STUDENT SHOULD KNOW

Essential Descriptive Inorganic Chemistry: What every chemistry student should know
1st edition

ISBN 978-87-403-1502-8
Peer review by Dr David A. Johnson, emeritus reader at the Open University, UK

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INTRODUCTION

Descriptive inorganic chemistry is a big subject. Comprehensive texts (e.g. *Comprehensive Inorganic Chemistry*) run into several volumes. No student is capable of learning all the facts.

Educators have responded to this by arguing that what students need to do is not learn facts but the principles and theories behind the facts. The problem with this approach is that chemical principles and theories are not good enough for this. They only explain a small fraction of all the facts. Teaching principles and theories without any facts therefore leaves students ignorant of many of the facts, including very basic ones.

This short text seeks to resolve this problem. It sets out the descriptive inorganic chemistry every chemistry student should know. Only the most important chemistry of the most important elements is included. These are the elements that come high in rankings based on natural abundance, world consumption, and number of compounds.[1] Elements are not grouped according to the Periodic Table as this can obscure their distinctive character. Considerations of periodicity complement the material presented here.

I have, for the most part, given substances their traditional names. These are the names in, for example, the *British National Formulary*, used by doctors and pharmacists. In some cases, these differ from the names recommended by the International Union of Pure and Applied Chemistry (IUPAC). In these cases, I also give the IUPAC name. I have followed IUPAC in my spelling of 'sulfur'.

I have also, for the most part, given substances their traditional formulae. Some of these are empirical (e.g. NaCl), some molecular (e.g. HCl), some mixed (e.g. Na_2O_2). Ideally, these should be differentiated as in, for example, (NaCl), [HCl], and ($Na_2[O_2]$), but this is cumbersome. As a general rule, (1) volatile substances are molecular, (2) involatile substances that are soluble in nonionizing volatile solvents are 'macromolecular' (i.e. they contain large molecules like C_{60}), and (3) involatile substances that are insoluble in nonionizing volatile solvents are 'nonmolecular' (i.e. have a framework structure like diamond or sodium chloride). Types (1) and (2) have molecular formulae, type 3 empirical formulae (or a mixed formula if they contain molecular ions).

In general formulae, M represents a metal atom, X a non-metal atom, and R a radical (CH_3, C_2H_5, etc.). 'Organic chemistry' is defined as the chemistry of hydrocarbons and their derivatives.

Acknowledgement

I am very grateful to Dr. David Johnson of the Open University for reading through drafts of this book and commenting extensively on them.

Illustrations

I have taken the illustrations from the internet, with my thanks. I have specified the sources in the captions. As far as I know, all are free to copy, but if any are not, I apologize.

1 HYDROGEN

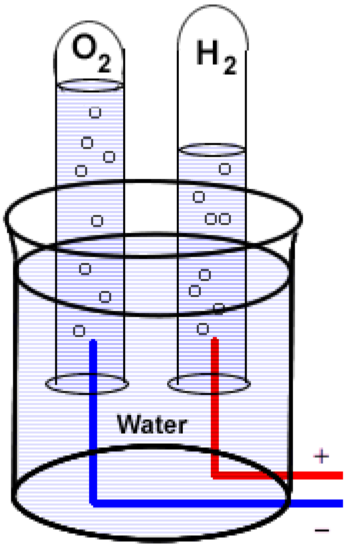
On earth, hydrogen occurs mainly as *water* (H_2O). Rain water contains dissolved carbon dioxide from the atmosphere and is slightly acidic:

$$CO_2 + H_2O = H^+(aq) + HCO_3^-(aq)$$

Mineral waters contain dissolved salts. Pure water is obtained by distillation. This conducts electricity slightly through self-ionization:

$$H_2O = H^+(aq) + OH^-(aq)$$

Hydrogen ions are hydrated [$H(H_2O)_4^+$ in dilute solution]. Acids increase the concentration of $H^+(aq)$ ions; alkalis increase the concentration of $OH^-(aq)$. Acids turn blue litmus red, alkalis red litmus blue.



Electrolysis of water in the laboratory
[LibreTexts]

Hydrogen (H_2) is obtained from water by electrolysis, the water being made more conducting by the addition of an acid or alkali:

$$2OH^-(aq) \rightarrow ½O_2\uparrow + H_2O + 2e^- \mid 2e^- + 2H^+(aq) \rightarrow H_2\uparrow$$

It is also prepared industrially by heating coke (from coal) or hydrocarbons (from petroleum oil) in steam:

$$C + H_2O \rightarrow CO + H_2$$

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n + 1)H_2$$

$$CO + H_2O \xrightarrow{\text{catalyst}} CO_2 + H_2$$

The mixture of CO and H_2 is called *water gas*.

In the laboratory, hydrogen can be made by the action of a dilute acid on zinc and other metals:

$$Zn + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2\uparrow$$

The gas is colourless, odourless, and very light. It burns in air or oxygen with a pale blue flame:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Some mixtures are explosive (hydrogen in a test-tube ignites with a ‘pop’).

Hydrogen combines with other non-metals, e.g.

$$H_2 + Cl_2 \rightarrow 2HCl$$

It also combines with some metals, e.g.

$$2Na + H_2 \rightarrow 2NaH$$

Sodium hydride is a colourless solid containing H^- ions and is a useful agent for converting RCl to RH:

$$RCl + NaH \rightarrow RH + NaCl$$

Large quantities of hydrogen are used to make ammonia (NH_3) and to hydrogenate unsaturated fats.

Prolonged electrolysis of water leads to a separation of isotopes, deuterium oxide (D_2O) accumulating in the residue.

2 OXYGEN

Oxygen (O_2) is a colourless, odourless gas, comprising about 1/5th of the atmosphere by volume. It is isolated by fractional distillation of liquid air and kept under pressure in steel cylinders.

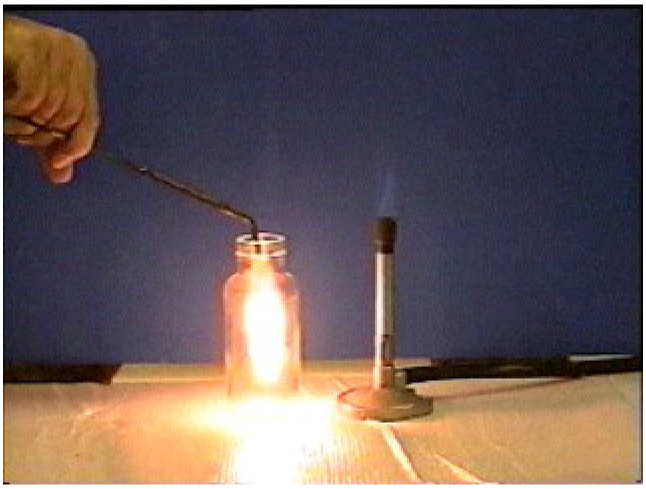
The gas combines with most other elements to form oxides. In these, oxygen atoms are almost always bivalent. For example, it combines with hydrogen to form water (H–O–H):

$$2H_2 + O_2 \rightarrow 2H_2O$$

There are a great many organic compounds containing oxygen atoms. They burn in air or oxygen to form carbon dioxide and water. The reaction is more vigorous in oxygen and can be dangerous (oxygen will reignite a glowing splint). Controlled oxidation of carbohydrates takes place in the body:

$$C_xH_{2y}O_y + xO_2 \rightarrow xCO_2 + yH_2O$$

The reverse process occurs in photosynthesis.



Wooden splint burning in oxygen
[Kevin A. Boudreaux]

Sodium burns in an excess of oxygen to give a pale yellow solid which, when added to an acid, gives a solution of hydrogen *peroxide* (H–O–O–H). (The solid is mainly sodium peroxide, $(Na^+)_2[O_2]^{2-}$, the yellow colour coming from a trace of *superoxide*, $(Na^+)[O_2]^-$.)

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2\uparrow$$

$$Na_2O_2 + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2O_2(aq)$$

The solution has strong oxidizing properties. It is used as a bleach and in the treatment of wastes. Pure hydrogen peroxide can be obtained by fractional distillation under reduced pressure, but the process is hazardous. The substance is made industrially by the oxidation of a quinol.

Oxygen can be prepared in the laboratory by a number of methods, e.g. by dropping water on sodium peroxide:

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2\uparrow$$

If an electric discharge is passed through oxygen, *ozone* is formed:

$$3O_2 \rightarrow 2O_3$$

This is a blue gas with a pungent smell. It is even more reactive than oxygen.

3 CARBON

Carbon exists in several forms. Important ones are *graphite* and *diamond*. Both occur naturally. Impure graphite is made by heating wood or coal in the absence of air to give respectively *charcoal* or *coke*. These are used as fuels, in metallurgy, and as absorbents. Diamonds are made by heating graphite under pressure. Diamond has a 3D framework structure, graphite a 2D one. Graphite is black, and conducts electricity in 2D. Both are very involatile. Other forms include *buckminsterfullerene* (C_{60}) and *graphene* (a single layer of graphite on a substrate).

Diamond and graphite
[Wikimedia]

Carbon burns in a limited supply of air to give carbon monoxide and in excess to give carbon dioxide:

$$2C + O_2 \rightarrow 2CO$$

$$2CO + O_2 \rightarrow 2CO_2$$

Carbon dioxide is a colourless, odourless gas, used in carbonated drinks. It is denser than air and does not support combustion, hence its use as a fire extinguisher. On freezing, it condenses under atmospheric pressure to a white solid (*dry ice*) and under higher pressure to a colourless liquid. Both are used as refrigerants.

Carbon dioxide dissolves in water to give weakly acidic solutions:

$$CO_2 + H_2O = H_2CO_3$$

$$H_2CO_3 = H^+(aq) + HCO_3^-(aq)$$

It reacts with alkalis to give salts of CO_3^{2-} and HCO_3^- ions:

$$CO_2 + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O$$

$$CO_3^{2-}(aq) + CO_2 + H_2O \rightarrow 2HCO_3^-(aq)$$

These are respectively carbonates and *bicarbonates* (hydrogencarbonates). They are colourless (unless the cation is coloured). Calcium carbonate occurs naturally (*limestone*). Carbon dioxide can be prepared in the laboratory by the action of an acid on a carbonate, e.g.

$$CaCO_3 + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2\uparrow + H_2O$$

Carbon monoxide is a colourless, odourless, very poisonous gas. It reacts with some metals to give *carbonyls*, from which useful derivatives can be made:

$$xM + yCO \rightarrow M_x(CO)_y$$

Metal carbonyls are very toxic.

Hydrocarbons occur in natural gas and petroleum oil. Natural gas comprises mainly methane (CH_4). The components of oil are reformed by heating (*cracking*) and separated by fractional distillation. Hydrocarbons burn in air or oxygen to carbon dioxide, e.g.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Carbon dioxide in the atmosphere affects the climate.

On heating, carbon combines with many metals to form carbides, e.g.

$$3Fe + C \rightarrow Fe_3C$$

Iron carbide is a grey, metallic compound and is present in steel.

4 CALCIUM

Calcium occurs naturally in *limestone* or *chalk* (calcium carbonate, $CaCO_3$). When heated, this is converted into *quicklime* or *lime* (calcium oxide, CaO):

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

Quicklime reacts vigorously with water to give *slaked lime* (calcium hydroxide, $Ca(OH)_2$):

$$CaO + H_2O \rightarrow Ca(OH)_2$$

All three compounds are white solids. Limestone is used to make cement by heating it with clay.

Lime works
[FreeFoto]

Calcium hydroxide is sparingly soluble in water to give an alkaline solution (*lime water*):

$$Ca(OH)_2 + aq \rightarrow Ca^{2+}(aq) + 2O_2H^-(aq)$$

Bubbling carbon dioxide through the solution gives a white precipitate of calcium carbonate:

$$Ca^{2+}(aq) + 2OH^-(aq) + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

This is a test for CO_2.

Treatment of calcium hydroxide with acids gives calcium salts:

$$Ca(OH)_2 + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2H_2O$$

These are colourless (unless the anion is coloured), but impart a brick-red colour to a flame. Calcium hydroxide is used to reduce acidity in soils.

Calcium sulfate occurs naturally as *gypsum* ($CaSO_4 \cdot 2H_2O$). This loses water on heating to give a powder that readily takes up water to form a solid mass. This is used as plaster.

Calcium chloride crystallizes as a hydrate ($CaCl_2 \cdot 6H_2O$). The anhydrous salt ($CaCl_2$) can be obtained by heating, and is used as a desiccant.

Calcium salts of the organic anions in soaps are insoluble, hence the scum formed when washing in hard water. Hard water produces a scale when heated because of the reaction:

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O$$

The reverse reaction occurs in the cold and leads to the erosion of limestone.

Calcium itself is made by electrolysis of molten calcium chloride:

$$2Cl^-(CaCl_2) \rightarrow Cl_2\uparrow + 2e^- \mid 2e^- + Ca^{2+}(CaCl_2) \rightarrow Ca$$

It is also be made by heating calcium oxide with aluminium (an example of the *thermit* reaction):

$$3CaO + 2Al \rightarrow 3Ca + Al_2O_3$$

The element is a fairly hard, grey metal. It reacts with water to give hydrogen:

$$Ca + 2H_2O \rightarrow Ca^{2+}(aq) + 2OH^-(aq) + H_2\uparrow$$

Calcium
[Metabunk]

5 SODIUM AND POTASSIUM

Sodium

Sodium occurs naturally in *rock salt* (common salt, sodium chloride, NaCl) and *brine* (aqueous NaCl).

Rock salt
[The Spice Lab]

Important compounds are *soda-ash* (sodium carbonate, Na_2CO_3), *sodium bicarbonate* (sodium hydrogencarbonate, $NaHCO_3$), and *caustic soda* (sodium hydroxide, NaOH). These are all white solids and used as alkalis.

Sodium is made by electrolysis of molten sodium chloride:

$$Cl^-(NaCl) \rightarrow \tfrac{1}{2}Cl_2\uparrow + e^- \mid e^- + Na^+(NaCl) \rightarrow Na$$

Sodium hydroxide is made similarly by electrolysis of aqueous sodium chloride:

$$Cl^-(aq) \rightarrow \tfrac{1}{2}Cl_2\uparrow + e^- \mid e^- + H_2O \rightarrow OH^-(aq) + \tfrac{1}{2}H_2\uparrow$$

Sodium bicarbonate is made by bubbling carbon dioxide through an aqueous solution of sodium chloride and ammonia (the *Solvay* process):

$$NaCl(aq) + NH_3(aq) + CO_2 + H_2O \rightarrow NaHCO_3\downarrow + NH_4Cl(aq)$$

Ammonia is regenerated from the aqueous ammonium chloride produced by heating it with lime (made, along with the carbon dioxide used, by heating limestone):

$$2NH_4Cl(aq) + CaO \rightarrow 2NH_3\uparrow + CaCl_2(aq) + H_2O$$

Heating sodium bicarbonate gives the carbonate:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2\uparrow + H_2O\uparrow$$

The carbonate is also formed by burning seaweed, hence the name 'soda-ash'.

Sodium bicarbonate is a mild alkali because of the equilibrium:

$$HCO_3^-(aq) + H_2O = H_2CO_3(aq) + OH^-(aq)$$

Sodium carbonate is a stronger alkali because of two equilibria, this and:

$$CO_3^{2-}(aq) + H_2O = HCO_3^-(aq) + OH^-(aq)$$

Sodium hydroxide is a very strong alkali and can burn the skin.

All three alkalis react with acids to form sodium salts, e.g.

$$NaOH + H^+(aq) \rightarrow Na^+ + H_2O$$

$$Na_2CO_3 + 2H^+(aq) \rightarrow 2Na^+(aq) + CO_2\uparrow + H_2O$$

Sodium salts are colourless (unless the anion is coloured), but impart a characteristic yellow colour to a flame. Most are freely soluble in water. Sodium nitrate ($NaNO_3$) occurs naturally as *Chile saltpetre*.

Sodium itself is a soft, grey metal. It tarnishes rapidly in air and reacts vigorously with water:

$$4Na + O_2 \rightarrow 2Na_2O$$

$$2Na_2O + O_2 \rightarrow 2Na_2O_2$$

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

It is accordingly kept under paraffin.

Sodium metal
[Weebly]

Potassium

Potassium is similar to sodium. An important difference is that it is essential for plant growth. The ash from burning land plants (*potash*) is potassium carbonate (K_2CO_3). The most important ore is *sylvite* (potassium chloride, KCl). This is used under the name 'potash' as a fertilizer. Potassium salts impart a lilac colour to a flame.

Potassium burns in air or oxygen to the yellow superoxide (KO_2).

6 CHLORINE

Chlorine (Cl_2) is a greenish yellow gas with a characteristic pungent smell. It is made by electrolysis of aqueous sodium chloride (NaCl):

$$Cl^-(aq) \rightarrow \tfrac{1}{2}Cl_2\uparrow + e^- \mid e^- + H_2O \rightarrow OH^-(aq) + \tfrac{1}{2}H_2\uparrow$$

Sodium chloride occurs naturally as *rock salt*. The gas is stored in metal cylinders.

Chlorine
[IndiaMART]

Hydrogen burns in chlorine to form hydrogen chloride:

$$H_2 + Cl_2 \rightarrow 2HCl$$

This is a colourless gas with a sharp, irritating smell. It fumes in moist air and dissolves very readily in water to give hydrochloric acid:

$$HCl + aq \rightarrow H^+(aq) + Cl^-(aq)$$

This is a strong acid with many uses.

Chlorine combines with other elements to form chlorides. These can also be made using hydrogen chloride or hydrochloric acid. For example, iron reacts with hydrogen chloride to give its lower chloride ($FeCl_2$), while chlorine gives the higher chloride ($FeCl_3$):

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

In most chlorine compounds, the element is univalent.

Chlorine combines with hydrocarbons to form chloro-compounds:

$$RH + Cl_2 \rightarrow RCl + HCl$$

These can also be made by treating alcohols with a hydrolysable chloride, e.g. PCl_5:

$$2ROH + PCl_5 \rightarrow 2RCl + POCl_3 + H_2O$$

Chlorine partially dissolves in water and is used to kill bacteria in water supplies. The gas dissolves in aqueous sodium hydroxide to give a solution used as a bleach. This contains *hypochlorite* ions (ClO^-, chlorate(I)):

$$Cl_2 + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O$$

With calcium hydroxide, *bleaching powder* is produced:

$$2Ca(OH)_2 + 2Cl_2 \rightarrow (Ca(OCl)_2, CaCl_2, 2H_2O)$$

Chlorine also forms *chlorite* (ClO_2^-, chlorate(III)), *chlorate* (ClO_3^-, chlorate(V)), and *perchlorate* ions (ClO_4^-, chlorate(VII)). Perchlorates are used when a non-complexing anion is required.

Chlorine is widely used in the manufacture of chlorinated plastics such as PVC.

Chlorine can be prepared in the laboratory by several methods, the simplest being by the action of hydrochloric acid on bleaching powder:

$$(Ca(OCl)_2, CaCl_2, 2H_2O) + 4H^+(aq) \rightarrow 2Ca^{2+}(aq) + 2Cl_2\uparrow + 4H_2O$$

Hydrogen chloride can be prepared by the action of concentrated sulfuric acid on sodium chloride:

$$NaCl + H_2SO_4 \rightarrow HCl\uparrow + NaHSO_4$$

7 FLUORINE

The most important fluorine mineral is *fluorspar* or *fluorite* (calcium fluoride, CaF_2). Treatment of this with sulfuric acid gives hydrogen fluoride:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF\uparrow$$

This is a colourless gas which condenses to a colourless liquid at 19°C. It is kept in steel cylinders. Because it attacks glass and causes serious burns, it has to be handled in metal or polyfluorocarbon apparatus using protective clothing. The liquid is a very good solvent.

Hydrogen fluoride readily dissolves in water to give *hydrofluoric acid*. This can be handled in polythene. Reaction with glass gives $[SiF_6]^{2-}$ ions:

$$SiO_2 + 6HF(aq) \rightarrow 2H^+(aq) + [SiF_6]^{2-}(aq) + 2H_2O$$

Hydrofluoric acid is a weak acid:

$$HF(aq) = H^+(aq) + F^-(aq)$$

$$F^-(aq) + HF(aq) = HF_2^-(aq)$$

Reaction with alkalis gives salts containing colourless F^- and HF_2^- ions (fluorides and hydrogendifluorides).

Hydrofluoric acid in polythene bottle
[Wikipedia]

Fluorine itself is obtained by electrolysis of hydrogen fluoride made conducting with potassium fluoride:

$$2F^-(HF) \rightarrow F_2\uparrow + 2e^- \mid 2e^- + 2H^+(HF) \rightarrow H_2\uparrow$$

This is a pale yellow gas with a sickly smell. It is stored in steel cylinders and handled in metal or polyfluorocarbon apparatus. It reacts readily with most other elements to give fluorides. It also readily displaces other non-metals from their compounds, e.g.

$$NaCl + F_2 \rightarrow NaF + ClF\uparrow$$

For elements having more than one valency, fluorine brings out a high valency. For example, sulfur burns in fluorine to give sulfur hexafluoride (SF_6):

$$S + 3F_2 \rightarrow SF_6$$

Chlorine under similar conditions gives SCl_2. Fluorine brings out high valencies in some metals. For example, nickel normally has a valency of two, but heating a mixture of 2KCl and $NiCl_2$ in fluorine gives quadrivalent K_2NiF_6. In its compounds, fluorine is always univalent.

Fluorine forms many organic compounds, with some or all of the hydrogen atoms replaced by fluorine. The latter are known as *perfluoro*-compounds, and are made by fluorinating the corresponding hydrogen compounds with fluorine or a reactive fluoride. Other fluoro-compounds are made by various methods, e.g.

$$RCl + HF \rightarrow RF + HCl$$

8 NITROGEN

Nitrogen (N_2) is a colourless, odourless gas, comprising about 4/5ths of the atmosphere by volume. It is isolated by fractional distillation of liquid air and kept under pressure in steel cylinders.

Nitrogen partially combines with hydrogen when these are heated together under pressure in the presence of an iron catalyst (the *Haber* process):

$$N_2 + 3H_2 = 2NH_3$$

The product (*ammonia*) is separated by liquefaction and kept in steel cylinders. It is a pungent gas which dissolves in water to give a weakly alkaline solution:

$$NH_3(aq) + H_2O = NH_4^+(aq) + OH^-(aq)$$

Addition of acids gives *ammonium* salts:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

These are colourless unless the anion is coloured. Ammonia can be prepared in the laboratory from ammonium chloride and slaked lime:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3\uparrow + 2H_2O$$

Liquid ammonia is a solvent. It dissolves metallic sodium and potassium to give blue solutions containing M^+ ions and free electrons.

Ammonia burns in air or oxygen to nitrogen:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

However, in the presence of a platinum catalyst, nitrogen monoxide (NO) is formed:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

This is a colourless gas, which, in excess of air or oxygen, reacts further to give nitrogen dioxide (NO_2):

$$2NO + O_2 \rightarrow 2NO_2$$

This is a brown gas, which reacts with water to give *nitric acid*:

$$3NO_2 + H_2O \rightarrow 2HNO_3(aq) + NO\uparrow$$

This can be concentrated by distilling it with concentrated sulfuric acid. The concentrated acid is a brownish liquid as a result of partial decomposition into nitrogen dioxide:

$$2HNO_3 = 2NO_2 + H_2O + \tfrac{1}{2}O_2$$

Nitric acid is a strong acid, and combines with alkalis to form *nitrates*:

$$HNO_3 + aq \rightarrow H^+(aq) + NO_3^-(aq)$$

These are colourless unless the cations are coloured. Sodium and potassium nitrates occur naturally (KNO_3, *nitre* or *saltpetre*; $NaNO_3$, *Chile saltpetre*). Ammonium nitrate (NH_4NO_3) is used widely as a fertilizer along with ammonia itself and other derivatives.

As well as being a strong acid, nitric acid is a strong oxidizing agent, and dissolves some metals that other acids will not, e.g. copper:

Dilute acid: $3Cu + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO\uparrow + 4H_2O$

Conc. acid: $Cu + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2\uparrow + 2H_2O$

Copper dissolving in concentrated nitric acid
[Exploratorium]

Nitrogen forms a second series of salts (*nitrites*). These can be made by reducing nitrates, e.g.

$$2NaNO_3 \xrightarrow{\text{heat}} 2NaNO_2 + O_2\uparrow$$

Nitrogen forms other hydrides and oxides. These include *hydrazine* (N_2H_4), made by oxidizing ammonia with aqueous sodium hypochlorite:

$$2NH_3(aq) + ClO^-(aq) \rightarrow N_2H_4(aq) + Cl^-(aq) + H_2O$$

This is a powerful reducing agent, being readily oxidized to N_2. Among the other oxides is *nitrous oxide* or 'laughing gas' (dinitrogen monoxide, N_2O), made by heating ammonium nitrate or, more safely, a mixture of ammonium sulfate and sodium nitrate:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

$$(NH_4)_2SO_4 + 2KNO_3 \rightarrow K_2SO_4 + 2N_2O + 4H_2O$$

The gas supports combustion and rekindles a glowing splint.

When ammonia is heated with methane over a platinum catalyst, *hydrogen cyanide* (HCN) is formed:

$$CH_4 + NH_3 \rightarrow HCN + 3H_2$$

This is a colourless gas with the smell of almonds. Its solution in water is weakly acidic, and reacts with alkalis to produce *cyanides*:

$$HCN(aq) + OH^-(aq) \rightarrow CN^-(aq) + H_2O$$

These are colourless when the cations are colourless. The gas and its salts are extremely poisonous. Cyanide ions form strong complexes with some metal ions, e.g. $[Fe(CN)_6]^{4-}$.

There are a great many organic compounds containing nitrogen. These include amines (RNH_2, R_2NH, R_3N) and nitro-compounds (RNO_2).

9 SULFUR

Sulfur occurs naturally in a few locations as a bright yellow crystalline solid (*brimstone*). This can be extracted by melting it (the *Frasch* process). In this form it comprises S_8 molecules in which sulfur atoms are bound into an eight-membered ring. It can be obtained in other forms (S_n). Since the atomicity varies, I shall use the empirical formula S.

Sulfur
[Mini Me Geology]

Sulfur burns in air to sulfur dioxide:

$$S + O_2 \rightarrow SO_2$$

This is a colourless gas with a choking smell. It dissolves in water to give a weakly acidic solution:

$$SO_2 + H_2O = H^+(aq) + HSO_3^-(aq)$$

Reactions with alkalis give salts of SO_3^{2-} and HSO_3^- ions:

$$SO_2 + 2OH^-(aq) \rightarrow SO_3^{2-}(aq) + H_2O$$

$$SO_3^{2-}(aq) + SO_2 + H_2O \rightarrow 2HSO_3^-(aq)$$

These are called respectively *sulfites* and *bisulfites* (hydrogensulphites). They are colourless (unless the cation is coloured) and are useful reducing agents, being readily oxidized.

Sulfur dioxide combines further with oxygen in the presence of a catalyst to give sulfur trioxide:

$$2SO_2 + O_2 = 2SO_3$$

This is a colourless gas which condenses to a white solid containing $(SO_3)_3$ molecules. It reacts vigorously with a stoicheiometric quantity of water to give hydrogen sulfate or *concentrated sulfuric acid* (*oil of vitriol*):

$$SO_3 + H_2O \rightarrow H_2SO_4$$

This is a colourless, oily liquid. It is very corrosive and burns the skin. It reacts vigorously with more water to form *sulfuric acid*:

$$H_2SO_4 + aq \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

This is a strong acid and widely used. Sulfates are colourless (unless the cation is coloured). Some occur naturally, e.g. $CaSO_4{\cdot}2H_2O$ (*gypsum*).

Sulfuric acid plant
[DSD Chemtech]

Sulfur dioxide can be prepared in the laboratory by the action of concentrated sulfuric acid on a sulfite, e.g.

$$2NaHSO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2SO_2\uparrow + 2H_2O$$

Sulfur forms other oxo-compounds. When a solution of a sulfite is boiled with sulfur, a *thiosulfate* is formed, analogous to SO_4^{2-}:

$$SO_3^{2-} + S \rightarrow S_2O_3^{2-}$$

Sulfur burns in fluorine to give sulfur hexafluoride:

$$S + 3F_2 \rightarrow SF_6$$

This is a colourless, odourless, unreactive gas. Its inertness makes it very useful.

On heating, sulfur combines with many metals to form sulfides, e.g.

$$Fe + S \rightarrow FeS$$

$$FeS + S \rightarrow FeS_2$$

Iron monosulfide is a grey, nonstoicheiometric solid. It reacts with acids to give hydrogen sulphide:

$$FeS + 2H^{+}(aq) \rightarrow Fe^{2+}(aq) + H_2S\uparrow$$

Iron disulfide is golden-yellow in colour and occurs naturally as *iron pyrites* or *fools' gold*. It contains S_2^{2-} ions.

Hydrogen sulfide is a colourless gas with the odour of bad eggs. It is extremely poisonous. It occurs naturally in sour natural gas, from which it can be extracted with an aqueous amine:

$$RNH_2(aq) + H_2S = RNH_3^{+}(aq) + HS^{-}(aq)$$

It can also be obtained by reducing organic sulfides in petroleum oil:

$$RSH + H_2 \rightarrow RH + H_2S$$

The gas is oxidized to sulfur using a catalyst (the *Claus* process):

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O$$

10 PHOSPHORUS

Phosphorus occurs most widely as *phosphate rock*. This has the approximate composition $Ca_3(PO_4)_2$. Treatment of this with concentrated sulfuric acid gives hydrogen phosphate:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4\downarrow$$

This is a colourless, low-melting solid, which readily dissolves in water to give *phosphoric acid*:

$$H_3PO_4(aq) = H^+(aq) + H_2PO_4^-(aq)$$

$$H_2PO_4^-(aq) = H^+(aq) + HPO_4^{2-}(aq)$$

$$HPO_4^{2-}(aq) = H^+(aq) + PO_4^{3-}(aq)$$

Concentrated solutions of this (typically 85%) are syrupy. Reaction with alkalis gives salts containing colourless PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ ions (phosphate, hydrogenphosphate, dihydrogenphosphate). Ammonium phosphate is used as a fertilizer.

Hydrogen-containing phosphate ions can combine together by loss of water molecules to form a wide variety of polynuclear ions. For example,

$$n\mathrm{NaH_2PO_4} \xrightarrow{\text{heat}} (\mathrm{NaPO_3})_n + n\mathrm{H_2O}\uparrow$$

The product in this case contains $-O-PO_2^--O-PO_2^--$ chains. DNA contains similar chains.

Phosphorus itself can be obtained by heating phosphate rock with sand (SiO_2) and coke (C):

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + P_2\uparrow$$

Condensation of the vapour gives white phosphorus, a waxy solid comprising P_4 molecules. Since this easily catches fire, it is kept under water. From it, red and black forms can be obtained by the application of heat and pressure. These have nonmolecular structures (P_n). I shall represent the element by the empirical formula P.

Red and white phosphorus
[BBC]

Phosphorus burns in an excess of air or oxygen to *phosphorus pentoxide*, $(P_2O_5)_2$:

$$4P + 5O_2 \rightarrow P_4O_{10}$$

This is a white solid that readily takes up water and is used as a drying agent:

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Phosphorus also forms lower oxides and acids.

Phosphorus burns in a limited supply of chlorine to phosphorus trichloride and in excess to phosphorus pentachloride:

$$2P + 3Cl_2 \rightarrow 2PCl_3$$

$$2P + 5Cl_2 \rightarrow 2PCl_5$$

The trichloride is a colourless liquid, the pentachloride a white solid. With a Grignard reagent, P–Cl can be converted to P–R:

$$P\text{–}Cl + RMgCl \rightarrow P\text{–}R + MgCl_2$$

Phosphorus combines with many metals to form phosphides, e.g.

$$3Ca + 2P \rightarrow Ca_3P_2$$

Hydrolysis of calcium phosphide gives *phosphine*:

$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3\uparrow + 3Ca(OH)_2$$

This is a colourless gas with the smell of rotten fish and is poisonous.

11 SILICON

Silicon occurs naturally in rocks and sands as silicon dioxide (*silica*, SiO_2) and metal silicates (e.g. *feldspars*). These are used as building materials. Silica is fused with alkalis (typically Na_2CO_3 and $CaCO_3$) to make glass. Feldspars are sodium, potassium, or calcium aluminosilicates (e.g. $NaAlSi_3O_8$).

Silicon also occurs in clays. These are baked to make bricks, and with limestone ($CaCO_3$) to make cement. Clays are aluminium silicates (e.g. china clay, $Al_2(OH)_4Si_2O_5$).

Silicon is extracted from silica by heating this with coke:

$$SiO_2 + 2C \rightarrow Si + 2CO\uparrow$$

Pure silicon is an involatile lustrous grey semiconductor. It can be doped with other elements to change its electrical properties and make 'silicon chips'.

Silicon
[WebElements]

Silicon combines with chlorine to form silicon tetrachloride:

$$Si + 2Cl_2 \rightarrow SiCl_4$$

This is a colourless liquid which fumes in moist air:

$$SiCl_4 + (4 - x)H_2O \rightarrow SiO_x(OH)_{4-2x}\downarrow + 4H^+(aq) + 4Cl^-(aq)$$

It is a starting point for the preparation of organosilicon compounds. For example, treatment with two moles of a Grignard reagent gives R_2SiCl_2:

$$SiCl_4 + 2RMgCl \rightarrow R_2SiCl_2 + 2MgCl_2$$

The same product can be obtained by passing RCl over hot silicon in the presence of copper:

$$Si + 2RCl \rightarrow R_2SiCl_2$$

Hydrolysis of this gives a polymer:

$$R_2SiCl_2 + H_2O \rightarrow (1/n)(–SiR_2–O–)_n + 2HCl$$

This is a *silicone*. Terminal groups are made by including R_3SiCl and branching groups, $RSiCl_3$. Silicones have a variety of uses.

When heated with an excess of carbon, silicon forms silicon carbide (SiC). When pure this is colourless, but the commercial material has a dark colour. It is very hard and used as an abrasive (*carborundum*).

Silicon combines with metals to form *silicides* (e.g. Mg_2Si). Treatment of these with acid gives silicon hydrides (*silanes*, SiH_4, Si_2H_6, Si_3H_8 etc.). These are inflammable in air.

12 IRON

Small quantities of iron occur naturally in meteorites. The metal is extracted from iron oxide ores (usually red-brown *haematite*, Fe_2O_3) by heating the ore with coke (C) and limestone ($CaCO_3$) in a blast of air to give *pig-iron*. The net reaction is

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2\uparrow$$

The limestone removes impurities from the ore as a slag. Pig-iron contains carbon in the form of iron carbide (Fe_3C). The concentration of this is reduced by blowing oxygen through molten pig-iron in a converter to make *steel*. Other metals are added to make the kind of steel required, e.g. chromium for stainless steel.

Iron ore
[Canadian Business Journal]

Blast furnace
[Pinterest]

Iron is a malleable grey metal, which rusts in moist air to a red-brown powder of approximate composition $Fe(OH)_3$:

$$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3$$

The element forms two main series of compounds: bivalent (*ferrous* or iron(II)) and trivalent (*ferric* or iron(III)). Thus it dissolves in mineral acids to form pale green $Fe^{2+}(aq)$ ions:

$$Fe + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2\uparrow$$

These are readily oxidized to $Fe^{3+}(aq)$ ions, e.g. with hydrogen peroxide:

$$2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O$$

Aqueous Fe^{3+} ions are pale violet, but solutions containing them are often yellow because of hydrolysis or complexing:

$$Fe^{3+}(aq) + H_2O = FeOH^{2+}(aq) + H^+(aq)$$

$$Fe^{3+}(aq) + Cl^-(aq) = FeCl^{2+}(aq)$$

In neutral or alkaline solutions, Fe^{2+} ions are oxidized by air. Thus addition of aqueous sodium hydroxide to a Fe^{2+} solution precipitates pale green ferrous hydroxide which darkens on exposure to air to form a red-brown, gelatinous precipitate of ferric hydroxide

$$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2\downarrow$$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3$$

Ferric hydroxide contains variable amounts of water.

Ferrous sulfate, $FeSO_4 \cdot 7H_2O$ (green vitriol)
[IndiaMART]

Both Fe^{2+} and Fe^{3+} ions form complexes, e.g. $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$. The pigment *Prussian blue* is a mixed Fe^{II}-Fe^{III} cyano-complex. In *haemoglobin*, an Fe^{2+} ion is coordinated by five nitrogen atoms, leaving one coordination position to bind an O_2 molecule.

Iron also forms organometallic compounds. For example, powdered iron combines with carbon monoxide to give iron pentacarbonyl:

$$Fe + 5CO \xrightarrow{\text{heat}} Fe(CO)_5$$

This is a toxic, yellow liquid. Treatment of anhydrous iron dichloride with sodium cyclopentadienyl in ether gives orange crystals of *ferrocene*:

$$FeCl_2 + 2NaC_5H_5 \rightarrow Fe(C_5H_5)_2 + 2NaCl$$

This has a sandwich structure. Both compounds satisfy the 18-electron rule.

13 ALUMINIUM

Large quantities of aluminium occur in silicate rocks, sands, and clays. The main ore is *bauxite* ($AlO_x(OH)_{3-2x}$). It also occurs as *cryolite* (Na_3AlF_6).

The metal is extracted by electrolysing a solution of aluminium oxide (Al_2O_3) in molten cryolite (cry.):

$$6O^{2-}(cry.) \rightarrow 3O_2\uparrow + 12e^- \mid 12e^- + 4Al^{3+}(cry.) \rightarrow 4Al$$

The oxide is made by dissolving bauxite in aqueous sodium hydroxide, removing insoluble impurities, precipitating aluminium hydroxide with acid, and heating:

$$AlO_x(OH)_{3-2x} + OH^-(aq) + xH_2O \rightarrow [Al(OH)_4]^-(aq)$$

$$[Al(OH)_4]^-(aq) + H^+(aq) \rightarrow Al(OH)_3\downarrow + H_2O$$

$$2Al(OH)_3 \xrightarrow{\text{heat}} Al_2O_3 + 3H_2O\uparrow$$

The cryolite, if not mined, is made from bauxite, fluorspar (CaF_2), and soda-ash (Na_2CO_3).

The metal is whitish grey, light, malleable, and a good conductor of electricity. It does not rust because its oxide forms a protective layer over the surface. The metal is widely used as a structural material, e.g. in aircraft.

Aluminium burns brightly when heated in air or oxygen:

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

The metal abstracts oxygen from many metal oxides when it is heated with them (the *thermit* reaction), e.g.

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

The reaction is so exothermic as to melt the iron.

In the presence of chloride ions, aluminium dissolves in mineral acids to give aluminium salts:

$$2\mathrm{Al} + 6\mathrm{H}^{+}(\mathrm{aq}) \rightarrow 2\mathrm{Al}^{3+}(\mathrm{aq}) + 3\mathrm{H}_2\uparrow$$

The chloride ions disrupt the protective oxide film. The salts are colourless when the anions are colourless. Addition of aqueous sodium hydroxide precipitates aluminium hydroxide:

$$\mathrm{Al}^{3+}(\mathrm{aq}) + 3\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{Al(OH)}_3\downarrow$$

This is a white, gelatinous solid containing variable amounts of water. The solid dissolves in excess of aqueous sodium hydroxide to give aluminate ions as in the purification of bauxite:

$$\mathrm{Al(OH)}_3 + \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow [\mathrm{Al(OH)}_4]^{-}(\mathrm{aq})$$

Aluminium hydroxide is thus amphoteric. The metal itself will dissolve in hydroxide solutions:

$$2\mathrm{Al} + 2\mathrm{OH}^{-}(\mathrm{aq}) + 6\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{Al(OH)}_4^{-}(\mathrm{aq}) + 3\mathrm{H}_2\uparrow$$

The double salt potassium aluminium sulfate (*alum*, $\mathrm{KAl(SO_4)_2{\cdot}12H_2O}$) is used as a mordant.

Alum crystals
[Natural Deodorant Store]

Aluminium burns in chlorine to give aluminium chloride:

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

This readily takes up water, but in its anhydrous state is used in organic chemistry to catalyse Friedel-Crafts reactions. With Grignard reagents, it forms air-sensitive organoaluminium compounds, which are also used as catalysts:

$$AlCl_3 + 3RMgCl \rightarrow (1/n)(AlR_3)_n + 3MgCl_2 \ (n = 1 \text{ or } 2)$$

Another useful reagent is lithium aluminium hydride ($LiAlH_4$) made by heating the elements together under pressure:

$$Li + Al + 2H_2 \rightarrow LiAlH_4$$

This is a white solid rapidly hydrolysed by moisture.

14 COPPER

Small quantities of copper occur naturally. Most is extracted from *iron pyrite* (FeS_2) containing small amounts of *copper pyrite* ($CuFeS_2$). This is fused with silica (SiO_2) and a blast of air forced through it. This converts the iron to iron silicate slag and releases the copper:

$$2FeS_2 + 2SiO_2 + 5O_2 \rightarrow 2FeSiO_3 + 4SO_2\uparrow$$

$$2CuFeS_2 + 2SiO_2 + 5O_2 \rightarrow 2Cu + 2FeSiO_3 + 4SO_2\uparrow$$

The copper is purified by electrolysis:

$$Cu(crude) \rightarrow Cu^{2+}(aq) + 2e^- \mid 2e^- + Cu^{2+}(aq) \rightarrow Cu(pure)$$

Copper is a reddish, malleable metal. It is an excellent conductor of electricity, widely used in electrical wiring. Its surface turns brown in moist air and then green. The brown colour is due to the formation of oxide, the green to copper salts derived from acid gases (CO_2, SO_2) in the air. The metal forms alloys with zinc (*brass*), tin (*bronze*) and nickel (*monel metal*).

Copper only dissolves in oxidizing acids, e.g. nitric acid:

Dilute acid: $3Cu + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO\uparrow + 4H_2O$

Conc. acid: $Cu + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2\uparrow + 2H_2O$

It will, however, dissolve in other acids in the presence of oxygen:

$$2Cu + 4H^+(aq) + O_2 \rightarrow 2Cu^{2+}(aq) + 2H_2O$$

Copper forms two main series of compounds: univalent (*cuprous* or copper(I)) and bivalent (*cupric* or copper(II)). Thus when heated in air or oxygen it forms black cupric oxide (CuO), which decomposes on stronger heating to red cuprous oxide (Cu_2O):

$$2Cu + O_2 \rightarrow 2CuO$$

$$4CuO \rightarrow 2Cu_2O + O_2\uparrow$$

Cu_2O and CuO dissolve in non-complexing mineral acids to give respectively colourless $Cu^+(aq)$ and blue $Cu^{2+}(aq)$ ions:

$$Cu_2O + 2H^+(aq) \rightarrow 2Cu^+(aq) + H_2O$$

$$CuO + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O$$

The former rapidly disproportionate:

$$2Cu^+(aq) \rightarrow Cu\downarrow + Cu^{2+}(aq)$$

This does not happen in strong hydrochloric acid because the cuprous chloro-complex is stronger than the cupric:

$$Cu^+(aq) + 2Cl^-(aq) \rightarrow [CuCl_2]^-(aq) \text{ (yellow)}$$

$$Cu^{2+}(aq) + Cl^-(aq) = CuCl^+(aq) \text{ (green)}$$

Indeed, the reverse reaction can take place under these conditions:

$$Cu + CuCl^+(aq) + 3Cl^-(aq) \rightarrow 2[CuCl_2]^-(aq)$$

Cupric sulfate, $CuSO_4{\cdot}5H_2O$ (blue vitriol)
[nontoxicprint]

Cupric complexes include dark blue $[Cu(NH_3)_4]^{2+}$ and the oxygen-carrier in many organisms (*haemocyanin*).

15 MANGANESE

Manganese is extracted from the mineral *pyrolusite* (manganese dioxide, MnO_2) by heating this with coke (C):

$$MnO_2 + 2C \rightarrow Mn + 2CO\uparrow$$

It is a grey metal and used to harden steel.

The element forms compounds in various valencies. The most important of these are *manganous* (manganese(II)) salts, the dioxide, and potassium *permanganate* (manganate(VII)).

Manganous salts can be made by dissolving the metal in mineral acids:

$$Mn + 2H^+(aq) \rightarrow Mn^{2+}(aq) + H_2\uparrow$$

Manganous ions are very pale pink (dilute solutions are colourless).

Manganese dioxide is a black solid, usually slightly deficient in oxygen. Potassium permanganate is made by first fusing the dioxide with potassium hydroxide in air to give potassium *manganate* (manganate(VI)):

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O\uparrow$$

The manganate then is oxidized to permanganate by electrolysis:

$$2MnO_4^{2-}(aq) \rightarrow 2MnO_4^-(aq) + 2e^- \mid 2e^- + 2H_2O \rightarrow 2OH^-(aq) + H_2\uparrow$$

Potassium manganate is dark green, the permanganate deep purple.

Potassium permanganate crystals dissolving in water
[Victoria State Government]

Potassium permanganate is a powerful oxidizing agent. Aqueous solutions are used to titrate reducing agents in the presence of sulphuric acid, e.g. oxalates:

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2 + 8H_2O$$

Treatment of a permanganate with cold concentrated sulphuric acid gives (di)manganese heptoxide, Mn_2O_7. This a green oil, and liable to explode violently.

Manganese forms organometallic compounds, e.g. $Mn_2(CO)_{10}$.

16 CHROMIUM

Chromium is extracted from the mineral *chromite* ($FeCr_2O_4$). It is a light grey metal and is used to produce stainless steel. For this purpose, the ore is heated with coke to give a chromium-iron alloy for addition to steel:

$$FeCr_2O_4 + 4C \rightarrow Fe + 2Cr + 4CO\uparrow$$

For other purposes, chromite is fused with sodium hydroxide in air and the product, sodium *chromate*, extracted from the iron oxide also produced with water:

$$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

Sodium chromate is yellow. Acid converts it into orange sodium *dichromate*:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O$$

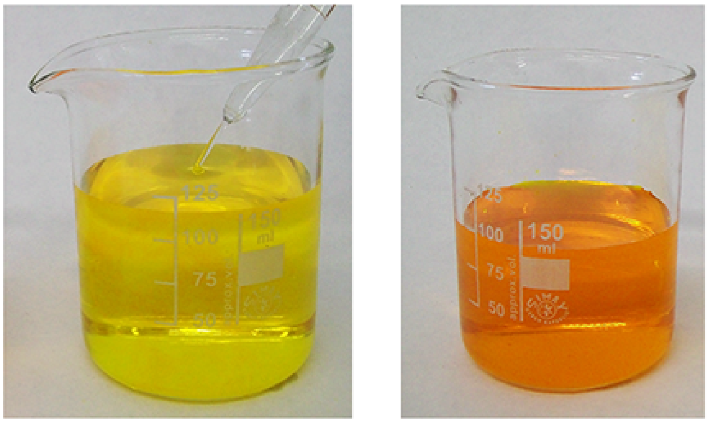
Chromates and dichromates are used as oxidizing agents. For example, sodium or potassium dichromate in acid is used to oxidize alcohols to aldehydes:

$$3CH_3CH_2OH + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CHO + 2Cr^{3+}(aq) + 7H_2O$$

The resulting solutions contain *chromic* (chromium(III)) ions. These are violet or, if complexed [as, e.g., in $CrSO_4^+(aq)$], green. Further reduction with zinc gives *chromous* (chromium(II)) ions:

$$2Cr^{3+}(aq) + Zn \rightarrow 2Cr^{2+}(aq) + Zn^{2+}(aq)$$

These are sky-blue and readily oxidized.



Solutions of chromate and dichromate
[ColourLex]

Treatment of a chromate or dichromate with concentrated sulfuric acid gives red crystals of chromium trioxide, CrO_3.

Reduction of anhydrous sodium dichromate with carbon gives green chromic oxide:

$$Na_2Cr_2O_7 + 2C \xrightarrow{\text{heat}} Cr_2O_3 + Na_2CO_3 + CO\uparrow$$

Heating this with aluminium gives chromium (thermit process):

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

Objects are chromium-plated by electrolysing a chromic solution with a chromium anode and the object as cathode:

$$\mathrm{Cr} \rightarrow \mathrm{Cr}^{3+}(\mathrm{aq}) + 3\mathrm{e}^- \mid 3\mathrm{e}^- + \mathrm{Cr}^{3+}(\mathrm{aq}) \rightarrow \mathrm{Cr(object)}$$

Chromic oxide
[Flying Sky Industries]

Chromic ions form many complexes, e.g. $[\mathrm{Cr(NH_3)_6}]^{3+}$ and $[\mathrm{Cr(CN)_6}]^{3-}$. Chromium also forms organometallic compounds, e.g. $\mathrm{Cr(CO)_6}$.

17 NICKEL

Nickel occurs along with other metals mainly in sulfide ores. Separation from other metals depends on the ore. The resulting nickel sulfide (~NiS) is roasted in air to the oxide and reduced with coke:

$$2NiS + 3O_2 \rightarrow 2NiO + 2SO_2\uparrow$$

$$NiO + C \rightarrow Ni + CO\uparrow$$

Nickel is malleable whitish-grey metal. It does not tarnish and is used in coinage. It and its alloy with copper (*monel metal*) are used to handle fluorine.

Nickel readily dissolves in dilute mineral acids to give solutions of nickel salts:

$$Ni + 2H^+(aq) \rightarrow Ni^{2+}(aq) + H_2\uparrow$$

Aqueous nickel ions are green. Addition of sodium hydroxide precipitates green nickel hydroxide, which is insoluble in excess:

$$Ni^{2+}(aq) + 2OH^-(aq) \rightarrow Ni(OH)_2\downarrow$$

Oxidation gives a black precipitate of variable composition with nickel in a higher valency.

Nickel sulfate, $NiSO_4{\cdot}7H_2O$
[IndiaMART]

Nickel forms complexes, e.g. $[Ni(NH_3)_6]^{2+}$ (octahedral) and $[Ni(CN)_4]^{2-}$ (square-planar). It also forms organometallic compounds, e.g. nickel carbonyl, $Ni(CO)_4$.This is a colourless, volatile, toxic liquid. Pure nickel is obtained by passing carbon monoxide over impure metal to give the carbonyl which is then decomposed by heating:

$$Ni + 4CO \rightarrow Ni(CO)_4 \xrightarrow{heat} Ni + 4CO\uparrow$$

18 ZINC

The main ore is *zinc blende* (zinc sulfide, ZnS). This is roasted to the oxide and reduced with coke:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$$

$$ZnO + C \rightarrow Zn + CO\uparrow$$

Zinc is a brittle, whitish-grey metal. It is used as a protective coating for iron (*galvanization*) and in copper-zinc alloys (*brass*). It dissolves in mineral acids to give solutions of zinc salts:

$$Zn + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2\uparrow$$

These are colourless unless the anion is coloured. Addition of aqueous sodium hydroxide precipitates white zinc hydroxide:

$$Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2\downarrow$$

This is amphoteric and dissolves in excess:

$$Zn(OH)_2 + OH^-(aq) \rightarrow Zn(OH)_3^-(aq)$$

Zinc itself dissolves in hot aqueous sodium hydroxide with the evolution of hydrogen;

$$Zn + OH^-(aq) + 2H_2O \rightarrow Zn(OH)_3^-(aq) + H_2\uparrow$$

Zinc oxide and carbonate (*calamine*, $ZnCO_3$) are white and used in ointments. Zinc sulfide is also white, but fluoresces when exposed to high-energy radiation (e.g. alpha-rays). Zinc oxide is yellow when hot.

Zinc sulfate, $ZnSO_4{\cdot}7H_2O$ (white vitriol)
[Wikipedia]

19 OTHER IMPORTANT ELEMENTS

Magnesium

Magnesium is similar to calcium. The chief difference is that the metal is very light, and is used for constructional purposes, e.g. in aircraft. So too are its alloys with aluminium.

A major source is *dolomite* ($MgCa(CO_3)_2$). This is calcined and then heated with an iron-silicon alloy (the *Pidgeon* process):

$$MgCa(CO_3)_2 \rightarrow (MgO,CaO) + 2CO_2\uparrow$$

$$2(MgO,CaO) + (Fe,Si) \rightarrow 2Mg\uparrow + Ca_2SiO_4 + Fe$$

Magnesium also occurs as magnesium chloride ($MgCl_2$) in some brines and is isolated electrolytically.

Magnesium compounds include *magnesia* (MgO), *Epsom salt* ($MgSO_4{\cdot}7H_2O$), and *chlorophylls* (Mg^{2+} complexes). *Milk of magnesia* is a suspension of $Mg(OH)_2$ in water.

Epsom salt
[Dr. Teal's]

Magnesium reacts with alkyl and aryl chlorides, bromides, and iodides in dry ether to give the Grignard reagents used widely in organic chemistry:

$$\mathrm{Mg + RX \rightarrow RMgX}$$

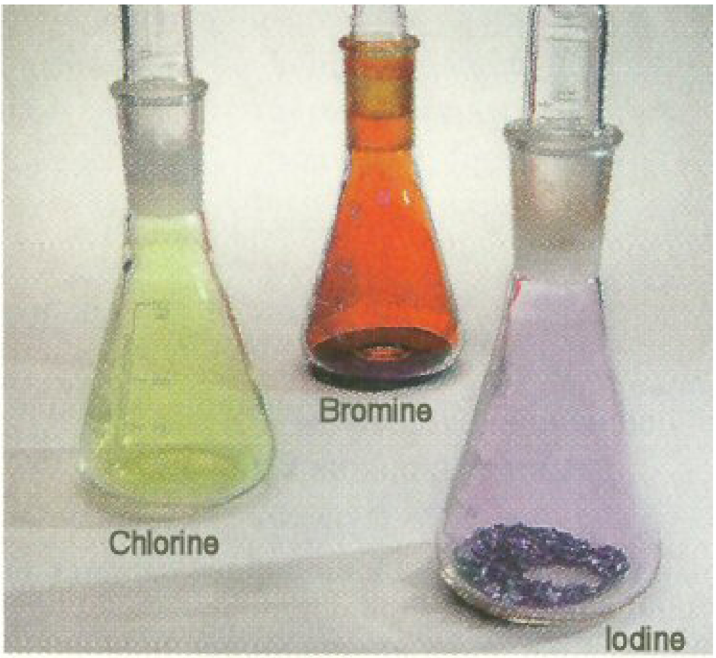
Bromine and iodine

Bromine and iodine are similar to chlorine. Some brines contain their ions, and bromine and iodine can be extracted from them by treatment with chlorine:

$$\mathrm{2X^-(aq) + Cl_2 \rightarrow X_2 + 2Cl^-(aq)}$$

Bromine (Br_2) is a dark red-brown liquid with a red-brown vapour. Iodine (I_2) forms shiny black crystals with a violet vapour. It dissolves in organic solvents to give violet solutions, but in aqueous potassium iodide to give a yellow-brown solution:

$$\mathrm{I_2 + I^-(aq) \rightarrow I_3^-(aq)}$$



[A Review of the Universe]

Like hydrogen chloride, hydrogen bromide (HBr) and hydrogen iodide (HI) are colourless gases, which dissolve readily in water to form strong acids (*hydrobromic* and *hydriodic* respectively).

Fluorine, chlorine, bromine, and iodine all form salts containing X^- ions and are known collectively as *halogens*.

Boron

Boron is similar to silicon except that it is trivalent in its compounds. It occurs as borates (e.g. *borax*, $Na_2B_4O_5(OH)_4{\cdot}8H_2O$). Treatment of these with hot mineral acids yields colourless crystals of boric acid on cooling. For example:

$$B_4O_5(OH)_4^{2-}(aq) + 2H^+(aq) + 3H_2O \rightarrow 4B(OH)_3$$

Boric acid is a weak monobasic acid:

$$B(OH)_3 + H_2O = H^+(aq) + B(OH)_4^-(aq)$$

It is used to make Pyrex glass. Heating it gives the oxide, B_2O_3:

$$2B(OH)_3 \rightarrow B_2O_3 + 3H_2O\uparrow$$

Boron trifluoride (BF_3) is an important catalyst. It is made by heating a borate or the oxide with fluorspar (CaF_2) and concentrated sulfuric acid:

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2BF_3\uparrow + 3CaSO_4 + 3H_2O$$

The trifluoride is a colourless gas and forms many adducts, e.g. with ammonia (H_3NBF_3). Reaction with metal fluorides gives $[BF_4]^-$ salts.

Boron trichloride (BCl_3) is made by heating the oxide with chlorine in the presence of carbon:

$$B_2O_3 + 3C + 3Cl_2 \rightarrow 2BCl_3 + 3CO$$

This reacts with Grignard reagents to form organoboron compounds (BR_3), used in organic synthesis.

Boron itself can be made by reducing boron compounds. The purest samples are black and, like silicon, involatile and semiconducting. They are either amorphous or crystalline, with many different structures.

Boron
[Lenntech]

Boron combines with metals to form *borides* (e.g. MgB_6). Treatment of these with acid gives boron hydrides (*boranes*, B_2H_6, B_4H_{10} etc.). Like silanes, these are inflammable in air.

Titanium

Titanium occurs as *ilmenite* ($FeTiO_3$) and *rutile* (TiO_2). It is extracted by heating the ore with coke and chlorine, e.g.

$$2FeTiO_3 + 6C + 7Cl_2 \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO\uparrow$$

Titanium tetrachloride is a colourless liquid and is separated from iron trichloride by distillation. It is then reduced by heating it with magnesium:

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

Titanium is a grey metal. It is used as a constructional material because of its high strength-to-weight ratio.

Titanium dioxide is widely used as a white pigment. One way of making it is to heat the tetrachloride in oxygen:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2\uparrow$$

Titanium dioxide
[Nanotech Etc.]

Titanium tetrachloride fumes in moist air and is used to make smoke screens:

$$TiCl_4 + 2H_2O \rightarrow TiO_2\downarrow + 4HCl$$

It is also mixed with $Al_2(C_2H_5)_6$ to catalyse the polymerization of olefins (*Ziegler-Natta* catalysis).

A solution of titanium tetrachloride in hydrochloric acid contains $Ti(OH)_2^{2+}$ ions and other species:

$$TiCl_4 + 2H_2O \rightarrow Ti(OH)_2^{2+}(aq) + 2H^+(aq) + 4Cl^-(aq)$$

Reduction of this with zinc gives a violet solution containing Ti^{3+} ions:

$$2Ti(OH)_2^{2+}(aq) + Zn + 4H^+(aq) \rightarrow 2Ti^{3+}(aq) + Zn^{2+}(aq) + 4H_2O$$

This is used as a reducing agent.

Cobalt

Cobalt occurs along with other metals in combination with sulfur and arsenic. The ores are roasted to oxides and separated by various methods. The resulting cobalt oxide (Co_3O_4) is reduced to the metal by heating it with coke:

$$Co_3O_4 + 4C \rightarrow 3Co + 4CO\uparrow$$

The metal is bluish grey and used in steel and magnets. It remains ferromagnetic to a higher temperature than other elements.

The chemistry of cobalt is similar to that of iron. Like the latter, it forms two main series of compounds: bivalent (*cobaltous* or cobalt(II)) and trivalent (*cobaltic* or cobalt(III)). Aqueous Co^{2+} ions are pink, Co^{3+} blue. The latter are unstable, being readily reduced by water:

$$4Co^{3+}(aq) + 2H_2O \rightarrow 4Co^{2+}(aq) + 4H^{+}(aq) + O_2\uparrow$$

Cobaltous sulfate, $CoSO_4{\cdot}7H_2O$
[Prayug Agro]

Both ions form complexes. Co^{3+} complexes are more stable than the aqueous ion and are particularly numerous, interconversions taking place only very slowly. For example, treatment of $CoCl_2(aq)$ with ammonia in the presence of air gives five different compounds depending on the conditions: golden-brown $[Co(NH_3)_6]Cl_3$, bright red $[Co(NH_3)_5(H_2O)]Cl_3$, purple $[CoCl(NH_3)_5]Cl_2$, deep violet *cis*-$[CoCl_2(NH_3)_4]Cl$ and green *trans*-$[CoCl_2(NH_3)_4]Cl$. These were used by Werner to develop his coordination theory. Most Co^{3+} complexes are octahedral. Vitamin B_{12} is a Co^{3+} complex.

Cobalt forms organometallic compounds. The simplest carbonyl is $Co_2(CO)_8$.

Silver

Small amounts of silver occur naturally. Most is obtained from the slime that is formed under the anode in the electrolytic purification of copper. Silver is isolated from this chemically and purified by electrolysis in dilute nitric acid:

$$Ag(crude) \rightarrow Ag^+(aq) + e^- \mid e^- + Ag^+(aq) \rightarrow Ag(pure)$$

Silver is a malleable, whitish grey metal and good conductor of electricity (the best of all the elements). It dissolves in dilute nitric acid to give a solution of silver nitrate:

$$3Ag + NO_3^-(aq) + 4H^+(aq) \rightarrow 3Ag^+(aq) + NO\uparrow + 2H_2O$$

This is colourless. Silver chloride (white), bromide (pale yellow), and iodide (yellow) are insoluble and darken on exposure to light:

$$Ag^+(aq) + X^-(aq) \rightarrow AgX\downarrow$$

Adding silver nitrate to sodium chloride
[BBC]

Silver forms complexes, e.g. $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$.

Gold and platinum

These occur naturally. Gold is a yellow metal, platinum whitish grey.

The two metals do not dissolve in ordinary acids, but they do dissolve in *aqua regia* (a mixture of concentrated nitric and hydrochloric acids). The resulting solutions contain respectively $[AuCl_4]^-$ and $[PtCl_6]^{2-}$ ions:

$$2Au + 3HNO_3 + 11HCl \rightarrow 2H[AuCl_4] + 3NOCl\uparrow + 6H_2O$$

$$Pt + 2HNO_3 + 8HCl \rightarrow H_2[PtCl_6] + 2NOCl\uparrow + 4H_2O$$

Gold also dissolves in aerated sodium cyanide solution, a process used to extract it from crushed rock:

$$4Au + 8CN^-(aq) + O_2 + 2H_2O \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

$$2[Au(CN)_2]^-(aq) + Zn \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au\downarrow$$

Gold forms two main series of compounds, *aurous* (gold(I)) and *auric* (gold(III)). Platinum likewise forms *platinous* (platinum(II)) and *platinic* (platinum(IV)) compounds. Auric and platinous complexes (d^8) are characteristically square-planar.

Chloroauric acid, $H[AuCl_4]\cdot 3H_2O$
[Alibaba]

Platinum is an important catalyst. It is used, for example, in catalytic converters in cars. Complexes of gold and platinum are used in medicine.

Tin

The most important ore is *cassiterite* (SnO_2). This is reduced by heating it with coke:

$$SnO_2 + 2C \rightarrow Sn + 2CO\uparrow$$

The metal is whitish grey and has a relatively low melting point (232°C). It forms two series of compounds: bivalent (*stannous*, tin(II)) and quadrivalent (*stannic*, tin(IV)), e.g.

$$Sn + 2HCl \rightarrow SnCl_2 + H_2\uparrow$$

$$Sn + 2Cl_2 \rightarrow SnCl_4$$

Stannous chloride is a white solid, stannic chloride a colourless liquid.

Stannous chloride, $SnCl_2{\cdot}2H_2O$
[SafestChina]

Stannous compounds are reducing agents. Aqueous Sn^{2+} ions are oxidized by air.

Tin forms important alloys with copper (*bronze*) and lead (*solder*), and is used to provide a protective cover for steel (*tin-plate*) used in canning. Molten tin is used in the manufacture of float glass.

Lead

The most important ore is *galena* (PbS). This is roasted in a limited supply of air:

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2\uparrow$$

The oxide is then reduced with coke:

$$PbO + C \rightarrow Pb + CO\uparrow$$

Lead a dense, grey, malleable metal. It is similar to tin in forming two series of compounds, bivalent (*plumbous*, lead(II)) and quadrivalent (*plumbic*, lead(IV)), e.g. colourless Pb^{2+} salts and brown PbO_2. The relative stabilities are, however, different: plumbic compounds are oxidizing agents; aqueous Pb^{2+} ions are stable in air.

Plumbous nitrate, $Pb(NO_3)_2$
[IndiaMART]

Lead-tin alloys are low-melting and used as solder.

Uranium

This occurs in oxide minerals (e.g. *pitchblende*, U_3O_8) dispersed in rocks. The rocks are crushed, leached with sulfuric acid, and the uranium isolated chemically. The resulting 'yellow cake' has the approximate composition U_3O_8 and, on one scheme, is reduced by heating it with hydrogen:

$$U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O\uparrow$$

The dioxide is converted to the tetrafluoride by heating it in hydrogen fluoride:

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O\uparrow$$

The tetrafluoride is reduced by heating it with magnesium:

$$UF_4 + 2Mg \rightarrow U + 2MgF_2$$

[Uranium Mining Museum]

Natural uranium comprises mainly ^{235}U (0.7%) and ^{238}U (99.3%), the first of which is used in nuclear reactors. To separate these, the tetrafluoride is converted to the hexafluoride by heating it in fluorine:

$$UF_4 + F_2 \rightarrow UF_6$$

The hexafluoride is volatile and is separated in a gas centrifuge, $^{238}UF_6$ concentrating towards the wall and $^{235}UF_6$ towards the centre. Chemists use 'depleted uranium' made by removing the $^{235}UF_6$ and reducing the $^{238}UF_6$.

Other sexivalent compounds include the oxide, UO_3, and salts of the yellow *uranyl* ion, UO_2^{2+}.

20 OTHER NOTABLE ELEMENTS

Lithium

This is similar to sodium and potassium. An important compound is lithium aluminium hydride, $LiAlH_4$, used as a reducing and hydrogenating agent in organic chemistry. Lithium salts are used in psychiatric medicine.

Lithium, sodium, and potassium, along with rubidium and caesium, are known collectively as *alkali metals*. They all react with water giving hydrogen and form basic hydroxides (MOH) and colourless $M^+(aq)$ ions. They are distinguished by their flame colours: lithium, crimson-red; sodium, yellow; potassium, lilac; rubidium, ruby-red; caesium, sky-blue.

Barium

This is similar to calcium. An important compound is barium sulfate ($BaSO_4$). This is insoluble in water, and the formation of a white precipitate on addition of $Ba^{2+}(aq)$ is used as a test for sulfate. Being dense, barium sulfate is given to patients when X-raying the stomach and intestine.

Calcium, strontium, barium, and radium are known collectively as *alkaline earth metals*. They all react with water giving hydrogen and form basic hydroxides [$M(OH)_2$] and colourless $M^{2+}(aq)$ ions. Their flame colours are: calcium, brick-red; strontium, crimson-red; barium, apple-green; radium, red-purple. Radium is radioactive.

Selenium

This is similar to sulfur. Like sulfur, it forms compounds in which it has a valency of two (H_2Se), four (SeO_2), and six (H_2SeO_4). It exists in several forms, from red (Se_8) to black (Se_n).

Black and red selenium
[Wikipedia]

Molybdenum and tungsten

These are whitish grey metals with high melting points. Their chemistry is dominated by oxo-compounds (*molybdates* and *tungstates*) in which they have a valency of six. Molybdenum trioxide is white (yellow when hot), tungsten trioxide yellow. Tungsten carbide (WC) is used to tip cutting tools. Both elements form organometallic compounds, e.g. $Mo(CO)_6$ and $W(CO)_6$.

Mercury

This is the only metal that is a liquid at room temperature. It dissolves other metals to form *amalgams*. It forms two series of compounds: *mercurous* (mercury(I), e.g. Hg_2Cl_2) and *mercuric* (mercury(II), e.g. $HgCl_2$). Aqueous Hg_2^{2+} and Hg^{2+} ions are colourless. Mercurous chloride (*calomel*) is insoluble in water. Mercury compounds are poisonous.

Mercury
[Mining Chemicals Trading Support]

Helium, neon, argon, krypton, and xenon

These are minor components of the atmosphere. All are monatomic. Chemically, they are almost completely or totally inactive. They are known as the *inert gases* (or, ineptly, ‘noble gases’). Argon is the most abundant, comprising about 1% of the atmosphere by volume.

Questions

1. Write a short account of the chemistry of (a) calcium, (b) nitrogen, (c) iron.
2. Compare and contrast the chemistry of (a) magnesium and zinc, (b) phosphorus and sulfur.
3. X is a non-metal. It combines with hydrogen to form a hydride. This dissolves in water to give an acid. The acid forms a series of salts. These give a pale yellow precipitate with silver nitrate. Identify X.
4. M is a metal. It forms two series of salts with valencies two and three. $[M(H_2O)_6]^{3+}$ ions oxidize water, $[M(NH_3)_6]^{3+}$ ions do not. Identify M.
5. Which of the following represent the highest oxides of iron, manganese, and chromium?
   a) FeO_3, MnO_2, CrO_3
   b) FeO_3, Mn_2O_7, CrO_3
   c) Fe_2O_3, MnO_2, CrO_3
   d) Fe_2O_3, Mn_2O_7, CrO_3
   e) Fe_2O_3, MnO_2, Cr_2O_3
   f) Fe_2O_3, Mn_2O_7, Cr_2O_3

Answers

1. See the sections on these elements in the text.
2. (a) Both are bivalent metals, but zinc hydroxide is amphoteric, whereas magnesium hydroxide is basic.
   (b) Their chemistries are similar, but their valencies are different (phosphorus: 3, 5; sulfur: 2, 4, 6).
3. Bromine
4. Cobalt
5. (d). Iron does, however, form derivatives of FeO_3, e.g. K_2FeO_4, made by suspending $Fe(OH)_3$ in KOH(aq) and oxidizing it with chlorine.

ENDNOTES

1. See my discussion in *Introduction to Inorganic Chemistry*, www.bookboon.com/en/introduction-to-inorganic-chemistry-ebook, and *J. Chem. Educ.*, 1991, **68**, 732–737.