INTERCHAPTER D

# The Alkali Metals

The alkali metals are soft. Here we see sodium being cut with a knife.

The website Periodic Table Live! is a good supplement to much of the material in this Interchapter. A link to this website can be found at www.McQuarrieGeneralChemistry.com.

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. They occur in Group 1 of the periodic table and so have an ionic charge of +1 in their compounds. All the alkali metals are very reactive. None occur as the free metal in nature. They must be stored under an inert substance, such as kerosene, because they react spontaneously and rapidly with the oxygen and water vapor in the air.

Figure D.1 Lithium floating on oil, which in turn is floating on water. Lithium has the lowest density of any element that is a solid or a liquid at 20°C.

## D-1. The Hydroxides of the Alkali Metals Are Strong Bases

The alkali metals are all fairly soft and can be cut with a sharp knife (Frontispiece). When freshly cut they are bright and shiny, but they soon take on a dull finish because of their reaction with air. The alkali metals are so called because their hydroxides, MOH(*s*), are all soluble bases in water (alkaline means basic). Lithium, sodium, and potassium have densities less than 1.0 $g \cdot cm^{-3}$ and so will float on water as they react.

The letter M is often used in chemical formulas to represent an element that could be any one of several choices, often from a given family or group of elements. For example, in the formula MOH(*s*), M represents any one of the alkali metals, and so MOH(*s*) can be LiOH(*s*), NaOH(*s*), KOH(*s*), or any of the other alkali metal hydroxides.

Lithium has such a low density that it will actually float on oil (Figure D.1). The physical properties of the alkali metals are given in Table D.1. There are no stable isotopes of francium; all of them are radioactive.

The alkali metals can be obtained by **electrolysis**, which is a decomposition reaction driven by passing an electric current through a liquid or a solution (Chapter 25). For example, sodium metal is obtained by electrolysis of molten mixtures of sodium chloride and calcium chloride. Sodium is the least expensive metal per unit volume.

$$2\,NaCl[\text{in } CaCl_2(l)] \xrightarrow[\text{electrolysis}]{600^\circ C} 2\,Na(l) + Cl_2(g)$$

TABLE D.1 The physical properties of the alkali metals

| Element | Symbol | Atomic number | Atomic mass | Metal radius/pm | Ionic radius of $M^+$/pm | Melting point/°C | Boiling point/°C | Density at 25°C/$g \cdot cm^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| lithium | Li | 3 | 6.941 | 145 | 60 | 180.50 | 1342 | 0.534 |
| sodium | Na | 11 | 22.989770 | 180 | 95 | 97.794 | 882.940 | 0.97 |
| potassium | K | 19 | 39.0983 | 220 | 133 | 63.5 | 759 | 0.89 |
| rubidium | Rb | 37 | 85.4678 | 235 | 148 | 39.30 | 688 | 1.53 |
| cesium | Cs | 55 | 132.90545 | 260 | 169 | 28.5 | 671 | 1.93 |
| francium | Fr | 87 | (223) | ~290 | ~180 | 27 | — | — |

Chlorine gas is a useful by-product of this electrolysis. The $CaCl_2(l)$ is added to the sodium chloride to lower the temperature necessary for the operation of the electrolysis cell. Pure $NaCl(s)$ melts at 800°C.

## D-2. The Alkali Metals Are Very Reactive

The alkali metals react directly with all the nonmetals except the noble gases. The increasing reactivity of the alkali metals with increasing atomic number is demonstrated in a spectacular manner by their reaction with water. When metallic lithium reacts with water, hydrogen gas is evolved slowly, whereas sodium reacts vigorously with water (Figure D.2). The reaction of potassium with water produces a fire because the heat generated by the reaction is sufficient to ignite the hydrogen gas evolved (Figure D.3). Rubidium and cesium react with water with explosive violence.

Molten lithium is one of the most reactive substances known. The only known substances that do not react with molten lithium are tungsten, molybdenum, low-carbon stainless steels, and the noble gases. If a piece of lithium metal is melted in a glass tube, the molten lithium rapidly eats a hole through the glass (Figure D.4). The reaction is accompanied by a brilliant green-yellow flame and a considerable evolution of heat.

Figure D.3 Potassium reacts violently with water to produce potassium hydroxide and hydrogen gas. The flame is a result of the explosive reaction of the evolved hydrogen gas with oxygen in the air. The molten potassium was blown out of the reaction vessel by the explosion.

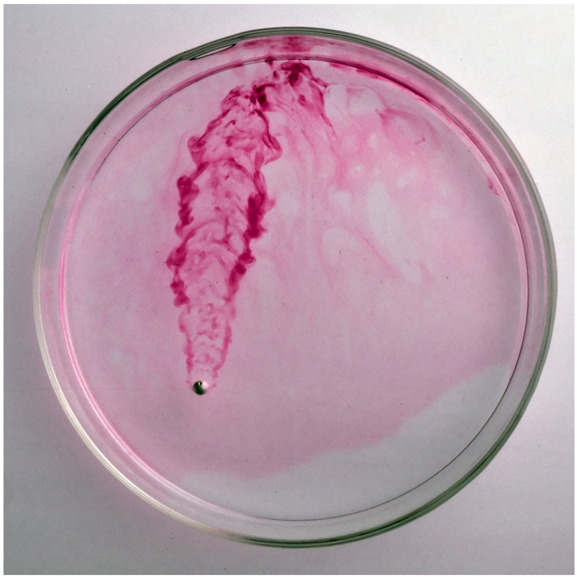

Figure D.2 The reaction of sodium with water. The sodium is propelled along the water's surface by the evolved hydrogen gas. The production of $NaOH(aq)$ is shown by the pink color of the acid-base indicator phenolphthalein, which is colorless in acidic or neutral solutions and pink in basic solution. The heat of the reaction is sufficient to melt the sodium.

The alkali metals react directly with oxygen. Molten lithium ignites in oxygen to form $Li_2O(s)$; the reaction is accompanied by a bright red flame. The reactions of the other alkali metals do not yield the oxides $M_2O(s)$. With sodium, the **peroxide** $Na_2O_2(s)$ is formed, and with potassium, rubidium, and cesium the **superoxides** $KO_2(s)$, $RbO_2(s)$, and $CsO_2(s)$ are formed.

Figure D.4 Molten lithium in a glass beaker. Molten lithium reacts with the glass with the evolution of a large amount of heat.

Both potassium superoxide and sodium peroxide are used in self-contained breathing apparatus. The relevant reactions for $KO_2(s)$ are described by

$$4\,KO_2(s) + \underset{\text{exhaled air}}{2\,H_2O(g)} \rightarrow 4\,KOH(s) + 3\,O_2(g)$$

$$KOH(s) + \underset{\text{exhaled air}}{CO_2(g)} \rightarrow KHCO_3(s)$$

The reactions for $Na_2O_2(s)$ are given by

$$2\,Na_2O_2(s) + \underset{\text{exhaled air}}{2\,H_2O(g)} \rightarrow 4\,NaOH(s) + O_2(g)$$

$$NaOH(s) + \underset{\text{exhaled air}}{CO_2(g)} \rightarrow NaHCO_3(s)$$

Note that $O_2(g)$ is generated and that $H_2O(g)$ and $CO_2(g)$ are absorbed in each case.

The alkali metals react directly with hydrogen at high temperatures to form hydrides. For example,

$$2\,Na(l) + H_2(g) \xrightarrow{500^\circ C} 2\,NaH(s)$$

The alkali metal hydrides are ionic compounds that contain the hydride ion, $H^-$. The hydrides react with water to liberate hydrogen,

$$NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$$

and are used to remove traces of water from organic solvents. In such cases, the metal hydroxide precipitates from the solution.

Lithium is the only element that reacts directly with nitrogen at room temperature (Figure D.4):

$$6\,Li(s) + N_2(g) \xrightarrow{\text{room T}} \underset{\text{lithium nitride}}{2\,Li_3N(s)}$$

The reddish black lithium nitride (Figure D.5) reacts directly with water to form ammonia according to

$$Li_3N(s) + 3\,H_2O(l) \rightarrow 3\,LiOH(aq) + NH_3(g)$$

This reaction can be used to prepare deuterated ammonia, $ND_3(g)$, by reacting lithium nitride with heavy water according to

$$Li_3N(s) + 3\,D_2O(l) \rightarrow 3\,LiOD(aq) + ND_3(g)$$

Some of the more common reactions of the alkali metals are summarized in Figure D.6.

Figure D.5 Lithium nitride, $Li_3N(s)$.

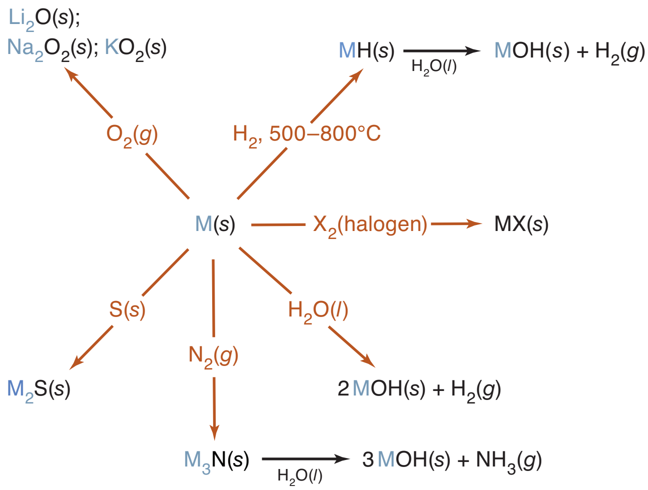


Figure D.6 Representative reactions of the Group 1 metals.

Compounds of the alkali metals are for the most part white, high-melting ionic solids. With very few exceptions, alkali metal salts are soluble in water and the resulting solutions conduct an electric current, as a result of the dissociation of the salt into its constituent ions.

Not all the properties of lithium are analogous to those of the other members of the alkali metal family. For example, in contrast to the analogous salts of the other alkali metals, $LiF(s)$ and $Li_2CO_3(s)$ are insoluble in water and $LiCl(s)$ is soluble in alcohols and ethers. The anomalous behavior of lithium is ascribed to the much smaller size of the $Li^+$ ion (Table D.1).

Lithium is also the element that produces the highest power-to-mass ratio when used in batteries (see Interchapter U). However, due to its high reactivity, the development of practical lithium batteries only became possible in recent decades. Today lithium batteries provide light, compact power for everything from cellular telephones to electric cars. Because lithium can explode or catch fire when exposed to air, used lithium batteries should always be disposed of in a proper electronics waste receptacle and never placed in the regular trash.


Figure D.7 Sodium dissolving in liquid ammonia. Solutions of sodium in liquid ammonia are deep blue in color and are able to conduct an electric current.

The alkali metals have the unusual property of dissolving in liquid ammonia to yield blue solutions that conduct an electric current (Figure D.7). The properties of such a solution are interpreted in terms of **solvated electrons** and alkali metal ions:

$$M(s) \xrightarrow[NH_3(l)]{} M^+(amm) + e^-(amm)$$

The solvated electrons are electrons surrounded by ammonia molecules. When the blue solutions are concentrated by evaporation, they become bronze in color and behave like liquid metals.

## D-3. Many Alkali Metal Compounds Are Important Commercially

Sodium hydroxide is among the top ten ranked industrial chemicals. Over nine million metric tons of it are produced annually in the United States alone. Sodium hydroxide is prepared by the electrolysis of concentrated aqueous sodium chloride solutions,

$$2\,NaCl(aq) + 2\,H_2O(l) \xrightarrow[\text{electrolysis}]{} 2\,NaOH(aq) + H_2(g) + Cl_2(g)$$

or by the reaction between sodium carbonate and calcium hydroxide given by

$$Na_2CO_3(aq) + Ca(OH)_2(aq) \rightarrow 2\,NaOH(aq) + CaCO_3(s)$$

The formation of the insoluble $CaCO_3(s)$ is a driving force for this reaction. The alkali metal hydroxides are white, translucent, corrosive solids that are extremely soluble in water; at 20°C the solubility of $NaOH(s)$ is 65 grams per 100 mL of $H_2O(l)$, and that of $KOH(s)$ is 100 grams per 100 mL of $H_2O(l)$.

Sodium carbonate is also among the top ten ranked industrial chemicals. About 90% of the sodium carbonate produced in the United States is obtained from natural deposits of the mineral trona (Figure D.8), which has the composition $Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O(s)$. When trona is heated, it yields sodium carbonate according to

$$2\,Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O(s) \xrightarrow{\text{high T}} 3\,Na_2CO_3(s) + CO_2(g) + 5\,H_2O(g)$$

Figure D.8 Underground deposits of trona being mined at Tenneco's Green River, Wyoming, mine.

The carbon dioxide is recovered as a by-product.

Sodium carbonate also is prepared from sodium chloride by the **Solvay process**, which was devised by the Belgian brothers Ernest and Edward Solvay in 1861. The Solvay process is used extensively in countries that lack large trona deposits. In this process, carbon dioxide is bubbled through a cooled solution of sodium chloride and ammonia. The reactions are described by

$$NH_3(g) + CO_2(aq) + H_2O(l) \rightarrow NH_4^+(aq) + HCO_3^-(aq)$$

$$NaCl(aq) + NH_4^+(aq) + HCO_3^-(aq) \xrightarrow{15°C} NaHCO_3(s) + NH_4Cl(aq)$$

At 15°C the sodium hydrogen carbonate precipitates from the solution. Part of the sodium hydrogen carbonate is converted to sodium carbonate by heating:

$$2\,NaHCO_3(s) \xrightarrow{80°C} Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

The carbon dioxide produced in this reaction is used again in the first reaction.

The commercial success of the Solvay process requires the recovery of the ammonia, which is relatively expensive. The ammonia is recovered from the $NH_4Cl(aq)$ by the reaction described by

$$2NH_4Cl(aq) + Ca(OH)_2(s) \rightarrow 2NH_3(g) + CaCl_2(aq) + 2H_2O(l)$$

The calcium hydroxide and the carbon dioxide used in the process are obtained by heating limestone, which is primarily $CaCO_3(s)$. The raw materials of the Solvay process are sodium chloride, limestone, and water, all of which are inexpensive. The principal use of sodium carbonate is in the manufacture of glass.

Table D.2 summarizes the principal sources and commercial uses of the alkali metals. Some other industrially important alkali metal compounds are listed in Table D.3.

**TABLE D.2** Sources and uses of the alkali metals

| Metal | Sources | Uses |
|---|---|---|
| lithium | spodumene, $LiAlSi_2O_6(s)$; certain mineral springs and salt lakes | alloys; organic reactions; batteries |
| sodium | salt waters, $NaCl(s)$, $NaNO_3(s)$ | production of titanium metal; small nuclear reactor coolant |
| potassium | ancient ocean and salt lake beds; occurs in numerous mineral deposits at low levels, $KNO_3(s)$, $KCl(s)$ | heat exchange alloys |
| rubidium | mineral springs (Searles Lake, California; Manitoba; Michigan brines) | photocells |
| cesium | water from certain mineral springs (Bernic Lake, Manitoba) | ion propulsion systems; atomic clocks |

**TABLE D.3** Commercially important alkali metal compounds and their uses

| Compound | Uses |
|---|---|
| lithium aluminum hydride, $LiAlH_4(s)$ | production of many pharmaceuticals and perfumes |
| lithium borohydride, $LiBH_4(s)$ | organic synthesis |
| lithium carbonate, $Li_2CO_3(s)$ | to treat schizophrenia |
| sodium hydrogen carbonate (sodium bicarbonate), $NaHCO_3(s)$ | manufacture of effervescent salts and beverages, baking powder, gold plating |
| sodium carbonate, $Na_2CO_3(s)$ | manufacture of glass, pulp and paper, soaps and detergents |
| sodium hydroxide, $NaOH(s)$ | production of rayon, cellulose, oven cleaner, drain cleaner |
| sodium sulfate decahydrate (Glauber's salt), $Na_2SO_4\cdot 10\,H_2O(s)$ | solar heating storage, air conditioning |
| sodium cyanide, $NaCN(s)$ | extraction of gold and silver from ores; electroplating solutions; fumigant for fruit trees |
| potassium carbonate (potash), $K_2CO_3(s)$ | manufacture of special glass for optical instruments, soft soaps |
| potassium nitrate, $KNO_3(s)$ | pyrotechnics, explosives, matches; tobacco treatment |
| dipotassium hydrogen phosphate, $K_2HPO_4(s)$ | buffering agent |

## TERMS YOU SHOULD KNOW

electrolysis *D1*
peroxide *D2*
superoxide *D2*
solvated electron *D4*
Solvay process *D5*

## QUESTIONS

**D-1.** Why must the alkali metals be stored under an inert liquid like kerosene or an inert gas like argon?

**D-2.** How are the alkali metals produced commercially?

**D-3.** Why do you think sodium metal is the least expensive metal per unit volume?

**D-4.** What is the only element that reacts directly with nitrogen gas at room temperature?

**D-5.** Outline, by means of balanced chemical equations, the Solvay process.

**D-6.** Outline, by means of balanced chemical equations, the operation of a self-contained breathing apparatus charged with sodium peroxide.

**D-7.** Explain why the alkali metals cannot be stored in water.

**D-8.** Superoxide ions, peroxide ions, and oxide ions can be thought of as arising from oxygen by the transfer of the appropriate number of electrons to $O_2$: $O_2 + e^- \rightarrow O_2^-$; $O_2 + 2e^- \rightarrow O_2^{2-}$; and $O_2 + 4e^- \rightarrow 2O^{2-}$. What are the chemical formulas for potassium oxide, potassium peroxide, and potassium superoxide?

**D-9.** What is the major commercial source of sodium carbonate?

**D-10.** Complete and balance the following equations:

(a) $Na(s) + O_2(g) \rightarrow$

(b) $Na(s) + H_2O(l) \rightarrow$

(c) $Li(s) + N_2(g) \rightarrow$

(d) $NaH(s) + H_2O(l) \rightarrow$

(e) $Li_3N(s) + H_2O(l) \rightarrow$

**D-11.** Complete and balance the following equations:

(a) $Na_2CO_3(aq) + Ca(OH)_2(s) \rightarrow$

(b) $NaHCO_3(s) \xrightarrow{80^\circ C}$

(c) $NH_3(aq) + CO_2(aq) + H_2O(l) \rightarrow$