

																		1	2																										
																		H	He																										
3	4																	5	6	7	8	9	10																						
Li	Be																	B	C	N	O	F	Ne																						
11	12																	13	14	15	16	17	18																						
Na	Mg																	Al	Si	P	S	Cl	Ar																						
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																												
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																												
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																												
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																												
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104																												
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub																																		
																		73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90										
																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu														
																		91	92	93	94	95	96	97	98	99	100	101	102	103	104	105													
																		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr														

4

Lithium, Sodium, Potassium, Rubidium, Caesium and Francium

4.1 Introduction

The alkali metals form a homogeneous group of extremely reactive elements which illustrate well the similarities and trends to be expected from the periodic classification, as discussed in Chapter 2. Their physical and chemical properties are readily interpreted in terms of their simple electronic configuration, ns^1 , and for this reason they have been extensively studied by the full range of experimental and theoretical techniques. Compounds of sodium and potassium have been known from ancient times and both elements are essential for animal life. They are also major items of trade, commerce and chemical industry. Lithium was first recognized as a separate element at the beginning of the nineteenth century but did not assume major industrial importance until about 40 y ago. Rubidium and caesium are of considerable academic interest but so far have few industrial applications. Francium, the elusive element 87, has only fleeting existence in nature due to its very short radioactive half-life, and this delayed its discovery until 1939.

4.2 The Elements

4.2.1 *Discovery and isolation*

The spectacular success (in 1807) of Humphry Davy, then aged 29 y, in isolating metallic potassium by electrolysis of molten caustic potash (KOH) is too well known to need repeating in detail.⁽¹⁾ Globules of molten sodium were similarly prepared by him a few days later from molten caustic soda. Earlier experiments with aqueous solutions had been unsuccessful because of the great reactivity of these new elements. The names chosen by Davy reflect the sources of the elements.

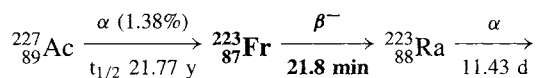
Lithium was recognized as a new alkali metal by J. A. Arfvedson in 1817 whilst he was working as a young assistant in J. J. Berzelius's laboratory. He noted that Li compounds were similar to those of Na and K but that the carbonate and hydroxide were much less soluble

¹ M. E. WEEKS, *Discovery of the Elements*, Journal of Chemical Education, Easton, 6th edn., 1956, 910 pp.

in water. Lithium was first isolated from the sheet silicate mineral petalite, $\text{LiAlSi}_4\text{O}_{10}$, and Arfvedson also showed it was present in the pyroxene silicate spodumene, $\text{LiAlSi}_2\text{O}_6$, and in the mica lepidolite, which has an approximate composition $\text{K}_2\text{Li}_3\text{Al}_4\text{Si}_7\text{O}_{21}(\text{OH},\text{F})_3$. He chose the name lithium (Greek $\lambda\iota\theta\omicron\varsigma$, stone) to contrast it with the vegetable origin of Davy's sodium and potassium. Davy isolated the metal in 1818 by electrolysing molten Li_2O .

Rubidium was discovered as a minor constituent of lepidolite by R. W. Bunsen and G. R. Kirchhoff in 1861 only a few months after their discovery of caesium (1860) in mineral spa waters. These two elements were the first to be discovered by means of the spectroscope, which Bunsen and Kirchhoff had invented the previous year (1859); accordingly their names refer to the colour of the most prominent lines in their spectra (Latin *rubidus*, deepest red; *caesius*, sky blue).

Francium was first identified in 1939 by the elegant radiochemical work of Marguerite Perey who named the element in honour of her native country. It occurs in minute traces in nature as a result of the rare (1.38%) branching decay of ^{227}Ac in the ^{235}U series:



Its terrestrial abundance has been estimated as 2×10^{-18} ppm, which corresponds to a total of only 15 g in the top 1 km of the earth's crust. Other isotopes have since been produced by nuclear reactions but all have shorter half-lives than ^{223}Fr , which decays by energetic β^- emission, $t_{1/2}$ 21.8 min. Because of this intense radioactivity it is only possible to work with tracer amounts of the element.

4.2.2 Terrestrial abundance and distribution

Despite their chemical similarity, Li, Na and K are not closely associated in their occurrence, mainly because of differences in size (see

Table on p. 75). Lithium tends to occur in ferromagnesian minerals where it partly replaces magnesium; it occurs to the extent of about 18 ppm by weight in crustal rocks, and this reflects its relatively low abundance in the cosmos (Chapter 1). It is about as abundant as gallium (19 ppm) and niobium (20 ppm). The most important mineral commercially is spodumene, $\text{LiAlSi}_2\text{O}_6$, and large deposits occur in the USA, Canada, Brazil, Argentina, the former USSR, Spain, China, Zimbabwe and the Congo. An indication of the industrial uses of lithium and its compounds is given in the Panel. World production of lithium compounds in 1994 corresponded to some 5700 tonnes of contained lithium (equivalent to 30 000 tonnes of lithium carbonate) of which over 70% was in the USA.

Sodium, 22 700 ppm (2.27%) is the seventh most abundant element in crustal rocks and the fifth most abundant metal, after Al, Fe, Ca and Mg. Potassium (18 400 ppm) is the next most abundant element after sodium. Vast deposits of both Na and K salts occur in relatively pure form on all continents as a result of evaporation of ancient seas, and this process still continues today in the Great Salt Lake (Utah), the Dead Sea and elsewhere. Sodium occurs as rock-salt (NaCl) and as the carbonate (trona), nitrate (saltpetre), sulfate (mirabilite), borate (borax, kernite), etc. Potassium occurs principally as the simple chloride (sylvite), as the double chloride $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ (carnallite) and the anhydrous sulfate $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ (langbeinite). There are also unlimited supplies of NaCl in natural brines and oceanic waters ($\sim 30 \text{ kg m}^{-3}$). Thus, it has been calculated that rock-salt equivalent to the NaCl in the oceans of the world would occupy 19 million cubic km (i.e. 50% more than the total volume of the North American continent above sea-level). Alternatively stated, a one-km square prism would stretch from the earth to the moon 47 times. Note also that, although Na and K are almost equally abundant in the crustal rocks of the earth, Na is some 30 times as abundant as K in the oceans. This is partly because K salts with the larger anions tend to be less soluble than the Na salts and, likewise, K is more strongly bound to

Lithium and its Compounds⁽²⁻⁴⁾

The dramatic transformation of Li from a small-scale specialist commodity to a multikilotonne industry during the past three decades is due to the many valuable properties of its compounds. About 35 compounds of Li are currently available in bulk, and a similar number again can be obtained in developmental or research quantities. A major industrial use of Li is in the form of **lithium stearate** which is used as a thickener and gelling agent to transform oils into lubricating greases. These "all-purpose" greases combine high water resistance with good low-temperature properties (-20°C) and excellent high-temperature stability ($>150^{\circ}\text{C}$); they are readily prepared from $\text{LiOH}\cdot\text{H}_2\text{O}$ and tallow or other natural fats and have captured nearly half the total market for automotive greases in the USA.

Lithium carbonate is the most important industrial compound of lithium and is the starting point for the production of most other lithium compounds. It is also used as a flux in porcelain enamel formulations and in the production of special toughened glasses (by replacement of the larger Na ions): Li can either be incorporated within the glass itself or the preformed Na-glass can be dipped in a molten-salt bath containing Li ions to effect a surface cation exchange. In another application, the use of Li_2CO_3 by primary aluminium producers has risen sharply in recent years since it increases production capacity by 7–10% by lowering the mp of the cell content and permitting larger current flow; in addition, troublesome fluorine emissions are reduced by 25–50% and production costs are appreciably lowered. In 1987 the price for bulk quantities of Li_2CO_3 in the USA was \$3.30 per kg.

The first commercial use of **Li metal** (in the 1920s) was as an alloying agent with lead to give toughened bearings; currently it is used to produce high-strength, low-density aluminium alloys for aircraft construction. With magnesium it forms an extremely tough low-density alloy which is used for armour plate and for aerospace components (e.g. LA 141, d 1.35 g cm^{-3} , contains 14% Li, 1% Al, 85% Mg). Other metallurgical applications employ **LiCl** as an invaluable brazing flux for Al automobile parts.

LiOH is used in the manufacture of lithium stearate greases (see above) and for CO_2 absorption in closed environments such as space capsules (light weight) and submarines. **LiH** is used to generate hydrogen in military, meteorological, and other applications, and the use of **LiD** in thermonuclear weaponry and research has been mentioned (p. 18). Likewise, the important applications of **LiAlH_4** , **Li/NH_3** and **organolithium reagents** in synthetic organic chemistry are well known, though these account for only a small percentage of the lithium produced. Other specialist uses include the growing market for ferroelectrics such as **LiTaO_3** to modulate laser beams (p. 57), and increasing use of thermoluminescent **LiF** in X-ray dosimetry.

Perhaps one of the most exciting new applications stems from the discovery in 1949 that small daily doses (1–2 g) of **Li_2CO_3** taken orally provide an effective treatment for manic-depressive psychoses. The mode of action is not well understood but there appear to be no undesirable side effects. The dosage maintains the level of Li in the blood at about 1 mmol l^{-1} and its action may be related to the influence of Li on the Na/K balance and (or) the Mg/Ca balance since Li is related chemically to both pairs of elements.

Looking to the future, **Li/FeS_x** battery systems are emerging as a potentially viable energy storage system for off-peak electricity and as a non-polluting silent source of power for electric cars. The battery resembles the conventional lead-acid battery in having solid electrodes (**Li/Si** alloy, negative; **FeS_x** positive) and a liquid electrolyte (molten **LiCl/KCl** at 400°C). Other battery systems which have reached the prototype stage include the **Li/S** and **Na/S** cells (see p. 678).

the complex silicates and alumino silicates in the soils (ion exchange in clays). Again, K leached from rocks is preferentially absorbed and used by plants whereas Na can proceed to the sea. Potassium is an essential element for plant life and the growth of wild plants is often limited by the supply of K available to them.

The vital importance of NaCl in the heavy chemical industry is indicated in the Panel opposite, and information on potassium salts is given in the Panel on p. 73.

Rubidium (78 ppm, similar to Ni, Cu, Zn) and caesium (2.6 ppm, similar to Br, Hf, U) are much less abundant than Na and K and have only recently become available in quantity. No purely Rb-containing mineral is known and much of the commercially available material is obtained as a byproduct of lepidolite processing for Li. Caesium occurs as the hydrated aluminosilicate pollucite, **$\text{Cs}_4\text{Al}_4\text{Si}_9\text{O}_{26}\cdot\text{H}_2\text{O}$** , but the world's only commercial source is at Bernic Lake,

² Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th edn., 1995, Vol 15, pp. 434–63.

³ J. E. LLOYD in R. THOMPSON (ed.) *Speciality Inorganic Chemicals*, Royal Society of Chemistry, London, 1981, pp. 98–122.

⁴ W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, VCH, New York, 1989, pp. 215–8.

Production and Uses of Salt⁽⁵⁻⁷⁾

More NaCl is used for inorganic chemical manufacture than is any other material. It is approached only by phosphate rock, and world consumption of each exceeds 150 million tonnes annually, the figure for NaCl in 1982 being 168.7 million tonnes. Production is dominated by Europe (39%), North America (34%) and Asia (20%), whilst South America and Oceania have only 3% each and Africa 1%. Rock-salt occurs as vast subterranean deposits often hundreds of metres thick and containing >90% NaCl. The Cheshire salt field (which is the principal UK source of NaCl) is typical, occupying an area of 60 km × 24 km and being some 400 m thick: this field alone corresponds to reserves of >10¹¹ tonnes. Similar deposits occur near Carlsbad New Mexico, in Saskatchewan Canada and in many other places. Production methods vary with locality and with the use to be made of the salt. For example, in the UK 82% is extracted as brine for direct use in the chemical industry and 18% is mined as rock-salt, mainly for use on roads; less than 1% is obtained by solar evaporation. By contrast, in the USA only 55% comes from brine, whereas 32% is mined as rock salt, 8% is obtained by vacuum pan evaporation, 4% by solar evaporation and 1% by the open pan process.

Major sections of the inorganic heavy chemicals industry are based on salt and, indeed, this compound was the very starting point of the chemical industry. Nicolas Leblanc (1742-1806), physician to the Duke of Orleans, devised a satisfactory process for making NaOH from NaCl in 1787 (Patent 1791) and this achieved enormous technological significance in Europe during most of the nineteenth century as the first industrial chemical process to be worked on a really large scale. It was, however, never important in the USA since it was initially cheaper to import from Europe and, by the time the US chemical industry began to develop in the last quarter of the century, the Leblanc process had been superseded by the electrolytic process. Thus in 1874 world production of NaOH was 525 000 tonnes of which 495 000 were by the Leblanc process; by 1902 production had risen to 1 800 000 tonnes, but only 150 000 tonnes of this was Leblanc. Despite its long history, there is still great scope for innovation and development in the chlor-alkali and related industries. For example, in recent years there has been a steady switch from mercury electrolysis cells to diaphragm and membrane cells for environmental and economic reasons.⁽⁷⁾ Similarly, the ammonia-soda (Solvay) process for Na₂CO₃ is being phased out because of the difficulty of disposing of embarrassing byproducts such as NH₄Cl and CaCl₂, coupled with the increasing cost of NH₃ and the possibility of direct mining for trona, Na₂CO₃·NaHCO₃·2H₂O. The closely interlocking chemical processes based on salt are set out in the flow sheet (Fig. 4.1). The detailed balance of the processes differs somewhat in the various industrial nations but data for the usage of salt in the USA are typical: of the 34.8 million tonnes consumed in 1982, 48% was used for chlor-alkali production and Na₂CO₃, 24% for the salting of roads, 6% for food and food processing, 5% for animal feeds, 5% for various industries such as paper pulp, textiles, metal manufacturing and the rubber and oil industries, 2% for all other chemical manufacturing, and the remaining 10% for a wide variety of other purposes. Further discussion on the industrial production and uses of many of these chemicals (e.g. NaOH, Na₂CO₃, Na₂SO₄) is given on p. 89.

Current industrial prices are ~\$5 per tonne for salt in brine and ~\$55 per tonne for solid salt, depending on quality.

Manitoba and Cs (like Rb) is mainly obtained as a byproduct of the Li industry. The intense interest in Li for thermonuclear purposes since about 1958, coupled with its extensive use in automotive greases (p. 70), has consequently made Rb and Cs compounds much more available than formerly: annual production is in the region of 5 tonnes for each.

4.2.3 Production and uses of the metals

Most commercial Li ores have 1-3% Li and this is increased by flotation to 4-6%. Spodumene, LiAlSi₂O₆, is heated to ~1100° to convert the α-form into the less-dense, more friable β-form, which is then washed with H₂SO₄ at 250°C and water-leached to give Li₂SO₄·H₂O. Successive treatment with Na₂CO₃ and HCl gives Li₂CO₃ (insol) and LiCl. Alternatively, the chloride can be obtained by calcining the washed ore with limestone (CaCO₃) at 1000° followed by water leaching to give LiOH and then treatment with HCl. Recovery from natural brines is also extensively used in the USA (Searles Lake, California and Clayton Valley, Nevada).

⁵ L. F. HABER, *The Chemical Industry during the Nineteenth Century*, Oxford University Press, Oxford, 1958, 292 pp. T. K. DERRY and T. I. WILLIAMS, *A Short History of Chemical Technology*, Oxford University Press, Oxford, 1960, 782 pp.

⁶ Kirk-Othmer *Encyclopedia of Chemical Technology*, 3rd edn., 1983, Vol. 21 pp. 205-23.

⁷ W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, VCH, New York, 1989, 149 ff., 218 ff.

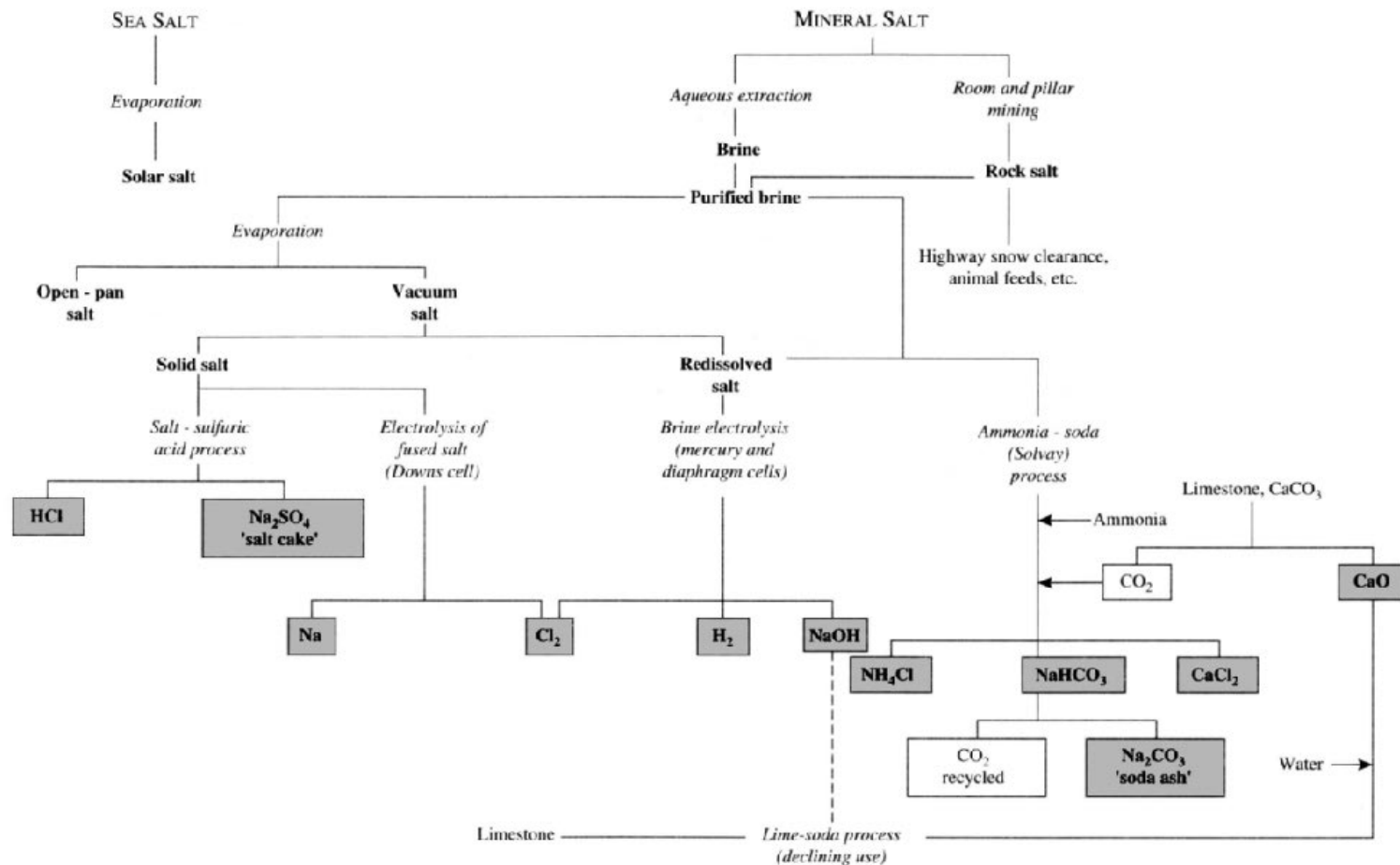


Figure 4.1 Flow sheet on chemical processes based on salt.

Production of Potassium Salts⁽⁸⁻¹⁰⁾

Sylvite (KCl) and sylvinit (mixed NaCl, KCl) are the most important K minerals for chemical industry; carnallite is also mined. Ocean waters contain only about 0.06% KCl, though this can rise to as high as 1.5% in some inland marshes and seas such as Searle's Lake, the Great Salt Lake, or the Dead Sea, thereby making recovery economically feasible. Soluble minerals of K are generally referred to (incorrectly) as potash, and production figures are always expressed as the weight of K₂O equivalent. Massive evaporite beds of soluble K salts were first discovered at Stassfurt, Germany, in 1856 and were worked there for potash and rock-salt from 1861 until 1972. World production was 28.6 million tonnes K₂O equivalent in 1986 of which 35% was produced in the USSR and 24% Canada.

In the UK workable potash deposits are confined to the Cleveland-North Yorkshire bed which is ~11 m thick and has reserves of >500 million tonnes. Massive recovery is also possible from brines; e.g. Jordan has a huge plant capable of recovering up to a million tonnes pa from the Dead Sea and the annual production by this country and by Israel now matches that of the USA and France.

Potassium is a major essential element for plant growth and potassic fertilizers account for the overwhelming proportion of production (95%). Again KCl is dominant, accounting for more than 90% of the K used in fertilizers; K₂SO₄ is also used. KNO₃, though an excellent fertilizer, is now of only minor importance because of production costs. In addition to its dominant use in fertilizers, KCl is used mainly to manufacture KOH by electrolysis using the mercury and membrane processes (about 0.7 million tonnes of KOH worldwide in 1985). This in turn is used to make a variety of other compounds and materials such as those listed below (the figures referring to the percentage usage of KOH in the USA in 1984): K₂CO₃ 25%, liquid fertilizers 15%, soaps 10%, liquid detergents (K₄P₂O₇) 9%, synthetic rubber 5%, crop protection agents 3%, KMnO₄ 2%, other chemicals 26% and export 5%. The manufacture of metallic K is relatively minor, the world production in 1994 amounting only to about 500 tonnes. Prices in 1994 were \$30-40 per kg for bulk K and \$16-22 per kg for NaK (78% K).

The main industrial uses of potassium compounds other than KCl and KOH are:

K₂CO₃ (from KOH and CO₂), used chiefly in high-quality decorative glassware, in optical lenses, colour TV tubes and fluorescent lamps; it is also used in china ware, textile dyes and pigments.

KNO₃, a powerful oxidizing agent now used mainly in gunpowders and pyrotechnics, and in fertilizers.

KMnO₄, an oxidizer, decolorizer, bleacher and purification agent; its major application is in the manufacture of saccharin.

KO₂, used in breathing apparatus (p. 74).

KClO₃, used in small amounts in matches and explosives (pp. 509, 862).

KBr, used extensively in photography and as the usual source of bromine in organic syntheses; formerly used as a sedative.

It is interesting to note the effect of varying the alkali metal cation on the properties of various compounds and industrial materials. For example, a soap is an alkali metal salt formed by neutralizing a long-chain organic acid such as stearic acid, CH₃(CH₂)₁₆CO₂H, with MOH. Potassium soaps are soft and low melting, and are therefore used in liquid detergents. Sodium soaps have higher mp's and are the basis for the familiar domestic "hard soaps" or bar soaps. Lithium soaps have still higher mp's and are therefore used as thickening agents for high-temperature lubricating oils and greases — their job is to hold the oil in contact with the metal under conditions when the oil by itself would run off.

The metal is obtained by electrolysis of a fused mixture of 55% LiCl, 45% KCl at ~450°C, the first commercial production being by Metallgesellschaft AG, in Germany, 1923. Current world production of Li metal is about 1000 tonnes pa. Far greater tonnages of Li compounds are, of course, produced and their major commercial applications have already been noted (p. 70).

Sodium metal is produced commercially on the kilotonne scale by the electrolysis of a fused eutectic mixture of 40% NaCl, 60% CaCl₂ at ~580°C in a Downs cell (introduced by du Pont, Niagara Falls, 1921). Metallic Na and Ca are liberated at the cylindrical steel cathode and rise through a cooled collecting pipe which allows the calcium to solidify and fall back into the melt. Chlorine liberated at the central graphite anode is collected in a nickel dome and subsequently purified. Potassium cannot be produced in this way because it is too soluble in the molten chloride to float on top of the cell for collection and because it vaporizes readily

⁸ Kirk-Othmer Encyclopedia of Chemical Technology, 4th edn., 1996, Vol. 19, pp. 1047-92.

⁹ P. CROWSON, *Minerals Handbook 1988-89*, Stockton Press, New York, 1988, pp. 216-21

¹⁰ Ref. 7 pp. 228-31.

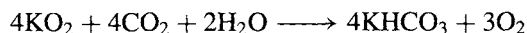
at the operating temperatures, creating hazardous conditions. Superoxide formation is an added difficulty since this reacts explosively with K metal. Consequently, commercial production of K relies on reduction of molten KCl with metallic Na at 850°C.[†] A similar process using Ca metal at 750°C under reduced pressure is used to produce metallic Rb and Cs.

Industrial uses of Na metal reflect its strong reducing properties. Much of the world production was used to make PbEt₄ (or PbMe₄) for gasoline antiknocks via the high-pressure reaction of alkyl chlorides with Na/Pb alloy, though this use is declining rapidly for environmental reasons. A further major use is to produce Ti, Zr and other metals by reduction of their chlorides, and a smaller amount is used to make compounds such as NaH, NaOR and Na₂O₂. Sodium dispersions are also a valuable catalyst for the production of some artificial rubbers and elastomers. A growing use is as a heat-exchange liquid in fast breeder nuclear reactors where sodium's low mp, low viscosity and low neutron absorption cross-section combine with its exceptionally high heat capacity and thermal conductivity to make it (and its alloys with K) the most-favoured material.⁽¹¹⁾ The annual production of metallic Na in the USA fell steadily from 170 000 tonnes in 1974 to 86 000 tonnes in 1985 and is still falling. Potassium metal, being more difficult and expensive to produce, is manufactured on a much smaller scale. One of its main uses is to make the superoxide KO₂ by direct combustion; this compound is used in breathing masks as an auxiliary supply of O₂ in mines, submarines and space vehicles:



[†] This reduction of KCl by Na appears to be contrary to the normal order of reactivity (K > Na). However, at 850–880° an equilibrium is set up: $\text{Na}(\text{g}) + \text{K}^+(\text{l}) \rightleftharpoons \text{Na}^+(\text{l}) + \text{K}(\text{g})$. Since K is the more volatile (p. 75), it distils off more readily, thus displacing the equilibrium and allowing the reaction to proceed. By fractional distillation through a packed tower, K of 99.5% purity can be obtained but usually an Na/K mixture is drawn off because alloys with 15–55% Na are liquid at room temperature and therefore easier to transport.

¹¹ C. C. ADDISON, *The Chemistry of Liquid Alkali Metals*, Wiley, Chichester, 1984, 330 pp.



An indication of the relative cost of the alkali metals in bulk at 1980–82 prices (USA) is:

Metal	Li	Na	K	Rb	Cs
Price/\$ kg ⁻¹	36.3	1.50	34.4	827	716
Relative cost (per kg)	24	1	23	550	477
Relative cost (per mol)	7.3	1	39	2050	2760

4.2.4 Properties of the alkali metals

The Group 1 elements are soft, low-melting metals which crystallize with bcc lattices. All are silvery-white except caesium which is golden yellow;⁽¹²⁾ in fact, caesium is one of only three metallic elements which are intensely coloured, the other two being copper and gold (see also pp. 112, 1177, 1232). Lithium is harder than sodium but softer than lead. Atomic properties are summarized in Table 4.1 and general physical properties are in Table 4.2. Further physical properties of the alkali metals, together with a review of the chemical properties and industrial applications of the metals in the molten state are in ref. 11.

Lithium has a variable atomic weight (p. 18) whereas sodium and caesium, being mononucleidic, have very precisely known and invariant atomic weights. Potassium and rubidium are both radioactive but the half-lives of their radioisotopes are so long that the atomic weight does not vary significantly from this cause. The large size and low ionization energies of the alkali metals compared with all other elements have already been noted (pp. 23–5) and this confers on the elements their characteristic properties. The group usually shows smooth trends in properties, and the weak bonding of the single valence electron leads to low mp, bp and density, and low heats of sublimation, vaporization and dissociation. Conversely, the elements have large atomic and ionic radii and extremely high thermal and electrical conductivity. Lithium is the smallest element in the group and has the highest ionization energy, mp and heat

¹² R. J. MOOLENAAR, *Journal of Metals* 16, 21–4 (1964).

Table 4.1 Atomic properties of the alkali metals

Property	Li	Na	K	Rb	Cs	Fr
Atomic number	3	11	19	37	55	87
Number of naturally occurring isotopes	2	1	2 + 1 ^(a)	1 + 1 ^(a)	1	1 ^(a)
Atomic weight	6.941(2)	22.989 768(6)	39.0983(1)	85.4678(3)	132.90543(5)	(223)
Electronic configuration	[He]2s ¹	[Ne]3s ¹	[Ar]4s ¹	[Kr]5s ¹	[Xe]6s ¹	[Rn]7s ¹
Ionization energy/kJ mol ⁻¹	520.2	495.8	418.8	403.0	375.7	~375
Electron affinity/kJ mol ⁻¹	59.8	52.9	46.36	46.88	45.5	(44.0)
$\Delta H_{\text{dissoc}}/\text{kJ mol}^{-1}$ (M ₂)	106.5	73.6	57.3	45.6	44.77	—
Metal radius/pm	152	186	227	248	265	—
Ionic radius (6-coordinate)/pm	76	102	138	152	167	(180)
E°/V for $\text{M}^+(\text{aq}) + \text{e}^- \longrightarrow \text{M}(\text{s})$	-3.045	-2.714	-2.925	-2.925	-2.923	—

(a) Radioactive: ⁴⁰K $t_{1/2}$ 1.277 × 10⁹ y; ⁸⁷Rb $t_{1/2}$ 4.75 × 10¹⁰ y; ²²³Fr $t_{1/2}$ 21.8 min.

Table 4.2 Physical properties of the alkali metals

Property	Li	Na	K	Rb	Cs
MP/°C	180.6	97.8	63.7	39.5	28.4
BP/°C	1342	883	759	688	671
Density (20°C)/g cm ⁻³	0.534	0.968	0.856	1.532	1.90
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	2.93	2.64	2.39	2.20	2.09
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	148	99	79	76	67
ΔH_{f} (monatomic gas)/kJ mol ⁻¹	162	108	89.6	82.0	78.2
Electrical resistivity (25°C)/μohm cm	9.47	4.89	7.39	13.1	20.8

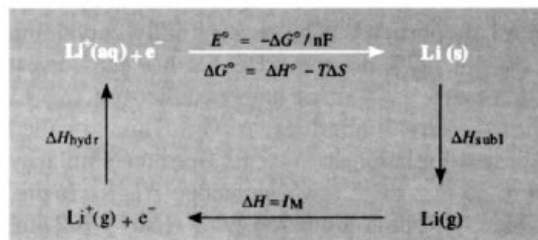
of atomization; it also has the lowest density of any solid at room temperature.

All the alkali metals have characteristic flame colorations due to the ready excitation of the outermost electron, and this is the basis of their analytical determination by flame photometry or atomic absorption spectroscopy. The colours and principal emission (or absorption) wavelengths, λ , are given below but it should be noted that these lines do not all refer to the same transition; for example, the Na D-line doublet at 589.0, 589.6 nm arises from the 3s¹ – 3p¹ transition in Na atoms formed by reduction of Na⁺ in the flame, whereas the red line for lithium is associated with the short-lived species LiOH.

Element	Li	Na	K	Rb	Cs
Colour	Crimson	Yellow	Violet	Red-violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

The reduction potential for lithium appears at first sight to be anomalous and is one of the

few properties that does not show a smooth trend with increasing atomic number in the group. This arises from the small size and very large hydration energy of the free gaseous lithium ion. The standard reduction potential E° refers to the reaction $\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$ and is related to the free-energy change: $\Delta G^\circ = -nFE^\circ$. The ionization energy I_M , which is the enthalpy change of the gas-phase reaction $\text{Li}(\text{g}) \longrightarrow \text{Li}^+(\text{g}) + \text{e}^-$, is only one component of this, as can be seen from the following cycle:



Estimates of the heat of hydration of Li⁺(g) give values near 520 kJ mol⁻¹ compared with

405 kJ mol⁻¹ for Na⁺(g) and only 265 kJ mol⁻¹ for Cs⁺(g). This factor, although opposed by the much larger entropy change for the lithium electrode reaction (due to the more severe disruption of the water structure by the lithium ion), is sufficient to reverse the position of lithium and make it the most electropositive of the alkali metals (as measured by electrode potential) despite the fact that it is the most difficult element of the group to ionize in the gas phase.

4.2.5 Chemical reactivity and trends

The ease of involving the outermost ns^1 electron in bonding, coupled with the very high second-stage ionization energy of the alkali metals, immediately explains both the great chemical reactivity of these elements and the fact that their oxidation state in compounds never exceeds +1. The metals have a high lustre when freshly cut but tarnish rapidly in air due to reaction with O₂ and moisture. Reaction with the halogens is vigorous; even explosive in some cases. All the alkali metals react with hydrogen (p. 65) and with proton donors such as alcohols, gaseous ammonia and even alkynes. They also act as powerful reducing agents towards many oxides and halides and so can be used to prepare many metallic elements or their alloys.

The small size of lithium frequently confers special properties on its compounds and for this reason the element is sometimes termed "anomalous". For example, it is miscible with Na only above 380° and is immiscible with molten K, Rb and Cs, whereas all other pairs of alkali metals are miscible with each other in all proportions. (The ternary alloy containing 12% Na, 47% K and 41% Cs has the lowest known mp, -78°C, of any metallic system.) Li shows many similarities to Mg. This so-called "diagonal relationship" stems from the similarity in ionic size of the two elements: $r(\text{Li}^+)$ 76 pm, $r(\text{Mg}^{2+})$ 72 pm, compared with $r(\text{Na}^+)$ 102 pm. Thus, as first noted by Arfvedson in establishing lithium as a new element, LiOH and Li₂CO₃ are much less soluble than the corresponding

Na and K compounds and the carbonate (like MgCO₃) decomposes more readily on being heated. Similarly, LiF (like MgF₂) is much less soluble in water than are the other alkali metal fluorides because of the large lattice energy associated with the small size of both the cation and the anion. By contrast, lithium salts of large, non-polarizable anions such as ClO₄⁻ are much more soluble than those of the other alkali metals, presumably because of the high energy of solvation of Li⁺. For the same reason many simple lithium salts are normally hydrated (p. 88) and the anhydrous salts are extremely hygroscopic: this great affinity for water forms the basis of the widespread use of LiCl and LiBr brines in dehumidifying and air-conditioning units. More subtly there is also a close structural relation between the hydrogen-bonded structures of LiClO₄·3H₂O and Mg(ClO₄)₂·6H₂O in which the face-shared octahedral groups of [Li(H₂O)₆]⁺ are replaced alternately by half the number of discrete [Mg(H₂O)₆]²⁺ groups.⁽¹³⁾ Lithium sulfate, unlike the other alkali metal sulfates, does not form alums [M(H₂O)₆]⁺[Al(H₂O)₆]³⁺[SO₄]²⁻ because the hydrated lithium cation is too small to fill the appropriate site in the alum structure.

Lithium is unusual in reacting directly with N₂ to form the nitride Li₃N; no other alkali metal has this property, which lithium shares with magnesium (which readily forms Mg₃N₂). On the basis of size, it would be expected that Li would be tetrahedrally coordinated by N but, as pointed out by A. F. Wells,⁽¹³⁾ this would require 12 tetrahedra to meet at a point which is a geometrical impossibility, 8 being the maximum number theoretically possible; accordingly Li₃N has a unique structure (see p. 92) in which one-third of the Li have 2 N atoms as nearest neighbours (at 194 pm) and the remainder have 3 N atoms as neighbours (at 213 pm); each N is surrounded by 2 Li at 194 pm and 6 more at 213 pm.

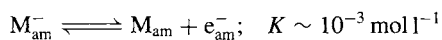
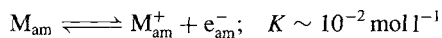
¹³ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984, 1382 pp.

4.2.6 Solutions in liquid ammonia and other solvents⁽¹⁴⁾

One of the most remarkable features of the alkali metals is their ready solubility in liquid ammonia to give bright blue, metastable solutions with unusual properties. Such solutions have been extensively studied since they were first observed by T. Weyl in 1863,[†] and it is now known that similar solutions are formed by the heavier alkaline earth metals (Ca, Sr and Ba) and the divalent lanthanoids europium and ytterbium in liquid ammonia. Many amines share with ammonia this ability though to a much lesser extent. It is clear that solubility is favoured by low metal lattice energy, low ionization energies and high cation solvation energy. The most striking physical properties of the solutions are their colour, electrical conductivity and magnetic susceptibility. The solutions all have the same blue colour when dilute, suggesting the presence of a common coloured species, and they become bronze-coloured and metallic at higher concentrations. The conductivity of the dilute solutions is an order of magnitude higher than that of completely ionized salts in water; as the solutions become more concentrated the conductivity at first diminishes to a minimum value at about 0.04M and then increases dramatically to approach values typical of liquid metals. Dilute solutions are paramagnetic with a susceptibility appropriate to the presence of 1 free electron per metal atom; this susceptibility diminishes with increase in concentration, the

solutions becoming diamagnetic in the region of the conductivity minimum and then weakly paramagnetic again at still higher concentrations.

The interpretation of these remarkable properties has excited considerable interest: whilst there is still some uncertainty as to detail, it is now generally agreed that in dilute solution the alkali metals ionize to give a cation M^+ and a quasi-free electron which is distributed over a cavity in the solvent of radius 300–340 pm formed by displacement of 2–3 NH_3 molecules. This species has a broad absorption band extending into the infrared with a maximum at ~ 1500 nm and it is the short wavelength tail of this band which gives rise to the deep-blue colour of the solutions. The cavity model also interprets the fact that dissolution occurs with considerable expansion of volume so that the solutions have densities that are appreciably lower than that of liquid ammonia itself. The variation of properties with concentration can best be explained in terms of three equilibria between five solute species M , M_2 , M^+ , M^- and e^- :



The subscript am indicates that the species are dissolved in liquid ammonia and may be solvated. At very low concentrations the first equilibrium predominates and the high ionic conductivity stems from the high mobility of the electron which is some 280 times that of the cation. The species M_{am} can be thought of as an ion pair in which M_{am}^+ and e_{am}^- are held together by coulombic forces. As the concentration is raised the second equilibrium begins to remove mobile electrons e_{am}^- as the complex M_{am}^- and the conductivity drops. Concurrently M_{am} begins to dimerize to give $(M_2)_{am}$ in which the interaction between the 2 electrons is sufficiently strong to lead to spin-pairing and diamagnetism. At still higher concentrations the system behaves as a molten metal in which the metal cations are ammoniated. Saturated solutions are indeed extremely concentrated as indicated by the following table:

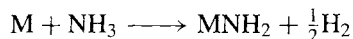
¹⁴ W. L. JOLLY and C. J. HALLADA, *Liquid ammonia*, Chap. 1 in T. C. WADDINGTON (ed.), *Non-aqueous Solvent Systems*, pp. 1–45, Academic Press, London, 1965. J. C. THOMPSON, The physical properties of metal solutions in non-aqueous solvents, Chap. 6 in J. LAGOWSKI (ed.), *The Chemistry of Non-aqueous Solvents*, Vol. 2, pp. 265–317, Academic Press, New York, 1967. J. JANDER (ed.), *Chemistry in Anhydrous Liquid Ammonia*, Wiley, Interscience, New York, 1966, 561 pp.

[†] Actually, the first observation was probably made by Sir Humphry Davy some 55 years earlier: an unpublished observation in his Notebook for November 1807 reads "When 8 grains of potassium were heated in ammoniacal gas it assumed a beautiful metallic appearance and gradually became of a pure blue colour".

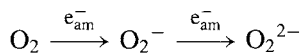
Solute	Li	Na	K	Rb	Cs
$T/^{\circ}\text{C}$	-33.2°	-33.5°	-33.2°	-	-50°
$g(\text{M})/\text{kg}(\text{NH}_3)$	108.7	251.4	463.7	-	3335
$\text{mol}(\text{NH}_3)/\text{mol}(\text{M})$	3.75	5.37	4.95	-	2.34

The lower solubility of Li on a wt/wt basis reflects its lower atomic weight and, when compared on a molar basis, it is nearly 50% more soluble than Na (15.66 mol/kg NH_3 compared to 10.93 mol/kg NH_3). Note that it requires only 2.34 mol NH_3 (39.8 g) to dissolve 1 mol Cs (132.9 g).

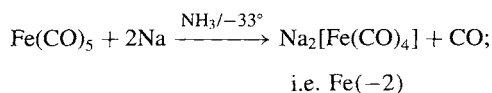
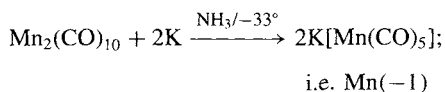
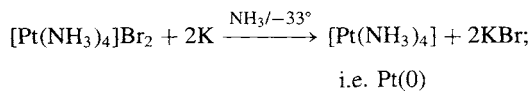
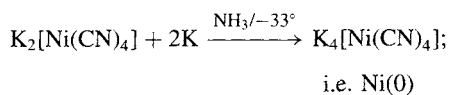
Solutions of alkali metals in liquid ammonia are valuable as powerful and selective reducing agents. The solutions are themselves unstable with respect to amide formation:



However, under anhydrous conditions and in the absence of catalytic impurities such as transition metal ions, solutions can be stored for several days with only a few per cent decomposition. Some reductions occur without bond cleavage as in the formation of alkali metal superoxides and peroxide (p. 84).

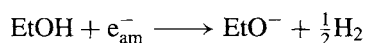
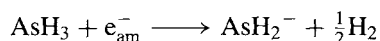
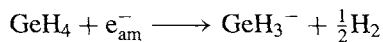


Transition metal complexes can be reduced to unusually low oxidation states either with or without bond cleavage, e.g.:

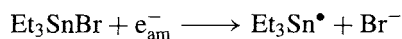
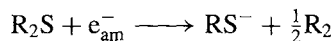


Salts of several heavy main-group elements can be reduced to form polyanions such as $\text{Na}_4[\text{Sn}_9]$, $\text{Na}_3[\text{Sb}_3]$ and $\text{Na}_3[\text{Sb}_7]$ (p. 588).

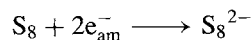
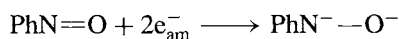
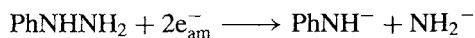
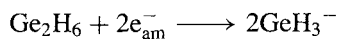
Many protonic species react with liberation of hydrogen:



These and similar reactions have considerable synthetic utility. Other reactions which result in bond cleavage by the addition of one electron are:



When a bond is broken by addition of 2 electrons, either 2 anions or a dianion is formed:



Subsequent ammonolysis may also occur:

