

SODIUM AND SODIUM ALLOYS

1. SODIUM

Sodium [7440-23-5], Na, an alkali metal, is the second element of Group 1 (IA) of the Periodic Table, atomic wt 22.9898. The chemical symbol is derived from the Latin *natrium*. Commercial interest in the metal derives from its high chemical reactivity, low melting point, high boiling point, good thermal and electrical conductivity, and high value in use.

Sir Humphry Davy first isolated metallic sodium in 1807 by the electrolytic decomposition of sodium hydroxide. Later, the metal was produced experimentally by thermal reduction of the hydroxide with iron. In 1855, commercial production was started using the Deville process, in which sodium carbonate was reduced with carbon at 1100°C. In 1886 a process for the thermal reduction of sodium hydroxide with carbon was developed. Later sodium was made on a commercial scale by the electrolysis of sodium hydroxide (1,2). The process for the electrolytic decomposition of fused sodium chloride, patented in 1924 (2,3), has been the preferred process since installation of the first electrolysis cells at Niagara Falls in 1925. Sodium chloride decomposition is widely used throughout the world (see SODIUM COMPOUNDS).

Sodium was first used commercially to make aluminum by reduction of sodium aluminum chloride. The principal application as of the mid-1990s is for the manufacture of tetraethyllead (TEL), the antiknock gasoline additive. However, TEL use is declining worldwide because of the recognized toxic effects of lead (qv) released to the environment (see LEAD COMPOUNDS, INDUSTRIAL TOXICOLOGY). Sodium use is growing for manufacture of sodium borohydride and agricultural crop protection chemicals (see BORON COMPOUNDS; FUNGICIDES, AGRICULTURAL). Smaller amounts of sodium are used to produce sodium hydride, indigo dyes,

Table 1. Radioisotopes of Sodium

| Isotope | CAS Registry Number | Half-life, s |
|-----------|---------------------|-------------------|
| sodium-20 | [14809-59-7] | 0.4 |
| sodium-21 | [15594-24-8] | 23.0 |
| sodium-22 | [13966-32-0] | 2.58 ^a |
| sodium-24 | [13982-04-2] | 15.0 ^b |
| sodium-25 | [15760-13-1] | 60.0 |
| sodium-26 | [26103-12-8] | 1.0 |

^aExpressed in years.

^bExpressed in hours.

tantalum metal powders, silicon, and sodium peroxide; in the preparation of many organic compounds, pharmaceuticals (qv), sodium azide, and copper; and in lead dross refining.

Sodium is not found in the free state in nature because of its high chemical reactivity. It occurs naturally as a component of many complex minerals and of such simple ones as sodium chloride, sodium carbonate, sodium sulfate, sodium borate, and sodium nitrate. Soluble sodium salts are found in seawater, mineral springs, and salt lakes. Principal U.S. commercial deposits of sodium salts are the Great Salt Lake; Searles Lake; and the rock salt beds of the Gulf Coast, Virginia, New York, and Michigan (see CHEMICALS FROM BRINE). Sodium-23 is the only naturally occurring isotope. The six artificial radioisotopes (qv) are listed in Table 1 (see SODIUM COMPOUNDS).

1.1. Physical Properties. Sodium is a soft, malleable solid readily cut with a knife or extruded as wire. It is commonly coated with a layer of white sodium monoxide, carbonate, or hydroxide, depending on the degree and kind of atmospheric exposure. In a strictly anhydrous inert atmosphere, the freshly cut surface has a faintly pink, bright metallic luster. Liquid sodium in such an atmosphere looks much like mercury. Both liquid and solid oxidize in air, but traces of moisture appear to be required for the reaction to proceed. Oxidation of the liquid is accelerated by an increase in temperature, or by increased velocity of sodium through an air or oxygen environment.

Only body-centered cubic crystals, lattice constant 428.2 pm at 20°C, are reported for sodium (4). The atomic radius is 185 pm, the ionic radius 97 pm, and electronic configuration is $1s^2 2s^2 2p^6 3s^1$ (5). Physical properties of sodium are given in Table 2. Greater detail and other properties are also available (5).

Sodium is paramagnetic. The vapor is chiefly monatomic, although the dimer and tetramer have been reported (6). Thin films are opaque in the visible range but transmit in the ultraviolet at ca 210 nm. The vapor is blue, but brilliant green is frequently observed when working with sodium at high temperature, presumably because of mixing of the blue with yellow from partial burning of the vapor.

At 100–300°C sodium readily wets and spreads over many dry solids, eg, sodium chloride or aluminum oxide. In this form the metal is highly reactive (7), but it does not easily wet stainless or carbon steels. Wetting of structural metals is influenced by the cleanliness of the surface, the purity of the sodium,

Table 2. Physical Properties of Sodium^a

| Property | Value | Property | Value |
|------------------------------------|--------------------|--------------------------------|-------------------|
| ionization potential, V | 5.12 | specific heat, | |
| melting point, °C | 97.82 | kJ/(kg · K) ^b solid | |
| heat of fusion, kJ/kg ^b | 113 | at 20°C | 2.01 |
| volume change on melting, % | 2.63 | mp | 2.16 |
| boiling point, °C | 881.4 | liquid | |
| heat of vaporization at bp, | 3.874 | at mp | 1.38 |
| MJ/kg ^b | | 400°C | 1.28 |
| density, g/cm ³ solid | | 550°C | 1.26 |
| at 20°C | 0.968 | electrical resistivity, | |
| 50°C | 0.962 | Ω · cm | |
| mp | 0.951 ^c | solid | |
| liquid | | at 20°C | 4.69 |
| at mp | 0.927 | mp | 6.60 ^c |
| 400°C | 0.856 | liquid | |
| 550°C | 0.820 | at mp | 9.64 |
| viscosity, mPa · s(=cP) | | 400°C | 22.14 |
| at 100°C | 0.680 | 550°C | 29.91 |
| 400°C | 0.284 | thermal | |
| 550°C | 0.225 | conductivity, W/(m·K) | |
| surface tension, mN/m(= dyn/cm) | | solid | |
| at mp | 192 | at 20°C | 1323 |
| 400°C | 161 | mp | 1193 ^c |
| 550°C | 146 | liquid | |
| | | at mp | 870 |
| | | 400°C | 722 |
| | | 550°C | 648 |

^aRef. 5.^bTo convert J to cal, divide by 4.184.^cValue is estimated.

temperature, and the time of exposure. Wetting occurs more readily at $\geq 300^\circ\text{C}$ and, once attained, persists at lower temperatures (5).

Sodium Dispersions. Sodium is easily dispersed in inert hydrocarbons (qv), eg, white oil or kerosene, by agitation, or using a homogenizing device. Addition of oleic acid and other long-chain fatty acids, higher alcohols and esters, and some finely divided solids, eg, carbon or bentonite, accelerate dispersion and produce finer (1–20 μm) particles. Above 98°C the sodium is present as liquid spheres. On cooling to lower temperatures, solid spheres of sodium remain dispersed in the hydrocarbon and present an extended surface for reaction. Dispersions may contain as much as 50 wt% sodium. Sodium in this form is easily handled and reacts rapidly. For some purposes the presence of the inert hydrocarbon is a disadvantage.

High Surface Sodium. Liquid sodium readily wets many solid surfaces. This property may be used to provide a highly reactive form of sodium without contamination by hydrocarbons. Powdered solids having a high surface area per unit volume, eg, completely dehydrated activated alumina powder, provide a suitable base for high surface sodium. Other powders, eg, sodium chloride, hydride, monoxide, or carbonate, can also be used.

The solid to be coated is placed in a vessel equipped with a stirrer, filled with pure, dry nitrogen or another inert gas, and heated to 110–250°C. Clean sodium is added with stirring. If enough is added, the sodium is rapidly distributed over the entire available surface. Depending on that available surface, up to 30 wt% or more sodium can be added without changing the free-flowing character of the system (7,8).

1.2. Chemical Properties. Sodium forms unstable solutions in liquid ammonia, where a slow reaction takes place to form sodamide and hydrogen, as follows:



Iron, cobalt, and nickel catalyze this reaction. The rate depends on temperature and sodium concentration. At -33.5°C , 0.251 kg sodium is soluble in 1 kg ammonia. Concentrated solutions of sodium in ammonia separate into two liquid phases when cooled below the consolute temperature of -41.6°C . The compositions of the phases depend on the temperature. At the peak of the conjugate solutions curve, the composition is 4.15 atom % sodium. The density decreases with increasing concentration of sodium. Thus, in the two-phase region the dilute bottom phase, low in sodium concentration, has a deep-blue color; the light top phase, high in sodium concentration, has a metallic bronze appearance (9–13).

At high temperature, sodium and its fused halides are mutually soluble (14). The consolute temperatures and corresponding Na mol fractions are given in Table 3. Nitrogen is soluble in liquid sodium to a limited extent, but sodium has been reported as a nitrogen-transfer medium in fast-breeder reactors (5) (see NUCLEAR REACTORS).

The solubility–temperature relationships of sodium, sodium compounds, iron, chromium, nickel, helium, hydrogen, and some of the rare gases are important in the design of sodium heat exchangers, especially those used in liquid-metal fast-breeder reactors (LMFBR). The solubility of oxygen in sodium is particularly important because of its marked effect on the corrosion of containment metals and because of problems of plugging narrow passages. This solubility S given in units of ppmwt O is

$$\log S = 6.239 - 2447/T \quad (1)$$

for temperature, T , in Kelvin from about 400 to 825 K (5). Solubility data for many other materials in sodium are also available (5). Because metallic calcium is always present in commercial sodium, and to a lesser extent in nuclear-grade

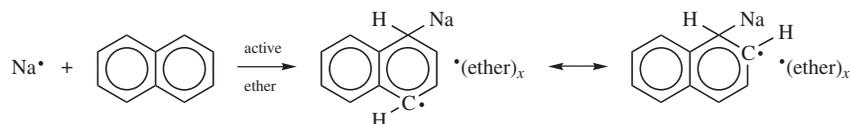
Table 3. Mutual Solubility of Sodium and Fused Sodium Halides

| Compound | Consolute temperature, °C | Na concentration, mol fraction |
|----------|---------------------------|--------------------------------|
| Na–NaF | 1182 | 0.28 |
| Na–NaCl | 1080 | 0.50 |
| Na–NaBr | 1025 | 0.52 |
| Na–NaI | 1033 | 0.50 |

sodium, the solubilities of calcium oxide and nitride in sodium are critical to the design of heat-transfer systems. These compounds are substantially insoluble at 100–120°C (15) (see HEAT-EXCHANGE TECHNOLOGY).

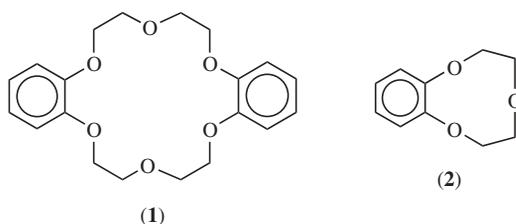
Sodium is soluble in ethylenediamine (16,17), but solubility in other amines such as methyl- or ethylamine may require the presence of ammonia. Sodium solubility in ammonia and ethylenediamine solutions has been extensively investigated (18). Sodium is insoluble in most hydrocarbons and is readily dispersed in kerosene or similar liquids toward which it is chemically inert. Such dispersions provide a reactive form of the metal.

In 1932 a class of complexes consisting of ethers, sodium, and polycyclic hydrocarbons was discovered (19). Sodium reacts with naphthalene in dimethyl ether as solvent to form a soluble, dark-green, reactive complex. The solution is electrically conductive. The reaction has been described as follows (8):



The addition product, $\text{C}_{10}\text{H}_7\text{Na}$, called naphthalenesodium or sodium naphthalene complex, may be regarded as a resonance hybrid. The ether is more than just a solvent that promotes the reaction. Stability of the complex depends on the presence of the ether, and sodium can be liberated by evaporating the ether or by dilution using an indifferent solvent, such as ethyl ether. A number of ether-type solvents are effective in complex preparation, such as methyl ethyl ether, ethylene glycol dimethyl ether, dioxane, and THF. Trimethylamine also promotes complex formation. This reaction proceeds with all alkali metals. Other aromatic compounds, eg, diphenyl, anthracene, and phenanthrene, also form sodium complexes (16,20).

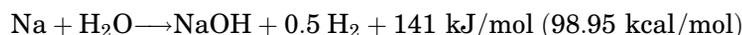
In 1967, DuPont chemist Charles J. Pedersen (21) discovered a class of ligands capable of complexing alkali metal cations, a discovery which led to the Nobel Prize in Chemistry in 1987. These compounds, known as crown ethers or cryptands, allow greatly enhanced solubility of sodium and other alkali metals in amines and ethers. About 50 crown ethers having between 9–60 membered oligoether rings were described (22). Two such structures, dibenzo-18-crown-6 (1) and benzo-9-crown-3 (2), are shown.



Sodium Reactions. Sodium reacts with many elements and substances (5,16,20) and forms well-defined compounds with a number of metals. Some of these alloys are liquid below 300°C. When heated in air, sodium ignites at

about 120°C and burns with a yellow flame, evolving a dense white acrid smoke. In the presence of air or oxygen a monoxide or peroxide is formed. Limited oxygen supply and temperatures below 160°C give sodium monoxide, Na₂O, as the principal reaction product. At 250–300°C in the presence of adequate oxygen, sodium peroxide, Na₂O₂, is formed along with very small amounts of superoxide, NaO₂ (see PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES). Sodium superoxide is made from sodium peroxide and oxygen at high temperature and pressure. Sodium does not react with extremely dry oxygen or air, except for the possible formation of a surface film of transparent oxide (23).

The reaction of sodium and water according to the following equation



has been extensively studied as it relates to the generation of steam in sodium-cooled breeder reactors (5). Under ordinary circumstances, this reaction is rapid. The liberated heat melts the sodium and frequently ignites the evolved hydrogen if air is present. In the absence of air and a large excess of either reactant, the reaction may be relatively nonviolent. Thus, dry steam or superheated steam may be used to clean equipment contaminated with sodium residues, but precautionary action must be taken to exclude air, avoid condensation, and design equipment to drain without leaving pockets of sodium. Any such sodium may become isolated by a layer of solid sodium hydroxide and can remain very reactive and hazardous.

Hydrogen and sodium do not react at room temperature, but at 200–350°C sodium hydride is formed (24,25). The reaction with bulk sodium is slow because of the limited surface available for reaction, but dispersions in hydrocarbons and high surface sodium react more rapidly (7). For the latter, reaction is further accelerated by surface-active agents such as sodium anthracene-9-carboxylate and sodium phenanthrene-9-carboxylate (26–28).

There is little evidence of the direct formation of sodium carbide from the elements (29,30), but sodium and graphite form lamellar intercalation compounds (16,31–33). At 500–700°C, sodium and sodium carbonate produce the carbide, Na₂C₂; above 700°C, free carbon is also formed (34). Sodium reacts with carbon monoxide to give sodium carbide (34), and with acetylene to give sodium acetylide, NaHC₂, and sodium carbide (disodium acetylide), Na₂C₂ (see CARBIDES) (8).

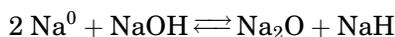
Nitrogen and sodium do not react at any temperature under ordinary circumstances, but are reported to form the nitride or azide under the influence of an electric discharge (14,35). Sodium silicide, NaSi, has been synthesized from the elements (36,37). When heated together, sodium and phosphorus form sodium phosphide, but in the presence of air with ignition sodium phosphate is formed. Sulfur, selenium, and tellurium form the sulfide, selenide, and telluride, respectively. In vapor phase, sodium forms halides with all halogens (14). At room temperature, chlorine and bromine react rapidly with thin films of sodium (38), whereas fluorine and sodium ignite. Molten sodium ignites in chlorine and burns to sodium chloride (see SODIUM COMPOUNDS, SODIUM HALIDES).

At room temperature, little reaction occurs between carbon dioxide and sodium, but burning sodium reacts vigorously. Under controlled conditions, sodium formate or oxalate may be obtained (8,16). On impact, sodium is reported to react explosively with solid carbon dioxide. In addition to the carbide-forming

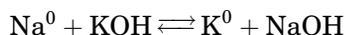
reaction, carbon monoxide reacts with sodium at 250–340°C to yield sodium carbonyl, $(\text{NaCO})_6$ (39,40). Above 1100°C, the temperature of the Deville process, carbon monoxide and sodium do not react. Sodium reacts with nitrous oxide to form sodium oxide and burns in nitric oxide to form a mixture of nitrite and hypoxynitrite. At low temperature, liquid nitrogen pentoxide reacts with sodium to produce nitrogen dioxide and sodium nitrate.

Phosphorus trichloride and pentachloride form sodium chloride and sodium phosphide, respectively, in the presence of sodium. Phosphorus oxychloride, POCl_3 , when heated with sodium, explodes. Carbon disulfide reacts violently, forming sodium sulfide. Sodium amide (sodamide), NaNH_2 , is formed by the reaction of ammonia gas with liquid sodium. Solid sodium reacts only superficially with liquid sulfur dioxide but molten sodium and gaseous sulfur dioxide react violently. Under carefully controlled conditions, sodium and sulfur dioxide yield sodium hydrosulfite, $\text{Na}_2\text{S}_2\text{O}_4$ (41). Dry hydrogen sulfide gas reacts slowly with solid sodium, but in the presence of moisture the reaction is very rapid. The product is sodium sulfide.

Sodium reacts with dilute acids about as vigorously as it reacts with water. The reaction with concentrated sulfuric acid may be somewhat less vigorous. At 300–385°C, sodium and sodium hydroxide react according to the following equilibrium:



The reaction is displaced to the right by dissociation of sodium hydride and liberation of hydrogen. This dissociation is favored under vacuum or when the reaction zone is swept with an inert gas to remove the hydrogen (24,25). In this manner, sodium monoxide substantially free of sodium and sodium hydroxide is produced. In the more complicated reaction between sodium metal and anhydrous potassium hydroxide, potassium metal and sodium hydroxide are produced in a reversible reaction (42,43):



Superimposed on this simple equilibrium are complex reactions involving the oxides and hydrides of the respective metals. At about 400°C, the metal phase resulting from the reaction of sodium and potassium hydroxide contains an unidentified reaction product that precipitates at about 300°C (15).

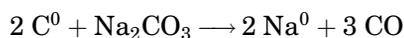
Data for the free energy of formation (44,45) indicate that sodium reduces the oxides of Group 1 (IA) elements except lithium oxide. Sodium does not reduce oxides of Group 2 (IIA) elements, but does reduce the Group 12 (IIB) mercury, cadmium, and zinc oxides. Many other oxides are reduced by metallic sodium. In some cases reduction depends on the formation of exothermic complex oxides. Iron oxide is reduced by sodium below ca 1200°C. Above this temperature the reaction is reversed. Sodium reduces most fluorides except the fluorides of lithium, the alkaline earths, and some lanthanides. It reduces most metallic chlorides, although some of the Group 1 (IA) and Group 2 (IIA) chlorides give two-phase equilibrium systems consisting of fused salt and alloy layers (43). Some heavy metal sulfides and cyanides are also reduced by sodium.

Sodium reacts with many organic compounds, particularly those containing oxygen, nitrogen, sulfur, halogens, carboxyl, or hydroxyl groups. The reactions are violent in many cases, for example, organic halides. Carbon may be deposited or hydrogen liberated, and compounds containing sulfur or halogens usually form sodium sulfide or sodium halides. Alcohols give alkoxides (see ALKOXIDES, METAL). Primary alcohols react more rapidly than secondary or tertiary. The reactivity decreases with increasing number of alcohol carbon atoms, or higher concentrations.

Organosodium compounds are prepared from sodium and other organometallic compounds or active methylene compounds by reaction with organic halides, cleavage of ethers, or addition to unsaturated compounds. Some aromatic vinyl compounds and allylic compounds also give sodium derivatives.

Sodium does not react with anhydrous ethyl ether but may react with higher ethers or mixed ethers. Organic acids give the corresponding salts with evolution of hydrogen or decompose. Pure, dry, saturated hydrocarbons, eg, xylene, toluene, and mineral oil, do not react with sodium at the hydrocarbon-cracking temperature. In the presence of unsaturated hydrocarbons, sodium may add at a double bond or cause polymerization. Sodium amalgam or sodium and alcohol are employed for organic reductions. Sodium is also used as a condensing agent in acetoacetic ester and malonic ester syntheses and the Wurtz-Fittig reaction (16,21) (see MALONIC ACID AND DERIVATIVES).

1.3. Manufacture. Thermal Reduction. Metallic sodium is produced by thermal reduction of several of its compounds. The earliest commercial processes were based on the carbon reduction of sodium carbonate (46–49) or sodium hydroxide (1,8,50):

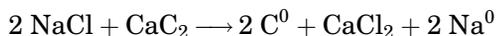


Sodium chloride is reduced by ferrosilicon in the presence of lime:



This process was operated briefly in vacuum retorts by Union Carbide in 1945 (51).

The chloride is also reduced by calcium carbide at 800–1200°C under vacuum (52).

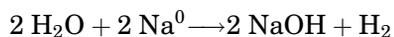


A number of other thermal reductions are described in the literature (8), but it is doubtful that any have been carried out on commercial scale.

Electrolysis of Fused Sodium Hydroxide. The first successful electrolytic production of sodium was achieved with the Castner cell (2):



The water formed at the anode diffuses to the cathode compartment where it reacts with its equivalent of sodium:



The net change is represented as follows:



Because the water reacts with half of the sodium produced by the electrolysis, the current yield can never be more than 50% of theoretical. Other reactions in the cell lower this yield still more.

The Castner cell was so simple in design and operation that over the years only minor changes have been made. A section of a cell used in England in the early 1950s is shown in Figure 1. The fused caustic bath is contained in the

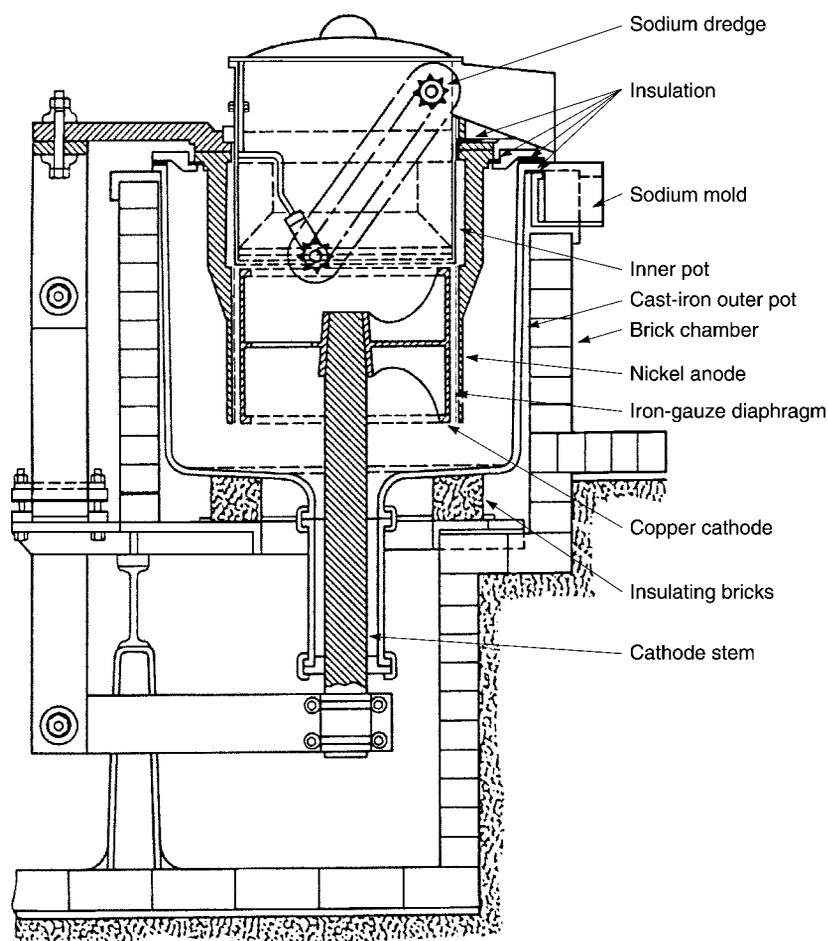


Fig. 1. Castner sodium cell (53). Courtesy of ICI, Ltd.

cast-iron outer pot, which rests in a brick chamber. The cylindrical copper cathode is supported on the cathode stem, which extends upward through the bottom of the cell. The cathode stem is sealed and insulated from the outer pot by a frozen portion of the bath. The cylindrical nickel anode concentric with the cathode is supported from the rim of the outer pot. The cylindrical iron-gauze diaphragm, located in the 2.5-cm annular space between the electrodes, is suspended from the inner pot. Because of the difference in density, sodium rises in the hydroxide bath and collects on its surface in the inner pot; the latter is electrically insulated from the top anode ring by which it is supported. The inner pot is closed by a cover that maintains an atmosphere of hydrogen over the sodium to prevent burning. No practical way has been found to collect the hydrogen, which is vented, as is the oxygen liberated at the anode. A perforated hand ladle was used to remove sodium from early Castner cells (54). Later, the sodium was removed using mechanically driven iron-gauze buckets. The cell shown in Figure 1 can hold approximately 1 t of molten bath, consisting primarily of mercury-cell caustic soda with up to 10% each of sodium chloride and sodium carbonate. Some salt is added initially to improve the bath conductivity, but the carbonate is an unwanted impurity. After several months of operation, the chloride, carbonate, and other impurities attain concentrations that seriously impair the efficiency of the cell. The bath is then renewed. Operating characteristics are given in Table 4. Small cells are heated externally to maintain operating temperature, but large cells are heated by the electrolysis current. Of the many ingenious systems proposed to prevent the reaction of sodium with the water produced at the anode, none are known to have been applied substantially commercially.

Electrolysis of Fused Sodium Chloride. Although many cells have been developed for the electrolysis of fused sodium chloride (8,55–60), the Downs cell (3) has been most successful (see ELECTROCHEMICAL PROCESSING). In cells in general use by 1945, a single cylindrical anode constructed of several graphite blocks was inserted through the center of the cell bottom and surrounded by an iron-gauze diaphragm and a cylindrical iron cathode. In the 1940s, the single anode and cathode were replaced by a multiple electrode arrangement consisting of four anodes of smaller diameter in a square pattern, each surrounded by a cylindrical

Table 4. **Operating Characteristics of the Castner Cell**

| Property | Value |
|--|-----------------|
| bath temperature, °C | 320 ± 10 |
| cell current, kA | 9 ± 0.5 |
| cell voltage, V | 4.3–5.0 |
| cathode current density, kA/m ² | 10.9 |
| current efficiency, % | 40 ^a |
| sodium produced | |
| g/(A·h) | 0.4 |
| g/(kW·h) | 90 |

^aValue is approximate.

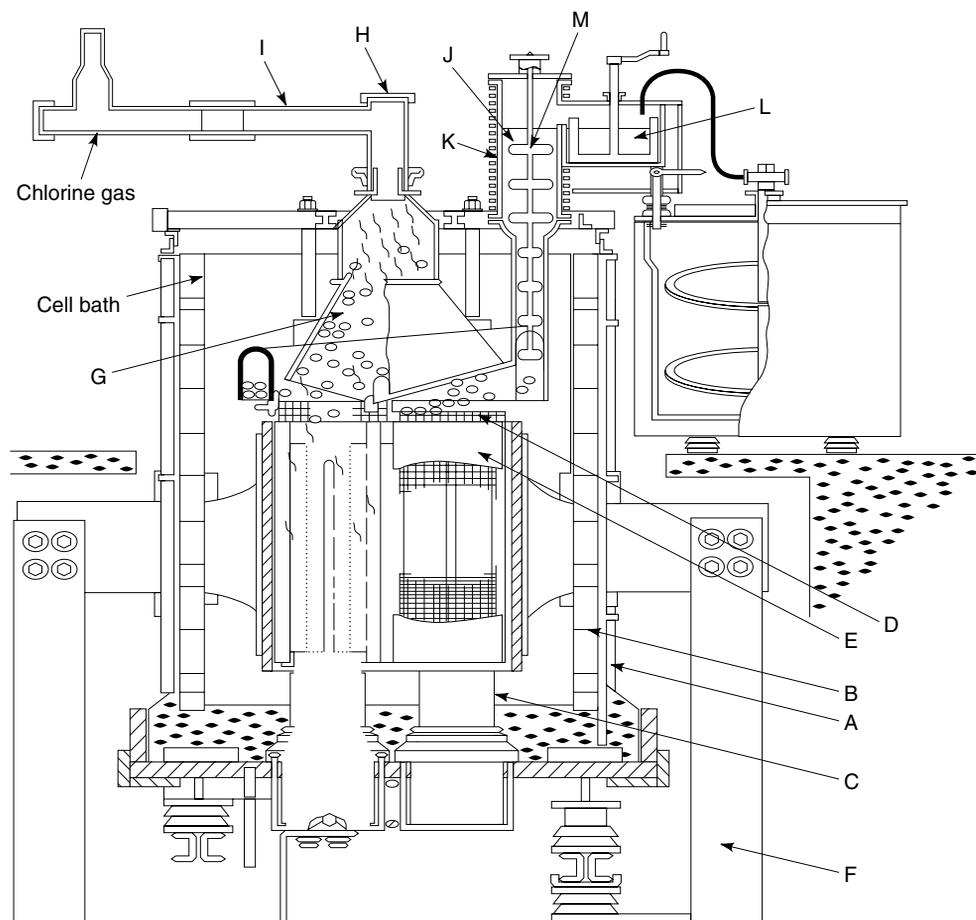


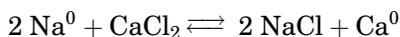
Fig. 2. Downs cell: A, the steel shell, contains the fused bath; B is the fire-brick lining; C, four cylindrical graphite anodes project upward from the base of the cell, each surrounded by D, a diaphragm of iron gauze, and E, a steel cathode. The four cathode cylinders are joined to form a single unit supported on cathode arms projecting through the cell walls and connected to F, the cathode bus bar. The diaphragms are suspended from G, the collector assembly, which is supported from steel beams spanning the cell top. For descriptions of H–M, see text.

diaphragm and cathode, as shown in Figure 2. Without increasing the overall cell dimensions, this design increased the electrode area per cell, allowing increased amperage.

The cell consists of three chambers. The upper chamber is outside the chlorine dome and above the sodium-collecting ring. The other two chambers are the chlorine-collecting zone inside the dome and diaphragm, and the sodium-collecting zone outside the diaphragm, and under the sodium-collecting ring of the collector unit. This arrangement prevents recombination of the sodium and chlorine. The collector is a complex assembly of inverted troughs and chambers arranged to collect the products in separate compartments as they rise through the bath.

The chlorine emerges through the nickel dome, H, and is removed through the chlorine line, I, to a header (see ALKALI AND CHLORINE PRODUCTS). Sodium, J, is channeled to a riser pipe, K, which leads to a discharge point above the cell wall. The difference in level between the overflowing sodium and the cell bath is due to the roughly 2:1 density ratio of the fused bath and liquid sodium. The upper end of the riser pipe is fitted with fins that cool the sodium and thereby precipitate dissolved calcium. The sodium, still containing some calcium, electrolyte, and oxide, overflows into a receiver, L. The calcium precipitated in the riser pipe tends to adhere to the wall from which location it is dislodged by the scraper, M, and returned to the base of the riser. The cell is fitted with a smoke-collection cover to collect particulate emissions and to protect the operators. A small area is left uncovered for visual observation, bath-level regulation, and salt-bath agitation and salt feed. Fine, dry crystalline salt is fed to the bath through a feed chute from a salt system conveyor (not shown).

The cell bath in early Downs cells (8,14) consisted of approximately 58 wt% calcium chloride and 42 wt% sodium chloride. This composition is a compromise between melting point and sodium content. Additional calcium chloride would further lower the melting point at the expense of depletion of sodium in the electrolysis zone, with the resulting complications. With the above composition, the cells operate at 580–600°C, well below the temperature of highest sodium solubility in the salt bath. Calcium chloride causes problems because of the following equilibrium reaction (56):



The alloy phase contains about 5 wt% calcium at cell conditions, an amount intolerable for most industrial uses. The bulk is removed by precipitation in the cooled riser pipe. Any precipitated calcium that adheres to the walls of the riser must be scraped off to prevent plugging. The precipitate drops to the bath–metal interface where it reacts to reform calcium chloride and sodium according to the above equilibrium. Calcium remaining in the sodium is largely removed by filtration at about 110°C. The filtered sodium contains <0.04 wt% calcium. The filtration operation produces a filter cake of calcium, sodium, chlorides, and oxides. High temperature sodium chloride reaction, and mechanical pressing of the sodium–calcium filter sludge are employed commercially in removing sodium from the calcium sludge, allowing recovery of most of the sodium content.

Characteristics of Downs cells are given in Table 5 (2).

Salt that is substantially free of sulfate and other impurities is the cell feed. This grade may be purchased from commercial salt suppliers or made on site by purification of crude sea or rock salt. Dried calcium chloride or cell bath from dismantled cells is added to the bath periodically as needed to replenish calcium coproduced with the sodium. The heat required to maintain the bath in the molten condition is supplied by the electrolysis current. Other electrolyte compositions have been proposed in which part or all of the calcium chloride is replaced by other salts (61–64). Such baths offer improved current efficiencies and production of crude sodium containing relatively little calcium.

Table 5. Characteristics of Downs Cells

| Property | Country of manufacture | | |
|--|------------------------|---------------|---------|
| | United Kingdom | United States | Germany |
| bath temperature, °C | 580 ± 15 | 580–600 | 590 ± 5 |
| cell current, kA | 25–35 | 43–45 | 24–32 |
| cell voltage, V | 7 ^a | 7 | 5.7–6.0 |
| cathode current density, kA/m ² | 9.8 | 11–12 | 9.8 |
| current efficiency, % | 75–80 | 85–90 | 78 |
| cell life, d | 500–700 | 600–800 | 300–350 |
| diaphragm life, d | 20–100 | 50–90 | 20–30 |

^aValue is approximate.

Cell life is determined by the loss of graphite from the anodes. Oxygen released at the anode by electrolysis of oxides or water in the bath reacts with the graphite to form CO and CO₂. In time, erosion of the anode increases the interelectrode spacing with corresponding increases in cell voltage and temperature. At this stage the cell is replaced.

A dimensionally stable anode consisting of an electrically conducting ceramic substrate coated with a noble metal oxide has been developed (55). Iridium oxide, for example, resists anode wear experienced in the Downs and similar electrolytic cells (see METAL ANODES).

Other commercial cells designed for the electrolysis of fused sodium chloride include the Danneel-Lonza cell and the Seward cell, both used before World War I. The former had no diaphragm and the sodium was confined to the cathode zone by salt curtains (ceramic walls); the latter utilized the contact-electrode principle, where the cathode was immersed only a few millimeters in the electrolyte. The Ciba cell was used over a longer period of time. It was an adaptation of the Castner cell to sodium chloride for fused caustic electrolysis. A mixture of sodium chloride and other chlorides, molten at 620°C, was electrolyzed in rectangular or oval cells heated only by the current. Several cells have been patented for the electrolysis of fused salt in cells with molten lead cathodes (65). However, it is difficult to separate the lead from the sodium (see ELECTROCHEMICAL PROCESSING).

Electrolysis of Amalgam. Sodium in the form of amalgam as made by the electrolysis of sodium chloride brine in mercury cathode cells is much less expensive than any other form of the metal, but commercial use of amalgam is restricted largely to production of caustic soda (see ALKALI AND CHLORINE PRODUCTS). Many efforts have been made to develop processes for recovering sodium from amalgam (66–69). Recovery by electrolysis with the amalgam serving as anode has been the favored approach. The electrolytes were generally low melting sodium salt combinations, although liquid ammonia (70) and organic solvents (71) have been reported. The addition of lead before electrolysis using a low melting salt electrolyte has been patented (72,73).

Sodium was made from amalgam in Germany during World War II (68). The only other commercial application appears to be the Tekkoshu process

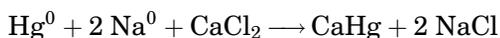
Table 6. Tekkosha Fused-Salt Electrolysis Cells^a

| Property | Value |
|------------------------------------|---------|
| voltage, V | 3.0–3.1 |
| current, kA | 60 |
| current density, kA/m ² | 4 |
| current efficiency, % | 96–98 |

^aRefs. (74–76).

(74–76). In this method, preheated amalgam from a chlor–alkali cell is supplied as anode to a second cell operating at 220–240°C. This cell has an electrolyte of fused sodium hydroxide, sodium iodide, and sodium cyanide and an iron cathode. Operating conditions are given in Table 6.

The sodium produced contains 0.1–0.5 wt% mercury. This mercury is converted to calcium amalgam by treating the crude sodium with powdered anhydrous calcium chloride:



The residual salts (CaCl₂, NaCl) and the calcium amalgam are removed by cooling and filtration. The Tekkosha process offers the advantages of moderate temperature, minimum corrosion, simple operation, high efficiency, low labor cost, good working conditions, and process adaptability. In the United States, these advantages would be largely offset by the environmental problems inherent in the handling of mercury and the need to produce some caustic soda to balance the in-process sodium inventory.

Electrolysis Based on Cationically Conducting Ceramics. Searching for a method for using sodium and sulfur (qv) as reactants in a secondary battery, the Ford Motor Company developed a polycrystalline β-alumina ceramic material that selectively transports sodium cations when subjected to an electric field (48,77,78) (see BATTERIES; CERAMICS AS ELECTRICAL MATERIALS). This ceramic, or any of its many variants, is useful as a diaphragm or divider in a two-compartment cell. In one compartment, the sodium is in contact with the ceramic; in the other, a suitable liquid electrolyte is in contact with the opposite side of the ceramic. Thus, the sodium is in electrochemical but not physical contact with the liquid electrolyte. Many low melting electrolytes can be used that are otherwise incompatible with sodium, eg, sodium polysulfides; sodium tetrachloroaluminate, NaAlCl₄; sodium hydroxide; and mixtures of sodium chloride and zinc chloride or sodium nitrite and nitrate. Because sodium is not in contact with the liquid electrolyte, the various reactions that usually lower the current efficiency of commercial cells do not occur. Cells based on this principle generally operate at close to 100% current efficiency (79). Sodium of exceptional purity is produced at satisfactory operating conditions. However, improved ceramics of predictable properties and long service life have not been commercialized as of this writing (ca 1996). Research on sodium–sulfur batteries is continuing (80–88). Operational prototypes are being tested for utility peak power load-leveling (89), and in early zero-emission electric vehicle (ZEV) trials. Solid electrolytes other than sodium beta-alumina are also reported (90,91). This technology, known as alkali metal thermal electric

Table 7. Sodium Process Energy Requirements^a

| Process | Total energy, MJ/kg Na ^b |
|-------------------------------|-------------------------------------|
| Downs, fused NaCl | 107 ^c |
| Castner, fused NaOH | 328 |
| Tekkosha, double electrolysis | 80 |
| sodium–lead, evaporation | 55 |

^aRef. 76.^bTo convert MJ/kg to Btu/lb, multiply by 430.2.^cRef. 92 gives a value of 97 MJ/kg.

conversion (AMTEC), was the topic of the 1995 Intersociety Energy Conversion Engineering Conference (IECEC) (see THERMOELECTRIC ENERGY CONVERSION).

Energy Requirements. The energy requirements of several sodium manufacturing processes are compared in Table 7 (76). The data contain some ambiguities because of the allocation of energy to the coproduction of chlorine. An independent calculation shows a somewhat lower energy consumption for the Downs process (92).

1.4. Specifications, Shipping. Sodium, generally about 99.9% Na assay, is available in two grades: regular, which contains 0.040 wt% Ca, and nuclear (low Ca), which has 0.001 wt% Ca. Both have 0.005 wt% Cl⁻. The nuclear grade is packed in specially cleaned containers, and in some cases under special cover atmospheres. A special grade of sodium low in potassium and calcium (<10 ppm) is achievable to meet requirements for use in manufacture of the more newly developed sodium–sulfur batteries.

Sodium is commonly shipped in 36- to 70-t tank cars in the United States. Smaller amounts are shipped in 16-t tank trucks or ISO-tanks. Sodium is also available in 104- and 190-kg drums, and in bricks (0.5–5 kg). A thin layer of oxide, hydroxide, or carbonate is usually present. Sodium is also marketed in small lots as a dispersion in an inert hydrocarbon, or produced in-process via high pressure injection into a pumped stream of inert carrier fluid, such as toluene or mineral oil.

1.5. Economic Aspects. Historically, U.S. production of sodium was 70–85% of world production. As lead compounds were phased out of gasoline in North America, this situation changed (Table 8).

1.6. Analytical Methods. Sodium is identified by the intense yellow color that sodium compounds impart to a flame or spectroscopically by the

Table 8. North American Sodium Production and Uses^a, t × 10³

| Use | 1959 | 1963 | 1967 | 1972 | 1978 | 1980 ^b | 1995 ^b |
|-------------------------|------------|------------|------------|------------|------------|-------------------|-------------------|
| gasoline additives | 72 | 93 | 124 | 121 | 101 | 78 | 1 |
| herbicides/insecticides | | | | | | | 6 |
| bleaching chemicals | | | | | | 4 | 8 |
| metals reduction | 5 | 5 | 12 | 6 | 14 | 13 | 8 |
| all others | 24 | 16 | 13 | 19 | 11 | 6 | 7 |
| <i>Totals</i> | <i>101</i> | <i>114</i> | <i>149</i> | <i>146</i> | <i>126</i> | <i>101</i> | <i>30</i> |

^aRefs. 93 and 94.^bEstimates.

characteristic sodium lines. The latter test is extremely sensitive, yet because many materials contain traces of sodium salts as impurities, it is not conclusive evidence of the presence of sodium in any considerable quantity.

The alkali metals are commonly separated from all other elements except chlorine before gravimetric determination. In the absence of other alkalies, sodium may be weighed as the chloride or converted to the sulfate and weighed. Well-known gravimetric procedures employ precipitation as the uranyl acetate of sodium–zinc or sodium–magnesium. Quantitative determination of sodium without separation is frequently possible by emission or atomic-absorption spectrometric techniques.

Metallic sodium is determined with fair accuracy by measuring the hydrogen liberated on the addition of ethyl alcohol. Sodium amalgam is analyzed by treating a sample with a measured volume of dilute standard acid. After the evolution of hydrogen stops, the excess acid is titrated with a standard base. Total alkalinity is calculated as sodium. Calcium in commercial sodium is usually determined by permanganate titration of calcium oxalate. The trace amounts of calcium present in nuclear-grade sodium, as little as 0.5 ppm, are determined by atomic absorption spectrometry. Chloride is determined as silver chloride by a turbidimetric method in which glycerol stabilizes the suspended precipitate. Sodium oxide is separated from sodium by treatment with mercury. The oxide, which is insoluble in the amalgam formed, can be separated and determined by acid titration. Methods for the determination of impurities in sodium are available (5,8,23,94).

1.7. Health and Safety Factors. The safe handling of sodium requires special consideration because of its high reactivity. Using properly designed equipment and strict safe-handling procedures, sodium is used in large- and small-volume applications without incident (96). The hazards of handling sodium are no greater than those encountered using many other industrial chemicals (5), although incidents can result in very serious injury, and fatalities have been known to occur from accidental contact with molten, burning sodium, or from contact with sodium finely dispersed in inert hydrocarbons such as mineral oil or toluene.

Direct contact of the skin with sodium can cause deep, serious burns from the action of sodium with the moisture present and the subsequent corrosive action of the caustic formed. Sodium can cause blindness on contact with the eyes. For these reasons, goggles, face shields, hard hat, hoods, long-gauntlet mittens, and multiple layers of flame-retardant protective clothing are recommended when working with molten sodium (97). All body parts should be protected and clothing needs to be designed for quick removal in case of emergencies. Contaminated clothing should first be steamed, then washed, or destroyed by burning.

Perhaps the greatest hazard presented by metallic sodium stems from its extremely vigorous reaction with water to form sodium hydroxide and hydrogen with the evolution of heat (5,14,98,99). In the presence of air this combination usually results in explosion; in a closed system where an inert atmosphere is present, the hydrogen evolved can cause a rapid increase in pressure. In the absence of air, the rate of reaction is substantially equal to the rate of mixing the reactants, and the reaction does not generally cause mechanical damage to

heat-transfer equipment. In the presence of air, the results cannot be predicted. Hydrogen evolved in a closed containers should not be allowed to mix with air.

Another hazard arises from the oxidation of sodium in air. Liquid sodium can autoignite at 120°C, although under some conditions dispersed or high surface sodium may ignite at much lower temperatures (7). A small local sodium fire can be extinguished by submerging the burning mass in the remaining pool of liquid sodium using an iron blade if the bulk of the sodium has not reached the ignition point. Larger fires are more difficult to handle. The common fire extinguishers, ie, water, CO₂, CCl₄, etc, should never be used. These only aggravate the existing situation by introducing additional explosion or reaction hazards. If the vessel containing the burning sodium can be flooded with nitrogen or closed to exclude air, the fire subsides and the material can be cooled. Fires that cannot be extinguished by excluding air may be quenched by large quantities of dry salts or other dry, cold, inert powder (100). Dry light soda ash, Na₂CO₃, is excellent for this purpose but must not be used if made damp on exposure in storage, and must be carefully protected from contact with exposure to moisture in air. Process areas and equipment should be designed to confine any sodium spills and permit recovery.

Techniques for handling sodium in commercial-scale applications have improved (5,23,98,101,102). Contamination by sodium oxide is kept at a minimum by completely welded construction and inert gas-pressured transfers. Residual oxide is removed by cold traps or micrometallic filters. Special mechanical pumps or leak-free electromagnetic pumps and meters work well with clean liquid sodium. Corrosion of stainless or carbon steel equipment is minimized by keeping the oxide content low. The 8-h TWA PEL and ceiling TLV for sodium or sodium oxide or hydroxide smoke exposure is 2 mg/m³. There is no defined ALD for pure sodium, as even the smallest quantity ingested could potentially cause fatal injury.

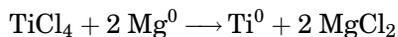
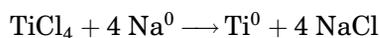
In the laboratory, sodium is best handled in a glove box filled with nitrogen or another inert gas, or in a water-free hood. When sodium is handled on the bench top, water and aqueous solutions must be excluded from the area. Tools for cutting or handling sodium must be clean and dry. Contact of sodium with air should be kept to a minimum because moisture in the air reacts rapidly with sodium. A metal catch pan under the equipment is essential to contain any spills or fires when breaking into pipe or equipment that previously contained liquid sodium. Provision should be made for safe removal of sodium residues from equipment and for cleaning the apparatus. Residue and sodium scrap can be destroyed by burning in a steel pan in a well-ventilated hood. Equipment may be cleaned by being opened to the air and heated until any sodium present is oxidized, or by purging thoroughly with nitrogen, then slowly admitting dry steam to the system while maintaining the nitrogen purge. The burning of sodium as part of any cleaning procedure produces an irritating and hazardous smoke of sodium oxide. This should be collected by an appropriate hood or duct and scrubbed. Dilute aqueous sodium hydroxide is a satisfactory scrubbing liquid.

Other methods for safely cleaning apparatus containing sodium residues or disposing of waste sodium are based on treatment with bismuth or lead (103), inert organic liquids (104–106), or by reaction with water vapor carried in an inert gas stream (107).

Most reactions of sodium are heterogeneous, occurring on the surface of solid or liquid sodium. Such reactions are accelerated by extending the sodium surface exposed. The sodium is generally dispersed in a suitable medium (108) or spread over a solid powder of high surface area (7,8). Dispersions in inert hydrocarbons may be briefly exposed to air and present no special hazards as long as the hydrocarbon covers the sodium. High surface sodium reacts very rapidly with air, however, and cannot be exposed without risk of fire. Dispersions of sodium spilled on cloth or other absorbent material may ignite quickly.

1.8. Uses. The largest consumption of sodium worldwide, as of the mid-1990s, is the production of tetraethyllead and tetramethyllead antiknock compounds for gasoline. This production is outside of North America. Sodium is also used for the production of the organometallic compounds such as methylcyclopentadienylmanganese tricarbonyl (MMT), another gasoline additive.

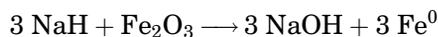
The manufacture of refractory metals such as titanium, zirconium, and hafnium by sodium reduction of their halides is a growing application, except for titanium, which is produced principally via magnesium reduction (109–114). Typical overall halide reactions are



Sodium reduction processes are also described for tantalum (115), silicon (116–118), magnesium (119), and other metals.

Metallic potassium and potassium–sodium alloys are made by the reaction of sodium with fused KCl (8,98) or KOH (8,15). Calcium metal and calcium hydride are prepared by the reduction of granular calcium chloride with sodium or sodium and hydrogen, respectively, at temperatures below the fusion point of the resulting salt mixtures (120,121).

Whereas manufacture of sodium peroxide has declined (122–126), Na_2O_2 is an excellent agent to liberate metal from complex ores, eg, silver tetrahedrites. Sodium hydride, made from sodium and hydrogen, is employed as catalyst or reactant in numerous organic reactions and for the production of other hydrides, eg, sodium borohydride (see HYDRIDES). Sodium is used indirectly for the descaling of metals such as stainless steel and titanium (41). Sodium and hydrogen are fed to a molten bath of anhydrous caustic to generate sodium hydride, which dissolves in the melt and is the effective descaling agent (see METAL TREATMENTS), according to the following reaction (127):



Many sodium compounds are made from sodium. Sodium is employed as a reducing agent in numerous preparations, including the manufacture of dyes (see DYES AND DYE INTERMEDIATES), eg, indigo; herbicides (qv) (128); pharmaceuticals (qv); high molecular weight alcohols (129); perfume materials (130) (see PERFUMES); and isosebacic acid (131,132).

Sodium is a catalyst for many polymerizations; the two most familiar are the polymerization of 1,2-butadiene (the Buna process) and the copolymerization

of styrene-butadiene mixtures (the modified GRS process). The alfin catalysts, made from sodium, give extremely rapid or unusual polymerizations of some dienes and of styrene (qv) (133-137) (see BUTADIENE; ELASTOMERS, SYNTHETIC; STYRENE PLASTICS).

Naphthalene sodium prepared in dimethyl ether or another appropriate solvent, or metallic sodium dissolved in liquid ammonia or dimethylsulfoxide, is used to treat polyfluorocarbon and other resins to promote adhesion (138-140). Sodium, usually in dispersed form, is used to desulfurize a variety of hydrocarbon stocks (140). The process is most useful for removal of small amounts of sulfur remaining after hydrodesulfurization.

Sodium as an active electrode component of primary and secondary batteries offers the advantages of low atomic weight and high potential (78,142, 143). In addition to the secondary battery for ZEVs, a remarkable primary cell has been developed by Lockheed Aircraft Corporation in which sodium metal and water (in the form of aqueous sodium hydroxide) are the reactants (144-147). No separators or diaphragms are used, the counterelectrode is mild steel, and the interelectrode distance is small. The unexpected discovery which makes this cell possible is that, given an external circuit of reasonable resistance, hydrogen is released on the iron counter-electrode rather than on the sodium surface. Thus, sodium dissolves as NaOH in a vigorous but nonviolent manner, and the released electrons traverse the external circuit to discharge hydrogen ions at the iron electrode. Concentration cells based on amalgams of differing sodium content that are regenerated thermally have been described (148,149).

Because of the electrical conductivity, low density, low cost, and extrudability of the metal, cables were made of sodium sheathed in polyethylene (150). An earlier application used sodium-filled iron pipe as a conductor (151); a more recent patent describes a conductor of sodium contained in aluminum, copper, or steel tubing (152). A corrugated flexible thin-walled copper tube filled with sodium and particularly well-adapted for use in gas-insulated high voltage transmission lines has been developed (153). Sodium conductor distribution cables offer both economic and energy-saving advantages (154), but have never gained wide acceptance for commercial use.

Sodium is used as a heat-transfer medium in primary and secondary cooling loops of liquid-metals fast-breeder power reactors (5,155-157). Low neutron cross sections, short half-life of the radioisotopes produced, low corrosiveness, low density, low viscosity, low melting point, high boiling point, high thermal conductivity, and low pressure make sodium systems attractive for this application (40).

Sodium has also been essential to new developments in heat transfer in advanced solar energy collectors (158,159) for powering systems remote from electrical distribution systems, and aerospace. A comparison of sodium with other working fluids in heat pipes is available (78,88,160,161) (see HEAT-EXCHANGE TECHNOLOGY, HEAT PIPES). Small amounts of sodium have been used widely to cool exhaust valves of heavy-duty internal combustion engines (8), affording longer valve or seat life by lower valve temperature in operation.

In metallurgical practice, sodium uses include preparation of powdered metals; removal of antimony, tin, and sulfur from lead; modification of the structure of silicon-aluminum alloys; application of diffusion alloy coatings to substrate metals (162,163); cleaning and desulfurizing alloy steels via NaH

(164); nodularization of graphite in cast iron; deoxidation of molten metals; heat treatment; and the coating of steel using aluminum or zinc.

Sodium vapor lamps, in use for many years, continue to be improved, both with respect to efficiency and color of emitted light. These lamps, however, contain only a few milligrams of sodium each.

A process development known as NOXSO (DuPont) (165,166) uses sodium to purify power plant combustion flue gas for removal of nitrogen oxide, NO_x , and sulfur, SO_x compounds. This technology relies on sodium metal generated *in situ* via thermal reduction of sodium compound-coated media contained within a flue-gas purification device, and subsequent flue-gas component reactions with sodium. The process also includes downstream separation and regeneration of spent media for recoating and circulation back to the gas purification device. A full-scale commercial demonstration project was under construction in 1995.

2. SODIUM ALLOYS

Sodium is miscible with many metals in liquid phase and forms alloys or compounds. Important examples are listed in Table 9; phase diagrams are available (4,5,14,35).

The brittleness of metals is frequently increased by the addition of sodium to form alloys. The metals vary in their ability to dilute the natural reactivity of sodium. Most binary alloys are unstable in air and react with water. Ternary and quaternary alloys are more stable.

Sodium-potassium alloy is easily prepared by melting the clean metals in an inert atmosphere or under an inert hydrocarbon, or by the reaction of sodium with molten KCl , KOH , or solid K_2CO_3 powder.

Alloys of lead and sodium containing up to 30 wt% sodium are obtained by heating the metals together in the desired ratio, allowing a slight excess of sodium to compensate for loss by oxidation. At about 225°C , the elements react and generate enough heat to cause a rapid temperature rise. External heating is discontinued and the mixture is cooled and poured into molds. The brittle alloys can be

Table 9. Metal-Sodium Systems^a

| Metal | Alloy formation | Compound formation | Consolute temperature, °C |
|----------------------|-----------------|--------------------|---------------------------|
| barium | + | + | miscible |
| calcium | + | | ca 1200 |
| lead | + | + | |
| lithium ^b | + | | 306 |
| magnesium | + | | >800 |
| mercury | + | + | |
| potassium | + | + | miscible |
| rubidium | + | | miscible |
| tin | + | + | |
| zinc | + | + | >800 |

^aRefs. 4, 5, 14, and 37.

^bRefs. 167 and 168.

ground to a powder and should be stored under a hydrocarbon or in airtight containers to prevent surface oxidation. The 30 wt% sodium alloy reacts vigorously with water to liberate hydrogen, providing a convenient laboratory source of this gas. An alloy containing 10 wt% sodium may be used in controlled reactions with organic halogen compounds that react violently with pure sodium. Sodium-lead alloys that contain large amounts of sodium are used to dry organic liquids.

Sodium-lead alloys that contain other metals, eg, the alkaline-earth metals, are hard even at high temperatures, and are thus suitable as bearing metals. Tempered lead, for example, is a bearing alloy that contains 1.3 wt% sodium, 0.12 wt% antimony, 0.08 wt% tin, and the remainder lead. The German Bahnmittel, which was used in axle bearings on railroad engines and cars, contains 0.6 wt% sodium, 0.04 wt% lithium, 0.6 wt% calcium, and the remainder lead, and has a Brinell hardness of 34 (see BEARING MATERIALS).

Up to ca 0.6 wt% sodium dissolves readily in mercury to form amalgams that are liquid at room temperature (169). The solubility of sodium in mercury is ca 1 wt% at 70°C (169) and 2 wt% at 140°C (37). Alloys containing >2 wt% sodium are brittle at room temperature. Sodium-rich amalgam may be made by adding mercury dropwise to a pool of molten sodium; mercury-rich amalgam is prepared by adding small, clean pieces to sodium to clean mercury with agitation. In either case an inert atmosphere must be maintained, and the heat evolved must be removed. Solid amalgams are easily broken and powdered, but must be carefully protected against air oxidation. Amalgams are useful in many reactions in place of sodium because the reactions are easier to control (169).

Sodium amalgam is employed in the manufacture of sodium hydroxide; sodium-potassium alloy, NaK, is used in heat-transfer applications; and sodium-lead alloy is used in the manufacture of tetraethyllead and tetramethyllead, and methylcyclopentadienylmanganesetricarbonyl, a gasoline additive growing in importance for improving refining efficiency and octane contribution.

Sodium does not form alloys with aluminum but is used to modify the grain structure of aluminum-silicon alloys and aluminum-copper alloys for improved machinability. Sodium-gold alloy is photoelectrically sensitive and may be used in photoelectric cells. A sodium-zinc alloy, containing 2 wt% sodium and 98 wt% zinc, is used to deoxidize other metals.

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- References 14 and 20 cover the inorganic chemistry of sodium.
- References 8 and 16 survey sodium organic chemistry.
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