IODINE AND IODINE COMPOUNDS

1. Introduction

Iodine [7553-56-2], (I), atomic number 53, atomic weight 126.9044, is a nonmetallic element belonging to the halogen family in Group 17 VII of the Periodic Table. Iodine is a simple element and the only known stable species with a mass number of 127. There are 22 other iodine isotopes having masses between 117 and 139, and 14 of these yield significant radiation.

Iodine was discovered by Bernard Curtois toward the end of 1811 or early 1812, when he observed violet vapors rising on heating saltpeter pots, in the factory in which he was engaged. However, its discovery was not made public until about 2 years later, when J. B. Désormes and F. Clement at a meeting of the Physical and Mathematical Section of the Institut Imperial de France on November 1813 announced its discovery by Curtois (1).

Following its discovery and examination, the new element was named *iode* in French after the Greek word *ioeides* meaning violet-colored. Shortly thereafter, Sir H. Davy invented the English term *iodine* from the same root (2).

Iodine is a bluish black, crystalline solid having a metallic luster. It is obtained in blocks or lumps like other elements, but in shiny flakes or prills that can be easily crushed to powder. Iodine crystallizes in rhomboidal plates belonging to the triclinic system.

2. Occurrence in Nature

No less than 99.6% of the earth's mass can be accounted for 32 of the chemical elements. The remaining 0.4% is apportioned among 64 elements, all of which are present as traces. Iodine is one of these 64 elements. Estimates on the abundance of constituent elements of the lithosphere place iodine 46th on a restricted list of 59 elements (37 very rare elements are excluded) and 61st on a list in which 96 elements are included. Iodine is, indeed, one of the scarcest of nonmetallic elements in the total composition of the earth (3).

Although not abundant in quantity, iodine is distributed almost everywhere. It is present in rocks, soils, waterbodies, plants, animal tissues, and foodstuffs (3,4). Except for the possible occurrence of elemental iodine vapor in the air near certain iodine-rich springs, iodine never occurs free in nature. It is always found in combination with other elements in the form of either more or fewer inorganic salts rather complex organic compounds such as thyroxin.

Wherever iodine occurs, its quantities are generally exceedingly small, and very sophisticated chemical methods are required to detect iodine. Only a few substances characteristically contain iodine in relatively large quantities. These are seaweeds, sponges, and chorales (5); the underground waters from certain deep oil-well boring and mineral springs (6); and, most impressive of all, the vast natural deposits of sodium nitrate, ("caliche" ore) found in the northern part of Chile. Even in these, however, the proportion of iodine is small, rarely exceeding 1 part in 500 (7–9).

Underground brines in Japan and caliche deposits in Chile are the largest current world sources of iodine (10). The caliche ore contains 3–12% sodium nitrate and its iodine content averages 0.04%. Lautarite [$Ca(IO_3)_2$] and dietzeite [$7Ca(IO_3)_2 \cdot 8CaCrO_4$] are the two crystalline forms in which iodine naturally occurs in caliche (11). In subsurface brines associated with oil and gas deposits, iodine occurs frequently as sodium or potassium iodide with an iodine concentration in the range of 30–150 ppm.

3. Properties

3.1. Physical Properties. The absorption of x-rays by iodine has been studied and the iodine crystal structure determined (12,13). Iodine crystallizes in the orthorhombic system and has a unit cell of eight atoms arranged as a symmetrical bipyramid. The cell constants at 18°C (14) are given in Table 1, along with other physical properties. From the interatomic distances of many iodine compounds, the calculated effective radius of the covalently bound iodine atom is 184 pm (15).

The density, d, of liquid iodine (16) is given by the expression

$$d = 3.94916 + 0.003267 \times (120 - t) \tag{1}$$

where t is temperature in °C. The specific volume at 120°C is 0.2532 mL. Measurements of the density of solid iodine have been extended to low temperatures, eg, d at $-195°C = 5.15$ g/mL; the atomic volume at $-273°C$ obtained by extrapolation is 24.5 mL (17,18). The experimental values for the viscosity of iodine vapor at 8 kPa (60 mm Hg), are determined over the temperature range 380–800°C, in reasonable agreement with those calculated by the Sutherland equation (19,20). The viscosity of liquid iodine at a temperature just above the melting point is 1.98 mPa(=cP) as compared to the 2.35 mPa (=cP) calculated by Andrade and Lindemann's equation. The coefficient of cubic expansion of solid iodine has been found to be 2.64×10^{-4} mL/°C, and that for liquid iodine 8.54×10^{-4} mL/°C (21,22). The critical temperature, T_c, of iodine has been determined as 553°C (23); the most probable value for the melting point of iodine is 113.6°C (24,25), although it has been claimed that a prolonged drying may raise it to 115.6°C (26). The change in volume on fusion is 2.04%.

The vapor pressure, p, of solid iodine has been redetermined using the gas current method and by a static method using a flexible metallic diaphragm (27,28). The data from the gas current method are well represented by equation 2 (27):

$$\log p_{\mathrm{kPa}} = -(3512.8/t) - 2.013 \log t + 15.3796 \tag{2}$$

The diffusion coefficient of iodine vapor between 14 and 30°C varies between 0.0767 to 0.0851 (29). The latent heat of fusion of molecular iodine has been found to be 15.66 ± 0.08 kJ/mol (3.74 ± 0.02 kcal/mol), and the latent heat of vaporization, calculated from vapor pressure data, to be 62.30 kJ/mol (14.89 kcal/mol) (28,30).

Temperature, °C	Vapor pressure, Pa (psi)
0	3.97 (0.0006)
10	10.64 (0.0015)
20	26.50 (0.0038)
30	61.90 (0.0090)
40	136.46 (0.0198)
50	285.56 (0.0414)
60	570.35 (0.0827)
70	1090.44 (0.1581)
80	2006.10 (0.2909)
90	3561.03 (0.5163)
100	6118.15 (0.8871)

The heat capacity of iodine at constant pressure has been redetermined for the temperature ranges −263 to −223°C (30) and −71 to 160°C (31). For solid iodine, in the interval 25−113.6°C, it can be expressed by equation 3:

$$C_p = 3.122 + 0.781 \times 10^4 \times (T - 298)^2 \qquad (3)$$

where C_p is the heat capacity in J/(mol·K) and T is the temperature in K (31). The heat capacities of iodine above its melting point are available (32). For the interval 113.6 to 160°C, a constant molal heat capacity for liquid iodine of 81.64 J/(mol·K) 19.51 kcal/(mol·K) is reported.

The thermal conductivity of solid iodine between 24.4 and 42.9°C has been found to remain practically constant at 0.004581 J/(cm·s·K) (33). Using the heat capacity data, the standard entropy of solid iodine at 25°C has been evaluated as 116.81 J/(moK), and that of the gaseous iodine at 25°C as 62.25 J/(mol·K), which compares satisfactorily with the 61.81 value calculated by statistical mechanics (34,35).

Iodine is only slightly soluble in water and no hydrates form upon dissolution. The solubility increases with temperature, as shown in Table 2 (36). Iodine is soluble in aqueous iodide solutions owing to the formation of polyiodide ions. For example, an equilibrium solution of solid iodine and $KI_7 \cdot H_2O$ at 25°C is highly concentrated and contains 67.8% iodine, 25.6% potassium iodide, and 6.6% water. However, if large cations such as cesium, substituted ammonium, and iodonium are present, the increased solubility may be limited, owing to precipitation of sparingly soluble polyiodides. Iodine is also more soluble in solutions of chlorides, bromides, and other salts than in pure water, but these salts have much less effect than do the iodides (36).

Iodine dissolves in many organic solvents (Table 3) (36), and the color of the resulting solutions varies with the nature of the solvent. This color variation results from the particular charge transfer possible upon complex formation. Complexation occurs with solvents that are electron donors. Aliphatic hydrocarbons and carbon tetrachloride give violet solutions, aromatic hydrocarbons give pink or brown-pink solutions, and alcohols, ethers, and high vapor amines give brown colors. Iodine readily sublimes, as is evident by the pressure below the melting point. It also exists as a black mobile liquid at atmospheric pressure over a range of more than 60°C. Iodine, a good solvent for alkali metal iodides and ammonium bases, dissolves sulfur, selenium, the covalent iodides of such metals as aluminum, tin, and titanium, and many organic substances.

Solutions of alkali metal and ammonium iodides in liquid iodine are good conductors of electricity, comparable to fused salts and aqueous solutions of strong acids. The liquid is therefore a polar solvent of considerable ionizing power, whereas its own electrical conductivity suggests that it is appreciably ionized, probably into I^+ and I_3^- (triodide). Iodine resembles water in this respect. The metal iodides and polyiodides are bases, whereas the iodine halides are acids.

Iodine vapor is characterized by the familiar violet color and by its unusually high specific gravity, approximately nine times that of air. The vapor is made up of diatomic molecules at low temperatures; at moderately elevated temperatures, dissociation becomes appreciable. The concentration of monoatomic molecules, for example, is 1.4% at 600°C and 101.3 kPa (1 atm) total pressure. Iodine is fluorescent at low pressures and rotates the plane of polarized light when placed in a magnetic field. It is also thermoluminescent, emitting visible light when heated at 500°C or higher.

3.2. Chemical Properties. The electron configuration of the iodine atom is $[\mathrm{Kr}]4d^{10}5s^25p^5$ and its ground state is $2p^0_{3/2}$. Principal oxidation states are $-1,\ +1,\ +3,\ +5$, and $+7$, but the oxide IO_2 where iodine has an oxidation state of $+4$ is also known. Iodine forms thermodynamically stable compounds in all these oxidation states, except the $+4$. Iodine is the heaviest of all the common halogens and the least electronegative. It is usually less violent in its reactions than the other members of the halogen family. Iodine presents mild oxidizing properties in acidic solutions.

Iodine forms compounds with all the elements except sulfur, selenium, and the noble gases. It reacts only indirectly with carbon, nitrogen, oxygen, and some noble metals such as platinum.

Iodine, as a vapor or as a solid, reacts at room temperatures with the vapors of the alkali metals in a highly luminous reaction (37,38). Iodine as a vapor or in the solid state reacts at room temperature with copper and silver to form the respective iodides. Iodine as a vapor or in the solid state reacts with magnesium, calcium, aluminum, zinc, tin, nickel, and iron, forming the corresponding iodides. It does not react with lead, bismuth, or gold (39). Platinum is not attacked at ordinary temperatures, but reacts readily at 1400°C, forming PtI and PtI_2. Tungsten is attacked by iodine at ordinary temperatures, forming the iodide, but is not attacked at high temperatures, where even atomic iodine has no effect. Iodine reacts with tantalum and niobium at 1300–1500°C (40), where the corresponding pentaiodides are formed. Iodine and vanadium react to form VI_5, which on heating decomposes to V_2I_3, which does not decompose on further heating.

Moist iodine vapor rapidly corrodes metals, including most stainless steels. The initial process is the formation of corrosion centers where small amounts of metal iodide are formed which deliquesce, and the corrosion then takes place electrochemically (41,42). Only titanium and molybdenum steels are unattacked by iodine (42,43). The corrosion of molten iodine has also been studied.

Under high pressures and temperatures, iodine reacts with oxygen to form iodine pentoxide [12029-98-0] (44). The reaction of iodine with carbon monoxide under acidic conditions is catalyzed by palladium salts (45). Phosphorous vapor and iodine react to form phosphorus triiodide [13455-01-1], PI_3 (46).

Iodine dissolves without reaction in concentrated sulfuric acid and with concentrated nitric acid it reacts to form iodine pentoxide (47). Iodine reacts with alkali metal hydroxide solutions to form the corresponding hypoiodite and the rate of the reaction increases with the alkali concentration and temperature. At 50°C, the reaction is almost instantaneous:

$$\mathrm{NaOH + I_2 \longrightarrow NaI + NaIO + H_2O}$$

Subsequently, the hypoiodite is oxidized to iodate, and this reaction is not influenced by the alkali concentration, temperature, or iodate concentration.

Iodine reacts with hydrocarbons to form iodine compounds, but compared to the other halogens, the equilibria are unfavorable because the displacement step with the iodine atom is endothermic, requiring 4066.3 J (971.9 cal) for methane and 799.9 J (191.2 cal) for toluene. Hydrogen iodide can be used to reduce an alkali iodide to hydrocarbon plus molecular iodine.

Complete iodination of organic compounds can be achieved by preventing the formation of free hydrogen iodide through the addition of an oxidizing agent, neutralization of the HI with a base, or combination using mercuric salts.

Iodine adds to carbon–carbon double bonds to form polyiodine derivatives. These addition reactions are reversible, however, and do not go to completion.

Reactions in Aqueous Media. The chemistry of aqueous iodine has been extensively studied because of the role of iodine as a disinfectant (see DISINFECTANTS AND ANTISEPTICS). The system is very complex, owing to the number of oxidation states available to iodine under ambient conditions (48).

Aqueous solutions of iodine are hydrolyzed according to

$$\mathrm{I_2 + H_2O \longrightarrow HIO + I^- + H^+}$$

The equilibrium constant of this reaction is 5.4×10^{-13} at 25°C, ie, iodine hydrolyzes to a much smaller extent than do the other halogens (49). The species concentrations are highly pH dependent: at $\mathrm{pH} = 5$, about 99% is present as elemental I_2; at $\mathrm{pH} = 7$, the I_2 and HIO species are present in almost equal concentrations; and at $\mathrm{pH} = 8$, only 12% is present as I_2 and 88% as HIO. The dissociation constant for HIO is ca 2.3×10^{-11} and the pH has little effect on the IO^- ion formation. At higher pH values, the HIO converts to iodate ion. This latter species has been shown to possess no disinfection activity. An aqueous solution containing iodate, iodide, and a free iodine or triodide ion has a pH of about 7. A thorough discussion of the kinetics of iodine hydrolysis is available (49).

Iodine is a mild oxidizing agent in acidic solutions, having an equilibrium potential of the iodine–iodide ion couple of −0.5345 V at 25°C (50,51). Iodine readily oxidizes sulfur dioxide to sulfate, thiosulfate to tetrathionate, and stannous and titanous salts to stannic and titanic salts. On the other hand, ferric and cupric salts, and salts of vanadium, chromium, and manganese in the respective highest oxidation states, oxidize iodide ion in acid solution, liberating free iodine.

Oxidizing agents such as chlorine, bromine, nitrous acid, and hot nitric acid liberate iodine from iodide solutions (52).

Iodine can be oxidized to iodate in acid solutions by concentrated nitric acid and, in more dilute solutions, by permanganate, bromates, chlorates, and even chlorine and bromine.

$$I_2 + 5\,Cl_2 + 6\,H_2O \longrightarrow 2\,HIO_3 + 10\,HCl$$

However, in strong hydrochloric acid, these reagents, as well as iodic acid, oxidize iodine to iodine monochloride or to the ICl_2 ion.

$$2\,I_2 + HIO_3 + 5\,HCl \longrightarrow 5\,ICl + 3\,H_2O$$

In alkaline solutions, iodine can be oxidized to iodate by sodium hypochlorite or hypobromite, whereas chlorine passed into a solution of iodine and alkali oxidizes all the way to periodate.

$$I_2 + 2\,OH^- \longrightarrow I^- + IO^- + H_2O$$

Hydroiodic acid reacts quantitatively with iodic acid to give iodine:

$$5\,HI + HIO_3 \longrightarrow 3\,I_2 + 3\,HO$$

The kinetics of this reaction, the conditions under which it goes to completion, and subsequent titration of the iodine with thiosulfate solutions have all been investigated (53–55).

Small concentrations of HI reduce concentrated sulfuric acid to sulfurous acid; high concentrations of HI reduce it to hydrogen sulfide (56).

4. Manufacture and Processing

The industry related to the iodine production began a few years after the discovery of the element by Courtois in 1811. The production processes are basically related to the raw materials containing iodine: seaweeds, mineral deposits, and oil-well or natural-gas brines.

Seaweeds. Although seaweeds are scarcely used nowadays, the earliest successful manufacture of iodine started in 1817 using certain varieties of seaweeds. The seaweed was dried and burned, and the ash was lixiviated to obtain iodine and potassium and sodium salts. The first process used was known as the kelp, or native, process. The name *kelp*, initially applied to the ash of the seaweed, has been extended to include the seaweed itself. About 20 tons of fresh seaweed was used to produce 5 tons of air-dried product containing a mean of 0.38% iodine in the form of iodides of alkali metals. The ash obtained after burning the dried seaweed contains about 1.5% of iodine, by weight. Chemical separation of the iodine was performed by lixiviation of the burned kelp, followed by solid–liquid separation and water evaporation. After separating sodium and potassium chloride, and sodium carbonate, the mother liquor, containing iodine as iodide was treated with sulfuric acid and manganese dioxide to oxidize the iodide to free iodine, which was sublimed and condensed in earthenware pipes (57).

Mineral Deposits. The only iodine obtained from minerals has been a by-product of the processing of nitrate ores in Chile. “Caliche” is the name for the nitrate deposits occuring in the Atacama desert of northern Chile and west of the Andes mountains. The Atacama Desert is known as the driest of the world’s deserts, where measurable rainfalls ($\geq$1 mm or more) may be as infrequent as once every 5–29 years (10). Associated with the caliche deposits, with an area averaging 700 km in an east–west) direction, it can be estimated, that the iodine may total over 5 million tons (58).

The first iodine recovery from caliche was opened in 1852, but the first iodine was exported to Europe in 1868, becoming the most important by-product of the nitrate production in terms of value. Presently there are two ways for producing iodine from caliche iodates: (*1* from solutions containing more equivalent iodine than its solubility as elemental iodine in the same solution ($\sim$0.4 g/L at 25°C) and *2* from more diluted equivalent iodine solutions.

First Alternative. The mother liquor from the sodium nitrate crystallization plant, containing normally about 1.5 1.5 g/L iodine as iodate, is decanted for clarification and concentration homogenization (see Figure 1). From there the solution is split. The larger fraction is fed into an absorption tower, where it is contacted with SO_2 obtained by sulfur combustion. In the absorption tower iodate is reduced to iodide according to the following reaction:

$$IO_3^- + 3\,SO_2 + 3\,H_2O \longrightarrow I^- + 3\,SO_4^{2-} + 6\,H^+$$

After leaving the absorption tower, the resulting iodide solution—together with the iodide solution coming from the kerosene extraction plant, as described below—is contacted with the smaller iodate fraction in the stoichometric proportion of 5 mol of iodide to 1 mol of iodate,producing iodine:

$$IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + 3\,H_2O$$

Up to 0.4 g/L of the iodine stays in solution, and the rest precipitates as crystallized iodine, which is removed by flotation. From the flotation cell a heavy pulp is obtained, which is water-washed and submitted to a second flotation step. The washed pulp is introduced into a heat exchanger where it is heated under pressure up to 120°C to melt the iodine that flows into a settling tank for decantation.

From there the melt flows into a second reactor forsulfuric acid drying. The refined iodine is either flaked or prilled, and packed in plastic-lined fiber drums. The solution leaving the flotation cell, containing about 0.4 g/L iodine, is sent to a kerosene solvent extraction process to recover the dissolved product; after neutralization with soda ash to the initial incoming alkalinity, the solution is returned to the nitrate lixiviation process. The iodine-charged kerosene is contacted with an acidic concentrated iodide solution containing SO_2, which reduces the iodine to iodide.

Second Alternative. The treatment of a diluted iodate solution does not require a flotation step, since all the iodine will stay in solution (see Figure 2). Therefore only the kerosene extraction unit is used, and the final product of this plant is a concentrated iodide solution, which is used to react with the iodate mother-liquor stream of the plants operating with concentrated iodate solutions.

Diluted iodate solutions are obtained not only from the tail leaching of the ore for nitrate recovery but also from special processes designed to obtain only concentrated iodide solution. These processes obtain their solutions by heap leaching of old waste dumps and low-grade nitrate caliche, such as blasted overburden, left over by former nitrate producers.

Until 1990, some flaked iodine and iodine containing wastes were sublimed to obtain an especially high-grade product. This process was dropped from the current industrial processes in view of the quality improvements reached in present operations. Sublimed iodine is produced only in small quantities by specialized companies that offer this product for special minor applications requiring the highest purity.

4.1. Subsurface Brines. About 50% of the iodine currently consumed in the world comes from brines processed in Japan, the United States, and the former Soviet Union (see CHEMICALS FROM BRINE). The predominant production process for iodine from brines is the blow-out process, which was first used in Japan. Iodine is present in subsurface brines as sodium and/or potassium iodide, and its concentration varies from about 10 to 150 ppm. The recovery process can be divided into brine cleanup, iodide oxidation to iodine followed by air blowing out and recovery, and iodine finishing. (see figure 3)

The brine cleanup consists of skimming and settling steps to free the solution from oil, clays, and other impurities. Sulfuric acid is then added until a pH of <2.5 is reached. This is to ensure iodine liberation by oxidation, by precipitation of the soluble barium contained in the brine.

The clarified and acidified brine is treated with gaseous chlorine, which is injected into the solution in a small excess over the theoretical stoichometric relation of 0.28 kg of chlorine per kilogram of iodide. The oxidation occurs according to the following reaction:

$$2\ \mathrm{I}^- + \mathrm{Cl}_2 \longrightarrow \mathrm{I}_2 + 2\ \mathrm{Cl}^-$$

The I_2 formed stays in solution, exerting a certain vapor pressure and is extracted from the brine in a countercurrent air blowout process. The extracted brine leaves the extraction tower and is discarded or reinjected into the wells to avoid sinking of the soil. The iodine-loaded air is then submitted to a cocurrent desorption process by means of an acidic iodide solution to which SO_2 is added. By this solution the iodine is reduced to iodide by the following reaction:

$$\mathrm{I}_2 + \mathrm{SO}_2 + 2\ \mathrm{H}_2\mathrm{O} \longrightarrow 2\ \mathrm{HI} + \mathrm{H}_2\mathrm{SO}_4$$

Part of the solution, which is continuously recirculated, is bled off and sent to the iodine finishing process. Iodine finishing consists of contacting this bleed of concentrated acidic iodide solution with gaseous chlorine, through which iodine is formed by oxidation and precipitated. After iodine precipitation, the resulting acidic mother liquor, saturated with free iodine, is pumped back to acidify the clarified brine and to rest iodine.

The crystallized iodine is decanted and transferred into a fusion kettle. The melted product is contacted with strong sulfuric acid to remove organic impurities and humidity. Finally the iodine is flaked or prilled and packed.

For brines having very low iodide concentrations, in some facilities in Japan and in the former Soviet Union, the activated carbon method of recovery is used. This method consists in treating the acidified brine with sodium nitrite in large tanks, where the following reaction takes place:

$$NaI + H_2SO_4 + NaNO_2 \longrightarrow 1/2\ I_2 + Na_2SO_4 + NO + H_2O$$

The free iodine, which stays in solution, is recovered by adsorption on activated carbon., and then the iodine is extracted from the activated carbon with hot caustic soda. The product obtained is an iodate–iodide solution, according to the following reaction:

$$6\ I_2 + 6\ NaOH \longrightarrow 5\ NaI + NaIO_3 + 3\ H_2O$$

This solution is treated with H_2SO_4 and $K_2Cr_2O_7$, precipitating the iodine crystals and filtering them out, and pressing the cake for removing impregnation. The rest of the process consists in subliming directly the cake, or in submitting it to melting and flaking.

The newest process uses ion-exchange resins on brines already oxidized to liberate iodine. The liberated iodine in the form of polyiodide is adsorbed on Amberlite IRA-400, an anion-exchange resin (Amberlite IRA-400). When the ion-exchange resin is saturated, it is discharged from the bottom of the column and then transferred to the elution column. Iodine is eluted (or desorbed) using caustic solution followed by sodium chloride. The regenerated resin is returned to the adsorption column. The elutriant, rich in iodide and iodate ions, is acidified and oxidized to precipitate iodine. The crude iodine is then separated in a centrifuge and purified with hot sulfuric acid or refined by sublimation. Although a patent for this process has been granted in the United States in 1939 (57); the first plants to use this process were located in Japan and went on-stream during 1963–1966. In 1991, two plants in Japan produced iodine by the ion-exchange process: Nihon Tennen Gas Kogio Co. Ltd. (NITTEN) and Kanto Natural Gas Co. (59).

5. Economic Aspects

Iodine haas traditionally seen boom and bust cycles. Tight supply sent prices up, reaching peaks of \$18 kg in 1988 and \$20 kg in early 1998. Price increase of the end of 1980s encouraged fast expansion of the capabilities of iodine-producing companies. Whereas the Chilean producers expanded via the caliche ore extracting route, Japanese companies made investments in the U.S. brine-based iodine production. Consequently, iodine prices fell from a\$19/kg level at the beginning of 1990 60 to a level of \$12/kg range by the end of the same year, reaching a level of \$9.50/kg in 1992. This situation is supposed to put margin pressure on some higher-cost brine-based producers, possibly forcing them to curtail production. A sustained increase in demand occuring since 1995 contributed to balance the market and even create tightness in the supply during 1997.

Iodine plant locations in the United States and Japan are dictated primarily by the availability of natural brines containing adequate amounts of iodine. In 1997, the United States had three iodine-producing companies: Woodward Iodine Corp., North American Brine Resources, and IoChem. In Japan there are seven iodine-producing companies: Ise, Godo, Nippo, Nitten, Kanto, Toho Gas, and Japan Energy, with over 30 plants. All these companies deliver iodine as flaked material except Ise, which also produces prilled iodine.

Plants in the United States are basically iodine producers and need to extract the solutions from deep wells (between 2000 and 3000 m) and then reinject the processed solutions because of environmental reasons and maintain the underground pressure of the exploitation area. In Japan, on the other hand, iodine is mainly a by-product of the natural-gas production, and the wells are less deep (about 1500 m). Depleted solutions are either discarded into the ocean or reinjected. Investment costs associated with deep wells are relatively high, reaching 1.7 to 2.0 million dollars in the United States and up to ca 0.7 million in Japan.

Total plant investment and maintenance costs are relatively high for a new iodine plant in the United States or in Japan because of the number of deep wells required and the corrosive nature of the iodine solutions.

For the Chilean iodine, which is associated mainly with nitrate production, plant location is adjacent to the nitrate plants, although some smaller installations are independent and are installed where high iodate containing old waste dumps or nitrate tailings are available. In 1997 in Chile there were three iodine-producing companies in operation. The most important of them, SQM, is the largest world iodine producer. Its production during 1997 was close to 6200 tons, accounting for 67% of the Chilean iodine output. Other Chilean producers were Cosayach and ACF. Like the Japanese Company Ise, SQM is also a prilled iodine producer with its own patended iodine prilling technology. By the end of 1997, the newcomer Minera Yolanda put in the market minor quantities of iodine. Their project is based mostly in nitrates, and their presence in the market is expected to be marginal.

Not considering the former Soviet Union, world production of iodine was about 17.500 tons in 1997. Chile became the largest producer with 53% of the world total, Japan provided about 38% and the United States provided 9%. The U.S. Geological Survey estimated production in 1996 in the former Soviet Union countries as 300 tons in Azerbaijan, 255 tons in Turkmenistan, and 150 tons in Russia. In 1997 these quantities should be lower because of adverse conditions of the production facilities. China produced approximately 200 tons as coproduct in the production of sodium alginate from seaweed, and Indonesia produced around 100 tons from brines.

6. Grade Specifications and Standards, and Shipping

Commercial iodine has a minimum purity of 99.8%. The Committee of Analytical reagents of the American Chemical Society (61) and the *U.S. Pharmacopoeia*

XXII (68) specify an iodine content not less than 99.8%, a maximum nonvolatile residue of 0.01%, and chlorine–bromine (expressed as chlorine) concentration of 0.005% [American Chemical Society (ACS)] and 0.028% (USP), respectively. In the past these requirements were attained basically only by sublimation, whereas nowdays these specifications can be met by direct-production iodine. Although the impurities of the Chilean product were chiefly water, sulfuric acid, and insoluble materials some years ago, improvements in the production process especially in the refining step, allow the direct obtainment of ACS-type iodine. Also, because of its origin and production process, the Chilean iodine has a chlorine–bromine impurity level of no more than 0.002%. For these reasons the main world producers seldom offer sublimed iodine.

Iodine is packed in fiber drums lined with double-ply polyethylene containing 10, 25, and 50 kg. There are no specific transportation, shipping, or safety requirements. As low temperatures reduce vapor presaure and therefore decrease the rate of loss, a cool, well-ventilated storage area is recommended. There is no specific freight classification; iodine is shipped as “chemicals”, and special labels are subject to specific country regulations.

7. Analytical Methods

Most analytical methods use the oxidizing power of iodine for its determination. The results are generally expressed as an equivalent concentration of elemental iodine. The choice of a method for the analysis of iodine depends on the concentration range to be determined.

Thiosulfate titration of iodine is limited to a concentration of 7.5 μg/mL (63). The use of organic solvents such as benzene, toluene, chloroform, and carbon tetrachloride as indicators in the titration of iodine have also been proposed. These procedures increase the sensitivity of the titration so that 6.0 μg/mL of iodine can be detected, although a sensitivity of 2 μg/mL has been claimed (64).

Arsenious oxide, trivalent antimony (73), sulfurous acid (74), hydrogen sulfide (75), stannous ion, and thiocianate (76) have been recommended for the titration of iodine. However, none of these appears to have a greater sensitivity for the determination of minute quantities of iodine than thiosulfate.

Titration methods using adsorption indicators based on the precipitation of insoluble iodides, have also been proposed. The sensitivity of these methods is less than that for the thiosulfate titration. Electrometric titration of the reaction between iodine and thiosulfate was not found practicable for routine determinations of minute quantities of iodine.

In view of the chromophoric character of the elemental iodine itself, many colorimetric methods have been proposed for the determination of inorganic iodine. These methods use the visible portion of the spectrum in reading iodine concentrations. In the visible range the extinction coefficient for iodine is not high enough for use with minute quantities of iodine in water and other solvents.

Methods for iodine determination in foods using colorimetry, ion-selective electrodes, microscale acid digestion methods, and gas chromatography, suffer some limitations such as potential interferences, possibility of contamination, and loss during analysis. More recently neutron activation analysis, which is probably the most sensitive analytical technique for determining iodine, has also been used (65,66).

Iodide ion, a moderately effective reducing agent, is used extensively for the determination of oxidants. In such applications, the iodine liberated by reaction between the analyte and the unmeasured excess of potassium iodide is ordinarily titrated with a standard solution of sodium thiosulfate 67. The reaction is between Inodine and thiosulfate ion is described by the following reaction:

$$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$$

The quantitative conversion of thiosulfate to tetrathionate is unique with iodine; other oxidant agents tend to carry the oxidation further to sulfate ion or to a mixture of tetrathionate and sulfate ions. Thiosulfate titration of iodine is best performed in neutral or slightly acidic solutions. If strongly acidic solutions must be titrated, air oxidation of the excess of iodide must be prevented by blanketing the solution with an inert gas, such as carbon dioxide or nitrogen.

8. Health and Safety Factors

Iodine is much safer to handle at ordinary temperatures than the other halogens, because it is a solid and its vapor pressure is only 1 kPa (7.5 mm Hg) at 25°C, compared to 28.7 kPa (215 mm Hg) for bromine and 700 kPa (6.91 atm) for chlorine. When handling properly packed containers, usual work clothes are sufficient. In the handling of solid, unpacked iodine, rubber gloves, rubber apron, and safety goggles are recommended. Respirators or masks are also recommended.

The maximum safe concentration for short-term exposure of up to 1 h is 1.0 ppm. Exposure of the lungs and eyes can be irritating at concentrations of 0.1 ppm and should be avoided. Exposure in concentrations higher than 0.1 ppm for extended periods causes severe irritation to the eyes and respiratory track, and may lead to pulmonary edema. The mean lethal dose for an adult is 2–4 g. Prolonged contact with skin may also be harmful and may cause burns.

The U.S. Occupational Safety and Health Administration (OSHA) has set for iodine a ceiling level of 0.1 ppm in air. The American Conference of Governmental Industrial Hygienists (ACGIH) established 0.1 ppm as the threshold limit value TLV [Time-weighted Average (TWA)] for iodine. The MAK value is also 0.1 ppm. (68–70).

Empty containers may be destroyed in an incinerator or decontaminated by washing with a dilute thiosulfate or sulfite solution. Bulk wastes should be treated by controlled iodine recovery processes.

Emergency treatment includes irritating the eyes with water or washing the contaminated body area with a 5% thiosulfate solution followed by saline catharsis. If swallowed, gastric lavage with 5% solution of thiosulfate, followed by saline catharis, should be accomplished, and medical attention should be provided. If pulmonary signs are severe, oxygen should be supplied with intermittent positive-pressure breathing apparatus.

Chronic absorption of iodine causes *iodism* characterized by insomnia, inflammation of the eyes and nose, bronchitis, tremor, diarrhea, and weight loss.

Iodine is not combustible itself, but can react very vigorously with reducing materials. It is incompatible with acetaldehyde, C_2H_2, Al, NH_3, NH_4, OH, Sb, BrF_5, $CsHC_2$, CsC_2, Cs_2O, CuC_2, ethanol, HgO, O_2, Li, LiC_2, Li_6C, Mg, F_2O, K, $RbHC_2$, Rb_2C_2, AgN_3, NaH, ZrC, SO_3, formamide, pyridine, P, ethanol and butadiene, and ethanol plus methanol and HgO.

9. Environmental Concerns

Pure *iodine* sublimates when heated and toxic fumes are released: thus iodine must be stored in sealed containers, away from heat and sunlight. In case of large spillage of material, use of an aqueous sodium thiosulfate solution or dry sodium carbonate is recommended to neutralize spilled iodine.

Most common iodine derivatives are not harmful to the environment, and they are quickly degraded into basic elements. As reference, inorganic iodides and iodates of calcium and potassium, which represent the main iodine use worldwide, are ingested by human beings and animals, as additives in edible salt and components in pharmaceuticals, for the prevention and treatment of different diseases.

Some processes for the production of chemical intermediates containing iodine produce waste streams that are recycled for both environmental and economic purposes. Recycling normally burns the impurities that should not be discharged into the environment and recovers the iodine in its elemental form or as a derivative.

10. Uses

The principal iodine consuming countries are the United States, Japan, France, the United Kingdom, Germany, and Italy. Together, these countries account over 70% of the world total iodine consumption, which is estimated to be approximately 17,500 tons/yr. Iodine is used in animal feed supplements, batteries, catalysts, colorants, fuels, inks, disinfectants for health and industrial use, iodized salt, lubricants, pharmaceuticals, photographic processes, and contrast media; in the production of high-purity metals; and in stabilizers. Iodine has a wide range of uses in chemical and related industries. There are some difficulties in compiling accurately the proportion of iodine consumption in the different areas because a high percentage of the initial use of iodine lies in the production of intermediates, which are frequently marketed as such before reaching their ultimate end use. However, the best information available from the market suggests a breakdown of world iodine consumption, as follows:

Iodine consumption	%
Catalysts	8
Stabilizers	6
X-rays contrast media	20
Sanitizers and disinfectants	17
Pharmaceuticals	8
Animal and fowl feeds	10
Photography	6
Herbicides	6
Ink, colorant and dyes	4
Other uses	15

The main specific uses of iodine are summarized below.

10.1. Industrial Uses. *Catalysts.* Iodine and its compounds are very active catalysts for many reactions (18,19), especially in the production of synthetic rubber via Ziegler–Natta catalyst systems. Iodine and certain iodides, for example, titanium tetraiodide [7720-83-4], are also employed for producing stereospecific polymers, such as polybutadiene rubber; about 75% of the iodine consumed in catalysts is assumed to be used for polybutadiene and polyisoprene polymerization (72) (see RUBBER CHEMICALS). The principal use of iodine compounds in the United States was reported by the U.S. Bureau of Mines to be in the production of polybutadiene and polyisoprene synthetic rubber via Ziegler–Natta catalyst systems.

Iodine catalysts are used in the production of synthetic rubbers for vehicle tire manufacture. The production of synthetic rubbers tends to be concentrated in the industrialized countries of North America, western Europe, and Japan.

Iodine catalyzes the conversion of amorphous selenium to the black, semiconducting “metallic” modification, and is used for this purpose in the manufacture of photoelectric cells and electric rectifiers (see SELENIUM AND SELENIUM COMPOUNDS).

Stabilizers. Potassium iodide is used as heat stabilizer in the manufacture of nylon and for converting rosins, tall oil, and other wood products to more stable forms. Nylon stabilization is necessary during polymerization as weak sites are formed that lead to chemical deterioration. The consumption of iodine in stabilizers is largely accounted for by the heat stabilization of nylon, which is used in tire-cord manufacture for several types of vehicle. Nylon suitable for tire cord must be of very high strength. Tire cord for trucks and off-road tires are the largest end use for this type of nylon.

In this tire-cord application, iodine is involved with copper acetate or borate and potassium iodide. During the process copper (II) is reduced to copper (I) and the potassium iodide is added to regenerate de copper (II) in order to regenerate the process.

Nylon stabilization is the second largest market for iodine compounds after rubber catalyst. This application accounts for ca 2250 tons/yr of iodine worldwide.

Iodine is used to stabilize tall oil for use in various tall-oil fatty acids and tall-oil rosins that compete with several types of oil used in polymers. When heated with small amounts of iodine, rosins, tall oil, and other wood products are converted to more stable forms. Iodine has been used with some tin salts as a catalyst in the hydrogenation of coal and its distillation products (73,74), and has been recommended as a catalyst for the production of drying oils from unsaturated animal fats (75,76).

Photography. The use of iodine in photographic uses, including photographic films and X-ray films, is an important application for iodine and its derivatives, and is expected to be one area for potential growth in the future. Silver iodide was the first silver halide to be used in photography, although this use has been superseded by silver bromide, which has a higher sensibility. Nevertheless, when silver iodide is incorporated into silver bromide, it provides a considerable increase in light sensitivity, compared with unaltered silver bromide. Triphenylphosfonium iodide is also among the iodine derivatives used in photography. This derivative permits faster development and higher contrast photography.

X-Ray Contrast Media. X-ray contrast media (CM) have been used since the first discovery of X-rays by Roentgen in 1895. The function of such media is to opacify an organ or portion of the body to X rays, providing greater diagnostic information to the physician. Many opaque atoms have been studied in many chemical forms; for example, bismuth, barium, tantalum, strontium, and bromine have all been used in a variety of compounds. Although many water-soluble compounds have been evaluated, by 1980 only two atoms—iodine and bromine—were found to be of significant diagnostic use.

Historically, iodinated CM have evolved from water-insoluble, highly toxic substances into water-soluble, reasonably safe compounds. Safety became increasing important as the radiologist recognized that higher and higher doses led to better diagnostic information. Salts of 3-amino-2,4,6-triodobenzoic acid derivatives were found most useful and versatile in most applications (77). The main requirements for diagnostically useful radiocontrast medium are high water solubility at high iodine concentrations, low viscosity, and low osmolality as close as possible to those of body fluids. Water solubility of ionic CM arises from a salt formation with an appropriate cation, generally sodium or *N*-methylglucamine, which can give highly concentrate solutions of up to 40%–50% w/v iodine.

The iodine content and viscosity of a formulation must suit the clinical use. Thus, intravenous urographic agents are formulated to contain between 28 and 40% iodine (280–400 mg/ml) and are administered in doses of 50–150 mL. For angiographic use, solutions of up to 37% iodine (370 mg/mL) are required.

The use of iodine in X-ray uses, including films and contrast media is currently a large application for iodine and its derivatives worldwide, and is also expected to be the principal area for future growth.

Dyes, Inks, and Colorants. Iodine is contained in a number of dyestuffs and is also used in the synthesis of intermediates. Red 3 dye [16423-68-0] contains 58% (w/w) iodine and is on the US Drug and Administration list of permitted color additives for food. Some other dyes containing iodine include 4′,5′-diiodoflourescein [38577-97-8], rose bengal [11121-48-5] and erythrosin [15905-32-5] (see XANTENE DYES), and members of the cyanine group (see CYANINE DYES). Erythrosine (disodium salt of 9-*o*-carboxiphenyl-6-hydroxy-2′,4′, 5′,7′-tertraiodo-3′-

isoxanthrone) is an orthochromatic sensitizer for photographic emulsions and also a certified food colorant (see COLORANTS FOR FOODS, DRUGS, COSMETICS, AND MEDICAL DEVICES). Iodine consumption in erythrosine may be estimated to be about 750 tons/yr (20). Dyes are not expected to show any major growth in the future.

10.2. Animal Feeds.

Iodine is required for the synthesis of the hormone thyroxine by the thyroid gland, the lack of which results in the condition known as *goiter*. To ensure this supply, iodine is added to salt for human consumption and to animal foodstuffs. To prevent the disease, a supplement of iodine is introduced either in the form of iodized salt or as an iodized salt additive to a feed concentrate mixture. Iodine deficiency during pregnancy and lactation increases birth of weak or dead offspring in cows, pigs, horses, and goats.

As an animal feed additives, iodized proteins in fowl and cattle feeds increase egg or milk yields, and iodine prevents foot rot in cattle. Iodine deficiency can result in weak or stillborn offspring and hairless pigs. In the United States the iodine is added to proteins in one of the following forms: potassium iodide, calcium iodate [7789-80-2], ethylene dihydroiodate (EDDI) [5700-49-2], or ethanediamine dihydroiodide. In the United Kingdom it is added as potassium iodide, calcium iodide or potassium iodate. The amount of added iodine varies from country to country, species to species, and breed to breed. Consumption of iodine in animal feeds in the United States was estimated by the U.S. Bureau of Mines to be over 500 tons/yr.

World consumption of iodine in animal foodstuffs has been estimated to between 8% (78) and 13% (79), the majority of which is used in the United States and western Europe.

10.3. Health and Sanitary Uses.

Iodine and iodine compounds are extensively used in health and sanitary applications, including sanitizers, cleaning products, water treatment chemicals, disinfectants, pharmaceuticals, X-ray contrast media, radiation protection, and medical research.

Sanitizers and Disinfectants. Iodine is extensively used in a variety of forms as both antiseptic and disinfectant. Iodophors, which are usually nonionic surfactants complexed with iodine, were developed in response to the need for more readily usable iodine-based antiseptics and disinfectants. They are used as disinfectants in dairies, laboratories, and food-processing plants, and for sanitation of dishes in restaurants. The reaction product of lanolin and iodine shows usefulness as a germicide (80).

Iodophors consist of elemental iodine in loose combination with surface-active agents (surfactants) that must be both highly water-soluble and also capable of varying large weights of iodine in solution in water without precipitation. Typical examples of suitable surfactants include nonylphenol polyethylene glycol ether, which can form a loose chemical combination with up to 20% by weight in iodine. Iodophors are used for a variety of combined detergent and antiseptic applications. The most common use is as germicidal agent in the form of a tincture of iodine, which is a solution of iodine in alcohol.

A poly(vinyl pyrrolidinone)–iodine complex [25655-41-8] (PVP–iodine) has been used extensively in hospitals and elsewhere because of its germicidal, bactericidal, fungicidal, and generally disinfecting properties (81). It is sold as a solution that contains about 10% available, or active, iodine and about 5% inactive iodine, in the form of iodide ion (see DISINFECTANTS AND ANTISEPTICS; INDUSTRIAL ANTIMICROBIAL AGENTS).

Pharmaceuticals. Iodine and iodine compounds and preparations are employed extensively in medicine, such as in antiseptics, drugs administrated in different combinations in the prophylaxis and treatment of certain diseases, and therapeutic agents in various thyroid dyscarsias and other abnormalities (see RADIOPHARMACEUTICALS). The principal active ingredients containing iodine have been classified as antiseptic, antispasmodic, coronary vasodilator, diagnostic, endocrinology, neuromuscular blocking agent, gastroenterology, metabolism and nutrition, neurology–psychiatry, ophthalmology, parasitology, pneumology, and rheumatology (82).

Protection from Radioactive Iodine. Iodine is absorbed by the human body and concentrated in the thyroid gland. To prevent radioactive iodides from lodging in the thyroid gland during exposure to radioactive iodine (^{131}I), which is released during nuclear accidents, a dose of potassium iodide administered before or shortly after exposure to radioactive iodine can limit the harmful effects of radiation by replenishing the thyroid with iodine and blocking the absorption of the radioactive iodine (72).

Water purification. Iodine effectively disinfects water against bacteria, viruses, and cysts. Globaline tablets were developed for the disinfection of small or individual water supplies in the U.S. Army during World War II. Studies of the disinfection of public water supplies with iodine were initiated in 1963 (83). These studies showed that concentrations of up to 5 ppm of iodine were not deleterious to health and that 1 ppm was sufficient to safely disinfect a water supply at the high pH values encountered in many treated supplies, with virtually no loss of effectiveness because of iodate buildup. Administration of approximately 2 mg of iodide in a single dosage induces the Wolff–Chaikoff effect (84): the inhibitory effect of iodine on hormone formation by the thyroid. Commercially available iodinators control potentially dangerous organisms by passing a side stream of water through a bed of prilled iodine to provide 0.5 ppm of iodine in a water supply.

Iodine may also be used as an effective microbicide for swimming pools (83, 85,86). It acts like free chlorine and is superior to chloroamines in bacterial, virucidal, and cysticidal efficiency (see also WATER, TREATMENT OF SWIMMING POOLS, SPAS, AND HOT TUBS). In addition, iodine shows decreased reactivity with organic matter, less variation in microbicidal efficiency over the typical pH range observed in pools, and potential for regeneration of free iodine through application of a suitable oxidant (eg, chlorine, ozone, or potassium monopersulfate). Other advantages of iodine over chlorine are its longer life, lack of odor, no bleaching action, and minimal eye irritation. Unfortunately, dependable control of algae proliferation in well-illuminated swimming pools has not been accomplished with iodine alone. Controlled field experiments have shown that compounds such as prometryne and terbutryne are effective algaecides compatible (nonreactive) with free iodine as microbicide (87). Chlorine can be used in combination with iodine as means of controlling algae and to reoxidize residual iodide to free iodine.

Radioactive isotopes. The basis of the utility of iodine radioactive isotopes is due to their constituent radionuclides that emit β- or γ-radiation (72).

Radioactive iodine has been used successfully for the treatment of cancer of the thyroid. Patients have remained apparently cancer-free for as long as 13 years following surgery. Iodine-131 is the most widely available and used isotope for the diagnosis and therapy of thyroid disorders. Iodine-125 has been useful for the delineation of superficial lesions. Iodine-123, which is produced in a cyclotron, is considered the agent of choice for imaging and uptake measurements despite the high cost, since it minimizes the patient's radioactive exposure; its half-life is only 13 h, and it emits a 159-keV photon (57).

10.4. Agriculture Applications. The use of herbicides based on iodine compounds has its main market in western Europe and the Far East, where the consumption of iodine in herbicides is thought to be in the order of 500 to 600 tons/yr (72). In Canada in the United States these compounds are used only to a small extent. The only significant iodine containing herbicide is ioxynil (4′-hydroxy-3′, 5′-diiodo-benzoic acid). This compound, often used in combination with other herbicides, is formulated for controlling many annual broad-leaved weeds, especially black bindweed, knotgrass, mayweeds, and corn marigold post-emergence in wheat, barley, oats, rye, and triticale (82). NaH, ZrC, SO_3, formamide, pyridine, P, ethanol + butadiene, and ethanol + methanol + HgO.

11. Iodine Derivatives

11.1. Inorganic Compounds. Iodides and Iodates are the principal iodine inorganic derivatives. Some of the more important inorganic iodine intermediate and derivatives are discussed

Iodides. Iodides range from completely ionic structures like, potassium iodide, to covalent structures such as titanium tetraiodide. Commercially, iodides are the most important class of iodine compounds. In general, they are very soluble in water and some are hygroscopic. However, some iodides such as cuprous, lead, silver, and mercurous, are insoluble. Chlorine and bromine readily displace iodine from the iodides, converting them to the corresponding chlorides and bromides.

Potassium iodide [7681-11-0] (KI), MW 166.02, mp 686°C, I 76.45%, forms colorless cubic crystals, which are soluble in water, ethanol, methanol, and acetone. KI is used in animal feeds, catalysts, photographic chemicals, for sanitation, and for radiation treatment of radiation poisoning resulting from nuclear accidents. Potassium iodide is prepared by reaction of potassium hydroxide and iodine, from HI and KHCO3, or by electrolytic processes (88,89). The product is purified by crystallization from water (see also FEED AND FEED ADDITIVES, RUMINANT FEEDS; PHOTOGRAPHY).

Sodium iodide [7681-82-5], (NaI), MW 149.92, mp 662°C, I 84.66%, forms colorless cubic crystals, which are soluble in water, ethanol, methanol, and acetone. It is used in photography, for the production of organic chemicals, and as an expectorant in cough medicines. NaI is separated by addition of sodium hydroxide or sodium carbonate to an acidic iodide solution (see also EXPECTORANTS, ANTITUSSIVES, AND RELATED AGENTS).

Hydrogen iodide [10034-85-2], (HI), MW 127.93, mp −50.9°C, bp −35.1°C, I 99.21%, is a colorless, nonflammable gas that fumes in moist air. It is decomposed by light. It is unstable at room temperatures and above, slowly decomposing to hydrogen and iodine. It is extremely soluble in water, forming an azeotrope: 234 g HI in 100 g H_2O at 10 °C and 900 g HI in 100 g H_2O at 0°C. Hydrogen iodide is prepared by catalytic reaction of iodine and hydrogen; or concentrated HI solutions with P_2O_5 (90–93). Hydrogen iodide is used in the manufacture of hydroiodic acid, organic iodo compounds, and to remove the iodine from iodo compounds. Hydroiodic acid is the colorless solution formed when hydrogen iodide gas dissolves in water. It is prepared by reaction of iodine with hydrogen sulfide or hydrazine, or by an electrolytic method. Typically commercial hydroiodic acid contains 40–55% HI. Hydroiodic acid is used in the preparation of iodides and many organic indo compounds.

Iodates. Iodates are stable at room temperatures but loose oxygen on heating. Metallic iodates, although stable and safe to handle, should be kept out of contact with organic substances and other combustible materials because such mixtures are explosive. Iodates can be prepared by strong oxidation of iodine to iodic acid, followed by neutralization with an oxide or hydroxide; or by electrolytic oxidation of an iodide solution (94,95).

Potassium iodate [7758-05-6], (KIO_3, MW 214.02, I 59.30%, forms white, odorless crystals or a crystalline powder. It has a density of 3.98 and mp 560°C with partial decomposition. Potassium iodate is rapidly formed when potassium iodide is fused with potassium chlorate, bromate, or perchlorate. It solubility in water has been studied extensively: 9.16 g/100 g H_2O at 25°C and 32.2 g/100 g H_2O at 100°C. KIO_3 is used extensively as an oxidizing agent in analytical chemistry, and as a maturing agent and dough conditioner (see BAKERY PROCESSES CHEMICAL LEAVENING AGENTS).

Sodium iodate [7681-55-2], ($NaIO_3$), MW 197.90, I 64.13%, is a white crystalline powder. Its solubility in water is similar to that of potassium iodate: 9.0 g/100 g H_2O at 25°C and 34.0 g/100 g H_2O at 100°C. It is insoluble in alcohol. The existence of two hydrates in a saturated solution has been confirmed: the pentahydrate up to 19.85°C, and the monohydrate from 19.85 to 73.4°C.

Calcium iodate monohydrate $[Ca(IO_3)_2] \cdot H_2O$, MW 407.90, I 62.22%, is a solid white powder with a density of about 4.5. Calcium monohydrate is stable up to 540°C, but it is very sensitive to reducing agents. It is slightly soluble in water, insoluble in alcohol, and more soluble in aqueous solutions of iodides. It is mainly used in animals and fowl feeds.

Iodic acid [7782-68-5], (HIO_3), MW 179.93, I 72.14%, mp 110°C (dec), density 4.650, forms orthorombic crystals that darken on exposure to light. Iodic acid is not hygroscopic and is very soluble in water: 269 g/100 mL H_2O at 20°C and 295 g/100 ml H_2O at 40°C. It is soluble in nitric acid and diluted alcohol. It is insoluble in absolute alcohol, ether, and chloroform. HIO_3 decomposes to $HIO_3 \cdot I_2O_5$ at 70°C, and decomposes completely to I_2O_5 at 200°C. It is prepared by oxidation of iodine with perchloric acid, nitric acid, or hydrogen peroxide. Oxidation of iodine proceeds in aqueous suspension to iodic acid by silver nitrate. Iodic acid is also formed by anodic oxidation at a platinum electrode of iodine dissolved in hydrochloric acid (96,97).

Iodine monochloride [7790-99-0], MW 162.38, I 78.16%, is a black crystalline solid or a reddish-brown liquid. Solid ICl exists in two crystalline modifications: (*1*) α-form, stable ruby-red needles, *d* 3.86 g/cm^3 and mp 27.3°C; and (*2*) metastable brownish-red platelets, *d* 3.66 g/cm^3, mp 13.9°C and bp 100°C (dec). Iodine monochloride is used as a halogenation catalyst and as an analytical reagent (Wij's solution) to determine fats and oils iodine values (see FATS AND FATTY OILS). It is prepared by direct reaction of iodine with liquid chlorine. Aqueous solutions are obtained by treating a suspension of iodine in moderately strong hydrochloric acid with chlorine gas or iodic acid (98,99).

11.2. Organic Compounds. The organic iodine compounds have lower heats of formation and greater reactivities than do their chlorine and bromine analogues. As in the case of the inorganic iodides, their indices of refraction and specific gravities are higher than the corresponding chlorine and bromine derivatives (100).

The aliphatic iodine derivatives are usually prepared by reaction of an alcohol with hydroiodic acid or phosphorous triiodide; by reaction of iodine, an alcohol, and red phosphorous; addition of iodine monochloride, monobromide, or iodine to an olefin; or replacement reaction by heating the chlorine or bromine compound with an alkali iodide. The aromatic iodine derivatives are prepared by reacting iodine and the aromatic system with oxidizing agents such as nitric acid, fuming sulfuric acid or mercuric oxide.

Methyl iodide [74-88-4], also known as *iodomethane*, (CH_3I, MW 141.95, I 89.41%, is a colorless pungent liquid with a density of 2.279 at 20°C, a melting point of −66.1°C, and a boiling point of 42.5°C. It turns brown on exposure to light. It is poisonous. Its solubility in water is 1.4 g/100 g H_2O at 20°C. It is miscible with alcohol and ether. Methyl iodide is prepared by reaction of methanol with phosphorous and iodine; from potassium iodide and methyl sulfate or methyl *p*-toluenesulfonate; by reaction of dimethyl sulfate with an aqueous iodine slurry containing a reducing agent such as iron or sodium bisulfite; by reaction of methanol and hydrogen iodide; and by reaction of methanol, iodine, and diborane (101,102). It is used as a methylation agent in organic synthesis; in microscopy (qv) because of its high refractive index; as an embedding material for examining diatoms; and in testing for pyridine.

Methylene iodide [75-11-6), (CH_2I_2), also known as diodomethane, MW 267.87, I 94.76%, mp 6.0°C and bp 181°C, is a very heavy colorless liquid; it has a density of 3.325 at 20°C and a refractive index of 1.7538 at 4°C. It darkens on contact with air, moisture, and light. Its solubility in water is 1.42 g/100 g H_2O at 20°C; it is soluble in alcohol, chloroform, benzene, and ether. Ethylene iodide is prepared by reaction of sodium arsenite and iodoform with sodium hydroxide; action of iodine, sodium ethoxide, and hydoiodic acid on iodoform; the oxidation of iodoacetic acid with potassium persulfate; and by reaction of potassium iodide and methylene chloride. It is used for determining the density and refractive index of minerals; it is also used as a starting material in the manufacture of X-ray contrast media and other synthetic pharmaceuticals (qv).

Thymol iodide ($C_2OH_24I_2O_2$, MW 550.23, I 46.13%, is a reddish-brown or reddish-yellow bulky powder that gives off iodine vapors when heated above 100°C and on prolonged exposure to light. Readily soluble in chloroform, ether, collodion, and volatile oils. Slightly soluble in alcohol and insoluble in water, glycerol, and alkaline solutions. Thymol iodide is prepared by treating a solution of thymol in sodium hydroxide with a potassium iodide–iodine solution. Its principal use is as an antiseptic disinfectant (10–105).

Iodoform [75-47-8], (CHI_3), is also known as triodomethane, MW 393.78, I 96.69%, mp ~ 120°C and 4.008 density at 20°C. Iodoform is a yellow crystalline powder, with an unctuous touch and disagreeable odor, that decomposes at high temperatures with iodine evolution. It is only slightly soluble in water: 0.01 g/100 g H_2O at 20°C. It is soluble in chloroform, benzene, and glycerol. Iodoform is prepared by treating acetone, sodium hypochlorite, iodine, and a sodium hydroxide; by reacting chloroform and methyl iodide; and by electrolysis of an iodide solution in dilute alcohol or acetone (106). Iodoform is used as wound dressing and as a sensitizing agent in certain printing processes.

Ethyl Iodide [75-03-6], (C_2H_5I), also known as iodoethane, is a colorless liquid with a density of 1.933 at 20°C and a boiling point of 72.2°C. Because of its high density it is used in petrology as a heavy liquid for determining the density of rock and mineral fragments. In medicine it has been used for the treatment of fungous diseases of the skin. It is only slightly soluble in water, but completely soluble in alcohol and ether. Ethyl iodide is prepared by reactions similar to those used for the methyl iodide preparation (101).

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ARMIN LAUTERBACH
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SQM Chemicals

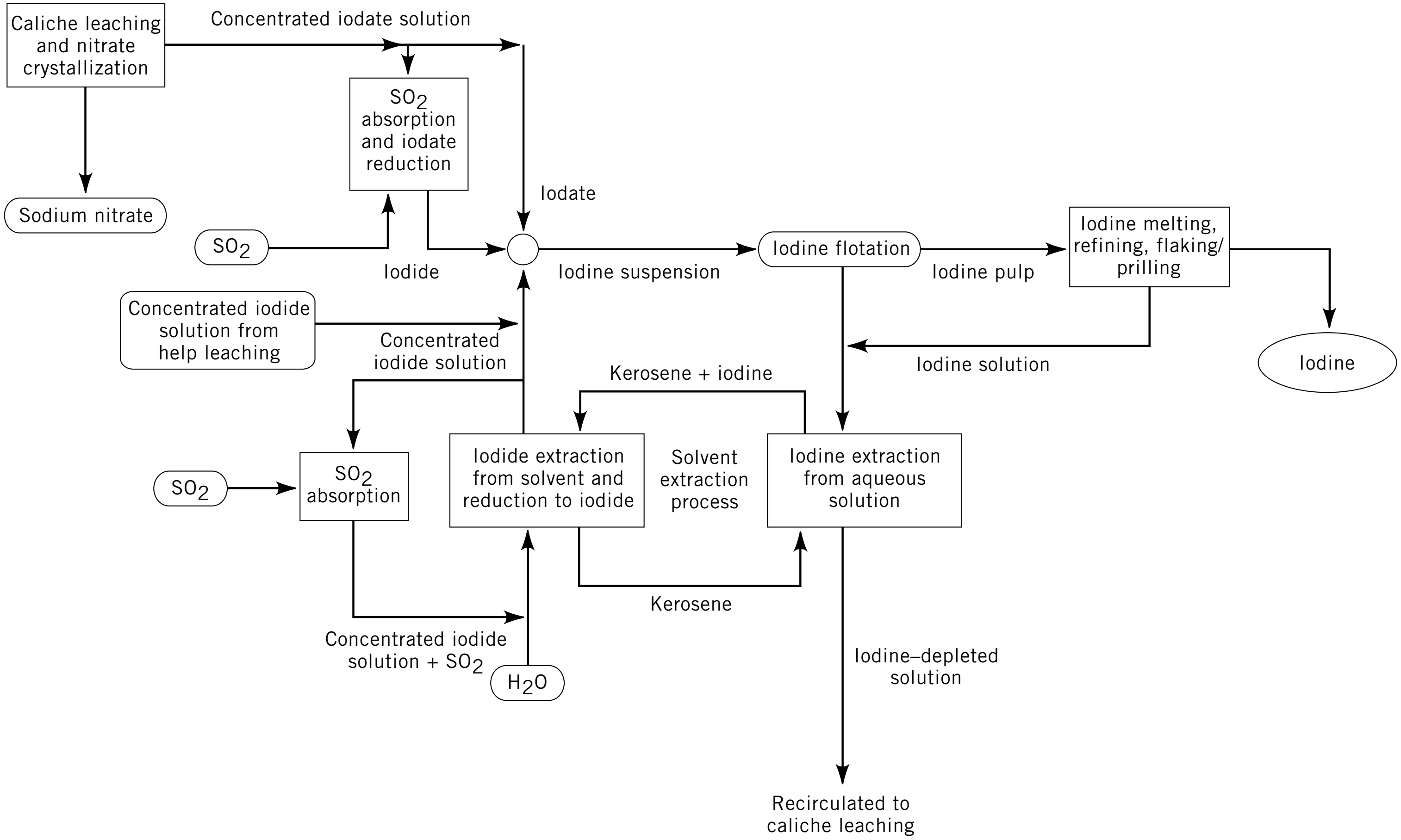

Fig. 1. SQM nitrate/iodine production process for obtaining iodine from concentrated iodate solutions.

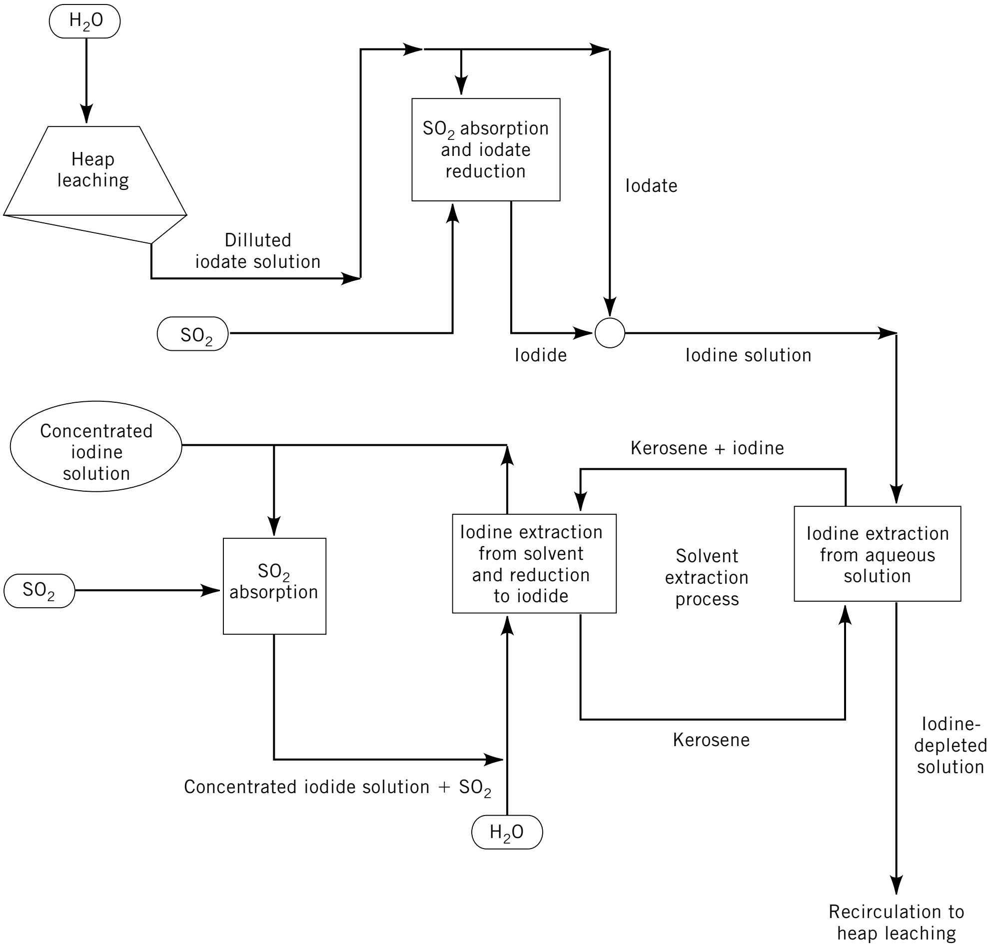

Fig. 2. SQM's heap leaching of caliche tailings for iodine recovery from diluted iodate solutions.

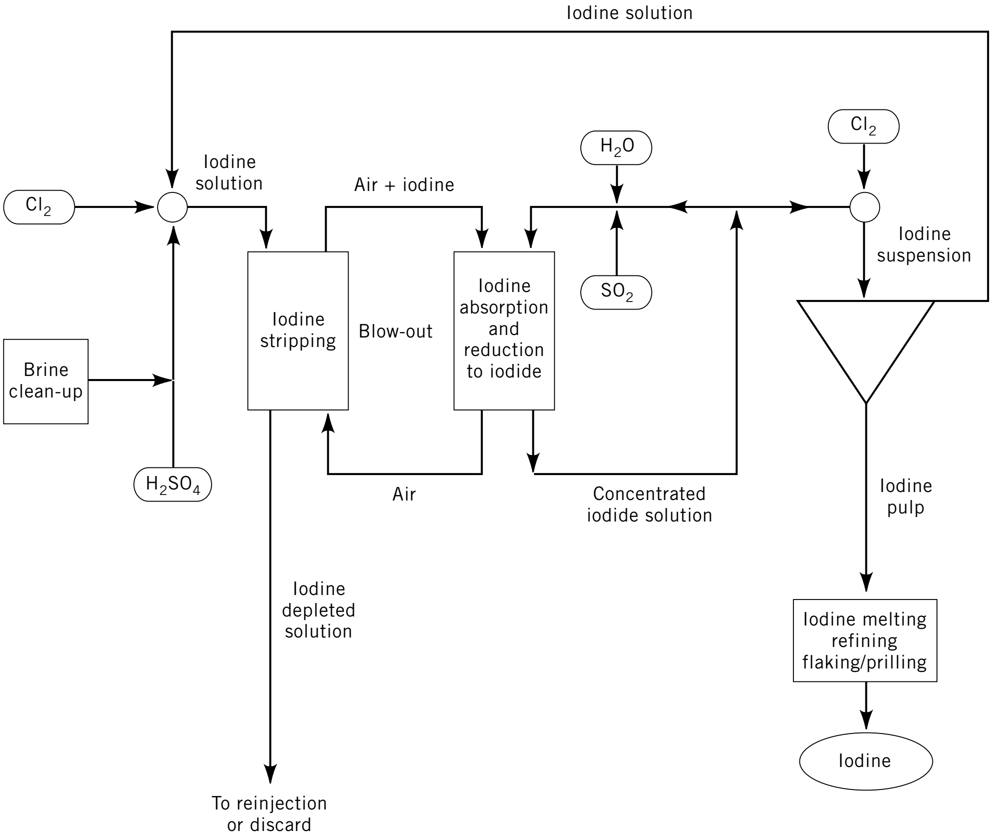

Fig. 3. Iodine production process from brines.

Table 1. **Physical Properties of Iodine**

Properties	Solid	Liquid	Gaseous
color	bluish black	bluish black	violet
melting point	113.6		
boiling point, °C		185	
critical temperature, °C		553	
critical pressure, kPa[c]		11753.7	
density, g/mL			
20°C	4.93		
60°C	4.89		
120°C		3.960	
180°C		3.736	
vapor density at 101.3 kPa,[d] g/L			6.75
cubic coefficient of expansion 0–113.6°C, $°C^{-1}$	2.81×10^{-4}		
crystal structure, 4 mol I_2 per unit cell	orthorhombic		
unit cell dimensions at 18°C, pm			
a	477.61		
b	725.01		
c	977.11		
entropy at 25°C, J/(mol · K)[e]	116.81		62.25
specific heat, J/(g · K)[e]			
25–113.6°C	$0.1582 + 1.9628 \times 10^{-4}\ T^{f}$		
113.6–184°C		0.3165	
25–1200°C			0.1465
heat of fusion at 113.6°C, J/g[e]	62.17		
heat of sublimation at 113.6°C, J/g[e]	238.40		
heat of vaporization at bp, J/g[e]		164.45	
viscosity, mPa(=cP)			
at 116°C		2.268	
at 185°C		1.414	
vapor pressure, kPa[d]			
at 25°C	0.04133[a]		
at 113.6°C	12.0655	[b]	
thermal conductivity at 24.4°C, W/(m · K)	0.4581		
electrical resistivity, Ω · cm			
at 25°C	5.85×10^{6}		
at 110°C	8.33×10^{5}		
at 140°C		1.1×10^{5}	
dielectric constant			
at 23°C	10.3		
at 118°C		11.08	
refractive index, n_D	3.34		

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[a] For the solid, between 0 and 113.6°C, $\log p_{\mathrm{kPa}} = -(3410.71/T) - 0.3523 \log T - 1.301 \times 10^{-3} T + 14.3140$ where T is in Kelvin.

[b] For the liquid, between 113.6 and 186°C, $\log p_{\mathrm{kPa}} = -(2300.24/T) + 10.025$, where T is in Kelvin.

[c] To convert kPa to atm, divide by 101.

[d] To convert kPa to mm Hg, multiply by 7.50.

[e] To convert J to cal, divide by 4.184.

[f] T is in Kelvin.

Table 2. **Solubility in Water**[a].

Temperature, °C	Solubility, g/kg	Temperature, °C	Solubility, g/kg
0	0.162	60	1.06
20	0.293	70	1.51
25	0.340	80	2.17
30	0.399	90	3.12
40	0.549	100	4.48
50	0.769	110	6.65

[a] Ref. 36.

Table 3. **Solubility in Organic Solvents**[a]

Solvent	Solubility, g/kg
benzene	164.0
carbon disulfide	197.0
carbon tetrachloride	19.2
chloroform	49.7
cyclohexane	27.9
ethyl acetate	157.0
ethyl alcohol	271.1
ethyl ether	337.3
ethylene bromide	115.1
ethylene chloride	57.6
glycerol	9.7
n-heptane	17.3
n-hexane	13.2
isobutyl alcohol	97
isooctane	13.2
tetrachloroethylene	69[b]
toluene	182.5
trichloroethylene	79[b]
p-xylene	198.3
water	0.34

[a] At 25°C. Ref. 36.

[b] Solubility is given in g/1000 mL of solution.