IODINE

Its Properties and
Technical Applications

CHILEAN IODINE EDUCATIONAL BUREAU, INC.

120 Broadway, New York 5, New York

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Contents

Foreword

The purpose of this booklet is to present to scientists and engineers engaged in research, development, and operation in the process industries, a survey of the physical and chemical properties of iodine and its compounds with emphasis on some of the unusual ones, which, it is believed, could serve as the foundations for new and expanded uses of these substances. A number of suggested applications will be discussed to illustrate the wide variety of fields in which these properties are, and may be, utilized.

The ultimate test of the economic utility of a material depends on a number of factors. If its use will result in greater output per unit of capital investment, labor, or other raw materials; if it will yield a product of higher quality; or if it can result in the production of new and useful substances, it should have a place in industry.

The most important applications of iodine are of three types: those in which relatively small quantities are used as catalysts; those in which relatively large amounts are employed to produce a given result, but the iodine is recovered and recirculated and does not appear in the final product; and, finally, those in which iodine is an essential constituent of a product because of the unusual properties which it confers. These types will be stressed in this booklet.

Such uses of special materials are common in the process industries. In the first category, the use of mercuric sulfate as a catalyst in the synthesis of acetaldehyde, and of iodine in that of cyclopropane, can be cited; in the second, iodine in the production of ductile zirconium metal, mercury in electrolytic alkali-chlorine cells, and ammonia in the Solvay process; and, finally, the presence of silver and iodine in the present day rapid negative photographic emulsions.

It cannot be emphasized too strongly that iodine is an element in its own right. It, therefore, has characteristics, undergoes reactions, and forms compounds which are different from those of any other element. An outstanding illustration is the fact that there is no substitute for the iodine needed by the thyroid gland. Just as a small amount is required by the human system to supply the thyroxine essential to health and vigor, it is believed that iodine can find an equally important role in many processes and products and, indeed, eventually earn the title of "The Thyroxine of Industry."

The reader will, of course, recognize that this booklet is a general survey and refers to only a very small fraction of the vast amount of literature on the properties, reactions, and applications of iodine and its compounds which has accumulated in the more than a century and a third since the discovery of the element.

The Bureau publishes "Iodine Abstracts and Reviews" which contains summaries of current scientific and technical articles relating to the properties, reactions and technical uses of iodine and its compounds. Copies are available upon request.

I

Chemistry of Iodine

and Its Compounds

A Short History of Iodine

Iodine was discovered by Bernard Courtois, a Frenchman, about 1811.[1] Whether it was the second or third halogen to be discovered is a matter of definition. The first place belongs to chlorine, which was isolated by Scheele in 1774, while it was not until 1826 that Balard discovered bromine. Fluorine, apparently, was recognized as an element by Ampere in 1810 when he presented arguments that hydrofluoric acid was analogous to hydrochloric acid and therefore a compound of hydrogen and an unknown element, but it did not receive its name until 1813, when Davy arrived at the same conclusion. It was not until 1886 that Moissan first isolated it in the elementary state. In the case of iodine, its discovery and isolation occurred simultaneously since Courtois recognized it as a new substance because of the violet color of its vapor.

The discovery of iodine may be looked upon as a result of war-fostered research. At the time, France was engaged in the Napoleonic wars and was isolated by the British Navy and the allied armies from foreign sources of the potassium nitrate required for gunpowder. To supply her requirements of this strategic material, nitre beds were established to produce calcium nitrate, which in turn was converted to the potassium salt by means of potash from wood ashes.

Courtois was one of those engaged in this industry. To conserve his supply of potash, he adopted the procedure of removing the major part of the impurities before conversion to the potassium salt and, in the course of this process, converted the calcium nitrate to the sodium salt by means of crude soda ash, which was obtained from the ashes of seaweed, and therefore contained iodine.

It seems that the copper vats in which this operation was carried out were rapidly corroded by the solutions, an effect which Courtois traced

1

to a reaction between the metal and an unknown substance introduced with the crude soda ash. He found that this substance could be precipitated as a black powder by adding sulfuric acid to the solutions and that it yielded a violet colored vapor when heated. He isolated some of the material, studied a number of its more obvious properties, and gave samples to J. B. Désormes and F. Clément. Some time later a sample came into the possession of J. L. Gay-Lussac who studied its properties more intensively, recognized it as a new element, and named it "iode," from the Greek word meaning violet colored.

Since its discovery, iodine has been a major factor in the advance of chemical science. Hofmann's researches on the reactions of alkyl halides with ammonia and the amines (1850) and the Williamson (1851), Wurtz (1855), and Grignard (1900) reactions, among others, established its importance in the development of synthetic organic chemistry; while its applications in analytical chemistry are so numerous that its use has acquired a special name of its own, "iodometry", suggesting that its application is so broad as to be a science in itself.

Iodine also has made important contributions to physical chemistry. The ready reversibility of the reactions between iodine and other substances has made them favorites for the study of the law of mass action and of reaction rates.

This importance is continuing. The present availability of the radioactive isotope I^{131} is aiding in the elucidation of reaction mechanisms. Furthermore, the number of reactions in which iodine and its compounds have found use, either as catalysts or as reagents, is growing more numerous year by year. To name only a few applications, the powerful oxidizing properties of periodic acid and its salts in aqueous solutions have opened up new avenues for the study of carbohydrates. Even in metallurgy, the application of the de Boer method of dissociation of the iodides on a hot filament has shown that titanium, zirconium, and hafnium, when sufficiently pure, are exceedingly malleable and ductile metals instead of the brittle semimetals which they were postulated to be on the basis of previous methods of preparation.

The Occurrence
and Production of Iodine

Iodine, according to the United States Geological Survey,[2] is the 47th most abundant element in the earth's crust, counting the rare earths as a single element. Although widely distributed in small quantities in rocks and soils, only about a dozen minerals containing iodine as an essential constituent have been discovered in nature, the most important probably being lautarite, $Ca(IO_3)_2$, found in the Chilean nitrate deposits. It is also present in appreciable quantities in some underground brines and, according to a recent compilation,[3] it occurs in sea water to the extent of about 0.05 part per million, or approximately 1/1300th the concentration of bromine. McClendon[4] has written an excellent summary of studies of the distribution of iodine.

Despite its low concentration in sea water, some seaweeds possess the ability to extract iodine and it remains in the ashes when they are incinerated. It was the use of soda ash from this source that led to the presence of iodine in Courtois' vats.

The ashes of seaweed were the first commercial source of iodine. Harvesting of these plants was an important industry along the coasts of France and of Scotland for a great many years, not only for iodine, but also for potash. However, in 1840, iodine was discovered in the Chilean nitrate beds and the first shipment made in 1868. This, together with the rise in the production of potash from the German deposits, resulted in a marked decline in the seaweed industry which, however, continued to supply important quantities of iodine right up to the beginning of World War II, particularly in Japan, and to a lesser extent in Scotland, France, and along the Asiatic coast of Russia. Iodine also has been produced from mineral waters in Northern Italy and from oil well brines in Java, Russia, and California.

The most important source of iodine, however, is the Chilean nitrate deposits. The nitrate ore, or "caliche," contains up to about 0.3% iodine, recent averages for mine-run ore being between 0.03 and 0.05%. As stated above, calcium iodate (lautarite) has been found in the nitrate deposits but, although practically entirely in the form of iodate, it is not certain that all of the iodine occurs as this mineral, since it is possible that some is present as one or both of the double salts of sodium iodate with sodium sulfate, discovered by Foote and Vance in their study of the system $NaIO_3$-Na_2SO_4-H_2O.[5]

The iodate dissolves with sodium nitrate when the caliche is leached for the recovery of the latter substance. It is allowed to build up in the leach solutions which are recycled until a reasonable concentration is obtained before being drawn off and treated with sodium bisulfite to precipitate the free iodine. This is filtered off and sublimed to form the crude iodine of commerce.

3

The Properties of Iodine

Iodine has an atomic number of 53 and an atomic weight of 126.92. As found in nature it is a simple element, only one stable isotope being known. Several radioactive isotopes have been prepared, one of which, I^{131}, is finding interesting applications as a tracer.

Solid Iodine

In massive form iodine is a bluish-black solid with a specific gravity of 4.93. The resublimed material usually seen in the laboratory consists of almost opaque, strongly doubly refracting crystals which have a metallic luster, the unusually high refractive index of 3.34, and pronounced pleochroism. They belong to the orthorhombic system.

The fact that iodine is the only halogen which is solid at ordinary temperatures (excluding, of course, the practically unknown element 85, recently named astatine) is an advantage both in shipment and in storage. Iodine is exported from Chile in wooden kegs containing 70 kilograms and can be stored in these with no special precautions for any reasonable length of time without serious loss due to volatilization.

Having the highest atomic weight of the common halogens, iodine begins to exhibit metallic properties. In addition to its luster and opacity, it is classed as a semiconductor of electricity.

Iodine is only slightly soluble in cold water (1 part in 3450 at 20°C.) but is much more soluble in hot water (1 in 250 at 100°C.). Kracek[6] estimated that the two substances would be completely miscible in the liquid state at temperatures of about 300°C. and above. Iodine is also soluble in aqueous solutions containing iodide ion, owing to the formation of polyiodide ions. Some of these solutions are very highly concentrated. Grace,[7] for example, found the composition of that in equilibrium with $KI_7 \cdot H_2O$ and solid iodine at 25°C. to be 68% iodine, 26% potassium iodide, and 6% water.

Some of the polyiodides, notably those of rubidium, cesium, ammonium, substituted ammonium, and iodonium, are stable in the solid state, while others, such as those of potassium, can exist as solids only when containing "solvent of crystallization."

Iodine is also very soluble in carbon disulfide and many organic solvents. Some of these solutions are violet in color, while others are brown. There is good experimental evidence that the iodine in the violet solutions is generally present as unsolvated diatomic molecules, although electrical conductivity[8] and ultraviolet absorption data[7] indicate that benzene solutions are an exception to this rule. In brown solutions the iodine is present as solvated molecules and, indeed, the solvates have been isolated in the cases of acetone and ether.[10] Kleinberg and Davidson[11] have recently published an excellent review of knowledge of the nature of iodine solutions.

Liquid Iodine

Iodine melts at 113.6°C. to a black mobile liquid. Unlike liquid chlorine and bromine, which have no solvent action on their binary ionic salts, liquid iodine is a good solvent for the alkali metal iodides and those of the ammonium bases. It also readily dissolves many other substances including sulfur, selenium, tellurium, and the iodides of iron, aluminum, and thallium, as well as those of such elements as tin, zirconium, and antimony. A number of organic compounds are also soluble.[12]

Studies of the electrical conductivities of solutions of various iodides in liquid iodine have given very interesting results.[13-17] The pure solvent itself has an appreciable conductivity, 0.9×10^{-5} at 140°C., and the solutions can be classified in the following categories:

1. Good conductors, conductivity greater than 10^{-1}; lithium, potassium, rubidium, and tetramethylammonium iodides
2. Fair conductors, greater than 10^{-3}; aluminum iodide
3. Poor conductors, greater than 10^{-4}; sodium iodide and phosphorus triiodide
4. Bad conductors, about 10^{-5}; stannic, mercuric, and antimony iodides.

It is to be pointed out that the conductivities of the solutions in the first group are of the same order as those for fused salts and aqueous solutions of strong electrolytes.

These data indicate that although its dielectric constant is relatively low, about 12.0, liquid iodine is a polar solvent of considerable ionizing power. It is therefore unique in being the only elementary substance exhibiting this property. The appreciable conductivity of the solvent itself suggests that it is ionized to a small extent in accordance with the equation

$$I_2 = I^+ + I^-$$

or, more probably,

$$2I_2 = I^+ + I_3^-$$
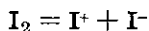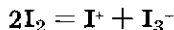
placing it with sulfur dioxide in the class of "acidic" solvents which form solvated anions rather than in the class of "basic" solvents such as water and ammonia which yield solvated cations.

If this viewpoint is correct, it follows that the normal iodides, polyiodides, and iodine monohalides are, respectively, the unsolvated bases, solvated bases, and acids in the iodine system corresponding to the metallic oxides, hydroxides, and hydrogen acids in the water system. The neutralization reaction is written either as

$$KI + ICl = KCl + I_2$$

or

$$KI_3 + ICl = KCl + 2I_2.$$
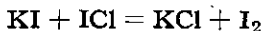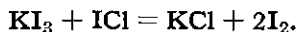
The iodine system naturally has some unusual characteristics compared to that based on water. In the first place, the solvent is an element. Secondly, the conductivity data reported above indicate that sodium is a weak base, weaker even than aluminum which is relatively strong in the iodine system. A third characteristic is the relatively small

5

number of cathodic reactions that can occur because of the overwhelming tendency of free iodine to be reduced to iodide ion. On the basis of data from aqueous solutions, it might be assumed that silver and the metals below it in the electromotive series could be deposited cathodically from solutions in iodine, but the special affinity of these metals for the element as well as their tendency to form complex iodides make it extremely doubtful that any such reaction would occur. Finally, there is the existence of "acid" salts which have no exact counterparts in the water system. Compounds of the alkali halides with the iodine monohalides, such as $KCl \cdot ICl$ and $KCl \cdot 2ICl$, are acid salts in the iodine system, analogous to the acid fluorides.

Iodine Vapor and Gas

Iodine boils at 184°C. under atmospheric pressure to produce the characteristic violet colored vapor. It has an appreciable vapor pressure at ordinary temperatures, a fact familiar to every chemist who has seen partly filled bottles containing solutions or crystals of iodine. At low temperatures, iodine vapor is made up of diatomic molecules, just as in the case of the other halogens; but, on heating, dissociation takes place. The concentration of monatomic molecules becomes appreciable at moderately elevated temperatures, reaching, for example, 1.4% at 600°C. and a total pressure of 1 atmosphere.

The concentration of iodine vapor in equilibrium with the solid at ordinary temperatures appears to be close to a critical point with reference to the type of electrical discharge it will carry. According to Mellor,[18] it conducts an oscillatory discharge, but this stops in a few minutes if excess solid is present and is replaced by a nonoscillatory type owing to the increased vapor pressure caused by the heat generated.

Iodine vapor produces a number of noteworthy effects with light. It is photosensitive; visible light of wave length 4995 A in the green-blue region of the spectrum causes dissociation to a normal and an excited atom. It exhibits fluorescence at low pressure, emitting a yellowish green light when illuminated by light from the sun or an electric arc, and it also rotates the plane of polarized light when placed in a magnetic field between crossed Nicol prisms. Describing this last phenomenon, Wood[19] states, "On exciting the magnet, an intense blaze of emerald green light at once appeared, wholly different in color from that of the fluorescent light."

One of the more interesting properties of iodine vapor is its thermo-luminescence. When heated to 500°C. or higher, it emits visible light. According to Wood,[19] it gives the appearance of a luminous red cloud in relatively thick layers at 700°C., but the light becomes almost white in thin layers at higher temperatures.

Chemical Properties

Iodine, like its sister halogens, fluorine, chlorine, and bromine, is very active chemically, and can be made to combine with all of the other elements, with the exception of the noble gases, sulfur, and selenium.

6

However, owing to the formation of protective films, a number of metals in massive forms are resistant to its action, particularly in the absence of water. Iodine also reacts with many organic compounds as will be seen later.

Iodine is usually less violent in its action than the other halogens. It combines with hydrogen only slowly, if at all, at ordinary temperatures, but may be made to do so at moderately high temperatures in the presence of a platinum catalyst.[20] Many metallic iodides can be made safely by direct union of the elements because of the relatively small evolution of heat.

Inorganic Compounds of Iodine

Because of the high atomic weight of iodine, its compounds are characterized by their high specific gravities. That of methylene iodide, 3.325, is the highest of any pure liquid except mercury. This is also true of their solutions and is especially marked in those of the more soluble salts. Saturated aqueous solutions of $KHgI_3$, $NaHgI_3$, and InI_3, have specific gravities of 3.19, 3.46, and 3.44, respectively, and, like methylene iodide, have been used to determine the specific gravities of minerals and other substances and to effect separations based on this property. For the same reason, compounds of iodine usually have higher indices of refraction than the corresponding chlorine and bromine compounds. That of methylene iodide, for example, 1.738, is greater even than carbon disulfide.

Compounds of Electropositive Iodine

The metallic properties of iodine also appear in its compounds. Hypoiodous acid is so weak that it has, indeed, been called iodine hydroxide. Iodine monochloride, although completely hydrolyzed in dilute aqueous solution, is stable in moderately concentrated hydrochloric acid solutions, and forms double salts with the alkali chlorides of the type KCl·ICl. Iodine monobromide behaves similarly. More recently, it has been shown[21] that alcoholic solutions of iodous nitrate, INO_3, prepared by precipitating alcoholic solutions of iodine itself, its monochloride, or monobromide with alcoholic silver nitrate solution, as well as similar solutions of the monochloride, deposit iodine on the cathode when electrolyzed. The iodous cation is greatly stabilized by coordinating it with a molecule of pyridine and to an even greater extent with two molecules.[22] The other pyridine bases, picoline, lutidine, and collidine, are also effective.[23] An excellent review of this subject has recently appeared,[24] and it has also been reported[25,26] that monopyridine iodous p-nitrobenzoate has interesting antibacterial properties.

The hypothetical sesquioxide, I_2O_3, also shows definite basic properties. Iodine trichloride forms double salts with the alkali chlorides just as does the monochloride; and basic phosphates, sulfates, and salts of organic acids corresponding to the sesquioxide are known.

Finally, iodine exhibits its basic character in the iodonium salts and other organic derivatives which will be taken up later when the organic compounds of iodine are discussed.

Compounds With the Other Halogens

Iodine forms five interesting compounds with the other halogens, two each with fluorine and chlorine and one with bromine. Three, the

monobromide, monochloride, and trichloride, are solids at ordinary temperatures; one, the pentafluoride, is a liquid; while the heptafluoride is a gas.

The stabilities of these substances and the number of atoms of the other halogens which combine with iodine increase in the order bromine, chlorine, fluorine. The monobromide readily dissociates but iodine takes fire in fluorine to form the pentafluoride.

The monochloride and monobromide in the liquid state are, like iodine itself, solvents with definitely polar characteristics. They have appreciable electrical conductivities of their own and dissolve the alkali and other metallic halides to form conducting solutions.[27,28]

These compounds are powerful halogenating agents but they differ in their action from the free halogens in several respects. In the first place, combination with iodine reduces the activity of the more reactive halogen so that the reaction, when once started, is less vigorous; secondly, in the case of the monochloride and monobromide, and possibly others, the reactions frequently start more readily because of reduced energies of activation; and, finally, both halogens usually take part in the reactions.

The Polyhalides

It was stated earlier that iodine monochloride combines with potassium chloride to form the solid compounds KCl·ICl and KCl·2ICl. These and the polyiodides are representative of an unusual class of compounds formed by the combination of iodine itself, its chlorides or bromide with the alkali metal, ammonium, substituted ammonium, and iodonium halides, and those of other strong bases. There is also evidence that similar compounds of somewhat less strongly electropositive elements, such as the alkaline earths and magnesium, can exist when stabilized by water of crystallization.

These substances, which are represented by such formulas as CsI_3, $KIBr_2$, $KIBrCl$, $KICl_2$, $KICl_4$, and $KICl_3F$, form crystals, usually orthorhombic, which are highly colored, ranging from deep black through red and orange to yellow. The more stable ones usually crystallize in the anhydrous condition.

They vary widely in their stability as shown by measurements of the concentration of iodine halide dissolved in carbon tetrachloride in equilibrium with the crystals of a number of alkali metal, ammonium, and alkylammonium compounds.[29] Among the iododibromides the potassium salt was the least and the quaternary ammonium salts the most stable. Indeed, tetraethylammonium iododibromide was so stable that it yielded no detectable quantity of iodine monobromide to the carbon tetrachloride. According to other measurements,[30] the dissociation pressure of iodine monochloride over the compound KCl·ICl at 25°C. is only 0.20 mm., which is very low compared to the vapor pressure of the pure monochloride at the same temperature, 28.3 mm. These substances therefore provide convenient means for shipping and storage of iodine and its halides, as well as for modifying their chemical activities over a wide range.

Hydrogen Iodide

Hydrogen iodide, like the other hydrogen halides, is a colorless gas at ordinary temperatures which fumes strongly when brought into contact with moist air. However, it is much less stable than the others and can readily be made to dissociate partly into hydrogen and iodine.

The gas is very soluble in water, forming hydriodic acid which, like hydrobromic and hydrochloric acids, is a very strong acid. It differs from the others in having pronounced reducing properties, iodine being liberated. In concentrated solutions even sulfates are reduced and for this reason the acid cannot be prepared by the action of sulfuric acid on an iodide.

Inorganic Iodides—Physical Properties

Crystal structure studies during recent years have shown that there are many exceptions to the general rule that the crystalline iodides are isomorphous with the corresponding chlorides and bromides. Indeed, additional data may show that it is more frequently false than true. It does hold, of course, in the case of the alkali metals, but it does not hold for thallous iodide below 170°C., nor for silver iodide at any temperature, the crystal structure of the latter being so close to that of ice that it can induce crystallization of this substance in clouds at temperatures very much above that at which simple cooling is effective. For this reason silver iodide has been found effective in the artificial production of rain.

The metallic diiodides are also important exceptions to the rule as they generally crystallize on a "layer lattice" of the so-called cadmium iodide type, the metal atoms forming a layer between two layers of iodine atoms. The result is a sort of a "sandwich" molecule of indefinite extent in two directions but only three atoms thick in the third. These "sandwich" molecules are held together by the comparatively weak attraction of iodine atoms for each other and there is consequently, as in the case of graphite and mica, excellent cleavage along these planes. Like graphite and mica, they also have pronounced lubricating properties. A few dibromides crystallize on this lattice, but there is no known case of a chloride doing so. Indeed, in the only two known instances in which the diiodides and dichlorides have the same crystal structures, those of barium and nickel, the iodides adopted the structures of the others.

The ionic triiodides also appear to have a characteristic structure of their own, belonging to the orthorhombic system, the typical substance being lanthanum iodide.

Large crystals of potassium iodide have been grown for optical purposes. In Germany, similar crystals of solid solutions of thallous bromide and iodide were made for use in the infrared region of the spectrum.[31]

Like the other compounds of their type, the solid iodides generally have very low electrical conductivities. Silver and cuprous iodides, however, are unusual in this respect,[32-34] as they are classed as semiconductors, their conductivities rising rapidly, in the order of 10,000 to 100,000 times, respectively, upon heating from 100° to 500°C. That

of cuprous iodide is further greatly increased by the presence of iodine vapor, the rise being proportional to its partial pressure.

Below 240°C., cuprous iodide is predominantly an electronic conductor, but at higher temperatures, ionic conduction gradually increases, the metal ions moving through the lattice. Silver ions also carry the current in silver iodide. The extreme mobility of the metal ions in these salts is shown by an experiment performed by Reinhold.[35] After holding a bar of a solid solution of 75 mol per cent silver iodide and 25 per cent cuprous iodide for four days with one end at 210° and the other at 325°C., he found that the concentration of the copper salt had risen to 37 per cent at the cold end and had fallen to 21 per cent at the hot end. Longer heating produced no further effect but shorter periods were not tried.

With the exception of the iodides of copper, silver, mercury, thallium, lead, and palladium, all iodides are soluble in water. There is some evidence that they are less readily hydrolyzed in solution than the chlorides or bromides. Anhydrous arsenic triiodide, for example, is stable in contact with its saturated aqueous solution, while stannic iodide requires much less free acid to prevent hydrolysis than does stannic chloride. Some recent work[36] has shown that addition of iodide to magnesium sulfate solutions reduces hydrolysis, whereas addition of chloride increases it.

An important property of the alkali metal iodides is their high solubilities in acetone, furfural, liquid sulfur dioxide, and other non-aqueous solvents. In many cases these are much greater than those of the corresponding chlorides and bromides. Metathetical reactions can therefore take place between organic chlorides and potassium or sodium iodides in these solvents with the formation of the organic iodides and precipitation of potassium chloride. This property is also shared by some of the diiodides, notably those of calcium, magnesium, zinc, and cobalt, and has led to the suggestion that they be used in wet type absorption refrigeration systems, while the ability of these same salts to take up organic liquids as "solvent of crystallization" has given rise to a similar suggestion for their use in dry type systems.

The high solubility of many iodides in liquid anhydrous ammonia may be of considerable future interest as this substance is one of the cheapest nonaqueous solvents, while its good solvent power and highly polar characteristics, similar to those of water, make it one of the most interesting.

There is an interesting relationship between the melting and boiling temperatures of the halides of the elements and the type of bond in the molecule. In the purely covalent halides the melting and boiling points rise in the order chloride, bromide, iodide. As the ionic character of the bond increases, however, this order tends to become reversed with the result that in the case of the most highly electropositive elements, the iodides usually have the lowest melting and boiling points. The low melting points of some of the metallic iodides have been applied in the preparation of low melting salt mixtures.

There is relatively little information on binary iodide systems, but what there is indicates that they are frequently quite different from the corresponding chloride systems. Magnesium and potassium chlo-

rides, for example, form two compounds and three eutectics, the lowest melting at 426°C. A recent study of the corresponding iodide system, however, showed no compound formation and a single eutectic melting at the extraordinarily low temperature of 255°C., 171 degrees below the lowest in the other.[42]

The vapors of the volatile iodides of the elements in the fourth column of the periodic table are among the heaviest known gases. Stannic iodide, for example, with a boiling point in the neighborhood of 350°C., has a molecular weight of 626, from which it can be calculated that a liter of the vapor at that temperature weighs over 12 grams at a pressure of 1 atmosphere. Further calculations show that the velocity of sound in this vapor under the same conditions is less than 100 meters per second, which suggests that it may have applications in acoustics and also provide a convenient medium for the study of supersonic phenomena.

Inorganic Iodides—Chemical Properties

The iodides are usually much less stable chemically than the other halides. Iodides of sulfur and selenium do not exist; those of phosphorus and bromine decompose at slightly elevated temperatures; while those corresponding to the highest chlorides of iron, copper, arsenic, vanadium, and other metals have not been prepared in the anhydrous state, and anhydrous chromic iodide is apparently unstable.[43,44] In general, these iodides do not exist in aqueous solution either, so that the presence of a small quantity of iodide ion in the solution is sufficient to maintain the metals in a lower valence state and to provide an indication, by liberation of free iodine, when oxidation is occurring. Some higher iodides, however, can be stabilized both in the solid state and in solution by attaching coordinating groups to the metal ions. Water appears to be effective in the case of chromium and europium, but copper and cobalt require ammonia or amines.

At higher temperatures, even the more stable iodides show appreciable dissociation. The nickel salt loses iodine at temperatures below its melting point.[45] Attempts to measure the absorption spectra of the vapors of the iodides of the other iron group metals have yielded, even in the case of manganese, only those of iodine and in some cases of the metal itself.[46] Recent work[47] has shown that even zinc and cadmium iodides are largely dissociated at temperatures in the neighborhood of 1000°C. This fact has been utilized as the basis of a method for preparing some of the more refractory metals in a highly pure state. A carbon almost entirely amorphous to x-rays was obtained by heating hexaiodobenzene to 1000°C.[48]

Another consequence of the low free energies of formation of the iodides is the ready replacement of the iodine by other substances. It is well known, for example, that treatment with fluorine, chlorine, or bromine will convert them to the corresponding salts with quantitative liberation of the iodine. Oxygen acts in a similar manner. Although the alkali iodides are very reasonably stable to this reagent, this is not the case with the iodides of the less electropositive elements, most of which, on heating in air or oxygen, are converted to oxides. They

therefore resemble the sulfides in this respect, but with the important difference that the iodine does not form an oxide, but is liberated as the free element, which can be recovered as such.

The more volatile covalent iodides, notably those of aluminum and titanium, actually burn in air with the production of flame and, at moderately high temperatures where their vapor pressures are appreciable, can even form explosive mixtures.

The iodine may be replaced even by much less active substances under the proper conditions. Hieber and his co-workers[49-57] and Manchot and Manchot[58] found that the iodides of many of the transition metals would react quantitatively with carbon monoxide under pressure to produce the carbonyls, whereas poor yields were obtained with the other halides.

Although iodine is readily displaced from the iodides by the other halogens, the opposite is the case with the hydrohalogen acids. Hydrogen iodide, either in the anhydrous state or in aqueous solution, will react with the other halides to convert them into iodides. In some cases the reaction is fairly vigorous. This method has been used to prepare anhydrous titanium iodides and similar substances and was recently made the subject of a patent[59] for the preparation of alkali and alkaline earth iodides from the corresponding chlorides, thereby avoiding the use of the hydroxides.

In the case of the halides of some weak bases which have a tendency to lose hydrogen halide, the iodides are the most stable. Phosphonium iodide is one of the most notable examples.

Complex Iodides

Iodides usually have less tendency to form complex anions than do the chlorides, but there are some exceptions to this rule, notably in the cases of cadmium, mercury, and silver. Some complex iodides are well known. Potassium iodomercurate, $KHgI_3$, is one of the most familiar as it is the basis of Nessler's reagent for the detection of ammonia and of other reagents for proteins and alkaloids, and, as previously stated, its saturated solutions in water have unusually high specific gravities. The sodium iodide-lead iodide complex is also extraordinarily soluble.[37] The most concentrated solution at 25°C. has a specific gravity of 2.542 and contains 879 grams of lead iodide and 1082 grams of sodium iodide per liter.

Even more remarkable is the silver iodomercurate, Ag_2HgI_4. This substance undergoes an allotropic transformation at 50°C., the crystal structure changing from tetragonal to cubic on heating and the color from yellow to red, the latter change being so pronounced and so sharp that the substance has been recommended as a constituent of thermosensitive paints to warn of overheating of bearings and other objects.

Study of this transformation in detail[38] indicates that it is of an unusual partial order-disorder type, the silver and mercuric ions acquiring a random distribution while the iodide ions retain their rigid lattice positions. This process probably becomes complete at 158°C., where the compound undergoes another transformation to a disordered

solid solution of mercuric iodide in the beta form of silver iodide.[39]

Accompanying the 50° transformation is a sharp increase of a hundred-fold in the electrical conductivity of the substance, making it about a thousand times better than any other solid electrolytic conductor in the temperature range between 50° and 150°C. According to Ketelaar,[38] there are only four good solid electrolytic conductors, three of which are iodides, namely the silver iodomercurate and cuprous and silver iodides.

The corresponding cuprous iodomercurate, Cu_2HgI_4, is isomorphous with the silver salt and undergoes a similar allotropic transformation accompanied by a sharp change in color from red to chocolate brown in the neighborhood of 70°C. Accordingly, it has also been recommended as a constituent of thermosensitive paints, both alone and mixed with the silver salt.[40,41] Investigation would probably show that it also possesses unusual electrical conducting properties.

The Oxides of Iodine

Mixtures of oxygen and iodine vapor, passed over the oxides and carbonates of the alkaline earth metals at high temperatures, combine with them to form the corresponding normal paraperiodates;[60] and sodium iodide, when heated in the presence of sodium oxide or hydroxide, absorbs oxygen to yield normal sodium paraperiodate;[61] but iodine itself has not yet been made to combine directly with oxygen. The two elements, however, unite indirectly to form a large number of interesting and important compounds which may be considered as derivatives of five oxides, namely, the monoxide, I_2O; the sesquioxide, I_2O_3; the dioxide, IO_2; the pentoxide, I_2O_5; and the heptoxide, I_2O_7. Only two of these, the dioxide and pentoxide, have been prepared in the free state.

The monoxide is the anhydride of hypoiodous acid. This acid is known only as an unstable, strongly oxidizing solution which rapidly disproportionates into iodic acid and free iodine. There is strong doubt that any of its salts have been prepared. As already noted, it is so weak an acid that it has been called iodine hydroxide. Iodine monochloride may be considered as one of its derivatives.

It was stated earlier that I_2O_3 also exhibits pronounced basic properties and that a number of its salts have been prepared. One of its most interesting derivatives is the Masson and Race reagent, made by dissolving iodine and iodine pentoxide, in the proper proportions to form this oxide, in strong sulfuric acid. This reagent converts many aromatic compounds directly to the corresponding iodoso and iodonium derivatives in high yields. (cf. pages 25 and 28)

Iodine dioxide, a yellow solid at ordinary temperatures, is at present no more than a laboratory curiosity.

Iodine pentoxide is a commercial product. It is easily made by oxidizing iodine to iodic acid, either electrolytically or with concentrated nitric acid, and dehydrating the product. It can be prepared readily on a large scale if the demand arises. It is by far the most stable of the halogen oxides, but is a powerful oxidizing agent, being one of the very few substances that will quantitatively oxidize carbon monoxide to carbon dioxide at ordinary temperatures.

14

Iodic Acid and the Iodates

When added to water, iodine pentoxide forms iodic acid, HIO_3, which is also a powerful oxidizing agent. Except in its formula and its oxidizing properties, this acid bears little resemblance to chloric and bromic acids. The latter are strong, monobasic acids which exist only in solution. Iodic acid, on the other hand, is a weak acid, of about the same strength as sulfurous acid, forms acid and pyro as well as normal salts, and can be obtained commercially as a stable, colorless, crystalline solid which is very soluble in water.

Iodates of most of the metals have been prepared. In general they are sparingly soluble in water but are usually soluble in dilute nitric acid. Probably the best known is potassium acid iodate, $KH(IO_3)_2$, which is recommended as an alkalimetric standard because of its stability, freedom from water of crystallization, and ease of purification.[62] Potassium iodate is used for the separation of thorium from the rare earths. Calcium iodate is found in the Chilean nitrate beds.

Periodic Acid and the Periodates

Another important oxygen compound of iodine is periodic acid, corresponding to the unknown oxide, I_2O_7. It is prepared by the electrolytic oxidation of iodic acid. Its salts can be formed by oxidation of iodates with chlorine in alkaline solution, while the action of oxygen, sodium nitrate, or sodium peroxide on mixtures of sodium iodide with sodium oxide or hydroxide at high temperatures yields normal sodium paraperiodate, Na_5IO_6.[61] Similarly, passage of a mixture of iodine vapor and oxygen over the oxides or carbonates of the alkaline earths yields the paraperiodates of these metals.[60]

As in the case of iodic acid, the resemblance of periodic acid to the other known member of its class, perchloric acid, is small. The latter is a strong monobasic acid with very little oxidizing power in dilute aqueous solution. Periodic acid, on the other hand, is a rather weak acid of about the same strength as iodic acid; is a powerful oxidizing agent even in dilute solutions; and, in its relationships as an acid, more nearly resembles the phosphoric acids, as it forms salts derived from metaperiodic acid, HIO_4, mesoperiodic acid, H_3IO_5, paraperiodic acid, H_5IO_6, and even $H_4I_2O_9$. Like the phosphoric acids, it also forms heteropoly acids with molybdenum and tungsten trioxides.

Metaperiodic acid has been prepared, but the most important form is paraperiodic acid which is the only one stable in contact with its aqueous solution. It is commercially available as colorless deliquescent crystals which are very soluble in water.

The activity of periodic acid as an oxidizing agent varies widely with conditions. In acid solution, it is one of the most powerful oxidizing agents known, and will readily convert manganese salts to permanganate, but in strongly alkaline solutions it is less strongly oxidizing than chlorine and, as noted above, its salts can be prepared from iodates by oxidation with this reagent under these conditions. Its activity can therefore be varied over a wide range simply by controlling the hydrogen ion concentration of the solutions.

One of the most interesting properties of periodic acid is the ability

15

of its aqueous solutions to oxidize cellulose and other carbohydrates. This reaction, which is discussed in greater detail on page 21, has become of considerable importance as a method of elucidating the structures of these substances. It may also become of commercial importance because of the unusual products formed.

The periodates of many of the metals have been prepared. However, because of the strongly oxidizing activity of periodic acid, such salts as ferrous and manganous periodates, if they exist at all, should be much less stable than the corresponding perchlorates.

Some of the periodates are remarkably resistant to heat. Zintl[61] found that sodium metaperiodate had to be heated to 300°- 400°C. to decompose it to iodine, oxygen, and normal sodium paraperiodate; and that the latter salt required a temperature above 800°C. to cause it to break down with evolution of oxygen. Indeed, that this salt can be prepared at only slightly lower temperatures by the action of oxygen on mixtures of sodium iodide and oxide or hydroxide, and that the normal alkaline earth paraperiodates are formed merely by passing oxygen and iodine vapor over the corresponding oxides or carbonates, demonstrate that these substances share with the iodides the distinction of being thermodynamically stable with respect to their constituents at ordinary and moderately elevated temperatures.

Complex periodates of copper, silver, and gold with the alkali metals have been reported in which the two first-named metals are in the unusual trivalent state.[63] Nickel forms complex paraperiodates with the alkali metals in which it is tetravalent.[64] They form insoluble, dark purple crystals which are unusual in that they have a metallic luster and form bright mirrors on glass. These properties resemble those of the tungsten bronzes and suggest that the crystals may be metallic conductors.

Like potassium and ammonium dihydrogen orthophosphates, silver and ammonium trihydrogen paraperiodates exhibit specific heat anomalies at low temperatures which are attributed to ordering of the hydrogen bonds.[65,66] Recent work has shown that the high temperature modifications of these salts also have pronounced electric polarization properties.[67] This suggests their possible use in electronics.

As in the case of the iodates, the periodates are, in general, sparingly soluble in water. The *meta* salts usually have the highest solubilities, those of the barium and sodium salts being quite high and moderate respectively. Where precipitation of hydroxides or basic salts does not interfere, the *meta* salts can be converted to the *para* compounds by increasing the alkalinity and vice versa.

Although they have not been studied from this viewpoint, the varying ease of replacement of the hydrogen ions in the paraperiodates indicates that they may show a sequestering action for calcium and other ions in aqueous solutions similar to the polymetaphosphates.

Reactions of Iodine
and Its Inorganic Compounds
with Organic Compounds

In general, iodine reacts with organic compounds in much the same manner as the other halogens, but, owing to the weakness of the carbon-iodine bond, the energy liberated is comparatively small and many reactions are readily reversible. In such cases, conditions can be chosen so that the reaction proceeds either to the formation of the iodo compound or to the complete elimination of the iodine as the free element, or to the unusual situation in which a free halogen exists in stable contact with the organic reactants as well as the products.

Iodine takes part in substitution reactions, just as do the other halogens, to form iodo derivatives and hydrogen iodide, but the equilibria are usually such that only small concentrations of the products result. Indeed, they generally favor the well-known reverse reaction, that of hydrogen iodide with an iodo compound to replace the iodine with hydrogen and liberate the former as the free element, which is the basis for one of the most important uses of hydrogen iodide in organic chemistry. To make the substitution reaction go to completion, it is necessary to have present an oxidizing substance to convert the hydrogen iodide to free iodine as quickly as it is formed, or a basic substance to neutralize it. The former is preferable as it results in a greater utilization of the iodine, practically all of which, according to Groggins and Newton,[68] enters the organic compound when nitric acid is used as the oxidizing agent.

Shepherd and Fellows[69] recently reported that the substitution of iodine on pyrimidine rings is greatly accelerated by the presence of mercuric acetate, probably owing to the conversion of the iodide ion formed to the stable iodomercurate ion. They give an interesting table comparing the relative efficiencies of potassium hydroxide-iodine mixtures, iodine monochloride, and their own iodine-mercuric acetate as iodinating agents for a number of nitrogen compounds.

Iodine will also add to unsaturated compounds to form polyiodo derivatives, although complete saturation is frequently not obtained and, again, the reactions are often readily reversible. The equilibria and kinetics of such reactions have been the subjects of many investigations. The thermal decomposition of ethylene iodide was studied in the gas phase by Mooney and Ludlam[70] and by Cuthbertson and Kistiakowski;[71] and in carbon tetrachloride solution by Polissar,[72] who found that the decomposition of both the solid iodide and its solution was catalyzed by iodine. The pure solid melted at 81.5°C. without decomposition, but decomposed in the presence of iodine at 45°C. Ire-

dale and Stephan[73] found that iodide ion catalyzed the reaction in aqueous alcohol. Ghosh and his co-workers[74-76] studied the iodination of beta-amylene, alpha-pinene, and phenylacetylene in benzene, alcohol, and other solvents. Unsaturated compounds other than hydrocarbons undergo the same type of reaction.

Ogg and Priest[77,78] found that cyclopropane reacts with iodine in the neighborhood of 250°C. to yield 1,3-diiodopropane and that the reaction is reversible. There was no evidence of formation of hydrogen iodide; some propylene was formed, but this reaction was relatively slow even though it was catalyzed by iodine.

The ready reversibility of the foregoing reactions, together with the relatively low vapor pressures of the iodo compounds, and their great reactivities, which will be discussed later, suggests that iodine could be used in many processes to reduce temporarily the vapor pressure, change the solubility, or increase the reactivity of organic compounds in order to effect separations and yield products otherwise difficult to obtain. Furthermore, the relative ease with which the carbon-iodine bond is made and broken suggests that iodine has possibilities as a catalyst in many reactions.

Iodine, of course, reacts with other organic compounds. Li[79] studied the kinetics and mechanism of the reaction between iodine and tyrosine to form diiodotyrosine. Another type of reaction which has received considerable attention recently is that of iodine and aryl ketones or hydroxy compounds on heterocyclic bases, such as pyridine, to produce substitution derivatives of the bases.[80,81]

Iodine Halides

The iodine halides also react with organic compounds. They are active halogenating agents but are usually less violent in their action than the more active halogens in the free state because of the energy liberated in their formation. However, in the case of the monochloride and monobromide at least, their reactions start more readily than those of the free halogens because of their low energies of activation. For this reason, iodine is widely used as a catalyst in chlorinations and brominations.

Iodine pentafluoride is receiving attention as a mild fluorinating agent. It was prepared and tested in Germany for the fluorination of hydrocarbons with some success, and has also been studied in the United States.[82]

Iodine monochloride has been used as an iodinating agent.[83-85] It also adds to unsaturated linkages to produce chloroiodo compounds, in which the position of the chlorine is governed to a certain extent by Markownikoff's rule, as the chlorine tends to add to the carbon atom with the smallest number of hydrogens. Advantage has been taken of the differences in reactivities of the iodine and chlorine in these substances to convert them into other products. An interesting reaction of the monochloride is that with calcium carbide to produce diiodoacetylene.[86]

The reactivities of iodine monochloride and monobromide can be further reduced, if desired, by converting them to the complex iodo-

chlorides and iodobromides by reaction with the corresponding potassium salts.

Iodine trichloride adds to unsaturated bonds in much the same way as the monochloride. Its most interesting reaction is that with acetylene to produce chlorovinyl iododichloride, in which the iodine is in a positive oxidation state. This type of compound is practically unique with iodine and will be discussed at some length later.

Hydrogen Iodide

Hydrogen iodide adds to unsaturated compounds much more readily than do the other hydrogen halides. In addition to the experimental evidence for this, Remick[87] arrived at the same conclusion on the basis of electron theory and also showed that hydrogen iodide should be the most reactive in the splitting of ethers or alcohols.

Some of these reactions are also reversible. Jones and Ogg,[88] for example, found that tertiary butyl iodide, which decomposes at relatively low temperatures, yielded isobutylene and hydrogen iodide between 134°C. and 190°C. if the pressure was kept reasonably low, that the reaction was reversible and the equilibrium concentrations measurable. A free energy equation was derived. At the highest temperatures some iodine was liberated when the initial pressure was greater than 150 mm., presumably by the action of hydrogen iodide on the butyl iodide.

Hydriodic acid reacts with alcohols more readily than the other hydrogen halides to produce the corresponding iodides with the elimination of water. This reaction works particularly well with the lower aliphatic primary alcohols. In other cases, there may be danger of the formation of an iodine-free compound owing to reaction between the iodide and the excess of hydriodic acid.

Inorganic Iodides

The inorganic iodides, and particularly those of the alkali metals, react with alkyl and acyl chloro and bromo compounds to form the corresponding iodo derivatives. Known as the "exchange reaction," it takes place readily with sodium and potassium iodides in acetone solution[89] since these salts are soluble in this liquid while the chlorides and bromides are not and are precipitated. Other solvents, such as methyl and ethyl alcohols and acetamide, have also been used.

This reaction is used for the convenient preparation of many iodo compounds and has been the subject of many kinetic studies as it has been employed to measure the relative reactivities of halo compounds and the effects of structure on this property.[90-95]

Conant and his co-workers[90-72] measured the reaction rates of a large number of chloro compounds. They found that primary straight chain alkyl chlorides from butyl to myricyl (C_{30}) react at about the same rate; ethyl chloride is about twice as reactive, and primary isoamyl chloride about half as reactive as the others. Secondary and tertiary chlorides are much less reactive. Cyclohexyl chloride is practically unreactive.

It was also found that the reactivity of a compound of the type ACH$_2$Cl, where A is an activating group, is roughly proportional to the acidity of the corresponding AOH compound. As the length of the methylene chain increases, the influence of such groups decreases rapidly. The benzoyl group is an exception to this rule as it retains its activating influence with at least three intervening methylene groups. Substitution of chlorine, bromine, or the nitro group in benzyl chloride greatly increases its reactivity.

Some substances were extremely reactive, chloroacetophenone being 105,000 times more so than butyl chloride. To secure measurable rates with this substance, it was necessary to conduct the experiments at 0°C.

Tamele and co-workers,[96] and Hatch, Gordon and Russ[97] have applied the reaction to the study of the relative reactivities of allylic chlorides. The latter authors conclude that the reaction rate increases with decreasing electronegativity of the radical attached to the number 2 carbon and that *trans* isomers should be more reactive than *cis* isomers.

Precipitation of the alkali halide reaction product does not appear to be necessary to make the reaction proceed to completion in the case of chlorides, as Conant and Hussey[91] found that lithium iodide gave the same reaction rates as the potassium and sodium salts, even though lithium chloride is soluble in acetone. Skolnik and his co-workers,[98] in their studies of the reactions of 2-(alpha-chloroalkyl)-benzimidazoles with potassium iodide in acetone solution, also concluded that the precipitation of potassium chloride was not the rate controlling factor. However, Dostrovsky and Hughes[93] found that precipitation was necessary to make the reaction go to completion in the case of the bromides, those with potassium iodide being complete because of precipitation of the bromide, but incomplete with lithium iodide, the bromide of this metal being soluble in acetone.

Skolnik and his co-workers[98] also concluded that, in general, the higher the dielectric constant of the reaction medium, the lower the specific reaction rate, as, in their experiments, the addition of nitrobenzene or water, with higher dielectric constants than acetone, resulted in a decreased reaction rate, while addition of benzene increased it.

Iodine can be made to replace other groups, such as the *p*-arylsulfonyl radicals, by this reaction. There is a great deal of present interest in applying it to various esters of *p*-toluenesulfonic acid, especially those of cellulose, the sugars, and other carbohydrates. The results of a study of the reactivities of a number of such compounds with sodium iodide in acetone were published recently.[99]

It is well known that potassium iodide will react directly with aryl diazonium salts to yield the corresponding iodo compounds without the necessity for the presence of metallic copper or a cuprous salt as a catalyst. This is in marked contrast to the other halides.

The extraordinary affinity of mercuric iodide for the iodide ion, its much greater solubility in acetone, alcohols, and other organic solvents than in water, and the probable stabilizing effect of the large iodomercurate anion on unstable cations, suggest that this substance can act as a condensing agent for iodo compounds. Silver, lead, and cadmium iodides should have similar but less powerful effects.

20

Periodic and Iodic Acids

Periodic acid in aqueous solutions oxidizes many organic compounds, being itself reduced to iodic acid. This reaction, introduced only in 1928, has rapidly become of increasing importance in recent years as a method for elucidating the structures of carbohydrates and similar compounds. Jackson[100] has written an excellent review of the nature, scope, and use of the reaction up to the year 1944. According to this authority, it is applicable to compounds having two hydroxyl groups or a hydroxyl and an amino group attached to adjacent carbon atoms, and is characterized by the cleavage of the carbon-carbon bond. If the groups are not attached to contiguous carbon atoms, no oxidation takes place. Compounds with a carbonyl group adjacent to a second carbonyl or hydroxy group are also oxidized. The author goes on to state:

"Although the widely applicable reaction has gained recognition chiefly through its use in analysis and determination of constitution, many compounds have been prepared for the first time by this method; some of them are available at the present time only through this type of oxidation. The reaction also has provided an improved method for the preparation of some compounds that usually have been obtained in other ways. An advantage in most periodic acid oxidations is the absence of side reactions and the consequent high yield.

"The more common oxidizing agents, such as permanganate and nitric acid, usually cannot be substituted for periodic acid, since they are not selective in their action. Also these reagents oxidize many of the compounds obtained as products of periodic acid oxidation."

Many new papers on this reaction have appeared since the time of this review. One[101] discusses the kinetics of the oxidation of cellulose by periodic acid; another[102] states that cotton can be made resistant to periodic acid by methylation with diazomethane; and a third,[103] dealing with the use of periodic acid in determination of the structures of polysaccharides, states that the tendency of the reaction of sodium periodate with these substances to go too far can be controlled by adding potassium chloride to the solution to form the less soluble potassium salt. Two others extend the scope of the reaction to compounds containing active methylene groups[104] and phenols.[105] Still another[106] deals with decarboxylations with periodic acid.

Iodic acid is also an effective oxidizing agent for many organic compounds. Hurka[107] has written an excellent review article on this subject.

The Organic Iodo Compounds

There is a general belief that the organic compounds of iodine are much less stable than the corresponding ones of the other halogens. This is true only for the iodo derivatives, although many of this class are adequately stable for all practical purposes. There are other interesting and potentially important classes of iodine compounds, containing the element in a positive oxidation state, which are much more stable than similar compounds of the other halogens, if, indeed, the latter exist at all.

The outstanding characteristics of the iodo compounds are their lower heats of formation, relative instabilities, and great reactivities. As in the case of the inorganic iodides, their specific gravities and indices of refraction are higher than those of the corresponding chloro and bromo derivatives and, since the C—I bond is covalent, their melting and boiling points are also higher.

They may be prepared by any of the reactions discussed in the previous section. However, a mixture of iodine and red phosphorus is frequently used with advantage instead of hydriodic acid in their preparation from alcohols.

Some of the iodo compounds are useful for their physical properties. The high specific gravity of methylene iodide has made it of value in determining this property for other substances and to effect separations on this basis. The fact that it is miscible in all proportions with benzene, with a specific gravity of 0.88, increases its range of usefulness. Because of its high index of refraction, 1.738 at 24°C., higher even than that of carbon disulfide, it is also used for determining this property of other materials. The salts of the iodo derivatives of quinine, cinchonine, and other alkaloids have an extraordinary ability to polarize light, and iodo-quinine sulfate has been used as the active material of a commercial polarizing plastic sheet. The dyestuff, erythrosin, which is tetraiodo-fluorescein, is a certified food color in the United States, a valuable orthochromatic sensitizer for photographic emulsions, and is highly fluorescent.

Among the alkyl monoiodo compounds, the stability is a function of the position of the iodine, those in which it is attached to a primary carbon being the most stable. Secondary compounds are less stable and tertiary least of all.

A number of kinetic and equilibrium measurements of the thermal decomposition of the lower alkyl halides have been made. The reversible dissociation of tertiary butyl iodide into isobutylene and hydrogen iodide has already been discussed in connection with the reactions of the last named substance with organic compounds. In the case of the more stable n-propyl, isopropyl, n-butyl, and sec-butyl iodides, Ogg and Polanyi[108] and Jones and Ogg[109, 110] found that they decompose at

higher temperatures to yield equimolar quantities of the corresponding alkane and alkene hydrocarbons and free iodine. These reactions were catalyzed by iodine and gave no evidence of reversibility. Their rates were measured, rate equations derived, and possible mechanisms discussed.

As will be inferred from the discussion of the reactions of iodine with unsaturated compounds, polyiodo alkyl compounds with iodine attached to adjacent carbon atoms tend to lose iodine with the formation of a double bond. However, the stability increases with the distance between the iodine atoms, approaching that of the monoiodo compounds.

Aromatic iodo compounds are apparently very reasonably stable and iodine attached to the ring appears to be less reactive than in aliphatic compounds. Iodobenzene, for example, can be boiled without decomposition and, indeed, its vapor pressure has been measured up to five atmospheres at 270°C. with only minor decomposition. This substance possesses an unusually long liquid range as its melting point is $-31.2°C$. and boiling point 188.6°C.

The iodo compounds are noted for their reactivities. According to Calloway,[111] "The studies generally made to determine the reactivity of a series of halides containing the same R group but different halogen atoms consist in measuring the velocity of a reaction with some type of substance that results in a reaction of the two molecules in a more or less direct manner. Such substances have been used as inorganic and organic bases, metals, or alcohols.

"Such studies have given a series of 'orders of reactivity' for a given R group connected to various halogens. In practically every case where R is acyl, aryl, or alkyl, the order found has been $I > Br > Cl > F$. Although variations have been observed in this series, unusual orders have generally been explained by side reactions."

Calloway himself found one reaction which was an exception to this rule, namely alkylation by the Friedel and Crafts method, but in acylation by this same method the order of reactivity was normal.

According to one estimate, the alkyl iodides are, as a general rule, about 50 to 100 times more reactive than the corresponding chlorides, with the bromides occupying an intermediate position.

Recent measurements of velocity constants for the reactions of seventeen organic halides with liquid ammonia by Markova and Shatenshtein[112] confirm the greater reactivity of the iodides in this case, while Watt and Otto[113] found that at 0°C. the reaction between ethyl iodide and ammonia started spontaneously about two minutes after mixing of the reactants, was vigorously exothermal, and was complete after about 15 minutes.

The same order appears also to apply to some reactions with metallic salts. According to Henne,[114] iodine is most, and chlorine least, easily replaced in the reactions between metallic fluorides and organic halides to produce organic fluorides. Although he states that side reactions are most prevalent with iodides, "which in consequence have not been used extensively," he goes on later to say that mercurous fluoride converts alkyl iodides readily to alkyl fluorides, and that methyl fluoride was

23

prepared in yields of better than 80% by adding mercurous fluoride to a solution of iodine in an excess of methyl iodide.

It is frequently unnecessary to use the pure iodo compounds to secure the advantage of their reactivity, but the ability of the alkali iodides to react with chloro and bromo compounds to form the corresponding iodo compounds by the exchange reaction described above can be utilized. This is the basis for one of the most important catalytic applications of iodine. The iodo compounds formed react rapidly, usually with the regeneration of the alkali iodide, which then is available for another cycle and accordingly acts as a catalyst. Such reactions are best carried out in acetone solutions, but, as will be seen later, other solvents, such as acetamide, and even none at all, have been used.

Organic Compounds of Polyvalent Iodine

Iodine forms four types of unusual compounds which have no counterparts among those of the other halogens, namely, the iodoso, iodoxy, iodyl, and iodonium compounds. Excellent reviews of the properties and reactions of these substances have been prepared by Willgerodt[115] and Sandin.[116]

The Iodoso Compounds

It was stated earlier that iodine trichloride adds to acetylene to produce chlorovinyl iododichloride. Better known is the fact that when chlorine is passed into a cold solution of iodobenzene in chloroform, the iodine is not replaced, but instead takes up a molecule of chlorine to produce a yellow crystalline solid, $C_6H_5ICl_2$, which is variously called iodobenzene dichloride, phenyliodosochloride or phenyliododichloride.[117]

Many other aryl iodo compounds undergo this reaction. Willgerodt[115] listed about 125 iodoso chlorides prepared in this manner and Nichol and Sandin[118] found that the reaction proceeds so smoothly that they recommended it for the identification of aryl iodo compounds.

Treatment of these substances with alkali[119, 120] yields the corresponding iodoso compounds, which have the general formula RIO, where R is a univalent aryl radical or an unsaturated alkyl radical of pronounced negativity such as chlorovinyl.

Some aryl iodoso derivatives have been prepared by direct oxidation of the corresponding iodo compounds by such reagents as fuming nitric acid, potassium permanganate, ozone, and peracetic acid. Probably the most effective reagent for this purpose is that discovered by Masson and his co-workers,[121] a solution in concentrated sulfuric acid of a mixture of iodine and iodine pentoxide in proportions to form I_2O_3, although its usefulness for the preparation of iodoso compounds appears to be limited to those containing *meta* directing groups, other substances yielding iodonium salts directly.

The iodoso compounds are likely to explode when overheated and therefore should be handled with this in mind. The explosion point of iodosobenzene is given as about $210°C$.

The iodoso compounds may be considered as being derived from the oxide I_2O_3, and, like it, have basic properties. They are weak diacid bases. Fluorides, nitrates, chromates, acetates, and salts of other organic acids have been prepared by reaction with the appropriate acids and even the chlorides have been prepared by this method in addition to those described above.

These salts are all fairly strong oxidizing agents. The fluorides have been used as a fluorinating agent by Bockemueller,[122] who found that the reactions were aided greatly by the presence of hydrogen or silicon fluorides, and also by Garvey and his co-workers.[123] The latter workers also investigated the chlorides as chlorinating agents and found that they yielded the same products as chlorine gas when they reacted, but were less vigorous in their action. Sandin and McCormack[124] and others have shown that iodosobenzene acetate resembles lead tetra-acetate in its reactions as an oxidizing and methylating agent.

In many of the reactions of these substances, the iodo compounds are reformed and can be recycled. An advantage of their use is that no metals are introduced.

Heating of the iododichlorides causes dissociation into the iodo compounds and free chlorine, which tend to react further to produce chloro substitution products, the extent to which this occurs varying with the particular substance. Caldwell and Werner[125] reported that about 27% of the chlorine in iodobenzene dichloride was released as the free halogen, the rest going to form p-chloroiodobenzene and hydrogen chloride, but that, with *ortho* and *para*—nitroiodobenzene dichlorides, the simple dissociation reaction was the only one that took place, all of the chlorine being liberated as the free element. Possibly others would decompose in the same manner if heated at lower pressures.

The Iodoxy Compounds

When iodosobenzene is heated with steam, disproportionation takes place, iodobenzene distills over, and a white solid, iodoxybenzene, remains behind.[126] The same compound can be obtained in a much better yield by oxidizing iodobenzene dichloride with sodium hypochlorite solution.[127]

The iodoxy compounds have the general formula RIO_2, where R is an aryl radical, and may be considered as derivatives of iodine pentoxide. They are powerful oxidizing agents and, like the iodoso compounds, should be handled with care as they explode on heating, the temperature at which this occurs in the case of iodoxybenzene being given as 236-7°C. This substance also explodes on impact.

These substances are sparingly soluble in water but insoluble in less polar solvents. They are amphoteric, but both the acidic and basic properties are weak.

The Iodyl Compounds

Masson and his co-workers[128] found that when a solution of iodoxybenzene in alkali is allowed to stand, half of the iodine is converted to the iodate ion and the remainder to the salt of a compound, $(C_6H_5)_2IOOH$, which they named diphenyliodyl hydroxide. This substance is also amphoteric and its salts with carbonic and acetic acids, which have been isolated, are more stable than those with strong acids, a circumstance which its discoverers attributed to ring formation. It is also an active oxidizing agent and is reduced by sulfur dioxide or iodide ion to diphenyliodonium ion.

26

The Iodonium Salts

These are probably the most interesting of the compounds of poly-valent iodine. They have the general formula R_2IX, where R is an organic radical and X an inorganic or organic anion, and are true salts, the group R_2I being a monovalent cation similar to the quaternary ammonium radicals. There is some doubt about the oxidation state of the iodine in these substances, but they may be considered simply as derivatives of hydrogen iodide, just as the quaternary ammonium salts are derivatives of ammonia. It is true that hydrogen iodide, when dissolved in water, forms one of the strongest acids and, unlike ammonia, shows no basic properties, but, on the basis of the rule that the "onium" cations formed by the elements of the fifth, sixth, and seventh columns of the periodic table contain one more hydrogen or equivalent radical than the highest hydrogen compound formed, the iodonium salts fall in their correct place in the order NR_4^+, SR_3^+, and IR_2^+. Indeed, they are the only known stable members of the last group.

Strangely enough, no stable iodonium compounds containing the comparatively electropositive saturated aliphatic groups, which would be expected to yield the strongest bases, are known. To stabilize the iodonium cations, the groups represented by R in the general formula must be of a more electronegative character, and therefore the most stable and best known derivatives are those with aryl radicals, such as the diphenyliodonium salts, although, as may be expected, some compounds with unsaturated chloro-aliphatic groups have been prepared. The chlorovinyl compounds are the best known of this type.

In spite of this apparent requirement for electronegative groups, the iodonium radicals are very strong bases. Although most of the hydroxides exist only in solution, that of the iodonium radical derived from diphenyl is reported as having been prepared in the solid state.[129] X-ray crystal analysis shows that the iodonium cations exist as such in the solid state. They are taken up by zeolites, just as are any other strong bases.

An unusual characteristic of the iodonium salts is that, instead of resembling those of the alkali metals as do most of the other "onium" salts, they are more nearly like those of the heavy metal thallium. The chlorides, for example, are sparingly soluble in water, while the iodides are almost insoluble and, as usually prepared, have a pronounced yellow color. This situation may account for the nonformation of iodonium amalgams, a fact which has been used as an argument against their strongly basic character. The compounds of the other onium salts with mercury are probably formed with the evolution of large quantities of energy like those of the alkali metals, and are therefore sufficiently stable to exist at least in dilute solution in mercury, while the iodonium-mercury compounds, like those of the heavy metals, are formed with the liberation of much less energy and therefore are not sufficiently stable to preserve the iodonium cation. This idea is supported by the fact that iodonium salts of weak acids, although formed initially, slowly decompose in solution.

Iodonium salts may be made by a number of methods. The classical one is that in which equal molar quantities of an iodoso and an iodoxy

compound are caused to react in the presence of water containing hydroxyl ion to form an iodonium iodate.[130] Sodium hydroxide or moist silver oxide may be used as the source of the hydroxyl ion.

This method is especially suited for the preparation of mixed iodonium compounds by using the iodoxy derivative of one radical and the iodoso derivative of another. In one case, the choice of which radical is to be supplied as the iodoxy compound was found to be a matter of great importance. Sandin and his co-workers[131] obtained a 75% yield of crude phenyl-p-anisyliodonium iodide starting from iodosobenzene and p-iodoxyanisole, but no yield at all from iodoxybenzene and p-iodosoanisole. Whether this can be generalized into the statement that the more electronegative radical must be present as the iodoxy compound has not been determined.

Another method, used by Freidlina and his associates, employs aryltin trichlorides as arylating agents for iodine trichloride and iododichlorides.[132, 133] It is reported that phenyltin trichloride reacts with 2-chlorovinyliodododichloride to give a 31% yield of (2-chlorovinyl) phenyliodonium chloride, and with iodine trichloride, with the evolution of heat, to give a quantitative yield of diphenyliodonium chloride.

By all odds the simplest, cheapest, most rapid, and efficient method for preparing iodonium salts is that developed by Masson and Race[134] in which an aromatic compound is treated with a mixture of iodine and iodine pentoxide, in the proportions to form I_2O_3, in an excess of strong sulfuric acid. It works best with hydrocarbons and those substitution derivatives having *para* directing groups; and when the compounds, such as the hydrocarbons themselves and their halogen derivatives, are sufficiently stable to resist the powerful oxidizing action of the reagent, the corresponding iodonium derivatives are produced in high yields. In all cases studied, where isomers are possible, the *para* derivative is practically the only product. With compounds having *meta* directing groups, the reaction may stop at the iodoso stage, and less stable compounds are likely to yield oxidation products.

There is every reason to believe that this process could be adapted for the large scale, low cost production of iodonium salts if a demand for them should arise.

Salts of many iodonium radicals with different anions have been prepared and studied. These include halides, polyhalides, sulfates, nitrates, chromates, dichromates, carbonates, bicarbonates, fluoborates, cyanides, acetates, oxalates, and salicylates. As stated previously, they generally resemble the thallium salts in their solubilities, but, as may be expected, have characteristics of their own. Some of the triiodides, for example, are stable salts, insoluble in water; other salts, including some of the iodides, are more soluble in alcohol and other organic solvents than in water; and Masson and Race[134] found that an acid sulfate of bis(p-chlorophenyl)iodonium could exist at ordinary temperatures in an oily as well as a crystalline form. There is also evidence that some of the acid sulfates of this radical and others are unusually resistant to hydrolysis and it is believed that a phase rule study of the system bis(p-chlorophenyl)iodonium sulfate-sulfuric acid-water would yield some interesting results.

Substitution reactions can be carried out on the aryl radicals, to

some extent at least, without destruction of the iodonium groups. Sandin and his co-workers, for example, found that both benzene rings in diphenyliodonium nitrate could be nitrated with a mixture of nitric and sulfuric acids, and that the positive iodine was predominantly *meta* directing, but not quite so strongly as in the iodoxy compounds, since about 14-20% of the product was the *para* derivative.[135]

Like all other substances in their class, the iodonium salts decompose on heating. The decomposition temperature varies with the acid strength of the anion, the sulfides and salts of other weak acids tending to decompose at room temperature, while the halides of the more stable radicals must be heated to 200°C. and even higher. These decomposition temperatures, which are usually reported as melting points with decomposition, since the products are usually liquids or liquids and gases, are characteristic of the different salts and may be used for their identification.

The thermal decomposition of iodonium salts has been the subject of many studies. The reactions of the iodides are the simplest, the products usually being the iodo compounds from which the iodonium salts were derived. That of diphenyliodonium iodide has been studied with the help of radioactive iodine as a tracer, and it has been shown that there is no interchange of iodine atoms between the positive valence state in the iodonium radical and the iodide ion even after considerable decomposition has occurred.[136]

Other decompositions are much more complex. In their study of that of phenyl-*p*-anisyliodonium chloride and bromide, Sandin and his co-workers[131] found that by far the major products were *p*-iodoanisole and chloro- or bromobenzene and, on the basis of this and other considerations, they concluded that the iodine tends to remain attached to the more electronegative radical.

The iodonium salts are active arylating agents. Sandin and his co-workers have shown recently that diphenyliodonium chloride reacts with thiol compounds, such as thioglycolic acid and cysteine, to produce the corresponding phenyl derivatives, and also with thiophenol, although in this case the reaction product was not given.[137] They state that these reactions should be of interest from the standpoint of enzyme studies. Still more recently Sandin and Brown[138] reported that, in the presence of sodium hydroxide, diphenyliodonium chloride reacts with pyridine to produce a mixture of phenylpyridines. No reaction took place in the absence of the alkali. According to Sandin, McClure, and Irwin,[139] the diaryliodonium chlorides react in boiling *n*-propanol solutions with mercury and tellurium to yield the corresponding aryl mercury chlorides and diaryltelluriums.

Some of these reactions were confirmed by Makarova and Nesmeyanov,[140] who found diphenyliodonium fluoborate a particularly active phenylating agent; pyridine, trimethylamine, triphenylphosphine, triphenylarsine, triphenylstibine, diphenyl sulfide, and diphenyl selenide being converted to the completely substituted onium compounds. The greater reactivity of the hydroxide, compared to the chloride, is probably due to its lower stability, but, in the case of the fluoborate, the anion may be exerting a catalytic effect, since this substance is very reasonably stable, its decomposition temperature being given as 190°C.

Sandin and Makarova and Nesmeyanov have pointed out the similarity of many of the reactions of iodonium salts to those of diazonium salts.

Heterocyclic Iodine Compounds

It was stated earlier that biphenyleneiodonium hydroxide is the only such compound reported to have been prepared in the solid state. It is also unusual in another respect, as it is one of a group of compounds in which the iodine is present as part of a five-membered heterocyclic ring. No other halogen forms such a structure and, indeed, it is so unique that those compounds in which it exists could properly form a separate class among the derivatives of polyvalent iodine.

In general, the compounds in which this structure exists resemble the other iodonium salts in physical properties and solubilities. Studies[29, 41] have also shown that their mode of decomposition on heating is generally similar in the absence of any catalytic agent, but Lothrop[42] found that, when heated in the presence of cuprous oxide as a catalyst, biphenyleneiodonium iodide and its dimethyl derivatives yield substances which he identified as the very rare hydrocarbon, biphenylene, and its corresponding dimethyl derivatives. Further study would probably disclose other unusual reactions of this class of iodine compounds.

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II

Applications of Iodine and Its Compounds

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Iodine in Organic Chemistry

The very important roles played by iodine and its compounds in the development of synthetic organic chemistry, and their continued widespread use in research laboratories devoted to the development of new processes and products, make it reasonable to predict that they will find many of their most important industrial applications in this field.

Iodine and Its Compounds as Catalysts

The characteristic reactivities of iodine and its compounds have led to their use as catalysts for increasing reaction rates and yields in a wide variety of reactions. In most cases, the concentrations required are so low that the cost of the iodine is small compared to the benefits secured. In others, recovery of the iodine would become desirable even though the amount required is much less than stoichiometric.

The catalytic uses of iodine and its compounds may be classified into ten categories depending on their specific action:

1. Exchange catalysis
2. Halogenation
3. Isomerization
4. Dehydration
5. Acylation
6. Carbon monoxide (and nitric oxide) additions
7. Reactions with oxygen
8. Homogeneous pyrolysis
9. Inhibitor
10. Other Applications.

Exchange Catalysis

The fundamental basis in this case is the ability of inorganic iodides to react with alkyl and acyl compounds of the other halogens to produce the more reactive iodo compounds which can then react with

35

other substances with the formation of the desired end products and the regeneration of the inorganic iodide for use in another cycle.

This principle has been applied to the reactions of alkyl and acyl halides with metals, metallic compounds, amines, and others in which the iodo compounds have been found to be more reactive than those of the other halogens.

Sodium and potassium iodides are generally used although, as will be seen later, others, such as lead iodide, can be employed under special conditions. Acetone is generally the most suitable solvent for this reaction, as the alkali iodides are more soluble in this medium than the other halides, but it is by no means the only one as the reaction has been found to work in acetamide, toluene, and others, and even in the absence of any additional solvent, a liquid reactant adequately serving the purpose. It is usually desirable to avoid the presence of water to prevent undesirable side reactions.

A number of examples taken from recent literature demonstrate the wide applicability of this method.

During their study of the synthesis of cyclopropane, Hass and his associates[1] found that, in the presence of a small amount of iodide, 1,3-dichloropropane, dissolved in a mixture of dibutyl ether and xylene, reacted with magnesium turnings at 140°C. to yield 70% of the theoretical amount of cyclopropane, but that, in the absence of the iodide, a similar mixture failed to react appreciably when heated overnight at 200°C., even when the magnesium was in powder form. The presence of the iodide was shown to be necessary even after the reaction had started, as its removal by metallic copper caused the reaction to stop.

The addition of sodium iodide to a refluxing mixture of zinc dust, ethanol, and 1,3-dichloropropane also markedly increased the rate of production of cyclopropane, but the effect was only temporary owing to the formation of inert zinc iodide. This difficulty could be resolved by adding sodium carbonate to regenerate sodium iodide or by using as a solvent, acetamide, in which the iodide ion retained its activity. A combination of sodium carbonate and acetamide was even more effective and consistently gave yields of pure cyclopropane in excess of 80% of theory within three or four hours, using only a 10% excess of zinc dust and 1/60 mole of iodine.

In a recent patent, Pearsall[2] specifies the use of a small amount of iodine or an iodide as a catalyst for the production of lead tetraalkyls directly from metallic lead and alkyl chlorides. The active substance is lead iodide which reacts with the alkyl chloride to produce the iodide, the latter reacting with metallic lead to yield the tetraalkyl and regenerate the lead iodide. Pearsall states, "Lead iodide is used here as a catalyst because it causes the reaction to take place at commercially attractive rates." No solvent other than the alkyl chloride is specified.

One of the most spectacular demonstrations of the effect of an iodide on the yield of a reaction is that described by Hurd and Perletz[4] in the preparation of phenoxyacetone. Earlier workers had reported yields of this substance of only 16 to 23% from the reaction of chloroacetone and phenol in the presence of an alkali, but the authors found that this was increased to 90 to 95% when an amount of potassium iodide equiv-

alent to a little over 1% of the weight of the reactants was added. Acetone was used as a solvent and it was found that adding the potassium iodide to a solution of the chloroacetone and allowing to stand for some time before adding to the phenol was beneficial.

Potassium iodide had a similar effect on the reaction of beta-naphthol with chloroacetone to produce β-naphthoxyacetone, a yield of 85% being secured compared to 21% reported by previous workers in the absence of the iodide.

Lawson[5] cites two examples in which an amount of sodium iodide equal to less than 1% by weight of the reactants was used to catalyze the reaction between a monochlorinated paraffin wax and potassium stearate to yield the corresponding ester. In one case the reaction was carried out in butyl alcohol, but no solvent was used in the other, the molten reactants apparently being adequate for that purpose.

According to Whitmore and his associates,[6] ethyl-β-bromopropionate reacted with m-chloroaniline in the presence of an amount of sodium iodide equal to one and a half per cent of their combined weights to give an 80% yield of ethyl-β-(m-chloroanilino)propionate with toluene as a solvent. It is of interest that the chlorine on the benzene ring took no part in the reaction.

Huber, Bair, and Laskowski[7] report that 4,7-dichloroquinoline, heated with 2-amino-4-morpholinobutane in the presence of about 0.2% of their weight of sodium iodide, yielded 88% of the theoretical quantity of 7-chloro-4-(1-methyl-3-morpholinopropylamino)quinoline. The chlorine attached to the pyridine nucleus of the quinoline reacted but that attached to the benzene nucleus did not. No special solvent was used.

Exchange catalysis should be applicable to all types of reactions in which iodo compounds are more reactive than the other halides, including acylation by the Friedel and Crafts method and alkylation of acetoacetic esters by halides. Calloway[8] found that the acyl iodides were the most reactive in the former case, and Renfrow and Renfrow[9] concluded that the alkyl iodides reacted faster than the corresponding bromides in the latter and usually gave better yields.

In some cases, the metallic iodides could probably be replaced by those of organic bases to advantage because of their high solubilities in organic solvents, as demonstrated by the general use of quaternary ammonium iodides for the investigation of conductivity and ionization phenomena in such solvents.

Not all cases of catalysis of metal reactions by iodine and its compounds can be attributed to the exchange reaction. It is general practice, for example, to initiate those between magnesium and other halides in the preparation of Grignard reagents by adding a crystal of iodine or a small amount of an iodo compound, while Sanderson[3] states that the same substances are effective catalysts in the preparation of methyl aluminum chloride from methyl chloride and aluminum or its alloys. At first sight it might be thought that the actual catalyst in such cases is iodide ion formed in situ, but the process is more likely an activation of the metal surface, since the addition of iodine is occasionally recommended even in the preparation of Grignard reagents from iodo compounds.

Halogenation

The knowledge that iodine catalyzes halogenations goes back at least to 1902, when Bruner published his extensive data on the iodine-catalyzed bromination of benzene.[10]

According to Groggins,[11] iodine is an excellent chlorination catalyst because of its ability to form iodine monochloride which has a low energy of activation, and he refers to its use in the chlorination of benzene and toluene, stating that it promotes substitution in the nucleus rather than in the side chain.[12] In another place,[13] describing the preparation of chloroacetic acid by the action of chlorine on acetic acid, he gives the composition of the catalyst as one part of iodine, five parts of phosphorus pentachloride, and five parts of red phosphorus in 200 parts of acetic acid.

Among the halogenations in which iodine has been reported to be an effective catalyst in recent years are the chlorination and bromination of aryloxyacetic acids and their homologues in glacial acetic acid;[14] the chlorination and bromination of ethyl cinnamate in carbon tetrachloride solution;[15] and the bromination of phenanthrene,[16,17] in which case it also was found that the iodine strongly inhibited the addition reaction between bromine and phenanthrene. Kinetic studies were made in the two last-mentioned investigations and it was concluded that the iodine monohalides are important factors.

A case in which iodine was found to be effective in a halogenation with a substance other than the free halogens themselves is one step in a new method for the synthesis of dl-lysine, reported by Galat.[18] This utilizes iodine as a catalyst in the chlorination of ε-benzoylaminocaproic acid to the corresponding α-chloro- acid by sulfuryl chloride. It is stated that the new method is simpler than the old one as the sulfuryl chloride reaction takes place at moderate temperatures, evolves no considerable amount of heat, and forms a homogeneous solution, whereas the one it replaced was not only violently exothermic, but formed mixtures of such consistency that efficient stirring was impossible. Furthermore, the new method is cheaper because of higher yields and the use of sulfuryl chloride.

Iodine is also useful as a catalyst in the chlorination of groups other than hydrocarbons. Kharasch and his co-workers[19] used a crystal of iodine as a catalyst in the preparation of 2,4-dinitrobenzenesulfenyl chloride by chlorination of 2,4-dinitrophenyl disulfide.

Isomerization

The ability of iodine to add to unsaturated bonds, together with the resulting instability of the polyiodo derivatives, suggests that it would be an effective catalyst for isomerization reactions. That this is actually the case is demonstrated by two recent series of patents.

According to Hasselstrom, and Hasselstrom and Brennan,[20-22] rosin, tall-oil, and other wood products can be stabilized by heating with 0.1 to 5% of their weight of iodine until molecular rearrangement is effected, and are thereby made more resistant to light, heat, and atmos-

pheric oxidation. It is believed that a stabilized rosin now on the market is produced by this process.

Ralston and Turinsky[23] state that drying or resinifying properties can be conferred upon soya bean, castor, fish, and other oils, and the acids derived therefrom, or these properties improved, by heating in the presence of 0.06 to 0.5% by weight of a large number of iodine compounds, to convert the double bonds to conjugated systems. Among the iodine compounds specified are inorganic covalent iodides, ammonium and substituted ammonium iodides, and alkyl iodides. They appear to be those which would be most likely to have appreciable solubilities in the oils in question.
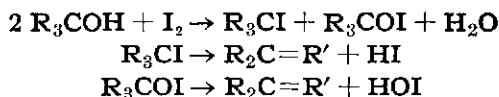
Dehydration

Dehydration consists of the removal of hydrogen and hydroxyl groups from organic compounds to yield unsaturated products and water. Since the water is not present as such in the original compound but is formed as a result of the reaction, the term dehydrohydroxylation would be more descriptive.

The fact that iodine is a catalyst for this reaction has been known for a long time and has been applied in many reactions in the laboratory. It was apparently discovered by Hibbert[24] who made a thorough study of the action of iodine and reported the following conclusions in an excellent paper:

1. Tertiary alcohols can be readily dehydrated.

2. Secondary alcohols are dehydrated only with difficulty.

3. Primary alcohols cannot be dehydrated with iodine.

He also concluded that the mechanism of the reaction is as follows:

$$2 R_3COH + I_2 \rightarrow R_3CI + R_3COI + H_2O$$
$$R_3CI \rightarrow R_2C = R' + HI$$
$$R_3COI \rightarrow R_2C = R' + HOI$$

and finally

$$HI + HOI \rightarrow I_2 + H_2O$$
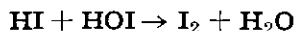
where R may be any saturated group and R' an unsaturated group formed from R by loss of hydrogen.

Later workers do not appear to have disputed this mechanism and it is in accord with the known instability of tertiary iodides and the comparatively high stability of the corresponding hypohalites.

Whitmore and co-workers[25] made detailed studies of the action of iodine on trialkyl carbinols up to and including the triamyl series. Nazarov[26-29] also made important contributions. In unsymmetrical carbinols, it was found that the direction of dehydration is governed by the relative ease with which hydrogen can be removed from the alpha carbon atoms of the three alkyl groups concerned. The ethyl group gives up hydrogen most readily, followed in order by n-propyl, n-butyl, n-amyl, and methyl. Introduction of branching in the alkyl groups complicates these reactions to some extent; a secondary alkyl group furnishes hydrogen about as readily as methyl but tertiary alkyl

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groups are much more resistant. In many reactions, of course, more than one isomer is produced.

Mosher[30] studied the dehydration of tertiary alcohols containing the cyclohexyl ring with iodine and found that 1-methylcyclohexanol yielded only 1-methylcyclohexene, but that, as the alkyl groups became larger, there was an increasing tendency for the formation of cyclohexylalkenes. He concluded that dehydration takes place in such a manner that the double bond enters the ring whenever possible, and that the cyclohexyl radical loses hydrogen more readily than methyl, ethyl, or isopropyl. Bogert and his associates[31] reported an 88% yield of 1-β-phenylethyl-1-cyclohexene from the corresponding tertiary cyclohexanol.

The presence of other groups affects the facility with which the reaction takes place. There are indications, for example, that carbonyl, aldehyde, and carboxy groups permit dehydration of secondary and even primary alcohols in the presence of iodine, while Campbell and Campbell[32] found that the dimethylamino group prevented the reaction unless a chain of at least four carbon atoms intervened between it and the carbon carrying the hydroxyl group.

The amount of iodine required is usually small, but varies with the substance being treated. Hibbert found that diacetone alcohol required only 0.01% of its weight of iodine to yield 97.8% of mesityl oxide, but used 0.23% with pinacol and dimethylethylcarbinol, and 1.9% with cyclohexanol; while Mosher used 0.25 and 0.5% in his experiments. Other workers state merely that they used "a trace" or a "crystal" in their laboratory work. Whitmore and his co-workers[25] reported that the reaction is helped sometimes by increasing the pressure with low-boiling alcohols and by reducing it with those of higher boiling points.

Many interesting compounds have been prepared by this method. In addition to mesityl oxide from diacetone alcohol, Hibbert prepared crotonaldehyde from aldol, dimethylbutadiene from pinacol, and a number of others. Whitmore and his co-workers[33-37] and Nazarov[26-29] prepared a number of unsaturated hydrocarbons.

More recently, Howard and his co-workers[38] reported that heating 2,2,3,4,4-pentamethyl-3-pentanol with one per cent of its weight of iodine yielded equal parts of the two isomeric decenes, the total yield being 78% of theoretical.

A recent patent to Morey[39] discloses a method by which the dehydration of aliphatic dihydric alcohols or diols containing a single tertiary hydroxyl group can be made to yield the intermediate unsaturated monohydric alcohol instead of going directly to the unsaturated hydrocarbon. This is accomplished by adding a controlled amount of water to the diol before the dehydration is started and by continuously returning the water produced to the reaction vessel during the operation. As may be expected from Hibbert's conclusions, the tertiary hydroxyl group is eliminated first.

Iodine can also catalyze other reactions in which hydrogen and hydroxyl are eliminated as water, possibly by the same mechanism. Its well-known ability to catalyze the alkylation of aromatic amines by aliphatic alcohols is an example.

40

Acylation

On the basis of an earlier report that acetyl iodide reacted with thiophene to yield a small amount of 2-acetylthiophene, Hartough and Kosak[40] tried the reaction between acetyl chloride and thiophene in the presence of "catalytic amounts of iodine" and obtained a 16% yield of this substance. Substituting acetic anhydride for the acetyl chloride, they secured yields as high as 86% of 2-acetylthiophene with 0.008 mole of iodine per mole of acetic anhydride as a catalyst. Even 0.00007 mole of iodine yielded traces, while with 0.04 mole the reaction was uncontrollably rapid. The reaction could be carried out at temperatures as low as −30°C., but not below, as iodine became insoluble in the acylating mixture.

Furan was also acetylated, a 60% yield of 2-acetylfuran being obtained with 0.0004 mole of iodine per mole of anhydride. One tenth this quantity of iodine had no catalytic effect in this case, while larger amounts gave reduced yields. Hydrogen iodide was even better than iodine as a catalyst for this reaction, as 0.01 mole per mole of anhydride resulted in a yield of 76%. The reaction was so rapid that a dry ice bath was necessary to keep it under control, and it was thought that a smaller quantity of catalyst could be used to advantage.

In general, it was found that aliphatic acyl chlorides gave poorer results than the corresponding anhydrides. On the other hand, benzoyl chloride yielded 90% of 2-benzoylthiophene in the presence of iodine as a catalyst. The powerful catalytic effect of iodine was demonstrated in this case also as the uncatalyzed reaction yielded only about 1% of product per hour.

The catalytic effect of iodine has been confirmed and the scope of this reaction extended by other workers. Bruson and Riener[41] used hydrogen iodide as a catalyst in the preparation of 2-propionylfuran and 2-butyrylfuran from the corresponding anhydrides and furan, while Kipnis and Ornfelt,[42] in the preparation of 2-acetylfuran, found it desirable to add the hydriodic acid catalyst at −10°C. instead of at 0° to aid in the control of the subsequent exothermic reaction. Benkeser and Currie[43] found that it was applicable to organosilicon compounds containing the thiophene and furan rings, as they were able to acetylate 5-trimethylsilylthiophene and 5-trimethylsilylfuran with acetic anhydride in the presence of a small amount of iodine as a catalyst.

Some of the more active derivatives of benzene can also be acylated by this method. Chodroff and Klein[44] showed that acetic anhydride and benzoyl chloride react with anisole and acetanilide to form p-acetylanisole, p-benzoylanisole and p-acetylaniline in the presence of iodine as a catalyst. The reactions, unlike those with furan and thiophene, are not exothermic, and require higher temperatures and longer times. Greater concentrations of the iodine catalyst are also generally needed for optimum yields; in the case of the reaction between naphthalene and benzoyl chloride, for example, the yield of α-phenyl naphthyl ketone rose from 15 to 52% when the iodine concentration was increased from 0.021 to 0.076 mole per mole of reactants.

Carbon Monoxide (and Nitric Oxide) Additions

There is considerable interest at the present time in the introduction of carbonyl groups into organic compounds by the direct addition of carbon monoxide. Iodine should be an effective catalyst for such reactions, in combination with one of the transition metals, since it accelerates the reaction of carbon monoxide with these metals to form carbonyls, and their iodides readily form addition complexes of the type $Fe(CO)_4I_2$.

Nickel iodide was used as a catalyst in a German process for the preparation of adipic acid, one of the constituents of Nylon, by reaction of carbon monoxide with tetrahydrofuran at 270°C. and 200 atmospheres pressure.[45] This salt was also used, in combination with metallic nickel, for the preparation of acrylic esters and amides from acetylene, carbon monoxide, and alcohols or amines.[46]

The iodides of the transition metals also form complexes with nitric oxide, suggesting that they may be effective catalysts for the addition of this substance to organic compounds.

Reactions with Oxygen

That iodine and its compounds have a marked effect on reactions involving oxygen has been known for a long time. In 1898, Centnerszwer[47] reported that methyl, ethyl, and allyl iodides and iodobenzene were by far the most effective of a large number of organic compounds in reducing the upper pressure limit of oxygen at which the luminescence of yellow phosphorus appeared. Later, Tanaka and Nagai[48] and Nagai[49] found that the alkyl iodides narrowed the composition ranges of mixtures of hydrogen and air, and ethyl ether and air in which ignition could take place, and that mixtures of methyl or ethyl iodides with air in any proportions would not propagate flames. Still later, Payman[50] reported that two parts of ethyl iodide in a thousand parts of a methane-air mixture raised the ignition temperature from 634° to 759°C. During the discussion of this paper Dixon stated that iodine is as effective as ethyl iodide.

It is well known that iodine was the first substance found by Midgely and his co-workers to have anti-knock properties. The experiments with iodine showed that the phenomenon was chemical rather than physical in nature, a fact which ultimately led to the discovery of tetraethyl lead.

Another very interesting series of observations was made by Jorissen,[51] who studied the effect of coating the walls of a reaction vessel with alkali halides on the temperature at which formation of carbon dioxide first became apparent in a mixture of methane and oxygen. These salts were found to be increasingly effective in raising this temperature in the order lithium, sodium, potassium, rubidium, and also fluorine, chlorine, bromine, and iodine, lithium fluoride giving an appreciable reaction at 190°C., while potassium iodide required 540°.

Jorissen also studied the effectiveness of these substances and others in the form of powders on the explosive reaction between methane and oxygen and found that, among the alkali halides, their effectiveness

was exactly the reverse of that given, lithium fluoride requiring the smallest quantity to prevent explosion and potassium iodide the largest.

The high temperature required for the formation of carbon dioxide in the presence of potassium iodide found by Jorissen suggests that, rather than preventing the oxidation of methane, the iodides caused it to take place in stages in which methanol and other intermediate oxidation products were formed; and that iodides should be studied as catalysts for the preparation of such partially oxidized compounds directly from hydrocarbons. This idea receives support from a recent patent to Harman[52] which claims that the addition to a benzene-air mixture of an amount of iodine vapor equal to 0.005 to 0.5% of the volume of the benzene vapor considerably increases the yield of phenol.

Another application of these phenomena is given in a patent to Claussen,[53] which states that the addition of 0.001 to 0.1 volume percent of iodine to the gases used for burning out carbon from petroleum catalysts favors the formation of carbon monoxide rather than the dioxide, with the result that considerably less heat is generated in the catalyst and danger of fusion due to excessive temperatures is avoided.

Homogeneous Pyrolysis

Glass and Hinshelwood,[54] in their study of the thermal decomposition of gaseous diisopropyl ether, found that it took place with measurable velocities at temperatures between 500° and 570°C., yielding carbon monoxide, methane, ethylene, and carbon. However, one sample decomposed rapidly to acetone and propane at 400°C. Investigation disclosed that this contained a small amount of isopropyl iodide, from which the ether had been made, and that this substance was an active catalyst for the reaction.

Subsequent studies by Hinshelwood and his co-workers[55-61] showed that the decompositions of several ethers, acetaldehyde, methyl formate and acetate, and some amines were also catalyzed, but those of formic and acetic acids and ethyl halides were not; that methyl and ethyl iodides were also effective catalysts; that iodine was the real catalyst; and that bromides were less effective and chlorides relatively ineffective. It was also found that the mechanism of the reaction involves the catalysis by iodine of the transfer of hydrogen from the carbon attached to the oxygen to a neighboring one.

On the basis of experiments with isopropyl iodide as a catalyst, Bairstow and Hinshelwood[60] concluded that iodine does not catalyze the decomposition of ketones. Gantz and Walters[62] found, however, that elemental iodine had a very marked effect on the reaction rate, increasing it as much as ten times at the optimum concentration ratio; that methyl iodide was equally effective and ethyl iodide less so; but, in agreement with Bairstow and Hinshelwood, that isopropyl iodide had practically no effect, a condition which was shown to be due to an inhibiting action on the iodine by the propylene liberated by decomposition of the iodide. Iodine also catalyzed the decomposition of methylethyl ketone, diethyl ketone, biacetyl, dioxane and tetrahydrofuran.

43

This type of catalytic action of iodine should be useful in hydrocarbon syntheses from oxygen-containing materials where it is desired to prevent the formation of oxy compounds.

Iodine as an Inhibitor

That iodine, like other catalysts, can sometimes act as a negative catalyst or inhibitor is brought out by two recent patents. Hansley[63] states that a serious obstacle to the more general utilization of cyanhydrins in chemical syntheses and as solvents is a pronounced tendency to decompose during storage or upon heating to a temperature necessary for distillation even under reduced pressure. He found that this could be greatly reduced by adding a small amount of iodine, usually from 0.001 to 1.0% of the weight of the cyanhydrin, but even traces were effective in some cases. Among other examples, he states that formaldehyde cyanhydrin containing 0.1% iodine was distilled under vacuum with substantially no decomposition, whereas in the absence of the iodine decomposition was substantially complete under the same conditions.

According to Stevens,[64] iodine is an effective preservative for organic peroxides and other liquid compounds containing peroxy oxygen. The iodine is preferably added in amounts up to 1% by weight and its use is particularly advantageous in that it does not impair the utility of the compounds. In an example showing the effect of iodine, it is stated that about one pound of isopropyl percarbonate containing 4 grams of iodine (about 1%) was allowed to stand for 10 days at room temperature without appreciable sign of decomposition, while a 10 gram sample decomposed in 12 minutes with a rapid evolution of gas when iodine was absent.

The stabilizing effect of iodine on peroxides also applies to their reactions with other substances. Perret and Perrot[65] report that benzoyl peroxide reacts with unsaturated aliphatic hydrocarbons in carbon tetrachloride to form many compounds, including some by reaction with the solvent. Upon addition of iodine, however, the reaction is normalized by elimination of almost all side reactions and the formation chiefly of diol benzoates.

Other Applications

Iodine has been found to be a very effective catalyst for many reactions which do not fall into any of the foregoing categories.

According to Gordon,[66] a mixture of tin oxalate and iodine was used as a catalyst for the large-scale liquid phase hydrogenation of coal, heavy oil and creosote oil at the coal hydrogenation plant at Billingham, England. A table summarizing the results of the operation shows that the treatment of the last-named substance with 4.7% of its weight of hydrogen in the presence of 0.02% iodine and 0.01% tin oxalate resulted in a yield of 11.2% as refined gasoline, 70.7% as middle oil boiling between 170° and 320° C., and 17% of hydrocarbon gas. It was thought that improved results could have been secured by using cor-

rosion resistant equipment and installing an iodine recovery system so that an increased concentration could be used.

Belokrinitskii reports[67] that iodine is a catalyst for the reaction between diphenylamine and sulfur to produce phenothiazine. In its absence the reaction mixture had to be heated for 160 minutes at 240° to 280°C. to produce a 50% yield. Addition of an amount of iodine equivalent to 1% of the weight of amine, however, gave a practically quantitative yield in 11 minutes at 190° to 200°C., with the theoretical amount, or a slight excess, of sulfur.

According to Tyurenkova,[68] the reactions in the last stage of the process for the preparation of thiuram are strongly catalyzed by small amounts of potassium iodide. In this operation, dimethyl dithiocarbamate is oxidized by a mixture of sodium nitrite and sulfuric acid. Under laboratory conditions, it was found that the addition of 0.05 mole of potassium iodide per mole of product resulted in an increase in yield from 80% to practically quantitative and reduced the reaction time from 2 to 2.5 hours to 10-15 minutes.

A very interesting example of the catalytic action of iodine is described by Hewitt and West in a British patent.[69] They state that, in the preparation of quinoline from aniline and glycerol in concentrated sulfuric acid by the Skraup synthesis, nitrobenzene and arsenic acid are unsatisfactory as oxidizing agents because of operating difficulties and poor yields, especially when based on the glycerol used. The addition of about one or two per cent of iodine, or an iodine compound such as potassium iodide or iodoform, to the reaction mixture, however, makes such oxidizing agents unnecessary and results in improved yields and simpler operation. The method is also applicable to the preparation of derivatives of quinoline, and that of 8-hydroxyquinoline from o-aminophenol is described.

The effect of the iodine may be partly due to its catalysis of the dehydration of the glycerol to acrolein, but its principal function is to increase the activity of strong sulfuric acid as an oxidizing agent, since sulfur dioxide is one of the reaction products. Knowing that hydrogen iodide reacts with concentrated sulfuric acid to yield sulfur dioxide and free iodine, the action of the iodine can be explained by formulating the reaction in two steps:

$$C_6H_5NH_2 + C_3H_5(OH)_3 + I_2 \rightarrow C_9H_7N + 3\,H_2O + 2\,HI$$
$$2\,HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2\,H_2O$$
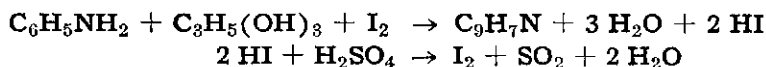
If this viewpoint is correct, there are probably many other reactions in which concentrated sulfuric acid could be used as a cheap and efficient oxidizing agent in the presence of iodine as a catalyst.

In a recent patent, Bowman[70] recommends a synthetic mixture of metallic magnesium and magnesium iodide as a dehydrohalogenation catalyst. Coupling also takes place. Among the reactions for which this catalyst is recommended are the conversion of benzyl chloride to stilbene, the formation of styrene from a mixture of methyl and benzyl chlorides, of butadiene from methyl chloride and ethylene dichloride, and maleic acid from chloroacetic acid.

Karrman[71] found that 3-retenol reacts briskly with some aromatic

amines in the presence of a small amount of iodine to form good yields of arylated aminoretenes, of interest to dye chemists and with possibilities as inhibitors for rubber and oils, and other applications. A mixture of 3-retenol and aniline, containing 0.3% iodine, gave a 95% yield of 3-phenylaminoretene when heated in a sealed tube for six hours at 250°C.

Lasher,[72] in a patent, states that 0.5% or less of iodine chlorides and bromide, added to drying oils, such as linseed oil, reduces the bodying time about one half.

Many other examples of the use of iodine and its compounds as catalysts could be cited, but it is believed that the foregoing will serve to demonstrate their wide applicability.

Iodine and Its Compounds as Process Reagents

There are many applications in which the advantages of the reactivities and other properties of iodine and its compounds can be secured by utilizing them cyclically as process reagents. Such applications, in order to be economical, may require the development of methods for the cheap and efficient recovery and recirculation of the iodine.

Separation and Refining Processes

The ability of iodine to combine with compounds having unsaturated bonds to form unstable derivatives of relatively low volatility has been utilized by Horeczy and Wadley[73,74] in a process to separate the lower olefins from saturated hydrocarbons and from each other. The gases are brought into contact with a solution of iodine in a solvent for aliphatic compounds, such as toluene, xylene, or carbon disulfide, to dissolve the olefins as their diiodo derivatives, while the saturated hydrocarbons are unaffected and pass on. The resulting solution is transferred to stripping equipment, where decomposition is effected in stages to separate the individual olefins. It was found that the separation of propylene from ethylene was aided by the ability of the former to react more rapidly and at a lower temperature with iodine than the other, as well as by the lower dissociation temperature of diiodopropane.

This principle should be of fairly wide applicability as advantage could be taken, not only of differences of stability and volatility, but also of solubility in such a process as countercurrent extraction. It could also be used to cause olefins to react with other substances, such as metallic salts of organic acids, to form the corresponding esters. In such cases, of course, the iodine would be converted to the metallic iodide.

Borglin[75] utilized the ability of sodium iodide to react with organic compounds by the exchange reaction to remove undesirable odor-producing compounds from organic thiocyanates. He extracted a solution of hexyl isothiocyanate in petroleum ether with one of the iodide in ethyl alcohol, and reported that after the petroleum ether had been separated by distillation, the treated isothiocyanate had a desirable odor in contrast to the undesirable one before treatment.

Wurtz, Grignard and other Reactions

The general opinion in the literature seems to be that, although complications sometimes enter because of side reactions, the Wurtz, Williamson, Grignard, and Ullmann reactions take place more readily with iodo compounds than with the other halides. Ziegler and his co-workers[76] state, for example, that in the preparation of long chain polymethylene dihalides up to C_{40} by the Wurtz synthesis, the iodides gave much better yields and purer products than the bromo compounds.

An interesting case in which the Grignard reaction took a different course when an iodide was employed was discovered by Fuson and Corse.[77] They found that when 2,4-trimethyl- or triethylbenzoyl chloride was added to an ether solution of methyl magnesium iodide, only the monoketone was formed. However, when the order of addition was reversed, the reaction produced a mixture consisting of 35% of the expected ketone and 38% of the substituted benzil.

Kharasch and his associates[78] studied this reaction further and found that no benzil was formed by methyl magnesium bromide, except in the presence of cobalt chloride as a catalyst, when a yield of 35% of the ketone and 31% of the benzil, plus some tar, was secured. Under the same conditions, the iodide gave 17% of the ketone and 63% of the benzil.

Rubber Treatment

The lower alkyl iodides can convert rubber to new and interesting products, and they can also serve as reclaim agents by removing the sulfur from vulcanized material. According to two patents,[79,80] these substances react with vulcanized and unvulcanized rubber at high temperatures to yield, first, a thermoplastic balata-like material, and, on continued action, one resembling shellac. With vulcanized rubber, up to 80 to 90% of the sulfur can be removed as thioethers or sulfonium compounds.

Later Selker and Kemp[81] reported that methyl iodide can differentiate between mercaptan, sulfide, and disulfide sulfur in anhydrous systems and they employed it[82] to study the manner in which sulfur was tied up in various vulcanized rubbers. In the course of this work, they found that up to 100% of the sulfur could be removed under the proper conditions. This process was aided by the presence of mercuric iodide or precipitated silver, which also delayed the conversion of the rubber into a thermoplastic resinlike material sufficiently to permit the recovery of elastic desulfurized products. Several samples of such materials were revulcanized; one, in which the sulfur had been reduced from about 1.5 to 0.2% by heating with methyl iodide for three hours at 100°C. in the presence of mercuric iodide, yielding a product in which hand tests indicated about 800 to 900 pounds per square inch at about 300% elongation.

The compounds of iodine can also be applied to advantage in the preparation of synthetic rubbers or elastomers, according to Vincent in a recent patent.[83] He states that iodoform, carbon tetraiodide, and other substances containing the $-CI_3$ group, when added as modifiers

in the polymerization of dienes, such as butadiene and chloroprene, yield products superior in such properties as workability, storage stability, and resistance to heat aging, to those obtained when sulfur compounds are used; and which are free from undesirable odor and other objectionable properties of the others. Furthermore, it is claimed that products free from metallic salts can be produced and smaller amounts of accelerators used, since the iodo compounds have much less retarding effect upon polymerization than other modifying agents.

Replacement by Other Radicals

Priestley and Hurd[84] utilized the ease of replacement of iodine by other radicals to prepare the nitro derivatives of aceto-2-thiophenamide by treating the iodo compounds with a mixture of nitric and sulfuric acids. They found that iodine was more readily replaced than bromine and were actually able to prepare the trinitro compound from 2-acetamido-3,4,5-triiodothiophene even though it could not be made by direct nitration of aceto-2-thiophenamide.

Selective Reactivity

Heitz and Livak[85] took advantage of the ability of iodine monochloride and monobromide to add to olefins and the relative inertness of alkyl iodine in the Friedel-Crafts reaction to devise a method for making alkaryl iodides and the corresponding alcohols. The olefins are caused to react with the iodine halides to produce a haloiodide which is then condensed with aromatic compounds in the presence of aluminum chloride to form the corresponding beta-arylalkyl iodides, which may be utilized as such or the iodine hydrolyzed off to form the alcohol.

Periodic Acid Oxidation

Periodic acid oxidation is another process utilizing an iodine compound which offers considerable promise of yielding products of commercial value. In this connection, Jackson[86] states, ". . . many compounds have been prepared for the first time by this method; some of them are available at the present time only through this type of oxidation. The reaction also has provided an improved method for the preparation of some compounds that usually have been obtained in other ways. An advantage in most periodic acid oxidations is the absence of side reactions and the consequent high yield."

One of the most interesting products of this reaction is that yielded by cellulose, which, if cotton is the starting material, can be recovered as a soft, cottony product by proper treatment. The secondary alcohol groups in the cellulose units are converted to aldehyde groups; and it may be possible, under the proper conditions, to condense these with phenols, amines, and other substances to produce polymers combining the properties of cellulose and the synthetic plastics.

In his statement, part of which was quoted above, Jackson goes on to say, "A disadvantage for large-scale operation is the relative expense of the reagent." This would be true only if the periodic acid were used once and then discarded; it would not be the case if its reduction

product, iodic acid, could be recovered and reoxidized efficiently. Under such conditions, the actual material consumed would be oxygen, the periodic acid acting as a carrier to deliver it to the compound to be oxidized under the proper conditions of reactivity and oxidation potential.

It should be readily possible to accomplish this. There are a number of ways of separating iodates from solution, one being the formation of the double salt, $NaIO_3 \cdot 4Na_2SO_4$, discovered by Foote and Vance,[87] while Willard and Ralston[88] have shown that iodine can be readily oxidized electrolytically to iodic acid, and iodic acid to periodic acid, with fair current efficiencies, the former at a platinum and the latter at a lead peroxide anode, processes already in commercial use.[89]

In many cases, such as when the organic reaction product is insoluble, or, better still, when this is true for both the raw material and the product, it may be unnecessary to separate the iodic acid at all, or at worst, separate it only from that part of the solution which must be discarded to avoid accumulation of impurities in the system. Under such conditions the main body or all of the solution, after removal of the product, would go to an electrolytic cell where the iodic acid would be reoxidized for use in another cycle. Indeed, if the periodic acid oxidation is sufficiently rapid, it may be possible to carry it out in the electrolytic cell itself, the iodic acid acting as a carrier of oxygen from the electrode to the material to be oxidized.

Such ideas are by no means new as they are merely adaptations of two old German processes for the electrolytic production of anthraquinone from anthracene.[70] In one of these a solution of chromic and sulfuric acids was used as the oxidizing agent, and in the other a solution of ceric sulfate and sulfuric acid. The reaction of chromic acid with the anthracene was slow compared to the electrolytic reoxidation of the chromic sulfate, so it was economical to use two separate units, a large tank for the former reaction and a small cell for the latter. The ceric sulfate, on the other hand, reacted so rapidly with the anthracene that the latter could be added directly to the cell and, if added at the proper rate, prevented the appearance of any appreciable amounts of ceric sulfate.

Products with Valuable Properties
Because of Their Iodine Content

Iodine, being a separate and distinct chemical element, can be expected to confer unusual and, in many cases, valuable properties upon substances of which it is an essential constituent.

Iodine in Plastics

A search of the literature made a number of years ago failed to disclose a single instance in which iodine had been used as an essential constituent of a synthetic resin. Considering the use of such relatively rare elements as beryllium, columbium, silver and gold in alloys, that other great class of materials valued primarily for their physical properties, this situation was surprising. There are, of course, good reasons

49

for it, one being the relative newness of synthetic resins, and another the extreme importance of structure as evidenced by the fact that nearly all of the plastics on the market today, with their wide range of physical properties, are derivatives of the five elements, carbon, hydrogen, oxygen, nitrogen, and chlorine.

However, interest in the effects of other elements is increasing as evidenced by the current attention to fluorine and silicon. Iodine is beginning to share in this trend. Rochow[91] mentioned an iodophenyl-silicone, stating that it can be polymerized to a brown resin; while Walling and his co-workers prepared and polymerized p-iodostyrene to a glassy light yellow product[92] and also copolymerized it with styrene and methyl methacrylate.[93]

It can be said with a reasonable degree of assurance that the substitution of iodine for hydrogen or chlorine in the present types of polymer will increase the specific gravity, index of refraction, and opacity to x-rays. Of even greater importance is the strong probability that it will also raise the softening point since the carbon-iodine bond is covalent. Walling and his co-workers reported a melting point of 44-44.5°C. for p-iodostyrene, compared to about $-10°$ for p-chloro-styrene and $-30.7°$ for styrene itself. The effects on other properties cannot be predicted but they could be very marked.

Iodine would probably exert its most unusual effect if it could be incorporated in one of its positive oxidation states. The iodonium salts are by far the most promising from this point of view. They are unique in containing the carbon-iodine-carbon linkage and could be used either to introduce this linkage alone with derivatives of the simple diphenyl-iodonium type or in parallel with a carbon-carbon bond with those derived from biphenyl and containing the heterocyclic iodine ring.

They would also introduce an ionic bond, the third of the iodine, but this might indeed be an advantage, considering that one of the most important plastics, glass, consists of alkali and alkaline earth ions embedded in silica chains. In this connection, it is of interest to note that the relative insolubility of their halides indicates that iodonium cations have little affinity for water.

Anion exchange resins containing iodonium radicals should be very interesting as the characteristic halide insolubility may give them a special affinity for such ions, even in the presence of large concentrations of sulfate and other polyvalent ions, while their strongly basic character would make them effective with weak as well as strong acids.

Iodine in Physiologically Active Substances

The necessity for a continuous supply of iodine to maintain health in human beings and the higher animals, the relatively minute amount required to fulfill that demand, and its widespread use in human and veterinary medicine, establish it as one of the most potent elements physiologically and suggest that some of its compounds should be unusually effective as rodenticides, insecticides, and plant growth inhibitors and stimulants.

There is much evidence in favor of this proposition. A review of the

literature on the use of organic iodine compounds against insects, fungi, and bacteria, compiled by C. V. Bowen of the United States Department of Agriculture and issued early in 1944,[94] lists 294 organic iodine compounds of which 112 were tested as insecticides or fungicides. Practically all of these were toxic to at least some degree.

More recently, the compound, 2-iodo-3-nitrobenzoic acid, has been shown to have plant growth inhibiting properties comparable to those of 2,4-D, and, when made from radioactive iodine, has been used to trace the course of this type of chemical through a plant system.[95] Swingle and his co-workers[96] studied the toxic effects of 883 organic compounds, including 34 containing iodine, on one or more of 20 species of insects, most of them leaf-feeding, and classified them on the basis of their toxicity. Of the iodine compounds, three were placed among the 25 selected as most toxic, 16 were among the 169 others found toxic to one or more of the species, while only 15 were included in the total of 689 found to be nontoxic. It will be seen that although only 22% of the total number of compounds tested were found to be toxic, 56% of those containing iodine were in this group.

The iodonium salts should be of particular interest in this field because of their resemblance to the highly toxic thallium salts and also because Sandin and his co-workers[97] have shown that they react with thiol compounds, some of which are essential to the growth of microorganisms. The high physiological activity of basic heterocyclic nitrogen compounds suggests that the iodonium derivatives of biphenyl containing the five membered heterocyclic iodine ring are worthy of special attention.

Dyes and Other Coloring Matters

Erythrosin and the other dyestuffs containing iodine now commercially available do not exhaust the possibilities of iodine in this field by any means. Many years ago it was discovered that addition of iodine to an alkaline solution of phenol resulted in the formation of a red substance which received the name of Lautemann's red. Hunter and Woollett[98] prepared it in fair quantities, studied some of its properties, and drew conclusions regarding its structure. They described it as a deep purple powder, insoluble in all aqueous solutions, alcohol, and ligroin, but soluble in carbon disulfide, ethylene bromide, and bromoform. It is very inert chemically, being unacted upon by acids, alkalies, or ordinary oxidizing agents, but is reduced by strong reducing agents, such as tin or zinc and hydrochloric acid, to a colorless product from which it can be regenerated by reoxidation with manganese or lead dioxide.

Study of its constitution led to the conclusion that it is a resinoid polymer of the composition $(C_6H_2I_2O)_n$ and that it has a linear polyquinoid structure of the type $=C_6H_2I_2=O=C_6H_2I_2=O=$, the double bonds being in the 1,4, and the iodines in the 2,6 positions on the quinone rings.

Some years later Woollett and his co-workers[99] found that 3,5,3′,5′-tetraiodo-4,4′-dihydroxydiphenyl, when oxidized by chromic acid in ethyl acetate solution, gave green crystals with a metallic luster and

for it, one being the relative newness of synthetic resins, and another the extreme importance of structure as evidenced by the fact that nearly all of the plastics on the market today, with their wide range of physical properties, are derivatives of the five elements, carbon, hydrogen, oxygen, nitrogen, and chlorine.

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a red streak. They could find no satisfactory solvent for this substance and reported that it could be reduced and reoxidized an indefinite number of times.

The intense color of these substances and their relative chemical inertness suggest that they may be useful as pigments. There is also the probability that other iodinated phenol derivatives will yield equally stable compounds with different colors.

Other Possibilities

Many iodonium compounds have been made much more readily available by the simple and efficient method of preparation developed by Masson and his co-workers,[100,101] in which they are produced directly in high yields from the aromatic hydrocarbons or their derivatives by treatment with a mixture of iodine and iodine pentoxide in concentrated sulfuric acid.

This fact should greatly stimulate interest in the properties of these unusual substances. They offer possibilities for new basic dyestuffs, detergents, flotation reagents, and other surface active agents, and other products similar to those derived from nitrogen bases.

According to Blanksma and his co-workers,[102] 2-amino-4-nitroiodobenzene is 1250 times as sweet as sucrose.

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Iodine in Inorganic Chemistry

A number of potential applications of iodine in inorganic chemistry will be discussed in connection with its use in metallurgy. However, there are three of considerable interest which cannot be so classified.

Preparation of Finely Divided Oxides

There is very definite evidence in the literature that the volatile iodides of the elements in the third, fourth, and fifth columns of the periodic table are combustible in air. In Vanino's handbook,[1] for example, it is stated that the vapor of aluminum iodide forms an explosive mixture with air and burns with an orange red flame, while Mellor,[2] in discussing titanium tetraiodide, states, "The solid fumes in air, and it is combustible, burning to iodine and titanium dioxide." These observations are supported by thermochemical data which indicate that the combustion of a mole of stannic iodide vapor to stannic oxide and iodine vapor should liberate about 80,000 calories.

These facts could serve as the basis for a very interesting process for the production of the oxides of these elements in a very finely divided state by forming the iodide, burning it in the vapor state, and collecting the finely divided oxide for use and the iodine for recirculation. Such oxides, like French process zinc oxide, lampblack, and other materials which are separated from the gaseous state, would probably have properties sufficiently different from those prepared by other methods to give them special fields of application at premium prices.

Causticization

The sodium paraperiodates seem to have definite possibilities as reagents for causticizing soda ash and even salts of stronger acids which yield volatile nonmetallic oxides upon decomposition at high temperatures. This statement is based on the following facts:

1. Normal sodium paraperiodate, Na_5IO_6, is thermodynamically stable with respect to its constituents up to temperatures of 800°C. and over.[3] The sodium atoms are rather tightly held as this salt is formed from sodium metaperiodate, $NaIO_4$, and sodium oxide with the evolution of a large amount of heat.

2. Normal sodium paraperiodate is hydrolyzed by water to caustic soda and either disodium or trisodium paraperiodate.[3,4]

3. Trisodium paraperiodate is sparingly soluble in dilute caustic soda solutions, and is practically insoluble in those containing 20% NaOH or more.[4] It is the stable solid phase at sodium hydroxide concentrations up to at least 30.75%, the highest investigated.

The process visualized is similar to the old Löwig process for causticization of soda ash with the periodate replacing ferric oxide. The salt to be causticized would be mixed with the trisodium paraperiodate, the

mixture heated to a temperature sufficiently high to drive off water vapor and the volatile nonmetallic oxide, and the reaction mass cooled and hydrolyzed with water to yield a solution of caustic soda and solid trisodium paraperiodate which would be recirculated.

Such a process, like that of Löwig, would have the advantage over the lime process of yielding much stronger caustic solutions. On the basis of the available data, 30% caustic soda solutions are definitely attainable with even higher concentrations possible. The periodate has the advantage over ferric oxide of being colorless and therefore would not discolor the product when present in small concentrations. It probably is also a stronger acid.

Catalysis of Sulfuric Acid Oxidations

Sulfuric acid, one of the cheapest and most plentiful of all chemicals, is not usually considered a particularly active and powerful oxidizing agent, although it is known that it shows some activity when hot and concentrated. According to thermodynamic data, however, it should be much more active, indicating that its sluggishness is due to a slow reaction rate and suggesting that if a suitable catalyst could be found, its utility as an oxidizing agent would be vastly increased.

Iodine may be such a catalyst. It is a well-known fact that hydrogen iodide cannot be prepared by heating a metallic iodide with concentrated sulfuric acid. Instead, the reaction products are free iodine, water vapor, sulfur dioxide, and sometimes even hydrogen sulfide. The usual explanation is that hydrogen iodide is first formed and reduces the sulfuric acid, being itself oxidized to iodine. If, therefore, a dilute solution of iodine in concentrated sulfuric acid is treated with a substance which will convert the iodine to an iodide, it may be expected that the latter will react with the sulfuric acid to liberate SO_2 and other reduction products of the acid and regenerate the iodine for another cycle. The process therefore becomes in effect an oxidation by sulfuric acid.

That such reactions do take place is illustrated by an example taken from organic chemistry. In a British patent, Hewitt and West[5] state that in the preparation of quinoline from aniline and glycerol in concentrated sulfuric acid by the Skraup synthesis, nitrobenzene and arsenic acid are unsatisfactory oxidizing agents because of operating difficulties and poor yields. The addition of about 1 or 2% of iodine, or of an iodine compound, such as potassium iodide or iodoform, to the reaction mixture makes such oxidizing agents unnecessary and results in improved yields and simpler operation.

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Iodine in Metallurgy

What may be called an early application of iodine in metallurgy is due to Moissan. For the preparation of high purity metallic calcium, he recommended heating anhydrous calcium iodide with sodium. A calcium-sodium alloy was formed which, when treated with alcohol to remove the sodium, left a residue of metallic calcium of unusually high purity for the time.

Preparation of Pure Metals

The intense current interest in metals and alloys suitable for use in gas turbines, jet engines and other high temperature applications, and continued interest in light weight structural materials and those highly resistant to corrosion, have resulted in intensive studies of the preparation and properties in a highly purified state of such metals as titanium, zirconium, hafnium, vanadium and chromium. As a result of this work, some of these metals have been shown to have properties which make them of interest in a number of important fields. High purity zirconium, for instance, with a specific gravity of only 6.5, is readily workable mechanically and is comparable in corrosion resistance to tantalum which has a specific gravity of 16.6 and is much less abundant; while titanium, with a specific gravity of 4.5, has been shown to have mechanical properties comparable to those of alloy steels, coupled with excellent corrosion resistance.

The vapors of many metallic iodides dissociate appreciably when heated to high temperatures. When the resulting partial pressure of the metal is greater than its vapor pressure at the same temperature, it will be deposited on any available surface, while the equivalent amount of iodine will be liberated.

On the basis of these considerations, van Arkel, de Boer, and Fast devised a process for the preparation of the refractory transition metals in states of such high purity that some, such as titanium and zirconium, which had previously been considered to be inherently brittle, were found for the first time to be exceedingly malleable and ductile.

The process has been described by these workers and others in an extensive series of articles.[1-11] It is fundamentally simple. Crude metal, together with a small amount of iodine, is placed in a bulb which can be evacuated to a very low pressure and is provided with a filament, suitably of tungsten, which can be heated to a high temperature by passage of an electric current. After evacuation, the iodine is allowed to react with the crude metal, the bulb is placed in an oven and heated to a temperature at which the vapor pressure of the iodide is appreciable, and a current passed through the filament. The iodide vapor striking the filament is dissociated, producing metal which is deposited thereon and free iodine which returns to react with a further quantity of crude

metal. Under the proper conditions, the metals are deposited in compact forms which require no further treatment to prepare them for working operations such as rolling and drawing.

The iodine is used over and over again; a small amount, therefore, serves to refine a large quantity of metal. Fast,[5] for example, produced 190 grams of refined zirconium with only 12 grams of iodine in an experiment limited to 30 hours' duration and with no attempt to recover the residual iodine.

The process can be compared to an electrolytic refining operation in which the crude metal acts as the anode, the purified metal as the cathode, the mixture of iodine and iodide vapors as the electrolyte, and the temperature difference between the filament and the bulb as the applied potential difference.

Rates of deposition are quite respectable. In the simple apparatus described above, Fast secured rates of about 0.057 lb. per sq. ft. per hour for titanium[6] and 0.15 lb. for zirconium.[5] Continuing the analogy with an electrolytic cell, these correspond to 100% current efficiencies at current densities of 58 and 80 amperes per sq. ft. respectively.

It is to be noted that the metals are deposited in the absence of all gases except iodine and the vapors of their own iodides. This is of extreme importance in the cases of those of the fourth, fifth, and sixth groups of the periodic table, as they react readily with carbon, nitrogen, and oxygen to form very stable compounds which either enter into solid solution in the parent metals or concentrate at the grain boundaries, in both cases producing brittle material. Any of these compounds present in the crude metal are not attacked by the iodine and remain in the residues with the other impurities.

A summary of the suitable conditions for the deposition of the different metals, taken chiefly from van Arkel,[7] is given in the following table:

Metal	Compound	Bulb Temp. °C.	Wire Temp. °C.
Chromium	CrI_2	800	1100
Copper	CuI	400	900
Iron	FeI_2	500	1100
Hafnium	HfI_4	400	1600
Thorium	ThI_4	400	1700
Titanium	TiI_4	200	1400
	$TiI_4 + TiI_2$	620	1400
Uranium	$UI_4(UI_3 + I_2)$	525	1100
Vanadium	VI_2	800	1200
Zirconium	ZrI_4	200	1400

Ductile metallic zirconium is now being produced commercially by this process. The properties of the metal and some of its applications are discussed in a paper by Alnutt and Scheer.[12]

Van Arkel[7] reported that he was unable to prepare cobalt, nickel, or uranium by this process. The reason for failure with the first two metals is given by Jellinek and Uloth[13] who showed that their iodides dissociate at temperatures in the neighborhood of 700°C., where they have very low vapor pressures. In a study for the Manhattan Project, Pres-

cott, Reynolds, and Holmes[14] showed that uranium could readily be deposited from its iodides. They found that the volatile tetraiodide, which would be most suitable for the purpose, dissociated at comparatively low temperatures to produce the nonvolatile triiodide. However, by maintaining an excess of iodine vapor in the bulb, they were able to secure a sufficient concentration of tetraiodide vapor to deposit the metal.

The work of Prescott, Reynolds, and Holmes was carried out principally at filament temperatures close to the melting point of uranium, but they refer to other work in which the metal was deposited in the molten state on a tungsten filament coated with thorium oxide to prevent alloying of the two metals. The uranium, which was of high purity, ran off as quickly as deposited and was caught in a receiver. Their paper also includes a very interesting thermodynamic analysis of the process.

No reference has been found to the preparation of metallic rhenium by the iodide process, but the fact that this metal gives a black volatile product, probably the tetraiodide, when heated to a relatively low temperature in iodine vapor[15] suggests that it could be so prepared.

Alloys also can be prepared by the iodide process. Indeed, owing to the reduction in vapor pressure which occurs on alloying, it should be possible to deposit as alloys many metals which cannot be deposited in the pure state because of their high vapor pressures. Fast[16] prepared alloys of zirconium and titanium and de Boer and Fast[4] those of zirconium and hafnium, both covering the range from 100% zirconium to 100% of the other metal. This is to be expected as all three metals are in the foregoing table. However, the two latter workers[3] also prepared alloys of zirconium with aluminum and with tin. The richest aluminum alloy reported contained 9.9% Al and is described as much harder than pure zirconium but still with good ductility.

As shown by van Arkel,[1] the nitrides and carbides of titanium and zirconium can be prepared in a very pure, compact state by admitting nitrogen or carbonaceous gases into the bulb.

It is believed that there is a good chance that by the application of modern chemical engineering techniques, this process could be developed on a large scale, not only for the economical production of metals, particularly those in the fourth, fifth, and sixth groups of the periodic table and their alloys, but also for the preparation of coatings of these metals on other objects.

No information has been published on the purity of the iron produced by this process. It would be of interest to find out how such metal prepared, say, from Armco or electrolytic iron, would compare in purity with high purity iron prepared by more elaborate methods.

The Carbonyl Process

Another method in which metal is deposited by dissociation of a vapor of a volatile compound, and in which iodine may have an important application, is the carbonyl process.

Applied to the refining of nickel, this is, of course, the well-known Mond process, and it was used in Germany for the production of high

grade iron and nickel powders. The Germans made radical changes in it during the war. They went to high pressures, 200 atmospheres, and comparatively high temperatures, 200° to 260°C., to secure greater reaction rates and higher conversions; condensed the carbonyls to the liquid state; and, at least in the case of nickel, submitted them to fractional distillation to remove impurities and to produce metal of high purity. They claimed that, as applied to nickel, this process was cheaper than either electrolytic refining or the original Mond process.

Of the metals important in ferrous metallurgy, iron, cobalt, and nickel unite directly with carbon monoxide to form carbonyls which are volatile at ordinary or slightly elevated temperatures, and dissociate to metal at somewhat higher temperatures. Chromium, molybdenum, and tungsten also form volatile carbonyls, but so far they have not been prepared directly from the metals.

Since they differ in volatility, the various carbonyls can be separated by fractional distillation and this fact, combined with their ease of dissociation, may make them of considerable importance in secondary metal operations.

The extensive investigations of Hieber and his co-workers[17-25] show that iodine is an effective catalyst in accelerating the reaction of carbon monoxide with iron, nickel, and cobalt. It was first found that the iodides of these metals react much more readily and completely with carbon monoxide to form the carbonyls than do the other halides. This is shown in the following table which gives the results of experiments in which the salts were exposed to carbon monoxide at 200 atmospheres pressure for 15 hours.[24]

YIELD OF IRON, COBALT, AND NICKEL CARBONYLS IN % FROM THEIR PURE HALIDES

	Temp. °C.	Chloride	Bromide	Iodide
Iron	200	0	0	50-75*
	250	0	1.5	—
Cobalt	200	2.5	4.5	100
	250	3.5	9.1	100
Nickel	250	2.0	1.0	100

* Remainder converted to iron carbonyl iodide, $Fe(CO)_4I_2$.

The released halogens combined with the copper lining of the autoclave which was not in direct contact with the salts.

Other work by Hieber and co-workers shows that cobalt iodide is more active than the sulfide.[17] When heated in the presence of copper, the iodide was completely converted to carbonyl in 12 hours at 160°C. and 145 atmospheres pressure, while the sulfide required a temperature of 190°C. and a pressure of 250 atmospheres to produce an equal yield in the same time.

It was found later that conversion of cobalt to the iodide was unnecessary[24] and that about one fifth of the stoichiometric amount of iodine greatly facilitated conversion of finely divided metal. In the case of iron, the effect of iodine was even more pronounced as only a

trace was necessary to produce practically complete conversion to the carbonyl.

Hieber attributes the activity of iodine to the greater ease of formation of carbonyl iodides, which break down into the normal iodides and the carbonyls. However, it is probably also connected with the lower free energy of formation of the iodides, as a result of which the iodine can be more readily replaced by carbon monoxide than can the other halogens.

Some of the platinum metals also form carbonyls and iodine plays a favorable role here also. Manchot and Manchot[26] found that direct action of carbon monoxide on ruthenium metal produced a maximum of only 10% conversion to the carbonyl even after 14 days at 300°C. and 400 atmospheres pressure, but a mixture of the triiodide and metallic silver was completely converted in 24 hours at 170° and 455 atmospheres. Hieber and co-workers[22,23] found that iridium iodide reacted more readily than the other halides.

Aluminum Refining

A third process in which iodine may have advantages is based on the observations of Friedel and Roux in 1885.[27] They found that passage of the vapors of aluminum chloride or bromide over metallic aluminum at a low red heat resulted in the formation of a deposit of the metal in a colder portion of the tube a short distance beyond the charge. They explained this result by assuming that the trihalides reacted with the metal to form gaseous lower halides which decomposed on cooling with reformation of the trihalide and liberation of metal.

A process for the refining of aluminum, based on this reaction, received considerable attention in Germany during the war. Although only meager details are available, it is reported that scrap metal containing 97.4% aluminum was refined to a purity of 99.98% by this process while an aluminum-silicon alloy, produced in the electric furnace and containing less than 60% aluminum, yielded metal with a purity of 99.85%.

According to reports, the Germans preferred the chloride or bromide, a situation which was to be expected since iodine was much less available than normally because of war conditions. Experimental data[28] indicate that there is little difference among the aluminum halides from a thermodynamic standpoint, but the iodide would appear to have definite practical advantages. Aluminum chloride, for example, must be condensed as a solid at atmospheric pressure, reacts with silica to form silicon tetrachloride,[29] and is rapidly hydrolyzed by moisture. Aluminum iodide, on the other hand, is readily condensed to a liquid at atmospheric pressure; it exists as a liquid over a range of almost 200°C.; does not react with silica; and should be less susceptible to hydrolysis than the chloride. It should also have less of a tendency to react with the impurities in the aluminum.

Copper Recovery

A Chilean engineer[30] has proposed the use of iodine in the hydrometallurgical recovery of copper from its ores. These would be leached

with dilute sulfuric acid to dissolve out the copper, which would be precipitated from the solution as cuprous iodide by addition of iodine and sulfur dioxide, sulfuric acid for further leaching being formed at the same time. The iodide would be roasted to liberate the iodine for recycling, and to convert the copper to the oxide, which, as a final step, would be reduced to metal. This process is interesting as it takes advantage of a number of characteristic reactions of iodine and its compounds.

Production of Alkali Metals

The ability of iodides to form low melting salt mixtures is utilized in the Gilbert process for the production of sodium and other alkali metals from aqueous solutions. The metal is electrolyzed into a mercury cathode just as in the well-known mercury alkali-chlorine cell. The resulting amalgam goes to a second cell containing a fused mixture of low melting salts of the metal, where it is made the anode and where the metal is electrolyzed out of the mercury and deposited on a steel cathode. In a patent,[31] the inventor recommends the following low melting salt mixtures among others, all of which are eutectic compositions:

Eutectic Mixture		Melting Point °C.
NaOH, 55 wt. %	NaI, 45 wt. %	225
KOH, 72 mol %	KI, 28 mol %	250
LiOH, 45.5 mol %	LiI, 54.5 mol %	183

There are no reports that this process has been developed beyond a laboratory scale in the United States, but during the war it was carried to a large pilot plant scale in Germany with satisfactory results.[32]

Electroplating

A number of investigators have recommended the use of iodides as constituents of solutions for the electrodeposition of metals. Perhaps the greatest interest has been shown in the electroplating of silver from iodide baths in an effort to avoid the use of the highly poisonous cyanides.

Silver iodide, although very insoluble in water, dissolves readily in strong potassium iodide solutions to form a complex anion. Such a solution therefore fulfills two of the requirements for producing a fine grained deposit, namely a low concentration of actual metal ions but a high concentration of metal in the form of a complex to act as a reservoir for supplying these ions.

Two investigations have shown that smooth, adherent plates can be obtained from such baths with high current efficiencies. Fleetwood and Yntema[33] recommend a solution containing 23.8 grams of silver, 520 grams of sodium iodide, and 60 grams of citric acid per liter of solution, while Alpern and Toporek[34] found that the organic acid could be replaced by sulfuric acid with no loss in plating characteristics. The latter authors conclude, "Electroplates of silver which appear to be of the same order of quality, and obtained at comparable efficiencies and costs as those from the cyanide baths, were obtained from solutions containing sulfuric acid, potassium iodide, and silver within a pH range from

3.0 to 0.65. The plates were bright, fine grained, and adherent to the basis metal."

The fact that cadmium, lead, and palladium also form iodide complexes in solution suggests that similar baths may be suitable for the electroplating of these metals.

Many investigators have tried to find baths from which aluminum can be electrolytically deposited as a smooth adherent plate for decorative and protective purposes. However, those proposed were made up with volatile organic solvents and had high resistances, or they were mixtures of fused salts which gave unsatisfactory deposits or operated at too high a temperature. Recent work by a Russian scientist[35] may provide a new approach to the problem. He found that aluminum and potassium iodides form a eutectic melting at 97°C. and containing 84.5% aluminum iodide. There is a good possibility that this melting point can be further reduced by the addition of other alkali iodides, thus bringing the operating temperature range down to a point where organic addition agents can be used to produce a smooth plate. Aluminum iodide has a definite advantage over the bromide and chloride for this purpose because of its much lower volatility, and it should be also considerably less sensitive to moisture. There is a considerable demand at the present time for a suitable bath to permit the electroforming of complex aluminum parts for electronic devices.

A similar process may be possible for magnesium. Klemm and his co-workers[36] found that magnesium and potassium iodides form a simple eutectiferous system with the extraordinarily low eutectic temperature of 255°C. It seems reasonable to suppose that the melting point of such a mixture could be reduced still further by the addition of other salts.

Casting and Heat Treatment

It is claimed in a British patent[37] that the addition of iodine to molten copper and brass prior to casting results in cleaner, denser, more readily worked metal, especially when there is a large proportion of scrap in the charge. It is also claimed that brass containing 61% copper and 39% zinc, treated by this process, is superior to the ordinary 70-30 grade for screws and other articles. A charge low in scrap may require as little as two grams of iodine per 100 lbs. of metal, but this will increase somewhat with the amount of scrap used.

The addition of low concentrations of iodine vapor to the atmospheres of heat treating furnaces is recommended in another British patent.[38] It is stated that more uniform physical properties are secured and that the iodine prevents harmful action on the metal by hydrogen, water vapor, and other atmospheric constituents.

Powder Metallurgy

The peculiar layer type of crystal structure of the divalent metallic iodides and their consequent good lubricating properties suggest their application in powder metallurgy as a lubricant in the pressing operation to reduce "bridging" and produce greater density in the compacts. Cadmium iodide appears to be especially suitable for this purpose

as it is nonhygroscopic, while the high position of cadmium in the electromotive series and the volatility of the salt and its components would insure its complete elimination during sintering.

The fact that many metallic iodides readily dissociate on heating and that the reaction is reversible suggests that a small amount of iodine in the atmospheres of furnaces used for the sintering of powder compacts should shorten the time required for that operation by promoting grain growth and recrystallization. The presence of the iodine would actually make the atmosphere a gaseous solvent for the metal.

Metallography and Inspection of Metals

Iodine also has applications in these fields. A mixture of one part methyl iodide and one part of dry methyl alcohol, to which is added a crystal or two of iodine, is recommended as a very suitable etching reagent for specimens of nearly all magnesium alloys which are to be examined in the electron microscope. According to Heidenreich, Gerould, and McNulty,[39] it fulfills nearly all of the requirements for a perfect etching reagent.

The high atomic weight of iodine makes it and substances containing it relatively opaque to x-rays. This property has resulted in the development of "radio-opaque" substances for use in diagnostic medicine to make the internal structures of the human body visible in x-ray photographs. Substances of the same type should find application in x-ray inspection of objects made of metal to delineate more sharply intricate internal openings which cannot be inspected by other methods and to make internal cracks, fissures, and other defects more clearly visible. It is believed that preparations with low surface tensions could be prepared which would readily penetrate small openings and be useful for the study of microporosity and similar phenomena.

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Iodine and Its Compounds
in Electricity and Electronics

The use of iodine and its compounds in electricity and electronics is relatively old. In the early days of electrical distribution, when the direct current system was in exclusive use, there apparently were many claims that incandescent electric lamps did not give satisfactory service. Some of these claims were known to be fraudulent, but there was no way of proving this until somebody thought of placing a plug of cotton moistened with an iodide solution in the stem of the lamp so that it came into contact with both lead-in wires. When the lamp was placed in service, a small amount of the current passed through the cotton and, owing to the liberation of iodine, gradually turned its color a darker and darker brown, making possible a reasonable guess of the length of time the lamp had been in use.

On a higher ethical plane, it can be reported that methylene iodide vapor was widely used by Bragg and his contemporaries in their ionization chambers in the early days of the investigation of crystal structure by x-ray diffraction.

There has been no regular pattern, other than that of utility, to the actual or suggested uses for iodine and its compounds in these fields. One depends on the intense colors of iodine itself and its complex with starch, another on the crystal structure of its compounds, and still another on their ease of dissociation. It is believed, however, that iodine fundamentally has properties which are of definite interest to electrical and electronic engineers. Since iodine is the heaviest of the common halogens, it has some semimetallic characteristics in the free state, and its compounds begin to exhibit unusual properties owing to their departure from the typical saltlike character of the compounds of the other halogens.

Electrical Recording Papers

The use of iodine for electrical recording papers goes back to the old polarity test paper, consisting of a piece of filter paper soaked in potassium iodide solution. Upon drawing the leads from the terminals of a direct current circuit over the test paper, a deep brown color is produced by the positive lead owing to the liberation of iodine by electrolysis, while the negative lead gives no color. The method is very sensitive. Quantities of electricity as small as 10^{-7} ampere hour should give a perceptible color in the presence of starch, and, under the proper conditions, the quantity of iodine liberated should be closely proportional to the rate of current flow, since the iodine coulometer has been used for years as a very accurate method of measuring quantities of current.

The simplest recording paper is one soaked in a solution of iodide and starch, and this has been widely used. Various means of improving its performance are recorded in the literature. A British patent[1] recommends the addition of a small amount of a strong reducing agent as a preservative to prevent the development of a blue color during storage. According to a German patent[2] addition of cadmium and zinc iodides improves the range of tones which may be reproduced.

The performance of such papers probably could be further improved by taking advantage of the new knowledge of the nature of the starch-iodine complex.[3] A somewhat different type of paper could be based on the solubility of the iodonium and some quaternary ammonium iodides in organic solvents, together with the ability of these substances to combine with the iodine liberated to form intensely colored poly-iodides of high stability and low solubility.

Ampere Hour Meters Containing Iodine

In the early days of this century there was considerable interest in the development of simple, compact, and rugged mercury coulometers in which the cathodically deposited mercury was collected in calibrated measuring tubes where its volume could be expressed in terms of ampere hours or any other desired unit. Of the various models, the most successful was probably the Wright Electrolytic Meter.[4] This was a glass electrolytic cell containing a mercury anode, an iridium cathode, and an electrolyte consisting of an aqueous solution of potassium and mercuric iodides. Iridium was chosen as the cathode material because it does not amalgamate with the deposited mercury, but instead permits it to run off into the calibrated tube in which its volume is measured.

The unit was ingeniously contrived to operate over long periods without attention. It was completely sealed, a feature made possible by the fact that no gas was generated either by chemical or electrochemical action. The anode and cathode were so placed that the convection currents produced by solution and discharge of the mercury tended to keep the solution composition uniform. The meter could be reset at any time by inverting and returning the deposited mercury to the reservoir which supplied the anode.

When first introduced, this meter apparently did not exhibit its inherent reliability and accuracy because solutions of simple mercury salts were used as electrolytes. These were not satisfactory. If the mercury was in the mercuric state it tended to react with the metal, while mercurous salts required the presence of some free acid to prevent hydrolysis and this, in turn, slowly reacted with the metal, sometimes with the evolution of gas. This problem was eventually solved by Hatfield[5] who recommended the potassium iodide-mercuric iodide solution. The mercury in such solutions is present as a complex for which no corresponding mercurous complex exists. They are, therefore, stable in contact with metallic mercury and the latter acts merely as a simple divalent element.

This electrolyte apparently proved entirely satisfactory, as it was later reported[6] that several thousand meters were in operation in

67

England and definite efforts were made to introduce them into Germany. According to Allmand and Ellingham[4] the meter was exceedingly reliable and constant in operation and needed no attention, while its accuracy was within 1% even though the current varied from 10% to 150% of the rated capacity.

Manufacture of this type of meter continued in Germany at least up to the beginning of the second World War[7] with improvements, such as the incorporation of fritted glass diaphragms, being added from time to time. Different designs were available for use in homes, factories, battery charging stations, electroplating establishments, and other locations.

Iodine in Primary and Secondary Cells

During World War II there was a large demand for cells of high capacity and small size to supply energy to portable electronic equipment and also for those which could operate under adverse conditions, particularly low temperatures. Iodine and its compounds were investigated with promising results. Garrett and his co-workers report that the characteristics of iodine make it a very promising cathode in a low temperature dry cell[8] while Schaschl and McDonald[9] took advantage of the solubility of "iodine tribromide" in liquid sulfur dioxide to develop a cell, using sodium as an anode, which has an open circuit voltage of 2.7 at $-60°C$. and 3.5 volts at room temperature.

There should be considerable use for iodine in both primary and secondary cells. The fact that it is a solid of relatively low vapor pressure at ordinary temperatures should make it very convenient for halogen-metal cells which may, under the proper conditions, be sufficiently reversible to serve as secondary cells. The tendency of the iodine to dissolve in the electrolyte as soon as iodide ion is formed can be avoided by adsorption on activated charcoal, or, possibly, by the use of iodonium bases which form insoluble iodides and polyiodides. Such a material in an electrode would take up and hold as polyiodide the free iodine formed during charge and release it during discharge.

The periodates also appear to offer the possibility of providing an efficient cathode, particularly in alkaline systems. Their activity as oxidizing agents can be varied over a wide range depending on the alkalinity of the system. Periodic acid itself is one of the most powerful oxidizing agents known and will readily convert manganese to permanganate, but as the system becomes more alkaline the oxidizing activity becomes less and the stability increases until finally, in anhydrous systems, the normal alkali and alkaline earth paraperiodates become thermodynamically stable with respect to their constituents. It may, therefore, be possible to select an alkalinity at which reduction of periodate no longer takes place in two steps, i.e., through iodate, but goes directly to iodide, a valence change of eight. If such a point could be realized, it would provide an efficient and relatively light weight electrode since one pound of iodine at 100% efficiency would yield 766 ampere hours compared to only 117 for lead. Of particular interest in this connection are the sodium paraperiodates, which are relatively insoluble in alkaline solutions, the solubility becoming negli-

gible when the sodium hydroxide concentration rises above 20%. The silver periodates are also insoluble, and, taking into account the insolubility of silver iodide, offer the possibility of a completely insoluble iodide-periodate electrode.

Finally there is the fact that silver, copper, and nickel, when combined with periodic acid, can exist as complexes in unusually high valence states, thus adding still another possibility for securing an efficient low weight electrode.

Iodine in Lubricants

Hughes and Whittingham reported[10] that exposure of a cadmium-nickel alloy surface to the vapor of iodine and heat resulted in a marked reduction in the friction of a stainless steel slider moving on it and changed the motion from a "stick-slip" type, in which the harder metal was digging into the softer, to a very smooth one. Other tests showed that the friction of a steel ball bearing, under a load of 200 to 600 kilograms, on a cadmium iodide surface was lower than on metallic cadmium or on other cadmium halides at ordinary temperatures, and that this advantage increased with temperature, the cadmium iodide surface still giving smooth sliding at 105°C whereas the others gave a "stick-slip" type of motion.

The reason for this action of iodine is the "layer-lattice" structure of cadmium iodide, consisting of sheets of atoms of indefinite extent in two directions but only 3 atoms thick in the third, the cadmium atoms being sandwiched in between the iodine atoms. Accordingly the layers are held together only by the comparatively weak attraction of the iodine atoms for each other and there is, therefore, excellent cleavage in the plane of the sheets as in the case of graphite and mica. Most of the other divalent metallic iodides, notably those of lead, iron, manganese, cobalt, titanium, and magnesium, have the same structure, suggesting that iodine should be an effective constituent of high pressure lubricants. Cadmium and lead iodides should be of special interest as solid lubricants, as they are nonhygroscopic and do not take up water of crystallization.

These substances can be used as lubricants for other purposes, such as reducing distortion of a desired crystal structure during crushing and grinding. Clark and Kern,[11] for example, found that when litharge was ground with lead peroxide, lead sulfate, and other compounds, it was so badly distorted that it lost its diffracting power for x-rays, but when mixed with lead iodide, its diffracting power remained but that of the iodide disappeared.

Iodides in Commutator Brushes

The commutators and brushes of generators and motors on military aircraft are designed to carry very heavy electrical loads in order to maintain lightness and compactness and, in general, give good service under normal conditions of atmospheric pressure and moisture. During the early stages of World War II, however, it was found that they gave considerable trouble owing to excessive sparking at high altitudes, resulting in rapid destruction of both the commutators and the brushes.

Considered at first to be a problem of lubrication, organic lubricants and molybdenum sulfide were tried without success. Attention was then turned to lead iodide because of its layer lattice structure and nonhygroscopicity. The results were successful beyond expectations.[12] Instead of the expected formation of a lubricating film on the commutator surface, a dark satiny one, very similar in appearance to the normal cuprous oxide film, was formed and remained stable even under the most adverse conditions. Cadmium iodide was also found to be effective, as were other metallic iodides.[13,14]

It is probable that the lubricating action of the lead and cadmium iodides plays some part in the phenomenon, but the ready oxidizability of the iodides of the heavy metals is probably even more important. Very likely a film of cuprous iodide is first formed on the commutator surface and this is converted to cuprous oxide by the combined action of heat and atmospheric oxygen during operation.

Brushes treated by this method have uses in other fields where commutating conditions are unusually difficult. Elsey reports that a group of treated test brushes were installed in an electric locomotive, and after 85,000 miles of high speed operation were in excellent condition, the average wear being only 0.01 inch per thousand miles of service.

Deposition of Metals

As described in the section, "Iodine in Metallurgy," the instability of the metallic iodides at high temperatures has been utilized by van Arkel and de Boer in a very elegant process for the production of many of the refractory metals, including copper, iron, chromium, vanadium, titanium, zirconium, hafnium, and thorium in a highly pure, compact, and coherent form.[15-17]

A quantity of crude metal and a small amount of iodine are sealed together into an evacuated glass bulb provided with a filament of tungsten or other refractory metal. The bulb is placed in an oven and heated to a temperature at which the vapor pressure of the metallic iodide is appreciable, and a current passed through the filament to heat it to a considerably higher temperature, suitably from 1000 to 1600°C. The iodide vapor striking the filament is dissociated, producing metal, which is deposited thereon, and free iodine which returns to react with an additional quantity of crude metal. A small amount of iodine therefore serves to transfer a much larger quantity of metal.

Since the deposition reaction is purely a thermal one, and metal will be deposited on any surface heated to the proper temperature with which the iodide vapor comes in contact, the process can be used for producing metallic coatings on other objects regardless of their nature, provided, of course, that they do not react either with iodine or the deposited metal and that they are sufficiently refractory to withstand the required temperature. Rentschler and Henry, for example, in a recent U. S. patent[18] describe a photoelectric cell for the ultraviolet region of the spectrum in which the photosensitive surface is a layer of metallic zirconium deposited on tungsten by dissociation of zirconium tetraiodide vapor.

70

In another place[17] these same authors describe how the photosensitivity of such surfaces can be altered by treating them with nitrogen, oxygen, and hydrogen after deposition, the process being, in effect, an alloying one. Alloys can also be prepared directly by the iodide process by simultaneous deposition of metals from mixtures of iodide vapors.

Iodine in Dry Rectifiers and Photoelectric Cells

There are many references in the literature to the beneficial effect of iodine and its compounds on selenium in its electronic applications. In a recent paper on the manufacture of selenium rectifiers, Escoffery[20] states that to improve the forward conductivity a small amount of iodine is added to the selenium which otherwise is of the highest possible purity. Penin and Astahov[21] report that the addition of 0.1% iodine increased the rectification ratio of selenium from 10 to between 20 and 30. Bismuth iodide has also been recommended for the same purpose.[22] In the case of selenium photocells, Hart[23] reported that he found their infrared sensitivity to be increased by treatment with solutions of pinacyanol and other iodine-containing dyes used as photographic color sensitizers. He finally concluded that iodine itself was the active ingredient and that an aged solution of iodine in ethyl alcohol was the most effective of all. In a British patent, Rupp[24] claims that about 0.1% iodine should be added to the selenium to be used for photocells, 0.1 to 5% for rectifiers, and 5% to that to be used for thermocouples to confer high electrical conductivity.

Iodine also apparently has an effect on alkali metal photocells. Olpin[25] reported that it increases the sensitivity of potassium cells to white light and that the increase is general for all wave lengths although more marked at both ends of the visible spectrum.

Other Items of Interest

Solid iodine has an appreciable electrical conductivity which increases from 1.71×10^{-7} at 25° to 12.0×10^{-7} at 110°C.[26] According to this same source, exposure to light increases the conductivity as much as 25 fold, and the greatest sensitivity is to the visible region of the spectrum.

Liquid iodine is a polar solvent of considerable ionizing power. Solutions of the alkali iodides in molten iodine have electrical conductivities of the same order of magnitude as those of fused salts and aqueous solutions of strong electrolytes. Some of these solutions have relatively low melting points, the eutectic mixture with potassium iodide, for example, fusing at 80.8°C.[27-29]

Iodine vapor exhibits unusual effects with light. It is fluorescent, emitting a yellowish-green light when illuminated by the sun or an electric arc; it is thermoluminescent, emitting a red glow when heated to about 500°C.; and it also rotates the plane of polarization of polarized light when placed in a magnetic field.[30]

Kovalenko[31] studied the breakdown potentials in hydrogen iodide and other gases. On the basis of his own findings and data in the litera-

ture, he concluded that the breakdown potentials of gases increase with the following:

1. Increasing molecular weight
2. Decreasing free path of molecules
3. Increasing critical temperature
4. Increasing distance between atomic nuclei in the molecule
5. Decreasing energy of dissociation.

On the basis of these conclusions, the vapors of volatile iodine compounds should have unusually high breakdown potentials.

According to a recent patent[32] molten potassium iodide is far superior to any other reagent for removing insulating enamel coverings from electric conductors prior to joining with other conductors.

A recent determination of the dielectric constant of lead iodide gave the extraordinarily high value of 113,[33] practically the same as that of rutile. Some earlier workers found similar values, but others reported figures as low as 2.4.[34] A clue to the reason for such a wide variation is given by the latter reference in which it is reported that melting of the iodide raised the dielectric constant to 62.5, suggesting that the high values are due to the presence of a small amount of lead oxide or a lower lead iodide. It also suggests that detailed study of the systems lead iodide-lead oxide and lead-iodine would yield materials of even higher dielectric constants. Such material should be of considerable interest even if values approaching those of the alkaline earth titanates are not obtained, as the low melting point of lead iodide, 412°C., together with its relatively high plasticity and formability should make it useful where the other materials cannot be applied.

Copper and silver iodides and their combinations with mercuric iodide exhibit extraordinary electrical and thermal properties. They are the best solid electrolytic conductors known, the conductivity of the compound silver iodomercurate, Ag_2HgI_4, increasing sharply a hundredfold at 50°C., owing to an allotropic transformation, to a value about a thousand times better than other solid electrolytic conductors in the temperature range between 50° and 150°C.,[35] while the conductivity of solid cuprous iodide is enormously increased by the presence of iodine vapor, the increase being a function of the partial pressure of the iodine.[36]

Coming to thermal properties, when a bar of a solid solution of cuprous and silver iodides is subjected to a temperature gradient, the copper ions migrate to the cold end and the silver to the warm end. In an experiment described by Reinhold[37] a bar of a solid solution of 75 mol per cent of silver iodide and 25 per cent of cuprous iodide was held for four days with one end at 210° and the other at 325°C., after which time it was found that the concentration of the copper had risen to 37% at the cold end and had fallen to 21% at the hot end.

Finally there is the fact that both cuprous and silver iodomercurates undergo allotropic transformations at 50° and about 70°C., respectively, accompanied by very sharp changes in color, a fact which has led to their use as constituents of thermosensitive paints for the protection of machinery by giving warning of overheating of vital parts.[38,39] By varying the relative proportions of·copper, silver, and mercuric iodides, the

sharpest change in color can be made to take place over a relatively narrow range almost anywhere in the temperature interval between 50° and 100°C., that of greatest interest for protection of electrical equipment.

Iodides are activators for zinc sulfide phosphors.[40]

Like potassium and ammonium dihydrogen orthophosphates, silver and ammonium trihydrogen paraperiodates undergo transitions at low temperatures, accompanied by sharp changes in their dielectric constants as well as by specific heat anomalies. The high temperature modifications of these salts have rather high dielectric constants.[41-43]

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