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THE DIRECT SYNTHESIS AND PURIFICATION OF SODIUM IODIDE

by

James Russell Johnson

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Dean of Graduate College

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INTRODUCTION AND HISTORY

The preparation and purification of sodium iodide is of great interest owing to the use of large single crystals of the material in optics and in radioactivity sensors.

Since the beginning of this work, considerable interest has developed in obtaining ultra-pure alkali halides. Such properties as nuclear magnetic resonance (87), ionic conduction and diffusion (105), electrical conductivity (31, 100, 223), photoconductivity (102), and photolytic behavior (143) are all affected by the presence of impurities. Other important physical behaviors of the alkali halides that are dependent on the amount of impurity present include electron spin resonance and relaxation (63, 214), Hall mobility at low temperatures (34), thermal conductivity (164), optical absorption and fluorescence (181), infrared and ultraviolet spectra (4), and deposition of thin films of metals (96). Duerig and Markham (60) conclude for optical work, that commercial crystals just aren't good enough, and further, that elemental impurities in excess of 1 part per million, or at most 10 parts per million, will interfere.

Color centers in alkali halides may be formed by three processes: addition of excess alkali metal, addition of excess halogen, and by radiation. When an alkali halide crystal is heated in an alkali metal vapor, metal atoms diffuse into the crystal and ionize. The electrons enter the anion holes, making the density less than the pure crystal (27). This type of coloration produces F (Farbe-color) centers in the crystal, and is of the trapped-electron type. A trapped-hole type of color center, called a V type, is formed when the alkali halide is heated with bromine or iodine (138). The pressure of halogen necessary to accomplish this is of the order of 50 atmospheres, and it has not been possible to form this type of color centers with chlorine. The third type of color center is formed by ionizing radiation, especially soft x-radiation, bombarding the alkali halide crystal. Trapped hole and trapped electron color centers may be formed (192). The mechanism of color center formation due to ionizing radiation is not well known, but experimental and theoretical work is currently quite extensive. The basis for the single point defects (F centers) has had the most analysis: the theories of Seitz, Varley, and Howard have been proposed (176). The theoretical foundation for the formation of complex color centers is not very well advanced.

The use of the above phenomenon to measure ionizing radiation came before many of the studies mentioned above. The technique is called scintillation counting. As high energy particles strike the crystal, electrons in the crystal are excited by photoelectric and Compton effects. These excited electrons strike fluorescent centers in the crystal. A fluorescent center has electrons which become excited. A transition occurs, then rearrangement to another excited state, and emission of luminescence takes place (67). Commonly, the luminescence is detected with a photomultipler tube and the signal fed through cathode follower circuit into a Geiger-Müller counter (12). The pulse-height analyzer usually used to record the counter output may be replaced by digital recording with further computing to separate the background count using a method of moments technique (76). Alternately, the background count may be separated by a differential coincidence counter using two electron photomultiplier tubes (141).

Sodium iodide-thallium iodide is the alkali halide and fluorescent center most used. For x-rays, this type of crystal appears to be far and away superior (30). Sodium iodide-thallium scintillation crystals are far more efficient than a Geiger-Müller counter for high energy gamma rays (55 times) (12), and are well adapted to beta and gamma ray determinations (64).

The theoretical basis of luminescence is not well established, but some facts are known and some models have been advanced (24, 108, 153). The luminescence near the surface of the crystal apparently occurs by a different mechanism that the luminescence in the interior. The presence of defects may provide sites for the processes to occur (108). Impurities other than thallium ion must be excluded, since they will cause spurious scintillations.

Analysis of a Harshaw Crystal

Keeping in mind the statement by Duerig and Markham (60) that commercial crystals are often not suitable for color center study, the following table will illustrate the problem. The analyses were done by emission spectrographic analysis at the National Bureau of Standards (60). Although the crystal is not sodium iodide, a qualitative similarity may be drawn. See Table 1 on page 5 for the analyses. Other crystals for which the analysis was given were potassium chloride, potassium bromide, and sodium fluoride. These other examples conformed to the analysis above in general outline.

It may be seen that the above crystal contains one element, calcium, which was present in the amount 1000 - 10,000 parts per million, and six elements, silver, aluminum, iron, lithium, magnesium, and silicon, which were present in the amount 100 - 1000 parts per million. Duerig and Markham stated above (60), that 1 part per million, or perhaps 10 parts per million is all that is allowable for optical work. The emission spectrographic analysis doesn't approach a sensitivity of this level, and even as it is, detects the presence of seven elements which are present in objectionable quantities.

Table 1. Emission spectrographic analysis of a Harshaw optical sodium chloride crystal

Element	Amount	Element	Amount	Element	Amount
Ag (silver)	T[a]	Hf (hafnium)	-	Rb (rubidium)	-
Al (aluminum)	T	Hg (mercury)	-	Rh (rhodium)	-
As (arsenic)	-	In (indium)	-	Ru (ruthenium)	-
Au (gold)	-	Ir (iridium)	-	Sb (antimony)	-
B (boron)	-	K (potassium)	-	Sc (scandium)	-
Ba (barium)	-	Li (lithium)	T	Si (silicon)	T
Be (beryllium)	-	Mg (magnesium)	T	Sn (tin)	-
Bi (bismuth)	-	Mn (manganese)	-	Sr (strontium)	-
Ca (calcium)	VW	Mo (molybdenum)	-	Ta (tantalum)	-
Cd (cadmium)	-	Na (sodium)	VS	Te (tellurium)	-
Ce (cerium)	-	Nb (niobium)	-	Th (thorium)	-
Co (cobalt)	-	Ni (nickel)	-	Ti (titanium)	-
Cr (chromium)	-	Os (osmium)	-	Tl (thallium)	-
Cs (cesium)	-?	P (phosphorus)	-	U (uranium)	-
Cu (copper)	-?	Pb (lead)	-?	V (vanadium)	-
Fe (iron)	T	Pd (palladium)	-	W (tungsten)	-
Ga (gallium)	-	Pt (platinum)	-	Y (yttrium)	-
Ge (germanium)	-	Ra (radium)	-	Zn (zinc)	-

[a] Key to amounts: VS- very strong: greater than 10% ; M-medium: 0.1 - 1.0% ; W-weak: 0.01 -0.1% VW-very weak: 0.001 - 0.01% (1000 - 10,000 p.p.m.); T - trace: 0.0001 - 0.001% (100 - 1000 p.p.m.) - not detected; -? -probably not detected

Single Crystal Growing

There are three common methods of crystal growing: the Stöber method, the Bridgman-Stockbarger method, and the Kyropoulos method. The technique pioneered by Stöber (194) involved the use of a temperature gradient around a crucible with a conical tip. The temperature gradient was approximately 50 degrees per centimeter, and the power was gradually reduced to allow crystal formation. Stockbarger first worked with the Stöber method (195), and then adapted the Bridgman technique to the growing of fluorite crystals (196, 197). This method utilized a steep temperature gradient at the center of the vessel by heating the top part and leaving the bottom part unheated. The vessel was then drawn through the heated and unheated areas after the material to be crystallized was first melted, as done by Slonaker, Smutz, and Olson at Iowa State University (188) and Dobrovinska and Eidel'man (58). The third method of growing crystals from a melt is the one developed by Kyropoulos (117). It appears to be the most versatile method, and enables growth of crystals of the order of twelve inches in diameter. First, a seed crystal is placed on a rod. The seed crystal is placed in contact with the melt and gradually withdrawn. Crystallization occurs because the rod is cooled.

Sodium iodide (thallium) crystals have been grown by the Stöber method (109), as have normal alkali halide crystals (172). Far more common, however, is the growth of alkali halide crystals by the Kyropoulos method (18), and the method has been applied to transition metal fluorides with success (37). Inert atmospheres are used in many cases (64, 154) as the introduction of oxygen or water has been shown to cause the formation of cloudy, colored crystals (205). The Kyropoulos method is most advantageous for growing large diameter crystals, but the thickness is limited due to the increasing distance from the cooled chuck holding the seed crystal (133). On the other hand, the Stöber process is best for growing crystals of great length, but the thickness is limited by the temperature gradient that can be maintained across the depth of the melt (133). In either case, it is the heat conduction problem that limits crystal size.

Industrially, the crystals of sodium iodide are grown by melting sodium iodide and letting the massive melt cool at a very slow rate. The process takes days and starts with the purest industrially available sodium iodide. If the crystal is to be a scintillator crystal, thallium iodide is added to make a mixed melt.

The salt is heated up prior to melting to volatilize water which is readily picked up by the deliquescent sodium iodide. Then it is placed in a sealed vessel, heated above its melting point, and allowed to cool at the rate of approximately one degree per hour. Many times, when the sealed vessel is opened after solidification has taken place, a large amount of iodine gas is given off. When all goes well, a clear cylindrical crystal with height and diameter of one foot is obtained. Then it is cut up for sale. Impurities present in the starting material are incorporated into the crystal with this technique. The heating of the salt prior to crystal formation also causes impurity problems because the volatilized water will react with iodide ions to produce free iodine and hydroxide ions. The overall reaction replaces iodide ions with hydroxide ions, and is the cause of the iodine cloud on opening the crystal growing vessels. The industrial method of growing alkali halide crystals is rather ineffective in preventing the addition of more impurity, not to mention the retention of the impurities already present.

Methods of Purifying Alkali Halides

General methods

High purity metals, organic materials, and salts have peen purified in recent years by a wide range of processes, some of which are quite new. Some of these methods are zone refining, electron beam melting, liquid-liquid extraction, ion exchange, chromatography, electrolysis, and thermal diffusion.

In a discussion of this problem by Carlson and Peterson (36), the prerequisite conditions are discussed. An equilibrium must be established between two phases for a segregation to take place. There are three possible phases, and hence six possible combinations. Gases are miscible in all proportions, so no segregation can take place with an all gaseous system. The all solid system is also eliminated, since it is impractical to separate the components of a solid solution. This leaves four useful phase combinations: the solid-liquid, the liquid-vapor, the solid-vapor, and the liquid-liquid.

Further, this discussion states that theoretical distribution of impurities and thermodynamic properties may not be known for multicomponent systems, especially if these systems are at very low, i.e., ultrapure concentrations. Phase diagrams are usually not available for this concentration region. Not the least of the problems is the contamination from the vessel or the atmosphere during the purification work. Kinetically, purification work becomes ever slower and less rewarding as the amount of impurity becomes smaller. Many workers who originate and use purification techniques are not interested in the theoretical basis of a separation, but merely want the process accomplished. This attitude does not ease the burden on those who wish to repeat or extend purification work.

Specific methods

Liquid-liquid extraction has provided the basis for the separation of several pairs of elements that are chemically quite similar. The pairs, tantalum-niobium and zirconium-hafnium, are particularly good examples of metals that have been extremely difficult to separate by ordinary chemical means such as crystallization, but have yielded to techniques forming different complexes of the metals under the same set of conditions, followed by extraction with the proper solvent (80, p. 440). Zirconium and hafnium are more alike in the tetravalent state than any other two elements, but have been separated by the use of thenoyltrifluoracetone to form chelates followed by extraction with an organic solvent, or by nitric acid and tributylphosphate. The pentavalent oxides of tantalum and niobium may be separated by treatment with a solution of potassium fluoride in hydrogen fluoride, which converts the oxides to potassium heptafluorotantalate (V) and potassium pentafluoromonoxoniobate (V). The tantalum complex is more soluble in the organic phase of the extraction mixture.

Ion exchange has allowed spectacular separations of the rare earth elements when complexed with citrate and eluted from an ion exchange resin. These procedures were developed at the Ames Lab during the period 1941-1945 by Spedding and his co-workers. Lately, use of EDTA and HEDTA have made possible even better separations of these elements in large amounts (45, p. 882). Inorganic synthetic ion exchange materials have made it possible to do the following: to remove rubidium from cesium (7), to distinguish between the alkali metals (6, 189), and to separate the alkali metals from other metals (151).

The type of ion exchange material used for this work is zirconium phosphate or ammonium molybdophosphate.

Entire analysis schemes have been set up using the techniques of chromatography, especially paper chromatography (185). Perhaps, it will be possible to separate salts by gas-liquid chromatography in the future. Partition media such as alumina, silica gel, and inorganic salt eutectics have already been used in operations up to 1000° C, but a resolution of five inorganic chloride salts was not very effective (70). In present day technology the materials to be separated by gas liquid chromatography must have a vapor pressure of at least 0.02 millimeters at 500° C (10). Materials that meet this specification include ammonia, carbon suboxide, sulfuryl chloride, nitrosyl chloride, and low-boiling gases. All that is necessary is the proper partition medium; for some, this has been found. The values of the heats of solution of arsenic (III) chloride, antimony (III) chloride, antimony (V) chloride, and titanium (IV) chloride were found by chromatographic means on a column with a fused bismuth (III) chloride-lead (II) chloride eutectic stationary phase (202).

The use of electrochemical potentials with corrections for the appropriate overvoltages makes it possible to separate aqueous solutions of metal ions. Sometimes the separation takes place in a reducing column.

Differences in volatility of materials has often allowed the materials to be made purer. Sublimation is a common technique for organic chemists, and similar use can be made of transport reactions for the purification of salts such as lithium fluoride (187). In such a case, there is a very definite distinction between the area where less volatile impurities are found, a pure material area, and the area where the impurities of greater volatility are found. Separations from such common materials in lithium fluoride as lithium oxide and hydroxide can be made. An added refinement is the condensation onto a heated surface to make more volatile impurities congregate in another section of the apparatus (150). Another example of this method is the crystal-bar or Van Arkel process, in which a metal is purified by forming an iodide in the apparatus, and decomposing the iodide on a hot wire (150).

Diffusion through membranes has been the basis for several separations of alkali metal halides. Passage through a porous membrane takes place by means of alignment-type diffusion for those materials that can form hydrogen bonds, while other materials are transported by hole-type diffusion. In this example, definite diffusion rankings may be set up for positive and negative ions (191). A porous cellulose filter saturated with a nonpolar organic solvent can differentiate between sodium and potassium ions with a permeability ratio of potassium ion to sodium ion of 30-40 (92). Osmotic transfer of solvent has been used to grow crystals, and the semipermeable membrane will certainly help purify the crystal formed by having a permeability ratio favoring the salt that is desired (208).

One of the most promising methods of purification has appeared in the last few years, i.e., the first paper on zone refining by the pioneer Pfann published in 1952 (159). For several years this technique was used almost exclusively with metals and was welcomed by metallurgists attempting to purify germanium and silicon for semiconductor use. Since then the process of zone refining has been extended to all kinds of preparative chemistry (68), pharmaceuticals (66), organic compounds (221), non-metallic elements such as phosphorus (49), and salts such as uranyl nitrate dihydrate (120), gallium trichloride (107), calcium tungstate (71), silver halides (142), and alkali metal halides (8, 9, 84, 100, 146, 163, 212, 213) and pseudo-halides (146).

The following examples are cited for alkali halides: 1) purification of the order of 10^4 has been effected in potassium chloride (84); 2) total impurity level has been reduced to less than 1 part per million using a floating zone technique with alkali halides and to approximately 0.02 parts per million using a horizontal boat refiner (212); and 3) potassium chloride has been purified to contain less than 2 parts per billion of oxygen impurities and less than 10 parts per billion of heterovalent ions (213). An analysis of potassium and potassium bromide subjected to

Table 2. Neutron activation analysis of zone refined potassium chloride and potassium bromide[a, b, c, d] (9)

Element	Concentration in KCl (p.p.m.)	Concentration in KBr (p.p.m.)
Br (bromine)	72.5	-
Cs (cesium)	<0.1	<0.1
Na (sodium)	<0.1	<0.1
Ni (nickel)	≤ 2	≤ 2
P (phosphorus)	-	<0.1
Rb (rubidium)	<0.1	<0.1
S (sulfur)	1-2	1-2
Zn (zinc)	0.46	0.45

[a] Harshaw Chemical Company starting material.

[b] Analysis performed at Oak Ridge Laboratory.

[c] In addition, these elements were present in amounts less than 0.1 parts per million: Ag, Si, Ta, W, Ti, Fe, Cr, Ga, Hf, In, Sc, Th, U, V, Y, Zr, rare earths, Ca, Ba, Sr, Mg, P (KCl only).
These elements were present in amounts less than 0.01 parts per million: Cu, As, Au, Bi, Cd, Ge, Hg, Ir, Os, Re, Mo, Pt, Ru, Sb, Se, Te, Sn, Mn.

[d] No analysis was done for: Al, B, F, I, Li, Pb, Tl.

zone refining was shown on page 14, Table 2, as an example of what this method can accomplish. The analysis was done with neutron activation at the Oak Ridge Laboratory of the Atomic Energy Commision. Analysis of organic compounds showed that naphthalene had been purified to contain 0.000947 mole per cent of other materials by zone refining (66), and cyclohexane was improved in purity from 98.93 per cent to 99.91 per cent in twelve passes at low temperature (33).

Synthesis of Sodium Iodide

The elements sodium and iodine were discovered almost simultaneously. Sodium was first formed by Davy (132, p. 421) in 1807 by means of electrolysis, and iodine was obtained by Courtois (46) in 1811 when he noticed that the copper vats being used to decompose calcium nitrate with kelp or varec were being corroded. Addition of sulfuric acid produced iodine, and sublimation purified it. Compounds of sodium had been known from antiquity, but the formation of it had to wait for non-chemical reduction (132, p. 419). Gay Lussac was the first to establish the similarity of iodine to chlorine (72). This work was done in 1813, and the following year Gay Lussac worked out the chemical properties of iodine in a paper that is a model of a thorough scientific investigation (73).

Indirect synthesis

With the similarities between the halogens established, Gay Lussac went on to prepare sodium iodide in 1813 by the action of an aqueous solution of hydrogen iodide on potassium carbonate or potassium hydroxide, followed by the concentration of the solution by evaporation (74). This method is still preferred as the most direct way to alkali halides.

Dumas and le Royer (177) set the pattern for a great number of syntheses of alkali halides by dissolving iodine in the alkali hydroxide to form a mixture of the iodide and iodate. Then the solution is evaporated to dryness and calcined until oxygen ceases to be evolved to reduce the iodate to iodide. Liebig (124) showed that the above process formed alkali hypohalite upon the action of iodine on the alkali hydroxide, and the hypohalite decomposed to halide and halate upon heating. Other investigators such as Preuss (166), used the same reactions. Pettenkofer (158) formed the hydriodic acid from the reaction of iodine and phosphorus in distilled water. Separation of the acid is accomplished by distillation. Hydriodic acid was formed by the reaction of copper (I) iodide on hydrosulfuric acid by Langbein (118).

Another method of attack involves the formation of a heavy metal iodide. The heavy metal iodide is decomposed with water and the resulting hydrohalic acid is neutralized with a base. Serulas (184) prepared antimony iodide by heating the elements together, and added water to form a solution of hydriodic acid and a precipitate of antimony oxyiodide. The acid was then neutralized with potassium carbonate. Liebig (122) took the alternate scheme of precipitating the heavy metal from solution with potassium carbonate, sulfate, or hydroxide, which at the same time formed potassium iodide. The barium iodide was formed by a reaction between baryta water and iodine, or iron (II) iodide could be substituted (121, 123). Other methods used a variation on the production of the original barium hydroxide (210) or in the substitution of calcium hydroxide (125).

In this century, most industrial processes for sodium and alkali halides have made use of the heavy metal iodide-alkali carbonate method. Examples of this also use barium sulfide to reduce the resulting iodate (40) or substitute zinc for iron (144). Organic impurities may be removed with activated charcoal (129).

The iodine-alkali hydroxide reaction is also used industrially to produce both potassium and sodium iodide (17, 218).

Other sodium iodide preparations include the reaction of iodine, sodium hydroxide, and sodium thiosulfate with a byproduct of sodium sulfate (135), and the reaction of sodium chloride with hydrogen iodide gas (93). Sodium hydrogen sulfite and iodine react to form sodium iodide and dithionic acid (190). Charcoal, iodine, and sodium carbonate can be reacted to form sodium iodide (15). Sodium hydroxide, hydrogen peroxide, and iodine react to form sodium iodide, water and oxygen (128).

Industrial purification steps often utilize the addition of sodium diethyldithiocarbamate (78, 128) to remove heavy metal impurities. Dithizone and 8-hydroxyquinoline (57) have been used to accomplish the same end. Dissolving an iodide in hot aqueous hydrogen iodide results in purer materials upon cooling to 30° C. At this point the purified crystals appear (97).

Direct synthesis

Synthesis of sodium iodide from the elements has not met with much success. In summarizing attempted reactions between alkali metals and halogens, Merz and Weith (134) in 1873 gave the data which is shown on Table 3, page 19. Other workers confirm their conclusions reached with regard to the action of sodium on chlorine (48) and bromine (193).

All the methods in this section for the production of sodium iodide utilize indirect methods and Table 3 confirms the reasons for this emphasis in light of the then-current knowledge regarding direct reactions between sodium and iodine.

Early in this century, Trautz (203) noted a chemiluminescence from the reaction of sodium or potassium in air or halogens, and Wilkinson (222) found luminescence occurred with alkali metals and halogens.

Table 3. Behavior of alkali metals and halogens according to Merz and Weith

Element pair	Behavior
Sodium and chlorine	No reaction when dry
Sodium and bromine	No reaction, even after heating
Sodium and iodine	No reaction, even when melted
Potassium and chlorine	Violent reaction even in the cold
Potassium and bromine	Very violent reaction; explosion
Potassium and iodine	Explosion, "welding flames"

This technique of converging gas streams led to a whole series of papers in the 1920's by a group of German and Russian physicists, who were investigating the energy spectrum of elements and conversions between these states. This work followed that of Bohr and was done concurrently with the development of the quantum mechanics. These workers sought to explain the mechanism of the reaction between an alkali metal with a halogen or oxygen in terms of the spectra obtained, or perhaps the reaction mechanism was to account for the spectra. According to Haber and Zisch (85), sodium atoms were thought to be excited by the exothermic reaction between sodium and the halogen and to produce the sodium D-line spectra without much luminescence. Investigators used a wide range of sodium and halogen pressures, from 10^{-3} millimeters (21) to 15 millimeters (127). In all cases, the sodium vapor and halogen vapor were swept along with a nitrogen gas stream. To bring the gas streams together, techniques of concentric tubes (19, 88), opposing entrances into a reaction vessel (22), or volatilization of the vapors from adjacent tubes (127) were employed. Iodine is present as atoms in flame conditions (162).

Examination of the precipitate and light distribution from the point where the flame occurred by Beutler and Polanyi (20) showed primary and secondary reactions corresponding to: 1) $Na + I_2 = NaI + I$

2) $Na + I + Na = NaI + Na + h\nu$

A discussion of the vapor reaction between sodium and iodine is the topic of a paper by Ootuka and Schay (152). Some difficulties arise in the measurement, in that it is possible for the nitrogen gas, used as a carrier stream, to be excited also and to interfere with the results, according to Ljalikov and Terenin (127) and Beutler and Polanyi (20). Hasche, Polanyi, and Vogt (89) found that, due to self absorption, the light emission from sodium vapor alone is the same as that for sodium vapor in reaction with iodine at low pressures. Fränz and Kallmann (65) used the excess energy of reaction of sodium and chlorine to excite mercury atoms to emission and determined energies of dissociation of halogen molecules.

Today this type of reaction is called a molecular beam reaction and is described in a reaction between potassium and alkali halides by Norris (148). A study of crossed molecular beams of cesium and bromine was made by Datz and Minturn (51), who postulated a stripping mechanism for the resulting reaction.

All of the work described above on the reactions of sodium and halogen gas streams swept along with nitrogen illustrates that physicists, not chemists, were doing the experimentation. Nowhere is a chemical test done to identify the products of the reaction, because these scientists were primarily interested in the energy states of sodium and the transitions between these states. The possibility that sodium vapor could react with the nitrogen carrier gas to form sodium nitride was not discussed, though this could certainly happen. The work is commonly done at moderate temperatures, which are less than the decomposition temperature of sodium nitride, 300° C. The reactions themselves seem quite possible under the conditions given, but the chemistry of the processes is accorded minor importance.

Methods Used for Producing Other Iodides

Direct union of elements is a favored means of forming metal iodides, and has been successful for such iodides as those of yttrium (112), boron (11), and niobium in the five (126), four, and three (43) valent states. Titanium (IV) iodide has been prepared by the reaction of aluminum, iodine, and titanium (IV) oxide in a sealed and evacuated vessel (23). This reaction took place by steps: first, the aluminum and iodine reacted violently at 100-110° C. and secondly, the reaction to form the titanium (IV) iodide took place at 450° C. The iodides of a wide variety of transition and representative metals were made by the action of aluminum iodide on the corresponding metal oxide (39). The driving force for these reactions is the high heat of formation of aluminum oxide. Another reaction process makes use of a very high pressure bomb with Hexogene giving pressures of 50,000 kilograms per square centimeter and temperatures of 30,000 atmospheres for the short time of 4×10^{-6} seconds (136).

EXPERIMENTAL PROCEDURES AND RESULTS

The experimental section is divided into two sections as set forth by the title : The Direct Synthesis and Purification of Sodium Iodide.

Direct Synthesis of Sodium Iodide

Review of previous work (98)

This summary is arranged by groups of reactions according to the phases of the elements reacting.

The reaction between solid sodium and solid iodine Attempts were made to seal samples of the two elements in a Pyrex tube while working in a dry box. Sealing was never accomplished satisfactorily, since the sodium metal formed an oxide coating in the two dry boxes used; one having the chamber and entrance port flushed with nitrogen purified over heated uranium turnings (77) and the other utilizing an entrance port which was evacuated and filled with helium. A resistance heater was used to make the seals of the Pyrex tubing.

Tubes sealed in this fashion were then exposed to ultrviolet radiation over a period of several days. Iodine molecules are dissociated by this treatment (44, 52, 116, 149, 211) and would then be in a more reactive state. A four hundred watt ultraviolet source was used for this purpose, but the reaction was incomplete. Tests for sodium ion by a flame test and for iodide ion with silver nitrate were weak.

The reaction between liquid sodium and liquid iodine This possibility was tried by means of two sets of conditions ; one of which was planned and the other completely unplanned.

The first method used as a source of sodium a dispersion prepared with a high speed stirring motor in a hydrocarbon solvent. The method made it possible to obtain very small particles of sodium in the micron range by means of a 17,000 revolutions per minute stirrer in a Morton designed flask(139, 140). A nitrogen gas purge of the apparatus was used to prevent oxidation by air, and mineral oil was chosen as the hydrocarbon solvent to permit higher temperature operation than the more common dispersion solvents. An iodine dispersion in the same solvent was then added to the sodium dispersion in a manner similar to the sodium hydride preparation by Whaley(220). Various conditions of stirring speed, temperature, and length of stirring were tried.

With this method, separation of the sodium iodide from the hydrocarbon solvent was the major problem. Positive tests for sodium ion and iodide ion were obtained, but the reaction was far from quantitative.

The second method of reacting the two elements in the liquid state occurred in a vessel held at a temperature of 150° C which contained molten sodium. The attempted reaction of sodium with iodine bubbling through the sodium was not successful, so iodine was added to the vessel and remained on top of the sodium crust, which had formed even in presence of a protective nitrogen purge. Six to twelve hours later, during the night, the reaction between the elements occurred with explosive force. The products gave strong sodium and iodide ion tests, which represented approximately 25 % conversion to sodium iodide. This method, though producing an appreciable amount of desired material, was not repeated due to the suddenness of the reaction.

The reaction between liquid sodium and vapor iodine This method was tried with many different approaches, which will be reviewed one at a time.

One trial made use of a Pyrex tube, which contained the elements, sealed in a dry box. The tube was heated until the sodium melted and the iodine turned into a vapor. Fairly strong sodium ion and iodide ion tests were obtained, but it was not possible to seal uncontaminated elements in a tube, as mentioned above.

An extended series of experiments was performed using the bomb technique to get liquid sodium and vapor iodine together. The dry box and gas-fired furnace, along with supplementary equipment, was made available in the metals reduction laboratories of Ames Lab. The practical experience of the Ames Lab workers was also put to use.

The bombs used were fabricated from steel pipe with a threaded or flanged and bolted cap. A magnesium oxide jarred and sintered liner was formed to fill the space between the bomb and the charge, as shown in Figure 1. Samples of sodium and iodine were weighed in the helium-protected dry box and placed in the bomb. After removal from the dry box, the bombs were placed in a steel drum furnace fired with an ordinary home gas burner. It was possible to insert a thermocouple lead in a well on the bombs to follow the rate of temperature increase. Temperature increase rate was difficult to control because the furnace was either on or off and there was no intermediate position. On several runs the temperature increase was slowed manually by switching the furnace on and off.

The first attempt using this equipment involved loading the two elements directly into the jarred and sintered magnesium oxide liner. By the inflection point on the temperature recorder chart, it was estimated that the reaction took place at approximately 200-300° C. The contents of the bomb, examined in the dry box, were a fused mass of reactants and liner. The fused material was insoluble in water, and showed that the liner had reacted with both sodium and iodine. Yield of sodium iodide was 7.79 %, which was determined gravimetrically by precipitation with silver nitrate.

After this run, all succeeding attempts were done with another liner material inside the steel bomb and magnesium oxide liner material. Most metals are eliminated as possibilities because they react extensively with iodine to form iodides. Experience with the crystal-

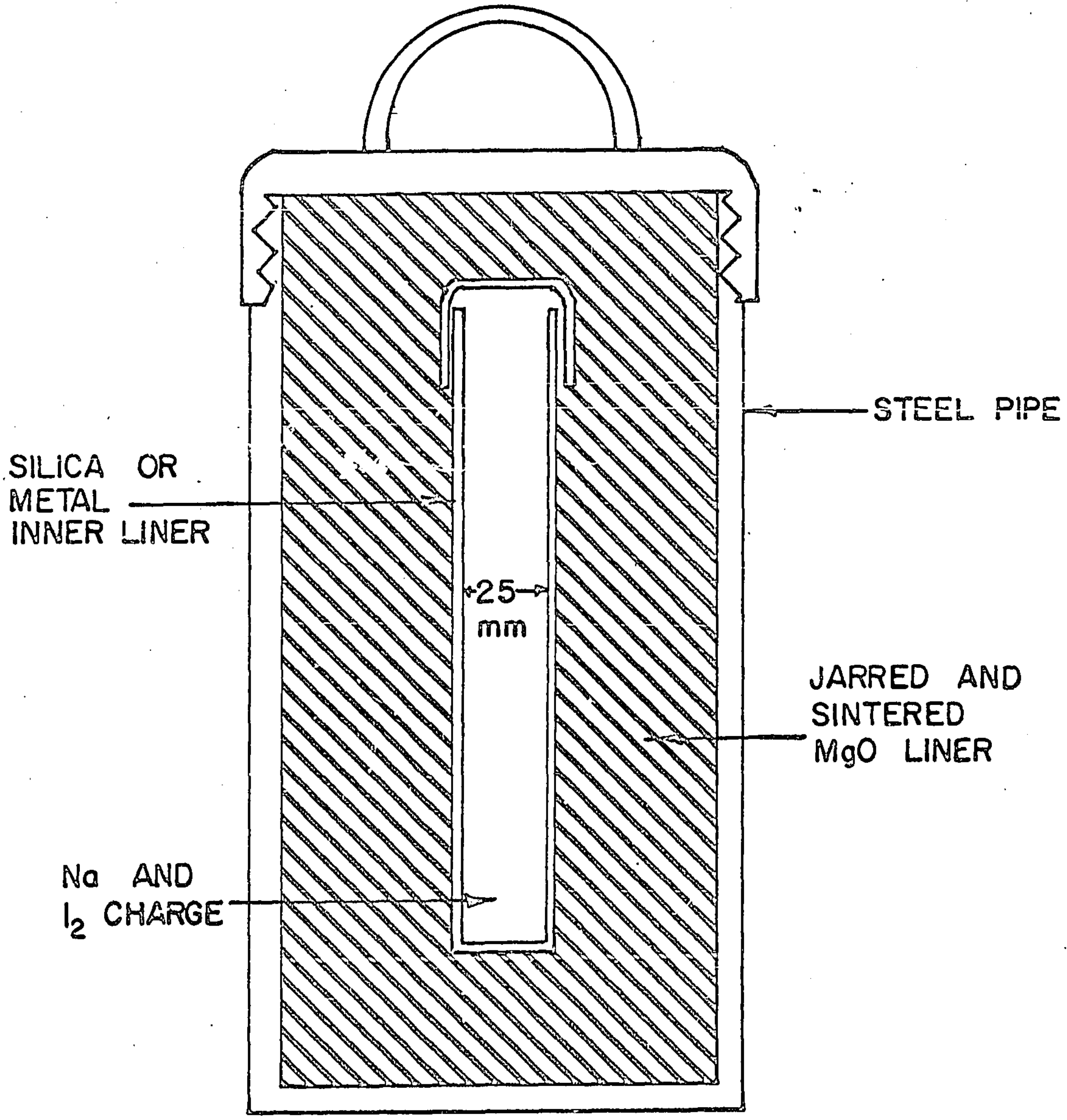


Figure 1. Bomb cross section

bar process of refining refractory metals has shown that molybdenum is the only metal that remains unaffected by iodine vapors at moderate to high temperatures, with nickel a relatively poor second choice.

With this in mind, a run was made with a quartz (fused-silica) liner inside the bomb and magnesium oxide liner. This was the most successful run, though the quartz liner cracked and the products showed the bluish tinge of colloidal sodium. The quartz liner also showed that both elements had been adsorbed on the inner walls. Analysis of this product follows in Table 4.

Table 4. Analysis of a sodium-iodine bomb reaction; quartz liner[a]

Compound		Percent yield[b]
Sodium iodide		69.76
Sodium hydroxide		25.30
	Total	95.06[c]

[a] Sodium iodide determined by the Volhard method(55, p. 332), sodium hydroxide by nitric acid standardized with sodium carbonate(55, p. 202).

[b] Based on weight of sodium.

[c] Some sodium lost by preliminary tests and adsorption.

Molybdenum is a difficult metal to fabricate, because it loses its ductility on heating and must be welded in an inert atmosphere. Nevertheless, a liner was made from molybdenum and loaded with sodium and iodine in the standard manner, and the bomb fired. On disassembling the bomb, it was found that the welded seams had shattered from the pressure increase in the bomb and that the reactants had fused almost beyond recognition with the magnesium oxide liner.

The next metal tried as a bomb liner was nickel. Though it is not as resistant to iodine vapors as is molybdenum, fabrication is considerably easier. This bomb using the nickel liner was loaded with weighed amounts of the two elements in the dry box and fired in the furnace. When the recording potentiometer reached 550° C (estimated bomb temperature was 200° C higher), the bomb exploded, causing extensive damage to the furnace. This was the reaction noted for its beauty by those in the rooms above in the Metallurgy Building. The contents of the bomb were never found, and bomb reactions were ceased by common consent.

On a new tack, an apparatus was fabricated to allow iodine vapor to pass over molten sodium as shown in Figure 2. Sodium metal was placed in the apparatus in the dry box, as was iodine. The sodium rested on the horizontal surface between the vertical tubes, and the iodine was placed in one vertical tube. Sublimation of iodine could

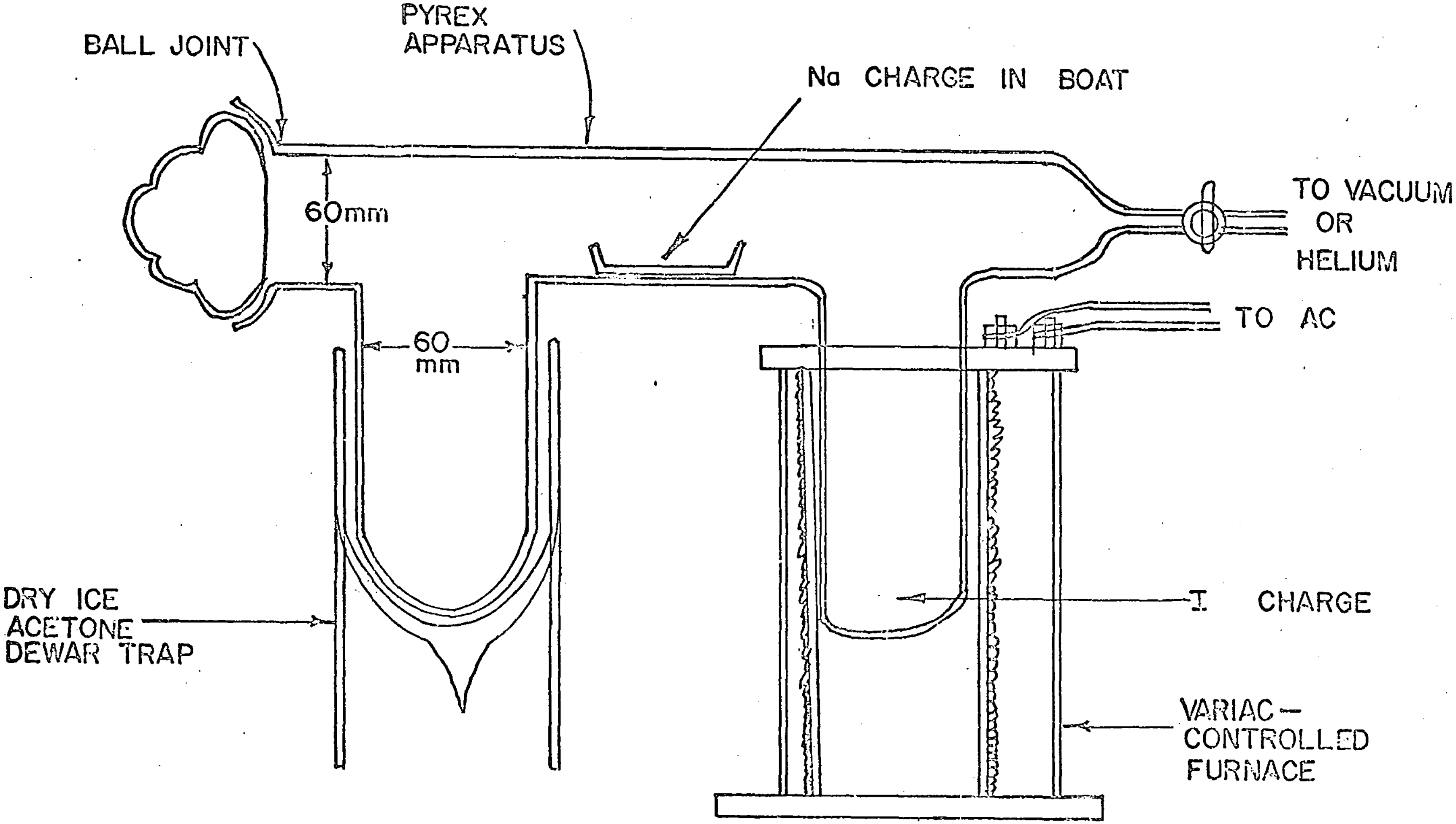


Figure 2. U-tube apparatus cross section

be carried out at one tube with heat from a furnace, and condensation occurred at the other vertical tube with liquid nitrogen.

The main difficulty with this method was that it was difficult to obtain a clean sodium surface to be exposed to the iodine vapor, which limited the reaction quite severely.

Attempts to overcome this difficulty by designing a boat to contain the sodium and heating the sodium to a higher temperature with heating tape and a split furnace were not successful. A two level boat with a stainless steel wool filter to remove sodium oxide from the sodium metal as shown in Figure 3 did not operate as hoped, and washing sodium metal in various organic solvents to remove the mineral oil protectant did not help.

The sodium oxide crust, which readily formed, prevented significant contact between the iodine vapor and the sodium, though each attempted reaction run produced a small quantity of sodium iodide, as shown by strong sodium and iodide ion tests. A quantitative determination of the percent iodide in one such run gave 36.37 %.

It was found during these experiments that a nitrogen gas purge formed a gray deposit on the sodium surface, and that this material was sodium nitride. For this reason, helium was used to protect the reactants. The last traces of oxygen and nitrogen were removed from the helium by passage over heated uranium turnings(77).

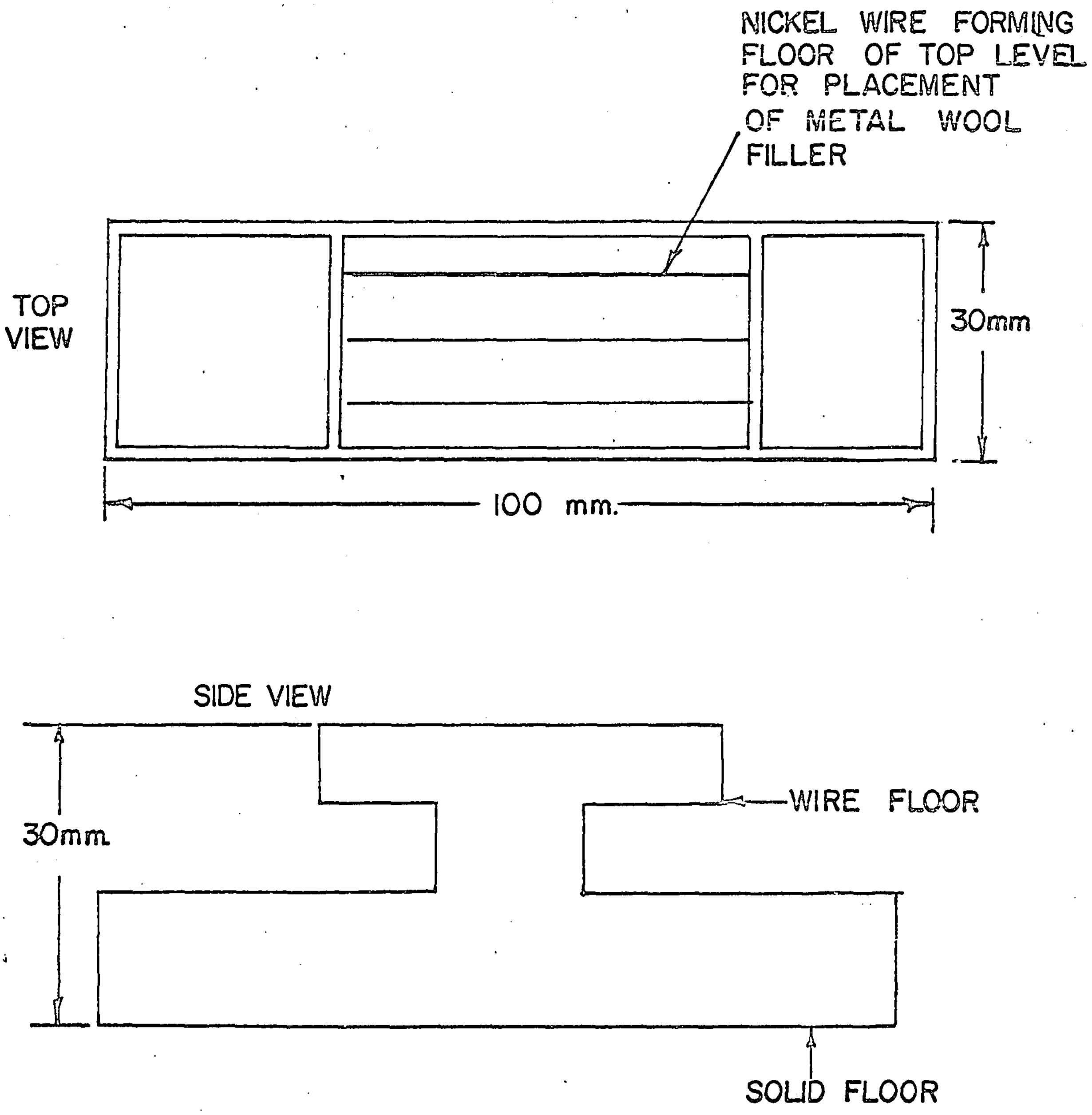


Figure 3. Two-level nickel boat

Another line of attack on the liquid sodium-vapor iodine reaction was to bubble iodine gas through molten sodium. An apparatus made for this attempt used a movable iodine delivery tube based on stirrer design, and had an inlet and outlet for helium purge gas. A separate iodine generator was the source of iodine vapor, and the delivery tube was heated with heating tape, as shown in Figure 4. Plugging of the iodine delivery tube under the surface of the molten sodium kept this method from working, even though the sodium and iodine were well above the melting point and sublimation point, respectively. An analysis of a product obtained by this method was done on a portion that obviously had reacted, and does not take into account the large amount of completely unreacted sodium. Most of the sodium that did react did so with oxygen and water vapor to form sodium hydroxide.

Table 5. Reaction analysis; iodine bubbled through molten sodium

Substance	Percent present
Sodium iodide; Volhard analysis	3.12
Sodium hydroxide; standard acid	77.67
Sodium; displacement of water in buret	19.21

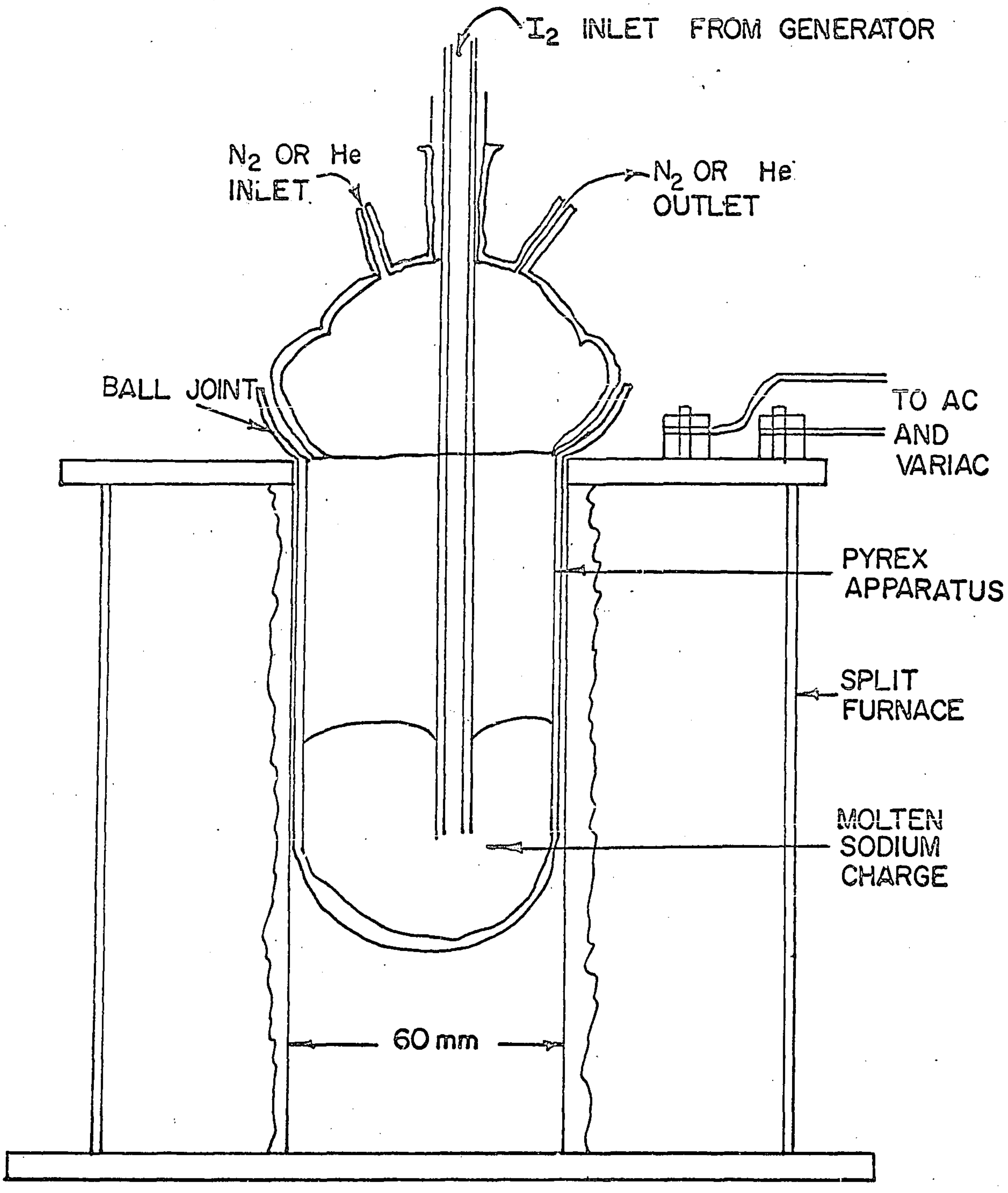


Figure 4. Cross section of apparatus for bubbling iodine into liquid sodium

The reaction between vapor sodium and vapor iodine This set of conditions put the elements in their most reactive and difficult-to-handle-form.

As a first trial, the common lecture demonstration for the production of sodium chloride from the elements was adapted to substitute iodine for chlorine. In this method, sodium which is burning on a deflagrating spoon is thrust into a chlorine (iodine) atmosphere. A white vapor is produced that upon condensation gives strong sodium and halide tests.

Naturally this method forms a rather appreciable amount of sodium hydroxide along with the desired product. To avoid this, a nitrogen gas flow was directed into the vessel containing the iodine, but the situation was not improved very much.

In a determination of the purity of the sodium iodide produced, a quantitative analysis of the product was made. This technique was necessary because the sodium was not weighed prior to the reaction, and some of the sodium iodide produced was lost to the atmosphere and was not condensed. It was therefore not possible to calculate the yield. The results of a typical run are shown in Table 6.

Another method used to test the vapor phase reaction utilized an apparatus made from Pyrex and consisting of a vertical arm for sodium and a horizontal arm for iodine. These vapor generation areas were heated with tube furnaces, and the whole apparatus was evacuated to a pressure of 2 X 10^{-5} millimeters of mercury. Heating above the sublimation temperature of iodine caused transport of that element, but this was not successful with sodium.

Table 6. Analysis of sodium iodide produced by burning sodium in an iodine atmosphere[a]

Compound		Percent present
Sodium iodide		97.02
Sodium hydroxide		2.98
	Total	100.00

[a] Sodium iodide determined by the Fajans method (55, p. 335), and sodium hydroxide determined by standardized nitric acid.

Additional synthesis work

The reaction between liquid sodium and vapor iodine

Maintenance of a clean sodium surface was the aim of an experiment utilizing the low-density properties of helium gas. An apparatus shown in Figure 5 was constructed, set up and rotated 180° in the clamp. Then the helium gas purge, which passed through a heated tube of uranium turnings as

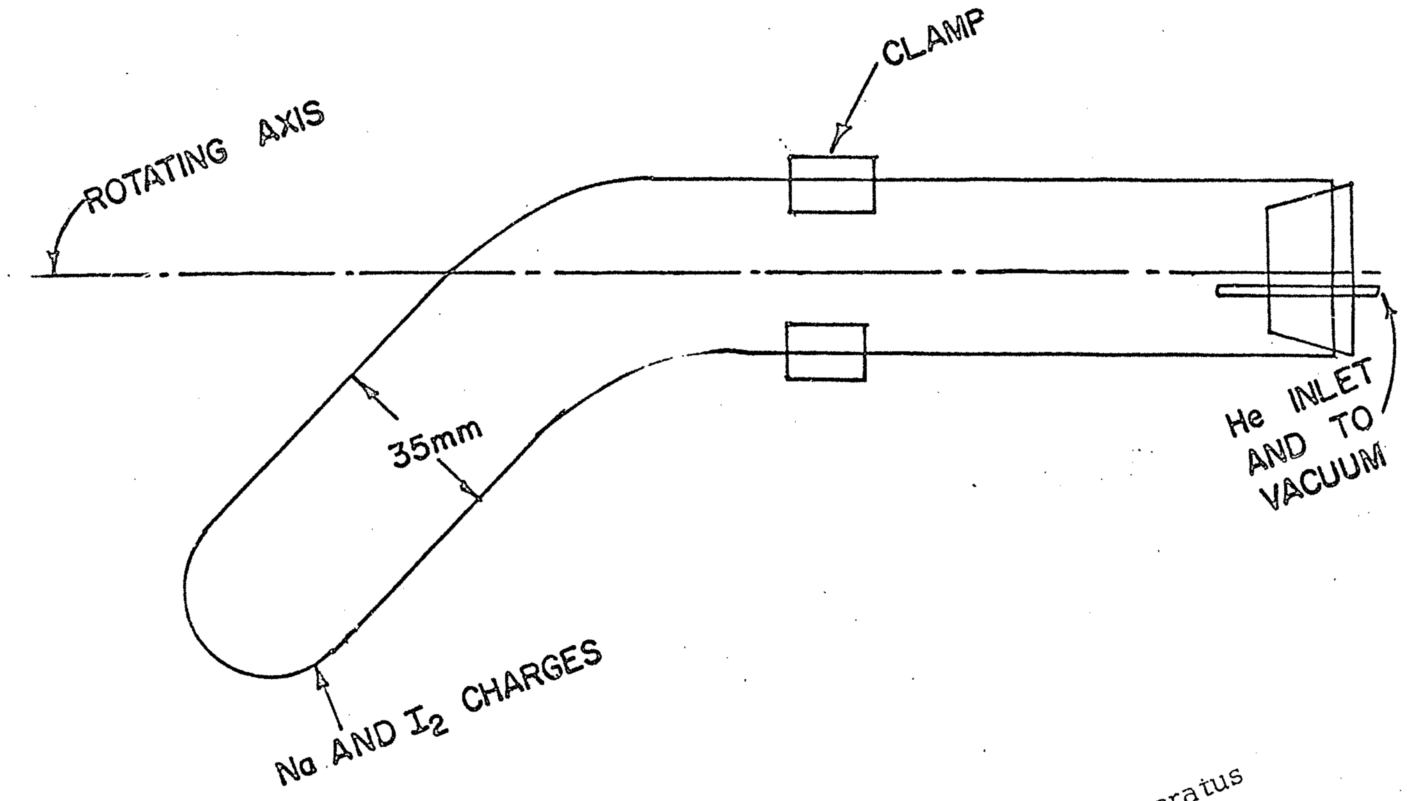


Figure 5. Bent tube reaction apparatus

described above, filled the tube by displacing the air. After fifteen minutes of flushing with helium, the bent tube was rotated to the position shown in Figure 5, which retained a pocket of helium gas at the closed end of the tube, even though this portion of the tube was no longer the highest point of the apparatus. A piece of sodium metal was cleaned and pushed to the protected end of the bent tube. The sodium was melted with a Bunsen flame, whereupon a black material formed on the surface and it was not possible to keep the surface bright, even by shaking the apparatus to try to clear the film. Iodine was added by means of a polyethylene cup on the end of a wire. No obvious reaction took place, though the iodine did volatilize. The problem is that the sodium oxide and other impurities formed should be dense enough to go to the bottom of the puddle of sodium metal, but are held in place by surface tension.

In another trial with the bent tube apparatus, the tube was evacuated before adding the elements and refilled with helium while in the inverted position described above. This process was repeated three times and the tube was rotated back into the position shown in Figure 5. When sodium was added and melted, the surface stayed much cleaner than in the previous trial. Iodine was added, and the tube was heated. Not much apparent reaction occurred. This method using the bent tube did not produce satisfactory results, and was abandoned.

To overcome the chief problem of the method described above, a new rotating double tube apparatus was designed and constructed, and is shown in Figure 6. This apparatus had a reaction chamber and a separate chamber for melting sodium metal. When the molten sodium was transferred to the reaction chamber, it was hoped that the oxide film and other impurities would be left behind.

The method of operation for the new apparatus was to flush it with purified helium, then to add a cleaned piece of sodium metal to chamber A, with the apparatus rotated so that chamber **A** would be in a vertical position. After melting the sodium with a Bunsen flame, the appartus was rotated in a counterclockwise direction to put chamber B in a vertical position. When this was done, the molten sodium flowed through the connecting tube to the reaction chamber, chamber B. The addition of the iodine took place in a similar manner, except that melting was not necessary. Flushing with purified helium took place at all times, and air and water vapor were removed by evacuating the whole apparatus prior to use.

During a run with this apparatus, the sodium metal turned black when placed in chamber **A**. Melting followed, which cleaned the surface of the sodium considerably. Transfer to chamber B was facilitated by wrapping heating tape around the connecting tube. When iodine was added to the vessel, and the reaction chamber heated, a flame occurred

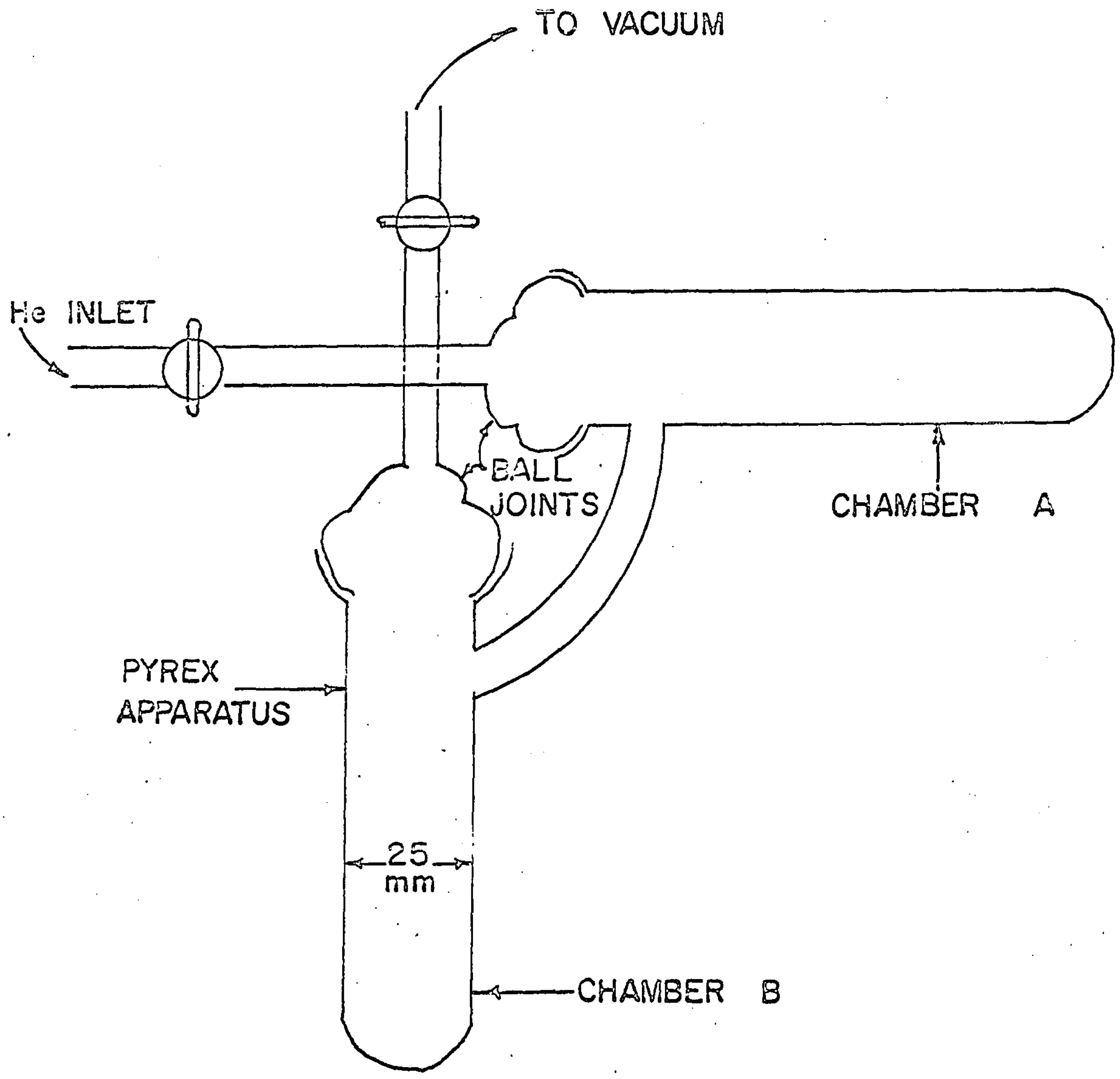


Figure 6. Rotated double tube apparatus

and small deposits of salt formed on the walls of the reaction chamber. Burning pieces of sodium devitrified and cracked the walls of this chamber and consequently ruined the apparatus. The amount of sodium iodide produced by this reaction was small, and a large amount of sodium hydroxide was present along with unreacted sodium. The chief conclusion from this work was that Pyrex glass is not a suitable container material for the reaction between sodium and iodine. Pyrex will not contain burning sodium.

Still another method which was used to promote the reaction between liquid sodium and vapor iodine was that of adding the elements to sodium iodide itself. Sodium and iodine were placed in a nickel crucible. Sodium iodide was placed on top of this mixture of the two elements. The first time this method was used a violent reaction took place and sputtered sodium iodide out of the crucible. This reaction, however, was attributed to the presence of water in the sodium iodide. Further runs utilized dried sodium iodide which had been under vacuum for more than a day. Under these conditions, no reaction was observed. The iodine all volatilized before the sodium reached a reactive stage. This difference in volatility had been the basic problem with several attempts, and is no doubt the reason for the lack of success cited in the literature for the direct synthesis of sodium iodide.

The last method used for this type of liquid sodium-vapor iodine was a modification to prevent occurrence of the problems preventing success in the last two examples cited directly above. The apparatus was made of nickel to overcome the problem of sodium attacking a glass container, and was sealed to keep the elements together while heating them. Disadvantages of this design are that nickel is not entirely inert to the attack of iodine vapor, and pressure built up in the apparatus due to volatilizing iodine. The pressure is further increased by the high heat of reaction of sodium and iodine. This piece of equipment is shown in Figure 7. The lid contained a groove to accept an "O" ring as a seal, and was held in place by a bail fastened to the sides of the nickel vessel. The lid could be tightened down by screwing a bolt in the bail against the lid. An auxiliary lid with an entrance tube was available for evacuating the apparatus or flushing with helium.

The apparatus was loaded with iodine after it was evacuated and flushed with helium. Next, a piece of stainless steel wool was stuffed in the container to form a bed for the sodium and to filter out impurities when the sodium was melted. Lastly, a piece of sodium was added, the "O" ring lid put in place, and the lid tightened. All possible operations were carried out under the protection of a stream of purified helium.

To start the reaction, a Fisher burner was used to heat the walls of the container. This treatment melted the sodium and allowed it to run

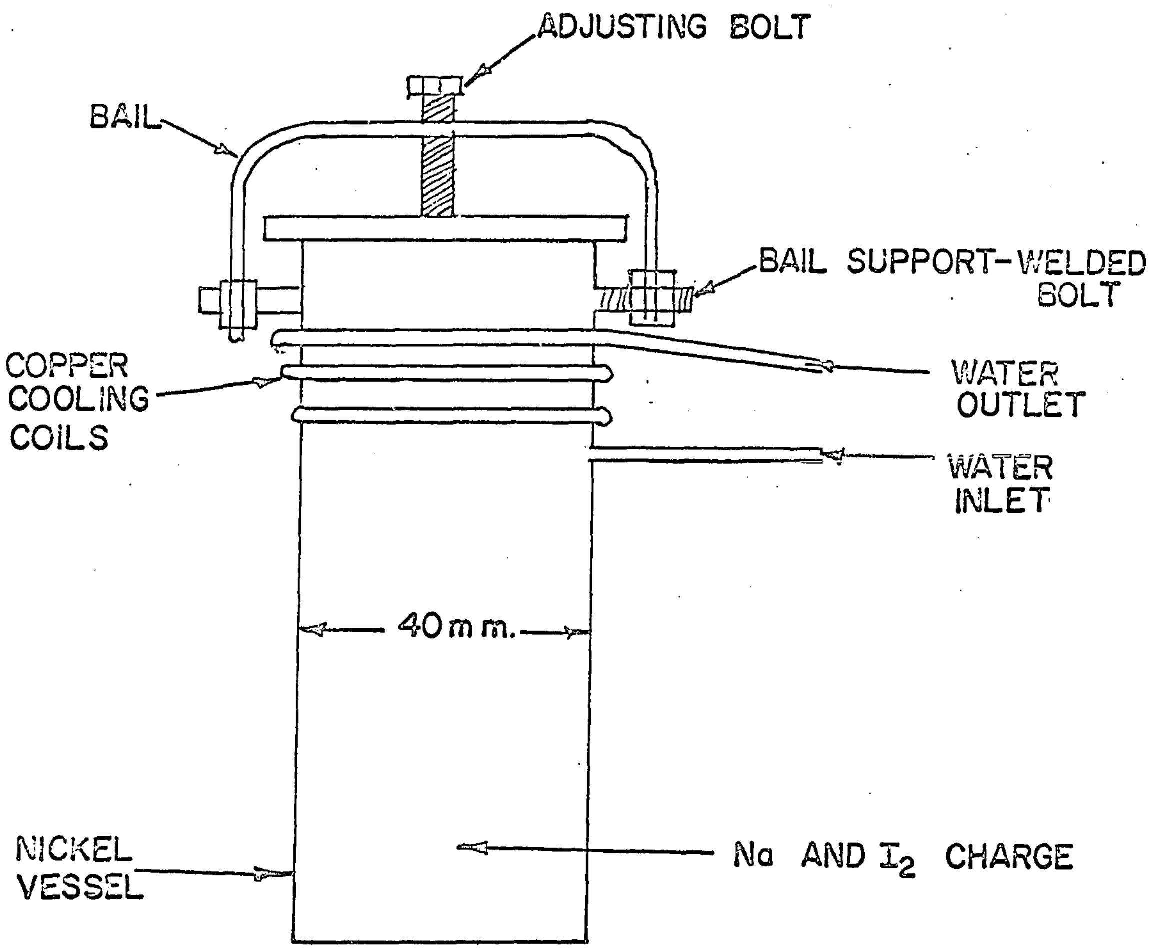


Figure 7. "O" ring sealed nickel apparatus

down through the stainless steel wool filter and come into contact with the iodine. While preparing to heat the resulting mixture of the elements, the "O" ring seal failed and released a cloud of iodine vapor. The seal was destroyed by the action of hot iodine which made it hard and brittle.

A coil of copper tubing was soldered around the top of the vessel just below the "O" ring seal area to protect the seal from heat. In the next trial, the vessel worked quite well. The melting of the sodium to allow it to pass through the filter and further heating of the two elements did not affect the seal. Upon opening the container, it was found that most of the sodium and iodine did not react. A greenish-white chalky powder, which was in the bottom of the vessel, turned into a mossy appearing precipitate when the products were dissolved in water. The solution was yellow and the precipitate gradually turned brown, indicating that iodine was dissolved in the solution. A test for nickel ion, performed by adding ammonia and dimethylglyoxime, showed the presence of a moderate amount. Prior to this test, iodide ion, which appeared to interfere, was removed with silver nitrate. Silver ion would also interfere by reacting with ammonia, so silver ions were removed with potassium chloride solution. All precipitates were discarded and the treatment had the effect of removing the iodine. This trial added nickel to the product, and was not tried again.

Analysis of the product from the above reaction showed it was quite impure. The method of analysis was used with a large number of products obtained and is described in detail.

Each product was dissolved from the reaction vessel with water. This solution was gently boiled over a Fisher burner until dryness. Still more heating often released a small amount of iodine, and in many cases, turned a rather dark-appearing product into a brilliant white material. It must be said that this treatment was happened on at least partially by mistake, when a beaker containing a product inadvertently was boiled to dryness and not noticed until the material had been heated quite strongly. After a product material cooled, it was placed in a weighing bottle and further dried in an oven operating at 110° C for a period of at least twelve hours. Samples of the product were titrated with standardized solutions of nitric acid and silver nitrate for the determination of sodium hydroxide and sodium iodide.

The nitric acid was standardized against primary standard trishydroxymethylaminomethane that had been dried in a vacuum desiccator, using metnyl purple as the indicator. The adsorption method was used to determine iodide. The silver nitrate solution was standardized against weighed samples of oven-dried potassium iodide. In this case, 5 milliliters of 1 % dextrin solution and 8 drops of a 0.1 % eosin solution were added to each portion. Dextrin was used as a protective colloid to keep the resulting silver iodide in a finely divided state, and eosin is highly colored when silver salts are present in excess in a solution containing silver iodide, thus indicating the end point(55, p. 335).

Two samples of each product were weighed, with both hydroxide and iodide determined on the same sample. The hydroxide is titrated first, using phenolphthalein as an indicator. Then the adsorption method may be used to determine iodide content, because the phenolphthalein is now in the colorless form and eosin works as the iodide indicator even in acidic solutions.

The calculations performed follow this scheme: the normality and volume of standardized nitric acid used allow calculation of the weight of sodium hydroxide present in the sample. This weight of impurity is then subtracted from the weight of the sample to obtain a weight which should be entirely made up by sodium iodide. Next normality and volume of standardized silver nitrate are used to calculate the number of equivalents of sodium iodide that are present. The number of equivalents and the corrected sample weight are used to calculate the corresponding equivalent weight of the sodium iodide found. This equivalent weight, if the sample is pure sodium iodide, should equal the equivalent weight of anhydrous sodium iodide: 149.92. Sample calculations follow for the reaction of sodium and iodine in the case of the reaction of sodium and iodine in the nickel apparatus sealed with an "O" ring, which is described above as the last liquid sodium-vapor iodine reaction.

Table 7. Sample purity calculations for a direct synthesis product

Value	Sample 1	Sample 2
Weight of product taken	0.2682 grams	0.2201 grams
Milliliters of nitric acid used	12.53	11.20
Equivalents of nitric acid (N= 0.09691) used; equal to equivalents of sodium hydroxide present	0.0012143	0.0010854
Weight of sodium hydroxide found	0.0453 grams	0.0405 grams
Corrected weight of sample (weight minus sodium hydroxide)	0.2229 grams	0.1796 grams
Milliliters of silver nitrate used	Void-over	5.54
Equivalents of silver nitrate used (N=0.11252); equal to equivalents of sodium iodide	Void	0.00061323
Equivalent weight of sodium iodide	Void	288.12

This table of calculations shows that experimental titration technique was not of the best order, due to the problem with the first sample, but this case is the first one described with regard to synthesis techniques and is used for that reason. The equivalent weight obtained also shows that the sodium iodide was quite impure, as already indicated above in the description of the method. The impurities included nickel from the vessel, and it can be noted that there were more equivalents of sodium hydroxide present than there were equivalents of sodium iodide.

Checks were made to see if the above technique of determining both hydroxide and iodide in the same sample was a valid method. Solutions of sodium hydroxide and sodium iodide were made up. The sodium hydroxide solution was protected from carbon dioxide by forcing air entering the container to pass through an Ascarite drying tube. Samples of sodium hydroxide and sodium iodide were taken with a pipette in a 1:5 ratio, and phenolphthalein was added to exactly duplicate experimental conditions. Results are shown in Table 8. The very small difference between titrations of reagents, separately and together, indicates that the procedure is justified and that the presence of phenolphthalein does not affect the result.

A large number of trials were made to see if the method of treatment of products of direct synthesis was a valid one and to check the method of calculation.

Table 8. Titration of sodium hydroxide and sodium iodide on a known sample

Compound found	Combined sample[a]	Separate sample[b]
Sodium hydroxide; milliliters of nitric acid required	# 1- 2.23	# 1- 2.22
	# 2- 2.24	# 2- 2.22
	# 3- 2.16	
Sodium iodide; milliliters of silver nitrate required	# 1 -9.50	# 1 -9.44
	# 2- 9.45	# 2- 9.50
	# 3- 9.50	# 3- 9.46

[a] Containing 10.00 milliliters of 0.09988 N sodium iodide, 2.00 milliliters of 0.1111 N sodium hydroxide, and two drops of phenolphthalein.

[b] Sodium hydroxide samples contain 2.00 milliliters of 0.1111 N sodium hydroxide and sodium iodide samples contain 10.00 milliliters of 0.09988 N sodium iodide.

Products were crystallized from ethanol during the purity trials, but initial trials indicated the presence of the dihydrate of sodium iodide. Titrations were done to determine the base content with nitric acid standardized as described above, and to determine iodide content with silver iodide by the Fajans or adsorption method(55, p. 335). The dihydrate form would cause great problems in crystal growing, because dihydrate decomposes at elevated temperatures. This in turn would lead to the formation of hydroxide in the crystal and the release of iodine gas.

Other trials were made to see if the weighing technique was adequate to obtain a condition of constant weight. A preliminary investigation showed that sodium iodide picks up moisture from the air on long exposure, especially in humid weather and in poorly sealed containers. A sample of commercial sodium iodide lost approximately 20 % of its weight on oven drying, but then remained at constant weight for four days even though the seal on the weighing bottle was not air tight. Another sample and its changes in weight with different treatments is shown in Table 9.

The next set of trials was to test the working up of the products obtained by direct synthesis. One sample of sodium iodide was treated as shown in Table 10.

Since the samples shown in Tables 9 and 10 did not contain sodium hydroxide, while typical products did, a product of direct synthesis was also tested to determine the effects of recrystallization. Tables 11 and 12 are similar in form to Tables 9 and 10, except that sodium hydroxide has been added to the samples in Tables 11 and 12.

Table 9. Testing for constant weight with a sodium iodide sample[a]

Steps in treating sodium iodide	Weight of sample
1. Oven and vacuum dried[b]	1.1778 grams
2. Exposed to air, then vacuum dried	1.1752 grams
3. Oven dried[c]	1.1778 grams

[a] Harshaw optical grade crystal.

[b] Weighing bottle previously treated in a similar fashion.

[c] Titrated with silver nitrate and shown to be 99.62 % sodium iodide with good precision on one sample, and to have an equivalent weight of 149.92 on a second sample.

Table 10. Testing the effects of recrystallizing sodium iodide[a]

Steps in treating sodium iodide	Weight of sample
1. Oven and vacuum dried	0.8273 grams
2. Recrystallized from absolute ethanol	0.8270 grams
3. Again recrystallized from absolute ethanol	0.8191 grams (transfer loss)

[a] Equivalent weight of the Harshaw optical grade material was 150.17.

Table 11. Testing for constant weight with sodium iodide-sodium hydroxide mixed samples[a]

Steps in treating the sample	Weight of sample and weighing bottle
1. Prior to treatment	6.7862 grams
2. Vacuum dried	6.7300 grams
3. Oven dried	6.7100 grams
4. Vacuum and oven dried	6.7098 grams
5. Twenty hour exposure to air	6.7204 grams

[a] Product of a direct synthesis run which was titrated with silver nitrate and shown to have an equivalent weight of 170.31 with fair precision. The amount of sodium hydroxide found by titration with nitric acid was subtracted from the sample weight before calculation of the equivalent weight.

The results on samples from experimental runs containing sodium hydroxide were far less satisfactory than those without sodium hydroxide. This material with sodium hydroxide is far more hygroscopic, as evidenced by the weight increase in Table 11 and the high equivalent weight in Table 12. During the weighing processes, the sample material was exposed to humid air, which definitely affected the material containing sodium hydroxide. This trend was further confirmed on a synthetic sample of sodium iodide and sodium hydroxide, made up to resemble a product of a direct synthesis trial. This synthetic product had a very high equivalent weight because it was an equi-molar mixture of sodium iodide and sodium hydroxide and therefore picked up a considerable amount of water.

Table 12. Testing the effects of crystallizing a mixture of sodium iodide and sodium hydroxide[a]

Steps in treating the sample	Equivalent weight of the sample[b]
1. Recrystallized from water	156.32
2. Again recrystallized from water and then from ethanol	157.44

[a] Product of a direct synthesis run.

[b] Average of two samples in each treatment, obtained with good precision.

Other trials used weighed amounts of sodium iodide and sodium hydroxide to test the efficiency of recrystallization from water, the purpose being to detect the same amounts before and after recrystallization. Typical results of these trials are shown in Table 13.

Table 13. Testing for constantcy of amount of sodium iodide[a] and sodium hydroxide[b] before and after recrystallization

Sample	Weight of sodium iodide, grams	Weight of sodium hydroxide, grams
Samples before recrystallization		
Combined sample # 1, weighings	0.5014	0.1842
Combined sample # 1, titrations[c]	0.5061	0.1668
Combined sample # 2, weighings	0.5281	0.1896
Combined sample # 2, titrations	0.5314	0.1698
Samples after recrystallization		
Separate sample # 1, weighing	-	0.1927
Separate sample # 1, titration	-	0.1698
Separate sample # 2, weighing	-	0.2202
Separate sample # 2, titration	-	0.1993
Separate sample # 3, weighing	-	0.1978
Separate sample # 3, titration	-	0.1809

[a] Harshaw optical crystal grade.

[b] Mallindrodt Analytical Reagent grade.

[c] Sodium iodide determined by titration with silver nitrate by adsorption indicator, and sodium hydroxide titrated with standardized nitric acid.

Table 13 (Continued)

Sample	Weight of sodium iodide, grams	Weight of sodium hydroxide, grams
Separate sample # 4, weighing	0.4646	-
Separate sample # 4, titration	0.4688	-
Separate sample # 5, weighing	0.5634	-
Separate sample # 5, titration	0.5656	-
Separate sample # 6, weighing	0.1988	-
Separate sample # 6, titration	0.1996	-
Separate sample # 7, weighing	0.2160	-
Separate sample # 7, titration	0.2166	-
Separate sample # 8, weighing	0.2177	-
Separate sample # 8, titration	0.2193	-
Separate sample # 9, weighing	0.2916	-
Separate sample # 9, titration	0.2925	-

A conclusion reached from the analyses presented in Table 13 is that all of the sodium iodide present is found, whether the sample is recrystalized or not, and whether the sample contains sodium hydroxide or not.

More sodium iodide was detected than was weighed out due to the slight amount of chloride which was present in the sodium iodide used. This impurity lowered the equivalent weight of the sample and caused the amount of total halide found by titration to slightly exceed the amount of sodium iodide weighed out.

The other important conclusion is that less than 100 % of the sodium hydroxide added is detected by titration, whether the sample contains sodium iodide or not, and whether it has been recrystallized or not. The amount of sodium hydroxide detected by titration was 90.1 percent of that weighed out in the combined samples before recrystallization, and 91.03 percent in the separate samples after recrystallization. The difference between the amount weighed out and the amount detected may be attributed to the fact that sodium hydroxide is only 97 percent pure, and further exposure to air will cause the formation of sodium carbonate which has a higher equivalent weight than sodium hydroxide.

The consistency of the results obtained in Table 13 is cited as evidence that the method of analysis is valid for determining the sodium iodide and sodium hydroxide content of products of direct synthesis, and that recrystallization does not affect the chemical state of either material. In all cases, the samples were vacuum and/or oven dried, and kept in a weighing bottle to minimize the

the effects of the hygroscopicity of both substances.

The fact that exposure to humid air affects samples was shown with a large number of synthetic products made up by dissolving various amounts of sodium iodide and sodium hydroxide in water. Upon treatment by the standard method of analysis, namely boiling dry followed by oven drying and titration with silver nitrate and nitric acid, it was found that the equivalent weight of sodium iodide was always high. The amount of sodium hydroxide detected by titration was subtracted from the total sample weight, and this corrected figure was used to calculate the equivalent weight. Further, there appeared to be a proportional relationship between the percent of sodium hydroxide present in a sample and the equivalent weight of sodium iodide calculated. This relationship contains many more variables than the percent of sodium hydroxide, such as chance exposure to humid air or analysis differences, but the proportionality of equivalent weight of sodium iodide to the percent of sodium hydroxide still remains clear. A graph of these two variables is presented in Figure 8, and a listing in Table 14. An added point at zero percent of sodium hydroxide is obtained from Table 15a. An allowance is made for the fact that the amount of sodium hydroxide detected by titration only makes up approximately 91 % of the total weight of impure sodium hydroxide added. In most cases, this made little difference.

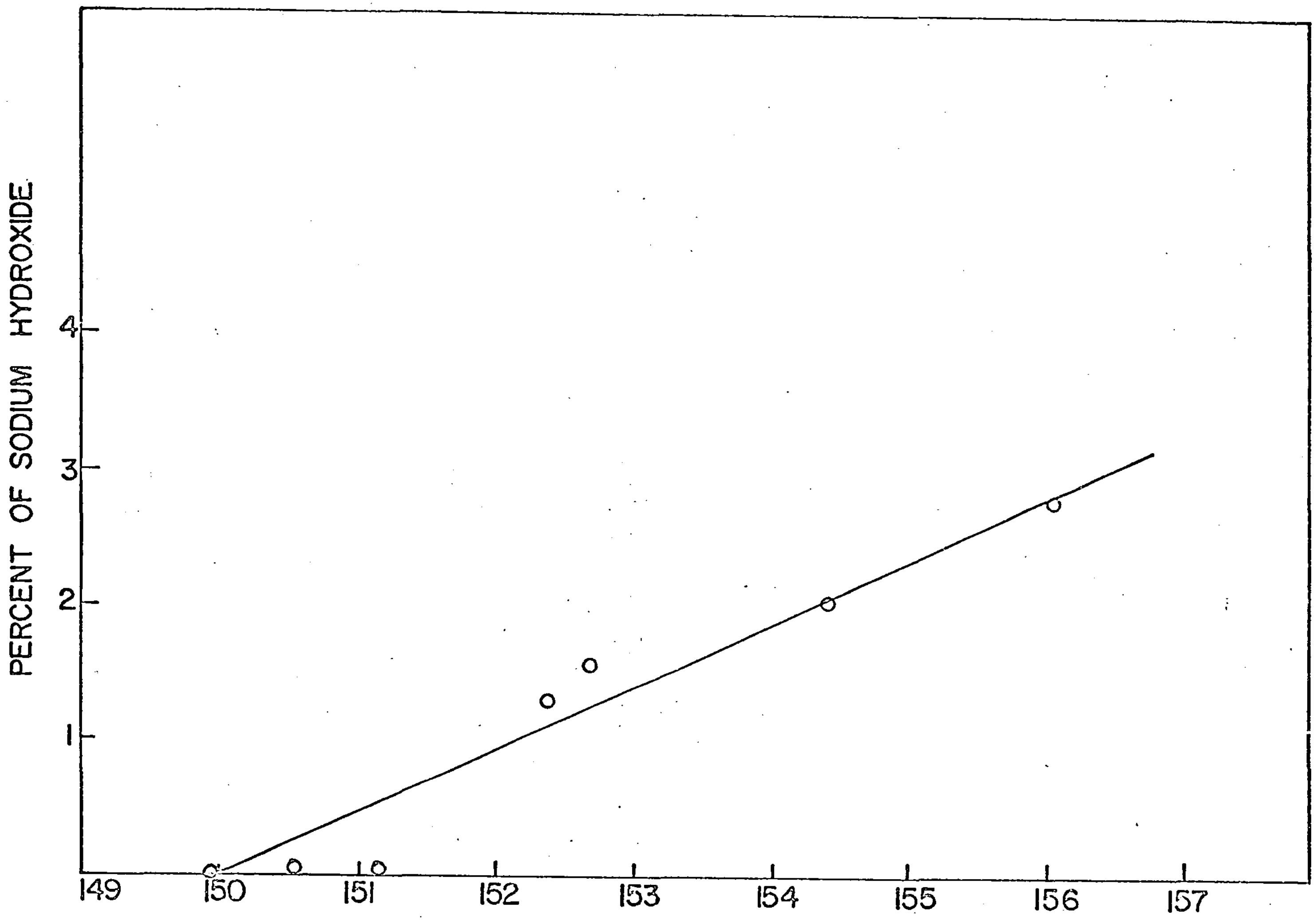


Figure 8. Graph of percent of sodium hydroxide versus equivalent weight of sodium iodide

Table 14. Correlation between percent of sodium hydroxide and equivalent weight of sodium iodide in synthetic combined samples

Sample	Percent sodium hydroxide	Equivalent weight of sodium iodide, uncorrected	Equivalent weight of sodium iodide, corrected[a]
Control # 1[b,c]	1.58	152.68	152.43
Control #2	2.10	154.39	154.17
Control #3	1. 35	152.37	152.14
Control #4	0.05	151.18	151.18

[a] Corrected to use the fact that the sodium hydroxide was 91 % pure by dividing the weight of sodium hydroxide by 0.91.

[b] Harshaw optical cyrstal grade sodium iodide and Mallinkrodt Analytical Reagent sodium hydroxide.

[c] Average of three samples for each control with good precision.

The equivalent weight of the samples after recrystallization from water shown in Table 15a averages 149.89, which can be compared to an average of 149.67 before recrystallization. Both equivalent weights incorporate very good precision and accuracy, and are within experimental error. The figures in Table 15a were used to establish a point of zero sodium hydroxide concentration and the corresponding sodium iodide equivalent weight for Figure 8, and also to show that recrystallization from water, under the proper conditions, has no effect on the degree of hydration of sodium iodide.

Table 15a. Effect of recrystallization from water on weights and equivalent weights of sodium iodide samples[a, b]

Sample	Weight before recrystallization	Weight after recrystallization	Equivalent weight[c]
# 1	1.3456	1.3451	149.79
# 2	1.2017	1.1998	149.98
# 3	1.1828	1.1814	149.89

[a] Harshaw optical crystal grade.

[b] All samples boiled dry, baked, and oven dried after recrystallization.

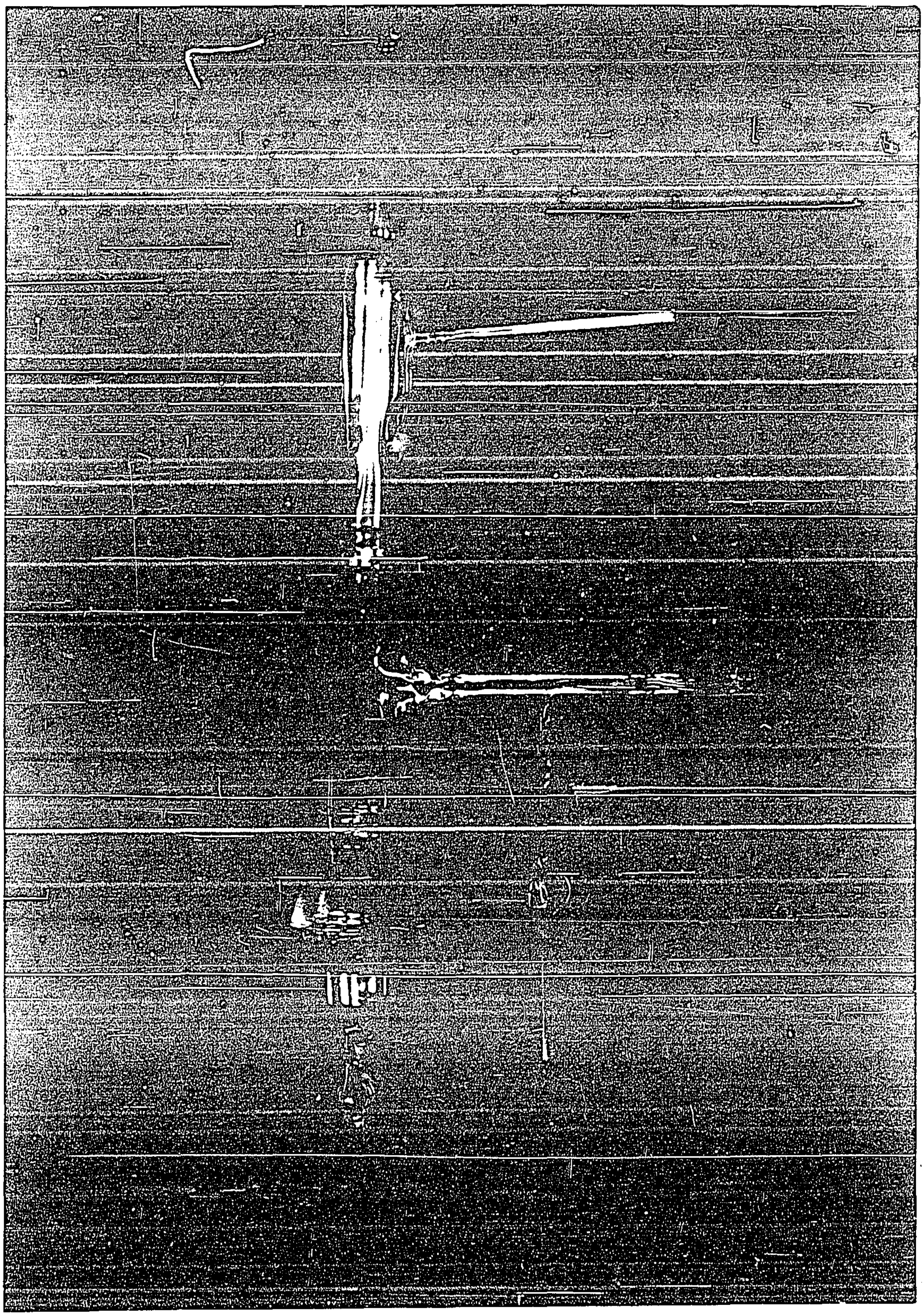
[c] Determined by titration with silver nitrate by the adsorption method.

Other results from the analytical analysis made above indicate that products of individual synthetic runs may be analyzed as shown. Titration for sodium hydroxide and sodium iodide may be done on the same sample without error, and recrystallization from water will not affect the degree of hydration if precautions to exclude moist air are taken. Further, the calculation of the equivalent weight of sodium iodide is a valid measure of the degree of purity of a product of direct synthesis, provided subtraction of the amount of sodium hydroxide is made from the sample weight taken. This method was used as a purity test for all further synthetic products.

The reaction between vapor sodium and vapor iodine The apparatus shown in Figure 2 was modified to allow a completely vapor phase reaction to take place in it. The iodine generator was a horizontal tube and the sodium generator was a vertical tube, as shown in Figures 9 and 10. A heating furnace was placed around each generator, and a Plexiglas safety shield was placed in front of the apparatus for personal protection in case of a violent reaction. Provision was made to evacuate the apparatus prior to use, with traps as an integral part of the apparatus and at an in-line position. The extensive trapping was necessary to prevent iodine from entering the pump and corroding the oil and pump mechanism. A thermocouple was used to measure the temperature in each furnace, so that the vapor pressure of the elements could be controlled.

The apparatus was loaded with iodine by means of a V-shaped device made of stainless steel in the form of a shovel. Sodium was cleaned and pushed into position in the vertical tube with the same

Figure 9. U-tube apparatus



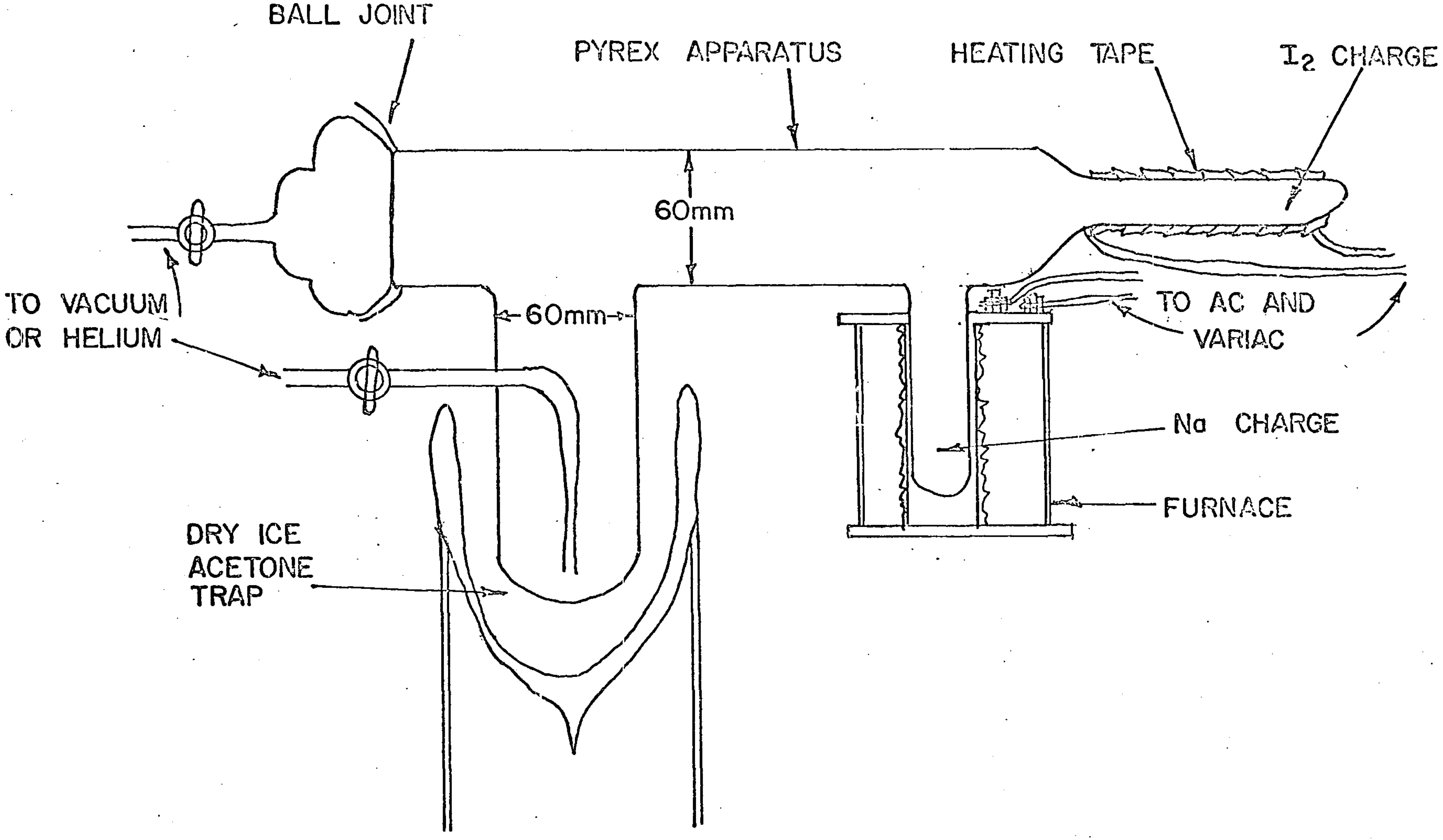


Figure 10. U-tube apparatus with sodium and iodine generators, cross section

device. The apparatus was immediately evacuated to minimize air oxidation of the sodium and to allow both elements to volatilize more easily; the sodium generator was heated to 450° C and the iodine generator to 80° C. The vapor pressures produced are shown in Figures 11 and 12 (26, 86, 91, 170, 171, 217).

The above conditions did not promote much reaction, so temperatures were increased to 500° C for the sodium generator and to 120°C for iodine generator, corresponding to 5 millimeters vapor pressure and 110 millimeters vapor pressure, respectively. A plug of white material, apparently sodium hydroxide, formed in the vertical tube. A small amount of white material was deposited on the walls of the apparatus near the juncture of the generators. This material did not react with water and therefore contained no unreacted sodium, and in solution did not affect pH paper and therefore did not contain sodium hydroxide. The white material tested above gave a copious precipitate with silver nitrate.

A modification to the apparatus was made to avoid the sodium hydroxide plug formation. A heating tape was wrapped around the area where the sodium generator joined the main tube, and was kept at 200° C. In a trial with this revised apparatus, it was found that the amount of sodium volatilized was very small, and that a plug of sodium hydroxide had formed again.

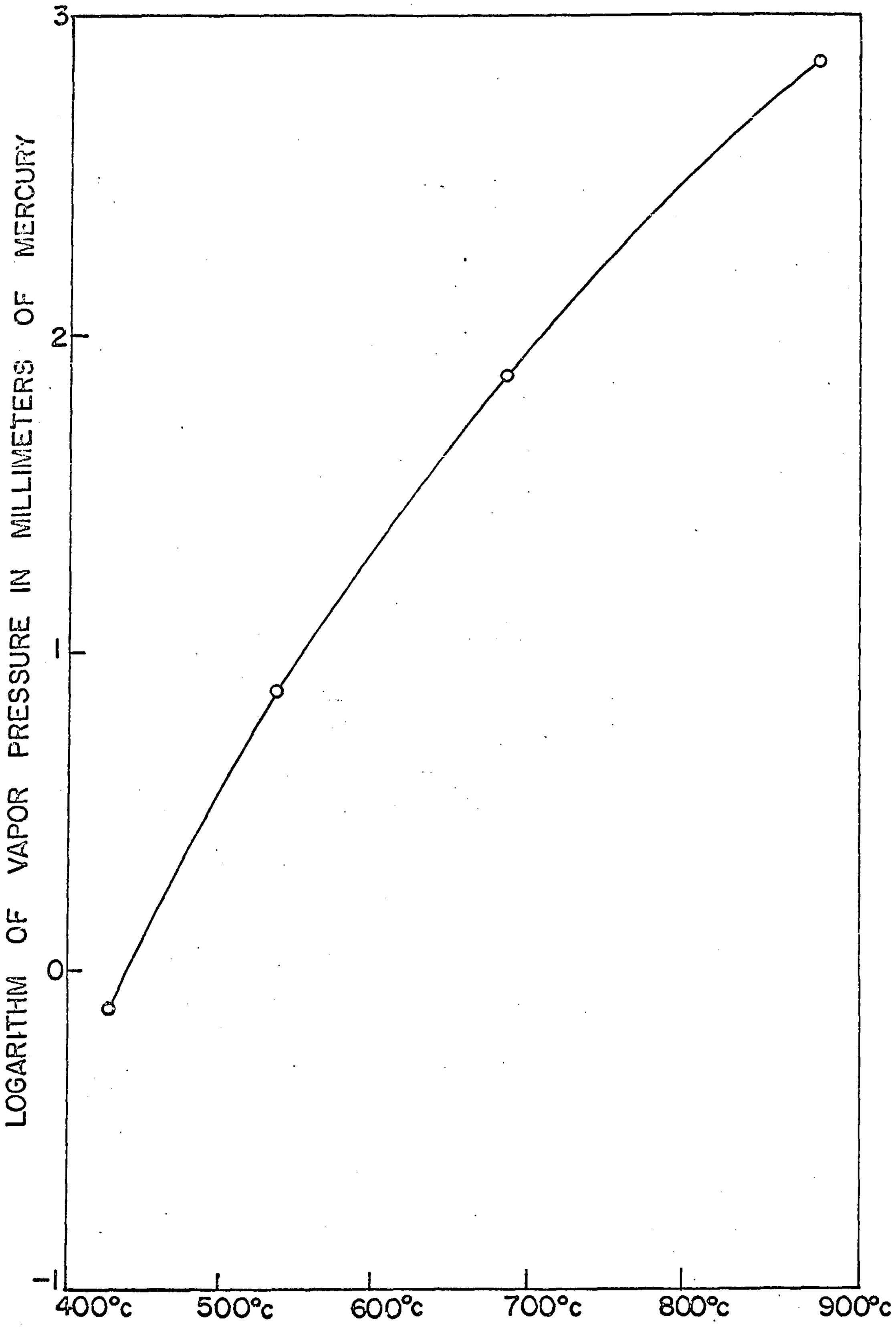


Figure 11. Vapor pressure of sodium at different temperatures

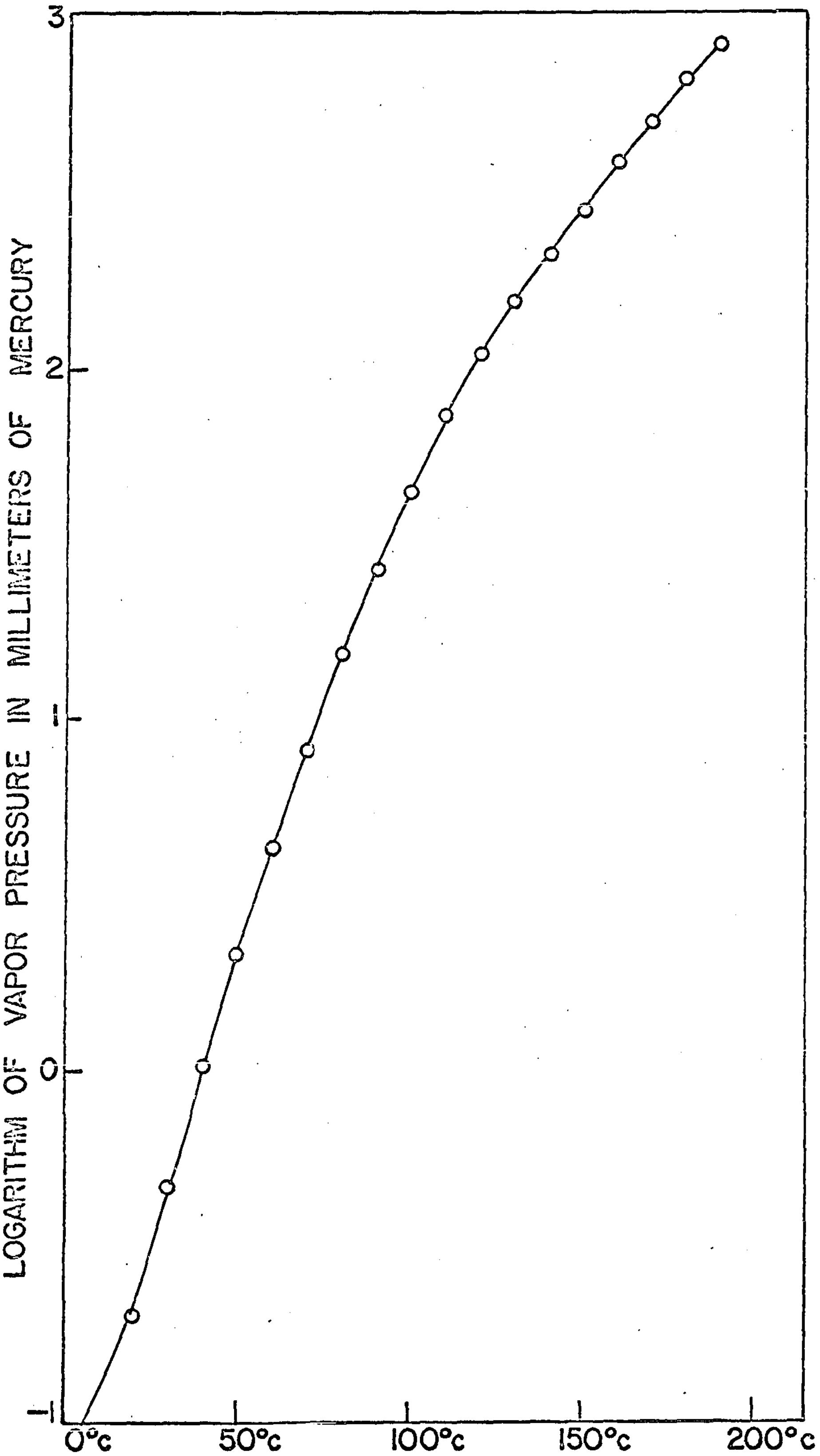


Figure 12. Vapor pressure of iodine at different temperatures

Flushing with purified helium was done prior to the next trial and the apparatus was outgassed by heating with the furnaces and heating tape. A supply of helium was passed through the apparatus while the xylene wash for the sodium was evaporated, but the results were not much better than those accomplished previously. The sodium surface was maintained without corrosion, which was a great improvement.

In a run similar to the last described above, the sodium was loaded first. During the loading of the iodine, some of that element came in contact with a fresh surface of sodium and reacted instantaneously and violently, leaving a yellowish deposit on the walls of the apparatus in that area. This deposited material did not contain sodium metal, but did contain a small amount of sodium hydroxide and a large amount of sodium iodide. The amount of product on this run far exceeded that on other runs of this type, but was still not satisfactory, so this method was not used again.

On most runs, a black material formed in the iodine area, indicating that the element was not pure. Further trials were performed with iodine that had been sublimed to remove nonvolatile impurities.

The apparatus shown in Figure 13 was designed to allow liquid sodium to be removed from the inevitable sodium hydroxide film while under a protective atmosphere of purified helium. During the entire

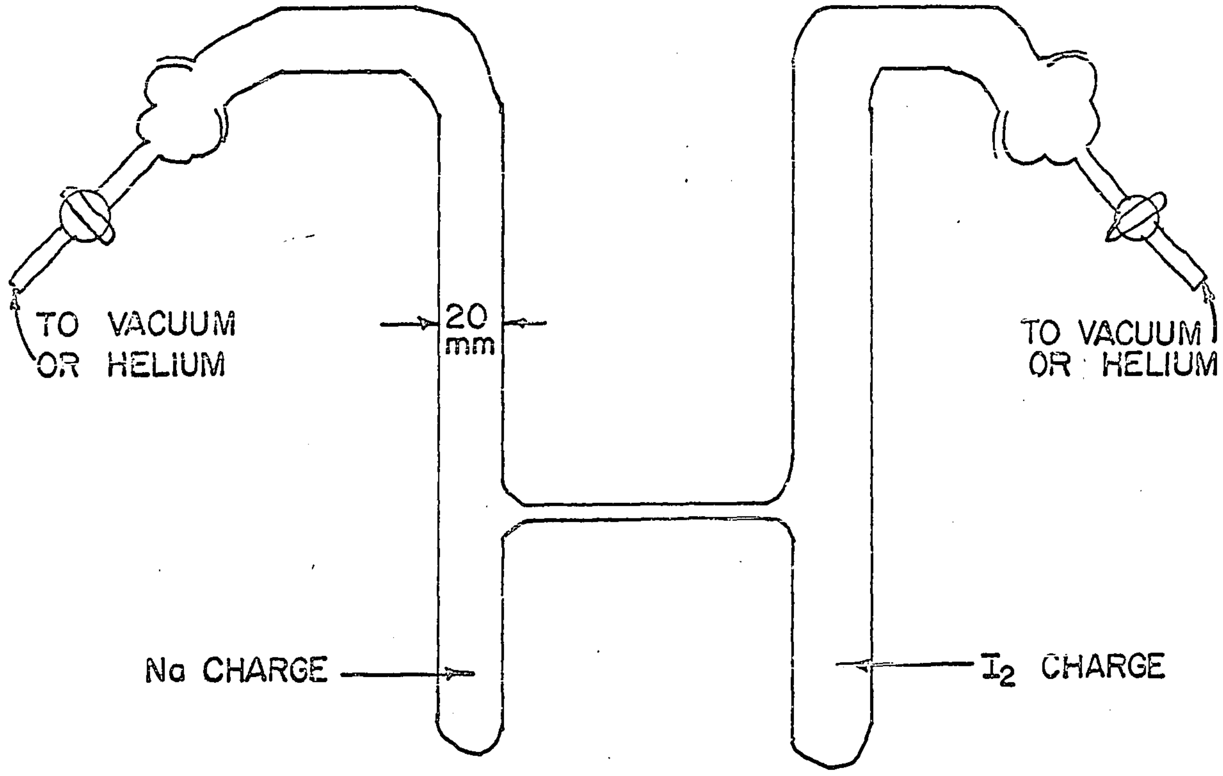


Figure 13. Vycor double tube apparatus

process of loading, melting, and reaction, the apparatus was flushed with helium. Sodium was loaded into one half of the apparatus, melted, and then allowed to flow to the other side of the apparatus by tilting it. It was hoped that a clean surface of sodium could be maintained while the sodium was flowing through the small tube connecting the two halves of the apparatus. The major part of the apparatus was made of Vycor to withstand the reaction heat.

In a trial with the apparatus described above, it was evacuated and flushed several times with purified helium prior to introduction of the sodium. After the inert atmosphere had been provided, the design of the apparatus was such that the helium would not diffuse away, because the purge gas is lighter than air and the reaction areas were protected by high points in the gas path. The sodium quickly became corroded when added and melted in this run due to a leak in the helium purge supply.

The second run started with removal of oxygen and moisture as above, but differed in that iodine was introduced before sodium. This was done in the hope that all possible sources of oxygen would be eliminated before sodium was present. Not much occurred until the apparatus was heated, at which point the sodium burned in the iodine atmosphere. The temperature of the reaction was approximately 500° C, and the sodium etched the Vycor quite badly. The resulting product was not very pure and this method was abandoned.

An apparatus was designed to be built of nickel, which is the only practical iodine-resistant metal. A metal apparatus is necessary, as sodium etches glass and Vycor quite strongly. Although nickel is only the second-best structural material to overcome iodine corrosion, it is far more easily formed than molybdenum. The nickel equipment, shown in Figure 14, consisted of two parts: an iodine generator and a reaction area. A welded tube connects the two nickel crucibles used as the basis for the device, and machined caps were made to closely fit the crucibles. One cap was solid, and the other had a vent tube which could be used as an entrance or exit port. The whole apparatus was made of nickel and all welding was done by the Heliarc process.

When first using the apparatus above, sodium metal was cleaned up and placed in the side with the ported cap, and iodine was placed on the other side. Both crucibles were heated, so that the iodine would volatilize and come in contact with a hot sodium surface. This method was not satisfactory, so in later trials the sodium was not added until heating of the iodine generator produced iodine vapor throughout the apparatus. The bottom of the reaction area was heated to a red heat, but the amount of reaction was still small. Further experimenting with temperatures in the reaction and iodine generating

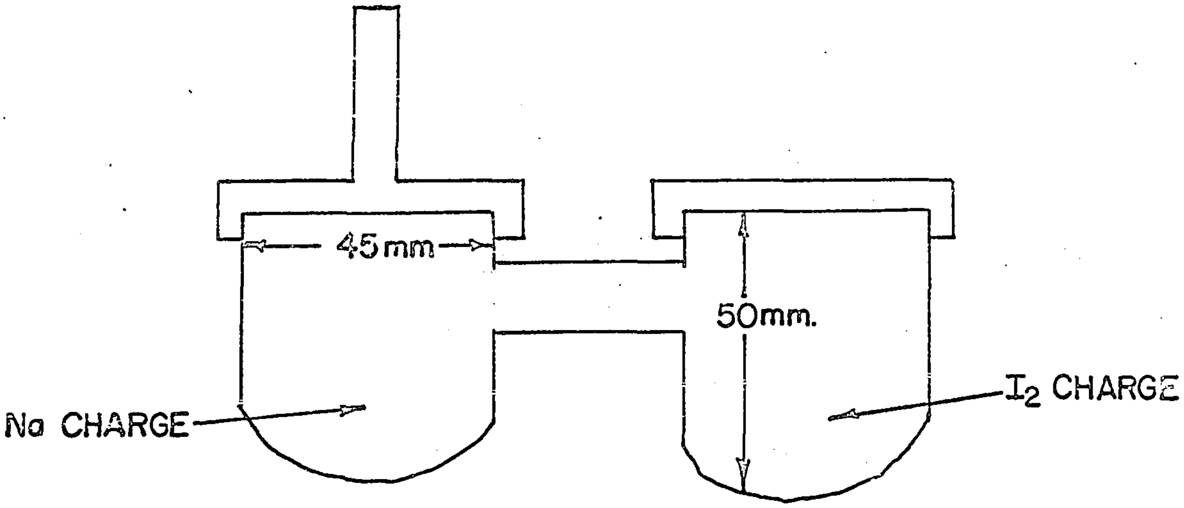


Figure 14. Nickel double crucible

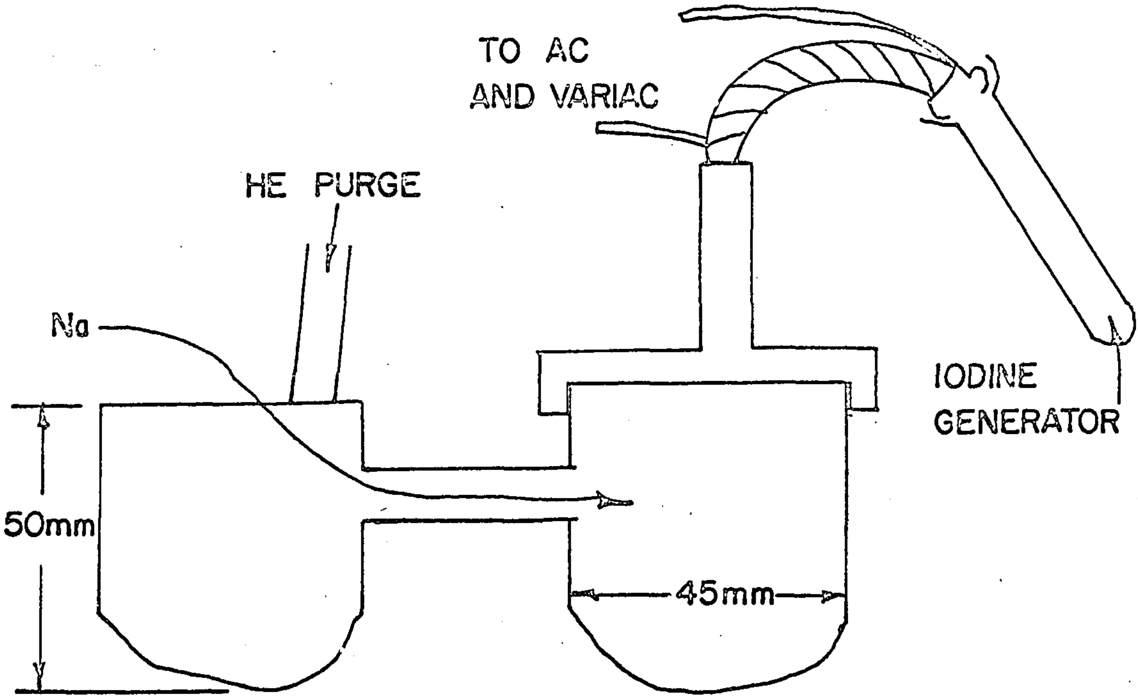


Figure 15. Nickel double crucible with iodine generator

areas showed that iodine would not come into contact with sodium if the reaction side of the vessel was heated to a high temperature. In this case, the iodine vapor merely left the reaction area through the port. Since the generation and reaction areas are necessarily connected, heat conduction makes it difficult to maintain a temperature differential between the two areas.

The apparatus put to use in the above method was also used with a separate iodine generator, shown in Figure 15. This time the cap with the port attached became the entrance rather than the exit port, and the iodine generator led directly through this cap. Sodium was added through the connecting tube. The generator contained a ball joint to facilitate disassembly and cleaning. A heating tape was wrapped around the iodine delivery tube, which was a close, but not tight, fit in the cap port. The generator was heated with a micro Bunsen burner.

Various conditions were tried in the experimental runs with the above device. Different rates and sequences of heating, and varying amounts of the two elements were tested for completeness of reaction. The products were tested by the analytical means described above and are listed in Table 15b.

A single nickel crucible was used for a large number of runs with a separate iodine generator, as in Figure 15. In the first series of of trials, the iodine generator was heated to initiate a flow of iodine vapor into the reaction crucible. When the flow was well established, cleaned pieces of sodium were placed in the crucible and the bottom of the crucible was heated with a Fisher burner. The purpose of the technique was to provide heat to overcome the energy of activation for the reaction while the sodium was protected from air and oxygen by iodine vapors. In this way, the oxide surface that almost inevitably occurs on sodium was broken down under an iodine atmosphere, followed by a reaction with the surrounding iodine. Results of this method are shown in Table 15b.

Although the technique described above did allow the reaction between the elements to take place under favorable conditions, improvements were sought. One such change was the use of the sodium transfer device shown in Figure 16. With this apparatus, sodium could be cleaned and transported to the reaction vessel without undue exposure to air. A helium gas purge was maintained through the open-end apparatus, and since helium is lighter than air, it caused downward displacement of air, and protected the sodium sample.

Another improvement in apparatus also was aimed at delivering sodium metal with a lesser amount of oxide coating to the reaction

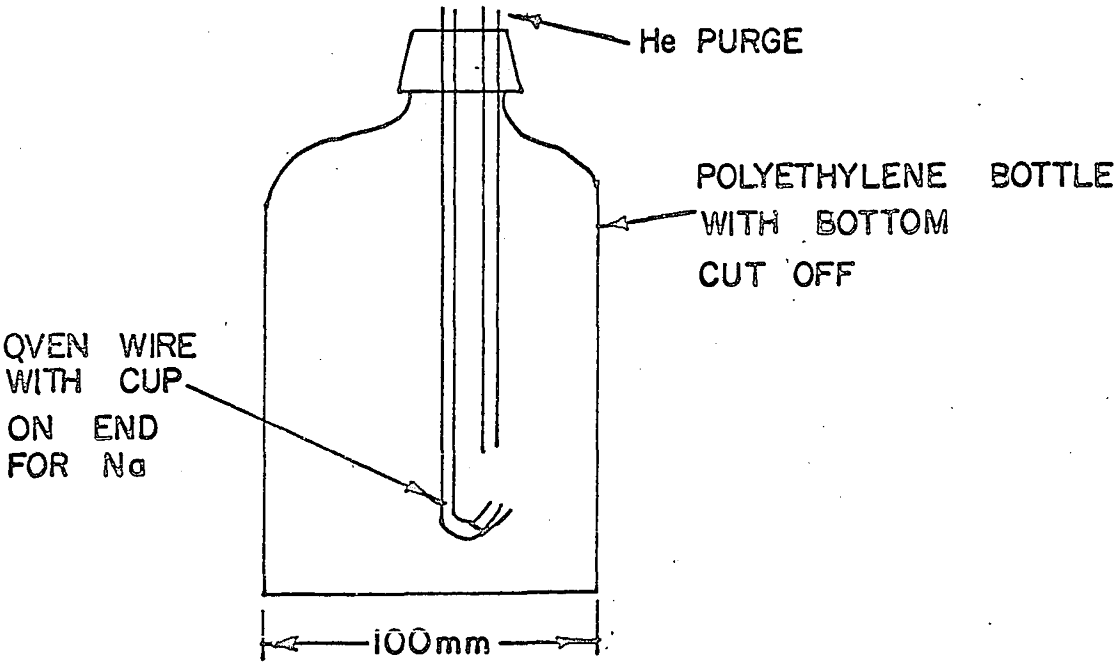


Figure 16. Sodium transfer device

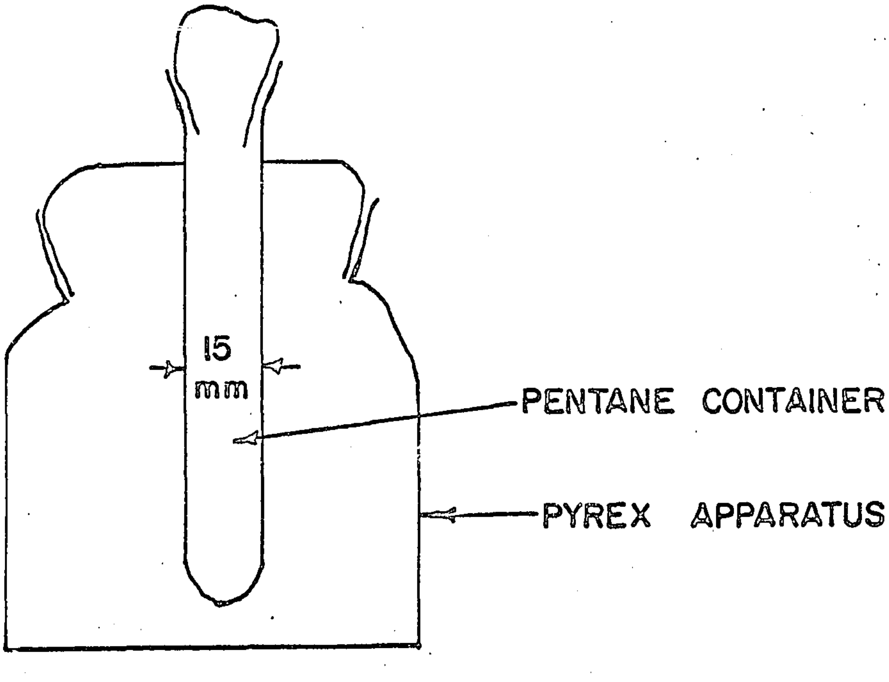


Figure 17. Pentane container-sodium cleaner

vessel. Sodium metal was kept under mineral oil after opening a can of the metal, and cut under the same solvent. Since mineral oil has a high boiling point, it is difficult to remove by blotting or evaporation, and its presence during the reaction led to the formation of carbonaceous material in the products. Use of the apparatus described immediately above made it possible to transfer sodium to the reaction area without further corrosion, which made it unnecesary to have a protective solvent on the sodium prior to introduction of the sodium into the iodine vapor. A suitable solvent for removal of mineral oil was sought, and pentane was decided upon because it has a low boiling point and could be easily removed by evaporation under the protective stream of helium gas. The apparatus shown in Figure 17 was designed to contain pentane under conditions such that the solvent would not evaporate rapidly. Ice placed in the outer chamber kept the pentane at a temperature below the boiling point of the solvent, and reduced the vapor pressure considerably from that at room temperature. Further refinement of this apparatus included the addition of sodium wire to the pentane to dry it before placing the sodium to be reacted in the pentane, and addition of ethanol to the pentane to remove any oxide film that might have formed on the sodium surface. The two techniques could be used together, if Dry Ice were used as the coolant in the outer chamber of the sodium washing device.

Improvements to the container for the reaction were also necessary. Some black material formed as a matter of course when using the nickel crucible or other nickel apparatus. It has been explained above that nickel is the most practical metal to fabricate for a piece of apparatus that will contain iodine, but is by no means inert to iodine. Tests of the black material formed in elemental runs confirmed a tendency to dislodge material from the reaction crucible. Dimethylglyoxime tests for nickel on the residue were positive. With this unwanted impurity in mind, a change in apparatus material was made, and a new crucible of molybdenum was fabricated. The sides were rolled from sheet molybdenum, the bottom was cut from sheet stock, and all joints were Heliarc welded. Many of the better runs were made using this crucible, although some black material still formed. The amount of black material was far smaller than the case with nickel crucibles. At first it was thought that this black material was molybdenum (VI) oxide, as oxygen attacks the metal at high temperatures. No positive tests could be made for this oxide, or other oxides of molybdenum, and it could well have been carbon formed from heating the pentane wash solvent. In some runs, this dark material did not appear.

The design of the iodine generator was also modified to increase its capacity by forming it from a round bottomed flask and a ball joint, which connected it to the delivery tube. This made it possible to maintain the iodine flow for much longer periods of time. Consequently, larger amounts of sodium iodide, such as 5.8 grams, could be made in one run, and the flow of iodine could be provided over the molybdenum crucible to protect it from oxygen while the reaction vessel cooled.

With the use of a molybdenum crucible, helium-protected sodium transfer device, Dry Ice-cooled pentane rinsing and cleaning device, and the large iodine generator with a heated delivery tube, the highest state of the art of the reaction between sodium and iodine was reached. The direct synthesis was accomplished as a matter of routine, using the principle that sodium could be burned in an atmosphere of iodine gas. The sodium iodide contained some sodium hydroxide in almost all cases, certainly in levels above that allowable for use of sodium iodide in fundamental crystal studies. A summary of the results of burning sodium in an iodine atmosphere is given in Table 15b.

Table 15b. Results and purity tests of sodium iodide produced by burning sodium metal in iodine vapor

Run	Crucible material and conditions	% sodium hydroxide	Equivalent weight of sodium iodide
ER # 1	Nickel double crucible	5.32	170.31
ER # 2	Nickel double crucible	not detected	151.01
ER # 3	Nickel double crucible, helium purge	1.93	156.32
ER # 4	Nickel double crucible, helium purge	28.5	very high
ER # 6	Nickel double crucible, helium purge	16.90	288.12
ER # 7	Nickel double crucible, helium purge	9.94	194.30
ER # 8	Nickel crucible	30.17	very high
ER # 9	Nickel double crucible, helium purge	1.253	153.82
ER # 10	Nickel crucible, iodine generator	34.0	very high
ER # 10a	Nickel crucible, iodine generator	0.664	153.16
ER # 11	Nickel crucible, iodine generator	0.0336	150.35
ER # 12	Nickel crucible, iodine generator	0.619	152.43

Table 15b(Continued)

Run	Crucible material and conditions	% sodium hydroxide	Equivalent weight of sodium iodide
ER # 13	Nickel crucible, iodine generator	0.0911	152.43
ER # 14	Nickel crucible, iodine generator	1.014	154.67
ER # 15	Nickel crucible, iodine generator	0.482	151.91
ER # 16	Nickel crucible, iodine generator	7.52	171.02
ER # 17	Nickel crucible, iodine generator	0.0577	149.89
ER # 18	Nickel crucible, iodine generator, pentane wash	1.6	153.69
ER # 19	Silica crucible, iodine generator, pentane wash	1.81	154.13
ER # 20	Molybdenum crucible, iodine generator, pentane wash	4.9	169.32
ER # 21	Molybdenum crucible, iodine generator, pentane wash	1.4 ca.	157.73
ER # 22	Molybdenum crucible, iodine generator, pentane wash	0.09	152.61
ER # 23	Molybdenum crucible, iodine generator, dried pentane wash	0.07	154.96
ER # 24	Molybdenum crucible, iodine generator, dried pentane wash	0.30	153.08

Table 16. Results and purity tests of sodium iodide produced by burning sodium metal in iodine vapor in the presence of materials tested for catalytic acitivity

Run	Crucible material and conditions	Material tested for catalytic activity	Percent of sodium hydroxide	Equivalent weight of sodium iodide
CR # 2	Nickel double crucible	Selenium dust	1.90	192.17
CR # 3	Nickel double crucible	Copper powder	7.76	221.76
CR # 5	Nickel double crucible	Copper (II) selenite	29.7	767.76
CR # 6	Nickel crucible, iodine generator	Silicon (IV) oxide	24.35	311.45
CR # 7	Nickel crucible, iodine generator	Silicon (IV) oxide	1.914	156.53
CR # 8	Nickel crucible, iodine generator	Copper (II) oxide	5.5	166.58
CR # 9	Nickel crucible, iodine generator	Copper (II) oxide	11.91	249.52
CR # 10	Nickel crucible, iodine generator	Lead (IV) oxide	39.30	224.31
CR # 11	Nickel crucible, iodine generator	Lead (IV) oxide	0.0	150.90
CR # 12	Nickel crucible, iodine generator, dried pentane wash	Glass beads	10.1	223.84

At the same time the series of reactions shown in Table 15, pp. 79-80, was done, trials were made with a selection of elements and compounds to see if they would exhibit catalytic activity. The results of these investigations are shown in Table 16 on p. 81.

The trials to identify a catalyst did not point out any material that could lower the activation energy for the reaction between sodium and iodine. In most cases, results with other materials present did not equal the results with the elements alone.

Purification of Sodium Iodide

Direct synthesis methods did not lead to extremely pure sodium iodide, so a study of purification techniques was made. Experimentation with the techniques and analysis of the results follows.

Ion exchange

Ion exchange is a well-known method of separating metal ions and radicals from one another; hence its application to purification of sodium iodide was thought possible.

Columns for ion exchange were made from a stopcock and a sealing tube containing a medium porosity glass frit. The dimensions of the ion exchange material were: 10 centimeters high and 2 centimeters in diameter. Dowex 50 X8, 200-400 mesh was used as the cation exchanger, and Dowex 1 X8, 100-200 mesh was used as the anion exchanger.

Preparation of the columns was carried out by placing ignited silicon (IV) oxide on the glass frit. The purpose of the frit is to prevent organic materials from leaving the column, and the sand is to keep the frit from plugging with the resin. The resins were made into a water slurry, and poured into the columns. A sodium citrate solution was then run through the columns to remove traces of iron that are common to ion exchange resins due to the manufacturing process containers. It was not possible to backwash the columns, due to the small mesh of the resin. Treatment with sodium citrate had already converted much of the hydrogen form cation exchanger to the sodium form, and further treatment with concentrated sodium iodide solution completed the conversion. During all operations with the ion exchange procedures, deionized water from an Amberlite MB-3 (mixed bed, indicating) resin was used to exclude all unnecessary introduction of impurities. The collection jug and deionization column were protected from the atmosphere by Ascarite drying tubes.

Column flow was quite slow, so the fluid head was increased to three feet by placing the columns on the floor and the feed solution dropping funnels on the bench top. This change gave a flow rate of approximately 1 milliliter per minute. Each column had an exchange capacity of 50 milliequivalents. The mass action effect of 2250 milliequivalents of sodium citrate and 2000 milliequivalents of sodium iodide were run through the cationic exchange column and should be sufficient to convert if from the hydrogen to the sodium form. Six thousand milliequivalents of sodium iodide were run through the anion exchange column to effect conversion to the iodide form. The column packings were then removed and washed with water prior to repacking and passage of more sodium iodide through the columns.

The data in Table 17 led to the replacement of deionized water used as described above by redistilled conductivity water made from Ames Lab deionized water.

Table 17. Conductivity of water supplies

Type of water		Conductivity
Ames tap water	<u>ca.</u>	6.5×10^{-4} mhos
Chemistry building distilled water	<u>ca.</u>	2.5×10^{-6} mhos
Own deionized water		9.7×10^{-7} mhos
Ames Lab tap deionized water		4.5×10^{-7} mhos
Ames Lab redistilled conductivity water		3.5×10^{-7} mhos

The columns, feed solution containers, and connecting tubes were wrapped with aluminum foil to minimize decomposition of the sodium iodide solution due to light. Such a solution exposed to air readily acquires a yellow tinge due to decomposition to iodine and hydroxide (35, 53, 83, 99, 169, 175) and is readily detected because the iodine color can be seen at concentrations as low as 10^{-6} molar (55 , p. 295). During passage through the ion exchange columns, a sodium iodide solution was decolorized in the anion exchanger and not affected in the cation exchanger. Whether this was due to the nature of the exchanger or the finer mesh of the anion exchanger was not determined.

Samples of the sodium iodide used to saturate and convert the ion exchange columns and samples of sodium iodide recovered after passage through the columns were submitted for emission spectrographic analysis, and are tabulated in Table 18, page 87.

Purification by ion exchange took place on potassium, lithium, iron, copper, and chromium, while additional amounts of silicon and magnesium were added to the sodium iodide. Concentrations of silicon and magnesium were probably increased by contact with glass apparatus. Emission spectrographic analysis does not completely describe the purity of a material, because the method cannot be used to determine non-metals, which are certainly of equal importance to metals in the analysis of sodium iodide.

An improved ion exchange apparatus shown in Figure 18 was built to include a provision for vacuum filtration and introduction of a protective gas purge. This purge gas was helium purified by treatment

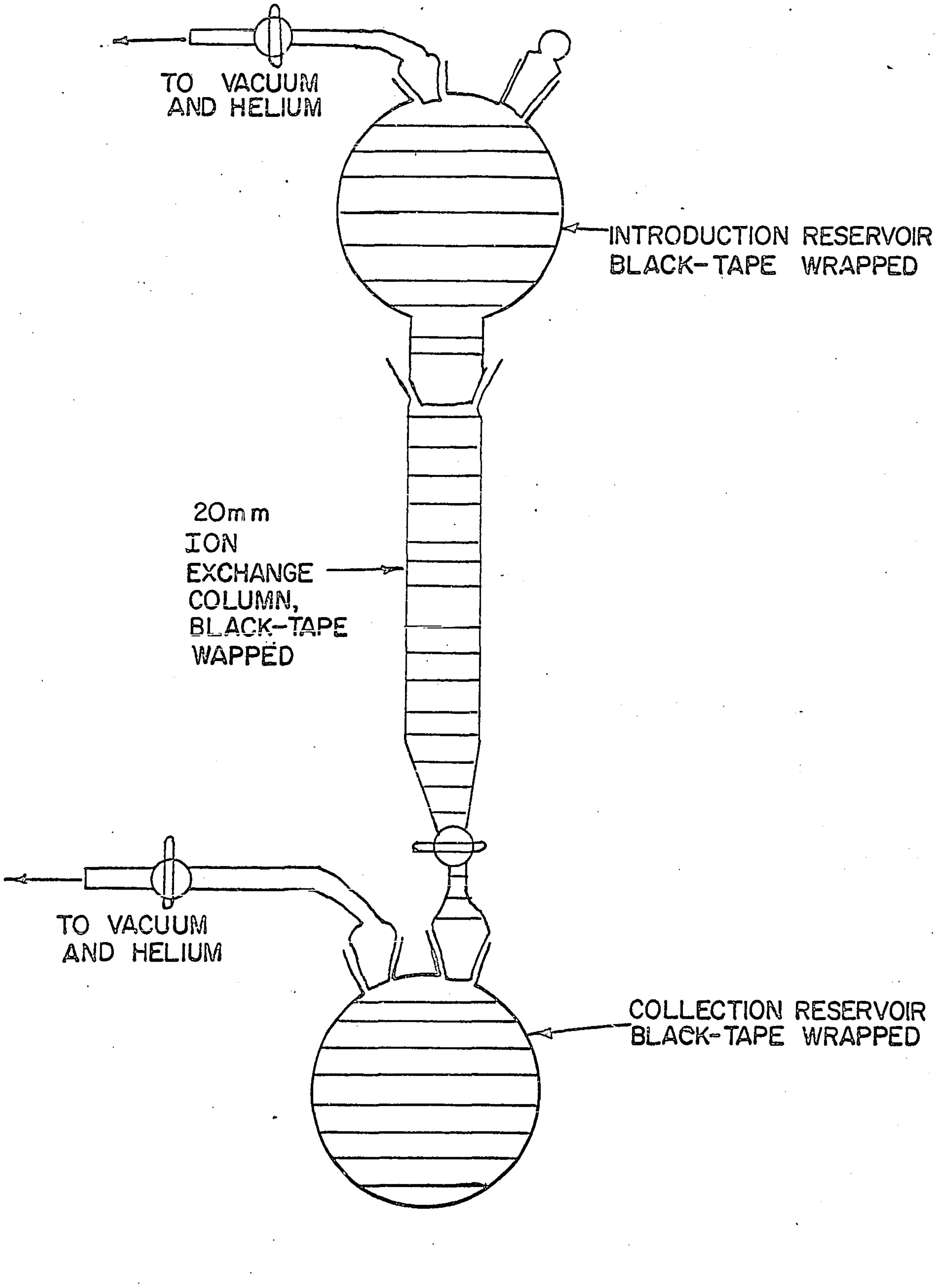


Figure 18. Vacuum ion exchanger-pyrex

Table 18. Results of ion exchange purification of sodium iodide[a] tested by emission spectrographic analysis

Element	IRA - 1 Sodium iodide starting material	IRA - 2 Sodium iodide, anion, cation	IRA - 3 Sodium iodide, cation, then anion
Na (sodium)	VS[b]	VS	VS
K (potassium)	VW	T	T
Rb (rubidium)	-	-	-
Cs (cesium)	-	-	-
Li (lithium)	T	FT	FT
Si (silicon)	FT	T	T
Mg (magnesium)	FT	T	T
Fe (iron)	VW	FT	T
Al (aluminum)	Tx	Tx	Tx
Cu (copper)	T	FT	FTx
Ca (calcium)	T	T	T
Cr (chromium)	FT	-	-

[a] Baker Analyzed sodium iodide.

[b] Key:
VS - very strong (*ca.* greater than 10 %)
M - medium (*ca.* 0.1 - 1.0 %)
W - weak (*ca.* 0.01 - 0.1 %)
VW - very weak (*ca.* 0.001 - 0.01 %)
T - trace (*ca.* 0.0001 - 0.001 %)

FT - faint trace
\- - not detected
x - interference

with vanadyl sulfate (131) and passed over heated uranium turnings (77). The vacuum source was an aspirator capable of lowering the pressure in the apparatus to 50 millimeters of mercury. The cation exchanger column packing was Amberlite IR-112(H) and the anion column packing was Amberlite IRA-401, both 50-100 mesh and packed in the form of a slurry, then backwashed. The helium purge gas was made available because it was noted that the yellow color due to decomposition of sodium iodide solution appeared much more slowly in a solution protected by helium gas.

The color removal of the anion exchange resin was again noted, showing that decolorization is due to the type of resin, not the particle size of the resin. Evaporation of the sodium iodide solution which was passed through the ion exchange resins was done with a vacuum evaporator from a water-warmed flask to a water-cooled flask. The last of the water was removed by a flask-to-flask distillation with the help of a mechanical vacuum pump and an isopropyl alcohol-Dry Ice trap. During the evaporation, the sodium iodide solution was protected from light by placing a sheet of rubber over the flask. These techniques were put into service one by one, and the results of an emission spectrographic analysis of a group of ion exchange products are shown in Table 19, on page 89. A description of the techniques used in the treatment of each sample is also given.

Table 19. Results of analysis of products of ion exchange purification of sodium iodide

Substance	IRA - 4 NaI boiled down, anion then cation exchanger	IRA - 5 NaI vacuum evaporated	IRA - 6 NaI vacuum evaporated	IRA - 7 NaI vacuum evaporated cation, then anion resin	IRA - 8 NaI vacuum evaporated, light shielded
Sodium hydroxide[a]	0.195 %	0.00 %[b]	0.00 %	0 00 %	0.00288 %
Ag (silver)	T[c]	FTx	NA	NA	NA
Al (aluminum)	VW	T	NA	NA	NA
Li (lithium)	NA	NA	FT	FT	FT
K (potassium)	NA	NA	T	T	T
Rb (rubidium)	NA	NA	-	-	-
Cs (cesium)	NA	NA	VFT	VFT	VFT
Mg (magnesium)	VW	T	T	FT	FT
Ca (calcium)	VW	T	T	FT	FT
Sr (strontium)	FT	-	FT	VFT	VFT

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[a] Titrated with 0.009333 M hydrochloric acid standardized with a sodium hydroxide solution. The sodium hydroxide was standardized using potassium acid phthalate. The indicator used was phenolphthalein.

[b] Since phenolphthalein was used as the indicator, it is possible to have up to 0.0001 % sodium hydroxide present even if the indicator remains colorless. A check of the pH, however, showed that it was the same as that of distilled water.

[c] See Table 18 for an explanation of the symbols used for amounts of the elements detected. The notation, NA meaning not analyzed for, is an addition to this table.

Table 19. (Continued)

Substance	IRA - 4 NaI boiled down, anion then cation exchanger	IRA - 5 NaI vacuum evaporated	IRA - 6 NaI vacuum evaporated	IRA - 7 NaI vacuum evaporated cation, then anion resin	IRA - 8 NaI vacuum evaporated light shielded
Ba (barium)	NA	NA	FTx	FTx	FTx
Cr (chromium)	FT	-	-	-	-
Cu (copper)	FT	-	T	FT	FT
Fe (iron)	T	_	W	FT	W
Hg (mercury)	-	FT	NA	NA	NA
Mn (manganese)	FT	T	NA	NA	NA
Si (silicon)	T	T	W	VW	VW

During the treatment of the samples obtained by ion exchange, it could be observed which samples were of good purity and which were not. The purer samples were more easily evaporated, and had less noticeable yellow iodine tinge. Elemental iodine is produced by decomposition of sodium iodide in direct proportion to the amount of sodium hydroxide formed simultaneously. Since the presence of iodine may be detected by eye at concentrations as low as 10^{-6} molar, practically all sodium iodide solutions had a yellow tinge (55, p. 295).

It can be seen from the analyses in Table 19 that the vacuum evaporation method of recovering sodium iodide from solution is superior to boiling the solution down, but no similar claim may be made for protecting the solution from light during evaporation. There are a large number of elements which are still present in the ion-exchanged sodium iodide, though such elements as potassium, lithium, iron, copper, and chromium were reduced in concentration. In the best sample, iron was present in the approximate amount of 0.01 - 0.1 % , silicon was present to the extent of 0.001 - 0.01 % , potassium was 0.0001 - 0.001 %, lithium, magnesium, calcium, and copper were present in less than 0.0001 % concentration. Barium, cesium, and strontium were detected in addition to those elements above.

Ion exchange methods do not reduce impurity concentrations to 1 part per million, or even 10 parts per million. These concentrations are the greatest allowable amounts of impurities that may be tolerated in scintillation and optical crystals.

Sublimation

The technique of sublimation has been used to purify salts (90, 187)

Table 20. Analysis of sodium iodide[a] sublimed in a tube

Element	IRA - 13, sodium iodide before sublimation	IRA - 12, sodium iodide after sublimation
Li (lithium)	T[b]	T - VW
K (potassium)	T	T - VW
Rb (rubidium)	-	-
Cs (cesium)	FTx	FTx
Mg (magnesium)	FT	T
Ca (calcium)	T	T
Sr (strontium)	FT	-
Ba (barium)	-	T
Si (silicon)	T	M
Fe (iron)	FT	VW
Mo (molybdenum)	-	-
Cu (copper)	FT	T

[a] Baker Analyzed Reagent, vacuum dried.

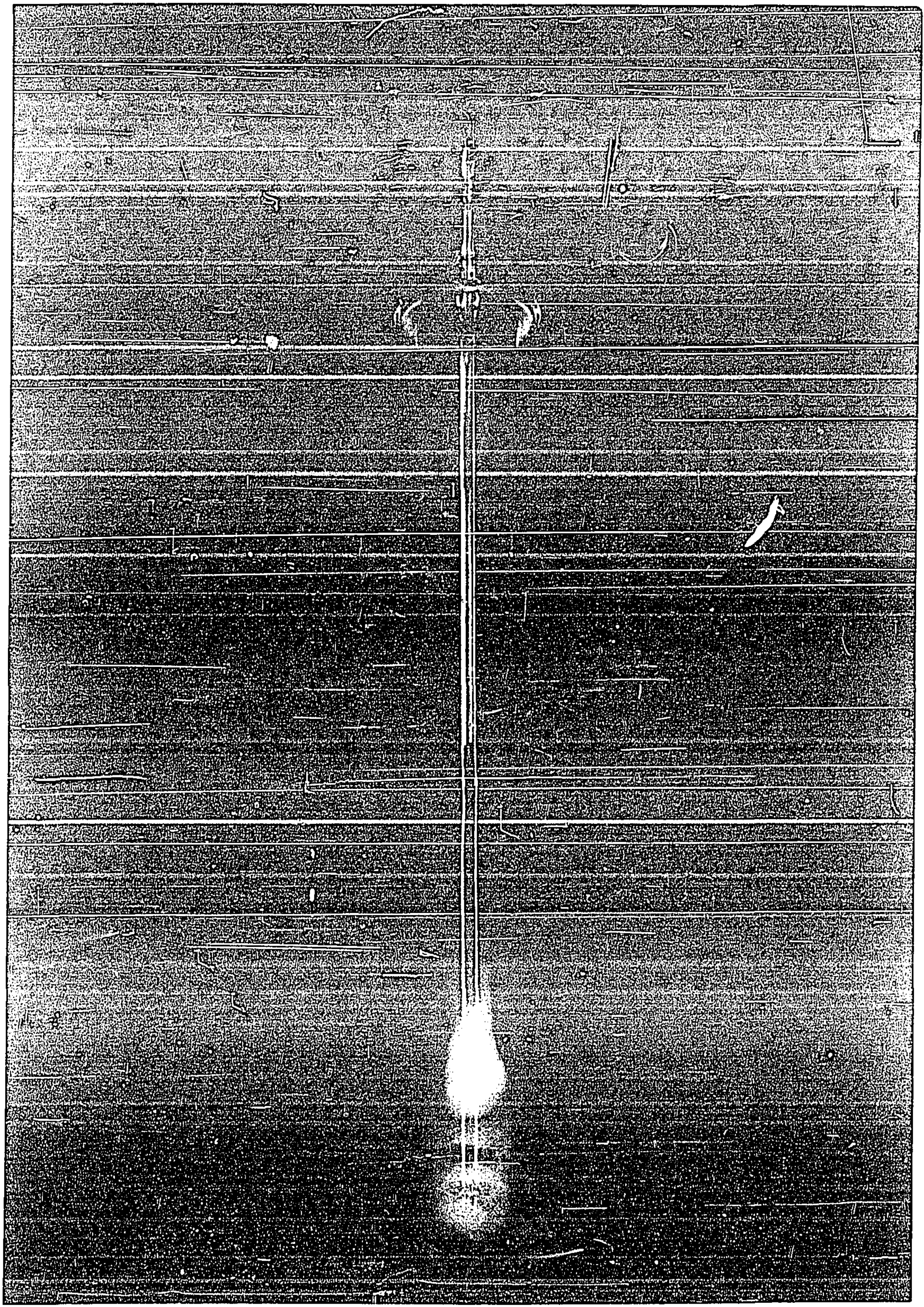
[b] See Table 18 for an explanation of the symbols used to denote amounts of elements detected by emission spectrographic analysis.

or to complement other purification methods such as zone refining (102).

The first apparatus used in an attempted sublimation purification of sodium iodide was simply a sealed tube heated with a coil of chromel wire. Sodium iodide was placed in the Vycor tube, which was evacuated and sealed. The temperature was measured with a thermocouple and current to the coil of wire was controlled with a Variac. The sodium iodide tended to turn yellow on heating, but an increase in the temperature to approximately $500 - 600^{\circ}$ C sublimed the yellow material to a cooler part of the tube. The heater did not extend the full length of the Vycor tube, which made it possible to gradually force the yellow impurity to move to one end of the tube where it was removed by sealing off the tube between the sodium iodide and the impurity. The analysis of this material is presented in Table 20, p. 92.

A tube sublimer designed to fit in a furnace and containing a cold finger cooled by an air stream is shown in Figures 19 and 20. The heated tube was connected to the sublimer head by means of a ball joint to ease disassembly problems. Cooling compressed air entered the cold finger at the top of the head, and left by the tube which extends to the bottom of the cold finger. This technique was used to keep

Figure 19.   Tube sublimer



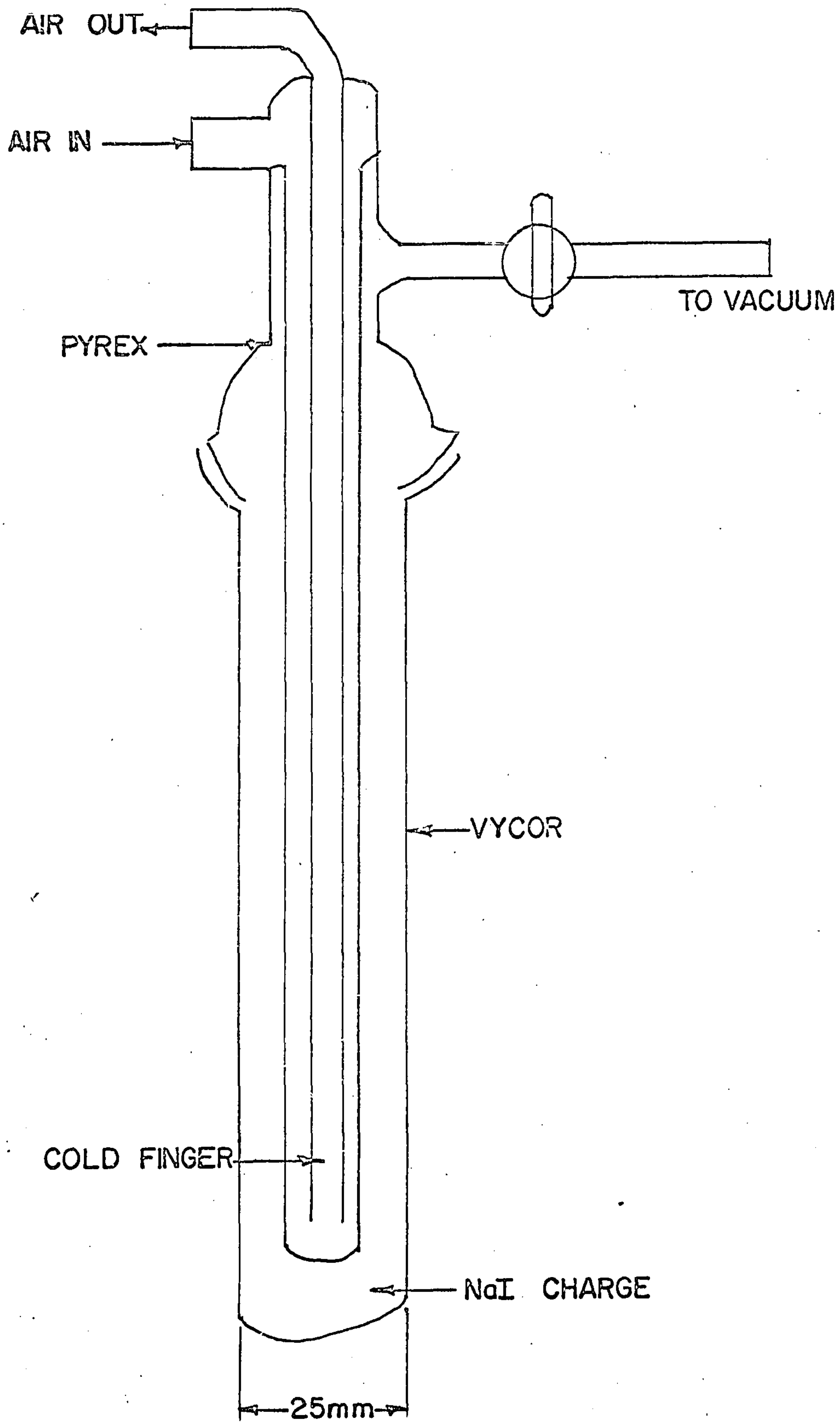


Figure 20. Tube sublimer

sodium iodide from condensing only at the tip of the cold finger. Since this part of the apparatus receives the cooling air last, it is not the coolest part, and the sodium iodide was distributed over a larger area of the cold finger. This gradual temperature gradation also had the effect of forcing less volatile impurities to condense at a higher position on the cold finger, giving a better separation.

On the first use of this tube sublimer, the heated tube collapsed at the heat necessary to cause sublimation. Temperatures lower than 520° C did not cause any noticeable sublimation, so the Pyrex tube was replaced with a Vycor tube. It was still possible to open the tube, even though collapsed, and gather samples for emission spectrographic analysis. One sample was taken from the material which first condensed on the cold finger, and another from the main body of the condensate. It was necessary in this run to reverse the inlet and outlet cooling tubes, so the materials of different volatility were not separated as described above. Analysis of these two samples and the original starting material is shown in Table 21, p. 98.

An analysis of the material sublimed in another run with a Vycor heated tube is shown in Table 22, p. 99. This run was identical to that presented in Table 21, except for the substitution of the Vycor tube for the Pyrex tube which collapsed.

Table 21. Analysis of sodium iodide[a] sublimed in a furnace

Element	IRA - 9 Sodium iodide starting material	IRA - 10 Sodium iodide first condensed	IRA - 11 Sodium iodide in main body of condensate
Li (lithium)	T[b]	T	T
K (potassium)	T	FT	T
Rb (rubidium)	-	-	-
Cs (cesium)	FTx	FTx	FTx
Mg (magnesium)	FT	T	FT
Ca (calcium)	T	T - VW	T
Sr (strontium)	-	-	-
Ba (barium)	-	-	-
Si (silicon)	VW	W	W
Fe (iron)	FT	W	FT
Cu (copper)	T	T - VW	T
Mo (molybdenum)	M	FT	-

[a] Sodium iodide from very good synthetic runs in a molybdenum crucible.

[b] See Table 18 for an explanation of the symbols used for emission spectrographic analysis.

Table 22. Analysis of sublimed sodium iodide[a] in a furnace sublimer

Element	SUB -6, starting material	SUB -1, material condensed on finger surface	SUB -2, material condensed on flank of crystal	SUB -3, material condensed on heel of crystal
Li (lithium)	VFT[b]	T	T	T
K (potassium)	T	T-VW	T-VW	T-VW
Rb (rubidium)	-	-	-	-
Cs (cesium)	FTx	FTx	FTx	FTx
Mg (magnesium)	FT	FT-T	FT	FT
Ca (calcium)	T	T	T	T
Sr (strontium)	VFT	-	-	-
Ba (barium)	T	T	T	FT
Si (silicon)	T	VW	T	T
Fe (iron)	FT	VW	T	T
Cu (copper)	FT	FT-T	FT-T	FT
Mo (molybdenum)	FT	VFT	-	-
Ni (nickel)	-	VFT	VFT	VFT
Al (aluminum)	FT	VW	T-VW	T-VW
Mn (manganese)	VFT	FT	VFT	VFT
Sn (tin)	-	FT	FT	-
Cr (chromium)	FT	T	FT	T

[a] Baker Analyzed Reagent.

[b] See Table 18 for an explanation of the emission spectrographic concentration terms.

The emission spectrographic analysis presented in Tables 20, 21, and 22 show that the sublimation in the Vycor tube heated in the furnace was the most successful trial. In the tube sublimer data shown in Table 20, strontium was the only element which was decreased in concentration by the sublimation operation. In Table 21 with the furnace sublimer shown in Figures 19 and 20, the only significant decrease occurred with molybdenum. Table 22 shows that four elements (lithium, potassium, iron, and aluminum) were increased in concentration, while strontium, barium, and molybdenum were decreased in concentration. Rubidium, cesium, magnesium, calcium, silicon, copper, nickel, manganese, tin, and chromium did not change in concentration.

The technique of sublimation improved the purity of sodium iodide with regard to several elements although this method was not used at optimum efficiency. Condensation of the sublimed sodium iodide onto a heated surface would help improve the results. The sodium iodide sublimed in the Vycor tube in the furnace was tested for the presence of hydroxide ion by dissolving samples in water and using a Beckman Expanded Scale pH meter. It was found that this sublimed sodium iodide contained 1.3×10^{-4} weight percent of hydroxide. The difficulty in separating sodium iodide and sodium hydroxide by sublimation is shown in Figure 21(2, 28, 42, 50, 81, 178, 179, 180, 215, 216), which

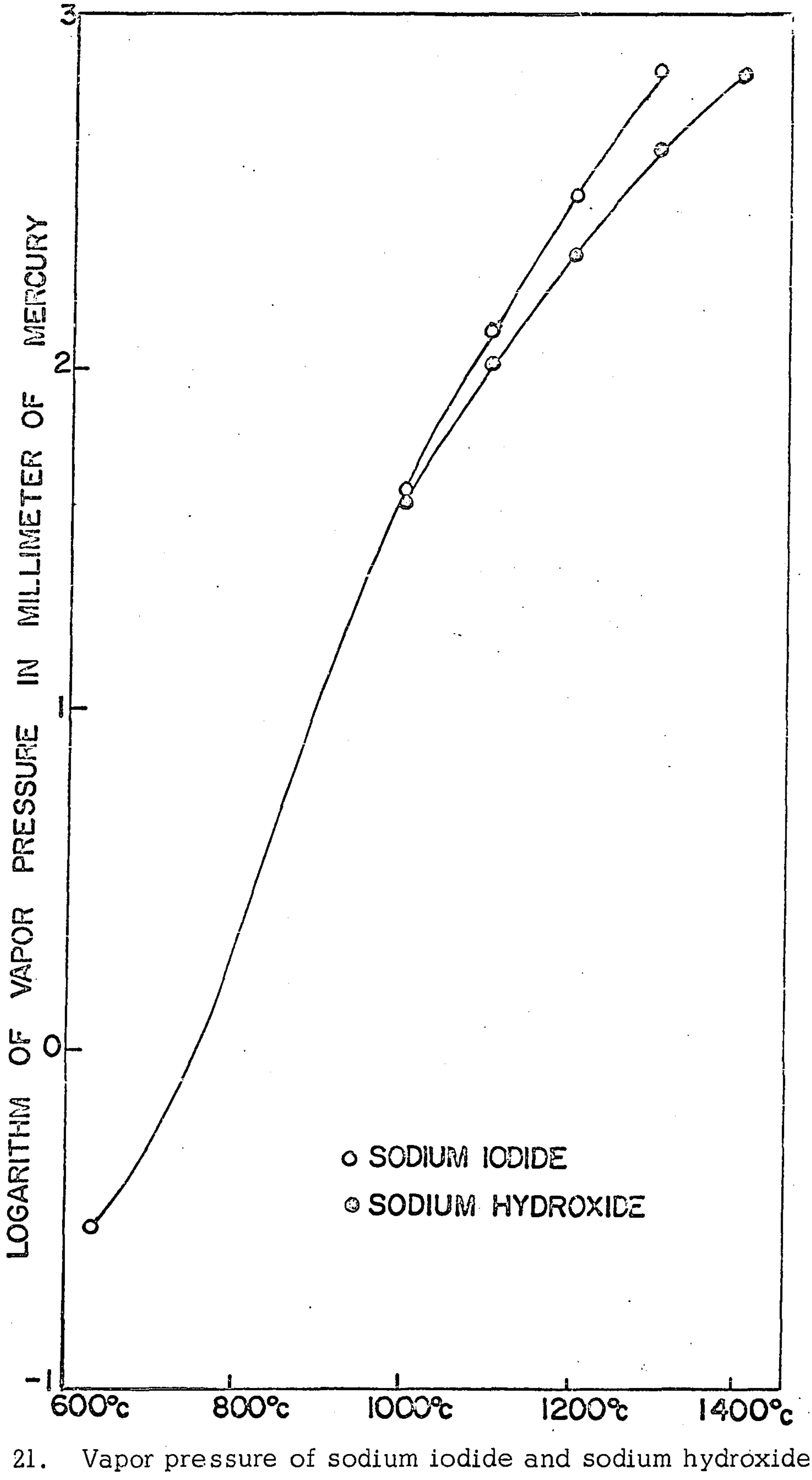


Figure 21. Vapor pressure of sodium iodide and sodium hydroxide

is a graph of the vapor pressures of sodium iodide and sodium hydroxide.

Zone refining

Since the first paper on this method appeared in 1952 by Pfann(159), interest in and use of zone refining has increased rapidly. Although originally applied to treatment of metals, its use has spread to other fields; the only requirement is that there be a difference in solubility of the impurity (solute) in the liquid and solid phases of the solvent. The distribution coefficient, k, is defined as the ratio of the solute in the solid phase compared to that in the liquid phase at equilibrium. If k is less than one, as in Figure 22(159), the freezing point of the solution is lowered and the solute will be concentrated in the last regions to freeze. In Figure 22, the liquidus and solidus lines slope downward, but this is not always the case. If the liquidus and solidus lines slope upward, the solute will raise the freezing point of the solution and k will be greater than one. In the case where k exceeds one, the solute is concentrated in the first regions to freeze.

The distribution of a solute in unequal fashion between solid and liquid phases has long been known and has been applied to the process of normal freezing. If a cylindrical bar of material is frozen, the concentration of solute at any point along the axis of the bar is given by:

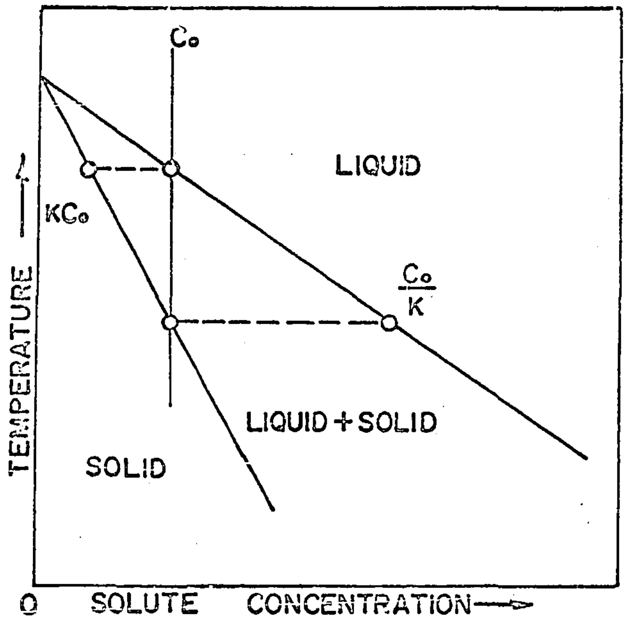


Figure 22. Portion of constitutional diagram for a solute which lowers the freezing point

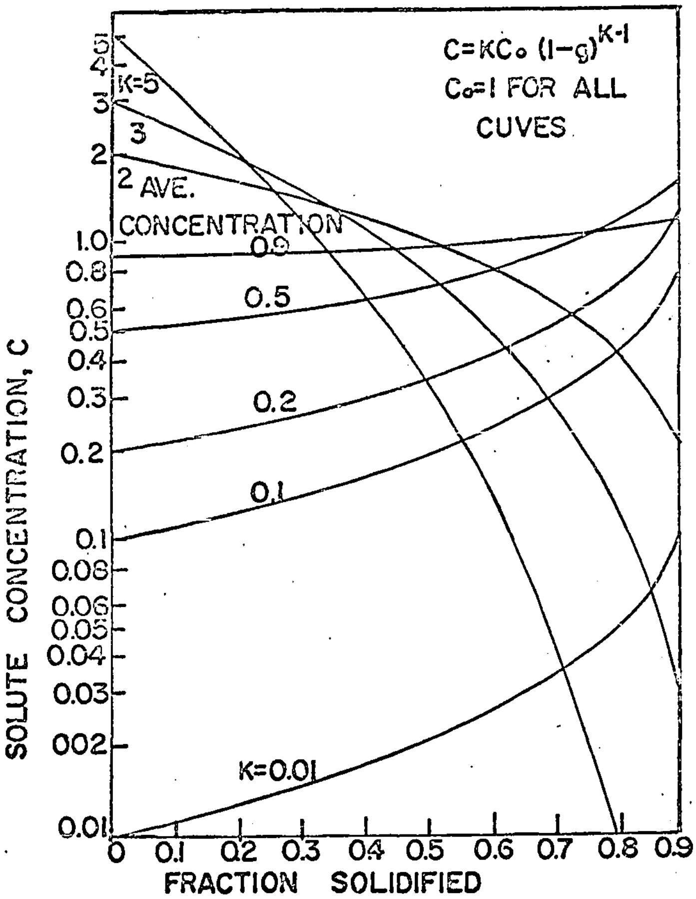


Figure 23. Curves for normal freezing showing dilute concentration in solid as a function of g

(1) $$C = kC_o (1 - g)^{k-1}$$

where: C = concentration of solute at any point along the axis of the bar,
C_o = concentration of solute initially,
g = fraction of the bar that has been solidified,
k = distribution coefficient as defined above, solid concentration to liquid concentration ratio.

Equation 1 is limited by the following assumptions:

1) that diffusion in the solid negligible,
2) that diffusion in the liquid is complete, i.e., concentration in the liquid is uniform,
and 3) that k is constant.

The change in concentration with normal freezing is plotted for decimal fractions of g in Figure 23(159), showing the influence of the value of k. For a real case, the assumptions limiting Equation 1 are not realized, so effective values of k are substituted for the equilibrium k defined above.

The zone melting process is discussed with reference to Figure 22. As the molten zone advances through the cylindrical bar of material, a fraction of the bar melts and an equal fraction freezes. If the measurement from the leading end of the bar is made in terms of length, x, a layer dx melts and a layer dx freezes. From Figure 22 it can be seen that the first solid to freeze, at x = 0, is of concentration kC_o. For the common case in which k is less than 1, kC_o will be less than C_o, and the liquid phase will be enriched in the concentration of the solute. Enrichment will continue at a decreasing rate until the liquid zone reaches the concentration C_o/k. At this point, the amount of solute leaving the liquid phase by freezing exactly balances the amount of solute entering the liquid phase by melting. No further changes in concentration occur in either phase until the last fraction of the bar freezes by normal freezing which is described in Equation 1. A diagram of the passage of a zone through a cylindrical bar is shown in Figure 24(159) and the resulting concentrations are shown in Figure 25(159). At the leading end of the bar, the concentration of solute decreases, and at the last part of the bar, the concentration of the solute increases. In between these two extremes, the solute concentration remains the same because it is C_o/k. The equation that describes the ratio of solute concentration at any point on the bar may be derived from the general zone melting equation(160):

$$(2) \qquad \left(\frac{l}{k}\right) dC_n(x) = \left[C_{n-1}(x+l) - C_n(x)\right] dx$$

where: $C_n(x)$ = solute concentration in the nth pass at a distance x from the leading end of the bar,
l = zone length,
and k = distribution coefficient.

Equation 2 is limited by the assumptions of Equation 1 and in addition:

1) that cross sectional area of the bar is constant,
and 2) that the density of the solid and liquid are equal.

The amount of solute in the zone is defined by:

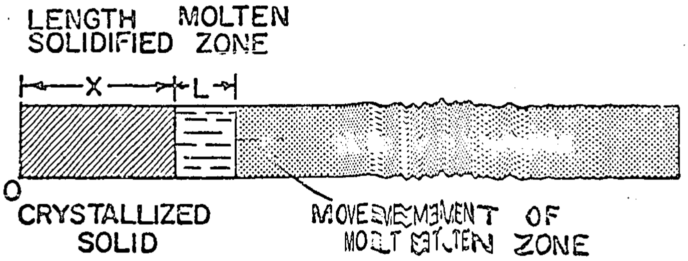


Figure 24. Solidification by zone-melting

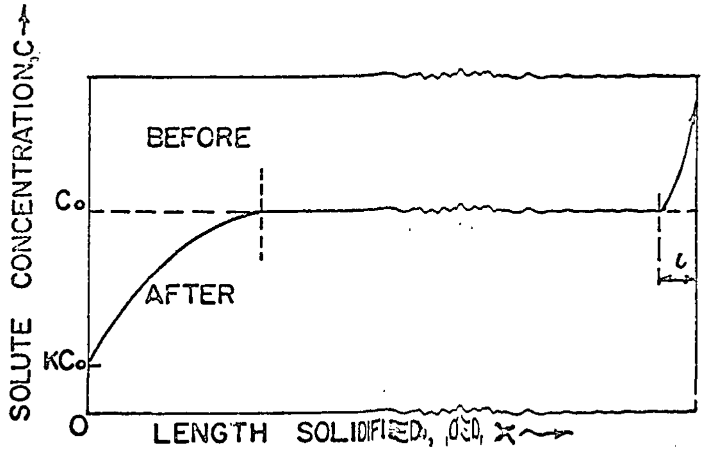


Figure 25. Approximate concentrations before and after single-pass zone-melting

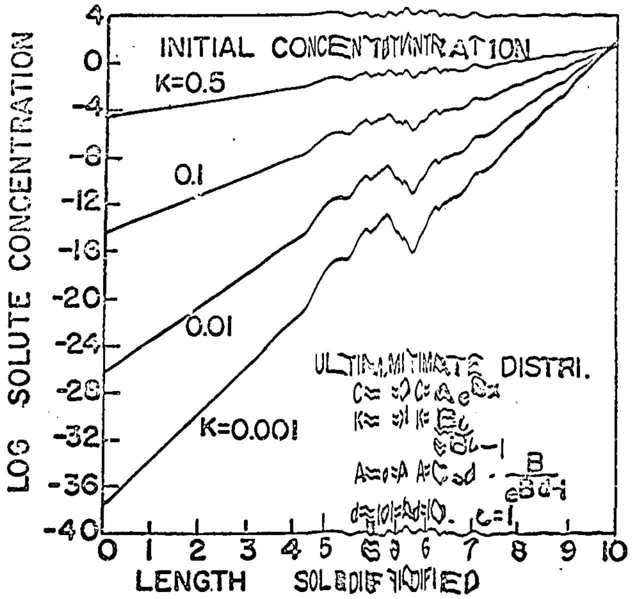


Figure 26. Solute concentration curves showing the ultimate distribution after multiple-zone-refining

(3) $$S = \left[\frac{C_n(x)}{k}\right] l$$

where S = the amount of solute in the molten zone,
so dS = the change in S as the zone advances and is equal to the right side of Equation 1.

The weight of solute entering the zone by melting is (see Figure 27):

(4) $A_s dx \rho_s C_o$,

and the weight leaving the zone is:

(5) $A_s dx \rho_s C_n(x)$

where A_s = area of the solid zone,
dx = change in distance from the leading end of the bar of the molten zone,
ρ_s = density of the solid,
C_o= original concentration of solute in the bar,
$C_n(x)$ = concentration of solute at distance x from the leading end of the bar after n passes.

The weight fraction of solute in the molten zone is:

(6) $$\frac{S}{l A_l \rho_l} = \frac{S}{l A_s \rho_s}$$

where S = the amount of solute in the molten zone,
A = area of the liquid zone,
l = length of the molten zone,
ρ_l = density of the molten zone,
A_s = area of solid zone,
ρ_s = density of the solid.

The differential equation of the material balance is:

(7) $$\left(\frac{l A_s \rho_s}{k}\right) dC_n(x) = \left[A_s \rho_s C_o - A_s \rho_s C_n(x)\right] dx$$

in which terms can be interpreted by referring to Equations 5 and 6.

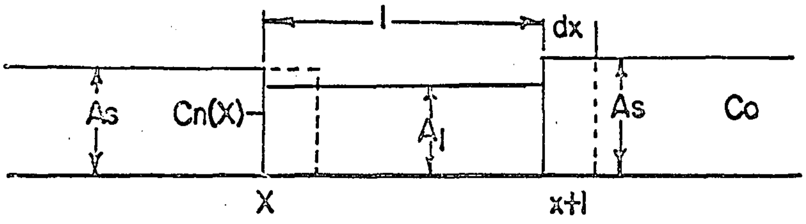


Figure 27. Diagram of moving zone (160)

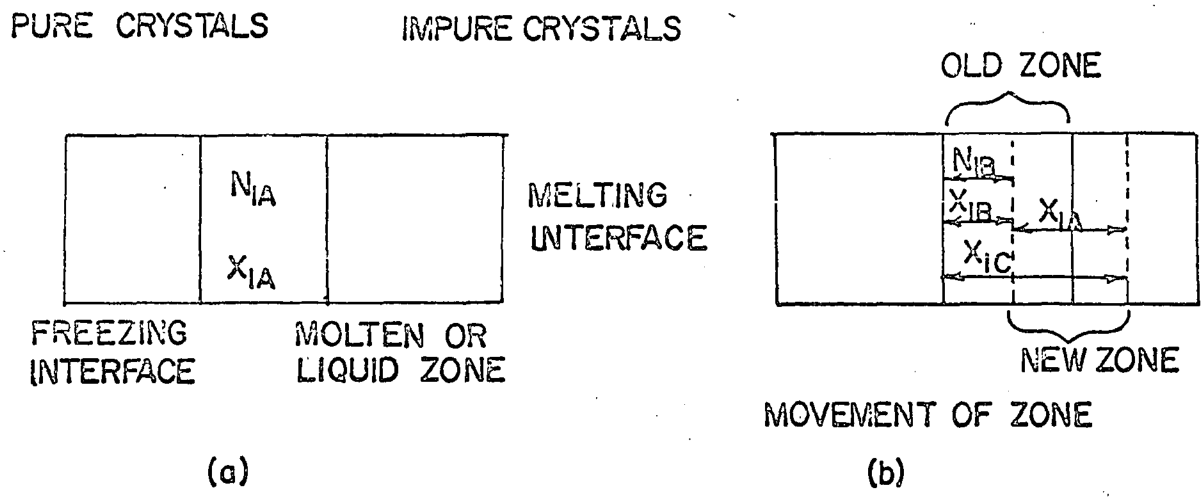


Figure 28. Zone movement (96)

Equation 7 can be written in the standard form:

$$\left[\frac{dC_n(x)}{x}\right] + \frac{k}{\ell} C_n(x) = \frac{k}{\ell} C_o. \tag{8}$$

The solution of Equation 8 is:

$$C_n(x)\, e^{\frac{k}{\ell} x} - C_n(0) = \frac{k}{\ell} \int_0^x e^{\left(\frac{k}{\ell}\right) x}\, dx \tag{9}$$

$$\text{where } C_n(0) = kC_o. \tag{10}$$

Equations 9 and 10 simplify to:

$$\frac{C_n(x)}{C_o} = 1 - (1 - k)\, e^{-\frac{k}{\ell} x} \tag{11}$$

where $C_n(x)$ = concentration of solute at distance x from the leading end of the bar after n passes,

C_o = original concentration of solute in the bar,

k = distribution coefficient or ratio of solute in solid to liquid,

ℓ = length of the molten zone,

and x = distance of the zone from the leading end of the bar.

After a number of passes of a molten zone through the cylindrical charge, the disiribution of solute along the bar will not change with any further passes, and the ultimate concentration will be reached. This has been likened to piling sand against a vertical wall; there will be a maximum attainable height. The solution of the equation which describes the concentration of the solute at ultimate concentration can be more easily solved than the equation for the concentration after any given zone pass. Approximate solutions for the latter case are available. The solution for concentration in the ultimate case is:

$$C = Ae^{Bx} \tag{12}$$

$$\text{where } k = \frac{B\ell}{e^{B\ell}-1} \qquad \text{and} \qquad A = \frac{C_oBL}{e^{BL}-1}$$

are used to evaluate A and B, and:

C = concentration of solute at any point x on the bar, since x is measured from the leading end of the bar,
x = distance from the leading end of the bar,
k = distribution coefficient, ratio of solid to liquid solute concentration,
ℓ = length of the molten zone,
L = length of the bar.

The ultimate distribution of solvent is shown in Figure 25(159) for different values of k as a function of the distance from the leading end of the cylindrical bar which is zone refined. If the value of k is small, the separation is quite sharp. For example, if $k = 0.1$, L (or d as shown on Figure 25) = 10, and $\ell = 1$, the ultimate concentration at $x = 0$ of the solute is less than the original concentration, C_o, by a factor of 10^{14}. Since the concentration of solute in the leading end of the bar is decreased by approximately the order of k in each pass, it would take at least 14 passes to approach the ultimate distribution of solute along the bar. The reason that it is not exactly 14 passes is that the concentration of the solute builds up in the last area to freeze; this increase affects the concentration of solute in the bar at longer distances from the trailing end of the bar with each pass.

Zone refining methods may also be treated by thermodynamic means to obtain the best conditions for a eutectic type mixture(95). The overall change in the chemical potential for zone refining is (see Figure 28):

$$(13)\quad \Delta\mu_i = N_{IA}RT \ln \frac{X_{IC}}{X_{IA}} + N_{IB}RT \ln \frac{X_{IC}}{X_{IB}} + N_{IIA}RT \ln \frac{X_{IIC}}{X_{IIA}} + N_{IIB}RT \ln \frac{X_{IIC}}{X_{IIB}}$$

where $\Delta\mu_i$ = change in the chemical potential,
I = impurity or solute,
II = solvent or major component,
A = the old zone,
B = the interface as a new zone is formed,
C = new zone,
N = number of moles,
X = mole fraction,
R = gas constant,
T = absolute temperature,
so X_{IC} = total mole fraction of impurity in the new molten zone that is formed as the zone moves,
X_{IA} = mole fraction of impurity in the old zone,
N_{IA} = number of moles of impurity in the old zone,
N_{IB} = number of moles of impurity left in the molten zone at the interface as pure solvent freezes out,
X_{IB} = mole fraction of impurity at interface as pure solvent freezes out,
N_{IIA} = number of moles of solvent present in the old zone,
X_{IIC} = mole fraction of solvent in the new molten zone,
X_{IIA} = mole fraction of solvent in the old zone,
N_{IIB} = moles of solvent left in the molten zone at the interface as pure solvent freezes out,
X_{IIB} = mole fraction of solvent at the interface as pure solvent freezes out.

If the impurity is present in the parts per million concentration range, the following inequalities may be applied:

for the solute: $N_{IA} > N_{IB}$, for the solvent: $N_{IIA} > N_{IIB}$,

$X_{IB} > X_{IC}$, $X_{IIC} > X_{IIB}$,

$X_{IB} > X_{IA}$, $X_{IIA} > X_{IIB}$,

$X_{IC} > X_{IA}$, $X_{IIA} > X_{IIC}$,

but: $N_{IIA} \gg N_{IA}$.

This development applies to a case in which k, the distribution coefficient, is less than 1, and leads to the following chemical potential for each part of the zone refining equation, Equation 13.

$\Delta\mu_{IA}$ = (+) large absolute magnitude,

$\Delta\mu_{IB}$ = (-) very small absolute magnitude,

$\Delta\mu_{IIA}$ = (-) very, very large absolute magnitude,

$\Delta\mu_{IIB}$ = (+) very small absolute magnitude approaching zero.

From this analysis, it can be seen that $\Delta\mu_i$ for the total process will be negative as expected. The determining factor is $\Delta\mu_{IIA}$, which is based on the magnitude of N_{IIA}. This would lead to the conclusion that the larger the molten zone, the larger the amount of solvent in the molten zone, the more negative the chemical potential for the entire process will be. Increasing the length of the zone would also increase the amount of solute or impurity in the zone, but this term is not the most important term determining the overall chemical potential.

The method of heating a molten zone is normally induction heating(186). This method, though it does not introduce any impurities and is convenient to use, is not as useful for salts such as alkali halides, which do not conduct electricity well. A flame is quite undesirable, due to contamination. Use of resistance heating by coils wound round the zone refining tube has been commonly used for alkali halides(62, 146, 200). The resistance method may be modified to handle low-melting materials by alternate heated and cooled zones(156, 157, 198, 199, 226). Arc imaging(165), glow discharge(204), electron beam with secondary emission(147, 183), induction heating(212), and flow through a hole in a heated strip(71) have been used as sources of energy for forming the molten zone. Another technique has made use of an internal heater to minimize zone lag(49, 54, 82).

The tube containing the charge may be advanced in a horizontal or vertical plane, with each method presenting certain advantages(120). Direction of linear movement of a vertical tube depends on the densities of the solid and molten phases and on stirring needs(221).

Movement of the zone is a compromise between speed and efficiency. Most workers in the field have used 10 millimeters per hour for zone speed(221), though this gives only 90 % impurity removal with one pass(95). To get 99 % efficiency, it is necessary to use the very slow speed of 0.06 millimeters per hour.

From a survey of the literature, the molten zone commonly used has been equal in length to the diameter of the tube. This dimension rarely exceeds 30 millimeters(221). Tube length found in the same survey was at least ten times the diameter.

Zone refining has been done almost entirely by the batch process to date, though devices to allow the automatic passage of more than one zone have often been used(101, 111, 200), and work is being done on continuous zone refiners which permit constant introduction of feed material and removal of refined products(106, 219).

Analysis of the results of zone refining of alkali halides has been done by a variety of methods. Chemical methods have been used, but often are not sensitive enough to determine the very small amounts of impurities present in zone refined materials(130). Divalent impurities have been checked by measuring the conductivity of the salt at different temperatures(84, 102, 212). Infrared absorption has been determined for alkali halides themselves(119, 167) to permit the identification and assignment of other bands to impurities such as carbonate (137, 145, 200, 209), cyanate(145, 200), nitrate(145, 209), and various oxygen-containing impurities(62, 110, 174, 225). Other oxygen-containing materials were identified by various colors of luminescence (224). Ultraviolet absorption spectra have been used to a great extent to identify hydroxide and related impurities in single crystals of alkali halides(3, 62, 94, 110, 155, 161, 168, 173, 174, 207, 213). Raman spectra of alkali halide crystals has been obtained(47, 113, 114, 115), making it possible to identify impurities by difference and comparison of spectra. Paraelectricity and ferroelectricity of hydroxide-type impurities has been determined by electron spin resonance to identify the form of this impurity(14, 84, 100, 103, 104, 213). Detection of impurities by means of radioactivity has been the basis of neutron activation(9, 79), gamma-active substitution(5, 56, 107), and beta-emitting atom substitution(13). Emission spectrographic analysis has been used(61), and mass spectrographic analysis was the basis for a study of gases evolved from the surface of a freshly cleaved alkali halide(206). Impurities congregate at dislocations in crystals, which made it possible to find the dislocations more easily by x-ray diffraction microscopy and to determine the amount of impurity present(182).

The first method of zone refining that was tried used the apparatus shown in Figure 29 to do an ice-eutectic separation. The apparatus was similar to that used by Pauly and Süe(156, 157, 198, 199) for alkali

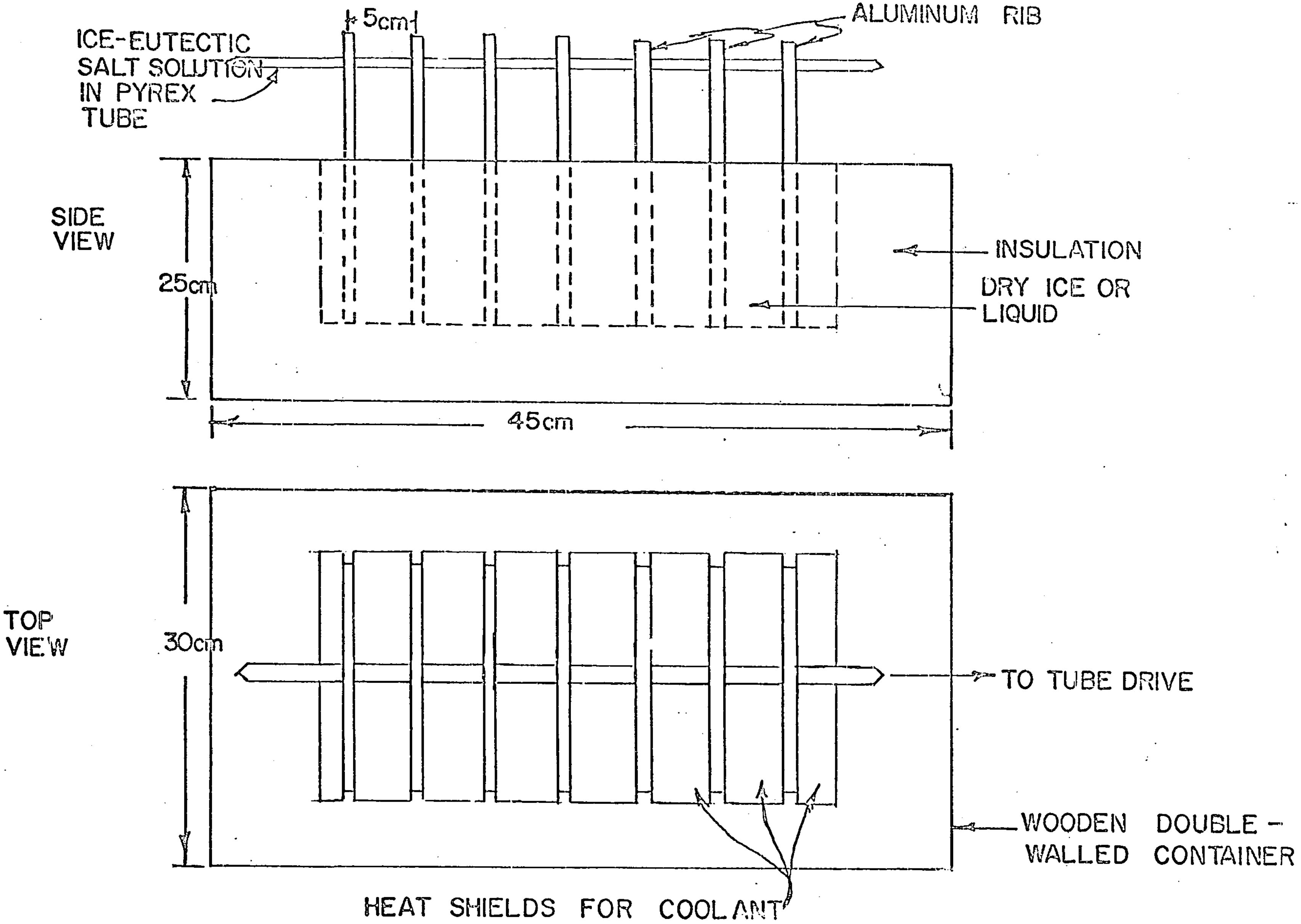


Figure 29. Ice-eutectic zone refiner

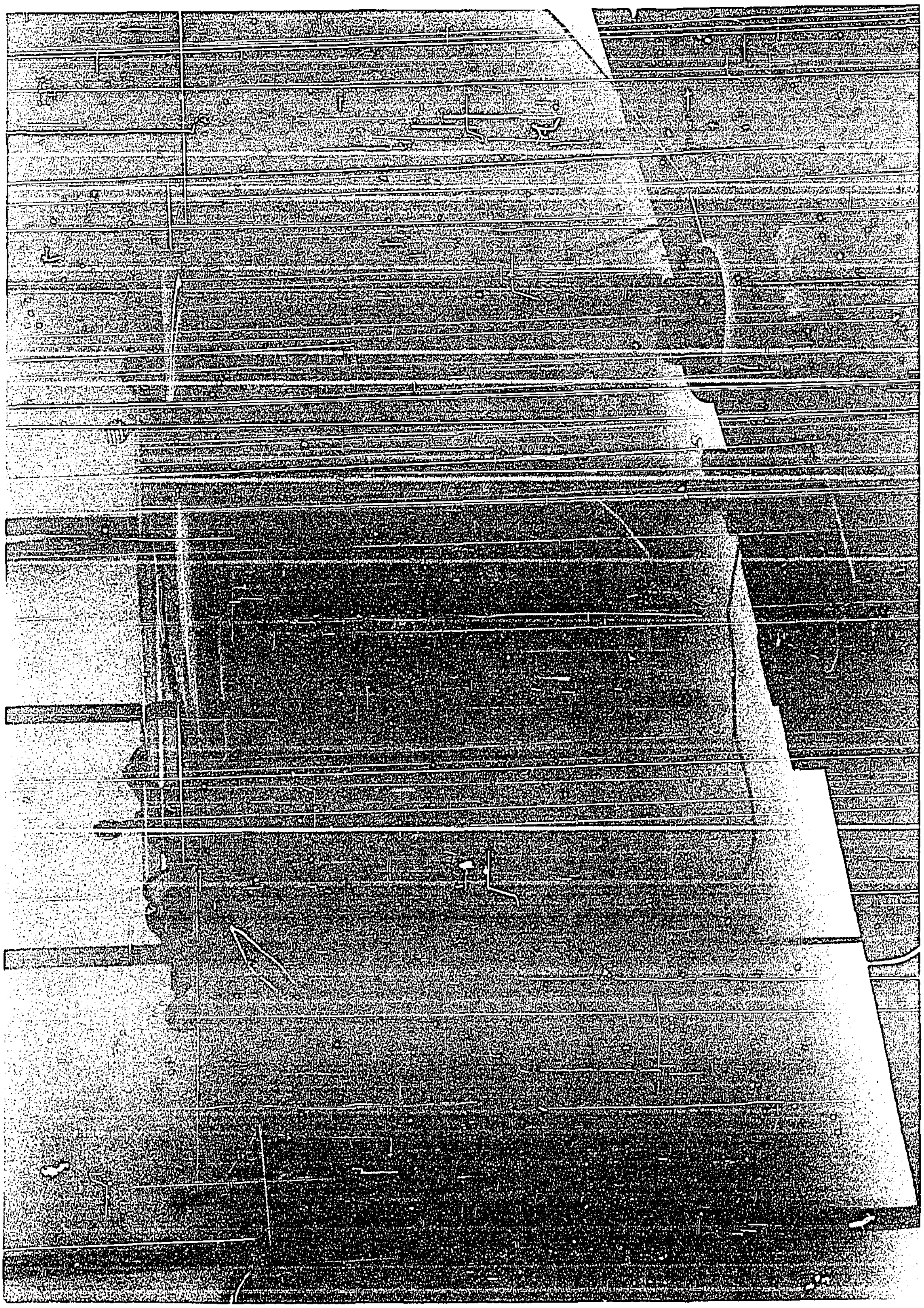
metal nitrates and chlorides. The eutectic point for sodium iodide solution occurs at -31.5° C with 90 grams of salt dissolved in 100 grams of water. The aluminum heat-conducting ribs shown in Figure 29 were 6 millimeters thick and contained three series of holes at different heights. With these different possibilities, it was possible to vary the amount of heat conducted by the ribs away from the ice-eutectic mixture sodium iodide solution by moving the tube closer or farther away from the coolant in the insulated box. A drive mechanism for advancing the zone was made from an electric clock motor by attaching a shaft to the minute hand shaft. The speed of this shaft was 1 revolution per hour which produced a linear speed of 1.3 centimeters per hour. A Pyrex tube containing 25 milliliters of the proper sodium iodide solution to give the eutectic mixture was sealed and placed in the apparatus described above. Dry Ice did not remove enough heat via the aluminum ribs to freeze the ice-eutectic mixture at its freezing point of -31.5° C, but liquid nitrogen did. Problems with the successful coolant occurred because liquid nitrogen evaporated rapidly and water vapor condensed on the aluminum ribs to the point where the sodium iodide ice-eutectic tube became frozen to the ribs. The fact that the tube shattered upon freezing could have been avoided, but the freezing of the tube to the aluminum ribs to prevent advancement of the molten zone is in part a tribute to the high humidity conditions possible at the heighth of an Iowa summer.

Attempts were made to avoid the condensation problem by changes in design, but this difficulty plus decomposition of sodium iodide solution(35, 53, 83, 99, 169, 175) led to the abandonment of this method.

Apparatus available for use in zone refining in Ames Lab included various sets of equipment primarily intended for metals and semiconductors. This equipment included heat sources such as arc imaging, electron beam, induction heating, and arc zone. Use of these methods was considered but adaptation problems and contamination problems from iodine discouraged use of Ames Lab equipment.

The next attempt at zone refining utilized the apparatus shown in Figures 30 and 31. The large Pyrex tube served as a holder for the Transite tube guides and as a heat shield. A ring resistance heater controlled by a Variac was the source of heat for the molten zone. Cooling took place on both sides of the heater by means of air jets directly radially at the sodium iodide tube from rings of copper tubing. The temperature was measured with a thermocouple placed next to the heater. Further estimation of temperature took place with a retinal optical pyrometer, which in spite of the lack of

Figure 30. Resistance heated zone refiner



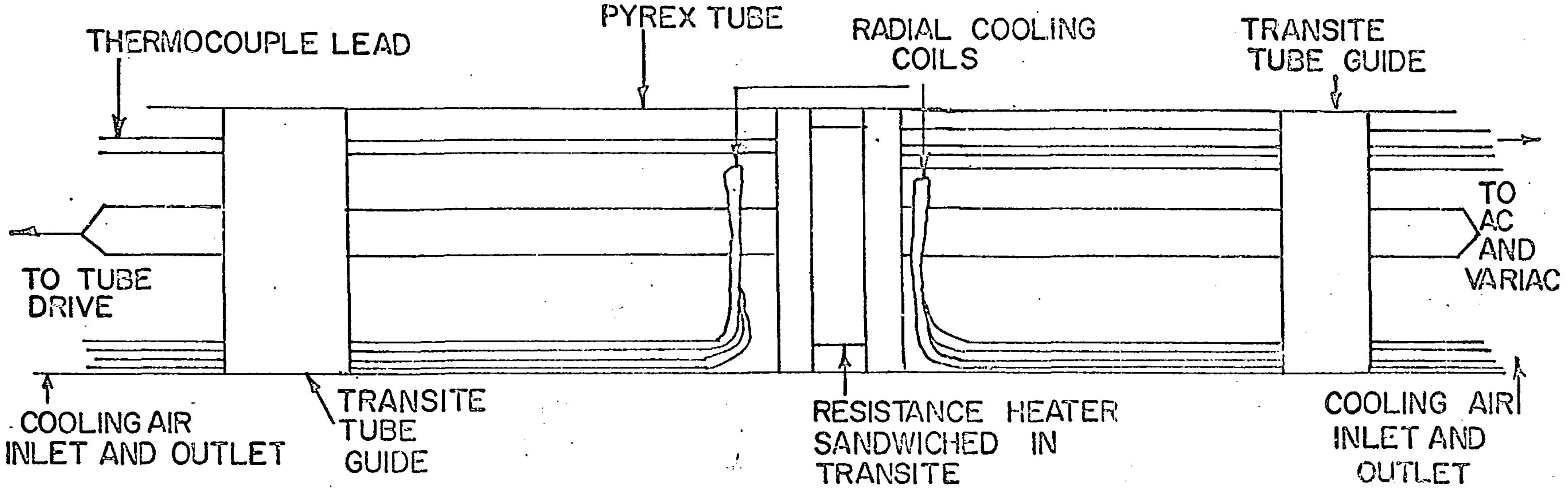


Figure 31. Resistance heated zone refiner

standards, gave a valuable indication of the amount of heat directly reaching the sodium iodide tube. Sodium iodide was sealed in quartz tubes after long pumping with a vacuum pump. Loading of the tubes took place in a dry box that was entered by means of an evacuated port.

The zone refining tube tried at first was 24 millimeters in diameter, which made it difficult to melt the sodium iodide all the way through. Upon melting, a belt of metallic material discolored the sodium iodide and made it gray. One zone was passed from end to end in this tube.

In the next trial with a Vycor tube of the same diameter as the first trial, heating the tube preparatory to sealing produced some iodine at each end of the heated area. This tube was loaded in the dry box described above, and was gradually heated until the temperature was 400° C. At this temperature some of the gray decomposition product formed. Caking also occurred, but shaking the tube broke up the caked material. Heating to melt this sample in the zone refiner led to the formation of a more pronounced gray color. Two passes of the molten zone through the tube were made.

Due to problems in getting the whole diameter of sodium iodide to melt, the next run utilized an eight millimeter Vycor tube. The tube was filled in the dry box, and nitrogen(purified by passage over copper turnings at 600-700° C) was swept through the sodium iodide to help remove water from the salt with the hope that decomposition would be decreased. The nitrogen was also trapped with liquid nitrogen to remove water vapor from the gas stream. The sodium iodide tube was heated to 80-90° C, which is above the decomposition temperature of the dihydrate; the hydrate which is stable at the highest temperature of all the hydrates. Heating and sweeping of nitrogen through this sodium iodide continued for 48 hours, and then the tube was sealed. The tube was advanced through the heater for two complete passages of the molten zone through the sodium iodide. The gray material formed in this run, even with the precautions described above.

Warren (213) used the technique of adding hydrogen halide gas to the zone refining tube and heating the salt above its melting point, which promotes the reaction between alkali hydroxide and the hydrogen halide. The net result is the conversion of alkali hydroxide to alkali halide by an acid-base reaction. This method could not be applied to sodium iodide, as the corresponding hydrogen halide, hydrogen iodide, decomposes at temperatures below the melting point of sodium iodide (25, 29).

Analysis of the results was attempted by emission spectrographic, infrared absorption, and ultraviolet absorption means. The ultraviolet analysis for oxygen-containing impurities was done first, and is described below.

Although the nature of the oxygen-containing impurity in alkali halide crystals has been thought to be hydroxide, a more likely material is the O_2^- ion(62, 110, 155, 174, 213). This impurity has been detected in single crystals of sodium chloride, potassium chloride, and potassium bromide, leading to the Ivey-type equation(62):

$$\lambda_{max} = 691\ d^{0.95} \tag{14}$$

where: λ_{max} = the wavelength of maximum absorption,
and d = interionic distance between nearest oppositely charged ions in the crystal lattice.

Upon using Equation 14, a wavelength of 2060 Ångstroms was obtained. Sodium iodide is also predicted to have no absorption all the way from the far ultraviolet wavelengths to the far infrared wavelengths(173), so no interference with the "hydroxide" band is expected.

Single crystals of sodium iodide were tested to see if this absorption band gave a valid method of analysis for oxygen-containing impurities. A large crystal of sodium iodide of optical purity was cleaved in a dry box to expose fresh surfaces and was then mounted in a cryostat. The cryostat was closed in the dry box to contain the dry box atmosphere and protect the crystal from water vapor and oxygen. After removal from the dry box, the cryostat was evacuated with a mechanical pump and a diffusion pump. The crystal was cooled by filling the cryostat with liquid nitrogen, which makes it possible to observe the spectrum at lower wavelengths. The hygroscopicity of sodium iodide voided several trials, but an adequate dry box was found that maintained the

the newly exposed cleaved surfaces of sodium iodide in a sufficiently dry atmosphere to permit the spectrum to be obtained. The spectrum was limited by the absorption edge of the sodium iodide crystal, which is characteristic of sodium iodide and its lattice spacing. When proceeding downward in wavelength from 3000 Ångstroms to 2000 Ångstroms, the absorption increased radically at 2500 Ångstroms. The only peaks obtained below 2260 Ångstroms were due to luminescence, due to the fundamental absorption of sodium iodide itself. (207). It was therefore not possible to observe a "hydroxide" absorption peak at 2060 Ångstroms. Ultraviolet absorption cannot be used as a method of analysis for oxygen-containing impurities.

Samples of sodium iodide were prepared for infrared absorption analysis by mixing the salt and a solvent to form a mull. Fluorolube and Nujol were the complimentary solvents used to form the mulls; they absorb at different wavelengths and make it possible to interpret the spectrum by difference between the two spectra obtained of the mulls. The mulls were prepared in a dry box between sodium chloride plates, and kept in a desiccator until the spectra were run to minimize introduction of water from the air into the sample. Infrared analysis has been used to detect the presence of oxygen-containing impurities in single crystals, but it was not possible to get any information on such anionic impurities by the mull method. Reproduction of the spectra obtained would not be of any more value than reproducing the spectra of Fluorolube and Nujol, and are in fact, identical.

The tubes containing zone refined sodium iodide were split lengthwise so that analysis of the material at different distances from the leading end of the bar could be done. Sawing the tubes on a glass saw was not feasible, because the saw blade is water-cooled. The nitrogen-flushed small diameter tube was ruined in this way. Upon inspection of the sodium iodide, it could be seen that the gray or black material formed in it due to decomposition of sodium iodide was distributed throughout the bar and not confined to the surface. The Vycor tubes used were etched, which is evidence for the presence of oxygen-containing impurities. Samples of zone refined sodium iodide were taken to determine the pH of a water solution and to then show the presence of hydroxide or carbonate. As the sodium iodide dissolved, a small amount of bubbles formed, which could have been from a minor amount of colloidal sodium in the crystalline sodium iodide. The zone refined sodium iodide did contain more base than the starting material, by 8×10^{-5} weight percent, as measured on a Beckman Expanded Scale pH meter.

Samples of sodium iodide were taken from the split tubes at intervals of ten centimeters for analysis by emission spectroscopy. The results are shown in Tables 23 and 24, and are inconclusive.

Table 23. Analysis of zone refined sodium iodide[a] with one zone pass

Element	Sodium iodide starting material	ZR 2-0, leading end of bar	ZR 2-10 10 cm. away	ZR 2-20, 20 cm. away	ZR 2-30, 30 cm. away	ZR 2-35, 35 cm. away
Li (lithium)	VFT[b]	T	T	FT	T	T
K (potassium)	T	T	T	T	T	T
Rb (rubidium)	-	-	-	-	-	-
Cs (cesium)	FTx	FTx	FTx	FTx	FTx	FTx
Mg (magnesium)	FT	FT	FT-T	FT	FT	FT
Ca (calcium)	T	T	T	T	T	T
Sr (strontium)	VFT	VFT	VFT	VFT	FT	FT
Ba (barium)	T	T	T	T	T	T
Si (silicon)	T	T	T	T	T	T
Fe (iron)	FT	T	T-VW	T	T	T-VW
Cu (copper)	FT	FT	FT	FT	FT	FT
Mo (molybdenum)	FT	-	VFT	VFT	VFT	VFT
Ni (nickel)	-	-	FT	-	-	FT
Al (aluminum)	FT	T-VW	T	T	T	VW
Mn (manganese)	VFT	FT	FT	VFT	VFT	VFT
Sn (tin)	-	VFT	T	VFT	VFT	VFT
Cr (chromium)	FT	FT	T	FT	FT	T

[a] Baker Analyzed Reagent.

[b] See Table 18 for an explanation of the emission spectrographic concentration symbols.

Table 24. Analysis of zone refined sodium iodide[a] with two zone passes

Element	Sodium iodide starting material	ZR 1-0 leading end of bar	ZR 1-10, 10 cm. away	ZR 1-20, 20 cm. away	ZR 1-30, 30 cm. away	ZR 1-40, 40 cm. away
Li (lithium)	VFT[b]	T	FT	FT	FT	FT
K (potassium)	T	T	T	T	T	T
Rb (rubidium)	-	-	-	-	-	-
Cs (cesium)	FTx	FTx	FTx	FTx	FTx	FTx
Mg (magnesium)	FT	FT	FT	FT	FT	FT
Ca (calcium)	T	T	T	T	T	T
Sr (strontium)	VFT	VFT	VFT	VFT	VFT	VFT
Ba (barium)	T	T	T	T	T	T
Si (silicon)	T	T	T	T	T	T
Fe (iron)	FT	T	FT	VW	T	T
Cu (copper)	FT	FT	FT	FT	FT	FT
Mo (molybdenum)	FT	VFT	VFT	VFT	VFT	-
Ni (nickel)	-	VFT	-	VFT	-	-
Al (aluminum)	FT	T	T	T	FT	T
Mn (manganese)	VFT	VFT	VFT	T	VFT	VFT
Sn (tin)	-	-	-	VFT	-	VFT
Cr (chromium)	FT	FT	FT	T	FT	FT

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[a] Baker Analyzed Reagent.

[b] See Table 18 for an explanation of the emission spectrographic concentration symbols.

Tables 23 and 24 show that there is no definite trend in concentration which is dependent on distance from the leading end of the sodium iodide bar, similar to behavior shown in Figure 25. Impurity ions in the zone refined bar should pile up at the end farthest from the leading end, as most of these impurities have distribution coefficients less than one in other zone refining processes, and should be carried along by the molten zone.

The gray or black material that accumulated in each tube of sodium iodide during zone refining could not be identified. Chemical and physical tests for carbon and silicon did not confirm the presence of either suspected material. Emission spectrographic analysis did not show any significant difference between the black material alone, compared to the sodium iodide it discolored, except for phosphorus. Perhaps the black material is present in such a small concentration that physical tests for carbon are inadequate, and this impurity is carbon. Emission spectroscopy cannot be used to detect the presence of carbon, due to the experimental procedure of the analysis.

DISCUSSION

It was shown to be possible to make sodium iodide directly from the elements by the vapor sodium-vapor iodine reaction, i.e., by burning sodium metal in an iodine atmosphere. The drawbacks of this method are quite fundamental and injurious to the purpose of this study: to obtain sodium iodide pure enough for scintillation and optical use of the highest order. The amounts of impurities in the best synthetic products exceeded the largest amount deemed allowable for fundamental studies, which is one to ten parts per million (60). Contamination from the crucible, either nickel or molybdenum, was enough to exceed this limit.

The heats of formation of the alkali metal compounds often produced in the synthesis of sodium iodide shows the relationship among the stabilities:

ΔH_f of $NaOH$ = -101 kilocalories per mole(132, p. 501),

ΔH_f of Na_2O = -99 kilocalories per mole(132, p. 486),

ΔH_f of Na_2O_2 = -112 kilocalories per mole(59, 132, p. 489),

ΔH_f of NaI = -68 kilocalories per mole(32, 69, 201).

Sodium iodide is the least stable of the substances listed, so heat of formation favors the production of oxygen-containing impurities in sodium iodide if there is any source of oxygen or water vapor present.

In dry oxygen, a protective film of sodium hydroxide covers the surface of the sodium, preventing further attack unless the film is broken down by temperatures above the melting point of sodium hydroxide(37) or by moist oxygen(38). The presence of sodium hydroxide as a film on sodium is the reason that it is difficult to get sodium and iodine to react; the film must be broken down. By the time increased temperature makes penetration of the sodium hydroxide film possible, the iodine has sublimed away from the reaction area.

The attention in producing ultrapure sodium iodide was then centered on the purification process. Experience with the ion exchange and ice-eutectic zone refining methods has shown that it is impractical to work with solutions of sodium iodide due to decomposition of iodide to iodine and hydroxide. In general, this leaves two avenues open: sublimation and zone refining of the solid.

Sublimation gave the best results in the experiments attempted. This method appears to be the best one to remove the divalent alkaline earth metal ions, which are the most difficult to separate by some other techniques.. The sublimation of sodium iodide can be further improved by forcing the salt to condense on a warm surface. The warm surface will force more volatile substances to be re-sublimed to a cooler region of the apparatus, while the sodium iodide condenses in a nearly isothermal area. Less volatile impurities can be left in the starting material. The method of sublimation bears further experimentation, especially as a step in the total purification procedure. Movement of a heated zone in repeated cycles over sodium iodide to cause mass transport and to emphasize volatility differences is another possibility.

The process of zone refining did not produce very good experimental results, but the success of this method with other materials, including alkali halides, encourages further work. Equipment for recycling multi-pass zone refining is quite expensive to build, especially if any other heating method than resistance is used, but experimentation can proceed on a modest scale with rather simple equipment.

Changes in technique to be investigated while using zone refining include the introduction of iodine gas or a mixture of iodine and hydrogen gases to the tube containing the sodium iodide charge. If the charge is heated above the melting point of sodium iodide, the gases come into contact with all of the charge by diffusion through the melt. Iodine or iodine and hydrogen gases might then react with hydroxide impurities in the sodium iodide and convert them to sodium iodide. The by-product, water, could then be swept out of the tube and the cycle could be repeated to remove all possible hydroxide and water vapor.

Sodium iodide etches and sticks to the walls of Vycor and quartz containers, which can cause fracture of the tube or the sodium iodide single crystal upon cooling of the entire charge to room temperature. Some workers have tried to avoid this problem by coating the walls of the vessel with carbon. Carbon can be deposited by decomposing an acetone stream in a hot tube. Another, more elegant, approach would eliminate the container and use the floating zone technique. It is just as important to keep impurities from being introduced as to remove them from commercial or direct synthesis sodium iodide.

Zone refining has the added advantage that well-formed single crystals of sodium iodide are obtained. These crystals are ideal for studies of scintillation or optical absorption behavior, if the crystal needed is not of very large dimensions. 20-30 millimeters is the limit in diameter, while length is almost unlimited.

Analysis was undertaken to determine if purification by zone refining did take place and if so, to determine the degree of purification. It was hoped that distribution coefficients for various impurities in sodium iodide could be calculated from the analyses, but zone refining did not work well enough to allow this.

An improvement in analysis by the method of mass spectroscopy was initiated, but at the present time results of the spark source mass spectrograph are returned extremely slowly due to the press of their work.

With this method of analysis, detection of impurities to one part per million would become routine to an accuracy of a factor of two or better, and it is possible in some instances to analyze at concentrations as low as ten parts per billion.

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