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A REVIEW OF THE ADSORPTION OF IODINE ON METAL AND ITS BEHAVIOR IN LOOPS

E. Hoinkis

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REACTOR CHEMISTRY DIVISION

A REVIEW OF THE ADSORPTION OF IODINE ON METAL AND ITS BEHAVIOR IN LOOPS

E. Hoinkis

MAY 1970

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A REVIEW OF THE ADSORPTION OF IODINE ON METAL AND ITS BEHAVIOR IN LOOPS

E. Hoinkis*

ABSTRACT

The partial pressures of the iron iodides at equilibrium with solid FeI_2 in the system Fe-I have been calculated for the regions where the solid phases are Fe(s) and Fe(s) + FeI_2(s) as function of temperature and pressure. The investigations of iodine adsorption on metal surfaces and of iodine deposition in loops has been reviewed. The methods used and the results of the experiments are discussed with respect to the behavior of iodine in coolant circuits of helium-cooled, graphite-moderated reactors.

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1. INTRODUCTION

The reasons for the escape of fission products into the coolant of helium-cooled, graphite-moderated reactors are the contamination of the fuel coatings with fuel and the failure of coated particles and the consequent diffusion of fission products through the fuel element wall. The release rate of the gaseous fission products and iodine during normal operation can be calculated with sufficient accuracy because many experimental and theoretical investigations have been made. Therefore, the amount of iodine entering the pressure circuit can be estimated. The ratio of the activities of the gaseous iodine plus the activity adsorbed on aerosol particles to the activity of the iodine plated out on the walls is known as the decontamination factor. Measurements at the Windscale AGR and the Dragon Reactor[1] provided values of the decontamination factor between 10^3 and 10^4. Yellowlees and Scheider[1] estimated with an assumed decontamination factor of 10^3 that 3000 Ci of ^{131}I will be plated out within the coolant circuit of a 600 Mw(e) reactor under normal operating conditions.

The situation within the coolant is very complicated from the chemical point of view. Iodine and other fission products are able to react with each other as well as with duct and heat exchanger material and with gaseous impurities within the coolant. The reactants and the reaction products are carried in a gas stream of varying temperature and high velocity and parts of them decompose due to radioactive decay. The materials present in the circuit are alloys with presumably oxidized surfaces. The amounts of long-lived fission product ^{129}I and stable ^{127}I increase during the operation of the reactor. Consequently, the total amount of iodine present in the circuit increases during reactor operation.

Because the chemical state of the iodine plated out within the coolant circuit is unknown, it is not possible at present to predict the behavior of the plated out iodine under abnormal operating conditions. For instance, it is not known whether the iodine plated out will become permanently gasborne if the water content of the coolant increases due to a leaky heat exchanger and more importantly how fast this will occur. Even without regard to safety considerations this question is important because of maintenance and repair.

The gaseous iodine species present in the coolants of the Dragon, Windscale, and AVR reactors have not been identified up to now. Investigations by Browning[24] carried out at the Dragon Reactor and many experiments on laboratory and technical scales lead to the conclusion that at least a part of the iodine present in the circuit reacts with the heat exchanger or pipe material. Up to now it has not been investigated whether solid metal iodides are able to exist at the high temperatures and low iodine vapor pressures within the coolant circuit. This question is of considerable interest, because rather large amounts of radioactive iodine could be accumulated in a part of the circuit where metal iodides are stable thermodynamically.

Therefore, the first task of this review was to examine how well the temperature and vapor pressure range in which the iodides of the alloy components are thermodynamically stable has been defined. This thermodynamic investigation has been done here only for the system iron-iodine, because the ducts within the coolant circuit and the heat exchanger are made mainly from steel and because it has been found in experiments on laboratory scale that only iron-iodides are formed if steel surfaces are exposed to iodine vapor. Nevertheless, this assumption is a considerable simplification because the high temperature part of the heat exchanger is made from nickel alloys. This assumption is only justified

if one assumes that the surface concentration of iodine in the high temperature part of the heat exchanger is so low that the formation of nickel-iodide can be neglected or if the oxide film on nickel alloys is of protective nature. According to fission-product release studies by Morgan[29] there is evidence that some iodine is released as CsI, but it is assumed here that iodine enters the coolant gas as almost completely dissociated $I_2(g)$ and not as a fission product iodide MI_x. Further it is assumed that the iodine partial pressure within the coolant is locally independent.

It is also of interest to what extent iodine present in the coolant will be dissociated. In the next two chapters of this study the dissociation of iodine and the partial pressures of the iodine species present in the system iron-iodide at temperatures and iodine partial pressures in the range of interest will be calculated using published thermodynamic data.

2. THE DEGREE OF DISSOCIATION OF IODINE

The degree of dissociation of iodine has been calculated taking into account the pressure of the additional helium present. The decrease of the degree of dissociation with increasing helium pressure can be neglected up to high pressures (200 atm He) as would be expected. The values of the equilibrium constant of the dissociation reaction has been taken from the JANAF Tables. The details of the calculation are given in Appendix A. Figure 1 is a graph of the degree of dissociation, α, for different temperatures, as a function of the sum of the partial pressure of atomic iodine plus the partial pressure of the molecular iodine ($P_{I_2}+P_I$). The degree of dissociation is very close to 100% at temperatures higher than 400°C and iodine pressures less than 10^{-9} atm.

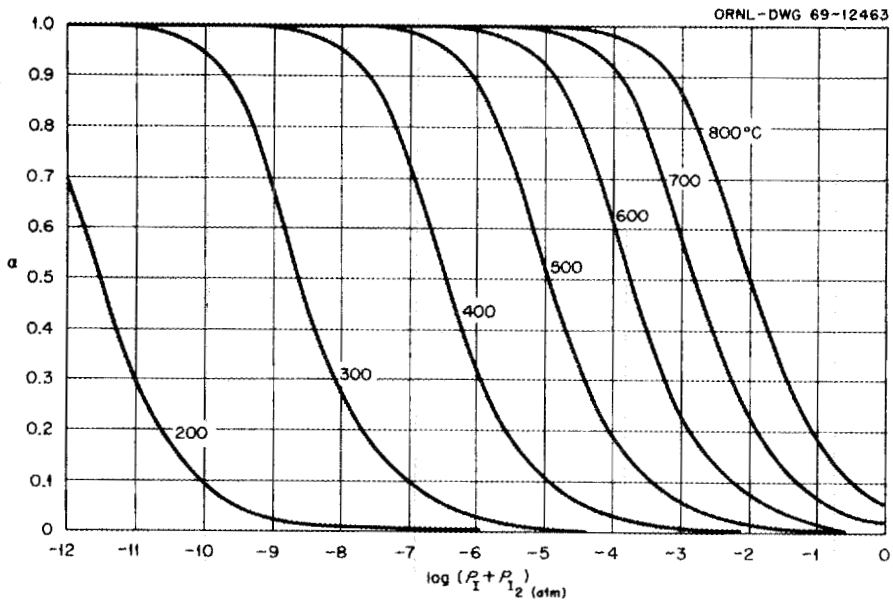


Fig. 1. The Degree of Dissociation α as a Function of the Total Pressure and Temperature.

3. THE THERMODYNAMICS OF THE SYSTEM IRON-IODINE

The system iron-iodine has been investigated by Schäfer and Hönes,[2] Sime and Gregory[3] and Zaugg and Gregory.[4,5] There is only one solid iron iodide, FeI_2, with a melting point of 587°C. There are four gaseous iron iodides: FeI_2, FeI_3, Fe_2I_4, and Fe_2I_6. Solid iron-II-iodide is thermodynamically stable only if the iodine partial pressure at a given temperature is at least equal or greater than the decomposition pressure above solid FeI_2 at equilibrium. The partial pressures of the iron iodides at equilibrium with iron or iron and solid FeI_2 can be calculated as a function of iodine partial pressure and temperature from the equilibrium constants of the reactions of formation of the iodides. The equilibrium constants have been measured at temperatures above 500°C only and over relatively small temperature intervals.

For the given problem partial pressures at lower temperatures down to 200°C are of interest also. Equations for the temperature dependence of the equilibrium constants of the reaction of formation of $FeI_2(s)$, $FeI_2(g)$ and $Fe_2I_4(g)$ valid between 200 and 587°C have been derived using the known specific heats.

The specific heats of $FeI_3(g)$ and $Fe_2I_6(g)$ are not known. For this reason the temperature dependences of the vapor pressures have been extrapolated linearly to lower temperatures. On account of this and because the equilibrium constants have been measured only over a rather narrow temperature range, all vapor pressures calculated here for lower temperatures could be at least a factor of about 10 too low or too high. The partial pressures of the iodine species at equilibrium with iron or iron plus solid iron-II-iodide have been calculated using a computer code. The equations used for the temperature dependence of the equilibrium constants along with a summary of the thermodynamic data measured

up to now are given in Appendix B. The results of the calculations are shown in Figs. 2, 3, and 4.

Figure 2 shows the logarithms of the partial pressures of the iron iodides above solid iron-II-iodide as a function of the reciprocal absolute temperature. The partial pressure of FeI_2 is up to 525°C higher than the partial pressures of atomic iodine and the other iron iodides. The partial pressure of Fe_2I_4 becomes higher than the one of FeI_2 at temperatures higher than 525°C. The partial pressure of Fe_2I_6 is at least two orders of magnitude lower than any of the other species present and can be neglected for all practical purposes.

With respect to the accumulation of solid iron-II-iodide in the coolant circuit the partial pressure of iodine above solid FeI_2 at lower temperatures is of interest. For 250° and 350°C the following partial pressures may be read from Fig. 2:

T(°C)	P_I (atm)	P_{FeI_2} (atm)
250	10^{-10}	$10^{-9.3}$
350	$10^{-7.5}$	$10^{-6.5}$

The value 10^{-10} atm for P_I corresponds to the upper limit of the iodine partial pressure range estimated for the coolant circuit of gas-cooled reactors. The lowest surface temperature in the circuit depends on the reactor design. At an iodine partial pressure of 10^{-10} atm, solid FeI_2 could be accumulated at points of temperatures lower or equal to 250°C.

The partial pressures of the iodine species in the system iron-iodine have been calculated for the case when the

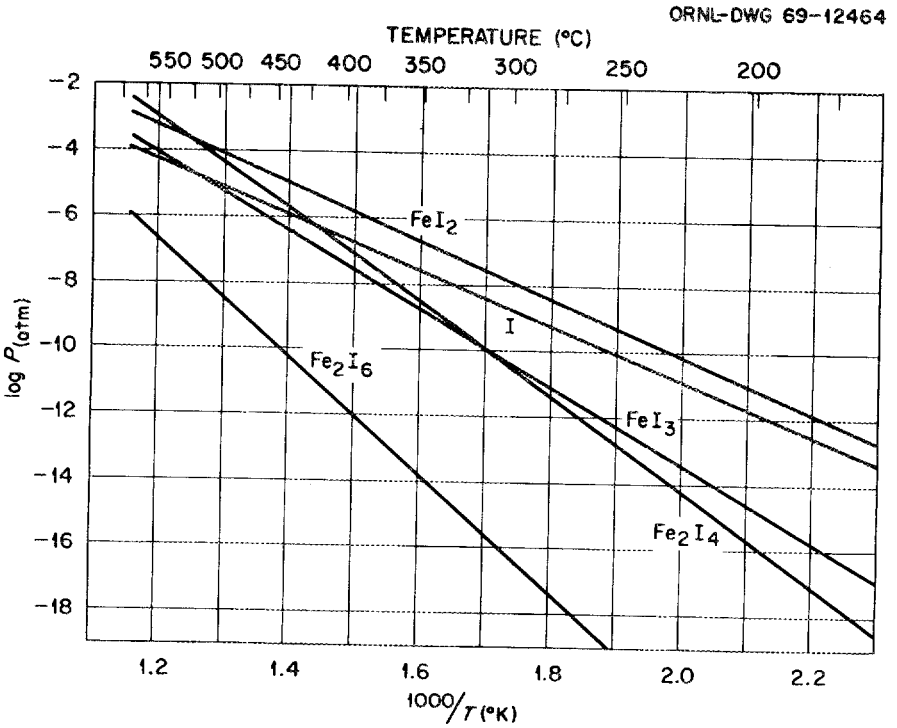


Fig. 2. The Partial Pressures of Iodine and the Iron Iodides above Solid FeI_2 as a Function of Temperature.

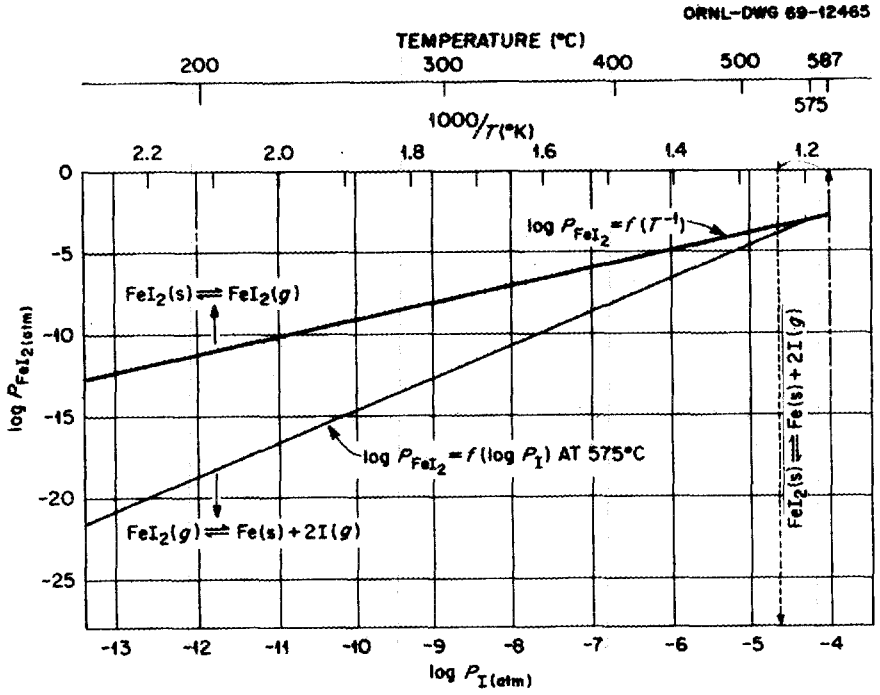


Fig. 3. The Partial Pressure of FeI_2 above Solid FeI_2 as a Function of the Temperature (Thick line) and the Partial Pressure of FeI_2 above Iron as a Function of the Partial Pressure of Iodine at 525°C (Thin line).

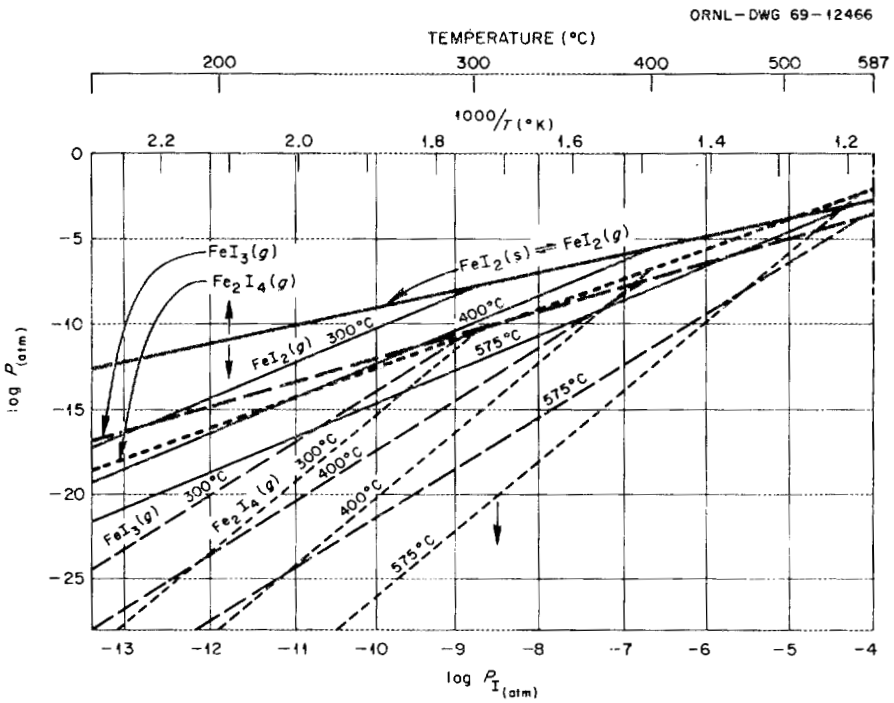


Fig. 4. The Partial Pressures of FeI_2, FeI_3 and Fe_2I_4 Above Solid FeI_2 as Functions of Temperature (Thick lines) and above Iron as Functions of Iodine Partial Pressure of 300, 400 and 525°C (Thin lines).

solid phase is only Fe(s). A plot of the partial pressures calculated for three different temperatures is shown in Fig. 4. Because Fig. 4 is difficult to survey, the construction of Fig. 4 will be explained using Fig. 3. The partial pressure of FeI_2 above iron at 575°C is plotted as a function of the partial pressure of atomic iodine P_I. Figure 3 gives, for example, $P_{FeI_2} \cong 10^{-15}$ atm at $P_I \cong 10^{-10}$ atm. The scale of the 1000/T-axis is arranged in this way that the partial pressure of atomic iodine at equilibrium with solid FeI_2 at the temperature T can be taken from the P_I-axis. This pressure is at 575°C, for example, $10^{-4.3}$ atm. The partial pressure of FeI_2 at equilibrium with solid FeI_2 is plotted as a function of the temperature. At 575°C, for example, $P_{FeI_2} = 10^{-3}$ atm.

Figure 4 is constructed in the same way as Fig. 3. The partial pressures of FeI_2, FeI_3 and Fe_2I_4 are plotted as functions of P_I for 300, 400 and 575°C. For $P_I = 10^{-9}$ at 400°C, Fig. 4 gives the following partial pressures:

$$P_{FeI_2} = 10^{-10.4} \text{ atm}$$

$$P_{FeI_3} = 10^{-14.4} \text{ atm}$$

$$P_{Fe_2I_4} = 10^{-16.3} \text{ atm}$$

At 575°C and $P_I = 10^{-9}$ atm, Fig. 4 gives

$$P_{FeI_2} = 10^{-12.7} \text{ atm}$$

$$P_{FeI_3} = 10^{-18.7} \text{ atm}$$

$$P_{FeI_4} = 10^{-22.1} \text{ atm} \quad .$$

In the iron-iodine system the gas phase contains practically only atomic iodine and FeI_2 at partial pressures P_I less than 10^{-9} atm and at temperatures higher than 400°C. The partial pressure of atomic iodine is at least ten times

higher than the partial pressure of FeI_2 under these conditions.

With respect to the behavior of iodine in coolant circuits of gas-cooled reactors, one arrives from the thermodynamic point of view, at the following conclusions:

Iodine is mainly present in atomic form under the conditions within the coolant circuit of a gas-cooled reactor. If the iodine present reacts with the heat exchanger and duct material forming gaseous FeI_2, the partial pressure of atomic iodine is at least ten times higher than the partial pressure of iron-II-iodide. The accumulation of solid FeI_2 as a solid phase within the coolant circuit at temperatures equal or less about 250°C seems to be probable.

4. THE ADSORPTION OF IODINE ON METAL SURFACES

Keilholtz and Barton[6] have written a comprehensive review of studies of the behavior of iodine in reactor containment systems. Davis[7] has discussed the mechanisms of sorption of iodine on different materials at lower temperatures. Milstead, Bell and Norman[8] investigated the iodine sorption on low chromium alloy and discussed from the thermodynamic point of view their own sorption data and in brief the data of other investigators. Here all data available including adsorption measurements on other materials and at lower temperatures will be dealt with in more detail.

In connection with the plateout of iodine in coolant circuits of gas-cooled reactors, iodine surface concentrations at partial pressures lower than 10^{-9} atm are of primary interest. Many experiments have been carried out at appreciably higher iodine partial pressures to prevent the huge experimental difficulties that arise at very low iodine partial pressures. Nevertheless, these experiments have been very

useful because the general chemical behavior of iodine adsorbed on oxidized metal surfaces has been discovered. The experiments performed can be divided into two groups depending on whether the iodine partial pressure above the specimen is lower or higher than the decomposition pressure above $FeI_2(s)$ at the same temperature at equilibrium. There is no solid FeI_2 as a pure phase on the surface of the specimen in the first case, but there is solid FeI_2 in the second case. Most experiments have been performed at 400°C. The partial pressures above $FeI_2(s)$ at equilibrium at 400°C are

$$P_I = 2.3\text{x}10^{-7} \text{ atm}, \; P_{I_2} = 1.17\text{x}10^{-7} \text{ atm}, \; P_{FeI_2} = 1.2\text{x}10^{-7} \text{ atm}.$$

The adsorption of iodine on metals has been investigated using both a transpiration method with a temperature distribution that is either isothermal or non-isothermal in the specimen range and a static method where the adsorbent is isothermal, but the whole apparatus non-isothermal. The first method is also called the dynamic flow method. The second one is referred to as the pseudo-isopiestic method.

Let us first consider experimental conditions where solid iron-II-iodide is not stable thermodynamically on the surface of the specimen. The surface concentration of iodine is thus determined by the amount of both the adsorbed iodine and the adsorbed gaseous metal iodides. In order to be able to compare iodine surface concentrations measured by different methods the actual partial pressures of iodine and the metal iodides above the specimen must be known. In case of the carrier gas method these partial pressures can be calculated using the mass balance equation and the temperature dependence of the equilibrium constants of the reactions of formation of the metal iodides and of the dissociation of iodine. In the case of the static non-isothermal method the thermal transpiration ratio of iodine in the given apparatus is also needed. The treatment of Milstead et al.[8] to calculate the partial pressures

above the specimen in the non-isothermal static method will be discussed in detail later on.

In cases where solid FeI_2 is present on the surface the deposit of iodine depends on the rate of formation and evaporation of FeI_2 and on the amount of iodine adsorbed on the oxide layer and on FeI_2.

4.1 Surface Concentration of Iodine on Metals Measured by the Transpiration Method

4.1.1 General Remarks

The attainment of equilibrium in chemical reactions investigated using the transpiration method can be checked out by determining the gas phase concentrations of the reaction products. These gas phase concentrations are independent of the flow rate if the flow rate is fast enough to eliminate gas phase diffusion effects, but also slow enough to allow establishing of the equilibrium partial pressures in the gas phase. The attainment of thermodynamic equilibrium has not been checked in all experiments mentioned in the following because some of the experiments are only of preliminary nature and because in some experiments the test section was not isothermal.

4.1.2 Experimental Results

Zumwalt, Hudson, Busch, Moses and Snow[9] investigated the deposition of iodine on isothermal samples of stainless-, low alloy- and carbon steel for an inlet iodine pressure of 10^{-6} atm in the temperature range 235-750°C. Samples in the form of plates were exposed in a quartz tube for about 65 hours to a slowly flowing helium carrier gas containing iodine, 100 ppm O_2, 5 ppm H_2O, and 370 ppm N_2. Thus at an iodine partial pressure of 10^{-4} atm the partial pressure of oxygen was about one hundred times greater than the one of iodine. The gas velocity was in the order of

1 cm sec^{-1}. The surface concentrations varied only slightly with the type of steel.

At 400°C and an iodine partial pressure of 10^{-6} cm the following iodine surface concentrations have been measured:

Table 1. Iodine Loading on Steel at 400°C and an Iodine Pressure of 10^{-6} atm from Carrier Gas Containing 100 ppm O_2, 5 ppm H_2O, and 370 ppm N_2

AISI 304 stainless steel	1.5 ($\mu g\ cm^{-2}$)
ASTM 387B low alloy steel	4 "
AISI 1030 carbon steel	4 "

The logarithm of the plateout of iodine (or metal iodides formed) appears to be roughly inversely proportional to the reciprocal absolute temperature. Substantial oxidation and scaling occurred at temperatures above 500°C. Gas chromatographic investigation showed that the incoming oxygen was apparently reacting with the carbon in the steel to produce a corresponding amount of CO and CO_2. The water reacted apparently to form hydrogen. The surface roughness and the nature of the reaction products were not investigated.

Browning and Davis[10,11] in experiments of preliminary nature investigated the deposition of iodine on stainless steel, copper, iron and nickel at partial pressures from 10^{-9} to 10^{-5} atm in the temperature range 24-700°C. Experimental details as well as quantitative data are not given in this report. Browning and Davis report the following qualitative results: the amount of iodine deposited on the metals varied in the order of Cu>Fe>Ni. Iodine reacted with the stainless steel surface forming metal iodides. Introduction of air seemed to cause loss of iodine from the surface deposit. The surface concentration on stainless steel with a preoxidized

surface (oxide layer thickness ~200-300 Å) at an iodine partial pressure of $\sim 10^{-9}$ atm is much lower than the surface concentration on stainless steel with an as-received surface, whatever this may have implied.

Creek and Parker[12] 1965 carried out preliminary investigations of the deposition of iodine on steel in the presence of hydrogen, air and steam. Iodine at a partial pressure of $\sim 10^{-7}$ atm at 400°C contained in mixtures of steam and helium as well as hydrogen and air was swept through stainless steel or carbon steel tubes for ~20 minutes with a linear flow rate of ~1.5m sec^{-1}. The temperature of the experimental tube was ~600°C at the entrance and gradually decreased to 100°C at the exit. The principal findings were: In helium and mixtures of hydrogen and steam, retention of iodine was much higher than in air and steam. Stainless steel retained much less iodine than did carbon steel. Lower fractions were retained at higher flow rates. Significant deposition begins at about 340°C and maxima in deposition occurred at 180-200°C. By no means all of the iodine was trapped by the metal surface. Retention values varied from 2-69%. Where the iodine has been carrier free, ~33% was retained by the stainless steel surface, whereas only ~2% was retained where stable iodine carrier had been added. The maximum retained on the carbon steel when the air-steam-mixture was used was about 69%. No significant fraction was retained above 400°C.

Burnett, Lofing and Allen[13] investigated the sorption of iodine on low chromium alloy, mild steel and Incoloy 800 at iodine partial pressures of $\sim 10^{-7}$ atm in helium as carrier gas. The heavy oxide scale on the surface of the specimen had been removed before the experiments by a chemical cleaning process. The metal surfaces were still noticeably oxidized. The helium flow rate was 5 cm sec^{-1}. The gas passed first through a U-tube filled with crystalline ^{131}I-tagged iodine held at temperatures between −78 and −40°C. The durations

of experiments varied between 184-508 hours, and was determined by the time desired to transport this amount of iodine into the tubes which corresponds to the steady-state-surface concentration. Iodine plateout along the length of each tube was measured. The amount of iodine deposited in that part of the tube above 400°C did not increase further after about 250 hours when the iodine partial pressure was approximately 10^{-7} atm. Apparently a steady state had been achieved where the amount of iodine deposited was equal to the amount of iodine and metal iodides desorbed. The iodine surface concentrations measured in a nearly isothermal part of the tube are given in Table 2.

Steady state was achieved only at the lowest iodine inlet pressures. Because these pressures are lower than the decomposition pressure above solid FeI_2 ($P_I+P_{I_2} = 3.4 \times 10^{-7}$ atm) the steady state could possibly correspond to thermodynamic equilibrium between the surface and the gas phase. There is no significant difference between the iodine loading on Fe materials and Incoloy 800. The experiments have shown that the plateout of iodine on a steel surface with a temperature distribution between 100 and 400°C is nearly quantitative at the very low linear flow rate of 5 cm sec^{-1} presumably mainly because the FeI_2 formed has been deposited, apparently along with the remaining iodine, in the low temperature parts of the tube.

Burnette et al. also performed experiments to investigate the transport behavior of iodine and the isotopic exchange between adsorbed iodine and iodine in the gas phase. One experiment was designed to investigate the transport behavior of adsorbed iodine. In this experiment iodine initially nearly uniformly distributed over the surface of a low chromium alloy tube was redistributed by purging the tube with helium. The "iodine" was transported to lower temperatures. The maximum of the iodine concentration

Table 2. Iodine Deposited on Different Materials Measured by Burnette, Lofing and Allen[13]

Material and Temperature	Iodine Inlet Pressure (atm)*	Iodine Sorption ($\mu g\ cm^{-2}$)	Condition
1-1/4% Cr,			
1/2% Mo at 400°C	9×10^{-8}	6.5	Steady state
300°C	1.4×10^{-7}	>45, >20	Not at steady st.
Mild steel at 425°C	8×10^{-8}	6.5	Steady state
400°C	4×10^{-7}	6 - 10	Not at steady st.
Incoloy 800 at 500°C	5×10^{-8}	0.5	Steady state
400°C	4×10^{-7}	~ 3	Not at steady st.
270°C	4×10^{-7}	~80	Not at steady st.

*The I_2 vapor pressure was calculated from the total amount of iodine transported into the tube and the charcoal trap.

appeared at approximately 180°C after 211 hours desorption. Burnette et al. assume that this downstream peak resulted from condensation of volatile iron iodide.

Another experiment was designed to investigate the isotopic exchange between adsorbed iodine and iodine in the gas phase. The surface of a mild steel tube was presaturated with stable iodine before the deposition of active iodine. After the presaturation ^{131}I tagged iodine at a partial pressure of $\sim 10^{-7}$ atm was swept over the surface for 226 hours. The same surface concentration of radioactive iodine was reached as in the experiment without presaturation of the surface within the same time and at the same temperature. Burnette et al. conclude from this result that the isotopic exchange between the adsorbed iodine (presumably FeI_2) and the gas phase is very fast. This conclusion holds only if one makes the unlikely assumption that the whole surface is covered entirely with FeI_2 which prevents further deposition of iodine and that this FeI_2 did not evaporate during the 226 hours sweeping of the tube with helium containing ^{131}I tagged iodine. Additionally in another experiment the desorption kinetics of iodine from a mild steel surface with and without inactive iodine at a partial pressure of $\sim 10^{-7}$ atm in the purge gas has been measured. In the case of a rapid isotopic exchange between the iodine in FeI_2 and the gas phase iodine, the desorption of active iodine should be faster if the surface is purged with helium containing inactive iodine. But the desorption rate was found to be the same in both experiments. Burnette et al. concluded from this result that there is a fast isotopic exchange between the solid and the gas phase. But it seems also reasonable to conclude that desorption of iodine activity is mainly due to evaporation of FeI_2.

Burnette et al. concluded from their adsorption experiments that the deposition of iodine on a stainless steel surface at 400°C from a gas stream is rapid and nearly

quantitative. It should be noted that the deposition velocity of iodine on stainless steel measured at the very low linear flow rate of 5 cm sec^{-1} in a temperature range ~100 to 400°C cannot be used to estimate the plateout factor in coolant circuits of gas-cooled reactors because the linear flow rate and the lowest temperature within the circuit is higher than in these experiments.

Rosenberg, Genco and Morrison[14] studied the deposition of iodine from helium containing air or steam-air mixtures at iodine partial pressure of ~10^{-5} atm within the temperature range 115 to 200°C.

In a simple flow system, the carrier gas containing the radioactive tagged iodine streamed slowly through an isothermal chamber where the specimen is placed. The activity of the specimen was continuously measured by a scintillation counter. The duration of the experiments was 20-320 hours and the linear flow rate 0.5 cm sec^{-1}. Preparation of test coupons involved polishing, degreasing, and drying in air. The amount of iodine deposited was found to be a linear function of time for mixtures of iodine with dry air, dry helium, helium-steam and air-steam. A change in the corrosion mechanism was observed to occur between 145 and 160°C. At 145°C the deposition is linear with respect to time, while at 160°C there is an initial burst of deposition followed by a rapid leveling off so that after 4 hours deposition has ceased. In order to investigate the effect of metal composition the corrosion rates of different metals were measured in iodine-steam-air mixtures at 115°C with a flow rate of 0.4 cm sec^{-1} and an iodine partial pressure of 5.6×10^{-5} atm. The corrosion rate and the total amount of iodine deposited increased in the order chromium, stainless steel, nickel, iron. The deposition rate at 115°C in iodine-steam-air mixtures increased with increasing gas phase concentration of the iodine. Desorption experiments at 115°C indicated that the deposition process was irreversible in a

steam-air-mixture at 115°C, yet reversible to a large extent in either air or under vacuum at the deposition temperature. This behavior is explained by Rosenberg et al. with the assumption that the iodine is present as $FeI_2 \cdot 4H_2O$ which does not decompose in the presence of steam; other metal iodides could be present also. It is not clear why at 115°C the iodine did not desorb in a mixture of steam and air. One possible explanation is that iodine deposited on stainless steel at 115°C from steam-air mixtures is incorporated into the growing corrosion centers and may be adsorbed on metal oxide-hydrates formed during the corrosion process. Desorption tests at higher temperatures have not been performed.

In connection with the accidental ingress of water into the coolant of a gas-cooled reactor, one is concerned whether the iodine plated out in the circuit will become gasborne. Experiments to investigate desorption of iodine under the conditions of this accident have not been performed as yet. However, some indirect conclusions can be drawn if the iodine deposition measured in the presence of steam is compared to iodine deposition measured at the same temperature and iodine partial pressures without steam. Unfortunately, measurements have been performed in the presence of steam and air; furthermore, there is a gap in the temperature range in which iodine deposition with and without steam and air has been measured. Nevertheless, it seems to be useful to investigate the influence of steam and air on the iodine deposition. The following considerations have been made in order to compare the amount of iodine deposited on low chromium alloy steel in the presence of air plus steam with the amount of iodine deposited from a pure helium stream. Burnette et al.[13] measured on 1-1/4% Cr, 1/2% Mo at 300°C at an iodine partial pressure of 1.4×10^{-7} atm an iodine loading of >45 $\mu g\ cm^{-2}$ and Milstead et al.[8] found on the same material at 316°C and 2.1×10^{-7} atm an iodine deposit of >190 $\mu g\ cm^{-2}$. Steady state had not been

established in either experiment. Iodine deposition in the presence of steam plus air has only been measured on stainless steel and iron but not on low chromium alloy steel. An iodine deposit of 2 $\mu g\ cm^{-2}$ on stainless steel at 160°C has been found at an iodine partial pressure of 6×10^{-5} atm in a mixture of helium plus 40 v/o air. In order to compare the amount of iodine deposited on low chromium alloy steel in the presence of air and steam with the amount of iodine deposited without steam and air, the difference between iron and stainless steel with regard to iodine deposition must be taken into account. For a very rough estimate, iodine loadings measured at a lower temperature may be considered in spite of the fact that the plateout mechanism at lower temperatures could be different from the one at high temperatures. The amount of iodine deposited from steam-air mixtures at 115°C on stainless steel within the same time has been found to be a factor of 5 lower than the amount deposited on iron. For this reason it is here assumed that at 160°C five times more iodine is deposited on a low chromium alloy steel than on stainless steel in a steam-air mixture. With regard to the 2 $\mu g\ cm^{-2}$ measured on stainless steel at 160°C, 10 $\mu g\ cm^{-2}$ iodine will be deposited on a low chromium alloy steel under the same conditions (160°C, iodine partial pressure is 6×10^{-5} atm). If one compares this value with the >45 to >190 $\mu g\ cm^{-2}$ measured at a lower iodine partial pressure and a higher temperature it follows that a higher iodine loading has been achieved in the absence of steam and air. So it is reasonable to conclude that at temperatures >160°C a mixture of steam and air prevents deposition of iodine on stainless steel to a large extent. One possible explanation for this behavior is that FeI_2 will be oxidized in the presence of air. The figures used in the evaluation given above are summarized in Table 3.

Similar investigations to those performed by Rosenberg et al. have also been made by Morris and Nichols.[15]

Table 3. Iodine Loading on Different Materials with and Without Steam and Air Present in the Gas Phase. Non-steady-state conditions are designated by the sign >

Material	Iodine Partial Pressure (atm)	Temperature (°C)	Conditions	Measured or Estimated	Iodine Loading g/cm^{-2}	Reference
Stainless steel	6×10^{-5}	160	Helium, iodine, air, steam	Measured	2	13
Iron	$\sim 10^{-5}$	115	Helium, iodine, air, steam	Measured	$>10^{3}$	14
Stainless steel	$\sim 10^{-5}$	115	Helium, iodine, air, steam	Measured	$>5 \times 10^{3}$	14
Low chromium alloy	6×10^{-5}	160	Helium, iodine, air, steam	Estimated	10	
1-1/4% Cr, 1/2% Mo	1.4×10^{-7}	300	Helium, iodine	Measured	>45	13
1-1/4% Cr, 1/2% Mo	2.1×10^{-7}	316	Iodine	Measured	>190	8

4.2 Surface Concentrations of Iodine on Metals Measured by the Non-Isothermal Static Method

4.2.1 General Remarks

The principle of the non-isothermal static (or pseudo-isopiestic) method is very simple. The specimen is placed in the horizontal leg of an L-shaped Pyrex tube heated by a furnace. The vertical leg contains iodine tagged with ^{131}I maintained at constant temperature using a refrigeration unit. The amount of iodine on the specimen is monitored with a calibrated gamma-scintillation counter.

The advantage of the method is the ease of performing an experiment. The disadvantages arise from the fact that the partial pressures of iodine and the gaseous metal iodides formed by reaction of the iodine with the specimen must be calculated making assumptions which are hard to justify under the conditions of the experiment. The attempt of Milstead, Bell and Norman[8] to calculate the actual partial pressures above the specimen under conditions at which solid FeI_2 is thermodynamically unstable is discussed in Appendix C. It is shown there that the treatment of Milstead et al. gives incorrect results, if applied to the measurement of the adsorption of iodine on steel in the given temperature and partial pressure range. Consequently, the relation of the measured iodine deposit to the partial pressures of iodine and, especially of the metal iodides, is uncertain. The partial pressures of iodine calculated with different assumptions agree for an iodine source pressure of $\sim 10^{-6}$ atm within a factor of about 3 as shown in Appendix C. Such a small difference is usually not important and in most cases could be neglected. But more serious with respect to the correlation of measured iodine surface concentrations with the iodine partial pressure above the specimen may be the fact that the partial pressures of the gaseous iodides above the specimen do not correspond to the partial pressures in an isothermal

static system at equilibrium. This is discussed in detail also in Appendix C and will be only briefly mentioned here: The pseudo-isopiestic system is not isothermal and the gaseous metal iodides formed diffuse in the gas phase from the high temperature specimen to the cooler parts of the apparatus where they condense. For this reason the actual partial pressure of the metal iodides above the specimen depend on the rate of formation of the iodides and do not correspond to the partial pressures at thermodynamic equilibrium. The rate of formation of the iodides is supposed to be low and for this reason the partial pressures of the metal iodides above the specimen are lower in the case of the non-isothermal static system than at the same iodine partial pressure and the same temperature in a truly isothermal static system at equilibrium. One cannot suppose a priori that the measured iodine deposition does not depend on the metal iodide partial pressures above the specimen. For this reason the iodine surface concentrations measured by the non-isothermal static method may be too low when compared to a surface concentration measured by an isothermal static method or a transpiration method at the same iodine partial pressure and the same temperature where thermodynamic equilibrium has been established. As shown in Appendix C, one is justified in calculating the partial pressure of atomic and molecular iodine above the specimen at low reaction rates and source iodine pressures $>10^{-6}$ atm simply assuming constant pressure within the whole apparatus and taking into account the dissociation of iodine. This simple treatment will be applied here later to compare the results of different investigators.

4.2.2 Experimental Results

The sorption of iodine by stainless steel at partial pressures from 10^{-9} to 10^{-6} atm and temperatures between 70 and 500°C has been measured in experiments of a preliminary nature by Davis and Browning.[12] In these experiments

iodine from an elemental iodine source diffused during 1 to 10 hours into an evacuated, heated stainless steel tube. The activity of the deposited iodine was measured. About two monolayer equivalents were adsorbed at 500°C at an iodine partial pressure of 10^{-9} atm. The sorption rate decreased if the stainless steel surface had been pre-oxidized. Only the early stage of the adsorption kinetics has been measured. Steady state was not achieved in these experiments.

Gray, Neill and Kress[16] investigated the adsorption of iodine on mild steel and stainless steel at iodine partial pressures between 10^{-9} and 4×10^{-5} atm at 400°C during runs of 12 to 100 hours duration using the apparatus described in 4.2.1. The steady state surface concentration of iodine on mild steel which had been previously annealed in hydrogen was 0.5 $\mu g\ cm^{-2}$ at an iodine partial pressure of 4×10^{-5} atm. The desorption of iodine from non-oxidized stainless steel surfaces was investigated at 650°C. The surface concentration was initially 0.2 $\mu g\ cm^{-2}$. This surface concentration corresponds to about a monolayer coverage if one assumes that the iodine is spread over the geometric surface uniformly. The gas phase iodine was purged with helium from the chamber and the desorption rate measured. Between 60 and 90% of the iodine desorbed from the surface within half an hour. The remaining iodine was equivalent to a tenth of a monolayer and was not removed by further purging with helium. FeI_2 was found in the cooler parts of the apparatus in all adsorption and desorption experiments. Autoradiographic investigations of both oxidized and H_2-annealed stainless steel surfaces exposed to iodine showed that the iodine deposition was not uniform.

Blasting an oxidized stainless steel surface contaminated with ^{131}I with wet steam and vigorous rubbing of the surface did not cause a removal or redistribution of the iodine. Information about the surface-concentration of iodine, the

temperature of the steam and whether air was present during the steam blasting is not given.

Bull and Neill[17] studied the desorption of iodine from hydrogen annealed mild steel at temperatures between 320 and 640°C. Iodine vapor (tagged with ^{131}I) at a partial pressure of $\sim 10^{-6}$ atm was adsorbed on the specimen. When a monolayer of iodine had deposited the pressure of both I_2 and I was reduced to $\sim 10^{-8}$ atm and the iodine source was placed in a liquid nitrogen bath. The desorption of the deposited iodine was followed by measuring the decrease of the activity with a gamma spectrometer. Approximately 50% of the iodine was desorbed within 20 hours at 370°C. The rate of desorption was considerably lower than in the experiment in which the specimen was purged with He. After the desorption process the surface concentration remained practically constant for the following 45 hours. The remaining surface concentration of iodine is proportional to the amount of iodine initially present on the surface. The measured desorption curve is probably the sum of different processes. Desorption of iodine adsorbed on FeI_2 and the oxide layer, evaporation of FeI_2 and decomposition of FeI_2 could be involved.

Bull and Neill[18] studied the reaction of iodine at 400°C with mild steel, stainless steel and steel wool at the rather high iodine partial pressure of 10^{-3} atm. Strips of the materials investigated were rolled into spirals and placed in the horizontal leg of the L-shaped Pyrex tube. Some strips had been previously oxidized. After four days ~ 1 g of iodine had reacted with the specimen. After 10 days the weight change of the specimen was measured and the reaction product deposited in the cooler parts of the apparatus analyzed. The product of reaction between a steel surface and iodine vapor was found to be FeI_2. The reaction took place in spite of the fact that the metal was covered by a 0.1 to 0.7 mm thick oxide layer. The amount of iodine found on the surface

of the steel specimens at the end of the experiment was quite high (~0.2 mg cm^{-2}). Photomicrographs showed a small amount of a new solid phase on the top of the oxide layer. This phase has not been investigated. Neglecting the minor constituents of the steel it seems to be clear from the thermodynamic point of view that the reaction product between iodine and steel is FeI_2. Because the metal is covered by an oxide layer the question is how was the FeI_2 formed. The oxide layer on the specimen which was exposed to iodine had a tendency to scale. A few cracks in the film were noted. It seems to be likely that iodine or iron diffuses through the cracks in or through the oxide film itself forming FeI_2 which evaporates. Photomicrographs have shown that the amount of FeI_2 on the oxide layer is inversely proportional to the thickness of the oxide layer.

To explain the formation of FeI_2, Bull and Neill considered a mechanism where iodine interacts with the oxide at the outer surface to form FeI_2 and an iron-deficient oxide according to the equations

$$Fe_3O_4(s) + 3/2\ I_2(g) \rightleftharpoons 4Fe_2O_3(s) + FeI_3(g) \qquad (1)$$

$$Fe_3O_4(s) + I_2(g) \rightleftharpoons 4Fe_2O_3(s) + FeI_2(g) \qquad (2)$$

Iron was then supposed to diffuse from the steel into the oxide layer. In order to prove the proposed mechanism Bull and Neill performed two experiments in which iodine vapor contacted Fe_3O_4 powder at 400°C. No reaction products were found during the two week duration of the runs. This result is in agreement with the fact that Fe_3O_4 is very stable against oxidizing agents, even against chlorine. An estimate of the change of the free energy for reaction (1) and for reaction (2) under the conditions of the experiment yielded positive values (~7 and ~21 kcal/mol).

In agreement with the experimental result of Bull and Neill a reaction between iodine and Fe_3O_4 is impossible from the thermodynamic point of view.

Milstead, Bell and Norman[8] studied the adsorption of iodine on low chromium alloy steel (1% Cr, 1/4% Mo alloy) over an iodine source-pressure range of 10^{-9} to 10^{-5} atm in the temperature range 316 to 482°C. In agreement with other investigators Milstead et al. found that iodine interacts with the steel surface to form volatile iron iodides and they pointed out that in these experiments a steady state must have been attained wherein the surface concntration of iodine depended on the net rates of formation and evaporation of FeI_2. The treatment of Milstead et al. to evaluate the adsorption measurements is discussed in detail in Appendix C. The loading of iodine on low chromium alloy steel at 400°C as a function of the iodine source pressure P'_{I_2} is given in Table 4.

Table 4. Sorption of Iodine on 1% Cr-1/4% Mo Alloy at 400°C Measured by Milstead, Bell and Norman[8]

Source Iodine Pressure (atm)	Loading ($\mu g/cm^2$)
1.1×10^{-5}	20.8
8.3×10^{-6}	23.2
4.0×10^{-6}	9.2
4.0×10^{-6}	9.3
2.8×10^{-6}	14.2
2.8×10^{-6}	12.2
1.3×10^{-9}	3.8

4.3 Summary and Discussion of the Adsorption Measurements

The discussion of the two methods applied to the measurement of iodine adsorption on metals has shown that the transpiration method is more suitable from the theoretical point of view than the non-isothermal static method. Most of the data available have been obtained by the non-isothermal static method.

The general results of the investigations mentioned here can be summarized as follows.

Iodine reacts with oxidized and clean metal surfaces forming metal iodides. The rate of the formation of metal iodides is presumably determined by diffusion of iron or iodine through cracks in the oxide layer. The distribution of iodine on the surfaces is not uniform. The surface concentrations on pre-oxidized alloys are lower than on alloys with as-received surfaces. The presence of steam and oxygen prevents deposition of iodine to an extent, depending on the concentration of $H_2O + O_2$ in the gas phase. The iodine deposition seems to be quite independent of the type of steel. There seems to be no significant difference between the iodine loading on ferrous materials and Incoloy. Iodine adsorbed on oxidized metal surfaces desorbs into carrier gas streams in elemental form as well as in the form of metal iodides.

Some of these general results will be discussed in more detail using Fig. 5. Iodine deposition on different materials measured by both the carrier gas and the non-isothermal static method is summarized in Table 4. Surface concentrations measured under non-steady state conditions are indicated by the sign >. The surface of the specimen is slightly oxidized if no other indication is given. The signs given in the last row of Table 5 refer to Fig. 5.

Figure 5 is a graph of iodine deposition ($\mu g\ cm^{-2}$) as a function of the logarithm of either the inlet or the iodine

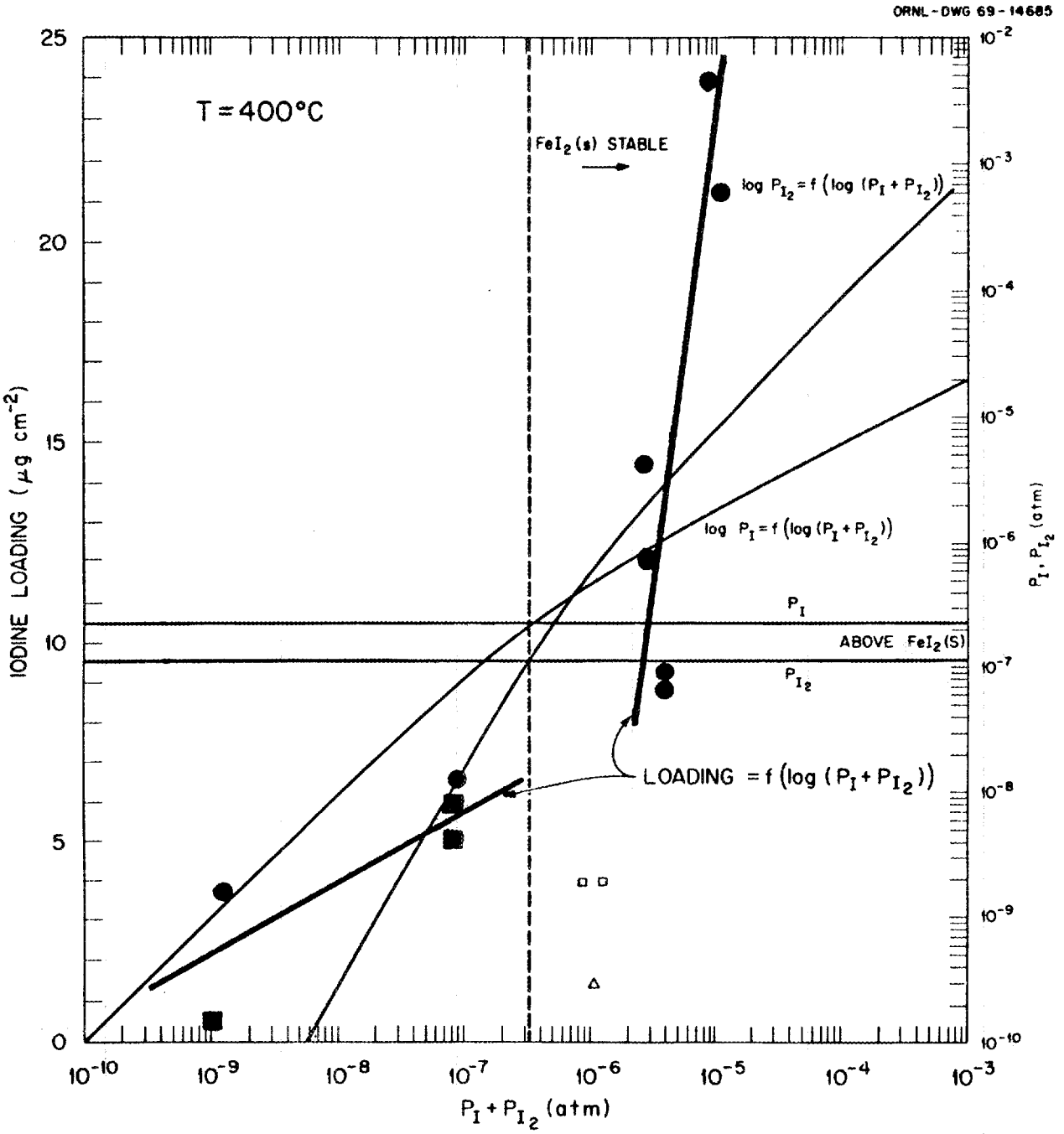


Fig. 5. The Iodine Loading at 400°C as a Function of Either the Inlet or the Source Iodine Pressure ($P_I + P_{I_2}$). The partial pressures P_I and P_{I_2} in a system containing only iodine are plotted as function of the total iodine pressure ($P_I + P_{I_2}$). FeI_2 is stable at total iodine partial pressures equal or higher than the pressure indicated by the dashed line.

Table 5. Iodine Loading on Different Materials Measured with the Carrier Gas Method or the Non-Isothermal Static Method

Method	Temp; (°C)	Inlet or Source Iodine Pressure (atm)	Material	Loading ($\mu g \cdot cm^{-2}$)	Ref.	Sign
Trans-piration Method	400	10^{-6}	AISI stainless steel	1.5	Zumwalt et al.[9]	△
	400	10^{-6}	ASTM 387B low alloy steel	4		□
	400	10^{-6}	AISI 1030 carbon steel (carrier gas contained 100 ppm O_2, 5 ppm H_2O)	4		□
	400	9×10^{-8}	1-1/4% Cr, 1/2% Mo	6.5	Burnette et al.[13]	○
	300	1.4×10^{-7}	1-1/4% Cr, 1/2% Mo	>45		
	425	8×10^{-8}	Mild steel	6		□
	425	8×10^{-8}	Mild steel	5		□
	400	4×10^{-7}	Mild steel	>10		
	500	5×10^{-8}	Incoloy 800	0.5		
	400	4×10^{-7}	Incoloy 800	>3		
	270	4×10^{-7}	Incoloy 800	>80		
Non-Isothermal Static Method	400	$\sim 10^{-9}$	Mild steel, H_2 annealed	0.5	Gray et al.[16]	■
	400	4×10^{-5}	Mild steel, H_2 annealed	>3		
	400	1.1×10^{-5}	1% Cr-1/4% Mo alloy	20.8	Milstead et al.[8]	●
	400	8.3×10^{-6}	"	23.2		●
	400	4.0×10^{-6}	"	9.2		●
	400	4.0×10^{-6}	"	9.3		●
	400	2.8×10^{-6}	"	14.2		●
	400	2.8×10^{-6}	"	12.2		●
	400	1.3×10^{-9}	"	3.8		●

source pressure ($P_I + P_{I_2}$) atm. The partial pressures P_I and P_{I_2} in a system containing only iodine at 400°C are plotted as functions of the logarithm of the total iodine pressure ($P_I + P_{I_2}$). The partial pressures P_I and P_{I_2} above solid FeI_2 at 400°C are also shown in Fig. 5. Solid iron-II-iodide is stable at 400°C at iodine pressures ($P_I + P_{I_2}$) $\geqslant 3.3 \times 10^{-7}$ atm. This value is indicated in Fig. 5 by the vertical dashed line. Only on the right hand side of the dashed line is solid iron-II-iodide as a pure phase stable and presumably present on the surface of the specimen.

The solid points represent iodine deposition measured by the non-isothermal static method. The other signs represent data measured by the transpiration method. Only steady-state data from Table 5 are plotted.

As can be seen from Fig. 5 the increase of the iodine loading with increasing iodine pressure ($P_I + P_{I_2}$) is more rapid when FeI_2(s) is thermodynamically stable. Data in this region have been measured by Milstead et al.[8] on low chromium alloy using the non-isothermal static method.

At iodine pressures higher than the pressure above solid FeI_2 the amount deposited should depend mainly on the rate of formation and evaporation of FeI_2, though elemental iodine is also adsorbed on FeI_2 and on any oxide layer. A saturation value for iodine deposition should be reached at a certain iodine pressure when the rate of formation of FeI_2 is equal to the rate of its evaporation. The observed increase of iodine deposition with increasing iodine pressure seems to indicate that the saturation value has so far not been reached.

The iodine loading measured at iodine pressures below the decomposition pressure of solid iron-II-iodide is more important with respect to the plateout of iodine within the coolant circuit. The data measured at low iodine pressures are quite scattered. These data were determined by different

investigators on different materials (mild steel and low chromium alloy) by two different methods. The few data available in this low pressure region cannot be used to extrapolate reliably into the partial pressure range of interest ($<10^{-9}$ atm). The dashed signs in Fig. 5 represent data measured on low alloy steel, carbon steel and stainless steel in the presence of 100 ppm O_2 plus 5 ppm H_2O. The iodine loading in the presence of an excess of oxygen and of some water is significantly lower than one would expect at the same relatively high iodine pressure without water and oxygen. On the other hand, it seems to be reasonable to conclude that adsorbed iodine will become gasborne if exposed to a mixture of water and air at temperatures > 160°C. However, no conclusions can be drawn about whether adsorbed iodine will desorb if exposed to water vapor alone.

5. DEPOSITION OF IODINE IN LOOPS

5.1 Experimental Results

The deposition pattern of iodine in loops has been investigated at Oak Ridge National Laboratory and Battelle Memorial Institute. Scott[19] performed one experiment on a laboratory scale to study the deposition of ^{131}I and ^{132}Te on stainless steel. ^{131}I and ^{132}Te were released along with other fission products from irradiated UC-particles heated to 790°C. The surface temperature within the stainless steel test section decreased from 660 to 36°C. About 10^{12} atoms of ^{131}I were released during the experiment into helium at a pressure of 0.7 atm recirculated with a linear flow rate of 6 cm sec^{-1}. The duration of the run was 24 hours. The highest surface concentration of ^{131}I within the test section was 10^{10} atoms cm^{-2}. Traces of ^{131}I were found even at the hottest points (660°C) of the deposition tube. The ^{131}I began to deposit in more than trace amounts where the tube

was at 440°C and showed a very intense maximum at 300°C. Most of the ^{132}Te deposited at 600°C. The independence of ^{131}I distribution from the flow rate and the duration of the experiment has not been checked.

Neill[20] investigated the deposition pattern of iodine within a loop on technical scale at Battelle Memorial Institute. The iodine was released from irradiated fuel into the recirculated carrier gas helium. The duration of one run was 48 hours. The flow rate of helium was 1.2 ℓ sec^{-1} at 400°C and the pressure 22 atm. The loop consists of a high temperature (650°C) and a low temperature (400°C) isothermal zone as well as non-isothermal zones (240-650°C). The deposited activity has been measured by scanning the deposition section with a gamma-scintillation detector. The surface concentration of ^{131}I varied between 10^8 and 10^{11} atoms cm^{-2} and was found to be about one hundred times lower in the high temperature isothermal zone than in the low temperature isothermal zone. The iodine deposit increases in the heat exchanger continually as the temperature decreased from 600 to 400°C. Conversely, the surface concentration of ^{137}Cs is independent of temperature and decreases monatonically throughout the test region. Apparently ^{131}I is released as iodine and not as cesium iodide because the distribution pattern of ^{137}Cs and ^{131}I are completely different.

Neill, Eissenberg and Gray[21] studied the adsorption of iodine on copper, silver, stainless steel and carbon steel in an isothermal deposition section of the ORNL fission product deposition loop in the temperature range 150-320°C. About 5 mg iodine tagged with ^{131}I and dissolved in benzene or cyclohexane had been injected within 1 to 2 hours into helium at 22 atm flowing with a linear flow rate between 1000 and 5500 cm sec^{-1} and Reynolds numbers between 25,000 and 80,000. Introduction of benzene and cyclohexane should not affect the principal findings. In some runs the iodine

was recirculated, in other runs a full flow silver filter was installed upstream of the point of injection to prevent recirculation of iodine remaining in the gas stream after a complete loop cycle. The activity was measured by scanning the deposition section with a gamma-scintillation detector. The deposition patterns of iodine on as-received stainless steel at 320°C and 22 atm became independent on the Reynolds number at high values. For example, the deposition patterns found at Re = 27,500 and Re = 50,000 differed only slightly. Iodine deposited on stainless steel at 205°C did not desorb in streaming helium within 20 hours at the same temperature but 80% of the initially deposited iodine desorbed within 124 hours after raising the temperature to 260°C.

The surface concentration of iodine was found to be lower at hot spots than in the surrounding isothermal region.

Neill, Gray and Kress[22] continued the experiments with the ORNL fission product deposition loop. A silver wool filter behind the test section was introduced into each experiment to remove the iodine not deposited. The iodine source was heated PdI_2. The estimated maximum iodine concentrations in the helium lay between 0.04 to 1.0 mg m^{-3} corresponding to iodine partial pressures between 10^{-8} and 3×10^{-7} atm. The helium pressure has been 22 atm, the linear flow rate 540 to 2000 cm sec^{-1} and the Reynolds number 2000 to 25,000. Deposition was investigated on copper, silver, mild steel and stainless steel at a surface temperature of 260°C within the isothermal test section. The duration of the adsorption and desorption experiments were 2 and 15 hours, respectively. Iodine surface concentrations of 0.8 $\mu g\ cm^{-2}$ for type 1015 mild steel and 0.04 $\mu g\ cm^{-2}$ for type 316 stainless steel was found within a deposition time of 2 hours and at a surface temperature of 260°C. It has not been proved whether the surface concentration was constant in the adsorption test after 2 hours. Neill et al. designed an

experiment to investigate the rate and extent of iodine deposition. They showed by measuring the iodine activity deposited on silver wires mounted in the flowing helium in a steel pipe that for low levels of surface concentration and negligible desorption the heat-mass-transfer analogy can be applied. Another interesting result of these experiments is that the deposition velocity of iodine on steel at high linear flow rates is relatively low. The iodine concentration in the gas phase remained practically constant over 320 cm from the iodine source. In this experiment a stainless steel pipe has been used. The linear flow rate was 2070 cm sec^{-1}, the Reynolds number 25,000, the temperature 260°C and the iodine partial pressure $\sim 10^{-13}$ atm. Only ~1% of the injected iodine was deposited within the test section. The deposition velocity is defined as the ratio of surface concentration and gas phase concentration multiplied by the injection time. The deposition velocity of iodine was found to decrease with increasing surface coverage, even at very low iodine surface concentrations. The deposition velocity increased with increasing surface roughness. A sudden enlargement in the flow passage caused an increase in the amount of iodine deposited after the enlargement.

Raines, Abriss, Morrison and Ewing[23] studied the deposition of trace amounts of fission products on stainless steel in the isothermal and non-isothermal zone (340 to 630°C) within the loop at Battelle Memorial Institute during runs of 55 hours. Helium at 20 atm was passed over a mildly irradiated fuel specimen and recirculated in a loop consisting of an isothermal high temperature zone (660°C), a heat exchanger, a low temperature isothermal zone (350°C) and a centrifugal blower. The helium passed the whole circuit about five times per sec. The Reynolds number was 5200 to 7300 within the different parts of the circuit. The amounts of the fission products deposited were determined by a least

squares computer analysis procedure developed to analyze the gamma spectra obtained on small sections of the loop.

In isothermal zones gross activity decreased roughly exponentially. There was an abrupt and significant increase in deposition at bends, thermocouples or other places where the hydrodynamic flow pattern was perturbed. Behavior of the fission products in the group, comprised of ^{141}Ce, ^{140}Ba-La, ^{95}Zr-Nb, and ^{103}Ru, was quite comparable and was most affected by hydrodynamic disturbances but not by temperature. The surface concentrations decreased roughly continuously with increasing distance from the source. Iodine-131 had its own unique deposition behavior. Small quantities deposited in the high temperature isothermal region. The bulk of it deposited in the heat exchanger. In the low temperature isothermal zone, iodine deposition appeared to be almost independent of position in the loop. According to Raines et al. behavior of iodine proved to be most difficult to interpret and the least amenable to theoretical treatment of all of the fission product deposited. There was a sharp peak in deposited ^{131}I in the low temperature isothermal section. Raines et al. considered a cold spot as reason of this peak. No corresponding increase in the deposition of a metallic fission product was apparent, at this point, suggesting that deposition was of elemental iodine.

Milstead[30] performed at Gulf General Atomic a long-term mixed fission product experiment to investigate the deposition of cesium, strontium, and iodine on low chromium alloy over a temperature range of approximately 300 to 500°C. The system was designed as a closed loop, whereby cesium, strontium and iodine were simultaneously carried by three separate helium streams to a tube where the gas streams were allowed to mix and pass through the tube. The partial pressures of strontium, cesium and iodine were $\sim 10^{-9}$ atm. The duration of the experiment was 3000 hours.

Examination of the plateout profiles of each of the three elements shows:

1. Cesium deposition was uniformly low ($<10^{-3}$ μg Cs cm^{-2} along the specimen tube in the range 483 to 312°C. Only 38% of the cesium was found in this area. The remainder passed through the system and condensed in cooler areas. No cesium was detected downstream of the rear connection to the specimen.

2. The deposition of strontium was initially high in the front section of the specimen tube, decreasing uniformly over the next eight inches, and finally reaching an approximate constant level at temperatures below about 430°C. No distinct effect of temperature on the deposition is discernible. Twenty-one percent of the strontium was found in the cooler regions below ~300°C.

3. Like strontium, iodine deposition occurred on the first metal surfaces contacted at temperatures above 450°C, decreased slightly until the metal temperature dropped below 300°C, and finally occurred in heavy amounts in the cooler region of the system. In this region the iodine surface concentration was higher by a factor of 1000 than on the first metal surface contacted. Seventy-seven percent of the iodine entering the system was found in the temperature range 100 to 200°C. Only 0.7% was found at temperatures above 312°C. Essentially no iodine was found downstream of the specimen tube. This deposition profile indicates that all of the iodine reacted with the metal surface to form FeI_2, which was subsequently evaporated from the surface and transported downstream to condense in an area where the partial pressure of FeI_2 was extremely low ($P_{FeI_2} = 7 \times 10^{-12}$ atm at 200°C).

The results showed that the deposition of cesium and strontium on low chromium alloy is relatively independent of

the temperature of the metal, with the heaviest strontium deposition occurring on the first surface contacted. There is no way to verify whether these two species were transported as iodides, but examination of the first three inches of the specimen tube showed a deficiency in the amount of iodine necessary for SrI_2 to be the deposited species. In all other areas there is a sufficient amount of iodine deposited to combine with the cesium and strontium.

The observed iodine deposition was 1.1 $\mu g/cm^2$ at 400°C.

5.2 Summary and Discussion of the Loop Experiments

The surface concentrations of the less volatile metallic fission products decrease roughly continuously with increasing distance from the source and are quite independent of the temperature. The deposition pattern of iodine, however, is mainly determined by the temperature distribution within the loop. Most of the iodine is deposited in a rather narrow temperature zone. It may be concluded from the different deposition patterns of metallic fission products on one hand and iodine on the other hand that iodine is released from the irradiated fuel into the helium mainly in elemental form and not as fission product iodide. But certainly there could be some MeI_x.

The deposition pattern of all fission products depends on hydrodynamic disturbances. There is an increase in deposition at bends, thermocouples or other places where the hydrodynamic flow pattern is perturbed. There is an increase in iodine deposition on cold spots.

No attempt has been made to find out whether gaseous metal iodides have been formed by reaction between iodine and the pipe material within the loop. The formation of gaseous iron iodides has been demonstrated in laboratory-scale experiments only. But it is very likely, that in loops gaseous

metal iodides were formed by reaction between pipe material and iodine. These metal iodides were then transported to regions of lower temperature where they deposit in a rather narrow zone, but some iodine sticks at high temperature.

The shape of the iodine distribution in a deposition zone and the temperature where the maximum of the surface concentration appears should depend on the iodine concentration in the gas and the molecular species and further on the linear flow rate and the duration of a run. The influence of the duration of a run on the deposition pattern has not been investigated.

It follows from experiments of Neill et al.[22] that only about 1% of the iodine contained in a helium stream of high linear flow rate and high Reynolds number is deposited within 0.15 sec on stainless steel at 260°C. In gas-cooled reactor circuits a volume element needs about 6 sec for one pass. Assuming in the reactor circuit the same deposition velocity as in the loop experiment mentioned above, about 40% of the iodine will be removed from the gas phase in one pass. Taking into account the much higher temperatures in the coolant circuit, it seems to be reasonable to conclude that the iodine concentration will be nearly constant within the whole circuit in the gas phase.

6. SUMMARY

The adsorption behavior of iodine adsorbed on oxidized metals in experiments on laboratory as well as on technical scale can be explained assuming chemisorption of iodine and formation of gaseous iron iodides.

Mainly iodine atoms will be present in coolant circuits of gas-cooled reactors. The iodine will react with the heat exchanger and pipe material to form gaseous metal iodides,

presumably mainly FeI_2 but the partial pressure of atomic iodine will be at least ten times greater than the partial pressure of FeI_2. The accumulation of solid FeI_2 as a pure phase within the circuit seems to be possible at temperatures <250°C. Rather large amounts of iodine activity could be accumulated in certain low temperature zones of the coolant circuit. Iodine will be chemisorbed at higher temperatures.

Adsorbed iodine or iodine present in the form of $FeI_2(s)$ will presumably become gasborne if exposed to a mixture of steam and air at temperatures >160°C. Whether the iodine will become gasborne if exposed to steam alone cannot be predicted.

A Van Arkel-type process seems to be possible resulting in the transport of metals into the core in the form of metal iodides.

APPENDIX A

THE DEGREE OF DISSOCIATION OF IODINE CONTAINED IN HELIUM

The degree of dissociation α is defined as the fraction of molecules which are dissociated at equilibrium with respect to the number of molecules present assuming there was no dissociation. If there are n'_{I_2} moles of I_2 at the beginning and n_{I_2} moles of molecular iodine after dissociation equilibrium has been established according to

$$I_2 \rightleftharpoons 2I \tag{A1}$$

the degree of dissociation is given by

$$\alpha = \left(n'_{I_2} - n_{I_2}\right) / n'_{I_2} = 1 - \left(n_{I_2} / n'_{I_2}\right) \quad . \tag{A2}$$

α may also be defined in terms of n_I the number of iodine atoms at equilibrium relative to the number of iodine atoms formed by 100% dissociation.

$$\alpha = n_I / 2n'_{I_2} \quad . \tag{A3}$$

For a reaction

$$n_A A + n_B B \rightleftharpoons n_C C + n_D D \tag{A4}$$

the equilibrium constant K_p is given by

$$K_p = P_C^{n_C} P_D^{n_D} / P_A^{n_A} P_B^{n_B} \quad . \tag{A5}$$

To express the equilibrium constant in terms of the mole fractions the following relations are used. The mole fraction X_i is given by

$$X_i = n_i / \Sigma n_i \tag{A6}$$

and the total pressure P by the sum of the partial pressures

$$P = \Sigma P_i \quad . \tag{A7}$$

Since

$$P_i = X_i P \tag{A8}$$

K_X is given by $K_X = K_p/P^{\Delta n_i}$. (A9)

For reaction (A1) the number of moles of various species present in a mixture of helium and iodine are given by

Table A-1. Species Present in the System Helium-Iodine

Without Dissociation	At Equilibrium
n'_{I_2} mole I_2	$n'_{I_2} - (n_I/2)$ mole I_2
0 mole I	n_I mole I
n_{He} mole He	n_{He} mole He

The mole fractions at equilibrium are:

$$X_{I_2} = \left[n'_{I_2} - \left(n_I/2\right)\right] / \left[\left(n'_{I_2} + n_{He} + \left(n_I/2\right)\right]\right. \tag{A10}$$

$$X_I = n_I / \left[n'_{I_2} + n_{He} + \left(n_I/2\right)\right] \tag{A11}$$

From Eq. (A9):

$$K_X = n_I^2 / \left[n'_{I_2} + n_{He} + \left(n_I/2\right)\right]\left[n'_{I_2} - \left(n_I/2\right)\right] = K_p/P \tag{A12}$$

It follows from (A12) substituting π for K_p/P that

$$n_I^2 + \frac{\pi n_{He} n_I}{2[(\pi/4) + 1]} - \frac{\pi n'_{I_2} (n'_{I_2} + n_{He})}{[(\pi/4) + 1]} = 0 \qquad \text{(A13)}$$

Solving of (A13) yields:

$$n_I = - \frac{n_{He} K_p}{(K_p + 4P)} + \left[\frac{K_p^2 (2n'_{I_2} + n_{He})^2 + 16\, K_p P (n'^2_{I_2} + n'_{I_2} n_{He})}{(K_p + 4P)^2}\right]^{\frac{1}{2}} \qquad \text{(A14)}$$

Equation (A14) provides the correct limiting value for α for a pure iodine system, because with $n_{He} = 0$

$$n_I = 2n'_{I_2} \left[\frac{K_p^2 + 4K_p P}{(K_p + 4P)^2}\right]^{\frac{1}{2}} \qquad \text{(A15)}$$

which is equal to

$$n_I = \left[\frac{K_p}{(K_p + 4P)}\right]^{\frac{1}{2}} \qquad \text{(A16)}$$

because

$$\alpha = \frac{n_I}{2n'_{I_2}} \quad \text{and} \quad \frac{K_p^2 + 4K_p P}{(K_p + 4P)^2} = \frac{K_p}{K_p + 4P} \quad . \qquad \text{(A17)}$$

Equation (A14) can now be used to calculate the degree of dissociation of n'_{I_2} moles of iodine in a certain volume of helium of a partial pressure P_{He}(atm) at temperature T using the known values of K_p. The equilibrium constant K_p has been taken from the JANAF Thermochemical Tables. The number of moles of helium, n_{He}, present per liter at a given temperature and pressure could be calculated using the ideal gas law. The deviations from this law in the pressure and temperature

range of interest in connection with gas-cooled reactors could be neglected. However, the Van der Waals equation has been used to calculate the number of moles He n_{He} to account to some degree for the deviations from the ideal gas law at higher pressures. Thus, the computer code mentioned later is more generally applicable than would be desired for the present purpose.

$$p_{He}V = n_{He}\ (RT + B_{He}p_{He}) \tag{A18}$$

where

$$B_{He} = X - Y/RT \quad . \tag{A19}$$

The values of the constants X and Y have been taken from Kortüm.[31]

$$X = 0.02370\ (\ell\ \text{mole}^{-1})$$

$$Y = 0.03412\ (\ell^2\ \text{atm mole}^{-2})\ .$$

For V = 1 liter, it follows:

$$n_{He} = p_{He}\left[0.08206T + p_{He}\left(0.02370 - \frac{0.41579}{T}\right)\right]^{-1} \tag{A20}$$

The total pressure at equilibrium P is given by

$$P = p_{He} + P_I + P_{I_2} \tag{A21}$$

The partial pressures P_I and P_{I_2} can be calculated only when n_I and n_{I_2} are both known. For this reason n_I must be calculated from Eq. (A14) by an iterative process. A convenient starting point is $P = p_{He}$. A computer program has been written to perform this iteration. Input data are the equilibrium constant K_p, the iodine concentration, the helium pressure and the temperature. Output data are the degree of dissociation, the partial pressures, the total pressure and the logarithm of the sum of the iodine partial pressures $\log\ [P_I + P_{I_2}]$.

APPENDIX B

THERMODYNAMIC DATA FOR THE SYSTEM IRON-IODINE AND THE EXTRAPOLATION OF MEASURED EQUILIBRIUM CONSTANTS TO LOWER TEMPERATURES

B.1 The Thermodynamic Data

All the data given have been taken from JANAF Thermo-Chemical Tables (1966).

B.1.1 FeI_2 (Crystal)

Heat of formation: $\Delta H^\circ_{f298.15} = -25 \pm 4$ kcal/mol

Entropy: $S^\circ_{298.15} = 40 \pm 2$ Gibbs/mol

Melting point: $T_m = 860 \pm 2°K$

The heat of sublimation of FeI_2 to monomer was calculated as the difference between $\Delta H^\circ_{f298.15}$ for $FeI_2(g)$ and $FeI_2(c)$. The heat of sublimation of FeI_2 to dimer was calculated as the difference between those for $Fe_2I_4(g)$ and $2FeI_2(c)$.

Heat of Sublimation:

To monomer $\Delta H^\circ_{S298.15} = 46$ kcal/mol

To dimer $\Delta H^\circ_{S298.15} = 52$ kcal/mol

The vapor pressure of FeI_2 has been measured by Schäfer and Hönes[2] using the transpiration method and by Sime and Gregory[3] using the torsion effusion method. The results of both methods are in excellent agreement and are represented[4] in the temperature range 150-587°C by:

$$\log p_{atm} = 16.742 - 9435/T - 2.969 \log T \quad .$$

B.1.2 FeI_2, Ideal Gas

Heat of formation: $\Delta H^\circ_{f298.15} = 21.0 \pm 3$ kcal/mol

Entropy: $S^\circ_{298.15} = 83.5$ Gibbs/mol

B.1.3 Fe_2I_4, Ideal Gas

Heat of formation: $\Delta H^\circ_{f298.15} = 20.0 \pm 5$ kcal/mol

Entropy: $S^\circ_{298.15} = 129.9$ Gibbs/mol

B.2 The Extrapolation of Measured Equilibrium Constants to Lower Temperatures

The temperature dependence of the equilibrium constant of the reaction $FeI_2(s) \rightleftharpoons Fe(s) + I_2(g)$ (B.1) has been represented between 500 and 587°C according to Zaugg and Gregory[4,5] by:

$$\log K = 5.2624 - 8192/T \ . \qquad (B.2)$$

An equation for the temperature dependence of K for reaction (B.1) approximately valid in the temperature range 200-587°C has been derived using the relationship:

$$\log K = -\frac{\Delta H_o}{4.574\ T} + \frac{\Delta C_p}{1.9865} \log T + i \qquad (B.3)$$

where ΔH_o and i are arbitrary constants. ΔC_p is the difference of the specific heats of the products and reactants and has been taken as 5.5 [cal/mol deg]. The determination of ΔH_o and i with $\Delta C_p = 5.5$ using Eq. (B.2) yields:

$$\log K = 14.525 - 9171/T - 2.769 \log T \ . \qquad (B.4)$$

The equilibrium constants for the following reactions have been determined by Zaugg and Gregory[4,5] and Schäfer and Hönes.[2] The equilibrium constant for the reaction

$$Fe(s) + 2I(g) \rightleftharpoons FeI_2(g) \qquad (B.5)$$

is given in the temperature range 587-791°C by:

$$\log K = -3.550 + 7540/T \ . \qquad (B.6)$$

Values of C_p have been taken from JANAF Thermochemical Tables and can be represented by

$$\Delta C_p = 1.604 + 7.1 \times 10^{-3} T \ .$$

The determination of ΔH_o and i in Eq. (B.3), using Eq. (B.6)

yields:

$$\log K = -4.806 + 7155.4/T + 0.8075 \log T - 7.776 \times 10^{-4}T \tag{B.7}$$

This formula is valid in the temperature range 150-800°C. The equilibrium constant of the reaction

$$2Fe(s) + 4I(g) \rightleftharpoons Fe_2I_4(g) \tag{B.8}$$

in the temperature range 587-791°C is given by:

$$\log K = -8.751 + 19,213/T \quad . \tag{B.9}$$

Values of C_p have been taken from JANAF Thermochemical Tables. ΔC_p can be represented by

$$\Delta C_p = 5.06 - 1.42 \times 10^{-2}T \ .$$

The determination of the arbitrary constants in Eq. (2) gives:

$$\log K = 18,833/T + 2.547 \log T - 1.552 \times 10^{-3}T - 14.452 \tag{B.10}$$

The equilibrium constant of the reaction

$$Fe(s) + 3I(g) \rightleftharpoons FeI_3(g) \tag{B.11}$$

is given by

$$\log K = -6.811 + 13,024/T \tag{B.12}$$

The equilibrium constant of the reaction

$$I_2(g) + 2FeI_2(s) \rightleftharpoons Fe_2I_6(g) \tag{B.13}$$

is given by

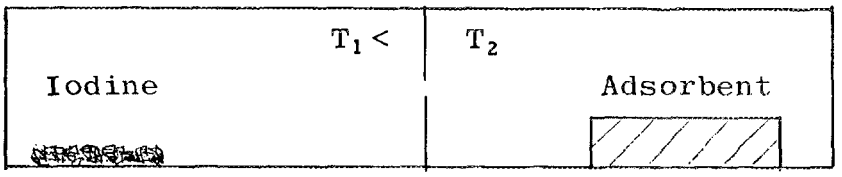
$$\log K = 9.017 - 9820/T \tag{B.14}$$

both in the temperature range 500-650°C. Values of the specific heat C_p of FeI_3 and Fe_2I_6 are not published.

APPENDIX C

THE NON-ISOTHERMAL STATIC METHOD FOR THE MEASUREMENT OF IODINE ADSORPTION ON METALS

The non-isothermal static method has been described in Chapter 4.2 and has been used frequently by different investigators. Milstead, Bell and Norman's[8] experiment, which is typical of the non-isothermal static method (pseudo-isopiestic) has been represented as a box containing a partition whose function is to separate the two temperature zones. The gaseous species diffuse through an orifice.



Initially the low temperature zone contains only iodine, the high temperature zone only the adsorbent. As the experiment proceeds iodine diffuses into the high temperature zone where it is adsorbed on the specimen. In the experiments of Milstead et al. iron iodides were formed and diffused into the low temperature zone where they condensed.

In order to be able to compare iodine surface concentrations measured by different methods it is important to know the real partial pressures of iodine and of the metal iodides within the apparatus. Milstead, Bell and Norman[8] have derived a steady-state transport equation to calculate the vapor pressures of the iodine species above the specimen. Their treatment will now be discussed in more detail. First let us consider the simpler isothermal static experiment.

If n'_{I_2} moles of iodine are introduced into a closed vessel made from pure iron under conditions where $FeI_2(s)$ is not stable

at the given temperature and iodine partial pressure, the following reactions occur:

$$2I(g) \rightleftharpoons I_2(g) \tag{C.1.1}$$

$$Fe(s) + 2I(g) \rightleftharpoons FeI_2(g) \tag{C.2.1}$$

$$Fe(s) + 3I(g) \rightleftharpoons FeI_3(g) \tag{C.3.1}$$

$$2Fe(s) + 4I(g) \rightleftharpoons Fe_2I_4(g) \tag{C.4.1}$$

$$2Fe(s) + 6I(g) \rightleftharpoons Fe_2I_6(g) \tag{C.5.1}$$

The equilibrium constants are given by:

$$K_1 = P_{I_2}/P_I^2 \tag{C.1.2}$$

$$K_2 = P_{FeI_2}/P_I^2 \tag{C.2.2}$$

$$K_3 = P_{FeI_3}/P_I^3 \tag{C.3.2}$$

$$K_4 = P_{Fe_2I_4}/P_I^4 \tag{C.4.2}$$

Reaction (C.5.1) can be neglected because the partial pressure of Fe_2I_6 is very low in comparison to the other iodides. The mass-balance equation expressed in moles I_2 is then

$$n'_{I_2} = n_{I_2} + 0.5\ n_I + 2n_{Fe_2I_4} + 1.5\ n_{FeI_3} + n_{FeI_2} \tag{C.6}$$

Using Avogadro's hypothesis, Eq. (C.6) can be written:

$$P'_{I_2} = P_{I_2} + 0.5\ P_I + 2P_{Fe_2I_4} + 1.5\ P_{FeI_3} + P_{FeI_2} \tag{C.7}$$

Introducing Eqs. (C.1.2) to (C.4.2) into Eq. (C.7) enables us to express all quantities in terms of P_I.

$$(P'_{I_2})_o = (K_1P_1^2 + 0.5\ P_I + K_4P_1^4 + 1.5\ K_3P_1^3 + K_2P_I^2) \text{ at equilibrium .} \tag{C.8}$$

Equation (C.8) relates the partial pressure of atomic iodine, P_I, at equilibrium to the partial pressure of molecular

iodine $(P'_{I_2})_o$ before the iodine reacts with the iron. After solving Eq. (C.8) the partial pressures of the other iodine species can be calculated using Eqs. (C.1.2) to (C.4.2). Equation (C.8) is valid for a closed system in which n'_{I_2} moles iodine have been introduced corresponding to an initial partial pressure P'_{I_2} of iodine, if equilibrium has been established and if there is no solid FeI_2 present in the system.

If thermodynamic equilibrium has not been established the partial pressure of atomic iodine would be found to be too low, if calculated according to Eq. (8). Correspondingly, the partial pressures of iron iodides would be found to be too high in comparison with the actual partial pressures in the system. If we consider the limiting case that there is no reaction at all, for instance, because the iron surface is covered with a protective layer, the partial pressures of the iron iodides are zero and the partial pressure of atomic iodine in the system is given by

$$P'_{I_2} = K_1 P_I^2 + 0.5\ P_I \quad . \tag{C.9}$$

Nevertheless, if Eq. (C.8) is applied to a system in which there is no reaction, equilibrium partial pressures will be calculated which don't correspond to the actual pressures within the system.

Equation (C.8) is valid for dynamic transpiration systems using a carrier gas stream if there is no solid FeI_2 present and if the flow rate is fast enough to eliminate gas phase diffusion effects and slow enough to allow establishment of the equilibrium partial pressures in the gas phase. For this reason the lack of dependence of all gas phase concentrations on the linear flow rate must be confirmed before Eq. (C.8) can be applied – as is well known.

The main difference between the isothermal and pseudo-isopiestic systems are:

1. The number of moles of iodine (I_2 + I) entering the high temperature zone where the specimen is placed must be calculated.
2. The gaseous reaction products leave the reaction chamber. Therefore, it is not possible to check whether thermodynamic equilibrium has been reached which can be done for both isothermal systems. The number of moles of the reaction products leaving the reaction chamber must therefore be calculated.

The pseudo-isopiestic method is applicable and equivalent to isothermal methods if the vapors are uncondensable. Point (2) needs to be discussed in more detail. The gaseous reaction products leave the reaction chamber by diffusion at a rate inversely proportional to the square root of their molecular weights. For this reason one could conclude that the ratios (P_I/P_{FeI_2}; P_I/P_{FeI_3} . . .) at steady state are different in the non-isothermal static system and in an isothermal static system at the same iodine partial pressure and temperature. This conclusion is obviously wrong because the ratios mentioned above are fixed for a given P_I and a given temperature by Eqs. (C.1.2) to (C.4.2). If, for instance, due to the mass dependence of the rate of diffusion $P_{Fe_2I_4}$ increases above the value fixed by the equilibrium constant, Fe_2I_4 will decompose and FeI_2 will be formed until the equilibrium partial pressures corresponding to the given P_I are established again.

In order to calculate the number of molecules entering and leaving the reaction chamber, Milstead et al.[1] assumed that the low temperature zones were separated by an orifice and introduced first the Knudsen equation into Eq. (C.6) and then Eqs. (C.1.2) to (C.4.2). The Knudsen equation allows us to calculate the number n(t) of moles of a gas at pressure P and the temperature T escaping from a vessel after time t through an orifice:

$$n(t) = KFP\ t/(MT)^{1/2} \quad \text{or} \tag{C.10}$$

$$P = n(t)(MT)^{1/2}/KFt \quad .$$

M is the molecular weight of the gas molecules, F (cm^2) the area of the orifice and $K = (2\pi R)^{-1/2}$.

The treatment of Milstead et al. implies three assumptions:

1. Thermodynamic equilibrium is established within the high temperature compartment of the apparatus.
2. There is no solid FeI_2 present.
3. The Knudsen-equation is valid for the given system.

At first, assumption (1) will be discussed assuming assumptions (2) and (3) are valid. Let us first consider again the limiting case where the specimen is covered with a protective layer. No reaction between iron and iodine occurs. In this case the partial pressures of the iron iodides are zero and the partial pressures P_{I_2} and P_I in the high temperature (T_2) region of the apparatus are related to the vapor pressure of the iodine source P'_{I_2} at the temperature T_1 according to Eqs. (C.6) and (C.10):

$$\frac{P'_{I_2}}{(M_{I_2}\ T_1)^{1/2}} = \frac{P_{I_2}}{(M_{I_2}\ T_2)^{1/2}} + \frac{P_I}{2(M_1\ T_2)^{1/2}}$$

$$\left[\frac{T_2}{T_1}\right]^{\frac{1}{2}} P'_{I_2} = P_{I_2} + (2)^{-1/2}\ P_I \quad . \tag{C.11}$$

There is no net flow of iodine between the two compartments and there is no atomic iodine in the low temperature zone. Obviously, Eq. (C.11) also holds if the reaction rate is low compared with the transport of iodine into the reaction chamber. Let us assume the system is at equilibrium (no net flow of iodine). The partial pressure of the iodine in the

reaction chamber decreases if some iodine is adsorbed on the oxide surface. Iodine from the iodine source will now diffuse into the reaction chamber until the initial partial pressure is established. Now there is again no net flow of iodine between the compartment with the iodine source and the compartment at high temperature. The adsorbed iodine diffuses on the surface or through the oxide layer or through cracks in this layer until it is able to react with the metal. The reaction product is now adsorbed and desorbs with a certain rate. The partial pressure of iodine in the gas phase remains constant during all these diffusion, reaction and desorption processes involving the formation of gaseous iodides and does not decrease according to the amount of iodine transformed into iron iodides as is required by Eq. (C.6). Only the amount of iodine present in the iodine source decreases.

The partial pressure of the iron iodides corresponds only to the partial pressure of iodine according to the steady-state transport equation derived by Milstead et al. using the mass-balance equation, the Knudsen equation and Eqs. (C.1.2) to (C.4.2), if the n'_{I_2} moles iodine entering the specimen range of the apparatus during the time t react without delay with the specimen forming gaseous iodides instantaneously. This statement will be discussed in more detail using the steady-state transport equation derived by Milstead et al.

Introducing the Knudsen-equation (C.10) into the mass-balance Eq. (C.6) gives:

$$\frac{P'_{I_2} t}{(M_{I_2} T_1)^{1/2}} - \left[\frac{P_{I_2} t}{(M_{I_2} T_2)^{1/2}} + \frac{P_I t}{2(M_I T_2)^{1/2}}\right] =$$

$$2\frac{P_{Fe_2I_4} t}{(M_{Fe_2I_4} T_2)^{1/2}} + 3/2 \frac{P_{FeI_3} t}{(M_{FeI_3} T_2)^{1/2}} + \frac{P_{FeI_2} t}{(M_{FeI_2} T_2)^{1/2}} \quad . \tag{C.12}$$

The left-hand side of Eq. (C.12) corresponds to the net transport of iodine per cm^2 of the aperture in time t,

$$n'_{I_2}(t) - \left[n_{I_2}(t) + 0.5\ n_I(t)\right] ,$$

into the hot zone (the constant K in Eq. (C.10) has been neglected).

Instantaneous reaction of the iodine entering the hot zone with the iron yields the vapor pressures $p_{Fe_2I_4}$, p_{FeI_3}, p_{FeI_2} and corresponding to Eq. (C.10) fluxes of these iron iodides from the hot zone to the lower temperature zone of the apparatus. The sum of these fluxes is equal to the net flux of iodine from the iodine source to the specimen at steady state.

$$n'_{I_2}(t) - \left[n_{I_2}(t) + 0.5\ n_I(t)\right] =$$

$$2n_{Fe_2I_4}(t) + 1.5\ n_{FeI_3}(t) + n_{FeI_2}(t) . \qquad (C.13)$$

Let us now examine the case where iodine and iron react slowly rather than instantaneously. To do this it is convenient to multiply the right-hand side of Eqs. (C12) and (C13) by a factor γ where $0 \leqslant \gamma \leqslant 1$.

$$n'_{I_2}(t) - \left[n_{I_2}(t) + 0.5\ n_I(t)\right] =$$

$$\gamma\left[2n_{Fe_2I_4}(t) + 1.5\ n_{FeI_3}(t) + n_{FeI_2}(t)\right] \qquad (C.14)$$

If the left-hand side of Eq. (C.12) is designated by F and the right-hand side by E, Eq. (C.12) becomes

$$F = \gamma E \quad . \qquad (C.15)$$

The value of γ depends mainly on the kind of the surface of the metal specimen and the temperature but also on the

vapor pressure of the iodine source and the shape of the apparatus. γ may approach unity at high temperature if the specimen is not protected, for example, by an oxide layer. Introducing Eqs. (C.1.2) to (C.4.2) in Eq. (C.15) gives:

$$\gamma 2P_I^4K_4 \ (2M_{I_2}/M_{Fe_2I_4})^{\frac{1}{2}} + \gamma 3P_I^3K_3 \ (M_{I_2}/2M_{FeI_3})^{\frac{1}{2}} +$$

$$2^{\frac{1}{2}} \ P_I^2 \left[K_1 + \gamma K_2 \ (M_{I_2}/M_{FeI_2})^{\frac{1}{2}}\right] + P_I - P'_{I_2}(2T_2/T_1)^{\frac{1}{2}} = 0 \ . \tag{C.16}$$

Equation (C.16) is identical to Milstead and co-worker's steady-state transport equation for $\gamma = 1$.

In order to compare the partial pressures calculated using different approaches, P_I and P_{I_2} have been calculated for an iodine source temperature $T_1 = -21°C$, an iodine source vapor pressure of 4×10^{-6} atm and a temperature within the reaction chamber of $T_2 = 400°C$. At first, P_I and P_{I_2} have been calculated assuming thermal transpiration and a very low reaction rate ($\gamma = 0$). Secondly, P_I and P_{I_2} have been calculated neglecting thermal transpiration and assuming constant pressure within the whole system according to:

$$P_I = P'_{I_2} \ 2\alpha/(1 + \alpha) \text{ and}$$

$$P_{I_2} = P'_{I_2} \ (1 - \alpha)/(1 + \alpha) \tag{C.17}$$

with $\alpha = 0.15$ at 400°C and $P'_{I_2} = 4 \times 10^{-6}$ atm. The results are given in Table C.1. The temperature in the hot zone is 400°C. The iodine source pressure is 4×10^{-6} atm and the source temperature -21°C.

The values of P_I calculated on the one hand assuming a very low chemical reaction rate and thermal transpiration and on the other neglecting thermal transpiration and assuming constant pressure within the whole apparatus are

Table C.1. Comparison of Atomic Iodine Partial Pressures Within the Reaction Chamber of a Non-Isothermal Static System Calculated According to Different Assumptions

	Thermal Transpiration		Constant Pressure Within the Whole Apparatus
	Milstead et al. $\gamma = 1$	$\gamma = 0$	
P_I (atm)	3.4×10^{-7}	1.6×10^{-6}	1.1×10^{-6}
P_{I_2} (atm)	2.9×10^{-7}	6.2×10^{-6}	2.9×10^{-6}
P'_{I_2} (atm)	4×10^{-6}	4×10^{-6}	4×10^{-6}

nearly equal. The equilibrium partial pressure P_I calculated assuming instantaneous chemical reaction and thermal transpiration ($\gamma = 1$) is approximately a factor of 3 lower than P_I calculated assuming no chemical reaction ($\gamma = 0$) and thermal transpiration. (The same figure in the case of P_{I_2} is about 10). The latter case is supposed to be equivalent to a process where the reaction rate is very low compared to the rate of the transport of iodine into the reaction chamber. The difference of the calculated P_I values may be important if P_I calculated according to Milstead and co-workers' steady-state transport equation is just below the decomposition pressure above solid FeI_2 whereas P_I calculated with $\gamma = 0$ gives a vapor pressure higher than the decomposition pressure of solid FeI_2. In the first case one has to conclude that there is no FeI_2 as a pure solid phase in the reaction chamber whereas there is solid FeI_2 in the second case. This makes a considerable difference to the interpretation of iodine surface concentrations in adsorption measurements.

Up to now it has always been assumed that there is no solid FeI_2 present in the system. If there is FeI_2 (solid) the reactions

$$Fe(s) + 2I(g) \rightleftharpoons FeI_2(g) \tag{C.18}$$

$$FeI_2(s) \rightleftharpoons FeI_2(g) \tag{C.19}$$

must be considered. Both, the partial pressures of iodine and of FeI_2 are fixed by Eqs. (C.18) and (C.19).

Use of Eq. (2a) in the steady-state transport equation now gives an erroneous result. One must therefore check whether there is solid FeI_2 in the reaction chamber before one starts the calculation of partial pressures.

The discussion of the non-isothermal static method up to this point has shown that the calculated equilibrium iodine pressures in the reaction chamber (and the relationship of the measured iodine-surface concentration to the iodine pressure) is quite sensitive to the rate of reaction and to the presence of solid FeI_2.

Finally assumption (3) of Milstead et al. will be discussed. Let us assume first that iodine neither reacts with the specimen nor dissociates. Introducing the Knudsen Eq. (10) into Eq. (6) gives

$$P'_{I_2}/P_{I_2} = (T_1/T_2)^{1/2}$$

P'_{I_2} and P_{I_2} are the iodine pressures at the temperature T_1 of the iodine source and at the temperature T_2 in the reaction chamber, respectively. In general, $R = P_1/P_2$ is known as thermal transpiration ratio and

$$R = P_1/P_2 = (T_1/T_2)^{1/2} \qquad \text{if } \lambda \gg d \quad . \tag{C.20}$$

P_1 and P_2 are the pressures in the two portions of an apparatus at temperature T_1 and T_2, λ is the mean free path of the molecules and d is the diameter of the apparatus in the region of the temperature gradient. Equation (C.20) is widely implied in textbooks as giving the limiting thermal transpiration ratio for all geometries. A careful investigation to

check the general applicability of Eq. (C.20) has been carried out only recently. Edmonds and Hobsen[25] have shown by measuring the thermal transpiration ratio R in helium and neon, that this equation is only valid for two compartments joined by an aperture of a diameter which is small compared with the diameter of the compartments. For long tubes and two bulbs connected by tubing the following equation is valid:

$$R = P_1/P_2 = A(T_1/T_2)^{1/2} \quad \text{if } \lambda >> d \tag{C.21}$$

where A is a constant greater than 1 if $T_1 < T_2$. In the case of helium and neon the constant A has been determined as 1.1 to 1.3. The equation for thermal transpiration has been derived from the kinetic theory of gases[26] assuming no net gas flow across the aperture and using the following assumptions:

1. A molecule accommodating to a surface simply disappears from the gas phase upon impact.
2. A reflected molecule suffers an elastic collision with the surface.
3. The desorbing molecules leave a surface with a velocity corresponding to the temperature of the surface.
4. The desorbing molecules leave a surface with a cosine distribution in angle.

Both Eqs. (C.20) and (C.21) are only valid for thermal transpiration in a single ideal gas. They are not proven for mixtures of gases which are condensable or chemical unstable under the conditions of the experiment. In agreement with the theoretical assumptions Edmonds and Hobsen[25] found experimentally that in the case for neon and helium, where physical adsorption of the gas within the apparatus is negligible, Eqs. (C.20) and (C.21) are valid only if the mean free path λ and the diameter of the aperture between the two compartments is $(\lambda/d) > 15$ and if the temperature gradient at

the aperture connecting the two compartments is sharp. Under the experimental conditions of the non-isothermal static method are some of the assumptions made during the derivation of Eq. (C.20) and (C.21) not applicable. First of all, the mean free path of the molecules is in the same order of magnitude as the diameter of the apparatus, as will be shown below.

According to Dushman and Lafferty[27] λ is given by

$$\lambda = [(2)^{\frac{1}{2}}\ n\pi r_o^2]^{-1}\ \text{(cm)} \qquad \text{(C.22)}$$

where n is the number of molecules/cm^3 and r_o the separation distance at which the Lennard-Jones potential between gas molecules becomes zero. This distance is considered as collision diameter for low energy collisions. According to Braune and Linke,[28] in the case of I_2-molecules r_o is 4.892 Å.

Expressing Eq. (C.22) in terms of the pressure P gives

$$\lambda = 7.3\ T/10^{20}\ P\ r_o^2\ \text{(cm)} \qquad \text{(C.23)}$$

where T is in °K, r_o in cm and P in torr. The experiments using the non-isothermal static method have been carried out at iodine pressures in the range of $P'_{I_2} = 10^{-6}$ atm at -20°C in the region of the iodine source. Equation (C.23) gives $\lambda = 3$ cm under these conditions. Neglecting dissociation of the I_2 molecules and assuming the same partial pressure of I_2 molecules in the region at 400°C gives $\lambda = 8.5$ cm. The diameter of the apparatus is about 3 cm and therefore $(\lambda/d) < 3$. Furthermore, there is adsorption of iodine and FeI_2 in nearly all parts of the apparatus on four different materials (iodine, glass, FeI_2 and an oxidized metal surface). In spite of the assumption mentioned above elastic collisions of I_2 molecules with an oxidized metallic surface as well as with surfaces covered with iodine or FeI_2 seemed to be unlikely. Where theory requires a single steep temperature gradient there

are two ill-defined temperature gradients in the apparatus used in the non-isothermal static method.

It follows that there is no basis to apply the equation for thermal transpiration to the non-isothermal static method without a careful experimental determination of the real thermal transpiration ratio R under the given conditions. If one assumes the validity of Eq. (C.21) and if the value of A is 1.3 as determined by Edmonds and Hobsen[25] for a system of similar geometrical shape but with a sharp temperature gradient and if $\lambda >> d$ we have

$$\frac{1}{A}\left[\frac{T_2}{T_1}\right]^{\frac{1}{2}} P'_{I_2} = P_{I_2} + (2)^{-1/2} P_I \quad ,$$

which, in turn, leads to

$$P_I = 1.4 \times 10^{-6} \text{ atm}$$

$$P_{I_2} = 4.7 \times 10^{-6} \text{ atm}$$

for

$$P'_{I_2} = 4 \times 10^{-6} \text{ atm and at } T_2 = 400°C \text{ and } T_1 = -21°C.$$

Comparison with Table C.1 shows that these partial pressures are higher than the partial pressures calculated neglecting thermal transpiration and assuming constant pressure within the whole apparatus. But the differences are certainly within the experimental error of maintaining a constant iodine pressure within the apparatus. Because in the non-isothermal static system is $\lambda \cong d$ and because the thermal transpiration ratio R approaches unity as λ decreases in comparison to d, it is relevant to calculate the partial pressures P_I and P_{I_2} within the reaction chamber simply using Eq. (C.17). Presumption for this treatment is, however, that the reaction rate is low compared to the transport rate of iodine and that the iodine source pressure is $P'_{I_2} > 10^{-6}$ atm.

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