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Adsorption of Iodine on Aerosols

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Chemical Technology Division

ADSORPTION OF IODINE ON AEROSOLS

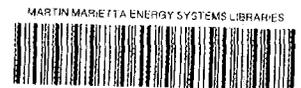
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Manuscript Completed: September 1990
Date Published: December 1990

Prepared for the
Electric Power Research Institute
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EPRI Project No. RP2802-16

Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6285
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400



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ABSTRACT

Molecular iodine adsorption on Cs_2O , Cs_2CO_3 , two-phase $\text{Cs}_2\text{CO}_3 \cdot 0.5\text{H}_2\text{O} + \text{Cs}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$, $\text{Cs}_2\text{CO}_3 + \text{saturated solution}$, and $\text{CsOH} + \text{saturated solution}$ was very rapid. The reaction was irreversible and formed iodide and iodate in a 5:1 ratio. There was no reaction of I_2 with CsNO_3 , HBO_2 , or MnO . Organic iodides CH_3I or $\text{C}_2\text{H}_5\text{I}$ reacted with Cs_2O , Cs_2CO_3 , or BaO to form inorganic iodide. The iodine potential, $RT \ln P_{\text{I}_2}$, or $P_{\text{CH}_3\text{I}}$, may be used to categorize oxide materials with regard to iodine adsorption by expressing the products of the I_2 reaction as iodide and iodate and the product of the CH_3I reaction as iodide.

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ADSORPTION OF IODINE ON AEROSOLS

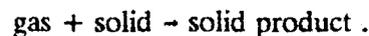
E. C. Beahm
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1 . INTRODUCTION

1.1 BACKGROUND

Iodine presents a unique challenge to the evaluation of fission product release in severe nuclear reactor accidents. It is the only fission product element that has a number of gaseous forms that are stable at conditions in containment, and it readily reacts to change its chemical and physical forms. Yet there is a need to anticipate iodine behavior in containment and release from containment so that the extent of the radioactive biohazard may be assessed. Iodine interactions will vary considerably, depending on the type of reactor system and the different accidents. The only meaningful way of dealing with this problem is to develop computer codes that track changes in the physical and chemical forms of iodine for a range of conditions. Models in such codes require data obtained from tests on relevant materials. In general terms, iodine in containment may chemically react in water, in gas, on stationary surfaces, or on aerosol particles. The reaction of iodine, in a gaseous form, with aerosols is the concern in this work.

The processes studied may be written as:



The rate expression for this general reaction is:

$$\frac{1}{A} \frac{dN_i}{dt} = V_d C_i \quad (1)$$

where

A = surface area,

N_i = mol of gas i reacted,

C_i = bulk concentration in gas,

t = time,

V_d = rate coefficient.

The rate coefficient has the units of distance divided by time and is often called a deposition velocity. Deposition expressed in terms of Eq. (1) does not require any specification of chemical form in the gas or in the solid product. However, care must be used in evaluating and using deposition velocities.

Because deposition velocities are based on specific experimental conditions with chemical interactions that are often unknown or unstated, their use should be restricted to the materials used in the measurements. In addition, deposition velocity measurements will give values that may result from a combination of rate resistance of gas phase mass transport, rate resistance of solid phase mass transport, and rate resistance of chemical reaction.¹ In tests where rate resistance of gas phase mass transport makes a significant contribution to the deposition velocity, the data will not be useful because it reflects only the specific test configuration and gas flow. This can create some difficulties when fast chemical reactions occur on the surface, resulting in a rate limitation due to gas phase mass transport. Once measurements have been made, the deposition velocities may be compared with expressions for gas phase mass transport to test their applicability.

For a flat plate surface, the deposition velocity limited by gas phase mass transfer may be written as:

$$V_d = \frac{0.664 D_{Ai}^{2/3} \sqrt{V}}{\sqrt{x}} \cdot \left(\frac{\rho_g}{\eta_g} \right)^{1/6} \quad (2)$$

where

D_{Ai} = diffusion coefficient for i in carrier gas, cm²/s;

V = bulk flow velocity of gas, cm/s;

ρ_g = density of gas, g/cm³;

η_g = viscosity of gas, g/cm·s;

x = distance from leading edge of sample, cm.¹

In general, in a system with specimens of some centimeters in length (x), gas phase mass transport will be significant as deposition velocities approach a value of ~0.1 cm/s.²

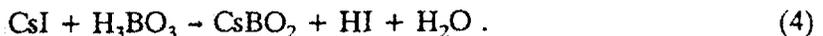
1.2 GASEOUS IODINE IN CONTAINMENT

Gaseous iodine may be in the form of I₂, organic iodide, and/or HI. There is no precise description of the chemical forms of iodine that emerge into containment from the

reactor coolant system (RCS) during severe accident sequences. Source term calculations presently specify the predominant chemical form of iodine and cesium to be CsI and CsOH, respectively, as they transport through the coolant system and enter containment. The relationship between cesium and iodine in the RCS can be illustrated by the reaction:



Reactions of cesium species that tend to lower the partial pressure of CsOH shift the equilibrium to the right, enhancing the formation of HI. Elrick et al.³ studied the instability of CsI interacting with stainless steel in a steam environment and proposed a cesium silicate, $\text{Cs}_2\text{Si}_4\text{O}_9$, as a reaction product. Bowsher and Nichols⁴ observed the formation of HI in the reaction of CsI and H_3BO_3 :



Hydrogen iodide will partially dissociate to produce some I_2 according to the reaction:



Organic iodides could form in the RCS from trace amounts of carbon in reactor fuel or from reaction with organic gas produced by the reaction of B_4C with steam.⁵ However, the conditions for forming both organic iodides and I_2 are more favorable in containment.^{5,6}

There are practical limits to the lowest and highest gaseous iodine concentrations in containment. Approximately 15 months after the accident at TMI-2, the concentration of ^{129}I in containment gas was $7.5 \pm 2.0 \times 10^{-11} \mu\text{Ci}/\text{cm}^3$.⁷ This corresponds to an ^{129}I concentration of $3.3 \times 10^{-12} \pm 8.9 \times 10^{-13}$ mols I/L. At that time, the containment gas was vented and purged, and the ^{129}I concentration was reduced by a factor of 20. However, the ^{129}I concentration returned to 90% of its original value in 15 d.

Methyl iodide is a "ubiquitous" halocarbon that is present at concentrations that vary somewhat with distance from the ocean.^{8,9} In a study of halocarbon concentrations at eight locations in the United States, Lillian et al.⁹ reported a maximum CH_3I concentration of 3.8 ppb ($\sim 10^{-10}$ mols $\text{CH}_3\text{I}/\text{L}$) and an overall mean value of 0.05 ppb ($\sim 2 \times 10^{-12}$ mols $\text{CH}_3\text{I}/\text{L}$). Thus, atmospheric iodine concentrations on the order of 10^{-12} mols I/L are the probable lower limits based on the evidence from TMI-2 and data on ubiquitous methyl iodide. Isotopic exchange between I_2 and CH_3I has been demonstrated by Behrens and Maddock.¹⁰

The upper limit of gaseous iodine will be restricted initially by the core inventory and the fractional release into containment. The mass of iodine in a water reactor core can be ~ 100 to 150 g/mol.¹¹ The total free volume of a PWR containment is on the order of 3.5×10^7 L, and BWR dry well volume is $\sim 4.5 \times 10^6$ L.¹¹ The maximum overall gaseous iodine concentration would be in the range of $\sim 5 \times 10^{-6}$ to $\sim 5 \times 10^{-5}$ gmol/L, or $\sim 10^{-5}$ gmol/L. Thus, in examining the interaction of iodine with aerosols, we are interested in gas concentration in the range of $\sim 10^{-12}$ mol I/L to $\sim 10^{-5}$ mol I/L. The experimental tests in this study were carried out at the upper end of the range. One reason for this is the difficulty in delivering predictable quantities of iodine at the lower concentrations and another difficulty is assaying product compounds to determine mechanisms of reaction. The experimental studies are supplemented by thermochemical calculations. In addition, caution should be exercised when interpreting information on iodine behavior at lower concentrations because anomalous behavior often occurs. Table 1 gives approximate ranges of concentration where difficulties in interpreting results of iodine studies may be encountered.

Table 1. Iodine behavior at different concentrations

Irreproducible behavior	Anomalous behavior	Predictable behavior
<ul style="list-style-type: none"> • Does not satisfy Maxwell-Boltzmann 	<ul style="list-style-type: none"> • Unexpected oxidation states • Colloid behavior • Adsorption behavior • Difficulty in identifying chemical forms 	<ul style="list-style-type: none"> • Behavior follows expectations with regard to pH, redox, etc. • Chemical forms easily identifiable
	$\sim 10^{-20}$ $(\sim 10^{-19} \text{ atm})$	$\sim 10^{-7}$ to $10^{-6} M$ $(\sim 10^{-6} \text{ atm})$

1.3 AEROSOL MATERIALS

Aerosols will consist of oxides, metals, and water.¹² In general, water soluble aerosol materials will be fission products, principally cesium compounds, and in some reactor systems, boron oxides. Cesium salts were featured in this study, and structural materials were represented by magnesium oxide.

In an accident sequence, computer codes such as Victoria and Vanessa can aid in predicting the overall composition of aerosols, but there are a number of problems in directly applying this information to adsorption of gaseous iodine. First, the bulk composition is not as important as the surface composition. Less volatile materials are more likely to condense first and can be found on the inside of aerosols. In addition, chemical changes can occur on aerosol surfaces in containment. Varying amounts of hydration may be expected, as well as reaction of CsOH to form carbonates, borates, and nitrates. Other aerosol oxides and metals may also react with HNO₃ (gas) produced from the interaction of radiation with humid air.¹³

Aerosols that contain liquid H₂O are a special case. The iodine adsorption behavior of an insoluble aerosol in an aqueous droplet would be that of the aqueous phase, and iodine phenomena expected in an aqueous solution such as mass transport, hydrolysis, and radiolysis effects would predominate. With water soluble aerosols, the same phenomena would occur along with additional pH and ionic strength effects of the aerosol material.

Although the interactions of iodine in aqueous solution are somewhat beyond the scope of this work, two aqueous systems peculiar to aerosols have been examined: (1) iodine reactions with a cesium salt plus saturated solution, and (2) gamma irradiation of >1 m HI solutions.

One aim of this study is to define how aerosol materials must be placed in different categories in order to have meaningful models of iodine adsorption.

2. EXPERIMENTAL SYSTEMS AND PROCEDURES

The primary requirement for materials in the test apparatus was that they be relatively unreactive with I₂, organic iodide, and HI. Quartz was selected for use in the reaction zone and as a vessel for holding the sample powder. HI is not a good material to work with in measured amounts; gas delivery systems must be made of brass, and everything that it contacts is degraded by repeated exposure.

2.1 ADSORPTION TEST APPARATUS

The adsorption system is shown schematically in Fig. 1. Iodine gas and air entered the quartz tube and passed over the sample material. Gas emerging from the tube passed through a glass frit into a trap solution. In test of I_2 and HI, a 0.1 M NaOH solution was used in the trap and the organic iodide tests used isooctane.

The amounts of both air and iodine plus air were measured with mass flow meters on the inlet side of the system. In most tests, total gas flow rates were 20 to 24 standard cubic centimeters per minute. The quartz sample boats were 3.4 cm long, and the surface area of the base was 3.6 cm².

Iodine gas as I_2 was produced from iodine crystals in a glass vessel that was surrounded by a controlled temperature bath. The amount of I_2 that entered the reaction zone could be controlled by the air flow rate through the iodine chamber and by the chamber temperature.

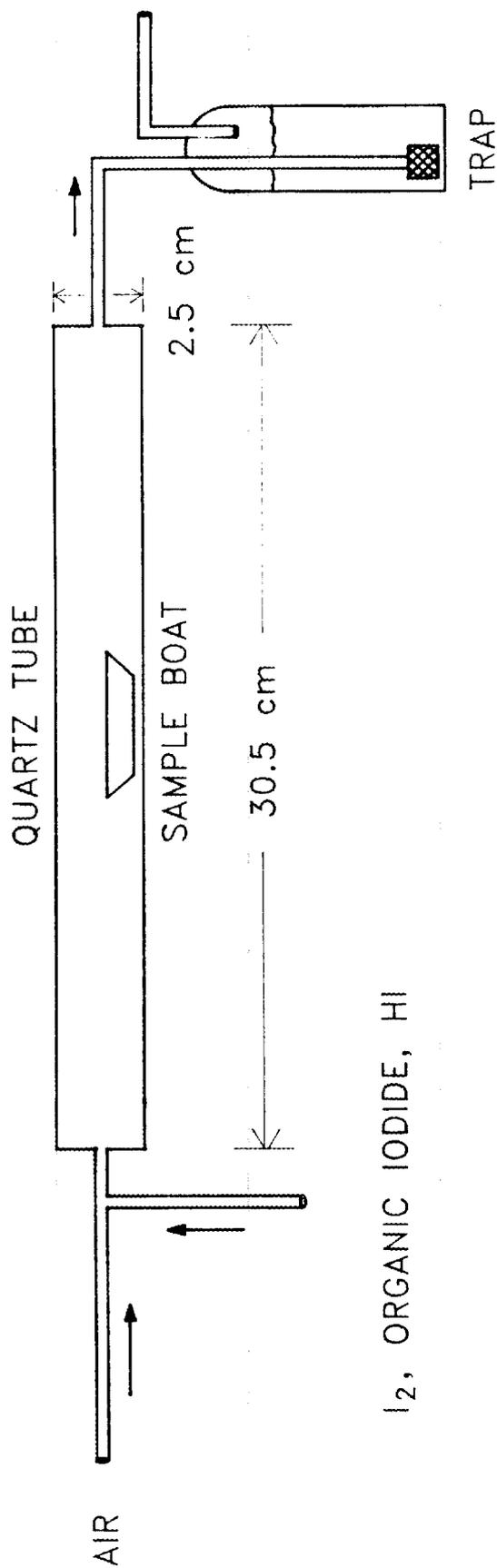
Gaseous organic iodide was introduced into the system from a small gas cylinder. Organic iodide was placed in the cylinder under a vacuum, and the cylinder was then pressurized with air to 100 psig. Hydrogen iodide was introduced into the system directly as Matheson 99% + HI gas.

Humidity was set on the inlet end of the tube by passing a portion of the air through a water bubbler and monitoring with a Humitemp Model 2200D humidity indicator.

2.2 MATERIALS AND PROCEDURES

Table 2 shows the surface area per gram and drying temperatures of the aerosol powders. Drying temperatures were obtained from the salt-H₂O phase diagrams to obtain an anhydrous material. Hydrated samples were first dried and then heated at a humidity to produce the desired phase(s).

Cesium oxide, Cs₂O, was used as a stand-in for anhydrous CsOH. The hydroxide may be dried, but it is difficult to ensure that the surface area remained constant from one sample to the next and for the measurement of the BET surface area.



I₂, ORGANIC IODIDE, HI

Fig. 1. Schematic diagram of adsorption system.

Table 2. Materials used in iodine adsorption

Compound	Source	BET surface area m ² /g	Drying temperature (°C)
Cs ₂ O	Johnson Matthey 99%	0.10	130
Cs ₂ CO ₃	Johnson Matthey	0.241	160
CsNO ₃	Johnson Matthey 99.9%	0.299	130
Cs ₂ B ₄ O ₇	a	0.665	235
MnO	Alfa 99.5%	0.483	125
Boric acid	Alfa 99.99%	0.391	175
CsOH	Alfa 99.9%	b	
BaO	Fisher ACS 99.3% ^c	1.08	150

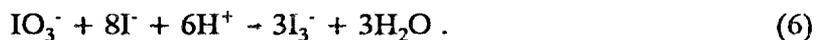
^aCs₂B₄O₇ was prepared by reacting CsOH with H₃BO₃.

^bCsOH was used only as CsOH + saturated solution. The surface area was the surface area of the quartz container, 3.6×10^{-4} m².

^cMade from Ba(OH)₂ · 8H₂O dehydrated at 200°C.

In a typical test, the powder material was dried in the quartz sample container. If necessary, the powder was hydrated. After the sample tube was flushed with air and iodine, the sample was placed inside and the trap was installed.

At the end of a test, the trap and sample were removed for analysis. The scheme for analysis is shown in Fig. 2. All analyses were begun immediately, within a few seconds, after each run. Iodate analysis was run by converting IO₃⁻ to I₃⁻ with an excess of I⁻ in acid solution:



The concentration of I₃⁻ was measured by a UV-visible spectrophotometer at 352 nm.

Thermochemical calculations were carried out with data obtained from the FACT system.¹⁴ Data for CsBO₂ were obtained from ref. 15, data for CsNO₃ were obtained from ref. 16, and data for CsIO₃ were obtained from refs. 16 and 17. Free energies of formation

I₂ TESTS

HI TESTS

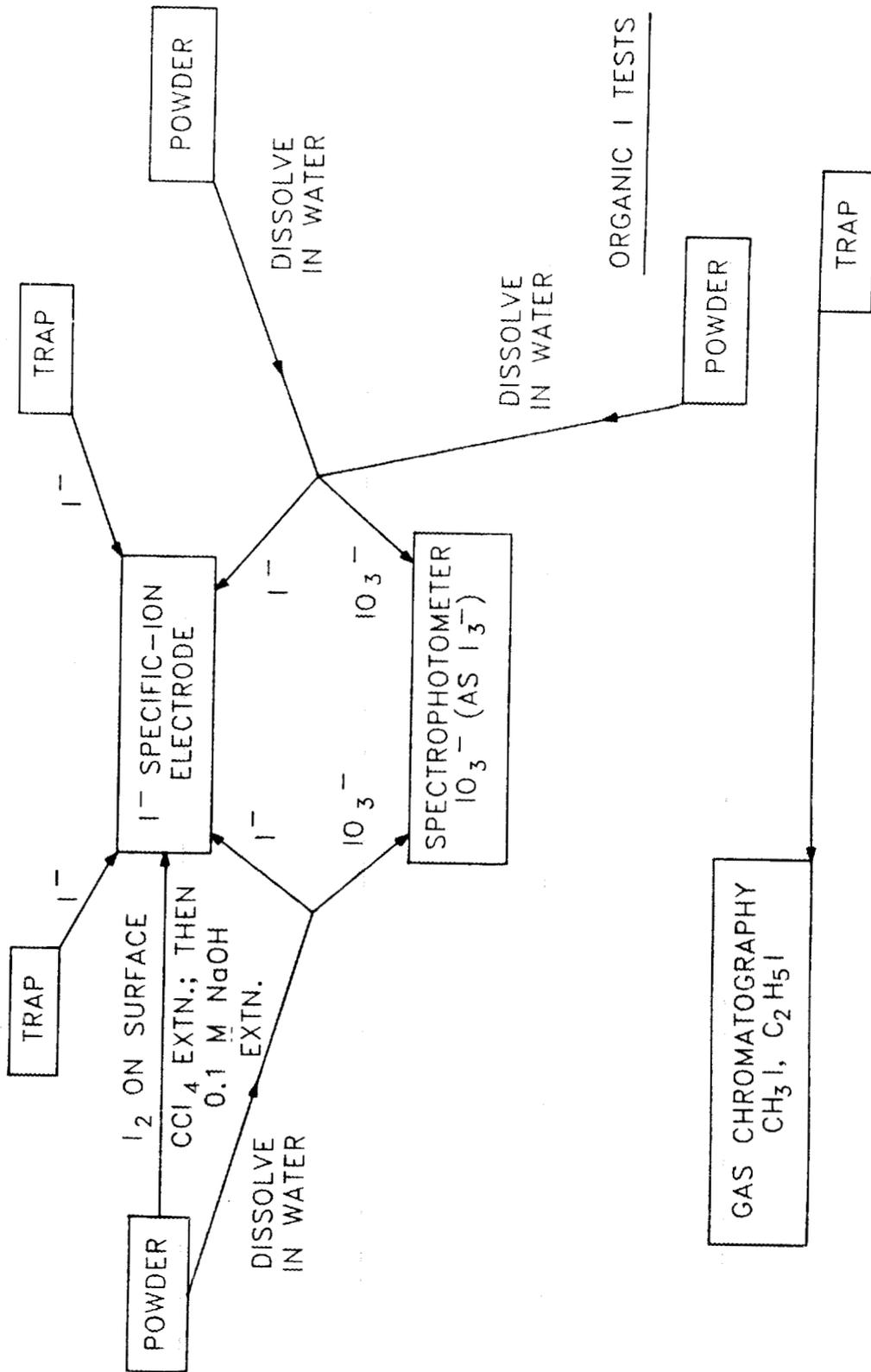


Fig. 2. Schematic diagram of analytical tests.

at temperatures greater than 298 K were extrapolated for CsNO_3 and the iodates using the relation:

$$\Delta G_f^\circ(T) = \Delta H_{298}^\circ - T\Delta S_{298}^\circ \quad (7)$$

where

$\Delta G_f^\circ(T)$ = standard free energy of formation at temperature T,

ΔH_{298}° = standard enthalpy of formation at 198 K,

ΔS_{298}° = standard entropy of formation at 298 K.

When components of air appear in reactions, the composition of dry air was used as $P_{\text{O}_2} = 0.209$ atm, $\text{CO}_2 = 0.00031$ atm, and $P_{\text{N}_2} = 0.781$ atm.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 I_2 ADSORPTION STUDIES

The materials and conditions used in the I_2 adsorption tests are given in Table 3.

Table 3. Materials and conditions in I_2 tests

Aerosol materials:

Cs_2O , Cs_2CO , two phase ($\text{Cs}_2\text{CO}_3 \cdot 0.5 \text{H}_2\text{O} + \text{Cs}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$), Cs_2CO_3 + saturated solution, Cs_2O , CsOH + saturated solution, $\text{Cs}_2\text{B}_4\text{O}_7$, HBO_2 , CsNO_3 , MnO

Temperatures: 100, 60, and 30°C

I_2 concentrations: -5×10^{-8} mol/L to -1×10^{-5} mol/L

3.1.1 I_2 Chemical Reaction Results

At 100°C, Cs_2O , Cs_2CO_3 , two phase ($\text{Cs}_2\text{CO}_3 \cdot 0.5 \text{H}_2\text{O} + \text{Cs}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$), Cs_2CO_3 + saturated solution, and CsOH + saturated solution reacted very rapidly and irreversibly with I_2 . The products of reaction were iodide and iodate in a ratio of ~5:1. A comparison of measured deposition velocities, with deposition velocities calculated from Eq. (2), indicates that the rates were determined only by gas phase mass transport. The CsOH + saturated solution gave an apparent deposition velocity of 8×10^{-2} cm/s. A

calculation using Eq. (2) and $D_{Ai} = 0.14 \text{ cm}^2/\text{s}$ gave a gas phase mass transport limited value of $4 \times 10^{-2} \text{ cm/s}$.

Cesium carbonate was initially chosen as an oxide of intermediate basicity between the very strongly basic Cs_2O or CsOH and the weakly basic $\text{Cs}_2\text{B}_4\text{O}_7$. However, at 100°C it too reacted at a rate that was limited by gas phase mass transport. In order to have the rate of adsorption of I_2 depend on surface interactions and not on gas phase mass transport, it is necessary that the quantity of I_2 removed from the gas stream and deposited on the specimen be small compared with the amount passed through the test system. This would ensure that the gas phase iodine concentration at or near the sample surface was the same as iodine concentration in the bulk gas stream. A wide range of gas flow rates and sample sizes were used in an attempt to conduct the I_2 adsorption tests at conditions where meaningful deposition velocities could be measured, but in all samples that contained Cs_2CO_3 , Cs_2O , or CsOH , more than one-half of the iodine introduced into the gas stream was adsorbed by the sample powder. Table 4 lists tests that were run with Cs_2CO_3 and the percentage of I_2 that was introduced into the system and adsorbed on the sample powder. These basic materials are effective getters for I_2 .

At 30°C , the rate of reaction of I_2 with Cs_2O was again determined by gas phase mass transport. However, the rate of reaction with Cs_2CO_3 decreased substantially. In two tests of the reaction of I_2 with Cs_2CO_3 at 30°C , deposition velocities of $7.1 \times 10^{-4} \text{ cm/s}$ and $6.1 \times 10^{-4} \text{ cm/s}$ were measured with gaseous I_2 concentrations of $3.3 \times 10^{-6} \text{ gram-atom I/L}$ and $5.1 \times 10^{-6} \text{ gram-atom I/L}$, respectively. It should be noted, however, that in these tests ~24% of the gaseous iodine deposited on the sample.

The $\text{Cs}_2\text{B}_4\text{O}_7$ powder reacted with I_2 to a limited extent as shown in Table 5. The rate of this reaction at 100°C was slower than the other reactive powders. Because of the limited extent of reaction, the rate could only be measured at low gaseous I_2 concentrations. The deposition velocity measured with $1 \times 10^{-7} \text{ gram-atom I/L}$ was $1 \times 10^{-3} \text{ cm/s}$ at 100°C .

Table 4. I₂ reaction with Cs₂CO₃ at 100°C

Total I ₂ introduced into system (gram-atom)	Gas flow rate (cc/min)	Cs ₂ CO ₃ sample mass (g)	Test duration (min)	Percent of total I ₂ that deposited on sample	
3.1 × 10 ⁻⁶	Static	0.5	60	95.4	Sample in center of closed tube
3.4 × 10 ⁻⁶	Static	0.5	60	99.8	Sample in center of closed tube
3.7 × 10 ⁻⁶	Static	0.5	60	98.1	Sample in center of closed tube
2.8 × 10 ⁻⁶	Static	0.5	60	99.6	Sample in center of closed tube
2.8 × 10 ⁻⁶	Static	0.05	60	99.6	Sample in center of closed tube
7.8 × 10 ⁻⁷	Static	0.05	15	66.7	Sample in center of closed tube
3.5 × 10 ⁻⁷	Static	0.05	7.5	85.3	Sample in center of closed tube
8.2 × 10 ⁻⁷	Static	0.05	15	66.5	Sample in center of closed tube
3.6 × 10 ⁻⁶	4	0.5	45	97.5	
7.5 × 10 ⁻⁶	4	0.5	90	98.6	
2.3 × 10 ⁻⁶	7	0.5	60	87.8	
3.0 × 10 ⁻⁶	11	0.5	60	83.2	
3.1 × 10 ⁻⁶	22	0.5	60	71.6	
3.4 × 10 ⁻⁶	22	0.5	60	76.7	
2.9 × 10 ⁻⁶	24	0.05	45	71.1	
3.7 × 10 ⁻⁶	24	0.05	60	60.3	
2.3 × 10 ⁻⁶	24	0.04	30	59.2	
2.7 × 10 ⁻⁶	24	0.07	30	62.5	
4.5 × 10 ⁻⁷	100	0.05	30	56.4	

Table 5. Extent of reaction with I₂

Anhydrous oxide	Monolayers (based on I)	gram-atom I (m ²)
Cs ₂ O	105	9.0 × 10 ⁻⁴
Cs ₂ CO ₃	52	4.3 × 10 ⁻⁴
Cs ₂ B ₄ O ₇	0.8	6.6 × 10 ⁻⁶

Three materials, CsNO₃, HBO₂, and MnO did not react chemically with I₂.

3.1.2 I₂ Physisorption Results

In addition to the chemical reaction of I₂ or chemisorption, there was also some physisorption. Measurements of physisorbed I₂ could only be made at temperatures below 100°C because of the rapid desorption when the powders were removed from the iodine containing gas at high temperatures. Thus, unlike the chemical reaction of I₂, which produced iodide and iodate and was irreversible, physisorbed I₂ desorbs easily.

Data on I₂ physisorption are given in Table 6. There was no physisorption of I₂ on Cs₂O even at temperatures as low as 30°C. This is probably because the rate of reaction between I₂ and Cs₂O at 30°C was limited only by gas phase mass transport. Even at this low temperature, all iodine that reached the surface was rapidly converted to iodide and iodate rather than remaining as physisorbed I₂.

Deposition velocities given in Table 6 can be used for intercomparison. Because physisorbed I₂ can be readily removed, these data should be used in adsorption isotherms or with desorption velocities. Deposition velocities for I₂ physisorption on Cs₂CO₃ or Cs₂B₄O₇ were approximately one order of magnitude greater than on CsNO₃, a material that did not react chemically with I₂.

Table 6. I₂ physisorption data

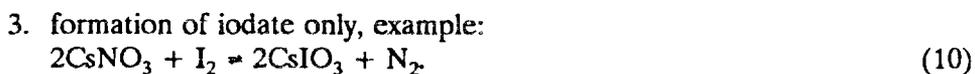
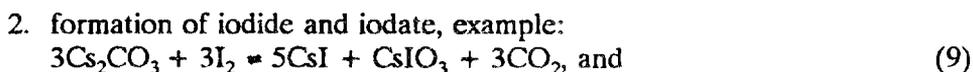
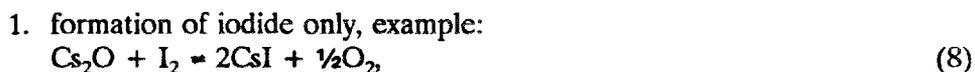
Material	Temperature (K)	Surface gram-atom I (cm ² /s)	Gas gram-atom I (cm ³)	Deposition velocity (cm/s)
CsNO ₃	303	1.0 × 10 ⁻¹³	3.7 × 10 ⁻⁹	2.7 × 10 ⁻⁵
CsNO ₃	303	6.2 × 10 ⁻¹⁴	2.9 × 10 ⁻⁹	2.1 × 10 ⁻⁵
CsNO ₃	333	1.2 × 10 ⁻¹⁴	3.4 × 10 ⁻⁹	3.5 × 10 ⁻⁶
Cs ₂ CO ₃	303	1.7 × 10 ⁻¹²	5.1 × 10 ⁻⁹	3.3 × 10 ⁻⁴
Cs ₂ CO ₃	303	5.8 × 10 ⁻¹³	3.1 × 10 ⁻⁹	1.9 × 10 ⁻⁴
Cs ₂ CO ₃	333	1.3 × 10 ⁻¹³	4.5 × 10 ⁻⁹	2.9 × 10 ⁻⁵
Cs ₂ B ₄ O ₇	333	1.3 × 10 ⁻¹³	2.1 × 10 ⁻⁹	6.2 × 10 ⁻⁵

No physisorption of I₂ on Cs₂O at 303 K or 333 K.

All tests were run for 1800 s.

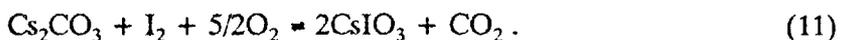
3.1.3 Discussion of I₂ Adsorption Tests

As reported previously, I₂ reacts with Cs₂O, Cs₂CO₃, Cs₂B₄O₇, CsOH + saturated solution, and Cs₂CO₃ + saturated solution to produce iodide and iodate. Giacalone and Indovina reported that I₂ and either MgO or CsO react in the anhydrous solvents CHCl₃, CCl₄, or C₆H₆ to form iodide and iodate on the oxide surface.¹⁸ It is conceivable that I₂ could have reacted in three ways:



The second kind of reaction, yielding approximately five iodides to one iodate, was the only reaction observed in these tests. The range of the iodide to iodate was 4.8 to 7.8 in the various tests. Thermochemical data show (see Fig. 3) that the formation of iodide and iodate would result in a lower free energy of reaction, or in more precise terms, a lower iodine potential ($RT \ln P_{I_2}$) than formation of iodide alone. However, formation of iodate alone would give a lower iodine potential than formation of iodide and iodate.

The formation of iodate must be limited by reaction kinetics. This can be appreciated by considering the reaction of Cs_2CO_3 with I_2 to produce $CsIO_3$:



This reaction includes oxygen as a reactant along with iodine. Reaction (10) is a more straightforward replacement of nitrogen by iodine. However, we have not detected any reaction of I_2 with $CsNO_3$ even though reaction (10) should lower the iodine potential. In a test at room temperature, iodine crystals and $CsNO_3$ were placed in a closed container for 186 h, but no iodate or iodide were detected on the nitrate.

Apparently, it is easier for I_2 to disproportionate on the surface to form iodide and iodate than it is to have a redox reaction with ions in the crystal. Having said this, it still must be acknowledged that iodide and iodate form on the surface as a result of interaction with the crystal. Cesium iodide crystallizes with the cubic cesium chloride structure where each ion is surrounded by eight ions of the opposite charge. Cesium iodate crystallizes in the perovskite structure.¹⁹ In this structure, the cesium ions are at the corners of a cube, the O^{2-} ions are face centered, and the I^{+5} is body centered. Iodate ions do not exist as IO_3^- units in this crystal structure. Table 7 shows interatomic distances in CsI , Cs_2O , and $CsIO_3$ crystals. The $Cs^+ - Cs^+$ distance in CsI and $CsIO_3$ are greater than in Cs_2O , also the $Cs-I$ distances are greater than the $Cs-O$ distances in Cs_2O . Thus, some expansion of the crystal lattice must occur as CsI and $CsIO_3$ form on the surface.

The reaction to form iodide and iodate requires a favorable free energy change that lowers the iodine potential. As shown in Fig. 3, $CsNO_3$ and MnO fail in this regard. The extent of reaction with anhydrous Cs_2O and Cs_2CO_3 is probably limited only by the surface concentration of iodide and iodate, which prevents further interaction between I_2 and the host crystal. In tests with saturated aqueous solutions present (i.e., $CsOH$ + saturated and Cs_2CO_3 + saturated solution), no such limit was expected or observed.

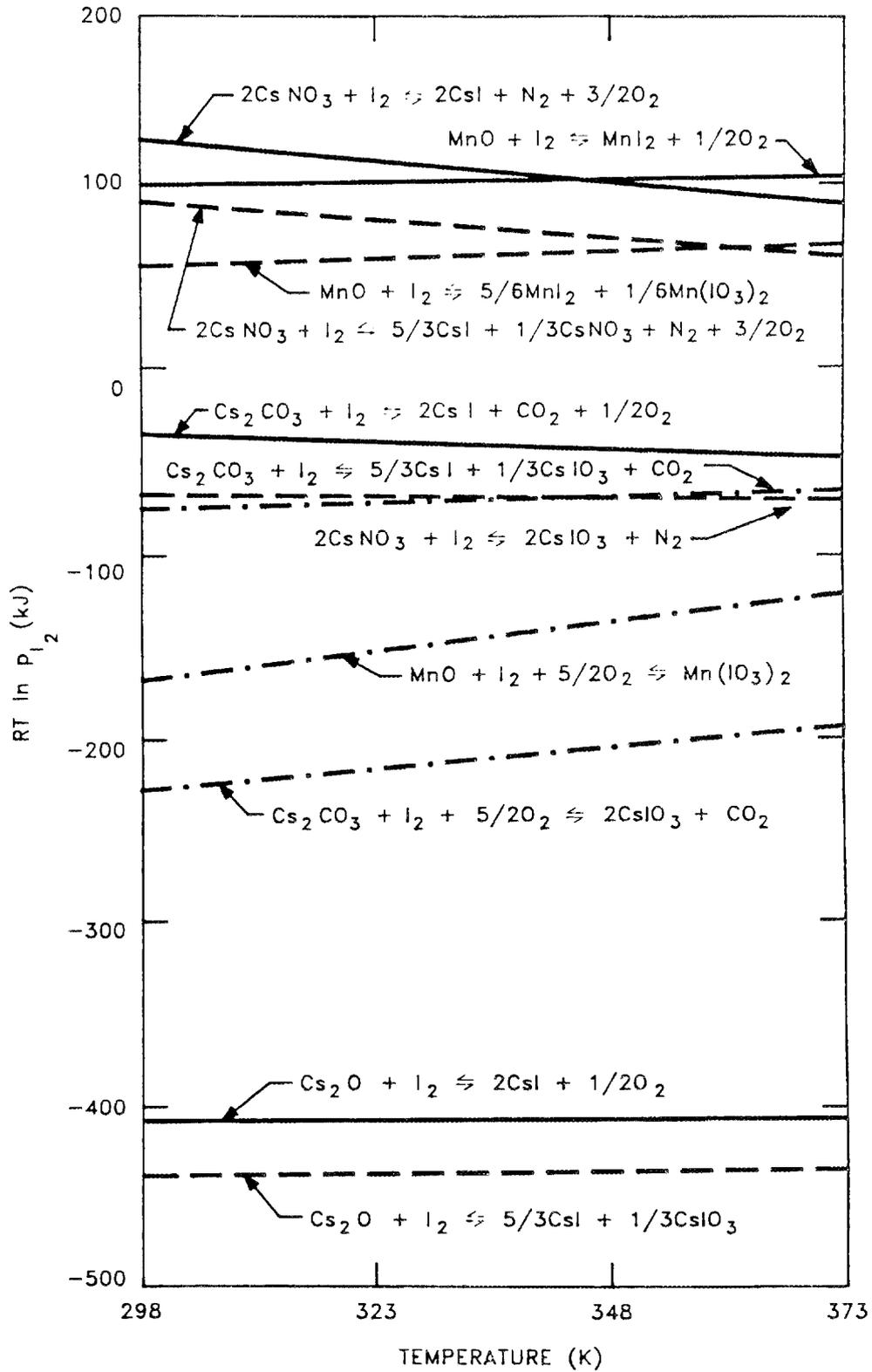
Fig. 3. Iodine potential in I_2 reactions.

Table 7. Interatomic distances in CsI, CsIO₃, and Cs₂O

Crystal	Interatomic distance Å	Reference
<u>CsI</u>		20
Cs ⁺ - Cs ⁺	4.568	
Cs ⁺ - I ⁻	3.96	
<u>CsIO₃</u>		21
Cs ⁺ - Cs ⁺	4.674	
Cs ⁺ - O ⁻²	2.70	
Cs ⁺ - I ⁺⁵	3.31	
<u>Cs₂O</u>		22
Cs ⁺ - Cs ⁺	4.19	
Cs ⁺ - O ⁻²	2.82	

The test results may also be characterized in terms of the Lux-Flood description of acidity and basicity of oxides.^{23,24} A basic oxide readily donates an O⁻² and an acid readily accepts an O⁻²:



In this case, I₂ is the acid and the prototype reaction is given by Eq. (8). The reaction with cesium carbonate [Eq. (9)] indicates that I₂ is a stronger Lux-Flood acid than CO₂. Similarly, the lack of reaction with CsNO₃ indicates that [(NO₂ + ½O₂) or N₂O₅] are stronger Lux-Flood acids than I₂.²⁴ The observation of iodide and iodate as products, similar to hydrolysis, suggests that I₂ reacts as an acid by disproportionation. In the case of I₂ in water, the fact that hydrolysis occurs only at high pH means that the hydrogen ion is a stronger acid than I₂ even in the Lux-Flood meaning of acids and gases.

3.1.4 Qualitative Tests of I₂ Reaction with a Variety of Aerosol Materials

A series of qualitative tests were run on a wide range of materials that may be present in aerosols in containment. The tests were run in the same way that tests on the cesium salts

were run, but they are qualitative in that with the exception of BaO, no BET surface areas were measured for these materials. The materials tested are listed in Table 8. The test results designated as very little reaction and small reaction are somewhat subjective. The results given as very little reaction produced amounts of iodide on the powders that were detectable, but very small compared to the cesium carbonate tests. The reaction with BaO was very similar in extent to the cesium oxide and cesium carbonate tests. The reaction with cadmium produced a combination of I_2 and I^- with ~30% of the surface iodine as I_2 . Beard et al.²⁵ studied the reaction of I_2 with cadmium aerosol and observed CdI_2 but did not mention adsorption of I_2 .

Table 8. Qualitative tests of I_2 with other materials
(tests at 100°C)

Material	Results and comments
Ni	No reaction
Cd	I_2 adsorption and formation of CdI_2 ($I^-/IO_3^- = 2I$)
CaO	Very little reaction
BaO	Extensive reaction ($I^-/IO_3^- = 5$)
In_2O_3	No reaction
ZrO_2	Very little reaction
Cr_2O_3	Very little reaction
SnO	Small reaction
CaO stabilized ZrO_2	No reaction

Table 9 lists calculated I_2 potentials, $RT \ln P_{I_2}$, for some possible aerosol materials. The materials were selected because there were some data on the free energy of formation of their iodides. However, in each case, the iodate data were only at 298 K and had to be extrapolated to 373 K. For comparison with data in Table 9, an I_2 potential of -5.7×10^4 J would result in an equilibrium I_2 pressure of 10^{-8} atm. In this list, the BaO, $CsBO_2$, SrO, and Ag_2O should react with I_2 at pressures of interest in containment.

Table 9. Calculated I_2 potentials, $RT \ln P_{I_2}$, for some possible aerosol materials at 373 K, 5:1 iodide to iodate as products

Material	$RT \ln P_{I_2}$ (J at 373 K)
CsBO ₂	-7.2×10^4
CaO	$+9.9 \times 10^3$
SrO	-5.6×10^4
Y ₂ O ₃	$+1.3 \times 10^5$
Ag ₂ O	-5.2×10^4
CdO	-2.1×10^4
BaO	-1.3×10^5

3.2 ORGANIC IODIDE ADSORPTION STUDIES

3.2.1 Organic Iodide Test Results

The aerosol materials that were used in these tests included Cs₂CO₃, Cs₂CO₃ + saturated solution, Cs₂O, CsOH + saturated solution, Cs₂B₄O₇, CsNO₃, BaO, HBO₂, and MnO. The tests were run with gaseous organic iodide concentrations in the range of $\sim 3 \times 10^{-7}$ to $\sim 4.5 \times 10^{-6}$ mol/L.

No physisorbed organic iodide was detected on the powders, however, chemisorbed inorganic iodide formed on some materials. Unlike the reactions with I₂, no iodate formed. The rate of reaction leading to I⁻ was sufficiently slow that it could be measured. There was no detectable reaction of CH₃I with Cs₂B₄O₇, CsNO₃, HBO₂, or MnO.

Deposition velocities for the reactions of Cs₂CO₃, Cs₂O, CsOH, and BaO are listed in Table 10. The amount of iodine deposited was approximately linear with time for surface loadings below a saturation limit. Maximum loadings are given in Table 11. The uniformity of deposited iodine was assessed by dividing the sample powder in half and analyzing each portion separately. These tests were run with Cs₂CO₃ at 100° C. In two tests, 43 and 55%,

Table 10. Reaction of aerosol materials with CH₃I or C₂H₅I

Aerosol material	Organic iodide	Temperature (°C)	Concentration of gaseous organic iodide (mol/L)	Duration of test(s)	Deposition velocity (cm/s)
Cs ₂ CO ₃	C ₂ H ₅ I	100	1.8 × 10 ⁻⁶	1800	8.3 × 10 ⁻⁵
Cs ₂ CO ₃	C ₂ H ₅ I	100	1.6 × 10 ⁻⁶	3600	7.4 × 10 ⁻⁵
Cs ₂ CO ₃	C ₂ H ₅ I	100	1.2 × 10 ⁻⁶	3600	7.6 × 10 ⁻⁵
Cs ₂ CO ₃	C ₂ H ₅ I	100	1.7 × 10 ⁻⁶	3600	6.5 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	50	1.4 × 10 ⁻⁶	900	4.3 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	50	1.2 × 10 ⁻⁶	1800	3.4 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	50	1.2 × 10 ⁻⁶	1800	3.9 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	70	1.2 × 10 ⁻⁶	900	6.7 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	70	1.4 × 10 ⁻⁶	1800	5.4 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	100	1.9 × 10 ⁻⁶	900	1.0 × 10 ⁻⁴
Cs ₂ CO ₃	CH ₃ I	100	1.3 × 10 ⁻⁶	1800	1.3 × 10 ⁻⁴
Cs ₂ CO ₃	CH ₃ I	100	3.1 × 10 ⁻⁶	900	8.1 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	100	3.1 × 10 ⁻⁶	900	5.9 × 10 ⁻⁵
Cs ₂ CO ₃	CH ₃ I	100	6.8 × 10 ⁻⁷	3600	5.6 × 10 ⁻⁵
Cs ₂ O	CH ₃ I	100	2.8 × 10 ⁻⁶	3600	1.3 × 10 ⁻⁴
Cs ₂ O	CH ₃ I	100	2.8 × 10 ⁻⁶	7200	1.9 × 10 ⁻⁴
Cs ₂ O	CH ₃ I	100	3.3 × 10 ⁻⁶	1800	4.5 × 10 ⁻⁴
Cs ₂ O	CH ₃ I	100	3.2 × 10 ⁻⁶	7200	9.8 × 10 ⁻⁵
Cs ₂ CO ₃ + saturated solution	CH ₃ I	100	3.5 × 10 ⁻⁶	1800	4.4 × 10 ⁻⁴
CsOH + saturated solution	CH ₃ I	100	4.1 × 10 ⁻⁶	1800	2.1 × 10 ⁻⁴
BaO	CH ₃ I	70	3.9 × 10 ⁻⁷	1800	4.1 × 10 ⁻⁵
BaO	CH ₃ I	70	3.0 × 10 ⁻⁷	900	6.9 × 10 ⁻⁵
BaO	CH ₃ I	100	2.1 × 10 ⁻⁶	1800	3.4 × 10 ⁻⁵
BaO	CH ₃ I	100	1.4 × 10 ⁻⁶	900	6.4 × 10 ⁻⁵

Table 11. Maximum loading of I⁻ from reaction with organic iodides

Material	Maximum loading	Monolayers
Cs ₂ O	$1.4 \times 10^{-4} \text{ mol I}^- \text{ m}^2$	17
Cs ₂ CO ₃	$4.1 \times 10^{-6} \text{ mol I}^- \text{ m}^2$	0.5
Cs ₂ B ₄ O ₇	$\leq 4.9 \times 10^{-8} \text{ mol I}^- \text{ m}^2$	≤ 0.006
CsNO ₃	$\leq 1.6 \times 10^{-8} \text{ mol I}^- \text{ m}^2$	≤ 0.002

respectively, were deposited on the upstream portion with the remainder on the downstream portion.

As in the tests of I₂ adsorption, the basic materials reacted. In this case, however, Cs₂B₄O₇ was not basic enough to give any appreciable reaction. The deposition velocities for CH₃I and C₂H₅I on Cs₂CO₃ were similar in value. The rate of reaction with anhydrous Cs₂O, Cs₂CO₃ + saturated solution, and CsOH + saturated solution were similar to each other and greater than the rate of reaction with anhydrous Cs₂CO₃ or anhydrous BaO.

The deposition velocities for the reaction of Cs₂CO₃ with CH₃I were fitted to an Arrhenius-type equation as:

$$\ln V_d = -4.72 - \frac{1.75 \times 10^3}{T}, \quad (13)$$

with a correlation coefficient of 0.80. The variation of the deposition velocity with temperature between 50 and 100°C was not large, and no variation could be discerned from the data at 70 and 100°C for BaO.

3.2.2 Discussion of Organic Adsorption Results

The most straightforward description of these test results is that the organic iodide undergoes a nucleophilic substitution reaction typical of alkyl halides:

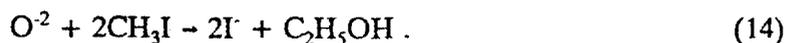
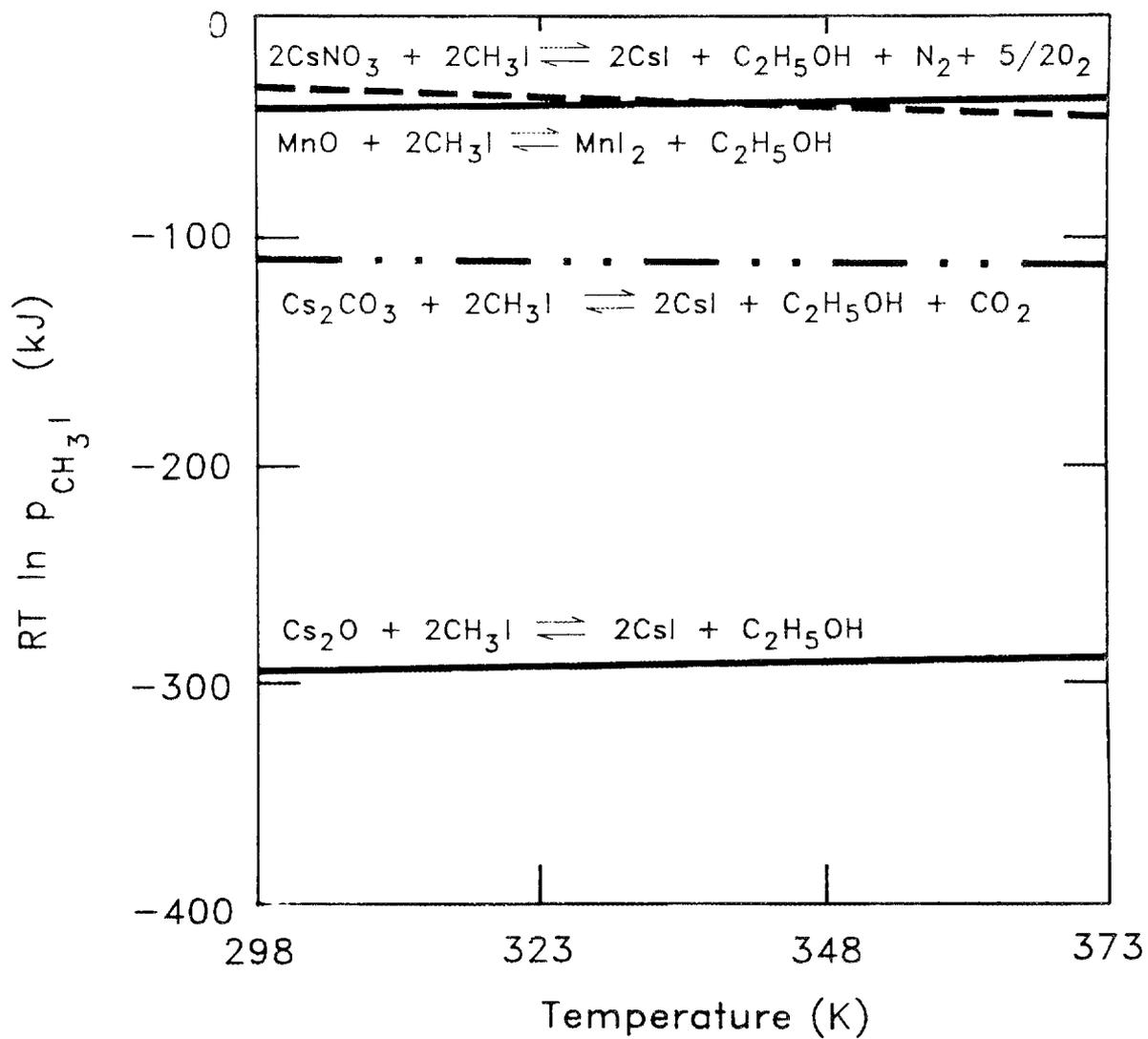


Figure 4 gives CH₃I potentials, RT ln P_{CH₃I}, for reaction with Cs₂O, Cs₂CO₃, CsNO₃, and MnO. As in Fig. 3, the O₂, N₂, and CO₂ pressures used in the calculation of this figure are

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Fig. 4. CH_3I potential in organic iodide reactions.

those in dry air. Also, a unit activity for C_2H_5OH was assumed even above its boiling point of 351 K. At 373 K, the calculated vapor pressure of CH_3I , using these assumptions, was 3×10^{-41} atm over Cs_2O ; that in equilibrium with Cs_2CO_3 was 6×10^{-16} atm, and over MnO , it was 2×10^{-5} atm. While it cannot be definitely claimed that reaction (14) describes the behavior of organic iodide in these tests, the results were consistent with the CH_3I potentials shown in Fig. 4 and indicate that materials such as $CsNO_3$ and MnO should react only at relatively high CH_3I vapor pressure.

The reaction of organic iodides may also be characterized in terms of Lux-Flood acids and bases. As depicted in Eq. (14), the oxide denotes an O^{2-} (base) and the CH_3I acts as an acid. In this sense, CH_3I is not as strong a Lux-Flood acid as I_2 because it cannot react with $Cs_2B_4O_7$.

3.3 HYDROGEN IODIDE ADSORPTION STUDIES

3.3.1 HI Test Results

As expected, HI proved to be quite reactive with both the equipment and the test aerosol powders. The materials evaluated in the tests included MnO , $CsNO_3$, HBO_2 , Cs_2CO_3 , and $CsOH$ + saturated solution. All tests were run at $100^\circ C$. Because of difficulties in controlling HI at low concentrations, the gaseous HI concentrations were $\sim 3 \times 10^{-5}$ to 7×10^{-5} mol/L.

All of the materials tested reacted with HI to form iodide on the surface of the powders. A small amount of iodine, amounting to 1 to 2% of the surface iodide, was in the form of iodate on the surface. Table 12 gives data on the rate of reaction with MnO , $CsNO_3$, HBO_2 , and Cs_2CO_3 . The reaction with $CsOH$ + saturated solution was limited only by the rate of transport to the surface.

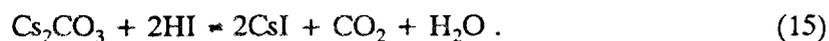
Table 12. Rate of reaction with HI at $100^\circ C$

Materials	Rate of reaction (gram-atom iodine/m ² s)
HBO_2	$1.7 \times 10^{-5} \cdot \text{concentration HI (mol/L)}$
$CsNO_3$	$1.5 \times 10^{-3} \cdot \text{concentration HI (mol/L)}$
MnO	$2.0 \times 10^{-3} \cdot \text{concentration HI (mol/L)}$
Cs_2CO_3	$9.4 \times 10^{-3} \cdot \text{concentration HI (mol/L)}$

The rates of reaction with CsNO_3 and MnO were quite similar. The reaction with HBO_2 was very slow.

3.3.2 Discussion of HI Adsorption Results

It is only a slight exaggeration to say that HI reacts with everything. Neither CsNO_3 nor MnO reacted with I_2 , so it is not likely that the small amount of iodate in their reaction with HI was a result of decomposition of HI into I_2 and H_2 with subsequent disproportionation into iodide and iodate. The reaction to form iodide could be viewed as an acid-base reaction; for example:



HI is so reactive because almost everything is more basic than it is.

3.3.3 Irradiation of Concentrated HI Solutions

The question considered here is whether HI in aqueous aerosols can become a source of I_2 under gamma irradiation. Irradiation of dilute iodide solutions results in the production of some I_2 when the pH is < -7 (ref. 26). The concentration of HI in aqueous aerosols could be much higher than iodide concentrations in sumps or water pools, and the pH would be very low.

The effect of gamma radiation on concentrated HI solutions was studied by irradiating 50 mL samples at 3.7×10^3 Gy/h. The samples were prepared by bubbling HI gas through water to attain a concentration of 1.5 M. The irradiation and analytical tests were carried out at room temperature. Conversion to I_2 was monitored by measuring the absorbance of I_3^- at 352 nm. At 298 K, an equilibrium constant of 690 ± 10 has been reported for the reaction:



A sample irradiated for 1 h resulted in a very small conversion to I_3^- or I_2 . The measured I_3^- concentration was only 3×10^{-4} M and the measured I^- concentration was 1.4 M. This would correspond to an I_2 concentration of 3×10^{-7} M. An unirradiated HI solution left for a similar time period gave a measured I_3^- concentration of 9×10^{-5} M and a measured I^- concentration of 1.4 M. Thus, the irradiation resulted in the conversion of an insignificant fraction of the HI into I_3^- or I_2 .

4. PERSPECTIVES ON IODINE ADSORPTION

Oxide aerosol materials may be categorized, with regard to interaction with iodine species, according to their basicity. The most basic materials such as CsOH, Cs₂O, and even Cs₂CO₃ react irreversibly with I₂ at 100°C with deposition velocities $> 10^{-1}$ cm/s. Cesium oxide reacts very rapidly even at temperatures as low as 30°C. Similar trends, but with smaller deposition velocities, were observed with reaction of organic iodides or HI. Rubidium salts should react in a manner similar to cesium salts. Other alkali metal oxides and hydroxides, such as Na₂O, K₂O, and CaO, can arise from core-concrete interactions. There are a host of other materials that are likely to contribute to the mass and surface area of containment aerosols,¹² but the extreme reactivity of some of the basic salts means that they may still dominate in iodine adsorption.

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