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THE CHEMISTRY OF IODINE IN CONTAINMENT

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Recent investigations of iodine behavior under radiolytic conditions have demonstrated that kinetics, not thermodynamics, will govern iodine speciation and partitioning under conditions typical of those expected in a reactor containment during an accident. In the presence of radiation, iodine volatility is orders of magnitude higher than that expected based on thermodynamic calculations. Kinetic studies have contributed extensively to the existing database of iodine chemistry and have several implications for modeling iodine behavior for safety analyses. For example, as a result of these investigations, many uncertainties in the iodine database, such as those regarding thermal oxidation of iodine, which were formerly regarded as reactor safety issues, are now considered to be relatively unimportant. In contrast, previously unconsidered factors, such as the effect on aqueous chemistry of impurities originating from surfaces, are now recognized as playing major roles in determining iodine volatility. An updated review of the existing literature regarding iodine behavior is provided, with a focus on recent developments. A critical evaluation of the data in the context of developing a model for iodine behavior under reactor accident conditions is also provided.

I. INTRODUCTION

It is generally recognized that radioiodine is potentially one of the most hazardous fission products that could be released from the fuel of nuclear reactors during a loss-of-coolant accident. This is due to the combination of its large inventory in nuclear fuel, a half-life of 8.04 days for the isotope of greatest radiological significance (^{131}I), a complex chemistry that could lead to formation of volatile species, and its hazardous biological effects.

Thermodynamic calculations and various experiments have established that under expected accident conditions the iodine released from fuel into containment would be primarily in its reduced state as cesium iodide.[1–4] This would initially be dissolved in the water originating from the discharged coolant and any safety spray systems present. Under accident conditions, nonvolatile I^- initially dissolved in the sump would be oxidized by radiolytic processes to form volatile molecular iodine that could become airborne. Molecular iodine in the aqueous phase could be further oxidized to nonvolatile iodine oxides or reduced by thermal or radiolytic processes to return to its original nonvolatile I^- state. Iodine species could also react with organic compounds present in containment to form organic iodides, which could subsequently either hydrolyze to give the corresponding alcohol and nonvolatile I^- or partition into the gas phase. Finally, surface deposition on both gas and aqueous surfaces could alter the steady-state concentrations of many of these iodine species or induce surface-catalyzed transformations. A simplified representation of the redox processes, chemical transformations, and partitioning that may occur in containment following an accident is given in Fig. 1.

Because controlled venting of the containment atmosphere is required following an accident in some reactor designs and because of the potential for release of a small fraction of volatile fission products out of containment as a result of leakage, it is important to be able to predict the volatility and speciation of iodine as a function of time following an accident. Many of the processes described in Fig. 1 circumvent the achievement of equilibria among aqueous iodine species that would be expected in nonradiolytic conditions. Therefore, the distribution and speciation of iodine expected

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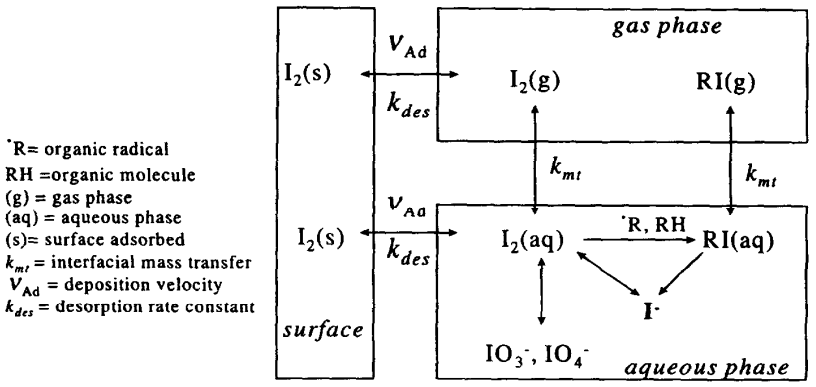

Fig. 1. Chemical reaction pathways for iodine in containment.

at thermodynamic equilibrium would not be observed in an accident scenario. Instead, time-dependent processes such as reactions of iodine with water radiolysis products, mass transfer, and surface adsorption would dominate iodine behavior and determine its speciation and partitioning. These processes are very complex and rely upon other time-dependent parameters such as iodine concentration, radiation dose, pH, temperature, the presence of organic and inorganic impurities, and the type of containment surfaces. Consequently, predicting iodine volatility in containment requires a sound understanding of a variety of kinetic phenomena.

Although there have been previous reviews on various aspects of iodine behavior in containment,[5,6] significant progress has been made in recent years in understanding the physical and chemical phenomena affecting iodine volatility. This paper reviews the current literature on iodine chemistry relevant to reactor accident conditions and provides a critical evaluation of recent developments in the area.

II. AQUEOUS CHEMISTRY

II.A. Thermodynamics of Iodine Species in the Aqueous Phase

Thermodynamic calculations using Gibbs energies of formation for chemical species in the aqueous phase allow the determination of the distribution of fission product species in aqueous solution at equilibrium. Although it is unlikely that a complete equilibrium among all the iodine species in solution would be achieved rapidly following a reactor accident, these calculations can provide valuable information on the natural tendency of the system and thus determine which reaction rates need to be known. Moreover, partial equilibria among a smaller set of iodine species, e.g.,

$$I_2 + H_2O = HOI + I^- + H^+ , \quad (1)$$

$$I_2 + OH^- = I_2OH^- , \quad (2)$$

$$I_2OH^- = HOI + I^- , \quad (3)$$

and

$$HOI = H^+ + OI^- , \quad (4)$$

are known to be achieved rapidly, and examination of these equilibria identify the species that may have a significant impact on iodine reaction kinetics.

Gibbs energies of formation of volatile iodine species both in the aqueous and the gas phases are also required to obtain the partition coefficients of these species. The partition coefficient, H, defined as the ratio of the concentration of a species in the aqueous phase to that of the gas phase at equilibrium, is an important parameter to be considered in defining iodine behavior. The partition coefficients of iodine species are reviewed in Sec. III.A.

Gibbs energies of formation in the aqueous phase are available in the chemical literature for various inorganic iodine species at the standard temperature of 25°C. The existing data are considered to be accurate and reliable except those for iodine species in the +1 oxidation state, such as IO^-, HOI, H_2OI^+, and I_2OH^-. The thermodynamic values at higher temperatures are also known or can be estimated for most of the iodine species of interest. Critically evaluated values of the thermodynamic parameters for inorganic iodine species are available in Ref. 7. No work has been performed recently that has significantly altered the values given in the references; however, a few high-temperature thermodynamic studies have been completed.[8–10] Gibbs energies of formation in the aqueous phase are not available for many organic iodides that may be present during an accident. Although it is not likely that the equilibria

involving organic iodides will dominate iodine behavior, the partition coefficients of organic iodides are required to determine the airborne iodine concentration. This is discussed in more detail in Sec. III.A.

The important chemical parameters that control speciation in aqueous solution at equilibrium are pH, redox potential, temperature, and total iodine concentration. Thus, at a given temperature and iodine concentration, potential-pH diagrams are often used to describe the iodine-water system at equilibrium. The potential-pH diagrams, calculated from Gibbs energies of formation, show the predominant species at equilibrium as a function of pH and redox potential.[7,11] For a total iodine concentration higher than 10^{-6} mol·dm^{-3}, nonvolatile iodide and iodate are the predominant iodine species for most of the redox potentials and pH ranges. Volatile molecular iodine dominates at equilibrium only under acidic and oxidizing conditions. The concentration of HOI at equilibrium also becomes important under those conditions, and more so at lower iodine concentrations. Early studies of iodine volatility assumed that HOI was highly volatile,[12] but this is no longer considered to be valid.[13,14] Nevertheless, this assumption and these thermodynamic calculations led to the conclusion that iodine volatility can be minimized by keeping the pH of the aqueous solution high.

Although some of the conclusions reached from thermodynamic calculations still hold, many of the assumptions made in deriving them are no longer considered valid. For example, the redox potential of water was originally assumed to be controlled by the concentration of dissolved oxygen in equilibrium with atmospheric oxygen. In a radiation field, however, water radiolysis significantly alters the redox characteristics of the aqueous phase. Under the radiation conditions expected in a reactor accident, iodine behavior is dominated by the reaction of iodine species with water radiolysis products that are being produced continuously.

Under radiolytic conditions, conversion of I^- to I_2 is dominated by the reaction of I^- with ·OH, which has a reaction rate orders of magnitude faster than corresponding oxidation of iodide by molecular oxygen. Likewise, under these conditions, the reduction of I_2 by water radiolysis products H_2O_2 and O_2 is responsible for an observed correlation between pH and iodine volatility that is greater than that predicted by a thermodynamic model. The redox behavior of iodine and its pH-dependent volatility under radiolytic conditions are therefore determined by the kinetics of the reaction of iodine species with water radiolysis products.

In summary, thermodynamic analyses do not provide information on how fast a chemical system will reach equilibrium. If chemical reaction rates involving important species are slow compared to the timescale of an accident, or if there are continuous processes such as radiolytic reactions resulting in production of these important species, the distribution of species during an accident will be different from that expected at equilibrium. To determine iodine speciation and volatility for conditions typical of those expected during accidents, it is essential to understand the chemical kinetics of iodine reactions under those conditions. Thermodynamic equilibria among the entire chemical system are reached slowly under the conditions expected in containment, although fast equilibria are attained among smaller sets of iodine species whose Gibbs energies of formation are well established. Therefore, more accurate thermodynamic calculations are unnecessary.

II.B. Thermal Reactions of Iodine Species

The reactivity of iodine in aqueous solutions was reviewed by Wren et al.[5] in 1987 and Sellers[6] in 1985, principally to establish a kinetic database of important reactions. Both reviews identified reactions for which rates and mechanisms were unknown. However, significant progress has been achieved in this area in recent years. Some important reactions are discussed in Secs. II.B.1 through II.B.5, with an emphasis on recent developments.

II.B.1. Thermal Oxidation of Iodide

Iodide is thermally oxidized to iodine in the presence of oxygen:

$$2I^- + 2H^+ + \tfrac{1}{2}O_2 \rightarrow I_2 + H_2O \quad . \qquad (5)$$

This oxidation reaction has been studied by Burns and Marsh[15] and Sigalla and Herbo,[16] and their proposed mechanisms and rate expressions differ significantly. This difference is likely to have arisen from different acidities and temperatures employed in the experiments and is an indication that the mechanism of this oxidation is complex. Moreover, the oxidation rate is easily affected by light, additives such as buffers, and impurities such as metal ions.[6,12] Nevertheless, since the counterpart radiation-induced oxidation of I^- to I_2 by ·OH is much faster (Sec. II.C), thermal oxidation is unlikely to be important under radiolysis conditions. Therefore, although the uncertainty regarding the mechanism and the rate expression of the overall thermal oxidation is large, the consequence of this uncertainty to predicting iodine volatility in an accident scenario should be minimal.

II.B.2. The Reaction of I_2/HOI/OI^- with H_2O_2

One of the key thermal reactions affecting iodine behavior is that of H_2O_2 with iodine species. Hydrogen peroxide is formed as a primary water radiolysis product, with a G value of 0.7 molecules·(100 eV)$^{-1}$ (Sec. II.C.2). It is less reactive than the other primary water radiolysis products such as e^-, ·OH, and ·H. As a result, hydrogen peroxide accumulates in aqueous solution to yield a steady-state concentration that is considerably higher than

the steady-state concentration of other radiolysis products (see Sec. II.C.2). Its high concentration, coupled with a large rate constant for its oxidation by I_2, has significant repercussions on the aqueous behavior of iodine. Sensitivity studies performed using a mechanistic modeling approach have predicted that gas-phase iodine concentrations are extremely sensitive to the rate of I_2 reduction by H_2O_2 (Ref. 17).

Hydrogen peroxide oxidizes iodide while reducing iodine:

$$2H^+ + 2I^- + H_2O_2 \rightarrow I_2 + 2H_2O \quad (6)$$

and

$$I_2 + H_2O_2 + 2H_2O \rightarrow 2I^- + 2H_3O^+ + O_2 \; . \quad (7)$$

Reaction (6) is of minor importance because radiation-induced oxidation by highly reactive radicals such as ·OH dominates iodide oxidation (Sec. II.C). The reduction reaction, however, strongly affects iodine volatility and is of particular importance in determining the relationship between pH and iodine volatility. Other key reduction reactions include hydrolysis of I_2 and its reaction with O_2^-, which are discussed later.

Although the kinetics of this reduction have been studied for more than a century,[18,19] there still remains a great deal of controversy about the mechanisms, the rates, and the catalytic roles of buffers. Liebhafsky[19] established the following rate law for the reduction reaction between pH 4 and 6 in phosphate buffer:

$$\text{rate} = \frac{k\cdot[H_2O_2]\cdot[I_2]}{[H^+]^2\cdot[I^-]} \; . \quad (8)$$

He suggested that the reduction occurred through the hydrolysis products of I_2, OI^-, and HOI:

$$OI^- + H_2O_2 \rightarrow I^- + H_2O + O_2 \quad (9)$$

and

$$HOI + HO_2^- \rightarrow I^- + H_2O + O_2 \; . \quad (10)$$

Subsequent studies by Fletcher and Miller[20] and Shiraishi et al.[21] reported that Reactions (9) and (10) were catalyzed by acetate and phosphate buffers, suggesting the rate obtained by Liebhafsky was influenced by the phosphate buffer.

A recent examination of the reduction reaction by Kassai-Rabia et al.[22] at pH 7 and 8 determined that the reaction rate is proportional to $1/[H^+]$ rather than $1/[H^+]^2$. The following mechanism was proposed, on the basis of the observed pH dependence:

$$I_2 + OH^- = HOI + I^- \quad (11)$$

and

$$HOI + HO_2^- \rightarrow O_2 + I^- + H_2O \; , \quad (12)$$

with Reaction (11) being rate determining at the studied pH.

Recently, we have undertaken an investigation of the reaction of I_2 with H_2O_2 in citrate, barbital (5,5-diethyl barbituric acid), and phosphate buffer over a pH range between 6 and 9 (Ref. 23). Our results with a citrate buffer in a pH range between 6 and 7 were in good agreement with those obtained by Shiraishi. However, at higher pH values, and using barbital buffer, measurements of the reaction rate as a function of peroxide, iodide, and buffer concentration led to the formulation of a new general rate expression:

$$\text{rate} = \frac{k'\cdot[H_2O_2]\cdot[I_2]}{([H^+]^2\cdot[I^-] + k''\cdot[H^+])} \; . \quad (13)$$

This is consistent with a mechanism in which I_2OH^- reacts with H_2O_2 to form IO_2H:

$$H_2O_2 + I_2OH^- = IO_2H + I^- + H_2O \; , \quad (14)$$

followed by the disproportionation of IO_2H:

$$IO_2H + OH^- = O_2 + H_2O + I^- \; . \quad (15)$$

An alternative mechanism, involving HOI and HO_2^- forming the same intermediate, is also possible. The important feature of this model is that, at low pH values, the reaction rate is dependent on $1/[H^+]^2$, while at high values of pH, it becomes dependent on $1/[H^+]$ because the production of IO_2H becomes rate limiting. This also explains the observation that the peroxide concentration dependence of the rate is more noticeable at high pH values.

We also observed that the rate of iodine reduction by H_2O_2 was catalyzed by all of the buffers (barbital, citrate, phosphate) employed. This is due to an increase in the IO_2H disproportionation rate [Reaction (15)] through

$$IO_2H + B^- \rightarrow O_2 + I^- + BH \; . \quad (16)$$

II.B.3. The Hydrolysis of Iodine

The hydrolysis of iodine,

$$I_2 + H_2O = HOI + I^- + H^+ \; , \quad (17)$$

plays an important role in iodine chemistry. Under most circumstances, this equilibrium is obtained rapidly, and the equilibrium constant, which is well established, is sufficient to predict the speciation. However, because the intermediates in the reaction may be important in predicting iodine behavior, the reaction is better represented by the mechanism proposed by Eigen and Kustin.[24] They studied the kinetics of iodine hydrolysis in the pH range between 4 and 5 and suggested a mechanism in which formation of an intermediate, I_2OH^-, by reaction of I_2 with water or the hydroxide ion, was the rate-determining step. Subsequent dissociation of I_2OH^- into HOI and I^-

was considered to be fast. Their suggested reaction scheme is

$$I_2 + H_2O = I_2OH^- + H^+ , \quad (18)$$

$$I_2 + OH^- = I_2OH^- , \quad (19)$$

$$I_2OH^- = HOI + I^- , \quad (20)$$

and

$$HOI = OI^- + H^+ . \quad (21)$$

A later study by Palmer and van Eldik[25] over a pH range between 3 and 7 found no pH dependence on the observed rate. They suggested that Reaction (20) is much slower than that estimated by Eigen and Kustin.[24] It is uncertain whether the limited data presented by Eigen and Kustin support the pH dependence of their derived rate law, but there are also inconsistencies in the analysis presented by Palmer and van Eldik,[25] for they propose the same reaction set as do Eigen and Kustin, which should lead to a pH-dependent rate.[26]

Uncertainty in the rate constant for formation of I_2OH^- could lead to uncertainties in calculating other iodine species concentrations if this step is the rate-determining step in a sequence of reactions. However, the only important reaction in which this species appears to be involved is the reduction of iodine by peroxide. Since it is not the rate-determining step in this reduction, even a large uncertainty in the rate of formation and disproportionation of I_2OH^- does not appear to influence calculated iodine volatility. This implies that the species can be assumed to be in rapid equilibrium with HOI and I_2. A more important uncertainty, and one that would seriously impact predictions of iodine volatility at higher temperatures, is that the only studies that have measured the temperature dependence of Equilibrium (17) over a large temperature range[27] were undertaken in a pH region where the buffer may have been ineffective.[a] Given that establishment of the equilibrium produces acid, which could change the calculated equilibrium constant, a more detailed study on the hydrolysis temperature dependence is required.

II.B.4. The Disproportionation of HOI and the Dushman Reaction

The disproportionation reactions of HOI,

$$3HOI \rightarrow IO_3^- + 2I^- + 3H^+ , \quad (22)$$

have been studied by a number of groups,[28–32] with somewhat conflicting results. Although these reactions are important in determining the equilibrium concentrations of iodine species in nonradiation conditions, they are generally too slow to have a significant effect on iodine volatility under radiolysis conditions. Therefore, uncertainties in the rate and equilibrium constants are not likely to have an impact on iodine volatility in postaccident containment.

The Dushman reaction,

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O , \quad (23)$$

an equilibrium involving the disproportionation reactions, has likewise been studied by numerous groups.[18,29,33,34] Recently, Palmer and Lyons[29] calculated the equilibrium constant to be 3.97×10^8 $dm^{12} \cdot mol^{-4}$, in good agreement with the value previously determined by Schildcrout and Fortunato.[33] The rate expression for the forward reaction appears to be a function of iodide concentration.[18,34] Prior to the spectrophotometric identification of I_2OH^- as an intermediate in the disproportionation of iodine,[28] it was speculated that a mechanism involving the formation of the polynuclear species $H_2I_2O_3$ at high iodide concentrations was responsible for the observed iodide dependence. However, the observed iodide dependence can be explained by the intermediate I_2OH^-, whose concentration depends on iodide concentration [see Reaction (20)].

II.B.5. Thermal Reactions of Organic Compounds

II.B.5.a. Formation of Organic Iodides. Measurements at the Three Mile Island (TMI)-2 reactor following the 1979 accident showed that organic iodides were a major component of the small amount of iodine that became airborne.[35] The origin of these organic iodides has not been established, and there is still controversy over what the major organic iodide formation mechanisms in postaccident containment will be.[36] This subject will be discussed in detail in Sec. II.D. Briefly, however, recent investigations have indicated that large quantities of water-soluble organic solvents could be leached into the containment sump water from paints. The potential high concentration of these species in a "wet" containment and the rapid rate at which their radiolytic decomposition products may react with molecular iodine in the aqueous phase make it very likely that this mechanism would predominate among organic iodide formation mechanisms[36] in many accident scenarios. Because, in general, the thermal reactions of alkanes and alcohols with I_2 are unlikely or very slow,[37] they will not influence the speciation of iodine. Certain classes of organic compounds do react rapidly with I_2, however, and these are discussed in this section.

The reaction of I_2/HOI with phenol to form iodophenol is fast at high pH, with its rate also dependent on the concentrations of phenol and iodine[38–41]:

$$C_6H_5OH + I_2 = C_6H_4IOH + H^+ + I^- . \quad (24)$$

[a] The authors of Ref. 27 report that boric acid was used to control the pH at 5.6; however, they do not report measuring the pH subsequent to the iodine hydrolysis. Boric acid has a pKa of 9.14 and would lose most of its buffer capacity at such low pH values.

This reaction converts a potentially volatile form of iodine to a less volatile form and thus may be an important reaction from the point of view of mitigating iodine volatility. The reaction is buffer catalyzed, and the general rate law can be expressed as a combination of the uncatalyzed rate, with a rate constant k_{obs}, and a catalyzed rate, with a rate constant k_{HA}, where *HA* is the concentration of buffer:

$$-\frac{d(I_2)}{dt} = k_{obs} \cdot \frac{[C_6H_5OH] \cdot [I_2]}{[H^+] \cdot [I^-]} + k_{HA} \cdot \frac{[C_6H_5OH] \cdot [I_2] \cdot [HA]}{[H^+] \cdot [I^-]} \quad (25)$$

Iodination of ketones at the α position can be either acid- or base-catalyzed and, depending on the conditions, can be quite rapid. In some base-catalyzed reactions, more than one iodination occurs. Methyl ketones and aldehydes, for example, react rapidly with I_2 under basic conditions to form iodoform (CHI_3) and the corresponding organic carboxylate, with the rate-determining step being a series of α-proton abstractions from the methyl group.[37] Iodoform, having a partition coefficient of 88 at 25°C (Ref. 38), is volatile and could have some effect on overall iodine volatility. Molecular iodine reacts readily with alkenes or unsaturated hydrocarbons to produce vicinal di-iodides.[37] Since unsaturated hydrocarbons may easily be formed on painted surfaces by thermal and radiolytic degradation of organic paints, these reactions may also be important in determining the adsorption characteristics of some organic coatings. They are unlikely, however, to lead to formation of volatile organic iodides because such formation would require breaking high-energy bonds in the polymer backbone structure (see Sec. II.D).

II.B.5.b. Hydrolysis of Organic Iodides. Hydrolysis of alkyl iodides to the corresponding alcohol and I^- is a facile process under certain conditions and plays an important role in determining the steady-state concentration of alkyl iodides expected in the aqueous phase. The hydrolysis rates for selected alkyl iodides (R-I) as reported in Ref. 36 are given in Table I. The mechanism, at pH values <10, proceeds primarily by formation of a carbocation, followed by reaction with water. As a result, the relative hydrolysis rates show a trend that can be predicted based on carbon structure and the presence of electron-donating and -withdrawing groups. Tertiary and benzyl iodides hydrolyze very rapidly, secondary iodides more slowly, and primary iodides very slowly. An electron-withdrawing functional group near the iodide results in a small hydrolysis rate constant. For example, iodo-ethanol and iodo-acetic acid hydrolyze very slowly due to destabilization of the intermediate carbocation by an electron-withdrawing group adjacent to the iodide.

Although the range of hydrolysis rate constants reported in Table I is quite wide, the measured activation energies for these reactions were all ~100 kJ·mol^{-1} (Ref. 36). This activation energy is in good agreement with those previously measured for CH_3I (Refs. 42 and 43). The similarity of the activation energies for hydrolysis of a large range of organic iodides is not surprising given that the mechanism, the nucleophile, and the leaving group are the same for all cases.

The large activation energy for hydrolysis of alkyl iodides has implications for their behavior at higher temperature. As an example, the rate constant for CH_3I hydrolysis is three orders of magnitude larger at 70°C than

TABLE I

Measured Hydrolysis Rates and Partition Coefficients of Organic Iodides

Compound	Partition Coefficient at 25°C	Hydrolysis Rate (s^{-1})	Activation Energy (kJ/mol)
Iodomethane	4.8	3.3×10^{-5} at 70°C	104 ± 10
Iodoethane	2.8	7.4×10^{-5} at 70°C	100 ± 6
2-iodobutane	2.2	1.0×10^{-3} at 70°C	97 ± 5
Iodoacetic acid	500 000	2.9×10^{-6} at 70°C	132 ± 10
Iodoethanol	71 000	1.8×10^{-5} at 90°C[a]	Not determined[a]
Benzyl iodide	Not determined	4.6×10^{-3} at 70°C	93 ± 5
2-iodophenol	725	$<6 \times 10^{-8}$ at 80°C[b]	Not determined[a]
2-iodo-2-methylpropane	Not determined[c]	$>1.2 \times 10^{-2}$ at 25°C[d]	105[e]

[a]Only one measurement made due to time required.
[b]Estimated upper limit.
[c]Hydrolysis is too fast to do partition determination.
[d]Lower limit estimated in a 70% methanol, 30% water solution.
[e]Estimate based on data from a 70% methanol, 30% water solution.

at 25°C. In contrast, the partition coefficient of CH_3I at 70°C is only about one-quarter that of its partition coefficient at room temperature.[44] In general, higher temperatures lead to lower overall volatility for organic iodides because hydrolysis becomes an efficient reduction path as temperature increases.

There have been limited investigations of the effect of inorganic impurities on the rate of alkyl iodide hydrolysis. The presence of the metal ions Hg^{2+}, Ag^{+}, and Pd^{2+} have been found to influence both the rate and mechanism of hydrolysis.[45–47] For example, the hydrolysis of methyl, ethyl, and isopropyl halides in aqueous solution containing Hg^{2+} was found to obey the general rate law:

$$\frac{d[RX]}{dt} = k_1[RX][Hg^{2+}] \ , \qquad (26)$$

where RX represents an alkyl halide.[47] Because mechanisms such as this could significantly decrease the steady-state concentration of volatile organic iodides, the effect of trace metal impurities on their rates may be an important consideration.

II.C. Radiation-Induced Reactions of Iodine Species

II.C.1. Radiolytic Oxidation of I^-

In a radiation field, I^- is oxidized by $\cdot OH$ to $I\cdot$, which eventually combines to form I_2:

$$I^- + \cdot OH \rightarrow HOI^- \ , \qquad (27)$$

$$HOI^- \rightarrow I^- + \cdot OH \ , \qquad (28)$$

$$HOI^- \rightarrow I\cdot + OH^- \ , \qquad (29)$$

$$I\cdot + I^- \rightarrow I_2^- \ , \qquad (30)$$

$$I_2^- + I\cdot \rightarrow I_3^- \ , \qquad (31)$$

$$I_3^- \rightarrow I_2 + I^- \ , \qquad (32)$$

and

$$I\cdot + I\cdot \rightarrow I_2 \ . \qquad (33)$$

Although the overall rate of formation of I_2 depends somewhat on subsequent reactions of $I\cdot$ and I_2^- (from $I\cdot + I^-$), it is particularly sensitive to the rate of Reaction (27). There are great discrepancies in the literature regarding the rate constant of Reaction (28), with reported values ranging from 20 s^{-1} (Ref. 21) to 2.3×10^6 s^{-1} (Ref. 48). However, because the competing Reaction (29) is much faster, with a rate constant of 1.2×10^8 s^{-1}, the wide variation in the reported rate constant of Reaction (28) does not have a significant impact on the overall oxidation rate. Reaction (27) is the rate-determining step, and these three reactions may be considered as a single irreversible reaction:

$$I^- + \cdot OH \rightarrow I\cdot + OH^- \ , \qquad (34)$$

with the rate constant of Reaction (27). Reported values for the oxidation rate constant are in good agreement, ranging from 0.9×10^{10} to 1.8×10^{10} $dm^3 \cdot mol^{-1} \cdot s^{-1}$ (Refs. 49, 50, and 51).

Because the rate of oxidation of iodide depends on the concentration of $\cdot OH$, it is important to accurately determine this concentration. The behavior of the $\cdot OH$ radical is discussed in detail in Sec. II.C.3.b.

II.C.2. Reactions of I_2 with O_2^- and HO_2

In oxygenated water, reaction of radiolytically produced electrons with oxygen produces superoxide (O_2^-) and peroxy (HO_2) radicals. Because O_2^- is a strong reductant of molecular iodine, the reactions of these species are important in determining iodine behavior. The reactions of these species with iodine have been studied by Schwarz and Bielski[52] using pulse radiolysis and spectrophotometry. The rates for various reactions were studied over a pH range of 2 to 12 in formate and phosphate buffer, and rate constants were determined for the following:

$$O_2^- + I_2 \rightarrow O_2 + I_2^- \ , \qquad (35)$$

$$HO_2 + I_2 \rightarrow H^+ + O_2 + I_2^- \ , \qquad (36)$$

$$O_2^- + HOI \rightarrow O_2 + I + OH^- \ , \qquad (37)$$

$$O_2^- + I_3^- \rightarrow O_2 + I_2^- + I^- \ , \qquad (38)$$

and

$$O_2^- + I^- + OI^- \rightarrow O_2 + I_2^- + 2OH^- \ . \qquad (39)$$

Schwarz and Bielski have established that formate buffer does not influence the kinetics of the system and have also calculated activation energies for Reactions (35) and (36). Reaction (35), an electron-transfer reaction, is the fastest, with a rate constant of 6×10^9 $mol^{-1} \cdot dm^3 \cdot s^{-1}$, and therefore dominates among the reduction processes.

II.C.3. Radiolysis of Water

Because water radiolysis forms reactive free radicals ($\cdot OH$, e^-, and $H\cdot$) and other products (H_2O_2, HO_2, and O_2^-) that play important roles in iodine chemistry in aqueous solution, it has great importance in determining iodine behavior in the presence of radiation. The water radiolysis processes are, in general, well understood, and comparisons between models[53,54] indicate that water radiolysis species concentrations agree to within a factor of two; therefore, the model is deemed to be adequate for the purpose of determining iodine behavior in the presence of radiation fields typical of those in an accident.

II.C.3.a. Water Radiolysis Model. The first proposed complete reaction kinetics model for the formation of overall water radiolysis products is that of Boyd et al.[53] This model reproduces the experimentally

observed concentrations of H_2O_2, H_2, O_2, etc. as a function of radiation dose. More recently, Buxton et al.[54] have compiled the rate constants of primary water radiolysis reactions with a new set of G values:

$$H_2O \rightarrow \cdot OH(2.7), e^- (2.6), H^+ (2.6), H\cdot (0.6),$$
$$H_2 (0.45), H_2O_2 (0.7) , \quad (40)$$

where the numbers in parentheses are the G values [molecules·(100 eV)$^{-1}$]. Secondary reactions, such as $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, and acid-base equilibria, such as $H^+ + O_2^- = HO_2$, which are required to assess the overall water radiolysis, were not included in the Buxton compilation.

Both the Boyd and Buxton data sets predict similar results for buffered water systems. For instance, calculated concentrations of most free radicals produced during the radiolysis of water are comparable within a factor of 2.

II.C.3.b. Behavior of Water Radiolysis Products. It was previously noted that the rate of iodide oxidation depends on the concentration of ·OH. In the presence of a gamma-radiation field, ·OH is formed as a primary radiolysis product of water with a G value of 2.7 molecules·(100 eV)$^{-1}$. At a dose rate of 2 kGy·h^{-1}, this corresponds to a zeroth-order rate constant of 1.6×10^{-7} mol·dm^{-3}·s^{-1}. However, the hydroxy radical immediately undergoes various reactions to reach a steady-state concentration. The key reactions in pure water that determine the steady-state concentration of ·OH are

$$H_2O \xrightarrow{h\nu} \cdot OH \ [G \text{ value of } 2.7 \text{ molecules}\cdot(100 \text{ eV})^{-1}] , \quad (41)$$

$$\cdot OH + OH^- = O^- + H_2O , \quad (42)$$

$$\cdot OH + HO_2^- \rightarrow HO_2 + OH^- , \quad (43)$$

$$\cdot OH + H_2O_2 \rightarrow HO_2 + H_2O , \quad (44)$$

$$\cdot OH + H_2 \rightarrow H\cdot + H_2O , \quad (45)$$

and

$$e^- + H_2O_2 \rightarrow \cdot OH + OH^- . \quad (46)$$

Any perturbation of the steady-state concentration of ·OH has an impact on the iodide oxidation rate. At iodide concentrations $>10^{-5}$ mol·dm^{-3}, a significant perturbation on the ·OH concentration might be expected from the iodide oxidation reaction itself. Another condition under which the concentration of ·OH is affected to a similar degree might be the presence of large quantities of organic compounds in the aqueous phase. The rate constants for reactions of organic species with ·OH are generally large, having a narrow range from $\approx 1 \times 10^9$ mol^{-1}·dm^3·s^{-1} to 1×10^{10} mol^{-1}·dm^3·s^{-1} [compare 9.7×10^8 mol^{-1}·dm^3·s^{-1} for methanol[55] and 7×10^8 mol^{-1}·dm^3·s^{-1} for methyl ethyl ketone (MEK) (Ref. 56)]. Calculations of the steady-state concentration of ·OH in the presence of such compounds predict that organic reactions would have a significant impact if the organic species concentration is greater than $\sim 10^{-4}$ mol·dm^{-3}.

Another primary water radiolysis product that plays a major role in iodine chemistry is hydrogen peroxide, because of its impact on the steady-state concentration of ·OH and O_2^- (via its reaction with e^-) and its ability to reduce I_2 to I^-, as discussed in Sec. II.C.2. Compared to free radicals, H_2O_2 is rather stable and its concentration is determined mainly by water radiolysis [G value = 0.7 molecules·(100 eV)$^{-1}$] and Reactions (47) and (48):

$$H_2O_2 + \cdot OH \rightarrow HO_2 + H_2O \quad (47)$$

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- . \quad (48)$$

At a dose rate of 2 kGy·h^{-1}, this G value corresponds to a zeroth-order rate constant for H_2O_2 production of 4.0×10^{-8} mol·dm^{-3}·s^{-1}. The H_2O_2 concentration thus would reach 2.5×10^{-5} and 1.4×10^{-4} mol·dm^{-3} within 10 min and 1 h, respectively. However, as the H_2O_2 concentration increases, the reactions of H_2O_2 with e^- and ·OH become important,[53,54] and the concentration of H_2O_2 levels off at a steady-state value of $\sim 1 \times 10^{-4}$ mol·dm^{-3}. This value may be affected by the presence of large ($>10^{-4}$ mol·dm^{-3}) quantities of organic impurities or by catalytic ($<10^{-6}$ mol·dm^{-3}) quantities of transition metals [see Reactions (53) and (55)]. Uncatalyzed thermal decomposition of H_2O_2 to 2·OH is slower than these reactions; therefore, its impact on H_2O_2 behavior is minimal.

Solvated electrons, which are products of water radiolysis, are strong reductants and play an important role in iodine chemistry through their reaction to form O_2^-. In an aerated solution, the steady-state e^- concentration is mainly determined by its formation from water radiolysis and by its reaction with oxygen and hydrogen peroxide:

$$H_2O \xrightarrow{h\nu} e^- \ [G \text{ value of } 2.6 \text{ molecules}\cdot(100 \text{ eV})^{-1}] , \quad (49)$$

$$e^- + O_2 \rightarrow O_2^- , \quad (50)$$

$$e^- + H_2O_2 \rightarrow \cdot OH + OH^- , \quad (51)$$

and

$$[e^-]_{ss} = \frac{k_{50}}{k_{50}\cdot[O_2] + k_{51}\cdot[H_2O_2]} . \quad (52)$$

For an air-saturated solution where the O_2 concentration is $\sim 2.5 \times 10^{-4}$ mol·dm^{-3} and the dose rate is ~ 2 kGy·h^{-1}, the steady-state e^- concentration is extremely low, of the order of 10^{-14} mol·dm^{-3}. In fact, the steady-state e^- concentration will be negligible for all

solutions containing even very low levels of dissolved oxygen. Hence, other electron reactions are not important, and their effect on the steady-state e^- concentration is, in turn, minimal.

Hydroxy radical and solvated electron reactions are uniformly fast, and the steady-state concentrations of these species, which are rapidly achieved, are therefore not significantly perturbed by trace impurities. Slower-diffusing molecular species such as superoxide and peroxide show a much greater range of reactivities, and their steady-state concentrations are more susceptible to perturbations. Because of their importance to the reduction of I_2 to I^-, reactions that can alter the concentration of these species could have a significant effect on the behavior of iodine. Sellers recognized the potential for inorganic impurities, such as trace metal ions, to affect the concentrations of these water radiolysis products[6] and included reactions of Cu and Fe in his model of aqueous iodine chemistry. His proposed reaction set for Fe is as follows:

$$Fe^{2+} + O_2^- \rightarrow H_2O_2 + Fe^{3+} + 2OH^- , \quad (53)$$

$$Fe^{2+} + e^- \rightarrow Fe^{3+} , \quad (54)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH , \quad (55)$$

$$Fe^{3+} + H\cdot \rightarrow Fe^{2+} + H^+ , \quad (56)$$

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- . \quad (57)$$

and

$$Fe^{3+} + O_2^- \rightarrow O_2 + Fe^{2+} . \quad (58)$$

Our preliminary sensitivity analysis study, using the Library of Iodine Reactions in Containment (LIRIC) (see Sec. VI) iodine chemistry model in combination with Reactions (53) through (58), indicates that iodine volatility at pH values >7 could be increased ten times by the presence of Fe^{2+} at concentrations $>10^{-6}$ mol·dm^{-3}. The calculated increase in iodine volatility results primarily from the catalytic consumption of the reductants H_2O_2 and O_2 by the metal. Large quantities of Fe, such as those observed in the aqueous phase in several Radioiodine Test Facility[57] (RTF) studies performed in stainless steel vessels, may therefore have some effect on iodine volatility.

II.D. Role of Organic Materials in Containment

II.D.1. Dissolution and Radiolysis

Results of recent intermediate- and bench-scale experiments simulating reactor accident conditions have shown that, in the presence of radiation, organic compounds could significantly alter the pH and dissolved oxygen concentration of the sump water.[58,59] The discussion in Secs. II.B and II.C has demonstrated that both pH and dissolved oxygen are important parameters in determining aqueous iodine behavior and therefore iodine volatility. The presence of organic impurities in the aqueous phase may also influence iodine behavior by inducing formation of organic iodides and altering the rate of oxidation of I^- to I_2 by competing with I^- for reaction with ·OH. An understanding of the effect of organic compounds on iodine chemistry is therefore important.

An example of the changes in pH, dissolved oxygen concentration, and iodine volatility that are induced by addition of an organic compound to an irradiated solution of CsI is shown in Fig. 2. These results were obtained in RTF experiments in which 1×10^{-3} mol·dm^{-3} MEK was added to an irradiated solution of CsI in a zinc primer–coated carbon steel vessel.[60] RTF tests in organic-painted vessels have also shown that in the absence of pH control, aqueous pH decreased in the presence of

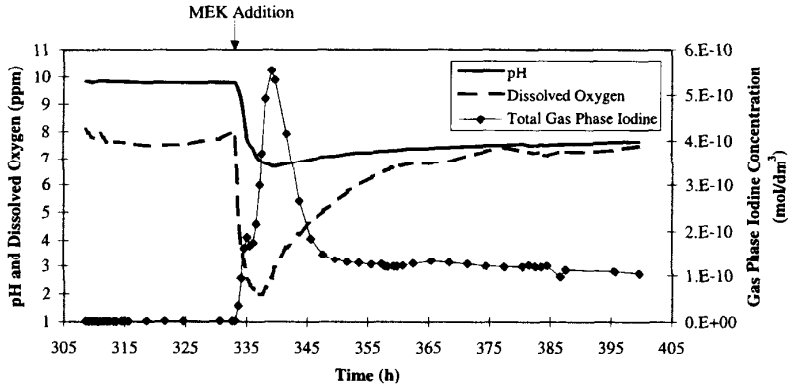

Fig. 2. Effect of MEK addition on pH, dissolved oxygen concentration, and airborne iodine concentration [I(*g*)] in an RTF test performed in a zinc-primed vessel. The test was performed in the presence of radiation at an absorbed dose rate of 1.8 kGy·h^{-1}

radiation.[59] This results in a decrease in the rate of reduction of volatile I_2 to nonvolatile I^-, thereby increasing the iodine concentration in the gas phase. Figure 3 shows both the total gas-phase iodine concentration and the solution pH as a function of time during the tests in organic-painted vessels. The increases in the gas-phase iodine concentration are closely related to decreases in pH.

The observation that irradiated CsI solutions in contact with organic-painted coatings undergo the same pH changes as do those in which organic impurities are purposely added suggests that the same mechanism could be responsible for this phenomenon. In both cases, the observed effect is the result of the radiolytic decomposition of an organic compound, which consumes oxygen and eventually forms organic acids and CO_2:

$$RH + \cdot OH \rightarrow R\cdot + H_2O \quad (59)$$

and

$$R\cdot + O_2 \rightarrow RO_2\cdot \rightarrow\rightarrow R'\cdot, \text{ alcohols, aldehydes, acids, and } CO_2 \; . \quad (60)$$

Surfaces painted with organic coatings in contact with water are a known source of organic impurities, an observation that is supported by the observed organic concentrations in RTF tests that had been performed in organic-painted vessels in the absence of radiation. Concentrations in the range of 1×10^{-3} dm^{-3} for methyl isobutyl ketone (MIBK), the major constituent of some paint thinners, and 1×10^{-6} $mol \cdot dm^{-3}$ for MEK, toluene, and xylene, other major components of paint solvents and thinners, have been observed in the aqueous phase in these experiments (Figs. 4 and 5). These organic compounds were not found at similar concentration levels in irradiated solutions in contact with the same surfaces, leading to the conclusion that at 25°C and at dose rates of 1 to 2 $kGy \cdot h^{-1}$, the rate at which solvents dissolved from the painted surfaces into the aqueous phase was slower than their subsequent radiolytic decomposition rates.

The relative rates of radiolytic decomposition versus dissolution can be estimated from a comparison of data from two RTF experiments. In the test shown in Fig. 2, an immediate decrease in pH and dissolved oxygen concentration (accompanying the decomposition of MEK) was observed when MEK was intentionally added to an irradiated solution of CsI to give a concentration of 1×10^{-3} $mol \cdot dm^{-3}$. Recovery of the dissolved oxygen concentration, which implies that radiolytic degradation to acids and CO_2 is essentially complete, requires only ~20 h. In contrast, dissolution of MIBK from vinyl paint to reach concentrations of 1×10^{-3} $mol \cdot dm^{-3}$ in the same water volume required almost 100 h (Fig. 4).

The relative rates of radiolytic decomposition versus dissolution have been confirmed by bench-scale studies that are discussed in Refs. 36, 61, 62, and 63. The rate of release of organic constituents from carbon steel

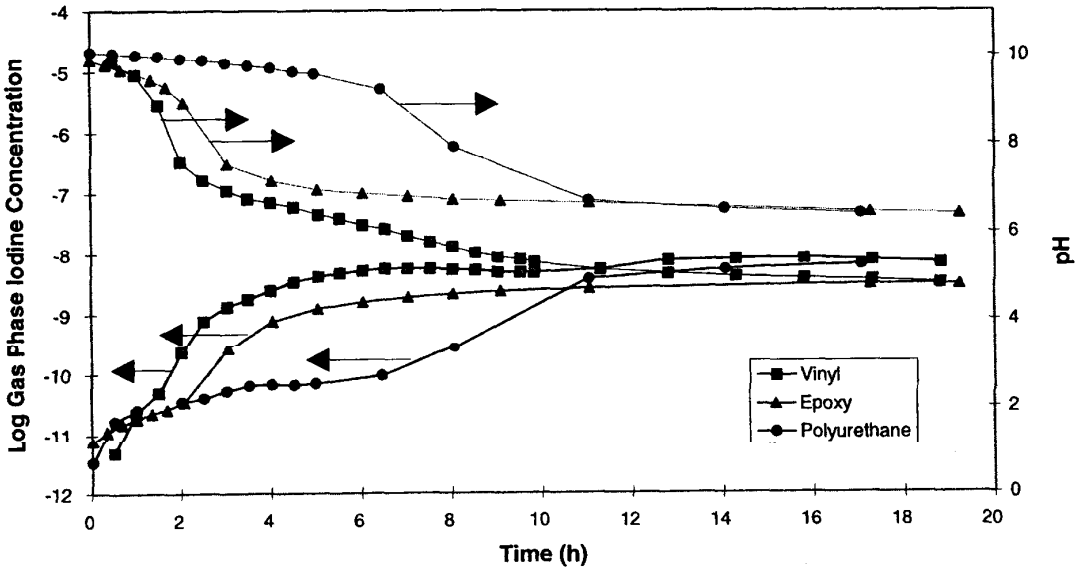

Fig. 3. Effect of surface coating on iodine volatility in the RTF. The tests were performed in the presence of radiation at an absorbed dose rate of ~1.5 $kGy \cdot h^{-1}$, with an initial pH of 10. The pH of the water was not controlled during the tests.

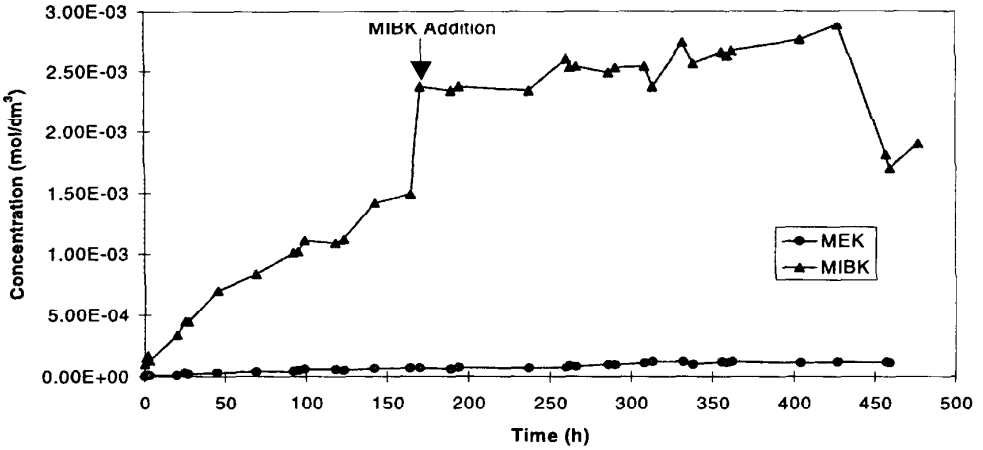

Fig. 4. Aqueous-phase concentration of MIBK and MEK in RTF tests performed in a vinyl-painted concrete-lined vessel in the absence of radiation. No measurable amounts of these organic compounds were present in a radiation field. The sudden increase in the MIBK concentration at ~170 h was due to a deliberate injection of 1.0×10^{-3} mol·dm^{-3} MIBK into the aqueous phase.

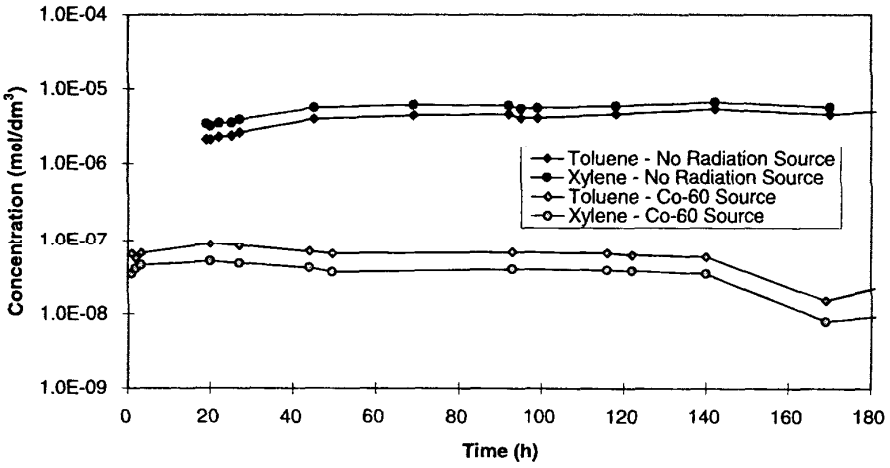

Fig. 5. Gas-phase concentrations of aromatics during RTF tests performed in vinyl-painted concrete-lined vessels with and without radiation. Other compounds were observed but have been omitted for clarity.

coupons coated with zinc-primed vinyl and zinc-primed polyurethane and epoxy paints in the absence of a radiation source and over the temperature range 25 to 90°C was studied.[61] These studies found that both aliphatic and aromatic organic compounds (paint solvents) were released from the painted surfaces in the absence of radiation. Figure 6 shows the organic compounds detected in the gas phase from immersed vinyl coupons that were previously aged in air for ~2 months at 40°C. The major component of the thinner present in this paint was MIBK, as determined by both gas- and aqueous-phase analysis. Smaller quantities of toluene, xylene, MEK, and acetone were observed. The concentration of organic solvent in aqueous solution [ORG(aq)] at time t follows first-order kinetics:

$$[\mathrm{ORG}(aq)]_t \propto [\mathrm{ORG}(ab)]_0 \cdot (1 - \exp(-kt)) \quad , \quad (61)$$

where

(aq) = aqueous phase

(ab) = absorbed phases

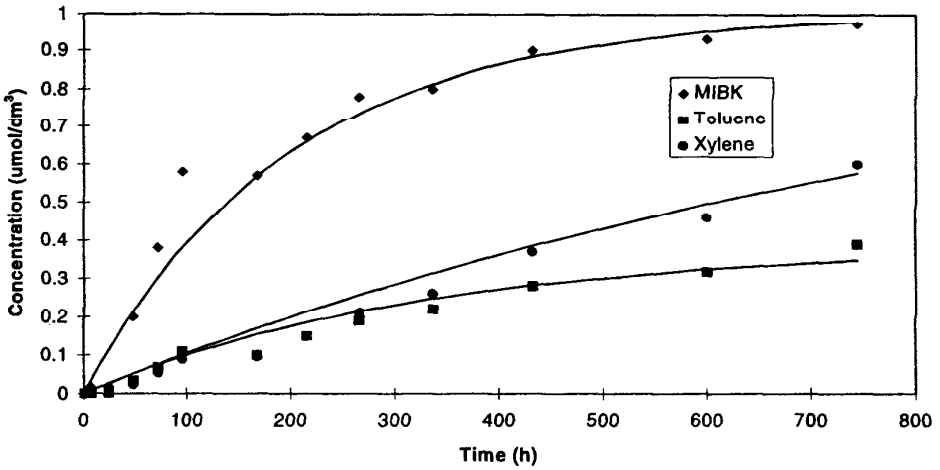

Fig. 6. Organic compounds detected by gas chromatography in the dissolution test with vinyl coupons at 40°C. The curves were fitted to the data using Eq. (34) in the text.

k = dissolution rate constant (s^{-1})

$[ORG(ab)]_0$ ($mol \cdot dm^{-3}$)

= maximum concentration of solvent in the paint polymer phase available to be released into water.

The dissolution rate constant for vinyl paint was observed to depend strongly on temperature, showing an Arrhenius temperature dependence with an activation energy of 82 ± 11 $kJ \cdot mol^{-1}$ (Fig. 7). Similar activation energies were observed for polyurethane and epoxy paint. The pH of the water did not have a significant impact on the dissolution process from any of the paints, and the maximum concentration of organic compound in the aqueous phase was found to depend only on the age of the coating. This implies that the initial solvent concentration within the coating controls the total amount of organic compound released and that the solvent content in the coating decreases with aging because of evaporative losses.

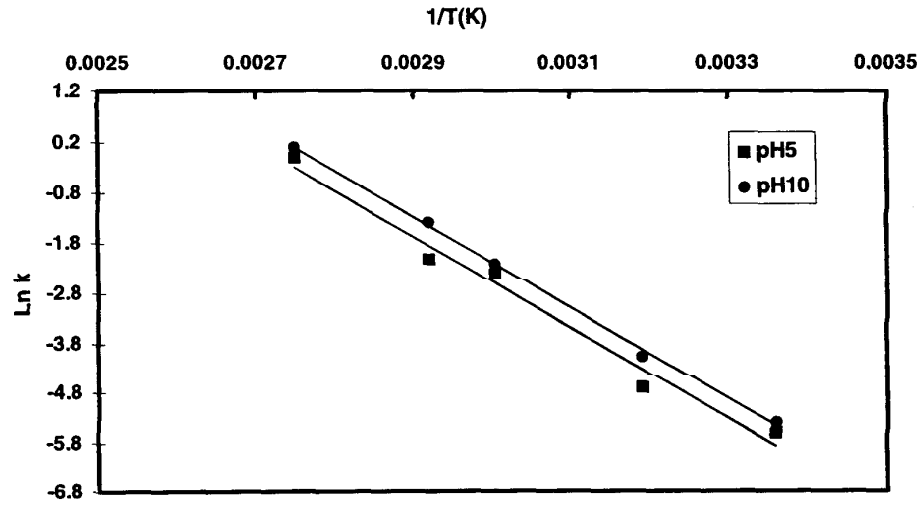

Fig. 7. Arrhenius plot for the dissolution of MIBK in water at pH 10 from vinyl-painted coupons. The line shows the fit for an activation energy of 82 ± 11 $kJ \cdot mol^{-1}$.

The effect of radiation on the rate of dissolution of the organic compounds was negligible. Release of MIBK from coupons in which dissolution followed a period of irradiation appeared to have the same rate constant, although the final concentrations of MIBK in solution were smaller. Radiation did, however, rapidly decompose the organic compounds once they had been released into the aqueous phase. Solutions in contact with vinyl-painted coupons that were irradiated subsequent to a dissolution period were found to yield increased gas-phase concentrations of acetaldehyde, acetone, and MEK and reduced concentrations of MIBK. The former three compounds were found to arise as a result of decomposition of dissolved MIBK.

The radiolytic decomposition of the common paint solvents, MEK, MIBK, and toluene in the aqueous phase, has also been studied as a function of radiation dose, initial organic concentration, and initial pH. Detailed studies were conducted primarily using MEK (Refs. 62 and 63), which was chosen as a model organic compound because it is a common solvent and is comparable to many of the other common organic species found in containment paints (e.g., acetone, heptanone, and MIBK). Based on the experimental results of the decomposition studies,[62] a detailed kinetic model for the steady-state gamma radiolysis of aerated aqueous solutions containing MEK was developed.[63] This full model reproduces the experimental data reasonably well; however, because MEK is only one of the many organic impurities expected to be found in the sump following an accident, a more generally applicable model was desired. Consequently, a simplified model, which is still based on the mechanistic understanding gained from the full model, was developed. Furthermore, its much smaller size (the full model contains >150 reactions) makes it much more practical for incorporation into a safety analysis code. A complete description of these models can be found in Ref. 63.

From the detailed mechanistic studies, at gamma-radiation dose rates in the aqueous phase of 10 and 1 $kGy \cdot h^{-1}$, 90% of a 1×10^{-3} $mol \cdot dm^{-3}$ solution of MEK would be decomposed within 20 min and 4 h, respectively, by which time the pH would drop to below 5. This decomposition rate is much faster than the rate for release of organic solvents from painted surfaces at room temperature observed in both our bench-scale and RTF studies. This supports our conclusion that the dissolution of organic solvents may be the key rate-controlling process for pH changes and organic iodide formation expected in containment after an accident.

Dissolution studies, in combination with extensive studies on the radiolysis of organic compounds[36] and various RTF test results, show that under many of the conditions expected to be typical of reactor accidents, the rates of radiolytic decomposition of organic compounds and formation of organic iodides are much faster than the rate of organic release from paints. The latter process appears to be the rate-determining step for the changes in pH, dissolved oxygen concentration, and organic iodide concentration observed when solutions of CsI are irradiated in the presence of painted surfaces. Consequently, detailed kinetic mechanisms for the radiolytic decomposition of all organic compounds and formation of all organic iodides may not be necessary.

II.D.2. Formation of Organic Iodides

Formation of organic iodides in containment could occur through homogeneous gas- or aqueous-phase reactions or through heterogeneous processes in either phase. Homogeneous gas-phase processes are dealt with in Sec. III.B, while heterogeneous processes are covered in Sec. IV.B. Because of the potential for the presence of large amounts of organic compounds in the aqueous phase and a higher I_2 concentration in the aqueous phase than in the gas phase, it is considered that the homogeneous aqueous-phase process is the main contributor to the formation and decomposition of organic iodides. Although there are still discussions regarding whether heterogeneous or homogeneous aqueous-phase reactions are the main mechanism for organic iodide formation, dissolution studies (see Sec. II.D.1) and intermediate-scale (RTF) tests strongly suggest that the latter dominates under conditions relevant to the RTF.

Intermediate-scale studies (see Figs. 8 and 9) have demonstrated that irradiated CsI solutions in contact with painted surfaces produce organic iodides whose concentration profiles closely followed that of I_2. Figure 9 also shows that when MEK was added into the aqueous phase, the increase in gas-phase CH_3I concentration closely followed that of the total gas-phase iodine concentration. These data suggest that the organic iodides (including CH_3I) are formed by the reaction of I_2 with organic compounds in the aqueous phase and that these reactions are relatively fast. Various ketone, alcohol, and alkyl radicals formed by the radiolysis of MIBK and MEK would easily react with I_2, methyl iodide being one of the products. Aromatic organic iodides can be formed by thermal and radiolytic reactions of I_2 with phenol derivatives,[15,16] which are formed in significant quantities during the radiolysis of aromatic solvents such as xylene and toluene.

Early studies on organic iodide formation focused mainly on CH_3I because of its high volatility and because methane or other low-molecular-weight alkanes were believed to be the major organic impurities in the containment atmosphere following an accident. However, RTF tests performed in organic-painted vessels have found that a large portion of the organic iodides formed from containment paint impurities are less volatile than CH_3I. Figure 8 shows iodine speciation measurements obtained in an RTF test performed with a vinyl-painted vessel. In later stages of the test, the concentration of organic iodides in the gas phase was orders of magnitude lower than that observed in the aqueous phase. If CH_3I were the predominant organic iodide, the gas-phase

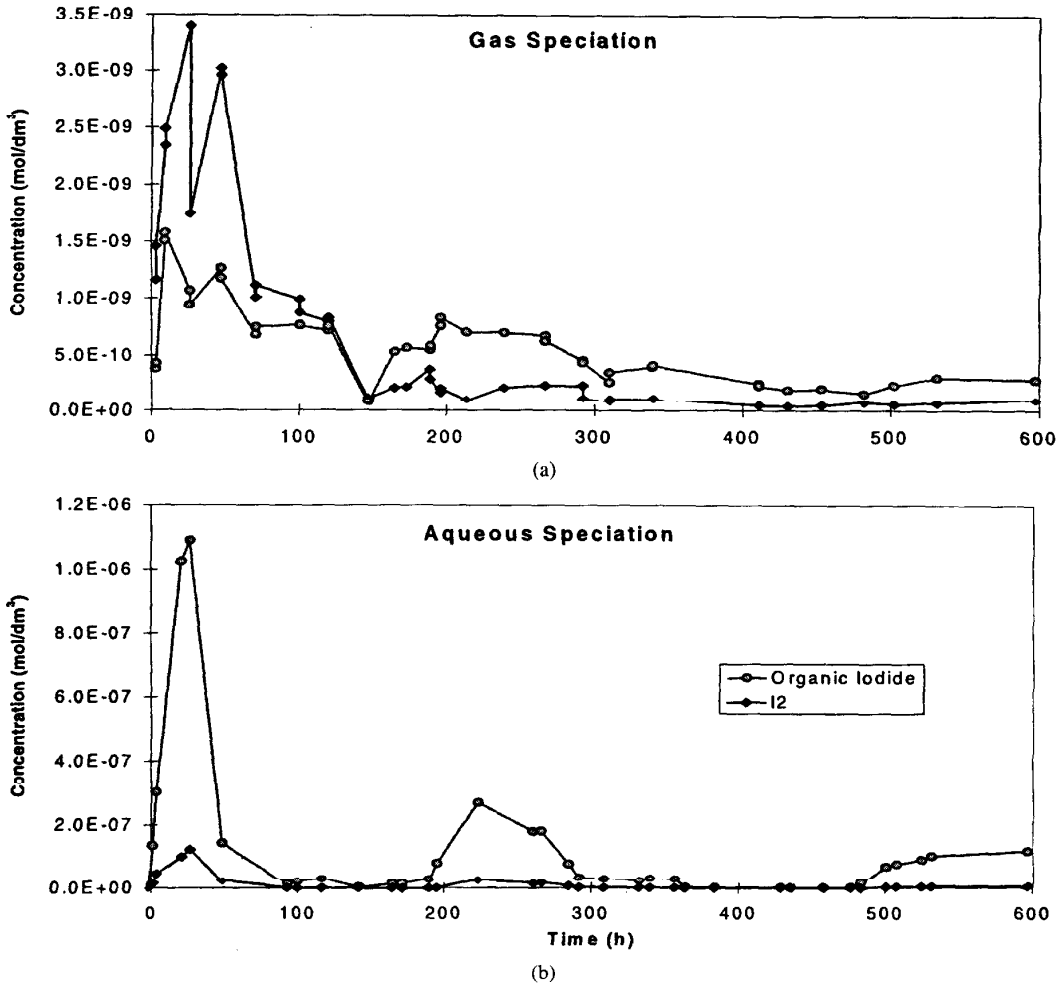

Fig. 8. Aqueous- and gas-phase iodine speciation in an RTF test performed in a vinyl-painted vessel.

concentration would be expected to be only five times less than the aqueous phase (based on a partition coefficient of 4.8 as given in Table I). It should also be noted that even when organic iodides constitute a large fraction of the iodine species concentration in the gas phase (compare Fig. 8, later stages of the test), they do so only because I_2, which dominated the gas phase in the earlier test stages, is preferentially adsorbed on the surface of the vessel over time.

RTF studies have established that a wide range of organic iodides, with varying volatilities, might be expected as the result of reaction of iodine species with organic impurities in containment. Establishing a range for the partition coefficients of these species and for the rate of their formation and destruction in the aqueous phase is necessary in order to determine an upper and lower limit for iodine volatility. However, conducting detailed studies of these parameters for every possible type of organic iodide would be impractical. Furthermore, modeling studies on RTF tests performed in vinyl-painted vessels[64] demonstrate that even without including organic iodide formation in the model, it is possible to reproduce RTF data reasonably well as long as the pH input is correct.

The explanation of this behavior involves the most important factors controlling iodine volatility under these conditions and deserves close attention. The effect of organic materials on iodine volatility is primarily due to their radiolysis in the aqueous phase, which leads to the formation of carboxylic acids and CO_2. These acidic

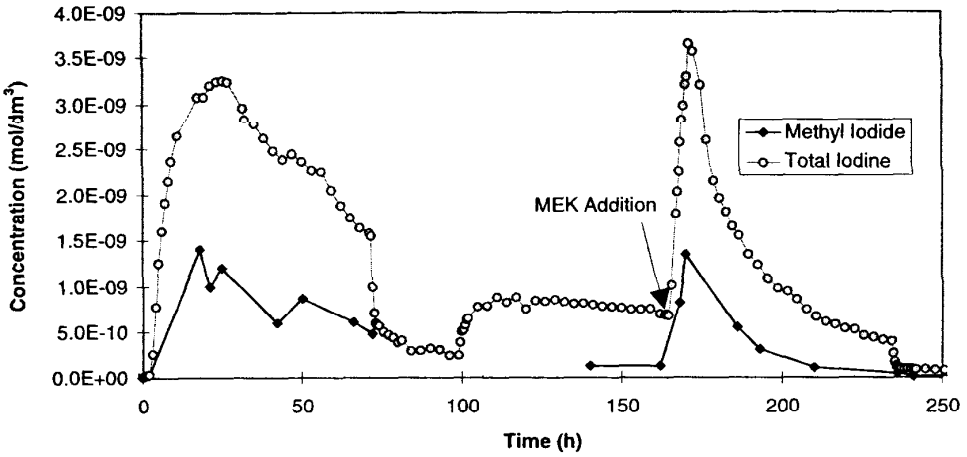

Fig. 9. Effect of organic addition to the aqueous phase on the gas-phase iodine concentration and speciation in an RTF test performed in an epoxy-primed, polyurethane-painted carbon steel vessel.

radiolysis products act to lower the aqueous pH, the most significant variable affecting the steady-state concentration of I_2 in the aqueous phase [see Reaction (6), Sec. II.B.2). The result of lower pH is that there is an increased concentration of I_2 in the aqueous phase.

Radiolysis of organic species also gives rise to organic radicals, which react readily with I_2 to generate organic iodides. Formation of these organic iodides is symptomatic of the higher I_2 concentrations generated by the pH changes accompanying organic radiolysis; i.e., it is a secondary effect that has the same pH dependence as that of I_2 formation. Furthermore, although some of these organic iodides, such as CH_3I, are more volatile than I_2, very few highly volatile species are generated under the conditions just described. Many other higher-molecular-weight organic iodides with volatilities that are lower than that of I_2 are produced. The presence of a few species more volatile than I_2 and many species less volatile than I_2 appears to compensate. Therefore, providing the correct pH input and making the assumption that all gas-phase iodine is in the form of I_2 gives a reasonable estimate of the total volatile iodine present in the gas phase.

III. GAS-PHASE REACTIONS

III.A. Thermodynamics of Gaseous Iodine Species

The main chemical forms of iodine that are likely to exist in the gas phase are molecular iodine and organic iodides. As mentioned previously, the volatility of HOI, which is easily formed in the aqueous phase by the hydrolysis of I_2 and has been observed spectroscopically in solution,[29,31,65] has been a controversial subject.[12,13,65-67] Gaseous HOI has not been detected unambiguously, except in matrix isolation studies[68-70] and a recent FTIR study using a long path cell.[14] A low value for the HOI partition coefficient, that reported by Lin,[12] has been used in some studies estimating iodine volatility for accident conditions[7]; however, subsequent studies have shown that Lin's value is too conservative, and the partition coefficient of HOI is now considered to be $>10^4$ (Ref. 13).

The potential for equilibrium among only the gas-phase species does not provide any valuable information on iodine behavior; the distribution of these gaseous species is determined by the aqueous-phase chemistry. Thus, this review of gas-phase thermodynamics is limited to partition coefficient determinations of the main gaseous forms of iodine.

Gibbs energies of formation of iodine species in both the gas and aqueous phases, obtained from vapor pressure and solubility measurements, respectively, allow the partition coefficients to be calculated. The partition coefficients of I_2 are well established: 80 and 12 at 25 and 80°C, respectively.[30]

Measured partition coefficients for several selected organic iodides are presented in Table I (Ref. 37). The partition coefficients of the organic iodides studied ranged over several orders of magnitude. Organic iodides with carbonyl, alcohol, or carboxylic acid substituents are more water soluble than their unsubstituted counterparts by virtue of their polarity. Since oxygen tends to react very rapidly with organic radicals to form perhydroxyl radicals and eventually alcohols and ketones, these types of organic iodides are expected to be created from organic impurities that may be present. Iodophenols are also likely to be formed because in the presence of radiation and in oxygenated aqueous solutions, aromatic compounds, such as toluene and xylene, undergo hydroxylation to form phenols, which react rapidly with I_2/HOI.

As discussed in Sec. II.D.2, comparison of the gas- and the aqueous-phase speciations from the RTF test in Fig. 8 indicates that the majority of organic iodides formed in the aqueous phase from solvents leached from paints are somewhat less volatile than I_2 and much less volatile than CH_3I. This comparison has also been made for several other RTF experiments, in vessels coated with a variety of paints, with the same conclusion. In general, it appears that in the presence of organic compounds, formation of organic iodides that are less volatile than I_2 (e.g., highly soluble iodo-ketones, alcohols, phenols, and acids) serves to reduce overall iodine volatility from that expected in the absence of organic species by reducing the molecular iodine concentration in the aqueous phase.

Because it would be extremely difficult to identify all of the organic iodides that could form and assign partition coefficients to each of them, developing an organic iodide model for predictions of iodine volatility will probably have to rely on obtaining an estimate for an overall partition coefficient for organic iodides. Detailed studies on organic iodide formation from several solvents found in paints will provide data on the distribution of organic iodides likely to be found. From these data, a weighted average for the partition coefficient for organic iodides can be obtained. Until then, using an estimate for H that assumes that the overall partition coefficient for organic iodides is the same as that for I_2 appears to be reasonable (see Sec. II.D.2) and conservative.

III.B. Thermal Organic Iodide Formation in the Gas Phase

Postma and Zavadoski[71] reviewed a number of experiments conducted prior to 1972 on the conversion of molecular iodine to organic iodides by thermal reactions. These experiments were done over a broad range of initial molecular iodine concentrations in the gas phase (10^{-13} to 10^{-6} mol·dm^{-3}) and in vessels ranging in size from 0.2 to 1.2×10^4 m^3. The only organic compound used in these experiments was methane at its natural concentration in air, of the order of 10^{-8} mol·dm^{-3}. Conversion to organic iodides (probably CH_3I), as measured with Maypack filters, ranged from $\sim 10^{-2}$% to ~10%, strongly depending on the iodine concentration. Postma and Zavadoski obtained the following linear least-squares fit to the data within a factor of 10:

$$\log_{10}(\% \text{ conversion}) = -0.726 + 0.26 \log_{10} C \ , \quad (62)$$

where C is the iodine concentration in mg·m^{-3}. They noted that the conversion varied by more than a factor of 10 among the various laboratories. Moreover, conversion to organic iodides appeared to decrease with increasing test-vessel size. The large variation in conversion factors is most likely due to difficulties in separating organic and inorganic forms of iodine with Maypack filters. These crude analytic tools appear to overestimate organic iodides by as much as a factor of 5 (Ref. 72).

The predominant organic materials in the atmospheres of containment buildings following an accident[73] may be quite different from methane in nature, and their concentrations could be several orders of magnitude higher (10^{-5} mol·dm^{-3}) than those used by Postma.[71] The sources of these materials are the constituents in paints, coatings, insulation, seals, gaskets, connectors, ion-exchange resins, lubricants, etc. According to Beahm et al.,[74] the largest amount of organic material in containment buildings is in the form of electrical cable insulation and jacketing, which is made mostly of ethylene-propylene rubber, hypohalon, and neoprene. He has estimated, based on data from Wing,[75] that one-half hour after an accident, radiation effects could result in a release of organic gases in the containment atmosphere at a rate of 0.48 mol·m^{-3}·s^{-1}. However, even if it is assumed that the total amount of iodine released into the containment atmosphere was in the form of I_2, its conversion to organic iodide would be only 0.38%, based on the relationship defined in Eq. (62). Since most of the iodine is expected to be released to containment as CsI, the percentage converted to organic iodide will be considerably less than this. Moreover, several intermediate-scale studies have shown that organic iodide formation in the aqueous phase and its subsequent partitioning to the gas phase are sufficient to account for the observed gas-phase organic iodide concentrations observed in these experiments.[37] Therefore, thermal conversion of I_2 to organic iodides in the gas phase is considered to be of little importance.

III.C. Radiolysis Reactions in the Gas Phase

Radiation induced reactions in the gas phase may affect iodine volatility in various ways: (a) Organic free radicals may be created, which react with airborne I_2 to produce organic iodides; (b) nitric acid produced by the radiolysis of N_2 and O_2 in moist air may change the pH of the aqueous phase, affecting iodine chemistry; and (c) ·OH radicals or ozone produced by the radiolysis of moist air may react with airborne iodine species to form soluble iodine oxides.

There have been several studies of the radiation-induced formation of organic iodide by homogeneous gas-phase reactions. Although these studies were conducted under conditions far different from those expected in an accident, they have established that the dominant mechanism of organic iodide formation involves the reaction of organic radicals with I_2:

$$R\cdot + I_2 \rightarrow RI + I\cdot \ . \quad (63)$$

The organic radicals are formed mainly by reactions of organic compounds with ·OH, which is generated by the radiolysis of water vapor:

$$RH + \cdot OH \rightarrow R\cdot + H_2O \ . \quad (64)$$

Postma and Zavadoski,[71] by interpolating between results of Barnes et al.[76] and those of Charamathieu

et al.,[77] estimated an upper limit for the conversion of molecular iodine to organic iodide as a function of iodine concentration. For an iodine concentration of 4×10^{-8} mol·m^{-3} (10 mg·m^{-3}), this interpolation yields a G value of $\sim 8 \times 10^{-4}$ molecules·(100 eV)$^{-1}$, which, for a total dose of 10 kGy, corresponds to ~1.4% conversion to organic iodides. Such an interpolation overestimates the yield of organic iodides because the studies by Barnes and Charamathieu were done either at iodine concentrations several orders of magnitude higher than those expected in an accident or with no oxygen present. The presence of oxygen would significantly reduce organic iodide formation by scavenging organic radicals and eventually forming alcohols and aldehydes:

$$R\cdot + O_2 \rightarrow ROO\cdot \rightarrow ROH, RCO_2H, \text{ etc } . \quad (65)$$

Model calculations, performed by Sagert[78] for an air mixture containing I_2 and methane in concentration ranges of 7.8 to 39×10^{-9} and of 2 to 8×10^{-8} mol·dm^{-3}, respectively, suggest that CH_3I cannot be formed from the attack of methyl radicals on I_2 as in Reaction (63), since the oxygen present in the air competes far too efficiently for the methyl radicals. Although the oxygen uptake by larger organic molecules may be slower, the formation of organic iodide in gas-phase reactions is not likely to be significant.

The study by Sagert also addressed other aspects of radiation-induced gas-phase reactions. A database used to model the radiolysis of moist air was based on the model developed by Busi et al. for the electron-beam-induced oxidation of SO_2 and NO_x in flue gases.[79,80] This database predicts the formation of nitric acid with a G value of ~3.19 molecules·(100 eV)$^{-1}$, in addition to a significant formation of ozone [G = 1.65 molecules·(100 eV)$^{-1}$]. Other significant yields are H_2 [G = 0.09 molecules·(100 eV)$^{-1}$] and H_2O_2 [G = 0.25 molecules·(100 eV)$^{-1}$]. In this model, a radiation dose rate of 2 kGy·h^{-1} in the aqueous phase corresponds to an absorbed dose rate of $\sim 4 \times 10^{14}$ eV·dm^{-3}·s^{-1} for the air mixture used. At this absorbed dose rate, the rate of production of nitric acid is calculated to be $\sim 2 \times 10^{-11}$ mol·dm^{-3}·s^{-1}. If most of the nitric acid produced in the gas phase by this process ended up in the aqueous phase (for gaseous and aqueous volumes typical of those expected in containment), it would result in a significant decrease in aqueous pH, which would increase iodine volatility. However, in intermediate-scale studies performed at similar dose rates, the pH changes expected due to formation of nitric acid in the gas phase were not observed. This discrepancy has not yet been resolved.

According to the calculations by Sagert, I_2 can be rapidly oxidized by radiolytically produced ·OH and eventually converted into water soluble oxygenated species, such as I_2O_5 and I_4O_9. The concentration of airborne I_2 was calculated to be reduced by several orders of magnitude in ~2 to 20 min at a dose rate of 10 kGy·h^{-1}, depending on whether the model included a reaction set involving HOI. Oxidation of I_2 in the gas phase may be important, but reactions involving species such as HOI and IO_2, whose stabilities in the gas phase are unknown, are speculative. Moreover, the concentrations of I_2 observed in several intermediate-scale studies are consistent with those expected for formation in the aqueous phase, implying that appreciable gas-phase oxidation does not occur.

Other radiolysis products that may influence iodine volatility are hydrogen peroxide and ozone. In the absence of I_2, the calculated G values for the formation of these species in the gas phase are 0.25 and 1.65 molecules·(100 eV)$^{-1}$, respectively.[73] In the presence of iodine, both ozone and hydrogen peroxide yields are lower. This occurs because these species are principally formed from hydroxy radicals. The G value for H_2O_2 in the absence of iodine corresponds to an H_2O_2 production rate of 1.6×10^{-12} mol·dm^{-3}·s^{-1} at a radiation dose rate of 2 kGy·h^{-1}. This is much slower than the H_2O_2 production rate in the aqueous phase. Therefore, the mass transfer of the H_2O_2 formed in the gas phase to the aqueous phase will have negligible impact on the aqueous H_2O_2 concentration.

IV. SURFACE EFFECTS

IV.A. Adsorption-Desorption on Surfaces

The interaction of iodine species with surfaces can also play a role in the determination of iodine volatility. Adsorption of iodine on surfaces may significantly deplete both gas- and aqueous-phase iodine concentrations, so these surfaces were recognized early as potentially important passive iodine sinks.[81-87] Adsorption-desorption phenomena may also play an important role in determining the time-dependent partitioning of iodine. Many studies have been performed to assess iodine adsorption rates on surfaces.[81-84,88] The resuspension or revolatilization of iodine from surfaces has also been investigated, though not as extensively. A thorough discussion of the existing literature is beyond the scope of this review; therefore, only the most significant work is presented here.

A number of large-scale experiments performed in the 1960s on iodine deposition in simulated containment environments[81-84] established that containment surfaces were effective sinks for iodine and that adsorption of iodine was dependent on many factors. The rate of deposition of I_2 from the gas phase onto most surfaces was found to increase with increasing humidity and to decrease with increasing temperature.[84]

The most complete set of smaller-scale deposition experiments on surfaces was performed by Rosenberg et al.[85,87] and Genco et al.,[86] who studied a variety of surfaces under various conditions. They found that the

initial deposition kinetics of gas-phase adsorption on most surfaces is a first-order process, physical in nature, and limited only by the rate of mass transfer of iodine to the surface. This behavior is also applicable to the long-term gas-phase deposition kinetics onto so-called inert surfaces, such as preoxidized Zircaloy and stainless steel.[86] For gas-phase deposition on reactive surfaces, diffusion-controlled first-order deposition was observed initially. At longer times, as saturation of the surface was approached, the adsorption was governed by simultaneous first- and second-order (chemical reaction) processes depending on paint type.[83-87] Many paints examined in the study by Rosenberg exhibited irreversible iodine adsorption for both aqueous- and gas-phase deposition. Methyl iodide was not retained in as large a quantity as was I_2; however, there was more irreversible adsorption of methyl iodide than of I_2. A summary of relevant gas-phase deposition data compiled in Ref. 86 is tabulated in Table II.

Recently, extensive studies on the adsorption/desorption behavior of iodine on stainless steel have established that it is also a complex process, despite the apparent "first-order" behavior from which a deposition velocity can be extracted.[88] The change in deposition velocity and desorption rate as a function of oxygen concentration and observations of changes of surface morphology as a result of corrosion have led the authors to propose a two-step process whereby iodine is adsorbed on active Fe sites on the metal surface and then reacts with oxygen to leave an iron oxy-iodide:

$$Fe + I_2 \rightarrow FeI_2 \qquad (66)$$

and

$$FeI_2 + (y/2)O_2 \rightarrow FeI_xO_y + (1 - x/2)I_2 \ . \qquad (67)$$

The rates of Reactions (66) and (67) are of similar order, and the overall rate of iodine adsorption increases in the presence of FeI_xO_y, suggesting that formation of an FeI_xO_y scale on the metal surface exposes more active Fe sites. The oxidation of iron in the presence of iodine has been observed by other workers.[89]

Despite a large body of literature on the surface adsorption of iodine, there are many areas that are not complete. The major problem with much of the existing data is that detailed kinetic studies have not been performed; rather, an integral first-order rate has been deduced from the overall observed adsorption. This simplification of the kinetics of deposition, which are in many cases more complex,[85,89] would lead to uncertainty in applying the existing data to conditions outside the studied range. An additional and more important gap in the literature is that the chemical nature of sorbed iodine on most surfaces and the rate at which it is desorbed have not been established. This leads to uncertainty in assessing the speciation of sorbed iodine, the potential for its revolatilization, and the ease of decontamination of surfaces. Finally, surface deposition as a function of temperature and relative humidity (including condensing conditions) has not been established rigorously.

IV.B. Formation of Organic Iodides on Surfaces

Direct chemical reaction of iodine with painted surfaces has been invoked in several studies[90,91] that have examined the formation of organic iodides on surfaces exposed to I_2 or I^-. Bennett et al.[20] have identified methyl, ethyl, n-propyl, and n-butyl iodide from the reaction of epoxy paints with I_2 in the gas phase at 100°C. Organic iodides were also observed in the gas phase at ambient temperatures from the reaction of I^- in the aqueous phase with painted and concrete surfaces followed by purging and/or irradiation of the surfaces after removing the solution.[91]

TABLE II

Summary of Gas-Phase Adsorption Data for Reactive Surfaces

Coating	Sorption of I_2[a]			Sorption of CH_3I[a]		
	Deposition Velocity ($cm \cdot s^{-1}$)	Amount Adsorbed at Saturation ($mg \cdot cm^{-2}$)	Irreversibly Adsorbed (%)	Deposition Velocity ($cm \cdot s^{-1}$)	Amount Adsorbed at Saturation ($mg \cdot cm^{-2}$)	Irreversibly Adsorbed (%)
Vinyl	5.9×10^{-3}	0.048	78	8.2×10^{-3}	0.0085	79
Acrylic	6.1×10^{-2}	0.21	33	9.8×10^{-4}	0.0010	78
Epoxy	2.8×10^{-1}	0.82	60	1.8×10^{-2}	0.025	100
Phenolic	1.3×10^{-1}	0.52	82	5.1×10^{-3}	0.0077	97
Zinc primer	6.2×10^{-1}	9.46	99	1.4×10^{-2}	0.0014	81

[a]Iodine loading conditions: 115°C, 7.6×10^{-6} $mol \cdot dm^{-3}$ I_2 or 115°C, 7.8×10^{-7} $mol \cdot dm^{-3}$ CH_3I, compare Type 304 stainless steel deposition velocity at 150°C $- 1.5 \times 10^{-3}$ (Ref. 87).

The reaction of molecular iodine with painted surfaces is easy to rationalize in view of the fact that many paints contain phenolic groups, unsaturated hydrocarbons, and ketones. In a radiation field, heterogeneous organic iodide formation could also occur if organic radicals are formed from radiolytic decomposition of the polymers that form the bulk of the organic coating. These could react with oxidized iodine species to form organic iodides. It is also possible that iodide could react with amine species on painted surfaces to form alkyl ammonium salts. However, it is difficult to formulate any radiolytic or thermal reaction that would cleave organic iodides from a polymer backbone at a rate sufficient to release large quantities of organic iodide into the gas phase. In fact, organic radicals formed at polymer surfaces are usually subject to rapid recombination, a phenomenon responsible for cross-linking of polymers.[92] The concentration of radicals available for reaction with I_2 to form organic iodides by radical I_2 interactions would therefore be small. In addition, irradiation of the surface after it was iodinated would also lead to cross linking rather than to cleavage. Organic iodides, once formed on a surface, would be far more likely to release iodine atoms upon exposure to radiation than organic iodides. Polyvinyl chloride, for example, readily loses the Cl· radical upon exposure to heat or radiation.[92]

In most of the studies cited in Ref. 90, measured gas-phase organic iodide concentrations represented a very small percentage of the iodine adsorbed on the surface. Furthermore, gas chromatography verified that at 100°C, there were significant concentrations of organic vapor in the gas phase during the experiments. Given the low yields of organic iodides in the gas phase, homogeneous gas-phase reactions of reversibly bound molecular iodine with various gas-phase organic materials could also have accounted for the measured gaseous organic iodides. In Ref. 91, there were significant concentrations of organic iodide detected in the gas phase, which one could infer were released from irradiated surfaces previously exposed to iodide in the aqueous phase. However, there was no direct evidence that the production of the gas-phase organic iodide species was a heterogeneous process. There was a considerable amount of residual water (containing iodide) remaining on the surfaces prior to the purging/irradiation process in which gaseous organic iodides were observed. The iodine behavior observed in these experiments was therefore also consistent with a process whereby organic compounds were released from a surface into an aqueous iodide solution. Radiolytic or thermal reactions of organic and iodine species in the film of solution remaining on the surfaces after their removal from the aqueous phase could have produced organic iodides, which were subsequently released to the gas phase.

In summary, although direct interaction of iodine species with painted surfaces to form organic iodides on the surface is possible, it does not seem likely that subsequent cleavage of these organic iodides from the surface would be a favorable enough process to contribute significantly to organic iodide concentration in the gas phase. The experimental evidence used to support heterogeneous formation[90,91] as a significant source of gaseous organic iodides is ambiguous.

V. INTERFACIAL MASS TRANSFER

Because iodine and most organic iodides formed in the aqueous phase are volatile, they become airborne under certain conditions. The determination of the volatility of iodine species as a function of time requires the inclusion of the mass transfer of each species considered.

According to the theory of boundary layers, the rate of mass transfer of a species between the gas and aqueous phases is defined by

$$\left(\frac{dC_1}{dt}\right)_{mt} = \frac{A_{g1}}{V_1}\cdot k_{mt}\cdot(H\cdot C_g - C_1) \tag{68}$$

and

$$\left(\frac{dC_g}{dt}\right)_{mt} = \frac{A_{g1}}{V_g}\cdot k_{mt}\cdot(C_1 - H\cdot C_g)\ , \tag{69}$$

where

C_g = gas-phase concentration

C_l = aqueous-phase concentration

k_{mt} = overall mass transfer coefficient

A_{gl} = interfacial mass transfer surface area

V_g = gas volume

V_l = aqueous solution volume

H = partition coefficient between the aqueous and gas phases.

The partition coefficient, being a thermodynamic property, depends only on the temperature and pressure of the system and can be calculated from known Gibbs energies of formation of the species in the gas and aqueous phases as discussed in Sec. III.A. Mass transfer coefficients show a small dependence on the nature of species and depend more strongly on thermal-hydraulic conditions within the stagnant boundary layers at the interface of the gas and liquid phases. The overall mass transfer coefficient k_{mt} is related to individual mass transfer coefficients by the expression

$$\frac{1}{k_{mt}} = \frac{H}{k_g} + \frac{1}{k_1}\ , \tag{70}$$

where k_g and k_l are the gas- and aqueous-phase mass transfer coefficients, respectively. For a dilute, homogeneous system, these can be calculated from fundamental quantities, $k_g = D_{AB}/\delta_g$ and $k_l = D_{Ao}/\delta_l$, where D_{AB} and D_{Ao}

are the diffusion coefficients in the gas and aqueous phases and δ_g and δ_l are the hypothetical gas- and liquid-phase boundary-layer thicknesses, respectively. The boundary-layer thickness is a function of the flow characteristics near the interface and of the transport properties of the fluid medium.

In practice, fluid flows and transport properties are often difficult to characterize. The values of k_{mt} required to reproduce various observed mass transfer rates are often very different from the values obtained from the calculated individual idealized mass transfer coefficients. In addition, because of the large number of iodine species likely to be produced in containment and the difficulty in assigning a value to the overall partitioning of organic iodides, uncertainties in the values for H will contribute directly to uncertainties in k_{mt} [Eq. (70)]. In RTF experiments, however, uncertainties in the value for k_{mt}, which could span perhaps an order of magnitude,[93,94] are less likely to be significant to the overall rate of transfer of species across the aqueous-gas interface [Eqs. (68) and (69)] than uncertainties in the values for H themselves, which could span several orders of magnitude (Table I). Furthermore, for the purposes of predicting iodine volatility, an uncertainty in k_{mt} is relatively unimportant when the rate of change of species concentrations in either the gas or the aqueous phase is slow, compared to the nominal mass transfer rate. Under these conditions, an uncertainty in k_{mt} would have only a small effect on calculated iodine volatility, and an equilibrium approximation (i.e., assuming mass transfer is fast with respect to changes in the concentration of individual species) suffices. Simulations of RTF experiments indicate that this approximation is reasonable under the conditions employed in these intermediate-scale studies[64] (see also Sec. VI.C).

VI. MODELING

VI.A. Empirical and Mechanistic Codes

There are two different approaches to model development for predicting iodine behavior for conditions expected to be typical of an accident: empirical and mechanistic. Empirical models, such as IODE, developed at Commissariat l'Énergie Atomique in France,[95,96] and IMPAIR, developed in Switzerland,[96,97] employ small reaction sets to represent many complex chemical processes. They use correlations to model the overall effects of key parameters such as pH and radiation dose on iodine volatility. For example, the IODE code contains about 15 chemical reactions and 8 other physical processes, whereas the IMPAIR code contains about 23 chemical reactions and 6 physical processes, to account for iodine behavior under accident conditions. Many of the reaction rates used in these codes are empirical. Although these empirical models are simple to use, code development relies on empirically adjusting the model to reproduce as closely as possible a large body of data obtained from bench-, large-, and intermediate-scale studies.

The observed differences in iodine releases at Windscale, TMI-2, and Chernobyl-4 indicate the need for a good overall understanding of iodine behavior and the complementary need to develop a general-purpose model for iodine behavior that takes into account accident-specific conditions. This has led to the incorporation of mechanistic chemistry into a few models. A fundamental aspect of these models is the ability to predict iodine behavior during the course of an accident in a time-dependent manner over a wide range of accident scenarios. The INSPECT code,[98] developed by AEA Technology (Harwell, United Kingdom), and the LIRIC code,[17,64,99–101] developed at Atomic Energy of Canada Ltd. (AECL), are examples of such models. They are mechanistic and consist of more than 300 reactions to cover the range of conditions of interest. Somewhere between the empirical and mechanistic models lies the TRENDS code[102] developed at Oak Ridge National Laboratory, in which some of the reaction sets are empirically formulated to fit the data.

The two mechanistic codes, INSPECT and LIRIC, contain very similar reaction sets, except those of less well understood reactions such as organic reactions and surface processes. Because the differences between the two codes are small, only the basic reaction sets included in LIRIC, as a representative mechanistic model, are briefly described in Sec. VI.B.

VI.B. LIRIC

The mechanistic model LIRIC has been described in detail elsewhere[64,101] and is therefore described only briefly here. The model contains a number of aqueous reaction subsets, including the water radiolysis model, reactions of aqueous iodine species with water radiolysis species, aqueous thermal iodine reactions, and reactions of inorganic impurities with water radiolysis products [e.g., Reactions (53) through (58)]. Gas-phase reactions are not included in LIRIC at the moment, since overall contributions to iodine volatility under conditions in which most of the iodine will be in the aqueous phase are considered to be relatively unimportant. Gas-phase concentrations of iodine are determined by means of the mass transfer of volatile iodine from the aqueous phase. The mass transfer model contained in LIRIC is the one described in Sec. V. Values of k_{mt} ranging from 1×10^{-4} to 1×10^{-3} dm·s^{-1} are used to model intermediate-scale studies, consistent with "lower-limit" estimates for mass transfer in the RTF under typical flow conditions.[60,99]

Reactions such as radiolytic degradation of organic-based–painted surfaces and surface-catalyzed formation of organic iodides are not included in LIRIC because of the lack of conclusive evidence for the existence of these processes. However, LIRIC contains a simple model for the radiolytic decomposition of MEK in the aqueous phase to

account for observed changes in pH and dissolved oxygen concentration in the presence of dissolved organic compounds, and a model for dissolution of organic compounds from painted surfaces, a key rate-determining step in the production of acid from organic impurities in the aqueous phase. These models are designed to estimate pH changes and organic iodide concentrations expected in accident conditions. However, the applicability of the MEK radiolysis model to the radiolysis of other "containment organic compounds" is still being established,[37] so the applicability of the LIRIC model is still somewhat limited in the area of predicting time-dependent pH, dissolved oxygen concentrations, and organic iodide concentrations.

In LIRIC, the adsorption and desorption on gas-phase surfaces is formulated using a reversible physical adsorption-desorption model.[64,101] The model also provides the option of using two other models, one based on chemisorption and the other based on reversible physical adsorption followed by a slower chemisorption, which may provide better descriptions of I_2 adsorption behavior on surfaces coated with organic paints.

Although a few important reaction mechanisms are still missing in LIRIC, mostly because of a lack of experimental data, the updated version of LIRIC includes mechanistic interpretations of many important processes that may occur in an accident. LIRIC is a useful tool for assessing iodine behavior under experimental conditions. Work is ongoing in areas of known deficiencies to provide a model that is adequate for predicting iodine volatility under all reactor accident conditions to the required degree of accuracy.

VI.C. Simulations of RTF Tests

LIRIC has been used successfully to simulate many RTF tests, demonstrating that the mechanisms and key processes within the model are adequate to predict iodine behavior under limited conditions. Two examples of the model's reproduction of intermediate-scale experiments are discussed here. These tests, which were performed in a stainless steel vessel with controlled pH, were designed to investigate the effect of pH on iodine volatility in the presence of radiation and were performed at an average radiation dose of 1.5 $kGy \cdot h^{-1}$. The experiments were initiated by introduction of 1×10^{-5} $mol \cdot dm^{-3}$ CsI, labeled with ^{131}I, into the water. The pH of the water was initially controlled at 10 and lowered in a stepwise manner during the experiments. The total gas- and aqueous-phase iodine concentrations were monitored during the tests, and iodine speciation measurements were performed periodically. The principal differences between the two tests were the rate of variation of pH and the final pH.

Figures 10a and 10b show the LIRIC calculations for the total iodine concentrations in the gas and aqueous phases as a function of time for the first test. Test results are also shown for comparison. In simulating the RTF test, the pH was adjusted in a stepwise manner to follow the test conditions (Fig. 10c), although the pH changes used in the calculations were more abrupt than those that occurred during the test. The calculation, using an effective metal ion concentration of 5×10^{-5} $mol \cdot dm^{-3}$, a value that was chosen based on experimental observations, reproduced the experimental data reasonably well, and no serious optimization regarding the metal ion concentration was performed. For I_2 adsorption and desorption on the gas-phase surfaces, the reversible physical model with deposition velocity of 9×10^{-3} $dm \cdot s^{-1}$ and desorption rate constant of 9×10^{-7} s^{-1} was used, and a geometrically calculated surface area was used.

Although small quantities of organic iodides were observed in both the gas and aqueous phases in these experiments, presumably as a result of impurities in the iodine source, organic iodides were not included in the calculations for this test since there were nominally no significant quantities of organic compounds present. Throughout the tests in stainless steel vessels, the gas-phase organic iodide concentration remained relatively small and constant, compared to the gas-phase I_2 concentration.

The calculations represented in Figs. 10 and 11 reproduce the observed iodine behavior very well in both the gas and aqueous phases. The discrepancies, particularly in the gas phase, may be due to the omission of the organic iodide formation submodel, an overestimation of the quantity of trace metals in solution, or to a small extent, the abrupt pH changes used in the calculations. The depletion of iodine in both the gas and the aqueous phases with time is due to the strong adsorption of gaseous I_2 on surfaces.

VII. SUMMARY

Sections II through V provide a summary of reactions and phenomena regarded to be important in predicting time-dependent iodine behavior under conditions expected to be typical of those prevailing in containment during a reactor accident. In addition to providing a critical review of existing information, an attempt has been made to focus on recent developments in this area. As the result of extensive investigation of iodine behavior under radiolytic conditions and the application of intermediate-scale studies to the development of a mechanistic model for iodine chemistry, the overall understanding of this area has improved significantly since the last review of this topic. Section VII.A summarizes important developments, and Sec. VII.B identifies areas in which there are still uncertainties.

VII.A. Important Developments

The most significant improvement in the understanding of iodine chemistry since the last reviews[5,6] of the topic lies in the recognition that kinetics, rather than thermodynamics, will determine the speciation and distribution of iodine after an accident. Since iodine species

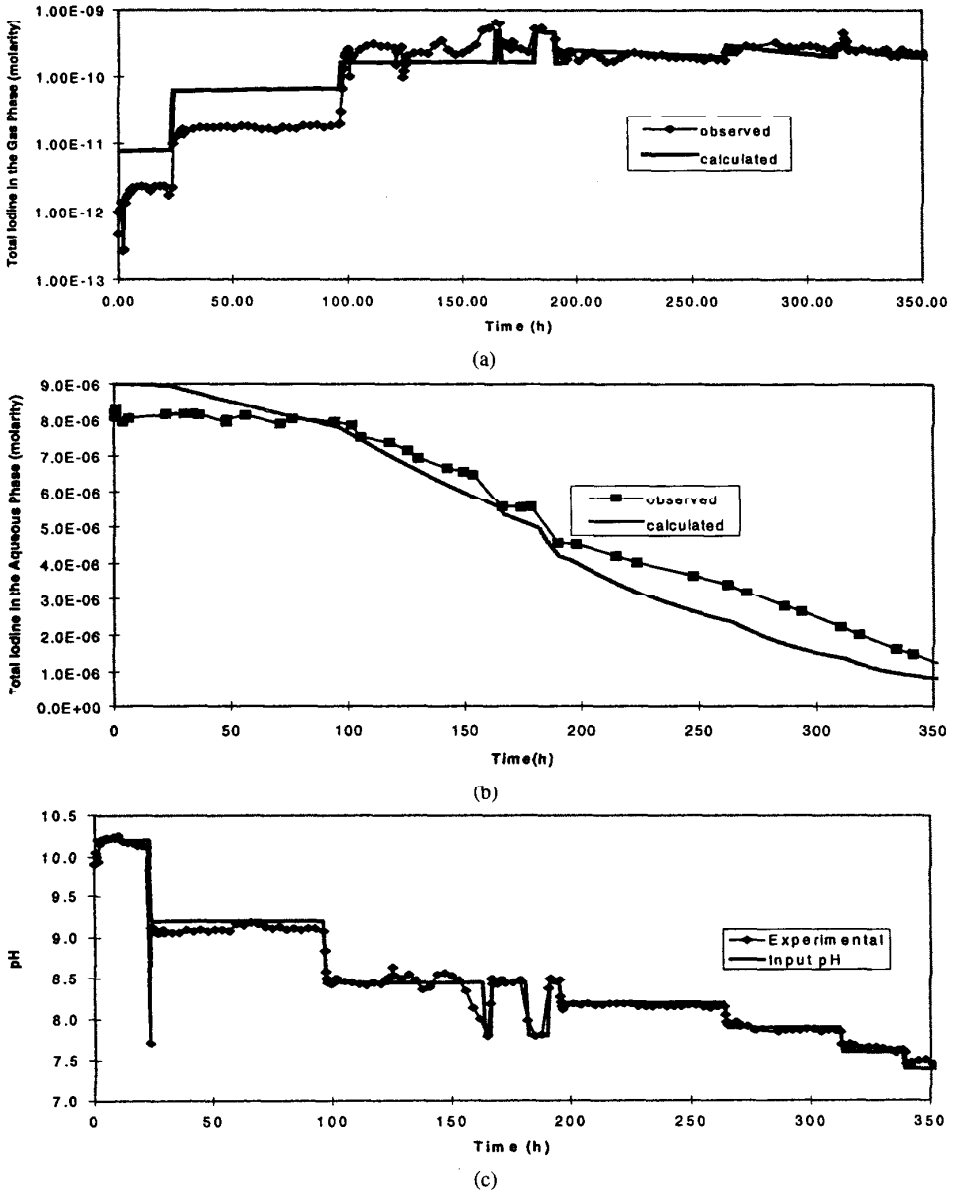

Fig. 10. Simulation of test 1, performed in a stainless steel vessel at room temperature and in the presence of radiation at an average dose rate of 1.5 $kGy \cdot h^{-1}$: (a) gas-phase iodine concentration, (b) aqueous-phase iodine concentration, (c) pH.

undergo rapid interconversions under radiolytic conditions, and since radiation may radically alter both the pH and redox characteristics of an aqueous solution, standard pH versus potential diagrams are not useful in predicting time-dependent iodine behavior. It has been demonstrated in the RTF and various bench-scale studies, however, that even under radiolytic conditions where kinetics determine iodine behavior, pH is still the key factor affecting iodine volatility. This pH dependence is largely due to the effects of iodine hydrolysis and of reactions of I_2 with O_2^- and H_2O_2 in the aqueous phase.

Integrated- and bench-scale studies have demonstrated that it is in the aqueous phase that organic impurities would have the largest impact on iodine

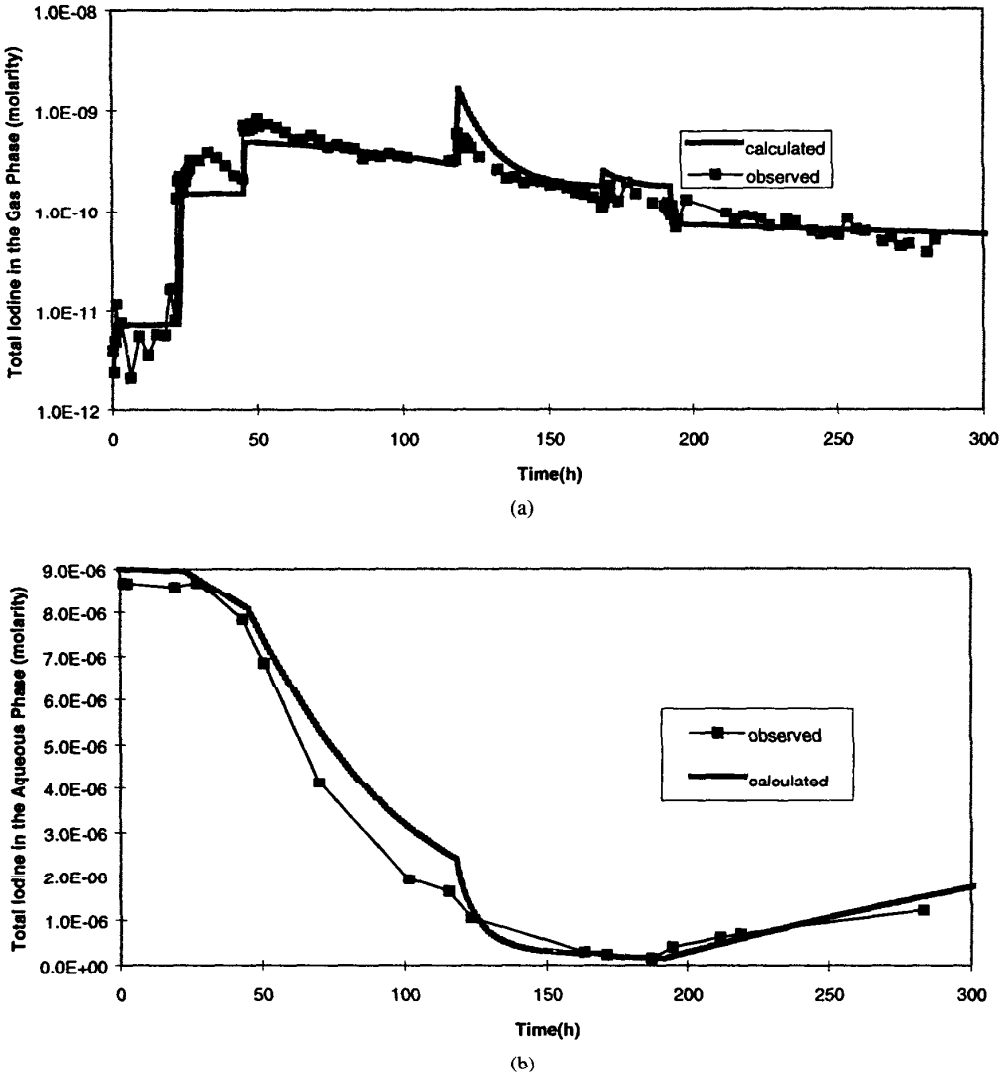

Fig. 11. Simulation of RTF test 2 performed in a stainless steel vessel in the presence of radiation: (a) gas-phase iodine concentration, (b) aqueous-phase iodine concentration.

volatility. This impact is primarily due to organic radiolysis altering the pH of the sump and, consequently, the steady-state I_2 concentration. Furthermore, since the concentration of both organic materials and of reactive iodine species is expected to be larger in the aqueous phase than anywhere else, organic iodide formation will be dominated by aqueous-phase processes. This has implications for modeling organic iodide production because the requirements for predicting organic iodide formation rates are reduced to knowledge of the time-dependent concentrations of organic radicals and of I_2.

The dissolution of organic solvents from paints is often slow in comparison to their radiolysis rates. These solvents could be the largest source of organic materials that would influence iodine behavior in containment. If the rate of their dissolution is considered to be the rate-determining step in controlling pH changes and organic iodide formation rates, it may not be necessary to develop detailed mechanistic models for all the processes involved in organic radiolysis and organic iodide formation. A model for dissolution of organic solvents from paint, coupled with a generalized organic radiolysis

model, could provide all of the kinetic information required to predict pH changes and organic radical concentrations resulting from organic radiolysis. This information, along with a semimechanistic model for reactions of organic radicals with I_2 in the aqueous phase and selected partition coefficients and hydrolysis rates for organic iodides, could be sufficient to predict time-dependent organic iodide concentration in the gas phase.

VII.B. Uncertainties

VII.B.1. Aqueous Chemistry

The kinetic database for aqueous iodine chemistry is relatively well established. A few areas exist where there are large uncertainties regarding rates and mechanisms, but for the most part, these reactions will not have a significant impact on iodine volatility under radiolytic conditions. The exceptions are in the area of organic radiolytic decomposition, which is crucial to modeling pH behavior (see Sec. II.D.1), and the temperature dependence of iodine hydrolysis. A simple mechanistic model for organic radiolysis, based on detailed investigation of MEK radiolysis, exists,[61,63] but its applicability to other ketones and alkyl organics needs to be established. It should be possible to evaluate the applicability of the model to other alkyl solvents and develop a similar model for "aromatic" compounds, such as xylene, with a limited number of experiments.

VII.B.2. Surface Reactions

The surface adsorption models within LIRIC are sufficiently versatile that they can adequately reproduce adsorption behavior on a variety of surfaces, for it has been demonstrated that even very simple modeling approaches, such as using "pseudo" first-order kinetics,[84–86] can be applied to describe deposition over a wide range of conditions. However, accurate modeling of adsorption behavior depends on having appropriate adsorption/desorption rate constants and on correctly characterizing the adsorbing surfaces and estimating the surface area. For RTF experiments in which there is a fixed geometric surface area and for which there are not sudden temperature or humidity changes, our modeling studies have indicated that a fairly narrow range of adsorption/desorption rate constants can be used to predict deposition behavior for a wide range of surface types. Modeling studies have also established that sudden changes in temperature and the presence of condensing conditions can significantly alter the adsorption/desorption rate constants required to reproduce RTF experimental results, but it is anticipated that only a limited number of parametric bench-scale studies are required to define the range of rate constants required to model adsorption behavior under these conditions. The data that are currently available on the adsorption of iodine species on containment surfaces are insufficient to describe an accident scenario in which temperature, humidity, and flow could vary and in which the containment surface morphology could change as a result of deposition or exposure of the surface to steam. However, the limited range of applicability of the current surface adsorption model within LIRIC can be vastly improved by the determination of a few key rate constants. Studies to determine these constants are part of our ongoing experimental program.

VII.B.3. Gas-Phase Reactions

Intermediate- and bench-scale studies, combined with reviews of the literature, have indicated that gas-phase reactions do not play a significant role in determining iodine volatility for any of the conditions examined. Therefore, although there are some uncertainties regarding gas-phase reactions of iodine species, it has not been demonstrated that these uncertainties are likely to influence the ability to predict iodine behavior in a reactor accident.

VII.B.4. Interfacial Mass Transfer

It is uncertain what the aqueous- and gas-phase mass transfer rates in postaccident containment would be. These rates could be reactor specific or accident specific and could also vary over the course of an accident. In modeling iodine behavior in intermediate-scale (RTF) studies, fast mass transfer is assumed, and the gas-phase iodine concentrations are determined primarily by the partition coefficient and not by the mass transfer rate. This assumption is valid under the conditions employed in intermediate-scale studies because the mass transfer rate is, in general, faster than the rate of change of iodine species in the aqueous phase and therefore is not rate determining. The assumption of fast aqueous/gas mass transfer could lead to errors in estimating the amount of iodine in the gas phase; however, it would always result in a bounding estimate. In view of the complexity of obtaining mass transfer information for accident- and reactor-specific conditions, assuming rapid interfacial mass transfer is probably the only practical solution to dealing with uncertainties in mass transfer rates.

VIII. CONCLUSIONS

This paper has discussed the current status of mechanistic modeling of the chemistry of iodine under conditions expected to prevail in a reactor containment during an accident. Under "wet" accident conditions, the volatility of iodine will be determined primarily by aqueous-phase chemical reactions and by adsorption of iodine on surfaces. Gas-phase reactions will have a limited impact on the behavior of iodine in these circumstances.

The key reactions that govern iodine speciation in the aqueous phase in the presence of radiation are the radiolytic oxidation of I^-, the hydrolysis of I_2, and the reaction of water radiolysis species with iodine species and with organic and inorganic impurities. There are still some uncertainties regarding aqueous-phase processes, namely, the temperature dependence of the iodine hydrolysis rate and the effect of organic radiolytic processes on iodine volatility. The former uncertainty should be relatively easy to address with a small experimental program. Significant progress has recently been made in developing models for the latter, and the completion of a model that has adequate predictive capability is foreseen in the near future.

In summary, our understanding of iodine chemistry has improved significantly since the last comprehensive review of this subject, and the areas that require further examination have narrowed. Mechanistic models to predict iodine behavior have improved, and the work needed to produce the remaining important model elements has been identified.

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