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**PART A - CALCULATION OF pH**

## 1. INTRODUCTION

Reactor safety studies<sup>1-3</sup> have shown that of all quantities affecting iodine volatilization, the pH of principal water pools is the most important. For values of  $\text{pH} > 7$ , the nonvolatile forms  $\text{I}^-$  and  $\text{IO}_3^-$  are found almost exclusively. However, as pH drops the creation of molecular iodine ( $\text{I}_2$ ) begins. For  $\text{pH} < 3$ ,  $\text{I}_2$  is the dominant form. This phenomenon varies somewhat with temperature, concentration, and radiation dose, although these are secondary effects.

Because of its consequences on iodine volatilization, the pH of water pools is a significant factor in reactor accidents. Sequence calculations must consider this variable if any aqueous iodine is present, even if present initially in stable forms. The purpose of this report is to briefly describe and document a simple procedure which can be used to calculate pH in water, given the inventories of various chemicals which affect pH.

## 2. MATERIALS THAT INFLUENCE pH

Numerous materials can influence pH in containment water pools during accident sequences, some of which are listed in Table 1. This list includes both acidic and basic materials, some present under normal operation, and some only occurring in accident conditions. For situations in which no chemical additives are present to control pH, the amounts of HI, cesium borate or hydroxide, and boron oxides reaching a sump will initially determine pH. In some sequences, the core-concrete interaction would produce aerosols that contain basic oxides, such as  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , and  $\text{CaO}$ . The influence of these oxides on pH will depend on the amount that has entered the water pool, the initial pH and buffering capacity of the solution, the quantity of water, and the extent of dissolution of the aerosol material. Further discussion of materials that could determine pH is given in ref. 1.

### 2.1 RADIOLYTIC ACID FORMATION IN CONTAINMENT

Water that is exposed to air absorbs  $\text{CO}_2$  to form carbonic acid, which lowers pH to a limiting value of 5.65. In addition, irradiation of various organic materials (paints, cable insulation, lubricating oil, etc.) could create large quantities of  $\text{HCl}$ .<sup>1</sup> When deposited or washed into pools and sumps, it could significantly lower pH. Another effect is the creation of nitric acid by the irradiation of water and air.

Table 1. Materials that affect pH in containment water pools

- 
- Boron oxides (acidic)
  - Fission-product compounds such as cesium hydroxide or cesium borates (basic)
  - Iodine as HI (acidic)
  - pH additives (basic)
  - Atmospheric species such as carbon dioxide or nitric acid (acidic)
  - Core-concentrate aerosols (basic)
  - Pyrolysis and radiolysis products from organic materials (acidic)
- 

### 2.1.1 Acids from Organic Materials

It has been shown that irradiation of electrical cable insulation produces HCl and, to a lesser extent, H<sub>2</sub>SO<sub>4</sub>. These acids can freely diffuse through the insulation into the containment atmosphere, and eventually end up in water pools or sumps. The formation rate can be estimated as follows:

$$R = R_{\gamma} + R_{\beta}$$

$$R_{\gamma} = 1.65 \times 10^{-14} \frac{\dot{E}_{\gamma} N}{V} (1 - \exp(-3.74 \times 10^{-5} r))$$

$$R_{\beta} = 8.70 \times 10^{-16} \frac{\dot{E}_{\beta} N}{V}$$

$R_{\gamma}, R_{\beta}$  = rate of HCl generation due to  $\gamma$  and  $\beta$  irradiation (gmol/s)

$\dot{E}_{\gamma}, \dot{E}_{\beta}$  = energy deposition rates of  $\gamma$  and  $\beta$  radiation due to fission-product decay (MeV/s)

$N$  = total weight of hypalon cable sheathing (lb)

$V$  = free volume of containment (cm<sup>3</sup>)

$r$  = average length of radiation travel in air (cm).

A good estimate of the radiation length  $r$  is the radius of the containment or half of the height.

## 2.1.2 Nitric Acid

Many experiments have indicated that in the presence of both air and water, irradiation can produce nitric acid. While the exact mechanism is somewhat in dispute, the acid always accumulates in the aqueous phase, indicating either a liquid phase or interfacial reaction. For this reason, the reaction rate is conveniently modeled by considering radiation dose to the water:

$$\frac{d[\text{H}^+]}{dt} = 10^4 g(\text{HNO}_3) \frac{E_{dep}}{V_L N_a},$$

where

$[\text{H}^+] =$  concentration of  $\text{H}^+$  (mol/L),

$g(\text{HNO}_3) =$  rate of  $\text{HNO}_3$  production due to irradiation (molecules/100 eV),

$E_{dep} =$  total energy deposition due to fission-product decay (MeV),

$V_L =$  volume of water (L),

$N_a = 6.022 \times 10^{23}$  (molecules/mol).

The quantity  $E_{dep}$  can be determined (see Weber<sup>4</sup>) from inventories of fission products in the water, which must be calculated. The volume of water also must be available from estimates or accident sequence computations. The data in ref. 3 indicate that at 30°C,

$$g(\text{HNO}_3) = 0.0068 \text{ molecules/100 eV} .$$

This quantity does not vary strongly with temperature.

## 2.2 CHEMICALS USED IN REACTORS

There are several chemicals present in many reactors which can have significant effects on containment pH. Borates may enter containment from the primary containment or through spray systems. Phosphate and hydroxide are frequently used as pH-control chemicals.

### 2.2.1 Borates

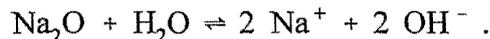
Boric acid will enter containment from accumulators, refueling water storage tanks, sprays, and the reactor coolant system (RCS). Boron concentrations of more than 4000 ppm (as boric acid) may be attained in the water pool. Boric acid sprays would have a pH of ~5 and would come into contact with most surfaces in containment. In systems that employ pH-control chemicals (Section 2.2.2), a large portion of the basic material is used to increase the pH of boric acid solutions.

## 2.2.2 Materials for pH Control

The pH buffer materials for use in containment must be borate or phosphate. No other chemical additives would have the desirable pH range and chemical stability. Typically, the phosphate is in the form of trisodium phosphate (TSP) that is held dry in baskets that are located in containment. The amounts of TSP may be quite large; 26,500 lb ( $3.2 \times 10^4$  mol) of the dodecahydrate\* is in place at Palo Verde, according to the updated final safety analysis report. Borate buffers are made up of sodium hydroxide and boric acid that are stored separately and combined in spray systems. Boric acid is also used in sprays, with passive pH control provided by TSP.

## 2.3 FISSION PRODUCTS

It is possible that some iodine could enter containment as HI, a fairly strong acid. However, most cesium is expected to be in the form CsOH, a strong base. If a core-concrete reaction takes place, then additional basic materials may be released and deposited in water pools, including CaO, Na<sub>2</sub>O, and K<sub>2</sub>O. Upon contact with water, these materials form hydroxides through reactions such as:



Thus, if such materials are freely dissolved in water, they may raise the pH significantly.

## 3. MODEL FOR CALCULATION OF pH

With knowledge of any additives and all species likely to be present, the solution pH at equilibrium can be determined by finding the minimum free energy. Such an approach assumes that all reactions that determine pH can be well characterized and proceed very rapidly. Within the range of interest for iodide conversion ( $3 < \text{pH} < 7$ ), this assumption is generally the case, as shown later by verifying calculations.

Free energy minimization, in water pools, is performed using the principal subroutine of the SOLGASMIX code,<sup>6</sup> which has been modified for use in accident sequence calculations. The species included in the calculation of pH are listed in Table 2, in the order that they are indexed in

---

\*According to Wendrow and Kobe,<sup>5</sup> the actual solid is probably  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \cdot \frac{1}{4}\text{NaOH}$ . Excess hydroxide is even present in reagent grade TSP, although rarely considered in safety evaluations (it is conservative to neglect the NaOH).

the calculational routine. Input data required for such a calculation include free energies of formation, activity coefficients, and mole inventories for each species. The first two have been determined from the literature and are described below. The mole inventories vary with each reactor and accident sequence, and must be supplied by the user.

Table 2. Thermodynamic parameters

Species	Free energy coefficients <sup>a</sup>			Activity constant <sup>b</sup>
	<i>a</i>	<i>b</i>	<i>c</i>	$a^0 \times 10^8$
1 Ar(g)	0.	0.	0.	0
2 H <sub>2</sub> O	-95.661	.949224	-.09634	0
3 Na <sup>+</sup>	-105.69	.85194	-.88327	3
4 H <sup>+</sup>	0.	0.	0.	9
5 Cl <sup>-</sup>	-52.928	.36800	-.35800	3
6 OH <sup>-</sup>	-63.534	.75606	-.74688	3
7 B(OH) <sub>3</sub>	-391.039	4.21268	-4.6180	0
8 B(OH) <sub>4</sub> <sup>-</sup>	-469.500	5.11900	-5.5217	4
9 B <sub>2</sub> (OH) <sub>7</sub> <sup>-</sup>	-856.472	9.31487	-10.123	3
10 B <sub>3</sub> (OH) <sub>10</sub> <sup>-</sup>	-1252.36	13.5904	-14.797	3
11 B <sub>4</sub> (OH) <sub>14</sub> <sup>-2</sup>	-1720.29	18.9053	-20.567	3
12 PO <sub>4</sub> <sup>-3</sup>	-411.190	4.33069	-4.3623	4
13 HPO <sub>4</sub> <sup>-2</sup>	-439.592	4.74018	-4.9977	4
14 H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-456.073	4.75994	-5.0339	4
15 H <sub>3</sub> PO <sub>4</sub>	-460.921	4.72657	-5.0064	0

<sup>a</sup>From Eq. (1).

<sup>b</sup>From Eq. (2).

Data for the free energies of formation of the borate and phosphate species were obtained from refs. 7 and 8, respectively. Free energy information for other species was obtained from the HSC system.<sup>9</sup> All free energy data were cast into a quadratic form,

$$\frac{\Delta G^0}{RT} = a + b (T - T_0) + c(T^2 - T_0^2) \quad (1)$$

where

$\Delta G^0 =$  the standard free energy of formation,

$R =$  the universal gas constant in energy units consistent with  $\Delta G^0$ .

$T_0 = 298.15$  K.

The best fit regression constants  $a$ ,  $b$ , and  $c$  are given in Table 2.

Activity coefficients for the aqueous ions were calculated from the modified Debye-Hückel expression,<sup>10</sup>

$$-\log_{10} \gamma_i = \frac{Az_i^2\sqrt{I}}{1 + a_i^0 B\sqrt{I}} \quad (2)$$

The quantities  $A$  and  $B$  are properties of water and, within our range of interest, can be described by:

$$A = 0.2053 + 106.43/(373 - T_c)$$

$$B = 0.32458 + 1.6464 \times 10^{-4} T_c$$

where  $T_c = T - 273.15$ .

The constants  $a_i^0$  are given for each ion of interest in the last column of Table 2. The ionic strength is given by

$$I = \frac{1}{2} \sum m_i z_i^2,$$

where  $z_i$  and  $m_i$  are the charge and molal inventory of the  $i^{\text{th}}$  ion, respectively. This approach is highly reliable for calculation of thermodynamic properties up to about  $I = 0.1$  m. While this is sufficient for many applications, the method also has been used successfully up to  $I = 0.3$ .

#### 4. DESCRIPTION OF CALCULATIONAL MODEL

As previously mentioned, the principal subroutines of the SOLGASMIX code are used to calculate the minimum free energy of a chemical system, from which the pH is derived from its definition

$$\text{pH} = -\log_{10} (a_{\text{H}^+}),$$

where  $a_{\text{H}^+}$  is the activity of the hydrogen ion. A main routine has been written, and is supplied with this program, to handle input/output and to set up the chemical system. All coding is done in FORTRAN, and has been compiled on both UNIX and PC-DOS systems. It is beyond the scope of this work to describe the detailed calculation steps for these routines. However, brief descriptions of the input and output are given in the following subsections. These include two input files 'setup.dat' and 'init.dat', and standard output.

#### 4.1 GENERAL INPUT

Thermodynamic information is contained in the input file 'setup.dat'. This includes the species parameters listed in Table 2 and stoichiometric variables which describe the chemical relationships between different species. Also included are various computational parameters which should not need adjustment. The information in this file does not depend on reactor or accident sequence; hence, it is applicable without modification to all accident sequences.

#### 4.2 PARTICULAR INPUT

Certain input is required which is highly dependent on the particular application. This is done using the file 'init.dat', which is illustrated in Fig. 1. Following a run title (Character format), each line of input contains a single variable (format F12.0), which may be followed by a comment. As seen in the figure, the variables represent temperature ( $^{\circ}\text{C}$ ), pressure (atm), water mass (kg), gas volume ( $\text{m}^3$ ), and quantities (gmol) of each solute listed in Table 2.

#### 4.3 OUTPUT

The equilibrium amounts (gmol) of each species listed in Table 2 are written to the standard output device (unit 6), as shown in Fig. 2. For aqueous ions, output also includes activity, activity coefficients, and molality.

#### 4.4 OPERATION

The FORTRAN source code is contained in two files 'phcalc.for' and 'gasolx.for'. These have successfully been compiled and run under both UNIX and DOS operating systems (the latter using Microsoft 6.0 Operating System and Microsoft 5.0 FORTRAN compiler).

NRC pH Calculation

```

25.0 Temperature (C)
 1.0 Pressure (atm)
.997 water (kg)
 0. gas volume (m3)
.0697 Na+ (mol)
.1290 H+ (mol)
 0. Cl- (mol)
.0697 OH- (mol)
.0430 B1.0 (mol)
 0. B1.1 (mol)
 0. B2.1 (mol)
 0. B3.1 (mol)
 0. B4.2 (mol)
.0430 PO4 --- (mol)
 0. HPO4-- (mol)
 0. H2PO4- (mol)
 0. H3PO4 (mol)

```

Figure 1. Contents of input file 'init.dat'.

NRC pH Calculation

Equilibrium Distribution of Species

Species	moles	molality	activity	act. coeff.
Ar	0.0000E+00			
H2O	5.5411E+01			
Na+	6.9700E-02	6.9823E-02	4.8691E-02	6.9735E-01
H+	1.4592E-07	1.4618E-07	1.1675E-07	7.9874E-01
Cl-	0.0000E+00	0.0000E+00	0.0000E+00	6.9735E-01
OH-	1.3637E-07	1.3661E-07	9.5264E-08	6.9735E-01
B1.0 (aq)	4.2692E-02	4.2767E-02	7.6830E-04	1.0000E+00
B1.1	3.0807E-04	3.0861E-04	2.2242E-04	7.2073E-01
B2.1	4.1900E-09	4.1974E-09	2.9271E-09	6.9735E-01
B3.1	4.1081E-10	4.1154E-10	2.8698E-10	6.9735E-01
B4.2	0.0000E+00	0.0000E+00	0.0000E+00	2.3649E-01
PO4---	5.3784E-07	5.3879E-07	2.8272E-08	5.2474E-02
HPO4--	2.6401E-02	2.6447E-02	7.1316E-03	2.6983E-01
H2PO4-	1.6589E-02	1.6618E-02	1.1977E-02	7.2073E-01
H3PO4 (aq)	9.9059E-06	9.9234E-06	1.7827E-07	1.0000E+00

```

pH = 6.93
Temp (C) = 298.15
ionic strength = 0.096

```

Figure 2. Sample output.

## 5. VALIDATION

The calculational model was applied to several chemical systems in which the pH is well known and verified. The experimental data are listed in Table 3. Figures 3–7 show that the calculation matches most experimental results within about 0.1 pH unit. For the trisodium phosphate system (Fig. 3) error is within 0.2 pH unit. In Figs. 3–6, an exact match of data and experiment would lie on the diagonal line. Fig. 7 indicates that the calculational model appropriately reflects pH changes with temperature throughout the range 25–95°C. It also appears that most calculation results are slightly low, although probably within experimental error. Overall, the calculation performs admirably on these test data even in cases where ionic strength exceeds 0.1 m.

Individual models that form the technical basis for the code have been validated. However, the code as a whole has not been subjected to rigorous verification and validation. Therefore, although the code is a useful tool, it should be applied by users familiar with the phenomena.

Table 3. Experimental data

Primary solutes	pH range	Temperature (°C)	Ionic strength (m)	Reference
Na <sub>3</sub> PO <sub>4</sub>	11.38 – 12.04	25–37	0.048–0.28	11
borax <sup>a</sup> + HCl	8.0 – 9.1	25	0.025	12
borax <sup>a</sup> + NaOH	9.2 – 10.8	25	0.026–0.049	12
KH <sub>2</sub> PO <sub>4</sub> + NaOH	5.8 – 8.0	25	0.056–0.14	12
Na <sub>2</sub> HPO <sub>4</sub> + NaOH	10.9 – 12.0	25	0.084–0.14	12
H <sub>3</sub> BO <sub>3</sub> + Na <sub>3</sub> PO <sub>4</sub> + NaOH	5.0 – 9.0	25	0.047–0.14	ORNL
KH <sub>2</sub> PO <sub>4</sub> + Na <sub>2</sub> HPO <sub>4</sub>	6.8 – 7.0	25–95	0.1	12
borax <sup>a</sup>	8.8 – 9.2	25–95	0.025	12

<sup>a</sup>Chemical formula Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10 H<sub>2</sub>O.

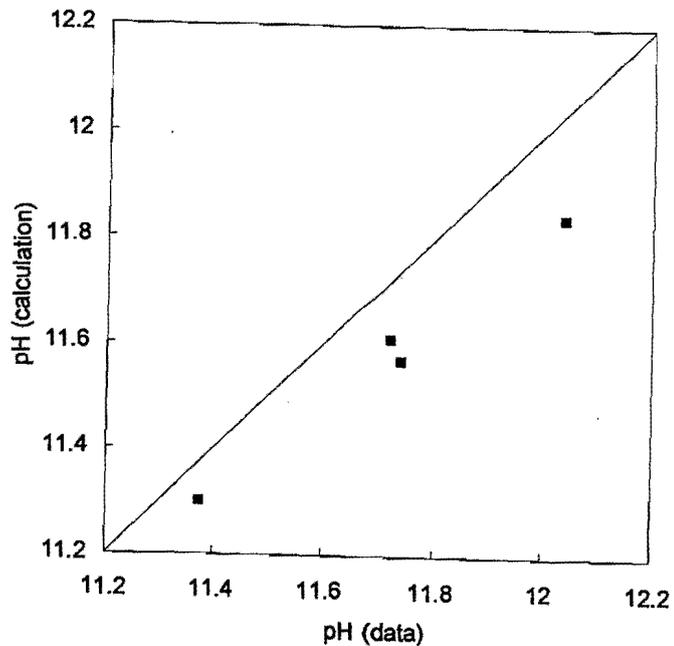


Fig. 3. pH in trisodium phosphate solutions at 25 and 37°C. Data from ref. 11.

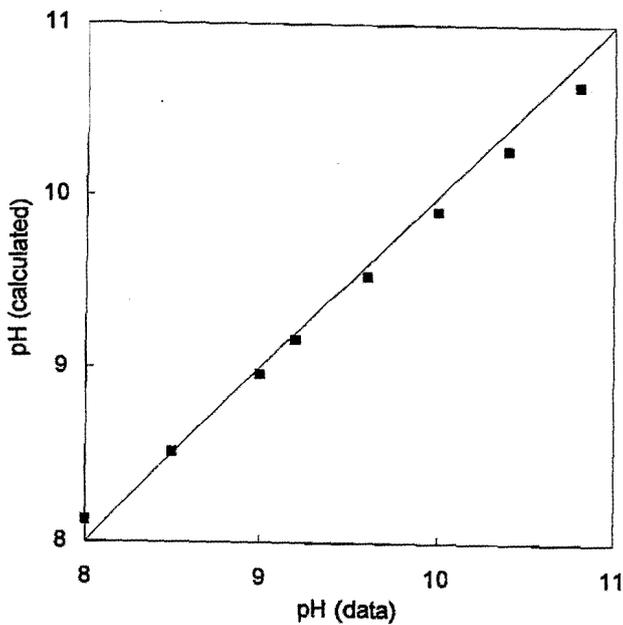


Fig. 4. pH in solutions of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ) and HCl or NaOH. Data from ref. 12.

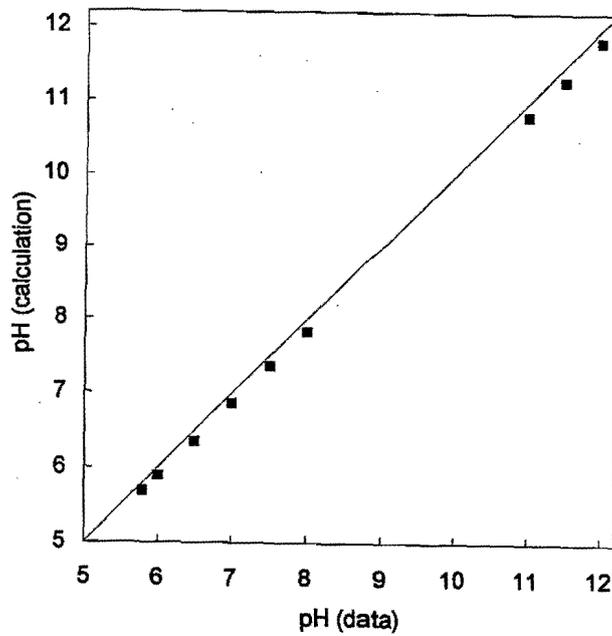


Fig. 5. pH in solutions of  $\text{KH}_2\text{PO}_4 + \text{NaOH}$  and  $\text{Na}_2\text{HPO}_4 + \text{NaOH}$ . Data from ref. 12.

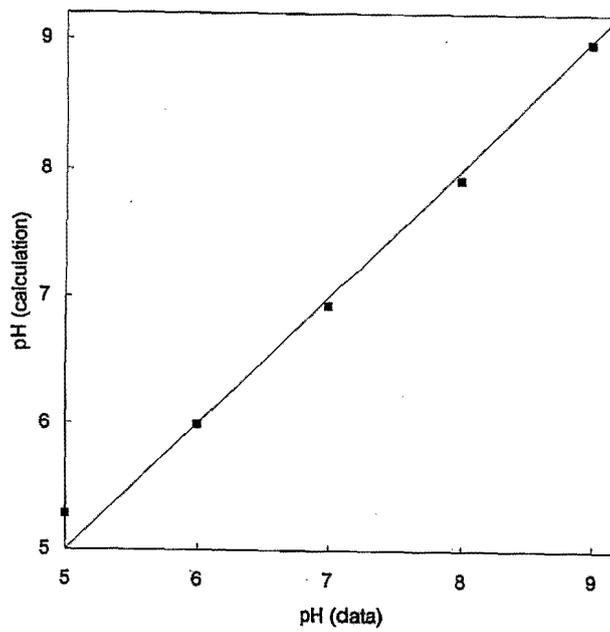


Fig. 6. pH in mixed phosphate-borate systems. Data from this study.

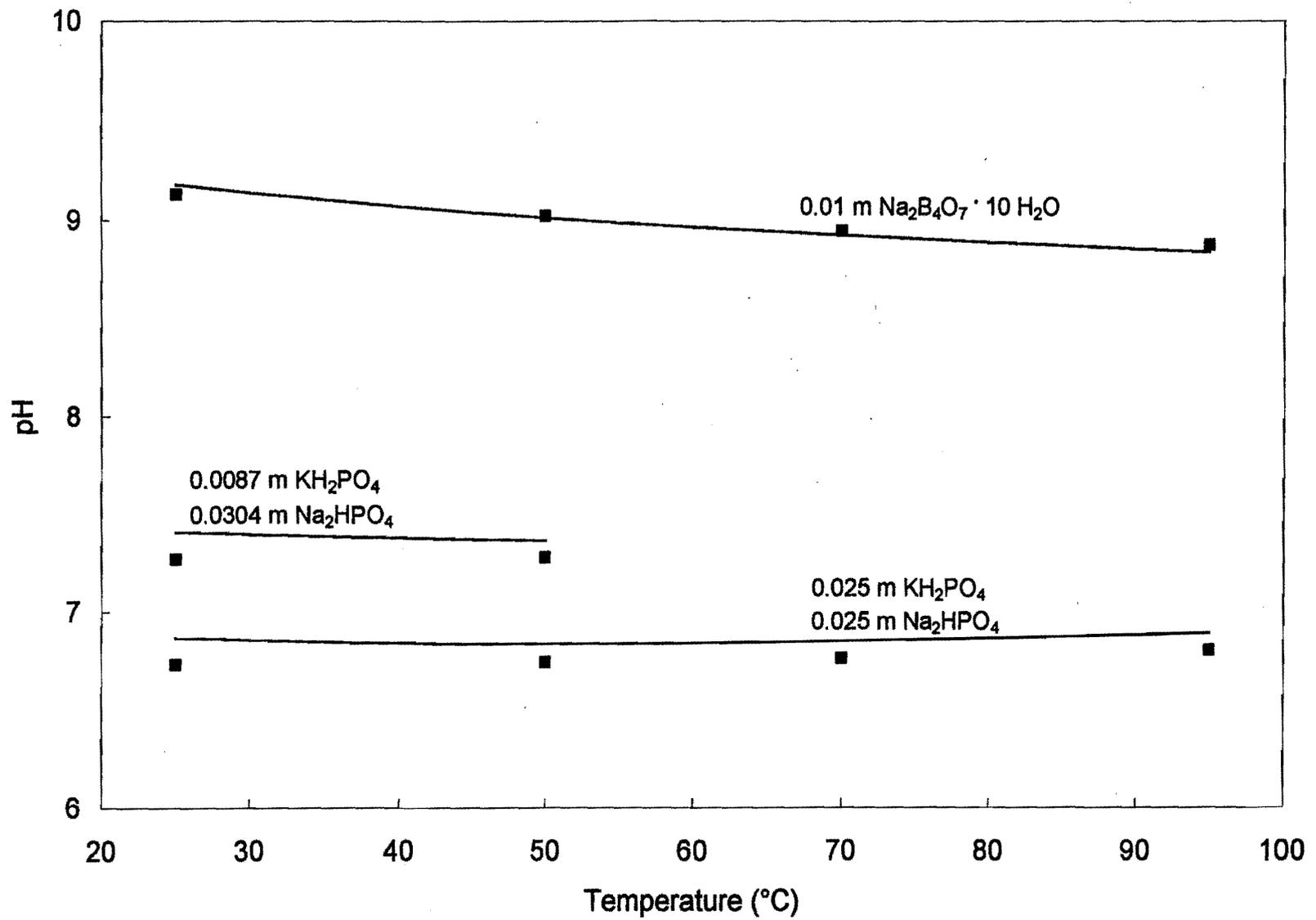


Fig. 7. Temperature variation of pH. Data from ref. 12.

## 6 REFERENCES

1. E. C. Beahm, R. A. Lorenz, and C. F. Weber, *Iodine Evolution and pH Control*, NUREG/CR-5950 (ORNL/TM-12242), 1992.
2. E. C. Beahm, C. F. Weber, T. S. Kress, and G. W. Parker, *Iodine Chemical Forms in LWR Severe Accidents*, NUREG/CR-5732 (ORNL/TM-11861), 1992.
3. C. F. Weber, E. C. Beahm, and T. S. Kress, *Models of Iodine Behavior in Reactor Containments*, ORNL/TM-12202, 1992.
4. C. F. Weber, *Calculation of Absorbed Doses to Water Pools in Severe Accident Sequences*, NUREG/CR-5808 (ORNL/TM-11970), Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., December 1991.
5. B. Wendrow and K. A. Kobe, *Chem. Rev.* **54**, 891 (1954). See also B. Wendrow and K. A. Kobe, *Ind. Eng. Chem.* **44**(6), 1439 (1952).
6. T. M. Besmann, *SOLGASMIX-PV, a Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems*, ORNL/TM-5775, Union Carbide Corp., Nucl. Div., Oak Ridge Natl. Lab., 1977; see also G. Eriksson, *Chemica Scripta* **8**, 100 (1975); G. Eriksson and E. Rosén, *Chemical Scripta* **4**, 193 (1973); G. Eriksson, *Acta. Chem. Scand.* **25**(7), 2651 (1971); Recent modifications described in C. F. Weber, *J. Comp. Phys.*, to be published (1998).
7. R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton, "Acidity Measurements at Elevated Temperatures. VI Boric Acid Equilibriums," *Inorg. Chem.* **11**(3), 537 (1972).
8. R. E. Mesmer and C. F. Baes, Jr., "Phosphoric Acid Dissociation Equilibria in Aqueous Solutions to 300°C," *J. Solution Chem.* **3**(4), 307 (1974).
9. HSC Chemistry for Windows, Version 2.0, Outokumpu Research, May 31, 1994.
10. H. E. Barner and R. V. Scheuerman, *Handbook of Thermochemical Data for Compounds and Aqueous Species*, Wiley, New York, 1978.
11. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions*, 3<sup>rd</sup> Ed., ACS Monograph Series 137, Reinhold Publishing Corp., New York (1958).
12. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2<sup>nd</sup> Ed., Butterworths, London (1959).

**PART B - CALCULATION OF IODINE SPECIATION AND TRANSPORT**

## 1. INTRODUCTION

Under Nuclear Regulatory Commission (NRC) guidance, models of iodine behavior under various severe accident conditions have been developed at Oak Ridge National Laboratory (ORNL), and came to be known collectively as the 'TRENDS' code. NRC support of model development ended in 1992, before any formal documentation or code development was undertaken. However, at the same time a need arose to actually apply most of the iodine chemistry and interaction models to postulated severe accident sequences at the High Flux Isotope Reactor (HFIR) in Oak Ridge. As a part of that work, substantial documentation was accomplished.<sup>1</sup> In addition, the code HFIR-TRENDS was developed to actually perform the calculations. This code is not easily exportable or transportable to other plants or sequences, inasmuch as many statements are tailored to the particular plant (HFIR) for which they were written. Later, certain parts of HFIR-TRENDS were appropriated and modified so as to simulate three Westinghouse AP-600 design basis accidents.<sup>2,3</sup> Most recently, a similar analysis was performed for the first time on an operating plant, a loss of coolant accident (LOCA) at the Grand Gulf Nuclear Plant.<sup>4</sup> In each of these cases, the code was specifically tailored to the plant and accident sequences.

The TRENDS models do not include primary system, aerosol, or thermal hydraulic analyses. In the past, basic plant analyses were done using the MELCOR code for the HFIR and Grand Gulf analyses and MAAP code for the AP-600. Transient variables such as temperatures, pressure and fission product inventories were then input into the TRENDS analysis.

The present set of models is a simplification of TRENDS used in each of the above applications. Its purpose is to calculate iodine speciation and transport within a single control volume. Thus, flows between control volumes, special systems (e.g., standby gas treatment system), and various other components are not included. In addition, some models of iodine chemistry are not included—only those which have been utilized in one of the previous applications. (No additional model development was undertaken as a part of this work.)

The control volume considered here contains a gas space, water pool, and steel surfaces. Models describe aqueous hydrolysis, radiolysis, transport to or from gas space (i.e., evaporation or dissolution), surface reactions and conversion to methyl iodide. Input variables remain fixed throughout the calculation.

It is beyond the scope of this document to provide detailed documentation for each of the models.<sup>1</sup> Fortunately, it has already been done for the most part, and will simply be referenced. However, brief descriptions are undertaken in Section 2. Input data requirements are discussed in Section 3 along with an explanation of output. A sample calculation is also given.

Individual models that form the technical basis for the code have been validated. However, the code as a whole has not been subjected to rigorous verification and validation. Therefore, although the code is a useful tool, it should be applied by users familiar with the phenomena.

## 2. IODINE CHEMISTRY AND INTERPHASE TRANSPORT

Evaluation of reactor accident sequences has generally assumed that the dominant form of iodine is CsI.<sup>5</sup> Emitted from the reactor coolant system as an aerosol, the iodide easily deposits on surfaces or enters water. Deposited particles may be washed into sumps or pools if water films from sprays or condensation are present on the containment surfaces. Otherwise, the deposited species are fairly stable and unlikely to move.

In water, CsI readily dissolves into the constituent ions Cs<sup>+</sup> and I<sup>-</sup>, both of which are quite stable. However, under certain conditions I<sup>-</sup> could react with various other aqueous species and could result in non-trivial amounts of I<sub>2</sub>. While some I<sub>2</sub> will stay dissolved, it evaporates from water much more readily than other species. Once in the gas space, it may be carried with leakage or venting flow into the environment. Thus, the aqueous conversion of I<sup>-</sup> to I<sub>2</sub> presents a significant additional threat of environmental release.

It has been shown<sup>6,7</sup> that the conversion of iodide to molecular iodine takes place only in acidic solutions. At 25°C, the reaction is quite slow for pH above 5, and quite rapid for pH under 3. At 90°C, the reaction proceeds rapidly for pH < 5. Thus, the revolatilization of iodine is dependent primarily on pH and, to a lesser extent, temperature.

In the gas space, I<sub>2</sub> could slowly be converted to organic iodide, an even more elusive and volatile form. Or it could deposit on surfaces, providing immobilization, but not as permanent as I<sup>-</sup> in solution. Other reactions are also possible. In water I<sup>-</sup> could react with metals and form insoluble products which would result in greater immobilization. Gas phase deposition onto painted or concrete surfaces could also occur. Surface iodine could be washed back into a sump by drainage of condensate or sprays. While these mechanisms might all occur in an actual reactor accident, they are not included in the present model, because no previous application has required them. Those mechanisms which are included are discussed briefly in the following subsections.

### 2.1 IODINE HYDROLYSIS

In aqueous solution, iodine can undergo hydrolysis (reactions with water molecules) which is described well by the reaction set<sup>1,8</sup>



The endpoint oxidation states  $I^-$  and  $IO_3^-$  (or  $HIO_3$ ) are highly soluble, and therefore highly desirable. The species  $HOI$  and  $HIO_2$  are reaction intermediates which may be volatile, but which are regarded as having short lifetimes. However, molecular iodine  $I_2$  is stable and sparingly soluble. It can be seen in the above reactions that low pH (i.e., large  $H^+$  concentration) will result in more  $I_2$ , and less  $I^-$  and  $IO_3^-$ . Each forward and reverse reaction gives rise to a single rate equation, with rate constants given in Table 1.

## 2.2 IODINE RADIOLYSIS

Fission product decay constitutes a significant radiation source to water, which catalyzes various iodine reactions. While many of the elementary reactions are still open to considerable debate, the overall results in terms of iodine speciation are well known and predictable. The primary mechanism is the catalytic decomposition of hydrogen peroxide ( $H_2O_2$ ), a substance which is formed when water molecules absorb radiation. Both  $I_2$  and  $I^-$  react with  $H_2O_2$ , and with a sufficient peroxide supply, an equilibrium distribution is established quickly.

The approach to equilibrium is simulated in a manner consistent with the model development in Ref. 1. The buildup of  $H_2O_2$  follows the empirical form

$$C_{H_2O_2} = C_{\infty}(1 - e^{-\alpha \dot{d}t}) \quad (2)$$

where

$\alpha, C_{\infty}$  = empirical constants,

$\dot{d}$  = dose rate (Mrad/h).

The rate of buildup is obtained by differentiating Eq. (2) and rearranging to get

$$\dot{C}_{H_2O_2} = \alpha \dot{d}(C_{\infty} - C_{H_2O_2}). \quad (3)$$

Reaction of iodine species with  $H_2O_2$  progresses with the rates

$$\text{(reduction of } H_2O_2) \quad r_r = k_7 [I^-] [H_2O_2] \quad (4a)$$

$$\text{(oxidation of } H_2O_2) \quad r_o = (a+b[H^+]) \frac{k_7 [I_2] [H_2O_2]}{[I^-] [H^+]^2} \quad (4b)$$

where  $k_7, a$ , and  $b$  are constants defined in Ref. 1, Sect. 3.2.1. The parameter  $k_7$  is actually a measured rate coefficient for the reduction reaction of  $H_2O_2$ .<sup>9</sup> The constants  $a$  and  $b$  arise from an expression for the steady-state distribution. The values for these quantities are given on Table 1. The species concentrations then satisfy

$$\frac{d}{dt} [I^-] = -2 \frac{d}{dt} [I_2] = -r_r + r_o \quad - \frac{d}{dt} [H_2O_2] = r_r + r_o \quad (5)$$

It is not intended that Eqs. (4) and (5) represent actual reaction mechanisms. Rather, they represent a reasonable set of rate expressions which serve to move the system quickly toward the steady-state distribution of  $I^-$  and  $I_2$  while maintaining a dependence on the concentration of  $H_2O_2$  to produce this movement.

### 2.3 GAS/LIQUID PARTITIONING

The same equation is used to describe evaporation of volatile iodine species from water ( $I_2$  or  $CH_3I$ ) or their dissolution from gas.<sup>1</sup> The model is based on the equilibrium partition coefficients (inverse of Henry's Law constant) for each species, and rate equations obtained from natural convection correlations, used with the two-film interface model. If a known surface velocity exists, then natural convection can be replaced by forced convection.

### 2.4 ORGANIC IODIDES

Organic iodides are described empirically by the formation of  $CH_3I$  from  $I_2$  in the gas phase. The model used is described fully in Ref. 1. As is  $I_2$ ,  $CH_3I$  is sparingly soluble in water, an effect which is negligible in the present sequence.

### 2.5 DEPOSITION ON STEEL SURFACES

The gas phase deposition of  $I_2$  onto base steel surfaces follows the two step process



The first step represents physical adsorption from bulk gas and includes mass transfer components. The second step represents a surface chemical reaction, which is irreversible. Complete documentation of the model is found in Ref. 1. The resulting rate constants are given in Table 1.

## 3. DESCRIPTION OF MODELS

The models described in the previous section have been encoded in a set of FORTRAN routines, described below:

MAIN PROGRAM - performs input and data initialization, sets up transient loop and calls principal subroutines for calculation and output.

LSODE - routine for solving systems of stiff ordinary differential equations (part of the public distribution CORLIB<sup>10</sup> set).

OUTPUT - a small routine to perform data output.

CHEM - The principal routine which sets up the rate equations in the form

$$\dot{\mathbf{y}}(t) = \mathbf{f}(\mathbf{y}(t), t)$$

This routine is called by LSODE during transient computations.

CJAC - A routine to analytically calculate the Jacobian

$$\mathbf{J} = \frac{d\mathbf{f}}{d\mathbf{y}}$$

This routine is also called by LSODE during transient calculations.

The models themselves make up the vector function  $\mathbf{f}$ ; changing a model requires changing the Jacobian (CJAC) as well as the function (CHEM). It is beyond the scope of this work to describe details of the coding. However descriptions of input and output are contained in the following sections.

### 3.1 INPUT

Variables required to run the calculation include parameters that describe the physical system, the numerical process, and the species inventories. Each quantity is contained on a separate line in the file 'initial.dat.' The format is 'f12.2' for floating point numbers and 'i12' for integers. Following each variable, a comment may be appended for the remainder of the line. A sample input file is shown in Fig. 1, and indicates the definition and units for each quantity. (The first line is a heading.) Note that some of the species inventories are not used in this version.

Some computational parameters are initialized by code statements rather than by input from a file. For example, all the control parameters for the LSODE routine are specified in the main program. Such parameters can be changed only altering the source code, in consultation with the extensive comments and definitions in the LSODE routine itself.

### 3.2 OUTPUT

Output occurs in three forms. On the screen, aqueous species inventories are printed at each print step as the transient progresses. A sample of this output is shown in Fig.2. The file 'output.dat' contains a much more extensive list of computed variables at each output timestep, listed in Table 2. These include most computed quantities of interest. The output format is '22e12.4,' indicating that each record will require continuation onto several lines. Finally,

diagnostic messages from the LSODE routine are output in the file 'lsoderr.dat.' See the routine itself for documentation of this output.

#### 4. SUMMARY

The 'TRENDS' models constitute a calculational tool to simulate iodine chemistry and transport within a single containment volume. It includes models for aqueous speciation via hydrolysis and radiolysis, evaporation/dissolution, gas phase speciation (conversion of I<sub>2</sub> to organic iodide), and gas phase deposition onto steel surfaces. It is a useful tool to evaluate iodine revolatilization, but does not accomplish a comprehensive accident sequence analysis.

#### 5. REFERENCES

1. C. F. Weber et al., *Models of Iodine Behavior in Reactor Containments*, ORNL/TM-12202, Oak Ridge National Laboratory, 1992.
2. E. C. Beahm, C. F. Weber, and T. A. Dillow, *Technical Assistance in Review of Source Term-Related Issues of Advanced Reactors*, NUREG/CR-6408 (ORNL/TM-13144), Oak Ridge National Laboratory (September 1998).
3. C. F. Weber and E. C. Beahm, *Iodine Volatility and pH Control in the AP-600 Reactor*, NUREG/CR-6599 (ORNL/TM-13555), Oak Ridge National Laboratory (September 1998).
4. C. F. Weber and E. C. Beahm, *Iodine Revolatilization in a Grand Gulf LOCA*, ORNL/M-6544, Oak Ridge National Laboratory, 1998.
5. E. C. Beahm et al., *Iodine Chemical Forms in LWR Severe Accidents*, NUREG/CR-5732 (ORNL/TM-1186 1), Oak Ridge National Laboratory (1992).
6. C.-C. Lin, "Chemical Effects of Gamma Radiation on Iodine in Aqueous Solution," *J. Inorg. Nucl. Chem.* **42**,1101-7 (1980).
7. E. C. Beahm et al., *Iodine Evolution and pH Control*, NUREG/CR-5950 (ORNL/TM-12242), Oak Ridge National Laboratory (1992).
8. C. F. Weber et al., "Optimal Determination of Rate Coefficients in Multiple-Reaction Systems," *Computers and Chem.*, **16**(4), 325-33 (1992).
9. H. A. Liebhafsky, "The Catalytic Decomposition of Hydrogen Peroxide by the Iodine-Iodide Couple at 25°C," *J. Amer. Chem. Soc.*, **54**,1792-1806 (1932).

10. A. C. Hindmarsh, "LSODE and LSODI, Two New Initial Value Ordinary Differential Equation Solvers," ACM-SIGNUM Newsletter **15**(4), 10-11 (1980).

Table 1. Rate Constants

Parameters	Defining Equation	Numerical Value	Units
$\ln k_1$	1a	23.05 - 8161/T	$s^{-1}$
$\ln k_2$	1a	25.59	$L^2/mol^2 \cdot s$
$\ln k_3$	1b	76.46 - 21049/T	$L/mol \cdot s$
$\ln k_4$	1b	40.18 - 6387/T	$L^2/mol^2 \cdot s$
$\ln k_5$	1c	9.527 - 601/T	$L/mol \cdot s$
$\ln k_6$	1c	12.48 - 612/T	$L^2/mol^2 \cdot s$
$k_7$	4	0.012	$L/mol \cdot s$
$\ln k_8$	6	28.24 - 12389/T	$s^{-1}$
$\ln k_9$	6	-2.563 - 3404/T	$s^{-1}$
$\ln k_{10}$	6	0.1142 - 3765/T	$s^{-1}$
$a$	4b	$6.05 \times 10^{-4}$	$(mol/L)^3$
$b$	4b	$1.47 \times 10^{-9}$	$(mol/L)^2$

Table 2. Detailed output description<sup>a</sup>

1. Time (s)	Aqueous Inventories (mol)
2. Total iodine in gas (g-atom)	10. $I^-$
3. Total iodine in water (g-atom)	11. $I_2$
4. Total iodine in surfaces (g-atom)	12. HOI
5. Total iodine in system (g-atom)	13. $HIO_2$
6. $I_2$ in gas (mol)	14. $HI_3^-$
7. $CH_3I$ in gas (mol)	15. $CH_3I$
8. $I_2$ adsorbed on steel (mol)	
9. Surface $FeI_2$ (mol)	

<sup>a</sup> Output format is '1p15e12.4'

Fig. 1. Input file 'input.dat' for sample calculation

```

NRC Iodine Chemistry Analysis
  1.   Pressure (atm)
 40.   Gas temperature (C)
 50.   Liquid temperature (C)
 40.   Wall temperature (C)
  0.   Gas volume (m3)
.0010 Liquid volume (m3)
 10.   Characteristic length (m)
1e17  Dose rate (MeV/s)
  .01  Gas-liquid interfacial area (m2)
  0.   Steel surface area (m2)
 4.5   Water pH
  0.   Forced convection gas velocity (m/s)
  0.   Beginning time (s)
28800. Ending time (s)
  24   Number of print steps (integer)
  0.   I2(g)                1
  0.   CH3I(g)              2
  0.   CsI(aero)            3
  0.   I2(aero)             4
  0.   -----              5
.00010 I-(aq)              6
.00000 I2(aq)              7
  0.   HOI(aq)              8
  0.   HI02(aq)            9
.00000 I03-(aq)           10
  0.   CH3I(aq)            11
  0.   -----             12
  0.   -----             13
  0.   -----             14
  0.   -----             15
  0.   -----             16
  0.   -----             17
  0.   -----             18
  0.   -----             19
  0.   -----             20
  0.   -----             21
  0.   -----             22
  0.   -----             23
  0.   I2(ads-Fe)          24
  0.   FeI2(s)            25
  0.   -----             26

```

Fig. 2. Screen output for sample calculation

Time (s)	Aqueous Iodine Species			Inventories (mol)		
	I-	I <sub>2</sub>	HOI	HI <sub>2</sub>	I <sub>3</sub> -	
1200.0	8.6524E-05	6.7370E-06	2.0908E-09	1.7965E-13	2.3702E-16	
2400.0	7.6131E-05	1.1932E-05	4.2087E-09	8.2765E-13	4.2612E-15	
3600.0	6.8364E-05	1.5815E-05	6.2120E-09	2.0082E-12	2.3231E-14	
4800.0	6.2745E-05	1.8623E-05	7.9702E-09	3.6023E-12	7.4619E-14	
6000.0	5.8811E-05	2.0590E-05	9.4014E-09	5.3479E-12	1.7520E-13	
7200.0	5.6132E-05	2.1929E-05	1.0490E-08	6.9763E-12	3.3365E-13	
8400.0	5.4352E-05	2.2818E-05	1.1273E-08	8.3212E-12	5.4853E-13	
9600.0	5.3189E-05	2.3400E-05	1.1813E-08	9.3378E-12	8.1120E-13	
10800.0	5.2437E-05	2.3775E-05	1.2175E-08	1.0061E-11	1.1104E-12	
12000.0	5.1957E-05	2.4015E-05	1.2412E-08	1.0552E-11	1.4362E-12	
13200.0	5.1652E-05	2.4168E-05	1.2564E-08	1.0878E-11	1.7798E-12	
14400.0	5.1458E-05	2.4265E-05	1.2662E-08	1.1089E-11	2.1354E-12	
15600.0	5.1336E-05	2.4326E-05	1.2725E-08	1.1225E-11	2.4988E-12	
16800.0	5.1258E-05	2.4365E-05	1.2764E-08	1.1312E-11	2.8673E-12	
18000.0	5.1209E-05	2.4389E-05	1.2789E-08	1.1368E-11	3.2388E-12	
19200.0	5.1178E-05	2.4405E-05	1.2805E-08	1.1403E-11	3.6125E-12	
20400.0	5.1158E-05	2.4414E-05	1.2815E-08	1.1425E-11	3.9874E-12	
21600.0	5.1146E-05	2.4421E-05	1.2821E-08	1.1439E-11	4.3631E-12	
22800.0	5.1138E-05	2.4425E-05	1.2825E-08	1.1448E-11	4.7394E-12	
24000.0	5.1133E-05	2.4427E-05	1.2828E-08	1.1454E-11	5.1159E-12	
25200.0	5.1130E-05	2.4429E-05	1.2830E-08	1.1457E-11	5.4927E-12	
26400.0	5.1128E-05	2.4429E-05	1.2831E-08	1.1459E-11	5.8696E-12	
27600.0	5.1127E-05	2.4430E-05	1.2831E-08	1.1461E-11	6.2465E-12	
28800.0	5.1126E-05	2.4430E-05	1.2831E-08	1.1461E-11	6.6235E-12	

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