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The Absorption of Gaseous Iodine by Water Droplets

Michael F. Albert

University of Tennessee - Knoxville

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To the Graduate Council:

I am submitting herewith a thesis written by Michael F. Albert entitled "The Absorption of Gaseous Iodine by Water Droplets." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Jack S. Watson, Major Professor

We have read this thesis and recommend its acceptance:

Joseph J. Perona, H. L. Dodds Jr.

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
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The Graduate School
THE ABSORPTION OF GASEOUS IODINE BY WATER DROPLETS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Michael F. Albert
March 1985
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ABSTRACT

A new model has been developed for predicting the rate at which gaseous molecular iodine is absorbed by water sprays. The model is a quasi-steady state mass transfer model that includes the iodine hydrolysis reactions. The parameters of the model are spray drop size, initial concentration of the gas and liquid phases, temperature, pressure, buffered or unbuffered spray solution, spray flow rate, containment diameter and drop fall height. The results of the model were studied under many values of these parameters. Plots of concentration of iodine species in the drop versus time have been produced by varying the initial gas phase concentration of molecular iodine over the range of $1 \times 10^{-5}$ moles/liter to $1 \times 10^{-10}$ moles/liter and a drop size of 1000 microns.

Results from the model are compared to results available from the Containment Systems Experiments at Pacific Northwest Laboratory. The difference between the model predictions and the experimental data ranges from -120.5% to 68.0% with the closest agreement 7.7%. The new spray model is also compared to previously existing spray models. At high concentrations of gaseous molecular iodine, the new spray model is considered to be less accurate but at low concentrations, the new model predicts results that are closer to the experimental data. Inclusion of the iodine hydrolysis reactions is shown to be a feature important to a model intended for determining the removal of molecular iodine over a wide range of conditions.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. BACKGROUND</td>
<td>1</td>
</tr>
<tr>
<td>1. Iodine and Nuclear Reactor Accidents</td>
<td>1</td>
</tr>
<tr>
<td>2. Existing Spray Models</td>
<td>5</td>
</tr>
<tr>
<td>II. MASS TRANSFER</td>
<td>12</td>
</tr>
<tr>
<td>1. General Mass Transfer with Reaction</td>
<td>12</td>
</tr>
<tr>
<td>2. Overall Mass Transfer Resistance for Iodine Absorption into Water Droplets</td>
<td>17</td>
</tr>
<tr>
<td>III. AQUEOUS IODINE CHEMISTRY</td>
<td>18</td>
</tr>
<tr>
<td>IV. DROP MODEL</td>
<td>37</td>
</tr>
<tr>
<td>V. SPRAY MODEL</td>
<td>60</td>
</tr>
<tr>
<td>VI. WALL-SPRAY MODEL</td>
<td>92</td>
</tr>
<tr>
<td>VII. EXPERIMENTAL DATA</td>
<td>108</td>
</tr>
<tr>
<td>VIII. COMPARISON TO DATA AND TO OLD MODELS</td>
<td>132</td>
</tr>
<tr>
<td>IX. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS</td>
<td>164</td>
</tr>
<tr>
<td>1. Summary</td>
<td>164</td>
</tr>
<tr>
<td>2. Conclusions</td>
<td>166</td>
</tr>
<tr>
<td>3. Recommendations</td>
<td>167</td>
</tr>
<tr>
<td>LIST OF REFERENCES</td>
<td>169</td>
</tr>
<tr>
<td>APPENDIXES</td>
<td>173</td>
</tr>
<tr>
<td>A. NUMERICAL TECHNIQUE</td>
<td>174</td>
</tr>
<tr>
<td>B. KINETIC MODEL, SAMPLE INPUT AND OUTPUT</td>
<td>177</td>
</tr>
<tr>
<td>C. DROP MODEL, SAMPLE INPUT AND OUTPUT</td>
<td>188</td>
</tr>
<tr>
<td>D. SPRAY MODEL, SAMPLE INPUT AND OUTPUT</td>
<td>206</td>
</tr>
<tr>
<td>E. WALL-SPRAY MODEL, SAMPLE INPUT AND OUTPUT</td>
<td>234</td>
</tr>
<tr>
<td>F. LIST OF SYMBOLS</td>
<td>268</td>
</tr>
<tr>
<td>VITA</td>
<td>274</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Values of rate and equilibrium constants (taken from Bell)</td>
</tr>
<tr>
<td>2</td>
<td>Partition coefficient of molecular iodine as a function of temperature</td>
</tr>
<tr>
<td>3</td>
<td>Physical conditions common to all spray experiments (Hillard)</td>
</tr>
<tr>
<td>4</td>
<td>Nozzles used in CSE spray experiments (Hillard)</td>
</tr>
<tr>
<td>5</td>
<td>Atmospheric conditions in CSE spray experiments (Hillard)</td>
</tr>
<tr>
<td>6</td>
<td>Spray flow rates and solutions used in CSE experiments (Hillard)</td>
</tr>
<tr>
<td>7</td>
<td>Timing of spray periods (Hillard)</td>
</tr>
<tr>
<td>8</td>
<td>Iodine material balances (Hillard)</td>
</tr>
<tr>
<td>9</td>
<td>Measured spray liquid distribution in CSE tests (Hillard)</td>
</tr>
<tr>
<td>10</td>
<td>Comparison of spray model to the CSE tests</td>
</tr>
<tr>
<td>11</td>
<td>Comparison of removal rate constant for spray model against CSE tests</td>
</tr>
<tr>
<td>12</td>
<td>Comparison of removal rate constant for spray model against previous models</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yield vs Mass Number for $^{235}U$ Fissions as a function of Incident Neutron Energy$^2$</td>
</tr>
<tr>
<td>2</td>
<td>BWR MARK I Primary Containment System</td>
</tr>
<tr>
<td>3</td>
<td>One Loop of the Residual Heat Removal (RHR) System for the BWR MARK I Containment. Containment Spray is one of the seven operating modes of this system</td>
</tr>
<tr>
<td>4</td>
<td>Comparison of Iodine Washout Predicted by Several Models with that Measured in CSE Using Caustic Spray$^5$</td>
</tr>
<tr>
<td>5</td>
<td>Concentration Profiles for the Two Resistance Models</td>
</tr>
<tr>
<td>6</td>
<td>Kinetic Model Flowsheet</td>
</tr>
<tr>
<td>7</td>
<td>Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-3}$ moles/liter a) Buffered pH of 9.0. b) Buffered pH of 7.0</td>
</tr>
<tr>
<td>8</td>
<td>Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-4}$ moles/liter a) Buffered pH of 9.0. b) Buffered pH of 7.0</td>
</tr>
<tr>
<td>9</td>
<td>Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-5}$ moles/liter a) Buffered pH of 9.0. b) Buffered pH of 7.0</td>
</tr>
<tr>
<td>10</td>
<td>Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-6}$ moles/liter a) Buffered pH of 9.0. b) Buffered pH of 7.0</td>
</tr>
<tr>
<td>11</td>
<td>Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-7}$ moles/liter a) Buffered pH of 9.0. b) Buffered pH of 7.0</td>
</tr>
<tr>
<td>12</td>
<td>Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-8}$ moles/liter a) Buffered pH of 9.0. b) Buffered pH of 7.0</td>
</tr>
<tr>
<td>13</td>
<td>Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-9}$ moles/liter a) Buffered pH of 9.0. b) Buffered pH of 7.0</td>
</tr>
</tbody>
</table>
Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-10}$ moles/liter
a) Buffered pH of 9.0. b) Buffered pH of 7.0

Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-6}$ moles/liter
Unbuffered pH of 9.5

Drop Model Flowsheet

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-5}$ moles/liter and a buffered pH of 9.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-6}$ moles/liter and a buffered pH of 9.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-7}$ moles/liter and a buffered pH of 9.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-8}$ moles/liter and a buffered pH of 9.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-9}$ moles/liter and a buffered pH of 9.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-10}$ moles/liter and a buffered pH of 9.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine as a function of time
Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-5}$ moles/liter and a buffered pH of 7.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-6}$ moles/liter and a buffered pH of 7.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-7}$ moles/liter and a buffered pH of 7.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-8}$ moles/liter and a buffered pH of 7.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-9}$ moles/liter and a buffered pH of 9.0
a) Concentration in the liquid drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-10}$ moles/liter and a buffered pH of 9.0
a) Concentration in the Liquid Drop as a function of time. b) Number of moles of molecular iodine transferred as a function of time

Spray Model Flowsheet

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-5}$ moles/liter and a buffered pH of 9.0 in the liquid phase
Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-6}$ moles/liter and a buffered pH of 9.0 in the liquid phase ........................................ 68

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-7}$ moles/liter and a buffered pH of 9.0 in the liquid phase ........................................ 70

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-8}$ moles/liter and a buffered pH of 9.0 in the liquid phase ........................................ 72

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-9}$ moles/liter and a buffered pH of 9.0 in the liquid phase ........................................ 74

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-10}$ moles/liter and a buffered pH of 9.0 in the liquid phase ........................................ 76

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-5}$ moles/liter and a buffered pH of 7.0 in the liquid phase ........................................ 78

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-6}$ moles/liter and a buffered pH of 7.0 in the liquid phase ........................................ 80

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-7}$ moles/liter and a buffered pH of 7.0 in the liquid phase ........................................ 82

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-8}$ moles/liter and a buffered pH of 7.0 in the liquid phase ........................................ 84

Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-9}$ moles/liter and a buffered pH of 7.0 in the liquid phase ........................................ 86
Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-10}$ moles/liter and a buffered pH of 7.0 in the liquid phase

Boundary Conditions for Falling Liquid Film

Wall-Spray Model Flowsheet

Results of Wall-Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-7}$ moles/liter and a buffered pH of 9.0 in the liquid phase

Results of Wall-Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-10}$ moles/liter and a buffered pH of 9.0 in the liquid phase

Schematic diagram of containment arrangement used in CSE spray tests (Hillard5)

Maypack Sampler

Concentration of elemental iodine in the main room, run A-3 (Hillard5)

Concentration of elemental iodine in the main room, run A-4 (Hillard5)

Concentration of elemental iodine in the main room, run A-6 (Hillard5)

Concentration of elemental iodine in the main room, run A-7 (Hillard5)

Concentration of elemental iodine in the main room, run A-8 (Hillard5)

Liquid volumes and concentration in vessel sumps, run A-3 (Hillard5)

Liquid volumes and concentration in vessel sumps, run A-4 (Hillard5)

Liquid volumes and concentration in vessel sumps, run A-6 (Hillard5)

Liquid volumes and concentration in vessel sumps, run A-7 (Hillard5)
57 Liquid volumes and concentration in vessel sumps, run A-8 (Hillard\textsuperscript{5}) ........................................ 127

58 Results of Spray Model for CSE run A-3 first spray period. Initial concentration of molecular iodine in the gas phase of $1.97 \times 10^{-7}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 133

59 Results of Spray Model for CSE run A-3 second spray period. Initial concentration of molecular iodine in the gas phase of $1.29 \times 10^{-8}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 135

60 Results of Spray Model for CSE run A-4 first spray period. Initial concentration of molecular iodine in the gas phase of $1.50 \times 10^{-7}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 137

61 Results of Spray Model for CSE run A-4 second spray period. Initial concentration of molecular iodine in the gas phase of $7.88 \times 10^{-10}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 139

62 Results of Spray Model for CSE run A-6 first spray period. Initial concentration of molecular iodine in the gas phase of $8.67 \times 10^{-8}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 141

63 Results of Spray Model for CSE run A-6 second spray period. Initial concentration of molecular iodine in the gas phase of $2.01 \times 10^{-9}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 143

64 Results of Spray Model for CSE run A-7 first spray period. Initial concentration of molecular iodine in the gas phase of $1.06 \times 10^{-7}$ moles/liter and a buffered pH of 5.0 in the spray solution .......... 145

65 Results of Spray Model for CSE run A-7 second spray period. Initial concentration of molecular iodine in the gas phase of $2.05 \times 10^{-8}$ moles/liter and a buffered pH of 5.0 in the spray solution .......... 147

66 Results of Spray Model for CSE run A-8 first spray period. Initial concentration of molecular iodine in the gas phase of $1.18 \times 10^{-7}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 149

67 Results of Spray Model for CSE run A-8 second spray period. Initial concentration of molecular iodine in the gas phase of $4.14 \times 10^{-9}$ moles/liter and a buffered pH of 9.5 in the spray solution .......... 151
CHAPTER I

BACKGROUND

1. Iodine and Nuclear Reactor Accidents

Radioactive isotopes of iodine are produced in abundance within the reactor cores of nuclear power plants. Much concern has been placed on the possible release into the atmosphere of radioactive iodine under accident conditions. Iodine can be inhaled or ingested and is quickly absorbed into the bloodstream. Once in the body, iodine concentrates preferentially in the thyroid gland, which is apparently the only tissue in the human body that uses iodine. As a result, the radiation dose to the thyroid is likely to exceed by far the dose to the rest of the body and is likely to affect more individuals than any other health effect from a nuclear reactor accident.

In a nuclear reactor, fissionable isotopes such as uranium-235 and plutonium-239 interact with neutrons resulting in a release of energy and the formation of fission product fragments. As can be seen in Figure 1, iodine (atomic number 53; mass numbers from 125 to 133) is an abundant fission product, and iodine can exist in a number of radioactive states; the most important is iodine-131. Radioactive iodine emits beta particles and gamma photons that can cause severe health effects.

There are several basic types of nuclear power plant designs. One classification (the most important in the United States) is the light water reactor. The two different types of light water reactors are pressurized water reactors (PWRs) and boiling water reactors (BWRs). In
Figure 1. Yield vs Mass Number for $^{235}\text{U}$ Fissions as a function of Incident Neutron Energy.\textsuperscript{2}
PWRs, the pressurized cooling water is not allowed to boil in the reactor core, but BWRs operate at lower pressure and have a different core design which allows the water boil. Power generation systems for both of these reactors are similar to those in other thermal electrical generating plants. Heat is produced and is used to generate steam which turns the turbine to generate electricity. In the case of a nuclear reactor, heat is produced by the fission process.

One serious accident sequence postulated that could result in release of iodine into the atmosphere is a "loss of coolant accident." For example, in the design basis accident sequence for a boiling water reactor, the recirculation system piping connected to the reactor vessel is presumed to break on the suction side of the pump, (see Figure 2) and it is assumed that the emergency cooling water systems do not function. The reactor control rods would be inserted to shut down the reactor, but heat would still be produced, due to decay of radionuclides in the reactor (decay heat), at an initial rate equivalent to approximately 7% of the normal operating power. The decay heat generation rate slowly decreases with time after reactor shutdown, but enough heat would be produced in the short term to boil off the water and expose the fuel rods to air. Without restoration of core cooling water systems, the fuel rods would eventually overheat and fracture, releasing the fission products. The fission products have a pathway into the primary containment (drywell) via the fractured cooling water pipe. The pressure in the drywell would increase and eventually the primary
Figure 2. BWR MARK I Primary Containment System.
containment would fail. The fission products would then be able to escape into the secondary containment or reactor building and from there into the outside atmosphere and expose the environment to radioactive iodine.

To minimize the release of radioactive iodine to the environment under the conditions of the design basis accident, all light water reactors have a containment water spray system. The spray systems are located outside of the reactor vessel and inside the primary containment for both PWR and BWR designs. Figure 3 shows the location of the containment sprays for the BWR Mark I containment design. The purposes of the spray systems are to remove the heat and thereby lower the pressure within the primary containment and to remove airborne fission products. As indicated, the BWR spray systems employ ordinary water taken from the pressure suppression pool. Models that predict the rate of iodine removal by the containment sprays are necessary for rational design of spray systems and for predicting the behavior of existing spray systems under accident conditions.

2. Existing Spray Models

In the past, most PWR containment spray systems used an aqueous sodium-thiosulfate solution. The reaction that occurs between sodium-thiosulfate and iodine is:

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \]  

(1)

This reaction is very fast, essentially instantaneous. However, sodium-thiosulfate has been found to be unstable in a radioactive atmosphere, breaking down into colloidal sulfur which is highly corrosive to ferrous
Figure 3. One Loop of the Residual Heat Removal (RHR) System for the BWR MARK I Containment. Containment Spray is one of the seven operating modes of this system.
metals. Because of this problem, sodium-thiosulfate solutions are no longer used.

The spray solutions now used for PWR spray systems are, for the most part, sodium hydroxide-boric acid solutions, while ordinary water is used in BWR spray systems. The chemical reactions that occur in these solutions are not as fast as the reactions for sodium-thiosulfate. The existing model for the removal rate of iodine is first order and can be expressed by:

\[ \frac{dC}{dt} = -\lambda C, \]  
(2)

where

\( C \) = concentration of iodine in the gas phase,

\( t \) = time,

\( \lambda \) = washout rate constant.

Integrating:

\[ C = C_0 \exp(-\lambda t) \]  
(3)

where \( C_0 \) is the initial iodine concentration.

The washout rate constant is defined as:

\[ \lambda = \frac{F P E}{V} \]  
(4)

where

\( F \) = spray flow rate,

\[ \frac{C_1}{C} \] = iodine partition coefficient for iodine between water and air (related to Henry's coefficient),

\( V \) = containment volume, and

\( E \) = removal efficiency.
The removal efficiency is defined as:

\[
E = 1 - \frac{6N_{Sh}^2 \exp\left(-a_n^2 \phi\right)}{a_n^2 (a_n^2 + N_{Sh}(N_{Sh}-1))} \text{ for a stagnant drop model,}\tag{5}
\]

\[
E = 1 - \exp\left[-\frac{6k \gamma_t e}{d(P + k_g/k_1^0)}\right] \text{ for a stagnant film model,}\tag{6}
\]

\[
E = 1 - \exp\left[-\frac{6k \gamma_t e}{dP}\right] \text{ for a well-mixed model,}\tag{7}
\]

and

\[
E = \frac{6k \gamma_h}{g} \text{ for a gas phase controlling resistance model.}\tag{8}
\]

In these equations,

- \(k_g\) = gas film mass transfer coefficient,
- \(k_1^0\) = liquid film mass transfer coefficient without reaction,
- \(t_e\) = drop exposure time,
- \(d\) = drop diameter,
- \(N_{Sh}\) = \(k_g d/(2 PC D_1)\),
- \(D_1\) = liquid diffusion coefficient,
- \(\phi = 4D_1 t_e/d^2\),
- \(a_n\) = \(n\)th root of \(a_n \cot(a_n) + (N_{Sh}-1) = 0\),
- \(h\) = drop fall height, and
- \(v_g\) = terminal settling velocity of the drop.

Equations 4 and 8 result in a washout rate constant:

\[
\lambda = \frac{6k \gamma_F h}{v_g d} \tag{9}
\]
Using this equation for the removal rate constant, the equation for the concentration in the gas is:

\[ C = C_0 \exp \left( \frac{-6 \frac{k}{g} \frac{F}{ht}}{V \frac{v}{g d}} \right). \] (10)

The property \( P \) is referred to as an "effective" partition coefficient because it relates the total concentration of species containing iodine, \( I^- \), in the liquid to the gas phase at the interface. The "effective" partition coefficient for aqueous iodine is defined as:

\[ P = \frac{[I_2 \text{ (liquid)}] + [I_2 \text{(reacted)}]}{[I_2 \text{ (gas)}]}, \] (11)

where the square brackets represent the concentration of the species.

A model often used today referred to as the "realistic" model is the well-mixed drop model with a partition coefficient of 100,000; this appears to give satisfactory results (see Figure 4 for comparison to existing data). The major problems with the "realistic" model are that it does not describe the iodine hydrolysis reactions, it does not deal with the liquid phase concentration, and it uses an effective partition coefficient. The effective partition coefficient is that it lumps the effects of the reactions into a single constant. The effects of the kinetics on the rate of mass transfer, under all conditions, are not constant (see Chapter 3). The temperature of the spray solution, the initial concentration of the spray solution, the pH of the spray solution, and the contact time of the individual drops all will significantly affect the rate of mass transfer. Therefore, a different effective partition coefficient is required for each condition which might
Figure 4. Comparison of Iodine Washout Predicted by Several Models with that Measured in CSE Using Caustic Spray.
exist. For these reasons, the "realistic" model will predict the same removal rate for an initial concentration in the liquid of molecular iodine of zero and for an initial concentration in the liquid near equilibrium.

The best available experimental results that might be used in an effort to judge the efficacy of the "realistic" model are the results obtained in the Containment Systems Experiments (CSE) which are discussed in Chapter 7. Briefly, these experiments are large scale containment system tests in which one of the goals of the tests was to determine the rate of removal of gaseous molecular iodine by water sprays. Some of the experimental runs used recirculatory sprays. For example, the third spray period for CSE experiment A-4 is for a recirculatory spray. The data show desorption of iodine from the spray solution. The so-called "realistic" model would predict that iodine is still being removed from the gas phase.

The objectives of this work are to develop a new model for the absorption of gaseous molecular iodine by water droplets which includes the iodine hydrolysis reactions and to determine if and under what conditions, the iodine hydrolysis reactions influence the rate of mass transfer. The parameters of the model are the initial gas phase concentration of molecular iodine, the initial concentration of the iodine species in the liquid (including pH), the gas phase temperature, the liquid phase temperature, the pressure, the diameter of the droplets, the spray flow rate, the spray time, the containment diameter and the containment height (drop fall height).
CHAPTER II

MASS TRANSFER

1. General Mass Transfer with Reaction

Mass transfer between two phases occurs because of a chemical potential driving force between the bulk of each phase and the interface. When the chemical potential driving force is greater in the gas phase than in the liquid phase (see Figure 5), the component being absorbed diffuses through the gas film to the interface of the drop where equilibrium is achieved. This phenomena is usually referred to as the "gas-film resistance", which suggests a stagnant gas film of finite thickness through which the soluble gas is transferred by molecular diffusion. The transferring species then diffuses from the liquid interphase to the bulk of the liquid. A concentration gradient exists in the liquid phase, just as in the gas phase, and this is referred to as the "liquid-film resistance", suggesting a stagnant liquid film of finite thickness at the interface. The bulk liquid may be completely mixed and thus have a uniform concentration, or it might be stagnant with the concentration of the transferring species decreasing as the distance from the interface increases, or the bulk liquid could be partially mixed. When chemical reactions occur in the bulk liquid, the concentration of the diffusing species can be reduced (or even eliminated) by the reactions. This can give a higher driving force due to the lower concentration of the transferring species in the bulk liquid.
Figure 5. Concentration Profiles for the Two Resistance Models.
Complications can occur when determining the effect of the chemical reactions on the mass transfer rate. As the transferring species diffuses through the liquid, that species is partially or possibly totally removed from the liquid by the chemical reactions. The rate of mass transfer may be increased further because the concentration gradient driving force at the interface becomes steeper (see Astarita\textsuperscript{6} or Dankwerts\textsuperscript{7} for more details). On the other hand, if the reaction in the liquid occurs very slowly, it might not affect the rate of mass transfer. A fast reaction in the liquid will increase the rate of mass transfer to a greater extent by removing the diffusing species from within the liquid film. A instantaneous reaction that occurs on the surface completely eliminates the contribution of the liquid phase to the rate of mass transfer.

The unsteady-state differential equation for diffusion with simultaneous reaction of the diffusing species is:\textsuperscript{6}

\[
D \Delta_2 C = u \cdot \nabla C + \frac{\partial C}{\partial t} + R .
\]

These terms represent the relation

\[
\text{molecular transport} = \text{convection} + \text{accumulation} + \text{reaction rate},
\]

where

\[
\Delta_2 = \text{Laplacian operator} = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} ,
\]

\[
\nabla = \text{Nabla operator} = \sigma_1 \frac{\partial}{\partial x_1} + \sigma_2 \frac{\partial}{\partial x_2} + \sigma_3 \frac{\partial}{\partial x_3} ,
\]

\[
u = \text{velocity <vector>},
\]

\[
C = \text{concentration of the diffusing species},
\]

\[
t = \text{time, and}
\]

\[
R = \text{reaction rate}.
\]
For the penetration theory in one-dimension in spherical coordinates, this equation reduces to:

\[
D_1 \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t} + R .
\]

(13)

Where \( r \) is the distance from the outer radius of the drop.

For the film theory (which assumes steady state in the film) in one-dimension, the unsteady-state diffusion equation reduces to

\[
\frac{D_1}{r^2} \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) = R .
\]

(14)

These equations can be solved analytically for simple kinetics. In general, the solution involves solving a series of differential equations for all species present. For the complex differential equations resulting from the iodine hydrolysis reactions (see Chapter 3), an analytical solution for the unsteady-state diffusion equation with reaction is not possible, and a numerical solution is required.
2. Overall Mass Transfer Resistance for Iodine Absorption into Water Droplets

When mass transfer occurs between two phases, the resistance to diffusion of both phases will influence the rate of mass transfer. If one phase's contribution to the overall resistance is much smaller than the contribution of the other phase, the effect of the phase, with the smaller resistance, may be ignored because it will not significantly affect the overall rate of mass transfer. The overall mass transfer resistance is the sum of the two resistances. For a soluble gas transported across both films, one can write for a completely mixed drop:

\[ M_r = k_g (C_g - C_{gi}) = k_1^o (C_{li} - C_l) \]  

(15)

where

- \( M_r \) = rate of mass transfer,
- \( k_g \) = gas-side mass transfer coefficient,
- \( k_1^o \) = liquid-side mass transfer coefficient with no reactions,
- \( C_g \) = concentration in the bulk gas,
- \( C_{gi} \) = concentration in the gas at the interface,
- \( C_l \) = concentration in the bulk liquid,
- \( C_{li} \) = concentration in the liquid at the interface.

Using a partition coefficient \( P = C_{li}/C_{gi} \):

\[ M_r = k_g (C_g - C_{gi}) = k_1^o (P C_{gi} - C_l) \]  

(16)

Solving for \( C_{gi} \):

\[ k_g (C_g - C_{gi}) = k_1^o (P C_{gi} - C_l) \]  

(17)
Substituting into Equation 16, one obtains:

\[
C_{g1} = \frac{k^0C_1 + k_g C_g}{k_g + k^0_1 p}.
\]  \hspace{1cm} (18)


\[
M_r = \frac{(P C_g - C_1)}{[1/(k^0_1) + P/k_g]} = K_{lov} (P C_g - C_1)
\]  \hspace{1cm} (19)

where

\[
K_{lov} = \frac{1}{1/k^0_1 + P/k_g}
\]  \hspace{1cm} (20)

where \(K_{lov}\) is the overall liquid-side mass transfer coefficient.

To estimate the relative contribution of the individual resistances (for the case of completely mixed bulk liquid and no chemical reactions), one can calculate the overall mass transfer coefficient and compare with the reciprocal of the individual gas and liquid mass transfer coefficients. (See Chapter 4, DROP MODEL, for calculation equations for mass transfer coefficients.) At 25°C:

\[
k_g = 10.75 \text{ cm/sec},
\]

\[
k^0_1 = 0.25 \text{ cm/sec},
\]

\[
P = 86.8,
\]

\[
\frac{1}{K_{lov}} = \frac{1}{0.25} + \frac{86.8}{10.75},
\]

\[
K_{lov} = 0.0826 \text{ cm/sec}.
\]

This indicates that there is significant resistance to mass transfer in both phases when no reactions occur. The chemical reactions that occur in the liquid (see Chapter 3, AQUEOUS IODINE CHEMISTRY) will tend to decrease the significance of the liquid phase.
CHAPTER III

AQUEOUS IODINE CHEMISTRY

The chemistry of aqueous iodine has been studied in depth by Bell, Sellers, and Eigen. The true reaction mechanisms of iodine and water are not known. The following reactions involving iodine and water are the best equation available for a mass transfer with reaction model:

1) \[ I_2 + H_2O \rightarrow HOI + I^- + H^+ \]

2) \[ 3HOI \rightarrow IO_3^- + 2I^- + 3H^+ \]

3) \[ 4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O \]

4) \[ I_2 + I^- \rightarrow I_3^- \]

5) \[ HOI \rightarrow H^+ + OI^- \]

6) \[ H_2O \rightarrow H^+ + OH^- \]

Note that this treatment essentially considers iodine hydrolysies as a two step mechanism given by equations 21 and 22. The other equations give terms related to this assumed two step process.

The kinetic rate equations developed for the chemical equations above are:
\[
\begin{align*}
\frac{d[I_2]}{dt} &= -k_1[I_2] + k_{-1}[I^-][HOI][H^+] + 0.5 k_3[H^+][O_2][I^-] \\
&- k_4[I_2][I^-], \\
\frac{d[I^-]}{dt} &= k_1[I_2] - k_{-1}[I^-][HOI][H^+] + (2/3) k_{20}[HOI]^2 \\
&+ (2/3) k_{21}[HOI][OI^-] - 2 k_{-2}[IO_3^-][I^-]^2[H^+]^2 \\
&- k_3[H^+][O_2][I^-] - k_4[I_2][I^-], \\
\frac{d[HOI]}{dt} &= k_1[I_2] - k_{-1}[I^-][HOI][H^+] - k_{20}[HOI]^2 \\
&- k_{21}[HOI][OI^-] + 3 k_{-2}[IO_3^-][I^-]^2[H^+]^2, \\
\frac{d[IO_3]}{dt} &= (1/3) k_{20}[HOI]^2 + (1/3) k_{21}[HOI][OI^-] \\
&- k_{-2}[IO_3^-][I^-]^2[H^+]^2, \\
\frac{d[I_3]}{dt} &= k_4[I_2][I^-] - k_{-4}[I_3] + k_3[H^+][O_2][I^-], \\
\frac{d[H^+]}{dt} &= k_1[I_2] - k_{-1}[I^-][HOI][H^+] + k_{20}[HOI]^2 \\
&+ k_{21}[HOI][OI^-] - 3 k_{-2}[IO_3^-][I^-]^2[H^+]^2 \\
&- k_3[H^+][O_2][I^-].
\end{align*}
\]

The stoichiometry of Equations 21 through 26 are not represented in the Equations 27 through 31 because Equations 27 through 31 are derived from experimental observations. Equation 32 was derived by incorporating the individual rate expressions used by Bell.

The first reaction has been assigned a pseudo first order rate constant for the forward reaction and a third order rate constant has been assigned to the reverse reaction. This reaction is fast and comes to equilibrium in a few seconds (see Table 1 for rate constants). There
Table 1. Values of rate of equilibrium constants (Bell⁹)

<table>
<thead>
<tr>
<th>Constant</th>
<th>Temperature (°C)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1^a$</td>
<td>20</td>
<td>3 $s^{-1}$</td>
</tr>
<tr>
<td>$k_{-1}$</td>
<td>20</td>
<td>$4.4 \times 10^{12} \ M^{-2} \ s^{-1}$</td>
</tr>
<tr>
<td>$k_{20}$</td>
<td>25</td>
<td>250 $M^{-1} s^{-1}$</td>
</tr>
<tr>
<td>$k_{21}$</td>
<td>25</td>
<td>120 $M^{-1} s^{-1}$</td>
</tr>
<tr>
<td>$k_{-2}$</td>
<td>25</td>
<td>$3 \times 10^{8} \ M^{-4} s^{-1}$</td>
</tr>
<tr>
<td>$k_3$</td>
<td>25</td>
<td>$3.475 \times 10^{-4} \ M^{-2} s^{-1}$</td>
</tr>
<tr>
<td>$k_4$</td>
<td>25</td>
<td>$3 \times 10^{6} \ M^{-1} s^{-1}$</td>
</tr>
<tr>
<td>$k_{-4}$</td>
<td>25</td>
<td>$4 \times 10^{3} s^{-1}$</td>
</tr>
<tr>
<td>$k_5$</td>
<td>25</td>
<td>736</td>
</tr>
<tr>
<td>$k_6$</td>
<td>25</td>
<td>$2.3 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

*The value of $k_1$ was calculated by Eigen and Kustin,¹¹ who assumed that $K_1 = 6.8 \times 10^{-13} \ M^2$.  

20
is a pH dependency since hydrogen ions (H+) are formed and the extent of the reaction varies greatly with the pH of the solution. The existence of hypoiodous acid, HOI, has not been proven; however, HOI is thought to be formed.9

The second reaction has been assigned a two term rate equation in which both expressions have a second order rate constant for the forward reaction and a fifth order rate constant for the reverse reaction. The second reaction is much slower than the first reaction and comes to equilibrium in a period of time varying from approximately fifteen seconds to well over one year depending on the pH. As in the first reaction, the higher the pH, the faster the reaction rate.

The third reaction is irreversible. The concentration of oxygen is assumed to be constant and is related to the concentration of oxygen in the gas by a Henry's coefficient. A pseudo second order rate constant kp3, can then be assigned to this reaction:9

\[ kp_3 = k_3 [O_2] \] (33)

In this third reaction, molecular iodine is a product, and the reaction is also pH dependent. At a low pH, the equilibrium shifts to the right, resulting in the production of more molecular iodine. But the production of molecular iodine by this reaction is small. Therefore, the third reaction also produces more beneficial effects, at a high pH, by producing molecular iodine than at a low pH.

Reaction four involves the formation of tri-iodide. This reaction is very important because it is essentially instantaneous and removes
molecular iodine from the solution. A second order rate constant is assigned to the forward reaction and a first order rate constant is assigned to the reverse reaction.⁹

Reaction five is the dissociation of hypoiiodous acid, and reaction six is the dissociation of water. Both reaction five and six are essentially instantaneous.

The most important reactions are the first and the fourth reactions. Both of these reactions remove molecular iodine from the solution, and by lowering the concentration of molecular iodine, the concentration driving force for mass transfer increases.

The most important species besides molecular iodine is the hydrogen ion concentration. Overall, the removal of molecular iodine from solution is increased when the pH of the solution is high and is decreased when the pH is low. All of the reactions except reaction four contain terms involving the hydrogen ion concentration.

At a high pH, the combined result of all reactions is to deplete the concentration of molecular iodine in solution. As a result, the concentration driving force for mass transfer is increased, and the mass transfer rate is increased. It is also very desirable to have the pH buffered because sufficient hydrogen ions are produced that otherwise would cause the pH to drop very quickly to a point where the reactions would essentially stop.

Little information is available concerning the temperature dependencies of these reactions. For reactions 1 through 3, no experimental information is available for the temperature dependencies. The
temperature dependence upon the equilibrium constants for reactions 4 through 6 are:

\[
\ln K_4 = 3727.86/T - 11.6326 + 0.0192212T \\
\log K_5 = 2800.48 + 0.7335 T - 80670/T -1115.1 \log T \\
\log K_6 = -4.098 -3245.2/T + 2.2367 \times 10^5/T^2 - 3.984 \times 10^7/T^3 \\
+ (13.957 - 1262.3/T) \log \text{DENLIQ}
\]

where \( \text{DENLIQ} \), the density of water which was derived by a numerical fit to experimental data \(^{17} \) is given by:

\[
\text{DENLIQ} = 6.0251147 \times 10^{-9} T^3 - 9.1329064 \times 10^{-6} T^2 \\
+ 3.573572 \times 10^{-3} T + 5.835882 \times 10^{-1}, \text{ and}
\]

\( T = \text{temperature, K.} \)

A numerical model which simulates the iodine hydrolysis reactions has been developed (see Appendix B). The model uses a Runge-Kutta-Felhburg (RKF) algorithm\(^{12} \) which numerically integrates the kinetic rate equations 27 through 32 as a function of time. Figure 6 shows the algorithm for the kinetic model. Inputs to the model are:

1) temperature of the solution,
2) initial concentration of all species in the solution,
3) whether buffered or unbuffered (see Appendix A, Numerical Technique), and
4) simulation time.

Output from the model produces one file and one plot. File FOR50.DAT contains the concentration of all species as a function of time (see
DETERMINE NEW STEP SIZE (LARGER)

DETERMINE NEW STEP SIZE (SMALLER)

UPDATE SPECIES CONCENTRATION

ACCEPT

CHECK ERROR

REJECT

CHECK TO SEE IF FINISHED

YES

STOP

INPUTS:
TEMP, WOLD(1), WOLD(2), WOLD(3),
WOLD(4), WOLD(5), WOLD(6), WOLD(7),
A, B, HMIN, HMAX, IN, TOLER.

DETERMINE THE CHANGE IN THE CONCENTRATION OF EACH IODINE HYDROLYSIS SPECIES, ACCORDING TO THE REACTIONS.

Figure 6. Kinetic Model Flowsheet.
Appendix B for a sample output). This file is used to make a plot of concentration of all species in the liquid versus time.

Figures 7 through 15 show the chemical kinetics as a function of time for initial concentrations of molecular iodine of $1.0 \times 10^{-3}$ to $1.0 \times 10^{-10}$ moles/liter and the initial concentration of the other species were zero. These plots were produced by numerically integrating the iodine hydrolysis reactions (see Appendix A for a description of the numerical technique). The fifteen-second time scale was chosen as the maximum drop lifetime because fifteen-seconds is the maximum time a drop would experience in a containment safety spray system (for longer reaction times see Reference 9).

These plots show that the concentration of molecular iodine decreases as the conversion of molecular iodine increases. For example, with an initial concentration of molecular iodine of $1 \times 10^{-3}$ moles/liter and with a buffered pH of 9.0, Figure 7a, the equilibrium concentration of molecular iodine is by a factor of approximately five less than the initial concentration. At an initial concentration of molecular iodine of $1 \times 10^{-10}$ moles/liter and a buffered pH of 9.0, Figure 14a, the equilibrium concentration of molecular iodine is almost seven orders of magnitude less than the initial concentration. The leveling-off of the change in the concentration of molecular iodine that occurs before 5 seconds is due mainly to the equilibration of the first reaction. The effects of the second reaction are not as obvious, but after the plateau has occurred, the concentration of molecular iodine is still dropping and the concentration of iodide, $I^-$, is increasing due to
Figure 7. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-3}$ moles/liter.

(a) Buffered pH of 9.0.
(b) Buffered pH of 7.0.
Figure 8. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-4}$ moles/liter.

(a) Buffered pH of 9.0.
(b) Buffered pH of 7.0.
Figure 9. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-5}$ moles/liter.

(a) Buffered pH of 9.0.
(b) Buffered pH of 7.0.
Figure 10. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-6}$ moles/liter.
(a) Buffered pH of 9.0.
(b) Buffered pH of 7.0.
Figure 11. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-7}$ moles/liter.

(a) Buffered pH of 9.0.

(b) Buffered pH of 7.0.
Figure 12. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-8}$ moles/liter.

(a) Buffered pH of 9.0.
(b) Buffered pH of 7.0.
Figure 13. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-9}$ moles/liter.

(a) Buffered pH of 9.0.
(b) Buffered pH of 7.0.
Figure 14. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-10}$ moles/liter.

(a) Buffered pH of 9.0.
(b) Buffered pH of 7.0.
Figure 15. Results of Kinetic Model. Initial concentration of molecular iodine $1.0 \times 10^{-6}$ moles/liter Unbuffered pH of 9.5.
the second reaction. The second reaction equilibrates very slowly and this equilibrium is shown in the figures provided by Reference 9.

In Figures 7 through 14, part a is for a buffered pH of 9 in the liquid while part b presents the results for a buffered pH of 7. Comparing the two parts, the conversion of molecular iodine for the same initial concentration is much greater for the pH 9 solutions than for the pH 7 solutions. For a pH of 7 and a high concentration of molecular iodine (above $1.0 \times 10^{-7}$ moles/liter), the fraction of molecular iodine converted is small but as the initial concentration of molecular iodine decreases, the conversion of molecular iodine increases. At an initial concentration of molecular iodine of $1.0 \times 10^{-10}$ moles/liter, the concentration of molecular iodine, at equilibrium, decreases by five orders of magnitude for a buffered pH of 7.0 as opposed to a decrease of 7 orders of magnitude for a buffered pH of 9.0.

Figure 15 represents results calculated for an unbuffered solution of pH 9.5 and an initial concentration of molecular iodine of $1.0 \times 10^{-6}$ moles/liter. The plotted results show quite clearly the effects of the enormous quantity of hydrogen ions produced, such that the pH very quickly drops from its initial value to a pH of approximately 6, and the reactions essentially cease.

A few important conclusions can be drawn from observing the plots of the iodine hydrolysis reactions and considering their effects on the rate of mass transfer:

1) For a solution that is buffered at a high pH, the reactions greatly increase the rate of mass transfer by decreasing the concentration
of molecular iodine in the liquid. This increases the concentra-
tion driving force for mass transfer, thereby increasing the over-
all rate of mass transfer.

2) For a solution that is buffered at a low pH, the reactions will
also increase the rate of mass transfer, but the increase will be
much less than for a buffered high pH.

3) For a solution that is unbuffered at essentially any pH, the pH
will almost immediately drop to a value at which reactions cease,
and the reactions, therefore, will not have any substantial further
effect on the rate of mass transfer.
CHAPTER IV

DROP MODEL

The drop model simulates a single droplet suspended in a gas containing molecular iodine for a specified amount of time. This model is used to calculate the rate of mass transfer for one drop and the concentration in the drop as a function of time. Water drops falling in air are essentially stagnant (non-circulating) if their diameter is less than 30 microns. Drops greater than 1000 microns are significantly non-spherical, and drops break-up before they reach a diameter of 10,000 microns. Safety spray systems in nuclear reactors have droplet mass medium diameters ranging from 700 microns to 1500 microns. According to Clift these drops are in the diameter range of non-spherical drops, with the bulk of the drop well mixed. Thus an approach was chosen such that the assumptions for the drop model are:

1) each drop has a completely mixed bulk liquid,
2) resistance to mass transfer in both the gas phase and the liquid phase,
3) molecular iodine (I₂) is the only species which transfers in or out of the drop,
4) reactions occur in the bulk of the liquid,
5) drops always fall at their terminal velocity,
6) the drop has a constant surface area and constant volume at all times,
7) the gas phase concentration is always constant (quasi-steady state), and
8) there is no transfer of heat or water between the drop and the gas phase.

The assumption of no heat transfer is made to make the model reflects only the mass transfer and the iodine hydrolysis reactions. Heat transfer will occur if there exists a temperature difference between the gas and liquid phases. Heat transfer would be important under certain conditions but consideration of it would add unnecessary complications to a completely new approach. If the results of this new approach are reasonable, then the addition of heat transfer models is the logical next step.

The drop is composed of water which may be unbuffered or buffered with a solution such as H2B03 and NaOH. The presence of these solutions would not change the iodine hydrolysis reactions. The gas phase is assumed to be a mixture of air and molecular iodine (I2). A two resistance model is used for the mass transfer rate:

\[
M_r = k_g \left( C_g - C_{gi} \right) = k_l^0 \left( C_{li} - C_l \right)
\]

where

- \( M_r \) = rate of reaction,
- \( k_g \) = gas phase mass transfer coefficient,
- \( k_l^0 \) = liquid phase mass transfer coefficient without reaction,
- \( C_g \) = concentration of molecular iodine in the gas phase,
- \( C_{gi} \) = concentration of the transferring species (molecular iodine) in the gas phase at the gas-liquid interphase,
- \( C_l \) = concentration of the transferring species in the liquid phase,
\( C_{1i} \) = concentration of the transferring species in the liquid phase at the gas liquid interphase.

Using an overall mass transfer coefficient, the mass transfer rate may be written as:

\[
M_r = K_{lo\nu} (C^*_1 - C_1)
\]

(40)

where

\( K_{lo\nu} \) = the overall mass transfer coefficient based on the liquid phase,

\( C^*_1 \) = the equilibrium concentration of the transferring species corresponding to the interphase liquid-phase concentration,

\( C_1 \) = the concentration of the transferring species in the bulk liquid,

and

\[
\frac{1}{K_{lo\nu}} = \frac{1}{K^0_{l}} + \frac{P}{K_{g}}
\]

(41)

where \( P \) is the partition coefficient (related to a Henry's coefficient).

The gas phase mass transfer coefficient is determined by a correlation given by Clift\(^{13}\) for drops in free fall in air and with diameter greater than 300 microns:

\[
k_g (Sc)^{2/3} = 0.83(\Delta \rho/\rho_g)^{1/4} g^{1/4} v^{1/2} d^{-1/4}
\]

(42)

where

\( k_g \) = gas phase mass transfer coefficient,

\( Sc \) = Schmidt number, \( Sc = \lambda/D_g \),

\( v \) = kinematic viscosity, \( v = \mu_g/\rho_g \),

\( \mu_g \) = viscosity of the gas,

\( \rho_g \) = density of the gas,
\( D_g \) = diffusion coefficient,

\( \Delta \rho = \) density of the liquid phase minus the density of the gas phase,

\( \rho_g = \) density of the gas phase,

\( g = \) acceleration of gravity, and

\( d = \) drop diameter.

This equation can be rearranged as:

\[
kg = 0.83 \left( \frac{\Delta \rho}{\rho_g} \right)^{1/4} g^{1/4} \left( \frac{\rho_g}{\mu_g} \right)^{1/6} D_g^{2/3} d^{-1/4}
\]  \( (43) \)

The diffusion coefficient is estimated by a binary gas system of air and molecular iodine. The mutual diffusion coefficient for a binary gas at low pressure is:

\[
D_g = \frac{0.001858 T^{3/2} \left( \frac{1}{M_a+1/M_b} \right)^{1/2}}{p \rho_{ab} \Omega_d} \text{ cm/sec}
\]  \( (44) \)

where

\( D_g = \) mutual diffusion coefficient for a binary gas,

\( T = \) temperature,

\( M_a = \) molecular weight of component a,

\( M_b = \) molecular weight of component b,

\( p = \) pressure, atm

\( \sigma_{ab} = \) Lennard-Jones force constant for the binary mixture, and

\( \Omega_d = \) collision integral.

There are very few successful attempts to correlate the inside the drop liquid phase mass transfer coefficient. This lack of correlations could be due to the inconsistent experimental results caused by surface impurities and other experimental problems. For this study, the liquid
phase mass transfer coefficient is approximated by using concepts Higbies penetration theory.

The liquid phase mass transfer coefficient is determined by Higbies penetration theory which leads to the following equation for droplets:

\[ k_1^0 = (4 \frac{D_1}{\pi} t^*)^{1/2} \]  

(45)

where

\[ t^* = \text{gas-liquid element contact time} \] [for a falling liquid drop in a gas phase: \( t^* = \frac{d}{u} \) (assumed)],

\[ d = \text{drop diameter}, \]

\[ u = \text{velocity of drop}, \]

\[ \pi = 3.1415\ldots, \text{ and} \]

\[ D_1 = \text{liquid diffusion coefficient}. \]

Higbies penetration theory was first applied to the liquid phase mass transfer coefficients between gas bubbles and bulk water for short periods of time. As a water drop falls through air, the water inside the drop circulates causing continual renewing of the surface. Garner and Lane\textsuperscript{15} have observed circulation within a drop as it falls in a gas. Previously reported studies\textsuperscript{16,17} have shown appreciably greater absorption rates of a gas by water drops than predicted by theoretical rates of mass transfer in stagnant drops; the difference due to circulation within the drops. The experimental results of Garner and Lane\textsuperscript{15} for CO\textsubscript{2} absorption from a gas into liquid water drops agree reasonably well within the values used in this study based upon the Higbies penetration theory. The penetration theory is only one approach for visualizing the mass transfer resistance in a liquid film. Other theories or correlations could be used which would give slightly different values.
for use in these models, but the liquid side coefficients used in this study are believed to be approximately correct and representative of values observed experimentally under similar conditions.

The liquid phase diffusion coefficient is determined by Wilke and Chang:\textsuperscript{14}

\[ D_l = 7.14 \times 10^{-8} [(\phi M_B)^{1/2} T/\mu_1 V_A^{0.6}] \]  \hspace{1cm} (46)

where

\[ D_l = \text{liquid diffusion coefficient}, \]
\[ V_A = 71.2 \text{ for molecular iodine}, \]
\[ T = \text{temperature}, \]
\[ M_B = 18.015, \]
\[ \phi = 2.26, \text{ and} \]
\[ \mu_1 = \text{viscosity of the liquid}. \]

Making these substitution, the liquid diffusion coefficient is

\[ D_l = 3.653 \times 10^{-8} [T/\mu_1]. \]  \hspace{1cm} (47)

The partition coefficient is determined by a fourth order numerical fit to the data presented in Table 2.\textsuperscript{18}

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Molecular Iodine Partition Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>292</td>
<td>108.</td>
</tr>
<tr>
<td>325</td>
<td>29.7</td>
</tr>
<tr>
<td>359</td>
<td>11.6</td>
</tr>
<tr>
<td>365</td>
<td>10.9</td>
</tr>
<tr>
<td>424</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The fourth order numerical fit to this data results in:
where $T$ is the absolute temperature, K.

The density, $\rho_{\text{ENGAS}}$, and the viscosity, $\nu_{\text{VIGAS}}$, of the gas phase are determined by a fourth order numerical fit to experimental data$^{19}$ for air. The fourth order fit for the density of the gas is:

$$
\rho_{\text{ENGAS}} = 8.2892005 \times 10^{-16} T^4 - 4.2656962 \times 10^{-12} T^3 \\
+ 8.0228283 \times 10^{-9} T^2 - 6.8325529 \times 10^{-6} T \\
+ 2.6129391 \times 10^{-3} \text{ gm/cc ,}
$$

(49)

where $T$ is in K. The viscosity of the gas in centipoise is expressed by:

$$
\nu_{\text{VIGAS}} = -2.8713193 \times 10^{-15} T^4 + 1.6909463 \times 10^{-11} T^3 \\
- 4.015468 \times 10^{-8} T^2 + 6.5679429 \times 10^{-5} T \\
+ 1.9523691 \times 10^{-3} ,
$$

(50)

where $T$ is in K.

The viscosity of the liquid, $\nu_{\text{VISLIQ}}$, is determined by a fourth order numerical fit to experimental data for water.$^{20}$ The expression for the viscosity in centipoise is:

$$
\nu_{\text{VISLIQ}} = 1.8662866 \times 10^{-8} T^4 - 2.633395 \times 10^{-5} T^3 \\
+ 1.3970607 \times 10^{-2} T^2 - 3.3074806 T \\
+ 2.9558666 \times 10^2 ,
$$

(51)

where $T$ is in K.

The density of the liquid, $\rho_{\text{DENLIQ}}$, is determined by a third order fit to experimental data for water.$^{20}$ The numerical fit results in

$$
\rho_{\text{DENLIQ}} = 6.0251147 \times 10^{-9} T^3 - 9.1329604 \times 10^{-6} T^2 \\
+ 3.573572 \times 10^{-3} T + 5.835882 \times 10^{-1} \text{ gm/cc ,}
$$

(52)
where $T$ is in K.

The Reynolds number of the drop is determined by a correlation by Cliff. The first step is:

$$N_D = 4 \rho g \Delta \rho g d^3/3\mu_g^2$$

(53)

where

$$N_D = "Best Number" \ (3N_D/4 \text{ is called Galileo number or Archimedes number}),$$

$\rho_g = \text{density of the gas},$

$\Delta \rho = (\text{density of the liquid} - \text{density of the gas}),$

$g = \text{acceleration of gravity},$

$d = \text{diameter of the drop},$ and

$\mu_g = \text{viscosity of the gas}.$

The Reynolds number can then be calculated by:

$$\log_{10}(N_{Re}) = -1.81391 + 1.34671 \log_{10} N_D - 0.12427 \left(\log_{10} N_D\right)^2$$

$$+ 0.006344 \left(\log_{10} N_D\right)^3,$$

(54)

where $N_{Re}$ is the drop Reynolds number.

The terminal velocity, $TRMVEL$, can then be determined from the drop Reynolds number:

$$TRMVEL = N_{Re} \mu_g / d \rho_g$$

(55)

where

$\mu_g = \text{viscosity of the gas},$ and

$\rho_g = \text{density of the gas}.$

The exposure time, $EXPTM$, can then be determined by:

$$EXPTM = \text{HEIGHT}/TRMVEL,$$

(56)

where $\text{HEIGHT}$ is the drop fall height.
The drop model is a quasi-steady state algorithm (see Figure 16 for DROP MODEL flowsheet). The algorithm is:

1) determine the number of moles of molecular iodine that are transferred to the drop from the gas phase,
2) calculate the concentration of molecular iodine in the liquid drop,
3) determine the concentration of all species in the liquid drop due to the iodine hydrolysis reactions, and
4) loop back to 1) until droplet fall time is reached.

The input parameters for the drop model are:

1) initial gas phase concentration of molecular iodine,
2) initial liquid phase concentration of all iodine hydrolysis species,
3) whether the liquid is buffered or unbuffered (see Appendix A for the Numerical Technique),
4) temperature of the liquid,
5) temperature of the gas,
6) pressure,
7) average drop surface area diameter,
8) average drop volume diameter,
9) exposure time, and
10) relative error control (see Appendix A for the Numerical Technique).

The output of the program is comprised of three files and two plots. File FOR22.DAT contains a summary of all of the conditions and calculations for the run. File FOR50.DAT contains the concentration of
INPUTS:
TEMPG, TEMPL, PRESS, DIAM, SAD, C12G,
WOLD(1), WOLD(2), WOLD(3), WOLD(4),
WOLD(5), WOLD(6), WOLD(7), A, B, HMIN,
HMAX, IN, TOLER.

CALCULATE: PROPERTY (EQN)
VISLIG(51), VISGA56(50), PC(48), DENLIG(52),
GENGAS(49), DIFTLIG(47), DIFGAS(44), NRE(54),
TRMVEL(55), KL2G(45), KI2G(43), KLOV(41),
RK4(34), RK5(36), RK6(38).

DETERMINE THE NUMBER OF MOLES OF
MOLECULAR IODINE TRANSFERRED AND
THE NEW CONCENTRATION OF MOLECULAR
IODINE IN THE DROPS.

DETERMINE THE CHANGE IN THE CONCEN­
TRATION OF EACH IODINE HYDROLYSIS
SPECIES, ACCORDING TO THE REACTIONS,
IN EACH DROP.

CHECK TO SEE IF FINISHED

CHECK ERROR

STOP

STOP

ACCEPT

REJECT

UPDATE SPECIES CONCEN­TRATION

Figure 16. Drop Model Flowsheet.
the drop as a function of time and is used to develop the plot of concentration in the liquid versus time. FOR51.DAT contains the gas phase concentration, number of moles of molecular iodine removed per step and the total number of moles removed as a function of time. This file is used to develop a plot of the number of moles removed as a function of time (see Appendix C for sample output files and for the FORTRAN program).

The results of this model are shown in Figures 17 though 28 for cases involving initial concentrations of molecular iodine in the gas phase from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-10}$ moles/liter, a drop diameter of 1000 microns, and a temperature of 298 K. Figures 17 through 22 represent the results for cases with a buffered pH of 9.0, and Figures 23 through 28 are for the cases with a buffered pH of 7.0. For each figure part a shows the concentration of the iodine hydrolysis species as a function of time and part b shows the gram-moles of molecular iodine removed as a function of time. If one compares the number of moles of molecular iodine removed per drop for a pH of 7 with the number of moles removed for a buffered pH of 9, it is seen that drops with a pH of 9 remove approximately one and a half times to five times as much iodine from the gas phase as drops with a buffered pH of 7.
Figure 17. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-5}$ moles/liter and a buffered pH of 9.0.
(a) Concentration in the liquid drop as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
Figure 18. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-6}$ moles/liter and a buffered pH of 9.0.

(a) Concentration in the liquid drop as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
Figure 19. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-7}$ moles/liter and a buffered pH of 9.0.

(a) Concentration in the liquid drop as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
Figure 20. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-8}$ moles/liter and a buffered pH of 9.0.

(a) Concentration in the liquid drop as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
Figure 21. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-9}$ moles/liter and a buffered pH of 9.0.

(a) Concentration in the liquid drop as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
Figure 22. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-10}$ moles/liter and a buffered pH of 9.0.

(a) Concentration in the liquid drop as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
Figure 23. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-5}$ moles/liter and a buffered pH of 7.0.

(a) Concentration in the liquid drop as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
Figure 24. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-6}$ moles/liter and a buffered pH of 7.0.

(a) Concentration in the liquid drop as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
Figure 25. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-7}$ moles/liter and a buffered pH of 7.0.

(a) Concentration in the liquid drop as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
Figure 26. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-8}$ moles/liter and a buffered pH of 7.0.

(a) Concentration in the liquid drop as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
Figure 27. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-9}$ moles/liter and a buffered pH of 7.0.

(a) Concentration in the liquid drop as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
Figure 28. Results of Drop Model. Initial concentration of molecular iodine in the gas phase of $1.0 \times 10^{-10}$ moles/liter and a buffered pH of 7.0.

(a) Concentration in the liquid drop as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
The spray model is an expansion of the single droplet model into a spray system. The drop model is expanded to be applicable to a system of many drops suspended in a gas during the period of the drop fall time. The assumptions for the spray model are:

1) each drop has a completely mixed bulk liquid,
2) resistance to mass transfer exists in both the gas phase and the liquid phase,
3) molecular iodine (I\textsubscript{2}) is the only species that transfers (has volatility) in or out of the drop,
4) reactions occur in the bulk of the liquid,
5) each drop falls at its terminal velocity,
6) every drop falls the same height,
7) each drop has a constant surface area and constant volume at all times,
8) there are no interactions between drops,
9) for the lifetime of a drop, the physical characteristics of the gas phase remains constant but the gas phase concentration can change slowly in a stepwise fashion over several drop lifetimes,
10) there is no transfer of heat or water between the drop and the gas phase (see Chapter 4, DROP MODEL), and
11) the containment height is the same as the drop fall height.
These assumptions are the same as for the drop model except for assumptions 6, 8, and 11. Both assumptions 6 and 8 deal with the relationship each drop has with the other drops and therefore would not be present in a single drop model. Assumption 11 is needed to calculate the containment volume, CVOL, by:

\[
CVOL = \pi \text{CDIAM}^2 \text{HEIGHT}/4.0 ,
\]  

where

\[
\text{CDIAM} = \text{containment diameter}, \text{ and }
\]

\[
\text{HEIGHT} = \text{drop fall height}.
\]

Since all drops are assumed to fall at the same velocity and fall the same height, their exposure time will be the same. The total duration of the spray can be broken into N segments, where N is determined by:

\[
N = \frac{\text{total spray time}}{\text{drop exposure time}} .
\]

The spray model determines the total volume and surface area of all of the drops suspended in the gas at any instant. The surface-to-volume ratio of one large drop having this volume and surface area will not be the same as the surface-to-volume ratio for the small drops, and the large drop would have to be significantly non-spherical. Nevertheless, the total volume and surface area is used to simulate one large non-spherical drop in which the drop model is applied to this large drop for N times. The algorithm used is (see Figure 29 for spray model flow-sheet):

1) determine all physical properties for the gas and liquid phases,
2) determine the number of loops required, \((N)\),
INPUTS:
TEMPG, TEMPL, PRESS, DIAM, SAD, CI2G, CI2SP, CISP, CHOISP, COISP, CI3SP, CHSP, A, HMIN, HMAX, IN, TOLER, FLRAT, DURTM, CDIAM, HEIGHT.

CALCULATE: PROPERTY (EQN)
VISLIQ(51), VISGAS(50), PC(48), DENLIQ(52), DENGAS(48), DIFLIQ(47), DIFGAS(44), NRE(54), TRMLVEL(55), KLI20(48), KI20(43), KLOV(41), RK4(34), RK5(35), RK8(38), ILKOPT(59).

DO I, FOR ILOOP NUMBER OF TIMES.

SET DROP CONCENTRATION EQUAL TO INPUT SPRAY CONCENTRATION.

DETERMINE THE NUMBER OF MOLES OF MOLECULAR IODINE TRANSFERRED AND THE NEW CONCENTRATION OF MOLECULAR IODINE IN THE DROPS.

DETERMINE THE CHANGE IN THE CONCENTRATION OF EACH IODINE HYDROLYSIS SPECIES, ACCORDING TO THE REACTIONS, IN EACH DROP.

UPDATE SPECIES CONCENTRATION

CHECK TO SEE IF FINISHED

CHECK ERROR

ACCEPT

REJECT

Figure 29. Spray Model Flowsheet.
DETERMINE THE CHANGE IN THE CONCENTRATION OF EACH IODINE HYDROLYSIS SPECIES, ACCORDING TO THE REACTIONS, IN THE SUMP.

Figure 29. (continued).
3) determine the total surface area and total volume for all of the drops in containment,

4) execute the drop model for the large drop with surface area and volume equivalent to these quantities for the actual system:
   a) determine the number of moles of molecular iodine that are transferred to the large drop from the gas phase,
   b) calculate the concentration of molecular iodine in the large liquid drop,
   c) determine the concentration of all species in the large liquid drop due to the iodine hydrolysis reactions,

5) calculate the new gas phase concentration, and

6) loop to step 4 until N loops have been completed.

A FORTRAN program that implements this algorithm is listed in Appendix E. Input parameters for the spray model are:

1) initial gas phase concentration of molecular iodine,

2) initial liquid phase concentration of all iodine hydrolysis species,

3) whether the liquid phase is buffered or unbuffered (see Appendix A, Numerical Technique)

4) temperature of both gas and liquid phases,

5) pressure,

6) average drop surface area diameter,

7) average drop volume diameter,

8) spray time,

9) spray flow rate,

10) drop fall height,
11) containment diameter, and

12) relative error control (see Appendix A, Numerical Technique).

Output from the program comprises four files and four plots. File FOR22.DAT contains a summary of all of the conditions and calculations of the run. File FOR50.DAT contains the concentration of the drops when they have fallen a distance equal to their input fall height and is used to create a plot of the concentration in the liquid drops versus time. File FOR51.DAT contains the gas phase concentration of molecular iodine, number of moles removed for each individual group of drops and the total number of moles removed versus time. FOR51.DAT is used to create a plot of concentration of molecular iodine removed versus time, and a plot of the number of moles of iodine versus time. File FOR52.DAT contains the concentration of the sprayed solution collected in the sump, and is used to create a plot of the concentration of iodine in the sump versus time.

A series of computer runs was performed for initial concentrations of molecular iodine in the gas phase from $1 \times 10^{-5}$ through $1.0 \times 10^{-10}$ moles/liter for 10 minute sprays times. Results for the cases with a buffered pH of 9 are shown in Figures 30 through 35 and results for the cases with a buffered pH of 7 are shown in Figures 36 through 41. The common inputs to the computer program for the cases whose results are shown in these figures are:

1) the initial liquid phase species concentrations are all zero except for the hydrogen ion concentration,

2) all of the spray solutions are buffered at pH 9 or pH 7,

3) the temperature of the gas is 298K and the temperature of the liquid is 298K,
Figure 30. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-5}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 30. (continued).
Figure 31. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-6}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 31. (continued).
Figure 32. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-7}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 32. (continued).
Figure 33. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-8}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.

(d) Concentration of iodine species in the sump as a function of time.

Figure 33. (continued).
Figure 34. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-9}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 34. (continued).
Figure 35. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-10}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 35. (continued).
Figure 36. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-5}$ moles/liter and a buffered pH of 7.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.

(d) Concentration of iodine species in the sump as a function of time.

Figure 36. (continued).
Figure 37. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-6}$ moles/liter and a buffered pH of 7.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 37. (continued).
Figure 38. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-7}$ moles/liter and a buffered pH of 7.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 38. (continued).
Figure 39. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-8}$ moles/liter and a buffered pH of 7.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 39 (continued).
Figure 40. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-9}$ moles/liter and a buffered pH of 7.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 40. (continued).
Figure 41. Results of Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-10}$ moles/liter and a buffered pH of 7.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 41. (continued).
4) the pressure is 1 atmosphere,
5) the drop surface area diameter is 0.1 centimeters,
6) the drop volume diameter is 0.1 centimeter,
7) the spray time is 10 minutes,
8) the spray flow rate is 37 liters/minute,
9) the drop fall height is 15.4 meters, and
10) the containment diameter is 3.3 meters.

These inputs were arbitrarily chosen, but are within the range of conditions that are likely to be encountered in potential reactor accident systems.

For these input parameters, Figures 30 to 41 show the results of these series of runs. Part a of each Figure shows the concentration of molecular iodine in the gas phase as a function of time. For the conditions of these tests, the gas phase concentration does not change very much. (This result is only valid for the conditions of these runs.) Part b of each Figure shows the number of gram-moles of molecular iodine removed versus time. These plots show a first order removal (a constant amount of molecular iodine is being removed between each time step). This is because the gas phase concentration of molecular iodine is remaining relatively constant. (Again this is only true for these conditions.) Part c of each Figure shows the concentration in the drops when they have fallen a distance equal to their fall height. These plots show that the concentration in the drops is not changing very much which is again because the gas phase concentration is not changing. Finally part d shows the concentration of iodine in the sprayed solution that is
collecting in the sump at the bottom of the containment. The concentration of molecular iodine in the sump decreases slowly with time because the solution is becoming slightly more diluted from the slightly lower concentration of molecular iodine in the drops and also because of the iodine hydrolysis reactions that are occurring in the sump.

A typical run on a Digital Equipment Corporation PDP-10 takes approximately 6 seconds of central processing unit (CPU) time for every minute of simulation. The CPU time depends upon the concentration of molecular iodine, the pH of the solution, whether it is buffered or unbuffered, and the error tolerance. For these simulations of 10 minutes of problem time, each run takes approximately 1 minute of CPU time.
CHAPTER VI

WALL-SPRAY MODEL

The wall-spray model calculates the removal of molecular iodine from the gas phase by a spray system and by contact with the wetted walls of the containment. This model incorporates the spray model to determine the removal by the sprays, and there is an additional falling liquid film routine to determine the removal of gaseous iodine by the walls that are wetted by the sprays. The vertical walls of the containment are cut into several horizontal cylindrical pieces in which molecular iodine is absorbed by the water flowing down the walls. The effect of variation in width is neglected within each cylindrical piece, and then the molecular iodine is reacted with the water in each piece. The height of each piece or section of the wall is determined by the drop exposure time and the velocity of the water on the walls. For this model, the percentage of water that flows down the walls must be known or estimated.

The assumptions for the wall-spray model are exactly those for the spray model plus assumptions for the wall. These assumptions are:

1) each drop has a completely mixed bulk liquid,

2) resistance to mass transfer exists in both the gas phase and the liquid phase,

3) the only species which transfers (has volatility) in or out of the drop is molecular iodine (I2),

4) reactions occur in the bulk of the liquid,

5) each drop falls at its terminal velocity,
6) every drop falls the same height,
7) each drop, at all times, has a constant surface area and constant volume,
8) there are no interactions between drops,
9) for the lifetime of a drop, the gas phase remains constant but the gas phase concentration can change slowly over several drop lifetimes,
10) there is no transfer of heat or water between the drop and the gas phase (see Chapter 4, DROP MODEL),
11) the fluid in each cylindrical piece or slice of the wall is well mixed,
12) reactions occur in the bulk liquid of each slice,
13) water only enters on the wall at the top, and
14) water only exits the wall at the bottom where it runs into a sump.

The boundary conditions for the wall are defined at the extremes of the y and x coordinates as defined on Figure 42, and are as follows:

1) at \( y = 0 \) and at all values of \( x \), the concentration of molecular iodine equals the concentration of molecular iodine in the liquid drop when it strikes the wall,
2) at \( x = 0 \) and at all values of \( y \), the concentration of molecular iodine in the liquid on the wall is equal to the interphase equilibrium concentration of molecular iodine in the gas, and
3) at \( x = 6 \) and at all values of \( y \), \( \partial[I_2]/\partial x = 0 \), (assume no diffusion into the wall).

The calculations for mass transfer to a falling liquid film are outlined in Treybal. One assumption in the outline by Treybal is that
Figure 42. Boundary Conditions for Falling Liquid Film.
no chemical reactions occur in the liquid. The concentration profile, \( C_A(x) \) (shown in Figure 42), is non-linear in shape (slope is a function of the distance from the interface). The mass transfer coefficient is proportional to the slope of the concentration profile at the interface. The local mass transfer rate can be expressed by:

\[
N_A = -D_1 \left( \frac{\partial C_A}{\partial x} \right)_{x=0} = k_1 (C_{A1} - \overline{C}_{A,L})
\]

where

- \( N_A \) = mass transfer flux across the interface of species A,
- \( D_1 \) = diffusivity of the transferring species in the liquid,
- \( \frac{\partial C_A}{\partial x} \) = concentration profile of the transferring species in the \( x \) direction,
- \( k_1 \) = local mass transfer coefficient, and
- \( \overline{C}_{A,L} \) = average bulk concentration of the transferring species after the water on the walls has Fallen a distance \( L \), the height of each horizontal piece.

When reactions occur in the liquid, the concentration profile, in the liquid will change. This will change the mass transfer coefficient in the liquid. Therefore, the assumption that the reactions induce a small error in the wall film mass transfer rate is made. However, since the transfer to the wall is only a small fraction of the total iodine absorption, small errors in this part of the wall-spray model will be insignificant. A more elaborate simulation of the transfer of iodine to the falling liquid film is not justified.
The average mass transfer flux for the wall liquid film, $N_{aw}$, is defined as:

$$N_{aw} = k_{1,av} ([I_2^1] - [I_{2,B}^1]) = \frac{u_y \delta}{H} ([I_{2,B}^1] - [I_2^0])$$  \hspace{0.5cm} (60)

where

- $k_{1,av} = \text{the average liquid mass transfer coefficient},$
- $[I_2^1] = \text{the concentration of molecular iodine at the interface},$
- $[I_{2,B}^1] = \text{concentration of molecular iodine at the bottom of the wall},$
- $[I_{2,B}^1] = \text{the average bulk concentration of molecular iodine},$
- $[I_2^0] = \text{the initial concentration of molecular iodine in the liquid},$
- $u_y = \text{average velocity of the liquid down the wall},$
- $\delta = \text{liquid thickness on the wall},$
- $H = \text{wall height},$ and
- $([I_2^1] - [I_{2,B}^1]) = \text{logarithmic average concentration gradient}.$

Values for $k_{1,av}$ and for the other parameters can be obtained as follows:

$$k_{1,av} = (6 D_1 \Gamma / \pi \rho_1 \delta \ H)^{1/2} \hspace{0.5cm} (61)$$

$$\Gamma = \text{mass rate of flow},$$
$$\pi = 3.1415... \hspace{0.5cm} ,$$
$$\rho_1 = \text{density of water},$$
$$\delta = (3 \mu_1 \Gamma / \rho_1^2 \ g)^{1/3} \hspace{0.5cm} (62)$$
$$g = \text{acceleration of gravity},$$
$$\mu_1 = \text{viscosity of water},$$
$$u_y = (\Gamma / \rho_1 \delta) \hspace{0.5cm} , \text{and} \hspace{0.5cm} (63)$$
Equation (60) can be solved by iterating for $[I^1_{2,B}]$:

$$
([I^1_{2,B}])_M = \frac{([I^1_{2}] - [I^0_{2}]) - ([I^1_{2}] - [I^1_{2,B}])}{\ln \left(\frac{([I^1_{2}] - [I^0_{2}])}{([I^1_{2}] - [I^1_{2,B}])}\right)}.
$$

(64)

Since all variables are known except for $[I^1_{2,B}]$, one can iterate for $[I^1_{2,B}]$, the concentration of molecular iodine at the bottom of each segment. Once $[I^1_{2,B}]$ is known, one can calculate the moles of molecular iodine transferred to the drop.

The algorithm for the wall spray model is (see Figure 43 for Wall-Spray Model Flowsheet):

1) determine all physical properties for the gas and liquid phases for both the spray and the wall section,
2) determine the number of loops, $N$, for the spray section of the program,
3) determine the number of pieces into which the wall will be broken,
4) determine the total surface areas and total volumes for the drops and for a wall slice,
5) execute the drop model until the drop reaches the wall,
   a) determine the number of moles of molecular iodine that are transferred to the large drop from the gas phase,
   b) calculate the concentration of molecular iodine in the large liquid drop,
Figure 43. Wall-Spray Model Flowsheet.
Figure 43. (continued).
DETERMINE THE CHANGE IN THE CONCENTRATION OF EACH IODINE HYDROLYSIS SPECIES, ACCORDING TO THE REACTIONS, IN THE SUMP.

Figure 43. (continued).
c) determine the concentration of all species in the large liquid drop due to the iodine hydrolysis reactions,

6) store the concentration of the drop (to be used as the initial concentration of the liquid of the wall),

7) continue execution of the drop model until the drop has reached the fall height,

8) execute the wall model for each section used to represent the wall,

9) execute the kinetic model on the liquid in the sump,

10) determine the total number of moles of molecular iodine transferred to the liquid and calculate the new gas phase concentration,

11) loop back to 5) until the spray part of the model is finished,

12) execute the wall model on the water that remains on the wall,

13) execute the kinetic model on the liquid in the sump,

14) determine the total number of moles removed and the new gas phase concentration of molecular iodine and,

15) loop back number to 12 until all of the water has flowed off the wall.

A FORTRAN program with this algorithm is shown in Appendix F.

Input parameters for this model are the same as those for the spray model with the addition of two more parameters for the wall section of the model. The inputs are:

1) initial gas phase concentration of molecular iodine,

2) initial liquid phase concentration of all iodine hydrolysis species,

3) whether buffered or unbuffered,

4) temperature of both gas and liquid phases
5) pressure,
6) average drop surface area diameter,
7) average drop volume diameter,
8) spray time,
9) spray flow rate,
10) drop fall height,
11) containment diameter,
12) relative error control (see Appendix A, Numerical Technique),
13) percentage of spray flow rate which flows down the wall, and
14) height of the wall.

A series of computer runs were performed for initial concentrations of molecular iodine in the gas phase of $1.0 \times 10^{-7}$ to $1.0 \times 10^{-10}$ moles/liter for 10 minute spray times for and a buffered pH valves of 9; the results are shown in Figures 44 to 45. The specific input parameters used for these runs are:

1) initial liquid phase concentrations are all zero except for the hydrogen ion concentration,
2) all spray solutions are buffered,
3) temperature of the gas is 298K and the temperature of the liquid is 298K,
4) pressure is 1 atmosphere,
5) drop surface area diameter is 0.1 centimeters,
6) drop volume diameter is 0.1 centimeter,
7) spray time is 10 minutes,
8) spray flow rate is 37 liters/minute,
9) drop fall height is 15.4 meters,
Figure 44. Results of Wall-Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-7}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 44. (continued).
Figure 45. Results of Wall-Spray Model. Initial concentration of molecular iodine in the gas phase of $1 \times 10^{-10}$ moles/liter and a buffered pH of 9.0 in the liquid phase.

(a) Concentration of molecular iodine in the gas phase as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 45. (continued).
10) containment diameter is 3.3 meters,
11) the percentage of spray that flows down the wall is 5%, and
12) the wall height is 3.3 meters.

The output parameters provided by the wall spray model are the same as those calculated by the spray model. If one compares the results of the spray model to those of the wall-spray model, one will find that there is not much difference in the calculated number of moles of molecular iodine removed from the gas phase and that most of the plotted results are nearly the same. These results show that the removal of gaseous iodine by the water on the wall is approximately as important as the removal of gaseous iodine by the spray drops. But wall spray model requires much more CPU time than does the spray model and yet does not predict significantly different results from the spray model. Therefore, it is suggested that the spray model can be used in most cases for predicting the absorption of gaseous iodine by water sprays. Nevertheless, there are probably times when the results of the two models would differ significantly such as for cases in which the wall surface area is very large.
CHAPTER VII

EXPERIMENTAL DATA

The experimental data used to compare with the results of the spray model are from the Containment System Experiments (CSE). Experimental runs A-3, A-4, A-6, A-7, and A-8 of this series are large scale spray system tests to determine the effectiveness of a spray system for removing airborne fission products. The results of these tests are reported in terms of the gas phase elemental iodine concentration versus time and also in terms of the liquid phase elemental iodine concentration versus time. The parameters for the spray experiments are the spray flux, the drop size, the gas phase temperature, pressure, and humidity, and the liquid spray composition. The physical dimensions of the CSE vessel are listed in Table 3 and are shown in Figure 46. Since these tests were made in realistic and not idealized equipment and conditions, the liquid and gas flow patterns are complex and not well characterized. The results from the new spray model will be compared with these results, but no better than approximate agreement can be expected. This data, however, can still provide a means for useful and meaningful evaluation of the spray model.

The CSE vessel is a large scale vessel (see Table 3 and Figure 46). The overall dimensions of the vessel are 20.34 meters high and a diameter of 7.62 meters. The vessel has a drop fall height of 15.4 meters. The overall volume of the vessel is 751 cubic meters.

The tests varied the temperature, pressure, pH of the drop, spray nozzle configuration and drop size. The conditions for run A-3 are a
Table 3. Physical conditions common to all spray experiments (Hillard5)

| Volume above deck including drywell | 21,005 ft³ | 595 m³ |
| Surface area above deck including drywell | 6,140 ft² | 569 m² |
| Surface area/volume | 0.293 ft⁻¹ | 0.958 m⁻¹ |
| Cross section area, main vessel | 490 ft² | 45.5 m² |
| Volume, middle room | 2,089 ft³ | 59 m³ |
| Surface area, middle room | 1,363 ft² | 127 m² |
| Volume, lower room | 3,384 ft³ | 96 m³ |
| Surface area, lower room | 2,057 ft² | 191 m² |
| Total volume of all rooms | 26,477 ft³ | 751 m³ |
| Total surface area, all rooms | 9,560 ft² | 888 m² |
| Drop fall height to deck | 33.8 ft | 10.3 m |
| Drop fall height to drywell bottom | 50.5 ft | 15.4 m |

**Surface coating**
- All interior surfaces coated with phenolic paint.\(^a\)

**Thermal insulation**
- All exterior surfaces covered with 1-in. fiberglass insulation.\(^b\)

\(^a\)Two coats Phenoline 302 over one coat Phenoline 300 primer. The Carboline Co., St. Louis, Missouri.

\(^b\)k = 0.027 Btu/(hr) (ft²) (°F/ft) at 200°F, Type PF-615, Owens-Corning Fiberglass Corp.
Figure 46. Schematic diagram of containment arrangement used in CSE spray tests (Hillard).
temperature of 298K, 1 atmosphere of pressure, pH of 9.5 and a drop diameter of 1210 microns. For all of the tests, the spray solution temperature was at 25°C, and the solutions were all buffered. For run A-4, the conditions were the same as for A-3 except for a higher spray flow rate and a different spray nozzle configuration. Run A-6 increased the temperature of the gas to 397K and the pressure to 3 atmospheres. Run A-7 changed the pH to 5, lowered the temperature to 394K and raised the pressure to 3.4 atmospheres. Run A-8 changed the drop diameter to 770 microns. See Figure 46 for spray nozzle arrangements, Table 4 for spray nozzles used, Table 5 for the atmospheric conditions, Table 6 for the spray flow rates and solutions used in the tests and Table 7 for the timing of the spray periods.

The experimental procedure for the molecular iodine spray absorption tests involved first heating the containment vessel with steam until the specified temperature was reached. A flask containing molecular iodine traced with 1 curie of iodine-131 was heated electrically. Air was passed over the flask to release molecular iodine. Samples were taken prior to turning on the sprays to determine how molecular iodine behaves without sprays. After the first spray period of each run was started, many samples were taken from the gas phase, from the liquid in the sump, from the wall trough and from the spray drop collectors. When the first spray period was ended, more samples were taken to determine how molecular iodine acts. A second, third, and sometimes a fourth spray period were used with many samples taken from the gas and liquid phases. The gas phase concentrations were determined by Maypack samplers (see Figure 47), and the liquid phase concentrations
Table 4. Nozzles used in CSE spray experiments (Hillard\textsuperscript{5})

<table>
<thead>
<tr>
<th></th>
<th>Runs A3, 4, 6, 7</th>
<th>A4, 6, 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle type:</td>
<td>Spraying Systems Co. 3/4 — 7G3</td>
<td></td>
</tr>
<tr>
<td>Nozzle characteristics:</td>
<td>Fog type, full cone</td>
<td></td>
</tr>
<tr>
<td><strong>Number</strong></td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td><strong>Layout</strong></td>
<td>Triangular</td>
<td>Square grid</td>
</tr>
<tr>
<td><strong>Spacing</strong></td>
<td>10 ft 5 in. apart</td>
<td>6 ft apart</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>40 psid</td>
<td>40 psid</td>
</tr>
<tr>
<td><strong>Rated flow</strong></td>
<td>4 gpm</td>
<td>4 gpm</td>
</tr>
<tr>
<td><strong>MMD</strong></td>
<td>1210 µ</td>
<td>1210 µ</td>
</tr>
<tr>
<td><strong>σ&lt;sub&gt;g&lt;/sub&gt;</strong></td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Run A8

<p>| | | |</p>
<table>
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<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle type:</td>
<td>Spray Systems Co. 3/8 A 20</td>
<td></td>
</tr>
<tr>
<td>Nozzle characteristics:</td>
<td>Fine atomization, hollow cone</td>
<td></td>
</tr>
<tr>
<td><strong>Number used</strong></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td><strong>Layout</strong></td>
<td>Square grid</td>
<td></td>
</tr>
<tr>
<td><strong>Spacing</strong></td>
<td>6 ft apart</td>
<td></td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>40 psid</td>
<td></td>
</tr>
<tr>
<td><strong>Rated flow</strong></td>
<td>4 gpm</td>
<td></td>
</tr>
<tr>
<td><strong>MMD</strong></td>
<td>770 µ</td>
<td></td>
</tr>
<tr>
<td><strong>σ&lt;sub&gt;g&lt;/sub&gt;</strong></td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Atmospheric conditions in CSE spray experiments (Hillard5)

<table>
<thead>
<tr>
<th></th>
<th>Run A3</th>
<th>Run A4</th>
<th>Run A6</th>
<th>Run A7</th>
<th>Run A8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Containment vessel insulated</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Forced air circulation(^a)</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Start of 1st spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor temperature, °F (^b)</td>
<td>77</td>
<td>77</td>
<td>255</td>
<td>248.7</td>
<td>250</td>
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<tr>
<td>Pressure, psia</td>
<td>14.6</td>
<td>14.6</td>
<td>44.2</td>
<td>50.0</td>
<td>50.7</td>
</tr>
<tr>
<td>Relative humidity, %</td>
<td>70</td>
<td>88</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>End of 1st spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor temperature, °F (^b)</td>
<td>77</td>
<td>77</td>
<td>229</td>
<td>234.5</td>
<td>243</td>
</tr>
<tr>
<td>Pressure, psia</td>
<td>14.6</td>
<td>14.6</td>
<td>38.6</td>
<td>44.4</td>
<td>48.2</td>
</tr>
<tr>
<td>Start of 2nd spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor temperature, °F (^b)</td>
<td>77</td>
<td>77</td>
<td>237</td>
<td>240</td>
<td>243</td>
</tr>
<tr>
<td>Pressure, psia</td>
<td>14.6</td>
<td>14.6</td>
<td>40.8</td>
<td>46.0</td>
<td>243</td>
</tr>
<tr>
<td>End of 2nd spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor temperature, °F (^b)</td>
<td>77</td>
<td>77</td>
<td>202</td>
<td>203</td>
<td>188</td>
</tr>
<tr>
<td>Pressure, psia</td>
<td>14.6</td>
<td>14.6</td>
<td>29.5</td>
<td>36</td>
<td>34.1</td>
</tr>
<tr>
<td>Start of 3rd spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor temperature, °F (^b)</td>
<td>77</td>
<td>77</td>
<td>233</td>
<td>230</td>
<td>218</td>
</tr>
<tr>
<td>Pressure, psia</td>
<td>14.6</td>
<td>14.6</td>
<td>40.7</td>
<td>41.8</td>
<td>32.2</td>
</tr>
<tr>
<td>Start of 4th spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor temperature, °F (^b)</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>232</td>
<td>247</td>
</tr>
<tr>
<td>Pressure, psia</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>42.4</td>
<td>52.4</td>
</tr>
<tr>
<td>End of 4th spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor temperature, °F (^b)</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>192</td>
<td>175</td>
</tr>
<tr>
<td>Pressure, psia</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>32.7</td>
<td>32.4</td>
</tr>
</tbody>
</table>

\(^a\) Fan without duct located in bottom of drywell. 2400 ft\(^3\)/min discharge.
\(^b\) Average of 5 thermocouples located at various elevations and radii.
\(^c\) No fourth spray.
<table>
<thead>
<tr>
<th></th>
<th>Run</th>
<th>Run</th>
<th>Run</th>
<th>Run</th>
<th>Run</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>A3</td>
<td>A4</td>
<td>A6</td>
<td>A7</td>
<td>A8</td>
</tr>
<tr>
<td><strong>1st spray</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total flow rate, gpm</td>
<td>12.8</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>50</td>
</tr>
<tr>
<td>Volume sprayed, gal</td>
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<td>490</td>
<td>490</td>
<td>490</td>
<td>150</td>
</tr>
<tr>
<td>Spraying pressure, psid</td>
<td>40</td>
<td>40</td>
<td>40</td>
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<tr>
<td>Solution</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>b</td>
</tr>
<tr>
<td><strong>2nd spray</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total flow rate, gpm</td>
<td>12.8</td>
<td>49</td>
<td>50</td>
<td>48.5</td>
<td>50</td>
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<tr>
<td>Volume sprayed, gal</td>
<td>385</td>
<td>1480</td>
<td>1500</td>
<td>1455</td>
<td>1850</td>
</tr>
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<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
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</tr>
<tr>
<td>Solution</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>b</td>
</tr>
<tr>
<td><strong>3rd spray</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total flow rate, gpm</td>
<td>12.5</td>
<td>42</td>
<td>16</td>
<td>45.5</td>
<td>47</td>
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<tr>
<td>Volume sprayed, gal</td>
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<td>1890</td>
<td>960</td>
<td>2730</td>
<td>2820</td>
</tr>
<tr>
<td>Spraying pressure, psid</td>
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<td>29</td>
<td>4</td>
<td>36.5</td>
<td>36.5</td>
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<tr>
<td>Solution</td>
<td>d</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td><strong>4th spray</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total flow rate, gpm</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td>48.6</td>
<td>50.4</td>
</tr>
<tr>
<td>Volume sprayed, gal</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td>2428</td>
<td>2520</td>
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<td>g</td>
<td>40</td>
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</tr>
<tr>
<td>Solution</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aFresh, room temperature. 525 ppm boron as H₃BO₃ in demineralized water. NaOH added to pH of 9.5.*

*bFresh, room temperature. 3000 ppm boron as H₃BO₃ in demineralized water. NaOH added to pH of 9.5.*

*cFresh, room temperature. 3000 ppm boron as H₃BO₃ in demineralized water. No NaOH added. pH 5.*

*dFresh, room temperature demineralized water.*

*eSolution in main vessel sump recirculated. No heat exchanger used.*

*fFresh, room temperature. 1 wt% Na₂S₂O₃, 3000 ppm boron as H₃BO₃ in demineralized water. NaOH added to pH 9.4.*

*gNo fourth spray.*
Table 7. Timing of spray periods
(Hillard5)

<table>
<thead>
<tr>
<th></th>
<th>Run A3</th>
<th>Run A4</th>
<th>Run A6</th>
<th>Run A7</th>
<th>Run A8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time after start of iodine release, min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>First spray</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start</td>
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<td>40.5</td>
<td>30</td>
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<tr>
<td>Stop</td>
<td>50</td>
<td>50.5</td>
<td>40</td>
<td>40</td>
<td>33</td>
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<tr>
<td>Duration</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>3</td>
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</tr>
<tr>
<td>Start</td>
<td>140</td>
<td>140</td>
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<td>Stop</td>
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<td>Duration</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
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<tr>
<td><strong>Third spray</strong></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Start</td>
<td>1473</td>
<td>1205</td>
<td>1565</td>
<td>1323</td>
<td>200</td>
</tr>
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<td>1533</td>
<td>1250</td>
<td>1525</td>
<td>1383</td>
<td>260</td>
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<tr>
<td>Duration</td>
<td>60</td>
<td>45</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td><strong>Fourth spray</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Start</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>1443</td>
<td>1350</td>
</tr>
<tr>
<td>Stop</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>1493</td>
<td>1400</td>
</tr>
<tr>
<td>Duration</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

*a* No fourth spray.
Figure 47. Maypack Sampler.
were determined by measuring the amount of iodine-131 tracer present.
For more information see Reference 1.

Results of these experimental tests are shown in Figures 48 through 57 and Table 8. Table 8 shows the material balance of iodine for all of the experimental runs. It should be noted in this table that between 25.65% and 57.58% of the iodine delivered to the containment vessel is unaccounted for and is assumed to be deposited on surfaces. Figures 48 through 52 show the concentration of elemental iodine in the gas phase as a function of time. The data is reported in terms of the half life of iodine, defined as

$$t_{1/2} = - \frac{\ln (1/2)}{\lambda},$$

$$= 0.693/\lambda,$$  \hspace{1cm} (66) \hspace{1cm} (67)

where $\lambda$ is the removal rate constant.

The reason the data are in this form is because the old spray models (Equations 2 through 8 of Chapter I, Section B) are in terms of the removal rate constant. Figures 53 to 57 shows the concentration of iodine in the liquid versus time. As can be seen in these figures, there is a delay in the response of the increase in the concentration of iodine in the liquid phase.

In these tests there are many processes for the removal of molecular iodine from the gas phase. In these large scale realistic tests, there are painted surfaces, non-painted surfaces, insulation, sprays, wet walls, and dry walls. All of these features can contribute to iodine sorption, and heat transfer can also have an effect on the removal rate of molecular iodine from the gas phase. Therefore, one can only hope to develop an approximate model which accounts for the major
Figure 48. Concentration of elemental iodine in the main room, run A-3 (Hillard5).
Figure 49. Concentration of elemental iodine in the main room, run A-4 (Hillard).
Figure 50. Concentration of elemental iodine in the main room, run A-6 (Hillard\textsuperscript{5}).
Figure 51. Concentration of elemental iodine in the main room, run A-7 (Hillard).
Figure 52. Concentration of elemental iodine in the main room, run A-8 (Hillard).
Figure 53. Liquid volumes and concentration in vessel sumps, run A-3 (Hillard⁵).
Figure 54. Liquid volumes and concentration in vessel sumps, run A-4 (Hillard^5).
Figure 55. Liquid volumes and concentration in vessel sumps, run A-6 (Hillard5).
Figure 56. Liquid volumes and concentration in vessel sumps, run A-7 (Hillard\(^5\)).
Figure 57. Liquid volumes and concentration in vessel sumps, run A-8 (Hillard$^5$).
Table 8. Iodine material balances (Hillard³)

<table>
<thead>
<tr>
<th>Location</th>
<th>Run A3</th>
<th>Run A4</th>
<th>Run A6</th>
<th>Run A7</th>
<th>Run A8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grams</td>
<td>Grams</td>
<td>Grams</td>
<td>Grams</td>
<td>Grams</td>
</tr>
<tr>
<td></td>
<td>x²</td>
<td>x²</td>
<td>x²</td>
<td>x²</td>
<td>x²</td>
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<tr>
<td><strong>Aerosol Generation</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Starting material</td>
<td>101.00</td>
<td>100.00</td>
<td>101.50</td>
<td>100.00</td>
<td>101.00</td>
</tr>
<tr>
<td>Generation apparatus</td>
<td>2.57</td>
<td>3.54</td>
<td>1.13</td>
<td>1.11</td>
<td>0.14</td>
</tr>
<tr>
<td>Injection line samples</td>
<td>0.36</td>
<td>0.36</td>
<td>0.15</td>
<td>0.15</td>
<td>1.03</td>
</tr>
<tr>
<td>Accounted for</td>
<td>25.25</td>
<td>25.00</td>
<td>30.59</td>
<td>30.14</td>
<td>2.66</td>
</tr>
<tr>
<td>Delivered to containment (by difference)</td>
<td>75.75</td>
<td>75.00</td>
<td>70.91</td>
<td>69.86</td>
<td>98.34</td>
</tr>
<tr>
<td></td>
<td>Grams</td>
<td>x²</td>
<td>Grams</td>
<td>x²</td>
<td>Grams</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
<td></td>
<td>b</td>
<td></td>
</tr>
<tr>
<td><strong>Containment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delivered to containment</td>
<td>75.75</td>
<td>100.00</td>
<td>70.91</td>
<td>100.00</td>
<td>98.34</td>
</tr>
<tr>
<td>In liquid pools (Prior to decontamination)</td>
<td>45.32</td>
<td>59.83</td>
<td>37.67</td>
<td>53.11</td>
<td>53.97</td>
</tr>
<tr>
<td>Samples</td>
<td>0.48</td>
<td>0.63</td>
<td>8.87</td>
<td>12.51</td>
<td>0.556</td>
</tr>
<tr>
<td>Purge to stack</td>
<td>0.52</td>
<td>0.69</td>
<td>0.73</td>
<td>1.03</td>
<td>0.086</td>
</tr>
<tr>
<td>Decontamination</td>
<td>5.90</td>
<td>7.78</td>
<td>5.46</td>
<td>7.70</td>
<td>0.820</td>
</tr>
<tr>
<td>Accounted for</td>
<td>52.22</td>
<td>68.93</td>
<td>52.73</td>
<td>74.35</td>
<td>55.43</td>
</tr>
<tr>
<td>On surfaces (by difference)</td>
<td>23.52</td>
<td>31.06</td>
<td>18.18</td>
<td>25.65</td>
<td>42.91</td>
</tr>
</tbody>
</table>

³Percent of starting mass.

bPercent of delivered mass.

Includes spray solution and steam condensate.
phenomena involved and considers only the removal by the sprays. If one looks at the drop data, these data are "difficult to interpret, not only because of sampling inadequacies but because the relative fractions of the various iodine forms and particle sizes were changing rapidly with time."5

The data for the gas phase are the result of the combined effects of all of the processes for the removal of molecular iodine from the gas phase. But if all of the processes except for the sprays exerted only a small overall effect in the removal of molecular iodine from the gas phase, then these data would be acceptable from the standpoint of usefulness in determining the efficiency of the spray model. The data for liquid in the sumps should eliminate some of the sources of error because these data shows how much molecular iodine is transferred to the liquid. Nevertheless, any iodine that is on the surfaces and is not chemically held to the walls could be washed off in the sumps. Since the sprays were not started at the instant the molecular iodine was released, a significant amount of molecular iodine released into the containment may have deposited on the surfaces, and subsequently been washed off into the sumps or might have been transferred back into the gas phase later when the partial pressure of molecular iodine in the gas phase was smaller than the partial pressure of molecular iodine on the surfaces. The latter effect could result in an underestimate of the removal rate of molecular iodine.

To remove some of the possible sources of error, the comparison of experimental results to the results of the spray model will be limited to the area of the drywell. The drywell had a cross sectional area of
8.8 square meters (which is a diameter of 3.35 meters), a drop fall height of 15.4 meters, and a volume of 135.52 cubic meters. For example, in run A-3, at the start of the first spray period, the initial gas phase concentration was approximately $5 \times 10^4$ micrograms/cubic meter ($1.97 \times 10^{-7}$ moles/liter) and the final concentration was approximately $1.25 \times 10^4$ micrograms/cubic meter ($4.92 \times 10^{-8}$ moles/liter). The amount of iodine removed from the gas phase during the first spray was 5.082 grams. Also, at the start of the first spray, the concentration of the liquid in the drywell sump was approximately $4 \times 10^4$ micrograms/liter ($1.58 \times 10^{-4}$ moles/liter) and the initial volume was approximately 150 liters. At the end of the first spray, the concentration in the drywell sump was $8 \times 10^2$ micrograms/liter ($3.15 \times 10^{-6}$ moles/liter), and the volume was approximately 332 liters. The number of grams of iodine transferred to the liquid in the drywell sump was 13.15 grams. The difference between the number of grams of iodine removed from the gas phase and the number of grams of iodine transferred to the liquid phase was $-6.78$ grams. The resulting relative error based on the gas phase is

$$\text{error} = \left( \frac{\text{grams removed from gas} - \text{grams transferred to liquid}}{\text{grams removed from gas}} \right) \times 100\% ,$$

$$\text{error} = \left( \frac{5.082 - 13.15}{5.082} \right) \times 100\% = -133.4\% .$$

130
Results of the other runs were similar with more iodine appearing transferred to the liquid than was removed from the gas. In fact, for many cases the error is much greater.

Some of the errors noted above may have resulted from iodine that had deposited on the walls before the sprays had started and that was subsequently washed off into the drywell sump. This explanation appears feasible, but may not be the total answer since the highest concentration of molecular iodine in the gas phase was reported to be $6.5 \times 10^4$ micrograms/cubic meter; and with a concentration at the start of the spray period of $5 \times 10^4$ micrograms/cubic meter it appears that only 2.03 grams were removed before the first spray (from gas above the drywell area). Another explanation would be that since the volume for this comparison is constrained to the volume of the drywell, there could be a transfer of additional iodine that was previously on the surfaces back to the gas. Most likely, however, much of the error is simply due to error sampling and analytical measurements in both phases.
CHAPTER VIII

COMPARISON TO DATA AND OLD MODELS

The spray model has been compared to the large scale tests from the Containment Systems Experiments,\(^5\) see Figures 58 through 67. The basis for the comparison is the number of grams of molecular iodine removed from the gas phase in the experimental test as opposed to the number of grams of molecular iodine that is predicted to be removed by the spray model. Since there is such a large discrepancy in the data between the gas and liquid phases (see Chapter 7, Experimental Data), only the experimental data from the drywell will be considered in an effort to eliminate some of the possible sources of error (see Table 9 for spray distributions). For run A-3 of the CSE tests, the initial conditions at the beginning of the first spray are:

Temperature of the liquid spray solution = 77°F = 298K,
Temperature of the gas = 77°F = 298K,
Pressure = 1 atmosphere,
Drop size = 1210 microns mass medium diameter,
(assumed) = 1210 microns average surface area diameter,
= 1210 microns average volume diameter,
Spray solution = buffered pH of 9.5 and all other liquid species have a concentration of 0.0 moles/liter,
Spray flow rate = 12.8 gallons/minute = 48.5 liters/minute (full containment),
= 4.8 gallons/minute = 18.18 liters/minute (drywell area),
Figure 58. Results of Spray Model for CSE run A-3 first spray period. Initial concentration of molecular iodine in the gas phase of $1.97 \times 10^{-7}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 58. (continued).
Figure 59. Results of Spray Model for CSE run A-3 second spray period. Initial concentration of molecular iodine in the gas phase of $1.29 \times 10^{-8}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 59. (continued).
Figure 60. Results of Spray Model for CSE run A-4 first spray period. Initial concentration of molecular iodine in the gas phase of $1.50 \times 10^{-7}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 60. (continued).
Figure 61. Results of Spray Model for CSE run A-4 second spray period. Initial concentration of molecular iodine in the gas phase of $7.88 \times 10^{-10}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 61. (continued).
Figure 62. Results of Spray Model for CSE run A-6 first spray period. Initial concentration of molecular iodine in the gas phase of $8.67 \times 10^{-8}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.

(d) Concentration of iodine species in the sump as a function of time.

Figure 62. (continued).
Figure 63. Results of Spray Model for CSE run A-6 second spray period. Initial concentration of molecular iodine in the gas phase of $2.01 \times 10^{-9}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.

(d) Concentration of iodine species in the sump as a function of time.

Figure 63. (continued).
Figure 64. Results of Spray Model for CSE run A-7 first spray period. Initial concentration of molecular iodine in the gas phase of \(1.06 \times 10^{-7}\) moles/liter and a buffered pH of 5.0 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.

Figure 64. (continued).
Figure 65. Results of Spray Model for CSE run A-7 second spray period. Initial concentration of molecular iodine in the gas phase of $2.05 \times 10^{-8}$ moles/liter and a buffered pH of 5.0 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.

(d) Concentration of iodine species in the sump as a function of time.

Figure 65. (continued).
Figure 66. Results of Spray Model for CSE run A-8 first spray period. Initial concentration of molecular iodine in the gas phase of $1.18 \times 10^{-7}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.

(b) Number of moles of molecular iodine transferred as a function of time.
(c) Concentration of iodine species in the liquid drops as a function of time.
(d) Concentration of iodine species in the sump as a function of time.
Figure 66. (continued).
Figure 67. Results of Spray Model for CSE run A-8 second spray period. Initial concentration of molecular iodine in the gas phase of $4.14 \times 10^{-9}$ moles/liter and a buffered pH of 9.5 in the spray solution.

(a) Concentration of molecular iodine in the gas phase as a function of time.
(b) Number of moles of molecular iodine transferred as a function of time.
(c). Concentration of iodine species in the liquid drops as a function of time.

(d) Concentration of iodine species in the sump as a function of time.

Figure 67. (continued).
Table 9. Measured spray liquid distribution in CSE tests (Hillard\textsuperscript{5})

<table>
<thead>
<tr>
<th>Cross section</th>
<th>Wall trough</th>
<th>Main sump</th>
<th>Dry well sump</th>
<th>Deck distribution ±(\sigma) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area, %</td>
<td>2.0</td>
<td>78.5</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>Run A3</td>
<td>0.7</td>
<td>62.8</td>
<td>37.5</td>
<td>64.8</td>
</tr>
<tr>
<td>Run A4</td>
<td>10.9</td>
<td>68.9</td>
<td>20.2</td>
<td>46.7</td>
</tr>
<tr>
<td>Run A6 and A\textsuperscript{7b}</td>
<td>2.1</td>
<td>68.4</td>
<td>28.5</td>
<td></td>
</tr>
<tr>
<td>Run A\textsuperscript{8a}</td>
<td>~6.0</td>
<td>73.0</td>
<td>21.0</td>
<td>46.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measured during shakedown test.

\textsuperscript{b} Measured from liquid level change during run. Normal condensation deducted.
Spray time = 10 minutes,
Containment height = 15.4 meters,
Containment diameter = 3.35 meters.

For the First Spray:

Initial concentration of elemental iodine in the gas phase =
\[ 5 \times 10^4 \text{ micrograms/cubic meter} = 1.97 \times 10^{-7} \text{ moles/liter}, \]
Initial concentration of iodine in the drywell sump =
\[ 8.0 \times 10^2 \text{ micrograms/cubic meter}, \]
Initial volume of liquid in the drywell sump = 150 liters.

Results of the CSE tests are:

Final concentration of elemental iodine in the gas phase =
\[ 1.25 \times 10^4 \text{ micrograms/cubic meter} = 4.92 \times 10^{-8} \text{ moles/liter}, \]
Number of grams removed from the gas phase =
\[ 3.75 \times 10^4 \text{ micrograms/liter} \times 15.4 \text{ meters} \times 8.8 \text{ square meters} = \]
\[ 5.82 \times 10^6 \text{ micrograms} = 5.082 \text{ grams}, \]
Final concentration in the drywell sump =
\[ 4 \times 10^4 \text{ micrograms/liter}, \]
Final volume in the sump = 331.8 liters,
Number of grams transferred to the liquid = 

\[(4 \times 10^4 \text{ micrograms/liter} \times 331.8 \text{ liters}) - (8 \times 10^2 \text{ micrograms/liter} \times 150 \text{ liters}) = 13.15 \times 10^6 \text{ micrograms} = 13.15 \text{ grams.}\]

These calculations show the discrepancy between the number of grams of iodine removed from the gas phase, 5.082 grams, and the number grams of iodine transferred to the liquid, 13.15 grams. This discrepancy is discussed in Chapter 7.

Results of the Spray Model (for run A-3 first spray figure 58) is:

Final concentration of the gas phase = 
\[2.4 \times 10^4 \text{ micrograms/cubic meter} = 9.45 \times 10^{-8} \text{ moles/liter},\]

Number of grams of iodine removed from the gas and transferred to the liquid = 3.54 grams.

Relative Percent Difference is:

Gas phase, 
\[\frac{(5.082 - 3.54)}{5.082} \times 100\% = 30.4\% ,\]

Liquid phase 
\[\frac{(13.15 - 3.54)}{13.15} \times 100\% = 73.1\% .\]

Table 10 contains the results of the comparisons for all of the runs. The third or fourth spray periods are not included in the comparison because these periods are for a sodium thiosulfate spray
<table>
<thead>
<tr>
<th>CSE run</th>
<th>Spray period</th>
<th>Initial gas phase concentration (moles/liter)</th>
<th>CSE experimental results</th>
<th>Spray model's results</th>
<th>Relative percent difference between the gas phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Final gas phase concentration (moles/liter)</td>
<td>Grams removed from the gas phase</td>
<td>Grams transferred to the liquid phase</td>
<td>Final gas phase concentration (moles/liter)</td>
</tr>
<tr>
<td>A-3</td>
<td>1st</td>
<td>$1.97 \times 10^{-7}$</td>
<td>$4.92 \times 10^{-8}$</td>
<td>5.082</td>
<td>13.15</td>
</tr>
<tr>
<td>A-3</td>
<td>2nd</td>
<td>$1.27 \times 10^{-8}$</td>
<td>$2.89 \times 10^{-10}$</td>
<td>0.426</td>
<td>4.90</td>
</tr>
<tr>
<td>A-4</td>
<td>1st</td>
<td>$1.50 \times 10^{-7}$</td>
<td>$1.97 \times 10^{-9}$</td>
<td>5.082</td>
<td>12.85</td>
</tr>
<tr>
<td>A-4</td>
<td>2nd</td>
<td>$7.88 \times 10^{-10}$</td>
<td>$7.88 \times 10^{-11}$</td>
<td>0.0244</td>
<td>1.124</td>
</tr>
<tr>
<td>A-6</td>
<td>1st</td>
<td>$8.67 \times 10^{-9}$</td>
<td>$2.36 \times 10^{-9}$</td>
<td>2.900</td>
<td>11.10</td>
</tr>
<tr>
<td>A-6</td>
<td>2nd</td>
<td>$2.01 \times 10^{-9}$</td>
<td>$1.10 \times 10^{-9}$</td>
<td>0.312</td>
<td>2.33</td>
</tr>
<tr>
<td>A-7</td>
<td>1st</td>
<td>$1.06 \times 10^{-7}$</td>
<td>$3.27 \times 10^{-9}$</td>
<td>3.547</td>
<td>8.08</td>
</tr>
<tr>
<td>A-7</td>
<td>2nd</td>
<td>$2.05 \times 10^{-9}$</td>
<td>$7.49 \times 10^{-10}$</td>
<td>0.0447</td>
<td>1.57</td>
</tr>
<tr>
<td>A-8</td>
<td>1st</td>
<td>$1.18 \times 10^{-7}$</td>
<td>$5.12 \times 10^{-9}$</td>
<td>3.889</td>
<td>7.57</td>
</tr>
<tr>
<td>A-8</td>
<td>2nd</td>
<td>$4.14 \times 10^{-9}$</td>
<td>$2.17 \times 10^{-9}$</td>
<td>0.0678</td>
<td>4.96</td>
</tr>
</tbody>
</table>
solution or for recirculatory spray solutions. The sodium-thiosulfate changes the chemical kinetics and therefore, the model developed in this report should not be expected to be valid. However, recirculatory spray solutions can be used in the spray model if one knows the concentration of all of the species in the solution. The experimental data do not report the concentration of all of the species and since the liquid phase data are questionable (discussed in Chapter 7), and any results would be essentially meaningless. Therefore no further comparisons were attempted.

With a high initial concentration of molecular iodine in the gas, such as those seen during the first spray period, the spray model predicts the number of grams of iodine removed within a relative difference of between 13.8% and 68%. At low concentrations of molecular iodine in the gas, such as those seen during the second spray period, the spray model predicts the number of grams of iodine removed within a relative difference of -120.0% to 68.0% with the closest result having a difference of 7.7%. At high concentrations, the model always underpredicts the number of moles transferred as indicated by the experimental data. At low concentrations of molecular iodine in the gas, the model over-predicted the removal rate 4 out of 5 times when compared to the gas phase data. It should also be noted that the spray model never over-predicts the number of grams removed when compared to the experimental data for the liquid.

The only difference between the conditions of experimental runs A-3 and A-4 is the spray flow rate. The model responds quite adequately
and, in fact, the difference in results decreases slightly. For experimental runs A-6, A-7, and A-8, the temperature and pressure of the gas are raised to approximately 397K and 3 atmospheres, respectively. The results of the spray model appear to have larger difference with the experimental data because the spray model does not contain calculations for heat transfer and the temperature of the drop always remain at its initial temperature of 298K. The properties of the liquid change with temperature and the kinetic rate constants will also change.

In run A-8, the drop size decreases to 770 microns. The model responds adequately and the error is most likely due to the higher temperature. It should be recalled that all of these results are produced with an input that assumes spherical drops. The drops are not spherical, but no information is available on the actual shape of the drops.

Comparing the new model to the previous models shows the new model has a better correlation with the experimental data than do the previous models. The data and the previous models are in terms of a removal rate constant and half lives of molecular iodine. The removal rate constant is expressed by Equation 3 of Chapter 1, Section B, repeated here:

\[ C = C_0 \exp(-\lambda t) \]  \hspace{1cm} (3)

where

- \( C_0 \) = initial concentration of molecular iodine in the gas phase,
- \( C \) = concentration of molecular iodine,
- \( \lambda \) = removal rate constant, and
- \( t \) = time.

Rearranging Equation 3 and solving for the removal rate constant:

\[ \lambda = - \frac{\ln \left( \frac{C}{C_0} \right)}{t} . \]  \hspace{1cm} (70)
The half life of molecular iodine is the period of time during which the concentration of molecular iodine in the gas phase decreases to one half of its initial concentration. The half life is determined by rearranging Equation 3 into:

\[ t_{1/2} = - \frac{\ln(C/C_0)}{\lambda} = - \frac{\ln(1/2)}{\lambda} = 0.693/\lambda \]  

(71)

Using these two equations, one can compare directly the experimental spray data and the results of the previous models in their existing form.

Note that the new spray model is not intended to determine a removal rate constant because removal rate constants tend to smooth out the data and can give false impressions since a logarithm is involved. The output of the new spray model is only put into this form to compare its results to the results of the existing models. The correct comparison would be to compare the number of moles removed or the resulting gas phase concentration.

Table 11 shows the comparison of the removal rate constant for the new model to that for the experimental data. As can be seen from Table 11, the new spray model always over-predicts the removal rate constant (under-predicts the removal rate) for the first spray period (high concentrations of molecular iodine). The absolute value difference for the new model is from 34.0% to 89.3% with an average difference of approximately 59.6%. One should notice that these differences do not have as wide a spread between the numbers as does the difference for the direct comparison of the number of grams of molecular iodine transferred to the liquid. This difference is due to the fact that the removal rate constant is calculated from a logarithm which smooths out the error. It is
Table 11. Comparison of removal rate constant for spray model against CSE tests

<table>
<thead>
<tr>
<th>CSE run</th>
<th>Spray period</th>
<th>Initial gas phase concentration (moles/liter)</th>
<th>CSE tests results</th>
<th>Spray model's results</th>
<th>Relative percent difference$^a$ between removal rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Final gas phase concentration (moles/liter)</td>
<td>Removal rate constant, $\lambda$ (min$^{-1}$)</td>
<td>Final gas phase concentration (moles/liter)</td>
<td>Removal rate constant, $\lambda$ (min$^{-1}$)</td>
</tr>
<tr>
<td>A-3</td>
<td>1st</td>
<td>$1.97 \times 10^{-7}$</td>
<td>$4.92 \times 10^{-8}$</td>
<td>0.139</td>
<td>5.0</td>
</tr>
<tr>
<td>A-3</td>
<td>2nd</td>
<td>$1.29 \times 10^{-8}$</td>
<td>$2.89 \times 10^{-10}$</td>
<td>0.126</td>
<td>5.5</td>
</tr>
<tr>
<td>A-4</td>
<td>1st</td>
<td>$1.50 \times 10^{-7}$</td>
<td>$1.97 \times 10^{-9}$</td>
<td>0.495</td>
<td>1.4</td>
</tr>
<tr>
<td>A-4</td>
<td>2nd</td>
<td>$7.88 \times 10^{-10}$</td>
<td>$7.88 \times 10^{-11}$</td>
<td>0.077</td>
<td>9.0</td>
</tr>
<tr>
<td>A-6</td>
<td>1st</td>
<td>$8.67 \times 10^{-8}$</td>
<td>$2.36 \times 10^{-9}$</td>
<td>0.365</td>
<td>1.9</td>
</tr>
<tr>
<td>A-6</td>
<td>2nd</td>
<td>$2.01 \times 10^{-9}$</td>
<td>$1.10 \times 10^{-9}$</td>
<td>0.022</td>
<td>32.0</td>
</tr>
<tr>
<td>A-7</td>
<td>1st</td>
<td>$1.06 \times 10^{-7}$</td>
<td>$3.27 \times 10^{-9}$</td>
<td>0.345</td>
<td>2.0</td>
</tr>
<tr>
<td>A-7</td>
<td>2nd</td>
<td>$2.05 \times 10^{-9}$</td>
<td>$7.49 \times 10^{-10}$</td>
<td>0.033</td>
<td>21.0</td>
</tr>
<tr>
<td>A-8</td>
<td>1st</td>
<td>$1.18 \times 10^{-7}$</td>
<td>$5.12 \times 10^{-9}$</td>
<td>1.08</td>
<td>0.64</td>
</tr>
<tr>
<td>A-8</td>
<td>2nd</td>
<td>$4.14 \times 10^{-9}$</td>
<td>$2.17 \times 10^{-9}$</td>
<td>0.017</td>
<td>40.0</td>
</tr>
</tbody>
</table>

$^a$Difference $\frac{|\lambda_{CSE} - \lambda_{SPRAY}|}{\lambda_{CSE}} \times 100\%$. 
far more realistic to use the number of grams of molecular iodine removed for comparison.

A comparison of the results of the previous spray models is shown in Table 12. Note that the "realistic model" is the name given to this model when it was first developed for inclusion in WASH-1329 and does not imply that it is the best model.

It is quite obvious that from Table 12 that for the first spray period of runs A-3, A-4, A-6, and A-8, the new spray model is not as accurate as some of the older models. Since the old models are not a function of the gas phase concentration of iodine and the parameters used in the old model for the first spray period and the second spray period are the same. The removal rate constant predicted by the old models would be the same for the first and second spray periods. The new model would predict results closer to the spray tests than would the "realistic" model for the second spray period. Although the "realistic" model does predict close results for the first spray period, it uses an effective partition coefficient of 100,000. For a drop fall height of 15.4 meters, the contact time of the drop with the gas phase is only 3.9 seconds and the effective partition coefficient at the conditions would only be approximately 2200. An effective partition coefficient of 100,000 would not be reached until approximately 10 days at a pH of 9.5. So this effective partition coefficient of 100,000 would not be reached until approximately 10 days at a pH of 9.5. So this effective partition coefficient consists of a true effective partition coefficient times an empirical factor. It is believed that this effective partition coefficient was picked so as to best describe the results for the first
Table 12. Comparison of removal rate constant for spray model against previous models

<table>
<thead>
<tr>
<th>CSE run number</th>
<th>Spray period</th>
<th>Experimental $\lambda$, min$^{-1}$</th>
<th>&quot;Realistic&quot;$^a$ film model $\lambda$, min$^{-1}$</th>
<th>Stagnant$^b$ drop model $\lambda$, min$^{-1}$</th>
<th>CSE model$^d$ $\lambda$, min$^{-1}$</th>
<th>New model $\lambda$, min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-3</td>
<td>1st</td>
<td>0.139</td>
<td>0.102</td>
<td>0.027</td>
<td>0.053</td>
<td>0.109</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.126</td>
<td>0.102</td>
<td>0.027</td>
<td>0.053</td>
<td>0.109</td>
</tr>
<tr>
<td>A-4</td>
<td>1st</td>
<td>0.495</td>
<td>0.39</td>
<td>0.093</td>
<td>0.195</td>
<td>0.408</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.077</td>
<td>0.39</td>
<td>0.093</td>
<td>0.195</td>
<td>0.408</td>
</tr>
<tr>
<td>A-6</td>
<td>1st</td>
<td>0.365</td>
<td>0.34</td>
<td>0.202</td>
<td>0.235</td>
<td>0.365</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.022</td>
<td>0.34</td>
<td>0.202</td>
<td>0.235</td>
<td>0.365</td>
</tr>
<tr>
<td>A-7</td>
<td>1st</td>
<td>0.347</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.033</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td>A-8</td>
<td>1st</td>
<td>1.08</td>
<td>1.02</td>
<td>0.483</td>
<td>0.527</td>
<td>0.978</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.017</td>
<td>1.02</td>
<td>0.483</td>
<td>0.527</td>
<td>0.978</td>
</tr>
</tbody>
</table>

$^a$Equation 7 with PC = $10^5$.

$^b$Equation 6 with PC = 5000.

$^c$Equation 5 with PC = 5000.

$^d$Equation 8.

$^e$Published results not found.
spray period. If a situation would arise for the need of the "realistic" spray model and it did not occur in this same vessel used in the CSE tests and under exactly the same conditions, the correction factor may be wrong.

The CSE model is a gas-film controlled model and is compared to tests maybe with a buffered high pH. The controlling resistance to mass transfer for iodine would be gas-film controlled under these conditions because the reactions quickly remove the molecular iodine in the liquid. However, when the pH is buffered at a low pH or when the pH is unbuffered, there will be significant resistance to mass transfer in both phases. BWRs use ordinary water for their sprays, so there will be significant resistance to mass transfer in both phases. Therefore, the CSE model would give incorrect results for BWRs and any other system not buffered at a high pH.

Since the iodine hydrolysis reactions are included in the new spray model, they can determine internally when the reactions play an important role in the mass transfer, and the new spray model should be valid for any conditions. The new spray model appears to give better results at low concentrations than for high concentrations of iodine in the gas phase. The difference between the experimental data and the new spray model can be caused by incorrect correlations for the mass transfer coefficients, incorrect data for the molecular iodine partition coefficient, incorrect expressions for the iodine hydrolysis reactions, or from incorrect reaction rate constants. But much of the difference is believed to be in the experimental spray data.
A new model has been developed for predicting the rate at which gaseous molecular iodine is absorbed by water sprays. The model is a quasi-steady state mass transfer model that includes the iodine hydrolysis reactions. The spray model was developed to determine numerically the influence of the iodine hydrolysis reaction on the mass transfer rates. The spray model is used to determine if inclusion of a representation of the iodine hydrolysis reactions increases the understanding of what is occurring and increases the realism of the actual process. The spray model is also used to see if the new models provide an increase in accuracy for the removal of gaseous iodine. The parameters of the spray model are the spray drop size, initial concentration of molecular iodine in the gas phase, the initial concentration of all of the iodine hydrolysis species (including pH), the temperature of the gas, the temperature of the liquid, the pressure, whether the spray solution is buffered or unbuffered, the spray flow rate, containment diameter, and containment height (drop fall height).

Three other models have also been developed; these are kinetic, drop, and wall spray models. The kinetic model simulates the solution to the equations to the iodine hydrolysis reactions as a function of time. The drop model simulates the absorption of gaseous iodine by a single water droplet. The drop model has a mass transfer with reaction algorithm and is the base model for the spray model. The wall-spray
model contains the spray model algorithm plus a falling-liquid film algorithm to simulate the removal of gaseous iodine by the water on the walls. The results of the wall-spray model are not significantly different from the results of the spray model and therefore the significantly longer computational time necessary to use the wall-spray model is not warranted.

The spray model shows a difference of -120.5% to 68.0% compared to the measured data of the Containment Systems Experiments with the closest result being within 7.7% of the experimental data. Some of the difference is believed to be due to error in the measured data from the experiment caused by the sampling techniques used and the fact that these tests are large scale with many removal processes occurring simultaneously. Molecular iodine is absorbed on paint, piping, insulation and particulates as well as on the spray drops. With all of these processes occurring simultaneously, it is extremely difficult to separate the contribution of the drops to iodine removal from the overall removed. Since literal interpretation of the experimental data show that twice as much iodine is transferred to the liquid phase as is removed from the gas phase, it is obvious that there are significant experimental errors present.

Other sources for the difference between the calculated results and the experimental data of error undoubtedly result from limitations in the spray model itself. The spray model does not include any representation of enhanced mass transfer during drop formation, and it has been shown by Simpson\textsuperscript{21} that significantly higher mass transfer rates do occur during drop formation. Another source of difficulty is
the unknown sphericity of the drops of the experiment. The new spray model has the ability to handle non-spherical drops, but there is no information on the sphericity for the spray drops and Clift\textsuperscript{13} indicates that drops of the size used in these tests are significantly non-spherical. Using non-spherical drops would increase the rate of mass transfer by increasing the surface area of the drops.

The spray model also does not consider heat transfer. Temperature changes in both the gas and liquid phases can alter the rate of mass transfer. The difference in results between the spray model and the experimental data increases when the initial temperature of the gas is not the same as the temperature of the liquid. Since there are no heat transfer calculations in the model, the gas and liquid phases are assumed to remain at the same temperature throughout the simulation.

2. Conclusions

In conclusion, the iodine hydrolysis reactions have a major influence on the removal of gaseous iodine by water droplets. The kinetics are influenced most when the water is buffered at a high pH. With a low pH or an unbuffered solution, the reactions essentially do not occur. The pH is the single most important kinetic rate-controlling parameter in the iodine hydrolysis reactions. A model for the absorption of gaseous iodine by water droplets will not be able to respond accurately to the different conditions that can occur if it does not include the iodine hydrolysis reactions. The new spray model gives better results when compared to the Containment Systems Experiment data for tests with low concentrations of molecular iodine but gives worse results at high
concentrations of molecular iodine than the previous models. The new spray model is more realistic since it contains the iodine hydrolysis reactions. It also provides information about the liquid phase and is able to handle a much greater range of conditions such as recirculatory sprays and unbuffered solutions. In any conceivable accident, radiation would be present and would alter the results based on hydrolysis alone by generating molecular iodine within the drops and by changing the pH in unbuffered sprays due to the formation of the acid.

3. Recommendations

It is recommended that all of the models: kinetic, drop, spray, and wall-spray models, be tested more extensively. It is recommended that both heat transfer and mass transfer during drop formation be incorporated into the spray model. Adding a representation of heat transfer would probably make the most significant improvement to the models and allow better comparison to experimental data taken from tests in which a temperature difference exists between the gas and liquid phases. The most important recommendation is that new smaller scale tests, which are more highly controlled, should be conducted. Presently there is a greater need for new data to which the results of these new models could be compared than there is a need for a more sophisticated model. Smaller scale experimental tests under better controlled conditions are suggested in which the only process for the removal of gaseous iodine would be by water drops or sprays. A small scale drop test could also be useful. Since the spray model is based upon the drop model, the drop model should be tested to see if it is correct. The drop model
must simulate a drop falling through gaseous iodine correctly; if not, then both the spray model and the wall-spray model would be incorrect.
LIST OF REFERENCES
LIST OF REFERENCES


APPENDIXES
APPENDIX A

NUMERICAL TECHNIQUE
All of the models involve the iodine hydrolysis reactions and an efficient numerical integration technique must be used. The kinetic model numerically integrates the iodine hydrolysis reactions with respect to time. The drop, spray and wall-spray models all contain mass transfer of molecular iodine to the liquid and the iodine hydrolysis reactions occurring in the liquid drop. Therefore, in all of the models the iodine hydrolysis reactions must be integrated.

The iodine hydrolysis reactions are integrated by a Runge-Kutta-Felhburg, RKF, 5(4) order numerical integration routine. RKF 5(4) has is a fifth order Runge-Kutta routine with a fourth order routine embedded in it. The RKF routine is a single step method with error control. To save computer calculation time the routine in the model only contains the parts of the RKF routine which are necessary to integrate these equations and the absolute error control has been replaced by a relative error control to improve accuracy and computer time. The error control is possible by comparing the difference between the two orders. The model requires as input the number of equations to integrate. For a buffered solution, there are four equations to numerically integrate. Equations 24, 25, and 26 are assumed to come to equilibrium instantaneously and since the hydrogen ion concentrations will not change, one would have to integrate Equations 27 through 30. For unbuffered solutions the pH would change, so Equation 32 would have to be integrated, so five equations would have to be integrated. Therefore, for a buffered solution the input parameter IN would be four and for an unbuffered solution IN would be equal to five.
Other numerical integration routines have been tried such as DGEAR and DVERK from the International Mathematics and Statistics Library, IMSL, and LSODE from Corlib. Neither of the IMSL routines would get started because the step size would drop below the accuracy of the machine. This is most likely due to the complexity of the differential equations. LSODE is a Gear's multistep integration routine. Gear's method works extremely well for the kinetic model. In fact LSODE works better in the kinetic model for longer periods of time. This is the routine that Bell$^3$ used. When mass transfer is included this routine becomes extremely slow, taking almost 10 times more computer time than does the RKF routine. This is because LSODE is a multistep method and each time mass transfer occurs a new concentration of molecular iodine is determined and the system must start over. So the RKF method was chosen because error can be minimized and efficiency can be achieved.
APPENDIX B

KINETIC MODEL, SAMPLE INPUT AND OUTPUT
KINETIC MODEL

The kinetic simulates the aqueous iodine hydrolysis reactions. Reactions 4, 5, and 6 (equations 24, 25, and 26) are assumed to come to equilibrium. The kinetic model numerically integrates equations 27 through 32 with a Runge-Kutta-Fehlberg 5(4) routine. Subroutine FUNCTN and ITER are called from this main program. Subroutine INTEGRATE contains the equations to be integrated. Subroutine ITER finds the root to the equilibrium equation of equation 24 by a secant method. This program is designed to run on a PDP-10 computer but should be easily converted to run on any Fortran computer.

IMPLICIT DOUBLE PRECISION (A-H,K-Z)
IMPLICIT INTEGER (I-J)

DIMENSION W(8), WOLD(8), K1(7), K2(7), K3(7), B(7), WB(7),
       DELTA(7), WES(7), F(7), K4(7), K5(7), K6(7), TOL(7)

READ (58,*) A, B, EMIN, HMAX, IN
READ (49,*) TOLER, TEMPL

! PLI CIT DOUBLE PRECISION (A-H,K-Z)
! PLI CIT INTEGER (I-J)

! DIMENSION W(8), WOLD(8), K1(7), K2(7), K3(7), B(7), WB(7),
! DELTA(7), WES(7), JF(7), K4(7), K5(7), K6(7), TOL(7)

! READ (58,*) A, B, EMIN, HMAX, IN
! READ (49,*) TOLER, TEMPL

! FORMAT (13, H, 13, TOL)
! FORMAT (13, H, 13, TOL)

! WRITE (50, 11)

READ IN INITIAL CONDITIONS

DO 20 J=1,7
READ (58,*) WOLD(J)
CONTINUE

TOLD=A
Q=1. 0D-1
H=1. 0D-2

WRITE (50,22) I, TOLD, WOLD(1), WOLD(2), WOLD(3), WOLD(4), WOLD(5), WOLD(6),
       , WOLD(7), B

CALCULATE THE EQUILIBRIUM CONSTANTS K4, K5, K6

DENLIQ=6. 02552247D-9*TEMPL**3-9. 1329604D-6*TEMPL**2+3. 573572D-3*TEMPL
       +5. 8358882D-1
RK6=-4. 098DD0-3245. 2DD0/TEMPL+2. 2363D5/(TEMPL**2)-3. 984D7/(TEMPL**3)+
(13. 957DD0-1262. 3DD0/TEMPL+8. 5641D5/(TEMPL**2))*DLG(DENLIQ)
RK6=10** (RK6)

178
RK5=10**(2800.48D00+0.7335E00*TEMFL-80670.0D00/TEMFL)

RK4=DEXP(3727.86D00/TEMFL-11.6326E00+0.0192212D00*TEMFL)

WOLD(8)=RK6/WOLD(5)

BEGIN THE RUNGE-KUTTA-FELBERG ROUTINE

CALCULATE K’S

DO 30 J=1,IN
W(J)=WOLD(J)
30 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)

DO 40 J=1,IN
K1(J)=B*P(J)
40 CONTINUE

DO 50 J=1,IN
W(J)=WOLD(J)+K1(J)/4.0D00
50 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)

DO 60 J=1,IN
K2(J)=H*P(J)
60 CONTINUE

DO 80 J=1,IN
W(J)=WOLD(J)+3.0D00*K1(J)/3.2D1+9.0D00*K2(J)/3.2D1
80 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)

DO 90 J=1,IN
K3(J)=B*P(J)
90 CONTINUE

DO 110 J=1,IN
W(J)=WOLD(J)+1.932D3*K1(J)/2.197D3-7.2D3*K2(J)/2.197D3
+7.296D3*K3(J)/2.197D3
110 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)

DO 120 J=1,IN
K4(J)=B*P(J)
120 CONTINUE

DO 130 J=1,IN
W(J)=WOLD(J)+4.39D2*K1(J)/2.162D2-8.0D00*K2(J)+3.68D3*K3(J)/5.13D2
-8.45D2*K4(J)/4.104D3
130 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)

DO 140 J=1,IN
K5(J)=B*P(J)
140 CONTINUE

DO 150 J=1,IN
W(J)=WOLD(J)-8.0D00*K1(J)/2.7D1+2.0D00*K2(J)-3.5440D3*K3(J)/2.565D3

179
CONTINUE
CALL PUNCTN(W,WCLD,F,IN)
DO 160 J=1,IN
K6(J) =F(J)
160 CONTINUE

DETERMINE THE NEW CONCENTRATION OF ALL OF THE IODINE HYDROLYSIS

DO 100 J=1,IN
WB(J) =WOLD(J) +1.6D1*K1(J)/(1.35D2+6.656D3+K3(J)/1.2825D4+
1.2861D4*K4(J)/5.643D4-9.0D00*K5(J)/5.0D1+2.0D00*K6(J)/5.5D1
R(J) =ABS(K1(J)/3.6D2-1.28D2*K3(J)/4.275D3-2.197D3*K4(J)/7.524D4
1 +K5(J)/5.0D1+2.0D00*K6(J)/5.5D1)/H
TOL(J) =ABS(WB(J)*TOL)
DELTA(J) =0.84*(TOL(J)/R(J))*0.25

DO 510 J=1,IN
WOLD(J) =WB(J)
510 CONTINUE

DETERMINE THE EQUILIBRIUM CONCENTRATIONS FOR EQUATIONS 24, 25 AND
26

BB= -1.0D00-(WOLD(2)+WOLD(1))*BK4
C=WOLD(2)*WOLD(1)*BK4-WOLD(7)
D=BE/(2.0D00*BK4)
E=((BB**2.0D00-4.0D00*BK4*C)**0.5D00)/(2.0D00*BK4)
V=BB**2.0D00-4.0D00*BK4*C
WOLD(7)=WOLD(7)+V
WOLD(1)=WOLD(1)-V
WOLD(2)=WOLD(2)-V

IF(IN.EQ.4)GOTO 600
RR=WCLD(6)+WCLD(5)+BK5
S=-BK5*WCLD(3)+WCLD(6)*WCLD(5)
M=(-BR+(BR-BR-4.0D00*SK5)**0.5)/(2.0D00)
WCLD(5)=WCLD(5)+M
GOTO 605

M=(BK5*WCLD(3)-WCLD(6)*WCLD(5))/(WCLD(5)+BK5)

WOLD(6)=WOLD(6)+M
WOLD(3)=WOLD(3)-M

IF(IN.EQ.4)GOTO 615

U=WOLD(8)+WCLD(5)-BK6
VV=WCLD(8)+WCLD(5)
X=(-VV+(VV-VV-4.0D00*U)**0.5)/(2.0D00)
WOLD(5)=WCLD(5)+X
WOLD(8)=WOLD(8)+X

GOTO 615

I=I+1
TOLD=TOLD+H

180
C WRITE(50,22) I, TOLD, WOLD(1), WOLD(2), WOLD(3), WOLD(4), WOLD(5),
     1 WOLD(6), WOLD(7), H
C DEL=DELTA(1)
C IF(IN .EQ. 1) GOTO 905
C DO 520 J=2, IN
     IF (DEL .LT. DELTA(J)) GOTO 520
     DEL=DELTA(J)
520 CONTINUE
C GOTO 905
C DETERMINE NEW STEP SIZE
C 900 DEL=DELTA(J)
C 905 IF (DEL .GT. Q) GOTO 910
     HNEW=Q*H
     GOTO 1000
C 910 IF (DEL .LT. 4.0) GOTO 920
     HNEW=4.0D00*H
     GOTO 1000
C 920 HNEW=DEL*H
C CHECK NEW STEP SIZE WITH MAX AND MIN STEP SIZE
C 1000 IF (HNEW .LT. HMAX) GOTO 930
     HNEW=HMAX
C 930 IF (HNEW .LT. HMIN) GOTO 1111
     LEFT=B-TOLD-HNEW
C IF (LEFT .GT. 0.0) GOTO 5000
     HNEW=B-TOLD
C 5000 H=HNEW
     IF (TCLD .GE. B) GOTO 999
     GOTO 1
C 1111 WRITE(40,21) HNEW
C 999 WRITE(23,25) I, IN
C STOP
C END
SUBROUTINE FUNCTN

THIS SUBROUTINE CONTAINS THE DIFFERENTIAL EQUATIONS (KINETIC RATE EQUATIONS) TO BE INTEGRATED. THIS SUBROUTINE IS CALLED FROM THE RUNGE-KUTTA-FELDMAN INTEGRATION ROUTINE IN THE KINETIC, DISP, SPRAY AND WALL-SPRAY MODELS.

SUBROUTINE FUNCTN (W,WOLD,F,IN)

IMPLICIT DOUBLE PRECISION(A-H,K-Z)
IMPLICIT INTEGER(I-J)

DIMENSION W(8),WOLD(8),F(7)

IF(IN .EQ. 5) GOTO 5

W(5)=WOLD(5)
W(6)=WOLD(6)

RK1=3.0D00
RK2=4.4D12
RK20=2.5D02
RK21=1.2D02
RK2R=3.0D08
RK3P=9.35D-8

R1=RK1*W(1)
R2=3*W(2)*W(3)*W(5)
R20=5*W(3)**2.0D00
R21=5*W(3)*W(6)
R28=5*W(4)*W(2)**2.0D00*W(5)**2.0D00
R3P=5*W(5)*W(2)

F(1)=-R1+RK1*5.0D-1*EE3
F(2)=R1-RK1+2.0D00*(R20+R21)/3.0D00-2.0D00*RR2-RP3
F(3)=R1-RK1-B20-B21+3.0D00*RR2
F(4)=B20+B21/3.0D00-RR2

IF(IN .EQ. 5) GOTO 10

F(5)=0.0D00
GOTO 11

F(5)=R1-RK1+E20+E21-3.0D00*RR2-4.0D00*RP3

F(6)=0.0D00
F(7)=0.0D00

RETURN
END
**SUBROUTINE ITTER**

This subroutine finds the root to the quadratic equilibrium equation for the formation reaction CP TB1-1OD1D2, I3- (Equation 24). A secant method is the routine used to find the root. This method is called whenever the quadratic formula results in less than approximately three significant figures. This subroutine is called by the programs KINETIC, DROP, SPRAY and WALL-SPRAY.

**SUBROUTINE ITTER(WOLD,RK4,C,V)**

IMPLICIT DOUBLE PRECISION (A-H,L-Z)
IMPLICIT INTEGER (I-K)

DIMENSION WOLD(7), W(7)

PO = 1.0D-16
P1 = 1.0D-18

Q0 = C - RK4 * PO * PO + RK4 * (WOLD(1) + WOLD(2)) - PO
Q1 = C - RK4 * P1 * P1 + RK4 * (WOLD(1) + WOLD(2)) - P1

NEW = P1 - Q1 * (P1 - PO) / (C1 - C0)

CHECK = ABS(NEW - P1) / P1

IF (CHECK .LT. 1.0D-4) GOTO 10

PO = P1
Q0 = Q1
P1 = NEW
GOTO 5

V = NEW
GOTO 10

RETURN

END
Kinetic Model sample input:

A = 0.0
B = 15.0
HMIN = 1.0 \times 10^{-10}
HMAX = 1.0 \times 10^2
IN = 4
TOLER = 1.0 \times 10^{-4}
TEMPL = 298 K
WOLD(1) = 1.0 \times 10^{-3}
WOLD(2) = 0.0
WOLD(3) = 0.0
WOLD(4) = 0.0
WOLD(5) = 1.0 \times 10^{-9}
WOLD(6) = 0.0
WOLD(7) = 0.0
APPENDIX C

DROP MODEL, SAMPLE INPUT AND OUTPUT
DROP MODEL

M. F. ALBERT

THE DROP MODEL SIMULATES THE ASPECTS OF ONE DROP SUSPENDED IN A GAS CONTAINING MOLECULAR ICINE. THE DROP MODEL IS A QUASI-
STEADY-STATE MODEL THAT CONSIDERS THE MASS TRANSFER INTO THE DROP AND THE ICINE HYDROLYSIS REACTIONS WHICH OCCUR IN
THE BULK LIQUID OF THE DROP. A TWC-RESISTANCE MODEL
IS USED TO DESCRIBE THE MASS TRANSFER. A RUNGE-KUTTA-FELHEUS
5(4) METHOD IS USED TO NUMERICALLY INTEGRATE THE ICINE
HYDROLYSIS EQUATIONS. SUBROUTINES PUNCTY AND ITTER ARE CALLED
FROM THIS MAIN PROGRAM. THIS PROGRAM IS DESIGNED TO RUN ON A
PDP-10 COMPUTER BUT SHOULD BE EASILY CONVERTED TO RUN ON ANY
FORTRAN COMPUTER.

IMPLICIT DOUBLE PRECISION (A-H, K-Z)
IMPLICIT INTEGER (I-J)

DIMENSION W(8), WOL(8), K1(7), K2(7), K3(7), B(7), WB(7),
1 DELTA(7), WES(7), F(7), K4(7), K5(7), K6(7), ICL(7)

READ (58,*), A, B, BMIN, BMAX, IN
READ (59,*), TMPG, TEMPD, DIAH
READ (60,*), CI2G, CHL
READ (69,*), TCI

FORMAT('AT A TEMPERATURE OF THE GAS ',F6.2, ' DEGREES KELVIN'/
1 ' THE VISCOSITY OF THE LIQUID (CP)' = ', E15.7/
2 ' THE VISCOSITY OF THE GAS (CP)' = ', E15.7/
3 ' THE PARTITION COEFFICIENT IS ' = ', E15.7/
4 ' THE DENSITY OF THE LIQUID (GMS/CC) ' = ', E15.7/
5 ' THE DENSITY OF THE GAS (GMS/CC) ' = ', E15.7/

FORMAT('THE DIFFUSION COEFFICIENT FOR THE GAS (SQ CM/SEC)' = ', E15.7/
1 ' THE DIFFUSION COEFFICIENT FOR THE LIQUID (SQ CM/SEC)' = ', E15.7/
2 ' THE GAS-SIDE MASS TRANSFER COEFFICIENT (CM/SEC)' = ', E15.7/
3 ' THE LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC)' = ', E15.7/
4 ' THE OVERALL MASS TRANSFER COEFFICIENT (CM/SEC)' = ', E15.7/
5 ' THE VOLUME FOR ONE DROP (LITERS)' = ', E15.7/
6 ' THE SURFACE AREA FOR ONE DROP (SQ CM)' = ', E15.7/
7 ' THE EXPOSURE TIME FOR THE DROP IS (SEC)' = ', E15.7/
8 ' THE REYNOLDS NUMBER FOR THE DROP ' = ', E15.7/
9 ' THE TERMINAL VELOCITY OF THE DROP (CM/SEC) ' = ', E15.7/

FORMAT('THE CONCENTRATION OF THE GAS IS (MOL/LITERS) : ', E15.7/
1 ' THE INITIAL CONCENTRATION OF THE DROP IS (MOL/LITERS) : '

FORMAT('TIME MOLES RBD FALL HGT STEP SIZE'
1 ' /

FORMAT(' THE FINAL CONCENTRATION OF THE DROP IS (MOL/LITERS) :

FORMAT('THE NUMBER OF MOLARITIES OF ICINE (I2) REMOVED IS = ', E15.7/
1 'THE NUMBER OF GRAMS OF IHCINE REMOVES IS = ', E15.7/

FORMAT(' TIME MOLES RBD FALL HGT STEP SIZE'
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
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FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /

FORMAT(' I2 = ',E15.7/
1 ' /

FORMAT(' ',E15.7/
1 ' /
2, /)

21 FORMAT('STEP SIZE WINOW STEP MIN',D15.7)
22 FORMAT(5S,D13.7)
23 FORMAT(4D15.7)
25 FORMAT(6)

C
WHITE(50,19)
WHITE(51,17)

C
SPA=3.1416D00*(DIA)**2
VOLD=(3.1416D00*(DIA)**3*D00)/(6.D00*1.0D3)

C
TEMPG4=TEMPG**4
TEMPG3=TEMPG**3
TEMPG2=TEMPG**2

C
TEMPL4=TEMPL**4
TEMPL3=TEMPL**3
TEMPL2=TEMPL**2

C
VL1=1.86628666E-8*TEMPL4-2.6333695D-5*TEMPL3+1.3976E07D-2*TEMPL2
VL2=3.3074E6D00*TEMPL+2.95986666D2
VSLIQ=VL1+VL2

C
PC1=9.981476D-7*TEMPL4-1.5730121D-3*TEMPL3+9.2785676D-1*TEMPL2
PC2=-2.42838E82*TEMPL+2.3624847D4
PC=PC1+PC2

C
DBL1=6.0251147E-9*TEMPL3-9.132604D-6*TEMPL2
DNL2=3.573572D-3*TEMPL+5.835082D-1
DENLIQ=DNL1+DNL2

C
VS1A=-2.871329D-15*TEMPG4+1.6909463D-11*TEMPG3-4.015468E-8*TEMPG2
VS1A=6.5679425D-5*TEMPG+1.5523691D-3
VISGAS=VS1A+VS1A2

C
TEMP=5.178D-3*TEMPG
OMEGA1=TMF**3*(-5.19047619D-2)+4.657142857D-1*TMF**2
OMEGA2=TMF*(-1.30423EC5D00)+2.315428571D00
OMEGA=OMEGA1+CEEGA2

C
VLWT=1/2.9D+1/2.53809D2

C
DIFGAS=1.858D-3*TEMPG**1.5*VLWT**0.5/(1.0D00*4.4355D0C**2*CEEGA)

C
DIFLIQ=3.91D-8*TEMP/VISLIQ

C
DNG1=8.2892055D-16*TEMPG4-4.2656962D-12*TEMPG3+8.0228283D-5*TEMPG2
DNG2=6.0325529D-6*TEMPG+2.6129391E-3
DENGAS=DNG1*DNG2

C
GSM1=0.83D00*(DENLIQ-DENGAS)/DENGAS)***0.25*9.81D2**0.25
GSM2=(VISGAS/(1.0D2*DENGAS))**-0.17*DIFGAS**0.67*DIA**-0.25
KG2=GS1*GS2

C
ND1=4.0D00*DENGA*(DENLIQ-DENGAS)*9.81D2*DIA**3
ND2=3.0D00*(VISGAS/1.0D2)**2
ND=NE1/ND2

C
WW=ALOG10(ND)

C
NBE1=(-1.81391D00+1.34671D00*WW-0.1247D00*WW**2+6.344D-3*WW**3)
NBE=LOG10*NBE1

C
TEMPV=EN1*(VISGAS/1.0D2)/(DIA*DENGA)

190
EXPTB=HEIGHT/TEMVEL

KLI2G=(4.00D0+LIPIQ*TEMVEL/(3.1415D0*DAM))**0.5

KLOV=KGI2*KLI2G/(PC*KLI2O+KGI2)

WRITE (22,10) TEMPG,VIPLIQ,VISGAS,EC,DEMPLIQ,DENGAS
WRITE (22,11) DIFGAS,LIPIQ,KGI2,KLI2O,KLOV,VOLD,SFA,E,NRE,TEMVEL

READ IN INITIAL CONDITIONS

DO 20 J=1,7
READ(N8,*)WOLD(J)
20 CONTINUE

TOLD=A
Q=1.0D-1
H=5.0D-2

CALCULATE EQUILIBRIUM CONSTANTS K4, K5 AND K6

RK6=4.098D00-3245.2D00/TEMPL+2.2363D5/(TEMPL**2)-3.986D7/(TEMPL**13)+(139.957D00-1262.3D00/TEMPL+8.5641D5/(TEMPL**2))*LIPIQ(LIPLIQ)
RK6=10**(RK6)

RK5=10**((2800.48D00+0.7335D00*TEMPL-80670.0D00)/TEMFL-1115.1D00*DLG610(TEMFL))

RK4=DEXP(3727.86D00/TEMPL-11.6326D00+0.079221ZD00*TEMFL)

WOLD(8)=RK6/WOLD(5)

WRITE (22,12)CI2G
WRITE (22,13)WOLD(1),WOLD(2),WOLD(3),WOLD(4),WOLD(5),WOLD(6),WOLD(7)

CALCULATE THE MASS TRANSFER

CI2L=WOLD(1)
T=TOLD
WOLD(1)=CI2L

MOLTE=H*KLOV*(EC*CI2G-WOLD(1))*SFA/1.0D3
NMOL=WOLD(1)*VOLD
WOLD(1)=(NECI+MOLTE)/VOLD

BEGIN THE RUNGE-KUTTA-HELLBORG ROUTINE

CALCULATE K'S

DO 30 J=1,IN
W(J)=WOLD(J)
30 CONTINUE

CALL FUNCTR(W,WOLD,F,IN)

DO 40 J=1,IN
K1(J)=H*F(J)
40 CONTINUE

DO 50 J=1,IN
W(J)=WOLD(J)+K1(J)/4.0D0
50 CONTINUE

CALL FUNCTR(W,WOLD,F,IN)

DO 60 J=1,IN

191
\begin{verbatim}
K2(J) = B * P(J)
DO 80 J = 1, IN
    W(J) = WOLD(J) + 3.0D0 * K1(J) / 3.2D1 + 9.0D00 * K2(J) / 3.2D1
80 CONTINUE
CALL FUNCTN(W, WOLD, F, IN)
DO 90 J = 1, IN
    K3(J) = B * F(J)
90 CONTINUE
DO 110 J = 1, IN
    W(J) = WOLD(J) + 1.932D3 * K1(J) / 2.197D3 - 7.2D1 * K2(J) / 2.197D3
110 CONTINUE
CALL FUNCTN(W, WOLD, F, IN)
DO 120 J = 1, IN
    K4(J) = B * F(J)
120 CONTINUE
DO 130 J = 1, IN
    W(J) = WOLD(J) + 4.39D2 * K1(J) / 2.16D2 - 8.0D00 * K2(J) + 3.68D3 * K3(J) / 5.13D2
130 CONTINUE
CALL FUNCTN(W, WOLD, F, IN)
DO 140 J = 1, IN
    K5(J) = B * F(J)
140 CONTINUE
DO 150 J = 1, IN
    W(J) = WOLD(J) - 8.0D00 * K1(J) / 2.7D1 + 2.0D00 * K2(J) - 3.54D3 * K3(J) / 2.56D3
150 CONTINUE
CALL FUNCTN(W, WOLD, F, IN)
DO 160 J = 1, IN
    K6(J) = B * F(J)
160 CONTINUE
Determine the new concentration of all icdine hydrolysis species and check error
DO 170 J = 1, IN
    W(B(J)) = WOLD(J) + 1.352D3 * K1(J) / 3.2D1 + 6.656D3 * K3(J) / 1.2D1 + 6.0D00 * K2(J) / 3.2D1
170 CONTINUE
B(J) = ABS(K1(J) / 3.6D2 - 1.28D2 * K3(J) / 4.275D3 - 2.197D3 * K4(J) / 7.52D4)
1 + K5(J) / 5.0D1 + 2.0D00 * K6(J) / 5.5D1
TOL(J) = ABS(WE(J) - TCLEB)
DELT(J) = 0.58D00 * (TOL(J) / B(J)) ** 0.25
DO 500 J = 1, IN
    IF (B(J) .GT. TOL(J)) GOTO 900
500 CONTINUE
DO 510 J = 1, IN
    WOLD(J) = WE(J)
510 CONTINUE
\end{verbatim}
DETERMINE THE EQUILIBRIUM CONCENTRATIONS FOR EQUATIONS 24, 25 AND 26

\[ \begin{align*}
BB &= -1.0D00 - (\text{WOLD}(2) + \text{WCLD}(1)) \times BK4 \\
C &= \text{WOLD}(2) \times \text{WCLD}(1) \times BK4 - \text{WCLD}(7) \\
D &= -2E / (2.0D00 \times BK4) \\
E &= (BB \times 2.0D00 - 4.0D00 \times BK4 \times C) \times 2D00 / (2.0D00 \times BK4) \\
V &= D - E \\
\end{align*} \]

IF \( V \) \LT \( 1.0D-18 \) CALL ITTER(\text{WOLD}, BK4, C, V)

WOLD(7) = WOLD(7) + V
WOLD(1) = WOLD(1) - V
WOLD(2) = WOLD(2) - V

IF \( \text{IN} \) \EQ \( 4 \) GOTO 600

BB = WCLD(6) + WOLD(5) \times BK5
S = BK5 \times WOLD(3) + WOLD(6) \times WOLD(5)
M = (-BB + (BB \times BK4 - 4.0D00 \times S) \times 0.5) / 2.0D00
WOLD(5) = WOLD(5) + M
GOTO 605

M = (BK5 \times WOLD(3) - WOLD(6) \times WOLD(5)) / (WCLD(5) + BK5)

WOLD(6) = WOLD(6) + M
WOLD(3) = WOLD(3) - M

IF \( \text{IN} \) \EQ \( 4 \) GOTO 615

U = WOLD(8) \times WOLD(5) - BK6
VV = WCLD(8) + WCLD(5)
I = (-VV + (VV \times VV - 4.0D00 \times U) \times 0.5) / 2.0D00
WOLD(5) = WOLD(5) + I
WOLD(8) = WOLD(8) + I

I = I + 1

TOLD = TOLD + H
PHT = TOLD \times TRAVEL
SUMMCL = SUMMCL + SLOTS
CI2L = WB(1)

WHITE(51, 23) TGLD, SUMMCL, PHT, H
WHITE(50, 22) I, TOLD, WOLD(1), WOLD(2), WOLD(3), WCLD(4), WCLD(5),
WOLD(6), WCLD(7), PHT

DEL = DELTA(1)

IF \( \text{IN} \) \EQ \( 1 \) GOTO 905

DO 520 J = 2, IN
  IF (DEL \LT \text{DELTA}(J)) GOTO 520
  DEL = DELTA(J)
520 CONTINUE

GOTO 905

DETERMINE NEW STEP SIZE

GOTO 905

DEL = DELTA(J)

IF (DEL \GT \text{Q}) GOTO 910

MNEW = Q \times H

GOTO 1000

193
C 91C IF (DEL .LT. 4.0) GOTO 920
HNEW=4.0D000*B
GOTO 1000
C 92C HNEW=DEL*B
C C CHECK NEW STEP SIZE WITH MAX AND MIN STEP SIZE
C 1000 IF (HNEW .LT. HMAX) GOTO 930
HNEW=HMAX
C 93C IF (HNEW .LT. HMIN) GOTO 1111
LEFT=B-TOLD-HNEW
C IF (LEFT .GT. 0.0) GOTO 5000
HNEW=B-TOLD
C 5000 H=HNEW
IF (TCLD .GE. B) GOTO 999
GOTO 1
C 1111 WRITE (40, 21) HNEW
STOP
C 999 WRITE (23, 25) I
GRMS=253.809DCG*SUMMCL
C WRITE (22, 15) SUMMOL,GRMS
WRITE (22, 14)
WRITE (22, 13) WOLD (1), WOLD (2), WOLD (3), WOLD (4), WOLD (5), WOLD (6),
1 WOLD (7)
STOP
END

194
**SUBROUTINE FUNCTN**

**IMPLICIT DOUBLE PRECISION (A-H, K-Z)**
**IMPLICIT INTEGER (I-J)**

**DIMENSION W(8),WOLD(8),F(7)**

**IF(IN .EQ. 5) GOTO 5**

**W(5) = WOLD(5)**
**W(6) = WOLD(6)**

**RK1 = 3.0D00**
**RK2 = 4.0D12**
**RK20 = 2.5D02**
**RK21 = 1.2D02**
**RK22 = 3.0D08**
**RK3 = 9.35D-6**

**R1 = RK1*W(1)**
**RB1 = RK1*W(2)*W(3)*W(5)**
**R20 = RK20*W(3)*2.0D00**
**R21 = RK21*W(3)*W(6)**
**RB2 = RK22*W(4)*W(2)**
**RB3 = RK3*W(5)*W(2)**

**F(1) = R1 + RB1 + 5.0D-1*B3**
**F(2) = R1 - RR1 + 2.0D00*R20 + B21 - 2.0D00*RB2**
**F(3) = R1 - RR1 + 5.0D00 + 3.0D00*RR2**
**F(4) = (R20 + R21)/3.0D00**

**IF(IN .EQ. 5) GOTO 10**

**F(5) = 0.0D00**
**GOTO 11**

**F(5) = R1 - RR1 + 5.0D00 + 3.0D00*RR2 - 4.0D00*BP3**

**F(6) = 0.0D00**
**F(7) = 0.0D00**

**RETURN**

**END**
**SUBROUTINE ITTER**

This subroutine finds the root to the quadratic equilibrium equation for the formation reaction of TBI-Iodide, I3- (Equation 24). A secant method is the routine used to find the root. This method is called whenever the quadratic formula results in less than approximately three significant figures. This subroutine is called by the programs KINETIC, DROP, SPRAY and WALL-SPRAY.

**SUBROUTINE ITTER(WCLD,BK4,C,V)**

```plaintext
IMPLICIT DOUBLE PRECISION (A-H,L-Z)
IMPLICIT INTEGER (I-K)

DIMENSION WCLD(7),W(7)

PO=1.0D-16
P1=1.0D-18

Q0=C-BK4*PO*F0-PO*BK4*(WCLD(1)+WCLD(2))-PO
Q1=C-BK4*P1*F1-P1*BK4*(WCLD(1)+WCLD(2))-P1

NEW=F1-Q1*(P1-F0)/(Q1-Q0)
CHECK=ABS(NEW-F1)/P1

IF (CHECK .LT. 1.0D-4) GOTO 10

P0=P1
Q0=Q1
P1=NEW
GOTO 5

V=NEW
RETURN

END
```
Drop Model sample input:

A = 0.0
B = 15.0
HMIN = $1.0 \times 10^{-10}$
HMAX = $1.0 \times 10^2$
IN = 4
TOLER = $1.0 \times 10^{-4}$
TEMP = 298
TEMPG = 298
DIAM = 0.1
SAD = 0.1
CI2G = $1.0 \times 10^{-5}$
WOLD(1) = 0.0
WOLD(2) = 0.0
WOLD(3) = 0.0
WOLD(4) = 0.0
WOLD(5) = $1.0 \times 10^{-9}$
WOLD(6) = 0.0
WOLD(7) = 0.0
PRESS = 1.0
AT A TEMPERATURE OF THE GAS 298.15 DEGREES KELVIN
THE VISCOSITY OF THE LIQUID (CP) = 0.8946000E+00
THE PARTITION COEFFICIENT IN = 0.06341528E+02
THE DENSITY OF THE LIQUID (GMS/CC) = 0.9966763E+00
THE DENSITY OF THE GAS (GMS/CC) = 0.1102988E-02
THE DIFFUSION COEFFICIENT FOR THE GAS (SQ CM/SEC) = 0.8086678E-01
THE DIFFUSION COEFFICIENT FOR THE LIQUID (SQ CM/SEC) = 0.1303670E-04
THE GAS-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = 0.11286248E+02
THE LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = 0.25586718E+00
THE OVERALL LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = 0.06519108E-01
THE VOLUME FOR ONE DROP (LITERS) = 0.5236000E-06
THE SURFACE AREA FOR ONE DROP (SQ CM) = 0.3141600E-01
THE EXPOSURE TIME FOR THE DROP IS (SEC) = 0.1500000E+02
THE REYNOLDS NUMBER FOR THE DROP = 0.25359298E+03
THE THERMAL VELOCITY OF THE DROP (CM/SEC) = 0.394423E+03
THE CONCENTRATION OF THE GAS IS (MOLES/LITER) = 0.1000000E-04
THE INITIAL CONCENTRATION OF THE DROP IS (MOLES/LITER):

12 = 0.0000000E+00
13 = 0.0000000E+00
801 = 0.0000000E+00
1001 = 0.0000000E+00
8 = 0.1000000E-08
10 = 0.0000000E+00
13 = 0.0000000E+00

THE NUMBER OF MOLES OF IODINE (12) REMOVED IS = 0.12695158E-08
THE NUMBER OF GRAINS OF IODINE REMOVED IS = 0.32224448E-06
THE FINAL CONCENTRATION OF THE DROP IS (MOLES/LITER):

12 = 0.8545203E-03
13 = 0.1433698E-02
801 = 0.4077559E-03
1001 = 0.8850566E-03
8 = 0.1000000E-08
10 = 0.2773791E-05
13 = 0.9033038E-03
APPENDIX D

SPRAY MODEL, SAMPLE INPUT AND OUTPUT
SPRINT MODEL

SPRINT MODEL SIMULATES THE REMOVAL OF MOLECULAR IODINE, I2,
FROM A GAS PHASE BY A SPRAY SYSTEM. THIS MODEL IS QUASI-STeady-
STATE MODEL THAT DETERMINES THE ABSORPTION OF GASEOS IODINE
INTO THE SPRAY DROPLETS AND THEN REACTS THE IODINE SPECIES
ACCORDING TO THE IODINE HYDROLYSIS REACTIONS. A TWO-RESISTANCE
MODEL IS USED TO DETERMINE THE MASS TRANSFER AND A STAGGERED-
YELLSBURG 5 (4) NUMERICAL INTEGRATION ROUTINE IS USED TO INTEGRATE
THE IODINE HYDROLYSIS REACTIONS. THIS MAIN PROGRAM CALLS THE
SUBROUTINES ITER AND FUNCT. THIS PROGRAM IS DESIGNED TO RUN
ON A PDP-10 COMPUTER BUT SHOULD BE EASILY CONVERTED TO RUN ON
ANY FORTRAN MACHINE.

IMPLICIT DOUBLE PRECISION (A-H, K-Z)
IMPLICIT INTEGER (I-J)

DIMENSION W(8), WOLD(8), K1(7), K2(7), K3(7), B(7), WB(7),
1 DELTA(7), RES(7), F(7), K4(7), K5(7), K6(7), TCI(7),
2 CCB(7), CC(7), CONFOL(8)

READ (58,*) A, BSH, HMAX, IN
READ (49,*) TOLER
READ (31,*) TEMPG, TEMPL, PBESS, DIAM, SAC, CI2SF, CISF
READ (31,*) CECISP, CCESF
READ (43,*) CI2G, CHSF, ITLINT, DURTH
READ (31,*) CIOSP, CI3SF
READ (30,*) CDIM, HEIGHT

FORMAT('CONCENTRATION OF THE DRUPS',/)
FORMAT('AT A TEMPERATURE OF THE GAS ', F6.2, ' DEGREES KELVIN'/
1 'THE VISCOSITY OF THE LIQUID (CP)=' , E15.7/
2 'THE VISCOSITY OF THE GAS (CP) = ','E15.7/
3 'THE PARTICLE COEFFICIENT IS = ','E15.7/
4 'THE DENSITY OF THE LIQUID (GAS/CC) = ','E15.7/
5 'THE DENSITY OF THE GAS (GAMS/CC) = ','E15.7)

FORMAT('THE DIFFUSION COEFFICIENT FOR THE GAS (SQ CM/SEC) = ','E15.7/
1 'THE DIFFUSION COEFFICIENT FOR THE LIQUID (SQ CM/SEC) = ','E15.7/
2 'THE GAS-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = ','E15.7/
3 'THE LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = ','E15.7/
4 'THE OVERALL LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = ','E15.7/
5 'THE VOLUME FOR ONE DROP (LITERS) = ','E15.7/
6 'THE SURFACE AREA FOR ONE DROP (SQ CM) = ','E15.7/
7 'THE EXPOSURE TIME FOR THE DROP IS (SEC) = ','E15.7/
8 'THE REYNOLDS NUMBER FOR THE DRUP = ','E15.7/
9 'THE THERMAL VELOCITY OF THE DRUP (CM/SEC) = ','E15.7)

FORMAT(15)
13 FORMAT('I2 = ','E15.7/
2 'I- = ','E15.7/
3 'BCI = ','E15.7/
4 'IC3- = ','E15.7/
5 'H+ = ','E15.7/
6 'IO- = ','E15.7/
7 'I3- = ','E15.7/

FORMAT('THE FINAL CONCENTRATION OF THE LIQUID IS (McL/S/LITRE) :')
15 FORMAT('THE NUMBER OF MOLES OF IODINE (I2) REMOVED IS = ','E15.7/
16 FORMAT('THE FINAL CONCENTRATION OF IODINE (I2) IN THE GAS IS ','

207
<table>
<thead>
<tr>
<th>Line</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1E15.7,' (MOLES/LITER)'://</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>FORMAT(' TIME MOLES RMD CCN GAS SUM MLS RM 10',//)</td>
</tr>
<tr>
<td>18</td>
<td>FORMAT(' CONCENTRATION OF THE SPRAYED SOLUTION IN THE SUMF ',//)</td>
</tr>
<tr>
<td>19</td>
<td>FORMAT(' N TIME 12 I- 00 I 10- I3, '/)</td>
</tr>
<tr>
<td>21</td>
<td>FORMAT('STEP SIZE BELOW STEP MIN',E15.7)</td>
</tr>
<tr>
<td>22</td>
<td>FORMAT(IS,6D13.7)</td>
</tr>
<tr>
<td>23</td>
<td>FORMAT(4D15.7)</td>
</tr>
<tr>
<td>32</td>
<td>FORMAT('// THE NUMBER OF DROPS IN THE CONTAINMENT IS',E15.7)</td>
</tr>
<tr>
<td>33</td>
<td>FORMAT('// THE NUMBER OF GRAMS OF IODINE REMOVED IN THE EXPERIMENT 11S',E15.7, '/ RESULTING IN AN ERROR OF',E15.7, ' PERCENT.')</td>
</tr>
<tr>
<td>34</td>
<td>FORMAT('// THE INITIAL CONCENTRATION IN THE GAS OF',E15.7, ' 1' (MOLES/LITER) '://')</td>
</tr>
<tr>
<td>C</td>
<td>WRITE(50,9)</td>
</tr>
<tr>
<td>C</td>
<td>WRITE(50,19)</td>
</tr>
<tr>
<td>C</td>
<td>WRITE(52,18)</td>
</tr>
<tr>
<td>C</td>
<td>WRITE(52,19)</td>
</tr>
<tr>
<td>C</td>
<td>WRITE(51,17)</td>
</tr>
<tr>
<td>C</td>
<td>SPH=3.1416D00*RAD**2</td>
</tr>
<tr>
<td>C</td>
<td>VOLD=(3.1416D00<em>DIA**3.000)/(6.000</em>1.0D3)</td>
</tr>
<tr>
<td>C</td>
<td>CI2G=CI2G</td>
</tr>
<tr>
<td>C</td>
<td>TEMP4=TEMPG**4</td>
</tr>
<tr>
<td>C</td>
<td>TEMP3=TEMPG**3</td>
</tr>
<tr>
<td>C</td>
<td>TEMP2=TEMPG**2</td>
</tr>
<tr>
<td>C</td>
<td>TEMPI=TEMPI**4</td>
</tr>
<tr>
<td>C</td>
<td>TEMPL3=TEMPI**3</td>
</tr>
<tr>
<td>C</td>
<td>TEMPL2=TEMPI**2</td>
</tr>
<tr>
<td>C</td>
<td>VSL1=1.8662866D-8<em>TEMPI-2.6333695D-5</em>TEMPI3+1.3976607D-2*TEMPI2</td>
</tr>
<tr>
<td>C</td>
<td>VSL2=3.307486D00*TEMPI+2.955866D2</td>
</tr>
<tr>
<td>C</td>
<td>VSLIQ=VSL1+VSL2</td>
</tr>
<tr>
<td>C</td>
<td>PC1=9.981476D-7<em>TEMPI-1.5730121D-3</em>TEMPI3+9.278567D-1*TEMPI2</td>
</tr>
<tr>
<td>C</td>
<td>PC2=-4.2428838D2*TEMPI+2.3624647D4</td>
</tr>
<tr>
<td>C</td>
<td>PC=PC1+PC2</td>
</tr>
<tr>
<td>C</td>
<td>DNL1=6.0251147D-9<em>TEMPI3-9.1329604D-6</em>TEMPI2</td>
</tr>
<tr>
<td>C</td>
<td>DNL2=3.573727D3*TEMPI5.835882D-1</td>
</tr>
<tr>
<td>C</td>
<td>DNLIQ=DNL1+DNL2</td>
</tr>
<tr>
<td>C</td>
<td>VSA1=2.8771329D-15<em>TEMPG+1.6909463D-11</em>TEMPI-4.155468D-8*TEMPG2</td>
</tr>
<tr>
<td>C</td>
<td>VSA2=6.5675429D-5*TEMPG+1.5523691D-3</td>
</tr>
<tr>
<td>C</td>
<td>VISGAS=VSA1+VSA2</td>
</tr>
<tr>
<td>C</td>
<td>TMP=5.178D-3*TEMPI</td>
</tr>
<tr>
<td>C</td>
<td>OMEGA1=TMP<strong>3*(-6.19047619D-2)+4.657142857D-1*TMP</strong>2</td>
</tr>
<tr>
<td>C</td>
<td>OMEGA2=TMP**(-1.30423805D00)+2.315428571D00</td>
</tr>
<tr>
<td>C</td>
<td>OMEGA=OMEGA1+OMEGA2</td>
</tr>
<tr>
<td>C</td>
<td>MLWT=1/2.91D+1/2.53809D2</td>
</tr>
<tr>
<td>C</td>
<td>DIFGAS=1.858E-3<em>TEMPG**1.5</em>MLWT<strong>0.5/(PRESS*4.4355D00</strong>2*OMEGA)</td>
</tr>
</tbody>
</table>
DIPLIQ = 3.91D-8*TEMPL/VISLIQ

dng1=8.2892055E-16*TEMGP4-4.2656962D-12*TEMPG3-8.0228283D-9*TEMGP2

dng2=-6.8325529E-6*TEHG1+2.6129391D-3

DENGAS=DNGL+DNG2

GS1=0.83D00*((DENLIQ-DENGAS)/DENGAS)**0.25*9.81D2**0.25

GS2=(VISGAS/(1.0D2*DENGAS))**-0.17*ZIPGAS**0.67*DIAM**-0.25

KGI2=GS1+GS2

ND3=4.0D00*DENGAS*(DENLIQ-DENGAS)**0.881D2*DIAM**3

WW=DLOG10(ND)

HBE1=-(1.81391D00+1.34671D00*WW-0.12427D0C*WW**2+6.344D-3*WW**3)

HBE=1.0D1**HBE1

TRWVEL=HBE*(VISGAS/1.0D2)/(DIAM*DENGAS)

EXPTH=HEIGHT/1.0D2/TRWVEL

KLI2O=(4.0D00*DIPLIQ*TRWVEL/(3.1415D00*DIAM))**0.5

INCMT=EXPTH/DLTH**1.0D00

KLO=KGI2*KLI2O/(FC*KLI2O+KGI2)

CCSA=(CEIAM/2.0D00)**2.0*3.1419265D00

DPMIN=FLRA/VCID

FLXDF=DPMIN/(CCSA**1.0D4)

ADABA=6.0D1/(EXPTH*FLIDP)

ILOGF=DRTM**6.0D1/EXPTH**1.0D00

VOLCCM=ADABA*HEIGHT/1.0D1

VOLSF=FLRA/DRTM

NUMBDS=DPMIN*EXPTH/6.0D1

CVOL=CCSA*HEIGHT/1.0D3

WHITE(23,12)ILLCF

WHITE(22,10)TEMPG,WISLIC,VISGAS,FC,DENLIQ,DENGAS

WHITE(22,11)DIPGAS,EIPLIC,KGI2,KLI2O,KLO,VOLD,SFA,EXPTH,HBE,1

TRWVEL

WHITE(22,32)NUMDFS,FLIDP,CVOL,ILCCF

WHITE(22,34)C12G,DRTM,VCLSP,FLRAI

C C DETERMINE THE EQUILIBRIUM CONSTANTS FOR K4, K5 AND K6

BK6=-4.098D00-3245.2D00/TEMPL+2.2363D5/(TEMPL**2)-3.984D7/(TEMPL**13)+(13.957D0C-1262.3DCG/TEMPL+8.564D5/(TEMPL**2))**DLCG(DENLIQ)

BK6=10**(BK6)

BK5=10**((2800.48D00+0.7335D00*TEMPL-8067C.CD00/TEMPL

1-1115.1D00/DLOG10(TEMP)])

BK4=EXP(3727.86D00/TEMPL-11.6326D00+0.0192212D00*TEMPL)

TOTAL=EXPTH/2.0D1

SFA=SFA*NUM DFS
VOLD=VOLD+VOLDS
TOLD=A
Q=Q+Q*1-1

DO 1100 II=1,ILCCF
INK=INK+1.0000
H=H+1.0000
TOLD=A
B=EXFTM
CI2G=(CI2G*CYCL)-SUMCL/CYOL
CI2L=CI2SP

INITIALIZE THE SPRAY DECEPS

DO 1100 II=1,IIU

BEGIN THE BUNGE-KUTTA-FELDEBURG INTEGRATION ROUTINE

T=TOLD

Determine the Mass Transfer to the Spray Droplets

WOLD(1)=CI2L
WML=WOLD(1)*WCLD
MOLT=KLOW*H*SFA*(CI2G*PC-WOLD(1))/1.000
WOLD(1)=(NMCL+MOLTB)/WOLD

DO 30 J=1,IN
W(J)=WOLD(J)
30 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)

DO 40 J=1,IN
K1(J)=R*F(J)
40 CONTINUE

DO 50 J=1,IN
W(J)=WOLD(J)+K1(J)/4.000
50 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)

DO 60 J=1,IN
K2(J)=R*F(J)
60 CONTINUE

DO 80 J=1,IN
W(J)=WOLD(J)+3.0000*K1(J)/3.2D1+9.0000*K2(J)/3.2D1
80 CONTINUE

CALL FUNCTN(W,WOLD,P,IN)
DO 90 J=1, I
   H3(J) = H*P(J)
90 CONTINUE

DO 110 J=1, I
   W(J) = WOLD(J) + 1.932D3*K1(J) / 2.197D3 - 7.23D3*K2(J) / 2.197D3 + 7.296D3*K3(J) / 2.197D3
110 CONTINUE

CALL FUNCTN(H, WOLD, P, IN)

DO 120 J=1, I
   K4(J) = H*F(J)
120 CONTINUE

DO 130 J=1, I
   W(J) = WOLD(J) + 4.39D2*K1(J) / 2.162 - 8.0D00*K2(J) / 5.13D2 - 8.45D2*K4(J) / 4.104D3
130 CONTINUE

CALL FUNCTN(H, WOLD, F, IB)

DO 140 J=1, I
   K5(J) = H*F(J)
140 CONTINUE

DO 150 J=1, I
   W(J) = WOLD(J) - 8.0D00*K1(J) / 2.7D1 + 2.0D00*K2(J) / 2.5D1 + 1.859D3*K4(J) / 4.104D3 - 1.1D00*K5(J) / 4.0D1
150 CONTINUE

CALL FUNCTN(H, WOLD, P, IB)

DO 160 J=1, I
   K6(J) = H*P(J)
160 CONTINUE

DETERMINE THE CONCENTRATION OF ALL IODINE HYDROLYSIS SPECIES
AND CHECK ERRCS

DO 100 J=1, I
   WR(J) = WOLD(J) + 1.6D1*K1(J) / 1.35D2 + 6.656D3*K3(J) / 1.2E25D4 + 2.856D4*K4(J) / 5.643D4 - 9.0D00*K5(J) / 5.13D1 + 2.0D00*K6(J) / 5.5D1
   R(J) = ABS(K1(J) / 3.6D2 - 1.28D2*K3(J) / 4.275D3 - 2.197D3*K4(J) / 7.524D4 + K5(J) / 5.0D1 + 2.0D00*K6(J) / 5.5D1) / H
   TOL(J) = ABS(WE(J) * TCLI5)
   DELTA(J) = C.94 * TOL(J) / R(J)) ** 0.25
100 CONTINUE

DO 500 J=1, I
   IF (R(J) .GT. TOL(J)) GC TO 900
500 CONTINUE

DO 510 J=1, I
   WOLD(J) = WE(J)
510 CONTINUE

DETERMINE THE EQUILIBRIUM CONCENTRATION FOR EQUATIONS 24, 25 AND 26

BB = - 1.0D00 - (WOLD(2) * WOLD(1)) * BK4
C = WOLD(2) * WOLD(1) * BK4 - WOLD(7)
D = BB / (2.0D00 * BK4)
E = ((BB**2.0D00 - 4.0D00 * BK4 * C) ** 0.5D00) / (2.0D00 * BK4)

211
V = D - E

IF (V .LT. 1.0D-18 .AND. V .NE. 0.0D00) CALL ITER(WCLL,BR4,C,V)

WOLD (7) = WOLD (7) + V
WOLD (1) = WOLD (1) - V
WOLD (2) = WOLD (2) - V

IF (IN .EQ. 4) GOTO 600

BR = WCLL (6) + WCLL (5) + EK5
S = - EK5 * WOLD (3) + WOLD (6) + WCLL (5)
M = (- BR + (BR + BB - 4.0D00 * 5) ** 0.5) / 2.0D00
WOLD (5) = WOLD (5) + M
GOTO 605

600 H = (BR5 * WOLD (3) - WOLD (6) + WCLL (5)) / (WCLL (5) + EK5)

605 WOLD (6) = WOLD (6) + H
WOLD (3) = WOLD (3) - H

IF (IN .EQ. 4) GOTO 615

U = WOLD (8) * WOLD (5) - EK6
V = WCLL (8) + WCLL (5)
I = (- VV + (VV + VV - 4.0D00 * U) ** 0.5) / 2.0D00
WOLD (5) = WOLD (5) + X
WOLD (8) = WOLD (8) + X

615 TOLD = TOLD + H
SUMCL = SUMCL + WCLL
PHT = TRAVEL * TIME
CIZL = W (1)
PHT = TOLD + TRAVEL
DEL = DELTA (1)
IF (IN .EQ. 1) GOTO 905

DO 520 J = 2, IN
   IF (DEL .LT. DELTA (J)) GOTO 520
   DEL = DELTA (J)
520 CONTINUE

GOTO 905

Determine new step size

900 DEL = DELTA (J)

905 IF (DEL .GT. Q) GOTO 910
   HNEW = Q * H
   GOTO 1000

910 IF (DEL .LT. 4.0) GOTO 920
   HNEW = 4.0D00 * H
   GOTO 1000

920 HNEW = DEL * H

925 CHECK NEW STEP SIZE WITH MAX AND MIN STEP SIZE

1000 IF (HNEW .LT. HMAX) GOTO 930
   HNEW = HMAX

930 IF (HNEW .LT. HMIN) GOTO 1111
   LEFT = B - TOLL - HNEW

212
IF (LEFT .GT. 0.0) G0T0 5000
HNEW=B-TOLD
C
5000
H=HNEW
C
IF (TCLD .GE. B) G0T0 999
G0T0 1
C
959
SUM=SUM+SUMCCL
TIME=TIME+TCLD/6.0D1
PST=TIME*TBRVEL
H=1.0D-2
TOLD=A
C
WRITE (50,22) II,TIME,WCLL(1),WOLD(2),WOLD(3),WOLD(4),WCLL(5),
1
WOLD(6),WCLL(7)
WRITE (51,23) TIME,SUMCCL,CI2G,SUM
C
DETERMINE THE CONCENTRATION IN THE SUMP
C
BEGIN RUNGE-KUTTA-FELDBURG INTEGRATION ROUTINE
C
CALCULATE K'S
C
2
DO 31 J=1,IN
CC(J)=CONPOL(J)
31 CONTINUE
C
CALL FUNCTN(CC,CONPOL,F,IN)
C
DO 41 J=1,IN
K1(J)=8*F(J)
41 CONTINUE
C
DO 51 J=1,IN
CC(J)=CONPOL(J)+K1(J)/4.0D00
51 CONTINUE
C
CALL FUNCTN(CC,CONFCL,F,IN)
C
DO 61 J=1,IN
K2(J)=8*F(J)
61 CONTINUE
C
DO 81 J=1,IN
CC(J)=CONPOL(J)+3.0D00*K1(J)/3.2D1+9.0D00*K2(J)/3.2D1
81 CONTINUE
C
CALL FUNCTN(CC,CONPOL,F,IN)
C
DO 91 J=1,IN
K3(J)=8*F(J)
91 CONTINUE
C
DO 111 J=1,IN
CC(J)=CONPOL(J)+1.932D3*K1(J)/2.197D3-7.2D3*K2(J)/2.197D3
1
+7.296D3*K3(J)/2.197D3
111 CONTINUE
C
CALL FUNCTN(CC,CONFCL,F,IN)
C
DO 121 J=1,IN
K4(J)=8*F(J)
121 CONTINUE
C
DO 131 J=1,IN
  CC(J) = CONPOL(J) + 4.39D2*K1(J) / 2.16D2 - 8.0D00*K2(J) +
            1 3.68D3*K3(J) / 5.13D2 - 8.45D2*K4(J) / 4.104D3
131 CONTINUE
C
CALL FUNCTN(CC,CONFCL,F,IN)
C
DO 141 J=1,IN
  K5(J) = H*F(J)
141 CONTINUE
C
DO 151 J=1,IN
  CC(J) = CONPOL(J) - 8.0D00*K1(J) / 2.7D1 + 2.0D00*K2(J) -
            1 3.54D3*K3(J) / 2.56D3 + 1.85D3*K4(J) / 4.104D3 - 1.13D1*K5(J) / 4.0D1
151 CONTINUE
C
CALL FUNCTN(CC,CONFCL,F,IN)
C
DO 161 J=1,IN
  K6(J) = H*F(J)
161 CONTINUE
C
Determine the Concentration of all of the Iodine Hydrolysis
C
DO 161 J=1,IN
  CC(J) = CONPOL(J) + 1.6D1*K1(J) / 1.35D2 + 6.65D3*K3(J) / 1.325D4 +
            1 2.856D4*K4(J) / 5.643D4 - 9.0D00*K5(J) / 5.5D1
  B(J) = ABS(K1(J) / 3.6D2 - 1.28D2*K3(J) / 4.275D3 - 2.197D3*K4(J) / 7.524D4 +
            1 K5(J) / 2.7D1 + 2.0D00*K6(J) / 4.0D1)
  TOL(J) = ABS(CCE(J)*TOLER)
  DELTA(J) = 0.84*(TOL(J) / H(J))**0.25
501 CONTINUE
C
DO 511 J=1,IN
  IF (B(J) .GT. TOL(J)) GOTO 901
501 CONTINUE
C
DO 511 J=1,IN
  CONFCL(J) = CCE(J)
511 CONTINUE
C
Determine the Equilibrium Concentration for Equations 24, 25 and
C
26
C
BB = -1.0D00 - (CONPOL(2) + CONPOL(1)) * BK4
C = CONPOL(2) * CONPOL(1) * BK4 - CONPOL(7)
B = BB / (2.0D00*BK4)
B = ((BB - 2.0D00 - 4.0D00*BK4*C)**0.5) / (2.0D00*BK4)
V = D - E
C
666 IF (V .LT. 1.0D-18 .AND. V .NE. 0.0D00) CALL ITER(CONFCL,BK4,C,V)
C
CONFCL(7) = CONFCL(7) + V .NE. 0.0D00) CALL ITER(CONFCL,BK4,C,V)
C
CONFCL(1) = CONFCL(1) - V
CONFCL(2) = CONFCL(2) - V
C
IF(IN .NE. 4) GOTO 601
C
BB = CHFCL(6) + CCBFCL(5) * BK5
S = BK5 * CONPOL(3) + CCBFCL(6) * CONPOL(5)
B = (-BB + (BB**2.0D00 - S)**0.5) / 2.0D00
CONFCL(5) = CCBFCL(5) * H
GOTO 601
C
601 M = (BK5*CONPOL(3) - CCBFCL(6)*CONPOL(5)) / (CONPOL(5)*BK5)
\[ \begin{align*}
C 606 & \quad \text{CONPCL}(6) = \text{CONPCL}(6) + M \\
C & \quad \text{CONPCL}(3) = \text{CONPCL}(3) - N \\
C & \quad \text{IF} (\text{IN} \geq \text{EQ} \geq 4) \quad \text{GOTO} \ 616 \\
C & \quad \text{U} = \text{CONPCL}(8) \times \text{CONPOL}(5) - EK6 \\
C & \quad \text{V} = \text{CONPOL}(8) + \text{CONPCL}(5) \\
C & \quad X = (-VV + (VV + \text{VV} - 4.0D00*U)^2 0.5) / 2.0D00 \\
C & \quad \text{CONPOL}(5) = \text{CONPCL}(5) \times X \\
C & \quad \text{CONPOL}(8) = \text{CONPCL}(8) \times X \\
C 616 & \quad \text{TOLD} = \text{TOLD} + S \\
C & \quad \text{DEL} = \text{DELTA}(1) \\
C & \quad \text{IF} (\text{IN} \geq \text{EQ} \geq 1) \quad \text{GOTO} \ 906 \\
C & \quad \text{DO} \ 521 \ J = 2, \text{IN} \\
C & \quad \text{IF} (\text{DEL} \geq \text{T}. \ \text{DELTA}(J)) \quad \text{GOTO} \ 521 \\
C & \quad \text{DEL} = \text{DELTA}(J) \\
C 521 & \quad \text{CONTINUE} \\
C & \quad \text{GOTO} \ 906 \\
C & \quad \text{Determine New Step Size} \\
C 901 & \quad \text{DEL} = \text{DELTA}(J) \\
C 906 & \quad \text{IF} (\text{DEL} \geq \text{GT} \geq \text{Q}) \quad \text{GOTO} \ 911 \\
C & \quad \text{HNEW} = Q \times B \\
C & \quad \text{GOTO} \ 1001 \\
C 911 & \quad \text{IF} (\text{DEL} \geq \text{LT} \geq 4.0) \quad \text{GOTO} \ 921 \\
C & \quad \text{HNEW} = 4.0D00 \times B \\
C & \quad \text{GOTO} \ 1001 \\
C 921 & \quad \text{HNEW} = \text{DEL} \times H \\
C & \quad \text{CHECK New Step Size with Max and Min Step Size} \\
C 1001 & \quad \text{IF} (\text{HNEW} \geq \text{LT} \geq \text{HMAX}) \quad \text{GOTO} \ 931 \\
C & \quad \text{HNEW} = \text{HMAX} \\
C 931 & \quad \text{IF} (\text{HNEW} \geq \text{LT} \geq \text{HMIN}) \quad \text{GOTO} \ 1112 \\
C & \quad \text{LEFT} = B - \text{TOLD} - \text{HNEW} \\
C & \quad \text{IF} (\text{LEFT} \geq \text{GT} \geq 0.0) \quad \text{GOTO} \ 5001 \\
C & \quad \text{HNEW} = B - \text{TOLD} \\
C 5001 & \quad \text{H} = \text{HNEW} \\
C & \quad \text{IF} (\text{VCLD} \geq \text{GE} \geq B) \quad \text{GOTO} \ 998 \\
C & \quad \text{GOTO} \ 2 \\
C 958 & \quad \text{DO} \ 800 \ \text{IQ} = 1, 7 \\
C 800 & \quad \text{CONPOL}(10) = (\text{VOLD}(10) \times \text{VCLD} + \text{CONPOL}(10) \times \text{POLVOL}) / (\text{POLVOL} + \text{VOLD}) \\
C & \quad \text{POLVOL} = \text{POLVOL} + \text{VCLD} \\
C & \quad \text{Write}(52, 22) \ \text{IX}, \text{TIME}, \text{CONPOL}(1), \text{CONPOL}(2), \text{CONPOL}(3), \text{CONPOL}(4), \text{CONPOL}(5), \text{CONPOL}(6), \text{CONPOL}(7) \\
C 1160 & \quad \text{CONTINUE} \\
C & \end{align*} \]
II=II-1
SUMGM=2.5380912*SUM
ERROR=1.0D2*(BDEXP-SUMGM)/BDEXP
C
WRITE (22, 16) CI26
WRITE (22, 15) SDE, SUMGM
WRITE (22, 14)
WRITE (22, 13) CONPOL (1), CONPOL (2), CONPOL (3), CONPOL (4), CONPOL (5),
        CONPOL (6), CONPOL (7)
C
GOTO 3000
C
1111 WRITE (40, 21) BNEW
1112 WRITE (40, 21) BNEW
3000 STOP
C
END
SUBROUTINE FUNCTN

THIS SUBROUTINE CONTAINS THE DIFFERENTIAL EQUATIONS (KINETIC RATE EQUATIONS) TO BE INTEGRATED. THIS SUBROUTINE IS CALLED FROM THE RUNGE-KUTTA-FELDENG Integration Subroutine IN THE KINETIC, DOP, SPRAY AND WALL-SPRAY MODELS.

SUBROUTINE FUNCTN (W, WOLD, P, IN)

IMPLICIT DOUBLE PRECISION(A-H, K-Z)
IMPLICIT INTEGER(I-J)

DIMENSION W(8), WOLD(8), P(7)

IF(IN .EQ. 5) GOTO 5

W(5) = WOLD(5)
W(6) = WOLD(6)

RK1 = 3.000
RKB1 = 4.412
RK20 = 2.502
RK21 = 1.202
RKB2 = 3.008
RKP3 = 9.350

B1 = RK1 * W(1)
B2 = RK2 * W(2) * W(3) * W(5)
B20 = RK20 * W(3) * 2.000
B21 = RK21 * W(3) * W(6)
B2B = RKB2 * W(4) * W(2) * 2.000 * W(5) * 2.000
BPF3 = RKP3 * W(5) * W(2)

F(1) = B1 + B2 + 5.00 - 1 * BPF3
F(2) = B1 - B2 + 2.000 * (B20 + B21) / 3.000 - 2.000 * B2 - BPF3
F(3) = B1 - B2 - B20 - B21 + 3.000 * B2B
F(4) = (B20 + B21) / 3.000 - B2B

IF(IN .EQ. 5) GOTO 10

F(5) = 0.000
GOTO 11


F(6) = 0.000
F(7) = 0.000

RETURN

END
SUBROUTINE ITER

THIS SUBROUTINE FINDS THE ROOT TO THE QUADRIC EQUILIBRIUM
EQUATION FOR THE FORMATION REACTION OF TRI-ICDIDE, I3- (EQUATION
24). A SECANT METHOD IS THE ROUTINE USED TO FIND THE ROOT. THIS
METHOD IS CALLED WHENEVER THE QUADRATIC FORMULA RESULTS IN LESS
THAN APPROXIMATELY THREE SIGNIFICANT FIGURES. THIS SUBROUTINE
IS CALLED BY THE PROGRAMS KINETIC, DROP, SPRAY AND WALL-SPRAY.

SUBROUTINE ITER(WCLD,RK4,C,V)

IMPLICIT DOUBLE PRECISION (A-H,L-Z)
IMPLICIT INTEGER (I-K)

DIMENSION WCLD(7),W(7)

P0=1.0D-16
P1=1.0D-10

Q0=C-RK4*PO*PO-RK4*(WCLD(1)+WCLD(2))-P0
Q1=C-RK4*P1*P1-RK4*(WCLD(1)+WCLD(2))-P1

NEW=F1-Q1*(P1-P0)/(Q1-Q0)

CHECK=ABS(NEW-P1)/P1

IF (CHECK .LT. 1.0D-4) GOTO 10

P0=P1
Q0=Q1
P1=NEW
GOTO 5

10 V=NEW
RETURN
END
Spray Model sample input

A = 0.0
B = DURTM = 10
HMIN = 1.0 × 10^{-10}
HMAX = 1.0 × 10^2
IN = 4
TOLER = 1.0 × 10^{-2}
TEMPL = 298
TEPG = 298
DIAM = 0.1
SAD = 0.1
CI2G = 1.0 × 10^{-5}
CI2SP = 0.0
CISP = 0.0
CHOISP = 0.0
COISP = 0.0
CHSP = 1.0 × 10^{-9}
CI03SP = 0.0
CI3SP = 0.0
PRESS = 1.0
CDIAM = 3.3
HEIGHT = 15.4
FLRAT = 37
At a Temperature of the Gas 298.00 Degrees Kelvin
The Viscosity of the Liquid (CP) = 0.09723348 x 10^-6
The Viscosity of the Gas (CP) = 0.13380738 x 10^-6
The Partion Coefficient is = 1.66 x 10^6 x 10^2
The Density of the Liquid (gms/cc) = 0.959146 x 10^3
The Density of the Gas (gms/cc) = 0.118294 x 10^3
The Diffusion Coefficient for the Gas (sq cm/sec) = 0.804076 x 10^-11
The Diffusion Coefficient for the Liquid (sq cm/sec) = 0.528637 x 10^-11
The Gas-Side Mass Transfer Coefficient (cm/sec) = 0.1127 x 10^3
The Liquid-Side Mass Transfer Coefficient (cm/sec) = 0.5736 x 10^3
The Overall Mass Transfer Coefficient (cm/sec) = 0.1502 x 10^3
The Volume for One Drop (liters) = 0.5236 x 10^-6
The Surface Area for One Drop (sq cm) = 0.314159 x 10^-1
The Exposure Time for the Drop is (sec) = 0.393846 x 10^-1
The Enthalpy Burden for the Drop = 0.2537 x 10^3
The Terminal Velocity of the Drop (cm/sec) = 0.3943 x 10^3
The Number of Drops in the Containers is 0.4723 x 10^3
The Drop Flux (number of drops/sq cm min) = 0.02477 x 10^1
The Container Volume (liters) = 0.1355 x 10^3
The Number of Outer Loops = 15
The Initial Concentration in the Gas is 0.1000000 x 10^3 (mols/liter)
The Duration of the Spray (min) = 0.1000000 x 10^2
The Volume of Liquid Sprayed (liters) = 0.3800000 x 10^3
And a Spray Flow Rate of 0.3800000 x 10^2 (liters/min)
The Initial Concentration of the Liquid (mols/liter) =

I1 = 0.0000000 x 10^6
I2 = 0.0000000 x 10^6
I3 = 0.0000000 x 10^6
H1 = 0.0000000 x 10^6
H2 = 0.0000000 x 10^6
H3 = 0.0000000 x 10^6
I0 = 0.0000000 x 10^6

The Final Concentration of Iodide (I2) in the Gas is 0.559702 x 10^-5 (mols/liter)
The Number of Mols of Iodide (I2) Removed is = 0.5596 x 10^-3
The Number of Grams of Iodine Removed is = 0.1520 x 10^-3
The Final Concentration of the Liquid is (mols/liter) =

I2 = 0.2780953 x 10^-3
I1 = 0.1939853 x 10^-2
H1 = 0.6201645 x 10^-4
I0 = 0.1000000 x 10^-6
H3 = 0.1000000 x 10^-6
I3 = 0.1324659 x 10^-3
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**Note:** The table represents the concentrations of various components over time, with columns for Budes, CO2, and Substrates.
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</table>

**Notes:**
- x1, x2, x3, x4 represent the variables in the dataset.
- The values range from 0.1 to 2.0.
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</table>

**Note:** The table continues with similar entries for various time points. The values in the table represent concentrations over time in a specified medium.
APPENDIX E

WALL-SPRAY MODEL, SAMPLE INPUT AND OUTPUT
WALL-SPRAY MODEL

M. P. ALBETT

THE WALL-SPRAY MODEL SIMULATES THE REMOVAL OF GASEOUS MOLECULAR
IODINE, I₂, BY WATER SPRAYS AND ALSO BY THE WATER ON THE WALLS
OF THE CONTAINMENT VESSEL. THIS MODEL IS ESSENTIALLY THE SPRAY
MODEL WITH THE ADDITION OF A SIMULATION OF THE ABSORPTION OF A
GAS BY A FALLING LIQUID FILM. A TWO-RESISTANCE MODEL IS USED TO
DESCRIBE THE MASS TRANSFER. A BUNGE-KUTTA-FELNBURG 5(4) NUMERICAL
INTEGRATION ROUTINE IS USED TO INTEGRATE THE IODINE HYDROLYSIS
REACTIONS. SUBROUTINE CALLED FROM THIS MAIN PROGRAM ARE ITER
FUNCTION, WALL AND FCOL. THIS PROGRAM IS DESIGNED TO RUN ON A
PDP-10 COMPUTER BUT SHOULD BE EASILY CONVERTED TO RUN ON ANY
PORTABLE COMPUTER.

IMPLICIT DOUBLE PRECISION (A-H, K-Z)
IMPLICIT INTEGER (I-J)

DIMENSION W(8), MOLD(8), X1(7), X2(7), X3(7), R(7), XW(7),
1 DELTA(7), WES(7), E(7), K4(7), K5(7), K6(7), XOL(7),
2 CCE(7), CC(7), COMPO(8), COMM(8, 300)

READ (59, *) A, EMN, HMAD, IN
READ (49, *) TGLER
READ (31, *) TEMP, TEMPL, PESS, DIAB, CADIC, CISP
READ (31, *) CCMIC, CISP
READ (43, *) CICSP, CISP, FLEB, DUBTM
READ (31, *)🕌P1SP, CISP
READ (30, *) CCIAN, HEIG, WPRAC, WHT

9 FORMAT (' CONCENTRATION OF THE DROPS ', /
10 FORMAT ('AT A TEMPERATURE OF THE GAS ', P6.2, ' DEGREES KELVIN', /
1 'THE VISCOSITY OF THE LIQUID (CP) = ', E15.7/)
2 'THE VISCOSITY OF THE GAS (CP) = ', E15.7/)
3 'THE VISCIBILITY COEFFICIENT IS = ', E15.7/)
4 'THE DENSITY OF THE LIQUID (GMS/CC) = ', E15.7/)
5 'THE DENSITY OF THE GAS (GMS/CC) = ', E15.7/)

11 FORMAT ('THE DIFFUSION COEFFICIENT FOR THE GAS (SQ CE/SEC) = ', E15.7/)
1 'THE DIFFUSION COEFFICIENT FOR THE LIQUID (SQ CM/SEC) = ', E15.7/)
2 'THE GAS-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = ', E15.7/)
3 'THE LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = ', E15.7/)
4 'THE OVERALL LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = ', E15.7/)
5 'THE VOLUME FOR ONE DROP (LITERS) = ', E15.7/)
6 'THE SURFACE AREA FOR ONE DBCP (SQ CM) = ', E15.7/)
7 'THE EXPOSURE TIME FOR THE DROP IS (SEC) = ', E15.7/)
8 'THE REYNOLDS NUMBER FOR THE DBCP = ', E15.7/)
9 'THE TERMINAL VELOCITY OF THE DBCP (CM/SEC) = ', E15.7/)
2 FORMAT (15)
13 FORMAT (' I2 = ', E15.7/)
14 FORMAT ('THE FINAL CONCENTRATION OF THE LIQUID IS (MCES/LITER) = '
15 FORMAT ('THE NUMBER OF ECLES OF IODINE (I2) REMOVED IS = ', E15.7/)
1 'THE NUMBER OF GRAMS OF IODINE REMOVES IS = ', E15.7/, )
DIPLIQ=3.91D-8*TEMP/1/VISLIQ

DN1=8.2892055E-16*TEMG*4.2656962D-12*TEMPG+8.0228283D-9*TEMPG2
DN2=6.8325529D-6*TEMG+2.6129391E-3
DENEG=ENG1+ENG2

GSM1=0.83D00*(((DENLIQ-DENGAS)/DENGAS)**0.25*9.81D2)**0.25
GSM2=((VISGAS/(1.0D2*DENGAS))**0.17*DIFGAS*0.67*DIAN**-0.25
KG12=GSM1*GSM2

ND1=4.0D00*DENGAS*(DENLIQ-DENGAS)*9.81D2*DIAN**3
ND2=3.0D00*(VISGAS/1.0D2)**2
ND=NL1/ND2

W=W=DLOG10(ND)

NRE1=(-1.81391E00+1.34671D00*W-0.12427D00*W**2+6.344D-3*W**3)
NRE=1.0D1**NRE1

TBWVEL=NRE*VISGAS/1.0D2/(DIAM*DENGAS)

EPTHEIGHT=HEIGHT/1.0D2/TBWVEL

KLI2C=(4.0D00*DIPLIQ*TBWVEL/(3.1415D00*DIAN))**0.5

KLOV=KG12*KLI2C/(PC*KLI2O+KG12)

CCSA=(CDIAM/2.0D00)**2.0*3.1419265D00

DPHMIN=PLRT/VOID

PLXDF=DPHMIN/(CCSA**1.0D4)

ADARA=6.0D1/(EPTHEIGHT*FLXDF)

ILOGE=DURTH*6.0D1/EPTHEIGHT*1.0D00

VOLCCN=ADARA*HEIGHT/1.0D1

VOLSE=PLRT*DURTH

NUMDIS=DPHMIN/EPTHEIGHT/6.0D1

CCVOL=CCSA*HEIGHT/1.0D3

WLM=(HEIGHT*WHT)/1.0D2/TBWVEL

WMFR=(WFRAC*PLRT/DELIQ*1.6667D1/(CDIAM**3.141593))

WPILC=(4.0D00*VISLIQ**MFR*1.0D-4/(DENLIC**2*9.81D2))**0.33

WVEL=WMFR/(LELIQ*WPILC*1.0D2)

WVOL=PLRT*WFRAC*EXTF/6.0D1

I=0

IAX=WHT/1.0D2/(EPTHEIGHT*WVEL)+1.0D00

KLW=(6.0D00*DIFLIC*WMFR/(1.0D2*3.141593*DELIQ*WPILC*EXTF*WVEL))

KLW=KLW**0.5

WAREA=WVOL*WPILC

WRITE(23,12)ILOGE
WRITE (22,10) TEMEG, VISLIQ, VISGAS, FC, DENLIQ, DENGAS
WRITE (22,11) DIFGAS, DIPLIQ, KG12, KLI2C, KLOV, VOID, SFA, EPTHEIGHT, NRE,
1

```
THREVEL
WRITE (22,32) NUNDFS,FLDP,CWOL,ILCCF
WRITE (22,34) CI2G,DOBTH,VOLSP,FLBAT

DETERMINE THE EQUILIBRIUM CONSTANTS FOR EQUATIONS 4, 5 AND 6
(EQUATIONS 24, 25 AND 26)

RK6=-4.098D00-3245.2D00/TEMP+2.2363D5/(TEMP**2)-3.964D7/(TEMP**4)
(TEMP**13)+13.957D00-1262.3D00/TEMP+8.5641D5/(TEMP**2))*(DLCG(DENLIQ))

RK6=10**-(RK6)

RK5=10**(2800.48D00+0.7335D00*TEMP-8067C.0D00/TEMP
1-1115.1D00*DLGG10(TEMP))

RK4=DEXP(3727.86D00/TEMP-11.632D00+0.019212D00*TEMP)

TOUTPL=EXPTM/2.0D1
SFA=SFA*NUNDFS
VOLD1=NUNDFS*VCLD
TCLD=A
Q=1.0CD-1
IF (VOLD(5) .GT. 0.0D00) GOTO 38
VOLD(8)=0.0D00
GOTO 37
38
VOLD(8)=RK6/VOLD(5)

WRITE (22,13) CI2SF,CISP,CHCISP,CIO3SF,CHSP,COISP,
1 CI3SF
WRITE (50,22) T,TIME,CI2SF,CISP,CHCISP,CIO3SF,CHSP,COISP
1 ,CI3SF

DO 1100 II=1,ILOOP
T=2K+1.0D00
H=1.0D-2
TOLD=A
B=EXITM

INITIALIZE THE CBHF CONCENTRATION

CI2L=CI2SP
VOLD(2)=CISP
VOLD(5)=CHSP
VOLD(4)=CI3SF
VOLD(7)=CI3SF
VOLD(3)=CHCISP
VOLD(6)=COISP

SUMCCL=0.0D00
WALCCL=0.0D00
IFLAG=1
SFA=SFA1
VOLD=VOLD1

BEGIN THE RUNGE-KUTTA-FELDBURG ROUTINE TO DETERMINE THE
ABSORPTION BY THE SPRAY DROPLETS

T=TOLD

DETERMINE THE MASS TRANSFER TO THE SPRAY DROPLETS

WOLD(1)=CI2L
WCL=WOLD(1)*VCLD
WOLT=KLV*P*SFA*(CI2G*PC-WOLD(1))/1.0D3
WOLD(1)=(WSCC+WOLTS)/VOLD

CALCULATE K'S
```

DO 30 J=1, IN
   W(J)=WCLD(J)
30 CONTINUE

CALL FUNCTN(W, WCLD, F, IN)

DO 40 J=1, IN
   K1(J)=B*F(J)
40 CONTINUE

DO 50 J=1, IN
   W(J)=WCLD(J)+K1(J)/4.200
50 CONTINUE

CALL FUNCTN(W, WCLD, F, IN)

DO 60 J=1, IN
   K2(J)=B*F(J)
60 CONTINUE

DO 70 J=1, IN
   W(J)=WCLD(J)+3.0DC*K1(J)/3.2D1+9.0DC*K2(J)/3.2D1
70 CONTINUE

CALL FUNCTN(W, WCLD, F, IN)

DO 80 J=1, IN
   K3(J)=B*F(J)
80 CONTINUE

DO 90 J=1, IN
   W(J)=WCLD(J)+1.932D3*K1(J)/2.197D3-7.2D3*K2(J)/2.197D3
90 CONTINUE

CALL FUNCTN(W, WCLD, F, IN)

DO 100 J=1, IN
   K4(J)=B*F(J)
100 CONTINUE

DO 110 J=1, IN
   W(J)=WCLD(J)+4.39D2*K1(J)/2.16D2-8.0DC*K2(J)+3.68D3*K3(J)/5.13D2
110 CONTINUE

CALL FUNCTN(W, WCLD, F, IN)

DO 120 J=1, IN
   K5(J)=B*F(J)
120 CONTINUE

DO 130 J=1, IN
   W(J)=WCLD(J)-8.0DC*K1(J)/2.7D1+2.0DC*K2(J)-3.54D3*K3(J)/2.56D3
130 CONTINUE

CALL FUNCTN(W, WCLD, F, IN)

DO 140 J=1, IN
   K6(J)=B*F(J)
140 CONTINUE

DO 150 J=1, IN
   W(J)=WCLD(J)-8.0DC*K1(J)/2.7D1+2.0DC*K2(J)-3.54D3*K3(J)/2.56D3
150 CONTINUE

CALL FUNCTN(W, WCLD, F, IN)

DO 160 J=1, IN
   K6(J)=B*F(J)
160 CONTINUE

DETERMINE THE NEW CONCENTRATION IN THE SPRAY DROPLETS FOR ALL OF
THE IODINE BHCACLISIS SPECIES AND CHECK ERROR

DO 160 J = 1, I8
WB (J) = WOLD (J) + 1.6D1*K1 (J) / 1.35D2 + 6.656D3*K3 (J) / 1.282D4 +
1 2.056D4*K4 (J) / 5.64D3 - 9.0D00*K5 (J) / 5.0D1 + 2.0D00*K6 (J) / 5.5D1
R (J) = A ES (K1 (J) / 3.6D2 - 1.282D3 - 2.197D3 - 4.275D3 - 2.0D00*K4 (J) / 7.524D4
1 + K5 (J) / 5.0D1 + 2.0D00*K6 (J) / 5.5D1) / R
TOL (J) = A ES (WB (J) * TCLEB)
DE LA (J) = 0.84 * (TOL (J) / R (J)) ** 0.25
D 100 CONTINUE

DO 500 J = 1, I8
IF (B (J) . GT. TOL (J)) GOTO 900
500 CONTINUE

DO 510 J = 1, I8
WOLD (J) = WB (J)
510 CONTINUE

DETERMINE THE EQUILIBRIUM CONCENTRATIONS OF EQUATIONS. 24, 25 AND
26
BB = 1.0D00 - (WOLD (2) * WCLD (1)) / RK4
C = WOLD (2) / WOLD (1) * RK4 - WOLD (7)
D = B / (2.0D00 * RK4)
E = (BB*2.0D00 - 4.0D00 * RK4 * C) / (2.0D00 * RK4)
V = D - E

IF (V . LT. 1.0D-18) AND V . NE. 0.0D00 CALL ITIEB (WCLE, RK4, C, V)

WOLD (7) = WOLD (7) + V
WOLD (1) = WOLD (1) - V
WOLD (2) = WOLD (2) - V

IF (IN . EQ. 4) GOTO 600

RB = WCLD (6) + WCLD (5) * RK5
S = RK5 * WOLD (2) * WCLE (6) * WOLD (5)
M = (-ER + (BB*ER - 4.0D00*S) ** 0.5) / 2.0D00
WOLD (5) = WOLD (5) + M

GOTO 605

M = (RK5 * WOLD (3) - WOLD (6) * WCLE (5) / WOLD (5) + RK5)
WOLD (6) = WOLD (6) + M
WOLD (3) = WOLD (3) - M

IF (IN . EQ. 4) GOTO 614

U = WOLD (8) * WCLD (5) - RK6
VV = WCLD (8) * WCLE (5)
X = (-ER + (VV*VV - 4.0D00*U) ** 0.5) / 2.0D00
WOLD (5) = WOLD (5) + X
WOLD (8) = WOLD (8) + X

IF (IFLAG . EQ. 2 OR TOLD . LT. WLTB) GOTO 615
IFLAG = 2

DO 620 J = 1, 7
CONVAL (J, 1) = WOLD (J)
620 CONTINUE

SPA = SPA1* (1- WFEAC)
VOLD = VOLD1* (1.0D00 - WFEAC)
615 TOLD=TOLD+B
SUMCL=SUMCL+CLF
PB1=PB1+TIME
C12L=WB(1)
PBT=TOLD*TBvel
DEL=DELTA(1)
C
IF(IN .EQ. 1)GCTC 905
C
DO 520 J=2,IN
IF(DEL .LT. DELTA(J)) GOTO 520
DEL=DELTA(J)
C
520 CONTINUE
C
GOTO 905
C
C DETERMINE NEW STEP SIZE
C
900 DEL=DELTA(J)
C
905 IF(DEL .GT. C) GOTO 910
HNEW=Q*B
GOTO 1000
C
910 IF(DEL .LT. 4.0) GOTO 920
HNEW=4.0000*B
GOTO 1000
C
920 HNEW=DEL*B
C
C CHECK NEW STEP SIZE WITH MAX AND MIN STEP SIZE
C
1000 IF(HNEW .LT. HMAX)GCTC 930
HNEW=HMAX
C
930 IF(HNEW .LT. HMIN)GCTC 1111
LEFT=B-TOLD-HNEW
C
IF(LEFT .GT. 0.0)GCTC 5000
HNEW=B-TOLD
C
5000 H=HNEW
C
IF(TCLD .GE. B)GCTC 999
C
GOTO 1
C
C BEGIN DETERMINATION OF THE REMOVAL BY THE WALLS
C
999 TIME=TIME+TOLD/6.001
C
PB1=TIME*TBvel
C
WRITE(5,43)II,ILOCF,IN,IMAX
43 FORMAT(4I6)
IF(IF .GE. IMAX)GOTO 79
IN=IN+1
C
C DETERMINE THE MASS TRANSFER TO THE WATER ON THE WALLS
C
79 DO 84 IQ=IN,1,-1
C
WRITE(5,44)IQ,IN
44 FORMAT(2I6)
WSUE=0.0000
CALL WALL(CCNWAL,A,B,HMIN,HMAX,IN,DIFLIQ,WMFR,WSUE,DENLIQ,KLW,
C          1W ARE1, W VOL, TCLEH, W FILE, W VEL, F LBAT, W FRAC, IQ, RR4, RR5, RR6, CI2G, FC, 2E XP TR  
C          WALMCL=W ALMCL+WSUM  
C          DO 85 J=1,7  
C          CONW AL (J, IQ+1)= CCNW AL (J, IQ)  
C          CONTINUE  
C          84 CONTINUE  
C          DETERMINE THE CONCENTRATION IN THE SUMP  
C          CALL POGL (CONPCL, A, B, BMIN, BMAX, IN, TOLER)  
C          IF ( IN . GT. IMAX) GOTO 83  
C          DO 81 J=1,7  
C          CONPCL (J) = (CONPCL (J) * POLVOL + WOLD (J) * VOLD) / (POLVOL + VOLD)  
C          CONTINUE  
C          POLVCL=POLVCL+VCLD  
C          GOTO 87  
C          83 DO 82 J=1,7  
C          CONPCL (J) = (CONPCL (J) * POLVCL + CCNW AL (J, IMAX+1) * W VOL + WOLD (J) * VCLD) / ( 
C          TW VOL + VOLD + FCLVCL)  
C          CONTINUE  
C          POLVCL=POLVCL+VCLD+VCL  
C          CI2G=(CI2G+C VOL-(SUMBOL+WALMCL)) / CVOL  
C          SUM=SUMBOL+SUM+WALMCL  
C          WRITE (50, 22) II, TIME, WOLD (1), WOLD (2), WOLD (3), WOLD (4), WCLD (5),  
C          WCLD (6), WCLD (7)  
C          WRITE (52, 22) II, TIME, CONPCL (1), CONPCL (2), CONPCL (3), CCNPCL (4),  
C          COMPOL (5), COMPOL (6), COMPOL (7)  
C          WRITE (51, 23) TIME, SUMBOL, CI2G, SUM  
C          1100 CONTINUE  
C          CONTINUE  
C          DETERMINE THE TRANSFERS BY THE WATER STILL DRAINING CPF THE WALLS  
C          DO 91 IQ=1,IM  
C          CALL WALL (CCNW AL, A, B, BMIN, BMAX, IN, DIFLIQ, WMFR, WSUM, DENLIQ, K LW,  
C          1W ARE1, W VOL, TCLEH, W FILE, W VEL, F LBAT, W FRAC, IQ, RR4, RR5, RR6, CI2G, FC,  
C          2E XP TR)  
C          WALMCL=W ALMCL+WSUM  
C          SUM=SUM+WSUM  
C          CI2G=(CI2G+C VOL-WSUM*GASFAC)/ CVOL  
C          CALL POGL (CONPCL, A, B, BMIN, BMAX, IN, TOLER)  
C          DO 92 J=1,7  
C          CONPCL (J) = (CONPCL (J) * POLVCL + CCNW AL (J, IQ) * W VOL) / (W CLD + POLVOL)  
C          CONTINUE  
C          POLVCL=POLVCL+W VOL  
C          CONTINUE  
C          IF (IN . LE. 1) GTC 2000  
C          IN=IN-1  
C          GOTO 91  
C
C
2000 SUMGEN=2.53809E2*SUM
ERROR=1.0D2*(RMEXP-SUMGRM)/RMDEXP
II=II-1
SUMGEN=2.53809E2*SUM
ERROR=1.0D2*(RMEXP-SUMGRM)/RMDEXP
C
WHITE(22,16) CI2G
WHITE(22,15) SDF,SUMBRM
WHITE(22,14)
WHITE(22,13) CONPOL(1),CONPOL(2),CONPOL(3),CONPOL(4),CCNCPOL(5),
1
CONPOL(6),CONPOL(7)
GOTO 3000
C
1111 WHITE(40,21) BENEW
C
3000 STOP
END
SUBROUTINE WALL

THIS SUBROUTINE IS CALLED FROM THE ROUTINE WALL-SPRAY. THIS
SUBROUTINE DETERMINES THE REMOVAL OF MOLECULAR IODINE BY THE
WATER FLOWING DOWN THE WALLS OF A CONTAINMENT VESSEL. THE
ALGORITHM USED FOR THE MASS TRANSFER IS FOR A FALLING LIQUID
FILM AND A BUNGE-KUTTA-FELDEBURG 5(4) ROUTINE IS USED TO
NUMERICALLY INTEGRATE THE IODINE HIDROLYSIS REACTIONS.

SUBROUTINE WALL(CONWAL,A,E,HMIN,HMAX,IN,DIPLIQ,WMFR,WSUM,DENLIC,
1KLW,AREA,WVCL,TOLEG,WFILM,WREL,FRAC,IG,ERK4,ERK5,ERK6,CI2G,PC
2,EXPM)

IMPLICIT DOUBLE PRECISION (A-H,K-Z)
IMPLICIT INTEGER (I-J)

DIMENSION W(8),CONWAL(8,300),K1(7),K2(7),K3(3),R(7),RF(7),
1DELTA(7),WES(7),F(7),K4(7),K5(7),K6(7),TCL(7),&ALCGN(2)

FORMAT('STEP SIZE EELCW STEP MIN',D15.7)

CI2W=CONWAL(1,IC)
TCLD=A
Q=1.0D-1
H=1.0D-2

CONWAL(8,IC)=ERK6/CONWAL(5,IC)

USE SECANT METHOD TO DETERMINE THE LOG MEAN BULK CONCENTRATION
IN THE LIQUID

CONWAL(1,IC)=CI2W
WNNCL=CCONWAL(1,IC)*WVCL/1.0D3
P0=CCONWAL(1,IC)*1.02D00
P1=CCONWAL(1,IC)*1.05D00
Q0=H*KLW*WFILM*(PO-CCONWAL(1,IC))/DLOG((CI2G*PC-CCONWAL(1,IC))/(CI2G
1*PC-PO)) +CCONWAL(1,IC)-PO
55 Q1=H*KLW/WFILM*(P1-CCONWAL(1,IC))/DLOG((CI2G*PC-CCONWAL(1,IC))/(CI2G
1*PC-P1)) +CCONWAL(1,IC)-P1
CI2LM=(Q1*PO-QO*P1)/(Q1-QO)
CHECK=ABS(CI2LM-P1)/P1
IF(CHECK .LT. 1.0D-3)GOTO 59
P0=P1
Q0=Q1
P1=CI2LM
GOTO 55

59 WMOLB=WFLIM*(CI2LM-CCONWAL(1,IC))*AREA/R/(1.0D3*EXPM)
WSUM=WRELE+WSUM
CONWAL(1,IC)=CCONWAL(1,IC)+WMOLB*1.0D3/WVCL

BEGIN BUNGE-KUTTA-FELDEBURG ROUTINE

CALCULATE K'S

DO 30 J=1,IB
W(J)=CONWAL(J,IC)
30 CONTINUE

244
CALL FUNCTN(W,CONWAL,F,IN)

DO 40 J=1,IN
K1(J)=B*F(J)
40 CONTINUE

DO 50 J=1,IN
W(J)=CONWAL(J,IQ)*K1(J)/4.D00
50 CONTINUE

CALL FUNCTN(W,CONWAL,F,IN)

DO 60 J=1,IN
K2(J)=B*F(J)
60 CONTINUE

DO 80 J=1,IN
W(J)=CONWAL(J,IQ)+3.0DC0*K1(J)/3.2D1+9.0D00*K2(J)/3.2D1
80 CONTINUE

CALL FUNCTN(W,CONWAL,F,IN)

DO 90 J=1,IN
K3(J)=B*F(J)
90 CONTINUE

DO 110 J=1,IN
W(J)=CONWAL(J,IQ)+1.932D3*K1(J)/2.197D3-7.23D1+1.296D3*K2(J)/2.197D3
110 CONTINUE

CALL FUNCTN(W,CONWAL,F,IN)

DO 120 J=1,IN
K4(J)=B*F(J)
120 CONTINUE

DO 130 J=1,IN
W(J)=CONWAL(J,IQ)+4.39D2*K1(J)/2.16D2-8.3D0*K2(J)+3.68D3*K3(J)/5.113D2-6.45D2*K4(J)/4.164D3
130 CONTINUE

CALL FUNCTN(W,CONWAL,F,IN)

DO 140 J=1,IN
K5(J)=B*F(J)
140 CONTINUE

DO 150 J=1,IN
W(J)=CONWAL(J,IQ)-8.3D0*K1(J)/2.7D1+2.6D0*K2(J)-3.54D3*K3(J)/2.156D3+1.859D3*K4(J)/4.104D3-1.101*K5(J)/4.0D1
150 CONTINUE

CALL FUNCTN(W,CONWAL,F,IN)

DO 160 J=1,IN
K6(J)=B*F(J)
160 CONTINUE

DETERMINE THE NEW CONCENTRATION OF THE IODINE HYDROLYSIS SPECIES
IN THE LIQUID CH WALLS AND CHECK ERROR

DO 170 J=1,IN
W(J)=CONWAL(J,IQ)+1.6D1*K1(J)/1.35D2+6.56D3*K3(J)/1.3525D4+
1 2.8561D4*K4(J)/1.543D4-9.3D0*K5(J)/1.0D1+2.2D0*K6(J)/5.5D1
170 CONTINUE
\[ R(J) = \text{ABS}(K1(J)/3.6D2 - 1.28D2*3.0573 - 2.19703K4(J)/7.524D4 + K5(J)/5.0D1 + 2.0D00*K6(J)/5.5D1) \]
\[ \text{TOL(J)} = \text{ABS}(\text{WE(J)} + \text{CNEF(J)}) \]
\[ \text{DELTA(J)} = 0.84*\text{TOL(J)}/\text{R(J)} ** 0.25 \]

100 CONTINUE

DO 50 J=1,IN
    IF(\( B(J) \) .GT. \( \text{TOL(J)} \)) GOTO 900
50 CONTINUE

DO 510 J=1,IN
    CONWAL(J,IQ) = \text{WE}(J)
51 CONTINUE

DETERMINE THE EQUILIBRIUM CONCENTRATION OF EQUATION 24, 25 AND 26 FOR THE CYLINDRICAL PIECE OF THE WALL

BB = \(-1.0D00 - (\text{CONWAL (2, IQ)} * \text{CONWAL (1, IQ)}) * \text{RK4} \)
C = \text{CONWAL (2, IQ)} * \text{CONWAL (1, IQ)} * \text{RK4} - \text{CONWAL (7, IQ)}
D = \((-\text{BE} + (\text{BE} * \text{RK5} - 4.0D00 * \text{S}) ** 0.5) / 2.0D00 * \text{RK5}) \)
E = \((\text{BB} * 2.0D00 - 4.0D00 * \text{RK4} * C) ** 0.5) / (2.0D00 * \text{RK4}) \)
V = \(\text{D} \)

IF(V .GT. 1.0D-18 .AND. V .EQ. 0.0D00) GOTO 575
WALCCH(1) = \text{CONWAL (1, IQ)}
WALCCN(2) = \text{CONWAL (1, IQ)}
CALL ITTER(WALCCH, RK4, C, V)
575 CONWAL (7, IQ) = \text{CONWAL (7, IQ)} + V
CONWAL (1, IQ) = \text{CONWAL (1, IQ)} - V
CONWAL (2, IQ) = \text{CONWAL (2, IQ)} - V

IF(IN .EQ. 4) GOTO 600

BB = \text{CONWAL (6, IQ)} * \text{CONWAL (5, IQ)} + \text{RK5}
S = \(-\text{RK5} * \text{CONWAL (3, IQ)} + \text{CONWAL (6, IQ)} * \text{CONWAL (5, IQ})
M = \((-\text{BE} + (\text{BE} * \text{RR} - 4.0D00 * \text{S}) ** 0.5) / 2.0D00 \)
GOTO 605

600 M = (\text{RK5} * \text{CONWAL (3, IQ)} - \text{CONWAL (6, IQ)} * \text{CONWAL (5, IQ)}) / (\text{CONWAL (5, IQ)} + \text{RK5})

605 CONWAL (6, IQ) = \text{CONWAL (6, IQ)} + M
CONWAL (3, IQ) = \text{CONWAL (3, IQ)} - M

IF(IN .EQ. 4) GOTO 615

\[ U = \text{CONWAL (8, IQ)} * \text{CONWAL (5, IQ)} - \text{RK6} \]
\[ \text{VV} = (\text{S} * 2.0D00 + \text{HK6} * \text{V}) \]
\[ X = \((-\text{VV} + (\text{VV} * \text{VV} - 4.0D00 * \text{U}) ** 0.5) / 2.0D00 \]
CONWAL (5, IQ) = \text{CONWAL (5, IQ)} + X
CONWAL (8, IQ) = \text{CONWAL (8, IQ)} + X

615 I = I + 1
TOLD = TOLD + 8

CIZW = \text{CONWAL (1, IQ)}
DEL = \text{DELTA (1)}

IF(IN .EQ. 1) GOTO 905

DO 520 J=2,IN
    IF(\( \text{DEL} \).LT. \( \text{DELTA(J)} \)) GOTO 520
    DEL = \text{DELTA(J)}
52 CONTINUE
GOTO 905

C DETERMINE NEW STEP SIZE
C
900 DEL=DELTA(J)
C
905 IF (DEL .GT. C) GOTO 910
   HNEW=Q*H
   GOTO 1000
C
910 IF (DEL .LT. 4.0) GOTO 920
   HNEW=4.0DCO*H
   GOTO 1000
C
920 HNEW=DEL*H
C CHECK NEW STEP SIZE WITH MAX AND MIN STEP SIZE
C
1000 IF (HNEW .LT. HMAX) GOTO 930
   HNEW=HMAX
C
930 IF (HNEW .LT. HMIN) GOTO 1111
   LEFT=B-TOLE-HNEW
C
   IF (LEFT .GT. 0.0) GOTO 5000
   HNEW=B-TOLE
C
5000 H=HNEW
C
   IF (ICLD .GE. B) GOTO 999
   GOTO 1
C
1111 WRITE(40,21) HNEW
999 RETURN
END
SUBROUTINE POOL

THIS SUBROUTINE DETERMINES THE CONCENTRATION OF THE IODINE HYDROLYSIS SPECIES IN THE SUMP POOL. A BUNGE-KUTTA-FELHEUG 5(4) ROUTINE IS USED TO INTEGRATE THE IODINE HYDROLYSIS REACTIONS. THIS SUBROUTINE IS CALL FROM THE WALL-SPRAY ROUTINE.

SUBROUTINE POOL(CONPOL,A,E,HMIN,HMAX,IN,TOLE)

IMPLICIT DOUBLE PRECISION (A-H,K-Z)
IMPLICIT INTEGER(I-J)

DIMENSION CONPOL(8),CC(7),K1(7),K2(7),K3(7),K4(7),K5(7),K6(7),
TCL(7),DELTA(7),B(7),CCB(7),F(7)

21 FORMAT('STEP SIZE BELOW HMIN ',E15.7)

H=1.0D-2
Q=1.0D-1
PTOL=A

BEGIN THE BUNGE-KUTTA-FELHEUG ROUTINE

CALCULATE K'S

DO 31 J=1,IN
   CC(J)=CONPOL(J)
   CONTINUE

CALL FUNCTN(CC,CONPOL,F,IN)

DO 41 J=1,IN
   K1(J)=H*F(J)
   CONTINUE

DO 51 J=1,IN
   CC(J)=CONPOL(J)*K1(J)/4.0D00
   CONTINUE

CALL FUNCTN(CC,CONPOL,F,IN)

DO 61 J=1,IN
   K2(J)=H*F(J)
   CONTINUE

DO 81 J=1,IN
   CC(J)=CONPOL(J)*3.0DCC*K1(J)/3.2D1+5.0D00*K2(J)/3.2D1
   CONTINUE

CALL FUNCTN(CC,CONPOL,F,IN)

DO 91 J=1,IN
   K3(J)=H*F(J)
   CONTINUE

DO 111 J=1,IN
   CC(J)=CONPOL(J)*1.932D3*K1(J)/2.197D3-7.2D3*K2(J)/2.197D3
   +7.296D3*K3(J)/2.197D3
   CONTINUE
111 CONTINUE
C CALL FUNCTN(CC,CONFC1,F,IN)
C DO 121 J=1,IN
   K9(J)=B*F(J)
121 CONTINUE
C DO 131 J=1,IN
   CC(J)=CONPOL(J)+4.39D2*K1(J)/2.16D2-8.0D00*K2(J)+
      1 3.68D3*K3(J)/5.13D2-8.45D2*K4(J)/4.104D3
131 CONTINUE
C CALL FUNCTN(CC,CONFC1,F,IN)
C DO 141 J=1,IN
   K5(J)=B*F(J)
141 CONTINUE
C DO 151 J=1,IN
   CC(J)=CONPOL(J)-8.0D00*K1(J)/2.7D1+2.0D00*K2(J)-
      1 3.54D3*K3(J)/2.565D3+1.859D3*K4(J)/4.104D3-1.1D1*K5(J)/4.0D1
151 CONTINUE
C CALL FUNCTN(CC,CONFC1,F,IN)
C DO 161 J=1,IN
   K6(J)=B*F(J)
161 CONTINUE
C DETERMINE THE NEW CONCENTRATION OF THE IODINE HYDROLYSIS SPECIES
C IN THE SUMP POOL AND CHECK ERROR
C DO 161 J=1,IN
   CCB(J)=CONPOL(J)+1.6D1*K1(J)/1.35D2+6.656D3*K3(J)/1.2825D4+
      1 2.8561D4*K4(J)/5.643D4-9.0D00*K5(J)/5.0D1+2.0D00*K6(J)/5.5D1
   R(J)=ABS(K1(J)/3.6D2-1.28D2*K3(J)/4.275D3-2.197D3*K4(J)/7.524D4+
      1 +K5(J)/5.0D1+2.0D00*K6(J)/5.5D1)*H
   TOL(J)=ABS(CCE(J)*TCLEB)
   DELTA(J)=0.84*(TOL(J)/R(J))*0.25
101 CONTINUE
C DO 501 J=1,IN
   IF(R(J).GT.TOL(J))GOTO 901
501 CONTINUE
C DO 511 J=1,IN
   CONFC(J)=CCB(J)
511 CONTINUE
C DETERMINE THE EQUILIBRIUM CONCENTRATION OF EQUATIONS 24, 25 AND
C 26
C BB=-1.0D00-(CONPOL(2)*CONPOL(1))*ER4
C C=CONPOL(2)*CONPOL(1)*ER4-CONPOL(7)
C D=BE/(2.0D00*ER4)
C E=((BB**2.0D00-4.0D00*ER4*C)**0.5D00)/(2.0D00*ER4)
V=D-E
C 666 IF(V.LT.1.0D-18.AND.V.NE.0.0D00)CALL ITER(Conpol,ER4,C,V)
C CONPOL(7)=CONPOL(7)+V
C CONPCL(1)=CONPCL(1)-V
C CONPCL(2)=CONPCL(2)-V
C IF(IN.EQ.4)GOTO 601
C  
BB=CCNPCL(6)+CCNPCL(5)+BK5  
S=BB*CCNPCL(3)+CCNPCL(6)*CONPOL(5)  
M=-5*BB+BB*4.0DOO*S**0.5)/2.0DOO  
CONPOL(5)=CONPOL(5)+M  
GOTO 606  
C  
601  
M=(BK5*CCNPCL(3)-CCNPCL(6)*CONPOL(5))/(CONPOL(5)+BK5)  
C  
606  
CONPOL(6)=CONPOL(6)+M  
CONPOL(3)=CONPOL(3)-M  
C  
IF(IN.EQ.4)GOTO 616  
C  
U=CONPOL(8)*CCNPCL(5)-BK6  
VV=CONPOL(8)+CCNPCL(5)  
X=(-VV+(VV*VV-4.0DOO*U)**0.5)/2.0DOO  
CONPOL(5)=CONPOL(5)+X  
CONPOL(8)=CONPOL(8)+X  
C  
616  
PTOLD=PTOLD+H  
DEL=DELTA(1)  
C  
IF(IN.EQ.1)GOTO 906  
C  
DO 521 J=2,IN  
IF(DEL.LT.DELTA(J))GOTO 521  
DEL=DELTA(J)  
521  
CONTINUE  
C  
GOTO 906  
C  
DETERMINE NEW STEP SIZE  
C  
901  
DEL=DELTA(J)  
C  
906  
IF(DEL.GT.Q)GOTO 911  
HNEW=Q*B  
GOTO 1001  
C  
911  
IF(DEL.LT.4.0)GOTO 921  
HNEW=4.0DOO*B  
GOTO 1001  
C  
921  
HNEW=DEL*B  
C  
CHECK NEW STEP SIZE WITH MAX AND MIN STEP SIZE  
C  
1001  
IF(BNEW.LT.BMAX)GOTO 931  
HNEW=BMAX  
C  
931  
IF(BNEW.LT.BMIN)GOTO 1112  
LEF=B-PTOLD-BNEW  
C  
IF(LEF.GT.0.0)GOTO 5001  
HNEW=B-PTOLD  
C  
5001  
H=HNEW  
C  
IF(PTOLD.GE.F)GOTO 998  
GOTO 2  
C  
C  
1112  
WRITE(40,21)BNEW  
998  
RETURN  
END  
250
SUBROUTINE FUNCTN

THIS SUBROUTINE CONTAINS THE DIFFERENTIAL EQUATIONS (KINETIC RATE EQUATIONS) TO BE INTEGRATED. THIS SUBROUTINE IS CALLED FROM THE RUNG-KEUTTA-FELDBURG INTEGRATION ROUTINE IN THE KINETIC, D&OP, SPRAY AND WALL-SHRA RIOUDL.

 SUBROUTINE FUNCTN (W,WCLD,F,IN)
 IMPLICIT DOUBLE PRECISION (A-H, K-Z)
 IMPLICIT INTEGER (I-J)
 DIMENSION W(8), WCLD(8), F(7)
 IF(IN .EQ. 5) GOTO 5
  W(5) = WCLD(5)
  W(6) = WCLD(6)
  RK1 = 3.0D00
  RKR1 = 4.4D12
  RK20 = 2.5D02
  RK21 = 1.2D02
  RKR2 = 3.0D08
  RKP3 = 9.35D-6
  B1 = RK1 * W(1)
  BR1 = RKR1 * W(2) * W(3) * W(5)
  B20 = RK20 * W(3) * 2.0D00
  B21 = RK21 * W(3) * W(6)
  BR2 = RKR2 * W(4) * W(2) * 2.0D00 * W(5) * 2.0D00
  RP3 = RKP3 * W(5) * W(2)
  F(1) = - B1 + BR1 + 5.0D-1 * BP3
  F(2) = B1 - BR1 + 2.0D00 * (B20 + B21) / 3.0D00 - 2.0D00 * R2 - RP3
  F(3) = B1 - BR1 - 2.0D00 * RR2
  F(4) = (B20 + B21) / 3.0D00 - RB2
  IF (IN .EQ. 5) GOTO 10
  F(5) = 0.0D00
  GOTO 11
  F(5) = B1 - BR1 + B20 + B21 - 3.0D00 * R2 - 4.0D00 * RP3
  F(6) = 0.0D00
  F(7) = 0.0D00
  RETURN
  END

251
SUBROUTINE ITER

THIS SUBROUTINE FINDS THE ROOT TO THE QUADRATIC EQUILIBRIUM
EQUATION FOR THE FORMATION REACTION OF TRI-IODIDE, I3- (EQUATION
24). A SECANT METHOD IS THE ROUTINE USED TO FIND THE ROOT. THIS
METHOD IS CALLED WHENEVER THE QUADRATIC FORMULA RESULTS IN LESS
THAN APPROXIMATELY THREE SIGNIFICANT FIGURES. THIS SUBROUTINE
IS CALLED BY THE PROGRAMS KINETIC, DROP, SPRAY AND WALL-SPRAY.

SUBROUTINE ITER(WCLD,RK4,C,V)

IMPLICIT DOUBLE PRECISION (A-H,L-Z)
IMPLICIT INTEGER (I-K)

DIMENSION WOLD(7),W(7)

PO=1.0D-16
PI=1.0D-10

Q0=C-RK4*PO*F0-PO*RK4*(WOL(1)+WOL(2)) - PO
Q1=C-RK4*PI*F1-PI*RK4*(WOL(1)+WCLD(2)) - PI

NEW=E1-Q1*(P1-F0)/(C1-C0)

CHECK=AES(NEW-P1)/P1

IF (CHECK .LT. 1.0D-4) GOTO 10

P0=P1
Q0=Q1
PI=NEW
GOTO 5

V=NEW

RETURN

END
Wall-Spray Model sample input:

\[ A = 0.0 \]
\[ B = DURTM = 10 \]
\[ HMIN = 1.0 \times 10^{-10} \]
\[ HMAX = 1.0 \times 10^2 \]
\[ IN = 4 \]
\[ TOLER = 1.0 \times 10^{-3} \]
\[ TEMPL = 298 \]
\[ TEMPG = 298 \]
\[ DIAM = 0.1 \]
\[ SAD = 0.1 \]
\[ CI2G = 1.0 \times 10^{-7} \]
\[ CI2SP = 0.0 \]
\[ CISP = 0.0 \]
\[ CHOSP = 0.0 \]
\[ COISP = 0.0 \]
\[ CHSP = 1.0 \times 10^{-9} \]
\[ CIO3SP = 0.0 \]
\[ CI3SP = 0.0 \]
\[ PRESS = 1.0 \]
\[ CDIAM = 3.13 \]
\[ HEIGHT = 15.4 \]
\[ FLRAT = 37.0 \]
\[ WFRAC = 0.05 \]
\[ WHT = 3.3 \]
AT A TEMPERATURE OF THE GAS 298.00 DEGREES KELVIN
THE VISCOSITY OF THE LIQUID (CP) = 0.89723484E-00
THE VISCOSITY OF THE GAS (CP) = 0.18638768E-01
THE PARTITION COEFFICIENT IS = 0.84629168E-02
THE DENSITY OF THE LIQUID (GMS/CC) = 0.99691660E+00
THE DENSITY OF THE GAS (GMS/CC) = 0.11629498E-02
THE DIFFUSION COEFFICIENT FOR THE GAS (SQ CM/SEC) = 0.82375648E-01
THE DIFFUSION COEFFICIENT FOR THE LIQUID (SQ CM/SEC) = 0.12964372E-04
THE GAS-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = 0.11279480E+03
THE LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = 0.25536588E+00
THE OVERALL LIQUID-SIDE MASS TRANSFER COEFFICIENT (CM/SEC) = 0.06100248E-01
THE VOLUME FOR ONE DROP (LITERS) = 0.52360000E-06
THE SURFACE AREA FOR ONE DROP (SQ CM) = 0.31916600E-01
THE EXPOSURE TIME FOR THE DROP IS (SEC) = 0.39004628E+01
THE NET WHEELS WHEELS FOR THE DROP = 0.25317234E+03
THE TERMINAL VELOCITY OF THE DROP (CM/SEC) = 0.39486012E+03
THE NUMBER OF DROPS IN THE CONTAINER IS = 0.72322222E+07
THE DROP PLUS (NUMBER OF DROPS/SQ CM HZ) = 0.82673538E+03
THE CONTAINER VOLUME (LITERS) = 0.13551508E+06
THE NUMBER OF OTHER LOOPS = 156
THE INITIAL CONCENTRATION IN THE GAS OF 0.10000000E-06 (BOLES/LITERS)
THE DURATION OF THE SPRAY (HZ) 0.10000000E+02
THE VOLUME OF LIQUID SPRAYED (LITERS) 0.38000000E+03
AND A SPRAY FLOW RATE OF 0.38000000E+02 (LITERS/HZ)
THE INITIAL CONCENTRATION OF THE LIQUID (BOLES/LITERS) :
12 = 0.00000000E+00
1 = 0.00000000E+00
NO = 0.00000000E+00
102 = 0.00000000E+00
80 = 0.00000000E+00
10 = 0.00000000E+00
I = 0.00000000E+00
THE FINAL CONCENTRATION OF IODINE (12) IN THE GAS IS = 0.16132500E-07 (BOLES/LITERS)
THE NUMBER OF MOLES OF IODINE (12) REACTED IS = 0.11330278E+01
THE NUMBER OF MOLES OF IODINE REACTED IS = 0.28777566E+01
THE FINAL CONCENTRATION OF THE LIQUID IS (MCARS/LITER) :
12 = 0.58056418E+06
1 = 0.63460943E+04
NO = 0.51079827E+05
103 = 0.46602638E+05
80 = 0.10000000E+08
10 = 0.49696444E+10
I = 0.76307699E-07
APPENDIX F

LIST OF SYMBOLS
A  Input starting time for all numerical models

\[ a_n \quad \text{nth root of} \quad a_n \cot(a_n) - (\text{sh} - 1) = 0 \]

B  Input stopping time for KINETIC and DROP models

BWR  Boiling Water Reactor

C  Concentration of a species

\[ C_g \quad \text{Concentration of a species in the gas phase} \]

\[ C_{gi} \quad \text{Concentration of a species in the gas phase at the interface} \]

\[ C_l \quad \text{Concentration of a species in the liquid phase} \]

\[ C_{li} \quad \text{Concentration of a species in the liquid phase at the interface} \]

cc  Cubic centimeter

CDIAM  Containment diameter in the SPRAY and WALL-SPRAY models, meters

CHL  Containment of hydrogen ions, \( H^+ \), in the liquid for the DROP and KINETIC models, moles/liter

CHOIL  Concentration of hypoiiodous acid, \( HOI \), in the liquid for the KINETIC and DROP models, moles/liter

CHOISP  Concentration of hypoiiodous acid, \( HOI \), in the spray solution for the SPRAY and WALL-SPRAY models, moles/liter

CHSP  Concentration of hydrogen ions \( H^+ \) in the spray solution for the SPRAY and WALL-SPRAY models, moles/liter

CIL  Concentration of Iodide, \( I^- \), in the liquid for the KINETIC and DROP models, moles/liter

CISP  Concentration of Iodide ion, \( I^- \), in the spray solution for the SPRAY and WALL-SPRAY models, moles/liter.

C103L  Concentration of Iodide ion, \( IO_3^- \) in the liquid for the KINETIC and DROP models, moles/liter.

C103SP  Concentration of Iodate ion, \( IO_3^- \), in the spray solution for the SPRAY and WALL-SPRAY models, moles/liter.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12L</td>
<td>Concentration of molecular iodine, I$_2$, in the liquid for the KINETIC and DROP models, moles/liter.</td>
</tr>
<tr>
<td>C12SP</td>
<td>Concentration of molecular Iodine, I$_2$, in the spray solution for the SPRAY and WALL-SPRAY models, moles/liter.</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeters</td>
</tr>
<tr>
<td>COIL</td>
<td>Concentration of Hypo-Iodate ion, OI$^-$, in the liquid for the KINETIC and DROP models, moles/liter.</td>
</tr>
<tr>
<td>COISP</td>
<td>Concentration of Hypo-Iodate ion, OI$^-$, in the spray solution for the SPRAY and WALL-SPRAY models, moles/liter.</td>
</tr>
<tr>
<td>cot</td>
<td>Cotangent</td>
</tr>
<tr>
<td>cP</td>
<td>CentiPoise</td>
</tr>
<tr>
<td>CPU</td>
<td>Central Processor Unit</td>
</tr>
<tr>
<td>CSE</td>
<td>Containment Systems Experiments</td>
</tr>
<tr>
<td>d</td>
<td>Drop diameter</td>
</tr>
<tr>
<td>Dg</td>
<td>Diffusion coefficient for the gas</td>
</tr>
<tr>
<td>D$_l$</td>
<td>Diffusion coefficient for the liquid</td>
</tr>
<tr>
<td>DENGAS</td>
<td>Density of air, gms/cc</td>
</tr>
<tr>
<td>DENLIQ</td>
<td>Density of water, gms/cc</td>
</tr>
<tr>
<td>DIAM</td>
<td>Drop diameter, cm</td>
</tr>
<tr>
<td>DURTM</td>
<td>Duration of spray, min</td>
</tr>
<tr>
<td>E</td>
<td>Spray removal efficiency</td>
</tr>
<tr>
<td>exp</td>
<td>exponential</td>
</tr>
<tr>
<td>EXPTM</td>
<td>Exposure time, seconds</td>
</tr>
<tr>
<td>F</td>
<td>Flow rate</td>
</tr>
<tr>
<td>FLRAT</td>
<td>Flow rate, liter/min</td>
</tr>
<tr>
<td>g</td>
<td>Acceleration of gravity</td>
</tr>
<tr>
<td>h</td>
<td>Drop fall height</td>
</tr>
<tr>
<td>H$^+$</td>
<td>Hydrogen ion</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>HEIGHT</td>
<td>Drop fall height, m</td>
</tr>
<tr>
<td>HMAX</td>
<td>Maximum step size for the RKF numerical integration routine</td>
</tr>
<tr>
<td>HMIN</td>
<td>Minimum step size for the RKF numerical integration routine</td>
</tr>
<tr>
<td>HOI</td>
<td>Hypoiodous Acid</td>
</tr>
<tr>
<td>IN</td>
<td>Number of equations to integrate. 4 for buffered solution; 5 for unbuffered solution</td>
</tr>
<tr>
<td>I⁻</td>
<td>Iodide</td>
</tr>
<tr>
<td>I₂</td>
<td>Molecular Iodine</td>
</tr>
<tr>
<td>I₃⁻</td>
<td>Tri-Iodide</td>
</tr>
<tr>
<td>IO₃⁻</td>
<td>Iodate ion</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>k₁</td>
<td>Reaction rate constant for equation i. (i &lt; 0: reverse reaction, i &gt; 0: forward reaction)</td>
</tr>
<tr>
<td>Kᵢ</td>
<td>Equilibrium constant for equation i.</td>
</tr>
<tr>
<td>k₉</td>
<td>Gas side mass transfer coefficient</td>
</tr>
<tr>
<td>K₉₀ᵥ</td>
<td>Overall gas side mass transfer coefficient</td>
</tr>
<tr>
<td>k₁</td>
<td>Liquid side mass transfer coefficient</td>
</tr>
<tr>
<td>K₁₀ᵥ</td>
<td>Overall liquid side mass transfer coefficient</td>
</tr>
<tr>
<td>kₗ₁,aᵥ</td>
<td>Average mass transfer coefficient for a falling liquid film</td>
</tr>
<tr>
<td>Ln</td>
<td>Natural logarithm</td>
</tr>
<tr>
<td>Log</td>
<td>Base 10 logarithm</td>
</tr>
<tr>
<td>M</td>
<td>Molarity, moles/liter</td>
</tr>
<tr>
<td>Mₐ</td>
<td>Molecular weight of species a</td>
</tr>
<tr>
<td>Mₐ</td>
<td>Molecular weight of species b</td>
</tr>
<tr>
<td>Mₜ</td>
<td>Mass transfer rate</td>
</tr>
<tr>
<td>Nₐ</td>
<td>Mass transfer flux to the drop</td>
</tr>
<tr>
<td>Nₐₘₜ</td>
<td>Mass transfer flux to the liquid on walls</td>
</tr>
</tbody>
</table>
$N_D$ "Best Number"

$N_{re}$ Reynolds number

$OI^-$ Hypo-Iodate ion

$OH^-$ Hydroxide ion

$p$ Pressure

$P$ Partition coefficient

PRESS Pressure, atm

PWR Pressurized water reactor

$r$ Distance from the outer radius of the drop

$R$ Reaction rate

$s$ Seconds

$sec$ Seconds

$Sc$ Schmidt number

$t$ Time

$t^*$ Contact time for each element in a drop

$t_e$ Exposure time of a drop

$t_{1/2}$ Half life

$T$ Temperature

$TEMPG$ Temperature of the gas, K

$TEMPL$ Temperature of the liquid, K

$TOLER$ Relative error control for RKF routine

$TRMVEL$ Terminal velocity of a drop, cm/sec

$u$ Velocity $< \text{ vector }$

$v$ Velocity

$V_g$ Terminal settling velocity

$V$ Containment volume

272
VISGAS  Viscosity of the gas phase, cP
VISLIQ  Viscosity of the liquid phase, cP
WFRAC  Fraction of spray flow rate which flows down the wall
WHT  Wall height, meters
WOLD(1)  Concentration of I₂ in RKF routine, moles/liter
WOLD(2)  Concentration of I⁻ in RKF routine, moles/liter
WOLD(3)  Concentration of HOI in RKF routine, moles/liter
WOLD(4)  Concentration of IO⁻ in RKF routine, moles/liter
WOLD(5)  Concentration of H⁺ in RKF routine, moles/liter
WOLD(6)  Concentration of OI⁻ in RKF routine, moles/liter
WOLD(7)  Concentration of I₃⁻ in RKF routine, moles/liter
λ  Removal rate constant
φ  4 Dₑtₑ/d²
σ  Thickness of water on the walls
Ω  Collision integral
ρ  Density
μ  Viscosity
∇  Nable operator
Δ²  Laplacian operator
VITA

Michael F. Albert was born in Lincoln Park, Michigan on June 30, 1960. He attended Lincoln Park elementary schools through the third grade. He and his family moved to Farmington, Michigan in 1968. He attended schools in Farmington until the eighth grade. In 1973 he and his family moved to Johnson City, Tennessee where he attended schools in that city through the ninth grade. In 1975, he and his family moved to Knoxville, Tennessee where he graduated from Doyle High School in June of 1978. In September of 1978 he entered The University of Tennessee, Knoxville and in December of 1982 he received his Bachelor of Science degree in Chemical Engineering. In January of 1983 he entered the Graduate School of The University of Tennessee, Knoxville and began his study toward a Master's degree. In June of 1983 he started his thesis in conjunction with Oak Ridge National Laboratory. He received his Master's degree in Chemical Engineering in March of 1985.