Estimation of pH in Iodine Solution on Equilibrium Condition

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1. Introduction

It is recognized that a radioiodine is potentially one of the most hazardous fission products that could be released from the fuel of nuclear reactors during severe accidents. The nuclear fuel has large inventories of various isotopes on iodine, and released iodine from the fuel makes complex chemical forms under a severe accident. According to the thermodynamic calculations and various experiments under the severe accident condition, the iodine released from the fuel would be primarily in its reduced state as cesium iodide in the containment [1-3]. This would be dissolved in the water by discharging of coolant and safety spray system, and be re-vaporized into the iodine by oxidization or radiolysis process.

There exist two basic approaches, that is, mechanistic and empirical models, to modeling on the generation of volatile iodine, I_2, from non-volatile iodide, I^-, in the aqueous phase by the radiolytic oxidation. The empirical models are practically used in the severe accident codes such as IODE, ASTEC, IMPAR *etc*. The mechanistic modeling tries to represent the whole set of elementary radiochemical reactions (typically included hundreds of the important reactions in water) and solves for the kinetics of these reactions using some ordinary differential equation solver. The typical codes adapted in the mechanistic approach are the INSPECT (IodiNe SPECiation and Transport) developed in AEAT, which has been integrated with some changes into MELCOR 1.8.5 [4] and the LIRIC model (Library of Iodine reactions in containment) developed in AECL [5].

We prepared a pool scrubbing code using the current iodine retention models, and performed sensitivity studies on the iodine retention such as the pool temperature, vapor velocity in a bubble, and iodine concentration [6]. We also issued a new correlation to estimate the iodate concentration in an acidic pool under irradiation conditions by identifying the key reactions and solving the differential equations based on the rate law. The correlation was also verified with experimental data using NaI solutions under gamma irradiation [7].

The important chemical parameters in aqueous solution at equilibrium on the iodine chemistry are pH, chemical potential, temperature, and total iodine concentration. The chemical potential and pH at a given temperature and iodine concentration are usually used to describe the behavior of iodine water system at equilibrium. Generally, Gibbs energies minimization is used to calculate species concentration in either solid, gas or mixture phase at equilibrium. In this paper, the Gibbs energies minimization method is set to calculate the iodine species and the concentration of H^+ or pH in solution.

2. Method

Chemical equilibrium calculations have traditionally been made through the use of equilibrium constants of known reactions – a procedure useful for simple problems. However, when the equilibrium composition is determined by a number of simultaneous reactions, the computation requires more complex. A direct and general method for solving this complicated problem is the direct minimization of the Gibbs function of the system, given by [8-9]:

$$G = \sum_{i=1}^{I} n_i(\mu_i^o + ln\hat{a}_i) \quad (1a)$$

Subject to the constraints of elemental balances:

$$\sum_{i=1}^{I} a_{ij} n_i = b_i, j = 1, \dots, J \quad (1b)$$

$$n_i \geq 0, \ i = 1, \dots, I \quad (1c)$$

The total Gibbs energy is changed as shown in equation (2), and should be minimized to get the concentration changes of the species in equilibrium state of the closed system.

$$dG = \sum_{i=1}^{I}(\mu_i^o + ln\hat{a}_i)dn_i = \sum_{i=1}^{I} \mu_i dn_i \quad (2)$$

And subject to the constraints:

$$\sum_{i=1}^{I} a_{ij} n_i - b_i = 0 \quad (3)$$

The equation (3) can be solved by multiplying each element balance by non-negative Lagrange multiplier, λ_j:

$$\lambda_j\left(\sum_{i=1}^{I} a_{ij} n_i - b_i\right) = 0 \quad (4a)$$

As summing over j, equation (4a) can be obtained.

$$\sum_{j=1}^{J} \lambda_j \left(\sum_{i=1}^{I} a_{ij} n_i - b_i\right) = 0 \quad (4b)$$

Function F can be defined by adding to G.

$$F = G + \sum_{j=1}^{J} \lambda_j \left(\sum_{i=1}^{I} a_{ij} n_i - b_i \right) \quad (5)$$

The minimum values of F and G are found when the partial derivatives of F with respect to n_i are set equation to zero:

$$\frac{\partial F}{\partial n_i} = \frac{\partial G}{\partial n_i} + \sum_{j=1}^{J} \lambda_j a_{ij} = 0 \quad (6a)$$

$$\mu_i + \sum_{j=1}^{J} \lambda_j a_{ij} = 0 \quad (6b)$$

for the gaseous phase,

$$\mu_i = \mu_i^o + RTlnP + RTln\frac{n_i}{N_g} \quad (7a)$$

for the mixture phase,

$$\mu_i = \mu_i^o + RTlnf_i + RTln\frac{n_i^k}{N_m} \quad (7b)$$

and for the condensed solid phase,

$$\mu_i = \mu_i^o \quad (7c)$$

A sufficient condition to ensure convergence to a single point is set [10];

$$\left|\frac{n^{k+1}-n^k}{n^k}\right| < 10^{-3} \quad (8)$$

3. Problems and Solutions

The purpose of this paper is to calculate the equilibrium compositions at 25°C and 1 bar of a liquid phase system. The species are determined by limited sets of equations:

$$\begin{gathered} I_2(s) \rightleftarrows I_2(l) \\ I_2(l) + H_2O \rightleftarrows H^+ + I^- + HIO \\ I_2(l) + H_2O \rightleftarrows I^- + H_2OI^+ \\ H_2O \rightleftarrows H^+ + OH^- \end{gathered} \quad (9)$$

In the initial unreacted state, there are present of iodine I_2 concentration from 10^{-4} to 10^{-7} M with H_2O concentration from $2x10^{-4}$ to 10^{-7} M. To solve the problem, the chemical identities, starting moles, temperature, pressure of the system, and the standard Gibbs free energy of formation of each species is given in Table I, II and III. And three cases of total iodine concentrations in the system, 10^{-4}, 10^{-6} and 10^{-7}M are considered.

To get the mole concentration of each species after chemical reactions including pH in solution, the minimization of the Gibbs free energy is performed. As considering the reaction system in equation (9), the equation (6b) can be described as the six equations for the six species as shown in equations (10).

$$\begin{aligned} I_2: &\quad \frac{16.4}{RT} + \ln\frac{n_{I_2}}{N_m} + 2\frac{\lambda_I}{RT} = 0 \\ H_2O: &\quad -\frac{192.42}{RT} + \ln\frac{n_{H_2O}}{N_m} + 2\frac{\lambda_H}{RT} + \frac{\lambda_O}{RT} = 0 \\ I^-: &\quad -\frac{51.92}{RT} + \ln\frac{n_{I^-}}{N_m} + \frac{\lambda_I}{RT} = 0 \\ H_2OI^+: &\quad -\frac{106.5}{RT} + \ln\frac{n_{H_2OI^+}}{N_m} + 2\frac{\lambda_H}{RT} + \frac{\lambda_O}{RT} + \frac{\lambda_I}{RT} = 0 \\ H^+: &\quad \ln\frac{n_{H^+}}{N_m} + \frac{\lambda_H}{RT} = 0 \\ OH^-: &\quad -\frac{157.28}{RT} + \ln\frac{n_{OH^-}}{N_m} + \frac{\lambda_H}{RT} + \frac{\lambda_O}{RT} = 0 \end{aligned} \quad (10)$$

The three material balance equations are:

$$\begin{aligned} H: &\quad 2n_{H_2O} + 2n_{H_2OI^+} + n_{H^+} + n_{OH^-} = 0 \\ I: &\quad 2n_{I_2} + n_{I^-} + n_{H_2OI^+} = 0 \\ O: &\quad n_{H_2O} + n_{H_2OI^+} + n_{OH^-} = 0 \end{aligned} \quad (11)$$

Nonlinear nine equations in equations (10) and (11) are solved to get nine unknowns by Newton-Raphson method [11].

Table I: The initial conditions of the problems

Temp. (K)	298.0		
Pressure (bar)	1.0		
Starting comp.	$I_{2(aq)}, H_2O, I^-, H_2OI^+, H^+, OH^-$		
	Case 1	Case 2	Case 3
Starting moles of I_2	10^{-4}	10^{-6}	10^{-7}
Starting moles of H_2O	$2x10^{-4}$	$2x10^{-6}$	$2x10^{-7}$

Table II: Initial estimate moles of each species

Component	Case 1	Case 2	Case 3
	Initial est.(M)	Initial est.(M)	Initial est.(M)
$I_2(l)$	0.25E-4	0.25E-6	0.25E-7
H_2O	0.25E-4	0.25E-6	0.25E-7
H^+	0.25E-4	0.25E-6	0.25E-7
OH^-	0.25E-4	0.25E-6	0.25E-7
I^-	2.50E-4	2.50E-6	2.50E-7
H_2OI^+	0.50E-4	0.50E-6	0.50E-7

Table III: The molar Gibbs energy at standard conditions

Components	Stand. molar Gibbs energy (kJ/mol)
$I_2(l)$	16.4
H_2O	-192.42
I^-	-51.58
H_2OI^+	-92.6
H^+	0.0
OH^-	-157.28

Table IV: The calculated concentrations of species

Comp.	Case 1 (M)	Case 2 (M)	Case 3 (M)
$I_2(l)$	3.0866E-5	3.0866E-7	3.08E-8
H_2O	4.29E-5	4.29E-7	4.29E-8
I^-	1.28E-4	1.28E-6	1.28E-7
H_2OI^+	1.03E-5	1.03E-7	1.027e-8
H^+	1.468E-6	1.468E-6	1.45e-7
OH^-	1.468E-6	1.468E-6	1.45e-7

Table V: The calculated fractions of species

Comp.	Fraction of species
$I_2(l)$	0.061
H_2O	0.0848
I^-	0.253
H_2OI^+	0.02
H^+	0.29
OH^-	0.29
Total	1.0

Table VI: The calculation of pH in solution

	Case 1	Case 2	Case 3
pH	4.83	5.83	6.83

The Tables IV and V show the calculated concentration and fractions of the species in solutions. The pH's in solutions are also calculated by using the H^+ concentration as shown in Table VI. As shown in Table IV and V, the pH increases from acidic to alkaline solution as the concentration of total iodine in the solution decreases, that is, the $[I_2]$ concentration decreases from 10^{-4} M to 10^{-7} M.

5. Conclusion

Gibbs energies minimization method is successfully set to calculate the iodine species and the concentration of H^+ or pH in solution. The pH increases from acidic to alkaline solution as the concentration of total iodine in the solution decreases.

NOMENCLATURE

$\hat{a}$	Chemical activity
f	Rational activity coefficient
I, J	Number of species, elements
I, j, k	Indices: species, elements, time step
a_{ij}	The stoichiometric coefficients (=moles of element j occurring in 1 mole of species i)
b_j	The mole inventory of element j
N_m	Total mole in mixture phase
μ	Chemical potential
n_i	Mole inventories

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