Development of the Thermochemical Equilibrium Module for SGTR Iodine Analysis

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1. Introduction

The amount of radionuclides released into the containment or to the environment is always the focus of public safety for a nuclear power plant. In particular, since a large amount of radioactive materials might be released under the condition of a core melt accident (that is, a severe accident), it is very important to estimate the behaviors of radioactive materials under severe accident conditions. According to the notice of the Nuclear Safety and Security Commission (NSSC) issued in July 2016 [1], all the utilities are required to show that the summed frequency of the accidents, in which environmental release amount of radionuclide *Cs-137* exceeds 100 TBq, is less than 1.0×10^{-6}/Rx-Yr and to submit the accident management plans including severe accident cases by June 2019. The steam generator tube rupture (SGTR) associated with a core melt under severe accident conditions might possibly releases large amount of radionuclides into the environment bypassing the containment building [2]. However, the radionuclides release mechanism for this case is very complex and the mechanistic analysis methodology has not been fully developed yet.

Iodine and Cesium are the major radionuclides released from the primary heat transfer system for operating light water reactors (LWRs), considering their core inventories and release fractions. The radionuclides that are released from the core and circulate inside the reactor coolant system (RCS) during a postulated severe accident are injected into the building (or containment) atmosphere in the forms of aerosol and gas. The released radionuclides would chemically react with air, water, organic materials, or other nuclides, so that iodine entering a building was estimated as at least 95% *CsI* with the remaining 5% as *I* plus *HI* for LWR severe accidents [3]. Transport mechanism of the radionuclides inside an auxiliary building is essential to the estimation of fission product (FP) release to the environment, to which chemical reactions of radionuclides affect seriously as well as aerosol dynamics and thermal hydraulics inside the building.

The Korea Atomic Energy Research Institute (KAERI) has developed a severe accident integrated analysis code system, CINEMA (Code for Integrated severe accident Management Analysis), since 2011. The CINEMA consists of three parts; 1) analysis module of in-vessel phenomenon (CSPACE), 2) analysis module of ex-vessel phenomenon (SACAP), and 3) analysis module of fission product (FP) behavior (SIRIUS) [4]. The SIRIUS (Simulation of Radioactive nuclides Interaction Under Severe accidents) code has been developed to predict the behaviors of the radioactive materials in the reactor coolant system and in the containment under severe accident conditions [5]. The objectives of this study are to develop some chemical reaction models such as the general equilibrium thermal-chemistry model and the frozen chemistry model for the FP behavior analysis under severe accident conditions and to implement those in C++ computer programing language separately from the SIRIUS analysis module. The developed models were successfully verified against conceptual simple problems, which will be used to develop an Iodine chemistry module in the SIRIUS analysis module.

2. FP Chemical Reaction Module

The chemical forms of iodine in the RCS are closely tied to the chemical forms of cesium. The relationship between cesium and iodine in the RCS can be expressed as follow chemical reactions [6]:

$$CsI + H_2O \leftrightarrow CsOH + HI \tag{1}$$

At temperatures in excess of 1,800K and at low hydrogen pressures, iodine in the form of *I* is the favored products of the reaction between *CsI* and *H₂O*.

$$CsI + H_2O \leftrightarrow CsOH + I + \frac{1}{2}H_2 \tag{2}$$
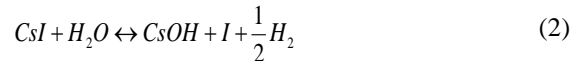
The chemical spectrum of chemical processes that could occur during a severe accident is extensive. Some chemical interactions are nonideal. Others are limited by mass transport kinetics, such as Zircaloy oxidation and the chemisorption of cesium onto oxidized Inconel or stainless steel. However, in most cases, chemical kinetics is rapid and the approach to equilibrium is well approximated as being instantaneous. This is generally true in regions where temperatures exceed 1,000 K; at temperatures well below 1,000 K, chemical kinetics may play a significant role [7]. In this study, the researches were limited to chemical equilibria in the reactor coolant system and in the buildings under severe accident conditions. And, treatment of chemical kinetics is remained for the future works.

2.1. General equilibrium thermal-chemistry model

At high temperature region under severe accident transients, chemical species react rapidly to attain thermochemical equilibrium. This rapid approach to equilibrium is treated as being instantaneous. Assume a chemical reaction as follows:

$$aA + bB \leftrightarrow cC + dD \qquad (3)$$

where A and B are reactants, and C and D are products of the chemical reaction in molar concentrations. And the constants a, b, c, and d are the stoichiometric coefficients. Then the equilibrium constant, K, becomes the following equation by the mass action law.

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (4)$$

Since the reaction quotient, Q, is defined as

$$\Delta G = \Delta G^o + RT \ln Q \qquad (5)$$

and $Q = K$ and $\Delta G = 0$ at equilibrium state,

$$K = \exp\left(-\frac{\Delta G^o}{RT}\right) . \qquad (6)$$

By using the solving mechanism in the VICTORIA code [7], the mole conservation equation for aerosol (condensed) and gaseous fission products becomes

$$\frac{n(i)}{V} = \sum_{j \in S} L_{ji} C(j) = \frac{1}{RT} \sum_{j \in G} L_{ji} p(j) + C_C \sum_{j \in C} L_{ji} x(j)$$
$$\text{for } i \in E . \quad (7)$$

where the set S, G and C are the sets of all species, all gas-phase species, and all condensed-phase species, respectively. Here $n(i)$ is the number of moles for element i and V is volume in m^3. $C(j)$ is the concentration of species j in kg-mol/m^3, $x(j)$ is the mole fraction of a condensed-phase species j, and C_C denotes the total concentration of a condensed-phase species. And, $p(j)$ is partial pressure of a vapor-phase species j, which is related to concentration by $p = CRT$ for an ideal gas. L_{ji} is the number of moles of element i in one mole of species j.

By applying a mass action law for gas-phase species with the obtained equilibrium constants, K's,

$$p(j) = C(j)RT = K_j \prod_{i \in E} p^{L_{ji}}(i) = K_j \prod_{i \in E} \left[C(i)RT\right]^{L_{ji}}$$
$$\text{for } j \in G . \quad (8)$$

Similarly for condensed-phase species, the mole fraction of a condensed-phase species j becomes

$$x(j) = \frac{C(j)}{C_C} = K_j \prod_{i \in E} p^{L_{ji}}(i) = K_j \prod_{i \in E} \left[C(i)RT\right]^{L_{ji}}$$
$$\text{for } j \in C . \quad (9)$$

Finally, the mole fraction of the condensed-phase species must sum to unity.

$$1 = \sum_{j \in C} x(j) = \sum_{j \in C} K_j \left[\prod_{i \in E} \left[C(i)RT\right]^{L_{ji}}\right] \qquad (10)$$

By substituting Eqs. (8) and (9) into Eq. (7), the mole conservation equation could be rearranged below.

$$\frac{n(i)}{V} = \frac{1}{RT} \sum_{j \in G} L_{ji} K_j \prod_{k \in E} \left[C(k)RT\right]^{L_{jk}} \text{, for } i \in E . \quad (11)$$
$$+ C_C \sum_{j \in C} L_{ji} K_j \prod_{k \in E} \left[C(k)RT\right]^{L_{jk}}$$

Now, the set of totally $(e+1)$ nonlinear equations composed of Eqs. (10) and (11) is solved using a dual iterative technique that uses both cyclic Newton and Newton-Raphson methods. Here, e is the number of elements in the set E.

For verification of the implemented general equilibrium thermal-chemistry model, a simple system containing 1.0 kg-mol/m^3 of gaseous oxygen, O_2(g), and 1.0 kg-mol/m^3 of gaseous europium, Eu(g), only was assumed. Here, g and c in the parenthesis denote respectively gas-phase and condensed-phases. All the possible chemical species that can be composed of O and Eu elements are O_2(g), O(g), Eu(g), Eu(c), EuO(g), EuO(c), Eu_2O_3(c), Eu_2O(g), and Eu_2O_2(g). Thus the initial concentrations, C_{ini}, were arbitrarily set to be as follows:

$C_{ini}[O_2(g)] = 1.0$, $C_{ini}[Eu(g)] = 1.0$, $C_{ini}[O(g)] = 0.0$, $C_{ini}[Eu(c)] = 0.0$, $C_{ini}[EuO(g)] = 0.0$, $C_{ini}[EuO(c)] = 0.0$, $C_{ini}[Eu_2O_3(c)] = 0.0$, $C_{ini}[Eu_2O(g)] = 0.0$, and $C_{ini}[Eu_2O_2(g)] = 0.0$ *The concentrations in kg-mol/m^3.

From the equation (7), the conservation of the numbers of moles of Eu and O elements per unit volume is expressed below:

$$\frac{n(Eu)}{V} = C[Eu(g)] + C[EuO(g)] + 2C[Eu_2O(g)]$$
$$+ 2C[Eu_2O_2(g)] + C[Eu(c)] + C[EuO(c)] + 2C[Eu_2O_3(c)]$$

$$\frac{n(O)}{V} = C[O(g)] + 2C[O_2(g)] + C[EuO(g)] + C[Eu_2O(g)]$$
$$+ 2C[Eu_2O_2(g)] + C[EuO(c)] + 3C[Eu_2O_3(c)]$$

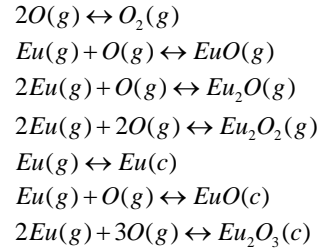Now, the formation reactions for each species from the vapor-phase elements Eu(g) and O(g) are as follows:

$$2O(g) \leftrightarrow O_2(g)$$
$$Eu(g) + O(g) \leftrightarrow EuO(g)$$
$$2Eu(g) + O(g) \leftrightarrow Eu_2O(g)$$
$$2Eu(g) + 2O(g) \leftrightarrow Eu_2O_2(g)$$
$$Eu(g) \leftrightarrow Eu(c)$$
$$Eu(g) + O(g) \leftrightarrow EuO(c)$$
$$2Eu(g) + 3O(g) \leftrightarrow Eu_2O_3(c)$$

Table I: Molar conservation of O and Eu elements at 2,000 K

Species	Concent-ration*	O element*	Eu element*
O_2(g)	2.49986E-1	4.9997E-01	-
O(g)	2.60978E-5	2.60978E-5	-
Eu(g)	1.1267E-13	-	1.1267E-13
Eu(c)	7.0331E-22	-	7.0331E-22
EuO(g)	4.8689E-09	4.8689E-09	4.8689E-09
EuO(c)	2.1080E-11	2.1080E-11	2.1080E-11
Eu_2O_3(c)	4.9999E-01	1.4999999	9.99999E-1
Eu_2O(g)	5.1109E-18	5.1109E-18	1.0221E-17
Eu_2O_2(g)	8.6193E-11	1.7238E-10	1.7238E-10
Total Mole Conc.		1.999974	1.0

* Concentrations in [kg-mol/m^3]

The mass action laws of the above reactions are

$$p(O_2) = K_1 p^2(O)$$

$$p(EuO) = K_2 p(Eu) p(O)$$

$$p(Eu_2O) = K_3 p^2(Eu) p(O)$$

$$p(Eu_2O_2) = K_4 p^2(Eu) p^2(O)$$

$$x(Eu) = K_5 p(Eu)$$

$$x(EuO) = K_6 p(Eu) p(O)$$

$$x(Eu_2O_3) = K_7 p^2(Eu) p^3(O)$$

With the relationship of $p = CRT$ and $x(i) = C(i)/C_C$, the conservation of the numbers of moles of *Eu* and *O* elements per unit volume become a form of the equation (11) as follows:

$$\frac{n(Eu)}{V} = C[Eu(g)] + K_2 RTC[Eu(g)]C[O(g)]$$

$$+ 2K_3(RT)^2 C^2[Eu(g)]C[O(g)] + 2K_4(RT)^3 C^2[Eu(g)]C^2[O(g)]$$

$$+ K_5 RTC[Eu(g)]C_C + K_6(RT)^2 C[Eu(g)]C[O(g)]C_C$$

$$+ 2K_7(RT)^5 C^2[Eu(g)]C^3[O(g)]C_C = 1\,\text{kg-mol/m}^3$$

$$\frac{n(O)}{V} = C[O(g)] + 2K_1 RTC^2[O(g)] + K_2 RTC[Eu(g)]C[O(g)]$$

$$+ K_3(RT)^2 C^2[Eu(g)]C[O(g)] + 2K_4(RT)^3 C^2[Eu(g)]C^2[O(g)]$$

$$+ K_6(RT)^2 C[Eu(g)]C[O(g)]C_C$$

$$+ 3K_7(RT)^5 C^2[Eu(g)]C^3[O(g)]C_C = 2\,\text{kg-mol/m}^3$$

Here, moles of *Eu* and *O* elements per unit volume are conserved to be 1.0 and 2.0 kg-mol/m^3, respectively.

Finally, the equation (10) can be rewritten for this case as follows:

$$1 = x(Eu) + x(EuO) + x(Eu_2O_3)$$

$$= K_5 RTC[Eu(g)] + K_6(RT)^2 C[Eu(g)]C[O(g)]$$

$$+ K_7(RT)^5 C^2[Eu(g)]C^3[O(g)]$$

This set of above three equations are iteratively computed in the developed module, for the three unknown concentrations of C[*Eu*(g)], C[*O*(g)], and C_C. For the temperature range of 1,000 K ~ 3,000 K, the equilibrium thermal-chemical states were computed as shown in Fig. 1. The trends of minor species such as *Eu*(g), *Eu*(c), *EuO*(c), and *Eu$_2$O*(g) can be identified in the log$_{10}$ Y-scale graph of Fig. 1(b). It is observed that the amounts of O_2(g), *O*(g), *Eu*(g), *Eu*(c), *EuO*(g), *EuO*(c), *Eu$_2$O*(g), and *Eu$_2$O$_2$*(g) increase with temperature rise, while only the concentration of *Eu$_2$O$_3$*(c) decreases.

To confirm conservation of the molar concentrations of *O* and *Eu* elements, the species molar concentrations are extracted at each temperature. Table I shows that molar concentrations of *O* and *Eu* elements are respectively ~2.0 and 1.0 at 2,000 K.

As a result, the developed subroutine was well verified to calculate the chemical equilibrium states depending on temperature. In the future study, some experimental data will be utilized for validation of the developed FP chemical reaction module.
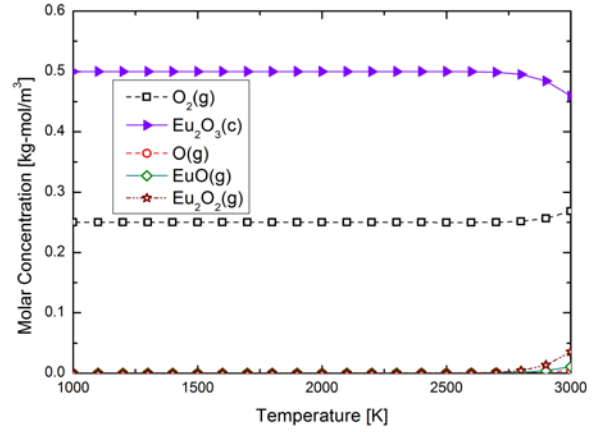
(a) Major species in linear Y-scale
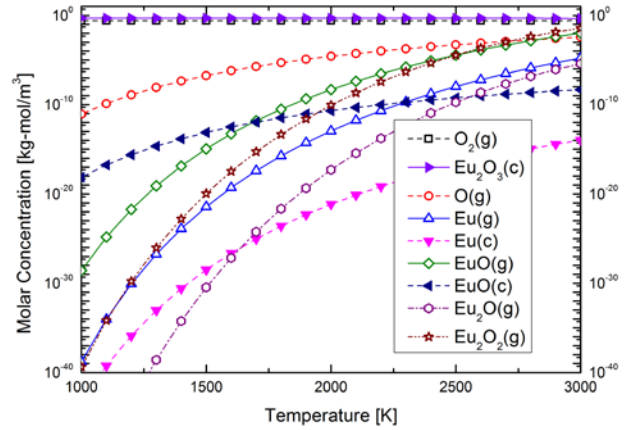
(b) All species in log$_{10}$ Y-scale

Fig. 1. Composition of Species of *Eu* and *O*, depending on temperature

2.2. Frozen chemistry model

The concept of the frozen chemistry model is that below a certain temperature threshold no chemical reactions occur, only simple phase changes. Since chemical interactions are not allowed in the frozen chemistry model, the following equation must be satisfied for all species *j*.

$$C_T(j) = C_G(j) + C_C(j) \tag{12}$$

where *C* is concentration in kg-mol/m^3, and subscripts *T, G* and *C* denote total, gas-phase, and condensed-phase, respectively. The equilibrium vapor-phase concentration can be expressed from Raoult's and the ideal gas laws as follows:

$$C_G(j) = \frac{n}{V} = \frac{p(j)}{RT} = \frac{p'(j)x(j)}{RT} = \frac{x(j)}{RT}\exp\left(-\frac{\Delta G}{RT}\right) \tag{13}$$

where *n* is the number of moles and *V* is volume in m^3 and *x(j)* is the condensed-phase mole fraction of species *j*.

By rearranging eqs. (12) and (13),

$$C_T(j) - C_C(j) - \frac{p'(j)}{RT}\frac{C_C(j)}{\sum_{k \in C_i} C_C(k)} = R_j = 0 \tag{14}$$

Here, the residual equation R_j is equal to zero as chemical equilibrium is attained.

In order to obtain a solution to Eq. (14), Newton-Raphson procedure is applied. The verification process and results are presented in the previous study [8].

2.3. Gas and liquid material properties

The equilibrium vapor pressure of pure species j is obtained by the following equation.

$$p'(j) = \exp\left(-\frac{\Delta G}{RT}\right) \tag{15}$$

Accordingly, the partial pressure of each vapor species j is expressed below by Raoult's law.

$$p(j) = p'(j)x(j) \tag{16}$$

The equilibrium vapor pressure of pure species j is calculated in the chemical reaction module, by rearranging eq. (15).

$$p'(j) = \exp\left(-\frac{\Delta G(j)}{RT}\right) = \exp\left(\frac{G_{gas}(j) - G_{con}(j)}{RT}\right) \tag{17}$$

where $G_{gas}(j)$ and $G_{con}(j)$ are respectively Gibbs free energies of the gas-phase and the condensed-phases species j, which are evaluated by the following equation.

$$G = a + bT + cT^2 + dT^3 \tag{18}$$

Here, T is temperature in Kelvin. The constants a, b, c, and d for totally 288 fission product species are stored as a lookup table in the chemical reaction module.

For the verification of the equilibrium vapor pressure calculation, the calculated equilibrium vapor pressures were compared with an empirical correlation from the NUREG/CR-5732 report [6]. The empirical correlation was calculated with data obtained from the FACT system. The FACT system has been transformed into FactSage© [9], which is one of the largest fully integrated database computing systems in chemical thermodynamics, a product of THERMFACT Ltd. The proposed vapor pressure of *CsI* over liquid for temperature range of 1,000 ~ 1,553 K was as follows:

$$p'(CsI) = \exp\left(-\frac{2.021 \times 10^4}{T[K]} + 1.307 \times 10\right) \tag{19}$$
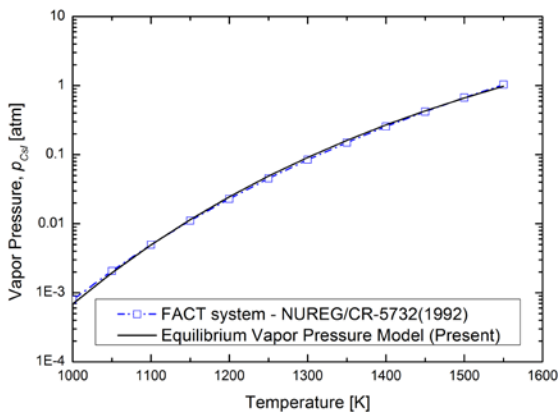

Fig. 2. Equilibrium vapor pressure of the pure *CsI* species

Figure 2 shows good agreement between the calculation result and the FACT equation. It was concluded that the equilibrium vapor pressure model has been implemented correctly.

3. Conclusions

In this study, the general equilibrium thermal-chemistry model and the frozen chemistry model were developed and implemented. The developed models were successfully verified against conceptual simple problems. For complete development of the FP chemical reaction module, development of the chemical kinetics model along with additional validation against experimental data is also in research schedule.

The developed FP chemistry module will be used to improve the iodine chemistry module in the SIRIUS analysis module, which would have the capability of mechanistic analysis of the FP release behavior under the SGTR accident conditions with a core melt.

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