

Implementation and Verification of the Chemical Reaction Models in the GAMMA-FP Fission Products Analysis Tool for VHTR Applications

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1. Introduction

The Korea Atomic Energy Research Institute (KAERI) has been developing a computer software to analyze the behaviors of the fission products (FP) circulating in the primary coolant loop and in the containment for a very high temperature gas-cooled reactor (VHTR). This software, named GAMMA-FP (GAs Multicomponent Mixture Analysis^[1] - Fission Products module), consists of four interconnecting modules, which are the thermal-dynamics module, the gaseous and the aerosol fission product analysis modules, and the chemical reaction module. The thermal dynamics module calculates the wall temperature and fluid properties as well as fluid velocities and temperatures within the control volumes, and transfers those data to the other modules. The aerosol FP module adopts a multi-component and multi-sectional aerosol analysis model (MAEROS^[2] model), and has been improved for 1-D aerosol transport.^[3] The gaseous FP module was developed to analyze the fission product plateau within the primary circuit as well as in the containment, which was validated against experiment data.^[4] In this study, some basic models of the FP chemical reaction module has been selected and implemented into the GAMMA-FP code. The general thermal equilibrium model was used for high temperature regions, and the frozen chemistry model was adopted for low temperature regions. A subsidiary subroutine calculating equilibrium gas pressure was also implemented and verified. These implemented chemical reaction models will be validated in the next stage of the research.

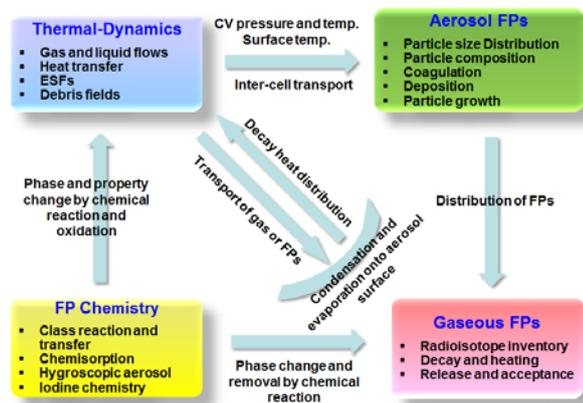


Fig. 1. Relationship and connectivity between the four modules of the VHTR FP analysis code, GAMMA-FP.

2. Model Implementation and Verification

2.1 Equilibrium Gas Pressure Calculation

When a simple phase change of the chemical species A occurs without any chemical reactions, reversible phase change reaction can be described as



Here, c and g denote the condensed-phase and the gas-phase respectively. The equilibrium vapor pressure of pure species A is obtained by the following equation.

$$p'(A) = \exp\left(-\frac{\Delta G}{RT}\right) \quad (2)$$

Accordingly, the partial pressure of each vapor species i is expressed as follows by Raoult's law.

$$p(i) = p'(i)x(i) \quad (3)$$

Here, $x(i)$ is the mole fraction of species i in the condensed phase in which it is soluble. The equilibrium vapor pressure of pure species is calculated in the subsidiary subroutine 'Relvp' of the GAMMA-FP chemical reaction module.

Rearranging eq. (2) gives

$$p'(i) = \exp\left(-\frac{\Delta G(i)}{RT}\right) = \exp\left(\frac{G_{\text{gas}}(i) - G_{\text{con}}(i)}{RT}\right). \quad (4)$$

where $G_{\text{gas}}(i)$ and $G_{\text{con}}(i)$ are respectively Gibbs free energies of the gas and the condensed phases of pure species i , which are evaluated by the following equation.

$$G = a + bT + cT^2 + dT^3 \quad (5)$$

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

For the verification of the equilibrium vapor pressure calculation, the calculated equilibrium vapor pressures were compared with those evaluated from empirical correlations. Blackburn and Johnson^[5] proposed the CsOH monomer pressure over liquid CsOH between 681 and 772 K by the equation.

$$\log_{10}(p_m [\text{atm}]) = -\frac{7217}{T[\text{K}]} + 5.640 \quad (6)$$

Konings and Cordfunke^[5] suggested the total vapor pressure above liquid CsOH between 676 and 976 K as follows.

$$\log_{10}(p_m + 2p_d [\text{atm}]) = -\frac{6414 \pm 148}{T[\text{K}]} + (4.763 \pm 0.180) \quad (7)$$

where p_m and p_d are the monomer and the dimer pressures in atm, respectively. The total pressure is assumed to be $(p_m + 2p_d)$.

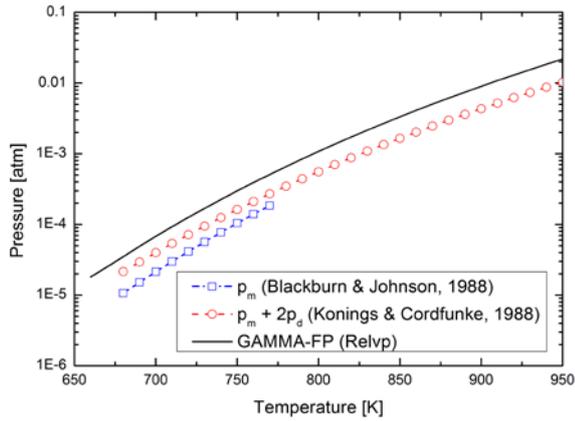


Fig. 2. CsOH equilibrium gas pressure.

Figure 2 presents the comparison result, which shows good agreement between the calculation result by 'Relvp' and the total vapor pressure by the Konings and Cordfunke equation. Therefore, it was concluded that the equilibrium vapor pressure model has been implemented correctly.

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.^[6] The frozen chemistry model would be activated and treated in the subroutine 'Chmfrz' of the GAMMA-FP chemistry module. Since chemical interactions are not allowed in the frozen chemistry model, the following equation must be satisfied for all species.

$$C_T(i) = C_G(i) + C_C(i) \quad (8)$$

where C is concentration in $\text{kg}\cdot\text{mol}/\text{m}^3$, 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:

$$C_G(i) = \frac{n}{V} = \frac{p(i)}{RT} = \frac{p'(i)x(i)}{RT} = \frac{x(i)}{RT} \exp\left(-\frac{\Delta G}{RT}\right), \quad (9)$$

where n is the number of moles and V is volume in m^3 . The condensed-phase mole fraction is defined as the following equation:

$$x(i) = \frac{C_C(i)}{\sum_{j \in C_i} C_C(j)} \quad (10)$$

By rearranging Eqs. (8), (9), and (10),

$$C_T(i) - C_C(i) - \frac{p'(i)}{RT} \frac{C_C(i)}{\sum_{j \in C_i} C_C(j)} = R_i = 0. \quad (11)$$

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

In order to obtain a solution to Eq. (11), Newton-Raphson procedure is applied. The Jacobian matrix of the residual equation R_i is obtained by taking the derivatives of the residual equations.

Table I: Verification calculation for the frozen chemistry model

Parameter	Resultant Value by GAMMA-FP
$C[\text{CsI}_c]$	9.999995E-1 [$\text{kg}\cdot\text{mol}/\text{m}^3$]
$C[\text{CsI}_g]$	5.223964E-7 [$\text{kg}\cdot\text{mol}/\text{m}^3$]
$p'(\text{CsI})$	5.863379E00 [Pa]
$x(\text{CsI}_c)$	0.6666846
$C[\text{CsOH}_c]$	4.999594E-1 [$\text{kg}\cdot\text{mol}/\text{m}^3$]
$C[\text{CsOH}_g]$	4.061228E-5 [$\text{kg}\cdot\text{mol}/\text{m}^3$]
$p'(\text{CsI})$	9.117383E02 [Pa]
$x(\text{CsOH}_c)$	0.3333154

$$J_{ij} = \frac{\partial R_i}{\partial C_c(j)} \quad (12)$$

$$\text{where } \frac{\partial R_i}{\partial C_c(i)} = -1 - \frac{p'(i)}{RT} \left[\frac{1}{\sum_{j \in C_i} C_c(j)} - \frac{C_c(i)}{\left(\sum_{j \in C_i} C_c(j)\right)^2} \right],$$

$$\text{and } \frac{\partial R_i}{\partial C_c(j)} = \frac{p'(i)}{RT} \left[\frac{C_c(i)}{\left(\sum_{k \in C_i} C_c(k)\right)^2} \right] \quad \text{for } i \neq j.$$

The final equation form of Newton-Raphson method is implemented as follows.

$$R_i + \sum_j J_{ij} \delta[C_c(j)] = 0 \quad (13)$$

where $\delta[C_c(j)]$ is correction to the concentration of the condensed-phase species j in $\text{kg}\cdot\text{mol}/\text{m}^3$. This system of equations is set to have converged when the largest relative correction is less than 10^{-3} .

For the verification of the implemented frozen chemistry model, a simple conceptual problem was raised and solved. We assumed that there exists the system containing gaseous and condensed phase CsI and CsOH at constant temperature of 900 K. Initial concentrations were arbitrarily set to be as follows:

$$\begin{aligned} C_{\text{ini}}[\text{CsI}_c] &= 1.0 \text{ kg}\cdot\text{mol}/\text{m}^3, & C_{\text{ini}}[\text{CsI}_g] &= 0.0 \text{ kg}\cdot\text{mol}/\text{m}^3, \\ C_{\text{ini}}[\text{CsOH}_c] &= 0.0 \text{ kg}\cdot\text{mol}/\text{m}^3, & C_{\text{ini}}[\text{CsOH}_g] &= 0.5 \text{ kg}\cdot\text{mol}/\text{m}^3, \\ & \text{and } C_{\text{C ini,tot}} &= 1.0 \text{ kg}\cdot\text{mol}/\text{m}^3 @ T = 900.0 \text{ K}. \end{aligned}$$

where subscripts *ini* and *tot* imply initial and total respectively. With this initial condition, the gas equilibrium pressure, the mole fractions in the condensed-phase, and the equilibrium concentrations as a result of 'Chmfrz' calculation are summarized in table I. It was confirmed that the subroutine 'Chmfrz' execute correctly, since the resultant values in table I satisfied the following equations with the gas constant R of $8314.3 \text{ J/kg}\cdot\text{mol}/\text{K}$.

$$C_G[\text{CsI}_g] = \frac{p'(\text{CsI}) \cdot x(\text{CsI}_c)}{RT}$$

$$C_G[\text{CsOH}_g] = \frac{p'(\text{CsOH}) \cdot x(\text{CsOH}_c)}{RT}$$

$$x(\text{CsI}_c) + x(\text{CsOH}_c) = 1$$

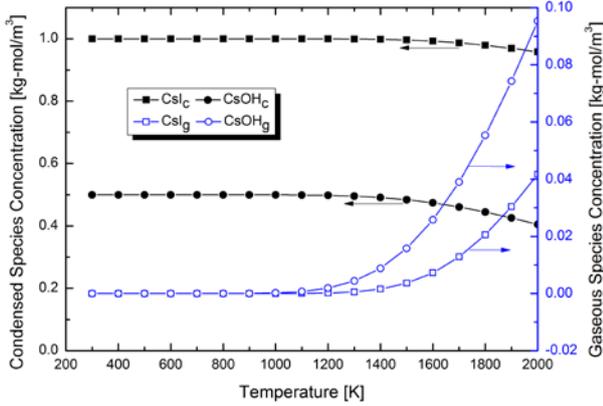


Fig. 3. Concentration variation as a function of temperature for the system containing CsI(1.0 kg-mol/m³) and CsOH(0.5 kg-mol/m³) only.

Figure 3 presents the equilibrium concentrations of the given system as a function of temperature calculated by the subroutine ‘Chmfrz’. The gas-phase concentration of both CsI and CsOH increase as temperature goes up.

2.3 General Equilibrium Thermochemistry Model

The general equilibrium thermochemistry model is implemented in the subroutine ‘Chmsty’ of the GAMMA-FP chemistry module, in which subroutine 26 basic elements and totally 288 fission product species are treated as like in the VICTORIA code^[6]. The fission product species consist of 110 aerosol species and 178 gaseous species. The mole conservation equation becomes

$$\frac{n(i)}{V} = \sum_{j \in S} L_{ji} C(j) = \frac{1}{RT} \sum_{j \in G} L_{ji} p(j) + C_c \sum_{j \in C} L_{ji} x(j) \quad \text{for } i \in E. \quad (14)$$

where S , G and C are the sets of all species, all gas-phase species, and all condensed-phase species, respectively. And 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,

$$p(j) = C(j)RT = K_j \prod_{i \in E} p^{L_{ji}}(i) = K_j \prod_{i \in E} [C(i)RT]^{L_{ji}} \quad \text{for } j \in G. \quad (15)$$

Similarly for condensed-phase species,

$$x(j) = \frac{C(j)}{C_c} = K_j \prod_{i \in E} p^{L_{ji}}(i) = K_j \prod_{i \in E} [C(i)RT]^{L_{ji}} \quad \text{for } j \in C. \quad (16)$$

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

$$1 = \sum_{j \in C} x(j) = \sum_{j \in C} K_j \left[\prod_{i \in E} [C(i)RT]^{L_{ji}} \right] \quad (17)$$

By substituting Eqs. (15) and (16) into Eq. (14), the mole conservation equation could be rearranged below.

$$\frac{n(i)}{V} = \frac{1}{RT} \sum_{j \in G} L_{ji} K_j \prod_{k \in E} [C(k)RT]^{L_{jk}} + C_c \sum_{j \in C} L_{ji} K_j \prod_{k \in E} [C(k)RT]^{L_{jk}}, \quad \text{for } i \in E. \quad (18)$$

Now, the set of totally $(e+1)$ nonlinear equations composed of Eqs. (17) and (18) 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 . The subroutine ‘Chmsty’ has been implemented, but the verification is being in progress.

3. Conclusions

Following development of other three modules such as the thermal-dynamics, the gaseous FP analysis, and the aerosol FP analysis modules, the FP chemical reaction module is being developed. For the basic FP chemical reaction model, the frozen chemistry model and the general equilibrium thermochemistry model have been implemented and partially verified in this study.

For complete development of the FP chemical reaction module in the GAMMA-FP code, the following researches should be conducted in the future.

- Accomplishment of the connectivity between the developed FP chemistry module with other modules in the GAMMA-FP
- Validation of the developed FP chemistry module
- Development of the FP chemisorption model onto structural surfaces
- Redistribution model of the decay heat and the heat of chemical reaction
- Iodine chemistry and other chemical models

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