

GAS-PHASE RESISTANCE TO THE VAPORIZATION OF MERCURIC HALIDES IN HIGH-TEMPERATURE ATMOSPHERIC GASEOUS CONDITION

Hee-Chul Yang[†], Joon-Hyung Kim, Yong-Chil Seo* and Yong Kang**

Department of Radwaste Treatment Technology, Nuclear Environment Management Center,
KAERI, P.O. Box 105, Yusong, Taejeon 305-600, Korea

*Department of Industrial Environment and Health, Yonsei University

**Department of Chemical Engineering, Chungnam National University

(Received 27 September 1995 • accepted 6 March 1996)

Abstract—Gas-phase resistances to the vaporization of three mercury halides into atmosphere at elevated temperatures were evaluated. Lab-scale vaporization experiments for mercuric bromide, mercuric iodide and mercuric chloride were performed and the results were analyzed to evaluate gas-phase resistance to vaporization of three mercuric halides using the vaporization and condensation model. Overall mass transfer coefficients, K_c , for the sample mercuric halides, were in the range between 4.8×10^{-6} and 1.6×10^{-5} g-mole $\text{sec}^{-1} \text{cm}^{-2} \text{atm}^{-1}$ at the temperatures from the subliming to boiling temperatures and were much smaller than interfacial mass transfer coefficients, k_c . It was estimated that resistance of pure gas-phase mass transfer is much larger than that of the phase transition between condensed and gas phases. It could be therefore said that gas-phase mass transfer coefficients, k_c , for mercuric halides, were nearly equal to overall mass transfer coefficient, K_c , which could be determined as a function of temperatures.

Key words: Mercuric Halides, Vaporization, Interfacial Resistance, Gas-phase Mass Transfer Coefficient, Condensation-vaporization Model

INTRODUCTION

Mercury is a naturally occurring substance, existing as a pure element or an organic and inorganic compound in different geologic circumstances [Aylett, 1975]. The element is used in a variety of industrial and consumer products and in a number of industrial processes. These industries and the products generate the waste containing mercury. Toxicity of mercury has led to increasingly stringent regulations on the treatment, storage and disposal of mercury-containing waste and also on use, recovery and recycle of the metal [USEPA, 1993].

Thermal treatment such as an incineration is an effective means to treat waste including metals containing hazardous organic constituents. It gives high volume reduction and safe disposal by the destruction of complex organic materials. Unlike hazardous organics, metals are not destroyed during thermal treatment but changed into the stable chemical forms in the combustion condition. Stable chemical forms of mercury in the oxidizing thermal conditions are elemental mercury (Hg) or mercuric oxide (HgO) depending on the local oxygen pressure. Both elemental mercury and mercuric oxide are volatile and mercury vapor coming out of the thermal treatment equipment could be condensed out of off-gas by cooling [Aulbau and Hawk, 1995]. In the presence of halogens the most stable forms of mercury are mercuric halides. If the halogens are present in the local surroundings, the elemental mercury and mercuric oxide may undergo a chemical reaction and form halides, which are more volatile than the oxide. Therefore the higher temperature and the longer residence time in an in-

cinerator, which are normally required for the destruction of halogenated organic materials such as polyvinylchloride (PVC) results in greater vaporization of mercury constituents. Recognizing the inability to control vapor-phase metal compounds and the submicron size range of their condensed form in the off-gas, the vaporization rates of mercuric halides during thermal treatment are much of concern.

Many studies on the behavior of toxic metals including mercury in a thermal treatment process have been brought to focus on the establishment of metals distribution, which is referred to as "partitioning" based on the examination of the metal elements found in fly ash, bottom ash and scrubber residue, etc [Law and Goldon, 1979]. Others are concerning about the computational modeling of the behavior of metals in the process based on the thermodynamic equilibrium calculation. There could have been significance differences between the results of partitioning in real thermal treatment process and equilibrium model calculations because of unknown kinetic factors such as the resistance of waste and/or ash matrices, interfacial resistance between gaseous and condensed phase and pure gas-phase resistance [Wu et al., 1994].

An attempt to relate the vaporization rate of several volatile metal chlorides with interfacial resistance was made in previous study [Yang et al., 1994]. Based on the assumption that interfacial resistance was much larger than that of gas-phase mass transfer, overall mass transfer coefficients were evaluated. If the condensation coefficient for vaporizing substance is known, however, interfacial and gas-phase resistance can be evaluated respectively without such an assumption. In this concern, interfacial and gas-phase resistances of three vaporizing mercuric halides, of which condensation coefficients are known, are investigated in this study.

[†]To whom all correspondences should be addressed.

EXPERIMENT

Mercuric bromide (HgBr_2), Mercuric chloride (HgCl_2) and Mercuric iodide (HgI_2) were used as sample mercuric halides. The purity of HgBr_2 was over 98%, and those of both HgCl_2 and HgI_2 were over 99.99%. Vapor pressure data, melting point and boiling point for sample compounds were compiled in Table 1.

The sample compounds were heated in the thermogravimetric device. Conditioning gas was fed with a flowrate of 5 L/min and the off-gas was withdrawn with the same volumetric flowrate in order to maintain atmospheric pressure in the furnace. Conditioning gas was composed of 21% O_2 and 79% N_2 . The system consisted of a furnace, a control and data acquisition system, and a gas-conditioning system for the furnace. A schematic diagram of the furnace is shown in Fig. 1. The temperature was increased with the rate of $4^\circ\text{C}/\text{min}$ from the room temperature to 400°C . The temperature of the furnace and the weight of sample were recorded and stored in the computer.

RESULTS AND DISCUSSION

1. Vaporization Flux

The weight changes for mercuric chloride (HgCl_2), mercuric bromide (HgBr_2), mercuric iodide (HgI_2) in the thermogravimetric furnace under experimental condition were shown in Fig. 2. All of the sample compounds were sublimed with the starting temperature of about 200°C .

The weight losses of the mercuric halides are basically attributed to the emitting of vapor-phase themselves because the stable form in the presence of halogens (X) are halides. Thus the general reaction form of the vaporization or sublimation is as follows;

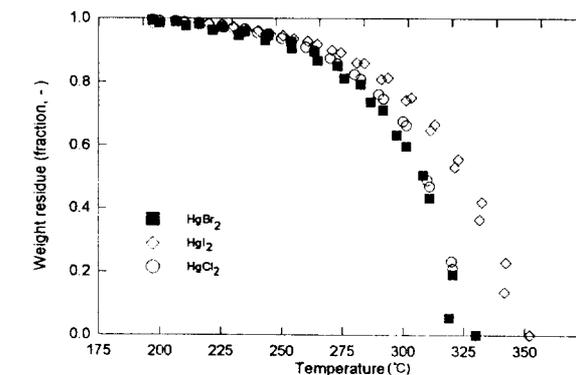


Fig. 2. Weight loss of sample mercuric halides with temperatures.



Assuming the interfacial area for vaporization is constant and equal to the inner cross-sectional area of the crucible above the melting temperatures, the vaporization flux of the sample compounds due to reaction Eq. (1) can be obtained from the weight loss per unit time and is given as follows;

$$N_v = \frac{1}{AM} \frac{dW}{dt} = - \frac{1}{AM} \frac{W_1 - W_2}{\Delta t} \quad (2)$$

A is the cross-sectional area of the crucible (cm^2), M is the molecular weight of sample mercuric halide (g/mole) and dW is the weight changes (g) during the differential time, dt (sec). Experimentally obtained vaporization fluxes for three mercuric halides are shown in Fig. 3, 4 and 5. The best fits for the experimentally obtained fluxes to the temperatures are exponential because the driving force for vaporization is vapor pressure which increases exponentially with temperature elevation. The vapor pressures, which could be normally obtained by Knudsen-Effusion Method in vacuum, are also noted as solid lines. The differences between solid and dashed lines are attributed to the resistance of foreign gas to the evaporating gas molecules. The following simple model was developed to evaluate gas-phase resistance to the evaporating gas molecules.

2. Condensation and Vaporization Model

The condensation and vaporization model for the evaluation of gas phase resistance to vaporization of metal compounds without any chemical reaction as in Eq. (1) is shown in Fig. 6. In equilibrium condition, vapor pressure at liquid-gas interface, P_v , is equal to vapor pressure at liquid surface, P_l . There is no net transfer from one phase to other phase in such condition. However, the gas molecules are moving at high speed. Some of the moving gas molecules strike liquid surface and a certain fraction of them are incorporated in the liquid. The rate of collision of the gas molecules with the surface is readily calculated from the classical kinetic theory of the gas [Lamoraux and Hildenbrand, 1987] and is given by,

$$\frac{dn}{dt} = P_l (2\pi mkt)^{1/2} \quad (3)$$

where (dn/dt) is the number of molecules per unit time, passing through an arbitrary plane of 1 cm^2 area randomly placed in the gas phase, m is the molecular mass, k is Boltzmann constant and t is time. Introducing the conventional units to Eq. (3)

Table 1. Vapor pressure data of sample mercuric halides

Substance	log p (mmHg)				Temperature range (K)
	A	B	$C \times 10^3$	D	
$\text{HgCl}_2(\text{s})^{(1)}$	-4,580	-2.0	-	16.39	298-m.pt.
$\text{HgBr}_2(\text{s})^{(1)}$	-4,500	0.05	-1.51	11.47	298-m.pt.
$\text{HgBr}_2(\text{l})^{(1)}$	-4,370	-5.03	-	24.18	m.pt.-b.pt.
$\text{HgI}_2(\text{s})^{(1)}$	-5,690	-6.47	-	30.27	298-m.pt.
$\text{HgI}_2(\text{l})^{(1)}$	-4,620	-5.53	-	25.72	m.pt.-b.pt.
	a		b		
$\text{HgCl}_2(\text{l})^{(2)}$	61,020		8.409		548-582

⁽¹⁾log p = $A \cdot T^{-1} + B \cdot \log T + C \cdot T + D$ (mmHg) [Kubasewski, 1979]

⁽²⁾log p = $-0.05223a/T + b$ (mmHg) [Weaf, 1989]

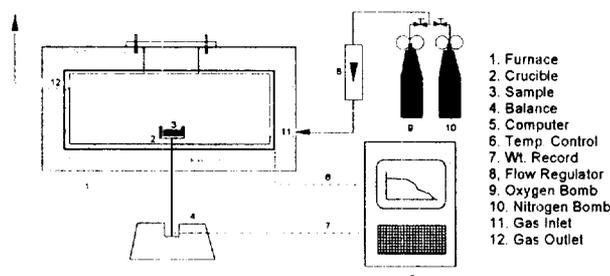


Fig. 1. A schematic diagram of thermogravimetric furnace.

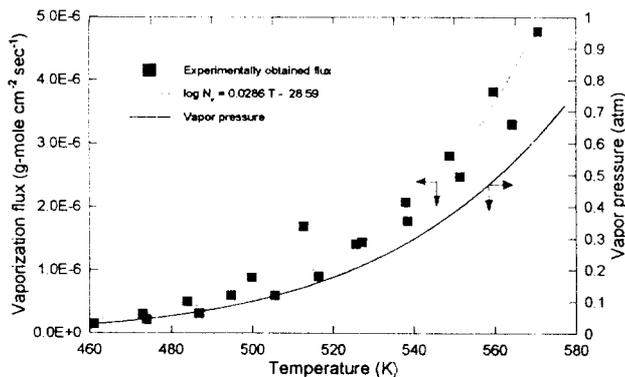


Fig. 3. Experimentally obtained vaporization flux and vapor pressure of Mercuric Bromide (HgBr₂).

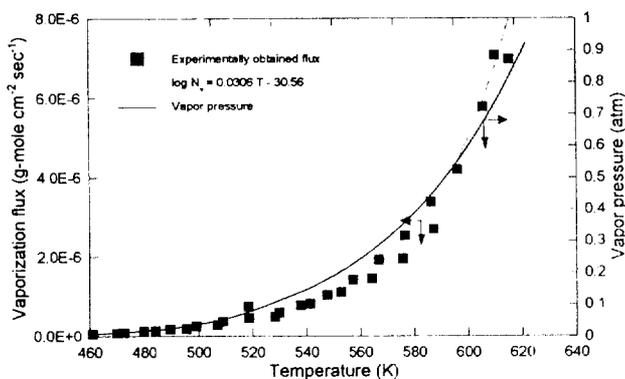


Fig. 4. Experimentally obtained vaporization flux and vapor pressure of Mercuric Iodide (HgI₂).

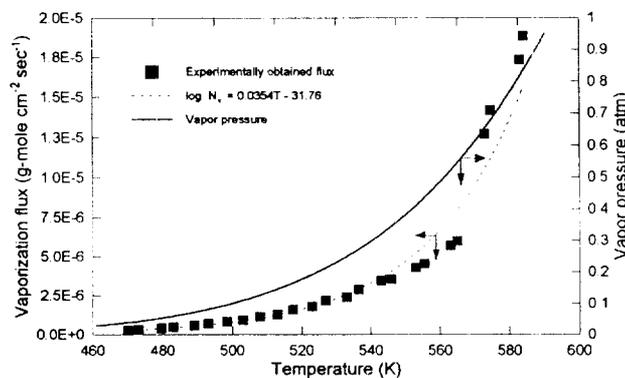


Fig. 5. Experimentally obtained vaporization flux and vapor pressure of Mercuric Chloride (HgCl₂).

gives the following equation for colliding mole flux with the liquid surface [Yang et al., 1994].

$$N = \frac{P_i}{(2\pi MRT_i)^{1/2}} \quad (4)$$

In Eq. (4), N is mole flux of colliding gas molecules with the liquid surface in $\text{g-mole cm}^{-2} \text{sec}^{-1}$, P_i is partial pressure of gas molecules at the interface in atm, and M is molecular weight of the gas molecules. Some fraction α of these colliding molecules remains in the liquid while the fraction $1-\alpha$ rebounds to the gas. In equilibrium condition, evaporation must occur at the same rate of condensing molecules. Therefore, net vaporization

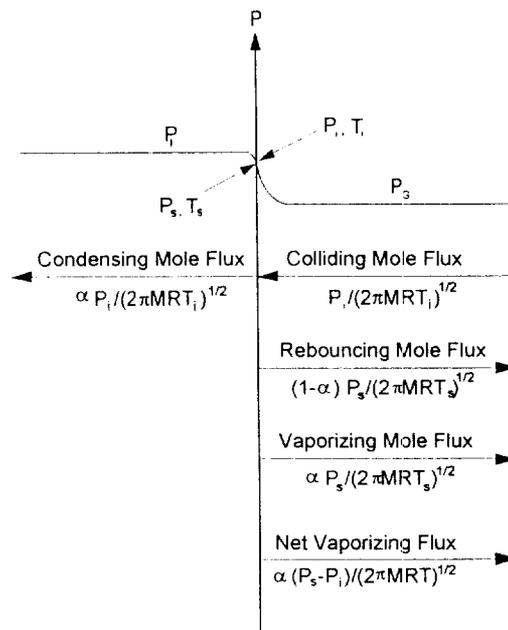


Fig. 6. Condensation and vaporization model at gas-liquid interface.

flux is given by the difference between the rates of vaporizing and condensing molecules at the liquid surface regarding that T_s is equal to T_i as T .

$$N_v = \frac{44.3\alpha(P_s - P_i)}{(MT)^{1/2}} \quad (5)$$

α is condensation coefficient. α and P_s are functions of only liquid surface at the temperature. In the equilibrium condition, P_i is equals to P_s and there is no net mass transfer between condensed phase and gas phase. In non-equilibrium condition which vaporization occurs, P_i is smaller than P_s since the gas molecules at interface are disappearing into the foreign gas. In such condition that the gas molecules at interface is completely removed without resistance of any foreign gas in vacuum, the maximum vaporization flux is given by introducing P_i as zero in Eq. (5).

In the normal atmospheric gaseous condition, foreign gas reduces the vaporization rate. One can evaluate this gas-phase resistance by introducing general gas-phase mass transfer coefficient, k_G , and is given by the Eq. (6).

$$k_G = N_v / (P_i - P_G) \quad (6)$$

In making assumption of interfacial equilibrium, P_i is replaced by P_s in the calculation of overall mass transfer coefficient, K_G with Eq. (6).

$$K_G = N_v / (P_s - P_G) \quad (7)$$

Combining Eq. (5) and (6) the rate of phase transition to the rate of transport into the foreign gas is given by Eq. (8).

$$k_G(P_i - P_G) = \frac{44.3\alpha(P_s - P_i)}{(MT)^{1/2}} \quad (8)$$

Solving Eq. (8) for P_i and substituting into Eq. (6) gives;

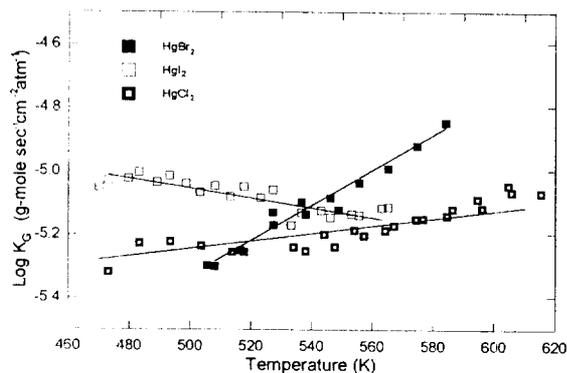


Fig. 7. Overall mass transfer coefficients for vaporization of mercury halides with temperatures.

$$N_v = \frac{k_G(P_s - P_G)}{1 + (MT_s)^{1/2}k_G/(44.3\alpha)} \quad (9)$$

Eq. (9) shows the relation between the experimentally obtained overall mass transfer coefficient based on the interfacial equilibrium and actual gas-phase mass transfer coefficient,

$$K_G = \frac{k_G}{1 + (MT_s)^{1/2}k_G/(44.3\alpha)} \quad (10)$$

where K_G is based on $P_s - P_G$, and k_G is based on the actual driving force $P_i - P_G$, namely. Rearranging Eq. (10) pure gas-phase mass transfer coefficient, k_G , can be readily obtained by interfacial resistance, R_i , and overall mass transfer coefficient, K_G .

$$\frac{1}{K_G} = \frac{1}{k_G} + R_i \quad (11)$$

In Eq. (11), R_i is equal to the reciprocal of the interfacial mass transfer coefficient k_i ,

$$R_i = 1/k_i = 0.0225(MT)^{1/2}/\alpha \quad (12)$$

3. Overall Mass Transfer Coefficient

The overall mass transfer coefficient for vaporization of the sample mercuric halide, K_G , is determined by the comparison of experimentally obtained vaporization flux in Eq. (2) to vaporization flux using Eq. (6) assuming the partial pressure in the bulk gas, P_G , is equal to zero. Obtained overall mass transfer coefficients for mercuric halides are shown in Fig. 7. The values of K_G were ranged between 3.17×10^{-6} and 4.96×10^{-6} g-mole sec⁻¹ cm⁻² atm⁻¹. K_G for HgBr₂ and HgCl₂ increased and that for HgI₂ decreased with temperature elevation. Logarithmic values of K_G changed linearly with temperatures. Overall mass transfer coefficients for the vaporization of sample mercuric halides could be determined as a function of the temperature. The values of overall mass transfer coefficients as a function of absolute temperature are noted as solid lines in Fig. 7.

4. Interfacial Resistance

Condensation coefficient for mercuric halides lies in the range of 0.1 to 0.64. Assuming the values of condensation coefficient, which was measured at limited temperature range, was not varying with the temperatures, the values of interfacial

Table 2. Condensation coefficient [Paul, 1962] and interfacial resistance for the vaporization of sample mercuric halides

Substance	Condensation coefficient, α	Interfacial resistance, $R_i \times 10$, sec cm ² atm g-mole ⁻¹	Temperature range, K
HgBr ₂	0.64(±0.1)	1.43-1.60	188-304
HgI ₂	0.53(±0.1)	7.96-9.73	188-349
HgCl ₂	0.1	1.94-2.26	188-416

Table 3. Pure gas-phase mass transfer coefficients for the vaporization of mercuric halides (log $k_G = AT + B$)

Substance	log k_G (g-mole sec ⁻¹ cm ⁻² atm ⁻¹)		Temperature range (K)
	10 ³ A	B	
HgBr ₂	5.59	-8.11	508-584
HgI ₂	-1.55	-4.28	506-549
HgCl ₂	1.19	-5.84	470-610

mass resistance for the vaporization of sample mercuric halides could be determined as a function of temperature by Eq. (12). Interfacial resistance, $1/k_i$, which determined by condensation coefficient α as a function of temperature, was listed in Table 2.

5. Gas-phase Mass Transfer Coefficient

To evaluate gas-phase mass transfer coefficients, overall mass transfer coefficients were compared to interfacial mass transfer coefficient, k_i . Overall mass transfer coefficients, K_G , were much smaller than interfacial mass transfer coefficient k_i . In other words, the resistance of gas-phase mass transfer is much larger than that of the phase transition between condensed and gas phases. Therefore it can be positively said that pure gas-phase mass transfer coefficients, k_G for tested mercuric halides, were nearly equal to experimentally obtained overall mass transfer coefficient, K_G . The estimated gas-phase mass transfer coefficients are listed in Table 3.

CONCLUSIONS

The resistance of gas-phase mass transfer for the vaporization of three mercury halides in atmospheric gaseous condition at elevated temperatures was much larger than that of interfacial resistance on phase transition between condensed and gas phase. Gas-phase mass transfer coefficients were nearly the same as overall mass transfer coefficients and the values were in the range between 4.8×10^{-6} to 1.6×10^{-5} g-mole sec⁻¹ cm⁻² atm⁻¹. Logarithmic values of gas-phase mass transfer coefficients changed linearly with the temperature increase. Gas-phase mass transfer coefficients for the vaporization could be obtained as a function of absolute temperatures.

ACKNOWLEDGEMENT

This work has been performed by Radioactive Waste Management Fund.

NOMENCLATURE

- A : cross-sectional area of the crucible [cm²]
 k : Boltzmann constant, 1.3805×10^{-16} erg K⁻¹ molecule⁻¹

M : molecular weight [g g-mole⁻¹]
K_G : overall mass transfer coefficient [g-mole sec⁻¹ cm⁻² atm⁻¹]
k_G : gas-phase mass transfer coefficient [g-mole sec⁻¹ cm⁻² atm⁻¹]
k_L : interfacial mass transfer coefficient [g-mole sec⁻¹ cm⁻² atm⁻¹]
m : mass of evaporating or vaporizing substance [g]
N : mole flux of colliding gas molecules with the liquid surface [g-mole cm⁻² sec⁻¹]
N_v : mole flux of evaporating gas molecules from the liquid surface [g-moles cm⁻² s⁻¹]
P_G : partial pressure in bulk gas [atm]
P_i : pressure due to gas molecules existing at the interface [atm]
P_v : vapor pressure at the surface of the liquid [atm]
R : gas constant, 82.03 cm³ atm g-mole⁻¹ s⁻¹
R_i : interfacial resistance [sec cm² atm g-mole⁻¹]
T : absolute temperature [K]
t : time [sec]
T_L : absolute temperature of liquid surface [K]
T_i : absolute temperature of gas at the interface [K]
W : weight of sample [g]

Greek Letter

α : condensation coefficient [-]

REFERENCES

- Aulbau, R. and Hawk, G., "High Temperature High Vacuum Mobile Retort for Recovery of Mercury and Removal of Organic Chemicals", 1995 International Incineration Conference, Bellevue, Washington, USA, 723 (1995).
- Ayllett, "The Chemistry of Zinc, Cadmium and Mercury", Pergamon Press, 275 (1975).
- Kelly, K., US. Bur. Mines. Bull., 383 (1935).
- Kiwa, K., "Vapor Pressure of Iodides, Bromides and Chlorides of Alkali Metals and Ti, Pb, Zn, Cd, Te and Hg", *J. Fads. Sci.*, **17**(5), 3 (1940).
- Lamoreaux, R. H. and Hildenbrand, D. L., "High-temperature Behavior of Oxides II. Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Ti, Si, Ge, Sn, Pb, Zn, Cd and Hg", *J. Phys. and Chem.*, **13**, 151 (1987).
- Law, S. L. and Goldon, G. E., "Source of Metals in Municipal Incinerator Emissions", **13**(4), 432 (1979).
- Paul, B., "Compilation of Evaporation Coefficients", *ARS J.*, 1324 (1962).
- USEPA/625/R-93/008, Operation Parameters for Hazardous Waste Combustion Devices, USEPA, 29 (1993).
- Weasf, R. C., Handbook of Chemistry and Physics, D-215 (1989).
- Wu, C. Y., Biswas, B. and Fendinger, N. J., "Models to Assess Heavy Metal Emission from Municipal Solid Waste Incineration", *Hazardous Waste and Hazardous Materials*, 71 (1994).
- Yang, H. C., Seo, Y. C., Kim, J. H., Park, H. H. and Kang, Y., "Vaporization Characteristics of Heavy Metal Compounds at Elevated Temperatures", *KJChE*, **11**(4), 232 (1994).