Determination of Optimal Vapor Pressure Data by the Second and Third Law Methods

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Though equilibrium vapor pressures are utilized to determine thermodynamic properties of not only gaseous species but also condensed phases, the obtained data often disagree by a factor of 100 and more. A new data analysis method is proposed using the so-called second and third law procedures to improve accuracy of vapor pressure measurements. It was found from examination of vapor pressures of cesium metaborate and silver that the analysis of the difference between the second and third law values can result in determination of an optimal data set. Since the new thermodynamic method does not require special techniques or experiences in dealing with measured data, it is reliable and versatile to improve the accuracy of vapor pressure evaluation.

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INTRODUCTION

Equilibrium vapor pressure data are utilized to determine thermodynamic properties of not only gaseous species but also condensed phases. But, vapor pressure measurement generally has a large uncertainty as mentioned in the preface of a handbook on thermodynamic data,1) “vapor pressures are not infrequently reported which disagree by a factor of 100 or more,” or as said in another paper,2) “experience in vapor pressure measurements, particularly at high temperatures, has shown that large systematic errors are common, even among experienced investigators.” Moreover, another thermodynamic data hand book3) says “when calorimetric data were available, they were given considerably more weight than values determined from vapor pressure data.” Based on this situation, the so-called second and third law procedures are considered as a method to improve accuracy of vapor pressure measurement. The second and third law methods4,5) are commonly used to determine reaction enthalpy from equilibrium constant measured in experiment, for example, to determine vaporization enthalpy in terms of vapor pressure measurement. In addition, examination of the difference of the determined enthalpies between those calculated by the second and third law methods has been utilized to check whether the Gibbs energy functions and equilibrium data are mutually consistent6) or to check whether cause of systematic errors are under control.7) As for Gibbs energy functions, even if in the absence of experimental data, satisfactory estimates can usually be made by a variety of procedures and uncertainties calculated from experimental molecular parameters are said to be small, i.e., ±0.2 to 0.4 J K⁻¹ mol⁻¹.8,9) These uncertainties could correspond to a two to five percent error in the equilibrium constant which is assumed to have the same uncertainty level as the Gibbs energy functions.

Therefore, such a thermodynamic method based on the second and third laws can be used to improve accuracy of vapor pressure data especially if Gibbs energy functions are determined based on experimental data. This paper concerns about application of the second and third law methods for determination of optimal vapor pressure data. The new evaluation method is practically applied for equilibrium vapor pressure data of cesium metaborate, CsBO₂, which is one of the most important chemical species having significant radiological impact in a severe accident like the one that occurred at Fukushima Daiichi Nuclear Power Station. Vapor pressures of silver given by nine laboratories7) were also evaluated by the present method.

THERMODYNAMIC METHOD FOR DETERMINATION OF OPTIMAL VAPOR PRESSURES

The new thermodynamic method to determine optimal vapor pressures proposed in this study is based on the second and third law methods. In the third law method,8,9) enthalpy changes of investigated reactions, Δ_rH°, can be determined from each experimental value of equilibrium constant, K_p°, using the following relation:
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\[ \Delta H^\circ_{\text{vap}}(\theta) = -RT \ln K_p(T) - T \Delta \text{geff}^\circ(T) \]  
(1)

where \( \theta \) is reference temperature of 0 or 298.15 K, \( R \) gas constant, \( T \) absolute temperature, and \( \text{geff} \) Gibbs energy function. \( \Delta \) signifies the difference between thermodynamic quantities of products and reactants. The subscript \( (\cdot) \) denotes reaction. The superscript \( \circ \) refers to standard-state pressure of 1 bar. The Gibbs energy function is defined as

\[ \text{geff}^\circ(T) = -S^\circ(T) + (H^\circ(T) - H^\circ(\theta))/T \]  
(2)

where \( S \) is entropy, \( \Delta \) Gibbs energy function of gaseous species can be calculated from molecular parameters by the use of statistical mechanics. While, Gibbs energy function of condensed phases can be obtained from heat capacity \( C_p \) by the use of the van't Hoff equation, Eq. (4), so that a plot of measured vapor pressure data, such compensations are unlikely to occur.

\[ \gamma_{\text{vap}} \text{average} \] is determined from the average value of \( 1/T \) over the temperature range. So more precise measurement of optimal data set of vapor pressures. In some cases, the choice of wrong data set of vapor pressures due to fortuitous analysis of an Arrhenius plot:

\[ \Delta H^\circ_{\text{vap}}(\theta) = -RT \ln K_p(T) - T \Delta \text{geff}^\circ(T) \]  
(3)

On the other hand, in the second law method, \( ^{10} \) van’t Hoff equation:

\[ \Delta H^\circ(T)/T^2 = R \ln K_p(T) - R \ln K_p(T) \]  
(4)

or

\[ \Delta H^\circ(T)/T = -R \ln K_p(T) \]  
(5)

is used. Equation (5) is derived by substituting \( dT = T^2 d(1/T) \) into Eq. (4) or from the relation:

\[ -R \ln K_p(T)/d(1/T) = d(\Delta G^\circ(T))/dT \]  
(6)

assuming that both of \( \Delta H^\circ(T) \) and \( \Delta S^\circ(T) \) are constant with temperature. Thus, \( \Delta H^\circ(T) \) at average temperature, \( T_{\text{ave}} \), is obtained from measured vapor pressure data, \( K_p(T) \) by a least-squares analysis of an Arrhenius plot:

\[ \ln K_p(T) = A - \Delta H^\circ(T_{\text{ave}})/T \]  
(7)

where both of \( A \) and \( \Delta H^\circ(T_{\text{ave}}) \) are fitting parameters. It is noted that \( T_{\text{ave}} \) is determined from the average value of \( 1/T \) for the measurements. Then, \( \Delta H^\circ(T) \) is reduced to the reference temperature \( \theta \) K through the use of heat content functions, \( \Delta H^\circ(T_{\text{ave}}) = \Delta H^\circ(\theta) \):

\[ \Delta H^\circ_{\text{vap}}(\theta) = \Delta H^\circ(T_{\text{ave}}) - \Delta H^\circ(\theta) \]  
(8)

But this procedure does not take into account for the temperature dependence of \( \Delta H^\circ(T) \) within the measured temperature range. So more precise \( \Delta H^\circ_{\text{vap}}(\theta) \) can be obtained from the so-called \( \Sigma \) plot:

\[ \ln K_p(T) = \frac{T^2}{R} \int_0^T \left[ \int_0^T \frac{\Delta C_p dT'}{T'^2} dT' + \Delta H^\circ(\theta) - \Delta H^\circ(0)/T \right] \]  
(9)

where \( T' \) and \( T'' \) are variables of the integrations and \( A' \) is a fitting parameter. This equation is obtained by integrating the van’t Hoff equation, Eq. (4), so that a \( \Sigma \) plot of measured \( K_p(T) \) will have linear dependence on \( 1/T \).

Now, this integration can further be changed to the following equation:

\[ \int_0^T \left[ \int_0^T \frac{\Delta C_p dT'}{T'^2} dT' + \Delta H^\circ(\theta) - \Delta H^\circ(0)/T \right] = -R \ln K_p(T) - R \ln K_p(T) \]  
(10)

Then, Eq. (9) can be transformed to the following equation:

\[ A' - \Delta H^\circ_{\text{vap}}(\theta)/T \]  
(11)

and, when temperature-independent constants of \( A' \) and \( \Delta S^\circ(0) \) are combined into a single constant \( \Delta \) for simplicity, similar equation to Eq. (1) can be obtained:

\[ \frac{R \ln K_p(T) - R \ln K_p(T)}{T} = A' + \Delta H^\circ_{\text{vap}}(\theta)/T \]  
(12)

Actually, this equation can also be derived by integrating the van’t Hoff equation, Eq. (4), from 0 K to the temperature of interest and we can find the following equation:

\[ -R \ln K_p(T) - R \ln K_p(T) = \Delta S^\circ(0) + \Delta H^\circ_{\text{vap}}(\theta)/T \]  
(13)

by use of the relation:

\[ -R \ln K_p(T) \rightarrow 0 \text{K} = \Delta G^\circ(0) = \Delta H^\circ(0) \]

Thus, in the case of the second-law method, two or more measured \( K_p(T) \) is necessary to determine the value of \( \Delta H^\circ_{\text{vap}}(\theta) \) since the second law of thermodynamics cannot provide the relation: \( \Delta S^\circ(0) = 0 \). On the other hand, the third law value can be obtained even from a single measured \( K_p(T) \) by use of Eq. (1) since the third law of thermodynamics can provide \( \Delta S^\circ(0) = 0 \). In addition, when the temperature is multiplied on both sides of Eqs. (12) or (13), the left-hand side is the same as the right-hand side of Eq. (1). Then, if both the measured \( K_p(T) \) and \( \Delta \text{geff}^\circ(T) \) are accurate, \( \Delta \) can become close to zero and \( \Delta H^\circ_{\text{vap}}(\theta) \) can also agree well with \( \Delta H^\circ_{\text{vap}}(\theta) \). Therefore, examination of difference of the values between \( \Delta H^\circ_{\text{vap}}(\theta) \) and \( \Delta H^\circ_{\text{vap}}(\theta) \) can result in determination of optimal data set of vapor pressures. In some cases, application of such a thermodynamic method might lead to choice of wrong data set of vapor pressures due to fortuitous compensations of errors between Gibbs energy function and vapor pressure data. However, since vapor pressure data are said to have a large uncertainty and accuracy of Gibbs energy functions is inferred to be commonly higher than that of vapor pressure data, such compensations are unlikely to happen. In other words, even if such compensations happen, vapor pressure data are considered to be the same level of errors as Gibbs energy functions.

APPLICATION TO VAPOR PRESSURE MEASUREMENT OF CESIUM METABORATE AND SILVER

Vapor pressure of CsBO₂

The detailed procedures of the sample and the Knudsen effusion mass spectrometric, KEMS, measurement


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Fig. 2. Temperature dependence of the vapor pressures of CsBO₂.

Table 1. The second-law and third-law sublimation enthalpies of CsBO₂.

| Authors         | \( \Delta H^{\text{sub}}_{\text{CsBO}_2}(298) \) (kJ/mol) | \( \Delta H^{\text{sub}}_{\text{CsBO}_2}(298) \) (kJ/mol) | Diff. (%) |
|-----------------|----------------------------------------------------------|----------------------------------------------------------|----------|
| Nakajima et al. | 292.8                                                    | 283.2                                                    | 3.4      |
| for CsBO₂(s)   | 287.1                                                    | 282.0                                                    | 1.8      |
| Nakajima et al. | 278.4                                                    | 279.9                                                    | 0.6      |
| for CsBO₂(l)   | 237.6                                                    | 284.3                                                    | 16.4     |
| Biswas and Mukerji | 286.5                                                  | 270.2                                                    | 6.0      |
| Cordfunke et al. | 289.1                                                  | 271.9                                                    | 6.3      |

are described in another paper. Briefly speaking, CsBO₂ sample used for the KEMS measurement was prepared from Cs₂CO₃ and H₃BO₃ mixed powders by heating at 873 K in air. In the KEMS measurement, the sample was heated and cooled stepwise in 30 K steps and the heating process was repeated two times. According to the paper examined an ionization behavior of CsBO₂ by a KEMS method, detected Cs⁺ ion results from the dissociative ionization of CsBO₂ molecule. So only the ion current of Cs⁺ ionized under 50 eV electron impact, \( I_{C^+} \), was monitored until the end of the KEMS measurement, as shown in Fig. 1. The measured ion current was converted into absolute vapor pressure by using the following equation:

\[
\rho_{\text{CsBO}_2} (t) = \frac{\sqrt{2 \pi R \Delta W_{\text{CsBO}_2} I_{C^+}(t) T(t)}}{a l \int_0^{t_{\text{eff}}} I_{C^+}(t') \sqrt{T(t')} \, dt' \sum_{i} \gamma_{i} \sqrt{M_i}}
\]

where \( \Delta W_{\text{CsBO}_2} \) is the weight of total amount of CsBO₂ effusing through the orifice, \( R \) the gas constant, \( a \) cross section of effusion orifice, \( L \) the Clausing factor, \( T \) absolute temperature, \( i \) an isotopic species, \( M \) the mass number of CsBO₂, \( \gamma \) isotopic abundance ratio of CsBO₂. \( \Delta W_{\text{CsBO}_2} \) is assumed to be the same as the weight difference of the samples before and after the KEMS measurement. Ion currents used in conversion into absolute vapor pressures were chosen for the last one minute before the next heating or cooling step.

Figure 2 shows the determined vapor pressures plotted in Arrhenius form. As shown in this graph, there is a certain difference of vapor pressures between the heating and cooling processes. The ion currents at each temperature ultimately seem to be independent of time from Fig. 1. So it is hard from the time dependence of the ion current to determine which data set of vapor pressures is more accurate. Therefore, sublimation enthalpies of CsBO₂ by the second and third law methods are examined to find optimal data set of the vapor pressures. The Gibbs energy function of gaseous CsBO₂ required in this method is derived from molecular parameters given by Ezhov and Komarov assuming a rigid rotor harmonic oscillator model. However, it is found that there is a negligible difference between the Gibbs energy functions calculated from other molecular parameters reported in the past. While, the Gibbs energy function of solid CsBO₂ is computed from its standard entropy of formation and heat capacity recommended by Cordfunke and Konings, which are regarded as good quality. Therefore, accuracy level of both of Gibbs energy functions of solid and gaseous CsBO₂ are expected to be better than that of vapor pressures of CsBO₂. Table 1 shows examination results of the second-law and third-law sublimation enthalpies. As shown in the table, the difference between the second-law and third-law values for the 2nd cooling stage of Nakajima et al. is the smallest. Indeed, Fig. 2 indicates the vapor pressures increase in the order of the 1st heating, 2nd heating and 2nd cooling stages. Further, when we take a closer look at Fig. 1, the ion currents at the heating stages, especially at the 2nd heating stage, still seem to increase with time and then the equilibrium might not be reached yet. Consequently, since the present thermodynamic method requires neither special technique nor experience when dealing with measured data, it can be useful to determine an optimal data set of vapor pressures.

Table 1 also includes the second-law and third-law sublimation enthalpies evaluated from vapor pressures of CsBO₂ reported in the past. Further, the values derived from the left-hand side of Eq. (12) and from the right-hand side of Eq. (1) are plotted in Figs. 3 and 4, respectively. Figure 3 also includes regression lines extrapolated to near the origin. As shown in these figures, the data of our work is the most reasonable because the intercept of the regression line is the nearest of the origin and temperature dependence of the third law values is the weakest. Thus, the second and third law methods can also allow us to find a more preferable data set among literature data.

Vapor pressure of Ag

Vapor pressure measurements of silver were conducted
at nine laboratories to establish vapor pressure standard reference materials.7) These data sets of vapor pressures were used to confirm validity of the second and third law methods. Gibbs energy functions of silver given by Cox et al.20) and Barin21) were used to identify their effect on the difference between the second and third law values. The examination results are summarized in Table 2. As shown in this table, the differences between the second and third law values using Gibbs energy functions given by Cox et al. are smaller than those in the case of Barin. Then, Cox et al.’s data is considered to be more reasonable. Further, it is shown that all the third law values of Lab. Nos. 1, 5 and 6, which have no greater than 1% of the difference between the second and third law values, lie between 285 and 286 kJ/mol and are close to the average third law value of 284.6 kJ/mol. Figure 5 shows all the data points of vapor pressures obtained from Lab. Nos. 1, 5 and 6 lie within the scatter of the data points obtained from other laboratories. Thus, examination of such a difference can lead to find more accurate data set of vapor pressures.

For comparison among 9 laboratories, the values derived from the left-hand side of Eq. (12) and from the right-hand side of Eq. (1) using Cox et al.’s Gibbs energy functions are plotted in Figs. 6 and 7, respectively. These figures show that, as the difference between the second and third law values becomes smaller, the intercept of the regression line approaches the origin and the temperature dependence of the third law values becomes weaker. Further, these plots can help us to easily find wrong data points which are largely deviated from the regression line or the average value. Therefore such a thermodynamic method including not only examination of the difference between the second and third

| Lab. No. | $\Delta H_{\text{sub}}^*(298)$ (kJ/mol) | $\Delta H_{\text{sub}}^*(298)$ (kJ/mol) | Diff. (%) | $\Delta H_{\text{sub}}^*(298)$ (kJ/mol) | $\Delta H_{\text{sub}}^*(298)$ (kJ/mol) | Diff. (%) |
|---------|--------------------------------------|--------------------------------------|---------|--------------------------------------|--------------------------------------|---------|
| 1       | 287.3                                | 285.1                                | 0.8     | 287.7                                | 284.9                                | 1.0     |
| 2       | 290.4                                | 281.5                                | 3.2     | 290.4                                | 281.4                                | 3.2     |
| 3       | 304.0                                | 284.6                                | 6.8     | 304.4                                | 284.3                                | 7.1     |
| 4       | 293.6                                | 286.6                                | 2.4     | 293.9                                | 286.3                                | 2.7     |
| 5       | 286.2                                | 285.7                                | 0.2     | 286.6                                | 285.5                                | 0.4     |
| 6       | 287.4                                | 285.2                                | 0.8     | 287.8                                | 285.0                                | 1.0     |
| 7       | 290.2                                | 283.2                                | 2.4     | 290.2                                | 283.1                                | 2.5     |
| 8       | 250.4                                | 285.5                                | 12.3    | 250.8                                | 285.4                                | 12.1    |
| 9       | 320.4                                | 279.5                                | 14.6    | 320.8                                | 279.3                                | 14.9    |
| Ave.‡   | 289.2                                | 284.6                                | 1.6     | 289.4                                | 284.3                                | 1.8     |

*Gibbs energy functions of Ag(s, l) and Ag(g) given by Cox et al.20)
# Gibbs energy functions of Ag(s, l) and Ag(g) given by Barin.21)
‡ The second law result from laboratory No. 3 and the second and third law results from laboratories Nos. 8 and 9 are discarded.

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**Table 2.** The second-law and third-law sublimation enthalpies of Ag.

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**Fig. 4.** Temperature dependence of the third law enthalpy of sublimation of CsBO$_2$6,18,19)

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**Fig. 5.** Temperature dependence of vapor pressures of silver.7)
Fig. 6. Values derived from the left-hand side of Eq. (12) by using vapor pressures of silver\(^{7}\) given by (a) laboratory No. 1, (b) laboratory No. 2, (c) laboratory No. 3, (d) laboratory No. 4, (e) laboratory No. 5, (f) laboratory No. 6, (g) laboratory No. 7, (h) laboratory No. 8, (i) laboratory No. 9.

Fig. 7. Temperature dependence of the third law sublimation enthalpy of silver\(^{7}\) given by (a) laboratory No. 1, (b) laboratory No. 2, (c) laboratory No. 3, (d) laboratory No. 4, (e) laboratory No. 5, (f) laboratory No. 6, (g) laboratory No. 7, (h) laboratory No. 8, (i) laboratory No. 9.
law values but also the plots such as shown in Figs. 6 and 7 can contribute to improvement of accuracy of vapor pressure measurement.

CONCLUSION

In this study, a new data analysis method is proposed to improve accuracy of vapor pressure measurements. The key of the new method is to use Eq. (12), which is derived from the van’t Hoff equation based on the second law of thermodynamics. The proposed method using the second and third law methods is found to be helpful to determine an optimal data set of vapor pressures when it is hard to know only measured data such as time dependence of ion currents in KEMS measurement. Further, examination results for vapor pressures of silver indicate that a smaller difference between the second and third law values can lead to find more accurate vapor pressure data. Therefore, such a thermodynamic method can contribute to improve accuracy of vapor pressure measurement.

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