REVIEW

**Thermodynamic Studies of Metallurgical Systems
by Mass Spectrometry**

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(Received July 28, 1993)

The application of the Knudsen cell-mass spectrometer technique to the thermodynamic studies of alloys and oxide melts which are called metallurgical slags is discussed in this review paper. Particular attention is paid to the development of such studies during the last twenty years.

In conducting mass spectrometric studies on the composition dependency of properties of mixtures, a series of measurements with the samples of different compositions are necessary, and in these measurements small changes in the instrumental sensitivity between experiments is unavoidable. Various methods have been developed in order to overcome this problem. Many alloy systems have been studied employing ion intensity ratio methods. Analytical expression of thermodynamic functions have enabled to compute the thermodynamic functions from the mass spectrometric data more accurately. The experimental technique of multi-Knudsen cell has been improved, and pulse-counting technique was used for the measurement of ion intensity. The determination of the thermodynamic properties of the alloys containing the components of very low vapor pressure were performed. There are many difficulties in conducting mass spectrometric studies with oxide melts, but some of such systems have been studied by applying various techniques. The phase boundaries of some alloy systems were determined using the data of activities or using another technique. A complete listing of the applications to date is presented.

1. Introduction

Mass spectrometry has made fruitful contribution to thermodynamic studies of many metallurgical systems. As is well known, the combination of a mass spectrometer and a Knudsen cell is a powerful tool for the determination of a vapor species and its equilibrium pressure above a condensed phase. Valuable thermodynamic information can be deduced from this vapor pressure. In 1975, Raychaudhuri and Stafford¹⁾ critically reviewed the methods which had been employed for the study of alloy thermodynamics by mass spectrometry, and Neckel²⁾ again reviewed the methods used for alloy thermodynamics by mass spectrometry in 1989. In the review paper of Raychaudhuri and Stafford, they summarized the results obtained prior to 1973. In this review paper, the studies which were performed after 1973 on the thermodynamics of alloys and oxide melts which are called metallurgical slags are described, and how the problems encountered during conducting such kinds researches were overcome are written. A listing of the papers to date is also presented. The alloys used for nuclear reactors, for instance U and Li alloys, are omitted from this review. Because the review

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Fig. 1. The N^+ and CO^+ ion peaks as an illustration of the resolution of repetitive scanning in pulse counting technique (Yamada and Kato⁴).

of mass spectrometric studies on such alloys will be published elsewhere.

2. Instrumentation

2.1 Mass analyzer

The most extensively used apparatus is the combination of a single-focusing magnetic deflection-type mass spectrometer and a Knudsen cell. Time-of-flight mass spectrometers, which were used in early days of thermodynamic study of alloys, have handicaps of lower resolution and less sensitivity than a magnetic sector instrument. The number of applications of quadrupole mass filters is increasing recently. The resolution of this instrument is less than that of a magnetic sector instrument. However, a quadrupole instrument is compact and sensitive, even though its sensitivity is strongly mass dependent.

Recently, Vrestal and Tomiska³) reported the combination of a monopole mass spectrometer with a Knudsen cell. This monopole analyzer is a simplified version of the quadrupole mass spectrometer. They determined the second law heats of sublimation for Co, Cu, Fe, and Ni using this instrument and the obtained results agreed well with the compiled literature values.

Pulse counting technique for ion detection can offer higher sensitivity and wide dynamic range. An electronic circuit arrangement for applying pulse counting technique to magnetic scanning type mass spectrometers was developed by Yamada and Kato.⁴) Mass discrimination caused by magnetic scanning is less than that caused by accelerating voltage scanning. This electronic circuit arrangement can smooth ion peaks and statistical fluctuations in the "counts per channel". Figure 1 indicates how such scanning is performed keeping good resolution. This technique was applied for the

Fig. 2. Device for measurements on multiple effusion cells (Chatillon *et al.*⁵⁾).

measurement of ion intensities of very low concentrations of P and Si in liquid iron.

2.2 Knudsen cell

The most studies in this area have been performed with a single Knudsen cell and some investigators used twin or multiple Knudsen cells. Since the most general and simplest way to determine a thermodynamic activity is to compare the partial pressure of the alloying element with that of the pure substance at a given temperature, the advantages of twin and multiple cells over a single cell are obvious. The disadvantages of such multiple cells are increased possibility of temperature gradients, bulk depletion and surface depletion of alloys, and the contamination of the Knudsen cell assembly during lengthened runs of enthalpy determination, and it is difficult by this arrangement to obtain good reproducibility of mechanical positioning of the ionizing conditions of the molecular beam in the ion source.

A new device for multiple cells was developed by Chatillon *et al.*⁵⁾ as indicated in Fig. 2. Multiple furnaces are moved by a direct-current electric motor, and the cells changed over within less than 6 sec. The positioning obtained from different directions is reproducible to within a few hundredths of a millimeter. This device could overcome some of the above mentioned disadvantages of the multi-cell, and has been used for many studies of alloys and oxide mixtures. Chatillon *et al.*⁶⁾ developed heat pipe device to maintain isothermal conditions in effusion cells. The maximum working temperature was 1,050°C, but they proposed that it was technically possible to reach temperatures of about 2,000°C. A valved Knudsen cell was developed by Howard.⁷⁾ In this

Fig. 3. Integration curve for the Fe-V system at 1,600°C (Furukawa and Kato⁸⁾).

Knudsen cell, preweighed sample beads are held in a sample wheel. After a bead is dropped into the cell the opening for feeding of the beads is closed and the ion intensity is measured. Then remaining beads are added one by one at a time and the ion intensity for the new alloy was measured after each addition. This technique decreases the time required for activity determination and simplifies the mathematical calculations required to obtain activities.

2.3 Compatibility of cell material with samples

The cell materials must be chemically inert towards samples. For the studies of alloys, metallic oxide which is stable against the alloy to be investigated is used as cell material. More strictly, the oxide which is "stabler" than the oxide of the components of the alloy is chosen as the material of the cell. However, thermodynamics suggests that such "stabler" oxide would dissociate from the following reason. The reaction of formation of an oxide M_xO_y at the temperature T is expressed as:

where M is the metal dissolved in the sample in the cell. The equilibrium oxygen partial pressure for this reaction is:

$$\ln p_{O_2} = \frac{2}{y} \ln a_{M_xO_y} - \frac{2x}{y} \ln a_M + \frac{2}{y} \cdot \frac{\Delta G_f^\circ}{RT} \quad (2)$$

where $a_{M_xO_y}$, a_M are the Raoultian activities of M_xO_y and M , respectively, and ΔG_f° is the standard Gibbs energy of the formation of the oxide. In the study of the Fe-V system by Furukawa and Kato,⁸⁾ Al_2O_3 cells were used. When the activity of V in iron is 0.1 and the activity of V_2O_3 is 1, the equilibrium value of $\log(p_{O_2}/MPa)$ is -1.27 . The activity of Al in iron in equilibrium with pure Al_2O_3 and with oxygen of the above partial pressure is calculated as 3.8×10^{-6} . When the activity of V_2O_3 is reduced to 0.1, the equilibrium activity of Al in iron becomes 1.2×10^{-5} . These computations suggest that Al_2O_3 can dissociate. Figure 3 shows Belton-Fruehan integration curve for the Fe-V system. When no Al was added to the sample, the measured ion intensity ratios scattered as indicated by open circles (○), but reproducible results as indicated by black circle (●) were obtained when the addition of a small amount of Al to the sample was made and the dissociation of Al_2O_3 was prevented. For the studies of oxide melts, metals are used for cell materials. The selection of cell material is the key to the success of the study of the oxides.

3. Measurement of Activity

3.1 Methods

The main task in alloy thermodynamics by mass spectrometry is the determination of the thermodynamic activity of a component in an alloy. Since the vapor pressure measured by a mass spectrometer is low, the fugacity of a monoatomic species can be taken equal to its partial pressure. Therefore, the activity can be obtained when the ratio of the ion intensity of a component of the alloy and of the pure component, because these ion intensities are proportional to the vapor pressures at a definite temperature. However, small changes in the experimental sensitivity between different experiments seem to be unavoidable and various methods have been proposed in order to overcome this undesired effect.

Raychaudhuri and Stafford¹¹ divided these methods into three groups in their review paper; *i.e.*, ion intensity ratio methods, methods using internal standards (I. S. methods), and methods used when polymeric vapor species are present. Among ion intensity ratio methods, those using the Gibbs–Duhem relation (ratio/G–D method) have widely been used. The first attempt to use the Gibbs–Duhem relation was reported by Lyubimov *et al.*³⁴; this method was subsequently developed independently by Belton and Fruehan⁹ and by Neckel and Wagner¹⁰. Belton and Fruehan derived the following relationships for a binary solution which vaporizes as free atoms:

$$\ln f_1 = - \int_{x_1=1}^{x_1=x_2} x_2 d[\ln(I_2/I_1) - \ln(x_2/x_1)] \quad (3)$$

$$\Delta H_1 = -R \int_{x_1=0}^{x_1=x_2} x_2 d \left[\frac{\partial \ln(I_2/I_1)}{\partial (1/T)} \right] \quad (4)$$

where f_1 is the activity coefficient of component 1, x_2 and x_1 are the mole fractions of the components 2 and 1, respectively, I_2 and I_1 are the ion intensities, and ΔH_1 is the partial molar enthalpy of mixing of the component 1.

Neckel and Wagner¹⁰ derived the following relationship for the excess Gibbs energy G^E and the ion intensities:

$$G^E(x_2) = RT \int_{x_2=0}^{x_2=x_2} \ln \frac{I_2(1-x_2)}{I_1 x_2} dx_2 - C^G(T) x_2 \quad (5)$$

$$C^G(T) = RT \ln \frac{\sigma_2(E) \gamma_2 P_2^\circ}{\sigma_1(E) \gamma_1 P_1^\circ} = RT \int_{x_2=0}^{x_2=1} \ln \frac{I_2(1-x_2)}{I_1 x_2} dx_2 \quad (6)$$

where σ is the electron impact cross section for the electron energy E , γ is the multiplier gain and P_1° and P_2° are the vapor pressures of component 1 and 2 in their standard states, respectively. The integrations involved in these equations are performed numerically after the experimental values for the functions $RT \ln(I_2 x_1 / I_1 x_2)$ are fitted graphically by a curve.

Tomiska *et al.*¹¹ developed an analytical procedure in order to avoid this cumbersome numerical integration. This procedure is based on the representation of an excess function by a polynomial. Further, among various kinds of polynomial, the “Thermodynamically Adapted Power-series” (T.A.P.-series) proposed by Tomiska¹² has been found to have special advantages. For instance, the measured ion intensities are related to the T.A.P.-series of the excess Gibbs energy by following equations:

Table 1. Thermodynamic Measurements of Binary Ferrous Alloys by Mass Spectrometry

Alloying element	Vapor pressure at 1,873 K (Pa)	State	Method	Investigators
Fe	8.0			
S	1.7	l	I.S./Fe	Kato and Minami (1973) ¹⁴⁾
	(1 mass%)	l	Ratio/G-D	Ichise, Kitao, and Mori (1975) ¹⁵⁾
P	1.4×10^{-4}	l	Ratio/G-D	Yamada and Kato (1980) ¹⁶⁾
	(1 mass%)			
Mn	5.2×10^3	s	Other	Zaitsev, Zemchenko, and Mogutnov (1989) ¹⁷⁾
		s	Other	Zaitsev, Zemchenko, and Mogutnov (1990) ¹⁸⁾
Al	1.8×10^2	l	Ratio/G-D	Belton and Fruehan (1969) ¹⁹⁾
		l, s	Ratio/G-D	Ichise, Yamauchi, and Mori (1977) ²⁰⁾
Sn	1.2×10^2	l	Ratio/G-D	Wagner and St. Pierre (1972) ²¹⁾
		l	Ratio/G-D	Yamamoto, Mori, and Kato (1983) ²²⁾
		l	Ratio/G-D	Nunoue and Kato (1987) ²³⁾
Cu	1.2×10^2	l	Ratio/G-D	Choudary, Serkin, and Belton (1975) ²⁴⁾
		l	Ratio/G-D	Timberg, Toguri, and Azakami (1981) ²⁵⁾
Ge	4.6×10^1	l	Ratio/G-D	Erdelyi, Tomiska, Neckel, and Nowotny (1978) ²⁶⁾
		l	Ratio/G-D	Nunoue and Kato (1988) ²⁷⁾
Cr	2.5×10^1	l	Other	Reese, Rapp and St. Pierre (1968) ²⁸⁾
		l	Other	Gilby and St. Pierre (1969) ²⁹⁾
		l, s	Ratio/G-D	Belton and Fruehan (1970) ³⁰⁾
		s	Other	Zaitsev, Zemchenko, and Mogutnov (1990) ³¹⁾
Au	8.1	l	Ratio/G-D	Tomiska, Nowotny, Erdelyi, and Neckel (1977) ¹¹⁾
Pd	7.3	l	Ratio/G-D	Tomiska, Krajnik, and Neckel (1989) ³²⁾
		s	Ratio/G-D	Tomiska (1989) ³³⁾
Co	3.7	l	Ratio/G-D	Lyubimov, Zobens, and Rakhovskii (1958) ³⁴⁾
		l	Ratio/G-D	Belton and Fruehan (1967) ⁹⁾
		l, s	Triple cell	Rammensee and Fraser (1981) ³⁵⁾
		s	Ratio/G-D	Tomiska (1986) ³⁶⁾
		l	Ratio/G-D	Tomiska and Neckel (1986) ³⁷⁾
Ni	3.8	s	Ratio/G-D	Lyubimov, Zobens, and Rakhovskii (1958) ³⁴⁾
		l	Ratio/G-D	Belton and Fruehan (1967) ⁹⁾
		l	Ratio/G-D	Kubaschewski, Geiger, and Hack (1977) ³⁸⁾
		l, s	Ratio/G-D	Conard, McAneney, and Sridhar (1978) ³⁹⁾
		l, s	Ratio/G-D	Rammensee and Fraser (1981) ³⁵⁾
		l	Ratio/G-D	Tomiska (1985) ⁴⁰⁾
		s	Ratio/G-D	Tomiska and Neckel (1985) ⁴¹⁾
Si	8.8×10^{-1}	l	Ratio/G-D	Yamada, Abe and Kato (1980) ⁴²⁾
		l, s	Ratio/G-D	Zaitsev, Zemchenko, and Mogutnov (1991) ⁴³⁾
Ti	1.5×10^{-1}	l	Ratio/G-D	Furukawa and Kato (1976) ⁴⁴⁾
V	2.0×10^{-2}	l	Ratio/G-D	Furukawa and Kato (1975) ⁸⁾
Mo	2.1×10^{-6}	l, s	I.S./Fe	Ichise, Maruo, Sasho, Ueshima, and Mori (1982) ⁴⁵⁾
Nb	1.0×10^{-7}	l, s	I.S./Fe	Ichise and Horikawa (1989) ⁴⁶⁾
Ta	4.3×10^{-10}	l, s	I.S./Fe	Ichise and Horikawa (1989) ⁴⁶⁾
W	6.7×10^{-11}	l, s	I.S./Fe	Ueshima, Yamana, Sugiyama, and Ichise (1984) ⁴⁷⁾

1. l and s refer to the liquid and solid state, respectively.

2. I.S./Fe: Fe is used as internal standard; "Other" refers to method not discussed here.

3. Ratio/G-D: Ion intensity ratio method by use of the Gibbs-Duhem relation.

Fig. 4. Experimental apparatus for effusion study by collection technique (Yamamoto *et al.*⁴⁸⁾).

$$RT \ln \frac{I_2(1-x_2)}{I_1x_2} = C^G(T) + \sum_{n=1}^N B_n^G [nx_2^{n-1} - (n+1)x_2^n] \quad (7)$$

where B_n^G are adjustable parameters and N is their total number. The constant $C^G(T)$ and the parameters B_n^G are adjusted by means of a least squares method to fit the experimental values of the intensity ratio function $RT \ln(I_2x_1/I_1x_2)$ as close as possible.

The enthalpies of mixing H^E and the excess entropies S^E can be determined from the temperature dependence of the excess Gibbs energy G^E .

The algebraic regression of all experimental values for the intensity ratio function, measured at various concentrations and temperatures, yields the parameters of the T.A.P.-series for G^E , H^E , and S^E . This approach has been termed "Algebraic Intensity Ratio" method. The advantages of this method were illustrated by applying this method to various systems.

Martin and Paulaitis¹³⁾ developed the technique for direct determination of infinite-dilution activity of the solute in a liquid mixture.

When polyatomic species are present in vapor phase, the activity can be determined by the use of the equilibrium of these species. However, only limited number of papers have been published, because the vapor pressures of oligomers above alloys are usually very low. Some applications of this technique for silicate systems have been reported as described later.

3.2 Ferrous alloys

Ferrous alloys are the most important industrial alloys, and the studies of the thermodynamic properties of these alloys have extensively been performed as indicated in Table 1. The mass spectrometer-Knudsen cell combination can determine the

Fig. 5. Vapor pressures of P, P_2 from Fe-P alloys (Yamamoto *et al.*⁴⁸⁾).

Fig. 6. Procedure for the determination of the activity of Fe in low Mo concentration range (Ichise *et al.*⁴⁵⁾).

activity of an alloy; the enthalpy and the entropy of forming the alloy can be deduced from the activity data.

For the determination of the activity, the ion intensity from the vapor of the component must be measured. The vapor pressures of the alloying elements of iron at 1,873 K (1,600°C) are indicated in Table 1; the temperature of steelmaking is around 1,600°C. In Table 1, the alloying elements are arranged in the order of increasing vapor pressure. The activities of the binary ferrous alloys with Al, Sn, Cu, Ge, Cr, Au, Pd, Co, Ni, Si, Ti, or V at 1,873 K have been determined mainly by ion intensity ratio methods, because these elements as well as Fe have measurable vapor pressures over wide composition ranges at this temperature.

The activity of the binary ferrous alloy with S or P has been determined by the ion intensity ratio method¹⁵⁾ or by the method using Fe as internal standard^{14), 16)} in the low concentration range of the alloying elements. However, S and P are in gaseous state at 1,600°C and the value of the standard Gibbs energy of the dissolution of these gaseous elements in liquid iron is necessary for the application of the activity data to the analysis of steelmaking process. In order to obtain this value, the vapor pressure of the element above the alloy at the concentration of the standard state of the element must be measured. If the ionization cross sections and the sensitivity factors of the ions are known, the vapor pressure can be computed from the ion intensities. However, the determinations of these factors are difficult, and the calculated tabulations of ionization cross sections given in literature are usually used. The relative multiplier gain of an ion

was sometimes assumed to be equal and sometimes was assumed to be proportional to the reciprocal of the square root of the weight of the ions.

Obviously, it is desirable not to use such assumptions. In the study of Fe-P alloys, Yamamoto *et al.*⁴⁸⁾ used the following technique. The ion source of their instrument was replaced by a gold target cooled by liquid nitrogen as shown in Fig. 4. This target was exposed to the effused vapors and the deposit on the target was chemically analyzed. The results of this analysis together with the ion intensity ratio $I_{P_2^+}/I_P^+$ which was obtained in the previous experiment gave the vapor pressures of P and P_2 as indicated in Fig. 5. In computing the vapor pressures, Hertz-Knudsen equation was used and ratio of the ionization cross sections σ_{P_2}/σ_P was assumed to be 1.5.

The vapor pressures of Mo, Nb, Ta, and W are too low for the measurement by mass spectrometry. The only possible method is to derive the activity of such alloying element from the Gibbs-Duhem treatment of the iron activities. For instance, Ichise *et al.*⁴⁵⁾ determined the activity of Fe in low Mo-Fe alloys by the following method. A small piece of iron was placed on a piece of Mo in a Knudsen cell as indicated in Fig. 6. In the course of raising temperature, the ion intensity of pure solid Fe was measured in the temperature range below the melting point of Fe. After the metals melted to form an uniform alloy, the ion intensity of Fe from the liquid alloy was measured. The values of the ion intensity of the solid Fe were extrapolated to liquid temperature range on the basis of linear relation of $\ln(IT)$ vs. $1/T$ plot for the purpose of obtaining the ion intensity of the internal standard. High Mo alloy can not be prepared in the cell, and the measurements for pure iron and that for the alloy were performed separately. In this case, Ag was used for calibrating the instrumental constant. The modifications of this method were used for Fe-W, Fe-Ta, and Fe-Nb alloys as indicated in Table 1.

3.3 Non-ferrous alloys

The activities of many non-ferrous alloy systems have been determined by mass spectrometry, as indicated in Table 2. The improvements of the apparatus, for instance, such as the improvement of the temperature distribution of the cell and the development of analytical treatment of the data have improved the accuracy of the data, especially those of the enthalpies of mixing.¹¹⁾ The accuracy of the activity data has been checked by deducing the phase diagrams from the activities and by comparing these phase diagrams with the phase diagrams in literature.¹⁰⁶⁾

3.4 Ternary and quaternary alloys

The thermodynamic studies of ternary and quaternary alloy systems by mass spectrometry are indicated in Table 3. Some ternary systems were studied using the ratio/G-D method. The activity of P in dilute solutions of P and another alloying element in liquid iron was determined using Fe as inner standard.¹³⁵⁾ Since the vapor of Sb contains Sb, Sb_2 , and Sb_4 , the activity of Sb in ternary and quaternary alloys containing Sb was determined using monomer-dimer method.^{134), 135)} The ion intensity ratio of Sb_4^+ to Sb_2^+ was also used for the determination of the activity.

3.5 Oxide melts related to metallurgical processes

Oxide melts which used for refining metals are called metallurgical slags and they play very important role in metallurgical processes. The data of the thermodynamic properties of these melts are necessary for the analysis of metallurgical processes. Only

Table 2. Thermodynamic Measurements of Binary Non-Ferrous Alloys by Mass Spectrometry

System	State	Method	Investigators
Ag-Al	l	Ratio/G-D	Belton and Fruehan (1969) ⁴⁹⁾
Ag-Al	l	Ratio/G-D	Cuthill, Brown, and Fabian (1969) ⁴⁹⁾
Ag-Cu	l	Dual cell	Cameresi, DeMaria, Gigli, and Piacente (1967) ⁵⁰⁾
Ag-Cu	l	Ratio/G-D	Nakamura, Yamaji, and Kato (1970) ⁵¹⁾
Ag-Cu	l	Ratio/G-D	Wagner, Sodeck, and Neckel (1971) ⁵²⁾
Ag-Cu	l	Ratio/G-D	Golonka, Botor, and Dulat (1979) ⁵³⁾
Ag-Cu	l	Other	Howard (1989) ⁷⁾
Ag-Ga	l	Ratio/G-D	Qi, Hino, and Azakami (1989) ⁵⁴⁾
Ag-Ge	l	Multiple cell	Martin-Garin, Chatillon, and Allibert (1979) ⁵⁵⁾
Ag-In	l	Ratio/G-D	Alcock, Sridhar, and Svedberg (1969) ⁵⁶⁾
Ag-In	l	Ratio/G-D	Qi, Hino, and Azakami (1989) ⁵⁴⁾
Ag-Mn	s	Dual cell	Gingerich, Kingcade, Stickney, and Chandrasekharaiah (1988) ⁵⁷⁾
Ag-Pd	s	Dual cell	Raychaudhuri (1971) ⁵⁸⁾
Ag-Sn	l	Ratio/G-D	Yamaji and Kato (1972) ⁵⁹⁾
Al-Au	l	Ratio/G-D	Erdelyi, Tomiska, Neckel, Rose, Ramakrishnan, and Fabian (1979) ⁶⁰⁾
Al-Co	l		Levin and Gel'd (1979) ⁶¹⁾
Al-Cu	l	Ratio/G-D	Perakis, Chatillon, and Pattoret (1973) ⁶²⁾
Al-Ni	l	Multiple cell	Jhonston, and Palmer (1980) ⁶³⁾
Al-Si	l	Multiple cell	Chatillon, Allibert, and Pattoret (1975) ⁶⁴⁾
Al-Te	l	Other	Said, Chastel, Bergman, and Castanet (1981) ⁶⁵⁾
Al-Ti	s	Ratio/Model	Hoch and Usell, Jr. (1971) ⁶⁶⁾
Al-Ti	s	Isotope	Hoch and Usell, Jr. (1971) ⁶⁶⁾
As-Cu	l	Dual cell	Hino and Toguri (1987) ⁶⁷⁾
As-Pd	l	Other	Storms and Szklarz (1987) ⁶⁸⁾
Au-Cu	l	Ratio/G-D	Neckel and Wagner (1969) ⁶⁹⁾
Au-Cu	l	Ratio/G-D	Hager, Howard, and Jones (1970) ⁷⁰⁾
Au-Ge	l	Ratio/G-D	Neckel and Sodeck (1969) ⁷¹⁾
Au-Ge	l	Ratio/G-D	Hager, Howard, and Jones (1973) ⁷²⁾
Au-Ni	l	Ratio/G-D	Tomiska, Erdelyi, Neckel, and Nowotny (1977) ⁷³⁾
Au-Pd	s	Dual cell	Bartosik (1971) ⁷⁴⁾
Au-Pd	s	Ratio/G-D	Bartosik (1971) ⁷⁴⁾
Au-Pd	l	Ratio/G-D	Tomiska, Kopecky, and Neckel (1990) ⁷⁵⁾
Au-Pd	s	Ratio/G-D	Tomiska (1990) ⁷⁶⁾
Au-Pt	s	Dual cell	Jones, Stafford, and Whitmore (1970) ⁷⁷⁾
Au-Si	l	Ratio/G-D	Bergman, Chastel, Mathieu, and Castanet (1978) ⁷⁸⁾
Au-Sn	l	Ratio/G-D	Howard and Hager (1978) ⁷⁹⁾
B-La	s	Other	Storms and Mueller (1978) ⁸⁰⁾
B-Mo	s	Other	Storms and Mueller (1977) ⁸¹⁾
B-Ni	l	Other	Storms and Szklarz (1987) ⁸²⁾
B-Pd	l	Other	Storms and Szklarz (1987) ⁸³⁾
B-Si	s	Multiple cell	Armas, Chatillon, and Allibert (1981) ⁸⁴⁾
Ba-P	l	Other	Zaitsev, Zemchenko, Litvina, and Mogutnov (1992) ⁸⁵⁾
Bi-In	l	Ratio/G-D	Lamparter, Cocke, and Steeb (1982) ⁸⁶⁾
Bi-Pb	l	Ratio/G-D	Fruehan (1971) ⁸⁷⁾
Bi-Te	l	Ratio/G-D	Belton and Fruehan (1971) ⁸⁸⁾
Bi-Tl	l	Ratio/G-D	Fruehan (1971) ⁸⁷⁾
Bi-Tl	l	Monomer-dimer	Fruehan (1971) ⁸⁷⁾
C-Nb	s	Other	Storms, Calkin, and Yench (1969) ⁸⁹⁾

Table 2. (Continued)

System	State	Method	Investigators
C-V	s	Other	Storms, Lowe, Baca, and Griffin (1973) ⁹⁰⁾
C-Y	s	Other	Storms (1971) ⁹¹⁾
C-Zr	s	Other	Storms, and Griffin (1973) ⁹²⁾
Ca-Ga	l	Dual cell	DeMaria and Piacente (1972) ⁹³⁾
Ca-Ga	l	Multiple cell	DeMaria and Piacente (1972) ⁹³⁾
Ca-P	l	Other	Zaitsev, Korolyov, and Mogutnov (1991) ⁹⁴⁾
Cd-Zn	l	Ratio/G-D	Nakazawa, Yazawa, and Taniuchi (1976) ⁹⁵⁾
Co-Cu	l	Ratio/G-D	Timberg, Toguri, and Azakami (1981) ²⁵⁾
Co-Ge	l	Ratio/G-D	Tomiska, Erdelyi, Nowotny, and Neckel (1982) ⁹⁶⁾
Co-Ni	l, s	Ratio/G-D	Tomiska, Nowotny, Erdelyi, and Neckel (1979) ⁹⁷⁾
Co-Ti	l	Ratio/G-D	Ueda, Nishi, Oishi, and Ono (1986) ⁹⁸⁾
Cr-Cu	l	Ratio/G-D	Timberg and Toguri (1982) ⁹⁹⁾
Cr-Mn	s	Other	Zaitsev, Zemchenko, and Mogutnov (1990) ¹⁰⁰⁾
Cr-Ni	l	Other	Gilby and St.Pierre (1969) ¹⁰¹⁾
Cr-Ni	l	Ratio/G-D	Wagner, Shade, and St.Pierre (1972) ¹⁰²⁾
Cu-Ga	l	Ratio/G-D	Alcock, Sridhar, and Svedberg (1970) ¹⁰³⁾
Cu-Ge	l	Ratio/G-D	Sodeck, Entner, and Neckel (1970) ¹⁰⁴⁾
Cu-Ge	l	Ratio/G-D	Alcock, Sridhar, and Svedberg (1970) ¹⁰³⁾
Cu-Ge	l	Ratio/G-D	Hager, Howard, and Jones (1973) ⁷²⁾
Cu-Ge	l	Ratio/G-D	Bergman, Chastel, Gilbert, and Castanet (1978) ⁷⁸⁾
Cu-Ni	s	Isotope	Hackworth, Hoch, and Gegel (1971) ¹⁰⁵⁾
Cu-Ni	l	Ratio/G-D	Tomiska and Neckel (1983) ¹⁰⁶⁾
Cu-Ni	s	Ratio/G-D	Tomiska and Neckel (1984) ¹⁰⁷⁾
Cu-Sb	l	Dual cell	Hino and Toguri (1987) ¹⁰⁸⁾
Cu-Si	l	Ratio/G-D	Riekert, Lamparter, and Steeb (1981) ¹⁰⁹⁾
Cu-Si	l	Ratio/G-D	Bergman, Chastel, and Mathieu (1986) ¹¹⁰⁾
Cu-Sn	l	Ratio/G-D	Alcock, Sridhar, and Svedberg (1969) ¹¹¹⁾
Cu-Sn	l	Ratio/G-D	Hager, Howard, and Jones (1970) ¹¹²⁾
Cu-Sn	l	Multiple cell	Paulaitis and Eckert (1983) ¹¹³⁾
Cu-Ti	s	Isotope	Hackworth, Hoch, and Gegel (1971) ¹¹⁴⁾
Cu-Ti	s	Ratio/G-D	Hackworth, Hoch, and Gegel (1971) ¹¹⁴⁾
Ga-Sb	l	Multiple cell	Bergman, Laffitte, and Muggianu (1974) ¹¹⁵⁾
Ge-Sn	l	Ratio/G-D	Howard and Hager (1978) ⁷⁹⁾
Ge-Ni	l	Ratio/G-D	Erdelyi, Neckel, Tomiska, and Nowotny (1977) ¹¹⁶⁾
Ir-Ti	s	I.S.	Choudary, Gingerich, and Cornwell (1976) ¹¹⁷⁾
Ir-Ti	l	I.S.	Pelino, Gupta, Cornwell, and Gingerich (1979) ¹¹⁸⁾
Mg-Sn	s	Other	Martin, and Paulaitis (1979) ¹¹⁹⁾
Ni-Pd	s	Ratio/G-D	Kopecky, Beleggratis, Neckel, and Tomiska (1992) ¹²⁰⁾
Ni-Pd	l	Ratio/G-D	Bitterman, Kopecky, and Tomiska (1993) ¹²¹⁾
Ni-Ti	l	Ratio/G-D	German and St. Pierre (1972) ¹²²⁾
Se-Te	l	Ratio/G-D	Nanjo, Nakazawa, Yazawa, and Taniuchi (1976) ¹²³⁾
Si-V	l, s	Other	Storms and Myers (1985) ¹²⁴⁾
Ti-V	s	Ratio/model	Rolinski, Hoch, and Oblinger (1971) ¹²⁵⁾

limited number of such melts have been studied by mass spectrometry as indicated in Table 4, because there are many difficulties in conducting the measurements of the thermodynamic properties of them.

Almost all components of alloys evaporate as monoatomic gases. On the contrary, the components of oxide melts evaporate in more complicated manner, and the vapor

Table 3. Thermodynamic Measurements of Ternary and Quaternary Alloys by Mass Spectrometry

System	State	Method	Investigators
As-Cu-S	l	Dual cell	Hino and Toguri (1987) ⁶⁷⁾
Au-Cu-Ge			Choudary and Gingerich (1975) ¹²⁶⁾
C-Cu-Fe	l	Ratio/G-D	Choudary, Serkin, and Belton (1975) ²⁴⁾
Co-Fe-Ni	l, s	Ratio/G-D	Fraser and Rammensee (1982) ¹²⁷⁾
Co-Fe-Ni	s	Ratio/G-D	Tomiska, Kopecky, Belegtratis, and Neckel (1993) ¹²⁸⁾
Co-Fe-Ni	l	Ratio/G-D	Tomiska, Belegtratis, Kopecky, and Neckel (1993) ¹²⁹⁾
Cr-Fe-Ni	l	Other	Gilby and St. Pierre (1969) ¹³⁰⁾
Cr-Fe-Ni	l	Ratio/G-D	Belton and Fruehan (1970) ³⁰⁾
Cr-Fe-Ni	l	Ratio/G-D	Wagner and St. Pierre (1971) ¹³¹⁾
Cr-Fe-Ni	l, s	Ratio/G-D	Wagner, Shade, and St. Pierre (1972) ¹³²⁾
Cr-Ti-V	s	Ratio/model	Rolinski, Hoch, and Oblinger (1972) ¹³³⁾
Cr-Fe-V	l	Ratio/G-D	Furukawa and Kato (1975) ⁸⁾
Cu-Fe-Sn	l	Ratio/G-D	Yamamoto, Mori, and Kato (1983) ²²⁾
Cu-Sb-Sn	l	Monomer-dimer	Szemla, Dziewidek, and Norwicz (1984) ¹³⁴⁾
Cu-Pb-Sb-Sn	l	Monomer-dimer	Szemla, Dziewidek, and Norwicz (1984) ¹³⁴⁾
Cu-S-Sb	l	Dual cell	Hino and Toguri (1987) ¹⁰⁸⁾
Fe-P-i	l	I.S.	Yamada and Kato (1983) ¹³⁵⁾
In-Sb-Zn	l	Other	Norman, Winchell, and Staley (1964) ¹³⁶⁾
N-O-Ti	s	Multiple cell	Grainer, Chatillon, and Allibert (1982) ¹³⁷⁾

i = Al, Co, Cr, Mo, Nb, Ni, Si, Ti, and V.

Table 4. Thermodynamic Measurements of Oxide Melts Related to Metallurgical Processes by Mass Spectrometry

System	State	Method	Investigators
Al ₂ O ₃ -CaO	l, s	Multiple cell	Allibert, Chatillon, Jacob, and Lourttau (1981) ¹³⁸⁾
Al ₂ O ₃ -CaF ₂ -CaO	l	Multiple cell	Allibert and Chatillon (1979) ¹³⁹⁾
Al ₂ O ₃ -CaF ₂ -CaO	l	Other	Zaitsev, Korolyov, and Mogutnov (1990) ¹⁴⁰⁾
Al ₂ O ₃ -SiO ₂	l	Multiple cell	Dhima, Stafa, and Allibert (1986) ¹⁴¹⁾
CaF ₂ -CaO-SiO ₂	l	Other	Zaitsev, Litvina, and Mogutnov (1992) ¹⁴²⁾
CaO-FeO-SiO ₂	l	Multiple cell	Dhima, Stafa, and Allibert (1986) ¹⁴¹⁾
CaO-SiO ₂	l	Other	Stolyarova, Shornikov, Ivanov, and Schultz (1991) ¹⁴³⁾
CaTiO ₃ -Ti ₂ O ₃ -TiO ₂	l	Multiple cell	Banon, Chatillon, and Allibert (1981) ¹⁴⁴⁾
FeO-MgO-SiO ₂	l	Ratio/G-D	E. R. Plante, W. Hastie, and M. Kowalska ¹⁴⁵⁾
Fe ₂ O-P ₂ O ₅	l	I. S.	Kambayashi, Awaka, and Kato (1985) ¹⁴⁶⁾
Fe ₂ O-P ₂ O ₅ -i	l	I.S.	Ohara, Nunoue, and Kato (1988) ¹⁴⁷⁾
FeO-SiO ₂	l	Multiple cell	Dhima, Stafa, and Allibert (1986) ¹⁴¹⁾
MgO-SiO ₂	l	Ratio/G-D	Kambayashi and Kato (1983) ¹⁴⁸⁾
MgO-SiO ₂	l	Ratio/G-D	Kambayashi and Kato (1984) ¹⁴⁹⁾
Na ₂ O-P ₂ O ₅	l	Multiple cell	Mahlheiors, Chatillon, and Allibert (1988) ¹⁵⁰⁾
PbO-SiO ₂	l	Monomer-dimer	Kato and Ouchi (1973) ¹⁵¹⁾
PbO-SiO ₂ -j	l	Monomer-dimer	Ouchi and Kato (1983) ¹⁵²⁾

i = CaO, MgO, MnO, and SiO₂; j = BaO, CaO, CoO, MgO, and NiO.

pressures of the components are usually low. Therefore, the methods using the Gibbs-Duhem relation can hardly be used. Further, it is not easy to find the materials of cells which are compatible with the samples.

The book "Mass spectrometric study of the vaporization of oxide systems" written by Semenov and Stolyarova¹⁵⁷⁾ is a comprehensive and good review of the studies in this

Table 5. Phase Diagrams of Alloys and a Metallurgical Slag System Studied by Mass Spectrometry

System	Investigators
Ag-Mn	Ichise, Ueshima, and Yamana (1989) ¹⁵³⁾
Al-Te	Said, Chastel, Bergman, and Castanet (1981) ⁶⁵⁾
Au-Ni	Tomiska, Erderyi, Neckel, and Nowotny (1977) ⁷³⁾
Au-Pd	Tomiska (1990) ⁷⁶⁾
B-La	Storms and Mueller (1978) ⁸⁰⁾
B-Mo	Storms and Mueller (1977) ⁸¹⁾
C-Nb	Storms, Calkin, and Yenchu (1969) ⁸⁹⁾
C-V	Storms, Lowe, Baca, and Griffin (1973) ⁹⁰⁾
C-Y	Storms (1971) ⁹¹⁾
C-Zr	Storms and Griffin (1973) ⁹²⁾
Co-Fe	Tomiska (1986) ⁹⁶⁾
Co-Ni	Tomiska, Nowotny, Erderyi, and Neckel (1979) ⁹⁷⁾
Cr-Cu	Timberg and Toguri (1982) ⁹⁹⁾
Cu-Ni	Tomiska and Neckel (1984) ¹⁰⁷⁾
Fe-Ge	Nunoue and Kato (1989) ¹⁶⁴⁾
Fe-Mo	Ueshima, Ichise, and Mori (1983) ¹⁵⁵⁾
Fe-Ni	Tomiska and Neckel (1985) ¹⁴¹⁾
Fe-Pd	Tomiska (1989) ⁹³⁾
Fe-Si	Zaitsev, Zemchenko, and Mogutnov (1991) ¹⁴³⁾
Fe-Sn	Nunoue and Kato (1987) ²³⁾
Fe-W	Ichise, Ueshima, and Miyagawa (1986) ¹⁵⁶⁾
Ni-Pd	Kopecky, Belegatis, Neckel, and Tomiska (1992) ¹²⁰⁾
Si-V	Storms and Myers (1985) ¹²⁴⁾
Al ₂ O ₃ -CaF ₂	Zaitsev, Korolyov, and Mogutnov (1990) ¹⁴⁰⁾

area, but this book is written in Russian.

The multiple-Knudsen-cell method has an advantage in the thermodynamic study of oxide melts, because often only a component of such melt has measurable vapor pressure. Allibert and Chailion and their co-workers applied this method to Al₂O₃-CaO, Al₂O₃-SiO₂, CaO-FeO-SiO₂, FeO-SiO₂, and Na₂O-SiO₂ systems as indicated in Table 4. Ouchi and Kato measured the activity of PbO in PbO-SiO₂¹⁵⁰⁾ and PbO-SiO₂-f¹⁵¹⁾ (*f* = BaO, CaO, CoO, MgO, and NiO) systems by the monomer/dimer method. Platinum cells coated with rhodium were used.

Kambayashi and Kato^{147), 148)} determined the activity of the MgO-SiO₂ system from the measurements of the relative intensities of SiO⁺ and Mg⁺, using the relation:

$$\text{SiO}_2(\text{in melt}) + \text{Mg}(\text{g}) = \text{MgO}(\text{in melt}) + \text{SiO}(\text{g}) \quad (8)$$

The activity ratio for SiO₂ to MgO in the Gibbs-Duhem relation was replaced by the ion-intensity ratio, and the activities of SiO₂ and MgO were computed by the equations:

$$\log a_{\text{SiO}_2} = - \int_{x=1}^x (1-x) d \log I_0^+ (I_+^{\text{Mg}} / I_+^{\text{SiO}}) \quad (9)$$

$$\log a_{\text{MgO}} = - \int_{x=0}^x x d \log I_0^+ (I_+^{\text{SiO}} / I_+^{\text{Mg}}) \quad (10)$$

where *x* is the mole fraction of SiO₂. They used platinum cells for the measurements at 1,873 K.¹⁴⁶⁾ For the measurements at 1,973 K,¹⁴⁷⁾ platinum-iridium cells and platinum-rhodium cells were used.

Kambayashi *et al.*¹⁴⁵⁾ determined the activity of P_2O_5 in Fe_2O_3 - P_2O_5 systems using the relation:

They measured the activity of P_2O_5 in the PbO - P_2O_5 system using this method. In this system, the activity of PbO was able to be determined by mass spectrometry. The calculated activity of P_2O_5 from the activity of PbO was in good agreement with the experimentally determined activity of P_2O_5 . These results indicate the validity of this method. The samples of the PbO - P_2O_5 system were held in palladium crucibles and the samples of the Fe_2O_3 - P_2O_5 systems were held in iron crucibles. Those crucibles were placed in alumina Knudsen cells. The palladium vapor in equilibrium with solid palladium and iron vapor in equilibrium with solid iron were used as the internal standards.

Ohara *et al.*¹⁴⁶⁾ applied this technique to the determination of the activity of P_2O_5 in the ternary Fe_2O_3 - P_2O_5 - i systems where i indicates CaO , MgO , MnO , and SiO_2 . The interaction parameters between P_2O_5 and these oxides in the melts were calculated from the activities of P_2O_5 in these ternary systems.

4. Studies of Phase Diagrams by Mass Spectrometry

The mass spectrometer-Knudsen cell combination has been used for the studies of phase diagrams of alloys as indicated in Table 5.

Phase diagrams can be obtained from activity data. Storms and his co-workers determined the phase boundaries of solid alloy systems from the activity data obtained by mass spectrometric measurements as indicated in Table 5.

The phase boundaries at a temperature have usually been obtained from the activities of the same temperature. Tomiska and his co-workers¹⁰⁶⁾ developed the technique which can determine phase boundaries at a temperature from the activities determined at another temperature. The condition for liquid-solid equilibrium at a temperature T in a binary system is expressed as:

$$\mu_j^l(x^l, T) - \mu_j^s(x^s, T) = 0 \quad (j=1, 2) \quad (12)$$

where μ_j^l and μ_j^s are the chemical potentials of component j in the liquid phase and in the solid phase, respectively, and x^l and x^s are the equilibrium compositions in the liquid phase and in the solid phase, respectively. The analytical expression of thermodynamic functions has been developed by Tomiska, and the thermodynamic data from mass spectrometric studies on liquid and solid phases and literature data for the heat capacities and enthalpies were used for the calculations.

Ueshima *et al.*¹⁵⁴⁾ determined the temperature of the invariant transformation of the Fe - Mo system by measuring the change of the ion intensity of Fe^+ with temperature. This technique was also applied to the Fe - W and Ag - Mn systems.

Gockcen *et al.*¹⁵⁸⁾ indicated that the phase boundaries could be determined by measuring the ion intensity ratio. This technique was applied to the Fe - Ge system by Nunoue and Kato.¹⁵³⁾ The relationship between $\ln(I_{Fe}^+/I_{Ge}^+)$ and $1/T$ is represented as follows:

$$\ln \frac{I_{Fe}^+}{I_{Ge}^+} = \frac{\Delta \bar{H}_{Fe}^M - \Delta \bar{H}_{Ge}^M - \Delta H_{ev, Fe}^\circ + \Delta H_{ev, Ge}^\circ}{RT}$$

Fig. 7. Temperature dependence of the ion current ratios for the Fe-Ge system (Nunoue and Kato¹⁵⁴).

Fig. 8. Summary of experimental results on phase equilibria in the Fe-Ge system (Nunoue and Kato¹⁵⁴).

$$-\frac{\Delta \bar{H}_{\text{Fe}}^{\text{M}} - \Delta \bar{H}_{\text{Ge}}^{\text{M}} - \Delta S_{\text{ev, Fe}}^{\circ} + \Delta S_{\text{ev, Ge}}^{\circ}}{R} + C \quad (13)$$

where $\Delta \bar{H}_i^{\text{M}}$ and $\Delta \bar{S}_i^{\text{M}}$ are the partial molar enthalpy and entropy of the solution of the component i , respectively, $\Delta H_{\text{ev}, i}^{\circ}$ and $\Delta S_{\text{ev}, i}^{\circ}$ are the molar enthalpy and entropy of evaporation of pure component i , respectively, and C is a constant. In general, the ion intensity ratio is a function of temperature and composition in the homogeneous regions. Equation (13) is linear in $1/T$ in a homogeneous solid or liquid region for a given composition, because the partial molar properties are independent of composition, and all of the molar properties are nearly independent of temperature in a limited temperature range. The temperature dependence of the ion intensity ratio is indicated in Fig. 7. In this figure, the straight solid lines indicate the ion current ratios measured in the homogeneous liquid phase region, and the straight broken lines indicate the ratios in the homogeneous solid phase region. In the region of twophase equilibrium, the ion current ratio is a function of only temperature. The phase boundaries determined from the results indicated in Fig. 7 is shown in Fig. 8, together with the boundaries obtained by other investigators.

5. Conclusions

The thermodynamic activities of many alloys and metallurgical slags have been measured by the Knudsen cell-mass spectrometer combination, and this technique has much contributed to the thermodynamic study of metallurgical systems. Almost all industrially important alloys which can be studied by high temperature mass spectrometry seem to have been studied. However, some important slag systems are still left to be studied. For instance, the activities of the compound of sulfur in slags may be measured by mass spectrometry. The activities of phosphorous oxides must be studied further. The thermodynamic data of the materials of electronic devices are still poor and mass spectrometric studies of this area should be performed.

If the sensitivity of the mass spectrometer should be improved, more systems can be studied by mass spectrometry. The lowest vapor pressure which can be measured by a Knudsen cell-mass spectrometer combination is about 10^{-6} Pa when a magnetic sector instrument is used. Pulse counting technique seems the ultimate technique for the measurement of ion intensity and has already been used for high temperature mass spectrometry. On the contrary, ion source efficiency may be increased further. For instance, Storms¹⁵⁹⁾ used an improved ion source and he could measure the vapor pressure of 10^{-8} Pa.

For high temperature mass spectrometry, magnetic sector instruments have widely been used, because this type instruments have good resolution and back ground peaks can be separated from the determined peaks. However, magnetic sector instruments are rather complicated and it requires trained technique for operation. The development of vacuum technique enables the intensity of the back ground peak very small, and another instrument, for instance, quadrupole mass spectrometers can widely be used.

High temperature mass spectrometry should be applied more to the study of phase diagrams, because this technique has an advantage over quenching technique which is usually used for the determination of phase boundaries at high temperatures: High temperature mass spectrometry can determine the phase boundaries "*in situ*" at a high temperature.

I expected the development of the transpiration-mass spectrometer system for the studies of vapors at near-atmospheric pressure. However, the problem of the error-inducing effects such as skimmer-interference have not been completely solved. If such problems should be solved, this technique would be very useful technique for high temperature studies of various materials.

The studies of thermodynamic equilibrium between condensed and gaseous phases are important for metallurgy, but no metallurgist is doing such studies by mass spectrometry.

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Keywords

High temperature mass spectrometry

Thermodynamic activity

Alloy

Metallurgical slag

Phase diagram