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THE APPLICATION OF A THERMOBALANCE FOR DETERMINING THE VAPOUR PRESSURE AND THERMODYNAMIC PROPERTIES

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Application examples of the thermobalance for vapour pressure and high-temperature thermodynamic properties of pure metals, their liquid solutions and molten sulphides measurements have been presented. The Knudsen method gives the possibility to determine the total vapour pressure over a given system. It allows also, in connection with a mass spectrometer, for determining the partial pressures in the gaseous phase and thus for describing the thermodynamic properties of the gaseous and condensed phases of the system examined.

The knowledge of the thermodynamic properties of the condensed and gaseous phases is necessary to analyse the phenomena occuring in high-temperature technological processes. To determine the thermodynamic data, three main methods are used:

- measurement of the electromotive forces (EMF) of electrochemical cells,
- colorimetric measurements,
- vapour pressure measurements.

The last group comprises the effusion Knudsen method, torsion method, and measurement of the ion currents intensity of the effusing vapour, by means of the mass spectrometer.

The measurements aim at fulfilling the following conditions: there is a thermodynamic equilibrium between the condensed phase and vapour in the cell, which can be achieved, when the effusion hole diameter is less than the mean free path of the vapours. During the measurement the rate of sample weight loss from the Knudsen cell is measured. The Knudsen cell is a crucible with a tight lid with an effusion orifice. The weight loss rate (dg/dt) measured in the function of temperature is connected with pressure inside the cell by the following equation:

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$$P = (\mathrm{d}g / \mathrm{d}t)\,\frac{\sqrt{2\pi RT/M}}{WA} \tag{1}$$

where:
P - vapour pressure,
T - temperature,
M - assigned molecular weight of the effusing vapour,
R - gas constant,
W - transmission probability of the orifice,
A - geometrical area of the orifice.
The Mettler thermobalance type TA1 of accuracy 10^{-5} g with results recording on a paper tape, vacuum of 10^{-3} Pa, heating temperature up to 1600°, has been used for Knudsen measurements.

Vapour pressure and thermodynamic of indium

The vapour pressure over liquid indium has been determined over the temperature range of 1096-1390 K by measuring the weight loss rate.

The pressure equation in the function of temperature has been described by the following relation [1]:

$$\log(P/Pa) = -\frac{12830}{T} + 10.706 \tag{2}$$

The value of standard sublimation enthalpy ΔH° (298 K) has been determined, basing on the relationships resulting from the second and third law, being 253.1 ± 1.2 kJ/mol and 242.5 ± 0.8 kJ/mol respectively. The standard sublimation enthalpy value, determined from the third law is, according to the usually assumed value, 243 kJ/mol [2].

The Fe-As system

The system has been examined over the arsenic concentration range of 22.58-35.89 mol%, over the temperature range 1100-1400 K at less than 12 mol% As by a mass spectrometer over the temperature range 1620-2010 K [3]. The arsenic vapour pressure over liquid arsenic-iron solution over the temperature range of 1220-1580 K for X_{As} = 0.2258 has been described by equation:

$$\ln(P/Pa) = 20.1445 - \frac{27699.3}{T} \tag{3}$$

The self-activity coefficient has been determined from the measurements of the I^+_{As} and I^+_{Fe} ion currents on the mass spectrometer. Its value at 1809 K is $\varepsilon^{As}_{As(Fe)} = 4.48 \pm 0.03$.

The complex results of both methods have been described by the Redlich-Kister equation, and the following equation for the arsenic activity coefficient has been obtained:

$$\ln\gamma_{As} = X^2_{Fe}\left\{b_0 + \sum_{i=1}^{n} b_i\,(X_{Fe} - X_{As})^{(i-1)}\,[X_{Fe} - (2i-1)X_{As}]\right\} \tag{4}$$

The highest consistency with the experimental data has been achieved for $i = 2$, where the constants are:

$b_0 = -2.348 - 6036/T$

$b_1 = 11.233 - 21771/T$

$b_2 = -11.422 + 23.423/T$

The value of the arsenic activity coefficient in a diluted solution has been determined from Eq. (4):

$$\ln\gamma^0_{As(Fe)} = -2.537 - 4383/T \tag{5}$$

The Cu_2S-PbS system

The first stage of the investigations aimed at determination of the vapour pressure and standard sublimation enthalpy of solid PbS. The measurements have been carried out over the temperature range of 878-1926 K and additionally in a mass spectrometer at 796-1096 K to determine the chemistry of pure PbS evaporation [4].

Basing on the ions identified in the gaseous phase, the courses of the following reactions in the gaseous phase have been confirmed:

$$PbS_{(s)} \rightleftarrows PbS_{(g)}$$

$$PbS_{(g)} \rightleftarrows Pb_{(g)} + S_{2(g)}$$

$$2PbS_{(g)} \rightleftarrows Pb_2S_{2(g)}$$

The determined PbS vapour pressures have been described by equation:

$$\log(P/Pa) = -11\,525.04\left(\frac{1}{T} - \frac{1}{960.9}\right) + 0.4065 \qquad (6)$$

The selected value of the standard sublimation enthalpy according to the third law is 232.4 ± 0.1 kJ/mol. The determined values of the pressures and the standard sublimation enthalpy show a very good consistence with the literature data.

The Cu_2S-PbS system has been examined by isothermal PbS evaporation from a sample containing approx. 80 mol% PbS over the temperature range of 1040-1103 K [5].

The results had been elaborated with an assumption, that only PbS evaporated from the sample, as the pure Cu_2S pressure is of the order of 10^{-4} Pa [5] over this temperature range.

From the results obtained the dependence of the PbS activity coefficient on the composition has been determined and described by the Redlich-Kister equation, obtaining:

$$\begin{aligned}\ln\gamma_{PbS} &= (1-X)^2[-2.7-391/T+(0.18+1285/T)(4X-1)- \\ &-(5.4-7149/T)(1-2X)(6X-1)] \qquad (7)\end{aligned}$$

The results obtained indicate a negative deviation of the PbS activity coefficient over the whole concentration range.

Moreover, the liquidus line position as well as the PbS activity in diluted solution coefficient value have been determined:

$$\ln\gamma^{o} = 2094.93/T-2.96 \qquad (8)$$

References

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Zusammenfassung — Es werden Anwendungen einer Thermowaage für die Messungen von Gasdruck und dynamischen Eigenschaften bei hohen Temperaturen von reinen Metallen, deren flüssigen Lösungen und geschmolzenen Sulfiden gezeigt. Das Knudsen-Verfahren ermöglicht die Bestimmung des Gesamtgasdruckes über einem gegebenen System. In Verbindung mit einem Massenspektrometer erlaubt es weiterhin die Bestimmung der partiellen Drücke in der Gasphase und somit die Beschreibung der thermodynamischen Eigenschaften der gasförmigen und kondensierten Phase des untersuchten Systemes.