Thermodynamic properties investigation of liquid metal alloys with application of the effusion method new variant in the pressure range between Knudsen’s and hydrodynamic efflux modes

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Abstract. A new variant of the effusion method for measuring the thermodynamic activity (Gibbs energy) in the alkali-metal binary and ternary systems (Cs-Na, K-Na, Cs-K, Cs-K-Na) is proposed. This activity is determined using the components partial pressures by the effusion method with measurement of atomic beam intensity. The pressure range was intermediate between Knudsen’s mode and hydrodynamic one. A detailed analysis shows that it is possible to operate outside the range where the Hertz-Knudsen equation applies. As oxygen inevitably reacts with a molten alkali metal, the effusion hole cannot be made in advance. Therefore, the effusive hole was machined directly in the vacuum chamber by the electron-ray pulse (the electron linear accelerator was located inside the chamber) after the cell acquired the working temperature.

1 Introduction

Multicomponent alloys of alkali metals are advanced coolants and working fluids for power engineering, technology and metallurgy because they are possessed the possibility of service characteristics control and the widest
temperature range of liquid phase being both highly effective high-
temperature and low-temperature coolants (Bystrov et al 1990).

Direct measurement of thermodynamic activity of components $a_i$ (or
Gibbs energy of alloy formation $\Delta G_i = RT \ln a_i$) for the liquid metal
alloys at high temperatures is extremely difficult with respect to alkali
metals. The reasons are:

- the absence of stable high-temperature solid electrolytes with the
  required ion composition to be used for concentration cell membranes (for
  EMF method),
- the interference of radiation of the respective lines (for the atomic
  absorption method) and
- too high saturation pressure (for effusion method).

Therefore instead of direct measurement of components activity of the
liquid alkali metal mutual alloys at high temperatures, use is made of the
determination of this function within a wide range of temperatures $T$ and
concentrations $x_i$ through integration of the differential equation of chemical
thermodynamics:

\[
\left[ \partial \ln a_i / \partial (1/T) \right]_{p, x_i} = \Delta \Pi_i / R ,
\]

(1)

the solution of which has a form:
\[
\ln a_i(T, x_i) = \ln a_i(T_1, x_i) - R^{-1} \int_{T_1}^{T} \Delta \overline{H}_i(T, x_i) T^{-2} dT.
\] (2)

The integrand \( \Delta \overline{H}_i(T, x_i) \), i.e. the partial enthalpy of formation within the entire region of parameters under the study \((400 \leq T \leq 1200K, 0 \leq x_i \leq 1)\), as well as boundary condition, \( \ln a_i(T_1, x_i) \), i.e. the concentration dependence of component activity only at one not high reference temperature \( T_1 \) \((400 \leq T_1 \leq 450K)\) within the entire range of \( x_i \), are determining in the experiment.

Thus the algorithm of the research allows determining thermodynamic activity at high temperatures without resorting to its direct measurements in this area. This method does not require any special assumptions and can be furnished with reliable input experimental data.

The object of this work is developing the method and measuring the activity (Gibbs energy) on the reference isotherm \( T_1 \), determining the boundary conditions \( \ln a_i = f(T_1, x_i) \) for integrating (1), which enables one to close the thermodynamic description for the alkali-metal binary and ternary systems (Cs-Na, K-Na, Cs-K, Cs-K-Na) in all above range of parameters under the study.

2 Experimental

The method is based on measuring the components partial pressures from the atomic-beam intensity provided by an effusion cell. As oxygen
inevitably reacts with a molten alkali metal, the effusion hole cannot be made in advance. Therefore (see Fig.1), the cell 7 filled with the liquid alloy under study by vacuum pouring, is placed (position I) in sealed form in the chamber 3. Then the chamber is being evacuated, after which the cell is brought to appropriate temperature $T_1$. Then a standardized electron-ray pulse 2 (the electron linear accelerator 1 was located inside the chamber) is used to make the effusion hole, and the cell is being transferred by a remote-controlled drive toward under the cryogenic condenser 5 (position II), which is cooled by liquid nitrogen 4. After the exposure time, the chamber is being filled with inert gas and the cryogenic condenser is being taken down and placed in a sealed vial in an inert gas atmosphere and then removed from the chamber. Spectrochemical analysis gives the condensate composition, and as this is equivalent to the vapor composition in the atomic beam 6, and the mass of condensate is known, one can determine the partial intensity and pressure for each component, and correspondingly the activity.

3 Results and discussion

Hertz-Knudsen equations:

$$q = P(2\pi RT\mu)^{-1/2}, \text{ mol}\cdot\text{m}^{-2}\cdot\text{sec}^{-1},$$

$$g = P(2\pi RT)^{-1/2} \mu^{1/2}, \text{ kg}\cdot\text{m}^{-2}\cdot\text{sec}^{-1}$$

(where $q$ and $g$ are the flux intensity in molar and mass units, $\mu$ - molecular mass) may be applied when Knudsen number
\[ Kn = \frac{\lambda}{2r_e} \geq 10 \]  
(5)

(where \( \lambda \) is mean free path and \( r_e \) is the effusion hole radius). In this case the reflected flux in the effusion hole zone is \( \leq 1\% \) (Sidorov et al 1985). The order of \( \lambda \) value is 
\[ \lambda = \left( \sqrt{2} \sigma n \right)^{-1} = \left( \frac{1}{2} \sigma \right)^{-1} kT/P \]  
(where \( \sigma \) is the effective particle cross sections and \( n \) is the number of particles in unit volume). So on the real conditions of experiment (400\( \leq T \leq 450\)K, \( r_e \approx 1\)mm) for alkali-metal alloys with components Na, K, Cs the requirement (5) is approximately answered only for pure Na (saturation pressure \( P_S \leq 1 \) Pa, \( \lambda \geq 10 \) mm). This aspect is important, since at working temperature \( T_1 \) and with real hole size \( r_e \), the flux in the hole zone in a general case may no longer be collision-free: saturation pressure of alloys \( P_S \approx 10 \) Pa, mean free path \( \lambda \approx 1 \) mm and Knudsen number \( Kn \approx 0.5 – 1 \).

In the hydrodynamic mode (\( Kn \leq 0.05 – 0.1; \lambda \leq 0.1 \) mm; \( P \geq 100 \) Pa) the efflux is supersonic (pressure ratio in effusion experiments >200), and correspondingly the mass flux is (Ewing and Stern 1974, 1975)
\[
g = PC_D \left\{ \gamma \left[ 2/\gamma (\gamma + 1) \right]^{(\gamma + 1)/(\gamma - 1)} \right\}^{1/2} (RT)^{-1/2} \mu^{1/2}, \]  
(6)
where \( \gamma = C_P/C_v \). Coefficient \( C_D \) is independent of the atomic composition in the gas and is dependent in a general way on the pressure ratio, but at large ratio it attains an asymptotic upper limit. The data (Ewing and Stern 1974, 1975) for monatomic, diatomic and triatomic gases give the general result \( C_D = 0.85 \pm 2\% \).
So, a general expression can be written for the mass flux rate in the free-molecular and hydrodynamic efflux modes:

\[ g = P \Gamma (RT)^{-1/2} \mu^{1/2} L, \]  

(7)

where the parameter \( \Gamma \) is introduced:

\[ \Gamma = \left\{ \begin{array}{ll}
\Gamma_k = (2\pi)^{-1/2} = 0.399 \text{ free-molecular (Knudsen’s) mode} \\
\Gamma_{hd} = C_D \{\gamma[2/(\gamma + 1)]^{(\gamma+1)/(\gamma-1)}\}^{1/2} \text{ - hydrodynamic mode.}
\end{array} \right. \]

(8)

Clausing factor \( L \) (account of a wall thickness) is the same (Ewing and Stern 1974, 1975) for both modes, for real conditions of experiment \( L \approx 0.77-0.87 \).

It is seen that the Hertz-Knudsen equation (HKE) (4) is a particular case of (7) with \( \Gamma = \Gamma_k = (2\pi)^{-1/2} \) and \( L = 1 \).

A monatomic vapour, such as an alkali metal saturated vapour at the temperature \( T_1 \), has \( \gamma = 1.67 \), and \( \Gamma = 0.617 \) for hydrodynamic mode. Thus the actual effusion flux in the hydrodynamic mode is 1.55 times that calculated from the HKE for the same pressures. In the range intermediate between the two modes, \( \Gamma \) for alkali-metal vapour increases from 0.399 to 0.617 (see Fig.2).

Important conclusions are that the effusion method can be used outside the Knudsen pressure range. The general form of the physical relationships persists, but there are numerical differences. In particular, if one neglects the transition to the intermediate or hydrodynamic modes, i.e., uses the HKE in pure form for this regions, one overestimates the
determined pressures, as is evident from \( g=f(P) \) for \( T=const \) on Fig.3 (\( P_K>P_t \) in regions 2 and 3, where \( P_K \) – saturation pressure derived from HKE, \( P_t \) – true saturation pressure).

4 Conclusions

- The method of the alkali-metal alloy activity (Gibbs energies) measuring on the reference isotherm \( 400 \leq T_1 \leq 450K \) is developed, determining the boundary conditions \( \ln a_i = f(T_1, x_i) \) for integrating (1), which enables one to close the thermodynamic description for the alkali-metal binary and ternary systems (Cs-Na, K-Na, Cs-K, Cs-K-Na) in the range of \( T \) and \( x_i \) \( 400 \leq T \leq 1200K, 0 \leq x_i \leq 1 \).

- The effusion method can be used outside the Knudsen pressure range. The general form of the physical relationships persists, but there are numerical differences.

- Developing the effusion method for alkali-metal alloys at pressures outside the HKE applicability range fills a gap in methods of examining such saturation pressures between the range for manometric methods \( (P>100Pa) \) and methods based on the HKE \( (P<1Pa) \).

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References


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FIGURE CAPTIONS (Kagan et al)

**Figure 1.** Functional scheme of installation:

1 – linear electron accelerator  
2 – electron beam  
3 – vacuum chamber  
4 – cryogenic cooler (liquid N₂)  
5 – interchangeable conical condenser  
6 – atomic beam  
7 – capsule containing liquid alloy under study (effusion cell)  
8 – thermostat  
9 – cell heaters  
10 – thermocouples  
11 – oscillatory unit for homogenization of liquid alloy  
12 – working-cell displacement direction from position I to position II  
I – position under electron beam for machining of effusion hole  
II – position under cryogenic condenser during effusion exposure

**Figure 2.** \( \Gamma \)-parameter for alkali metal alloys vapour as a function of mean free path:

\( \Gamma \) – parameter (see relationships 7,8 in the text)  
\( \lambda \) – mean free path  
1 – free-molecular (Knudsen’s) efflux mode  
2 – transitional efflux mode  
3 – hydrodynamic efflux mode

**Figure 3.** Flux as a function of pressure

\( P \) – saturation pressure  
\( g \) – flux intensity  
\( g_{\text{exp}} \) – experimental flux  
\( P_t \) – true saturation pressure  
\( P_K \) – saturation pressure derived from Hertz-Knudsen equation  
\( P_{\text{hd}} \) – saturation pressure calculated for hydrodynamic efflux mode  
1 – free-molecular (Knudsen’s) efflux mode  
2 – transitional efflux mode  
3 – hydrodynamic efflux mode  
\( \Gamma, \Gamma_K, \Gamma_{\text{hd}} \) – see relationships 7,8 in the text
1 – linear electron accelerator
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Fig. 1. Functional scheme of installation

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$g$, $g_{\exp}$, $g$, $P$, $P_{1}$, $P_{K}$, $P_{hd}$, $\Gamma$, $\Gamma_{K}$, $\Gamma_{hd}$

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- $P_{1}$ – true saturation pressure
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