Elaborating and applying a new method of Gibbs energy determination for multicomponent alkali-metal coolants

D N Kagan, G A Krechetova and E E Shpilrain
Joint Institute for High Temperatures of Russian Academy of Sciences;
13/19 Izhorskaya, Moscow 125412, Russia
E-mail: d.n.kagan@mtu-net.ru

Abstract. A new variant of the effusion method for measuring the thermodynamic activity (Gibbs energy) in the liquid alkali-metal binary and ternary systems (Cs-Na, K-Na, Cs-K, Cs-K-Na) is proposed. The activity is determined using the components partial pressures by the effusion method with measurement of atomic beam intensity. 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. 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. Applying this method allowed to supply with the boundary conditions the differential equation of chemical thermodynamics, the solution of which enables one to construct Gibbs energy of above alloys in the range of temperatures $400 \leq T \leq 1200$ K and concentrations $0 \leq x_i \leq 1$.

1. Introduction
Multicomponent mutual liquid solutions 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 high effective both high-temperature and low-temperature coolants simultaneously [1]. For example eutectic point of the ternary system Na-K-Cs is the lowest-melting metallic liquid of the known on the Earth (crystallization temperature $T_{cr} = -78^\circ$C).

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 and practically impossible with respect to alkali metals.

2. General method
Therefore instead of direct measurement of components activity of the liquid alkali metal mutual alloys at high temperatures, use is made of the calculation-experimental method [2, 3] based on determination of this function within a wide range of temperatures $T$ and concentrations $x_i$ through integration of the differential equation of chemical thermodynamics:

$$
[\partial \ln a_i / \partial (1/T)]_{p,x_i} = \Delta \overline{H}_i / R,
$$

(1)
the solution of which has a form:

\[
\ln a_i(T, x_i) = \ln a_i(T_1, x_i) - R^{-1} \int_{T_1}^{T} \frac{\Delta H_i(T, x_i)}{T} \, dT.
\]  
(2)

The integrand \(\Delta H_i(T, x_i)\), i.e. the partial enthalpy of formation within the entire region of parameters under the study \((400 \leq T \leq 1200 \text{K}, 0 \leq x_i \leq 1)\), 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 \(T_1\), \((400 \leq T_1 \leq 450 \text{K})\) 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 experimental data for \(\Delta H_i(T, x_i)\) in the range of the temperatures \(400 \leq T \leq 1200 \text{K}\) and the concentrations \(0 \leq x_i \leq 1\) are available in [4]. So the object of this work is elaborating 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.

3. Experimental

The experimental method for solution of this task is based on measuring the components partial pressures via 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, the cell filled with the liquid alloy under the study by vacuum pouring, is placed in sealed form in the chamber. Then the chamber is being evacuated, after that the cell is being brought to appropriate temperature \(T_1\). Then a standardized electron-ray pulse (the electron linear accelerator was located inside the chamber) is used to make the effusion hole, and the cell is being transferred by a remote-controlled drive towards under the cryogenic interchangeable conical condenser, which is fitted to the cooler with liquid nitrogen. After the exposure time, the chamber is being filled with inert gas, and the cryogenic condenser in this atmosphere is being removed from the chamber. Spectrochemical analysis gives the condensate composition, and as this is equivalent to the vapor composition in the atomic beam, one can determine the partial intensity and pressure for each component, and the activity correspondingly.

4. A new variant of the effusion method

But there is a problem. Hertz-Knudsen equations:

\[
q = P(2\pi RT\mu)^{-1/2}, \quad \text{mol-m}^{-2}\text{-sec}^{-1},
\]
(3)

\[
g = P(2\pi RT)^{-1/2} \mu^{1/2}, \quad \text{kg-m}^{-2}\text{-sec}^{-1}
\]
(4)

\((q \text{ and } g \text{ are the flux intensity in molar and mass units, } \mu \text{ - molecular mass}) \text{ may be applied when Knudsen number}

\[Kn = \frac{\lambda}{2r_e} \geq 10\]
(5)

\((\lambda \text{ is mean free path and } r_e \text{ is the effusion hole radius). In this case the reflected flux in the effusion hole zone is } \leq 1\% \text{ [5].}

The order of \(\lambda\) value is \(\lambda = \left(\frac{\sigma}{\sqrt{2} n}\right)^{-1} = \left(\frac{\sigma}{\sqrt{2}}\right)^{-1} kT/P\) (\(\sigma \text{ is the effective particle cross sections and } n \text{ is the number of particles in unit volume}). It is found that in the real conditions of experiment \((400 \leq T_1 \leq 450 \text{K}, r_e \approx 1 \text{mm})\) for alkali-metal alloys with components Na, K, Cs the requirement (5) is answered only for pure Na (saturation pressure \(P_s \leq 1 \text{ Pa, } \lambda \geq 10 \text{ mm}\)). In a general case, i.e. for
other components and alloys, the flux in the hole zone is not longer collision-free and begins to transfer into the hydrodynamic mode (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 [6, 7]

$$g = PC_D\left[2/(\gamma + 1)\right]^{\gamma (\gamma + 1)/(\gamma - 1)}(RT)^{1/2}\mu^{1/2},$$

where $\gamma = C_P/C_v$. Coefficient $C_D$ is independent on 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 [6, 7] 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:

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

where the parameter $\Gamma$ is introduced:

$$\Gamma = \Gamma_K = (2\pi)^{-1/2} = 0.399 \text{ – free-molecular (Knudsen’s) mode} \quad (8)$$

$$\Gamma = \Gamma_{hd} = C_D\left[2/(\gamma + 1)\right]^{\gamma (\gamma + 1)/(\gamma - 1)}(RT)^{1/2} \text{ – hydrodynamic mode.} \quad (9)$$

Clausing factor $L$ (account of a wall thickness) is the same [6, 7] 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 vapor, such as an alkali metal saturated vapor 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 larger than calculated from the HKE for the same pressures. In the range intermediate between the two modes, $\Gamma$ for alkali-metal vapor increases from 0.399 to 0.617.

Important conclusion is that the effusion method can be used outside the Knudsen pressure range. The general form of the physical relationships persists, but there are significant numerical differences. If one neglects the transition to the intermediate or hydrodynamic modes, i.e. uses the HKE in pure form for this regions, one sufficiently overestimates the determined pressures.

5. Results and discussion

The results are presented in table 1.

| Table 1. Activity of components in binary and ternary mutual solutions of alkali metals at 400K, experimental results ($x_i$ – mole fractions, $a_i$ – activity). |
|-----------------|--------|--------|--------|--------|--------|
| Cs-Na           | $x_{Na}$| 0.152  | 0.250  | $a_{Na}$| 0.302  | 0.463  |
|                 | $a_{Cs}$| 0.863  | 0.779  |         |        |        |
| K-Na            | $x_K$  | 0.200  | 0.319  | 0.334  | 0.500  | 0.668  |
|                 | $a_K$  | 0.358  | 0.475  | 0.493  | 0.658  | 0.741  |
|                 | $a_{Cs}$| 0.833  | 0.753  | 0.735  | 0.639  | 0.531  |
| Cs-K            | $x_{Na}$| 0.149  | 0.350  | 0.499  | 0.499  | 0.700  | 0.850  |
|                 | $a_{Na}$| 0.159  | 0.366  | 0.496  | 0.493  | 0.687  | 0.843  |
|                 | $a_{Cs}$| 0.847  | 0.653  | 0.528  | 0.525  | 0.316  | 0.150  |
| Na-K-Cs         | $x_{Na}$| 0.139  | 0.435  | 0.426  |        |        |
|                 | $a_{Na}$| 0.260  | 0.473  | 0.465  |        |        |
The following mutual solutions of alkali metals (mole fractions) were studied: Cs-Na (Na fractions) – 0.152, 0.250; K-Na (Na fractions) – 0.200, 0.319, 0.334, 0.500, 0.668; Cs-K (K fractions) – 0.149, 0.350, 0.499 (two samples), 0.700, 0.850; Na-K-Cs – 0.139Na, 0.435K, 0.426Cs. All the results were obtained at temperatures 400 ≤ T ≤ 450K and reduced to 400K using the partial enthalpy of formation data [4].

The analysis of errors gives the approximate value 5% for average magnitudes of activity.

The above results were compared with literature data that are available only for two of the investigated systems at temperatures of about 400K: Cs-Na [8, 9] – emf method, a\textsubscript{Na}; K-Na [10] – atomic absorption method, a\textsubscript{Na}, a\textsubscript{K}. The comparison showed quite satisfactory agreement, which makes it possible to form a general file of the data at this temperature and plot the isotherms T=400K for binary systems. The Gibbs-Duhem equation was used when tracing a\textsubscript{Cs} curve in Cs-Na solution. As it is indicated above these results are the boundary conditions for integrating the equation (1) in the state variables range 400 ≤ T ≤ 1200K, 0 ≤ x\textsubscript{i} ≤ 1.

6. Conclusions
The method of the alkali-metal mutual solutions activity (Gibbs energies) measuring on the reference isotherm 400 ≤ T ≤ 450K is developed, determining the boundary conditions ln a\textsubscript{i} = f(T\textsubscript{i}, x\textsubscript{i}) for integrating (1), which enables one to close the thermodynamic description for the liquid alkali-metal binary and ternary systems (Cs-Na, K-Na, Cs-K, Cs-K-Na) in the range of T and x\textsubscript{i} 400 ≤ T ≤ 1200K, 0 ≤ x\textsubscript{i} ≤ 1.

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

And finally one additional conclusion: development of the effusion method for alkali-metal alloys at pressures outside the HKE applicability range fills a gap in the saturation pressure examining methods between the range for manometric methods (P > 100Pa) and methods based on the HKE (P < 1Pa).

Acknowledgements
The authors are grateful for support of this work to the Russian Foundation for Basic Research (grant number 05-02-16129) and Ministry of Education and Science of Russian Federation (grant number SS-7261.2006.8).

7. References
[1]. Bystrov P I, Kagan D N, Krechetova G A and Shpilrain E E 1990 Liquid-Metal Coolants for Heat Pipes and Power Plants (New York: Hemisphere) pp 127-162
[2]. Kagan D N, Krechetova G A and Shpilrain E E 2001 High Temperature 39 840-845
[3]. Kagan D N, Krechetova G A and Shpilrain E E 2003 Journal of Molecular Liquids 103-104 395-404
[4]. Komarek K L et al. 1985 Handbook of Thermodynamic and Transport Properties of Alkali Metals, ed R W Ohse (Oxford: Blackwell) pp 913-977
[5]. Sidorov L N, Korobov M V and Zhuravleva A V 1985 Mass-spectral Thermodynamic Studies (Moscow: Moscow State University Press) pp 124-132
[6]. Ewing C T and Stern K H 1974 J. Phys. Chem. 78 1198-2005
[7]. Ewing C T and Stern K H 1975 J. Phys. Chem. 79 2007-2017
[8]. Ichikawa K, Granstaff S M and Thompson J C 1974 J. Chem. Phys. 61 4059-4062
[9]. Neale F E and Cusack N E 1982 J. Phys. F: Met. Phys. 12 2839-2850
[10]. Cafasso F A, Khanna V M and Feder H M 1967 Adv. Phys. 16 535-543