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# CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

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## Vapor pressure of alkali-metal binary alloys in glass cells



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### ABSTRACT

The alkali partial pressures of composite alkali-metal vapor are crucial in atomic-physics optical experiments. The vapor pressures of alkali-metal binary alloys can be calculated by using the activity and the mixing enthalpy for homogeneous alloys from early measurements. We show that the results of sodium-containing alloys deviate appreciably from the prediction of Raoult's law. Experimentally, the phase and the mixing ratio of binary alloys are non-destructively measured by nuclear-magnetic-resonance spectroscopy in glass cells. We find that many droplets of the sodium-rubidium alloy exist on the cell walls, and they have different mixing ratios. Therefore, the vapor density varies microscopically around the glass cells. To achieve precision optical measurements, we should take account of the pressure change due to the equilibrium process and further sodium contamination over the lifetime of glass cells.

### 1. Introduction

A transparent glass container of alkali metal, called glass vapor cell, is used in many experiments of atomic spectroscopy [1–3] because the isolated atomic system is especially suitable for precision metrology. The dynamical behaviors of the gas-phase atoms are stimulated and probed by irradiating laser, electric, and magnetic fields. However, the atomic dynamics is disturbed by surface potential produced by the metal film on the glass wall as well as atomic collisions [4]. A tiny amount of alkali metal forms non-metallic alkali-compound layer on the glass surface [5] and it affects atomic energy levels in a way different from metal film [6]. In the manufacturing process, the alkali metals are generated by chemical reaction such as decomposition and reduction of corresponding alkali salts with metal calcium [7] and alloys [8], or transferred from break-seal ampule of pure metal. The contamination by metal reductant is negligible because of its low vapor pressure. The metals are distilled in glass bulbs sequentially for getting extra-pure metal in the final cells [9–11]. Although distillation is believed important for better performance in optical experiments, it can introduce additional impurities, because alkali metals are highly-reactive chemicals. For example, sodium (Na) becomes dissolved in one other alkali metal such as rubidium (Rb) due to cation replacement in glass materials when a container consists of sodium borosilicate glass [12]. Therefore, to avoid impurities, we should not heat alkali metal too much but chase the liquid metal on a clean slope, counter-intuitively, without distillation. After metal transfer, the glass cells are filled with and without buffer gas and then sealed off.

In addition to macroscopic metal drops, the spherical metal

droplets often appear in micrometer-scale on the walls and the metal is sometimes crystallized as whiskers in the organic coating [13,14]. The vapor density is low at beginning in newly-manufactured cells and increased through curing process [5]. Even when the density is saturated, it is often smaller than literature data for unknown reasons [15]. To achieve precision measurements, therefore, the vapor density is routinely measured in each cell by optical absorption [16] and Faraday rotation [17,18]. The vapor density and the surface potential depend on the condition of alkali metal such as metallic film and droplet, non-metallic compound, and contaminated alloy. For control of the density of component atoms either in single or binary alkali-metal vapor [19], it is important to analyze the chemical state and the constituents of alkali metal on the walls. However, only a few works have been demonstrated to detect impurity in non-destructive ways [20]. Recently, we found that nuclear magnetic resonance (NMR) can be very useful for *in situ* analysis of alkali binary alloys, and investigated the phase of binary alkali system and the impurities such as oxygen and sodium, where a small amount of metal used in real optical experiments has been diagnosed in glass cells [12,21].

In this paper, we study the vapor pressure of alkali-metal binary alloys in glass cells. The vapor is properly described as an ideal gas because it is sufficiently dilute in our temperature range, and because the reactive gases such as oxygen and hydrogen are not present. According to Raoult's law, the partial pressure of the component in vapor is proportional to the mixing ratio in an ideal solution [22]. However, the real alloys do not always follow that law, because the interactions are not entirely identical between elements in the solution. After considering the thermodynamic equations, the vapor pressure is

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calculated by using the literature data, that is, the activity measured from mixing enthalpy for real alkali-metal binary alloys [23–26]. It should be noted that the behavior of sodium-containing alloys deviate appreciably from Raoult's law. Although the calculation indicates true pressure for homogeneous binary alloys, non-destructive NMR measurements in this work show a different situation of the Na-Rb system in real glass cells, that is, the mixing ratio of Na and Rb varies randomly across droplets on the walls. Since the vapor pressure is a function of mixing ratio, the alkali vapor density varies microscopically from droplet to droplet. Although atoms are exchanged between droplets through vaporization and condensation, it takes months to years, depending on the temperature, to achieve the equilibrated mixing-ratio and then vapor-pressure. Persistent chemical reactions are also expected to change constituents in glass cells. Even at a constant temperature, the vapor pressure of alkali metals will change for the entire lifetime of glass cells.

## 2. Ideal mixture and real alloy

The basic equations of thermodynamics are introduced in this section. From the chemical potentials of the liquid and the gas phases in equilibrium, the vapor pressure is expressed by the activity, the effective molar ratio. The activity is related with the interaction coefficients of the excess molar Gibbs function. Since the coefficients have been known for alkali binary alloys in the past works, the vapor pressure of binary alloy is straightforwardly obtained.

Dalton's law states that the total pressure of an ideal gas mixture is equal to the sum of the partial pressures of the individual gases A and B,  $p = p_A + p_B$ . The molar (mixing, atomic) ratio of A in the gas phase is

$$y_A = p_A/p, \quad (1)$$

and  $y_A + y_B = 1$  in the absence of buffer gas. Raoult's law for an ideal liquid mixture is  $p_A = x_A p_A^*$ , where  $p_A^*$  is the vapor pressure of pure liquid A,  $x_A$  is the molar ratio of A in a binary mixture AB, and  $x_A + x_B = 1$ . The total pressure is

$$p(x_A) = p_A + p_B = (p_A^* - p_B^*)x_A + p_B^*. \quad (2)$$

From Eqs. (1) and (2),

$$p(y_A) = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}. \quad (3)$$

If the liquid alloy Na-Rb is an ideal mixture, Eqs. (2) and (3) give the vapor pressure, as shown by dotted curves in Fig. 1(b). Since the pressures,  $p_{Na}^*$  and  $p_{Rb}^*$ , are sufficiently low at the temperature of 384 K [15], the vapor is an ideal gas in a good approximation. Because  $p_{Rb}^* \gg p_{Na}^*$ ,  $y_{Rb} \sim 1$  for a wide range of  $x_{Rb}$  in the equilibrium. Therefore, the alloy can be distilled for high purity Rb metal when contained in a sodium-free vessel.

The chemical potential of an ideal gas at the temperature  $T$  is

$$\mu_A^g(T) = \mu_A^* + RT \ln(p_A/p_A^*), \quad (4)$$

where  $R$  is the gas constant and  $\mu_A^*$  is the chemical potential in the gas phase at  $x_A = y_A = 1$ . For a real liquid mixture, using the activity  $a_A = \gamma_A x_A$ , the chemical potential of element A is expressed as

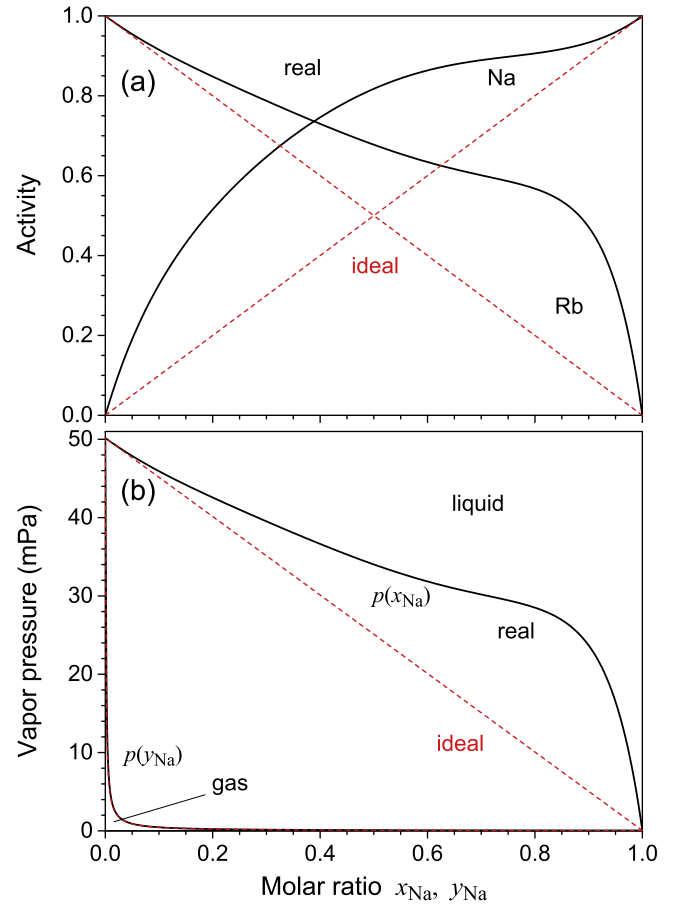
$$\mu_A^l(T) = \mu_A^* + RT \ln(a_A), \quad (5)$$

where  $a_A + a_B \neq 1$ . Since  $\mu_A^g(T) = \mu_A^l(T)$  in equilibrium,

$$p_A = a_A p_A^*. \quad (6)$$

Therefore, the vapor pressure is calculated from the activity of a real solution. Using Eq. (5), the chemical potential of the liquid mixture is

$$\mu^l(T) = x_A(\mu_A^* + RT \ln x_A) + x_B(\mu_B^* + RT \ln x_B) + RT(x_A \ln \gamma_A + x_B \ln \gamma_B), \quad (7)$$



**Fig. 1.** (a) Activity and (b) vapor pressure of ideal solution (dotted curve) and real liquid alloy Na-Rb (solid curve). Total pressures,  $p(x_{Na})$  and  $p(y_{Na})$ , are functions of molar ratio in the liquid alloy ( $x_{Na}$ ) and in the gas phase ( $y_{Na}$ ), respectively. The vapor pressures of pure metal,  $p_{Na}^* = 46$  mPa and  $p_{Rb}^* = 50$  mPa, at 384 K [15] are low enough to consider the vapor as ideal gas. Because  $p_{Na}^* \ll p_{Rb}^*$ , total pressure is nearly equal to the partial pressure of Rb metal.

where the first and the second terms are due to the chemical potential for ideal solution. The third term is the excess molar Gibbs function,  $\mu^e(T)$ , equal to the enthalpy of mixing (the excess enthalpy). For alkali-metal binary alloys, it has been obtained in the Redlich-Kister Polynomial,

$$\mu^e(T) = x_A x_B \sum_{i=0}^n RT \ell_i(x_{AB})^i, \quad (8)$$

from measurements and calculations [24–26], where  $x_{AB} = x_A - x_B$ , and  $\ell_i$  is the interaction coefficient between the elements A and B. In the case of  $x_j = 1$ , the coefficient  $\gamma_j$  should be unity. Therefore, we obtain the solution in the form  $\gamma_j = e^{(1-x_j)\delta_j}$  [23]. From Eqs. (7) and (8),

$$\delta_A + \delta_B = \sum_{i=0}^n \ell_i(x_{AB})^i. \quad (9)$$

Using the Gibbs-Duhem equation,  $x_A d\mu_A + x_B d\mu_B = 0$ ,

$$x_A x_B \left( \frac{\partial \delta_A}{\partial x_A} - \frac{\partial \delta_B}{\partial x_B} \right) = x_A \delta_A - x_B \delta_B. \quad (10)$$

From Eqs. (9) and (10) for  $n = 2$ ,

$$\delta_A/x_B = \ell_0 + \ell_1(2x_{AB} + 1) + \ell_2(3x_{AB} + 2)x_{AB}, \quad (11)$$

$$\delta_B/x_A = \ell_0 + \ell_1(2x_{AB} - 1) + \ell_2(3x_{AB} - 2)x_{AB}. \quad (12)$$

In the case,  $\ell_i = 0$  ( $i > 0$ ), the mixture is called regular solution. Eqs. (11) and (12) lead to the Margules equations,  $\ln \gamma_A = \ell_0 x_B^2$  and

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