

SATURATED VAPOUR PRESSURE OF Cs OVER Na-Cs SOLUTION

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By means of the resonant line absorption method, cesium activities in the Na-Cs solution as well as the saturated vapour pressures of metal over this solution have been measured.

In our previous papers we have reported results of cesium vapour pressure measurements over pure metal [1], and over Cs-Rb [12] and Cs-K [3] solutions.

This paper deals with Cs vapour pressure investigation over Cs-Na system.

The method of atomic absorption of cesium D_1 resonance line has been used in the manner described elsewhere [1, 2].

The apparatus, experimental procedure, accuracy of measurements, and cell filling technique were the same as in our preceding works [2, 3].

Figure 1 shows the results of saturated Cs vapour density measurements over Na-Cs solution as function of concentration and temperature. One can notice that the saturated Cs vapour density alters only slightly in the temperature range of 293—313 K for solutions with Cs molar fractions smaller than 0.4.

Figures 2 and 3 present the calculated Cs activities a_{Cs} and logarithms of Cs activity coefficients $\ln \gamma_{Cs}$ which are given by

$$a_i = \frac{P_i}{P_i^0}, \quad (1)$$

$$\gamma_i = \frac{a_i}{X_i}, \quad (2)$$

where P_i is a saturated vapour pressure of the i component over the solution, P_i^0 — saturated vapour pressure over pure metal, X_i — molar fraction of the i component in the solution. The activity coefficients of condensed solutions in isothermic-isobaric conditions obey

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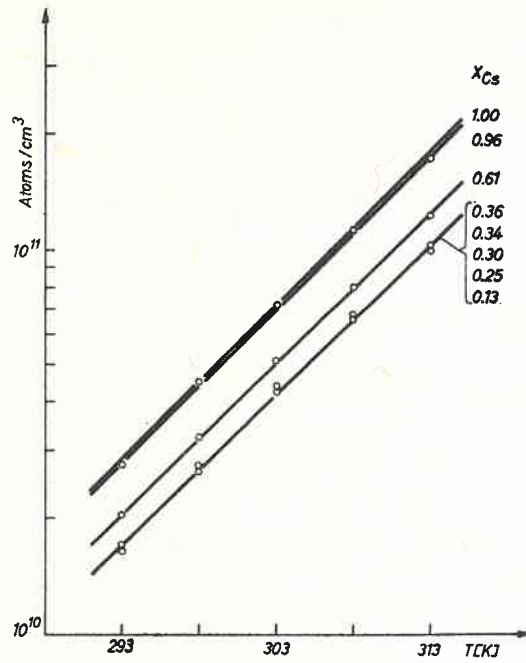


Fig. 1. Variation of saturated Cs vapour density over Cs-Na solutions with temperature

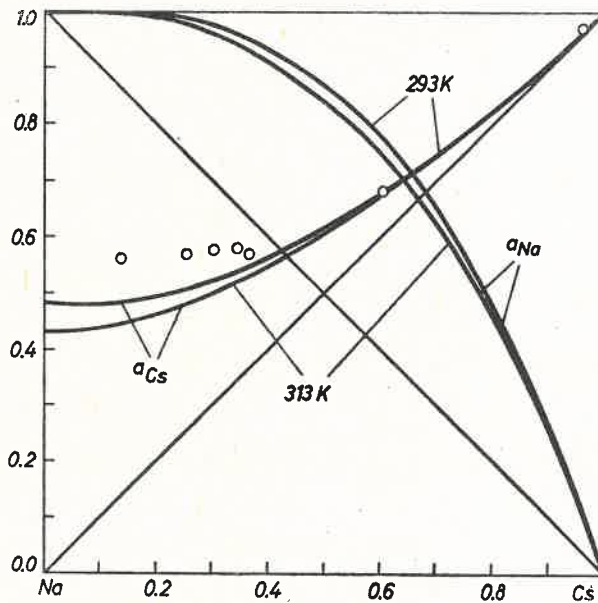


Fig. 2. Cs and Na activity isotherms calculated from formulae (8) and (9). ○ — Cs activities determined experimentally

the Gibbs-Duhem equation

$$\sum_{i=1}^n X_i d \ln \gamma_i = 0. \quad (3)$$

According to the solution of equation (3) proposed by Krupkowski [4] the activity coefficients for a two-component solution can be expressed by

$$\ln \gamma_1 = \omega(T) X_2^m, \quad (4)$$

$$\ln \gamma_2 = \omega(T) \left(X_2^m - \frac{m}{m-1} X_2^{m-1} + \frac{1}{m-1} \right), \quad (5)$$

where $\omega(T)$ is the energetic index dependent on temperature, m — thermodynamic function assymetry index.

For $m = 1$ formulae (4) and (5) become [5]

$$\ln \gamma_1 = \omega(T) X_2; \quad (6)$$

$$\ln \gamma_2 = -\omega(T) (\ln X_2 + 1 - X_2). \quad (7)$$

Formulae (6) and (7) correspond to the case of precipitation of pure component from the solution and this is exactly what tends to happen to the Na-component in Cs-Na system.

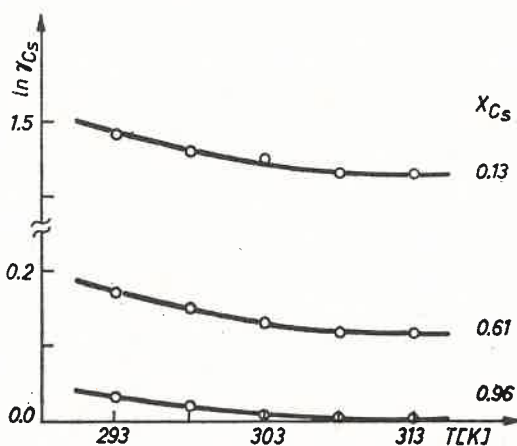


Fig. 3. Variation of $\ln \gamma_{Cs}$ with temperature for respective solutions

$\omega(T)$ has been calculated with the use of phase equilibrium diagram of Cs-Na system and is shown in Figure 4 [6]. Consequently formulae (6) and (7) become

$$\ln \gamma_{Na} = \frac{329}{T} X_{Cs}, \quad (8)$$

$$\ln \gamma_{Cs} = -\frac{329}{T} (\ln X_{Cs} + 1 - X_{Cs}). \quad (9)$$

The calculated from formulae (8) and (9) Na and Cs activity isotherms for two fixed temperatures are represented by continuous lines in Figure 2.

Taking into consideration formulae (8) and (9) the formation enthalpy per one mole of solution may be expressed by

$$\Delta H^M = -653X_{Cs} \ln X_{Cs} \quad (10)$$

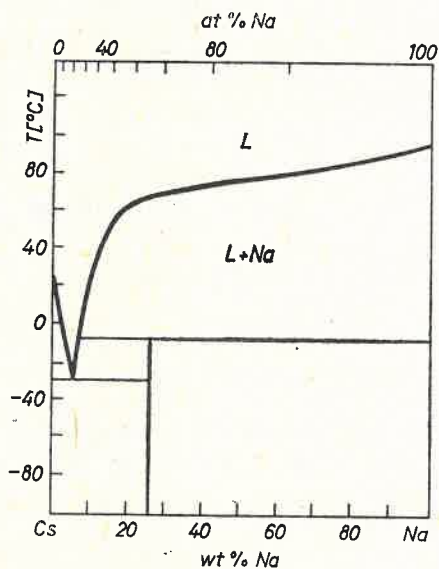


Fig. 4. Phase equilibrium diagram of Cs-Na system [6]

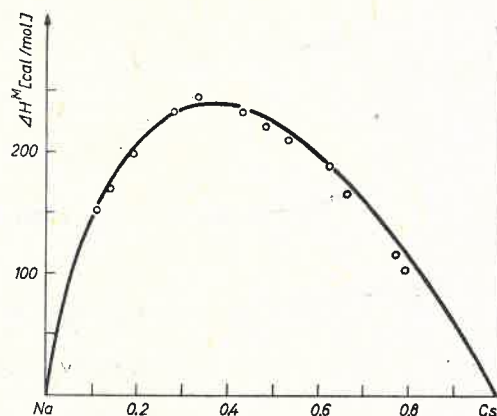


Fig. 5. Variation of the formation enthalpy per one mole of solution ΔH^M with solution composition calculated with the use of formula (10). \circ — results of Yokokawa and Kleppa [7]

The variation of function (10) is represented by the continuous line in Figure 5. Experimental data points obtained by Yokokawa and Kleppa [7] with the use of calorimetric method have been plotted as well. A satisfactory agreement of calculated values with the experimental data points indicates on the possibility of using Krupkowski's solution to the analysis of systems mentioned above.

The presented here experimental measurements and calculations show that the Na-Cs system is characterized by a positive deviation in the entire range of concentrations. This leads to the conclusion that the interaction forces between atoms of the same kind are larger than that which take place between different atoms in a solution [8]. The increase of temperature is accompanied by the decrease of activity coefficients (see Figure 3) and this indicates on the tendency of a solution to approach the ideal system. The calculated Cs activities with the use of formula (9) as well as that determined experimentally for solutions with small amount of Cs happened to be relatively large and alter slightly with the composition variation. This is thought to be due to the fact that the hypereutectic solutions, in which Na-component tends to precipitate (see Figure 4) below the liquidus line, possess a constant liquid phase composition at temperatures which mainly determine the Cs vapour density. The experimental value of Cs activity are large compared to that calculated from formula (9) (see Figure 2). This can be explained by the fact that Krupkowski's formulae do not take into consideration the presence of surface energy. Results presented in Ref. [9] indicate that cesium is an active surface component and this may be explained by the existence of significantly large surface tension for sodium $\left(\sigma_{\text{Na}} = 0.1937 \frac{\text{J}}{\text{m}^2}, \sigma_{\text{Cs}} = 0.0705 \frac{\text{J}}{\text{m}^2}\right)$. Thus, the surface phase may be expected to contain much more Cs than the bulk. In this work small amounts of metals as the whole have been used therefore the Cs vapour density was strongly influenced by the surface phase which being rich in Cs is most likely responsible for larger than have been anticipated values of experimentally measured activities.

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