

SATURATED VAPOUR PRESSURE OF Cs OVER A K-Cs SOLUTION

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By means of the resonant line absorption method, cesium activities in K-Cs solutions as well as the saturated vapour pressures of the metal over this solutions have been measured. Some values of the thermodynamic functions have been estimated.

1. Introduction

In the investigation of the thermodynamic properties of metal alloys knowledge of the activity and activity coefficient for each component is indispensable. In order to determine the component activity, measurements of saturated metal vapour pressure a solution were carried out.

In the case of an ideal solution, the vapour pressure of the i th component obeys Raoult's law

$$P_i = X_i P_i^0, \quad (1.1)$$

where X_i — molar fraction of the i th component in the solution, P_i — saturated vapour pressure over the solution, P_i^0 — saturated vapour pressure over the surface of a pure metal.

For a non-ideal solution, under the assumption that the metal vapour satisfies the conditions for an ideal gas equation (1.1) becomes

$$P_i = a_i P_i^0, \quad (1.2)$$

where a_i is the activity of the i th component in the solution.

The vapour density and, consequently, the vapour pressure can be calculated from the well known formula

$$S = \int k_v dv = \frac{g_2 \lambda_0^2}{g_1 8\pi\tau} N, \quad (1.3)$$

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where k_ν is the absorption coefficient, λ_0 is the peak wavelength of the absorption line, g_2 and g_1 are degeneracies of the excited and ground states, respectively. τ is the life time of the excited state, and N denotes the vapour number density.

Evaluating experimentally the integral $\int k_\nu d\nu$ for a pure metal S^0 and for a solution S it is possible, using formulas (1.2) and (1.3), to calculate the activity of the i th component

$$a_i = \frac{S_i}{S_i^0} \quad (1.4)$$

Thus, the activity coefficient is

$$\gamma_i = \frac{a_i}{X_i} = \frac{S_i}{S_i^0 X_i} \quad (1.5)$$

Knowledge of activity and activity coefficient of the components is essential in determining the basic thermodynamic functions for a given solution.

Potassium and cesium form a solution with unlimited solubility. The K-Cs solution reaches the lowest melting point at 233 K for $X_{Cs} = 0.5$ [1]. Up to now, the results for heat of formation obtained by Yokokawa and Kleppa [2] in calorimetric measurements of the analysed solution were the only ones known. The theory of liquid alloys of alkalis, in particular for the K-Cs system, has been developed by Christman [3]. Tanigawa and Doyama [4] applying the method of pseudopotential calculated the enthalpy of the solid solution formation. All previous investigations indicate that the formation of a K-Cs solution in the solid as well as the liquid state is endothermic.

The purpose of this work was to examine the dependence of cesium vapour on temperature for K-Cs solutions with different concentrations, and to determine the thermodynamic functions of such a system. This is of importance in the technology of metals as well as in spectroscopy, optical pumping and so on.

2. Results

Measurements have been carried out by applying the use of a Fabry-Perot scanning interferometer to atomic absorption spectroscopy. The apparatus and experimental procedure have been described elsewhere [5, 6]. The values of integrals S_{Cs}^0 and S_{Cs} were determined using the D_1 line hf components for cesium corresponding to the electronic transitions $^2S_{1/2}(F=4) \leftrightarrow ^2P_{1/2}(F=3)$ and $^2S_{1/2}(F=4) \leftrightarrow ^2P_{1/2}(F=4)$. The activities and activity coefficient for cesium in solution were calculated from formulas (1.4) and (1.5), respectively. Using the activities for cesium in K-Cs solutions and vapour pressures P_{Cs}^0 over pure metal obtained in Ref. [5], metal vapour pressures over the solution have been calculated applying formula (1.2). The dependence of saturated vapour density on temperature for several K-Cs solutions is shown in Fig. 1. Fig. 2 presents the activity coefficient dependence on temperature for solutions with different concentrations. According to the

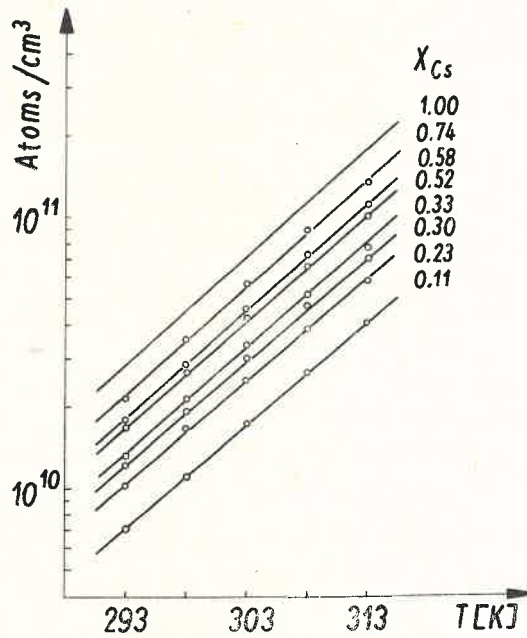


Fig. 1. Saturated cesium vapour density over a pure metal and over various K-Cs solutions versus temperature

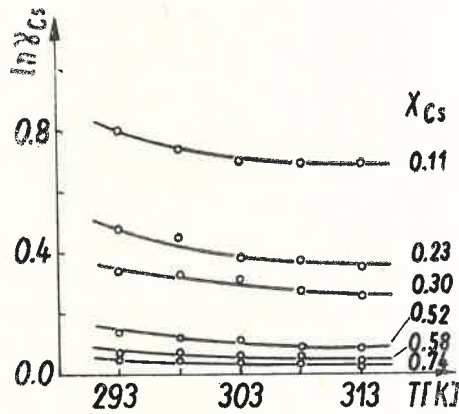


Fig. 2. Cesium activity coefficient for different K-Cs solution concentrations versus temperature

solution of the Gibbs–Duhem equations proposed by Krupkowski [7] the activity coefficients in a two component solution may be expressed by

$$\ln \gamma_1 = \omega(T)X_2^m, \quad (2.1)$$

$$\ln \gamma_2 = \omega(T) \left[X_2^m - \frac{m}{m-1} X_2^{m-1} + \frac{1}{m-1} \right], \quad (2.2)$$

where $\omega(T)$ is a factor dependent on temperature, m is a constant characteristic of a given solution. Using the activity coefficient values for cesium, and assuming that their dependence on concentration and temperature is in accordance with formula (2.2), parameters and m have been determined.

Finally, the activity coefficient dependence on the concentration and temperature for potassium and cesium is of the form

$$\ln \gamma_K = \left(\frac{819}{T} - 2.08 \right) X_{Cs}^{1.5} \quad (2.3)$$

$$\ln \gamma_{Cs} = \left(\frac{819}{T} - 2.08 \right) [X_{Cs}^{1.5} - 3X_{Cs}^{0.5} + 2] \quad (2.4)$$

The activity isotherms for cesium and potassium calculated from formula (2.3) and (2.4) as well as the activity values for cesium obtained experimentally are shown in Fig. 3. One can notice a relatively good agreement between the experimental a_{Cs} values and those

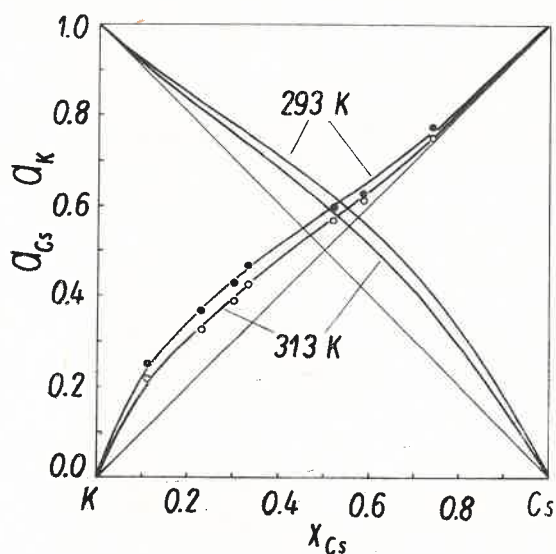


Fig. 3. Cesium and potassium activity isotherms determined with the use of formulas (2.3) and (2.4).
●, ○ — cesium activities determined experimentally

calculated from formula (2.4). Therefore, formulas (2.3) and (2.4) may be used to determine the thermodynamic functions which describe the K-Cs system under certain experimental conditions. The excess free energy ΔF_i^x for cesium and potassium, and the excess free energy of formation of 1 mole of solution ΔF^x can be expressed as

$$\Delta F_i^x = RT \ln \gamma_i, \quad (2.5)$$

$$\Delta F^x = RT \sum_i X_i \ln \gamma_i. \quad (2.6)$$

Taking into consideration formulas (2.3) and (2.4), the excess free energy of formation of 1 mol of solution has been calculated according to

$$\Delta F^x = (3254 - 8.26T)X_{Cs}[1 - X_{Cs}^{0.5}]. \quad (2.7)$$

The results obtained for 313 K are presented in Fig. 4.

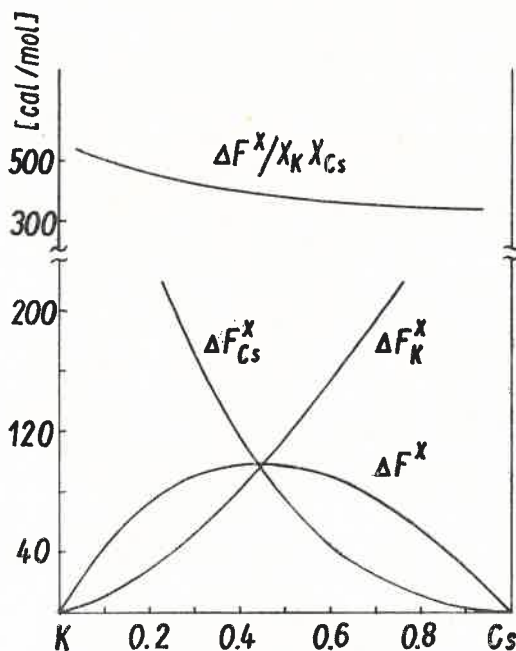


Fig. 4. ΔF_K^x , ΔF_{Cs}^x , ΔF^x and $\frac{\Delta F^x}{X_K X_{Cs}}$ at 313 K versus solution composition

3. Discussion

The results of measurements of saturated vapour densities for cesium over K-Cs solution enable us to consider the system from the thermodynamic point of view. Investigations of the activity coefficient dependence on temperature for cesium (see Fig. 2) indicate the tendency of solutions to approach an ideal system when temperature increases. This indicates a gradual increase in disorder in the liquid phase. From runs of activity isotherms (Fig. 3) one can observe that cesium exhibits a positive deviation from Rault's law in the entire range of concentrations. The excess free energy ΔF^x appears to be a measure of deviation of the solution from an ideal system.

The results presented in Fig. 4 show that the K-Cs solutions are characterized by a positive deviation in the entire range of concentrations. The dependence of the excess free energy on concentration exhibits an asymmetry. The maximum of this function is shifted toward solutions rich in potassium. The ratio of the excess free energy and the

product of molar fractions of the solution components does not remain constant. This results from the fact that the K-Cs solution cannot be regarded as regular in the investigated range of temperature employed in this experiment. Our observations presented here are in accordance with the results of other authors [2-4].

With respect to the Gugenheim theory the positive deviation of the K-Cs solution from an ideal system indicates that the interaction between atoms of the same kind in large compared with that between Cs atoms and K atoms.

The evaluated values of the excess free energy exceed the values obtained by Yokokawa and Kleppa. However, one has to notice that in our experiment only small amounts of metals have been investigated and all measurements have been carried out at low temperatures (293÷313 K). In this case the metal vapour density is influenced by the surface zone. Thus, the results presented for ΔF^x are a measure of the difference between the free energy of the real and the ideal solutions, and include information concerning the properties of the surface layer of the solution in question.

4. Conclusions

On the basis of the results presented here we conclude that the saturated vapour pressure for cesium over K-Cs solution may be described by $P_{Cs} = X_{Cs}\gamma_{Cs}P_{Cs}^0$, where γ_{Cs} can be obtained from the semiempirical formula (2.4). The correctness of using formula (2.3) in order to determine the potassium vapour pressure over K-Cs solution has to be confirmed experimentally.

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