VAPOR PRESSURE MEASUREMENTS IN K-KBr MIXTURES :
METHOD AND PRELIMINARY RESULTS

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ABSTRACT

In order to obtain thermodynamic information on mix­tures constituted with alkali metals with their halides, we investigated the K-KBr system by vapor pressure measure­ments.

The method chosen uses the features of both the Rodebush-Dixon and ebullition methods. The apparatus, consistent with the experimental requirements of such a system, allows one to investigate a wide temperature and pressure range.

The determination of the vapor pressure of potassium between 719K and 1045K was a check on the operation of the apparatus.

Vapor pressure measurements above the K-KBr liquid bath between 1000 and 1070K yielded the activity of potas­sium at $X_K=0.2$, $X_K=0.5$ and $X_K=0.8$.

INTRODUCTION

Between liquid alloys and molten salt mixtures, there is an intermediate class of liquids - metal-molten salt systems - which has never been subject to intensive research from both theoretical and practical points of views. These mixtures which show a continuous tran­sition from metallic to non-metallic character and a liquid miscibility gap are of special interest; therefore, a good knowledge of their thermodynamic properties could afford a better understanding of these phenomena.

We therefore decided to study the solutions of alkali me­tals in their halides for which some physico-chemical determinations are available (1-4).

The present work deals with the K-KBr system and shows on one hand the feasibility of thermodynamic measurements for such a mixture and provides on the other hand results on the activity of potas­sium in some K-KBr mixtures.

Many practical reasons explain the few measurements availa­ble for such systems. These are:
- the chemical reactivity of these mixtures
- the high vapor pressure of the metal
- the existence of a single-phase liquid only at very high temperature
- the occurrence of a wide miscibility gap that does not promote the estimation of the thermodynamic functions.

We choose to measure the vapor pressure of potassium above a K-KBr bath in order to deduce the activities and the Gibbs free energies.

**EXPERIMENTAL**

The vapor pressure of one component A in equilibrium above a liquid bath AB, when compared with that of the pure component A at the same temperature, yields the activity \( a_A \) and the chemical potential \( \mu_A \) of this component in the mixture.

**Principle of measurement**

For the present work, the following hypothesis was adopted: the difference between the vapor pressures of the two components is large enough to assume that the vapor above the liquid is only constituted with the more volatile component.

When the total pressure above a liquid bath maintained at constant temperature is decreased, ebullition takes place when pressure becomes equal to the vapor pressure of the liquid; the total vapor pressure should therefore be measured at the same time as the ebullition process is detected.

This determination can be done:
(i) either by recording the pressure variation against time arising from a microleak in the gas circuit above the liquid bath: when the pressure becomes equal to the vapor pressure, the rate of the pressure variation changes suddenly (point a on the curve figure 1): this is Rodebush-Dixon method (5).
(ii) or by recording the temperature T of the liquid during a variation linear against time of the pressure above the bath.

The ebullition, endothermal process, creates a cooling of the liquid, therefore a break on the curve \( T = f(t) \) (point b on the curve, figure 1).

In practice, it is much more interesting to couple these two methods in order to survey a wide investigation range.

The diagram of figure 1 shows the curves obtained with the two detection systems (points a' and b').

**Realization**

Figure 2 makes it easier to understand the principle of this method and of the working of the apparatus.

The experimental set-up consists of:
- the experimental cell (C) containing the mixture
- a vertical tubular furnace (F) with temperature regulation
- a primary and diffusion pumping group (V)
- a neutral gas tank (G)
- a system for measuring and recording against time the cell temperature (T) and the gas pressure (P)
- a network of pipes with gauges, valves, manometers, connections...:
Each part of the assembly can be insulated and an adjustable micro-leak valve (L) allows one to vary the pressure.

This apparatus, its construction and its setting as well as the several types of experimental cells tested were already described in detail (6).

Only the cell used for the K-KBr mixture will be described here with the experimental care necessary to obtain reliable measurements.

Experimental cell (figure 3)

The part containing the liquid mixture consists of a hollow cylinder 36mm diameter and 107mm high topped by a cylindrical pipe which connects the cell to the rest of apparatus. This connection is made owing to two isolation valves located in (5) and (6).

In the upper end of the pipe, there is a gastight outlet for the protection tube of the temperature thermocouple.

This location of the thermocouple is most suitable:
- the position of the thermocouple junction is height-adjustable, which is necessary for different fillings of the cell.
- a motion to and fro of the protection tube of the thermocouple permits stirring the liquid and therefore an homogenization (this is essential when the liquid mixture exhibits a demixing phenomenon)
- the protection tube of the thermocouple, centered in the connection tube, limits its section which results in a decrease of metallic vapor losses: the concentration of the liquid bath remains therefore quasi-constant.

Experimental care

A large set of trials on many pure substances and mixtures (Cd, Cd-Ga, K, KBr) made it clear that:
- much attention should be paid to the construction of this cell; the metallic weldings and the junction should be gas-tight at every temperature. The pipes must be very clean and the welding burrs removed.
- before each experiment, the whole assembly must be perfectly evacuated.

For the investigation of the K-KBr mixture, in the whole concentration and temperature range, a refractory stainless steel type NS 22S was found suitable for the construction of the cells.

It is obvious that the cell must be an isothermal system: accordingly, it is located in the uniform temperature zone of a furnace (200mm high) and surrounded with a refractory felt in order to lessen the convection losses.

Auxiliary equipment

Pressure is measured continuously by means of a piezoelectric detector, the sensing element of which is a cap of pure single-crystal silicon. The experimental range is between 0 and 1100 mbars. The electric signal of the detector is recorded continuously on a two

\[ \text{Schlumberger, type CZ 1080} \]
The neutral gas used is purified argon. The experimental temperature of the bath is measured by a platinum/platinum-rhodium thermocouple and recorded on the second channel of the previous recorder†. The furnace is regulated with an electronic system‡ driven by a Pt/Pt-Rh 10% thermocouple. The sensitivities of the systems for pressure and temperature measurements allows one to detect variations of the order of $5 \times 10^{-2}$ Torr and 0.5 K, respectively. The sample mass is known with a precision of $10^{-2}$ g. Weighings and filling of the cell are made within a glove-box filled with purified argon.

**Experimental Results**

The relation $a_K = \frac{P_K}{P_0}$ shows obviously that the determination of activity at temperature $T$ implies the measurements of the vapor pressures of pure potassium and of potassium above a liquid bath of $X_K$ composition.

**Vapor Pressure of Pure Potassium**

Measurements were carried out between 719K and 1045K. All the results obtained are reported in figure 4 as the logarithm of the vapor pressure of potassium against reciprocal temperature.

The A and B coefficients of the equation:

$$\log_{10} P = A + B/T \quad (P : \text{torr}, \quad T : \text{Kelvin})$$

were fitted by a least-square method. From 53 experimental values, the values 7.1510 and 4401.0487 were obtained for A and B respectively. The mean relative uncertainty of our pressure is about 1.5%. Our results were compared with those given by Hultgren (7) in his critical compilation. The agreement was found very satisfactory in our experimental temperature range.

From the previous equation, we calculated the enthalpy of vaporization of potassium at 952K (normal ebullition temperature); the value obtained 20.1 kcal.mol$^{-1}$ is to be compared with the mean value 21.33 kcal.mol$^{-1}$ obtained from the many previous works and also with that from Kelley's compilation (8) 19.0 kcal.mol$^{-1}$. The reliability of the vapor pressures measured for pure potassium points out the validity of the method. These experimental values will be used in the following to evaluate the activity of potassium in K-KBr mixtures.

† Sefram, type Servorac BPD

‡‡ Setaram, type PRT 3000
Figure 5 recalls the equilibrium lines of the phase diagram proposed by Bredig (1). The K-KBr system exhibits a wide miscibility gap in the liquid state and the activity of potassium above a single-phase liquid bath can only be measured in the whole concentration range above 1000K.

All our experiments were therefore carried out between 1000K and 1070K.

We investigated the mixtures with the respective compositions:

\[ X_K = 0.2 \quad , \quad X_K = 0.5 \quad , \quad X_K = 0.8 \]

The results are reported in figures 6, 7 and 8. On each diagram \( \log P = f(1/T) \), the straight line corresponds to the equation given previously with coefficients obtained from least-square analysis of data.

The results obtained for the vapor pressure of potassium, pure and above a liquid mixture, were corrected for taking into account the dissociation of K vapor into mono and diatomic molecules (9):

\[ 2K \rightleftharpoons K_2 \]

This method of correction is similar to that used (3) for the similar system Cs-CsCl.

The activities of potassium were then calculated at several temperatures: 1005K, 1035K, 1044K and 1065K and are plotted against the potassium mole fraction \( X_K \) in figure 9.

CONCLUSION

In spite of the experimental difficulties encountered in the investigation of metal-molten salt systems and particularly of alkali metal-halide mixtures, the determination of the metal vapor pressure at many temperatures and concentrations seems to be a good approach for determining their thermodynamic properties.

The experimental method chosen was first checked by measuring the vapor pressure of potassium at many temperatures. The activity of potassium was then measured, between 1000K and 1070K, in the mixtures \( X_K = 0.2 \), \( X_K = 0.5 \) and \( X_K = 0.8 \). The departure from ideality is large and the trend of the activity variation against temperature is a precursory sign of the demixing phenomenon.

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Fig. 1 - Principle diagram of the method.

Fig. 2 - Diagram of apparatus
Fig. 3 - Experimental cell.

1: cell
2: lid
3: connexion pipe
4: gastight junction
5: isolation valve
6:"
7:"
8: protection tube of thermocouple
Fig. 4 - $\log_{10} P = f\left(\frac{10^3}{T}\right)$ for pure potassium

Fig. 5 - Equilibrium phase diagram.

Fig. 6 - $\log_{10} P = f\left(\frac{10^3}{T}\right)$

Fig. 7 - $\log_{10} P = f\left(\frac{10^3}{T}\right)$
Fig. 8 - $\log_{10} P = f\left(\frac{10^3}{T}\right)$

Fig. 9 - $a_K = f(X_K)$

$\Theta(1005K)$ $O(1035K)$ $\Phi(1065K)$