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CONTRIBUTION TO THE LIQUID-VAPOUR EQUILIBRIUM
OF POTASSIUM AND SODIUM MIXTURES

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ABSTRACT

In this paper the phase diagram of the binary system potassium-sodium in the liquid-vapour range was calculated for different pressures and temperatures, assuming the two metals acting as ideal solution. The assumption was verified by experimental results. It is thus possible to calculate the separation factor for the rectification of potassium and to estimate the content of sodium in the vapour phase during experiments with vapourized potassium from the data of the vapour pressures of the pure metals.

Key words: phase diagram/binary system/potassium-sodium/liquid vapour equilibrium

ZUSAMMENFASSUNG

Das Phasendiagramm des binären Systems Kalium - Natrium wurde für den flüssig-gasförmigen Bereich für verschiedene Temperaturen und Drücke berechnet unter der Annahme, daß die beiden Flüssigmetalle als ideale Mischung dem Raoult'schen Gesetz folgen. Die berechneten Kurven wurden experimentell bestätigt. Es ist daher möglich, aus den Dampfdruckkurven der reinen Metalle den Trennungsfaktor für die Reinigung von Kalium mittels Destillation zu berechnen und den Gehalt an Natrium in der Dampfphase bei Kalium Dampfprozessen abzuschätzen.

Stichworte: Phasendiagramm/binäres System/Kalium-Natrium/Siedelinie-Taulinie

Contribution to the liquid-vapour equilibrium
of potassium and sodium mixtures.

Introduction

For future experiments with boiling and superheated potassium for the application as a heat carrier and as a thermodynamic working fluid (topping cycles) at highest temperatures, a stainless steel experimental facility is now being built as a combined project of SGAE and VEW (former BÖHLER).

Since the grade of purity of the potassium on the market, especially to the respect of sodium as impurity, is in direct correlation to the price of the metal, we do accept a few percent of sodium with the aim of rectifying the potassium by distillation.

For the calculation of the efficiency of a fractionating process by distillation the knowledge of the thermodynamic equilibrium between the liquid and gaseous phases of potassium and sodium at a certain temperature and pressure is essential (1). Searching through literature no diagram of the temperature versus composition of the system K - Na involving the gaseous and the liquid phases could be found. In this paper the equilibrium of the binary system potassium-sodium in the liquid-vapour range was studied for varying pressures and temperatures. The theoretical calculated curves were verified by experimental results, so that it seems reasonable to extrapolate the results in the low pressure region to the condition which will prevail during the above mentioned experiments.

Calculation

Assuming the two alkali metals potassium and sodium forming an ideal binary solution the diagram of temperature versus composition at constant pressure involving the gaseous and liquid phases was calculated (2). The known data of vapour pressures (3), plotted in an Arrhenius' diagram, shown in figure 1

served as basis for the calculation. Starting from given compositions of potassium and sodium in the liquid phase, the composition of the gaseous phase for different pressures and also in dependence of the temperature was of interest.

An ideal solution follows Raoult's law, i.e. for all temperatures the total pressure being the sum of the partial pressures of the two components,

$$p = P_K + P_{Na} \quad (1)$$

whereas the partial pressure of one component is in direct proportion to its molar fraction in the liquid phase as well as to the pressure of the pure component at a given temperature.

$$\begin{aligned} P_K &= f_{l,K} \times P_{O,K} \\ P_{Na} &= f_{l,Na} \times P_{O,Na} \end{aligned} \quad (2)$$

therefore the pressure of the system at a given temperature is

$$p = f_{l,K} \times P_{O,K} + f_{l,Na} \times P_{O,Na}$$

The concentration of the gaseous components in equilibrium with the ideal solution at this temperature is

$$\begin{aligned} f_{g,K} &= \frac{f_{l,K} \times P_{O,K}}{p} \\ f_{g,Na} &= \frac{f_{l,Na} \times P_{O,Na}}{p} \end{aligned} \quad (3)$$

the composition of the liquid phase at constant pressure with varying temperature is given by

$$\begin{aligned} f_{l,K} &= \frac{P - P_{ONa}}{P_{ONa} - P_{OK}} \\ f_{l,Na} &= \frac{P - P_{OK}}{P_{OK} - P_{ONa}} \end{aligned} \quad (4)$$

For varying amounts of potassium and sodium in the liquid phase the composition of the gaseous phase in equilibrium at given total pressures are plotted in diagram, figure 2. Each line represents the equilibrium for a

constant total pressure. The temperature at which the system is in equilibrium is fixed by the equation of the vapour pressure and lies between the two boiling points of the pure components potassium and sodium at the chosen pressure.

By the different shapes of the curves it is indicated, that the effect of the separation of potassium and sodium is improved with lower pressures.

In another diagram (see fig.3) the composition of the liquid phase (full line) with the corresponding composition of the gaseous phase (dotted line) is plotted against the temperature at the constant pressure of 10^{-2} torr. This diagram makes apparent the rate of rectification at a single step. By heating for instance a mixture of alkalis with about 20 weight percent of potassium the vapour at the boiling point at 10^{-2} torr would consist of about 80 % of potassium.

Experimental

It had to be proved, whether the assumption potassium and sodium being miscible over the whole range of composition and reacting as an almost ideal solution, is acceptable.

Weighed mixtures of potassium and sodium were heated to boiling and a small amount of escaping vapour was collected for chemical analysis. Thus the composition of the liquid phase, the boiling point of the mixture and the composition of the gaseous phase in equilibrium are known. The corresponding pressure may be calculated from the equations for the vapour pressures.

Since the amount of vapour withdrawn from the system is kept small in comparison to the initial amount of the alkalis, the system may be looked at as being static at the moment of the removal of the vapour.

Within a glovebox crucibles of stainless steel were filled with definite amounts of potassium and sodium. A lid with small holes was placed on top in order to avoid splashing. A thermocouple was led through the lid into the

mixture of the alkalis. In a short distance above the crucible a cup of stainless steel at a lower temperature was placed where the escaping vapour was collected. The setup was centered in the middle of a glass tube which was connected to a vacuum pump. The crucible with the alkali metals was heated to boiling by induction heating. After a short period, the induction was switched off. Within the glovebox the vapour collector was dismantled and the solidified vapour was dissolved in alcohol and water. The quantitative composition of the vapour in respect to potassium and sodium was determined by flamephotometry.

Results

In the following table the results of a series of experiments are listed.

Nr.	LIQUID (given)					GASFOUS (found)				
	weight (g)			fraction K		weight (mg)			fraction K	
	Na	K	Σ	w/o	mole	Na	K	Σ	w/o	mole
II/1	2,54	0,23	2,77	8,3	0,05	2,4	6,0	8,4	71,4	0,59
II/2	2,80	0,56	3,36	16,7	0,10	4,85	30,0	34,85	86,1	0,78
II/3	2,95	0,98	3,93	25,0	0,16	3,75	32,5	36,25	89,7	0,83
II/4	2,90	2,05	4,95	41,4	0,29	2,05	35,0	37,05	94,5	0,91
II/5	2,94	1,57	4,51	34,8	0,21	3,0	41,5	44,5	93,3	0,88

In order to be able to compare the experimental results with the calculated lines, the vapour pressure of the system had to be determined. For experimental reasons it was not possible to measure the pressure of the gaseous phase within the vicinity of the surface of the liquid during boiling. According to the boiling points of the mixtures during our experiments the pressure of the system is expected to have been at 10^{-2} torr. By plotting the experimental results onto the calculated diagram of the concentration in equilibrium

at constant pressure of 10^{-2} torr and varying temperatures, see fig.3, the values prove to be in good agreement with the theoretical assumption. (The dotted and the full line give the calculated curve, whereas the marked points denote the experimental results.)

Discussion

Since it is evident that liquid potassium and sodium act as an ideal solution, it is possible to calculate the separation factor for the distillation process at a given temperature and pressure. For experiments with boiling potassium the amount of sodium in the vapour phase may be estimated according to the content in the initial potassium. This fact may be of importance when vapour phase corrosion phenomena have to be estimated and interpreted.

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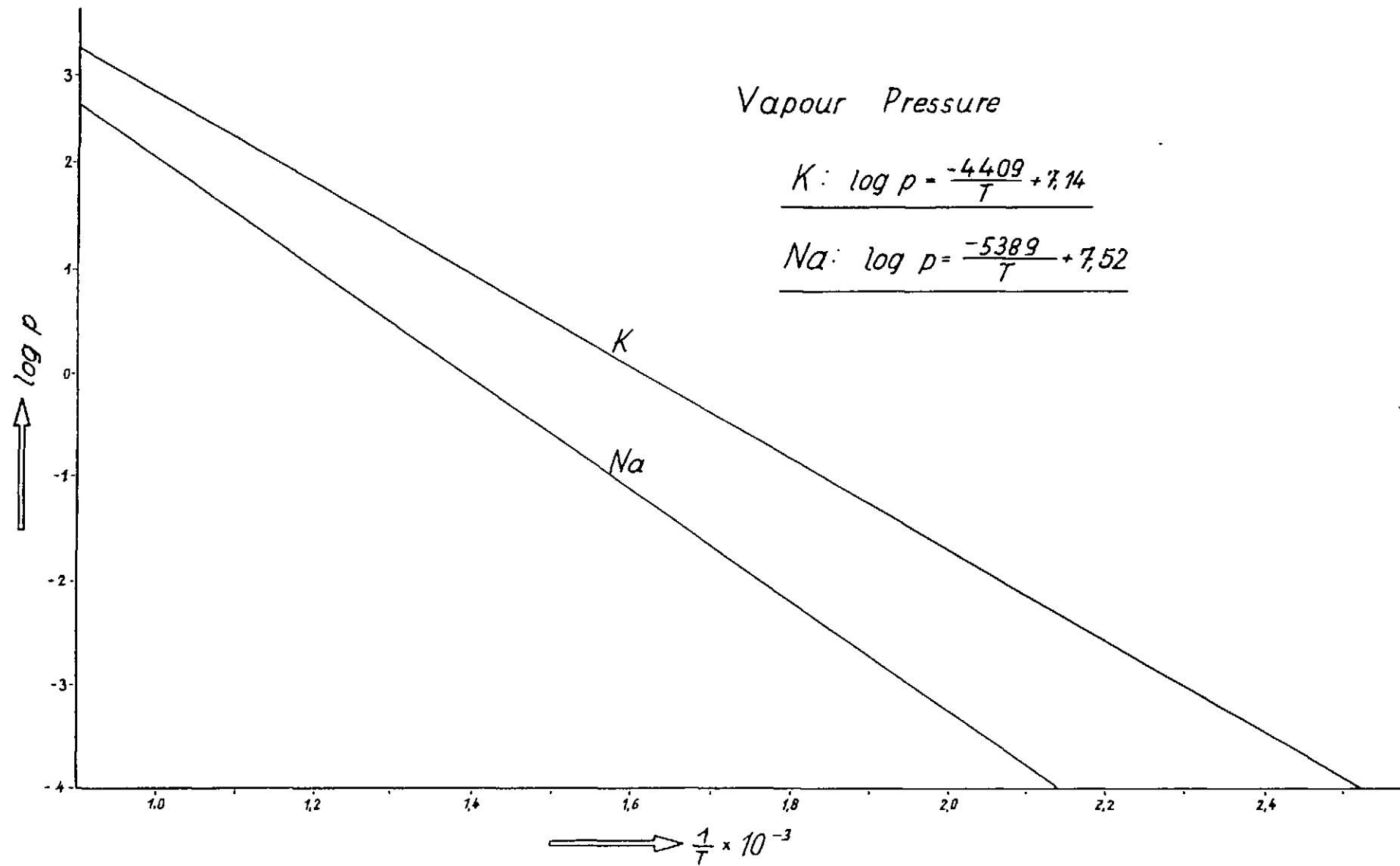


Figure 1

K - Na
Liquid-Vapour
Equilibrium at Constant Pressure

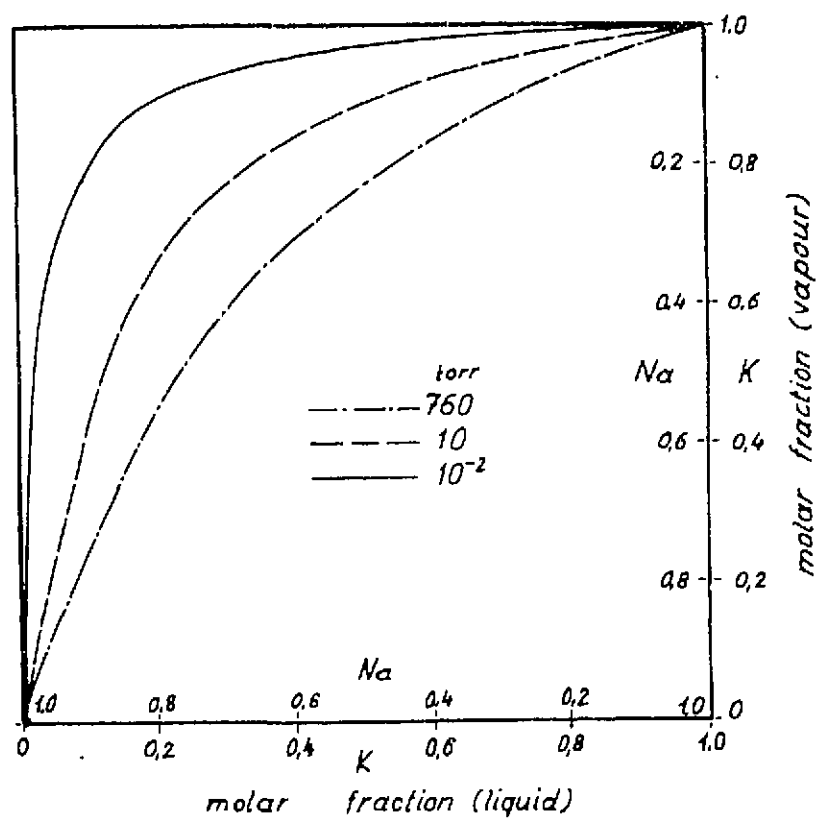


figure 2

K-Na
Liquid Vapour
Equilibrium at Constant Pressure
 10^{-2} torr

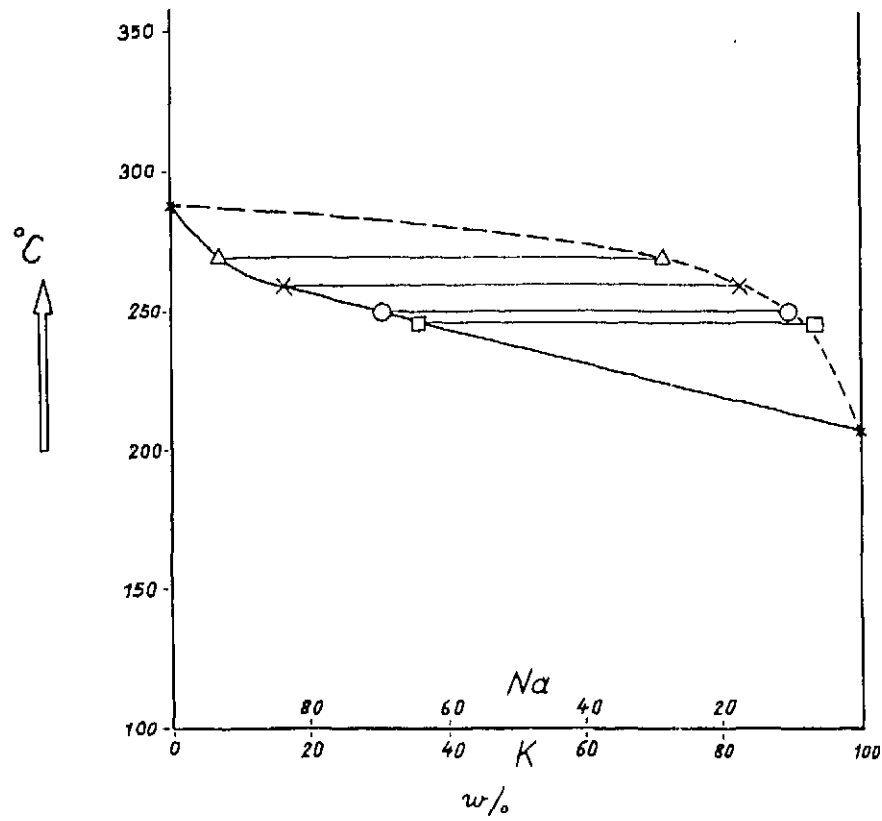


figure 3



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