

CONTRIBUTION TO THE CONSTRUCTION OF THE PHASE DIAGRAM OF THE BINARY SYSTEM $\text{PbCl}_2\text{--AgCl}$

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ABSTRACT

The phase diagram of the binary system $\text{PbCl}_2\text{--AgCl}$ was compared with the liquidus curves obtained from the thermodynamic model. The good agreement between the calculated and measured values of $\Delta H_{\text{E}}^{\text{melt}}$ indicates the possibility of the application of this procedure to the above system.

INTRODUCTION

The phase diagram of the binary system $\text{PbCl}_2\text{--AgCl}$ was studied for the first time by Treis [1] who determined the composition (40.5 mol% PbCl_2) and the melting point of the eutectic (583 K). Later it was studied by Tubandt and Eggert [2] who found that both compounds form perfectly miscible solutions in the liquid phase, whereas in the solid state they are mutually immiscible. According to their data, a mixture of both components froms the eutectic containing 39.96 mol% lead chloride (PbCl_2) with a melting point of 587 K. The same results are given by Urazov and Karnauhov [3]. Palkin and Afinogenov [4] showed that the composition of the eutectic was 39.85 mol% lead chloride and the melting temperature was found to be 591 K. Lower values (39 mol% lead chloride and 564 K) were found by Pélabon [5] and Urazov and Sokolova (38.07 mol% lead chloride and 587 K) [6]. The liquidus curves exhibit, according to ref. 1, a nearly linear dependence on the composition of the system. The eutectic composition varies according to the literature in the range 38.08–40.5 mol% lead chloride and the melting point is between 564 and 591 K.

The correlation of the thermodynamic data with the measured values enables us to determine their mutual agreement and presents an important procedure in the processing of both types of data. Calculation of the phase parameters on the basis of the thermodynamic data represents a very important contribution to data determination in regions where the available

techniques of phase analysis fail. The thermodynamic data can be used for the calculation of systems which have not been investigated yet by phase analysis and enable us to obtain an approximate idea of their phase boundaries.

The present work deals with the simple system lead chloride–silver chloride, where only one eutectic was found. The aim of this work was to compare the thermodynamic data known from the literature with measured values, and to calculate liquidus curves in the phase diagram of $\text{PbCl}_2\text{--AgCl}$ with the help of thermodynamic relationships and numerical procedures.

EXPERIMENTAL

Sample preparation

Lead chloride p.a. (Lachema Brno) and silver nitrate p.a. (Lachema Brno) were used as starting materials. Lead chloride was refined by fifteenfold zone melting in a quartz ampoule. In all experiments a stream of phosgene was passed through the ampoule before melting. Silver chloride was precipitated from the silver nitrate with hydrochloric acid, washed with water, dried and refined by zone melting (15-fold) in the quartz ampoule. The eutectic of both chlorides was prepared from the mixture corresponding approximately to the eutectic composition with a slight excess of lead chloride. The mixture was zone-refined three times. It is important to point out that by zone melting, the excess of lead chloride is transferred to the front of the ingot. In the centre, there is a pure eutectic and in the rear an elevated concentration of silver, mainly as silver chloride, occurs. The compositions of both compounds and of the eutectic were checked by chemical analysis.

DTA measurements

A commercial DuPont apparatus with a 1200°C cell was used for the thermoanalytical measurements. For measurements of T and ΔT a Pt/Pt–13%Rh thermocouple, with a sensitivity 0.05 K cm^{-1} , was used. ICTA standards were followed for the temperature calibration. The heating rate employed was 5 K min^{-1} . The enthalpy change of the eutectic melting ($\Delta H_{\text{E}}^{\text{melt}}$) was measured in a DSC apparatus (Perkin-Elmer DSC 2). The data obtained are listed in Table 1. The eutectic composition and the enthalpy change of the eutectic melting were further specified by the linear extrapolation method described by Gäumann [10].

Calculation of the phase diagram

The analysis of the thermodynamic data was carried out on the basis of equations derived from the thermodynamic condition for the coexistence of

both phases in equilibrium

$$(x_{\text{PbCl}_2} - x_E) \frac{\partial G_m^L(x, T)}{\partial x} = G_m^L(x, T) + \Delta H_{\text{PbCl}_2}^{\text{melt}} \left(1 - T/T_{\text{PbCl}_2}^{\text{melt}}\right) \quad (1)$$

$$(x_{\text{AgCl}} - x_E) \frac{\partial G_m^L(x, T)}{\partial x} = G_m^L(x, T) + \Delta H_{\text{AgCl}}^{\text{melt}} \left(1 - T/T_{\text{AgCl}}^{\text{melt}}\right)$$

where x and T are the composition and the temperature of the eutectic melting, respectively, and ΔH_i^{melt} and T_i^{melt} are the enthalpy change and the melting point, respectively, of the individual components (G_m^L is the molar mixing Gibbs energy given by the following relationship) [7]

$$G_m^L = \Delta G_m^L = RT [x \ln x + (1 - x) \ln(1 - x)] + \Omega x(1 - x)(1 + kx) \quad (2)$$

where Ω and k are the interaction parameters describing the non-ideal behaviour of the melt, both of which had to be determined by calculation. The consistency of the experimentally determined thermodynamic data was tested by comparing them with those obtained from the literature. For this purpose the relationship between the melting enthalpy of the eutectic, ΔH_E^{melt} , and the melting enthalpy of both components PbCl_2 and AgCl was used. ΔH_E^{melt} was calculated from eqn. (3), derived by Holba [8]

$$\Delta H_E^{\text{melt}} = \Omega x_E(1 - x_E)(1 + kx_E) - (1 - x_E)\Delta H_{\text{PbCl}_2}^{\text{melt}} - x_E\Delta H_{\text{AgCl}}^{\text{melt}} \quad (3)$$

RESULTS AND DISCUSSION

From DTA measurements of lead and silver chlorides, melting points of 768 and 728 K were obtained, respectively. The melting point of the eutectic is 583 K. The value of ΔH_E^{melt} determined from the DSC measurements is 19.05 kJ mol⁻¹.

TABLE 1
Thermodynamic data used for the calculation

	T^{melt} (K)	H^{melt} (kJ mol ⁻¹)	Composition (molar fraction)
AgCl	728 ^a	13.23 ^c	0
PbCl ₂	768 ^a	23.86 ^c	1
Eutectic	583 ^a	19.05 ^a 20.67 ^b	0.4068

^a Determined experimentally.

^b Calculated.

^c Rjabin et al. [9].

The spectral analysis of lead chloride showed the presence of traces of Fe, Mg, Al and Si. In silver chloride, only traces of metallic silver were found. The eutectic was analysed and was found to contain 57.09 wt% PbCl_2 , i.e., 40.68 mol% PbCl_2 .

For the calculation of the liquidus curves the system of equations (1) was used. The data employed for the calculation (listed in Table 1) lead to the following values for the interaction parameters: $\Omega = -13.6 \text{ kJ mol}^{-1}$; $k = -0.08$. Using these parameters in equations (1), the equilibrium composition at the phase boundaries can be determined for chosen temperatures. From the pairs of values obtained in this way, the liquidus curves were constructed. These are shown in Fig. 1, together with the data from ref. 1.

It follows from Fig. 1 that the course of the calculated liquidus curves differs considerably from the straight lines published previously [1]. The good mutual agreement of the calculated curves with our experimentally determined liquidus points, also outlined in Fig. 1, validates the present construction of the phase diagram of the binary system $\text{PbCl}_2\text{-AgCl}$. The reliability of our experimental data was also confirmed by the test of the consistency of the data using eqn. (3). The small difference between the calculated value of ΔH_E^{melt} ($20.67 \text{ kJ mol}^{-1}$) and the experimentally determined one ($19.05 \text{ kJ mol}^{-1}$) indicates a good agreement between our experimental data and those from the literature.

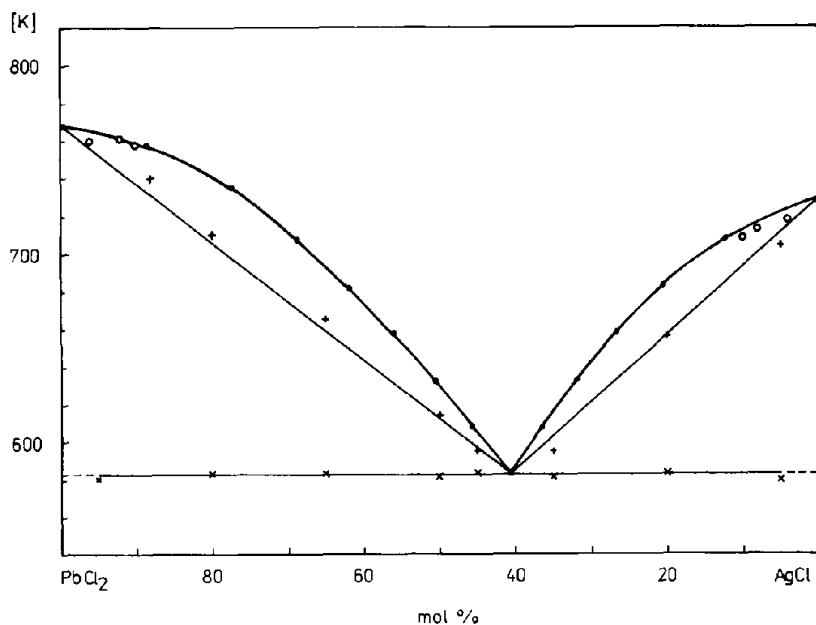


Fig. 1. Liquidus curves in the phase diagram of the system $\text{PbCl}_2\text{-AgCl}$. (+) From ref. 1; (●) calculated; (○) present work.

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