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A THERMODYNAMIC METHOD FOR THE DERIVATION OF THE SOLIDUS AND LIQUIDUS CURVES FROM A SET OF EXPERIMENTAL LIQUIDUS POINTS

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ABSTRACT

A thermodynamic method is presented which makes possible the correct derivation of solidus and liquidus curves from a set of experimental liquidus points. In an iterative procedure, which is based on the equal-G curve and which uses intermediate phase diagram calculations, the liquidus of the calculated phase diagram is made to run through the experimental liquidus points. In addition, information about the thermodynamic mixing properties of the system is obtained. Results are given for the systems *p*-dichlorobenzene + *p*-dibromobenzene, K_2CO_3 + K_2SO_4, KCl + NaCl.

INTRODUCTION

In this paper we consider TX phase diagrams which depict the equilibrium between a continuous series of mixed crystals and liquid mixtures, i.e. phase diagrams of types I, II and III in the sense of Bakhuis Roozeboom [1]. Phase diagrams of these types are usually obtained by means of a "vertical" technique whereby an amount of substance of given overall composition is subjected to a gradual change in temperature. During a vertical experiment the temperature is plotted against some physical property. The resulting cooling or heating curves are subsequently translated into liquidus and solidus points. Although such a procedure yields accurate liquidus points, it normally fails to provide reliable solidus points. By drawing a line through the "experimental" points one would obtain in extreme cases an obviously accurate liquidus of type I along with an inaccurate solidus of type III. This is in fact what could occur on the K_2CO_3 side of the K_2CO_3 + K_2SO_4 system [2] (see Fig. 2).

In this paper a thermodynamic procedure is presented by means of which the experimental liquidus points can be fitted and a thermodynamically sound solidus can be obtained simultaneously.

The thermodynamic formulation which is given first makes use of the con-

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cept of the equal-G curve (EGC) which we used previously in studies on isobaric [3] and isothermal [4] equilibria between two mixed states.

The computational procedure, which is an iterative one that uses intermediate phase diagram calculations, is described next and applied to the following real systems: p-dichlorobenzene + p-dibromobenzene, K_2CO_3 + K_2SO_4 and KCl + NaCl. The method not only provides a correct phase diagram, but also yields information about the thermodynamic mixing properties of the system.

THERMODYNAMIC FORMULATION

For isobaric conditions the Gibbs energy of a mixture which is formed by $(1 - X)$ moles of the first component and X moles of the second is usually presented as

$$G(T, X) = (1 - X)\,\mu_1^*(T) + X\,\mu_2^*(T) + RT\ln(X) + G^E(T, X) \tag{1}$$

where T is the thermodynamic temperature, R the gas constant and $\ln(X)$ a short notation defined as

$$\ln(X) = (1 - X)\ln(1 - X) + X\ln X \tag{2}$$

The first two terms on the right-hand side of eqn. (1) represent the Gibbs energy of the unmixed state (asterisks are used to denote pure components). The third term is the contribution due to ideal mixing, and the last term, the excess Gibbs energy, gives the deviation from ideal behaviour. Note that the mixing properties of a given mixture are known if its excess Gibbs energy is known.

In solid—liquid equilibria between two mixed states two Gibbs energy functions of the type expressed by eqn. (1) are involved; one for the solid and one for the liquid mixtures. At fixed temperature each of the functions corresponds to a curve in the GX plane. On passing through the temperature region in which the solid—liquid equilibrium takes place these two curves intersect; at every intermediate temperature the coexisting phases are given by the points of contact of the common tangent. The two sets of points of contact obtained in this manner represent the solidus and liquidus curves of the phase diagram. A third curve which can be plotted in the TX plane is the equal-G curve: the set of points of intersection of the two G-curves. It is clear that the EGC always runs between the solidus and liquidus.

If one makes use of the general relationship between the Gibbs energy G, enthalpy H and entropy S, which is $G = H - TS$, and therefore $\mu^* = H^* - TS^*$ and $G^E = H^E - TS^E$, eqn. (1) yields the following two expressions for the liquid(l) and solid(s) mixtures

$$G^l(T, X) = (1 - X)\,H_1^{*l} + XH_2^{*l} - (1 - X)\,TS_1^{*i} - XTS_2^{*l} + RT\ln(X) + H^{El} - TS^{El} \tag{3}$$

$$G^s(T, X) = (1 - X)\,H_1^{*s} + XH_2^{*s} - (1 - X)\,TS_1^{*s} - XTS_2^{*s} + RT\ln(X) + H^{Es} - TS^{Es} \tag{4}$$

The EGC, which is the solution of

$$\Delta G = G^{l} - G^{s} = 0 \tag{5}$$

is given by

$$(1 - X)\,\Delta H_1^* + X\,\Delta H_2^* - T[(1 - X)\,\Delta S_1^* + X\,\Delta S_2^*] + \Delta H^{E} - T\,\Delta S^{E} = 0 \tag{6}$$

In this equation ΔH_1^* and ΔH_2^* are the heats of melting of the pure components, and ΔS_1^* and ΔS_2^* are the entropies of melting of the pure components. These quantities are related as: $\Delta H_1^* = T_{01}\Delta S_1^*$ and $\Delta H_2^* = T_{02}\Delta S_2^*$, where T_{01} and T_{02} are the melting points of the pure components. If we neglect heat-capacity influences, i.e. if we ignore the dependence on temperature of all the difference functions in eqn. (6), the EGC can be given by the following explicit relation

$$T_{EGC}(X) = \frac{(1 - X)\,\Delta H_1^* + X\,\Delta H_2^* + \Delta H^{E}(X)}{(1 - X)\,\Delta S_1^* + X\,\Delta S_2^* + \Delta S^{E}(X)} \tag{7}$$

Because it is not possible without additional assumptions [5] to derive uniquely two functions (ΔH^{E} and ΔS^{E}) of X from one single other function (T_{EGC}) of X, we return to eqn. (6) and write it as follows

$$(1 - X)\,\Delta H_1^* + X\,\Delta H_2^* - T_{EGC}[(1 - X)\,\Delta S_1^* + X\,\Delta S_2^*] + \Delta H^{E}(X) - T_{EGC}\Delta S^{E}(X) = 0 \tag{8}$$

The last two members of the left-hand side of eqn. (8) now represent the difference between the excess Gibbs energies of the liquid and solid mixtures along the EGC

$$\Delta H^{E}(X) - T_{EGC}\,\Delta S^{E}(X) = \Delta G^{E}_{EGC}(X) = G^{El}_{EGC}(X) - G^{Es}_{EGC}(X) \tag{9}$$

The EGC can now be given by the following relation, which serves as the basis for the interpretation of TX phase diagrams

$$T_{EGC}(X) = T_{ZERO}(X) + \frac{\Delta G^{E}_{EGC}(X)}{(1 - X)\,\Delta S_1^* + X\,\Delta S_2^*} \tag{10}$$

where the "zero line" is given by

$$T_{ZERO}(X) = \frac{(1 - X)\,\Delta H_1^* + X\,\Delta H_2^*}{(1 - X)\,\Delta S_1^* + X\,\Delta S_2^*} \tag{11}$$

The EGC and the zero line have been drawn in Fig. 3, the phase diagram for the KCl + NaCl system. The EGC always runs between the solidus and liquidus. The zero line usually approaches the straight line connecting T_{01} and T_{02} (the smaller the difference between ΔS_1^* and ΔS_2^* and the difference between T_{01} and T_{02} the closer the zero line is to the straight line). With the help of the EGC and the zero line, the difference excess Gibbs energy can be read almost directly from the phase diagram: it is the distance from the zero line to the EGC, multiplied by the entropy of melting.

COMPUTATIONAL PROCEDURE

We start the procedure by estimating the position of the EGC, from which we calculate the corresponding difference excess function with the help of eqns. (10) and (11). The ΔG^E values are fitted to a four-parameter Redlich—Kister expression

$$\Delta G^E_{EGC}(X) = X(1-X)\{\Delta G_1 + (1-2X)\,\Delta G_2 + (1-2X)^2\,\Delta G_3 + (1-2X)^3\,\Delta G_4\} \tag{12}$$

If G^{El} is known from another source we combine it with ΔG^E_{EGC} to calculate G^{Es}. If G^{El} is not known we put $G^{El} = 0$ and consequently $G^{Es} = -\Delta G^E_{EGC}$. Next the phase diagram is calculated with the excess functions and the properties of the pure components; the calculations are carried out at a number of horizontal cross-sections, i.e. for a number of temperatures. The calculated liquidus is compared with the experimental one. A new cycle starts by shifting the EGC in the direction in which the difference between the experimental and calculated liquidus will decrease. The shift of the EGC can be approximated by

$$X(\text{improved EGC in cycle } j+1) - X(\text{EGC in cycle } j) = X(\text{experimental liquidus}) - X(\text{calculated liquidus in cycle } j) \tag{13}$$

Note that the use of a damping factor is optional; in order to avoid oscillations, the EGC shift may be weakened by multiplying the right-hand side of eqn. (13) by a fraction of 1.

With the new EGC position an improved difference excess function is calculated for the various cross-sections and fitted to eqn. (12). Next an improved phase diagram is calculated, the liquidus of which is again compared with the experimental liquidus. If there is a difference between the two liquidi the EGC is shifted again, and so on. The procedure is repeated until the best possible agreement is obtained between the calculated and experimental liquidus. The remaining disagreement is expressed with the help of the indices D_X and D_T, which are defined as

$$D_X = \frac{1}{p}\sum_{i=1}^{p} |X^l_{i\,\mathrm{exp}} - X^l_{i\,\mathrm{calc}}| \tag{14}$$

and

$$D_T = \frac{1}{p}\sum_{i=1}^{p} |T^l_{i\,\mathrm{exp}} - T^l_{i\,\mathrm{calc}}| \tag{15}$$

Here p stands for the number of cross-sections, $X^l_{i\,\mathrm{calc}}$ and $X^l_{i\,\mathrm{exp}}$ are the calculated and experimental mole fractions of cross-section i, and $T^l_{i\,\mathrm{calc}}$ and $T^l_{i\,\mathrm{exp}}$ are the temperatures of the calculated and experimental liquidus of mole fraction i.

The intermediate phase diagram calculations are made with the help of linear contributions: the minima of the two G-functions are brought to the same level; the abscissae are then the mole fractions of the coexisting phases [6].

The calculations, based on the procedure outlined above, are carried out with a computer program denoted here as LIQFIT. Some examples of the calculations are given in the next section.

EXAMPLES

In this section we give the results of calculations made on three systems, viz., *p*-dichlorobenzene + *p*-dibromobenzene, $K_2CO_3 + K_2SO_4$ and KCl + NaCl. Table 2 shows the properties of the pure components as well as the final results. In the case of the system *p*-dichlorobenzene + *p*-dibromobenzene we also made calculations (including phase diagram calculations) in a simplified manner using a programmable desk calculator. The course of that calculation is a good illustration of the method.

p-*Dichlorobenzene* + p-*dibromobenzene*

The liquidus and solidus points which are shown in Fig. 1 were derived by Campbell and Prodan [7] from cooling curves. From these data we took five liquidus points; the latter are given in Table 1 under the heading "experimental". Excess properties of the liquid state are not known. The calculation given here is a simplified one, because we take the two-parameter version of eqn. (12) for the difference excess Gibbs energy

$$\Delta G^{E}_{EGC}(X) = X(1 - X)\{\Delta G_1 + (1 - 2X)\,\Delta G_2\} \qquad (12a)$$

In the first cycle we took $\Delta G_2 = 0$ and derived ΔG_1 from the estimated position of the EGC for $X = 0.5$ ($T = 336.5$ K), which is marked in Fig. 1 with a cross (note that this choice implies the a priori expectation that the experi-

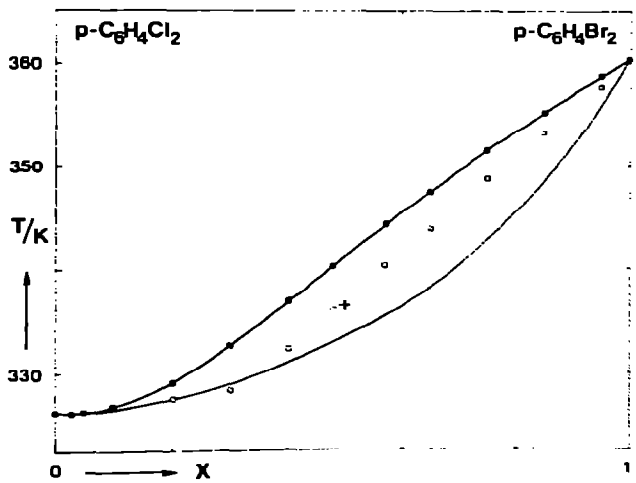

Fig. 1. The *p*-dichlorobenzene + *p*-dibromobenzene system. ● and ○, Experimental data. Curves: calculated solidus and liquidus curves.

TABLE 1

Survey of calculations made with the help of a desk calculator for the system *p*-dichlorobenzene + *p*-dibromobenzene

The excess Gibbs energy values are in kJ mole^{-1}.

Experimental		Cycle I					Cycle II		
T_{exp}	$X^{l}_{e,exp}$	$X^{l}_{e,calc}$	X^{EGC}_{calc}	$X^{s}_{e,calc}$	$X^{EGC}_{corr.}$	$\Delta G^{E}_{EGC,corr}$	$\Delta G^{E}_{EGC}/X(1-X)$	$X^{l}_{e,calc}$	$X^{s}_{e,calc}$
326.83	0.0990	0.0623	0.0693	0.0769	0.1060	−0.173	−1.83	0.0937	0.1158
332.64	0.3003	0.3056	0.3739	0.4586	0.3686	−0.359	−1.54	0.2997	0.4744
340.20	0.4796	0.4950	0.5988	0.7105	0.5834	−0.349	−1.44	0.4748	0.6959
347.33	0.6489	0.6633	0.7605	0.8487	0.7461	−0.260	−1.37	0.6434	0.8287
355.26	0.8501	0.8608	0.9117	0.9502	0.9010	−0.107	−1.19	0.8503	0.9393

mental two-phase region is too narrow, otherwise the cross would have been placed about 2 K higher). The resulting value for ΔG_1 is -1577 J mole^{-1}. With this value the liquidus, solidus and EGC positions were calculated for the five selected temperature cross-sections; the results are given in Table 1 under the heading "cycle I"; the value for the indices D_X and D_T are 0.016 and 0.5 K, respectively.

Improved EGC positions were next obtained by using eqn. (13). The improved EGC positions and the corresponding values for ΔG^{E}_{EGC} are given in Table 1. The linear part in curly brackets of eqn. (12a) can be found by plotting $\Delta G^{E}_{EGC}/X(1-X)$ vs. X. In round numbers it is given by $-1500-400(1-2X)$ J mole^{-1}, i.e. $\Delta G_1 = -1500$ J mole^{-1} and $\Delta G_2 = -400$ J mole^{-1}. The solidus and liquidus points corresponding to the improved excess function are given in the last two columns of Table 1. We observe that just after these two cycles the calculated liquidus points are in close agreement with the experimental ones. The corresponding value for D_X is 0.003 and for D_T 0.1 K.

For the calculations with LIQFIT we used 10 temperature cross-sections. The resulting values for the parameters are shown in Table 2. The calculated solidus and liquidus curves and the experimental data are shown in Fig. 1. As can be inferred from Table 2, there is excellent agreement between the calculated and experimental liquidus data.

$K_2CO_3 + K_2SO_4$

The experimental liquidus and solidus points are given by Barde et al. [2]. For our calculations on this system we replaced the experimental liquidus points by a number of dummy points. The latter were read from the curve which was drawn "by eye" through the experimental points. The excess Gibbs energy of the liquid phase is not known. The results are given in Table 2 and Fig. 2.

KCl + NaCl

The experimental data are those given by Coleman and Lacy [8]. The liquidus points at the NaCl side are in conflict with van't Hoff's Law, which is

$$\left(\frac{d(1-X_c^s)}{dT} - \frac{d(1-X_c^l)}{dT}\right)_{T=T_{02}} = \frac{\Delta S_2^*}{RT_{02}} \tag{16}$$

because they would result in a solidus curve extending beyond the phase diagram. The calculations were therefore based on the curve which was drawn "by eye" through the liquidus points, except for the part at the NaCl side, where it was drawn with an initial slope of $\Delta S_2^*/RT_{02}$.

Neglecting the excess entropy, for G^{El} we used the experimental excess enthalpy function derived by Hersh and Kleppa [9], which is given by: $X(1-X)\ \{-2.19 + 0.14\,(1-2X)\}$ kJ mole^{-1}. Therefore it was possible to calculate not only the difference excess Gibbs energy, shown in Table 2, but

TABLE 2

Properties of the pure components (1) and (2): the entropies of melting (ΔS^*, J K^{-1} $mole^{-1}$) and melting points (T_0, K)

Computations with LIQFIT: damping factors (DF) used and number of cycles (N) needed. Results: values for the four constants in the difference excess Gibbs energy functions (ΔG's kJ $mole^{-1}$) and values of the disagreement indices (D_T, K and D_X).

System	ΔS_1^*	ΔS_2^*	T_{01}	T_{02}	DF	N	ΔG_1	ΔG_2	ΔG_3	ΔG_4	D_T	D_X
p-Dichlorobenzene (1) + *p*-dibromobenzene (2)	55.7	57.0	326.23	360.45	0.6	5	−1.48	−0.24	−0.16	−0.33	0.05	0.0017
K_2CO_3 (1) + K_2SO_4 (2)	27.8	27.3	1175	1343	0.6	3	−3.90	1.73	0.17	−2.54	2.2	0.0134
KCl (1) + NaCl (2)	25.4	26.1	1047	1078	0.1	15	−14.75	1.93	−1.99	2.81	3.6	0.0124

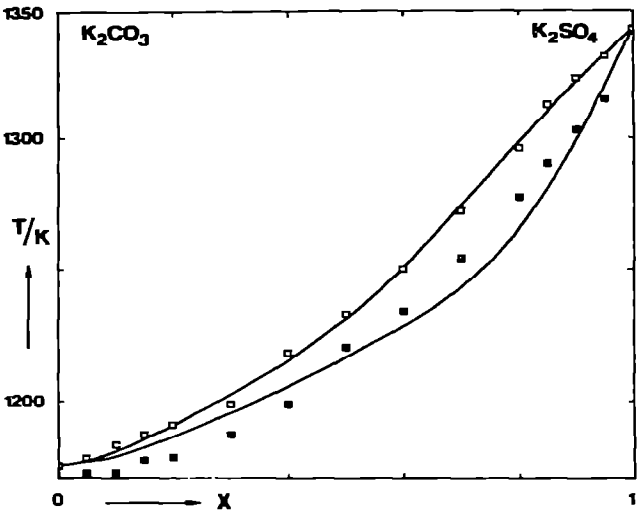

Fig. 2. The $K_2CO_3 + K_2SO_4$ system. ■ and ○, Experimental data. Curves: calculated solidus and liquidus curves.

also the excess Gibbs energy of the solid state, which is given by: $X(1-X)\{12.57 - 1.80\,(1-2X) + 2.00\,(1-2X)^2 - 2.81\,(1-2X)^3\}$ kJ mole^{-1}. The phase diagram obtained is shown in Fig. 3, together with the EGC calculated in the last cycle of the procedure and the experimental data. The G^{Es} value at $X = 0.5$, which is 3.14 kJ mole^{-1}, is in good agreement with the value (3.08 kJ mole^{-1}) which can be calculated for $X = 0.5$ and $T = 918$ with the excess enthalpy and excess entropy functions which were derived from the miscibility gap [5].

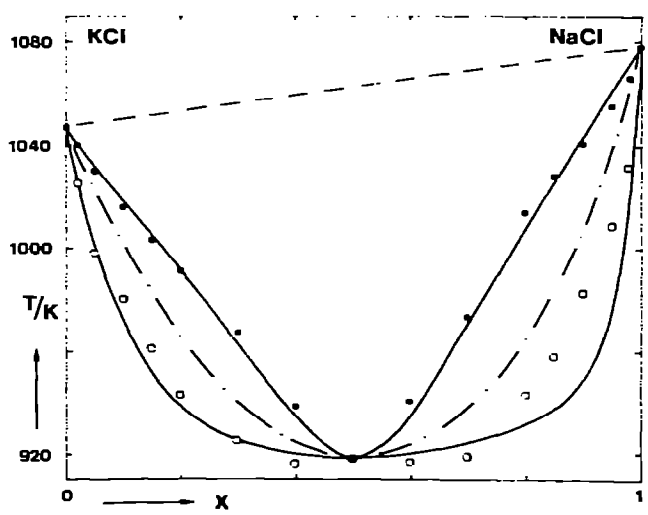

Fig. 3. The KCl + NaCl system. ● and ○, Experimental data. ———, Calculated solidus and liquidus curves; - - - - -, zero line; · — · — ·, equal-G curve.

DISCUSSION

The calculated phase diagrams (Figs. 1—3) show that the actual position of the solidus invariably deviates from that assumed by the investigators.

It is well known that the difficulty in determining the solidus is due to the absence of thermodynamic equilibrium between the liquid mixture and the bulk of the solid material, and that this in turn is due to the low diffusion rates in the solid state. In cooling experiments, thermodynamic equilibrium is appoached only when the first amount of solid material forms from the liquid (the liquidus can be correctly determined). On further solidification the composition of the solid material changes continually, and the last amount of liquid certainly does not disappear at the solidus point corresponding to the mean composition. In many heating experiments the same events take place in the reverse order.

The situation changes in those cases where a subsolidus equilibration, carried out for the purpose of preparing a homogeneous solid mixture, precedes the heating experiment. When a homogeneous solid mixture, which can also be obtained by the technique of zone levelling, is heated in a rapid experiment, i.e. rapid with respect to the diffusion rates in the solid state, it can only yield a liquid mixture of the same composition. The consequence of this is that such homogeneous material melts sharply at the temperature where solid and liquid mixtures, being of the same composition, have equal Gibbs energies. In other words, in rapid experiments homogeneous mixtures melt at the EGC! This behaviour has been observed by van Genderen et al. [10] for mixtures of *p*-dichlorobenzene + *p*-dibromobenzene prepared by zone levelling. It is possible that such behaviour was also observed for the $K_2CO_3 + K_2SO_4$ system by Levin et al. [11] who performed DTA experiments after heating three times below the solidus. They state that the liquidus was indistinguishable from the solidus. Their observations apparently differ from those of Barde et al. [2], who carried out DTA experiments on mixtures "homogénéisés par agitation mécanique", which gave rise to the points shown in Fig. 2.

In conclusion, it is recommended that calculations of the kind presented here be carried out in the pre-publication stage of the investigations. The effort required to perform these calculations is small compared to that required for the experiments. Furthermore, such calculations could be coupled back to the experimental information and, for instance, used to determine whether or not a region of demixing in the solid state interferes with the solid—liquid equilibrium.

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