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Estimation of the Activity Coefficients in a Liquid Mixture of Na_2CO_3 and Na_2S

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Activity coefficients for the components in Na_2CO_3—Na_2S liquid mixtures are calculated from the freezing point data of Courtois [2], assuming the solutions to be "regular solutions".

We have recently studied [1] the thermodynamics of equilibria on gasification of sodium-base pulping liquors. We then showed that under certain conditions, the condensed phase at equilibrium would be likely to consist mainly of a liquid mixture of Na_2CO_3 and Na_2S. For an accurate calculation of the equilibrium composition of the gas phase and condensed phase obtained, it was desirable to have an estimate of the activity coefficients of the two components, Na_2CO_3 (= 1) and Na_2S (= 2).

The experimental data on the system Na_2CO_3—Na_2S are rather meagre. Courtois [2] has given the temperature of solidification for various mixtures (circles in Fig. 3). He found no intermediate phase, and a simple eutectic equilibrium at 1 068°K. There is no evidence for solid solutions. From his work we may take the melting points to be 1 125°K for Na_2CO_3 and 1 453°K for Na_2S. These values are in good agreement (± 2°) with the work of other investigators [3-5].

Tammann and Oelsen [10] have also measured the freezing point curve. They give fewer points which agree well at low x_2 but deviate seriously at high x_2. We have decided to use Courtois' values; an experimental reinvestigation is however desirable.

The heat of fusion of Na_2CO_3, $L_{f1} = 7.3$ kcal mole^{-1}, has been determined calorimetrically by Ginzburg [3]. The heat of fusion for Na_2S, $L_{f2} \approx 1.6$ kcal mole^{-1}, has been estimated by Kubaschewski and Evans [6]. We have not been able to find any other data, such as heats of mixing, that could be used in the calculation of the activity coefficients of Na_2S and Na_2CO_3.

The two components Na_2S and Na_2CO_3 have the cation in common, and anions of the same charge and roughly the same "ionic radius". It seems likely that the Temkin [7] model can be used for such a mixture, as a good approximation; in this case, it means that the anions are randomly mixed. Then

$$s_1 - s_1^0 = -R \ln x_1; \qquad s_2 - s_2^0 = -R \ln x_2 \tag{1}$$

Let us now assume that the melts behave as "regular solutions" according to Hildebrand[8], which means that eqn (1) is valid and also that the molar heat of mixing is

$$\Delta H = bx_1x_2 \tag{2}$$

Then we can derive, from the definitions of partial molar quantities

$$h_1 - h_1^0 = bx_2^2; \qquad h_2 - h_2^0 = bx_1^2 \tag{3}$$

From the definitions of the thermodynamic quantities, with eqns (1) and (3) we may prove

$$RT \ln f_1 = bx_2^2; \qquad RT \ln f_2 = bx_1^2 \tag{4}$$

These are the well-known relationships for regular solutions[8]; the symbols have their usual significance: s_1, s_2 partial molar entropies; h_1, h_2 partial molar enthalpies; x_1, x_2 molar fractions ($x_1 + x_2 = 1$);

$$f_1 = a_1/x_1; \qquad f_2 = a_2/x_2 \tag{4a}$$

are activity coefficients, and the superscript "^{0}" refers to the standard state, which is the pure liquid in our case.

The constant b is assumed to be independent of temperature, so that a knowledge of this constant makes it possible to calculate f_1 and f_2 for all temperatures. We shall now set out to calculate the constant b, using the available experimental data.

In those parts of the phase diagram where a liquid is in equilibrium with the solid substance 1, we have

$$1 \text{ (solid)} \rightleftharpoons 1 \text{ (liquid, activity } a_1); \; K = a_1; \; \Delta H = L_{f1} \tag{5}$$

where K is the equilibrium constant. By integrating van't Hoff's equation

$$\int_K^{K=1} \mathrm{d} \ln K = R^{-1} \int_T^{T_{f1}} L_{f1} \frac{\mathrm{d}T}{T^2}$$

and assuming L_{f1} to be approximately constant over the interval studied, we obtain

$$RT \ln K = -L_{f1}(1 - TT_{f1}^{-1}) \tag{6}$$

Here, T_{f1} is the melting point for pure Na_2CO_3. From eqns (4), (4a), (5), and (6) we find

$$bx_2^2 + RT \ln x_1 = -L_{f1}\,(1 - TT_{f1}^{-1}) \tag{7}$$

which may be rewritten in the form

$$T = (L_{f1} + bx_2^2)[L_{f1}T_{f1}^{-1} - R \ln (1 - x_2)]^{-1} \tag{8}$$

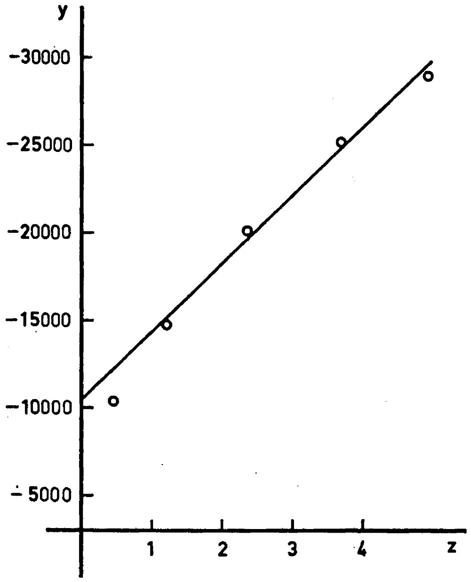

Fig. 1. Plot according to eqn (9). Circles calculated from data of Courtois [2]. Straight line calculated with $L_{f1} = 10.50$ kcal mole^{-1}, $b = 3.84$ kcal mole^{-1}.

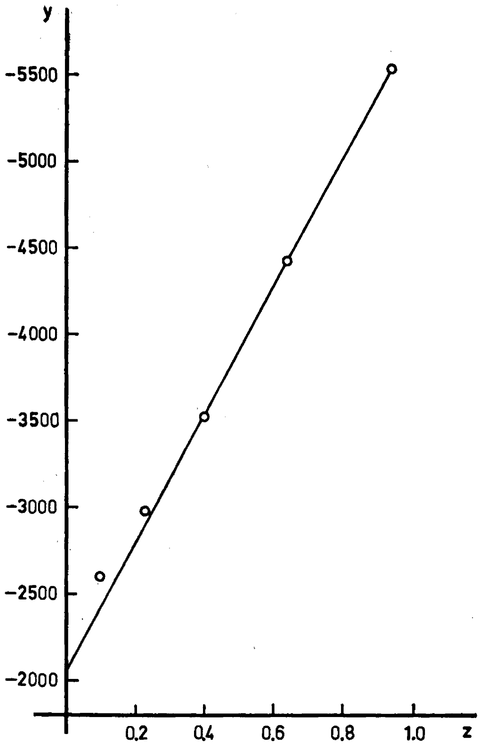

Fig. 2. Plot according to eqn (9) with indices 1 and 2 exchanged. Points calculated from data of Courtois [2]. Straight line calculated assuming $b = 3.69$ kcal mole^{-1} and $L_{f2} = 2.05$ kcal mole^{-1}.

If b, L_{f1} and T_{f1} are known, we may thus give T as a function of x_2. In the present case, this function is approximately known[2]; in order to calculate the unknown constants b and L_{f1} we may transform eqn (7) to the form

$$L_{f1} + y + bz = 0 \tag{9}$$

where

$$y = RTT_{f1}(T_{f1}-T)^{-1} \ln (1-x_2)$$

$$z = T_{f1}(T_{f1}-T)^{-1} x_2^2$$

Eqn (9) has been used by Flood, Förland and Roald [9] for calculating the heat of fusion of $CaCO_3$, from the melting diagram. If y is plotted as a function of z, one will obtain b and L_{f1} from the slope and intercept of the straight line. — One may easily derive equations that are symmetrical to eqns (8) and (9), with 1 and 2 exchanged.

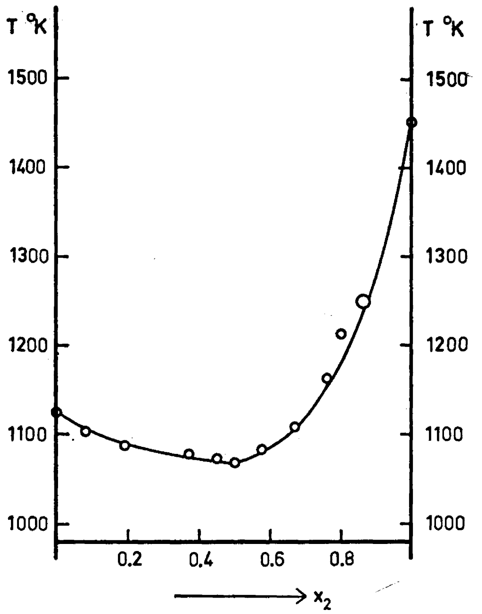

Fig. 3. Freezing point diagram $T(x_2)$ for system $Na_2CO_3-Na_2S$. Points: data of Courtois [2]. For the larger circle, Courtois gives a higher uncertainty than for the rest. Curve calculated from eqn (8) and its symmetrical form with 1 and 2 reversed, assuming $b = 3.75$ kcal mole^{-1}, $L_{f1} = 10.50$ kcal mole^{-1} and $L_{f2} = 2.00$ kcal mole^{-1}.

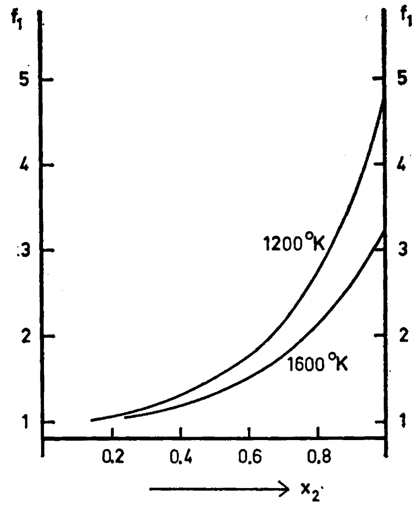

Fig. 4. Activity coefficient f_1 of Na_2CO_3 in melts $Na_2CO_3-Na_2S$, calculated by means of eqn (4), assuming $b = 3.75$ kcal mole^{-1}.

Fig. 1 gives a linear plot of Courtois' data according to eqn (9); it leads to the values $L_{f1} = 10.50$ kcal mole^{-1} and $b = 3.84$ kcal mole^{-1}. A plot of the symmetrical function is given in Fig. 2; it leads to $L_{f2} = 2.05$ kcal mole^{-1} and $b = 3.69$ kcal mole^{-1}.

Fig. 3 gives the diagram $T(x_2)$ calculated using eqn (8) and its symmetrical analog, with the average value of $b = 3.75$, and the value $L_{f1} = 10.50$ kcal mole^{-1}, and $L_{f2} = 2.00$ kcal mole^{-1}. Here, L_{f2} has been slightly adjusted to give a somewhat better agreement with the (anyway somewhat crude) experimental data.

The good agreement of the values for b obtained from the two independent diagrams (Figs. 1 and 2), and the good agreement of $T(x_2)$ with the experimental data indicate that the "Temkin regular solution" may be used as an approximate model for the melts of $Na_2CO_3 + Na_2S$.

Finally, Fig. 4 gives the activity coefficient, f_1, as a function of x_2, calculated by means of eqn (4), for temperatures 1 200°K and 1 600°K. For 1 200°K, values for f_1, when $x_2 > 0.8$ cannot be obtained experimentally since $Na_2S(s)$ crystallizes.

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