

Phase Diagram by the Conductance Method

The System Na_2SO_4 — Na_2CO_3

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The conductance of the salt mixtures as function of temperature has been used to determine the solidus and liquidus lines for the system Na_2SO_4 — Na_2CO_3 . A thermodynamic discussion of the results is given, based on the assumptions of ideal mixing in the liquid and a slight positive deviation in the solid phase.

In thermal analysis, the same instrument is used both to determine the temperature and to detect the heat effect that occurs at the phase transformation. In principle, one might as well detect the phase transformation by the change in some property of the system which is more conveniently measured than its heat content, simultaneously measuring the temperature separately.¹

Thus, for example, Øye² recently established the rather complex phase diagram for the system Li_2SO_4 — Ag_2SO_4 by measuring the electromotive force of concentration cells. The method has the advantage that the EMF can be measured accurately, and measured under equilibrium conditions. It appeared to the authors that the same advantage would be inherent when using the electrical conductance of the system to detect the transition points. A conductance cell for this purpose is very simply established since no knowledge of the cell constant is required, and it seemed that such a method might also offer a valuable supplement to the tracer technique developed by Flood and Seltveit³ for the determination of solidus curves.

A survey of the literature reveals that Benrath⁴ and Tubandt and Lorenz⁵ used conductivity measurements for phase studies of nonmetals already more than fifty years ago, but only brief reference to the method is given in more recent texts.⁶ Phase diagrams for salt mixtures have in some cases been established as by-products of conductivity measurements.^{7,8} For solid metal systems, on the other hand, the method appears to be well established.⁹

It was decided to gain some experience with the conductance method by using it on the system Na_2SO_4 — Na_2CO_3 , which has a certain interest in con-

nection with the oxygen electrode measurements previously done in this laboratory.¹⁰ This system has previously been studied by several investigators,¹¹⁻¹⁵ who all report a continuous liquidus curve with a flat minimum around 60–70 mole % carbonate. The older papers do not report the solidus line. At 600°C and below, a number of solid-solid transitions occur, these have been extensively studied by Khlapova^{14,15} but are outside the scope of the present paper. Her solidus curve,¹⁵ on the other hand, is rather inaccurate (and also thermodynamically impossible since the liquidus and solidus do not coincide at the minimum). The liquidus was redetermined by Nebell and Skarbø¹⁶ by means of cooling curves, using essentially the same furnace and procedure as described below. For the melting point of sodium carbonate, they obtained 858°C, which is also the value reported by Janz and Lorenz.¹⁷ Nebell and Skarbø also attempted to determine the solidus by the tracer method,³ using ⁶⁰Co (in the form of chloride), but the attempts were unsuccessful because the cobalt separated from the liquid (probably as cobalt oxide).

EXPERIMENTAL

A vertical resistance heated tube furnace (the standard design of this laboratory¹⁸, was used for the experiments. A cylindrical platinum crucible of 38 mm diameter was used as the container and at the same time served as one electrode. The other electrode, in the form of a hollow platinum cylinder with a diameter of about 10 mm, was placed concentrically in the crucible.

The charges were made by weighing the properly dried salts (*pro analysi*, E. Merck, Darmstadt). The furnace was flushed with a stream of dry carbon dioxide during the

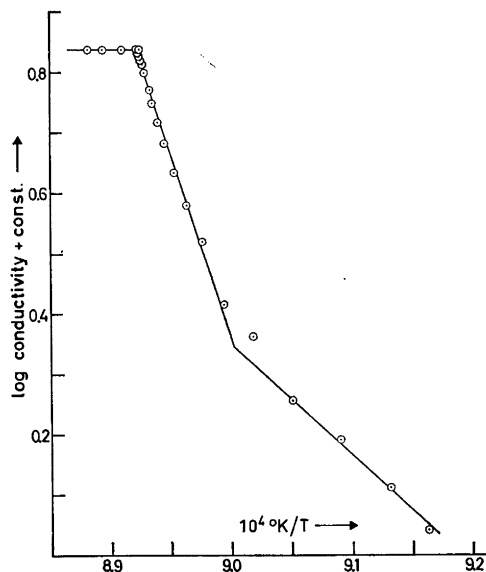


Fig. 1. Log conductance versus reciprocal abs. temperature, for a mixture with 91.6 mole % Na_2CO_3 .

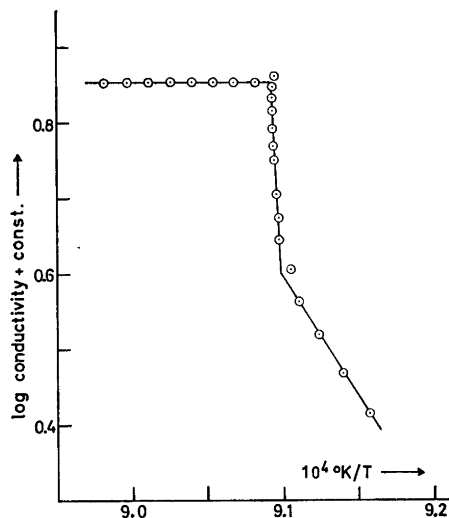


Fig. 2. Same as Fig. 1, but for 65.0 mole % Na_2SO_4 .

experiments to prevent thermal decomposition of the carbonate.¹⁹ Conductance was measured by a combined bridge and oscillator operating at 1000 c/s and 3 V (Philoscop Type GM 4249/01, Philips). Temperature was measured with a Pt/90Pt10Rh thermocouple placed with the bare leads into the salt mixture. Thus, for this simple system the phase transformations were checked by heating or cooling curves as well, using a rate of change of about 1° per minute. All conductance values were determined during cooling. The reported temperatures are based on the melting point of Na₂SO₄, 884°C²⁰⁻²² as the reference point.

RESULTS

As expected from the Arrhenius equation, the plots of the logarithm of conductance *versus* the inverse absolute temperature gave straight lines within each phase region, and distinct breaks at the transition points, see Figs. 1 and 2. The cooling curves (temperature *versus* time) showed definite breaks only at the liquidus points, whereas the solidus points appeared in heating curves. This is accordance with the statement by Kingery¹ that, as far as thermal analysis is concerned, heating curves are preferable for solidus points.

The measured points and the ensuing diagram are shown in Fig. 3, with the melting point for the pure carbonate taken from the previous work.¹⁶ It is noted that the solidus points obtained from conductance measurements during cooling agree well with the points obtained from thermal analysis

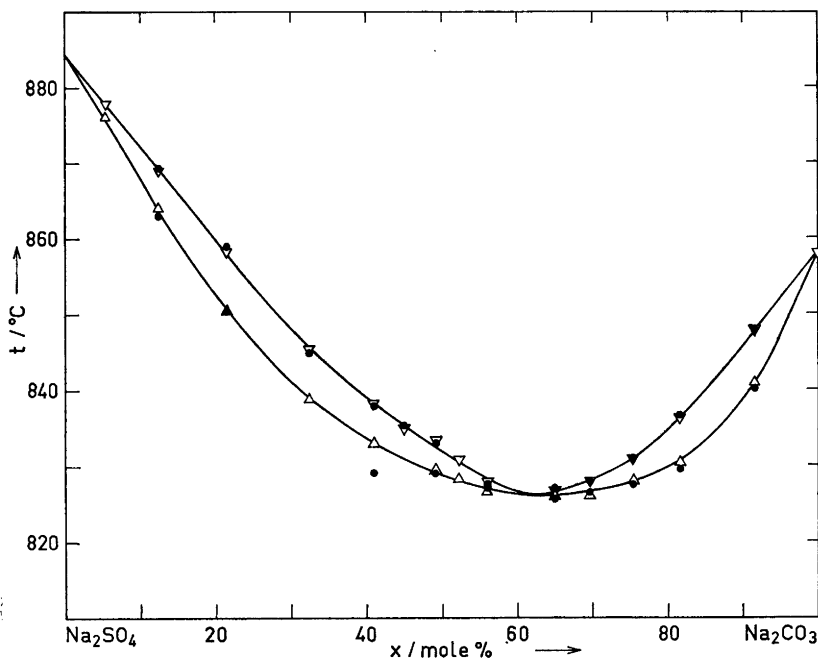


Fig. 3. Experimental liquidus and solidus curves for the system Na₂SO₄-Na₂CO₃. Solid circles: Results from conductance measurements. Triangles, point down: Cooling curves. Triangles, point up: Heating curves.

during heating (with one, un-explained exception). The minimum appears at 826°C and 62 mole % carbonate.

THERMODYNAMIC CALCULATIONS

The diagram of Fig. 3 invites some interpretation. The general relationship between temperature and composition for the solidus and liquidus lines may be written:

$$\ln \frac{X_1 \gamma_1}{N_1 f_1} = \frac{\Delta H_1^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_1^\circ} \right) - \left(C_{p1(l)}^\circ - C_{p1(s)}^\circ \right) \left(\frac{T_1^\circ}{T} - 1 - \ln \frac{T_1^\circ}{T} \right) \quad (1)$$

Here X_1 and N_1 are the mole fractions of one component, say, the sulphate, in the solid and the liquid mixtures in equilibrium at the temperature T , and γ_1 and f_1 are the corresponding activity coefficients; ΔH_1° is the heat of fusion at the melting point T_1° ; $C_{p1(s)}^\circ$ and $C_{p1(l)}^\circ$ are the molar heat capacities of pure solid and pure liquid component 1. In eqn. (1) these heat capacities have been assumed independent of temperature. Changing subscripts, we have the equivalent eqn. (2) for the carbonate.

The heats of fusion have been determined calorimetrically both for sodium sulphate²²⁻²⁴ and for sodium carbonate.^{23,24} The values selected from these investigations are $\Delta H_1^\circ = 5670$ ^{22,25} and $\Delta H_2^\circ = 7300$ cal·mole⁻¹.²⁴ The heat capacity differences are $\Delta C_{p1} \simeq -4.5$,²² $\Delta C_{p2} \simeq +2.0$ cal·mole⁻¹·deg⁻¹.²⁴

In order to calculate a theoretical diagram from the eqns. (1) plus (2), some knowledge, or assumptions, are also needed concerning the activity coefficients. The type of diagram shown in Fig. 3 occurs when the solid mixtures exhibit more positive (or less negative) deviations from ideality than the liquid. (It should be noted that only the *ratio* between the activity coefficients appear in eqn. (1).) The measurements with the oxygen electrode in concentration cells with liquid sodium sulphate-sodium carbonate mixtures¹⁰ were interpreted by the two mutually dependent assumptions that the mixtures behaved ideally and that the liquid junction potential was negligible. More recently, Førlund²⁶ has shown that the junction potential will vanish if the amount of electricity transported by each of the cations are in direct proportion to their mole fractions in the mixture. This seems plausible for ions of the same charge and about the same size, and hence lends support to the conclusions of the concentration cell measurements. In the following, then, the liquid will be regarded as an ideal mixture, and various assumptions concerning the solid phase are introduced.

Model I. For illustration it is first assumed that the solid phase also behaves ideally. In this case, eqns. (1) and (2) can be solved to give the mole fractions explicitly (see, *e.g.*, Hildebrand and Scott²⁷). The curves thus calculated are shown as the upper pair in Fig. 4.

Model II. The solid mixture exhibits a positive deviation from ideality which can be expressed by the symmetric expression for the excess free energy

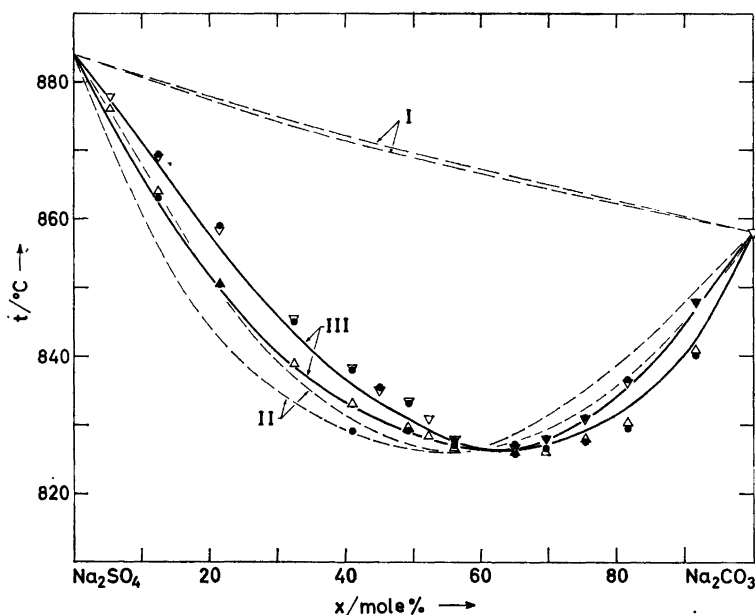


Fig. 4. Theoretical liquidus and solidus curves calculated on the assumptions of ideal mixing in the liquid and I: Ideal mixing in the solid, II: Symmetric positive deviations in the solid, III: Unsymmetric positive deviations in the solid.

Experimental points are identical with those of Fig. 3.

of mixing, $\Delta G^{xs} = b \frac{n_1 n_2}{n_1 + n_2}$, where the n 's are the number of moles in the solid, and b is a constant. This leads to the well-known expressions for the activity coefficients

$$RT \ln \gamma_1 = b X_2^2; RT \ln \gamma_2 = b X_1^2$$

The combination of these two equations with eqns. (1) and (2) is solved by successive approximations. With a value of 950 cal for the constant b , the pair of curves designated II in Fig. 4 is obtained. It is seen that the calculated diagram has the correct shape, but the experimental diagram is less symmetric.

Model III. Some additional asymmetry is introduced in the calculated diagram by using an asymmetric expression for the excess free energy,

$$\Delta G^{xs} = \alpha \frac{n_1 n_2}{\beta n_1 + n_2} \quad (3)$$

where α and β are constants.

Differentiation gives the activity coefficients

$$RT \ln \gamma_1 = \alpha \left(\frac{X_2}{\beta X_1 + X_2} \right)^2; RT \ln \gamma_2 = \alpha \beta \left(\frac{X_1}{\beta X_1 + X_2} \right)^2$$

The "best" values for the constants are obtained by solving the equations to match the experimental diagram in the minimum point, this leads to the values $\alpha = 1300$ cal, $\beta = 1.90$. Combining again with eqns. (1) and (2) gives the calculated diagram designated III in Fig. 4. It is seen that rather good agreement with the experimental points is obtained.

DISCUSSION

The models II and III above corresponds to the concept of regular solutions^{27, p. 46} if we assume that the entropy of mixing has the ideal value and hence that $\Delta G^{\text{xs}} = \Delta H_{\text{mix}}$. The phase diagram alone does not, however, warrant such an assumption. This is most clearly seen if we assume, for the sake of illustration, that $\Delta H_{\text{mix}} = 0$, $\Delta G^{\text{xs}} = -T\Delta S^{\text{xs}}$. This introduces a temperature dependence in the expressions for the activity coefficients, but because of the small temperature range of the diagram, the curves thus calculated (with parameters adjusted to match in the minimum point) are almost indistinguishable from those calculated with temperature-independent activity coefficients.

Eqn. (3) for the excess free energy corresponds formally to the equation given by Scatchard²⁸ for mixtures of liquid non-electrolytes. His equation may be written

$$\Delta G^{\text{xs}} = \alpha_{12}v_1 \frac{n_1n_2}{(v_1/v_2)n_1 + n_2}$$

where v_1 and v_2 are the molar volumes of the components. It is seen that the parameter β used above corresponds formally to the ratio between the molar volumes. It is interesting to note that this ratio works in the right direction, the introduction of the larger ion (sulphate) into an excess of the smaller ion (carbonate) requires a greater energy than the opposite. This trend would be expected to be particularly prominent for solid mixtures. In the present case, the value found to give best fit with experiments, $\beta = 1.90$, is considerably larger than the ratio $v_{\text{Na}_2\text{SO}_4}/v_{\text{Na}_2\text{CO}_3} = 1.25$. In a model proposed by Scott^{27, p. 304} taking into account the strain energy of solid solutions, the parameter β corresponds to the *square* of the volume ratio, which still falls short of the observed value. The volume analogy, although qualitatively useful, should not be stressed.

It would seem reasonable to consider the ideal behaviour of the liquid and the nearly ideal behaviour of the solid mixtures in this system in connection with the free rotation of the anions, as suggested by Bredig²⁹ for the high-temperature modification of sodium sulphate. But Fischmeister³⁰ has shown more recently that the available space is too small for rotation of the sulphate ion in the solid. Hence the process in the solid cannot be regarded as a mixing of spheres.

The calculated diagram, curves III of Fig. 4, differs from the experimental points in that the two-phase region is somewhat too narrow throughout. This seems to indicate that the dependence of the excess free energy on composition is slightly different from that given by eqn. (3), if the other data used for the calculation are accepted as correct.

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