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Determination of the Solidus Curve by a Tracer Technique. The System $CaCl_2$—NaCl

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Based on a modification of the high-temperature filtration previously described [1], a new technique for the determination of the solidus curve of a phase diagram is described. A small amount is added of a third, radioactive component which is soluble in the liquid, but insoluble in the solid phase in question.

The method is applied to the system calcium chloride — sodium chloride. The data of the composition of the solid phase are in favour of the existence of an incongruently melting compound Na_4CaCl_6. The solubility of calcium chloride in solid sodium chloride reaches a maximum of 15 mole percent. A discussion of the data indicates the occurrence of $CaCl_4^{--}$ ions in the liquid phase.

METHOD

In phase diagrams involving solid solutions, the extent of this solid solution, described by the solidus line, is often difficult to establish. This is particularly true for high-temperature systems. Thermal analysis will in general give only very approximate results for the solidus curve. Quenching techniques, with microscopic and/or X-ray examination of the quenched sample, have given a considerable amount of information, particularly in silicate systems where the phase transformations appear sufficiently slowly for the quenching to be effective. High-temperature X-ray techniques have also been used, but this method is rather elaborate and, notably at higher temperatures, difficult.

A knowledge of the solidus curve, however, is of decisive importance for a discussion of the thermodynamic and structural properties of the liquid (as well as the solid) solution, based on the phase diagram. Such discussion has yielded information of considerable interest for a number of systems, but so far the work has been limited to the consideration of systems without solid solution, since the solidus curves for other systems are in general not known with sufficient accuracy. Hence it became desirable to devise a method

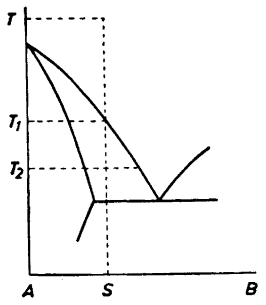

Fig. 1. Binary phase diagram where component A forms solid solutions with component B (schematic).

for reliable determination of the solidus curve in high-temperature systems. Such a method, employing the addition of a radiactive tracer, will be described.

The procedure is in principle as follows. To the components of the system (mixed in known amounts) is added a small amount of a third, radioactive component, which is so chosen that it cannot enter into the solid phase in question. The procedure may be illustrated by considering the binary system A—B (Fig. 1). The components A and B are mixed to give the chosen composition *s*, a small amount of radioactive tracer (order of magnitude 0.05 %) is added, and the mixture is brought to the temperature T where only liquid is present. A sample is withdrawn from this liquid and its radioactivity per gram is determined. (Eventually the composition of the melt may also be checked by chemical analysis of the same sample.) Next, the system is cooled. The system is then brought to equilibrium at the temperature T_2 (which for practical reasons must be so chosen that the ratio of liquid to solid phases is roughly within the limits 1.5 and 0.5). At this temperature, another sample is withdrawn from the liquid phase, and its radioactivity is determined. The radioactivity per gram of this second sample must necessarily be higher than that of the first, since the total amounts of liquid phase in the system has diminished while all of the radioactive tracer is present in that phase only. The ratio between these two specific activities gives directly the fraction of the total system present in the liquid state at temperature T_2.

The composition of the second sample, *i.e.* the liquid phase, is determined by chemical analysis. This analysis may be checked against the liquidus curve obtained from thermal analysis, or otherwise, one might rely upon the thermal analysis and omit the chemical analyses altogether.

Now, the gross composition is known from the outset, the relative amounts of liquid and solid has been determined from measurements of the radioactivity, and the composition of the liquid is known. By combination of this information, the composition of the solid phase may easily be calculated.

ON THE SYSTEM SODIUM CHLORIDE — CALCIUM CHLORIDE

As the first system to be investigated by the method outlined above was chosen the system sodium chloride — calcium chloride. At least five earlier investigations of this system are to be found in the literature. Lamplough [2] concluded from his work in 1911 that probably neither solid solution nor any compound between the components exist in this system. Menge [3] on the other hand, found in the same year a compound to which he attributes the formula $4\,NaCl \cdot CaCl_2$, and he also found that solid solutions are formed on the sodium chloride side. He indicates a maximum solid solubility of about 10 weight-%. His conclusions are based on thermal analysis in combination with microscopy.

In 1920, Scholich [4] re-investigated the system, and concluded that neither solid solution nor any compound is present. According to this author, Menge's results may probably be explained by assuming the presence of hydrated calcium chloride in his samples.

The presence of solid solutions is again maintained by Sato and Amano in 1935 [5] who find a maximum solid solubility of 4 to 5 % calcium chloride in sodium chloride, but no compound formation. These results are again supported by Miyake and Suzuki in 1954 [6] on basis of their X-ray investigations which were, however, carried out on slowly cooled samples.

EXPERIMENTAL

In the tracer method, the first question concerns the choice of a suitable tracer. In the case at hand, some radioactive ion which cannot enter into the solid sodium chloride lattice had to be used. As such, cobalt (^{60}Co) was used, and later on cesium (^{134}Cs), both in the form of the chlorides. Cobalt ion has about 18 % lower ionic radius than sodium ion, in addition to its double charge, and there are also reasons to believe that Co will be present in the NaCl-melt as $CoCl_4^{-2}$ complexes. Cesium ion has an ionic radius about 65 % higher than that of sodium ion. The fact that points obtained with the two different tracers agree may be taken as an indication that neither of them have entered the solid phase to any measurable extent.

Sodium chloride and calcium chloride (both *fusum pro analysi* from E. Merck A.G., Darmstadt) were weighed into a platinum crucible to a total of about 40 g for each run, with about 20 mg of radioactive cobalt chloride or cesium chloride added.

The furnace is shown in Fig. 2. It consists essentially of a Pythagoras tube wound with Kanthal resistance wire, the windings being closer spaced towards the ends to compensate for the extra heat loss at the ends. The furnace shell was water-cooled to do away with the influence of changes in ambient temperature. The temperature was controlled by a Kent Multelec potentiometric controller in connection with a platinum-platinumrhodium thermocouple located closely outside the heater windings. The temperature in the melt was followed with another thermocouple with the bare wires of the hot junction dipping directly into the melt. This thermocouple was connected to a Tinsley thermoelectric-free potentiometer in combination with a recording galvanometer (Multiflex galvanometer with Nachlaufschreiber from Dr. B. Lange, Berlin). This equipment will record, *e. g.*, a coolingcurve with an accuracy of about 0.07° per mm. The thermocouple was checked against the melting points of pure sodium chloride (800.6°) and sodium sulphate (885.0°). The furnace was equipped with a rotating stirrer which was lowered into the crucible after the salts had melted, to insure thorough mixing as well as even temperature. The stirrer shaft and thermocouple were running through packing glands in the top lid. A third packing gland was provided for the sample takers, an open scoop for sampling the homogeneous liquid and a platinum filter for sampling the heterogeneous system.

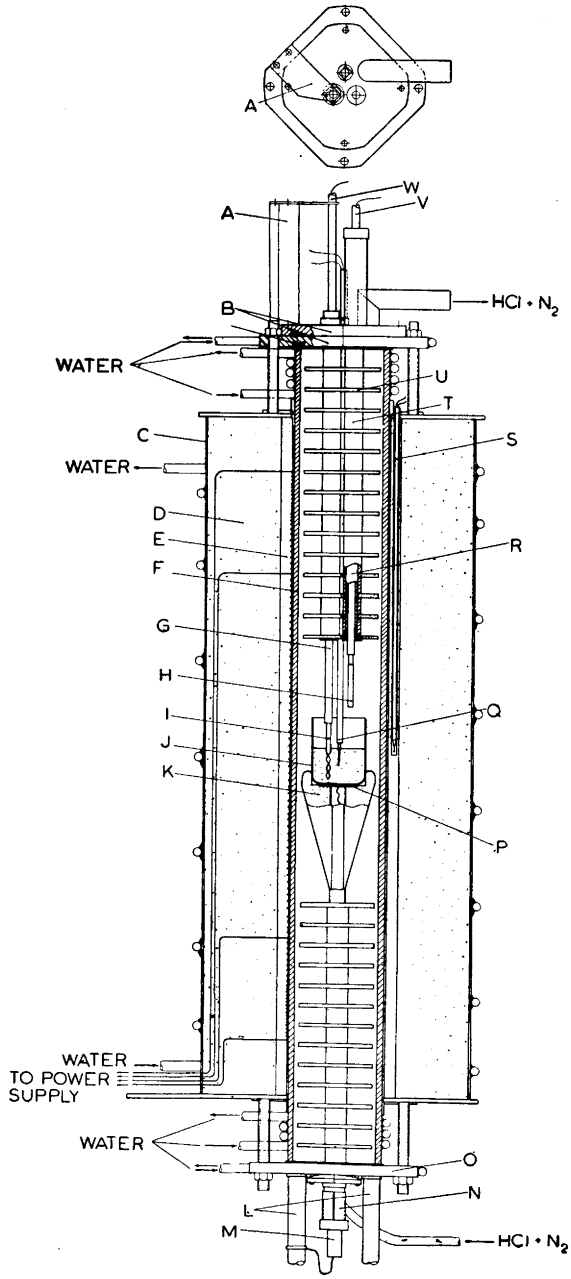

Fig. 2. High-temperature filtration furnace.

H = filtration tube
I = Pt stirrer on ceramic shaft
J = crucible with the equilibrium mixture
K = supporter
Q = thermocouple
U = radiation shields

The cobalt and calcium chlorides were protected from hydrolysis and oxidation by using an atmosphere of nitrogen plus hydrogen chloride in the furnace. In order to withstand this atmosphere, the top and bottom lids were made of pure nickel, with rubber gaskets.

A typical run was as follows. The platinum crucible with contents was placed in the furnace, which was then closed and a slow stream of the protective gas mixture was conducted through the furnace while it was heated. When a temperature was reached at which all of the charge would be molten, the stirrer and thermocouple was lowered into the melt. After 10—15 min of stirring, a sample (varying from about 0.2 to 0.5 g) was taken from the homogeneous melt, and the sample taker removed from the furnace and replaced by the platinum filter tube (see below). The furnace was then allowed to cool at a rate of about 1° per min, while the temperature of the melt was followed by the recording galvanometer described above.

After the break had been recorded (corresponding to temperature T_1 of Fig. 1) the cooling was continued to the chosen temperature (T_2), and the melt was held constant at this temperature sufficiently long for the equilibrium to be established. Experiments showed that 2 h was sufficient, but for practical reasons the constant temperature was usually held overnight. (Some particular run in which equilibrium was difficult to establish will be discussed under "Results".)

After equilibrium was supposedly established, the platinum filter assembly was lowered into the crucible. This consisted essentially of a platinum tube about 40 mm long, closed at the lower end by a platinum bottom with fine needle holes. The platinum tube was joined moderately gas-tight to a fused-quartz tube running through the packing gland at the top of the furnace. An electrical lead to the crucible and another to the filter, in combination with a low-voltage source and a pilot light, showed when the filter was in contact with the melt. The filter was then lowered some 5 mm more, and a sample sucked into the filter by application of a syringe at the top of the quartz tube. The filter assembly was then removed and replaced by a sample taker.

The temperature was then raised again until all of the charge had melted, stirred for a while, and another sample taken from this homogeneous liquid. This last sample served to check the total radioactivity present, *i. e.*, that nothing had disappeared from the crucible except for the samples.

Analysis for composition and radioactivity.

Each of the samples was dissolved in water and diluted to a known volume. In one part of the solution, the calcium content was determined by titration with ethylenediamine-tetraacetic acid, disodium salt ("Titriplex III", E. Merck A. G., Darmstadt) with "Eriochrome black T" as indicator. The sodium chloride content was determined as difference.

In another part of the solution, the radioactivity was measured with a scintillation counter for liquids (Scintillation Counter for Ultrasensitive Measurements, Type N 550, in connection with a Decatron Scaler N 530 A, both from E. K. Cole, Ltd., London). Only the ratios between the radioactivities (per gram) of the three different samples from the same run were of interest.

RESULTS

A part of the experimental data are given in Table 1, and the phase diagram is shown in Fig. 3. The eutectic lies at 500 $\pm$ 2°C and 48 mole percent NaCl. At 600°C the solubility of $CaCl_2$ in solid NaCl is about 15 mole percent (24 weight percent), hence is appreciably higher than estimated by earlier investigators. In the solid $CaCl_2$, on the other hand, no solubility of NaCl was detected.

The observations regarding the composition of the solid phase on the NaCl side of the diagram are not entirely unambiguous, and two different interpretations seem possible:

Table 1. Data of thermal analysis and high temperature filtrations of the system $NaCl-CaCl_2$.

Mole % NaCl	Cooling curve T_1 (°C)	Filtration T_2 (°C)	Mole % $CaCl_2$		Tracer
			liq.	sol.	
NaCl Side					
100	800.6				
96.0	789.5				
91.0		748.8	13.9	2.7	^{60}Co
92.5		721.5	18.7	4.4	^{134}Cs
82.3	729.6	689.4	25.4	7.4	^{60}Co
77.3	703.8	649.3	30.8	11.3	^{60}Co
74.0	686.6				
70.0		571.8	41.9	13.5	^{60}Co
70.0		594.3	38.6	13.5	^{60}Co
69.6	659	594.4	37.9	15.3	^{60}Co
66.7		550.7	45.2	19.8	^{134}Cs
65.7	632	605.9	37.8	15.0	^{60}Co
62.0	602.5	569.3	43.1	14.4	^{60}Co
61.0	590.8	554.6	44.0	9.2	^{60}Co
60.0		525.0	47.8	20.1	^{134}Cs
60.0		578.2	40.3	12.3	^{134}Cs
58.2	572.0	515.4	50.1	18.8	^{60}Co
58.2		515.7	49.2	19.0	^{134}Cs
58.2		529.9	47.6	18.8	^{134}Cs
56.1	560.4				
$CaCl_2$ Side					
0	771.6				
6	748.0				
17.4	695.8	631.8	69.78		
38.7	566.5	525.0	54.85	100.0	^{134}Cs

Column 1: Total composition solid + liquid.
» 2: Temp. of the first crystallization.
» 3: Filtration temperature.
» 4 and 5: Calculated composition of liquid and solid solutions.
» 6: Tracer.

1. As assumed by Menge, there exists a compound of the composition $CaCl_2 \cdot 4$ NaCl, which melts incongruently at 594°C (*cf.* the full lines in the diagram, Fig. 3).

2. No compound exists, but the content of $CaCl_2$ in the solid NaCl increases with decreasing temperature, reaching the maximum value of 20 mole percent at the eutectic temperature (*cf.* the broken line in Fig. 3). In favour of this latter alternative is that we have not yet succeeded in obtaining any X-ray evidence for the existence of a compound. Melts with about 58 mole percent NaCl were slowly cooled, or quenched, in both cases powder patterns showed strong lines of NaCl.

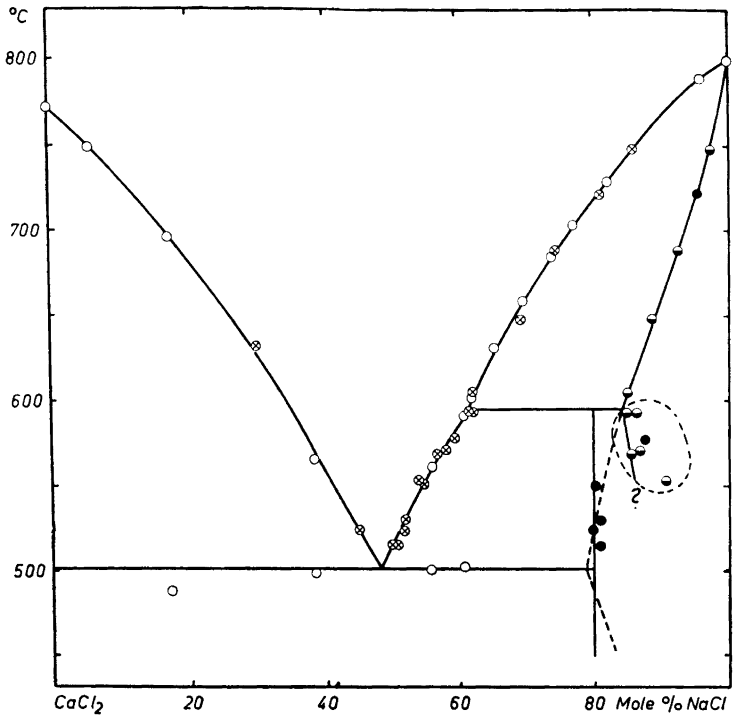

Fig. 3. The system NaCl—$CaCl_2$.

Open circles: Liquidus line determined by thermal analysis.
Crossed » » » » » high-temperature filtration.
Half filled circles: Solidus line determinations with ^{60}Co-tracer.
Filled circles: » » » » ^{134}Cs-tracer.

The data in the composition of the solid phase in the temperature range 500 to 550°C are not incompatible with this interpretation, but they fit better with the assumption of a compound $CaCl_2 \cdot 4\ NaCl$. Two other arguments also favour the existence of this compound. First, the liquidus curve has a weak but definite discontinuity at 594°C (as also observed by Menge). The second argument is the group of obviously erratic points for the solid phase composition in the temperature range 550 to 600°C (inside the circled area in the diagram Fig. 3). These points have been obtained using both CsCl and $CoCl_2$ tracers, and they seem to indicate that in this area it is difficult to attain true equilibrium between solid and liquid. This would be difficult to explain if a continuous range of solid solutions exists down to the eutectic temperature. If on the other hand the compound exists below 594°C, the following explanation seems reasonable. Our filtration technique demands that the system is cooled at least some 50° below the temperature of the first crystallization in order to get an appropriate ratio between the amounts of liquid and solid

compositions. In the range 550 to 600°C it is therefore necessary to start with melts containing more than 62 mole % NaCl, resulting in primary cyrstallization above 594°C. When next the melt is cooled below this temperature, a certain amount or $NaCl-CaCl_2$ solid solution will have to react with the liquid to form the compound before equilibrium is established. This reaction may very well be a slow process. Difficulties of this kind should be absent when the compound is the primary product of crystallization, and this is just what is observed. Starting with mixtures with less than 62 mole percent NaCl, the results for the solid phase composition show very little scattering.

If the existence of the compound is accepted, one will have to explain why it does not appear in the X-ray powder patterns. One reason might be that it is unstable at room temperature. It is evident that the solid solubility decreases strongly with decreasing temperature, (compare Sato and Amano [5]), furthermore the weakness of the break in the liquidus line at the peritectic temperature may indicate that the stability of the compound does not greatly exceed that of the undercooled solid solution. The final answer in this case should be given by high-temperature X-ray examination.

Another possibility is that the compound is stable down to room temperature, but has a crystal lattice very similar to that of NaCl. The solid solution in all probability has a NaCl lattice in which part of the Na^+ ions are replaced by Ca^{++} ions and cation vacancies (eventually forming pairs), distributed at random over the cation sites. The compound might have a similar structure, but with 1/5 of the Na^+ ions replaced by 1/10 Ca^{++} ions and 1/10 cation vacancies in an *ordered* distribution over the cation sites. In this case, X-ray examination at elevated temperatures would not be expected to furnish further evidence.

The question cannot be considered to be finally settled. When we have discussed it in some detail here, one reason is that if the compound formation is real (as we believe) the observations indicate a difficulty in the present method of determining the solidus line which may be expected to occur also in other systems.

STRUCTURAL INTERPRETATIONS

Considerable evidence favours the view that molten salt mixtures can in many cases be considered as ideal or regular mixtures of simple ionic components over certain ranges of composition. The study of phase diagrams may give valuable information about the validity of any chosen model for the structure of the melt, compare the alkali chloride — magnesium chloride systems, where the formation of $MgCl_4^{--}$ complex ions in the molten mixtures is strongly indicated [7]. In the following the system $NaCl-CaCl_2$ is examined from similar points of view.

In a system of coexisting solid and liquid phases, the equilibrium condition for the major component can be expressed by the well-known equation

$$\ln a_{(l)} - \ln a_{(s)} = \frac{\Delta H_m}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

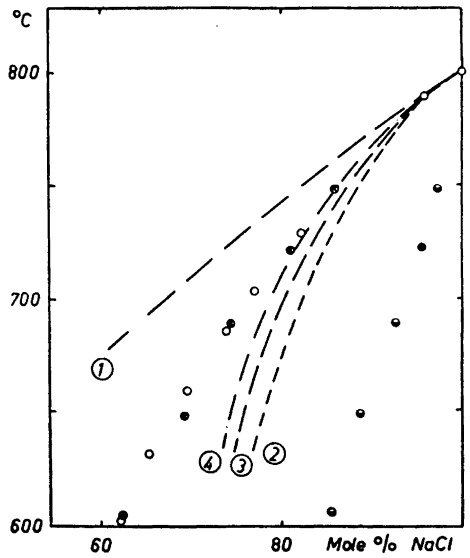

Fig. 4. The NaCl side of the diagram. Experimental data compared with calculated curves.

Here $a_{(l)}$ and $a_{(s)}$ are the activities of the component in the two phases, referring to its pure liquid and its pure solid respectively as standard states, and ΔH_m is the molar heat of melting of the component, considered to be independent of the temperature over the range studied.

a) *The NaCl side.* The molar heat of melting of NaCl is determined calorimetrically by Lyashenko [8] to 6.8 kcal, and by Roth and Berthrand [9] to 7.4 kcal. Careful investigations of the systems NaCl—Na_2SO_4 (Flood, Förland and Leirnes [10]) and NaCl—NaF (Grjotheim [11]), however, are in agreement with 7.1 kcal; this value will be adopted in the following.

We will first examine the possibility that the melt behaves as an ideal Temkin mixture of Na^+, Ca^{++} and C^- lions. This would give

$$a_{NaCl} = N_{Na+} \cdot N_{Cl} = \frac{n_{Na}}{n_{Na} + n_{Ca}} \cdot 1 = \frac{n_{NaCl}}{n_{NaCl} + n_{NaCl_2}} \qquad (1)$$

If, as a first approximation, the correction for the solid solubility is neglected, a calculation according to this model gives curve 1 in Fig. 4. It is evident that the real melt shows strong negative deviations from ideality according to this model, or in other words, the components seem to be more strongly bonded in the melt than corresponding to the ideal Temkin mixture of simple ions.

The second model to be tried is the same as proved valuable in the corresponding magnesium system [6], *viz.*, that tetrachloro complexes are formed in the melt according to the reaction

$$2\ Cl^- + CaCl_2 = CaCl_4^{--}$$

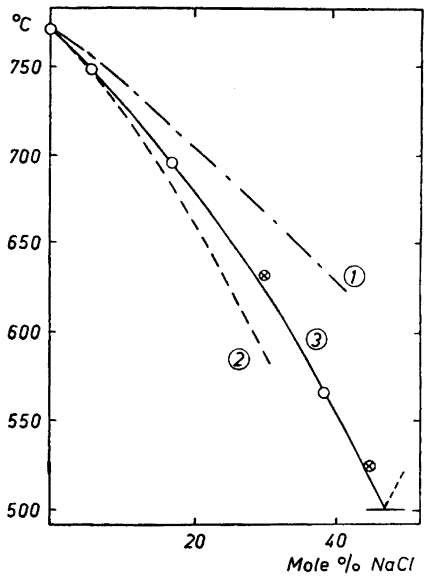

Fig. 5. The $CaCl_2$ side of the diagram. Experimental data compared with calculated curves.

Again assuming ideal Temkin ionic mixture:

$$a_{NaCl} = N_{Na^+} \cdot N_{Cl^-} = \frac{n_{Cl^-}}{n_{Cl^-} + n_{CaCl_4^{--}}} = \frac{n_{NaCl} - 2\, n_{NaCl_2}}{n_{CaCl_2} - n_{CaCl_2}}$$

Neglecting the solid solubility correction, the curve 2 in Fig. 4 is calculated. This curve shows a better agreement with the experimental data, remembering that the correction for the solid solubility will tend to lift the curve and thus bring it closer to the experimental points.

The calculation of the solid solubility correction depends upon the chosen model for the solid solution. Assuming a Temkin ideal solution for the solid (and no complex ions), the calculation gives curve 3 of Fig. 4. The second (more probable) model for the solid is the "equivalent fraction" model, which gives

$$a_{NaCl} = \frac{n_{NaCl}}{n_{NaCl} + 2\, n_{CaCl_2}}$$

The calculation based on this model for the solid and tetrachloro complexes for the liquid is shown as curve 4 in Fig. 4. This curve shows excellent agreement with the observations up to about 20 mole percent $CaCl_2$. The introduction of the "equivalent fraction" is in accordance with present ideas regarding solid solutions, when $CaCl_2$ is introduced in a NaCl lattice it is assumed that two Na^+ ions are exchanged with one Ca^{++} ion and one cation vacancy.

The deviations that occur between calculation and experiment at higher $CaCl_2$ concentrations may be explained either as a negative deviation from ideality in the solid solution or positive deviation in the liquid solution. Since the solid solubility is limited, negative deviations in the solid is improbable. Positive deviations in the liquid, on the other hand, could be explained simply as due to incomplete complex formation at the higher $CaCl_2$ concentrations.

b) *The $CaCl_2$ side.* The curve 1 in Fig. 5 has been calculated on the assumption of a simple Temkin mixture, and shows that this model disagrees with experiment also on the $CaCl_2$ side of the diagram. A formation of tetrachloro complexes could take place according to the following scheme

$$CaCl_2 + 2\ NaCl = CaCl_4^{2-} + 2\ Na^+$$

The corresponding expression for the (ideal) activity of $CaCl_2$ is:

$$a_{CaCl_2} = \left[\frac{n_{Na}}{n_{Ca} + n_{Na}}\right]\left[\frac{n_{Cl}}{n_{Cl} + n_{CaCl_4}}\right]^2 =$$

$$\left[\frac{n_{CaCl_2} - 1/2\, n_{CaCl}}{n_{CaCl_4} + 1/2\, n_{CaCl}}\right]\left[\frac{2\, n_{CaCl_2} - n_{NaCl}}{2\, n_{CaCl_2} - 1/2\, n_{NaCl}}\right]$$

and the result of the calculation is given as curve 2 in Fig. 5. Although this curve is in somewhat better agreement with the experiments than curve 1, the deviations are still considerable at NaCl concentrations above 5 mole percent. It should be noted that this latter model results in a mixture composed of two different anions (Cl^- and $CaCl_4^{2-}$). Theoretical considerations [12] have shown that such mixtures with both mixed cations and mixed anions in general would be expected to show considerably larger deviations from ideality than mixtures with one common ion.

According to the theory, the expression for the activity of $CaCl_2$ should be corrected by an activity coefficient

$$\gamma_{CaCl_2} = \exp\ (N'_{Na} N'_{CaCl_4}\ \Delta G/RT)$$

where the N's are equivalent fractions and ΔG is the free enthalpy change for the reaction

$$CaCl_2 + Na_2(CaCl_4) \rightleftharpoons Ca(CaCl_4) + 2\ NaCl$$

But a calculation along these lines would need support from other evidence before it could be considered to be of more than formal interest. The possibility of a treatment based on an entirely different type of model should be kept in mind, and will be considered in connection with a more extensive study now in progress regarding systems of this type.

It should finally be mentioned that surprisingly good agreement between calculation ad experiment can be obtained over the whole range by assuming the formation of $CaCl_6^{4-}$ complex ions in the melt, see curve 3 of Fig. 5. But it seems difficult to believe in the existence of discrete $CaCl_6^{4-}$ units in such a melt.

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