

Transition Point Depression and its Structural Interpretation in the Binary System Sodium Sulfate-Potassium Sulfate

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The heat content curves of K_2SO_4 and of $NaKSO_4$ have been determined in the temperature range from 25°C to 850°C. The depression of the transition point of sodium sulfate by the addition of potassium sulfate has been determined experimentally. The equilibrium lines of transitions in the phase-diagram of the binary system, sodium sulfate-potassium sulfate have been calculated from the heats of transition of these two compounds together with the heat of transition found for $NaKSO_4$.

A consistent treatment of the system is shown to require that in the high temperature solid solution of sodium sulfate with potassium sulfate there is a cation disorder. The second order transition in $NaKSO_4$ is established as an order-disorder transition.

For regions of solid solution high in potassium sulfate the data available indicate that the sodium ions occur in groups, probably consisting of two ions occupying neighbouring cation positions.

The system sodium sulfate-potassium sulfate exhibits a continuous series of solid solutions in a limited temperature range below the liquidus curve. This is shown in the phase diagram in Fig. 1 taken from the work of Nacken¹. For compositions from 50 to 75 mole-% potassium sulfate, the hexagonal (high temperature) structure is preserved below the transition temperature². Several authors observed a thermal effect in this composition range¹⁻⁵. Bredig states that the thermal effect is due to a second order transition, since he found only a change in the axial ratio of the hexagonal crystals on passing the transition point². He further suggests that this transition is due to the excitation of at least one rotational degree of freedom of the sulfate ion in the high temperature range. The possibility of an order-disorder reaction is

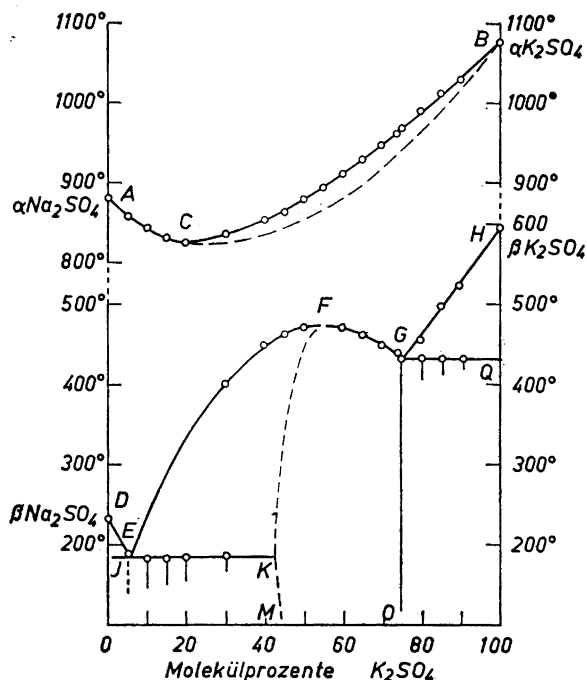


Fig. 1. Phase diagram of the system sodium sulfate-potassium sulfate according to Nacken.

also considered, but is believed to be less likely because of the speed of the transition. An order-disorder reaction is not ruled out by this argument, however. The average diffusion distance necessary to establish the ordered state and the activation energy of diffusion are probably small in this case, so that the reaction should be expected to proceed rapidly. In the following it will be shown that the phase diagram of the system sodium sulfate-potassium sulfate, observed by Nacken^{1,3}, can be interpreted on the basis of an order-disorder transition.

In the high temperature solid solution it is reasonable to assume that the sodium and potassium ions can replace each other on any one of the cation positions, since the solid solution extends across the whole diagram. Just below the transition point the solid solution extends only from about 50 to 75 mole-% potassium sulfate. This indicates that only in one fourth of the cation positions can sodium and potassium ions replace each other. Thus in the low temperature solid solution one-half of the cation positions have become permanent potassium ion positions and one-fourth of the positions are permanently filled with sodium ions. Hence an ordering has taken place.

The crystal structures of NaK₃(SO₄)₂ and Na₂K₂(SO₄)₂ determined at room temperature give additional evidence for this particular ordering. In these structures the cations are distributed over three different kinds of positions.

One kind of cation position takes potassium ions, another takes sodium ions and, finally, the last cation position takes either a sodium or a potassium ion⁶⁻⁸. There are twice as many of the former cation positions as of either of the two others.

Hilmy⁸ investigated the composition of crystals formed from a water solution of sodium and potassium sulfate, and he found that below 35°C the solid solubility range is very narrow and close to the composition $\text{NaK}_3(\text{SO}_4)_2$.

The lines in the phase diagram corresponding to the transition are analogous to the liquidus lines in a binary system with limited solid solution, and the depression of the transition temperature can be treated in the same way as the depression of a freezing point.

On the basis of the structural model outlined above, the change in configurational entropy with the sodium potassium ratio may be calculated in the high temperature and low temperature modifications. With an additional knowledge about the change in heat content by the transition from high to low temperature modification, the equilibrium lines of the phase diagram may be calculated. In the following, equilibrium lines of the phase diagram calculated on the basis of the structural model and calorimetric measurements of heat of transitions, will be compared with experimental points on the equilibrium lines.¹

DEPRESSION OF THE TRANSITION POINT OF SODIUM SULFATE

The depression of the transition point of sodium sulfate by addition of potassium sulfate can, according to classical thermodynamics, be derived briefly as follows:

At the transition point of a solid solution of potassium sulfate in sodium sulfate the partial free energy of sodium sulfate in the high temperature state ($\bar{F}_{\text{Na}_2\text{SO}_4}$) is equal to the free energy of pure sodium sulfate in the low temperature state ($F_{\text{Na}_2\text{SO}_4(\text{low})}$):

$$\bar{F}_{\text{Na}_2\text{SO}_4} = F_{\text{Na}_2\text{SO}_4(\text{low})}$$

Here an eventual small solubility of potassium sulfate in the low temperature phase is disregarded.

We will now choose pure sodium sulfate in the high temperature state as standard state. Referring to this state the above equation can be written:

$$\begin{aligned} \bar{F}_{\text{Na}_2\text{SO}_4} - F_{\text{Na}_2\text{SO}_4(\text{high})} &= \Delta\bar{F}_{\text{Na}_2\text{SO}_4} \\ &= F_{\text{Na}_2\text{SO}_4(\text{low})} - F_{\text{Na}_2\text{SO}_4(\text{high})} = -\Delta F_{\text{tr}} \end{aligned}$$

where $F_{\text{Na}_2\text{SO}_4(\text{high})}$ is the free energy of sodium sulfate in the standard state and ΔF_{tr} is the free energy of transition. Neglecting a minor correction term due to the difference in specific heat of sodium sulfate in the two states, we can introduce

$$\Delta F_{\text{tr}} = \Delta H_{\text{tr}} - T\Delta S_{\text{tr}} = \Delta H_{\text{tr}} \left(1 - \frac{T}{T_{\text{tr}}}\right) = -\Delta\bar{F}_{\text{Na}_2\text{SO}_4}$$

where ΔH_{tr} is the heat of transition, T is the temperature of the equilibrium and T_{tr} is the transition temperature of pure sodium sulfate. If further $\Delta \bar{F}_{\text{Na}_2\text{SO}_4}$ is expressed by the partial entropy $\Delta \bar{S}_{\text{Na}_2\text{SO}_4}$ and the partial heat content $\Delta \bar{H}_{\text{Na}_2\text{SO}_4}$, we finally obtain

$$\Delta \bar{S}_{\text{Na}_2\text{SO}_4} = \Delta H_{\text{tr}} \left(1 - \frac{T}{T_{\text{tr}}} \right) + \frac{\Delta \bar{H}_{\text{Na}_2\text{SO}_4}}{T} \quad (1)$$

Introducing the assumption of complete sodium-potassium disorder in the solid solution, the entropy of mixing due to this disorder can be expressed as

$$\Delta S = -R(n_{\text{Na}} \ln N_{\text{Na}} + n_{\text{K}} \ln N_{\text{K}}) \quad (2)$$

where n_{Na} and n_{K} are the molar amounts of sodium and potassium ions in the mixture and N_{Na} is defined by

$$N_{\text{Na}} = \frac{n_{\text{Na}}}{n_{\text{Na}} + n_{\text{K}}}$$

and N_{K} is defined correspondingly.

Differentiating with respect to n_{Na} , one obtains

$$\frac{\partial \Delta S}{\partial n_{\text{Na}}} = \Delta \bar{S}_{\text{Na}} = -R \ln N_{\text{Na}}$$

and as

$$\frac{\partial \Delta S}{\partial n_{\text{Na}_2\text{SO}_4}} = 2 \frac{\partial \Delta S}{\partial n_{\text{Na}}}$$

one obtains the partial entropy of sodium sulfate

$$\Delta \bar{S}_{\text{Na}_2\text{SO}_4} = -2 R \ln N_{\text{Na}} \quad (3)$$

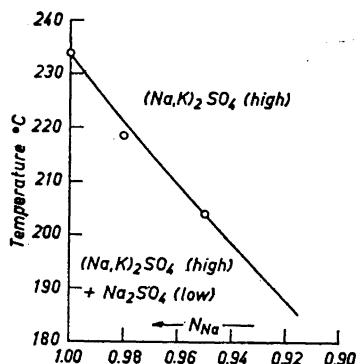
Introducing this into eqn. (1) one obtains

$$-2 R \ln N_{\text{Na}} = \Delta H_{\text{tr}} \left(\frac{1}{T} - \frac{1}{T_{\text{tr}}} \right) + \frac{\Delta \bar{H}_{\text{Na}_2\text{SO}_4}}{T} \quad (4)$$

For mixtures of this kind the partial heat content of a component will generally be proportional to the square of the fraction of the second component. If N_{Na} is close to unity, N_{K}^2 will be small, and $\Delta \bar{H}_{\text{Na}_2\text{SO}_4}/T$ will be small compared to $-2 R \ln N_{\text{Na}}$. The change in partial heat content of sodium sulfate may, therefore, be expected to be insignificant for systems with a high sodium sulfate content.

Calorimetric measurements of the heat content of sodium sulfate by Coughlin⁹ give 1.68 kcal for the heat of transition. The transition temperature is 234°C according to Nacken. The same value was found in the present investigation. Using these data, the transition temperature T of the solid solution

Fig. 2. Transition point depression of sodium sulfate by potassium sulfate. Circles represent observed points. Solid line is calculated.



may be calculated as a function of the composition N_{Na} and a comparison with the experimental data can be done.

No good previous determination of the depression of the transition point of sodium sulfate by addition of potassium sulfate was found in the literature. (One point on the depression curve indicated by Nacken⁷ is more likely to be the eutectic point). Therefore, measurements of the transition point depression were carried out by the present authors.

Experimental

The transition point was determined by ordinary thermal analysis. A sample of approximately 200 g with a Pt-PtRh thermo-couple in the center was cooled at a speed of about 0.1° C/min, and the break in the temperature-time curve was observed. The accuracy of the temperature measurement was of the order $\pm 1^\circ$ C. The results are given in Table 1.

Table 1.

| Mole % Na_2SO_4 in the solid solution in the high temperature phase | Temperature at which transition starts |
|---|---|
| 100 | 234°C |
| 98 | 218°C |
| 95 | 204°C |

On Fig. 2 is shown a plot of the transition temperature, T , as a function of N_{Na} as given by eqn. (4) omitting the term $\Delta\bar{H}_{Na_2SO_4}/T$. The circles represent the observed transition temperature for different compositions. As is seen from the figure, the agreement between calculated and observed values is good. One may conclude that the K^+ ions introduced into the high temperature modification of sodium sulfate are randomly distributed over all positions which are available for the K^+ ions. Further, one may conclude that the partial heat of mixing of sodium sulfate is small in this composition range.

It should be emphasized that the above results do not give information about whether the K^+ ions are randomly distributed over all cation positions

or a fraction of them. Assuming, *e.g.*, that in this concentration range only half of the cation positions can be occupied by K^+ ions, one will have a system where $1/2 (n_K + n_{Na}) - n_K$ moles of Na^+ ions and n_K moles of K^+ ions are distributed over $1/2 (n_K + n_{Na})$ moles of cation positions. If this distribution is random, the entropy of mixing due to this disorder can be expressed by the equation

$$\Delta S = -R \left[1/2 (n_{Na} - n_K) \ln \frac{1/2 (n_{Na} - n_K)}{1/2 (n_{Na} + n_K)} + n_K \ln \frac{n_K}{1/2 (n_{Na} + n_K)} \right] \quad (5)$$

$$\overline{\Delta S}_{Na,SO_4} = -R \ln(1 - 2N_K) \quad (6)$$

Comparing eqns. (3) and (6) one can see that in both cases will the calculated partial entropy of sodium sulfate be approximately equal to $2RN_K$ when N_K is small. Thus, in the concentration range in question it is not possible to determine whether the entropy of the system corresponds to eqn. (3) or to eqn. (6) when only $\overline{\Delta S}_{Na,SO_4}$ is known.

THE DEPRESSION OF THE TRANSITION POINT OF POTASSIUM SULFATE

Analogous to the above treatment, the depression of the transition point of potassium sulfate by additions of sodium sulfate can be expressed by the equation

$$\overline{\Delta S}_{K,SO_4} = \Delta H_{tr} \left(\frac{1}{T} - \frac{1}{T_{tr}} \right) + \frac{\Delta \overline{H}_{K,SO_4}}{T} \quad (7)$$

where $\overline{\Delta S}_{K,SO_4}$ and $\Delta \overline{H}_{K,SO_4}$ are partial entropy and heat content of potassium sulfate in the high temperature modification, and T_{tr} and ΔH_{tr} are the transition temperature and heat of transition of pure potassium sulfate. As for the region high in sodium sulfate, one may assume that also in this concentration region the cations are randomly distributed over all cation positions giving an entropy of mixing

$$\Delta S = -R(n_{Na} \ln N_{Na} + n_K \ln N_K)$$

and

$$\overline{\Delta S}_{K,SO_4} = -2R \ln N_K \quad (8)$$

Introducing this into eqn. (7), one obtains

$$-2R \ln N_K = \Delta H_{tr} \left(\frac{1}{T} - \frac{1}{T_{tr}} \right) + \frac{\Delta \overline{H}_{K,SO_4}}{T} \quad (9)$$

The transition temperature is according to Nacken¹ 595°C, and calorimetric measurements by Shomate and Naylor¹⁰ give 1.94 kcal for the heat of transition of pure potassium sulfate. Assuming that the term $\Delta \overline{H}_{K,SO_4}/T$ is of minor importance, at least for mixtures high in potassium sulfate, one can thus calculate the transition temperature as a function of composition.

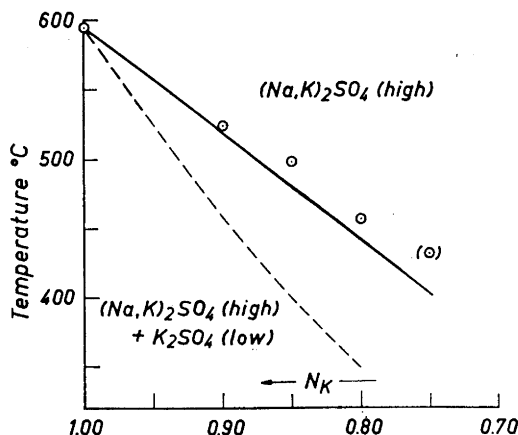


Fig. 3. Transition point depression of potassium sulfate by sodium sulfate. Circles represent points observed by Nacken. Dotted line is calculated assuming independent sodium ions and solid line is calculated assuming sodium pairs.

This is shown on Fig. 3 where the transition temperature is plotted as a function of N_K , giving the dotted line. This calculated line may be compared with the transition temperatures observed by Nacken and given as small circles in the figure. As is seen from the figure, there is a large discrepancy between observed and calculated values.

One will notice that the deviations are very closely proportional to N_{Na} . This indicates that the discrepancy is not due to a change in the partial heat content of potassium sulfate, as this term generally would give a deviation proportional to N_{Na}^2 . The partial entropy of potassium sulfate, on the other hand, would vary approximately proportionally to N_{Na} as $-\ln N_K \approx N_{Na}$ in the concentration range in question. Actually the observed change in transition temperature by addition of sodium sulfate is only one-half of the calculated. This corresponds to a partial entropy of potassium sulfate, only one-half of that expressed by eqn. (8).

The only reasonable interpretation of this is that the Na^+ ions occur in groups probably consisting of two ions. The entropy of mixing for a mixture of K^+ and Na^+ ions where the Na^+ ions occur in groups of two ions occupying neighboring positions can be expressed by the equation (compare Flory¹¹):

$$\Delta S = -R(n_K \ln \frac{n_K}{n_{Na} + n_K} + \frac{n_{Na}}{2} \ln \frac{n_{Na}}{n_{Na} + n_K}) \quad (10)$$

From this the partial entropy of potassium sulfate is:

$$\bar{\Delta S}_{K,SO_4} = -2 R \ln N_K - R(1 - N_K) \quad (11)$$

Introducing this into eqn. (7), the equation for the transition temperature, T , as a function of composition N_K , will be:

$$-2 R \ln N_K - R(1-N_K) = \Delta H_{tr} \left(\frac{1}{T} - \frac{1}{T_{tr}} \right) + \frac{\Delta \bar{H}_{K_2SO_4}}{T} \quad (12)$$

A plot of this function (omitting the term $\Delta \bar{H}_{K_2SO_4}/T$) is shown on Fig. 3 as the solid curve. As can be seen, the agreement between this calculated curve and the observed transition temperatures is good. One may conclude from this that for solid solutions with a high content of potassium sulfate the Na^+ ions occur in groups of two, and these groups are randomly distributed over the positions available for them.

One could also assume that the cation positions themselves occur in groups of two which either can be occupied by two Na^+ ions or two K^+ ions. The entropy of mixing for such a mixture is given by

$$\Delta S = -R \left(\frac{1}{2} n_K \ln \frac{1/2 n_K}{1/2 n_K + 1/2 n_{Na}} + \frac{1}{2} n_{Na} \ln \frac{1/2 n_{Na}}{1/2 n_K + 1/2 n_{Na}} \right) \quad (13)$$

Differentiation gives for the partial entropy of potassium sulfate

$$\Delta \bar{S}_{K_2SO_4} = -R \ln N_K \quad (14)$$

It can be easily shown that this expression for mixtures high in potassium sulfate is almost identical with the previous entropy expression (eqn 11), so that a distinction between the two types of disorder is not possible on the basis of the above data.

The inversion point depression could also be explained by the assumption of groups consisting of 3 Na^+ ions. This model would, however, give a larger difference between observed and calculated inversion point at the lowest content of sodium sulfate. As one should expect the agreement to be better in this region, groups of 3 Na^+ may be considered less probable.

The formation of pairs of Na^+ ions on neighbouring sites in the sodium-potassium sulfate mixture was certainly not expected. The conclusion depends on the applied value of the heat of transition of potassium sulfate (besides on the phase diagram measurements), and thus it could possibly be due to an error in this quantity. For this reason the heat of transition was redetermined.

Experimental

The heat content of potassium sulfate as a function of temperature was obtained with a calorimeter fairly similar to that first used by Oelsen, Rieskamp and Oelsen¹² and later modified by Tashiro¹³. This apparatus is designed to allow a simultaneous recording of the sample temperature and the water temperature of the calorimeter. For details of the experimental technique employed, Tashiro's paper should be consulted. Our calorimeter differed from his mainly in having two more radiation shields around the sample container to decrease the rate of cooling of the sample.

A sample of 65.8 g K_2SO_4 was fused in the sample container, and then kept at a temperature of about 1 000°C before being placed in the calorimeter. During the cooling in

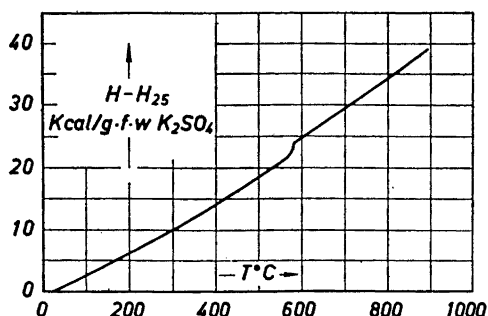


Fig. 4. Experimental heat content curve for K_2SO_4 .

the calorimeter the temperature of the sample was recorded at intervals of about $15^\circ C$. The observed heat content as a function of temperature is shown in Fig. 4. The heat of transition was found to be

$$H_{tr} = 1920 \text{ cal/g.f.w. } K_2SO_4$$

Average specific heat for the following temperature regions are:

$$\begin{aligned} 25 \text{ to } 595^\circ C: \bar{c}_p &= 39.2 \text{ cal/deg.g.f.w.} \\ 595 \text{ to } 850^\circ C: \bar{c}_p &= 48.4 \text{ cal/deg.g.f.w.} \end{aligned}$$

As is seen from the figure, the specific heat of the low temperature modification increases considerably with increasing temperature.

The value for the heat of transition (1.92 kcal) agrees very well with the previous value (1.94 kcal) obtained by Shomate and Naylor, and thus it confirms our conclusion that groups of Na^+ ions are formed in the high temperature modification of potassium sulfate.

DEPRESSION OF THE TRANSITION POINT OF $NaKSO_4$ BY ADDITIONS OF SODIUM SULFATE

Analogous to the two preceding calculations the depression of the transition point of $NaKSO_4$ by additions of sodium sulfate can be expressed by the equation

$$\Delta \bar{S}_{NaKSO_4} = \Delta H_{tr} \left(\frac{1}{T} - \frac{1}{T_{tr}} \right) + \frac{\Delta \bar{H}_{NaKSO_4}}{T} \quad (15)$$

where $\Delta \bar{S}_{NaKSO_4}$ and $\Delta \bar{H}_{NaKSO_4}$ are the partial entropy and the partial heat of mixing of $NaKSO_4$ in a mixture in the high temperature modification, the standard state being pure $NaKSO_4$ in the same modification. T_{tr} and ΔH_{tr} are the transition temperature and the heat of transition of $NaKSO_4$, respectively. The equation is based on the assumption that there is no sodium-

potassium disorder in the low temperature modification of NaKSO_4 . (The phase diagram by Nacken indicates that NaKSO_4 in the low temperature modification can only have a very small amount of excess sodium. It should be noted, as indicated by the dotted curves for this region of the phase diagram shown in Fig. 6, that NaKSO_4 does not have a sharp transition point, but rather a transition region. However, the major change appears (*e.g.*, from the heat content curve) to take place over a fairly short temperature interval so that the expression $\Delta S_{\text{tr}} = \Delta H_{\text{tr}}/T_{\text{tr}}$ may be considered to be a good approximation.)

Assuming a complete sodium potassium disorder in the high temperature modification, the entropy due to this disorder is equal to

$$S = -R(n_{\text{Na}} \ln N_{\text{Na}} + n_{\text{K}} \ln N_{\text{K}})$$

Differentiation with respect to n_{Na} and n_{K} gives:

$$\frac{\partial S}{\partial n_{\text{NaKSO}_4}} = \frac{\partial S}{\partial n_{\text{Na}}} + \frac{\partial S}{\partial n_{\text{K}}} = -R(\ln N_{\text{Na}} + \ln N_{\text{K}})$$

As we have chosen pure NaKSO_4 in the high temperature modification as the standard state, the partial entropy of NaKSO_4 in the mixture referring to this standard state will be:

$$\Delta \bar{S}_{\text{NaKSO}_4} = -R \ln(N_{\text{Na}} N_{\text{K}}) + R \ln 1/4 \quad (16)$$

Introducing (16) into (15) one obtains

$$-R \ln N_{\text{Na}} N_{\text{K}} + R \ln 1/4 = \Delta H_{\text{tr}} \left(\frac{1}{T} - \frac{1}{T_{\text{tr}}} \right) + \frac{\Delta \bar{H}_{\text{NaKSO}_4}}{T} \quad (17)$$

Neglecting a change in the heat of mixing in the concentration range in question, one may thus calculate the transition temperature as a function of composition if the transition temperature and heat of transition of pure NaKSO_4 is known.

From Nacken's measurements the transition temperature is equal to 470°C. No data were available for the heat of transition, however, and a calorimetric determination was, therefore, carried out.

Experimental

The heat content of NaKSO_4 as a function of temperature was determined by the method described in the previous part of this paper. A sample of 63 g NaKSO_4 was made by fusing together equal molar amounts of *pro analysi* potassium and sodium sulfate. The observed heat content curve is given in Fig. 5. The heat of transition was found to be:

$$\Delta H_{\text{tr}} = 1750 \text{ cal/g.f.w. NaKSO}_4$$

at 470°C. The heat of fusion was found to be

$$\Delta H_f = 4650 \text{ cal/g.f.w.}$$

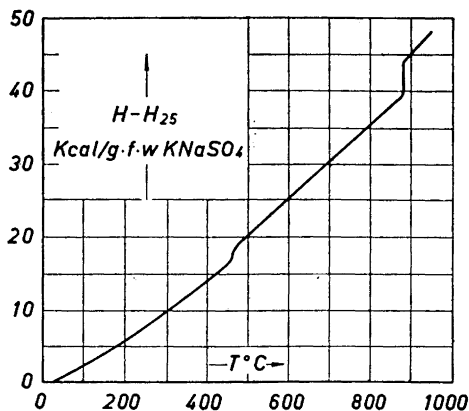


Fig. 5. Experimental heat content curve for NaKSO_4 .

with a fusion point of 884°C . Average specific heats for the following two regions are:

$$25 \text{ to } 450^\circ\text{C} \quad \bar{c}_p = 37.4 \text{ cal/deg.g.f.w.}$$

$$500 \text{ to } 850^\circ\text{C} \quad \bar{c}_p = 50.3 \text{ cal/deg.g.f.w.}$$

The specific heat in the low temperature region increases considerably with the temperature, so that the specific heat just below the transition is not very different from the specific heat above the transition. This speaks against the view that the transition releases new degrees of freedom.

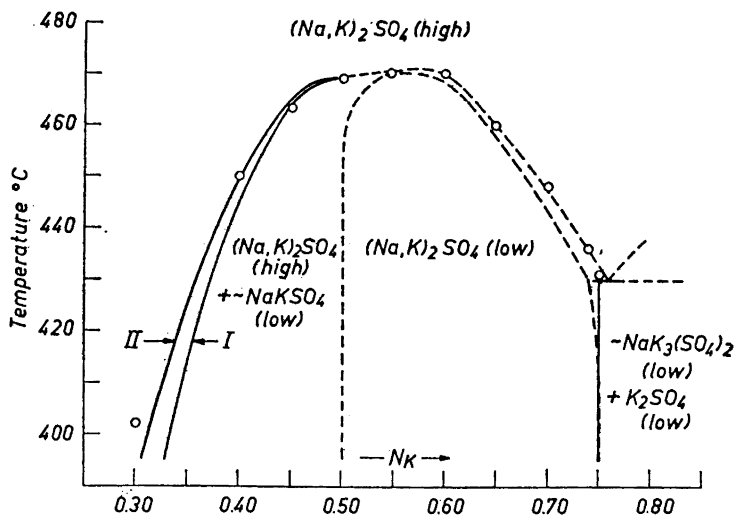


Fig. 6. Part of the phase diagram of the sodium potassium sulfate system in the composition range around the compound NaKSO_4 . Circles represent points observed by Nacken. The solid lines are calculated on the basis of certain models for the structure of the solid solution.

Knowing the heat of transition of NaKSO_4 it is now possible to calculate the transition temperature of mixtures having an excess of Na_2SO_4 , according to eqn (17).

A plot of such a calculation is shown on Fig. 6, curve I. The circles represent the transition temperature observed by Nacken. As can be seen from the figure, the agreement between calculated and observed transition temperature is good. Before concluding that this structural model is therefore the most likely, one should however calculate the partial entropy of NaKSO_4 based on other postulates about the cation disorder in the solid solution.

Previously it was shown that in solid solutions with a high sodium sulfate content the K^+ ions were randomly distributed over certain cation positions. But on the basis of measurements one could not say whether this applied to all cation positions or only a fraction (*e.g.*, $1/2$) of them. Assuming that only half of the positions can be occupied by K^+ ions, the entropy of the solid solution is given by eqn (5). Differentiation gives the following expression for the partial entropy of NaKSO_4 :

$$\Delta\bar{S}_{\text{NaKSO}_4} = -R\ln N_{\text{K}} - R\ln 2$$

This calculated entropy is in distinct disagreement with the experimental results.

The formation of pairs of Na^+ ions may possibly persist for $N_{\text{Na}} > 1/2$. It is, therefore, of interest to calculate the depression of the transition point of NaKSO_4 on this basis. The entropy of mixing for such a system is given by eqn (10). Differentiation gives the following expression for the partial entropy of NaKSO_4 :

$$\Delta\bar{S}_{\text{NaKSO}_4} = -R\ln(N_{\text{K}}\sqrt{N_{\text{Na}}}) - \frac{R}{2}(N_{\text{Na}} - N_{\text{K}}) + R\ln\frac{1}{2}\sqrt{\frac{1}{2}}$$

Substituting this entropy expression into eqn (15) the change in transition temperature for NaKSO_4 as a function of composition can be calculated (omitting the term $\Delta\bar{H}_{\text{NaKSO}_4}/T$). A plot of this function is shown on Fig. 6, curve II. As is seen from the figure, the agreement between the calculated and observed transition temperature is even better than for the previous calculation based on complete $\text{Na}^+ - \text{K}^+$ disorder. However, without more accurate information on the thermodynamic properties of the solid solution, a distinction between the two kinds of disorder cannot be made. However, the possibility that the cation positions as well as the cations occur as pairs may be excluded in this concentration range. According to eqn (13) we have:

$$\Delta S = -1/2 R(n_{\text{K}}\ln N_{\text{K}} + n_{\text{Na}}\ln N_{\text{Na}})$$

Differentiation with respect to the NaKSO_4 content gives

$$\Delta\bar{S}_{\text{NaKSO}_4} = -1/2 R\ln N_{\text{K}}N_{\text{Na}} + 1/2 R\ln 1/4 \quad (18)$$

which gives a transition point depression only half of that experimentally found.

In region $1/2 < N_K < 3/4$ a solid solution exists both in the high and the low temperature state of the mixture. A calculation of the change in transition temperature with composition could be based on an assumption about the disorder in the high temperature state as discussed in the preceding paragraphs combined with a limited disorder over one-quarter of the positions in the low temperature state. Such a calculation would give curves of the type as indicated by the dotted lines on Fig. 6. However, without more experimental data than available now, such calculations would not be of much value. One would have to know the compositions of both the high and low temperature phase in equilibrium. Further, more thermal data should be available, particularly the heat of transition of $K_2Na(SO_4)_2$. Without these data the calculations would contain at least one freely chosen parameter and, thus, an agreement between experiment and calculation could always be obtained.

CONCLUSION

The preceding discussion has shown that consistent values for the structural entropies can be obtained by assuming a random distribution of K^+ ions and a random distribution of pairs of Na^+ ions over all cation positions in the high temperature solid solution. This proves that the second order transition of $NaKSO_4$ is an order-disorder transition.

Acknowledgement. Thanks are expressed to *Norges Teknisk-Naturvitenskapelige Forskningsråd* for financial support.

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Received February 19, 1959.