

Decomposition of NaCl-KCl Mixed Crystals *

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(Z. Naturforsch. 21 a, 165–169 [1966]; received 13 September 1965)

Dedicated to Prof. J. MATTAUCH on his 70th birthday

The decomposition of equimolar NaCl–KCl mixed crystals was studied at different temperatures with calorimetric and capacitance measurements. Comparison with other studies indicates that the decomposition proceeds in three steps. The main heat emission and change of the dielectric constant take place during the second step. The activation energies of the steps are nearly equal.

NaCl and KCl form a complete range of stable mixed crystals only at high temperatures. The solubility gap appears² at about 495 °C with 65 mol % NaCl. At 300 °C KCl will dissolve about 10% NaCl, while NaCl will dissolve only about two per cent of KCl.

The decomposition of the mixed crystals observed in the region of incomplete mutual solubility has been the subject of several studies. EITEL³ and SCHEIL and STADELMAIER⁴ used optical methods to measure the decrease of light transmission in the mixed crystals during their ageing at a constant temperature. HYVÖNEN⁵ used a direct calorimetric method to measure the rate of heat evolution from the mixed crystals during their ageing at close to room temperature.

TICHELAAR⁶ studied the development of birefringence on the surface of a mixed crystal specimen during its decomposition. His results on the speed of the process extend from 150 °C to 441 °C. NURMIA⁷ used an automatic capacitance recorder to study the decomposition in the temperature range of 110 °C to 150 °C.

The object of the present study was to correlate the often conflicting results obtained with the various methods and to obtain a general picture of the decomposition process over a wide temperature range.

1. Calorimetric Measurements

OSTWALD⁸ reported already in 1882 that the heat of solution of a freshly prepared equimolar NaCl–

KCl mixed crystal was 40% less than that of a mechanical mixture. As the mixed crystal was aged at room temperature, its heat of solution was found to approach that of the mechanical mixture.

N. and W. BEKETOFF⁹ repeated these experiments and found that an equimolar NaCl–KCl mixed crystal aged at room temperature for eight months still had a heat of solution 15% less than that of the mechanical mixture.

Because the heat of formation is of the same order of magnitude as the heats of solution of the components (17.5 and 4.2 kJ/mol for KCl and NaCl⁶), a simple calorimeter consisting of a vacuum-jacket glass vessel, a stirrer, and a Beckman thermometer was sufficient for this study. At room temperature NaCl–KCl mixed crystals decompose under the influence of moisture within a few minutes; therefore accuracy had to be sacrificed for speed and simplicity. All the measurements were performed with samples of equimolar composition.

The specimens were prepared by melting together weighed amounts of the components, pouring the melt on a cooled copper plate, and crushing the still hot mass before it was placed in oven for the ageing. At intervals, samples were removed from the oven and cooled on the copper plate. A mass of 10.200 grams of the specimen was then weighed and immediately dissolved in 500 cm³ of water at 24 °C in the calorimeter.

Results of the calorimeter measurements are shown in Fig. 1 and Table 1. The heat of solution is found to increase with time and approach a constant value,

* This research has been supported by the Finnish State Committee for Natural Sciences (G. G.) and the Wihuri Foundation (M. N.).

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which still differs by 0.93 kJ/mol from the heat of solution of the mechanical mixture. Thus the whole heat of formation does not leave the crystal in the decomposition process studied.

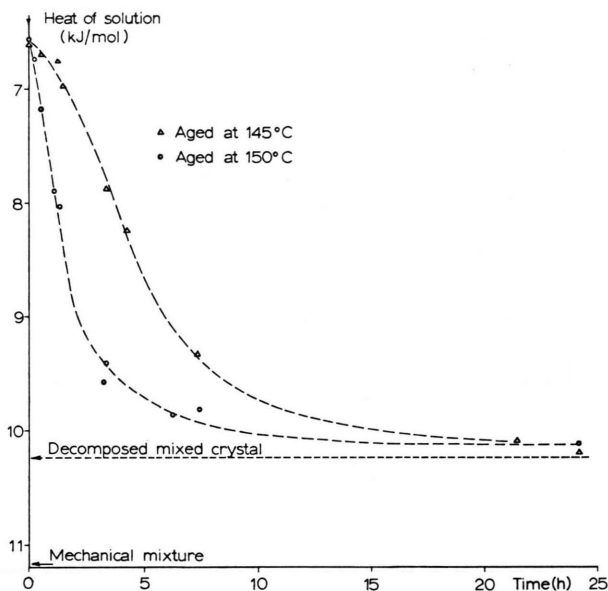


Fig. 1. Decay of the heat of formation of equimolar NaCl-KCl mixed crystals as a function of their ageing time.

Specimen 1		Specimen 2	
Aging time at 145° (h)	Heat of solution (kJ/mol)	Aging time at 150° (h)	Heat of solution (kJ/mol)
0	6.58	0	6.60
0.25	6.74	0.51	6.71
0.55	7.18	1.24	6.75
1.10	7.89	1.47	6.98
1.35	8.03	3.28	7.87
3.25	9.57	4.29	8.23
3.35	9.40	7.35	9.32
6.30	9.85	21.40	10.10
7.45	9.81	24.18	10.20
24.20	10.12		
Specimen 3 (aged several days at 150°)		10.22 kJ/mol	
Equimolar NaCl-KCl mixture (mean)		11.15 kJ/mol	
Heat of formation of unaged mixed crystal (11.15–6.59)		4.56 kJ/mol	

Table 1. Calorimetric studies of the decomposition of equimolar NaCl-KCl mixed crystals.

From the observed heat of solution of an unaged mixed crystal (mean value 6.59 kJ/mol) and that of a mechanical mixture of the components (mean of three measurements 11.15 kJ/mol), a value of 4.56 kJ/mol is obtained for the heat of formation of the mixed crystal. It agrees exactly with the value found by TICHELAAAR⁶ at 25 °C.

2. Capacitance Measurements

The changes in the dielectric constant of the mixed crystals during their decomposition were studied with the apparatus described by NURMIA⁷. The equimolar NaCl-KCl melt was poured directly into the 3 mm wide space between the concentric electrodes of the measuring condenser. After the melt had solidified, the condenser was maintained at constant temperature while a continuous record of its capacitance was obtained by means of a servo system coupled to an electronic recorder.

The recorder had a linear capacitance scale, but for analysis the data were plotted on a semilogarithmic coordinate system as shown in Fig. 2.

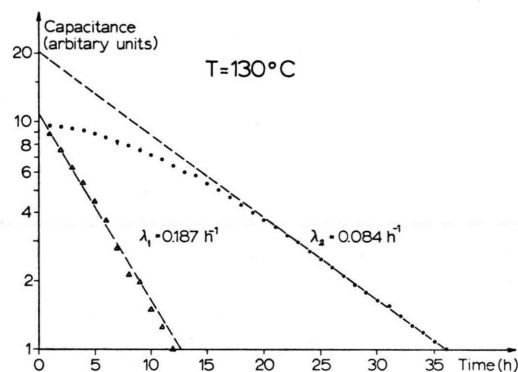


Fig. 2. Analysis of the results of a capacitance measurement.

It is observed that the latter part of the capacitance curve follows an exponential decay law characteristic to simple relaxation processes. However, the beginning of the curve deviates from this law so that the deviation again decays exponentially. Thus, the change of the capacitance of the specimen with time can be presented by a law of the form

$$C = C_2 e^{-\lambda_2 t} - C_1 e^{-\lambda_1 t},$$

where λ_1 and λ_2 are two decay constants as shown in Fig. 2.

A number of measurements were performed at temperatures from 110 °C to 200 °C; the results are given in Table 2.

Both λ_1 and λ_2 are seen to decrease regularly with increasing temperature so that their ratio remains approximately constant. The ratio C_1/C_2 , which determines the initial deviation from the simple exponential law, varied in different measurements from about 0.5, as in Fig. 2, to 0.2. This was possibly caused by differences in the rate of cooling

Temperature °C	Capacitance measurements		Calorimetric measurements	
	$\lambda_1(\text{h}^{-1})$	$\lambda_2(\text{h}^{-1})$	$\lambda_1(\text{h}^{-1})$	$\lambda_2(\text{h}^{-1})$
110	0.069	0.0198		
125	0.19	0.063		
130	0.19	0.084		
135	0.35	0.11		
140	0.55	0.174		
145	0.83	0.19	0.80	0.22
150		0.35	1.1	0.42
160	2.1	0.62		
170	4.2	1.0		
180		1.24		
190		2.17		
200		5.3		

Table 2. Decay constants of the decomposition of equimolar NaCl-KCl mixed crystals.

of the specimen prior to the start of the measurement.

After the processes described above had subsided, a further slow decrease of the capacitance of the measuring system was observed at temperatures above 170 °C. The decay constant of this process was of the order of 0.02 h⁻¹ at 200 °C.

Table 2 also contains values for the decay constants derived from the calorimetric measurements described in the previous section. A comparison indicates that the results of the two methods are in good agreement with each other. Thus it is possible to use the capacitance method, which is non-destructive and produces a continuous record, instead of the calorimetric method in the study of the decomposition process.

3. Measurements of Hyvönen

HYVÖNEN⁵ measured the rate of heat evolution during the ageing of equimolar NaCl-KCl mixed crystals at several temperatures between 25 °C and 50 °C. He postulated the presence of two distinct ageing processes: a fast exponentially decaying effect and a slower, slowly increasing effect. The former had a decay constant of 5·10⁻³ h⁻¹ to 85·10⁻³ h⁻¹ at temperatures from 25 °C to 45 °C, and an energy of activation of 1.1 eV. In addition, violent thermal effects of a much shorter time scale are seen in most of HYVÖNEN's measurements.

However, one of his slowly cooled mixed crystals (No. 4 in Table 7) exhibited an almost steady rate of heat emission at 35 °C and above after the effects caused by the temperature changes had subsided.

This steady emission of heat is now interpreted as the actual decomposition of the mixed crystal, and an estimate of the decay constant of the process is derived in the following way.

We assume that the decrease of the heat of formation, Q , of the mixed crystal follows a simple exponential law:

$$dQ/dt = -\lambda Q.$$

HYVÖNEN did not detect any decomposition in X-ray powder diffraction photographs taken after the calorimetric measurements. Thus the heat of formation cannot have decreased much from its initial value and

$$\lambda = \frac{dQ/dt}{Q_0}$$

Using for Q_0 the value 1000 cal/mol (4.17 kJ/mol) the results given in Table 3 are obtained.

Temperature °C	dQ/dt (mcal/h · mol)	λ (h ⁻¹)
25.12	11.5	1.15 · 10 ⁻⁵
30.19	13.6	1.36 · 10 ⁻⁵
35.19	22.7	2.27 · 10 ⁻⁵
40.18	27.9	2.79 · 10 ⁻⁵
45.07	43.7	4.38 · 10 ⁻⁵
49.80	50.5	5.04 · 10 ⁻⁵

Table 3. Decay constants calculated from HYVÖNEN's measurements. The values given in the second column are averages of two last values of dQ/dt given by HYVÖNEN in Table 7.

The above results are based on the assumption that the decomposition obeys a simple exponential law, i. e. that $C_1 \ll C_2$ (see section 2). Any deviation from this would result in too small values of the decay constant. On the other hand, residual thermal effects of different origin would tend to increase the observed rates of heat emission and yield too large values of the decay constant.

4. Measurements of Tichelaar

TICHELAAR⁶ studied the decomposition of equimolar NaCl-KCl mixed crystals with a polarization microscope by determining the time required for the surface of a mixed crystal to become completely birefringent. In order to compare this results with the present measurements, the decay constant was found from the equation

$$\lambda = 600/(t_1 + t_2),$$

where the t 's are the two values of time, in minutes, given by TICHELAAR for each temperature. The

numerical normalizing factor was chosen so that TICHELAAR's results agree with the present ones in the temperature range of 150 °C to 200 °C.

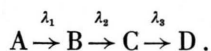
The values found for the decay constant are given in Table 4.

Tem- per- ature °C	<i>t</i> min.	λ h ⁻¹	Tem- per- ature °C	<i>t</i> min.	λ h ⁻¹
150	< 1080	—	318	2.5–3	110
166	260–350	0.98	326	1.5–2.5	150
192	78–93	3.51	335	1.5–2.5	150
203	48–68	5.17	354	1.5–2.5	150
213	32–45	7.80	364	2–3	120
221	21–24	13.3	368	1.5–2.5	150
235	12–14	23.1	376	2–3	120
246	8–9	35	384	4–5	67
250	7–8	40	401	5–6	55
260	6–7	46	404	5–6	55
262	6–7	46	412	10–12	27.3
274	3–4	86	415	10–11	28.5
281	3.5–4.5	75	425	19–20	15.4
294	3.5–4.5	75	434	34–35	8.70
304	2.5–3	110	441	70–90	3.75

Table 4. Decay constants calculated from TICHELAAR's measurements by fitting them with the present results between 150 °C and 200 °C.

5. Details of the Decomposition Process

The above results can be explained by assuming that the process from a homogeneous mixed crystal to a completely decomposed state with zero heat of formation takes place in three steps:



It is suggested that the step $A \rightarrow B$ is nucleation, step $B \rightarrow C$ the decomposition of the mixed crystal into a mosaic of submicroscopic crystallites of nearly pure NaCl and KCl, and step $C \rightarrow D$ the growth of the crystallite size.

If the phases A and B have the same dielectric constant and the same heat of formation, the capacitance and calorimetric measurements pertain almost entirely to the step $B \rightarrow C$ because the next step is much slower. If the initial concentration of phase A is A_0 and no other phases are present initially, we have

$$[A+B] = A_0 \left(\frac{\lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_2 t} - \frac{\lambda_2}{\lambda_1 - \lambda_2} e^{-\lambda_1 t} \right),$$

which is of the same form as the law observed experimentally. Thus $C_1/C_2 = \lambda_2/\lambda_1$ (cf. section 2),

and the initial rate of change of $[A+B]$ is zero. This situation is nearly attained in one of the calorimetric measurements and some of the capacitance measurements (see Figs. 1 and 2), and also in some of HYVÖNEN's specimens, which had a very small rate of long-term heat evolution. However, most mixed crystals seem to contain considerable amounts of nuclei already in the early phases of a measurement, so that their rate of capacitance change or heat evolution does not differ markedly from that predicted by the simple exponential law.

There is satisfactory evidence^{5,6} that phase C is transparent and clear, birefringent, and shows X-ray reflections of the pure components only. Thus the crystallites must have dimensions of the order of 1000 Å in order to cause sharp X-ray reflections and yet be optically invisible. The observed heat of formation of this phase, 0.93 kJ/mol, is of the order of 10^{-3} of the total lattice energy; this is of the magnitude expected of the surface energy of the small crystallites.

The growth of the size of the crystallites, or the step $C \rightarrow D$, will cause the specimen to turn milky. The optical studies of SCHEIL and STADELMAIER⁴ refer to this part of the decomposition process.

The activation energies of the various steps of the decomposition can be determined from the temperature dependence of the appropriate decay constant. Results obtained in this and other investigations are given in Table 5.

Step	Activation energy		Observer
	eV	kJ/mol	
A → B B → C	0.97	94	This study TICHELAAR (at 350°–250 °C)
	0.70	67	
C → D	0.96	92	TICHELAAR (at 250°–160 °C)
	1.09	105	NURMIA
	0.99	95	This study
	0.96	92	SCHEIL and STADEL- MAIER

Table 5. Activation energies of the various steps in the decomposition of NaCl-KCl mixed crystals.

Of these values, only those of TICHELAAR⁶ have been corrected for the change in the energetics of the process with temperature. The constancy of the activation energy indicates that all these processes are based on the same diffusion mechanism.

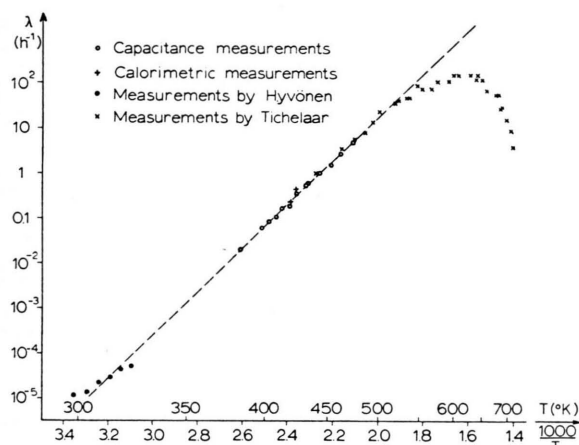


Fig. 3. Decay constant of the main step of the decomposition of equimolar NaCl-KCl mixed crystals at different temperatures.

The values of the decay constant pertaining to the process $B \rightarrow C$ are plotted in Fig. 3 as a function of the inverse of the absolute temperature. It can be observed that the linear relationship between $\log \lambda$ and $1/T$ is maintained over a range of nearly seven orders of magnitude in λ .

The decay constant of the process at room temperature is of the order of 10^{-5} h^{-1} , which corresponds to a "half-life" of about nine years. Thus even a completely nucleated crystal will decompose to an extent of only a few per cent per year at room temperature. This is in agreement with the observations of HYVÖNEN⁵ and TICHELAAR⁶ that the crystals can be kept at room temperature for long periods without detectable decomposition.

Thermolumineszenzspektren dotierter NaCl-Kristalle

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(Z. Naturforsch. 21 a, 169–173 [1966]; eingegangen am 3. Oktober 1965)

Herrn Professor J. MATTAUCH zum 70. Geburtstag gewidmet

Die im Bereich von 180° – 220° C gelegene Thermolumineszenz-Emission des NaCl wird für Ca, Sr, Ba, Cu, Fe, Mn und Cr-dotierte kristalline Proben untersucht. Insgesamt sind die erhaltenen Spektren mit Ausnahme des NaCl : Mn uncharakteristisch für die jeweiligen Aktivatorzusätze. Diese Messungen zeigen eine Analogie zu den Ergebnissen vergleichbarer Untersuchungen an natürlich thermolumineszierenden Flußspatmineralien. Auch hier sind Anzahl und Lage der auftretenden Banden weitgehend unabhängig von der Art der eingeschlossenen Fremdionen.

Untersucht man die spektrale Verteilung der natürlichen Thermolumineszenzemission von Flußspäten verschiedener Fundorte, so ergibt sich eine unerwartet geringe Abhängigkeit der Anzahl und Lage der Banden von den vorhandenen Verunreinigungen. Die hier ablaufenden Rekombinationsprozesse sind wegen der Verschiedenheit der Verunreinigungen nicht zu durchschauen. Eine Reihe von Autoren finden nun in dotierten Alkalihalogeniden eine charakteristische Aktivatorwirkung, die es in manchen Fällen ermöglicht, eine Zuordnung der auftretenden Banden zu bestimmten Aktivatortermen durchzuführen (10^{-3} u. a.). Um die Wirkungen einer

Reihe in Flußspäten vorkommender Ionen auf experimentell einfache Weise zu überprüfen, haben wir die Thermolumineszenz-Spektren entsprechend dotierter NaCl-Kristalle aufgenommen.

Die spektrale Verteilung der Thermolumineszenz-Emission an reinen NaCl-Kristallen untersuchten bereits mehrere Autoren^{4–9}. Über den Einfluß von speziellen Aktivatorzusätzen ist im Falle des NaCl jedoch wenig bekannt. Nur das System NaCl : Cu wurde bisher eingehender studiert.

Wir verwendeten NaCl-Kristalle¹⁰, die in der Schmelze mit 0,1 Mol-Proz. Ca, Sr, Ba, Cu, Fe, Mn und Cr dotiert worden waren. Mit Ausnahme von

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