

Decomposition of Equimolar NaBr-KBr Mixed Crystal

M. AHTEE, O. INKINEN, H. KOSKI, S. PEHKONEN, and P. VIKBERG

Department of Physics, University of Helsinki, Finland

(Z. Naturforsch. **25 a**, 1732–1736 [1970] ; received 3 June 1970)

The decomposition of equimolar NaBr-KBr mixed crystal has been studied within a temperature range of 115 to 251 °C. The measurements were made with an apparatus suitable for continuous recording of the changes in specimen capacitance. The results indicated that the decomposition takes place in three steps. A report is made on the decay constants, half-lives, and activation energies of the first two steps — the nucleation of a freshly prepared specimen, and the subsequent decomposition of the nucleated mixed crystal into components which are nearly pure. It was found that above 150 °C the rate of these processes is affected by a temperature-dependent effect of domain formation. The experimental result for the activation energy associated with the processes, 0.84 ± 0.05 eV, compares favourably with the value derived from a simple diffusion model.

NaCl-KCl solid solution is the only binary alkali halide system with a decomposition process which has been studied previously. Measurements have been made by optical¹, calorimetric², x-ray³, and capacitance⁴ methods. The results of these experiments have been summarized by GRAEFFE and NURMIA⁵, who concluded that the process from a homogeneous mixed crystal to a completely decomposed state with zero heat of formation takes place in three steps: the first of these is nucleation, the second the decomposition of the mixed crystal into a mosaic of submicroscopic crystallites of components which are nearly pure, and the third the growth in crystallite size. The activation energies of the steps were found to be nearly equal.

For further exploration of the decomposition of alkali halide solid solutions, the system NaBr-KBr was chosen for the present study. This solid solution exhibits limited mutual solubility; the critical solution temperature is about 395 °C, with a composition of 65 mole per cent NaBr⁶. Although the decomposition is very slow, both near the critical temperature and at low temperatures, it occurs within a reasonable time interval within the temperature range of 110 to 250 °C. The capacitance method originally proposed by NURMIA⁴ was applied for study of the decomposition process. Automatic recording of the changes of the specimen capacitance, which arise from changes in the dielectric constant

of the mixed crystal during its decomposition, was effected with an electronic apparatus. All the measurements were made with samples of equimolar composition. The result obtained for the activation energy of the transformation processes was compared with the value derived from a simple diffusion model.

1. Apparatus

The apparatus comprises an oven, and an electronic circuit for recording of the specimen-capacitance changes.

The construction of the oven is illustrated in Fig. 1. A quartz tube (A) containing the mixed crystal was placed between the steel plates (B), which served as the electrodes of the specimen capacitor. This capacitor was mounted in a brass cylinder (C), with insulators between B and C. The whole system was introduced into another brass cylinder (D), provided with heating resistors (E). The oven was surrounded with an aluminium box (F), which was insulated with mineral wool (G). The temperature of the specimen was measured with a calibrated copper-constantan thermocouple (T_1). The temperature of the oven was kept constant by a Servotronic controller manufactured by Honeywell (England), with a copper-constantan thermocouple (T_2) as sensor.

The capacitance meter, of which the circuit is shown in Fig. 2, consists of a saw-wave generator (A), an operational amplifier (B), and a recorder. The pulses with an amplitude of 5.8 V, and a frequency of 145 kc/s produced by the saw-wave generator pass through

¹ E. SCHEIL and H. STADELMAIER, Z. Metallkde. **43**, 227 [1952].

² L. J. HYVÖNEN, Soc. Sci. Fenn., Comm. Phys. Math. **16**, No. 15 [1952].

³ G. W. TICHELAAR, Thesis, Delft Institute of Technology, Delft 1956.

⁴ M. J. NURMIA, Ann. Acad. Sci. Fenn. A VI, No. **22** [1959].

⁵ G. GRAEFFE and M. NURMIA, Z. Naturforsch. **21 a**, 165 [1966].

⁶ NGUYEN-BA-CHANH, J. Chim. Phys. **61**, 1428 [1964].



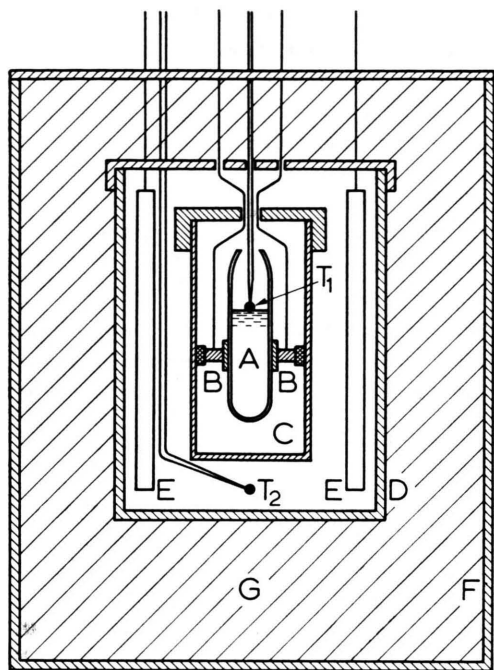


Fig. 1. Construction of the oven used in the capacitance measurements.

the specimen capacitor (C_x) to the operational amplifier. This performs the amplification and rectification of the a. c. signal. It proved that the thermal stability of the whole electronic system was better than $10^{-4}/^{\circ}\text{C}$. The outgoing d. c. signal was fed into a two-pen recorder (Honeywell K 194). One pen indicated the capacitance changes of the oven capacitor, and the other

the temperature of the specimen. The temperature changes in the specimen were found to be less than 0.5°C .

The apparatus was calibrated against a capacitor of capacitance 9.95 ± 0.05 pF. With this capacitance, the output voltage was adjusted to 4.975 V by a proper choice of R_{21} (see Fig. 2). The slope of the calibration straight line was then 500 mV/pF. The differential linearity of the apparatus was also investigated, and it was found that, within the capacitance range covered in the measurements, the deviations from linearity were insignificant.

2. Measurements

The equimolar NaBr-KBr mixed crystals were prepared by melting weighed amounts of "pro analysi" component salts, supplied by E. Merck AG (Darmstadt, Germany), together in a quartz tube at about 750°C . Since the decomposition is quickest at about 200°C , the melt was cooled rapidly with liquid nitrogen. It was found that the dry mixed crystals could be kept at room temperature for several days without detectable decomposition.

After cooling to room temperature, the quartz tube was placed in the oven, and its temperature was raised manually to the value desired. It took about 10–15 minutes to stabilize the temperature. A number of measurements were made at temperatures from 115 to 251°C . The decomposition process was followed till completion. The total length of a run varied from 4 to 72 hours, depending upon the temperature. When the specimens were removed from the oven after a completed run, they were opaque and milky; before disintegration they were transparent and clear.

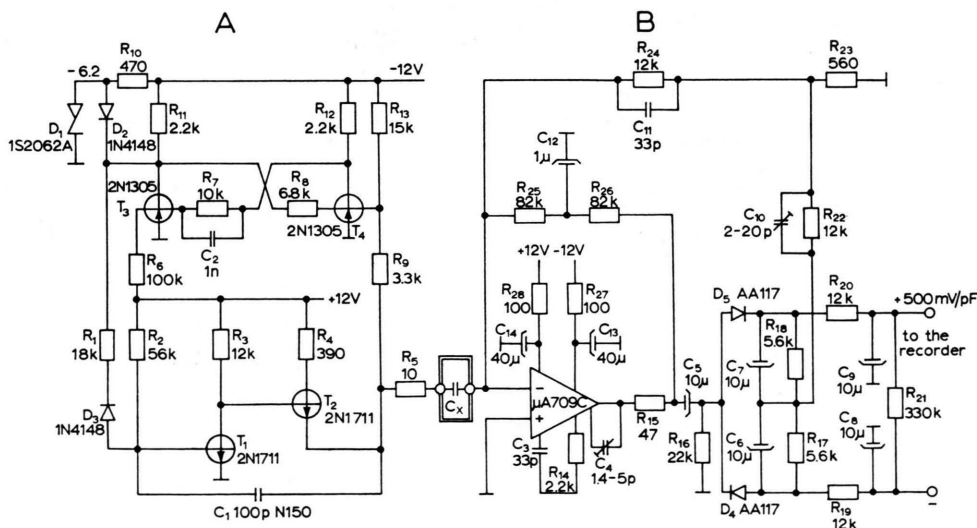


Fig. 2. Circuit of the capacitance meter. A=saw-wave generator, the schema of which is essentially the same as that in the Rochar A 1613 digital multimeter, C_x =oven capacitor, and B=operational amplifier.

3. Results and Discussion

The results of a capacitance measurement at 134 °C are indicated in Fig. 3, where the logarithms of the specimen capacitance are plotted against the ageing time. It is observable that at small values of time the capacitance changes quite slowly. This incubation period is connected with the nucleation of a freshly prepared specimen. Not until the number of nuclei is large enough, the actual decomposition process becomes observable. As seen from the latter part of the curve, the decomposition follows an exponential decay law, whereas at small values of time the curve deviates from this law. However, the deviation again decays exponentially. A further, very slow change in specimen capacitance was re-

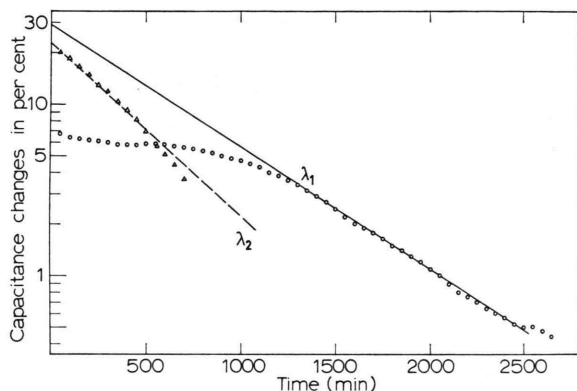


Fig. 3. Analysis of the results of a capacitance measurement at 134 °C. Circles denote the original experimental data plotted on a semilogarithmic coordinate system, whereas triangles stand for the differences between the extrapolated curve (indicated by λ_1) and experimental data.

marked after the two processes indicated in Fig. 3 had subsided, but the data did not permit of a detailed analysis of this process which causes the specimen to turn milky.

The above results indicate, in agreement with the observations made on NaCl-KCl mixed crystals, that the decomposition takes place in three steps. Since it was proved that the first two processes, the nucleation of a freshly prepared specimen, and the subsequent decomposition of the nucleated mixed crystal into components which are nearly pure, follow an exponential decay law, the change in specimen capacitance with time can be presented by the equation

$$C(t) - C(\infty) = C_1 \exp\{-\lambda_1 t\} - C_2 \exp\{-\lambda_2 t\}.$$

Here, λ_1 and λ_2 are the decay constants of the decomposition and nucleation processes, respectively (see Fig. 3). The half-lives of the processes can be calculated from the well-known equation

$$t_{1/2} = \ln 2 / \lambda. \quad (1)$$

The observed values of λ and $t_{1/2}$ pertaining to nucleation and decomposition processes have been compiled in Table 1.

The rate of a transformation process of a mixed crystal can be represented by an equation of the form⁷

$$v = F(T, x) \exp\{-E_a/kT\}, \quad (2)$$

where E_a is the activation energy associated with the process, k Boltzmann's constant, and $F(T, x)$ a function of the absolute temperature T and the composition x of the mixed crystal. If it is assumed

Temperature (°C)	Decomposition		Nucleation	
	$\lambda_1 (\times 10^{-3} \text{ min}^{-1})$	$t_{1/2} (\text{min})$	$\lambda_2 (\times 10^{-3} \text{ min}^{-1})$	$t_{1/2} (\text{min})$
115	0.578 ± 0.024	1200 ± 50	0.603 ± 0.024	1150 ± 50
134	1.92 ± 0.09	359 ± 20	2.09 ± 0.09	332 ± 20
148	5.42 ± 0.40	128 ± 10	5.71 ± 0.40	121 ± 10
155	7.72 ± 0.58	90 ± 7	8.04 ± 0.58	86 ± 7
167	11.9 ± 0.7	58 ± 4	12.4 ± 0.7	56 ± 4
178	15.9 ± 0.8	43 ± 3	17.0 ± 0.8	41 ± 3
187	22.2 ± 1.1	31 ± 2	23.2 ± 1.1	30 ± 2
196	34.7 ± 3.2	20 ± 2	36.3 ± 3.2	19 ± 2
208	41.3 ± 4.8	17 ± 2	43.8 ± 4.8	16 ± 2
218	44.7 ± 5.1	16 ± 2	45.3 ± 5.1	15 ± 2
227	30.2 ± 2.5	23 ± 2	31.0 ± 2.5	22 ± 2
251	22.7 ± 1.1	30 ± 2	23.9 ± 1.1	29 ± 2

Table 1. Decay constants λ and half-lives $t_{1/2}$ of the decomposition and nucleation processes of equimolar NaBr-KBr mixed crystal at various temperatures.

⁷ S. GLASSTONE, K. LAIDLER, and H. EYRING, *The Theory of Rate Processes*, McGraw-Hill Book Co., New York 1941.

that the energy and concentration differences between the initial and final states are not dependent upon temperature, function $F(T, x)$ can be regarded as a constant for a given composition. Since v is proportional to λ , there is obtained from Eqs. (1) and (2) the relation

$$\ln t_{1/2} = B + (E_a/kT), \quad (3)$$

where B is a constant. Thus the logarithm of the half-life will depend linearly upon $1/T$.

According to the solubility curve measured by NGUYEN-BA-CHANH⁶, the equilibrium phases of NaBr-KBr solid solution have almost constant compositions within the temperature range of 110 to 170 °C, containing about 3 and 98 mole per cent NaBr, respectively. However, at higher temperatures the equilibrium concentrations vary more appreciably. For example, at 250 °C the equilibrium phases contain 10 and 95 mole per cent NaBr. This means that the function $F(T, x)$ is no longer constant. BECKER⁸ has presented a theory for the domain formation, according to which this function is expressed as

$$F(T, x) = K \exp\{-A/kT\}, \quad (4)$$

where K is a constant, and A the domain-formation energy, which depends upon temperature for a given composition. By combination of Eqs. (2) and (4), there is derived the formula

$$v = K \exp\{-(A + E_a)/kT\}. \quad (5)$$

The logarithms of the observed half-lives of the nucleation and decomposition processes have been plotted against $1000/T$ in Fig. 4. It is observable

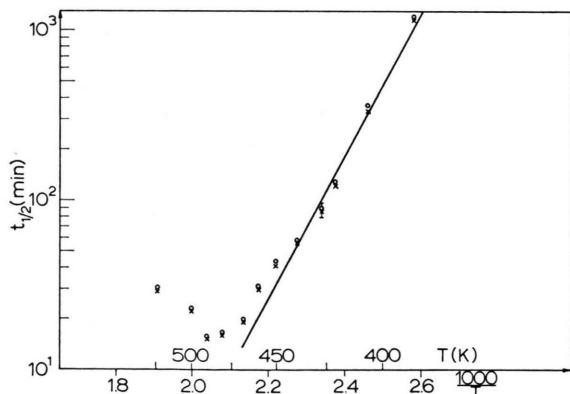


Fig. 4. Dependence of the logarithm of the half-life, $\ln t_{1/2}$, upon $1000/T$, where T is the absolute temperature. Circles and crosses indicate the results for the decomposition and nucleation processes, respectively.

that within the temperature interval from 390 to about 440 K, a linear relationship exists between $\ln t_{1/2}$ and $1000/T$, whereas clear deviations from linearity appear above 440 K. This indicates that the domains are so small below 440 K that the energy required for their formation is negligible as compared with E_a , and Eq. (3) is valid. From the slope of the straight line in Fig. 4, the activation energy of both the nucleation and decomposition processes was determined as 0.84 ± 0.05 eV. The constancy of the activation energy indicates that the processes are based upon the same diffusion mechanism. At higher temperatures, A increases by reason of the increasing size of domain. For the domain-formation energy, Eqs. (3) and (5) lead to the formula

$$A = kT \ln(t_{1/2}/t'_{1/2}),$$

where $t'_{1/2}$ is the half-life corresponding to the straight line in Fig. 4, and $t_{1/2}$ denotes the experimental result. Fig. 5 presents the values of A as a function of temperature.

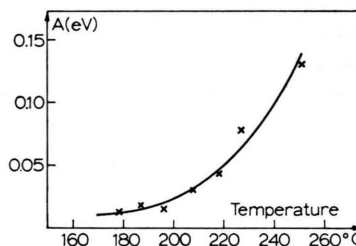


Fig. 5. Dependence of the domain-formation energy, A , upon the temperature.

Finally, the experimental result for the activation energy of the decomposition of random equimolar NaBr-KBr solid solution will be compared with the value derived from a simple diffusion model. If the final state contains only pure components, the decomposition process can be regarded as the diffusion of Na^+ in KBr and K^+ in NaBr. In addition to the energy for motion of a substitutional impurity ion into a vacancy, the energy required for the impurity ion to place itself at the vacancy (energy of solution) must be taken into account. The following expression will be adopted for the activation energy:

$$E_a = \frac{1}{2} [(E_{m1} + E_{s1}) + (E_{m2} + E_{s2})]. \quad (6)$$

Here, E_{mi} and E_{si} ($i = 1, 2$) denote the energies of motion and solution for Na^+ in KBr and K^+ in NaBr, respectively.

⁸ R. BECKER, Ann. Physik **32**, 128 [1938].

For the energy of motion of monovalent-impurity diffusion, MULLEN⁹ has derived the expression

$$E_m = c k_s \{ [r_I - r_+ + (1 - 1/\sqrt{2}) r_0]^2 - 3(r_I - r_+)^2 \}, \quad (7)$$

where $c = 0.68$ is an empirical constant, $k_s = 2 c_{11} r_0$ the Einstein spring constant for the host ion in the lattice (c_{11} is the elastic constant, and r_0 the nearest-neighbour distance), and r_I , r_+ the ionic radii of the impurity ion and the positive host ion, respectively. With the values reported by MULLEN⁹ for c_{11} and r_0 , and with the ionic radii¹⁰ $r_I = 1.50 \text{ \AA}$, $r_+ = 1.18 \text{ \AA}$, Eq. (7) gives the result $E_{m2} = 1.10 \text{ eV}$. The energy of motion for Na^+ diffusion in KBr cannot be calculated from Eq. (7), as it is not valid when the impurity ion is smaller than the host ion it replaces. According to the calculations of TOSI and DOYAMA¹¹, the energy of motion for K^+ diffusion in NaCl is 1.14 eV , which agrees with the above result for E_{m2} . Consequently, justification exists for replacing the energy of motion for Na^+ diffusion in KBr, E_{m1} , with that for Na^+ diffusion in KCl, which according to TOSI and DOYAMA's¹¹ calculations is 0.42 eV .

The energy of solution is determinable from the heat of formation of solid solution plotted against the composition data. The theory presented by HIETALA¹² states that the composition-dependence of the molar heat of formation of NaBr-KBr solid solution can be expressed by the equation

$$\Delta H = 4 b x(1-x) [1 + d(1-2x)], \quad (8)$$

where b is the heat of formation of a 50 mole per cent solid solution, x the mole fraction of NaBr, and $d = 0.30 (\Delta a/\text{\AA})$, with Δa representing the difference in the lattice constants of the pure components. From Eq. (8) are derived the expressions

$$\begin{aligned} E_{s1} &= \left(\frac{\partial \Delta H}{\partial x} \right)_{x=0} = 4 b (1 + d), \\ E_{s2} &= - \left(\frac{\partial \Delta H}{\partial x} \right)_{x=1} = 4 b (1 - d). \end{aligned} \quad (9)$$

With the values $b = 3720 \text{ J/mol}$ ¹³ and $d = 0.19$, Eqs. (9) give the results $E_{s1} = 0.18 \text{ eV}$ and $E_{s2} = 0.12 \text{ eV}$.

On substitution of the above values of E_m and E_s into Eq. (6), the result $E_a = 0.91 \text{ eV}$ is obtained. The agreement with the experimental value ($0.84 \pm 0.05 \text{ eV}$) can be considered good, as the theory is based on a simple model. For comparative purposes, the activation energy associated with the decomposition of equimolar NaCl-KCl solid solution was calculated from Eq. (6) by use of the energies of motion and solution derived by TOSI and DOYAMA¹¹ for Na^+ in KCl and K^+ in NaCl. The result arrived at, $E_a = 0.96 \text{ eV}$, compares favourably with the experimental value of 0.99 eV determined by GRAEFFE and NURMIA⁵.

Acknowledgement

The financial support of the Finnish Cultural Foundation (M. A.) and of the National Research Council for Sciences (O. I.) is gratefully acknowledged.

⁹ J. MULLEN, Phys. Rev. **143**, 658 [1965].

¹⁰ P. SYSIÖ, Acta Cryst. **B 25**, 2374 [1969].

¹¹ M. P. TOSI and M. DOYAMA, Phys. Rev. **151**, 642 [1966].

¹² J. HIETALA, Ann. Acad. Sci. Fenn. A VI, No. **122** [1963].

¹³ M. W. LISTER and N. F. MEYERS, J. Phys. Chem. **62**, 145 [1958].