die beiden hexagonalen Proben meßbare kubische Strukturanteile besitzen, wo das $\text{ZnS}/(5 \cdot 10^{-4})\text{Cu}/150^\circ\text{C}$ einen etwas größeren kubischen Anteil aufweist als $\text{ZnS}/(5 \cdot 10^{-4})\text{Cu}/350^\circ\text{C}$. Durch das Tempern wird in den mit $(5 \cdot 10^{-4})\text{Cu}$ -dotierten ZnS -Leuchtstoffen das Verhältnis von kubischen zu hexagonalen Strukturanteilen etwas verändert. So zeigen auch Gobrecht et al.⁴, daß die Aktivatorkonzentration einen wesentlichen Einfluß auf die Kristallstruktur der dotierten Zinksulfide hat.

Spektrale Untersuchungen der Thermolumineszenz der $\text{ZnS}/(5 \cdot 10^{-4})\text{Cu}$ -Leuchtstoffe ergeben, daß das Glowlicht beider Proben aus blauer und grüner

Emission zusammengesetzt ist. $\text{ZnS}/(5 \cdot 10^{-4})\text{Cu}/150^\circ\text{C}$ emittiert im wesentlichen blaues Thermolumineszenzlicht. Für das Verhältnis der Intensitäten der blauen Spontanlumineszenz des $\text{ZnS}/(5 \cdot 10^{-4})\text{Cu}/150^\circ\text{C}$ bei der Temperatur des flüssigen Stickstoffs (TfS) und Raumtemperatur (RT) finden wir bei 320 nm-Anregung $I_{\text{TfS}}/I_{\text{RT}} = 1,1$, bei 360 nm-Anregung 1,2. Daraus folgt, daß auch bei den $\text{ZnS}/(5 \cdot 10^{-4})\text{Cu}$ -Leuchtstoffen eine Temperaturlöschung der Lumineszenz die Abnahme der Höhe der Hochtemperatur-Glowmaxima nicht erklären kann.

¹ N. Riehl u. H. Ortmann, Monographie, Verlag Chemie, Weinheim 1957.

² D. Curie, „Luminescence in Crystals“, Methuen, London 1963.

³ L. Mader u. N. Riehl, Z. Phys. **206**, 319 [1967].

⁴ H. Gobrecht, H. Nelkowski u. P. Albrecht, Z. Naturforsch. **16a**, 857 [1961].

Interdiffusion of Silver Ions in Molten Thallous Nitrate

Anders Behn and Carl-Axel Sjöblom

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden.

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The interdiffusion coefficient of silver ions in molten thallous nitrate has been determined with the gravimetric technique. The observed data can be "least-squares" fitted into an Arrhenius equation

$$D_{12} = 1.07 \times 10^{-3} \exp - (4130 \pm 400)/RT$$

where D_{12} is expressed in cm^2s^{-1} , R in calories equivalent⁻¹, and T in degrees K. Friction coefficients r_{AgTl} calculated according to the Klemm¹ model indicate association between the cations, as has been indicated in mixtures of silver nitrate with heavy alkali nitrates also.

The interdiffusion coefficients of silver ions in mixtures of silver nitrate with other nitrates have been measured with different techniques and by different workers as reviewed most recently by Mazzocchin and Schiavon². The agreement between the different sets of data is generally very good, although some differences still seem to exist between the results of different methods: The chronopotentiometric results by Bowcott and Plunkett³ deviate from the rest. This difference might be systematic in nature, as argued by Angell and Tomlinson⁴, who have observed considerable discrepancies in measurements with the chronopotentiometric method in solutions of cadmium in molten cadmium chloride. The results

by Mazzocchin and Schiavon² on the other hand, which are also obtained chronopotentiometrically, agree very well with data from "conventional" methods (i.e. tracer, optical, and gravimetric methods). Since no independent interdiffusion coefficients for silver ions in thallous nitrate are available it was decided to measure them with the gravimetric technique^{5, 6}.

Experimental

Commercially available reagent grade salts were used after drying at 150°C for 50 hours. AgNO_3 was obtained from Riedel de Haen AG, Hannover, BRD, and TlNO_3 from E. Merck AG, Darmstadt, BRD.

The general features of the experimental procedure are described elsewhere⁶. Commercial fritted quartz glass discs (diameter 20 mm, thickness 3.5 mm) were used. The disc was filled with an AgNO_3 – TlNO_3 mixture containing 10 mole% AgNO_3 which was allowed to diffuse out into a pure TlNO_3 melt. The diffusion coefficient determined in this way is the interdiffusion coefficient of Ag^+ -ions in TlNO_3 ⁶. No additional salt flow due to the density difference between the melts inside and outside the disc was detected. The buoyancy of the disc during the diffusion was determined with an electrical balance, Mettler H20EGD, which was connected to a 2-channel potentiometric recorder, Goerz Servogor 2. The temperature of the melts was measured with a Platinel⁷ thermocouple connected to a Zeref temperature reference chamber and the second channel on the recorder. The experiments were performed in an electrical furnace to which a

Reprint requests to Dr. C.-A. Sjöblom, Department of Physics, Chalmers University of Technology, Gothenburg, Sweden.

constant heating current was fed from a voltage stabilizer and a variable transformer. The room temperature was thermostated. In this way the melt temperature could be kept constant to better than 1 °K (the reading accuracy of the recorder). Linear regression performed on a Canola 164P calculator was used in order to calculate the slope of the logarithm of the apparent weight of the cell versus time. An improvement in accuracy and speed in determining the interdiffusion coefficients was obtained in this way.

Results and Discussion

The observed interdiffusion coefficients of silver ions in molten thallous nitrate are plotted in Figure 1. The data can be "least squares" fitted to an Arrhe-

Fig. 1. The interdiffusion coefficient D_{12} of silver ions in molten thallous nitrate. Arrhenius line according to the present work —, according to Mazzocchin and Schiavon² ---. (The value $D=3.05 \text{ cm}^2/\text{s}$ at 321 °C in the present work was obtained twice.)

nus equation in the temperature interval 519–608 °K:

$$D_{12} = 1.07 \times 10^{-3} \exp(-4130 \pm 400)/RT \quad (1)$$

(the stated error is a standard deviation) where D is expressed in $\text{cm}^2 \text{s}^{-1}$, R in cal equiv^{-1} , and T in degrees K. The standard error of estimate⁸ of this equation is about 6%. The corresponding equation by Mazzocchin and Schiavon² is

$$D_{12} = 1.22 \times 10^{-3} \exp(-4470/RT) \quad (2)$$

which is calculated for the temperature interval 490–578 °K [Equations (1) and (2) are plotted in Figure 1]. The temperature ranges do not coincide exactly, but the agreement between the pre-exponential factors and between the activation energies in the two equations is still very good (the difference between the observed data is on the average less than 7%). It may thus be concluded that no systematic differences between the chronopotentiometric technique and the present technique can be observed in the case of silver ion interdiffusion in molten thallous nitrate.

Previous work on silver ion interdiffusion in nitrates of heavy alkali metals (Rb and Cs) give evidence of association between the two different kinds of cations⁶. The same kind of argument, based on the friction-coefficient formalism by Klemm¹ may be applied here⁹. It is found that the friction coefficient $r_{\text{AgTl}} = -3.2 \times 10^8 \text{ joule s cm}^{-2} \text{ mole}^{-1}$ at 250 °C and -2.2×10^8 at 300 °C. As expected, the degree of association decreases when the temperature increases.

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¹ A. Klemm, *Z. Naturforsch.* **15 a**, 173 [1960].

² G.-A. Mazzocchin and G. Schiavon, *J. Electroanal. Chem.* **33**, 229 [1972].

³ J. E. L. Bowcott and B. A. Plunkett, *Electrochim. Acta* **14**, 363 [1969].

⁴ C. A. Angell and J. W. Tomlinson, *Electrochemistry*, Proc. 1st Austral. Conf., Pergamon Press, London 1964, p. 557.

⁵ C.-A. Sjöblom, *Z. Naturforsch.* **20 a**, 1572 [1965].

⁶ D. Andréasson, A. Behn, and C.-A. Sjöblom, *ibid.* **25 a**, 700 [1970].

⁷ Obtained from Engelhard Industries AB, Stockholm, Sweden.

⁸ A. G. Worthing and J. Geffner, *Treatment of Experimental Data*, John Wiley & Sons, Inc., N. Y., 3rd, ed. 1964, p. 273.

⁹ In order to calculate the cation-cation friction coefficient r_{AgTl} one has to assume that the cation-anion coefficients r_{AgNO_3} and r_{TlNO_3} are equal to each other. This is a quite reasonable assumption, as pointed out by C.-A. Sjöblom and A. Behn, *Z. Naturforsch.* **23 a**, 1774 [1968].