Self-diffusion in Molten Zinc Bromide

By **Carl-Axel Sjöblom**

Department of Physics, University of Gothenburg, Sweden

(Z. Naturforschg. **18 a**, 1247—1248 [1963]; eingegangen am 22. November 1963)

The diffusion coefficient of the bromide ion in molten zinc bromide has been measured in the temperature range 415—547 °C. The results can be described by the following equation[1]:

$$D = 0.114 \exp[-(17\,050 \pm 500)/R\,T] .$$

D is expressed in $cm^2\,s^{-1}$, R in $cal \cdot mole^{-1} \cdot degree^{-1}$ and T in degrees Kelvin. A comparison with earlier measurements[2] shows that the activation energies of cation and anion are equal within the experimental error, and that D^- is considerably greater than D^+ in the whole temperature range.

In a previous paper[2], a modification of the capillary method[3, 4] for diffusion measurements, previously used by Djordjevic and Hills[5], has been described. This "D – H method" was tested with measurements of the self-diffusion coefficients of the following ions: The Tl^+-ion and the Cl^--ion in molten TlCl, and the Zn^{2+}-ion in molten $ZnBr_2$. The results have shown that the method had certain advantages in comparison with both the conventional capillary method[4] and the "W-method"[6]. Therefore the investigation has now been completed by measuring the self-diffusion coefficient of the Br^--ion in molten $ZnBr_2$. Only two other divalent halides, $PbCl_2$[7] and $CdCl_2$[8], have been investigated previously.

The experiments were performed in the same way as described earlier[2]. However, the whole sintered Pyrex glass disc was now analysed. This was possible, since the disc always could be filled completely with radioactive salt, without any air bubbles remaining in the upper part of the disc.

The radioactive isotope, ^{82}Br with $T_{1/2} = 35.5$ h, was made by irradiating zinc bromide in the RISÖ reactor at Roskilde, Denmark. After each experiment the specific activities of the samples were measured with a scintillation counter. The small traces of zinc activity were cut away with suitable discrimination.

Temp. (°C)	Time (sec.)	l (cm)	L	P (%)	I/I_0	$D^- \cdot 10^7$ ($cm^2\,s^{-1}$)
415.5	147 980	0.93	1.34	53	0.438	4.85
429.4	87 850	0.86	1.29	56	0.493	5.13
442.1	90 000	1.00	1.35	56	0.508	7.10
460.7	59 130	1.00	1.24	55	0.528	9.22
471.2	43 940	0.89	1.33	56	0.511	11.1
492.0	36 260	0.90	1.32	56	0.480	15.6
505.5	27 590	0.91	1.26	54	0.486	19.4
527.4	20 500	0.88	1.28	54	0.481	25.6
547.5	22 890	0.96	1.33	58	0.454	31.9

Table 1. Experimental results. The self-diffusion coefficient of the bromide ion in molten zinc bromide.

The obtained values of the self-diffusion coefficient of the bromide ion in molten zinc bromide are given in Table 1. The describing Arrhenius equation, obtained with "least squares fitting"[1, 9], $D^- = D_0^- \exp\{-Q^-/R\,T\}$, has the constants

$$D_0^- = 0.114\ cm^2\,s^{-1} ,$$
$$Q^- = 17\,050 \pm 500\ cal/mole \cdot degree.$$

The corresponding constants in the equation describing the behaviour of the zinc ion in molten zinc bromide are[2]

$$D_0^+ = 0.080\ cm^2\,s^{-1} ,$$
$$Q^+ = 16\,900 \pm 990\ cal/mole \cdot degree.$$

Lines corresponding to these two equations are shown in Fig. 1 together with the experimental points. The results show clearly, that the activation energies Q^+ and Q^- are equal within the experimental error. The values of D^- are greater than those of D^+ at corresponding temperatures. This was also found for the divalent salt $PbCl_2$[7], but, in $CdCl_2$ at 585 and 595 °C, Angell and Tomlinson[8] find D^+

---

[1] All stated errors in this paper are standard deviations, obtained according to ref. [9].

[2] C.-A. Sjöblom and A. Lundén, Z. Naturforschg. **18 a**, 942 [1963].

[3] J. S. Anderson and K. Saddington, J. Chem. Soc., Lond. **1949**, Suppl. p. 381.

[4] L. E. Wallin and A. Lundén, Z. Naturforschg. **14 a**, 262 [1959].

[5] S. Djordjevic and G. J. Hills, Trans. Faraday Soc. **56**, 269 [1960].

[6] L. E. Wallin, Z. Naturforschg. **17 a**, 191 and 195 [1962].

[7] G. Perkins, Jr., R. B. Escue, J. F. Lamb, and J. W. Wimberley, J. Phys. Chem. **64**, 1792 [1960].

[8] C. A. Angell and J. W. Tomlinson, Disc. Faraday Soc. **32**, 237 [1961].

[9] A. Hald, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 522, 627 and 649.

to be slightly greater than D^-. Their use of Pyrex glass above its softening temperature, 560 °C, has been criticized[10].

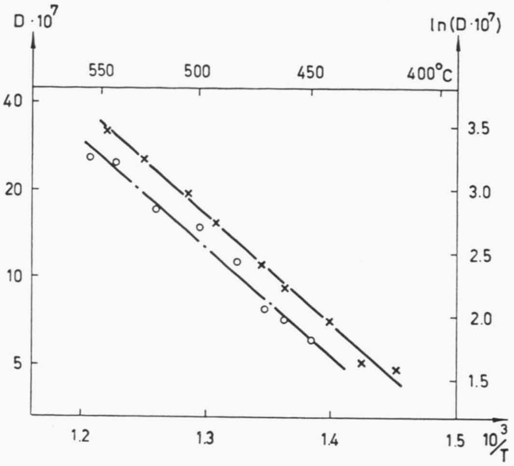

Fig. 1. The self-diffusion coefficients of the cation, D^+, (○), and the anion, D^-, (×), in molten $ZnBr_2$. The lines correspond to the equations quoted in the text.

The reproducibility of the D – H method is considerably improved by the fact that it is not necessary to divide the Pyrex-disc into two halves. It compares well with those obtained in the measurements made by Wallin and Lundén[4] and by Wallin[6] on $ZnBr_2$.

The measurements by Wallin[6] indicate that the "apparent activation energy" in $ZnBr_2$ might be temperature-dependent, and therefore the results of the D – H method are alternatively given in the form[9]

$$\ln(D^+ \cdot 10^7) = (2.54 \pm 0.03) + (27.6 \pm 25.5)(x - 1.30) - (13.9 \pm 9.9)(x^2 - 1.70) \quad (449 - 555\ ^\circ\mathrm{C}),$$

$$\ln(D^- \cdot 10^7) = (2.47 \pm 0.02) - (13.4 \pm 10.7)(x - 1.34) + (1.8 \pm 4.0)(x^2 - 1.79) \quad (415 - 547\ ^\circ\mathrm{C}),$$

where $x = 10^3/T$.

The downward curvature is not as pronounced in the values obtained with the D – H method for D^+ as in the values according to the W-method, and for D^- the curvature is upwards. This difference is easily explained by the extremely big standard deviation in the coefficients of the x- and x^2-terms. The corresponding equation for D^+ according to the W-method is

$$\ln(D^+ \cdot 10^7) = (2.45 \pm 0.02) + (7.47 \pm 6.02)(x - 1.33) - (6.36 \pm 2.24)(x^2 - 1.79) \quad (400 - 564\ ^\circ\mathrm{C}).$$

The estimate of errors shows that there is no statistical support for using a quadratic equation in desribing the results this far obtained for $ZnBr_2$.

The required diffusion times of the D – H method are much shorter than those of other methods. This simplifies the temperature-constancy problems very much and, also, makes it possible to use isotopes with a relatively short half-life, such as ^{82}Br.

With the present measurements of D^- it is now possible to complete the calculation[2, 11] of friction coefficients[12] for $ZnBr_2$. The previous calculation was based on the D^+ obtained by the W-method, but in Table 2 the results obtained by the D – H method are used for both D^+ and D^-.

I wish to express my gratitude to Dr. A. Lundén for encouraging discussions and helpful criticism of my work. It has been supported financially by a grant from "Anslaget för främjande av ograduerade forskares vetenskapliga verksamhet". The regression analysis was made free of charge on the FACIT EDB computer, which is gratefully acknowledged.

	$\zeta=1$ 2 components + = cations – = anions			3 components 1 = cations 2 = lattice 3 = anions		$\zeta_1=1$ lattice complex neutral	$\zeta_i=1$ 4 components 1 = cations 2 = neutral complexes 3 = anions 4 = lattice		
Ions	$\frac{10^{16}}{r_{++}}$	$\frac{10^{16}}{r_{+-}}$	$\frac{10^{16}}{r_{--}}$	$\frac{10^{16}\gamma_1}{r_{12}}$	$\frac{10^{16}\gamma_3}{r_{32}}$	$\left(\frac{t^+}{t^-}\right)_{\text{inner}}$	$\frac{10^{16}\gamma_1}{r_{14}}$	$\frac{10^{16}\gamma_2}{r_{24}}$	$\frac{10^{16}\gamma_3}{r_{34}}$
Zn^{2+}, 2 Br^-	−0.29	0.18	5.04	0.13	0.33	1.09	0.046	0.24	0.17
$ZnBr^+$, Br^-	0.30	0.53	0.46	0.19	0.24	0.80	0.24	0.098	0.29
$ZnBr^+$, $ZnBr_3^-$	0.23	1.06	0.32	0.19	0.24	0.90	0.50	−0.62	0.57

Table 2. Friction coefficients according to different simple models[11]. Temperature = 550° C, $D^+ \cdot 10^{16}/R\,T = 0.380$[2]; $D^- \cdot 10^{16}/R\,T = 0.494$[13]; $\Lambda \cdot 10^{16}/F^2 = 0.529$. Λ = equivalent conductivity, F = Faraday's constant (CGS-units).

---

[10] J. O'M. Bockris, Disc. Faraday Soc. **32**, 266 [1961].

[11] A. Klemm, Z. Naturforschg. **15 a**, 173 [1960].

[12] In Table 4 of ref. [2], for $ZnBr^+ + ZnBr_3^-$, $10^{16}/r_{++}$ should read 0.35 instead of 0.04.

[13] This paper.