Self-diffusion Measurements in Molten Salts

A modified diffusion couple technique

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A new technique has been developed for the determination of self-diffusion coefficients in molten salts. Two chemically identical columns of salt, one of which is radioactive, are allowed to diffuse into each other in a capillary. The diffusion is interrupted by means of freezing from the bottom. Equations are derived for the calculation of the disturbed concentration distribution, assuming that the contraction on freezing causes a Poiseuille flow in the melt above.

Since 1953, when the first determination of a self-diffusion coefficient in a molten salt was reported[1], some ten papers on this subject have been published[2–11] (work on fused silicates and sulphides not included). In general, the open-ended capillary method[12], or a modification of it[9], has been employed. This technique suffers from serious sources of error, mainly due to the difficulty of estimating the appropriate degree of stirring in the outer bath (Δl-effect).

Successful attempts to overcome this difficulty have recently been made for water solutions[13–15]; an application of such techniques in the high temperature field is, however, likely to be somewhat cumbersome.

Another source of error in the conventional capillary method is due to unavoidable fluctuations of temperature, especially at elevated temperatures. The material forced out on expansion is effectively lost in the large bath, and on the following contraction it is replaced by fresh material of zero concentration.

With the diffusion couple[16a] method on the other hand, though not entirely without importance, the temperature fluctuations cause no loss of material. Also convection disturbances can be effectively avoided by suitable choice of experimental conditions. In one case, such a technique has been used for molten salt systems[5a, b]. Here the diffusion process was interrupted before the freezing of the melt. Of course, this is an elegant solution of the problem that the melt is changing volume on solidification, with a considerable disturbance of the concentration distribution as a result. However, very elaborate precautions must be taken in order that the method shall give reliable results. In fact, both authors seem to have abandoned the technique in favour of the open-ended capillary method in one form or another[10, 11].

If the other alternative is chosen, i. e. first freezing the melt and then analysing the solid salt, some kind of correction must be applied to the resulting data. The simplest way to do this is to assume an "ideal contraction", which in this case means that a

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plane, perpendicular to the direction of diffusion, is preserved as a plane and only displaced towards the bottom of the diffusion vessel. Then the necessary correction consists only of a multiplication of measured distances with a constant factor [16b]

$$k = \frac{\varrho_s}{\varrho_l} \cdot \frac{r_s^2}{r_l^2} \simeq \frac{\varrho_s}{\varrho_l}$$

where ϱ and r are density and radius of diffusion sample, and subscripts s and l refer to solid and liquid state, respectively. This method of correction has, to the authors knowledge, not been applied to molten salts, although for molten metals and alloys it has been reported in several papers [17]. Whether the procedure is justifiable or not might perhaps depend on the extent to which the walls of the capillary are wetted by the melt; for zinc bromide, on which the present technique has been tried [18], it is certainly not suitable. Here the freezing results in a "funnel-effect", which produces an intermixing of different layers.

Another possibility would be rapid quenching of the capillary, in the hope that no contraction would have time to occur. However, even if the salt at the walls is instantaneously solidified, the inner part of the melt is most likely to freeze somewhat later, which none the less results in a "funnel-effect".

In the present work, the other extreme is chosen, instead of "instantaneous" quenching: the melt is allowed to freeze slowly from the bottom of the capillary. The liquid above the freezing zone is then slowly flowing downwards in the tube. Assuming a laminar flow with zero velocity at the capillary wall, the concentration distribution after solidification may be calculated if the one before is known. In this way it is possible to calculate corrected values of the diffusion coefficient from data of analysis of the solid salt.

Theory

General. The salt solidifies from the bottom of the diffusion capillary. The solid zone propagates with the velocity v_s. The freezing is connected with a contraction, which causes a downward flow in the melt above. Assuming a POISEUILLE flow in the liquid, the flow velocity is a maximum $(= v_0)$ on the axis of the tube and decreases towards the walls according to the equation

$$v(\eta) = (1 - \eta^2)\, v_0 \,. \qquad (1)$$

Here $v(\eta)$ = velocity at distance r from axis, R = radius of capillary tube, $\eta = r/R$.

An equation of continuity may be stated as follows, counting velocities positive upwards:

$$\int_0^1 [v_s - v(\eta)]\, \varrho_l \cdot 2\,\pi\,\eta\, d\eta = v_s\, \varrho_s\, \pi \,. \qquad (2)$$

ϱ_l and ϱ_s are the densities of liquid and solid salt, respectively. The difference of the cross sections of the glass capillary before and after solidification of the salt is neglected.

From equations (1) and (2) we have

$$v(\eta) = -2(k-1)(1-\eta^2)\, v_s \,, \quad \text{where } k = \varrho_s/\varrho_l \,. \qquad (3)$$

If the diffusion is slow compared to the solidification, we have in the liquid

$$c[z = s, t = s/v_s] = c[z = s - v(\eta)\, s/v_s, t = 0] \equiv c(\eta)\,, \qquad (4)$$

where z is the length coordinate in the direction of the capillary axis, and the abbreviation $c(\eta)$ is introduced for convenience.

In the solid, the mean concentration in the plane $z = s$ is called c_s. If concentrations are expressed in "activity per unit mass", the connection between c_s and $c(\eta)$ is:

$$v_s\, c_s\, \varrho_s\, \pi = \int_0^1 [v_s - v(\eta)]\, c(\eta)\, \varrho_l \cdot 2\,\pi\,\eta\, d\eta \,. \qquad (5)$$

Utilizing (3), we finally have

$$c_s = \frac{2(2k-1)}{k} \int_0^1 \eta\, c(\eta)\, d\eta - \frac{4(k-1)}{k} \int_0^1 \eta^3\, c(\eta)\, d\eta \,. \qquad (6)$$

Application to diffusion. With the initial conditions

$$\left.\begin{matrix} c = 1 & \text{for} & z < a \\ c = 0 & \text{for} & z > a \end{matrix}\right\} t = 0 \qquad (7)$$

the solution of the diffusion equation

$$\partial c/\partial t = D \cdot \partial^2 c/\partial x^2 \qquad (8)$$

may be written:

$$c = \tfrac{1}{2}[1 - \operatorname{erf}\{(z-a)/(2\sqrt{D\,t})\}] \,. \qquad (9)$$

From this follows [cf. (3) and (4)]:

$$c(\eta) = \tfrac{1}{2}[1 - \operatorname{erf}\{f(\eta)\}]\,, \qquad (10)$$

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[17] See e. g.: G. CARERI, A. PAOLETTI and F. L. SALVETTI, Nuovo Cim. (9) **11**, 399 [1954].

[18] L.-E. WALLIN, Z. Naturforschg. **17 a**, 195 [1962].

where

$$f(\eta) = \frac{1}{2\sqrt{D\,t}}\{[1+2(k-1)(1-\eta^2)]\; s-a\}\,. \tag{11}$$

Introducing (10) and (11) into (6), we have after some simplification:

$$c_s = \frac{1}{2} + \frac{2(k-1)}{k} I_1 - \frac{2k-1}{k} I_2 \tag{12}$$

with
$$I_1 = \int_0^1 \eta^3 \operatorname{erf}\{f(\eta)\}\,\mathrm{d}\eta \tag{13}$$

and
$$I_2 = \int_0^1 \eta \operatorname{erf}\{f(\eta)\}\,\mathrm{d}\eta\,. \tag{14}$$

By means of reversing the order of integration, the double integrals (13) and (14) can be transformed into a sum of terms, readily evaluable with the aide of standard tables. Setting

$$f(\eta) = \beta + (\alpha - \beta)\,\eta^2\,, \tag{15}$$

where $\alpha = \frac{1}{2\sqrt{D\,t}}(s-a)$, $\beta = \frac{1}{2\sqrt{D\,t}}[s(2k-1)-a]$ (16)

and
$$\eta = g[f(\eta)] = [A - B\,f(\eta)]^{1/2} \tag{17}$$

where
$$A = \frac{s(2k-1)-a}{2s(k-1)}\,, \qquad B = \frac{\sqrt{D\,t}}{s(k-1)}\,, \tag{18}$$

we have:

$$I_1 = \frac{2}{\sqrt{\pi}}\int_0^\beta\left[e^{-x^2}\int_0^1 \eta^3\,\mathrm{d}\eta\right]\mathrm{d}x + \frac{2}{\sqrt{\pi}}\int_\beta^\alpha\left[e^{-x^2}\int_{g(x)}^1 \eta^3\,\mathrm{d}\eta\right]\mathrm{d}x\,, \tag{19}$$

$$I_2 = \frac{2}{\sqrt{\pi}}\int_0^\beta e^{-x^2}\left[\int_0^1 \eta\,\mathrm{d}\eta\right]\mathrm{d}x + \frac{2}{\sqrt{\pi}}\int_\beta^\alpha\left[e^{-x^2}\int_{g(x)}^1 \eta\,\mathrm{d}\eta\right]\mathrm{d}x\,. \tag{20}$$

Using (17), this gives

$$I_1 = \frac{1}{4}\left[\operatorname{erf}(\alpha) + A^2\frac{2}{\sqrt{\pi}}\int_\alpha^\beta e^{-x^2}\,\mathrm{d}x - 2AB\frac{2}{\sqrt{\pi}}\int_\alpha^\beta x\,e^{-x^2}\,\mathrm{d}x + B^2\frac{2}{\sqrt{\pi}}\int_\alpha^\beta x^2\,e^{-x^2}\,\mathrm{d}x\right], \tag{21}$$

$$I_2 = \frac{1}{2}\left[\operatorname{erf}(\alpha) + A\frac{2}{\sqrt{\pi}}\int_\alpha^\beta e^{-x^2}\,\mathrm{d}x - B\frac{2}{\sqrt{\pi}}\int_\alpha^\beta x\,e^{-x^2}\,\mathrm{d}x\right]. \tag{22}$$

After some lengthy but elementary calculations, we get from (12), utilizing (18), (21) and (22):

$$\begin{aligned} c_s = {} & \tfrac{1}{2}[1-\operatorname{erf}(\alpha)] - \frac{s^2(2k-1)^2-a^2-2Dt}{4s^2k(k-1)}\cdot\tfrac{1}{2}[\operatorname{erf}(\beta)-\operatorname{erf}(\alpha)] \\ & + \frac{(s+a)\sqrt{D\,t}}{4s^2k(k-1)\sqrt{\pi}}\cdot e^{-\alpha^2} - \frac{[s(2k-1)+a]\sqrt{D\,t}}{4s^2k(k-1)\sqrt{\pi}}\cdot e^{-\beta^2}\,. \end{aligned} \tag{23}$$

The first term in (23) represents the concentration at s before freezing; the cause of the other terms is the downward flow. Fig. 1 shows an example of penetration curves 1. before freezing, 2. after "ideal contraction" as defined above, 3. calculated from equation (23); the two latter curves intersect practically at $c = \frac{1}{2}$, $s = a/k$. In order to show more clearly the difference between the curves, they are based on a rather short diffusion time ($\sqrt{D\,t}$ = 0,21 cm). As the diffusion proceeds, curves 2) and 3) will approach each other more and more closely. – The value of a in the example is 5.0 cm.

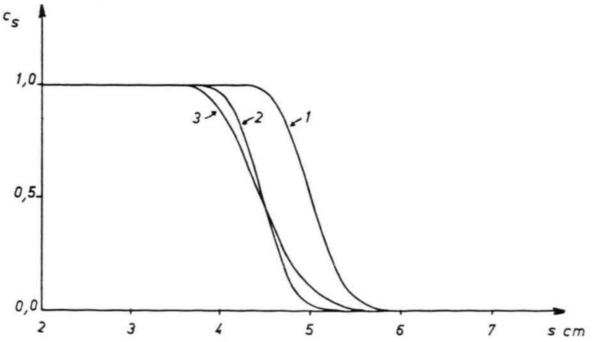

Fig. 1. Concentration distribution 1) before freezing, 2) after "ideal contraction", 3) calculated from equation (23).

In practice, the value of k

$$k = \varrho_s/\varrho_l$$

cannot be used, since the conglomerate of crystals after freezing has a lower mean density than the tabulated value ϱ_s for the solid salt. An experimentally determined value k must therefore be used in the calculations. Though theoretically not quite correct, the k-value, determined as the quotient between the distances from the bottom of the point $c_s = \frac{1}{2}$ before and after freezing, is sufficiently close to the proper one.

In evaluation of diffusion coefficients from experimental data by means of (23), it is suitable to calculate c_s-values for the experimental s-values. A comparison of the calculated and the experimental c-values will give a Δc for each s; the sum $\Sigma(\Delta c)^2$ is a minimum for the value of D, which best fits the data (method of least squares). Thus a few points in a diagram of $\Sigma(\Delta c)^2$ versus D will suffice to give a curve, the minimum of which indicates the "correct" D-value [19] (cf. [20]).

Check with experiments

The possibilities to prove the correctness of the simplifications made for the calculations are of course rather limited, as the true diffusion coefficients are not known, and accordingly not either the real concentration distribution before solidification of the melt. One possible way is to interrupt the diffusion process immediately after it is started. Then the boundary between radioactive and non-radioactive salt is still as sharp as it can be made experimentally. The resulting concentration distribution after freezing is easily calculated with equation (6) as starting-point.

According to (4) we have

$$c(\eta) \equiv c[z = \{1 + 2(k-1)(1-\eta^2)\}\, s, t = 0]. \tag{24}$$

We now define a value η_0 by the equation

$$\{1 + 2(k-1)(1-\eta_0^2)\}\, s = a. \tag{25}$$

With the same initial conditions as before, (7), it is evident that

$$\begin{array}{l} \eta < \eta_0 \Rightarrow z > a \Rightarrow c(\eta) = 0, \\ \eta > \eta_0 \Rightarrow z < a \Rightarrow c(\eta) = 1. \end{array} \tag{26}$$

We can then divide the equation (6) into two parts:

$$c_s = \left[\frac{2(2k-1)}{k}\int_0^{\eta_0} \eta\, c(\eta)\, d\eta - \frac{4(k-1)}{k}\int_0^{\eta_0} \eta^3\, c(\eta)\, d\eta\right] + \left[\frac{2(2k-1)}{k}\int_{\eta_0}^{1} \eta\, c(\eta)\, d\eta - \frac{4(k-1)}{k}\int_{\eta_0}^{1} \eta^3\, c(\eta)\, d\eta\right]. \tag{27}$$

The two terms in the first brackets are zero. We get

$$c_s = (1-\eta_0^2)\,[1 - \eta_0^2 (k-1)/k]. \tag{28}$$

Combination of equations (25) and (28) finally yields:

$$c_s = [a^2 - s^2]/[4\, s^2\, k(k-1)]. \tag{29}$$

Here $$a/(2k-1) \leqq s \leqq a,$$

since always $c_s \leqq 1$ and since $c_s = 0$ for $s \geqq a$.

In general, the agreement between theory and experiment is fairly good. Fig. 2 shows a comparison of experimental points to a curve, calculated by means of (29), for the case where $a = 7$ cm.

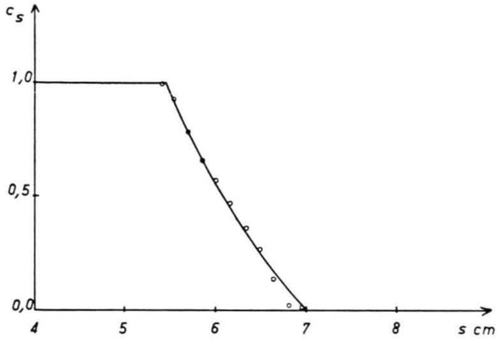

Fig. 2. Disturbance of "sharp" boundary. Solid line: theoretical curve, equation (29); circles: experimental points.

It should be noted that in experiments of this kind, the discontinuity at the top surface will cause a complicated situation in the uppermost part of the capillary; here the deduced equations cannot be expected to hold. More exactly, they will be valid from a point

$$s = L/(2k-1) \tag{30}$$

and downwards; L is the position of the original top surface [cf. eqn. (24)]. It is therefore necessary to have enough salt above the region of interest, so that disturbances of this kind are avoided.

Other applications of equation (6)

Equation (6) should of course in principle be applicable to any original concentration distribution. As measurements of thermal diffusion in molten salts are also made in this institute, it seemed to be of interest to see what happens to a linear distribution in a tube, freezing from the bottom.

Starting with an equation of the form

$$c = a\,z + b \tag{31}$$

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[19] Since these calculations are rather time-consuming, an electronic computer (ALWAC III E) was programmed to deliver directly the best D-value from the experimental data. The programme was made by Mr. GUNNAR HÄGGSTRÖM. Another possibility would have been to have the programme so devised that the machine could make a "two-dimensional" fitting to find both the best k-values and the best D-values.

[20] W. L. KENNEDY, U.S.A.E.C. Research and Development Report, IS-137.

we have, according to (24),

$$c(\eta) = a\,\{1 + 2\,(k-1)\,(1-\eta^2)\}\;s + b\,. \qquad (32)$$

After freezing, eqn. (6) holds. Elementary calculations yield

$$c_{\mathrm{s}} = \left[k + \frac{(k-1)^2}{3\,k}\right] a\,s + b\,, \qquad (33)$$

i. e., the linear relationship should remain linear (except for the top section, as mentioned above). The slope of the line should increase by a factor very nearly equal to k. However, hitherto no attempt has been made to utilize this relationship.

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Zinc Ion Self-diffusion in Molten Zinc Bromide

A re-determination

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The diffusion coefficient of zinc in molten zinc bromide has been re-measured with a new technique over the temperature interval 400 − 565 °C. The result is a downward shift of the values as compared to previous data. Assuming a relation of the form

$$D = D_0 \cdot e^{-Q/RT}$$

the values of the constants are:

$$D_0 = 0{,}405\ \mathrm{cm^2/sec}, \qquad Q = 19\,000\ \mathrm{cal/mole}.$$

In a previous paper [1], a modified diffusion couple method was described for the measurement of self-diffusion coefficients in molten salts. The technique is here used for a re-determination of the zinc ion self-diffusion in zinc bromide. This salt was chosen in order to have a direct comparison with previous data, obtained with the open-ended capillary method in the same laboratory [2].

Experimental

The oven, in which the diffusion runs were carried out, was built of a vertical glass tube with a Kanthal winding (see Fig. 1). This winding was supplied with some extra terminals; shunting parts of it allowed the temperature to be kept constant (or slightly increasing upwards) over a sufficient length in the oven.

The insulation consisted of rockwool, a section of which could be removed temporarily, thus providing a window for observation of the interior. A lamp, placed in the opposite wall, served for illumination. (At the higher temperatures the life-time of this lamp was of course rather short.)

During the runs the diffusion capillaries were placed in holes, drilled in a cylindrical block of aluminium bronze (30% Al). (This is a suitable material, since it combines three important features: it is a good heat conductor, is easily machined and does not scale at high temperatures [3].) Eight such holes were drilled, so that several values of the diffusion constant could be obtained in each run.

A chromel-alumel thermocouple, the hot junction of which was placed close to the oven winding, was fed into an AEG temperature regulator. Five other thermocouples of the same kind were placed at different heights in the wall of the metal block, thus allowing observation of the temperature distribution. The e.m.f. of the central thermocouple was almost compensated through a Leeds and Northrup potentiometer; the small unbalance was fed directly to the galvanometer of a commercial point recorder. The sensitivity thus obtained was 2 °C per scale division, so the temperature fluctuations could be recorded through a complete run. The absolute values of temperature were measured directly with the potentiometer and a mirror galvanometer.

The controlling and recording instruments were kept in a constant temperature box, since the long durations of the runs made it necessary to have uniform conditions

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[1] L.-E. Wallin, Z. Naturforschg. **17 a**, 191 [1962].

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[3] C. L. Thomas and G. Egloff, Temperature, Its Measurement and Control, Ed. American Institute of Physics, Reinhold Publ. Corp., New York 1941, p. 617.