

109. *The Self-diffusion of Lead in Lead Sulphide.*

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Some preliminary measurements of the self-diffusion of the lead ion in lead sulphide have been made between 733° K. and 1043° K., the radioactive isotope Ra-D being used as tracer. A modified technique, particularly suited for the measurement of diffusion coefficients not less than *ca.* 10^{-18} cm.² sec.⁻¹ in compressed powder specimens, is described. Under standardised conditions, the diffusion is represented by $D = 1.4 e^{-42,000/RT}$, but evidence is presented that D depends upon small variations in the stoichiometric Pb : S ratio. The relation between self-diffusion coefficient and the nature and concentration of lattice defects is discussed, and from the relationship between D and the Pb : S ratio, the presence of Schottky defects is inferred.

MEASUREMENTS of the rate of self-diffusion of lead in lead sulphide were undertaken originally in order to obtain data concerning the diffusion process in a typical polar solid built up from bivalent ions. Many experimental studies on reactions in oxide and sulphide systems have been made in recent years, but knowledge of the fundamental processes underlying reaction is still very scanty. One aspect of this problem, to which our attention had been drawn in the course of measurements on the relation between stoichiometric deficiency and semi-conducting properties of stannous and lead sulphides (Anderson and Morton, *Proc. Roy. Soc.*, 1945, *A*, 184, 83; Morton, unpublished), is the readiness with which a crystal lattice can attain thermodynamic equilibrium with respect to lattice defects. Lattice "holes" are necessarily created at the surface, but should ultimately be distributed at random throughout the lattice through the occurrence of self-diffusion.

Lead sulphide appeared to be a very suitable compound for study, since diffusion measurements could be made by the radioactive indicator method. For reasons set out below, however, our measured diffusion coefficients cannot be regarded as true material constants. Nevertheless, the results seem worth setting on record, since they reveal an effect which is not only of interest for the statistical mechanical model of the solid state, but is undoubtedly important in reaction processes between solids at elevated temperatures. This effect arises from that variability in stoichiometric composition which, in principle, is common to all solids of atomic lattice type (cf. Schottky and Wagner, *Z. physikal. Chem.*, 1930, *B*, 11, 163; Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge, 1940, pp. 549—554), and is particularly marked in the case of the heavy-metal sulphides.

Whereas most previous workers on self-diffusion have measured only the decrease in radioactivity at the surface of the specimen, due to the occurrence of diffusion (cf. Hevesy and Seith, *Z. Physik*, 1929, **56**, 790; Seith, *Z. Elektrochem.*, 1933, **39**, 538; Mackay, *Trans. Faraday Soc.*, 1938, **34**, 845), we measured the concentration gradient of the radioactive isotope (Ra-D) directly. We found thereby that the self-diffusion coefficient was not constant with depth. This effect, which can be correlated with minute changes in the stoichiometric composition of the solid, was not recognised until most of the experimental work was complete, although the relation between stoichiometric composition and self-diffusion coefficient should have been foreseen. Previous workers have—permissibly in most cases, no doubt—ignored it. It is evident that the determination of true self-diffusion coefficients in non-stoichiometric solids entails very considerable difficulties.

EXPERIMENTAL.

Lead sulphide was prepared by the direct union of lead (B.D.H. assay quality) with sulphur, purified as described by Bacon and Fanelli (*Ind. Eng. Chem.*, 1942, **34**, 1043). Details of the method are given by Ridge and Anderson (*Trans. Faraday Soc.*, 1943, **39**, 93). Some of the later measurements were made on resublimed lead sulphide.

Radioactive Lead Sulphide.—As no source of Th-B was available, we extracted Ra-D from the active deposit in old glass radon capillaries. The crushed capillaries were leached with 5*N*-nitric acid, and 0.1 g. of pure lead nitrate was added to the solution. The lead was deposited anodically as peroxide and subsequently precipitated as sulphide.

Lead Sulphide Pellets.—For the measurements, the finely powdered (inactive) lead sulphide was compressed into cylindrical pellets, 8 mm. in diam. and 4–7 mm. thick, in a hardened steel die, between plungers ground truly plane and square to the axis. The pellets had a black metallic lustre, and were strong enough to be handled without any loss in weight. The space-filling amounted to 90–95%.

Application of Radioactive Indicator.—For each measurement, one pellet was coated on one end face with a deposit of the radioactive sulphide. This was evaporated in a vacuum (10^{-4} mm.) from a small electrically heated oven, provided with collimating apertures to limit the molecular beam to a small solid angle. The pellet was held in place behind a mica disc, provided with a central hole of diameter just less than that of the pellet. By this means, contamination of the side of the pellet with radioactive sulphide vapour was avoided. Conditions yielding deposits with the optimum initial activity (deposits about 0.4–0.9 μ thick) were found by trial and error. Ra-E sulphide sublimed more readily than Ra-D sulphide, but owing to the short half-life of Ra-E, the initial count of fairly thick deposits soon settled down to a steady value.

Diffusion Measurements.—Two pellets, one of them bearing the radioactive deposit, were clamped tightly, end to end, between graphite discs, in a small steel press. The graphite prevented direct contact between the sulphide and the metal, with consequent reduction at high temperatures. The press was heated in an evacuated silica tube, in an electric furnace fitted with a rough thermostatting device.

Even at the lowest temperature employed, some volatilisation of lead sulphide occurred, and there was some loss of radioactive sulphide from this cause. Photographic investigation of a pellet, sectioned lengthways, showed that a very low concentration of active material had covered the entire outer surface, although in amount too small to affect the counter measurements. Superficial sulphiding of the press was observed, due (as discussed below) to evaporation of sulphur out of the sulphide.

After being heated, the two pellets were separated and embedded in "Perspex" resin, according to the procedure employed for setting metallographic specimens. The end face of the pellet, from which diffusion had occurred, was placed flat upon the base of the mould, so that it was ultimately flush with and parallel to one surface of the "Perspex" disc. The purpose of embedding the pellet was to enable thin parallel cuts to be made from the pellet with ease and precision. It is hardly possible to grind down the face of a pellet (8 mm. diam.) without producing curvature of the surface and obliquity to the axis, but the "Perspex" disc (21 mm. diam.) provides a bearing surface of sufficient size to ensure that the central region remains truly flat. The rear surface was first lapped on coarse carborundum paper until the thickness was uniform to within 0.01 mm. all over, as measured with a micrometer at four marked positions round the cylinder. Between successive radioactive counts, the front surface was lapped down on wet 360-mesh carborundum paper. At each step, two sets of four micrometer readings were made; the average of each set never varied by more than 0.002 mm., and in any one step the deviation from parallelism with the original surface did not exceed 0.005 mm. Any such deviation was corrected at the next step. This procedure enabled the concentration gradient to be measured at several different levels below the original surface, even though the depth of penetration was very small; e.g., in one pellet (No. 14) six steps were measured within 0.064 mm. of the original surface, and the steep fall within the first 0.02 mm. was clearly shown.

Counting Technique.—An argon-alcohol filled Geiger-Müller counter was used, without a scaling circuit; this limited adversely the maximum activity that could be recorded. The thin window of the counter actually admitted only the β -rays from Ra-E, not those of Ra-D; due time was therefore given before measurement, to establish radioactive equilibrium between Ra-D and Ra-E. Counter and pellet were brought always into the same relative positions.

Evaluation of Results.—The arrangement used, in which Ra-D diffused roughly symmetrically from a thin layer into the underlying and superimposed pellets, corresponds to the case of diffusion from a finite source along an infinite cylinder (cf. Barrer, "Diffusion in and through Solids," Cambridge, 1942, p. 45). The particular solution of the Fick equation for this case is

$$c_x = \frac{Q}{\sqrt{\pi Dt}} e^{-x^2/4Dt} \quad \dots \quad (1)$$

where Q = amount of diffusion material originally deposited, c_x = concentration at the distance x from the original surface after the time t , and D = diffusion coefficient.

The measured radioactivity corresponds, not to that of the radioactive material on the exposed surface, but to the integrated effect of β -radiation issuing, subject to the exponential absorption law (coefficient = k), from all depths. If, in a column of unit area, the concentration of radioactive material between x and $(x + dx)$ from the surface be c_x , it contributes an amount proportional to $c_x \cdot e^{-kx} \cdot dx$ to the radioactive count at the surface. Then the total activity A_0 measured at the surface is given by

$$A_0 = \frac{Q}{\sqrt{\pi Dt}} \int_0^{\infty} e^{-(x^2/4Dt + kx)} dx \quad \dots \quad (2)$$

Similarly, if the surface has been lapped down to a depth x_1 below the original level, the new activity is

$$A_{x_1} = \frac{Q}{\sqrt{\pi Dt}} \int_{x_1}^{\infty} e^{-(x^2/4Dt + kx)} dx \quad \dots \quad (3)$$

Changing the variable, writing

$$y = x/\sqrt{4Dt} + k\sqrt{Dt} \dots \dots \dots (4)$$

and integrating between the limits $y = y_0 = k\sqrt{Dt}$ and $y = \infty$, we transform (2) into

$$A_0 = \frac{2Q}{\sqrt{\pi}} e^{k^2Dt} \int_{y_0}^{\infty} e^{-y^2} dy = Q \cdot e^{k^2Dt} (1 - \text{erf } y_0) \dots \dots \dots (5)$$

Similarly for (3),

$$A_{x_1} = Q \cdot e^{k^2Dt} (1 - \text{erf } y_1) \dots \dots \dots (6)$$

Hence

$$A_{x_1}/A_0 = (1 - \text{erf } y_1)/(1 - \text{erf } y_0) \dots \dots \dots (7)$$

As a means of combining measurements, we may notice that $\text{erf } y_0 < 1$, so that if $A_x/A_0 \ll 1$ (as it is for measurements made at any appreciable depth below the original surface), (7) reduces approximately to

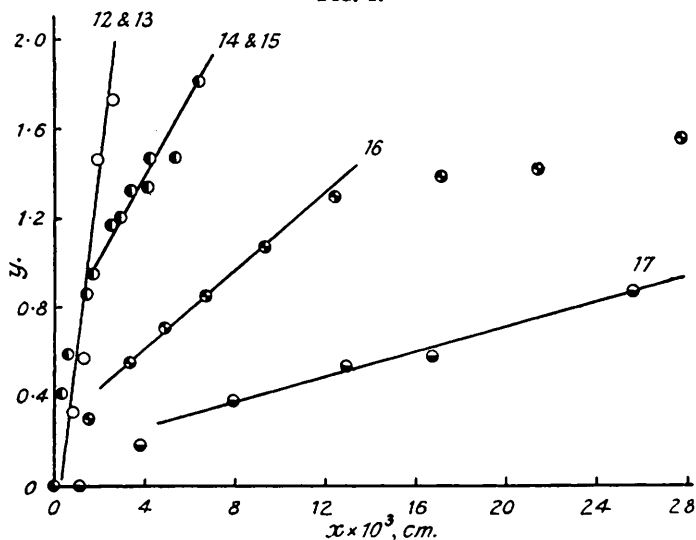
$$\text{erf } y = 1 - A_x/A_0 \dots \dots \dots (8)$$

Values of y obtained from probability tables may be plotted against x ; the resulting graph should be asymptotic to a straight line of slope $1/\sqrt{4Dt}$. Alternatively, for each depth x , the appropriate value of A_x/A_0 may be used to solve (7) by successive approximation.

RESULTS AND DISCUSSION.

The experimental measurements were first treated by the approximate graphical method outlined above, thereby obtaining smoothed values for the diffusion coefficient on the assumption that the error-function

FIG. 1.



distribution of radioactive isotope was valid. Plots of y against x [equation (8)] are given, for the main series of experiments only, in Fig. 1. The following table gives the corresponding values of D

| | | | | |
|--------------------------------------------|-----------------------|-----------------------|-------------------------|----------------------|
| $T^\circ \text{ K.}$ | 733° | 833° | 938° | 1043° |
| $D, \text{ cm.}^2 \text{ sec.}^{-1}$ | 4.3×10^{-13} | 2.2×10^{-11} | $1.3_8 \times 10^{-10}$ | 1.4×10^{-9} |
| Time of diffusion expt., hours | 265 | 97.5 | 71 | 67 |

In Fig. 2, $\log D$ is plotted against the reciprocal of the temperature; the results fall fairly well on the line $D = 1.3_8 e^{-42,000/RT}$. The activation energy of diffusion, 42,000 cal., is comparable with that found for lead in lead chloride and iodide.

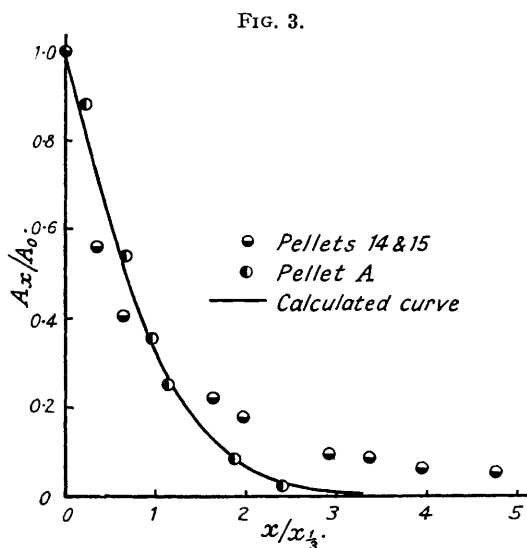
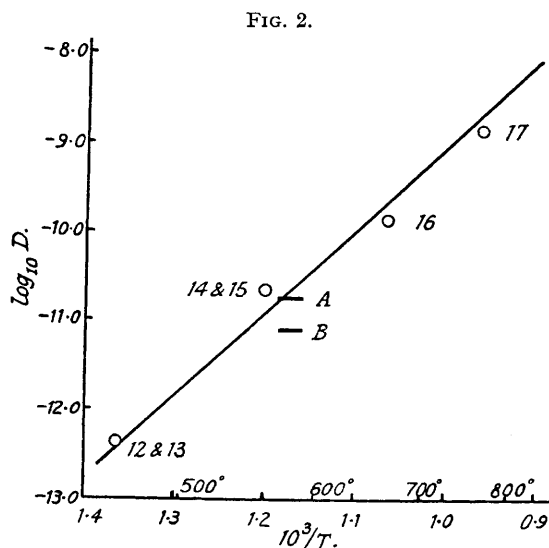
These values for the diffusion coefficient prove to be self-consistent chiefly because they were obtained under standardised experimental conditions. Further analysis shows that they are not true constants of the material.

If the apparent diffusion coefficient corresponding to the radioactive count at each depth be calculated from (7) by successive approximation, the result is less satisfactory: D varies continuously with depth; the radioactive isotope is not distributed according to the error-function law. Using the values of D from the above table, calculation of the ratio A_x/A_0 for various values of x shows how the radioactive count would vary with depth x if the error-function distribution were obeyed. In Fig. 3 such a curve is compared with the experimental data for the 833° K. pellet, the co-ordinate scales being adjusted so that the curves coincide at the two points for which $A_x/A_0 = 1$ and $\frac{1}{3}$ respectively. It may be seen that the apparent diffusion constant must be relatively *too small* close to the original surface, and *too large* at greater depths. The same is true for all the diffusion experiments carried out as described above. For the pellet A, in which diffusion occurred under different conditions (see below), agreement with the error-function curve is better, but deviation occurs in the opposite sense.

These results can be correlated with the possibility of departure from the ideal Pb : S ratio. Lead sulphide, like many of the chalcogenides of the heavy metals, is a "non-stoicheiometric" compound; *i.e.*, the PbS

crystalline phase is stable over a limited range of composition on either side of the ideal Pb : S ratio. There is apparently no recorded evidence that variability of composition has been detected analytically (it is, in any case, unlikely that so familiar a compound has been subjected to critical analysis since analytical technique was adequate to reveal small variations); nevertheless, it is clearly indicated by the semiconducting properties of the compound (cf. Hintenberger, *Z. Physik*, 1942, **119**, 1, whose results have been confirmed by one of our colleagues). Prepared by our method, lead sulphide contains a small stoichiometric excess of sulphur. If the partial pressure of sulphur vapour be kept low (*e.g.*, absorption of sulphur by another metal in the gas space), the excess of sulphur would be progressively lost during heating, and lead sulphide with a stoichiometric excess of lead would ultimately result. This could and did occur under the conditions of our main series of experiments. At the temperatures of the experiments, diffusion was slow, so that a composition gradient, changing with time, must have been set up in the outer portion of each pellet. If the self-diffusion coefficient is dependent on the stoichiometric composition, no true solution of the Fick equation can be found for such ill-defined conditions.

Variation in Self-diffusion Rate with Changes in Stoichiometric Composition.—The general model for diffusion and allied processes in crystals is based on Schottky and Wagner's theory (*loc. cit.*) of "ordered mixed phases." In developing the theory of diffusion, Wagner (*Z. physikal. Chem.*, 1931, Bodenstein Festb., p. 186) stated that the self-diffusion constant must be a function of the composition, but did not elaborate the problem. Our measurements provide the first opportunity to put the matter to a qualitative test.



In thermodynamic equilibrium at temperatures above the absolute zero, a crystal lattice must contain a certain concentration of lattice defects—atoms in interstitial positions, or vacant lattice sites. The process of self-diffusion represents the random migration of these defects through the crystal lattice. The effect of changes in stoichiometric composition may be foreseen by considering the alternative mechanisms discussed by Wagner. We may recognise two cases that can arise.

Case A. The stoichiometric compound AX contains predominantly defects of Frenkel type: with one species of ion (most probably the A cations) in interstitial positions, and vacant sites in the corresponding lattice. This model has been shown to be valid for *e.g.*, silver bromide. If we denote by N_A^i , N_A^* the number of vacant cation sites and interstitial cations respectively, we have in the stoichiometric compound $N_A^i = N_A^*$ (symbols relating to the stoichiometric phase being marked with an asterisk), and we may recognise two partial processes operative in self diffusion: (i) diffusion of ions between adjacent interstitial positions, with activation energy U^i ; (ii) diffusion of cation holes, *i.e.*, the jump of a cation into an adjacent vacant cation site, with activation energy U^h . The corresponding partial self-diffusion coefficients are $D^{i*} = kN_A^i e^{-U^i/kT}$ and $D^{h*} = kN_A^* e^{-U^h/kT}$. The relative importance of these will not be equal, since we may in general expect that $U_A^i \neq U_A^h$. Departure from stoichiometric composition occurs when $N_A^i \neq N_A^*$. For a crystal containing an excess of metal, $N_A^i > N_A^*$, $N_A^h < N_A^*$. If the concentration of defects in the lattice of the stoichiometric compound is small, the number of defects introduced by even a minute change of composition can far outweigh those present in thermal equilibrium; *i.e.*, $N_A^i \gg N_A^*$, $N_A^h \rightarrow 0$. Conversely, for an appreciable excess of non-metal, $N_A^h \gg N_A^*$, $N_A^i \rightarrow 0$. Thus, with increasing departure from ideal composition, one or other component of the diffusion process becomes predominant. At the same time, the partial self-diffusion coefficients change; thus, on the metal-rich side, $D^i = (N_A^i/N_A^*)D^{i*}$; $D^h \rightarrow 0$. The resultant effect of any appreciable change in composition is that the increase in one partial diffusion coefficient more than compensates for the decrease in the other; the net self-diffusion rate must therefore increase with rising

departure from stoichiometry on both sides of the ideal formula, the self-diffusion coefficient being at a minimum at some temperature close to, but not necessarily identical with, the ideal composition. The case is essentially similar to the effect of anomalous solid solution on the ionic conductivity of polar crystals, discussed by Koch and Wagner (*Z. physikal. Chem.*, 1938, B, 38, 295).

Case B. The stoichiometric compound contains defects of Schottky type—vacant sites in both cation and anion lattices, but no interstitial ions. Then $N_A^* = N_X^*$. For self-diffusion of the cations there is then only the one process—migration of vacant sites, with the self-diffusion coefficient $D^{A*} = k'N_A^*e^{-U^*/kT}$. For this type of crystal phase, deviation from stoichiometric composition arises if $N_A^* \neq N_X^*$; increase in the partial pressure of, e.g., the non-metal in equilibrium with the crystal results in building additional X atoms on to the lattice, N_A^* increasing and N_X^* decreasing thereby. It follows that changes in composition must be reflected in a monotonic change in the self-diffusion rate for the cation A; D must increase with increasing excess of non-metal, and diminish asymptotically to zero with increasing excess of metal.

It follows, therefore, that the effect of variability of composition upon self-diffusion rate should be detectable. It remains to be shown that it underlies our own experimental observations. To this end, we sealed up a pair of pellets, prepared for diffusion to occur, in each of two Pyrex tubes; no metal was present, the pellets being pressed into contact by glass-enclosed weights, which filled the tubes except for a dead space of about 5–6 c.c. All pellets were made from a sample of resublimed lead sulphide. The tubes were heated for 52½ hours at $853^\circ \pm 10^\circ \text{K}$. Tube A contained 0.5 mg. of pure sulphur, giving about 60–80 mm. pressure of S_2 vapour during the experiment; tube B was evacuated. In B a minimal change of stoichiometric composition should have occurred during heating, whereas in A the composition gradient should have been the reverse of that set up in the main series, with the sulphur-richest material on the exterior of the pellet. The diffusion constants (D , in $\text{cm}^2 \text{sec}^{-1}$) calculated by the graphical method for these two experiments were: Pellet A, 2.3×10^{-11} ; Pellet B, 7.9×10^{-12} . That of Pellet A is significantly greater, as predicted.

In the following table, the trend of diffusion coefficients is compared with depth in pellet A and in one of the pellets of the main series respectively.

| | | | | | | | | |
|------------------------------------------|----------------------------------|-------------------------------------------------|------|-----|-----|-----|-----|-----|
| <i>Pellet A.</i> Excess of sulphur de- | $\int x, \text{cm.} \times 10^3$ | 0.6 | 1.9 | 2.6 | 3.1 | 5.2 | 6.6 | |
| creasing inwards. | $843 \pm 10^\circ \text{K}$ | $D, \text{cm}^2 \text{sec}^{-1} \times 10^{11}$ | 33.0 | 6.1 | 4.0 | 3.4 | 4.0 | 3.3 |
| <i>Pellet 14.</i> Lead excess decreasing | $\int x, \text{cm.} \times 10^3$ | | 0.3 | 1.7 | 2.9 | 4.1 | 5.3 | 6.4 |
| inwards. | 833°K | $D, \text{cm}^2 \text{sec}^{-1} \times 10^{11}$ | 0.04 | 0.3 | 0.5 | 0.9 | 1.3 | 1.2 |

Note.—Because of the departure from the true error-function law, diffusion coefficients calculated from individual points are not identical with those derived from the graphical method, though of the same order of magnitude.

The self-diffusion coefficient, from these data, appears to vary monotonically with composition. We conclude that lead sulphide contains lattice defects of predominantly Schottky type. The values of D approach asymptotically to a constant value, which may be taken as characteristic of the particular sample of material composing the pellet.

The compressed powder pellets must, necessarily, have possessed a large internal surface. It is therefore relevant to enquire whether bulk diffusion or surface diffusion was observed in these experiments. The occurrence of both bulk and surface diffusion might, in fact, simulate a rise of D with increasing depth below the original surface, as observed in the main series of experiments; † it could not, however, account for the reversal of this trend under conditions where excess sulphur could be incorporated in the crystal lattice (Pellet A). Moreover, it is significant that diffusion assumes a just conveniently measurable magnitude at 460°C ., being 0.53 of the absolute melting point of lead sulphide ($T_m = 1112^\circ \text{C}$). According to Tammann's rule, "Platzwechsel" processes in solids become detectable at $0.52\text{--}0.57T_m$, as indicated by the onset of fritting (Tammann, *Z. anorg. Chem.*, 1926, 157, 321). For lead sulphide, Tammann and Kordes (*ibid.*, 1925, 149, 62) give 470°C . as the fritting temperature. Although any criterion of "perceptible diffusion" is arbitrary, the Tammann rule is in substantial agreement with the temperatures of incipient reactivity of solids (cf. the work of Hedvall and of Hüttig, particularly Hüttig, *Z. Elektrochem.*, 1935, 41, 527; *Angew. Chem.*, 1940, 53, 35; *Kolloid-Z.*, 1942, 98, 6, 263). Tammann (*Z. anorg. Chem.*, 1925, 149, 67) found the reaction temperature of the reaction $\text{PbS} + \text{CdO} \rightarrow \text{PbO} + \text{CdS}$ to be 440°C . Further, the onset of recrystallisation in solids, as shown by Hahn's emanation method (cf. Hahn and Senftner, *Z. physikal. Chem.*, 1934, 170, 191; Schröder and Schmah, *Z. Elektrochem.*, 1942, 48, 248), is at about the same fraction of the absolute melting point. The physical significance of the Tammann rule is that the mean diffusion path shall be sufficiently large to produce sensible effects within some interval of time determined by the type of criterion employed experimentally. For fritting experiments, such as those of Tammann and Kordes, this requires that D shall be of the order $10^{-13} \text{cm}^2 \text{sec}^{-1}$, i.e., about that found by us at the temperature $0.53T_m$. This agreement is evidence that bulk diffusion was actually measured in our experiments.

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† Three experimental points belonging to Pellet 16, which have been neglected in Fig. 1, fall on a second line, indicative of a higher diffusion coefficient, and may perhaps represent a surface diffusion process.