Diffusion of Silver into Glass from a Melt of Silver Nitrate
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Diffusion of silver into Pyrex glass from an AgNO₃ melt was studied with a radioactive tracer technique in the temperature interval 216—354 °C. The results can be described by an Arrhenius' equation

\[ D = A \exp \left( - \frac{E_a}{R T} \right) \]

where \( D \) is the diffusion coefficient, \( A \) is a pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature.

The first quantitative investigations of the diffusion of silver into glass were made by Schulze 1. Since then, several experiments concerning the diffusion of metal ions with different kinds of glass have been reported 2–17. These investigations show that Fick's law experimentally holds when metals diffuse into glass (cf. however, cit. 6). The metal ions of the melt exchange with the sodium ions in the glass, and the rate at which this exchange proceeds is controlled by the diffusion of the ions in the glass 15. The mechanism of ionic transport in glass is not quite understood. Moreover, only very few data concerning the exchange of ions between a salt melt and Pyrex 18 brand glass are available. Since Pyrex glass is very widely used for making diffusion and conductivity cells, where the construction material is supposed to be chemically inert, it was considered valuable to investigate the diffusion of silver into Pyrex glass from a silver nitrate melt as a function of temperature. Since Ag¹⁰ᵐ was readily available, a radioactive tracer technique was chosen for this work.

**Experimental**

The diffusion experiments were performed in a conventional, wire-wound, electrical furnace. The glass was measured with a scintillation counter. The temperature of the melt was kept constant to better than ±1 °C with a temperature controller (West, type Gardsman JP). The glass specimen was immersed for about an hour into a radioactive Ag¹⁰ᵐ melt. After the diffusion, the specific activity of the glass was measured with a scintillation counter. The diffusion takes place by exchange between the Ag⁺-ions of the melt and the Na⁺-ions of the glass, thus the saturation specific activity of the glass can be calculated from the Na₂O concentration of the glass 18 and the specific activity of the melt, which can be measured separately. If the surface area through which the diffusion takes place is known, the diffusion coefficient can be calculated from a suitable solution of the diffusion equation.

The diffusion coefficient is of the order of 10⁻¹² cm² s⁻¹, therefore the surface to volume ratio of the glass specimen must be as big as possible in order to obtain measurable glass activities within a reasonable time. Thus Pyrex glass frits manufactured at our laboratory were used. The fritted discs were sintered from glass powder that had passed through a 100 DIN sieve. The effective radii of the particles ranged from 10 to 40 μm.

Since the total surface area of each frit is unknown, only the temperature dependence of the diffusion coefficient was investigated.

4. O. von KUBASCHENSKI, Z. Elektrochem. 42, 1 [1936].
The diffusion coefficient can be determined with this type of experiment. A quantity proportional to the diffusion coefficient can be calculated, and the proportionality factor is the same for all frits provided that they all have the same structure. To obtain this, all frits were made at the same time and in an identical way. Only frits with a porosity \( \leq 1\% \) from the mean were used.

The proportionality factor mentioned above was determined in a separate experimental series at 255 °C. Experiments were performed both with glass plates and glass cylinders, and with diffusion times ranging from 2 700 to 78 000 seconds. The reproducibility of the results was not as good as in the other series since the glass-melt interfaces in these cases were much smaller.

If the specific activity of the silver in the silver nitrate is known, the diffusion coefficient can be calculated according to the following equation:

\[
D = \frac{(M/2N)^2}{(\pi/\tau)}
\]

where \( M \) is the immigrated amount of silver per cm\(^2\) of glass surface exposed to the melt, \( N \) the saturation concentration of silver in the glass, and \( t \) the diffusion time. \( N \) can be taken as the concentration of sodium ions in the glass. This equation is strictly valid for the linear case only, but it can be used, since \( D \) is of the order of \( 10^{-12} \) cm\(^2\) s\(^{-1}\).

### Results and Discussion

The diffusion coefficient of silver into Pyrex glass from a silver nitrate melt at 255 °C was determined to \((1.95 \pm 0.75) \times 10^{-12} \) cm\(^2\) s\(^{-1}\). \( ^{22} \) No time dependence could be detected. Using this value, the results of the “fritted disc” series could be converted to diffusion coefficients, given in the table. The corresponding Arrhenius’ equation (obtained by a “least squares” fitting) \( ^{23} \) is

\[
D = 6.0 \times 10^{-4} \exp \left( - \frac{20500 \pm 1050}{RT} \right) \text{ (cm}^2\text{ s}^{-1})
\]

where \( R = 1.9869 \) cal mole\(^{-1}\) degree\(^{-1}\), \( T \) = degrees Kelvin.

![Fig. 1. The relation between \( \log D \) and the reciprocal of the absolute temperature.](image)

The experimentally obtained diffusion coefficient is of a reasonable magnitude. If the Arrhenius’ equation is extrapolated to 540 °C, the present values are lower than those of Halberstadt \( ^{2} \) but higher than those of Kubaschewski \( ^{4} \). The marked difference between the results obtained by different investigators is not surprising since different kinds of glass have been used. The “activation energy” \( Q = 20.5 \) kcal/mole agrees well with the values reported for similar experiments performed in air. \(^{11, 12, 15, 16} \) The order of magnitude of both the diffusion coefficient and the activation energy is typical for diffusion in the solid state. The rate of diffusion is affected by the atmosphere in which the experiment is performed, and also by the type of melt from which a certain ion diffuses into the glass. \(^{6} \) During an investigation of self-diffusion of Ag\(^+\)-ions in an eutectic mixture of AgNO\(_3\) and KNO\(_3\), \(^{24} \) it was found that the diffusion coefficient of silver into Pyrex glass was about 1/10 of that from a melt of pure AgNO\(_3\) at the same temperature. Thus, the diffusion into the glass was negligible for the mixture.

\[^{20}\] Porosity = porous volume / total volume.
\[^{22}\] All stated errors are standard deviations, obtained according to ref. \(^{23}\).
It is evident that a quantitative theory for the diffusion of silver into glass must consider that the rate of diffusion depends on the glass, the melt and the atmosphere surrounding them. Such a theory is not yet available, and more experiments are probably needed in order to solve the problem. It is reasonable to believe, however, that the diffusion coefficients of other metals into Pyrex glass are of the same order of magnitude as that of silver. Therefore the exchange between a salt melt and a diffusion apparatus made of Pyrex glass should not be a serious problem. However, when the diffusion times are very long and when the glass surface exposed to the melt is very large (as in a fritted disc) special care should be taken.

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Self-Diffusion in Molten Silver Nitrate

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The self-diffusion coefficient of the Ag\(^+\)-ion in molten AgNO\(_3\) has been measured with the glass fibre paper strip technique in the temperature interval 220—336 °C. The result can be described by the equation

\[
D = 3.2 \times 10^{-4} \exp\left(-\frac{3400}{RT}\right) \text{ cm}^2 \text{s}^{-1}
\]

A comparison with the results obtained by other workers shows good agreement between the two sets of values. Possible sources of error are discussed.

Several different methods for self-diffusion measurements in molten salts have been used, e.g. different capillary methods, the shear cell method, and the fritted disc method. Another method, the paper strip technique, has been proposed by Honig. Self-diffusion measurements in molten NaNO\(_3\), KNO\(_3\), and CsNO\(_3\) showed good agreement between the results of this method and those obtained by previous workers. In his original paper, Honig discussed many aspects of using the paper strip method for diffusion measurements in molten AgNO\(_3\) also, but he gave no experimental results. Since the relative merits of the different methods for diffusion measurements have been a matter of considerable discussion, we found that a closer investigation of the possibilities of the paper strip technique would be valuable. We decided to use it for investigation of the self-diffusion coefficient of the Ag\(^+\)-ion in molten AgNO\(_3\). Such an investigation has been performed previously by Dworkin, Escue and Van Artsdalen, using the open-ended capillary technique, and the exchange between an AgNO\(_3\) melt and a borosilicate glass has been studied recently at this laboratory. From a comparison between the results of these two investigations and the present results, conclusions could be drawn concerning the value of the paper strip technique.

Experimental

The experimental equipment was similar to that previously used by Honig. A strip, 15 cm long and 0.5 cm wide was cut from Whatman GF 81 (GF/A) borosilicate glass fibre paper. It was impregnated with molten AgNO\(_3\) and placed on a Pyrex glass plate in a paper strip technique, has been proposed by Honig. Self-diffusion measurements in molten NaNO\(_3\), KNO\(_3\), and CsNO\(_3\) showed good agreement between the results of this method and those obtained by previous workers. In his original paper, Honig discussed many aspects of using the paper strip method for diffusion measurements in molten AgNO\(_3\) also, but he gave no experimental results. Since the relative merits of the different methods for diffusion measurements have been a matter of considerable discussion, we found that a closer investigation of the possibilities of the paper strip technique would be valuable. We decided to use it for investigation of the self-diffusion coefficient of the Ag\(^+\)-ion in molten AgNO\(_3\). Such an investigation has been performed previously by Dworkin, Escue and Van Artsdalen, using the open-ended capillary technique, and the exchange between an AgNO\(_3\) melt and a borosilicate glass has been studied recently at this laboratory. From a comparison between the results of these two investigations and the present results, conclusions could be drawn concerning the value of the paper strip technique.

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