The Behavior of Silver in Glass. I. The Diffusion of Silver into Glass from a Melt of Silver Nitrate*[1]

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(Received February 10, 1962)

Previously the present author, together with his co-worker, studied[1] the diffusion of silver into a glass material in a temperature range somewhat below the softening temperature, namely, from 500 to 600°C. It was ascertained that a colorless glass gradually turned yellow or, further, brown as a result of the immigration of silver therein. According to previous authors, the following three consecutive stages of change are involved: first, the immigration of silver ions due to exchanges between silver

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*[1] The major part of this report was presented at the 8th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1955.

[1] S. Kinumaki and T. Ito, *Sci. Repts. Research Inst., Tohoku Univ.*, **A8**, 60 (1956).

and sodium ions²⁾, second, the reduction of the ions³⁾, and, last, the formation of silver colloid in the glass medium⁴⁾. The first quantitative investigations of the immigration were done by Schulze²⁾, who observed that silver diffuses from a silver nitrate melt into Thuringian glass and stains it intensively and that ions of silver and of sodium are exchanged. However, as to how each of these stages contributes respectively to the coloring, we do not have sufficient knowledge, especially in the former two cases; the problem must be studied in the future. However, in any cases, the degree of coloring may be taken as a measure corresponding to the immigration of silver into the glass material.

Consequently, the amount of silver immigrated in the glass material can be estimated by measuring the absorption of light at a characteristic wavelength, if it exists. The present investigation attempted to study the problem of the penetration of silver into a glass medium in particular connection with the light absorption.

Experimental

Material and Measurement of Absorbance.—The specimens were made from a glass plate, 1.93 ±0.03 mm. thick, the composition of which was the same*2 as that glass used in the previous work. This glass plate was cut into rectangles 12×50 mm² as the optimum size of the specimens; in addition, as a point of reference, a piece was cut out of the same glass plate next to every piece, in order to eliminate the discrepancies in the following observations due to fluctuation in the composition or in the thickness of the glass material.

The specimens were immersed for definite periods in melts of silver nitrate, which were kept at the constant temperatures of 250, 280, 310, 340, 370 and 400±1°C. Then they were taken out of the melts, cooled and washed with distilled water to remove the salt clinging to the surface of the glass.

Absorption spectra were measured on these glass plates with a Shimadzu QB-50 type spectrophotometer.

After the optical measurements, the border parts of the glass plates were cut off in order to avoid the boundary effects in the diffusion processes; then the residual parts were cut into rectanglar pieces 6×12 mm² for the sake of simple calculation. These pieces were used as specimens for measuring the changes in density due to the silver immigration. As points of reference, pieces cut out of the original pile, as mentioned above, were used, having been heat-treated to have the same thermal histories as salt-immersed pieces.

Measurement of the Shifting of Glass Densities.—We know that we can coveniently determine the density of a tiny piece of a solid material when we have a liquid the density of which can vary over a range including that of the specimen. Thus, if the density of the liquid be adjusted so that the specimen can stay at any depth in the liquid, neither rising nor sinking, then the density of liquid, determinable with a pycnometer or by other means, can be taken to be that of the solid. For this purpose, in the present work, solutions were prepared as follows: a suitable quantity of red mercuric iodide was suspended in water; then potassium iodide was added thereto, enough for the bulk to become a clean solution, probably due to the formation of some complex ions. By such processes we can obtain solutions of desired densities, in the range from unity to 3.5, corresponding to the concentrations; moreover, we can, in the above-mentioned range, increase or decrease the densities of given solutions by the evaporation or addition of water. Thus, the solution consisting of 113 g. of mercuric iodide, 91 g. of potassium iodide and 46 g. of water, the total weight amounting to 250 g. and the volume to 100 ml., has a density of 2.5, which is nearly equal to those of the glasses. This was, therefore, suitable as the starting solution.

As, in the present work, the change in the density of the glass due to the immigration, rather than its absolute values, was essential, the following procedures were preferred: a piece of salt-treated glass, together with a piece of the original glass, was put into a solution denser than both of them, and thereinto was poured, little by little, pure water from a micro buret, the volume being read frequently. First, the denser one of the two pieces reached the state of suspension; then, after the addition of a definite quantity of water, the other reached suspension. Thus, from the quantity of added water between the two suspensions, the required value can be calculated.

Then, because of the small density differences, the density differences between the specimens were evaluated by interpolation from the rising or sinking velocity measures instead of adjusting the densities of the liquids exactly to the perfect suspension of the specimens.

On the original glass, it was confirmed by the same procedure that the density remains unchanged on the thermal exposure in the temperature range from 250 to 400°C; this fact about glass of a similar kind has already been indicated by previous authors⁵⁾.

Thermostat.—All through the measurements of the densities, the temperature was kept at 25± 0.001°C by means of a thermostat regulated by a combination of an infrared radiator and a water cooler. The room temperature was 25±3°C.

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2) For instance, A. G. Schulze, *Ann. Phys.*, **40**, 335 (1913).

3) J. Halberstadt, *Z. anorg. allgem. Chem.*, **211**, 185 (1933).

4) W. Jander, ibid., **143**, 277 (1925); W. A. Weyl, "Coloured Glasses", Soc. Glass Tech., Sheffield, England (1951), p. 407; H. Tober, *Glastech. Ber.*, **34**, 456 (1961).

*2 Composition of sample glass: SiO_2, 70.89; Na_2O, 14.11; CaO, 8.22; MgO, 4.43; Al_2O_3, 1.31; Fe_2O_3, 0.13; TiO_2, 0.03; total, 99.12 wt.%.

5) H. Salmang und K. von Soesser, *Glastech. Ber.*, **8**, 463 (1930).

Results and Calculation

Absorbance.—The absorption spectrum of non-treated sodium-glass was obtained with the usual profile, as is shown in Fig. 1; it was ascertained that this spectrum does not suffer any annealing effect. The absorption of silver-glass was obtained with reference to this non-treated glass. Accordingly, the measure of absorbance is the difference between the absorptions of silver- and sodium-glasses and may be regarded as corresponding to the change in composition due to the immigration of silver. Typical curves of the absorbance spectra of silver-glass obtained as mentioned above are shown in Fig. 2. These curves all have one resemblance. The depth of penetration layer was estimated by the diminution of the thickness of the specimen ground until the yellow layer had disappeared. Now it was obtained as about 0.4 mm. under these conditions of treatment. As is seen in Fig. 2, the maxima of the absorbance curves lie at a wavelength of 314±1 mμ. Thus, the wavelengths of maximum absorption can be taken to have a constant value, the small deviation in the above-mentioned results being attributable to the fluctuation in the properties of the particular glass pieces. The heights of peaks are dependent on the time and the temperature of treatment. The relations, at various temperatures, between the heights of the maxima and the times of treatment are shown in Fig. 3.

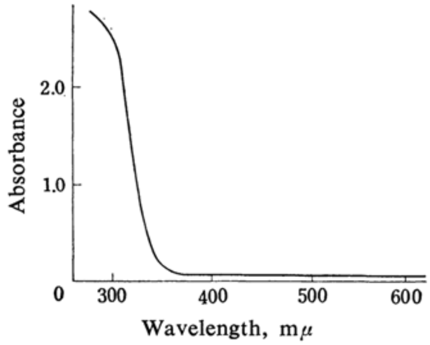


Fig. 1. Absorbance spectrum of sample glass refered to air. Since the conversion into the value per unit thickness is not important in this case, this is a figure obtained from non-converted values.

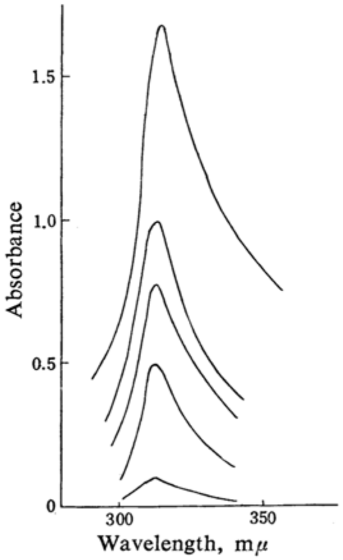


Fig. 2. Absorbance spectra of silver-containing glasses refered to the glass of Fig. 1.

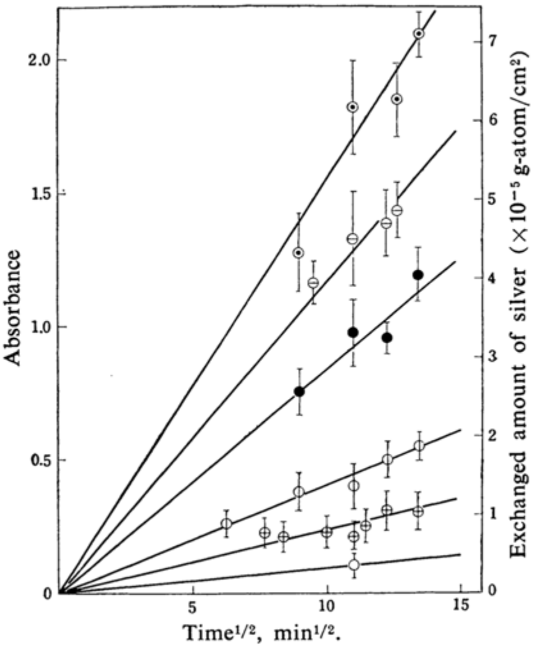
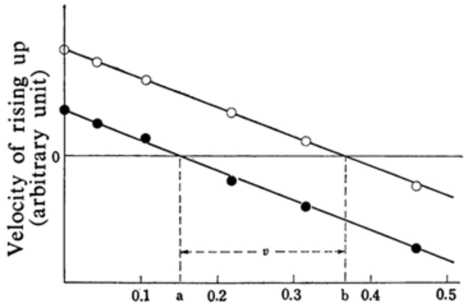


Fig. 3. Values of absorbance maxima as function of time at five temperatures:
○ 250, ⊕ 280, ⦶ 310,
● 340, ⊖ 370, ⊙ 400C
Errors are indicated by the lengths of the vertical lines.

Calculation of Density.—The pieces used in the measurement of density differences were selected particularly from those specimens which had reasonable values of absorbance as ascertained by the above-mentioned methods. We will denote the volume of water added to the reference solution from the beginning to the first suspension state by a in ml., and the volume, the weight and the density of the solution in this state by V, W and ρ respectively. Further, the volume of water added from the first to the second suspension states is v, the volume, the weight and the density of the solution thus arrived at being V_0, W_0



Volume of water withdrawn from a buret, ml.

Fig. 4. The relation of the velocity of rising up against the volume of water withdrawn.
-○- Sodium-glass -●- Silver-glass

and ρ_0 respectively. One of the relations of the rising or sinking velocity against the volume of withdrawn water was plotted as shown in Fig. 4. The difference in density between the two glass pieces is given by:

$$\Delta\rho=\rho-\rho_0=\frac{W}{V}-\rho_0$$

Then $\quad W=W_0-w=V_0\rho_0-vd$

where v, w and d are the volume, the weight and the density[*3] of the water withdrawn from the buret.

So
$$\Delta\rho=\frac{V_0\rho_0-vd-V\rho_0}{V}$$
$$=\frac{(V_0-V)\rho_0-vd}{V}$$

In the present work, it was confirmed that the volume contraction due to the dilution of the solution does not exceed the limit of acceptable approximation, namely $V_0-V=v$.

Consequently, $\quad \Delta\rho=\dfrac{v(\rho_0-d)}{V}$

The value thus obtained is the change in the weight of the glass per ml. caused by the immigration of silver. The area of the precise rectangle through which silver ions had penetrated into the glass was measured with a screw micrometer. The penetrated amounts per unit area thus calculated are plotted against absorbance in Fig. 5.

Diffusion Constant.—It has been described how both the absorbance and the change in density resulting from an immersion treatment occur as a result of a diffusion of silver ions and depend on the total amount of exchanged silver. With the inclination of the straight line given in Fig. 5, the absorbance can be converted into the amount of silver. The ratio of the exchanged amount of silver per unit area vs. the absorbance was obtained as follows:

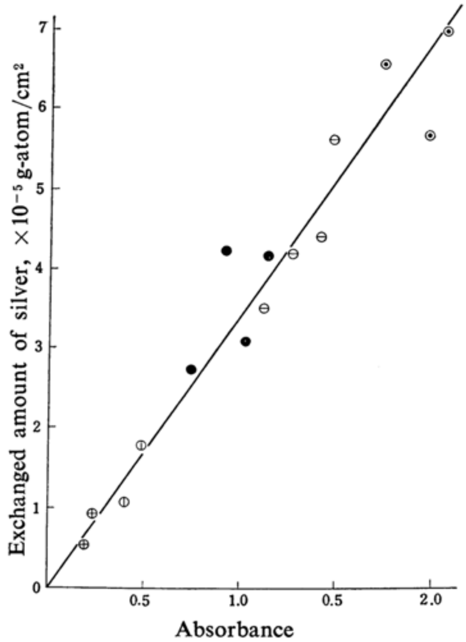


Fig. 5. The relation of the exchanged amount of silver against absorbance (cf. Fig. 3 for notes).

$$r=\frac{\text{amount per area}}{\text{absorbance}}=3.408\times10^{-5}\ \text{g-atom/cm}^2$$

The results of the conversion are placed vertically on the right of Fig. 3. On the other hand, according to Fick's law[6], the amount of silver can be represented with

$$M=2N\sqrt{\frac{Dt}{\pi}} \tag{1}$$

Accordingly, $$D=\left(\frac{M}{\sqrt{t}}\right)^2\frac{\pi}{4N^2} \tag{2}$$

where M is the immigrated amount of silver, N the saturation concentration, and t the reaction time. The $M/\sqrt{t}$ was obtained from the inclination of the straight lines in Fig. 3 at the respective temperatures. N can be taken as the concentration of sodium ions in the glass. It was calculated with the following equation:

$$N=\rho_0\times C\times\frac{1}{1/2(\text{Na}_2\text{O})}$$

Inserting $\rho_0=2.511$, $C=14.11/100$ (the wt.% of Na_2O) and $Na_2O=61.98$ (molecular weight),

$$N=1.31\times10^{-2}\ \text{g-atom/ml.}$$

Putting these values into Eq. 2, the diffusion constant, D, was obtained. The logarithms of

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[*3] $d=0.9971\pm0.0007$ (at 25±3°C), according to Landolt-Bernstein, "Physikalisch-Chemische Tabellen".

[6] J. Crank, "The Mathematics of Diffusion", Clarendon Press, Oxford (1956), p. 31.

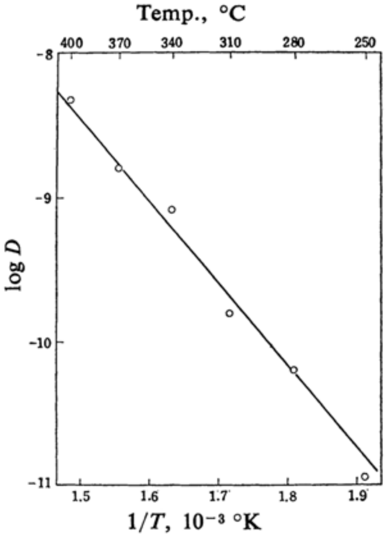

Fig. 6. The relation between $\log D$ and $1/T$.

D thus obtained are plotted against the reciprocal absolute temperature in Fig. 6. The relation of $\log D$ to $1/T$ is linear, as is seen in this figure. From the inclination of the line, the energy of activation, E, can be calculated to be

$$E=26.3\ \text{kcal./mol.}$$

also $$D_0=9.85\times 10^{-1}\ \text{cm}^2/\text{sec.}$$

Discussion

By measuring the electrical resistance, the diffusion of sodium in glass was studied⁽7⁾. In this work the means of absorbance has been successfully applied to the calculation of the diffusion, accompanied with the measurement of density difference.

The value of $E=26.3$ kcal./mol. is of the same order as that obtained in the previous work⁽1⁾. The value of $D_0=9.85\times 10^{-1}$ cm^2/sec., on the other hand, is slightly larger than that obtained previously. However, they are both reasonable values. In this work, treatment at temperatures above 400°C could not be carried out because of the instability of the nitrate and because of the anomaly of glass-density in its thermal history.

The figures in many reports of the absorption spectra of silver-containing glass have not agreed with each other. According to Wells⁽8⁾, the coloration of silver salts depends on the length of the Ag—O bonds. Helmholz⁽9⁾, on the contrary, has suggested that the color is related to the nature of the Ag—O bonds.

Most silver salts are colorless, although some of them are yellow or a similar color. Their absorption spectra have relatively low bands at wave lengths near 300 mμ⁽10⁾. Glass is not crystalline but amorphous. Therefore, the coloration, as well as the diffusion, involves more complicated problems than the salts, the space conditions in the glass media being in chaos. The absorption spectrum of silver-containing glass annealed at higher temperatures had a different band⁽1⁾. The coloration of glass has been, hitherto, dealt with in terms of the formation of the colloid of some metals in glass. The color of various kinds of silver glass would depend on the chemical state of silver, that is, on whether it is ionic, atomic or colloidal. The color obtained in the present experiment was yellow and not fluorescent, so it should be regarded as due to the state of the ions⁽11⁾. A detailed study of this problem will be carried out in the future.

The author wishes to express his deep gratitude to Professor Susumu Kinumaki of the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, for his helpful counsel and for supplying the author with material help of various kinds in the course of this study.

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7) R. W. Douglas and J. O. Isard, *J. S. Glass Thechnol.*, **33**, 289 (1949).

8) A. F. Wells, "Structural Inorganic Chemistry", 2nd ed., Clarendon Press, Oxford (1950), p. 215.

9) L. Helmholz and R. Levine, *J. Am. Chem. Soc.*, **64**, 354 (1942).

10) Y. Shibata et al., *J. Tokyo Chem. Soc.*, **40**, 411 (1919); J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. III, Longmans Green and Co., London (1923), p. 463; H. Fesefeldt, *Z. Physik*, **64**, 741 (1930); A. R. Ubbelohde et al., *Proc. Roy. Soc.*, **A251**, 156 (1959).

11) W. A. Weyl, "Coloured Glasses", loc. cit., p. 459; W. A. Weyl, *J. Phys. Chem.*, **57**, 756 (1953).