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A STUDY OF THE MIGRATION OF IONS IN GLASS

BY

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THESIS

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A STUDY OF THE MIGRATION OF IONS IN GLASS

I. Introduction

The study of migration of ions in glass is directly associated with that of diffusion since migration of any type will not occur unless forces promoting diffusion are present. In general, diffusion under proper conditions of constant temperature is the tendency on the part of any material -- in the form of ions, atoms, molecules or colloidal particles -- to disseminate and to establish a uniform distribution or concentration in some medium such as gas, liquid or solid.

It would be expected that in the study of diffusion in glass, laws analagous to those proposed by various investigators for liquids should apply. According to the theories of Tammann 1) and Zachariasen 2) glass is a liquid at high temperatures and a supercooled liquid or amorphous solid with a random network structure at temperatures below the softening point.

The study of diffusion is not only of theoretical interest but its practical importance is easy to point out in numerous familiar examples which are readily recognized in many branches of the ceramic industry. The application of diffusion laws, however, is usually ignored because they are not understood. Some of the chemical-physical processes in which diffusion plays a leading role are:-

a.) Velocity of solution of a solid
b.) Velocity of crystallization
c.) Reaction velocities
d.) Homogeneity

In (a) the rate of solution is proportional to the rate of diffusion of the substance from the saturated layer in contact with the crystal to the surrounding solution. In (b) the crystal growth occurs at the expense of the molecules in the adsorption layer, and the adsorption layer is replenished by molecules from the surrounding solution by means of diffusion. Johnston 3) promoted the growth of large crystals of sparingly soluble substances by allowing each of the reacting solutions to diffuse separately into a large volume of liquid within which they came together slowly. In (c) the reaction velocity may be determined by measuring the diffusion of the products found at the interface. In (d) homogeneity of a glass is dependent upon the diffusion of its constituents. This, however, is a very slow process and experimental batches are or should be ground, mixed, and remelted several times in order to insure satisfactory uniformity.

A few specific examples related to problems of ceramics are:- the diffusion of iron oxide from the hot end to the cold end of a silica brick used in the crown of an open hearth furnace; possible occurrence of halos about crystals which may be present in colored glazes; growth of crystals at devitrification temperatures of glass; and sintering in portland cement depending upon the diffusion of the components below the melting temperature.

Of still greater practical importance is the possible application of such studies to new methods of decoration, especially in cases where a discoloration sets in with the migration of the substance into the glass surface.

The research reported in this thesis is of an exploratory nature. A series of fundamental experiments were made to study the nature of and the rates of diffusion from certain compounds for a number of time and temperature intervals. In all cases diffusion took place from a salt into a commercial flint glass, i.e. a lime-soda-silica glass. One or more salts of Cu, V, Th, Pb, Au, Cr, Pt, Co, Fe and Ag were tried. However, silver was used for most of the experiments because of its rate of migration and its pronounced tendency for coloration, thus allowing use of relatively simple methods for measurement of the diffusion.

II. Review of Literature

Literature on the general subject of diffusion is relatively meager. Articles discussing diffusion in glasses or silicate fusions are especially few in number and most of these have originated in Germany.

Nernst in one of his writings points out that the force behind diffusion is essentially the same force as the osmotic pressure. The gas laws of Boyle, Gay-Lussac and Avogadro are found to apply in general to osmotic pressures, providing the solute is a non-electrolyte.

The principle of Soret which becomes important in a number of ceramic operations is based on diffusion. It states that a dissolved substance will diffuse from the warmer into the colder part of the solution.

A compilation from literature of some of the determined diffusion coefficients are:-

Most salts in aqueous solution = 0.26 cm.^{2}per day
Molten metals in molten metals = 2.59 "
Diopside in liquid mixture at 1500°C.= 0.14-0.2 "
Common salt in water at 15°C. = 1.00
Gold in molten lead at 492°C. = 3.00
Solid gold in solid lead at 150°C. = 4.3 x 10^{-3}
Silver into glass at 354°C. = 2.20 x 10^{-5}
Aqueous N. H_2SO_4 in water at 8°C. = 1.01

A. Equations Relating to Diffusion

1. Fick's Law

Fick's law has been the fundamental basis for the study of diffusion in liquids on a quantitative basis. The original law as stated by Fick in 1855 reads, "The dissemination of a dissolved substance through a solvent, as far as it takes place undisturbed under the influence of molecular forces alone, obeys the same laws which Fourier established for the dissemination of heat in a conductor, and which Ohm announced for the conduction of electricity. In the Fourier law it is only necessary to replace the words Quantity of heat with the words Quantity of dissolved substance, and the word temperature with density of solution."

Specifically, the law states that the driving force which impells a dissolved substance to move from the place in the solution of higher concentration to one of lower concentration, and which also determines the rapidity of the movement of the particle, is proportional to the drop in concentration. A mathematical representation of an equation to fit this law is as follows:-

$$\frac{dc}{dt} = -q D \frac{dc}{dx} \tag{1}$$

where c is the concentration, t the time, q the cross-section in square centimeters, x the distance of point in the interior of the sample from the surface, and D the diffusion coefficient. D can be expressed as the number of grams which diffuse past one sqaure centimeter of any plane in unit time when the concentration gradient normal to the plane is unity.

With the assumption that D is independent of the concentration and is a constant, one then obtains the following general form of the diffusion equation:-

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{2}$$

for diffusion only in the x-direction. Jost 4) discusses cases and presents equations to cover any concentration distribution.

A calculation of the above equation can be made directly on the basis of the excess of the entering over the leaving amount of substance in a volume element. Newman and Searle 5) used this method and based their procedure on the illustration in Figure 1.

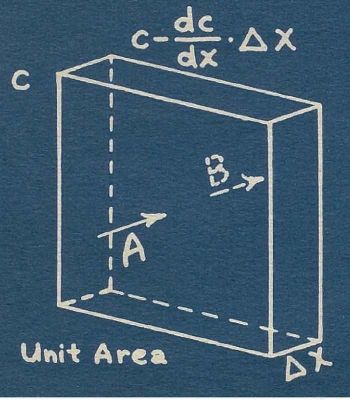


FIGURE 1. Volume element used as an aid for calculation of diffusion equation according to Newman and Searle 5)

The drawing represents a plane of finite thickness, Δx, along a direction of constant density in the liquid. The derivation follows:-

$\frac{dc}{dx}$ = concentration change with distance measured at right angles to the plane

then

$D\frac{dc}{dx}$ = mass of dissolved substance crossing unit area of the plane per second.

Inflow of dissolved substance at A in time Δt will be $D\frac{dc}{dx}\Delta t$, while the outflow from B will be

$$D\Delta t\frac{d}{dx}\left[c-\frac{dc}{dx}\Delta x\right] = D\frac{dc}{dx}\Delta t - D\frac{d^2c}{dx^2}\Delta x\,\Delta t.$$

Thus, the space between A and B has a net gain of $D\frac{d^2c}{dx^2}\Delta x\Delta t$. Since the volume enclosed is Δx, the change of concentration is $c = D\frac{d^2c}{dx^2}\Delta t$ or the rate of change is $\frac{dc}{dt} = D\frac{d^2c}{dx^2}$.

The equation in this form is not valid for all cases, for it has shown small deviations from the experimental results because of the assumption that D was a constant. Actually, it has been found to be a constant only for nonelectrolytes at low concentrations, for some solid substances, and in silicate melts for small masses of dissolved substances. Otherwise, it changes with concentration. However, a solution of the equation with a variable D would be a most difficult one and would be integrated by a given process of Boltzmann, whereas with a constant D a simple integral can be stated. One must also consider the fact that Fick's equation is only valid for a single homogeneous phase, and with polyphase systems a corresponding equation would have to be established for each phase. Also, a consideration of the interfaces in a polyphase system would have to be taken into account.

2. Solving for D from Fick's Law

Integration of Fick's equation according to Stefan 24) and also by Warburg 6) gives

$$(3) \qquad D = \left(\frac{M}{\sqrt{t}}\right)^2 \cdot \frac{\pi}{4N^2}$$

where N is the saturation concentration per cubic centimeter and M the amount of material immigrating per square centimeter. Since D is a constant, the following equation can be obtained

$$(4) \qquad \frac{M}{\sqrt{t}} = k$$

This form has been used quite extensively by investigators to study experimental data.

If the limiting assumption that D is a constant is relinquished, Jost arrives at the known Einstein relation:-

(5) $$D = \frac{RTB}{N}$$

B is the particle mobility and the reciprocal of the frictional resistance working on the particle. Taylor 7) presents another solution of this relation. Assuming the independent motion of the several constituents of a mixture, the relationship between molecular motion and diffusion is given by means of the equation

(6) $$D = \frac{\overline{\Delta^2}}{2t}$$

where $\overline{\Delta^2}$ is the mean square of the displacement which takes place in a given direction in time t. If one further assumes that the particles possess the same mean kinetic energy as a gas molecule at the same temperature, then the Einstein equation $\overline{\Delta^2} = \frac{2RT}{N} Bt$ holds.

By combining these equations the relation presented by Jost is again derived. Now, if Stoke's law for frictional resistance is substituted, then the Stokes-Einstein relation is obtained

(7) $$D = \frac{RT}{6\pi \eta r N}$$

where R is the gas constant, T the absolute temperature, η the viscosity, and r the true particle radius. This form may be rewritten to solve for r if D is known or derived experimentally. This equation had been prepared especially for molecules that are large in comparison to those of the solvent or colloids. Direct proof of the applicability of this equation to diffusing molecules is not possible and it can be tested by one of the following alternative methods:

$$D \cdot \Lambda = \text{constant} \qquad (8)$$

where the solvent is the same, the temperature is constant and a variety of diffusing substances is used. On the other hand, if a given substance is used in a variety of solvents, the following relation is possible

$$D \cdot \eta = \text{constant} \qquad (9)$$

For salts dissociated in solution into ions the problem is a little more complex. Nernst developed a diffusion equation whereby the diffusion coefficient, D, is expressed by the equation

$$D = \frac{2UV}{U+V} RT \qquad (10)$$

where U and V are mobilities of two ions. This equation has been found to agree with experimental results providing that for the chosen concentrations of the solutions the dissociation is approximately complete.

3. Solving for Concentration from Fick's Law

Another method of determining the validity of Fick's law is to compare the actual measured concentrations in a mass undergoing diffusion with the calculated values obtained from the law. Warburg derives the following expression for this purpose:-

$$c = c_0 \left\{ 1 - \frac{2}{\pi} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\beta^2} d\beta \right\} \qquad (11)$$

assuming that D is a constant and integrating with the limitations $x = 0, N_2 = N$; $x = \infty, N_2 = 0$; and $t = 0, N_2 = 0$. N is the molar concentration of replaceable ions; N_2 is the molar concentration of silver ions replacing the sodium ions. For specific application to his experimental set-up Bowen 8) uses the following form of this equation:

$$(12) \qquad 2c = c_0 \left[\frac{2}{\sqrt{\pi}} \int_{\frac{-l-x}{2\sqrt{Dt}}}^{\frac{l-x}{2\sqrt{Dt}}} e^{-\beta^2} d\beta + \frac{2}{\sqrt{\pi}} \int_{\frac{-l-(2m-x)}{2\sqrt{Dt}}}^{\frac{l-(2m-x)}{2\sqrt{Dt}}} e^{-\beta^2} d\beta + \text{etc.} \right]$$

where the term in the brackets in the limits is successively $x, 2m-x$, $2m+x, 4m-x, 4m+x$, etc., c is the volume concentration at any point at distance x from base of column, l the thickness of bottom layer of original uniform concentration c_0, m the total length of column. However, these equations are not as formidable as they may appear since

$$\frac{2}{\sqrt{\pi}} \int_0^q e^{-\beta^2} d\beta$$

is the probability integral whose value, for various values of q in limits, can be found in proper tables.

4. Temperature Coefficient of Diffusion Processes

An equation is set up, according to Taylor 7), to determine the temperature coefficient employing two measurements of the diffusion coefficient at two temperatures:

$$(13) \qquad \frac{D_2}{D_1} = 1 + \alpha (T_2 - T_1)$$

In liquids it has been found that the greater the ionic mobility the less is the temperature coefficient, and high diffusion rate is generally accompanied by a low temperature coefficient.

5. Diffusion in Solids

Dorn and Harder 9) discuss an equation for application to diffusion in solids as originally presented by Dushman and Langmuir. On the basis of the theory, it is assumed that the probability that an atom will jump from one atomic plane to a second is precisely analagous to the probability for a unimolecular chemical reaction to occur. The resulting equation becomes

$$(14) \qquad D = K\delta^2 = \frac{E}{Nh}\,\delta^2 e^{-\frac{E}{RT}}$$

where K is the probability an atom will jump, δ the jump distance, E the energy of activation per mole, N the Avogadro number, h the Planck constant, e the base of natural logarithms, R the gas constant, and T the absolute temperature. The equation may be simplified by letting

$$A = \frac{E\,\delta^2}{Nh}$$

then

$$(15) \qquad D = A e^{-\frac{E}{RT}}$$

In this form numerous experimental tests of the equation have demonstrated its validity and usefulness. This equation has been used as a basis for derivation of other similar equations which bring in the factor of time.

B. Diffusion of Silver in Glass

The first quantitative investigations on the diffusion of silver into glass were conducted by Günther Schulze 10) in 1913. His work was prompted by that of Heydweiller and Kopfermann 11) who found that silver introduced from molten silver nitrate is not only readily electrolytic but also migrates without any difference of electrical potential merely by diffusing in the glass.

In Schulze's work the test glass tubes were immersed in a bath of silver nitrate. The depth of penetration and change of concentration were obtained by first cleaning the tubes after the test, eating away a layer of glass with dilute hydrofluoric acid, determining the silver content of each corrosion analytically as silver chloride, and making the proper calculations. The temperature range covered was from 238 to 422°C. This is within the molten range of the nitrate whose melting point is 212°C. and the decomposition temperature is 444°C. It was found that the silver diffuses into the glass in the form of free ions and for every entering silver-ion there is a sodium-ion leaving, thus establishing the fact that diffusion is an ionic process.

Schulze's results showed that at a constant temperature the amount of silver diffusing into the glass is proportional to the square root of the time of diffusion (Equation 4). It was also demonstrated that, within the limits of observational errors, the decrease of concentration of the silver in the glass as it penetrates into the interior of the specimen is directly proportional to the

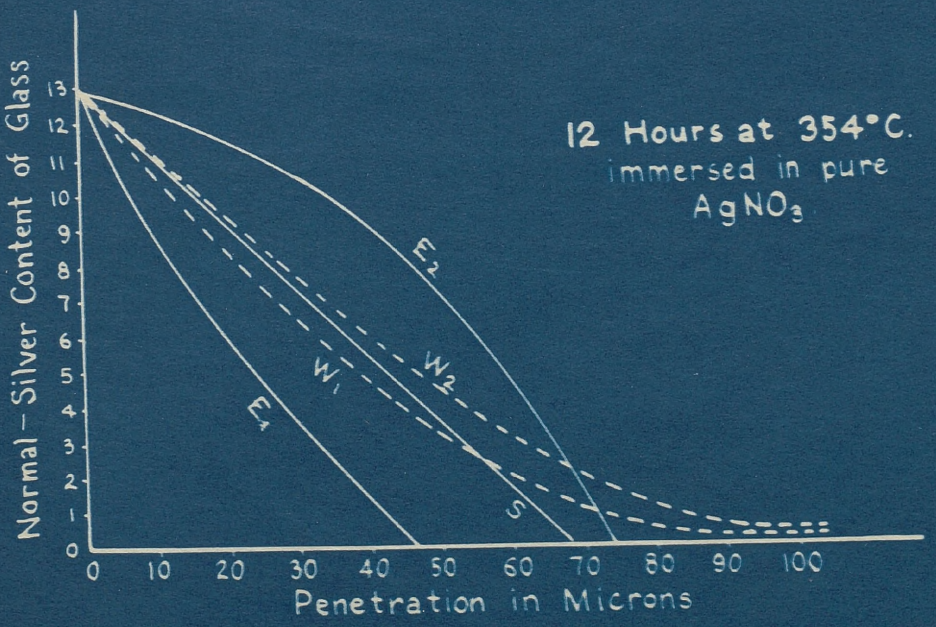


FIGURE 2. Relation of silver content of glass to depth of penetration according to Schulze[10)]

distance and is represented by a straight line. Curve S in Figure 2 represents this condition. Of interest are the theoretically calculated curves of Warburg which follow the experimental results fairly well except at the lower concentrations. A single curve cannot be calculated (Equation 11) since D is not strictly a constant and changes with silver migration. However, curves can be determined for either limiting case:- D_{Na}, diffusion constant in unchanging glass, and D_{Ag}, diffusion constant with full replacement of sodium by silver. Curve W_1 is obtained using the value for D_{Ag} as 2.09×10^{-5} cm.^{2} per day and curve W_2, using D_{Na} as 3.14×10^{-5} cm.^{2} per day.

Curves E_1 and E_2 are included to show the general effect of electrolysis in addition to diffusion. The former is for electrolysis acting in the direction opposite to that of diffusion, and the latter in coincidence with diffusion.

Halberstadt 12), twenty years later, also worked on the problem of diffusion of silver into glass. A silver foil wrapped tightly around a glass rod was the source of silver. The diffusion tests were run within a narrow temperature interval limited by the softening point and the region of appreciable softening. For the glass tested this range was 565 to 615°C. A series of tests at each of these temperatures were also found to agree with Equation 4. Halberstadt, however, suggests that silver atoms diffuse into the glass instead of silver ions. He supports this assumption with the knowledge of an atomic dispersed condition of metals in glass based on the Nernst distribution law. It was found for instance that the ratio of concentration of Au in Ag to Au in glass is a constant. Therefore; since gold dissolves monatomically in silver, gold must also be atomically dispersed in the glass.

The diffusion coefficient was not found to have a relationship with the viscosity as suggested for aqueous solutions by Equation 9 since the increase of D in the temperature interval is smaller than the decrease in viscosity. The use of Stokes-Einstein law (Equation 7) for calculation of particle size indicated a particle radius radius below the atomic order of magnitude. This meant that the diffusion coefficient was abnormally high. Since the value of the coefficient is somewhat dependent on the magnitude of the particles, then solvolysis of the atoms must have occurred.

Since the two investigators reporting on the subject presented differing viewpoints as to the nature of the silver particles diffusing into the glass, Kubaschewski 13) made a series of tests to prove that the silver in both cases migrated as silver ions. In his experiments the source of silver was from a dense, solidly fixed coating of silver which was deposited on test platelets by evaporation in a vacuum; and the range of test temperatures was from 466 to 568°C.

Equation 4 was again found to hold at the test temperature of 540°C. In order to calculate the coefficient of diffusion according to Equation 3 the saturation concentration must be known. Also, from this experimentally obtained value it was calculated that about every 25th sodium ion is replaced by a silver ion. An increase of temperature through the softening point was accompanied by a quick rise in values of the increase of weight on diffusion.

The argument set forth by Kubaschewski to prove that silver diffused into glass as ions was based on the formation of an intermediate oxide. If atoms diffuse into the glass, then the process must be independent of the oxygen pressure of the surroundings. On the other hand the suggested mechanism of reaction stating that primary Ag_2O first forms on the surface of the glass and then upon its decomposition silver ions diffuse into the glass, while the sodium ions function as oxygen-acceptors, would be dependent upon oxygen pressure. The validity of this reasoning was substantiated by the actual experimental results. Below a pressure of 40 mm. of Hg of oxygen the diffusion was strongly dependent upon the oxygen content.

Alexander 14) mentioned the work of R. Zsigmondy with respect to silver-glasses. His experiments showed that silver first goes into solution in the glass as oxide, but is reduced to the metal, and is finally found in the chilled glass as a colloidal dispersion.

Summarizing, it is shown that Equation 4 has been found to hold experimentally in all cases. Three possible theories were reported for diffusion of silver into glass -- as ions, as atoms or aggregated particles, and as the oxide.

Table I
Diffusion Coefficients of Ag into Glass

Temperature	D (cm.^{2}/day)	Author
354°C.	$.22 \times 10^{-4}$	G. Schulze
540°C.	$.95 \times 10^{-4}$	Kubaschewski
565°C.	9.85×10^{-4}	Halberstadt
590°C.	11.32×10^{-4}	Halberstadt
615°C.	13.65×10^{-4}	Halberstadt

Table I is a compilation of the diffusion coefficients as determined by the indicated workers. The values, however, are just an indication of the trend and magnitudes since all three investigators used glasses of different compositions. This fact and the probability that the softening temperature lies between 540 and 565°C.

account for the rapid rise of coefficients between these two temperatures.

C. Other Diffusion Experiments

Though some geological phenomena are explained on the basis of diffusion, actual related experimental work on this problem has been meager. Endell 15) has demonstrated the interdiffusion of lime and microcline glasses. He also showed that at temperatures above 1300°C. TiO_2, Fe_2O_3, MnO, CoO and NiO diffuse in a melt of microcline forming a colored halo around the corresponding oxide. The oxides are here arranged in the order of increasing range of the halos.

The most important work in this field is that of Bowen's 8) who made quantitative experiments on the diffusion of diopside, a heavy liquid, into a plagioclase, a light liquid, at temperatures above the fusion point of both, about 1500°C. The test cylinders were arranged so that the diopside was on the bottom. The extent of diffusion was measured by determining indices of refraction of the cooled glass cylinders along their vertical axis with a goneometer. The indices vary progressively with change of composition. Consequently, after developing a calibration curve the indices were used for determining compositions which were then plotted against distance from the bottom.

Using Equation 12 theoretical curves for concentration distribution were calculated assuming various values of the diffusion coefficient until the closest match to the experimental curve was obtained. However, none of the curves coincided completely. Since the equation was derived from Fick's law on the basis of a constant coefficient, it was then concluded that the coefficient varied with the composition. Bowen accordingly derived a number of "average diffusivities" for the mixtures he studied. From his research, he also determined that the rate of cooling was faster than the rate of diffusion in large molten igneous masses. There consequently would not occur a great deal of differentiation due to diffusion. However, reaction rims around foreign crystals in a fusion have sufficient time to develop.

Wessels 16) studied the thermolytic concentration changes in glass in relation to the Ludwig-Soret effect. This effect was first observed in homogeneous solutions by Ludwig in 1856 and then later by Soret in 1881. The phenomenon is the movement of a dissolved material from the hot portion to the cold ortion of an originally homogeneous medium and is attributed to differences of osmotic pressure. Glasses colored with iron, manganese and chromite showed a migration of their color to the cold end. Cobalt glasses did not seem to show this phenomenon. Further, this rule does not apply to colored glasses of the colloidal dispersion type. The experiments were carried out at a temperature slightly below the softening point of the glass. The test specimens were glass rods coated with nickel foil on the end immersed into a furnace having a potash glass tube for a lining. Curves showing relative intensities were drawn by visual inspection. Figure 3 gives typical curves for 2 days and 10 days test time for a green glass colored with chromium. The indicated changes in color from the normal seem to occur only through the temperature gradient portions on either side of the furnace opening.

Fettke and Stewart 17) discussed the rate of diffusion and rate of solution with respect to attack of refractories by slag.

The equation, another form of Fick's law, used by them was

$$\frac{dc}{dt} = D\,q\,(S_{sat.} - S_{act.}) \qquad (16)$$

where $S_{sat.}$ is the amount of diffusion substance that the glass can hold and $S_{act.}$ is the amount of diffusing substance already present in the glass. This equation is identical in form with that of a unimolecular reaction on the assumption that the rate of diffusion determined the total reaction rate. Actual tests made indicated that the diffusion of the solution materials from the interface was not the controlling factor in the slagging action of coal ash on aluminous silicate refractories.

An attempt to determine some of the controlling factors on the degree of coloration with silver and copper staining, as a prac-

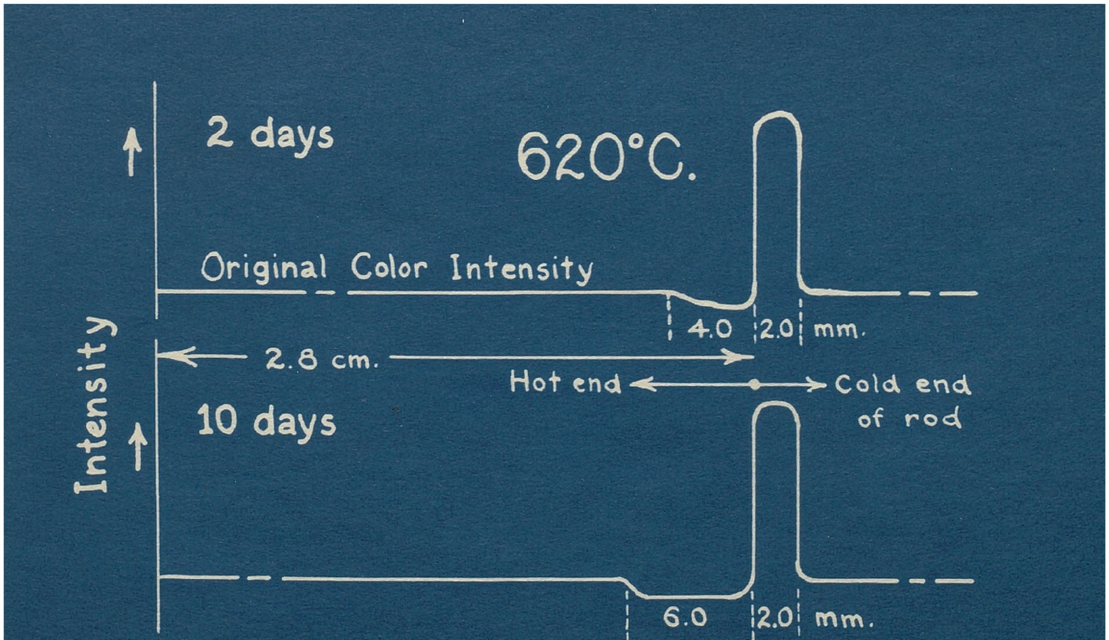


FIGURE 3. Illustration of Ludwig-Soret phenomenon by curves showing relative intensities of color along the length of green glass rods colored with Chromium according to Wessels (16).

tical application of thermal diffusion, was made by Gilard and Dubrul[18]. Their method was to note the effect of small concentrations of different materials on the intensity of transmitted light through the sample.

Halberstadt measured the diffusion velocity of copper into glass and found D_{Cu} to be 1.79 x 10^{-4} cm.^{2} per day at 650°C. in comparison with D_{Ag} of 13.65 x 10^{-4} cm.^{2} per day at 615°C.

D. Liesegang Rings

In the study of crystallization processes within gels Liesegang was the first to notice that under certain conditions these reactions lead to the formation of rhythmic bands of precipitates instead of large crystals. The particular experiment which attracted his attention was the formation of rhythmic rings of silver chromate when a drop of silver nitrate was placed on a gelatin film containing dilute potassium chromate.

Since the time of his discovery many investigators have repeated the experiment with various kinds of salts and theorized about the causes for this phenomenon. The following theories have been suggested:- (1) the precipitating salt forms a supersaturated solution which diffuses along with the added reactant until the metastable limit is reached when it precipitates, and by repetition of the process, alternate gaps and bands are introduced; (2) the precipitate which constitutes the bands is slightly soluble in the reaction products, and hence new bands can form only after a point is reached where the concentration of the reaction products is sufficiently small; (3) one of the reacting solutes is absorbed by the growing precipitate, thus giving zones which are practically free from it;

and (4) conditions affecting the rate of diffusion of the reacting ions are the controlling factors. The latter is now the most widely accepted.

Of considerable interest is the fact the the rhythmic bands of agates closely resemble Liesegang rings. Thus, the evidence points strongly to the genesis of agates as gels.

Endell 15) states that Liesegang has explained the rhythmic concentration texture of agates by supersaturation phenomena of iron salts diffused in silica gel. Another explanation is that of rhythmic formation of crystal nuclei. After reaching the metastable limit, spontaneously formed nuclei separate from the solution or become ineffective, thereupon a new supersaturated zone forms, whereby with repetition a rhythmic preparation is possible according to the principle of separation of nuclei. The latent heat of crystallization released affects the degree of saturation of the surrounding zone, and new nuclei may form at a certain distance. Thus, isolation of nuclei appears to be a necessary and perhaps also sufficient condition for the formation of rhythmic rings. The relatively high viscosity of the glasses at the devitrification temperature makes the nuclei inactive.

III. Experimental Procedure

The experiments were concerned with the effects of different salts as sources of diffusing material and the nature of the diffusion rather than the effect of the glass composition.

A. Glass Samples

Instead of using a melt of a salt containing the diffusing ion and submerging the glass sample, as had been done by previous investigators, it was decided to use the sample itself as the salt container. This allowed the possibility of determination of diffusion above the softening point of the glass.

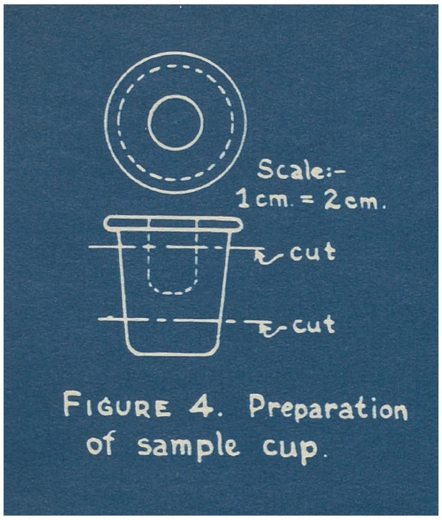


FIGURE 4. Preparation of sample cup.

The samples were prepared from a special glass article shaped by a candle holder mold with a plunger forming a well about one cm. in diameter. A diamond wheel was used to cut this article in two places as shown in the adjoining Figure 4. The bottom piece was then available as a cover for the center piece, the sample cup, whenever desirable. The glass was a commercially used flint glass whose composition, as calculated from the raw batch, was as follows:-

SiO_2	-	74.5%
Na_2O	-	16.5
CaO	-	4.0
MgO	-	2.8
Al_2O_3	-	0.5
B_2O_3	-	0.5
BaO	-	0.5

The softening point was 565°C. and the thermal expansion coefficient from room temperature to 500°C. was 9.9×10^{-6} cm. per cm. per °C.

The same equivalent weight of the different salts was always added. For use at test temperatures above the softening point of the glass the sample cups were placed in specially prepared Alundum crucibles of a size to fit the shape of the cut pieces so as to prevent too much deformation.

B. Sources of Diffusion Material

Since silver was found to diffuse the most readily, the major portion of the experiments were performed with silver salts.

Those used were $AgNO_3$, $AgCl$, Ag_2SO_4 and Ag_2O.

For the purpose of determination of their diffusibility, of relative rates of diffusion of their cations, and of the resulting colors other salts were also tested. Included in this group were Cu_2Cl_2, $CuSO_4.5H_2O$, V_2O_5, $CrCl_3$, $PbCl_2$, Tl_2SO_4, $AuCl_3$, $PtCl_4$, Co_3O_4 and $FeCl_3$.

C. Tests

The experiments were performed in a small laboratory furnace wound with Kanthal-wire. In heating the furnace the rate was about 10°C. per minute, and a potentiometer controller maintained constancy within ± 5°C.

The above furnace was used at a number of test temperatures, the highest being 900°C. and the longest time interval being 108 hours. The cooling procedure consisted of quickly removing the test pieces, placing them in another furnace at 500°C and subsequently cooling with the furnace. At temperatures below 500°C the cooling was accomplished either in the test furnace itself or after transferring the pieces to another furnace at the particular test temperature. The latter procedure allowed the running of several samples at varying time intervals.

A Pt-wire wound furnace was used for a few experiments at 1100°C. Also, the tests made in a reducing atmosphere of CO required a different type of furnace through which the gas could be passed.

D. Measurements

1. Increase of Weight

The amount of material diffusing into the glass cups was determined by weighings. For calculation the following weights were obtained:

(1) Weight of glass cup
(2) Weight of cup plus salt
(3) Weight of cup plus diffused material.

The difference between (2) and (1) was the weight of salt used. For purposes of elimination of as many variables as possible this weight always corresponded to 0.0043 equivalents of salt. This amount filled about half the well.

After the experiment the residue in the well was dissolved in a suitable solvent, such as dilute hydrochloric acid, the sample cup was washed and dried, and the third weight (3) was obtained. Then, the difference between (3) and (1) was the increase in weight due to the material diffused into the glass. However, this was not the true weight since there was simultaneously a diffusion of sodium from the glass into the salt. This exchange was shown to be true by the works of Schulze and Kubaschewski. Therefore, in the case of silver, the true weight of the material diffused into the glass can be calculated according to the following equation:-

$$M - M\frac{Na}{Ag} = G \qquad (17)$$

where M is the amount of silver entering into the glass, G is the increase of weight of the sample cup, and Na and Ag represent the corresponding molecular weights. Stated in words, the equation reads -- the weight of incoming silver minus an equivalent weight of outgoing sodium is equal to the actual increase of weight. Substituting known values, then

$$M = 1.272\ G$$

which gives the weight of silver diffused into the test glass sample. These values are recalculated on the basis of grams per unit area of diffusion interface and grams per unit volume of diffusion.

2. Extent of Diffusion

After weighing, the sample cups were cut in half vertically with a diamond wheel, ground and polished. The polished cut faces of the sample cups to be used for quantitative measurements and those showing unusual and significant effects were photographed at a magnification of 5x with the use of a Micro-Tessar IIb lens. The necessary arithmetical measurements were then made from the photographs.

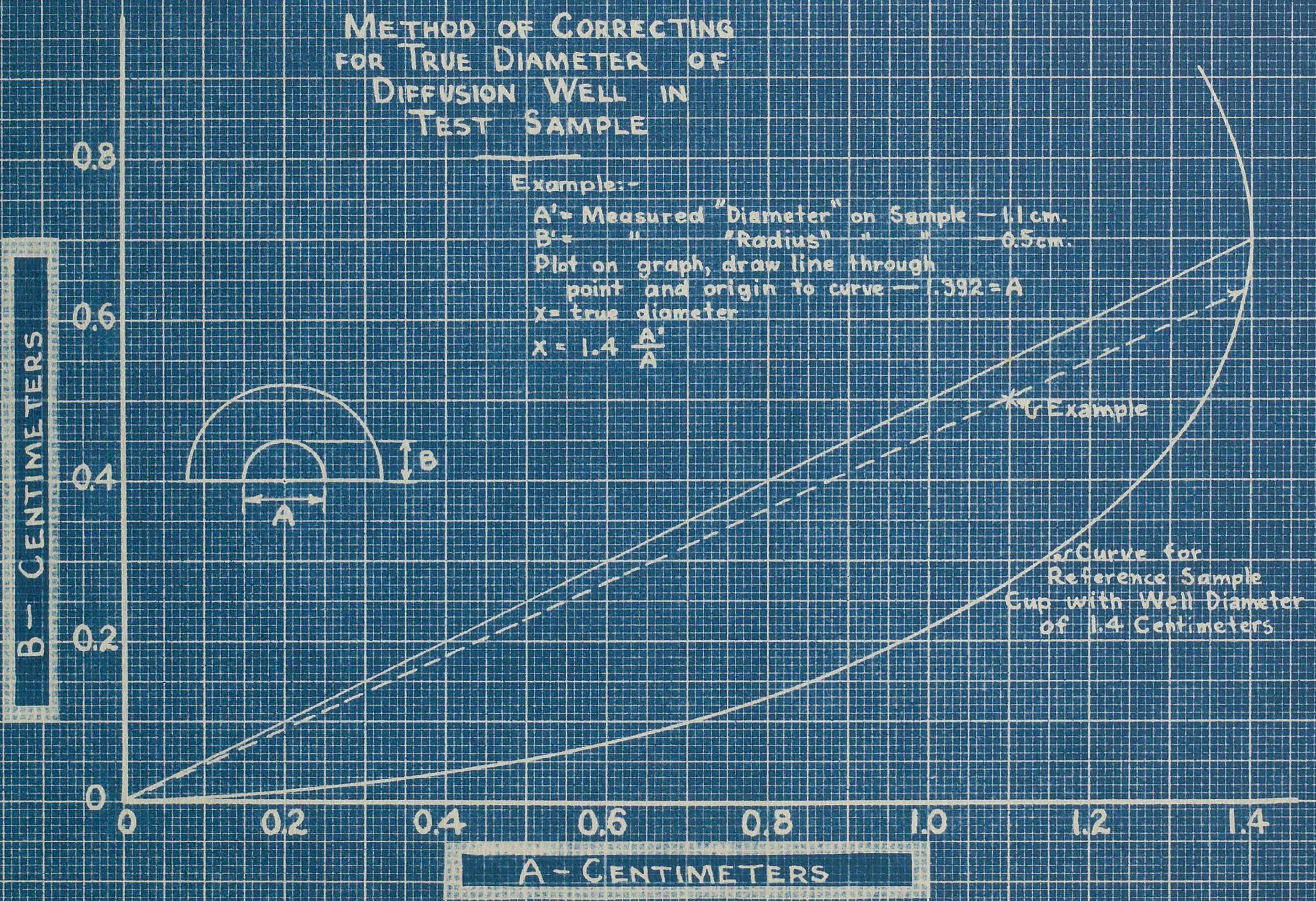
In order to compensate for the possibility of a non-center slice through the sample, and thus the measurement of an incorrect diameter on the photograph, the method illustrated in Figure 5 for determining the true diameter was derived. Micrometer calipers were used for measuring the "radius" of the well. The correction ratio of 1.4/A obtained from the above Figure applied to all linear and areal measurements on the particular photograph.

An application of a modified Simpson's rule or a graphical and arithmetical integration was used to obtain the area of the diffusion interface and the diffusion volume from the above-mentioned photographs. This method was necessary since it was found that the vertical cross-section of the bottom of the well did not correspond to the trace of any of the simple curves, such as circle, parabola, or ellipse.

The procedure consisted of first lining out horizontal strips on the photographs, a greater number being present in the portion of greater curvature. The average length of each strip was calculated and a correction made using the ratio obtained from Figure 5. The surface area of diffusion for each strip was then calculated from the formula:- Area of strip $= \pi d_{ave.}$ x the height or thickness of the strip, since a horizontal cut through the sample shows a circular

FIGURE 5

METHOD OF CORRECTING FOR TRUE DIAMETER OF DIFFUSION WELL IN TEST SAMPLE



Example:-

A' = Measured "Diameter" on Sample — 1.1 cm.
B' = " "Radius" " " — 0.5 cm.
Plot on graph, draw line through point and origin to curve — 1.392 = A
x = true diameter
$x = 1.4 \frac{A'}{A}$

trace. The total area would thus be the arithmetical summation of the strips:-

(18) $$A = \sum \pi d_{ave.} \times h$$

The calculation of the volume of diffusion is also performed with the aid of these strips. However, now the average length of the strip including the extent of the diffusion (d_2) is obtained in addition to the length of the well itself (d_1). The following formula is thus evolved:-

(19) $$V = \sum \frac{\pi}{4} h(d_2^2 - d_1^2).$$

In cases where the salt had flowed over the edges of the well the increased area and volume of diffusion was calculated with the use of the proper geometric formulas for circles and cylinders.

Dividing the volume by the area for a given sample gives the distance of diffusion. This value corresponded within experimental error with the actual measured distance from the photographs.

3. Observation of Colors

In all of the tests the color of the diffused portion of the sample and its change and appearance for different temperatures and times was noted.

The samples were also exposed to ultraviolet light with a wavelength of 3650 Å, and the presence and type of fluorescence was observed.

4. X-rays

In order to determine the nature of the colloidal particles Laue X-ray patterns were obtained of several samples into which diffusion from $AgNO_3$ had taken place. A thin wedge of the glass was ground for this purpose.

5. Ultramicroscope

A slit ultramicroscope was used for observation of a glass sample into which diffusion from $AgNO_3$ had been maintained for 36 hours at 900°C. Two surfaces were ground at right angles and highly polished. This was then used in the setup in place of the ordinary cell.

A thin section of the same sample was also made by petrographic methods and examined with a cardioid ultramicroscope.

6. Spectrograph

An approximate quantitative concentration gradient was determined for the above-mentioned sample with a Bausch & Lomb Medium Quartz Spectrograph using spark excitation. This method offers excellent opportunities for further work.

A working or calibration curve was first obtained by making a series of glasses with known silver concentrations, with AgCl as the source of silver. Silicon was used as the internal standard because of its comparatively high concentration with respect to the silver content. The intensities of one of the silver and silicon lines was measured with a microphotometer and their ratios were then plotted against silver concentration as shown in Figure 6. For the determination of an unknown the ratio of the intensities of the same two lines was located on the calibration curve and the silver percentage was read off.

7. Spectrophotometer

A thin slice, about 0.3 millimeters thick, of the above-mentioned sample was prepared. A transmittance curve for various

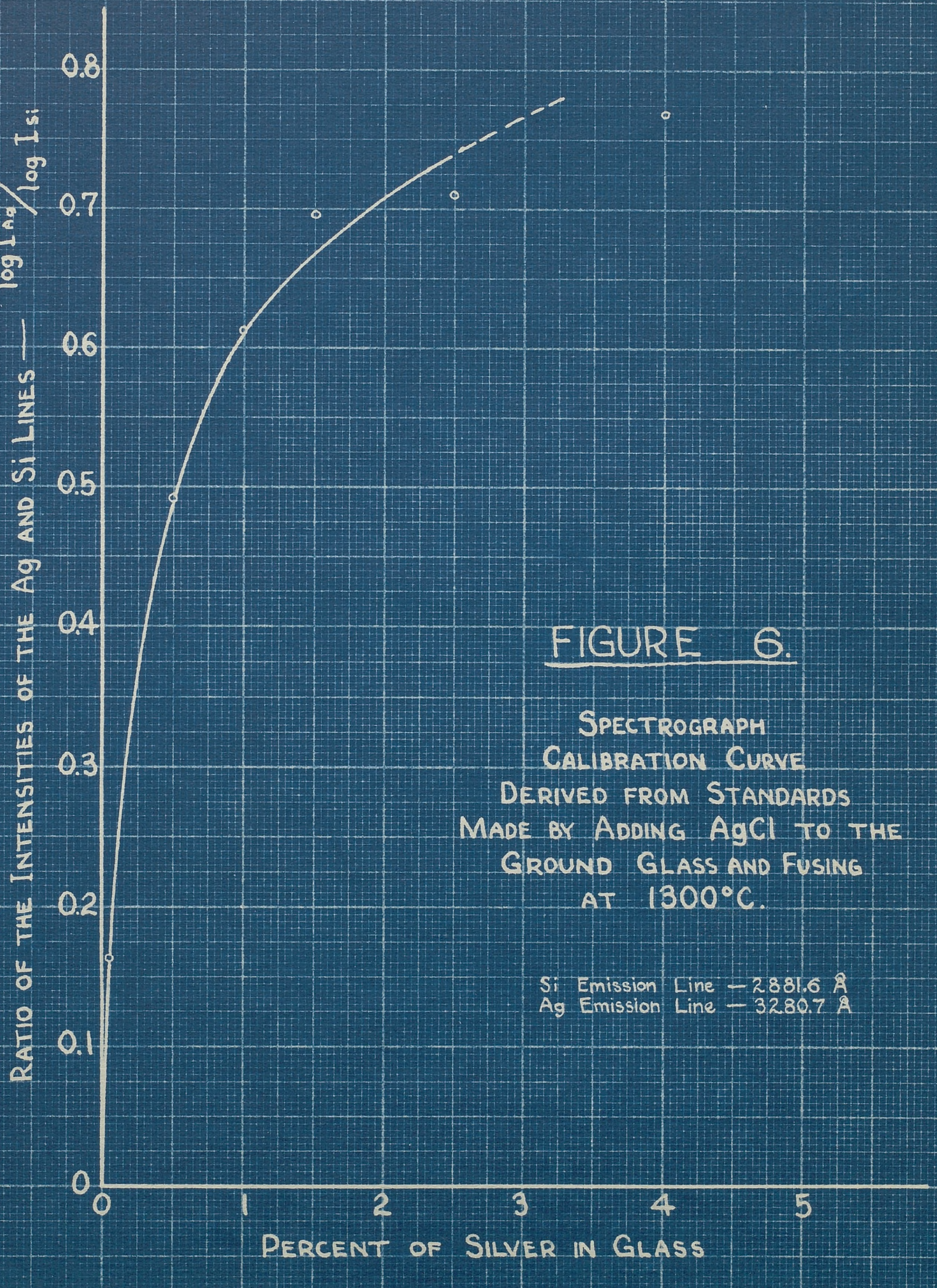


FIGURE 6.

Spectrograph Calibration Curve Derived from Standards Made by Adding AgCl to the Ground Glass and Fusing at 1300°C.

Si Emission Line — 2881.6 Å
Ag Emission Line — 3280.7 Å

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wavelengths was obtained for each of the distinctive areas of diffusion indicated in Plate IV with a G. E. Recording Spectrophotometer.

IV. Results

A. Diffusion from $AgNO_3$ as a Source

Of the silver salts $AgNO_3$ was used the most extensively, and the most complete results were thus obtained with it.

$AgNO_3$ melts at 212°C. and decomposes at 444°C., which is above the decomposition temperature for Ag_2O at 300°C., to form metallic silver. This decomposition is rapid causing some of the contents to boil over the edge of the well forming a larger area and volume of diffusion. It is noted that above the decomposition temperature the source of silver is no longer $AgNO_3$ but metallic silver which is in very close contact with the glass.

All of the tests were performed under nonrestricted diffusion since the samples were thick enough so that the diffusing material at no time reached the outer edges of the cups.

1. General Appearance

Examination of Table 2 shows that color variation is dependent mainly upon the temperature and that extended time has little effect. Below the softening point of the glass the diffusion color is a dark reddish-brown. Above, bands of different shades of color and translucency are formed in addition to the brown which is the furthest from the source of diffusion.

With ultraviolet light, however, it is observed that both temperature and time are important. For instance, for samples exposed to diffusion for 108 hours the brightest fluorescence was present at 400°C. On the other hand at 500°C. the fluorescence was good

Table 2.

Diffusion Data with Regard to $AgNO_3$

Temp. °C.	Time Hrs.	Area of Diffus. Cm.^{2}	Volume of Diff. Cm.^{3}	Distance of Diff. Cm.	Wt. Inc. per Area Gm/Cm.^{2}	Wt. Inc. per Vol. Gm./Cm.^{3}	Color	Fluorescence
200	108						Faint brown	Very faint yel.
300	108	3.87	.031	.008	.0081	1.614	Reddish brown	Yel.-brown
400	108	3.16	.129	.036	.0931	.811	" "	Bright yellow
500	108	10.00	.768	.080	.0058	.076	" "	Faint lt. Br.
500	36	7.86	.390	.050	.0069	.139	" "	Yellow
500	12	8.46	.350	.040	.0096	.231	" "	"
500	6	6.28	.204	.034	.0097	.298	" "	"
*500R	12	5.30	.133	.026	.0049	.193	" "	"
600	12	9.56	.699	.076	.0053	.072	Brown	Very faint br.
700	12	8.74	1.850	.19	.0133	.063	Dark br. with lt. band on edge	None
900	36	8.53	3.477	.44	.0421	.103	Bands of diff. colors - yel.-white, clear & gray, br.yel., red.-brown.	Yellow bands give yel.-wh. flu., red.-br. gives yel.
900	12	7.76	2.960	.34	.0390	.102		
900	6	7.63	1.922	.22	.0308	.122		
900	3	7.57	1.550	.18	.0242	.118		
900	0	8.55	.858	.10	.0136	.135		
1100	6						Br., Yellow rings	Yellowish around edges

* Reducing conditions

(Br. = brown; lt. = light; yel. = yellow; wh. = white) for short test time intervals but began to fade in pieces held for 108 hours. At higher temperatures fluorescence is present only in some of the rings.

After the residue had been dissolved, it was noted that there was some reaction between the salt and the glass surface because the surface was rough and pitted.

$AgNO_3$ was also tried in a tube made of Corning D172 glass at temperatures up to 700°C. with no appearance of diffusion or reaction. With Pyrex glass tubes a lighter brown color and a smaller distance of diffusion was noted with presence of some reaction.

2. Effect of Time on Distance of Diffusion

The curves for $AgNO_3$ at 500°C and 900°C. are shown in Figure 7, drawn with data from Table 2. The curves do not start at zero distance since the samples were heated with the furnace and some diffusion had occurred before the constant test temperature was reached.

The time rate of diffusion is not constant for extended times. In the early stages it is rapid and close to constancy, followed by a decrease.

The photographs in Plate I show the actual appearance of the samples at 500°C. for varying test time intervals.

3. Effect of Temperature on Distance of Diffusion

Figure 8 illustrates the curves for $AgNO_3$ at 12 and 108 hours. Both are seen to approach the temperature axis asymptotically and do not have a constant temperature rate.

For 108 hours at 200°C. there was no measurable distance of diffusion, but a surface discoloration was present. At about 500°C. there is a comparatively rapid increase in diffusion which may be due

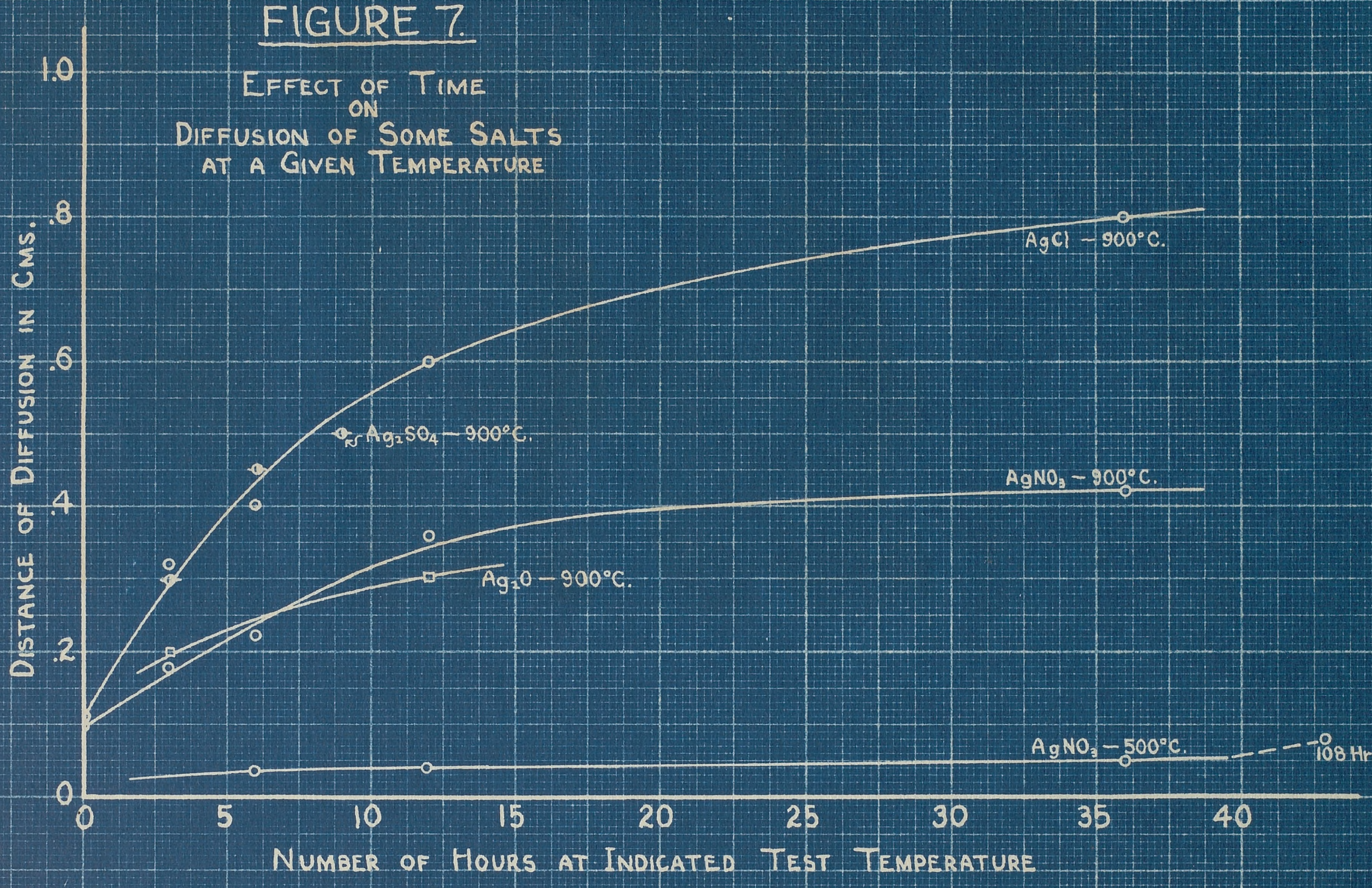

FIGURE 7.

EFFECT OF TIME
ON
DIFFUSION OF SOME SALTS
AT A GIVEN TEMPERATURE

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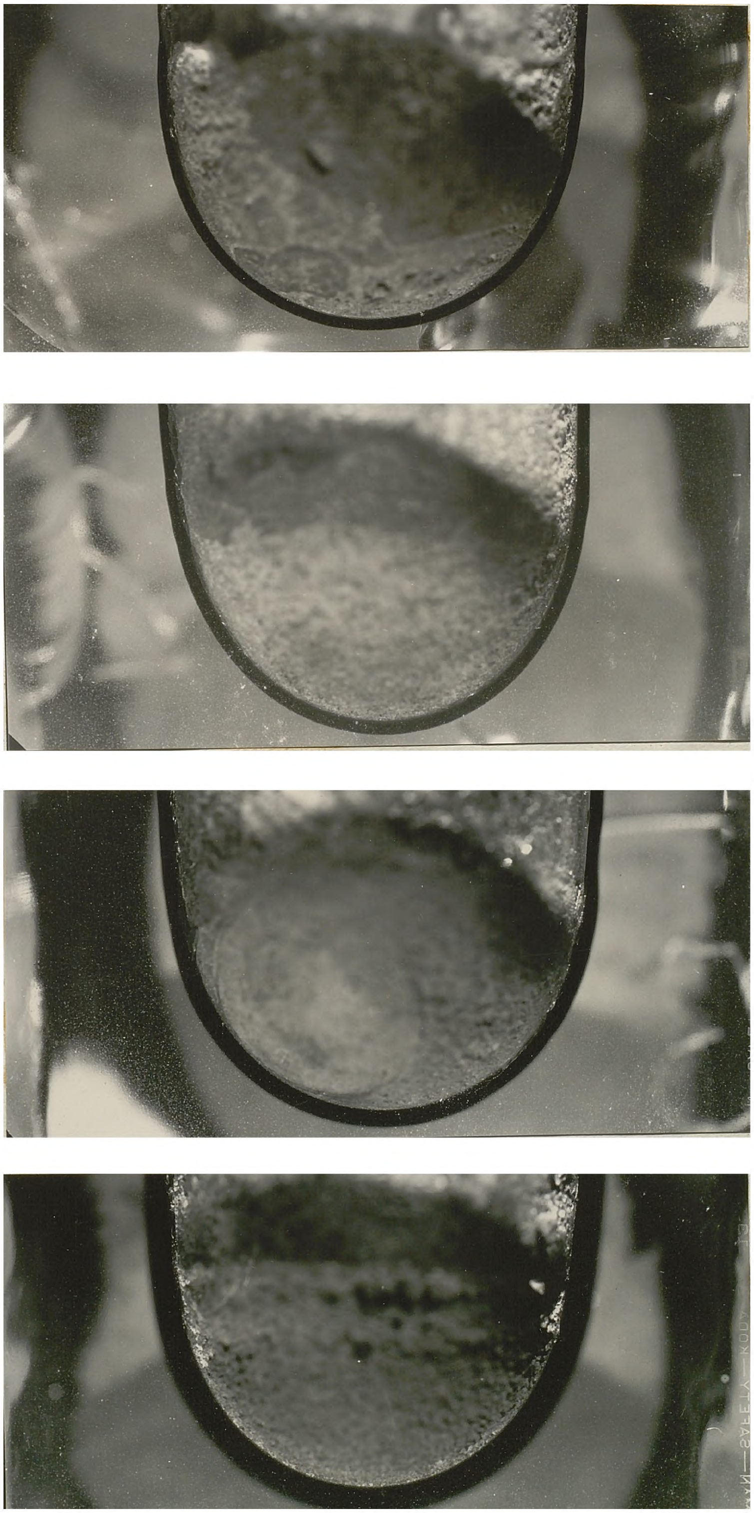


6 Hours

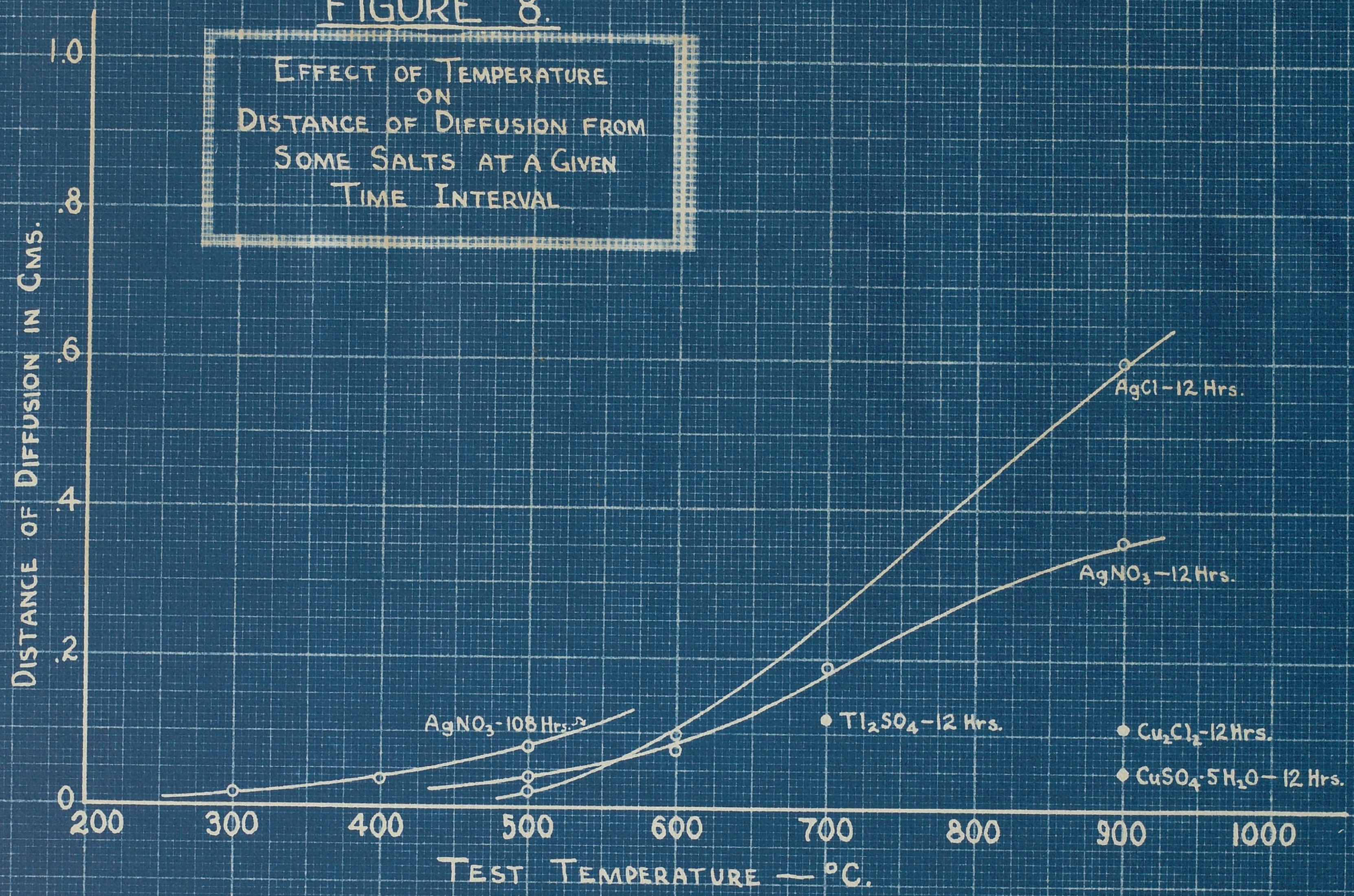
12 Hours

36 Hours

108 Hours

PLATE I: Amount of Diffusion with Varying Time at 500°C.
Using $AgNO_3$ at the Start of the Test.
5X Magnification.

FIGURE 8.



EFFECT OF TEMPERATURE ON DISTANCE OF DIFFUSION FROM SOME SALTS AT A GIVEN TIME INTERVAL

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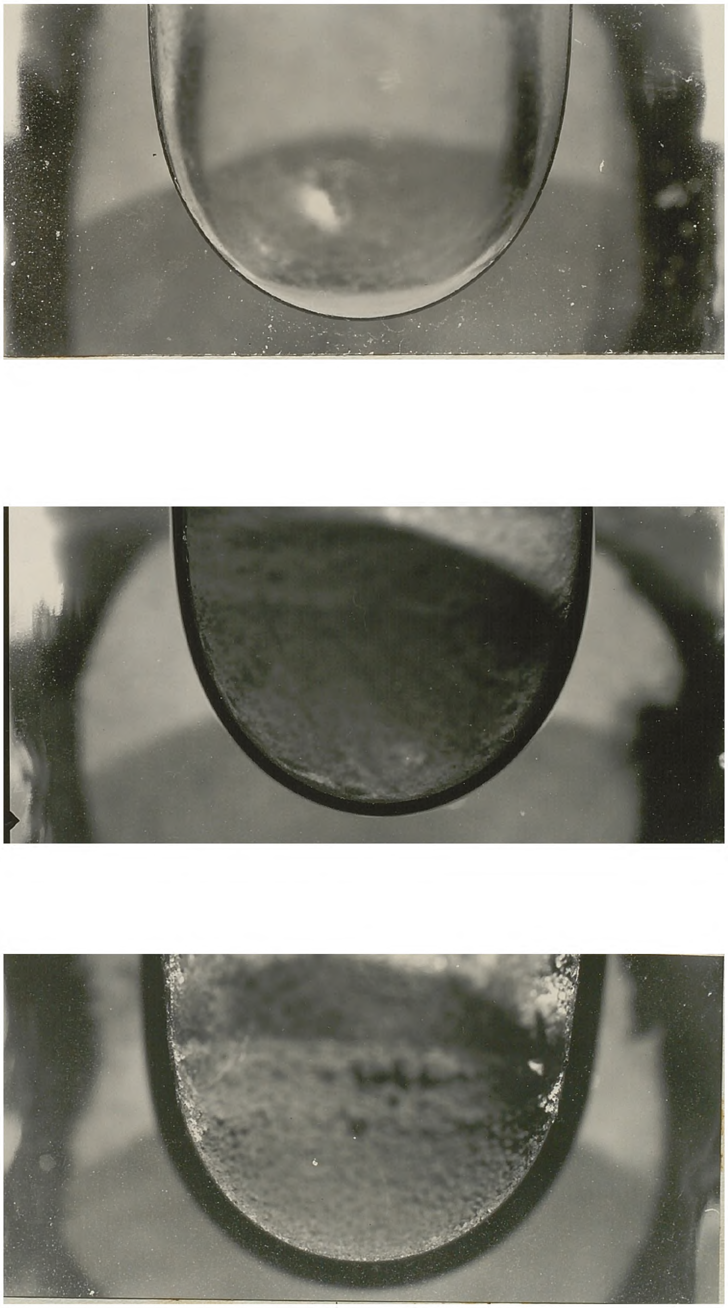
to the decomposition of the nitrate. Plate II shows photographs from which data for this curve was obtained.

For 12 hours test time there is a rapid increase in distance of diffusion at about 700°C. This is due to less resistance offered to the passage of silver particles. At temperatures above the softening point a large number of bonds in the glass structure are broken resulting in larger holes. The curve flattens out at 900°C, but probably would again increase rapidly at about 1100°C. due to accelerated decrease of the viscosity of the glass. Plate III shows the appearance of these samples. Especially noticeable is the presence of a number of layers above 600°C.

At temperatures up to 900°C. convection currents, which are the most difficult factor to cope with in diffusion experiments with aqueous solutions, offer no difficulties since the viscosity of the glass is sufficiently high. Above this temperature, however, convection currents were present and interfered with measurements of diffusion.

4. Variation of Concentration with Diffusion

Relation of the silver concentration in the diffused portion of the glass at 500°C. and 900°C. to the time of test is shown in Figure 9. There is a considerable drop in concentration at 500°C. indicating that the migration of new silver ions into the glass is greatly slower than the diffusion of the ions already in the glass. At 900°C. the drop is slight, in turn, indicating that the passage of the silver particles into the glass is practically as rapid as the diffusion of the particles into the glass. According to Fick's law the rate of diffusion within a medium is proportional to the concen-

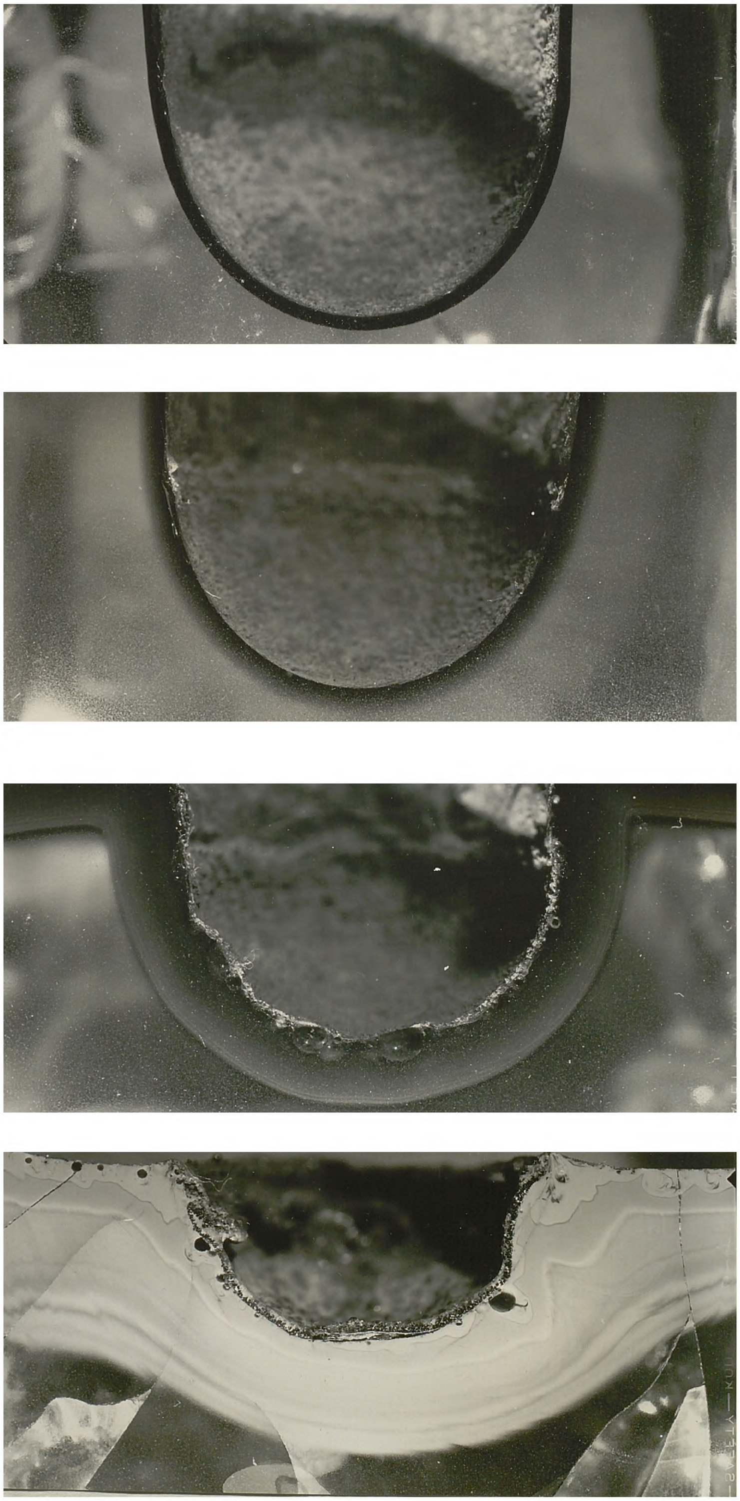


300°C.

400°C.

500°C.

PLATE II: Amount of Diffusion with Varying Temperature at 108 Hours Using $AgNO_3$ at the Start of the Test. 5X Magnification.



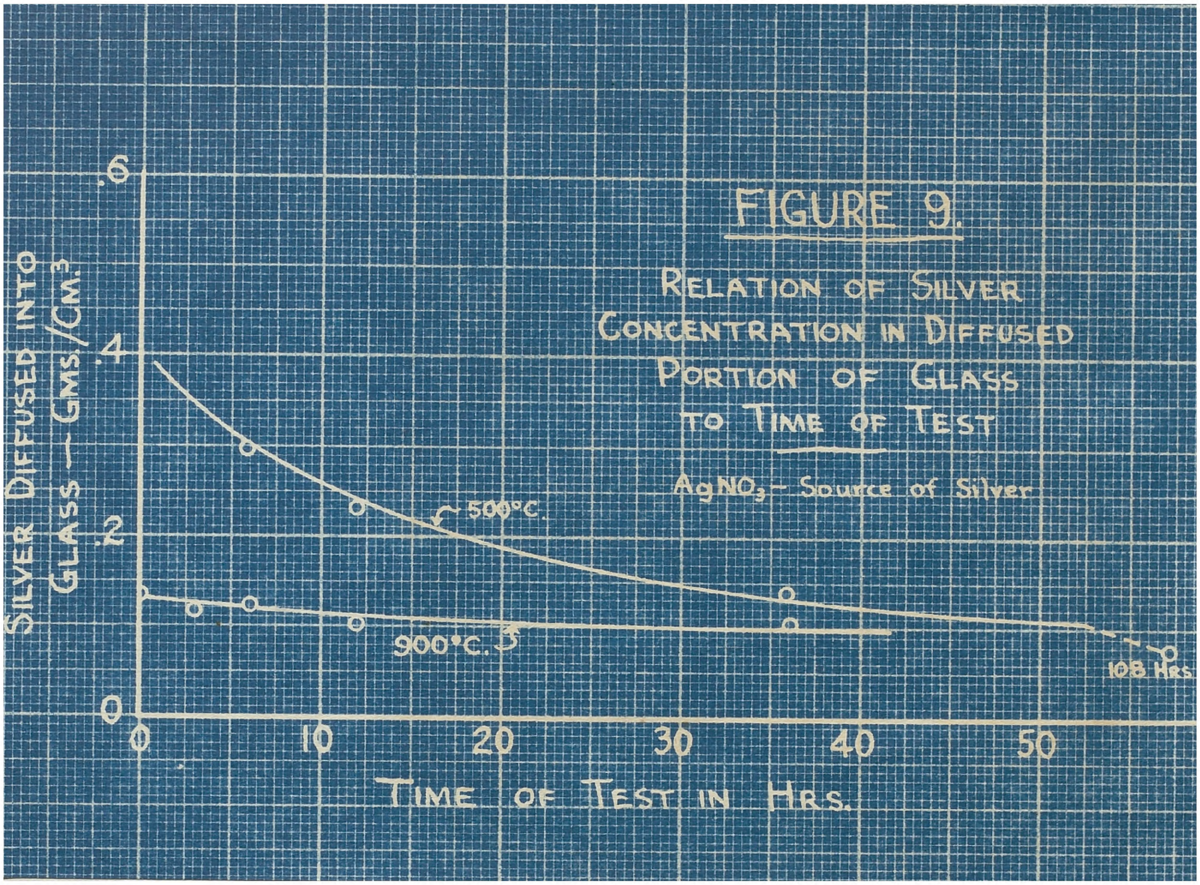
500°C.

600°C.

700°C.

900°C.

PLATE III: Amount of Diffusion with Varying Temperature at 12 Hours Using $AgNO_3$ at the Start of the Test. 5X Magnification.



tration difference. The difference within the glass is greater at 900°C., thus resulting in a faster rate of diffusion.

On the other hand, Figure 10 is a plot of the concentration in the diffused portion against the distance of diffusion. All the test points for $AgNO_3$ are located and marked. The curve shows a marked break in slope in the region of the softening point of the glass. It is reasoned that there is a marked difference in the nature of the diffusion on either side of this temperature range. The rapid drop in concentration at the lower temperatures indicates a marked resistance on the part of the glass to diffusion. At higher temperatures the glass offers relatively little resistance since the concentration is practically constant with increased distance of diffusion. At higher temperatures where a marked decrease of viscosity

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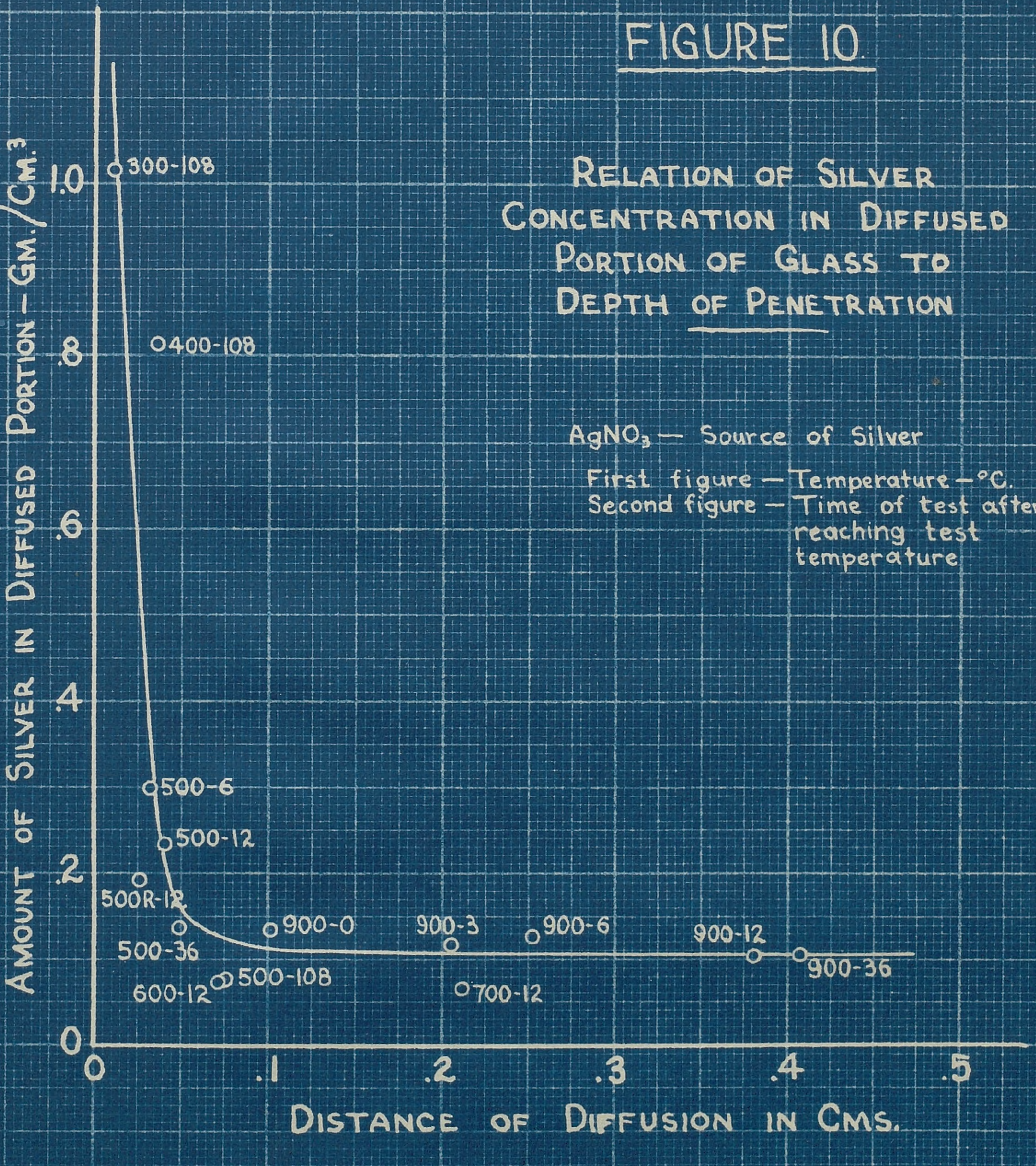
FIGURE 10

RELATION OF SILVER CONCENTRATION IN DIFFUSED PORTION OF GLASS TO DEPTH OF PENETRATION



$AgNO_3$ — Source of Silver

First figure — Temperature — °C.
Second figure — Time of test after reaching test temperature

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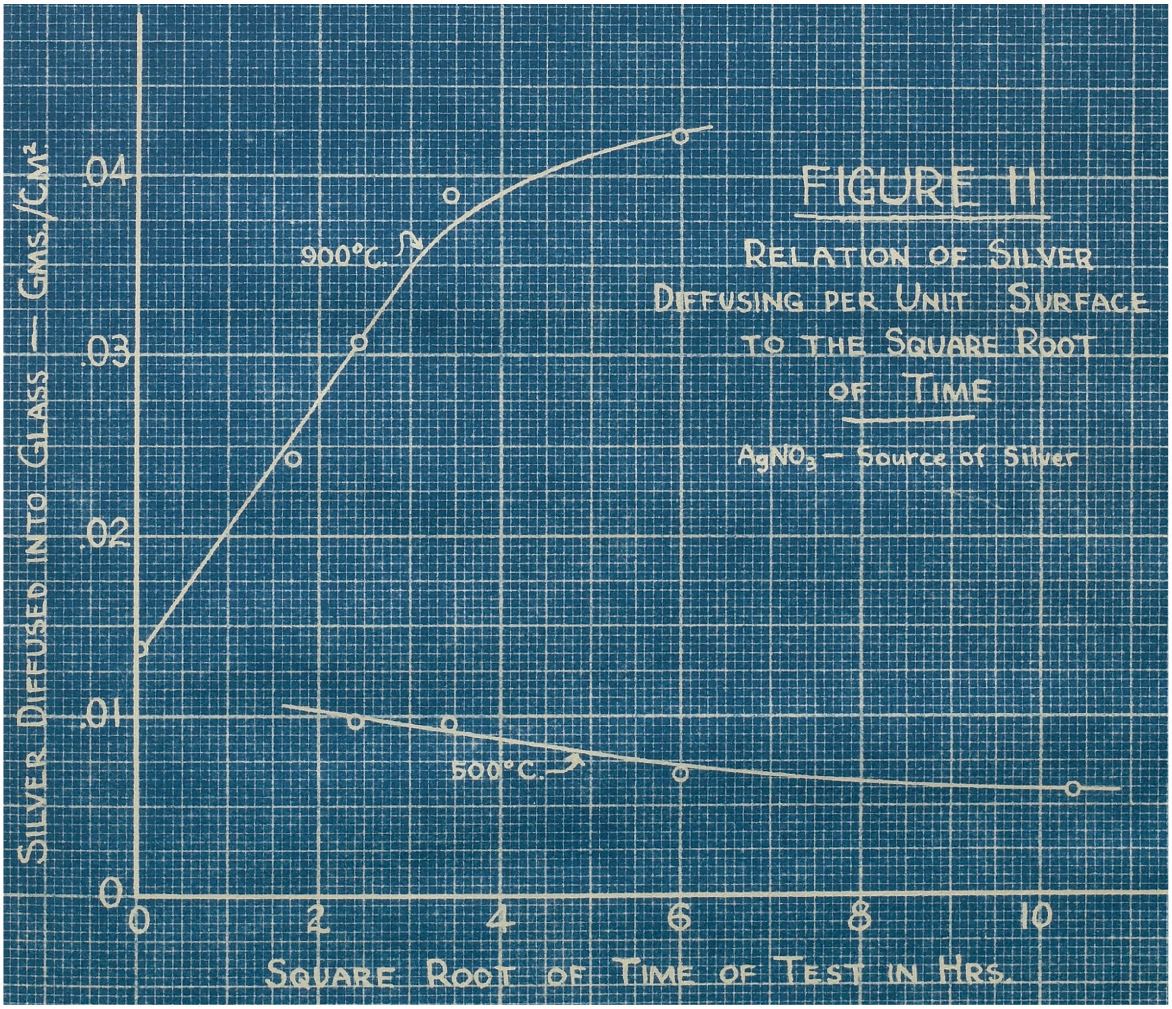
would occur it is logical that the curve would again have a change of slope and start to show an increase in concentration with distance.

5. Test of Fick's Law

According to Equation 4 if Fick's law with a constant diffusion coefficient applies, M, the grams per square centimeter, should be proportional to the square root of time. Graphically a straight line should be obtained. Figure 11 indicates this relation. At 900°C. a straight line is obtained for the early stages of the experiment, but as indicated by the point off the line at 36 hours the so-called diffusion constant changes for longer times. The high



resistance of the glass to diffusion at 500°C. is again indicated by the curve in this Figure. The slightly negative slope of the curve is doubtful since small experimental errors can produce this effect. However, the indication of a curve with a flat slope is still present. The extent of the straight line portion is thus unknowm.

6. Silver Concentration Gradient

Schulze [10) showed in his work at temperatures of about 400°C. that there was a straight line drop in concentration of silver from the surface to the interior of the specimen. At temperatures above the softening point, or specifically 900°C. in this case, rings of different colors were obtained. It was of interest to determine if there also was a straight line drop in concentration here.

Plate IV is a photograph with 5x magnification of a sample exposed to 900°C. for 36 hours. The areas referred to below are indicated on the Plate:-

Area 1 -- Clear glass
Area 2 -- Clear amber brown
Area 3 -- Opaque bluish-white, with transmitted light - brown
Area 4 -- Clear gray with yellowish tinge
Area 5 -- Opaque yellowish-white

Examination with an ultramicroscope revealed that all of the colored areas produced a Tyndall cone. However, a continuous change in the number of particles was not present. A relative approximation of particles per unit microscopic area showed:- Area 1, none; Area 2, too concentrated to make a count; Area 3, about 475; Area 4, about 6; and Area 5, about 1300.

A graphical analysis of the colors of the areas is shown by means of Spectrophotometric curves, as in Figure 12. Areas 2, 3 and 5 show a high transparency in the long wavelengths, thus producing

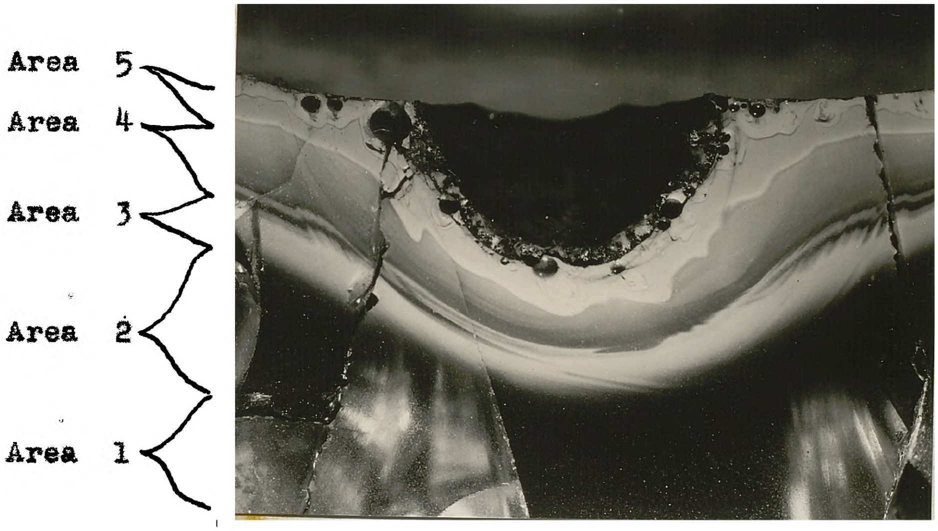
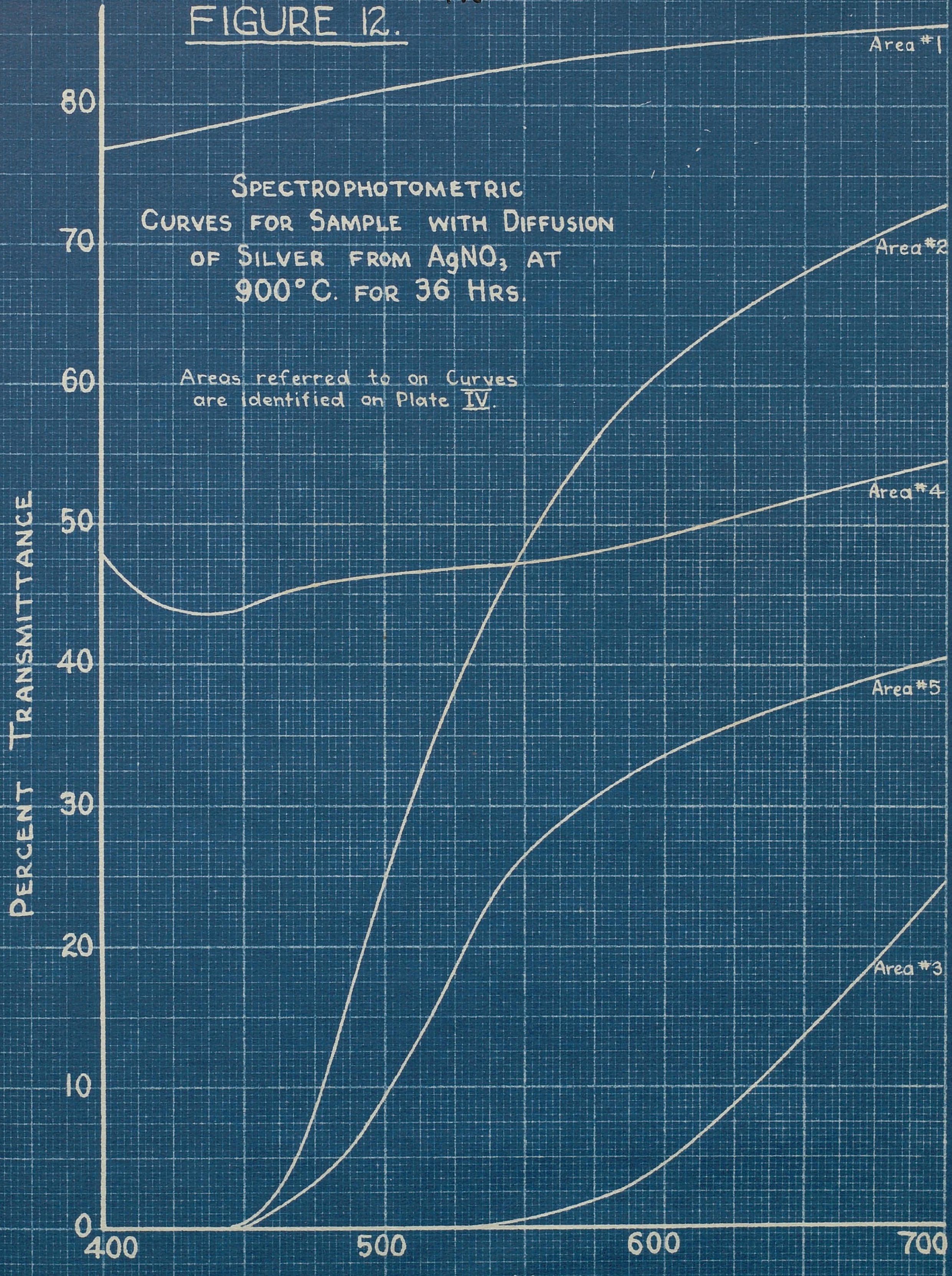


PLATE IV: Sample Showing Diffusion at 900°C. for 36 Hours Using AgNO$_3$ at the Start of the Test. 5X Magnification.

FIGURE 12.



SPECTROPHOTOMETRIC CURVES FOR SAMPLE WITH DIFFUSION OF SILVER FROM $AgNO_3$ AT 900°C. FOR 36 HRS.

Areas referred to on Curves are identified on Plate IV.

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the yellows and the browns. Curve for Area 4 indicates a grayish color since transparency is practically constant for all wavelengths.

Figure 13 was drawn with spectrographic data, using Figure 6 and measurements from Plate IV. A straight line drop in concentration was obtained down to the low percentages of silver where it deviated to approach the distance axis asymptotically. This curve and the ultramicroscopic observations indicated that the number of particles is not a criteria of concentration and that the size of the particles must vary considerably. The data agreed with the theory presented by Warburg 6), and varied slightly from Schulze's experimental results.

X-ray photographic exposures of the brownish and yellowish-white areas showed very faint presence of lines corresponding to those for metallic silver.

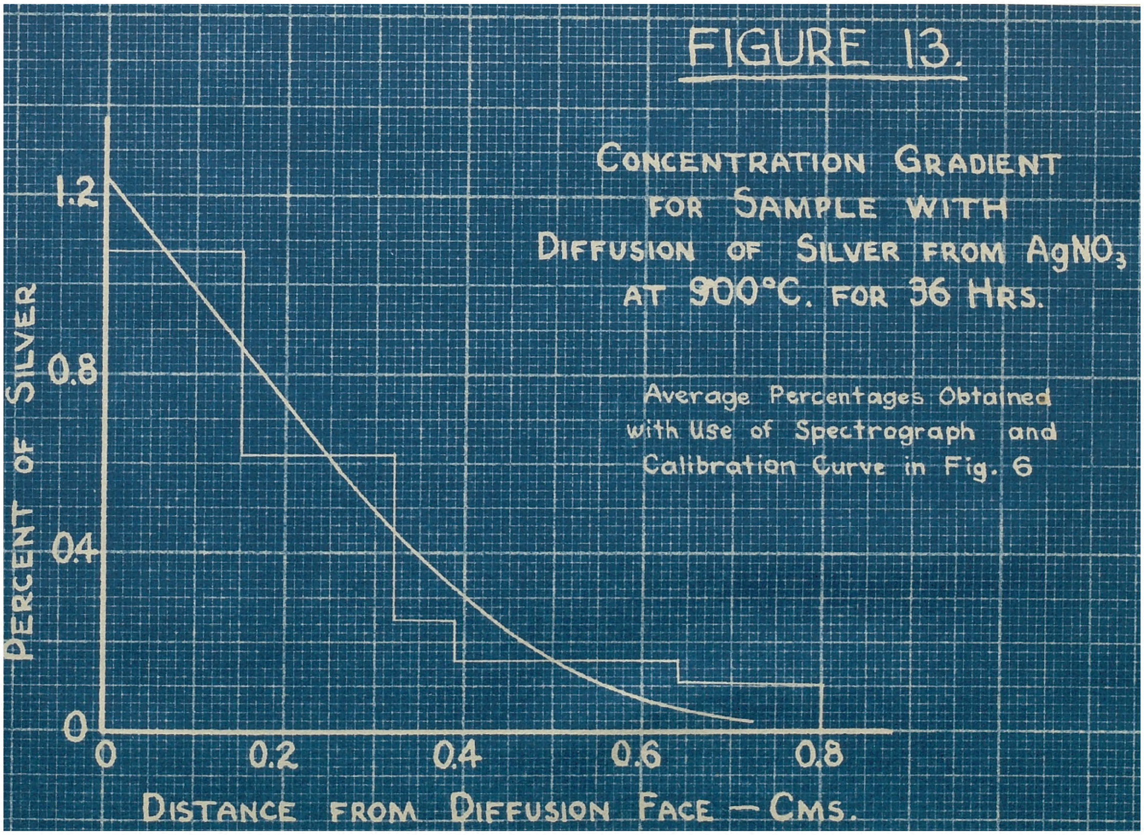


FIGURE 13.

CONCENTRATION GRADIENT FOR SAMPLE WITH DIFFUSION OF SILVER FROM $AgNO_3$ AT 900°C. FOR 36 HRS.

Average Percentages Obtained with Use of Spectrograph and Calibration Curve in Fig. 6

7. Diffusion Constant

The diffusion constant as calculated with Equation 3 can not be obtained since M_s, the silver saturation value, was not determined. However, with the data available in Figure 11 it is indicated that D would be a constant only in the comparatively early stages of diffusion since the curves are not straight lines for the entire test time interval.

B. Diffusion from Other Silver Salts as a Source

In addition to the $AgNO_3$, $AgCl$, Ag_2SO_4 and Ag_2O were used for a number of tests. For these salts, the following data is listed:

Salt	Melting Point	Boiling Point
$AgCl$	455°C.	1550°C.
Ag_2SO_4	652°C.	decomposes
Ag_2O	decomp., 300°C.	------

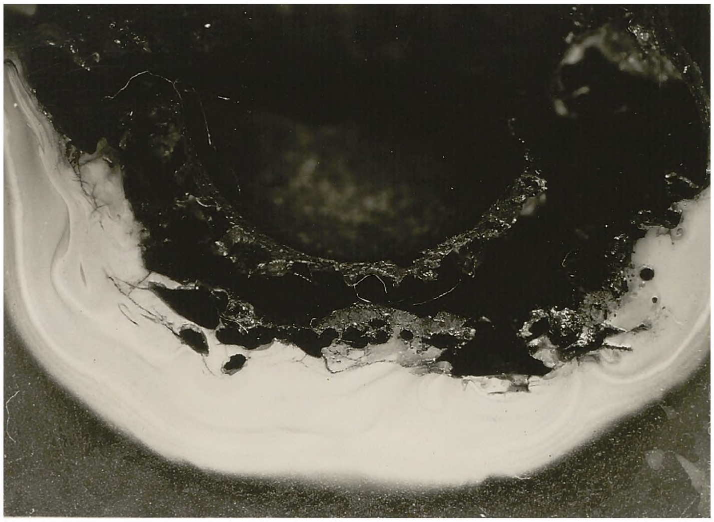
1. General Appearance

Table 3 lists the colors and the fluorescence of the samples in this group. The colors are, in general, the same as for $AgNO_3$ indicating that regardless of the manner of migration of the particles their physical nature is approximately the same.

Plate V-A pictures the appearance of a sample with Ag_2SO_4 as a source of diffusion. An area showing a marked cellular structure is present between the normal diffusion and the outline of the original well formed by metallic silver from the decomposition of the sulphate. A reaction or strong effusion of a gas is evidently responsible.

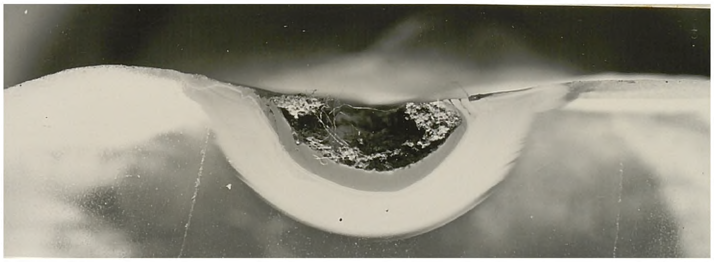
With Ag_2O as a source the results both in oxidizing and CO atmospheres are shown in Plate V-B. Blebs are formed with a reducing atmosphere which do not appear under oxidizing conditions, and also

A.



B.

Oxidizing
Atmosphere



Reducing
Atmosphere

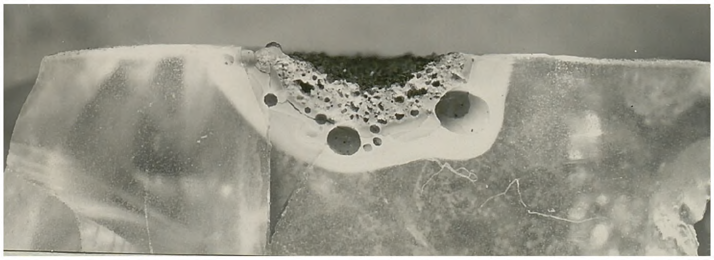


PLATE V: A. Ag_2SO_4 as Source of Diffusion at 900°C. for 6 Hours.
B. Ag_2O as Source of Diffusion at 900°C. for 3 Hours in Oxidizing and Reducing Atmospheres.
5X Magnification.

Table 3.

Diffusion Date with Regard to Other Silver Salts

Salt	Temp. °C.	Time Hrs.	Distance of Diff. Cm.	Color	Fluorescence
$AgCl$	500	12	.020	Clear amb. brown	Yellow
	*500R	12	.015	" " "	"
	600	12	.10	" " "	Faint yel.br.
	900	36	.80	Rings of brownish-yellow, yellow, dark gray	Faint brown in certain portions
		12	.60		
		6	.40		
		3	.32		
		0	.11		
Ag_2SO_4	700	12	.30	Brown, with bands of yel. and blue	None
	900	12	.60	Yellowish, also bluish-gray. Cellular react. layer present	Yellow and orange in some of the rings
		9	.50		
		6	.45		
		3	.30		
Ag_2O	900	12	.3	Yellowish	Yellowish - str. around center
		3	.2	Yel.-blue gray	
	*900R	3	.12	Yellowish	

* Reducing conditions.

the extent of the diffusion is not as great.

Samples with AgCl as a source of silver do not show any cellular structure. At 500°C. there was no noticeable attack on the glass.

2. Diffusion Data

Distance of diffusion against temperature at 12 hours test time for AgCl as a source is plotted in Figure 8. The curve is similar in shape to the others, but rises more rapidly, being diffused roughly twice as far as that for $AgNO_3$ at 900°C.

Figure 7 shows the curves for distance against time of test. All of them are again similar in shape. At 900°C. and 36 hours distance is about twice as far with AgCl as with $AgNO_3$. The Ag_2SO_4 curve roughly corresponds to that for AgCl and Ag_2O to that for $AgNO_3$.

In the case of AgCl and Ag_2SO_4 the particles diffusing therefrom must be smaller. Also, due to the fact that no reaction was present with the use of AgCl, the diffusing particle was likely a simple ion. In the case of the other silver salts the diffusing particle was probably a complex one and may have consisted of some complex ion or atom.

3. Effect of Reducing Atmosphere

Plate V-B and data in Table 3 indicate that a reducing atmosphere of CO had a considerable effect on diffusion from Ag_2O. This corresponds with Kubaschewski's theory that oxygen plays an important part. It is possible that the diffusing particle at some stage is a combination of silver and oxygen. However, the theory does not have general application since the distance of diffusion from AgCl in both atmospheres is within experimental error.

C. Diffusion from Non-Silver Salts

A number of other salts were selected to determine their tendency for diffusion and the resulting colors. The properties of these salts are:-

Salt	Melting Point	Boiling Point
$AuCl_3$	254°C. decomp.	
Co_3O_4	?	?
$CuSO_4$	d. 650°C. to CuO	
Cu_2Cl_2	422°C.	1366°C.
$CrCl_3$	?	1200-1500°C.
$FeCl_3$	282°C.	315°C.
$PbCl_2$	501°C.	950°C.
$PtCl_4$	decomposes	
Tl_2SO_4	632°C.	decomposes
V_2O_5	800°C.	?

The results with the above salts are listed in Table 4. Only those of copper, thallium and vanadium showed any diffusion. The copper formed a blue coloration, and the others, colorless. In all cases of diffusion fluorescence was also found to be present.

Figure 8 includes the measured points for these salts. It is noted that the order of increasing diffusion with the salts as a source is $CuSO_4.5H_2O$, Cu_2Cl_2, Tl_2SO_4, $AgNO_3$, AgCl.

Some type of reaction between the copper salts and the glass occurred since a cellular structure was formed. Tl_2SO_4 as a source showed a colorless but easily noticeable diffusion because of the large difference in indeces of refraction. Thallium remains in solution on cooling rather than segregating at crystallization centers as the silver.

D. Liesegang Rings

A Liesegang ring development was observed in some of the specimens with diffusion from all of the silver salts at temperatures above the softening point of the glass.

Table 4.

Diffusion Data with Regard to Non-Silver Salts

Salt	Temp. °C.	Time Hrs.	Distance of Diff. Cm.	Color	Fluorescence
$AuCl_3$	600	12	None	Reduced to metallic Au	
	900	12	None		
Co_3O_4	900	12	None		
$CuSO_4$	900	12	.05	Blue, slight reaction	Yellowish around center
Cu_2Cl_2	600	12	None	Blue surface.	None
	900	12	.11	Vesicles present	Bluish & Yel.
$CrCl_3$	900	12	None	Surface discol.	
$FeCl_3$	900	12	None	" "	
$PbCl_2$	700	12	NoneGla	Glass attacked along melt line	None
$PtCl_4$	600	12	None		
Tl_2SO_4	700	12	.12	None, but diff. index present	Faint yellow
	900	12	?		Yellow
V_2O_5	900	12	?	None	Yellow on surface

Plate VI shows photographs of a specific case of diffusion from $AgNO_3$, as the original source, at 900°C. for 12 hours. The magnification is 9.2 times. A was taken with transmitted light using Wratten filters D + H and B with ultraviolet illumination. In the latter the yellowish fluorescent areas appear as the lighter portions, and the darker portions represent areas of absorption or non-emission. The Liesegang rings appear in the grayish area, corresponding to Area 3 in Plate IV.

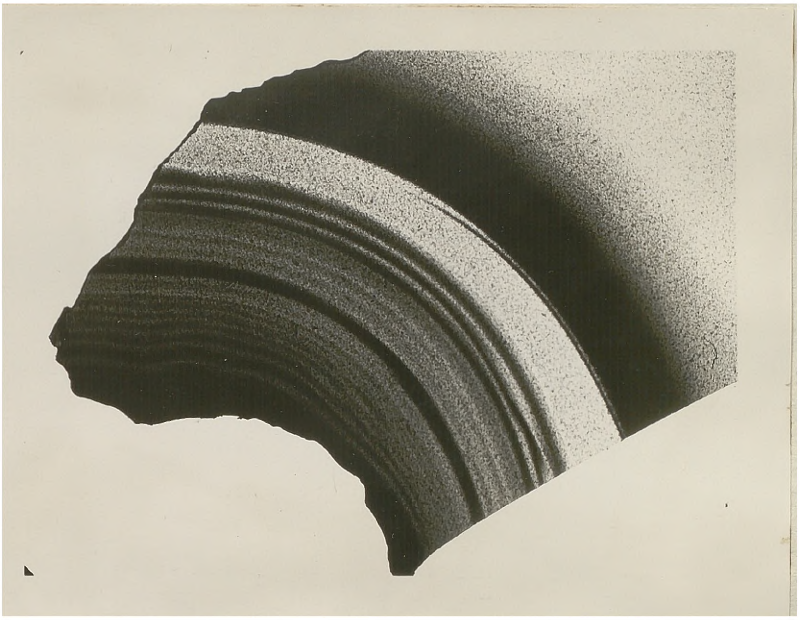
Though this phenomenon had appeared in several tests for all the silver salts, it was not simple to reproduce. Since there was no introduction of impurities, it was theorized that the rings would appear with variation in either the cooling or heating schedule. Accordingly, samples were prepared and the cooling was varied as follows -- cooling with the furnace, holding at 600°C. for one hour -- with no appearance of strong rings. In one test a heating cycle was followed whereby the temperature was held at 600°C. with better appearance of rings.

However, in the time available it was not possible to satisfactorily reproduce this condition which had appeared more or less accidently. It is thought that at some point during the long constant temperature period there was actually a drop in temperature for a short time. It is probable that in the grayish portion of the diffusion the concentration of silver particles is such that conglomeration readily occurs and any thermal disturbance would cause a departure from uniformity.

V. Discussion

The occurrence and rate of diffusion is dependent on both the glass and the salt providing the diffusing particles.

A. Transmitted Light with D+H Filters



B. Ultraviolet Light

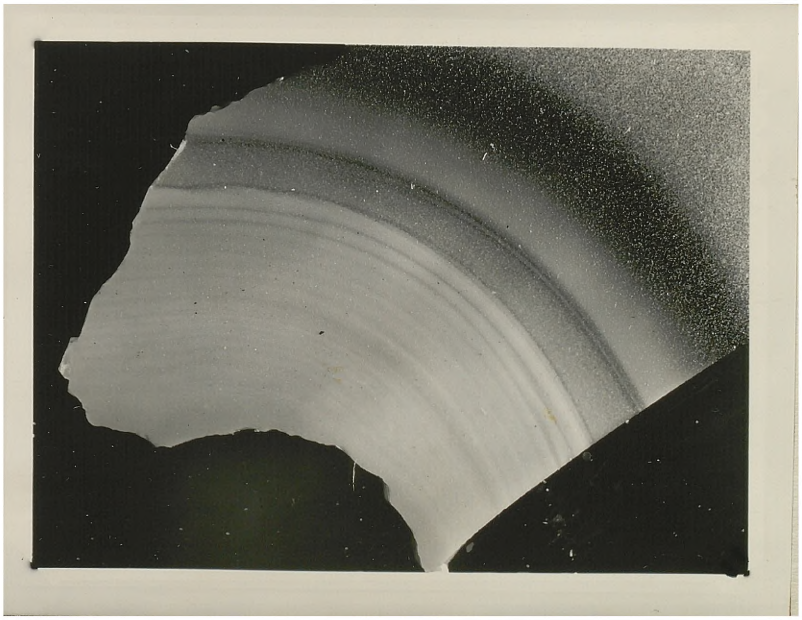


PLATE VI: Liesegang Rings in Sample with $AgNO_3$ as Source of Diffusion at 900°C. for 12 Hours. 9.2X Magnification.

The flint glass used permitted diffusion, but a few samples of glass high in silica did not do so under the same conditions. Two types of diffusion are present: replacement of alkali ions within the glass or penetration of particles of some kind into the holes of the glass.

The former type is present at all times providing ions from the salt are available and, in general, it is the predominant type for cases occuring at temperatures below the softening temperature of the glass. The latter type is commonly present, usually in addition to the former, at temperatures above the softening point. Here, the expansion of the glass and the breaking of bonds in the glass structure form openings for passage of larger particles. In a pure silica glass, for instance, the latter type of diffusion would be the only kind present and, consequently, would be slow and would occur at elevated temperatures.

The source of diffusing particles is a controlling factor in the diffusion process. At temperatures below the softening point of glass the salt must provide simple cations. Complex ions, however, may also penetrate into the surface layers a short distance. These ions can be provided in one of the following ways:- a) molten salt with sufficiently high ionization constant at the test temperature, b) sufficiently high vapor or dissociation pressure, and c) reaction with the glass resulting in the formation of cations. After their formation the ions then must be of such a size as to be able to penetrate into the glass openings. Those particles that enter the glass will have their rate of movement controlled by their effective size -- the smaller ones moving the fastest.

Above the softening temperature of glass the rate of diffusion is found to increase due to easier passage for the cations and also because larger complex ions and perhaps atoms are capable of penetration. The presence of complex forms is suggested by two conditions. First, with a salt containing oxygen the oxygen content or pressure of the atmosphere affected the rate of diffusion. Secondly, cellular surfaces indicated movement of complex ions or molecules with subsequent decomposition or reaction in the glass.

Therefore, it is apparent that it is difficult to compare different salts at a given temperature as to their ability to provide diffusing particles since there are so many conditions involved. Also, just a few of the salts tested showed occurrence of diffusion under the present experimental methods. However, entirely different results may be obtained if diffusion of a certain cation is promulgated from a different source -- as two glasses in contact, for instance, one already containing the diffusing ion and the other not.

The results indicate that the physical nature of the glass is important and that broadly the type of diffusion changes at critical temperature ranges, such as the softening point temperature and probably the temperature at which an appreciable drop in viscosity occurs. Below the softening point the glass offers greater resistance to entrance of ions into the glass and there is a rapid drop in concentration in comparison to the movement of ions into the glass. Whereas, above the softening point the entrance of particles is as great as their movement into the glass thus maintaining practically a uniform concentration with increased distance of diffusion.

The colors appearing on diffusion are due to different states of dispersion of the particles as a result of the crystallization of the material diffused into the glass. It is possible that certain concentrations are subject to a definite degree of crystallization. Consequently, with the presence of a range of concentrations a series of colored rings are formed.

One of these areas of a given concentration is probably more sensitive to thermal effects than the others resulting in different states of aggregation which in turn form bands resembling Liesegang rings. The theory is then proposed that the rings in an experimental condition of this type are a result of a combination of a definite concentration and the presence of certain thermal conditions rather than the result of a precipitation due to supersaturation alone or to a reaction with the formation of a new salt.

VI. Summary

A. Experimental Work

Instead of having a molten bath of the salt into which the sample was immersed, as done by the previous investigators, a sample was devised which acted as the salt container itself thus enabling the extension of the test temperature range up to 1100°C.

Of the following salts tested -- $AgNO_3$, $AgCl$, Ag_2SO_4, Ag_2O, Cu_2Cl_2, $CuSO_4$, V_2O_5, $CrCl_3$, $PbCl_2$, Tl_2SO_4, $AuCl_3$, $PtCl_4$, Co_3O_4 and $FeCl_3$ -- those of silver, thallium and vanadium diffused. The increasing order of ionic sizes is vanadium, silver, and thallium which also approximately corresponded to the rates of diffusion. Copper salts showed a reaction with the glass with a possible diffusion. If that were the case, the diffusing particle probably was a complex one since its apparent diffusion was much less than that for silver even though its cation is smaller than the silver cation.

The rate of diffusion for $AgNO_3$ at a given temperature is practically constant up to about 10 hours test time and then falls off. In 36 hours the distance of diffusion at 900°C. is 0.42 cm. and at 500°C. is 0.05 cm. AgCl at 900°C is 0.8 cm.

The increase of diffusion for a given time with temperature rise is more rapid. A break is shown at the softening temperature and another is probably present at the temperature of rapid decrease of viscosity.

Concentration of silver from $AgNO_3$ with distance of diffusion shows a sharp change at the softening temperature of the glass.

Fick's law as generally given holds for a limited time at the beginning of the experiment. Consequently, the so-called diffusion constant is not constant throughout the entire test period.

The concentration gradient is a straight line approaching the distance axis asymptotically. Therefore, the size of the particles in the colored bands in the specimens above the softening point do not vary progressively since the number does not vary continuously.

In the gray diffused portion Liesegang rings were found to occur under certain experimental conditions.

B. Suggestions for Future Work

Future experimental work on this subject can make greater use of the spectroscope. A more careful calibration curve can be obtained with the use of an internal standard providing a line closer to the silver. This, then, in combination with the ultramicroscope offer possibilities of determination of the particle sizes and their relation to the appearance of the different silver colors.

The instrument can undoubtedly also be used for study of diffusion of non-coloring material including essential constituents in the glass. This would benefit studies on homogeneity.

Variation of the compositions of the glasses and their effect on the rate of diffusion would offer suggestions as to the types of glasses that are more easily obtained in a homogeneous condition. Presence of certain catalyzers with the diffusing salts may have an accelerating effect.

Diffusion phenomena should also be studied with the diffusing particle originating from some other source rather than the salt itself, such as the application of the Ludwig-Soret effect.

AgCl, which showed the apparent diffusion of silver ions should be studied at more temperatures and more extended times to verify the theories as suggested with the $AgNO_3$ experiments.

VII. Acknowledgments

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IX. Vita

Joseph Adam Pask was born in Chicago, Illinois on February 14, 1913. He attended Lindblom High School in that city. On graduation he entered the University of Illinois where the degree of Bachelor of Science in Ceramic Engineering cum Laude was obtained in June, 1934. He then received a Cooperative Fellowship offered by the U. S. Bureau of Mines and College of Mines at the University of Washington in Seattle, Washington where he obtained the degree of Master of Science in Ceramic Engineering in June, 1935. This was followed by a position as Ceramic Engineer at the Willamina Clay Products Co. in Willamina, Oregon. After a year he returned to the University of Illinois on an Engineering Experiment Station Fellowship. In February, 1938 he joined the teaching staff as Assistant, followed by an Instructorship in September, 1938. During the summer of 1941 he worked as Assistant Ceramic Engineer at the Electrotechnical Laboratory of the U. S. Bureau of Mines in Norris, Tennessee. In September, 1941 he is joining the staff at the University of Washington as Acting Assistant Professor and head of the Department of Ceramic Engineering. Publications are as follows:-

With Hewitt Wilson, "Talc and Soapstone in Washington," A. I. M. M. E., Contrib. No. 99, 25 pp. (1936).

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