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The Diffusion of Helium and of Hydrogen Through Pyrex Chemically Resistant Glass

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The effects of temperature and of heat treatment on Pyrex chemically resistant glass have been studied by measuring the rate of diffusion of helium and of hydrogen through a tube of about one millimeter wall thickness. Measurements were made with helium between 180°C and 590°C, and with hydrogen at 512°C. The influence of gas pressure was determined and the diffusion rate was found to be directly proportional to the pressure for both helium and hydrogen.

The diffusion data throw light on the processes of molecular rearrangement involved in stabilization of the glass. Below 548°C the rates of diffusion (R) were increased about 10 percent by giving the glass sufficient heat treatment to assure "stabilization," i.e., equilibrium in the processes of dissociation and association. This increase occurred despite the fact that such heat treatment normally increases the density of the glass and therefore points to a chemical theory rather than a simple theory of holes governing the diffusion process.

The data also showed a continuous linear dependence for the stabilized glass of $\log R$ on $1/T$ from 440°C–590°C.

This range extends into the region of a true viscous liquid and it follows that the properties of a stabilized glass are continuous with that of a viscous liquid and that there is no need to postulate a separate glassy state. The "transformation point" mentioned by some investigators is merely the temperature of rapid strain release of an unannealed sample.

At or near 440°C the $\log R$ versus $1/T$ curve takes a lesser slope (for lower temperatures) and this change is attributed to the loss of rotational or vibrational freedom in the silicate complex, analogous to that frequently found in dielectric studies on solids. Activation energies have been calculated for the two temperature ranges.

At 512°C the rate of helium diffusion is approximately 45 times that of hydrogen, and it is believed that chemical forces delay the progress of the hydrogen molecule through the silicate network.

The general conclusion is drawn that gas diffusion furnishes a highly sensitive method for studying the molecular condition of silicate glasses and similar materials.

THE principal feature distinguishing the glassy state from the ordinary liquid state is a very high viscosity which delays the establishment of equilibrium of molecular processes in glass. The result of this delay is that the properties of a glass depend to an important degree on its thermal history or heat treatment. Examples are expansion coefficient,¹ viscosity,² elastic properties such as Young's modulus,³ electrical conductivity,⁴ absorption spectrum,⁵ and dielectric constant.⁶ When the temperatures are sufficiently high equilibrium is very rapidly attained in a

glass and it cannot be distinguished in its behavior from an ordinary viscous liquid.

The nature of the liquid state partakes in part the properties of crystals,⁷ and in part the properties of a condensed gas, but its study has proven rather difficult. One may say that at present we have less knowledge of the structure of liquids than we have of either gases or crystalline solids. One of the difficulties lies in the fact that dynamic equilibrium is rapidly attained in ordinary liquids and that it is impossible to "freeze in" or preserve a certain molecular condition, for later study. In glasses this is not so. One may by quenching or rapid chilling preserve a high temperature structure down to low temperatures, or one may anneal a glass at any desired temperature and study the properties of the molecular configurations so developed. These characteristics of glass are utilized industrially in many ways.

There are various physical methods for investigation of the structure of glass. Several have

¹ M. E. Spaght and G. S. Parks, *Glass VIII*, "The Coefficient of Thermal Expansion of Boron Trioxide," *J. Phys. Chem.* **38**, 103–10 (1934).

² H. R. Lillie, "Viscosity-Time-Temperature Relations in Glass at Annealing Temperatures," *J. Am. Cer. Soc.* **16**, 619–631 (1933).

³ N. W. Taylor, E. P. McNamara and J. Sherman, "A Study of the Elastico-Viscous Properties of a Soda-Lime-Silica Glass at Temperatures near the Transformation point," *J. Soc. Glass Tech.* **21**, 61–81 (1937).

⁴ J. T. Littleton and W. L. Wetmore, "The Electrical Conductivity of Glass in the Annealing Zone as a Function of Time and Temperature," *J. Am. Cer. Soc.* **19**, 243–245 (1936).

⁵ W. Weyl and E. Thümen, "The Constitution of Glass, II. Theoretical Basis of Glass Coloration," *Glastech. Ber.* **11**, 113–120 (1933).

⁶ W. Weyl, personal communication.

⁷ G. W. Stewart, "X-Ray Diffraction in Liquids," *Rev. Modern Physics* **2**, 116–122 (1930). "Molecular Structure as Interpreted by X-ray Diffraction Measurements in Liquids," *Chem. Reviews* **6**, 483–501 (1929).

been mentioned. X-ray analysis⁸ has demonstrated a certain regularity of atomic or ionic arrangement. This technique, however, presents a statistical picture of average interatomic distances and does not show the result of heat treatments in much detail, i.e., it is not particularly sensitive to heat treatment of the glass.

A method which depends on individual atomic properties, or on the properties of small groups of atoms or ions, rather than on the whole complex, is the method of gas diffusion through the solid. The progress of the diffusing atom is delayed by its binding (electrical interaction) with neighboring host atoms and the rate of diffusion is proportional to a quantity $e^{-A/RT}$ where A is the activation energy necessary to overcome these atomic forces. Diffusion thus becomes a property subject to study and mathematical treatment by the usual procedures of chemical reaction kinetics, and precise data can be obtained which lead to rather direct interpretation in terms of atoms and molecules.

As an example of the success of the diffusion method in the study of solids we may mention the work of W. R. Ham,⁹ on the diffusion of hydrogen through iron and nickel. It was found that "the magnetic changes at about 360° (Ni) and 750° (Fe) were clearly defined by diffusion data. In addition, iron exhibits changes in the isobars at 945°, 900° and at between 200° and 550°C. A definite difference in temperature is observed between Ar_3 and Ac_3 , and this appears to be a true hysteresis. The other points are all ascribed to electronic changes of the iron atom and it is suggested that the well known maximum in the tensile value of iron at 200–350° is explained in part by one of these electronic shifts. The general conclusion is reached that the isobars from hydrogen diffusion tests furnish an accurate means of tracing phase or electronic changes in iron and nickel, and that the change in slope of the isotherms provides a means in some instances of determining small amounts of foreign elements in solution in the metals."

⁸ B. E. Warren and J. Bischof, "Fourier Analysis of X-ray Patterns of Soda-Silica Glass," *J. Am. Cer. Soc.* **20**, 259–65 (1938).

⁹ W. R. Ham, "The Diffusion of Hydrogen Through Nickel and Iron," *Trans. Am. Soc. Metals* **25**, 536–64 (1937).

CHEMICAL THEORY OF DIFFUSION

The simple physical picture of diffusion as a movement of atoms through open channels or cracks which are large compared to atomic diameters, does not offer an explanation for much of the most accurate and reliable experimental work in this field. On the other hand, several workers, notably Dushman and Langmuir,¹⁰ and later Eyring,¹¹ have treated the diffusion process by the same methods as for chemical reaction rates. The fundamental assumption is made that the diffusing atom moves from lattice point to lattice point through the solid and is subjected to the influence of strong electrical fields of a periodic nature. In order for a diffusing atom to break away from its immediate environment and move to a new position of stability in the solid, it requires an amount of energy, E , to activate it. By application of the Boltzmann principle, the probability that a diffusing atom can cross this energy barrier is proportional to $e^{-E/kT}$, where k is the Boltzmann constant. For a gram molecular weight of diffusing atoms, since $R = Nk$ and $A = NE$ where N is the Avogadro number, the expression becomes $e^{-A/RT}$.

The quantity A is sometimes called the activation energy, the energy of transfer, or the heat of loosening per gram atomic weight. This is where the chemistry of diffusion may enter the theory, for obviously those atoms which can exert a strong attraction for the diffusing atom (large A value) will delay the progress of the diffusing atom through the solid. Thus for example at 500°C, helium has a rate of diffusion through silica glass about 22 times faster than has hydrogen, as shown by Williams and Ferguson¹² "Were it a case of effusion the ratio would be less than unity," that, is approximately $\sqrt{2/4} = 0.7$, since the molecular weights of helium and hydrogen are 4 and 2 respectively.

This large difference is to be expected on the theory that H_2 forms temporary attachments to

¹⁰ S. Dushman and I. Langmuir, "The Diffusion Coefficient in Solids and its Temperature Coefficient," *Phys. Rev.* **20**, 113 (1922).

¹¹ H. Eyring, "Viscosity, Plasticity and Diffusion as Examples of Absolute Reaction Rates," *J. Chem. Phys.* **4**, 283–291 (1937).

¹² G. A. Williams and J. B. Ferguson, "The Diffusion of Hydrogen and Helium through Silica Glass and other Glasses," *J. Am. Chem. Soc.* **44**, 2160–2167 (1922).

the oxygen ions which are of greater stability than that which helium may form with these ions. The two gases have nearly the same diffusion velocities through rubber ($C_{10}H_{16}$) which has a low oxygen content.¹³ In fact, because of the chemical inertness of the helium atom, it is probable that the only forces which tend to bind it to the ions of the glass are the so-called van der Waals forces which arise from the interaction of dipoles between the two kinds of atoms.

Our own experiments show that at 512°C the rate of helium diffusion through Pyrex glass is approximately 45 times as fast as that of hydrogen, and this despite the fact that the diameters of He and of H_2 are nearly the same, namely 4.00 and 3.94 Å, respectively. These values are computed from the densities of the two liquids, at -271.5° for He and at -258° for H_2 .

The theory that weak bonds between diffusing atoms and host atoms lead to relatively rapid diffusion has been also emphasized in another paper by one of the authors,¹⁴ in discussing the diffusion of gold, silver bismuth, thallium, and tin into lead, and the self-diffusion of lead. Further evidence that diffusion is essentially controlled by chemical factors has been given by W. R. Ham⁹ who has shown that a mixture of N_2 and H_2 diffuses through metallic iron very much more rapidly than either gas alone. This effect may be explained by assuming that N_2 and H_2 together form a complex molecule, possibly of an amide type, which has less attraction for the iron atoms than have the two H atoms which form when N_2 is not present.

In connection with the problem of the glassy state there are several questions which might be clarified by gas-diffusion studies. The first question was concerned with the nature of the so-called "transformation point:" is it a true thermodynamic property of a glass or is it simply interpreted as such because of a confusion of rate effects with equilibrium properties? Most expansion measurements are dynamic, in the sense that the temperature is rising or falling at a finite rate. It was considered desirable to measure some prop-

erty such as diffusion under constant temperature conditions, above and below the "transformation point." The second question is related to the first one and may be stated: "What influence does thorough annealing have on the permeability of glass to gas, and how shall the results be interpreted?"

MATERIALS AND METHODS

Earlier work on gas diffusion through glass has shown that hydrogen and helium diffuse more easily than do other gases. For this reason, and because of the relative simplicity of atomic structure of these gases, they have been chosen for this study. For the glass, Pyrex chemically-resistant glass was chosen, primarily because it was easily made into a suitable shape for the diffusion sample and also because it could readily be sealed to the rest of the vacuum system. From the standpoint of theoretical interpretation a glass of simpler chemical composition, such as fused silica or boric oxide would have been better, but from the practical standpoint Pyrex is of greater interest.

EXPERIMENTAL METHOD

The diffusion sample was a 41.0 cc Pyrex test-tube, having 94.6 cm² effective diffusing area and 1.1 mm wall thickness, sealed into a larger Pyrex tube as in Fig. 1. It was placed in a wire wound cylindrical muffle furnace, whose temperature was maintained uniform to $\pm 0.25^\circ\text{C}$ by three thermocouples, at ends and center, and by automatic control to $\pm 0.5^\circ\text{C}$. The temperature of the "sample" was read from a thermocouple placed inside the inner tube. The high pressure side connected with a manometer and gas supply, the low pressure side with a calibrated McLeod gauge and mercury diffusion pump and oil pump. Vacuum stopcocks (Hg seal) were used throughout. The apparatus was thoroughly tested for leaks, using air, before introduction of helium or hydrogen. These gases were from commercial sources and were purified before use, by contact with charcoal at liquid-air temperatures. This treatment probably removed water vapor or hydrocarbons, but would have no effect on any nitrogen which might be present. The speed of

¹³ J. D. Edwards and S. F. Pickering, "Permeability of Rubber to Gases," U. S. Bureau of Standards, Scientific Paper 387 (1920).

¹⁴ N. W. Taylor, "Reactions Between Solids in the Absence of a Liquid Phase," J. Am. Cer. Soc. **17**, 155-163 (1934).

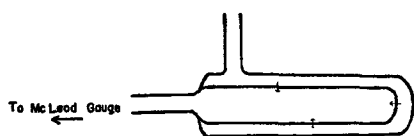


FIG. 1. Diffusion sample. Direction of diffusion indicated by arrows.

nitrogen diffusion through glass is extremely slow in comparison to that of helium, however.

The procedure consisted of trapping the diffused gas for definite intervals from 15 seconds to 30 minutes depending on the temperature, compressing this gas in the McLeod gauge and reading its volume at barometric pressure and room temperature which were of course known. At least 3 hours were devoted to each temperature, so that the glass had an opportunity to reach a steady state during that period. The diffusion data therefore represent essentially static conditions as compared with ordinary expansion studies.

PRESENTATION OF DATA

In view of the fact that the properties of a glass depend in part on the thermal history of the sample, the schedule of heat treatment will be given.

The rate measurements fall into five groups:

- I. August 4–August 11, 1936. Temperature rising from 406°C to 590°C.
- II. August 11–August 27. Temperatures falling from 590°C to 180°C.
- III. August 28–September 11. Temperatures rising and falling between 352° and 570°C for 2½ cycles. This series will be described as “the isotherms.”
- IV. September 12–September 14. Temperatures rising from 187° to 367°C.
- V. September 14–September 27. Glass held at 350° to 400°C. September 27–October 1. Temperatures rising from 242° to 544°C.

Group I. August 4–August 11. Temperature rising from 406° to 590°C (curve A)

After the whole vacuum system had been demonstrated to be free of leaks, measurements of diffusion rate for helium were begun at a temperature of 406°C. Since the glass sample had not been made strain-free by annealing at a temperature in the annealing range (approximately 545°C or above), the glass was really in a condition of strain. For this reason the rates of

diffusion are less than those obtained later. The experimental points are plotted in Fig. 2, Curve A. It will be seen that at temperatures of 548°C or above the rates obtained on the strained glass are almost the same as those obtained later in the Group II series (Curve B) which presumably represents strainfree glass. Below 548°, however, i.e., between 406° and 548°C, the helium diffusion rates are about 10 percent less than those of Group II. Previous workers in the field of gas diffusion through glass have nearly always failed to remove the condition of strain in the glass before taking precise measurements, and it is therefore doubtful whether much of the published work on gas diffusion should be accepted in a quantitative sense.

Group II. August 11–August 27. Temperature falling from 590° to 180°C (curve B)

The data of Group II were taken over a period of 17 days, measurements made at 590, 584, 574, 567°C, etc., until a low point of 180°C had been reached. As in Group I and all other groups, each temperature was held constant for approximately 3 hours before the rate data were obtained. At all temperatures down to about 525° ample time was available to permit complete or nearly complete stabilization (molecular rearrangement) of the glass to a condition characteristic of that temperature. At or near 525°C there was a very slight change in direction of the log R versus $1/T$ curve which thereafter continued as a straight line down to about 440°C. Below 440°C the log R versus $1/T$ line was again straight, but had a somewhat lesser slope. Note that on Fig. 2 it diverges from the broken line which is a

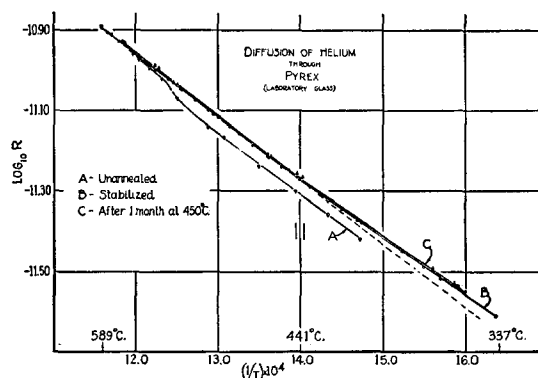


FIG. 2.

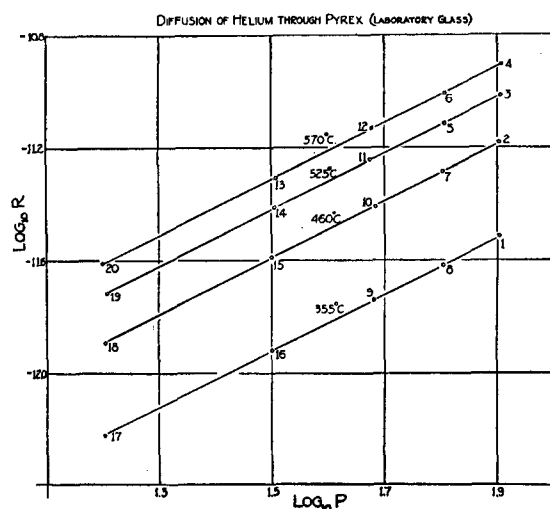


FIG. 3.

continuation of the upper slope. At about 225°C the line again changed direction, but as the rate measurements are less certain in this low temperature region, no emphasis will be laid on this effect, at present. The significance of the 525°C and 440°C breaks will be discussed later. Data below 337°C are not shown in Fig. 2.

Group III. The isotherms, August 28–September 11

The relation between diffusion rate and gas pressure was a subject of special interest, not only to permit reducing all rate data to a common pressure basis of 1 atmosphere, but also in connection with the more general problem as to the "molecular" state of the helium atom as it worked its way through the glass. For these reasons a series of isotherms were made at 5 different pressures, 16, 32, 48, 64 and 80 cm Hg. respectively, and at 4 different temperatures, 355°, 460°, 525° and 570°C. It was convenient to work at one helium pressure over the four temperatures, then to reduce its pressure and work back over the same four temperatures in reverse direction, etc. This resulted in heating the glass from 352 to 568, cooling to 355, heating to 570, cooling to 305 and finally heating to 571°C. The rate values are plotted in Fig. 3, and in Fig. 2, Curve C.

These cycles of alternate heating and cooling apparently produced no major effect on the diffusion rates except a slight increase, ca. 1 per-

cent above 450°C and about 2½ percent at or near 355°C. The "transformation point" at about 525 was wiped out, however, and its disappearance was confirmed by later tests, Group V.

The accuracy and reproducibility of the diffusion rates of Group III are shown by Fig. 2 where the plotted points fall nicely on the straight lines at each temperature.

Table I exhibits values of dm/dt for various values of p , and also shows values of R , the characteristic rate per atmosphere pressure gradient (g helium per cm² per sec. per mm wall thickness), calculated from the data of the two columns by means of the relation $R = 76/p \, dm/dt$. The temperature is also shown. It will be seen that the values of R are practically constant, except for small shifts due to temperature.

In the range 440°–600°C, the data of Curve C, Fig. 2, may be satisfactorily expressed by the equation

$$-\log R = 9.075 + 1562/T,$$

where R has the units already stated, and T is the absolute temperature, degrees Kelvin. This equation leads to rate values approximately 1 percent higher than those given in Table I, but is representative of the later data.

The linear relation between rate of diffusion and gas pressure is not surprising, since helium

TABLE I. Rate of helium diffusion through stabilized Pyrex glass.

TEMP. (°C)	PRESSURE (CM HG)	dm/dt	R
355	80.11	3.05×10^{-12}	2.82×10^{-12}
355.5	63.71	2.42×10^{-12}	2.89×10^{-12}
357	47.96	1.83×10^{-12}	2.94×10^{-12}
355	31.69	1.23×10^{-12}	2.88×10^{-12}
359	15.96	0.59×10^{-12}	2.90×10^{-12}
465	80.97	7.62×10^{-12}	6.29×10^{-12}
455.5	63.87	5.18×10^{-12}	5.96×10^{-12}
461	48.32	3.86×10^{-12}	6.15×10^{-12}
459	31.59	2.56×10^{-12}	6.12×10^{-12}
460.5	16.03	1.28×10^{-12}	6.10×10^{-12}
521.5	80.48	9.65×10^{-12}	8.92×10^{-12}
526	64.08	7.69×10^{-12}	9.15×10^{-12}
525	47.28	5.73×10^{-12}	9.21×10^{-12}
526	32.01	3.86×10^{-12}	9.20×10^{-12}
529	16.16	1.93×10^{-12}	9.27×10^{-12}
568	80.76	12.50×10^{-12}	11.62×10^{-12}
573	64.15	9.84×10^{-12}	11.84×10^{-12}
569	47.65	7.39×10^{-12}	11.70×10^{-12}
570	32.18	4.93×10^{-12}	11.66×10^{-12}
571	15.86	2.46×10^{-12}	11.83×10^{-12}

is normally monatomic. It may be mentioned that the solubility of helium in silica glass is in direct proportion to the pressure.¹⁵

Group IV. Temperatures rising from 187 to 367°C

Following the series of isotherms, a group of 5 determinations were made at temperatures between 187 and 367°C. They are consistent with Curve C, Fig. 2. This confirms the small increase in rate due to the heat treatment received by the glass sample in the 2½ weeks subsequent to August 27.

Group V. Temperature rising from 242 to 544°C following 2 weeks heat treatment at 400–350°C

After the series known as Group IV had been completed the sample stood one week at 400°C and one week at 350°C. Rate measurements were then made at approximately 244°, 440°, and 542°C. They indicate a further small increase, about 1–1.5 percent, over the rates in Group III and IV taken two weeks previously. They support the conclusion that further stabilization took place in the glass during this period. Secondly, they confirm the disappearance of the "transformation point." On the other hand, they appear to confirm the reality of a change in slope of the log R versus $1/T$ curve at or near 440°C.

DISCUSSION

Interpretation of the energies of activation

The heats of activation computed from the log R versus $1/T$ curves for the temperature ranges 350°–440°C and 440°–600°C are 6480 and 7150 calories per mole respectively. For the unannealed glass it is 6920 calories (Temp. 400–500°C). These values may be compared with Van Voorhis¹⁶ value of 8700 cal. for helium through Pyrex (200° to 500°C), and W. D. Urry's¹⁷ value of 5340 cal. for helium through unannealed Pyrex in the temperature range 81°–283°C.

¹⁵ G. A. Williams and J. B. Ferguson, "The Solubility of Helium and Hydrogen in Heated Silica Glass and the Relation of this to the Permeability," J. Am. Chem. Soc. **46**, 635–639 (1924).

¹⁶ C. C. V. Voorhis, "The Diffusion of Helium Through Several Widely Different Glasses," Phys. Rev. **A23**, 557 (1924).

¹⁷ W. D. Urry, "Further Studies in the Rare Gases. I. The Permeability of Various Glasses to Helium," J. Am. Chem. Soc. **54**, 3887–3901 (1932).

Two possible factors may determine the magnitude of the activation energy barriers. One is the attraction of helium for the ions of the glass, which we believe to be small compared to the second which is the repulsive force acting on the helium atom as it moves from "hole" to "hole" in the molecular network. This quantity might be quite large in magnitude if the passages through which the helium has to move are very small. The term "hole" as used here indicates a space of about atomic dimensions which is not occupied by any of the ions constituting the glass. Just as a silicate crystal is formed of SiO₄ tetrahedra linked, by sharing of corners, into chains and rings and sheets, these larger units being joined through positive ions, so we believe a silicate glass to have a similar structure, the essential difference being that there is no repeating "unit cell" in the liquid, but only a random arrangement of SiO₄ tetrahedra in space, and secondly, that the centers of gravity about which the atoms oscillate or rotate, themselves move around in a kind of Brownian motion. This sort of structure provides small "open spaces" or "holes" of atomic size in which the diffusing helium atoms may easily stay. On the other hand, considerable energy may be required by a helium atom to allow it to squeeze past its nearest oxygen neighbors and find a similar "hole." The magnitude of the repulsive energy developed as the helium atom passes through a small molecular orifice will depend on an inverse 6th or 7th power

TABLE II.

DIAMETER OF SQUARE	ENERGY (CAL/MOLE)
3.6A	13,920
3.8	8,393
4.0	4,250
4.2	2,183
4.4	1,078

law integrated over all the ions which act on a given helium atom as it moves from the center of its "hole" to the tightest point in the orifice. At present exact calculation of this energy from fundamental electrostatic or wave-mechanical theory cannot be made. Analogous calculations have, however, been made by Barrer,¹⁸ who has

¹⁸ R. M. Barrer, "The Mechanism of Activated Diffusion Through Silica Glasses," J. Chem. Soc. (London) 378–86 (1934).

considered how the size of a hole between four helium atoms arranged at the corners of a square affects the energy required to bring in a fifth helium atom from an infinite distance normal to the square so that it finally rests in the center of the plane. Table II is taken from Barrer's article, page 385.

It will be seen that not only are the repulsive energies several thousand calories in magnitude and therefore comparable to those actually observed in the present work, but also they are quite sensitive to small changes in the size of the hole when the size is nearly the same as that of the atom which is being squeezed. This may partly explain why heat treatment of the glass changes the activation energy for helium diffusion.

Changes resulting from heat treatment

1. *The "transformation point."*—One question to which the diffusion data have given a clear answer is the nature of the "transformation point." The $\log R$ versus $1/T$ plot for the stabilized glass (Curve C) is exactly linear from about 440°C to 600°C and shows no discontinuity or change in direction at or near 550°C which is the approximate temperature at which the expansion coefficient shows large increase. Since each diffusion measurement was of several hours duration the data may be regarded as static, in contrast to the dynamic expansion measurements. The conclusions must be drawn that a viscous liquid and a stabilized glass are continuous with one another in properties and that the "transformation point" is purely a property of the unstabilized glass. It is merely a temperature at which the viscosity is low enough to permit rapid stabilization by molecular rearrangement, thus leading to equilibrium between the forces of association and dissociation. These views are in harmony with those of Lillie,² Littleton,⁴ and Weyl¹⁹ but contrary to those of Berger²⁰ and others.

2. *Strained and annealed glass.*—Various workers have noted that heat treatment affects the

permeability of glass to gases. Tsai and Hogness²¹ state "We find that silica glass when heated to a high temperature undergoes a permanent change which results in a noticeably greater permeability for helium. The permeability depends somewhat on the previous heat treatment of the glass." Other workers have recorded that various samples of the same glass, e.g. fused silica, gave different permeabilities, without ascribing any reason for it. An examination of Fig. 2 shows that the rate of diffusion of helium through the Pyrex glass after annealing (Group II) was about 10 percent greater than that through the unannealed Pyrex (Group I). This large increase occurs despite the fact that Pyrex glass becomes denser (of higher specific gravity), as a result of annealing. This is shown by the density values 2.236 (annealed) and 2.233 (chilled).²²

These densities do not show the maximum spread which may be obtained under special conditions. On the other hand, they are in line with the usual experience that the chilled glass is less dense, and they fail to explain the lower permeability of this glass. The conclusion must follow that the chilled or unannealed glass is in a dissociated and unsaturated state which for some reason, either purely geometric or because of stronger chemical binding forces, delays the progress of the diffusing atoms. The idea of chemical unsaturation of the unannealed glass is in agreement with the views of W. Weyl based on absorption spectra. It has also been known for many years that unannealed glass is more susceptible to chemical attack than the annealed product.

The 440°C effect.—Figure 2, Curve C, shows two straight lines which meet at approximately 440°C. Above this temperature the rate of diffusion is expressed by

$$-\log R = 9.075 + 1562/T,$$

while below it, at least down to 350°C, the rate is given by

$$-\log R = 9.285 + 1415/T.$$

This change in slope occurs whether one approaches 440°C from above or below and with

¹⁹ W. Weyl, "On The Constitution of Glasses," *Glastech. Berichte* **10**, 541 (1932).

²⁰ A. Klemm and E. Berger, "The Change in Transmission of Glasses with Temperature Above and Below the Transformation Point," *Glastech. Berichte* **14**, 194-206 (1936); E. Berger, "Contributions to the Theory of Glass Formation and the Glassy State," *J. Am. Cer. Soc.* **15**, 647-677 (1932).

²¹ L. S. Tsai and T. R. Hogness, "Diffusion of Gases Through Fused Quartz," *J. Phys. Chem.* **36**, 2595-2600 (1932).

²² H. R. Lillie, personal communication.

essentially static measurements (three hours per point).

Since there is no known peculiarity in the properties of helium at 440°C it is believed that the effect is due to the Pyrex glass. The following hypothesis is tentatively advanced. The thermal energy of the glass at any temperature consists in atomic and molecular motion of translation, oscillation and rotation. It is possible that at or near 440°C a new degree of freedom is gained, i.e., above this temperature some molecule like SiO_4 may rotate about one axis with respect to the rest of the complex, while below 440°C it may not.

A recent paper by Smyth²³ presents evidence pertaining to rotation in crystal lattices. In NH_4NO_3 and NaNO_3 the NO_3 ion begins to rotate in the plane of its ions at 84°C and at 275° respectively. Similarly in NH_4Cl , NH_4Br and NH_4I rotation of the NH_4 ion sets in at -30°, -38° and -42°, respectively. Many other examples are discussed by Smyth, who points out that the shape of the molecule is an important factor, and that symmetrical groups like NH_4 , PH_4 (or SiO_4) rotate more easily than groups of lower symmetry.

No claim is made for great sharpness (small temperature range) of the "break" at 440°. As far as the experimental evidence is concerned it may actually extend over several degrees. In crystals the effect may be sudden or gradual. The writers have no data on dielectric constants for Pyrex in this temperature range, but such information would be useful to test this hypothesis. Since we regard glass as a highly viscous liquid, the following statement by Smyth is of interest. "From a molecular point of view, the essential difference between a solid with rotating molecules and a liquid is that the molecules of a solid are vibrating about points fixed in a lattice, while molecules of the liquid are vibrating about points

which migrate slowly and irregularly through the liquid."

It is obvious that more glasses and in particular glasses of simple composition should be studied in order to get more light on this hypothesis. It seems highly probable that the increased loosening of the lattice because of a rotation (or an extra degree of vibrational freedom) would permit more rapid diffusion of helium, as observed.

It is also clear that exact specific heat or similar information on crystalline silicates of simple chemical composition would be of value in connection with the above mentioned hypothesis.

DIFFUSION OF HYDROGEN

Two determinations were made at 787.5°K (512.5°C) on the rate of diffusion of hydrogen. The first, with the hydrogen under a pressure of 78.04 cm Hg, led to a value $dm/dt = 1.908 \times 10^{-13}$, from which $R = dm/dt = 1.858 \times 10^{-13}$ when calculated for a pressure drop of 1 atmosphere (76 cm Hg). The second, with a measured hydrogen pressure of 41.44 cm, gave a value of $dm/dt = 1.017 \times 10^{-13}$ from which $R = dm/dt = 1.865 \times 10^{-13}$ when calculated for a pressure drop of 1 atmosphere.

The agreement between these two results shows that the rate of diffusion of hydrogen is directly proportional to the pressure, and not to the square root of the pressure as is the case when hydrogen diffuses through metals. It appears that the two hydrogen atoms diffuse through Pyrex glass in pairs, rather than as separate atoms.

A comparison of the rate of diffusion of hydrogen and helium at 787°K (512°C) indicates that the helium diffuses about 45 or 46 times as fast as does hydrogen at this temperature.

Even at 120°C the diffusion of hydrogen into glass is perceptible. W. Weyl²⁴ has produced fluorescence by reduction of dissolved Ag_2O to the free atoms by hydrogen at this temperature.

²³ C. P. Smyth, "The Dielectric Constants of Solids and Molecular Rotation," *Chem. Review* **19**, 329-361 (1936).

²⁴ W. Weyl, "Contribution to the Fluorescence of Glasses," *Sprechsaal* **70** (1937), No. 46.