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DIFFUSION IN ZEOLITES AND GLASSES

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TECHNICAL PROGRESS REPORT

(Document # COO-1550)

I. Publication Status

A. Manuscripts Mentioned in Earlier Reports

(1) "Diffusion of Several Gases in Vitreous Boric Trioxide," W. W. Brandt, T. Ikeda, Z. A. Schelly (COO-1550-04*) has been presented at the Great Lakes Regional Meeting of the ACS, Milwaukee, Wisconsin (June, 1968), and has been extended during the past year, and is presently submitted to the Journal of Chemical Physics.

(2) "Diffusion and Chemi-Desorption Rate Coefficients from Desorption Transient Measurement," W. W. Brandt (COO-1550-10). This manuscript resulted from recent work, it also has been extended and has been accepted by the International Journal of Heat and Mass Transfer.

(3) "Computation of Desorption Transients; Computer Programs and Representative Results," W. W. Brandt (COO-1550-11). This material is supplementary to (1) above, and will be published by the American Society for Information Sciences, Document No. NAPS—00939.

B. New Manuscript

(1) "Diffusion of He, Ne, and Ar in Vitreous and Partially Devitrified Germanium Dioxide," W. W. Brandt, B. Rauch (COO-1550-13). This work resulted from the present project period. The manuscript has been submitted to the Journal of the American Ceramic Society. The present draft of this manuscript is Section (II) of this Report.

* Document number assigned by Mr. Douglas J. Arthur of UWM, memo dated May 21, 1968; see letter of W. W. Brandt to H. Miller, USAEC, dated May 31, 1968.

C. Manuscript in Preparation

(1) "Diffusion of Several Noble Gases in Conventional and Invert Silicate Glasses." A short outline of the results obtained in this area of study are described in Section (III) of this Report.

II

Diffusion of He, Ne, and Ar in Vitreous and Partially Devitrified Germanium Dioxide

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ABSTRACT

The diffusion coefficients of He, Ne, and Ar in various samples of GeO_2 were measured, using a newly developed nonisothermal desorption technique. Some of the samples used were annealed and partially devitrified, and in a few cases the desorption rates were measured on samples in and above the glass transition temperature range. A simple static model of the glass network was containing various crevices of different critical dimensions was found to be consistent with the observed diffusion coefficients and the approximate and relative noble gas solubilities.

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INTRODUCTION

The diffusion coefficients of several noble gases and of D_2 in vitreous B_2O_3 have recently been measured in this laboratory⁽¹⁾ and interpreted by making reference to structural heterogeneities probably present in that particular glass. Specifically, it was found that the pre-exponential factor, D_0 , of the Arrhenius equation for the diffusion coefficient, D ,

$$D = D_0 \exp(-E/RT) \quad (1)$$

decreases very strongly with increasing diffusate molecular size, presumably because only very few diffusion paths are available to large diffusing molecules. [E, R, and T have their standard meaning.] Vitreous B_2O_3 is known to differ from other glasses in several important respects, as reviewed earlier⁽¹⁾, and it is therefore desirable to study other typical vitreous materials to determine whether the results reported earlier are characteristic of that particular substance only, or are perhaps typical of many different glasses. Vitreous GeO_2 is an important case in point. Its physical properties have been studied by a variety of methods⁽²⁻⁶⁾ but very little is known about the diffusion of small molecules in this substance⁽⁷⁾. Also, the glass transition temperature of GeO_2 is experimentally easily accessible ($T_g \sim 570^\circ C$) and the diffusion properties can be investigated above as well as below this transition. Finally, GeO_2 is readily devitrified and interesting comparisons of partially devitrified samples with glassy ones are therefore possible.

A secondary goal, as in the earlier study⁽¹⁾, consists of testing whether the diffusion coefficients of inert gases are possibly far more sensitive to the presence of structural heterogeneities, such as cracks or crevices, on the near-molecular scale, than the more conventional surface area and pore volume determinations

EXPERIMENTAL

The germanium dioxide used was of Alfa Inorganics Ventron grade, 99.999% pure, except for a small and variable amount of water present. The granular material was either studied in its original condition, or it was melted at about 1470°C for about one half hour, broken up, ground, and sieved several times in an atmosphere of 10 to 15% relative humidity. The size distributions of the resulting batches were determined microscopically as described earlier⁽¹⁾, and the principal results are collected in Table (I). The densities of the original and of the remelted material were found to be $3.81 \pm 0.03(\text{g/ml})$ and $3.612 \pm 0.004(\text{g/ml})$, using a pycnometer and benzene as immersing liquid.

Several small batches of the remelted, ground, and sieved material were annealed between 630 and 890°C, for a number of hours, so as to obtain partially devitrified samples.

The X-ray diffraction patterns of the commercial granular material, Sample (M), of several remelted samples, and of all annealed samples were obtained on a Jarrell-Ash Model 80-000 diffractometer, using CuK_α radiation. Since perfect crystals were not available, Sample (M) was used as a relative standard: to determine its crystallinity, the amorphous scatter was measured in the range $2\theta = 47^\circ$ to 56° , where θ is the angle of incidence,

Table (I): Description of Samples. Average Grain Diameters and Half Widths of Size Distributions

Sample	Melt (c)	Number average Diameter	Weight average Diameter	Half widths of Distribution Number Average Diameter
(A)	(a)	3.0 mm	3.5 mm	~ 0.1
(B)	(a)	3.2 mm	3.3 mm	~ 0.1
(C)	(b)	770 μ		0.4
(D)	(b)	510 μ		0.7
(E)	(c)	121 μ	160 μ	0.9
(F) (a) } (G) (a) }	(d)	172 μ	217 μ	1.1
(H)	(d)	18.0 $\pm$ 3.3 μ (d)	32 μ	1.6
(I)	(e)	10.4 to 16.2 μ (b)	41 μ	high
(J)	(e)	14.9 to 20.6 μ (b)		1.5
(K)	(d)	105 μ		0.5
(L)	(f)	1.0 cm		~ 0.2
(M)	/	14.0 μ		0.9

NOTES: (a) Samples (F) and (G) were portions of a single sample. (b) The lower estimate of the number average diameter of Samples (I) and (J) is based on all particles present while the higher estimate is based on a fairly distinct group of larger particles present only and is considered more appropriate in view of the graphical evaluation method used in this work. (c) The melting conditions (a) to (f) differed only little from one case to the next. The commercial Sample (M) was used as received. (d) The random error estimate for the diameter originates from replicate

microscopic determinations of the size distribution histogram and is considered typical for all samples listed.

they were corrected for the small background originating from the sample holder material, and compared to the corresponding values of a nearly amorphous sample. Next, from the amorphous content so obtained, the crystallinity of Sample (M) was calculated by difference. Finally, the crystalline diffraction peak heights of the various other samples were divided by those of Sample (M), at $2\theta = 47^\circ$, 52° , and 56° , and their crystallinities estimated indirectly from the averages of these ratios. The results are listed in Table (II). Only the hexagonal modification was detected in the samples used; this is reasonable since this form is known to form first when devitrification occurs⁽⁸⁾. It turned out that GeO_2 samples of small grain size easily devitrified at high relative humidity, even at room temperature⁽⁹⁻¹⁰⁾. Presumably this crystallization is confined to the surface of the grains and is possibly very different from that produced by annealing. To minimize changes on the surfaces, the samples were handled and stored at low relative humidities.

The relative amounts of crystalline material present in the annealed samples and in Sample (M) were also determined from the height of a small sub-maximum in the IR absorbance near 970 cm^{-1} , known to be characteristic of the hexagonal modification of GeO_2 ⁽¹¹⁻¹⁴⁾. The absorbance values were found to be more reproducible than the X-ray data, and both sets of data showed a linear correlation. The IR measurements based on the KBr pellet method were very convenient, they required only very small amounts of samples, but the resulting measures of crystallinity are only relative ones, at this time.

Most of the desorption experiments reported here were done under non-isothermal condition⁽¹⁵⁾, the sample being heated at a constant rate. The principal advantage of this method lies in that the GeO_2

Table (II): Summary of Results from
Nonisothermal Desorption Experiments

Run No.	Sorbate gas	Sample (a)	Sorption time (hrs.)	Sorption temp (°C)	T _{max} ^(b) (°C)	ΔT ^(c) (°)	E ^(d) (Kcal/ mole)	log D ₀ ^(e)	x ^(f) (%)
9/1	Ne	M	23	450	648	262	22.8	-4.48	31.0
10/2	Ne	M	15	450	668	336	18.0	-5.7	31.0
21/1	Ne	E	36	400	223	149	11.9	-3.3	
21/3	Ne	E	3	400	236	133	13.7	-2.45	
23/1	Ne	E	16	400	247	104	18.3	-0.5	
23/2	Ne	E	2	400	232	138	13.0	-2.75	
24/1	Ne	E	3	400	239	124	14.9	-1.95	3
25/1	Ne	B	20	400	544	357	13.0	-1.99	
26/2	Ne	A	12	400	272	235	8.75	-1.81	
28/1	Ne	H	40	325	156	136	9.5	-5.2	
28/2	Ne	H	15	325	156	130	10.0	-4.9	
29/1	Ne	H	10	290	157	125	10.5	-4.7	
29/2	Ne	H	10	400	156	125	10.5	-4.7	
30/2	Ar	H	12	400	526	223	20.3	-4.7	2.5
34/1	He	C	20	300	175	158	8.9	-2.52	
34/2	He	C	12	250	180	165	8.8	-2.66	
36/1	Ne	C	18	300	417	222	15.0	-2.22	
37/1	He	D	12	200	87	103	9.0	-1.73	

(Table (II) con't)

Run No.	Sorbate gas	Sample (a)	Sorption time (hrs.)	Sorption temp (°C)	T _{max} ^(b) (°C)	ΔT ^(c) (°)	E ^(d) (Kcal/Mole)	log D ₀ ^(e)	x ^(f) (%)
37/2	Ne	D	12	400	344	213	12.6	-2.90	
38/1	Ne	D	12	400	303	188	12.5	-2.64	
38/2	He	D	30	200	90	104	9.1	-1.76	
40/3	Ne	I	30	200	158	109	12.0	-3.85	
41/1	Ne	I	12	200	152	98	13.0	-3.27	
42/1	Ar	I	30	350	576	198	26.0	-3.58	5.5
44/2	Ne	K	14	600	253	139	14.0	-2.04	<0.5
46/1	Ne	K	15.5	690	257	128	15.3	-1.39	<0.5
46/2	Ne	K	14.8	740	250	122	15.6	-1.05	2.5
47/1	Ne	K	12	790	373	197	14.75	-3.00	7.5
47/2	Ne	K	14.5	830	367	171	17.0	-2.23	13.0
48/1	Ne	K	13.5	765	346	169	15.9	-2.36	14.5
61/1	Ne	F	40	400	262	128	15.7	-1.58	
62/2	Ne	F	12	400	252	159	12.25	-3.07	
65/1	Ne	G	12	830	617	235	24.0	-1.82	24.0
78/1	Ne	J	14	250	140	104	11.6	-2.75	
78/2	Ne	J	15	400	138	99	12.0	-3.02	
79/1	Ne	L	14	575	673	271	23.5	1.16	

(Table (II) con't)

Run No.	Sorbate gas	Sample (a)	Sorption time (hrs.)	Sorption temp (°C)	T _{max} ^(b) (°C)	ΔT ^(c) (°)	E ^(d) (Kcal/mole)	log D ₀ ^(e)	x ^(f) (%)
80/1	Ar	J	15	400	335	235	11.0	-5.65	
80/2	Ar	J	15	500	656	349	17.5	-5.65	
93/1	Ne	G	12	600	674	271	29.0	-0.28	22.5

NOTES: (a) Sample characteristics are summarized in Table (I); (b) T_{max} is the temperature at which the desorption rate reached its maximum; (c) ΔT is the half-width of the desorption transient curve; (d) and (e), see equation (1), for method of evaluation, see Text; (e) The units of D₀ are (cm²/sec); (f) x is the crystallinity determined by X-ray diffraction measurements after each (series of) desorption experiments listed, except in Runs 9/1 and 10/2 where it was obtained on separate batches of Sample (M). The samples for Runs 44/2 to 48/1, 65/1, and 93/1 were annealed before the desorption experiments to produce partially devitrified samples.

samples were not normally exposed to high temperatures for a very long time, and therefore the devitrification which occurred during the desorption runs was minimized. Also, the method was found to be relatively fast, and this more than compensated for the fact that the random errors in the resulting D_0 and E values (see equation (1)) were somewhat larger than those obtained from isothermal experiments.

A number of isothermal runs were performed to check the results. Both methods, including the internal sensitivity calibration of the mass spectrometer by standard leaks were described earlier^(1, 15), as was the semi-automatic operation of the mass spectrometer⁽¹⁶⁾.

To characterize the GeO_2 samples further, the pore volumes were measured by a mercury intrusion method as discussed in the earlier report⁽¹⁾; the results obtained on two typical samples are shown in Figure (1). The BET surface area was measured on a sample of small grain size (Sample (M)), using Kr as sorbate at liquid N_2 temperatures⁽¹⁾, and found to be $0.46 \pm 0.04 (\text{m}^2/\text{g})$. This is two to four times larger than the microscopically visible area.

RESULTS

Some typical results from replicate nonisothermal desorption experiments are shown in Figure (2). The small amount of Ne detected early in each run probably constitutes gas left in the interspaces between the sample grains in spite of the repeated flushing of the sample at the end of the sorption process, using small portions of an inert gas, such as nitrogen. The Ne desorbing toward the end of each experiment possibly originates from the sample itself, but more likely from the platinum sheet metal sample

buckets, judging from blank experiments. The reproducibility of the center part of the curves shown in Figure (2) is typical of the nonisothermal method.

Some very different and non-typical curve shapes of low reproducibility were found with samples which had been subjected to a drastic high temperature treatment, i.e., they were sent through a plasma arc in order to produce spherical particles from the irregular grains originally present. A typical result of this type is shown in Figure (3) (lower curve).

Next, in a few cases, the desorption experiments were extended into and above the glass transition range and distorted transient curves were obtained as shown in Figure (3) (upper curve). This result is consistent with the very nonuniform thermal expansion encountered in this temperature range⁽¹⁷⁾.

Finally, the desorption transient curves obtained with several partially devitrified samples are presented in Figure (4); it is seen that the maximum rate of desorption shifted to relatively high temperatures, and that the curves from samples of intermediate or low crystallinities were often very irregular and non-reproducible. The principal numerical results from the nonisothermal and isothermal methods are summarized in Tables (II) and (III), respectively. The evaluation of methods used for both groups of data were described earlier⁽¹⁾.

To summarize the results, the logarithms of D_0 (see equation (1)) were plotted against the activation energies, E , in Figure (5). There are fairly large random errors in both quantities, D_0 and E , but they are apparently related in such a way that the resulting data points lie close to a straight line of positive slope.

Table (III): Summary of Results from
Isothermal Desorption Experiments

Run No.	Sorbate gas	Sample(a)	Sorption time (hrs.)	Sorption temp. (°C)	Desorption temp. (°C)	$D \times 10^{10}(b)$ (cm ² /sec)
1/1	Ne	M	~ 14	~ 210	210	0.0049
4/2	He	M	~ 14	~ 210	210	0.056
5/1	He	M	14.2	~ 180	182	0.029
59/1	Ne	G	12	215	192	1.9
66/1	Ne	G	12	240	230	5.8
67/1	Ne	G	12	250	144	0.49

NOTES: (a) See Table (I); (b) for method of evaluation see Text

Sample (M) is moderately crystalline, Sample (G) is nearly amorphous
(not annealed).

This "diagonal scatter" has been investigated by fitting the experimental curves at the temperature at which maximum desorption rate is found ($T_{\max}$), and at temperatures corresponding to the left and right half-heights ($T_{1/2\ell}$ and $T_{1/2r}$, respectively). The program uses the size distribution histograms as determined for each sample (see Table (I) for selected data), and the solutions to the diffusion equation for spherical grains⁽¹⁵⁾. It is found that an error in $\Delta T (\equiv T_{1/2r} - T_{1/2\ell})$ of $+10^\circ$ assumed for Run #40/3 resulted in decreases of the computed activation energy, E , by 1.1 Kcal/mole, and of $\log D_0$ by 0.71. Similarly, an error in $T_{\max}$ of $+10^\circ$ caused increases in E , by 0.6 Kcal/mole, and in $\log D_0$ by 0.16. A second important type of random error was traced to the accidental differences and the uncertainties in the grain size distributions, if one compares data obtained on different samples⁽¹⁾. This is borne out by Table (II) and Figure (5), and verified by computation; for example in Run 40/3 the E value given would be higher by 0.9 (Kcal/mole), and $\log D_0$ by 0.41, if the (very wide) grain size distribution of the particular sample used (Sample (I), see Table (I)) had been properly taken into account. The errors in most other data points due to the presence of a size distribution are of course far smaller, and they are always in the same direction.

To cope with the errors discussed above one must average many points to get final data of good precision. Also, one should attach most significance to the distances of the groups of data points for He, Ne, and Ar, in a direction perpendicular to that of the "diagonal scatter".

The Ar results are based on measurements on small samples of fairly wide size distribution (see Table (I)). The very small Ar background present in the mass spectrometer constitutes an appreciable fraction of the total Ar measured during the desorption experiments and is responsible for additional random errors in the final results.

As in the earlier study⁽¹⁾, the D_0 value obtained from isothermal measurements using Ne as sorbate gas (see Figure (5)) is lower than the corresponding D_0 from the group of nonisothermal runs selected for the same value of E . This difference is most likely due to the grain size distributions present, as they affect the two principal evaluation methods⁽¹⁾. A further systematic error originates from the fact that the sample grains are of irregular shape, rather than spherical. Possibly only the D_0 values are affected, and all data obtained are effected to the same extent.

DISCUSSION

As the primary result from this work one notes that $\log D_0$ (see equation (1)) decreases and E increases in the series He, Ne, Ar (see Figure (4)). This is similar to the trend found in the case of B_2O_3 ⁽¹⁾, but it is more uniform. The "diagonal scatter" discussed above is appreciable, but it does not invalidate this trend. Possibly in vitreous GeO_2 , like in B_2O_3 , there exist many diffusion paths of different widths, such that the small He atoms have a very wide choice of paths, and can diffuse far more quickly than the larger Ne or Ar species.

Secondly, one notes that all the D_0 values found for GeO_2 are lower than the corresponding ones for B_2O_3 , so the pores or crevices which are thought to constitute the useful diffusion paths may be less numerous in GeO_2 than in B_2O_3 . By contrast, the BET surface area and Hg intrusion pore volumes of GeO_2 were found to be distinctly larger than those of B_2O_3 , and one is left with the tentative conclusion that the internal surfaces of pores or crevices postulated here to interpret the diffusion data are perhaps not included in the surface areas measured by the BET method; presumably the Kr sorbate atoms are far too large to gain access to the crucial portions of the random network structure, at liquid nitrogen temperatures. Parenthetically we may note that the difference in the specific volumes of hexagonal crystalline and glassy GeO_2 is far lower than that between crystalline and vitreous B_2O_3 ⁽¹⁸⁾.

As a next finding, and in support of this tentative static model of the glass network structure, one may compare the relative amounts of He, Ne, and Ar taken up and then desorbed from the GeO_2 samples. The ratios of the uptakes for He : Ne : Ar, calculated as described for the Ne: Ar ratio in B_2O_3 ⁽¹⁾, is roughly equal to 1 : 2.8 : 18.4. These ratios are similar to what was found earlier for samples of a natural zeolite⁽¹⁹⁾, even though the actual amounts sorbed are much smaller.

The static model discussed up to now, of course, does not furnish the only possible basis for interpreting the data. In particular, the appreciable activation energies may indicate that random lattice motions are needed for each diffusive jump. The amplitudes of these motions determine the activation energies,

while the degree of cooperation between lattice motion necessary to produce a successful jump is related to the activation entropy, and thus to the pre-exponential factor D_0 of equation (1). The random network structure needs to be known in considerable detail if one wishes to develop a theory suitable to explain the trends found in this study, based on this second model. Moreover, it is quite conceivable that the static and the dynamic models mentioned are both valid to some extent, and novel experimental approaches are needed to determine their relative merits in each particular case studied.

Related to this general question, one notes that E and D_0 are vastly increased as one goes above the glass transition temperature, T_g , (Figure (5)). This is very similar to the data obtained on organic high polymers⁽²⁰⁾. Probably the dynamic model is far more appropriate for $T > T_g$ than for $T < T_g$.

Finally, the data show a strong and nonuniform dependence of the diffusion parameters D_0 and E on the sample crystallinity. In Figure (5) the data point for samples of low crystalline content (up to 5%) form a distinct group, those for slightly more crystalline samples lie close to this group, but those for the most strongly devitrified materials (22.5 and 24%) lie far to the right. Moreover, the latter data points show very high scatter, and the results obtained on the fairly crystalline commercial powder, Sample (M), are quite different again. Presumably the mode of crystallization and the details of the sample treatment affect these data very much. From the scatter described here and the irregularity of the second desorption rate curve in Figure (4) it is clear that a simple two-phase model as suggested by Maxwell and as applied to diffusion results for example by Jeschke and

Stuart⁽²¹⁾ will not explain these results.

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LEGENDS TO FIGURES

Figure (1): Pore volume as a Function of Pressure by the Mercury Intrusion method; dashed line, approximate average blank correction. $\bigcirc$, Sample similar to (K); $\square$, similar to (E) (see Table (1)).

Figure (2): Typical Neon Desorption Transients Obtained on a single sample of GeO_2 . Run designations are: $\square$, 23/2; $\bigcirc$, 24/1; $\triangle$, 23/1. The abscissa values are shifted to make the maxima coincide. The ordinate values are comparable, using a single (relative) scale. For additional details, see Table (II).

Figure (3): Distorted Desorption Transients, $\square$, Run 30/2, sample entering glass transition range; Ar sorbate. $\bigcirc$, 43/2, sample superficially melted in plasma arc, to produce spherical grains. For details on Run 30/2 see Table (II).

Figure (4): Neon Desorption Transients from Partially Devitrified GeO_2 . Run designations: $\triangle$, 47/2; $\square$, 48/2; $\bigcirc$, 65/1. The abscissa values are approximately comparable and they reflect the temperatures during each run. The ordinate values are comparable. See Tables (I) and (II) for additional details.

Figure (5): Logarithm of D_0 plotted against E (see eq. (1)).

Nonisothermal Experiments: the sorbate gas used, the sample designation (see Table (I)), average diameter used in the calculation, and the designations of the experiments used to derive (average) D_0 and E values (see Table (II)) are as follows;

(Legends to Figures con't)

, He, (A), 3.0 mm, 26/2; , He, (C), 770μ, 34/1 and 34/2;
, He, (D), 510μ, 37/1 and 38/2; , Ne, (B), 3.2 mm,
 25/1; , Ne, (C), 770μ, 36/1; , Ne, (D), 510μ, 37/2 and
 38/1; , Ne, (F), 172μ, 61/1 and 62/2; , Ne, (E), 121μ,
 21/1, 21/3, 23/1, 23/2, and 24/1; , Ne, (H), 18.0μ, 28/1,
 28/2, 29/1, and 29/2; , Ne, (I), 16.2μ, 40/3 and 41/1;
, Ne, (J), 20.6μ, 78/1 and 78/2; , left, Ne, (K),
 105μ, 44/2 and 46/1; , right, Ne, (K), 105μ, 46/2 and 48/1;
, left, Ne, (K), 105μ, 47/1; , right, Ne, (K), 105μ,
 47/2; , left, Ne, (G), 172μ, 65/1; , right, Ne, (G),
 172μ, 93/1; , Ne, (M), 14.0μ, 9/1 and 10/2; , Ar, (H),
 18.0μ, 30/2; , Ar, (I), 16.2μ, 42/1; , Ar, (J), 20.6μ,
 80/1, and 80/2; , Ne, (L), 79/1 ($T_{\max} > T_g$).

Isothermal Experiments: Ne, (G), 172μ, from Arrhenius plot
 based on runs 59/1, 66/1, and 67/1.

Figure 10

FIGURE (2)

TIME (10 min.)

FIGURE (3)

Fig. (4) TIME (10 min.) →

III. Diffusion of Several Noble Gases in Conventional and Invert Silicate Glasses.

Usually most physical properties of glasses change as one varies the composition and comparative studies attempting to relate such properties to molecular parameters are seriously hampered. One interesting exception to this is the series of conventional and invert glasses investigated by Stevels and his co-workers.^(1,2) The glasses in question contain SiO_2 , TiO_2 , equimolar amounts of K_2O , CaO , SrO , and BaO , and in some series also PbO . The conventional glasses contain 50 mole % SiO_2 , the invert glasses less. The latter category of glasses do not contain a continuous 3 dimensional random network, even though short chains or some complex silica ions may exist. Some properties, notably the density and refractive index, depend on composition in a simple way, they are nearly additive, while the viscosity and frequently the dielectric and mechanical losses show extrema at intermediate compositions, near the "inversion," that is for glasses of 50 mole % SiO_2 .

In the present study, we seek to decide whether the diffusion rates of inert gas atoms and the corresponding activation energies fall into one of these two categories, and whether the results permit one to describe the diffusion mechanism in some detail.

The results obtained thus far using He and Ne as diffusate species show that the activation energies for diffusion have a maximum at or near the composition corresponding to inversion, somewhat like the activation energies of the melt viscosities.

(1) H. J. L. Trap, J. M. Stevels, Phys. Chem. Glasses 1, 107(1960).

(2) idem., ibid., 1, 181(1960).

At present, we are attempting to measure Ar diffusion rates in these glasses, and to determine whether the packing efficiency alone might furnish a basis for interpreting our results, or whether one must assume that motions of the network modifier ions, or even of the silicate species present are likely to have a strong influence on inert gas diffusion.