FINAL REPORT

Study of Diffusion Coefficients of Glasses Under Zero-G

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Abstract: The present report details the results of two efforts. The first consists of the definition of a glass diffusion experiment to be conducted in a weightless environment and the conduct of those ground based studies which form a part of that experiment. The second portior of the work is the actual measurement of the best values of the diffusion coefficient which are obtainable under 1-G conditions. The 1-G measurements indicate that the diffusion coefficient in the potassium-germanate glasses has an activation energy of 170 Kcal/mole and the diffusion process is quite sensitive to water in the glasses.

DIFFUSION COEFFICIENTS OF GLASSES UNDER ZERO-G

Introduction

This final report summarizes the work and results conducted in the period from June 1, 1974, through November 30, 1976. The objective of this program was to formulate a diffusion experiment for glasses, outline such theoretical and earth bound results as were available and do the preliminary earth based experimental work in preparation for a weightless experiment. The fundamental premise of the work was that diffusion studies of the glass forming ion can be conducted in zero-g environments and diffusion data obtained from these experiments will be unique and valuable because of earth based experimental difficulties. A great deal of the time during the latter 18 months of this program was devoted to preparation of proposals to gain access to weightless facilities and to hardware definition for that program. That opportunity has not been forthcoming at this time.

Literature Survey

The diffusion literature in glasses is most abundant and will be reviewed by reference to a relatively recent article by Williams[1] and the text by Doremus.[2] This literature contains only scanty reference to the diffusion of the glass forming ion in glasses. This lack of experimental results is a direct consequence of the experimental difficulties associated with earth based diffusion experiments in these systems. The only work related to diffusion of the glass former which we have located is the work of Towers and Chipman[3] and that which is summarized in Terai and Hayami's[4] recent work. These works are severely hampered by experimental difficulties. They are, in fact, only capable of determining effective diffusion coefficients from

indirect observations. The only conclusion which can be advanced from these studies is that the diffusion of silica appears to involve "something other than simple ion movement." This conclusion is supported by the similar but nonequivalent studies of viscosity in similar glasses which reveal similar insights into the structure of the liquid silicate.

Initial System Selection

At the time of the original selection of a candidate for conducting these diffusion studies, the equipment which was to be available for a flight experiment was of primary importance. The boundary conditions, insofar as they influence the glass system, were perceived to be: (a) 1100°C maximum temperature and diffusion period of the order of 4 to 6 minutes. An experimental limitation inherent in diffusion measurements is the necessity of having an appropriate tracer with half life adequate for the time frames typical of flight experiments (packaging to recovery times of not less than 60 days). It was also obvious that the literature left almost all systems as available choices, hence, it appeared advisable to select a system which was fundamentally informative as well as of practical importance.

After a survey of the potential glass forming systems with these criteria in mind, the binary K_2O-GeO_2 glass system was selected for these experiments. This glass is quite analogous to the corresponding silicate systems but has the advantage of lower melting points with appropriate tracer ion availability.

Processing

Lab Processing:

Glasses are to be prepared by melting of electronic grade GeO_2 with reagent grade K_2CO_3 in the platinum ampule. Furnace atmosphere is to be

laboratory air with a temperature of at least 100°C above the liquidous for a minimum of one hour. Samples are to be annealed one hour at 25 to 50°C below the Littleton softening point then cooled to ambient.

The glass will be etched back into the ampule to allow insertion of the closure for sealing. The radiotracer Ge 68 is to be painted on the exposed surface of the glass and dried. The tracer deposit concentration is to be chosen such that a minimum activity in each anticipated diffusion slice is a minimum of 50 microCuries. The capsule is to be sealed using a electric arc welding with cooling as appropriate to minimize thermal effects on the glass sample.

The samples are to be enclosed in a sample capsule to be furnished by MSFC and sealed off with a helium atmosphere (pressure chosen to be such that one atmosphere is achieved at treatment temperature). The capsule and contents is then to undergo space processing.

Space Processing

The space processing of each capsule is to consist of a heating cycle designed to maximize time exposed to the diffusion temperature without exposing the low viscosity melt to gravitational forces. The cycles envisioned for each of the three different capsules is graphically depicted in Figure 1.

Post Processing Analysis

The post processing analysis is to consist of opening the sample ampules using an appropriate chemical machining solution. The diffusion profile is to be analyzed by etching the sample with dilute nitric acid to remove a predetermined section thickness. The section contained in the solution is to be counted to determine the activity of each section.

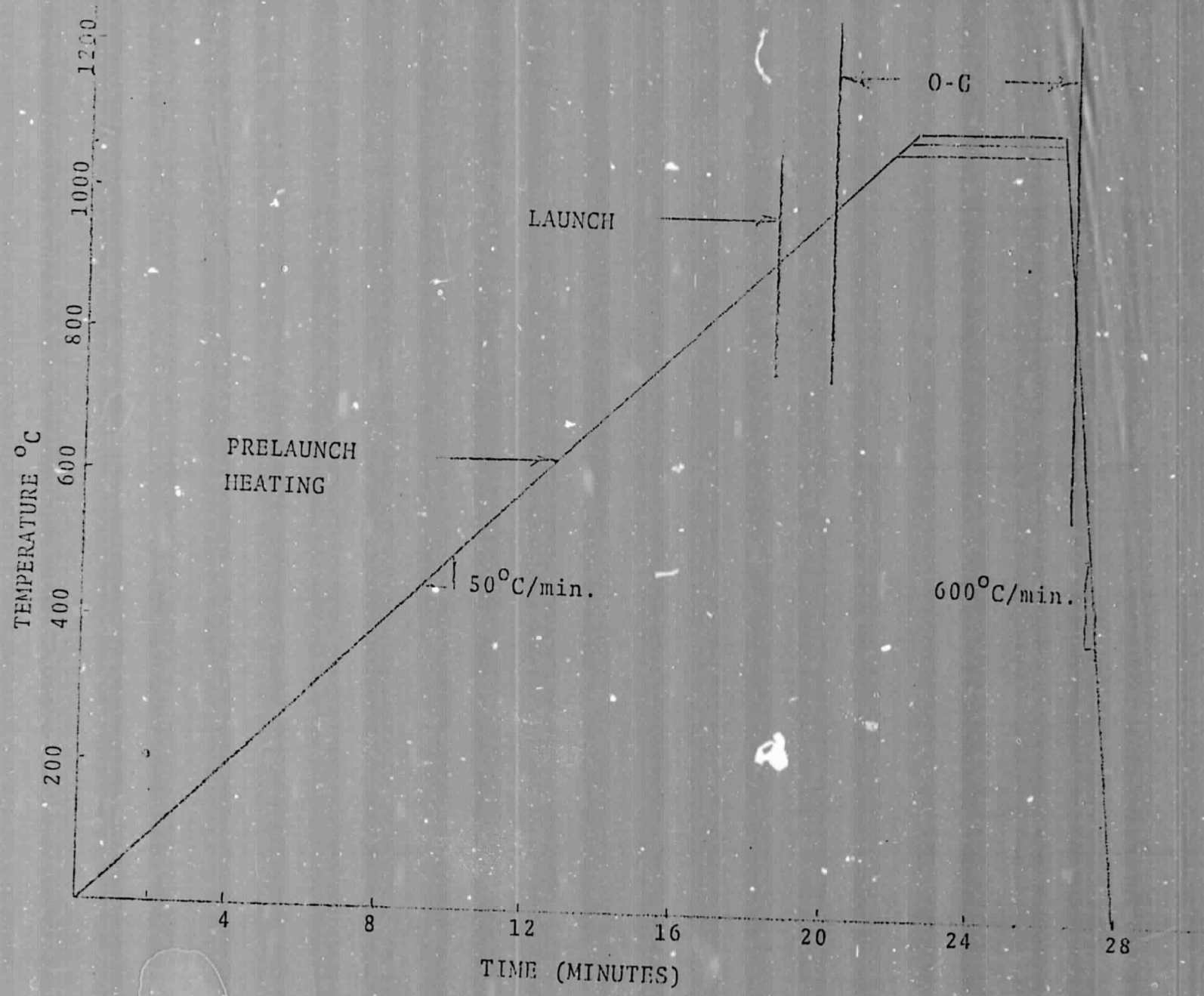


Figure 1: Space Process

Experimental Analysis

The appropriate solution to the diffusion equation for the present geometry is:

$$c(x,t) = \frac{S}{\sqrt{\pi D_t t}} \ell^{-\frac{x^2}{4D_t t}}$$

where c(x,t) is the concentration of radioactive atoms at a distance x from the initial face, S is the initial total activity, t is the diffusion time and D_t is the diffusion coefficient at a temperature T. By examination it is apparent that a plot of ℓn c(x) versus x^2 will be linear with a slope - $1/4D_t t$, thence with a given time t one can obtain D_t from the slope of the ℓn $c(x)/x^2$ plot.

The diffusion coefficient in a liquid can be related to the viscosity of the liquid by the Nabarro-Herring equation

$$\eta = \frac{kT}{\alpha a_o D}$$

or by the Stokes-Einstein formula

$$\eta = \frac{kT}{6\pi a_o D}$$

where a_o is the diameter of the diffusing species.[5]

The validity of these expressions was examined by comparing the measured diffusion coefficient for silicon in a 39% CaO, 40% SiO_2, 21% Al_2O_3 slag,[3] with the viscosity of the slag. Unfortunately, the viscosity was not reported in the article, so the viscosity for a 38% Ca, 42% SiO_2,

20% Al_2O_3 slag was used; this paper gives the viscosities of a large number of slags of different ratios of $CaO:SiO_2:Al_2O_3$ and the viscosity does not change appreciably with composition around the composition of the slag in which the diffusion coefficient was measured.

TABLE I

Slag Data[6]

T(°C)	$D(x10^8)^2cm^2/sec$	η poise
1350	3.7	46
1400	7.0	26
1450	13.5	16

Using $D = \frac{kT}{\alpha a_o \eta}$

1350°C $\alpha a_o = \frac{kT}{D\eta} = \frac{1.38x10^{-16}(1.62x10^3)}{3.7 \times 10^{-8}(46)} = 13.1 \times 10^{-8}$ cm

1400°C $\alpha a_o = \frac{1.38x10^{-16}(1.67x10^3)}{7.0 \times 10^{-8}(26)} = 12.7 \times 10^{-8}$ cm

1450°C $\alpha a_o = \frac{1.38x10^{-16}(1.72x10^3)}{13.5 \times 10^{-8}(16)} = 11.0 \times 10^{-8}$ cm

if $a_o = 10^{-8}$ cm, $\alpha \simeq 12$

The Nabarro-Herring equations are:[7]

$$\eta = \left[\frac{3}{32\pi}\right]^{2/3} \frac{kT}{D\Omega_o} Vg^{2/3}$$

(Equal Quasi-spherical grains, No grain boundary flow)

$$\eta = \frac{1}{10}\left[\frac{3}{4\pi}\right]^{2/3}\frac{kT}{D\Omega_o}\,Vg^{2/3}$$

(Equal Quasi-spherical grains, tangential stress relaxes at the boundaries). In our case, the "grain volume" Vg is the same as the volume of the mobile particle, so $Vg = \Omega_o = a_o^3$

$$\eta = \frac{1}{\alpha}\,\frac{kT}{Da_o}$$

from the first equation

$$\alpha = 1/\left[\frac{3}{32\pi}\right]^{2/3} = 10.4$$

and from the second

$$\alpha = 10/\left[\frac{3}{4\pi}\right]^{2/3} = 26.0$$

giving good agreement with the experimental value of $\alpha \simeq 12$ and with the Stokes-Einstein formula where $\alpha = 6\pi = 18.8$.

A large compilation of viscosity data is given by Riebling[8] for binary germanates containing Li_2O, Na_2O, K_2O and Rb_2O. Using his Figure 3, the viscosity of a 4.29 mole% Na_2O melt at 993°C is 240 poise, therefore

$$D = \frac{kT}{\alpha a_o \eta} = \frac{1.38\times10^{-16}\,\text{erg/°K}(1266\text{°K})}{15(10^{-8}\text{cm})\ \ (240\text{ poise})}$$

$$= 5 \times 10^{-9}\ \text{cm}^2/\text{sec.}$$

The following table is based on Riebling's viscosity data and the Nabarro-Herring equation with $\alpha = 15$.

TABLE II

Viscosity Data for Germania Glasses

Modifier	Mole %	T/°C	η(poise)	D Theoretical cm^2/sec	t=4min $\sqrt{Dt}$ mils
Na_2O	4.29	1108	100	$1.3 \cdot 10^{-8}$	0.70
	7.79	1108	26	$4.9 \cdot 10^{-8}$	1.4
K_2O	7.5	1000	76	$1.5 \cdot 10^{-8}$	0.7
	11.25	1000	28	$4.2 \cdot 10^{-8}$	1.2
	15.0	1000	13	$9.0 \cdot 10^{-8}$	1.8
	7.5	1100	35	$3.6 \cdot 10^{-8}$	1.2
	11.25	1100	14.8	$8.5 \cdot 10^{-8}$	1.8
	15.0	1100	7.6	$1.9 \cdot 10^{-7}$	2.5

After Riebling[8]

Ground Based Experimental Work

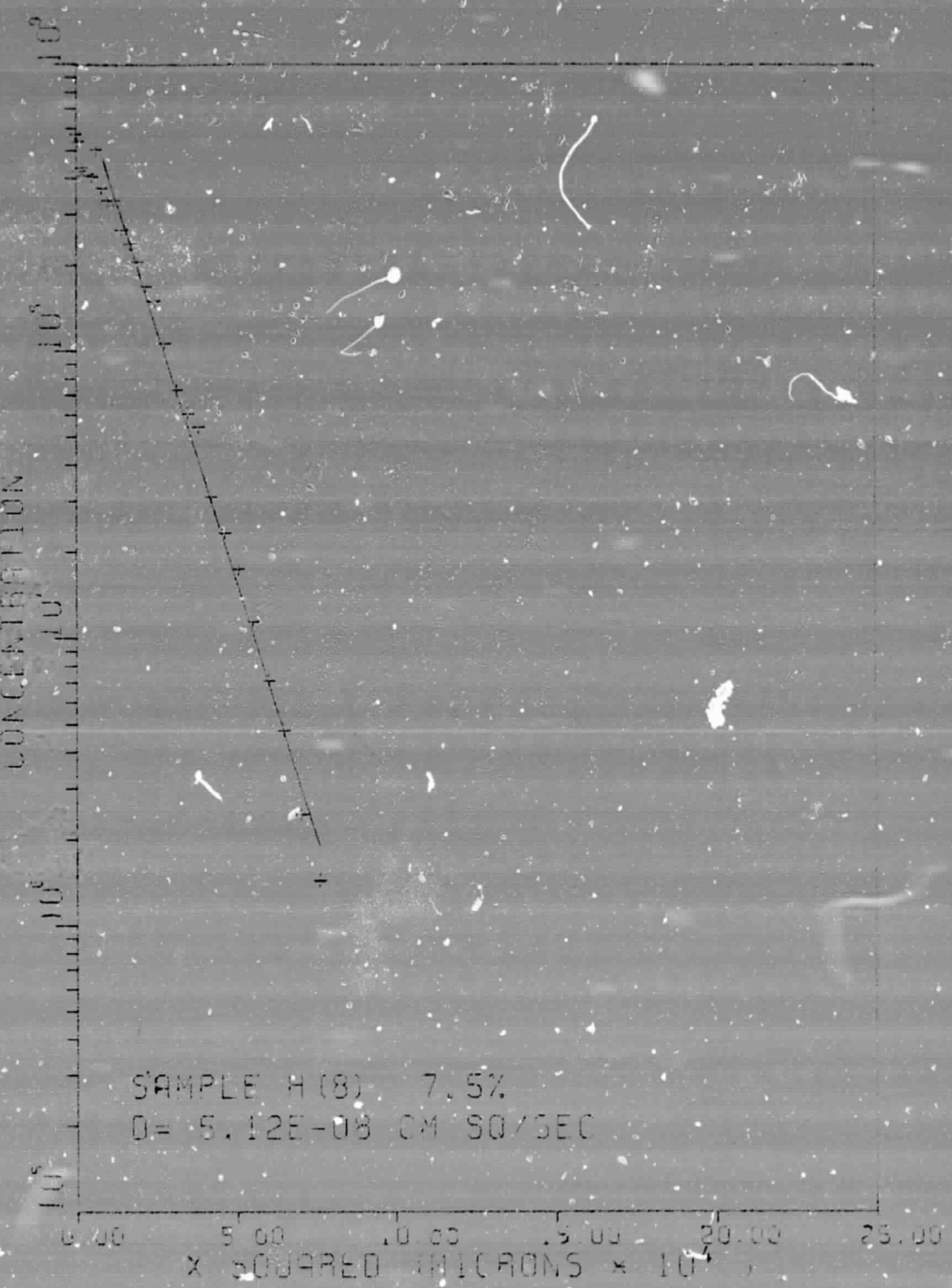
After the initial experimental formulation, the ground based simulation of the space experiments was undertaken. This led to the fabrication of samples in the geometry and type containers which were discussed earlier for the space experiment. The three glasses were prepared and radiotracers were placed on one end of the samples which were then heat treated at the diffusion temperatures for the appropriate times. The samples were sectioned using a technique which was developed especially for the potassium-germanate

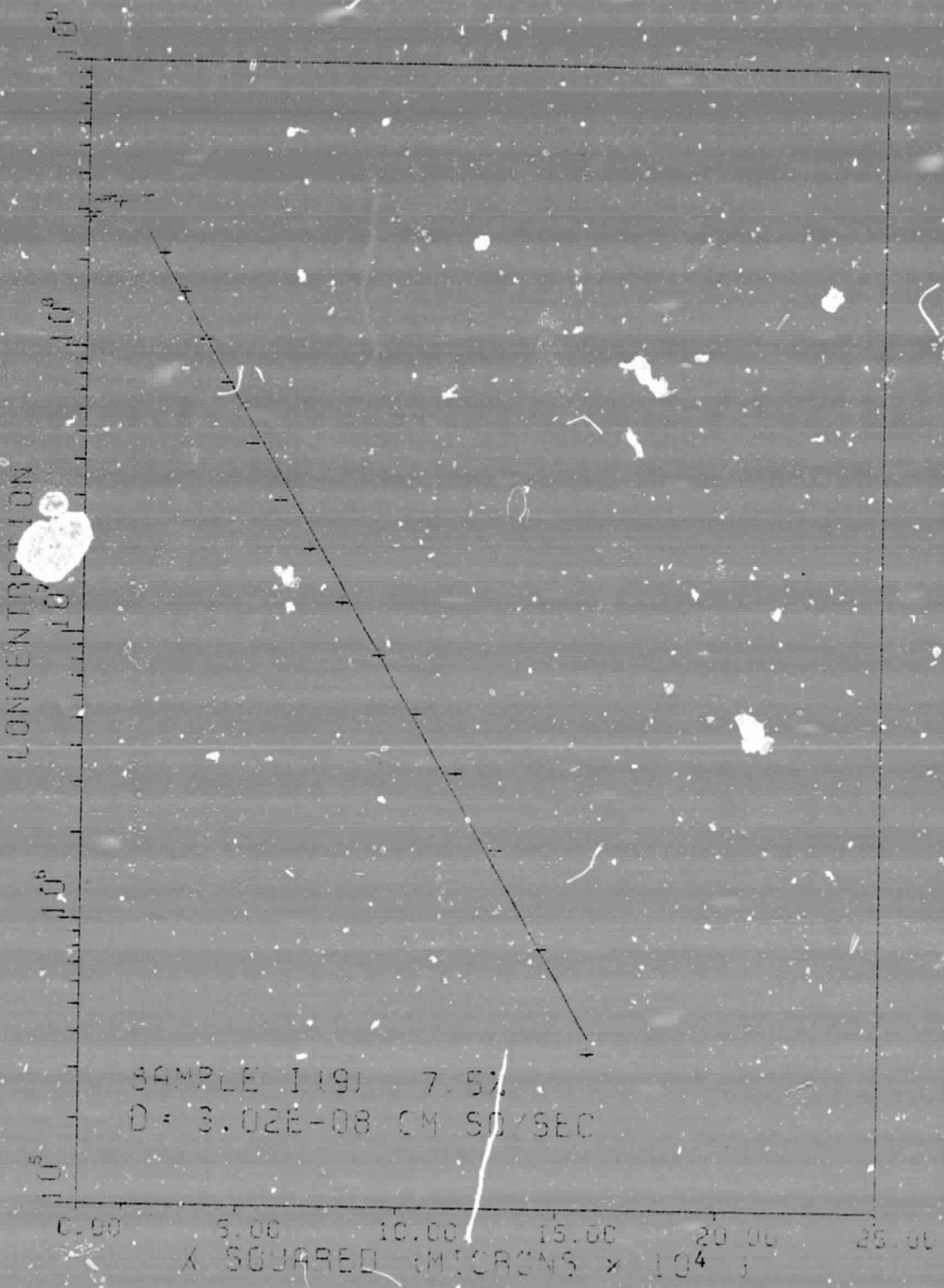
glasses. The solution which was used was a dilute nitric acid solution. The layers were removed from the actual sample in a counting vial which was subsequently placed in the NaI counting well. The results were plotted as corrected count rates as a function of distance squared.

Results

The data obtained for a 7.5%K_2O glass diffused 10 minutes at 1005°C are shown in Figure 2. The value of the diffusion coefficient extracted for this sample was 5.06 x $10^{-8}cm^2$/sec. A second experiment conducted with the same composition at the same temperature but for a longer time yielded the results as shown in Figure 3. The diffusion coefficient extracted from this result was 3.06 x $10^{-8}cm^2$/sec which compares favorably for the sample examined after the shorter diffusion time. It is also apparent upon examination of Figure 3 that significant deviation from the anticipated linearity occurs. It appears that this deviation is a result of the onset of convective mixing at the longer time. The results of a diffusion in the 7.5%K_2O glass for 10 minutes at 1030°C are shown in Figure 4. The diffusion coefficient extracted from this data was 1.85 x $10^{-7}cm^2$/sec. The activation energy obtained from these two data points is 171 Kcal/m. The examination of a 11.25% K_2O glass after a diffusion of 10 minutes at 1005°C gives the results shown in Figure 4 which yield a diffusion coefficient of 1.63 x $10^{-7}cm^2$/sec. This plot also shows considerable deviation from the anticipated linear behavior which appears to be the result of convective mixing. Attempts to obtain data for the 15%K_2O glass have proven fruitless because of either convective mixing at elevated temperatures or crystallization at the lower temperatures.

The data obtained is summarized in Table III which contains not only the experimental data but also the computed theoretical values discussed





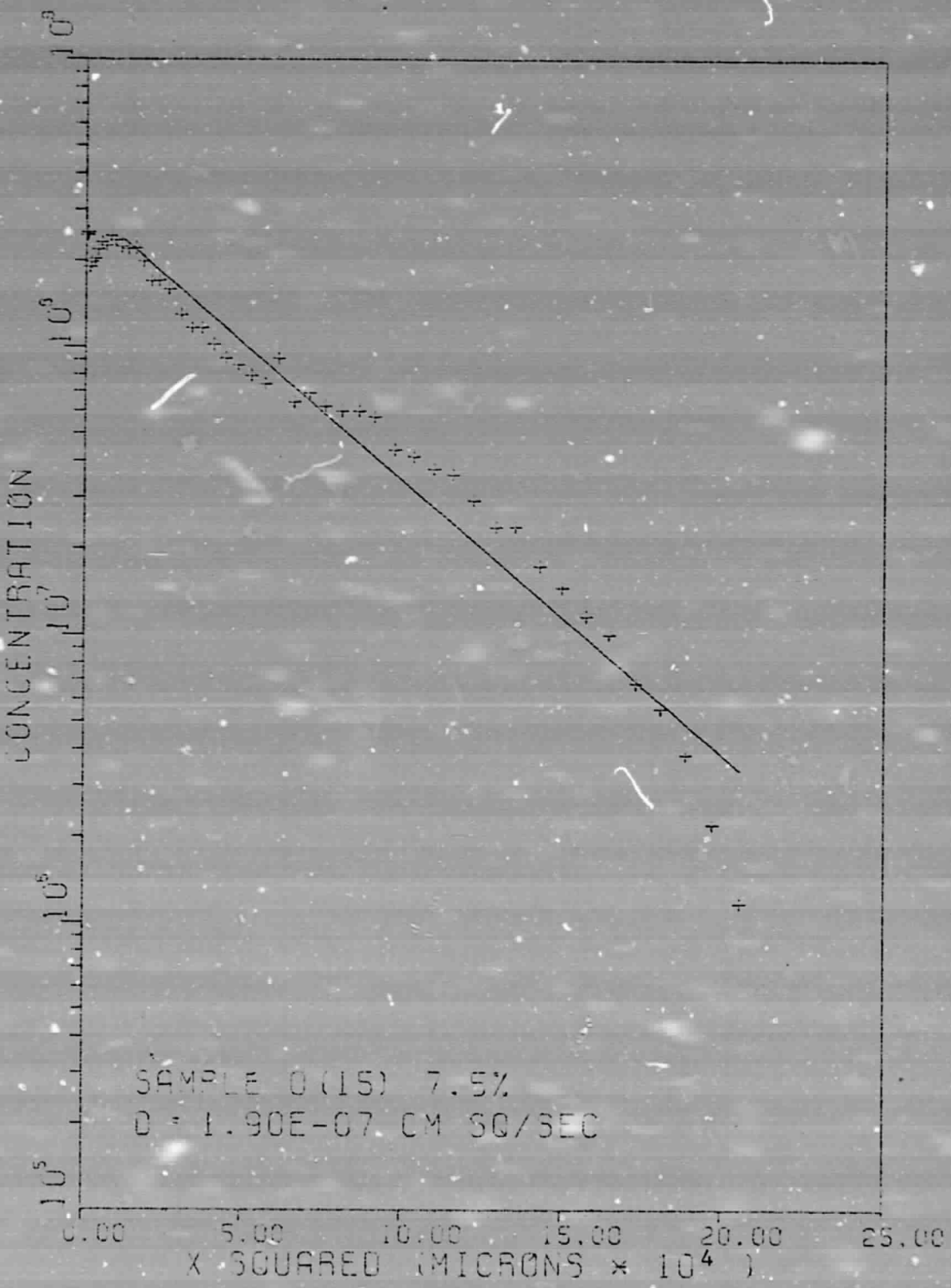

CONCENTRATION
10^8
10^7
10^6
10^5
SAMPLE 0(15) 7.5%
D = 1.90E-07 CM SQ/SEC
0.00
5.00
10.00
15.00
20.00
25.00
X SQUARED (MICRONS * 10^4)

TABLE III

K_2O (mole %)	Temp (°C)	η[1] (poise)	$D_{theor.}$[2] (cm^2/sec)x 10^8	$D_{meas.}$ (cm^2/sec)x 10^8	E_D (Kcal/mole)	E_{Flow}[1] (Kcal/mole)
7.5	1005	72.4	1.62	5.06		
					172	30.5
	1030	57.5	2.08	18.5		
11.25	1005	27.5	4.28	16.3		
15.0	1030	11.5	10.4			

[1] E. F. Riebling, J. Chem. Phys., 39, 1881, 1963.

[2] Calculated using $\alpha a_o = 15 \times 10^{-8}$ cm.

earlier. These results are best discussed by reference to the attached plot of viscosity and crystallization as a function of temperature and composition. These data were obtained from the literature and from work conducted in this study. It is apparent that the "best" data obtained in the present work was obtained from the 7.5 mole % K_2O glass at the temperatures corresponding to the two points shown in Figure 5. The two data points for the other glass compositions are also plotted and, as can be seen, lie in a different area of the plot. A detailed analysis of the present plot and the data provided in the Figures 2 - 5 indicate that the experimental data obtained for the 7.5 mole % K_2O glass is quite good, while that obtained for the other glasses is inaccurate because of either crystallization and convective mixing or of convective mixing. It thus appears that the diffusion coefficients can be measured in earth based experiments in those glasses of 7.5 mole % K_2O or less.

The deviations from linearity in the near surface region of the data reported in Figures 2 - 4 has been observed in several additional samples and is observed to become more pronounced with storage of the glass sample before isotope coating. The water content of the glass was measured and has been observed to increase with storage time, hence, these near surface results are doubtless a consequence of water absorption on the surfaces. The IR measurement of the water content could not, of course, determine the location of the water, but it is clear that the surface region is the only region which should be accessable to moisture under ambient conditions.

Summary

The work conducted under the present contract has taken two principal courses: First, the experiment for the weightless measurement of diffusion

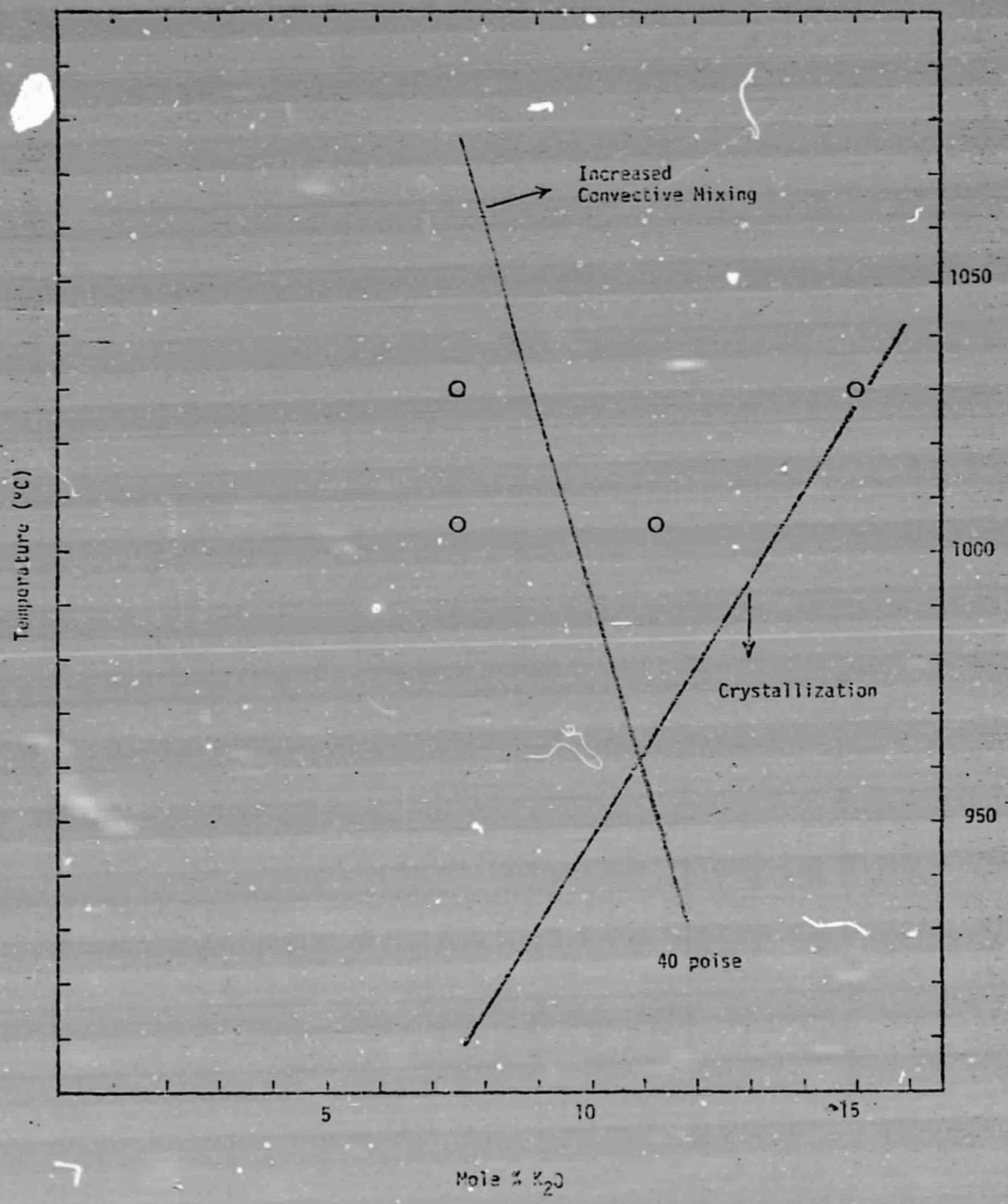


Figure 5: Plot of the temperature at which viscosity reaches 40 poise and observable crystallization occurs in 10 minutes at the temperature for the composition in question. Viscosity data from Riebling.

coefficients in glasses has been defined and the ground based experiments were conducted. Second, the measurements of diffusion coefficients which can be obtained under 1-G conditions were obtained and are here reported.

The space experiment was not accepted for flight, hence, no results were obtained from that portion of the program. The diffusion results obtained indicate that the activation energy for diffusion in the potassium germanate glasses is in the range 170 Kcal/mole, and the diffusion behavior is quite sensitive to water content of the glasses employed.

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