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Composite Diffusion Mechanisms and Diffusional Anisotropy
of Helium in Beryl, Aquamarine, Quartz, and Related Glasses

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Abstract

The rates of desorption of helium from several types of beryl, from aquamarine, and from quartz have been measured using a mass spectrometer type leak detector of high sensitivity. The rates measured on beryl or aquamarine slabs cut perpendicularly and parallel to the hexagonal axis of symmetry at 680°C are very different but conform to the appropriate solution of the diffusion equation. Diffusion through the channels present in the beryl crystal structure is probably the controlling process at this temperature. The extent of anisotropy, the conformance to the ideal curve shape and the sample to sample reproducibility correlate with the quality of the various beryls investigated. At low temperatures relatively little helium is evolved and the process does not conform to the solution of the diffusion equation mentioned above, probably because grain boundaries of various dimensions furnish the preferred diffusion paths. Fused beryl and quartz yield very anomalous (non conforming) rate curves while crystalline quartz is intermediate between the glasses and the crystalline beryls. Defect diffusion is probably of considerable importance in these cases. Results obtained on a beryl powder indicate that surface desorption is negligibly small in comparison to bulk and defect diffusion.

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INTRODUCTION

The study of diffusion rates in silicates is of great interest because the many known structures of natural or synthetic origin¹ afford an opportunity to see how the diffusion mechanism is affected or determined by the structural details. Much is known about diffusion properties of glasses of various compositions,² and about zeolites^{3,4} but few other crystalline silicates have been investigated in detail. Single crystals are usually not available and it is, therefore, very important to develop methods for distinguishing bulk and defect controlled diffusion processes.

Harrison has shown that if two different processes contribute to the overall diffusion, these can sometimes be characterized independently, i.e. the two rate constants in question can be determined by a detailed analysis of the desorption rates.⁵ To accomplish this, or to at least demonstrate the effects of two separate diffusion mechanisms in a given sorption experiment, non-steady state diffusion measurements must be carried out over an extended temperature and/or time range, the experimental precision must be high, and the two processes in question must proceed at very different rates. In view of Harrison's results, a very sensitive method was used in the present study to follow the desorption process over an extended time range, and the experiments were carried out over a temperature range of several hundred degrees centigrade, the upper limit being determined by the thermal stability of the material. Helium

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- (1) W. Eitel, "The Physical Chemistry of Silicates", U. of Chicago Press, Chicago (1954).
 - (2) J. D. MacKenzie, ed., "Modern Aspects of the Vitreous State", Vol. II, (1960); Butterworths, (London), Vol. II, pp. 1-71.
 - (3) W. W. Brandt, W. Rudloff, Z. phys. Chemie (Frankfurt), in press.
 - (4) R. M. Barrer, B. E. F. Fender, J. Phys. Chem. Solids, 21, 12 (1961), and references cited there.
 - (5) L. G. Harrison, Trans. Far. Soc., 57, 1191 (1961).

is an ideal diffusate molecule since, due to its small size, it is most likely to diffuse through the ordered crystalline regions ("bulk"). Beryl (and aquamarine) have well defined channels parallel to the axis of symmetry and should thus be very anisotropic with respect to bulk diffusion. There are some data in the older literature which show this effect,⁶ while a more recent study⁷ may have dealt with a composite diffusion process (say bulk and grain boundary) because the apparent activation energy for He diffusion was found to be somewhat larger than that obtained for Ar. In any case, the diffusional anisotropy of various beryl samples of very different quality are compared in the present study, so that the importance of bulk diffusion may become clear. As will be seen later, this approach will also test the validity of Harrison's suggestion that the desorption rate curve shapes can be analyzed to describe the principal contributing processes.

To gain a broad basis for the interpretation, crystalline quartz, fused specimens of beryl and quartz, as well as powdered crystalline samples were included in this work.

EXPERIMENTAL

The origin, appearance, general nature of X-ray diffraction pattern, and the results of etching experiments are summarized in Table (I). Macroscopically, the second and third beryls investigated do not differ much, but the X-ray powder diffraction patterns indicate that the latter contains some other crystalline silicate, probably α -quartz.⁸ The etching was done by immersing the polished specimens in fused NaOH for 30 to 300 seconds at about 320°C.

(6) Lord Rayleigh, Proc. Royal Soc. (London), A164, 470 (1924).

(7) K. K. Abdulgafarov, V. V. Cherdyn'tsev, N. P. Talobskaya, Optika Yadernye Protssessy, Alma-Ata, Shornik, 1959, 47-50.

(8) National Bureau of Standards Circular, 539, 9, (1959).

Table (1) Characteristics of Aquamarine, Beryls, and Quartz

Specimen	Appearance	X-ray diffraction pattern	Dimensions of Etch Pits (mm) on surfaces perpendicular ($\perp$) and parallel ($\parallel$) to axis of symmetry.
Aquamarine	Clear, light yellow-green	-----	$\perp$, 0.030; $\parallel$, 0.192 by 0.083.
Beryl, from Minas Geraes, Brazil	Clear, colorless	Very high crystallinity, excellent agreement with literature ⁸	$\perp$, 0.0471; $\parallel$, 0.107 by 0.042.
Beryl, from Ampangabe, Madagascar	Dark gree, near opaque but very uniform		$\perp$, 0.029; $\parallel$, 0.051 by 0.023.
Beryl, from Keystone, South Dakota	Off-white, opaque, rough surfaces	Low crystallinity, some α -quartz mixed in	very irregular and uncertain, but quite small
Quartz, from Hot Springs, Arkansas	clear and colorless	-----	-----

The desorption experiments were carried out as follows: First, the samples were degassed for 10 to 20 minutes at the experimental temperature and then over night exposed to He at approximately 500 mm Hg pressure. Next, the sample containers were quickly disconnected from the vacuum system and the specimens cooled to room temperature and stored. To measure the desorption rates, the sample is introduced into the vacuum and degassed for a short time at normal temperature to free it from much of the superficially sorbed atmospheric gases. Finally, it is dropped into the hot zone of the apparatus and the rate of He desorption is measured as a function of time. A sensitive mass spectrometer type leak detector (Model MD-140 of the Vacuum Instruments Corporation, Huntington Station, L.I., N.Y.) is used in a way described previously in some detail.⁹

RESULTS

The logarithm of the desorption rates measured are plotted against the logarithm of time so that the details of the rate process over several decades of logarithmic time and desorption rates can be shown and analyzed. The bend occurring in the desorption rate curves near completion allows an unambiguous superposition of the solution of the diffusion equation for an infinite slab and for the appropriate initial conditions.¹⁰ In this way apparent diffusion rates, $D^* = \frac{D}{2}$, can be obtained. Here D is the actual diffusion coefficient and l is the half thickness of the slab, diffusion being assumed to proceed perpendicular to the surface of the slab for the purpose of the data evaluation. Figures (1) and (2) show the rate data obtained at several temperatures on the aquamarine and beryl from Brazil, both materials being of high

(9) W. W. Brandt, M. Hattori, V. R. Sreenivasan, J. Chem. Phys., submitted for publication.

(10) K. Haruta, W. J. Spencer (Bell Telephone Laboratories), Bull. Am. Phys. Soc., 119, 219 (1964).

quality. The first three rate curves listed in the Legend to Figure (1) show the curve fits discussed above. Figure (3) shows data obtained on the beryls from Madagascar and South Dakota. Finally, some desorption runs on the fused beryl (from Brazil) and quartz samples, as well as on powders of these materials are given in Figure (4). A good deal of gas, presumably H_2O vapor, escaped from the two samples on fusion.

Quartz exhibits desorption rate curves which are intermediate between the curves for crystalline and fused beryls (Figures (1) to (4)). There are strong sample to sample differences in the quartz data, and hence they are not reported in detail.

At $790^{\circ}C$ the samples slowly deteriorate; presumably the thermal expansion causes mechanical stresses which lead to the formation of irregular cracks. The degraded specimens are opaque and yellowish. If there is little degradation, the desorption rate curves are somewhat steeper than the ideal ones at the very beginning and they approach low temperature curve shapes if the thermal degradation is excessive.

The experimental errors are quite unimportant in the Figures (1) to (4), except for the last few points of each run. Here the probable error range is indicated in each case and must be taken into account in the subsequent discussion of desorption rate curve shapes.

DISCUSSION

There is a strong dependence of desorption rate curve shapes on temperature evident in Figures (1) and (2), provided one considers only data obtained on a single specimen. At low temperatures, ($370^{\circ}C$) the initial desorption rates decrease very rapidly and several of the curves are convex to the abscissa. This is in marked contrast to the appropriate solution of the diffusion equation which is straight at short times and concave to the abscissa at

long times if plotted as in Figures (1) to (4).⁹ At intermediate temperatures (about 480°C) however, the long time portion of the desorption rate curve approaches this ideal curve shape, while at higher temperature (680 to 760°C) the fit is almost perfect over the entire experimental time range.

All the findings mentioned here are readily explained if one assumes bulk diffusion control in the temperature range of approximately 680°C to 760°C, grain boundary or defect diffusion at 370°C and below, and a wide transition region in between where both processes appear more or less side by side. The thermal degradation at high temperature causes defect diffusion through open cracks or crevices to play an increasingly important role. This is noticeable first at the beginning of the rate curves.

Other features of the experimental data are in accord with this interpretation: in the temperature range of 680°C to 760°C, the anisotropy of the process is strongest as one would expect if bulk diffusion is controlling. The diffusion rates for the sample slabs cut perpendicularly to the c-axis, $D^*_{\perp}$, are 10 to 20 times larger than those for the slabs cut parallel to this axis, $D^*_{\parallel}$, at 680°C (see Legends to Figures (1) to (4)). Hence, the corresponding ratio of effective diffusion lengths is about 4. On the other hand, the sample width which presumably is a measure of the length of the diffusion paths in samples cut parallel to the hexagonal axis of symmetry, divided by sample thickness, giving the diffusion length in perpendicular cuts, is close to 16. It is possible that there are some crevices or fissures of submicroscopic dimensions which are responsible for this numerical discrepancy; on the other hand, the effect of grain boundaries is perhaps not quite negligible even in the high temperature range (680 to 760°C). The effect cannot be a major one, though, because there is no correlation between the length to width ratios of the individual crystallites, as reported in Table (1), and the ratios

$D_{\perp}^*/D_{\parallel}^*$ of the corresponding samples. Also, the actual values of $D_{\perp}^*$ and $D_{\parallel}^*$ do not strongly increase with decreasing length of the individual crystallites present, and there is appreciable diffusional anisotropy even in the opaque and defect beryl from Madagascar.

At low temperatures, the total amount of He evolved over the experimentally accessible time range is much smaller than that desorbed at high temperatures. Presumably the "bulk" regions of the sample, that is the well formed crystallites, are effectively inaccessible to the He atoms since the bulk diffusion rate is far too low in this temperature range.

As mentioned earlier, the desorption rate curves obtained on crystalline quartz have a shape intermediate between the curves obtained on the crystalline and fused beryls. Presumably, the compact crystal structure of quartz is less permeable to He than is beryl, and defect diffusion remains relatively important, even at 680°C. Grass-shaped defects running parallel to the c-axis have been observed in natural quartz pieces,¹⁰ and ionic diffusion is known to be much easier along this axis than perpendicular to it.¹¹ The defect density may well vary from one specimen to the next and thus cause the observed sample to sample variations.

The fused quartz and beryl lead to desorption rate curves (Figure (4)) which deviate very strongly from the computed solution. This is readily understood if we assume a multitude of defects to be present, differing widely in shape and dimensions. They may range from small channels or crevices like those postulated to exist in some melts (lacunar structure¹²) to fissures of hundreds of angstroms dimensions. "Bulk" diffusion, that is permeation of the

(11) W. J. Spencer, private communication

(12) J. J. Zarzycki, J. Phys. Radium (Suppl. Phys. Appl.) 18, 65A (1957).

possibly disordered by compact regions of the network, thus contributes perhaps only little to the overall mass transport. Interestingly, McAfee postulated¹³ that submicroscopic defects of glasses can furnish preferred diffusion paths, in order to interpret the dependence of apparent gas diffusion coefficients on mechanical stresses. Also, Rayleigh assumed such defects to explain the very large difference in the diffusivities of mica and silica glass.¹⁴ Much additional work will be required to test the hypothesis offered here.

Finally, the rate curve for the beryl powder are shifted relative to the desorption rate curves for similar temperatures shown in Figures (1) to (3), consistent with the change in sample dimensions. Thus desorption from the surface cannot be an important contribution to the overall desorption processes discussed above. The quartz powder result cannot be compared to the results on crystalline quartz because of the strong sample to sample variations mentioned earlier but the total amount of He desorbed is much lower than in the beryl powder experiments, in agreement with the interpretations offered here.

ACKNOWLEDGMENT

This work has been supported by the U.S. Atomic Energy Commission under Contract AT-(11-1)-920.

(13) K. B. McAfee, Jr., J. Chem. Phys., 28, 218 (1958).

(14) Lord Rayleigh, Proc. Royal Soc. (London), A163, 376 (1937).

Legends to the Figures

Figure (1): Logarithm of Helium Desorption Rate against Logarithm of Time.

Aquamarine, cut perpendicular ($\perp$), or parallel ($\parallel$) to axis of symmetry. The direction of cutting, temperature of desorption, sample thickness (mm); sample weight (g), and relative diffusion rates, D^* , (sec^{-1}), for the individual curves are as follows: , $\perp$, 377°C , 0.60, 0.147, 4.8×10^{-5} ; , $\perp$, 465°C , 0.60, 0.147, 5.3×10^{-6} ; , $\perp$, 688°C , 0.60, 0.147, 5.0×10^{-5} ; , $\perp$, 688°C , 0.74, 0.180, 6.5×10^{-6} ; , $\perp$, 732°C , 0.60, 0.147, 8.7×10^{-5} ; , $\parallel$, 484°C , 0.44, 0.089, 4.5×10^{-6} ; , $\parallel$, 677°C , 0.53, 0.042, 5.8×10^{-6} ; , $\parallel$, 676°C , 0.57, 0.145, $\leq 4 \times 10^{-7}$; , $\parallel$, 708°C , 0.53, 0.042, 6.5×10^{-6} ; , $\parallel$, 726°C , 0.53, 0.042, 8.1×10^{-6} . The dashed curves next to the first three rate curves listed represent positions of the solution to the diffusion equation,¹⁰ used to derive values of $D^* = D/l^2$ (see text for more details).

Samples of equal thickness and weight are identical.

Figure (2): Logarithm of Helium Desorption Rate against Logarithm of Time.

Beryl from Brazil (for designations, see Legend to Figure (1)); , $\perp$,
 465°C, 0.42, 0.084, 8.5×10^{-6} ; , $\perp$, 690°C, 0.42, 0.084, 1.7×10^{-5} ;
, $\perp$, 692°C, 0.63, 0.121, 1.2×10^{-5} ; , $\perp$, 741°C, 0.42, 0.084,
 3.5×10^{-5} ; , $\perp$, 750°C, 0.42, 0.084, 4.5×10^{-5} ; , $\parallel$, 467°C, 0.46,
 0.071, 2.0×10^{-5} ; , $\parallel$, 689°C, 0.46, 0.071, 1.4×10^{-6} ; , $\parallel$, 694°C,
 0.70, 0.267, 1.2×10^{-6} ; , $\parallel$, 691°C, 0.50, 0.057, 1.7×10^{-6} ; , $\parallel$,
 731°C, 0.46, 0.071, 1.7×10^{-6} ; , $\parallel$, 755°C, 0.46, 0.071, 1.7×10^{-6} .

Figure (3): Logarithm of Helium Desorption Rate against Logarithm of Time.

Beryl from Madagascar (for designations, see Legend to Figure (1)): ;
 $\perp$, 675°C, 0.49, 0.089, 4.8×10^{-6} ; , $\perp$, 717°C, 0.49, 0.089, 1.1×10^{-5} ;
, $\perp$, 728°C, 0.49, 0.089, 1.4×10^{-5} ; , $\parallel$, 670°C, 0.51, 0.082,
 2.2×10^{-6} ; , $\parallel$, 708°C, 0.51, 0.082, 3.7×10^{-6} ; , $\parallel$, 727°C, 0.51,
0.082, 2.6×10^{-6} . Beryl from South Dakota: , direction uncertain, 682°C,
1.02, 0.323.

Figure (4): Logarithm of Helium Desorption Rate against Logarithm of Time

, Beryl from Brazil, .396 g powder, grain size about 90μ 373°C , ,
same, 690°C . Quartz powder, same grain size, , 0.522 g, 694°C , ,
0.232 g., 690°C . , Fused beryl from Brazil, thickness 0.79 mm., weight
0.088 g., 687°C . , Fused quartz, thickness 0.85 mm., weight 0.148 g.,
 691°C .

FIG. 1

FIG. 2

FIG. 3

FIG. 4