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## DIFFUSIVITY OF HELIUM IN FUSED SILICA

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## ABSTRACT

A statistical mechanical model of diffusion is applied to helium diffusion in fused silica. The number of gas atoms moving between solubility sites is related to the number of atoms in those sites. The number of atoms in the excited state, between two adjacent solubility sites, relative to the number occupying solubility sites can be described by their partition functions. The process of diffusion is treated as a random walk process which results in a diffusion equation in terms of the temperature, fundamental constants, and material parameters. The model is compared to data reported in the literature on He diffusion in fused silica in order to determine the unknown parameters. The model also shows that absolute rate theory is not able to account for the non-linearity observed in  $\log D$  vs  $1/T$  for this system.

## INTRODUCTION

The permeability of gases in fused silica at moderate pressures has been studied extensively over the past half century and is reviewed in recent publications.<sup>1,2,3</sup> At moderate pressures the solution of the gas in the glass is reasonably dilute, i.e. the mole fraction of He in SiO<sub>2</sub> at 1 atm is  $\approx 10^{-5}$ . If Henry's Law is applied to the physical solution of a gas in a solid, it can be shown that the Permeability = Diffusivity x Solubility. A statistical model describing the gas solubility has been derived by Studt, Shackelford, and Fulrath;<sup>4</sup> however, no attempt has been made to obtain a comparable quantitative model for the diffusion process. It is assumed that a reasonably idealized diffusion model can provide a worthwhile explanation of this physical process. Therefore, this paper proposes the application of a statistical mechanical model for the diffusion of helium gas in fused silica glass.

Diffusion in solids has been studied extensively with models usually expressed in an Arrhenius-type form

$$D = \gamma a_0^2 \nu \exp(-\Delta G_m / RT),^5$$

where  $D$  = the diffusivity,  $\gamma$  = a geometrical constant,  $a_0$  = the jump distance,  $\nu$  = the jump frequency,  $\Delta G_m$  = the activation free energy for diffusion,  $R$  = the gas constant and  $T$  = the absolute temperature.

Studies on the diffusion of gases in glass have used the more simplified version of the above expression,  $D = D_0 e^{-\Delta H / RT}$ , where  $D_0$  = the pre-exponential factor and  $\Delta H$  = the activation enthalpy for diffusion. Swets et al.<sup>6</sup> have observed that this expression did not accurately

describe their experimental data over the entire temperature range studied but that the data appeared to fit into two distinct temperature ranges with different activation energies. They explained this behavior in terms of changes in the residual crystallinity of the glass. Other experimenters<sup>7,8</sup> have attempted to describe this apparent non-linear behavior of an Arrhenius-type expression by assuming a temperature dependent pre-exponential factor,  $D_0$ . If this temperature dependence is accounted for, the experimental data appear to be described by only one activation energy over the entire temperature range. Consequently, they have argued that the Arrhenius expressions should be written as  $D = D_0' T^N e^{-\Delta H/RT}$  where  $N = 1/2$  or  $1$ . Shelby<sup>8</sup> found empirically that  $N = 1$  gave the best fit and noted that this was to be expected from the theory of absolute reaction rates<sup>9</sup> which predicts a pre-exponential term proportional to  $T$ . This is correct; however, the pre-exponential also contains partition functions which are temperature dependent. These partition functions contain terms such as  $e^{hv/2kT}$  which cause the proportionality between the pre-exponential and the temperature to be somewhat more complex than simply  $T$ . The diffusion model used here which is based on statistical mechanics shows that  $D_0$  is a complicated function of temperature. The entire pre-exponential factor, not just the first terms, must be considered when evaluating any temperature dependence.

As in the type of statistical model proposed for surface diffusion<sup>10</sup> and previous solubility models,<sup>4,11,12</sup> the vibrational motions of the dissolved gas atom will be treated as Einstein oscillators and the translational motion as that of the momentum of a particle in an element

of phase space. The model used here for diffusivity will be combined with the solubility model of Studt et al.<sup>4</sup> to obtain the complete expression for gaseous permeability.

#### MODEL

In order to obtain a diffusion model, the structure of the host material must be known. This model will be based on the structure of fused silica which has been described as a disordered form of  $\beta$ -cristobalite by Hicks.<sup>13</sup> The solubility sites in fused silica are approximately 3 Å in diameter<sup>4</sup> with "doorways" made up of oxygen rings connecting these sites. It is generally thought that these "doorways," which consist of a distribution of 5, 6 and 7 membered rings,<sup>13</sup> are large enough to permit easy movement of small gas atoms, i.e. He and Ne, through the larger 6 and 7 membered rings. It has been suggested<sup>14</sup> that the activation energy for diffusion is the elastic energy required to enlarge (dilate) a doorway sufficiently to accommodate or permit passage of an atom or ion. This may apply to motion of large modifier ions or inert atoms (e.g. argon); however, this is not expected to be valid for small atoms such as He because of the relatively high permeation rates observed in silica glasses as compared to other solids. Perkins et al.<sup>15</sup> have also stated that it is difficult to apply the dilation concept because one cannot define exactly how large the doorway must be dilated to permit movement of any given atom.

It is assumed that the process of gas atom movement between sites in the glass is a random walk process with an equilibrium established between atoms in solubility sites and those moving between sites (in a "doorway"). Therefore, at any temperature there is a certain fraction

of atoms in the solubility sites and a certain fraction moving between sites. These fractions vary with temperature. Since about one in  $10^5$  sites in fused  $\text{SiO}_2$  is occupied, it is highly improbable that neighboring sites will be occupied. Thus the diffusing species can be assumed to be moving in a truly random fashion. Hill<sup>10</sup> has shown that the number of atoms crossing a potential barrier ("doorway")/unit time is

$$N^* \left( \frac{kT}{2\pi m} \right)^{1/2} \quad (1)$$

where  $N^*$  = the number of atoms in a "doorway",  $k$  = Boltzmann's constant,  $T$  = temperature and  $m$  = the mass of the diffusing species. If  $N$  is the number of atoms in solubility sites and each atom spends time  $\tau$  in this site before jumping to the next site, then  $N/\tau$  is the number of atoms crossing a barrier per unit time; therefore,

$$N/\tau = N^* \left( \frac{kT}{2\pi m} \right)^{1/2} \quad (2)$$

Since the movement of the atoms is random throughout the structure, then jump vectors in all directions will be equally probable and  $D = \frac{1}{6} f d^2 \frac{1}{\tau}$  where  $D$  = the diffusion coefficient,  $d$  = the jump distance, and  $f$  = a correlation coefficient. For interstitial diffusion,  $f = 1$ . Combining the above expressions,

$$D = \frac{1}{6} d^2 \frac{N^*}{N} \left( \frac{kT}{2\pi m} \right)^{1/2} \quad (3)$$



When an atom moves from one site to a neighboring site, it must pass over a potential barrier,  $\epsilon_0$ , which is the result of attractive and repulsive forces of the solid acting upon the dissolved gas atom. This potential barrier is the difference in energy of the atom in the center of a solubility site relative to the same atom in the center of the "doorway" at the top of the potential barrier. This amount of energy,  $\epsilon_0$ , which the atoms must acquire to move between sites is essentially the activation energy,<sup>9</sup>  $\Delta H$ , for diffusion. For further discussions, it will be assumed that the activation energy is independent of temperature.

Shackelford<sup>16</sup> has shown that the motion of the atom in a solubility site contains three vibrational degrees of freedom with a characteristic vibrational frequency of  $6.9 \times 10^{12} \text{ sec}^{-1}$ . For the motion between sites it will be assumed that the atom has two vibrational degrees of freedom and one translational degree of freedom as it moves through the center of a "doorway." The vibrational components will be considered as simple harmonic oscillators and the translational component will be considered as a particle moving in an element of phase space.<sup>10</sup> It is also possible that intermediate stages of motion such as hindered translation<sup>10</sup> might occur. However, as in the model of Studt et al.<sup>4</sup> such refinement of the theory is not warranted at the present time because of the non-crystalline structure of fused silica glass.

The ratio of the number of atoms in "doorways" to those in solubility sites is equal to the ratio of the partition functions of the atom in the respective positions and can be expressed as<sup>10</sup>

$$\frac{N^* d\zeta}{N} = \frac{q_x^{++} q_z^{++} (2\pi mkT/h^2)^{1/2} d\zeta e^{-\epsilon_0/kT}}{q_x q_y q_z} \times \frac{M^{++}}{M} \quad (4)$$

where  $(2\pi mkT/h^2)^{1/2} d\zeta$  is the translational partition function,  $q_x^{++}$  and  $q_z^{++}$  are the vibrational partition functions associated with the motion of an atom at the barrier,  $q_x$ ,  $q_y$  and  $q_z$  are the vibrational partition functions associated with the motion of an atom in a solubility site,  $M^{++}/M$  is the ratio of the number of activated states to the number of solubility sites, and  $\epsilon_0$  ( $\Delta H$ ) is the difference in the energy of the potential energy surface at the barrier and in the solubility site. For the diffusion of monatomic gases in fused silica it will be estimated that  $q_x^{++} = q_z^{++}$  and  $q_x = q_y = q_z$ .

In  $\beta$ -cristobalite, the solubility sites are tetrahedrally coordinated and  $M^{++}/M = 2$ . However, in fused silica, each site has "doorways" which can consist of 5, 6 or 7 membered rings. Diffusion will be preferred through the larger "doorways." Thus a solubility site must contain two larger "doorways" to contribute to atomic movement and  $M^{++}/M = 1$  for this case, since no diffusion occurs through the smaller ones. When the proper partition functions are substituted into the above expression, it becomes

$$\frac{N^*}{N} = \frac{\left( e^{\frac{hv}{2kT}} - e^{-\frac{hv}{2kT}} \right)^3}{\left( e^{\frac{hv^*}{2kT}} - e^{-\frac{hv^*}{2kT}} \right)^2} \left( \frac{2\pi mkT}{h^2} \right)^{1/2} e^{-\frac{\Delta H}{RT}}, \quad (5)$$

which leads to the diffusivity expression

$$D = \frac{1}{6} \frac{kT}{h} d^2 \underbrace{\frac{\left( e^{\frac{hv}{2kT}} - e^{-\frac{hv}{2kT}} \right)^3}{\left( e^{\frac{hv^*}{2kT}} - e^{-\frac{hv^*}{2kT}} \right)^2}}_{D_0} e^{-\frac{\Delta H}{RT}} \quad (6)$$

where  $d$  = the distance an atom moves between the sites,

$v$  = the vibration frequency in solubility sites,

$v^*$  = the vibration frequency in "doorway",

$\Delta H$  = the activation energy for diffusion,

$D_0$  = the pre-exponential term.

#### DISCUSSION

In the diffusion model,  $d$ ,  $v^*$  and  $\Delta H$  are unknowns;  $v$  has been determined elsewhere.<sup>16</sup> Thus the unknown parameters  $v^*$  and  $\Delta H$  and the material parameter,  $d$ , must be determined in order to test the validity of the model. It is possible that there is wide range of translation distances,  $d$ , in the glass because every solubility site is not identical due to the amorphous nature of glass.  $\Delta H$  can be calculated by summing the attractive and repulsive forces acting on the diffusing atom if the structure were precisely known. Likewise, the calculation of the vibration frequency in the "doorway,"  $v^*$ , also requires knowledge of the exact structure. Even if the structure is well known, calculation of the binding energies between rare gas atoms and the ions of a solid are

only approximations<sup>12</sup> which may vary by a factor of three. Since accurate calculations of  $\Delta H$  and  $v^*$  are not possible and the translation distance,  $d$ , varies among the sites, these terms will have to be determined by fitting the model to experimental data. The literature contains consistent values of diffusion coefficients of various gases in glasses. Using the data of Swets, Lee, and Frank<sup>6</sup> for He diffusion in  $\text{SiO}_2$ , we have diffusion coefficients ranging over 4 orders of magnitude and which extend from  $300^\circ$  to  $1300^\circ\text{K}$ . Figure 1 shows the results of a least squares analysis when the model was fitted to the data by varying the three unknowns. The best fit (solid line) yields values of  $d = 2.5 \pm .5\text{\AA}$ ,  $v^* = 7.8 \pm .1 \times 10^{12} \text{ sec}^{-1}$  and  $\Delta H = 6100 \pm 50 \text{ cal/mole}$ . These values are in good agreement with those in the literature.<sup>4,16</sup> The jump distance,  $d$ , is approximately the distance between the centers of the adjacent solubility sites. The vibration frequency in a "doorway" would be expected to be somewhat higher than that in a solubility site ( $6.9 \times 10^{12} \text{ sec}^{-1}$ ), because the atom must "squeeze" through an opening smaller than the site, resulting in a steeper potential well. Activation energies have been reported<sup>8</sup> in the range of 4600-7000 cal/mole in the literature, assuming various temperature dependencies of the pre-exponential factor of the Arrhenius equation. This temperature dependence will be determined. When the data of Swets, Lee, and Frank,<sup>6</sup> over the whole temperature range, are subjected to a conventional Arrhenius plot ( $D_0$  independent of temperature), a value for the activation energy,  $\Delta H$ , of  $6063 \pm 46 \text{ cal/mole}$  is obtained. Figure 2 shows the variance in  $D_0$  with temperature when  $d = 2.5\text{\AA}$ ,  $v = 6.9 \times 10^{12} \text{ sec}^{-1}$  and

$v^* = 7.8 \times 10^{12} \text{ sec}^{-1}$ . It can be seen that this pre-exponential factor is essentially independent of temperature over the range of room temperature to infinity. In most diffusion experiments one usually assumes that  $D_0$  is temperature independent over the range of consideration. This is shown to also apply to the diffusion of He in fused silica. The small systematic deviations (Fig. 1) of the data from the model at lower and higher temperatures are probably a result of a slight temperature dependency in the activation energy. This deviation is considered small enough not to warrant further sophistication in trying to describe the complex variation of  $\Delta H$  with temperature.

When the above diffusion model is combined with the solubility model of Studt et al.<sup>4</sup>, an expression for the permeability is obtained:

$$K = \frac{1}{6} \frac{d^2}{h} \left( \frac{h^2}{2\pi mkT} \right)^{3/2} \frac{N_s}{\left( e^{\frac{hv^*}{2kT}} - e^{-\frac{hv^*}{2kT}} \right)^2} e^{-\left( \frac{\Delta H_K}{RT} \right)} \quad (7)$$

where  $K$  = the permeability,  $N_s$  = the number of solubility sites/cc and  $\Delta H_K$  is the activation energy for permeation. Figure 3 shows the permeability versus temperature for the data of Swets et al.,<sup>6</sup> versus the model (solid line). Again, reasonable agreement is obtained.

#### CONCLUSIONS

A diffusivity model has been applied to monatomic gaseous diffusion in glass. This model can be applied to diatomic molecules if the intrinsic rotations and vibrations of the molecule are known. If these are the same in the doorway and solubility site, then the partition functions for these terms would cancel, resulting in an expression

identical to that derived for the monatomic case. This diffusivity model need not be restricted to gaseous diffusion in glass, but also may be applied to such areas as the interstitial diffusion of He in Si and Ge. This could also be done with the solubility model, thus rendering the overall permeation expression valid for the general case of interstitial diffusion in solids where the gas does not react chemically with the solid or dissociate.

Non-linearity of  $\log D$  vs  $1/T$  has been observed in the diffusion of monatomic gases in fused silica. This behavior has been explained either in terms of the structure of fused silica or by the application of absolute rate theory to the diffusion of gases in glass. It has been claimed that the pre-exponential term,  $D_0$ , was best represented as being proportional to  $T$  as predicted in absolute rate theory.<sup>8</sup> However, a more complete treatment of absolute rate theory, similar to that proposed for surface diffusion,<sup>10</sup> has been applied to the diffusion of monatomic gases in fused silica. The resulting expression for diffusion shows that the pre-exponential is a complicated function of temperature, due to the vibrational partition functions, and not just simply proportional to  $T$ . When this model is applied to the diffusion of He in fused silica, it shows that the dependence of  $D_0$  on  $T$  in the temperature range 300-1300°K is almost non-existent. The application of absolute rate theory does not explain the small non-linearity observed in  $\log D$  vs  $1/T$ . This may be due to the fact that this theory in its present form neglects the effects of temperature on the potential surface by assuming it is constant throughout the temperature range.

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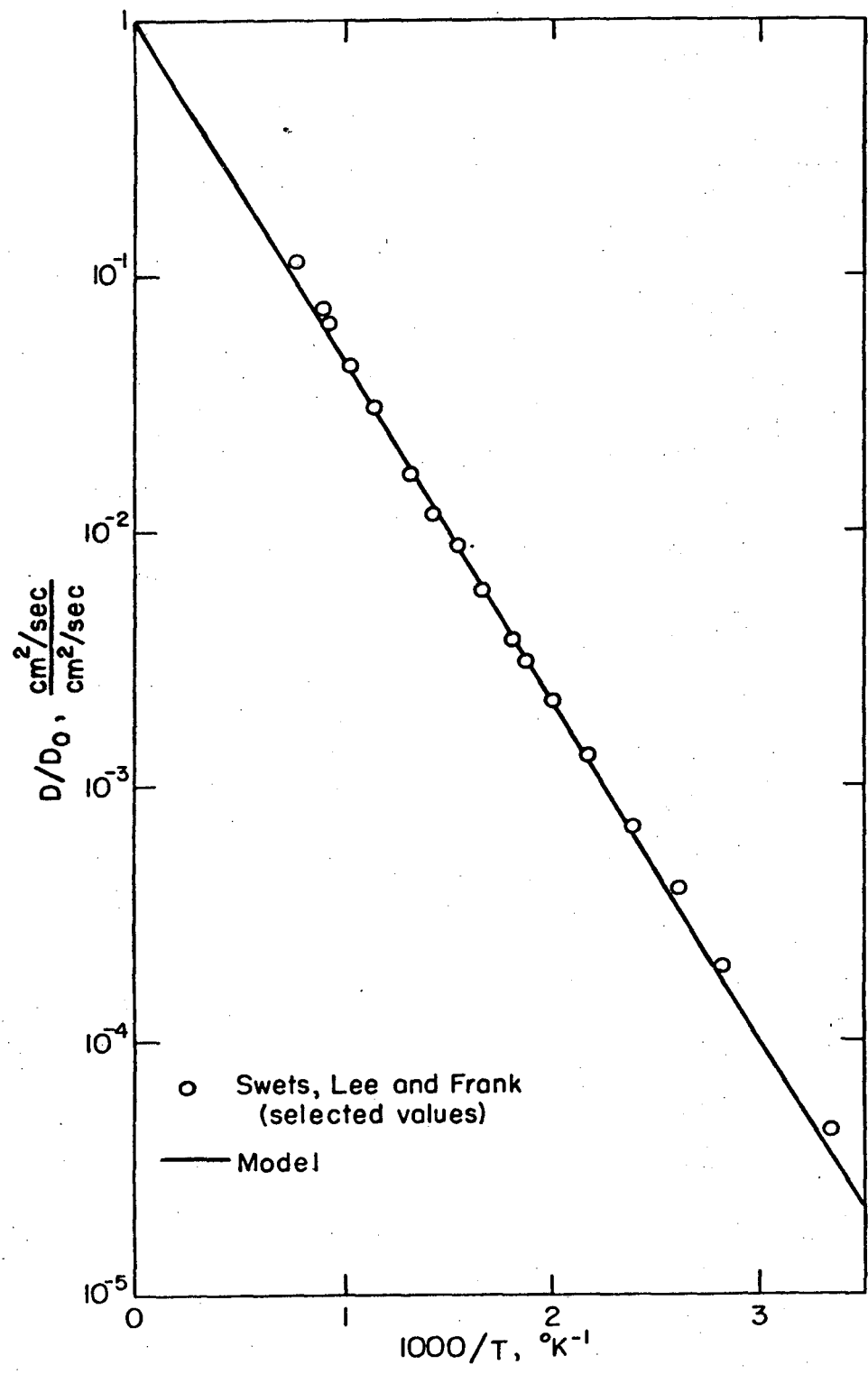
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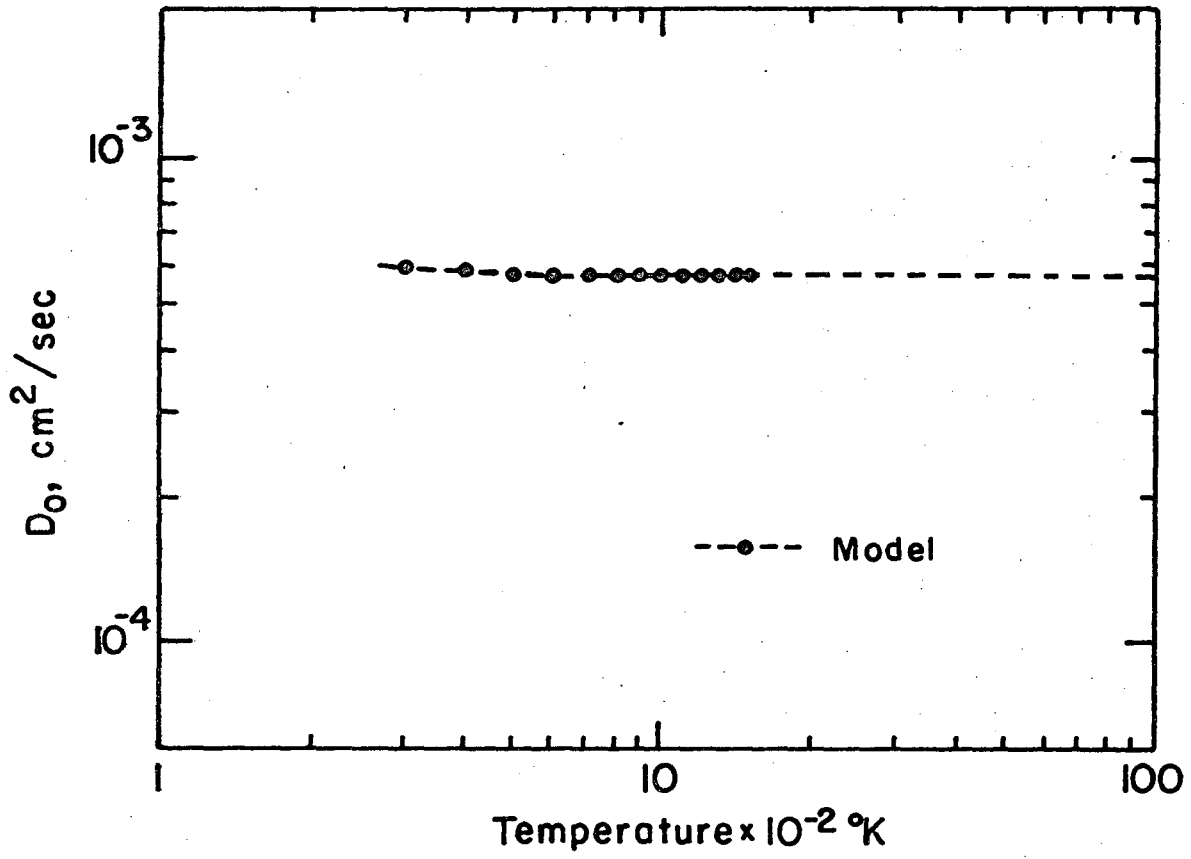
## FIGURE CAPTIONS

- Fig. 1. Comparison of experimental diffusivity data for helium in fused silica with a plot of Eq. (7), using the parameters of  $\bar{d} = 2.5 \text{ \AA}$ ,  $v = 6.9 \times 10^{12} \text{ sec}^{-1}$ ,  $v^* = 7.8 \times 10^{12} \text{ sec}^{-1}$  and  $\Delta H = 6100 \text{ cal/mole}$ .
- Fig. 2. Variation of the value of the pre-exponential factor,  $D_0$ , with temperature of the Arrhenius equation for helium diffusion in fused silica.
- Fig. 3. Comparison of experimental permeability data for helium in fused silica with a plot of Eq. (8), using the parameters  $\bar{d} = 2.5 \text{ \AA}$ ,  $v^* = 7.8 \times 10^{12} \text{ sec}^{-1}$ , and  $\Delta H_k = 4600$ .



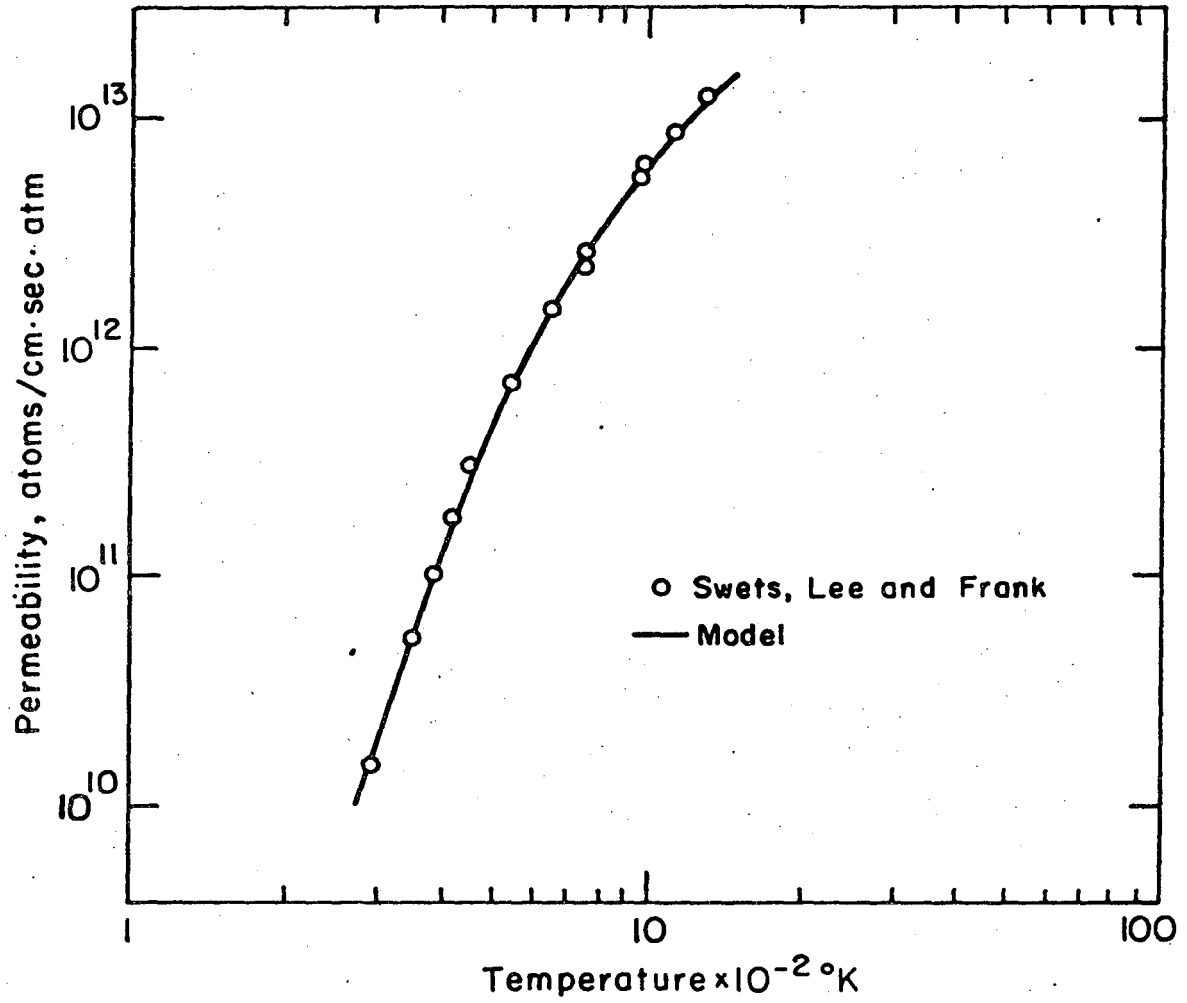
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Fig. 1



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Fig. 2



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Fig. 3

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