Title
DIFFUSIVITY OF MONATOMIC GASES IN FUSED SILICA

Author
Masaryk, Joseph S.

Publication Date
1972-06-01

Submitted to J. of Applied Physics

LBL-847
Preprint

DIFFUSIVITY OF MONATOMIC GASES IN FUSED SILICA

Joseph S. Masaryk and Richard M. Fulrath

June 1972

AEC Contract No. W-7405-eng-48

DIFFUSIVITY OF MONATOMIC GASES IN FUSED SILICA

Joseph S. Masaryk and Richard M. Fulrath

Inorganic Materials Research Division, Lawrence Berkeley Laboratory,
and Department of Materials Science and Engineering,
College of Engineering; University of California,
Berkeley, California 94720

ABSTRACT

A statistical mechanical model of gas diffusion in fused silica is presented. 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.

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.[1,2,3] At these pressures the solution of the gas in the glass is reasonably dilute, i.e. the mole fraction of He in SiO_2 at 1 atm is $\approx 10^{-6}$. 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;[4] 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 a statistical mechanical model for the diffusion of a monatomic gas in fused silica glass.

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

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

where D = diffusivity, γ = geometrical constant, a = jump distance, ν = jump frequency, ΔG_m = activation free energy for diffusion, R = gas constant and T = temperature. Studies on the diffusion of gases in glass have used the more simplified version of the above expression, $D = D_o e^{-\Delta H/RT}$, where D_o = pre-exponential factor and ΔH = activation enthalpy for diffusion. Swets et al.[6] 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[7,8] have attempted to describe this apparent non-linear behavior of an Arrhenius type expression by assuming a temperature dependent pre-exponential factor, D_o. 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 $D = D_o' T^N e^{-\Delta H/RT}$ where $N = 1/2$ or 1. Unfortunately most of these arguments have been empirical in nature and have not attempted to analyze the problem completely. The diffusion model presented here shows that D_o 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[9] and previous solubility models,[4,10,11] the vibrational motion of the dissolved gas atom will be treated as an Einstein oscillator and the translational motion as a particle-in-a-box. The model developed here for diffusivity will be combined with the solubility model of Studt et al.[4] 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 β-cristobalite by Hicks.[12] The solubility sites in fused silica are approximately 3 Å in diameter[4] with "doorways" made up of oxygen rings connecting these sites. It is generally thought that these "doorways," which consist of distribution of 5, 6 and 7 membered rings,[12] are sufficiently large enough to permit easy movement of small gas atoms, i.e. He and Ne, through the larger 6 and 7 membered rings. This is consistent with the relatively high permeation rates observed in silica glasses as compared to other solids.

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"); that is, 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 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[9] has shown that the number of atoms crossing a potential barrier ("doorway")/unit time/unit distance =

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

where N^* = the number of atoms in a doorway, k = Boltzman's constant, T = temperature and m = mass of the diffusing species. The number of atoms crossing the barrier per unit time would be

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

where d = distance that the atom moves between sites. If N if the number of atoms in solubility sites and each atom spends τ, time, in this site before jumping to the next site, then N/τ = number of atoms crossing a barrier per unit time; therefore,

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

Since the movement of the atoms is at random through the structure, then jump vectors in all directions will be equally probable and $D = \frac{1}{6}\, fd^2\, \frac{1}{\tau}$ where D = diffusion coefficient and f = correlation coefficient. In fused silica each site has several "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 $f \approx \frac{1}{2}$ because only 50% of the jumps will contribute to diffusion. Combining the above expressions:

$$D = \frac{1}{12}\; d\, \frac{N^*}{N}\left(\frac{kT}{2\pi m}\right)^{1/2} \tag{4}$$

When an atom moves from one site to a neighboring site, it must pass over a potential barrier, ε_o, 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 at rest (zero point energy) in the center of a solubility site relative to the same atom at rest in the center of the "doorway," top of the potential barrier. The amount of energy, ε_o, the atoms must acquire to move between sites is essentially the activation energy,[13] ΔH, for diffusion at 0°K. The ratio of the number of atoms in a "doorway" to those in a solubility site, $\frac{N^*}{N}$, is equal to the ratio of the partition functions[9] of the atom in the respective positions because of the equilibrium established between N* and N:

$$\frac{N^*}{N} = \frac{Q^*}{Q} e^{-\varepsilon_o/kT} \qquad (5)$$

where Q* is the partition function associated with the motion of an atom moving between sites, Q is the partition function associated with the motion of an atom in a solubility site, and ε_o (ΔH) is the difference in zero point energies.

For further discussions, it will be assumed that the activation energy is independent of temperature. Shackelford[14] has shown that the motion of the atom in a solubility site contains three degrees of vibrational freedom with a characteristic vibrational frequency of 6.9×10^{12} $\sec^{-1}$. For the motion between sites it will be assumed that the atom has two degrees of vibrational freedom and one degree of translational 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 classical particle-in-a-box motion, with the translational and vibrational motion being independent of each other. Treatment of the translational motion classically is valid down to a few angstroms and temperatures greater than room temperature. The error in using the classical solution versus the quantum result for He translation distances of 2.5 Å is 20% at 100°K and 5% at 1500°K. The use of the quantum expression requires summation of at least 100 terms in a series solution. Such detail as a series solution, therefore, is not necessary in expressing an idealized model, as the exact nature of glass structures is not precisely known. It is also possible that intermediate stages of motion such as hindered translation[9] might occur. However, as in the Studt et al.[4] model, such refinement of the theory is also not warranted at the present time in light of the previous comments on the nature of the structure of fused silica glass. When the proper partition functions are substituted into the above expression it becomes

$$\frac{N^*}{N} = \frac{2\left(e^{\frac{hv}{2kT}} - e^{-\frac{hv}{2kT}}\right)^3 \left(\frac{2\pi mkT}{h^2}\right)^{1/2} d\, e^{-\frac{\Delta H}{RT}}}{\left(e^{\frac{hv^*}{2kT}} - e^{-\frac{hv^*}{2kT}}\right)^2} \qquad (6)$$

which leads to the diffusivity expression

$$D = \underbrace{\frac{1}{6}\frac{kT}{h}\, d^2 \frac{\left(e^{\frac{hv}{2kT}} - e^{-\frac{hv}{2kT}}\right)^3}{\left(e^{\frac{hv^*}{2kT}} - e^{-\frac{hv^*}{2kT}}\right)^2}}_{D_o}\; e^{-\frac{\Delta H}{RT}} \qquad (7)$$

where d = distance atom moves between the sites

v = vibration frequency in solubility sites

v* = vibration frequency in "doorway"

ΔH = activation energy for diffusion

D_o = pre-exponential term

DISCUSSION

In the diffusion model, d, v^* and ΔH are unknowns; v has been determined elsewhere.[14] Thus these fundamental constants v^* and ΔH 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. ΔH 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. These are difficult calculations even if the structure is well defined because there are several expressions in the literature[10,11] that describe the van der Waals interaction between gas atoms and the solid which yield constants that vary by a factor of three. As in the case of the translation distance, d, the doorways between such sites are not identical, thus making it practically impossible to obtain accurate v^*'s and ΔH's. Therefore, these unknowns need be only approximated to test the model. The literature contains consistent values of diffusion coefficients of various gases in glasses. When the data of Swets, Lee and Frank[6] for He diffusion in SiO_2 is combined with experimental values obtained in this laboratory, we have diffusion coefficients ranging over 5 orders of magnitude and which extend from 200° to 1300°K. Figure 1 shows a computer analysis of model fitted to the data by varying the three unknowns. The best fit (solid line) yields values of

$d = 3\ \mathring{A}$, $v^* = 9.3 \times 10^{12}\ \text{sec}^{-1}$ and $\Delta H = 6150$ cals/mole. These values are in good agreement with those in the literature.[4,14] The vibration frequency in a "doorway" would be expected to be somewhat higher than 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[7] in the range of 4600-7000 cals/mole in the literature assuming various temperature dependencies of the pre-exponential factor of the Arrhenius equation. Thus when this model was fitted to the data no a priori temperature dependence of D_o was assumed. This temperature dependence will be determined. When the data of Swets, Lee and Frank[6] and that obtained in this laboratory are subjected to a conventional Arrhenius plot, (D_o independent of temperature) a value for the activation energy, ΔH, of 6149 ± 79 cals/mole is obtained. Figure 2 shows the variance in D_o with temperature when $d = 3\ \mathring{A}$, $v = 6.9 \times 10^{12}\ \text{sec}^{-1}$ and $v^* = 9.3 \times 10^{12}\ \text{sec}^{-1}$. 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_o is temperature independent over the range of consideration. This is shown to also apply to the diffusion of He in fused silica. The systematic deviation (Fig. 2) of the model at higher temperatures is probably a result of a slightly non temperature independent activation energy. This deviation is considered small enough not to warrant further sophistication in trying to describe the complex variation of ΔH with temperature.

When the above diffusion model is combined with the solubility model of Studt et al.[4] an expression for the permeability is obtained:

$$K = \frac{1}{6}\frac{d^2}{h}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \frac{N_s}{\left(e^{\frac{hv^*}{2kT}} - e^{-\frac{hv^*}{2kT}}\right)^2} e^{-\left(\frac{\Delta H_K}{RT}\right)} \qquad (8)$$

where K = permeability, N_s = number of solubility sites/cc and ΔH_K is the activation energy for permeation. Figure 3 shows the permeability versus temperature for the data of Swets et al.[6] and this laboratory versus the model (solid line). Again, reasonable agreement is obtained.

CONCLUSIONS

A diffusivity model has been derived for 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[4] 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 solid or dissociate.

ACKNOWLEDGMENT

The authors wish to thank Dr's. J. F. Shackelford, J. W. Morris and D. J. Meschi for helpful discussions.

This work was supported by the United States Atomic Energy Commission.

REFERENCES

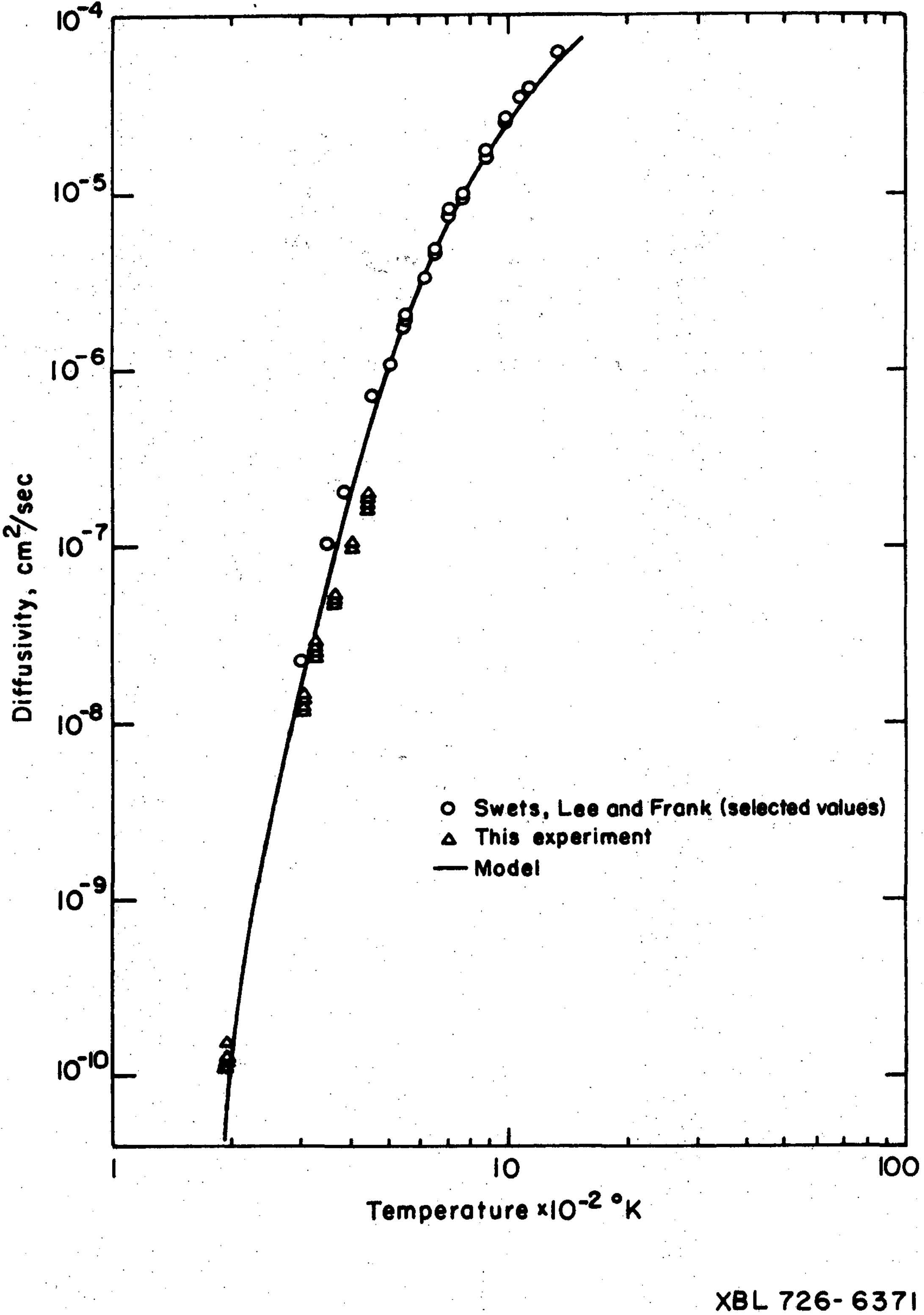
1. R. H. Doremus, in Modern Aspects of the Vitreous State, J. D. McKenzie, Ed. (Butterworths, Washington, D. C., 1962) Vol. 2.
2. E. L. Williams, Glass Ind. 43 [3], 113 (1962).
3. H. Scholze, Glass Ind. 47, 546 (1966).
4. P. L. Studt, J. F. Shackelford and R. M. Fulrath, J. Appl. Phys. 41 (7), 2777 (1970).
5. P. G. Shewmon, Diffusion in Solids, (McGraw-Hill, New York, 1963).
6. D. E. Swets, R. W. Lee and R. C. Frank, J. Chem. Phys. 34 (1), 17 (1961).
7. J. E. Shelby, J. Am. Ceram. Soc. 54 (2), 125 (1971).
8. W. M. Jones, J. Am. Chem. Soc. 75, 3093 (1953).
9. T. L. Hill, Introduction to Statistical Thermodynamics, (Addison-Wesley, Reading, Mass., 1960).
10. D. R. Olander, J. Chem. Phys. 43 (3), 779 (1965).
11. R. M. Barrer and D. E. W. Vaughan, Trans. Fara. Soc. 63 (9) 2275 (1967).
12. J. F. G. Hicks, Chemistry 58, 437 (1967).
13. K. J. Laidler, Theories of Chemical Reaction Rates (McGraw-Hill, New York, 1969).
14. J. F. Shackelford, Ph. D. thesis, University of California, Feb. 1971 (UCRL-20399).

FIGURE CAPTIONS

Fig. 1. Comparison of experimental diffusivity data for helium in fused silica with a plot of Eq. (7), using the parameters of $d = 3\ \text{Å}$, $v = 6.9 \times 10^{12}\ \text{sec}^{-1}$, $v^* = 9.3 \times 10^{12}\ \text{sec}^{-1}$ and $\Delta H = 6150$ cals/mole.

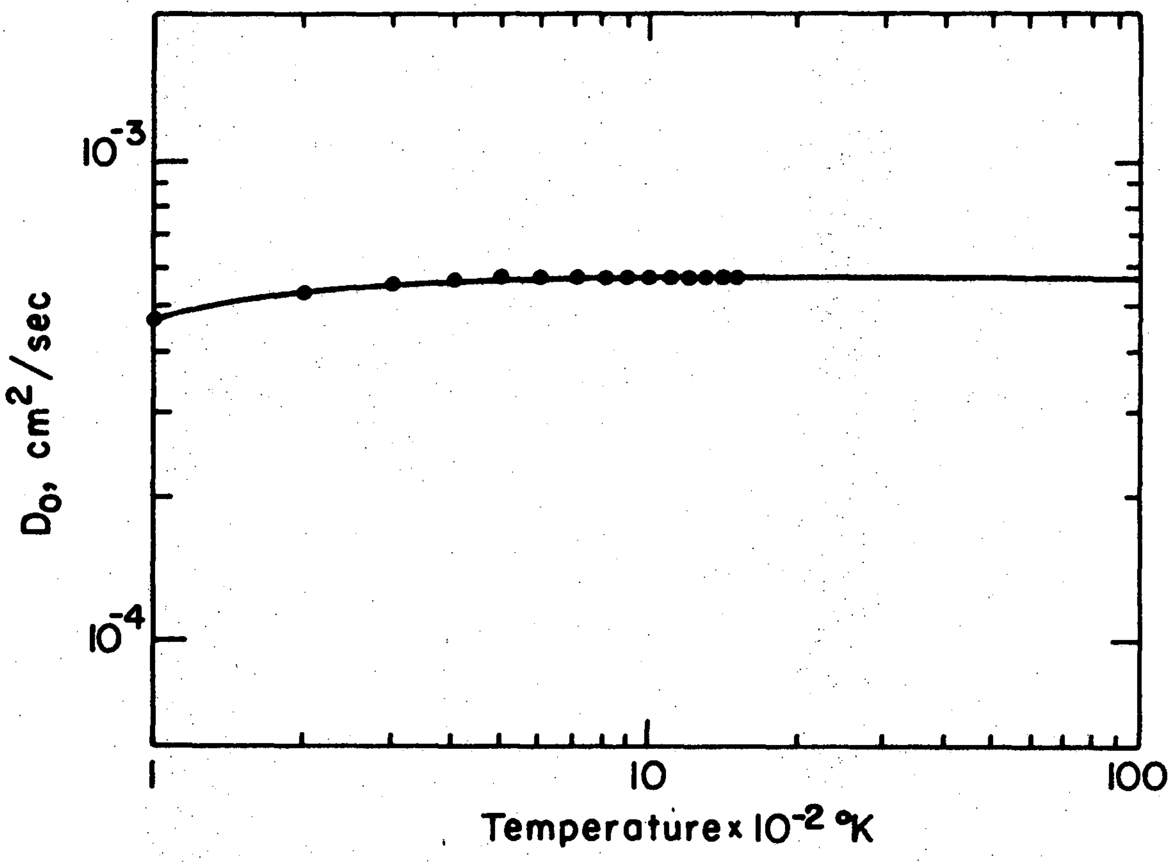
Fig. 2. Variance of the value of the pre-exponential factor, D_o, with temperature of the Arrhenius equation for helium diffusion in fused silica.

Fig. 3. Comparison of experimental permeability data for helium in fused silica with a plot of Eq. (8), using the parameters of $d = 3\ \text{Å}$, $v^* = 9.3 \times 10^{12}\ \text{sec}^{-1}$ and $\Delta H_k = 4650$.



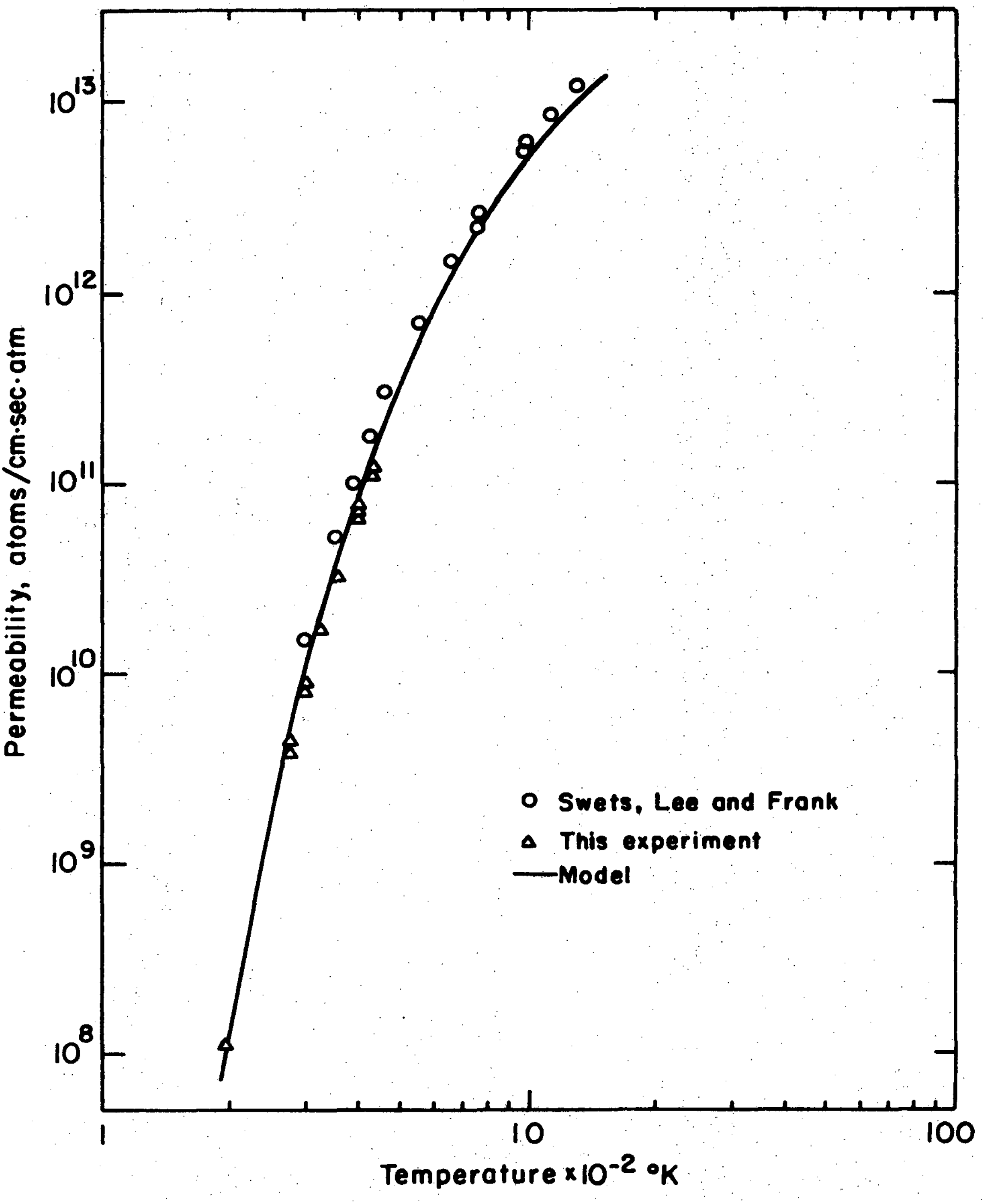
XBL 726-6371

Fig. 1



XBL726-6374

Fig. 2



XBL 726-6375

Fig. 3

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720