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LAWRENCE RADIATION LABORATORY
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THE SOLUBILITY OF GASES IN GLASS

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THE SOLUBILITY OF GASES IN GLASS

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ABSTRACT

January 1971

The statistical thermodynamics of the gas-in-glass system provides a basic model of the solubility. Equations are derived which give the solubility (in atoms or molecules per cubic centimeter of glass) as a function of gas pressure, temperature, fundamental constants, and material parameters. Three main categories of solubility are considered: (a) physical solubility of monatomic gases, (b) physical solubility of polyatomic gases, and (c) chemical solubility of polyatomic gases. The results for (a) and (b) are essentially equivalent. The results for (c) are dependent upon the specific system involved.

The model was compared with the experimental results for a variety of systems. Case (a) was observed for helium and neon in fused silica. Variations of the thermal history of the fused silica did not appear to have a measurable effect on physical solubility as evidenced in the helium data. Case (b) was observed for hydrogen in fused silica. Physical solubility was measured by a modified Seiverts' technique and was characterized by a linear dependence on pressure. Binding energies for the physically dissolved species were of the order expected for van der Waals bonding. Vibrational frequencies were on the order of $10^{13}$ sec$^{-1}$ with the heavier species having the lower frequencies. Case (c)
was observed for hydrogen in fused silica using previous literature data. The fused silica of this study did not display chemical solution of hydrogen perhaps due to the presence of water-produced hydroxyls. Comparison of the model with the literature data showed a $p^{1/2}$ pressure dependence for the solubility (indicative of dissociation) and a binding energy of about 63 kcal/mole (indicative of chemical bonding).
I. INTRODUCTION

Glasses are used in a wide variety of gas atmospheres. A number of gases are known to be soluble in glasses even at room temperature. A large body of experimental data on gas solubility in glass is available in reviews.\(^1,2\) However, almost all of the data are over a limited temperature range or were obtained indirectly (usually from permeation and diffusion measurements).

The thermodynamics of these generally dilute solutions is interesting in itself. It should be emphasized that the solubility to be discussed is in glasses below their glass transition temperatures where glass is truly a rigid solid rather than a supercooled liquid, as it is above the transition temperature. Solubility in the solid glass is that which would arise from exposure to gases during material application while that in the liquid glass would arise during fabrication.

Adequate quantitative models for gas in glass systems are lacking. However, statistical models have been proposed for gas solubility in metals.\(^3-6\) These theories have successfully described the solubility of \(\text{H}_2\) both with and without the formation of an hydride phase. Monatomic gas solution in crystalline oxides has been treated for \(\text{UO}_2\), tridymite,\(^7\) and cristobalite.\(^8\) Studt\(^9\) first suggested a similar approach for helium solution in glass. This paper will develop a comprehensive statistical mechanical model for gas solution in glass.

Experimental measurements of gas solution in glass have been made in order to test the model mentioned above and to provide improved data for some common systems. The glass used was fused silica, the simplest of the silicate glasses and a commonly used material. The gases used
were those known to be most soluble in fused silica, viz. helium, neon, and hydrogen. The primary experimental technique was a modification of Seiverts' method\textsuperscript{10} used for measuring gas solubility in liquid metal alloys. Also, the chemical absorption of hydrogen was measured from the infrared absorption spectra. Hydrogen is of special interest as it shows both physical and chemical solubility.
II. THE MODEL

The model assumes an ideal gas in equilibrium with the species in solution. The ideal gas is represented by free particles in a three-dimensional box (translation) with any internal molecular motion represented by independent rigid rotors (rotation) and simple harmonic oscillators (vibration). The dissolved species may be considered as a similar combination of fundamental modes of motion. However, the restriction of any molecular motion in the dissolved state is assumed to produce a corresponding vibrational mode of the simple harmonic oscillator type.

Such a model is considered reasonable in light of the success of similarly idealized models in treating gaseous equilibria, Langmuir adsorption, and, as mentioned in the previous section, gaseous solubility in crystalline solids.

Various types of solubility are possible. Noble gases dissolve as atoms. Polyatomic gases may dissolve with or without dissociation. Here, physical solubility is defined as solution without molecular dissociation and with relatively weak van der Waals bonding of the dissolved atom or molecule with the glass. Chemical solubility infers molecular dissociation and relatively strong chemical bonding of the dissociated species with the glass. However, it must be noted that the solution of gases in the glass solid is generally restricted to the smaller molecular species which can interstitially diffuse through the glass network structure.

Again, it should be emphasized that the glass being discussed is a rigid solid, i.e. below its glass transition temperature. This is important in the development of the model as the rigidity allows the
assumption that the dissolved species are localized.

A. Previous Models

Doremus has proposed a "free volume" model of the solubility of gases in glass. This model considers the free volume or "openness" of the glass structure to determine the magnitude of solubility. However, the model is qualitative and considers only one of many factors which can affect gas solubility. Statistical mechanical models of gas solubility in crystalline solids can serve as obvious guides for gas-in-glass systems. Studt first suggested that helium solubility in glass could be treated this way. A revision of Studt's approach is given in the next section on monatomic gas solution. This section is the basis of a recent publication. Further extensions of the approach to polyatomic solution are given in the last two parts of the Model section.

B. Monatomic Gas Solution

Equilibrium between the gaseous and dissolved states requires that the Gibbs free energy of the gaseous state, \( G(g) \), equal that of the dissolved state, \( G(s) \). Expressions for the Gibbs energies can be obtained from the assumed atomic model using

\[
G = kT \left( \frac{\partial \ln Q}{\partial \ln V} \right)_{T,N} - kT \ln Q
\]  

(1)

where \( Q \) is the canonical ensemble partition function, \( k \) is Boltzmann's constant, \( T \) is the absolute temperature, and \( V \) is the volume containing a number of particles, \( N \).

Assuming the gas to be ideal, the \( Q \) is that for a system of \( N \) indistinguishable particles in a three-dimensional box
where $m$ is the mass of one atom, $h$ is Planck's constant, and $q$ is the partition function for a single particle. Substituting Eq. (2) into Eq. (1) and using $pV = NkT$ (the ideal gas law) one obtains

$$G(g) = -RT \ln \left[ \frac{kT}{N!} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right]$$

where $R$ is the gas constant and $p$ is the pressure of the gas atmosphere.

For the dissolved state,

$$G(s) = G(Q) + E(0) - TS_m$$

with $G(Q)$ given by Eq. (1) where $Q$ is now the partition function associated with the motion of the gas atom in the dissolved state. For the monatomic case, the motion shall be assumed to be combinations of translation (the particle in the box) and vibration (the simple harmonic oscillator). $E(0)$ is the energy of the atom at rest (the lowest quantum state) in solution relative to the similar rest state in the free gas, i.e., removed from the potential field of the solid. This binding energy, $E(0)$, will be discussed further in section IV. $S_m$ is the partial molal entropy of mixing for the gas. It is of the form

$$S_m = R \ln \left( \frac{N_s}{n_s} \right)$$
where $N_S$ is the number of solubility sites available per cubic centimeter, and $n_S$ is the number of gas atoms dissolved per cubic centimeter of glass. The value of $n_S$ at one atmosphere pressure will be called "the solubility." The derivation of Eq. (5) assumed that $N_S$ and $n_S$ were large numbers and that $N_S > n_S$. These assumptions should be valid for all real systems discussed in this paper.

Four cases of solubility could occur. The dissolved species could have three degrees of translational freedom, two degrees of translational and one degree of vibrational freedom, one degree of translation and two degrees of vibration, or three degrees of vibration. Also, the translational motion could be localized or non-localized. The degrees of vibrational freedom would occur when the structure of the glass restricts the translational motion of the gas. Localized translation could occur in relatively large solubility sites such as pores. Nonlocalized translation could occur throughout the solid structure with the solid serving as a potential field with the potential being $E(0)$.

For the systems discussed in this paper, only the case of three degrees of vibration will be developed. Noble gas solubility is assumed to be in the interstitial openings of fused silica with the openings only slightly larger than the gas atoms. As long as there is a significant structural barrier between solubility sites, the assumption of localized vibration rather than nonlocalized translation is preferable. Also, for translational distances which are on the order of interatomic spacings in solids, the potential well would be expected to be nearly parabolic as associated with the harmonic oscillator rather than square as associated with the particle in a box. Therefore, small solubility
sites would again be expected to produce vibrational motion rather than translation.

For dissolved atoms with three degrees of vibrational freedom,

\[ Q = \frac{N}{q} = \left( \frac{e^{-\frac{\nu}{2kT}}}{1 - e^{-\frac{\nu}{kT}}} \right)^3 \]  

(6)

where \( \nu \) is the vibrational frequency of a simple harmonic oscillator.

Substituting Eqs. (5) and (6) into Eq. (4) gives

\[ G(s) = -RT \ln \left[ \frac{N}{n_s} \left( \frac{1}{1 - e^{-\frac{\nu}{kT}}} \right)^3 \right] + E(0). \]  

(7)

Equating \( G(g) \) and \( G(s) \) and rearranging terms gives the final expression for monatomic solubility

\[ \frac{n_s}{p} = \left( \frac{\hbar^2}{2\pi mkT} \right)^{3/2} (kT)^{-1} N \left( \frac{e^{-\frac{\nu}{2kT}}}{1 - e^{-\frac{\nu}{kT}}} \right)^3 e^{-E(0)/RT}. \]  

(8)

C. Polyatomic Gas Solution - Physical Solubility

The approach used in the monatomic case is extended, but the principle of the problem is unchanged. In fact, the result can be essentially the same as Eq. (8). For convenience, a specific example will be used, viz. the homonuclear diatomic.

The diatomic case is complicated primarily by the addition of internal degrees of freedom (two rotational and one vibrational). Equations (1), (4), and (5) are still valid. The partition function for the ideal gas is
$$Q = q^N / N! = (1/N!) \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{T}{\sigma} \left( \frac{e^{-\theta_{vl}/2T}}{1 - e^{-\theta_{vl}/T}} \right) \right]^N$$

(9)

with $\sigma$ the symmetry number ($\sigma = 2$ for H$_2$), $\theta_r$ the characteristic temperature for rotation ($\theta_r = h^2/8\pi^2 I k$ where $I$ = moment of inertia), and $\theta_{vl}$ is the characteristic temperature for vibration ($\theta_{vl} = h\nu/k$). This assumes the rotation to be that of a rigid rotor and the vibration to be that of a simple harmonic oscillator and that rotation and vibration are independent. Substitution of Eq. (9) into Eq. (1) gives

$$G(g) = -RT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \left( \frac{kT}{p} \right) \left( \frac{T}{\sigma} \right) \left( \frac{e^{-\theta_{vl}/2T}}{1 - e^{-\theta_{vl}/T}} \right) \right].$$

(10)

For the dissolved state, the internal vibration is assumed to be retained, i.e. the molecule does not dissociate and the vibrational frequency is not significantly altered. This leaves nine possible configurations depending upon the number of rotational and translational degrees of freedom that would be transformed to vibrational degrees of freedom. For the specific case to be discussed later (H$_2$ in fused silica), the solubility sites are slightly larger than the dissolved molecule and are separated by slight structural barriers. The dissolved state for this case would be assumed to retain the two degrees of rotational freedom but have the three degrees of translational freedom become three degrees of vibration. Basically, the undissociated molecule is assumed to retain its internal motion but loses the translational motion of the center of mass. The single molecule partition function for this case is
where $\theta_v$ is the characteristic temperature for vibration of the center of mass of the dissolved molecule. The resulting $G(s)$ is

$$G(s) = -RT \ln \left[ q \frac{N_s}{n_s} \right] + E(0)$$

with $q$ given by Eq. (11). Equating $G(g)$ and $G(s)$ and rearranging terms gives the final solubility equation for homonuclear diatomic physical solubility:

$$\frac{n_s}{p} = \left( \frac{\hbar^2}{2\pi m kT} \right)^{3/2} (kT)^{-1} N_s \left( \frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} \right)^3 e^{-E(0)/RT}$$

which is equivalent to Eq. (8) for the monatomic case.

Actually, Eq. (13) is quite general for any polyatomic physical solubility in which the internal degrees of freedom are retained and the external translation is transformed to localized vibration. The internal rotational and vibrational motions contribute to both $G(g)$ and $G(s)$ similarly so that these factors cancel when $G(g)$ and $G(s)$ are equated.

In applying the model to hydrogen, special care must be exercised. The high characteristic temperature of rotation for $H_2$ ($\theta_r = 87.5^\circ K$) means that the high temperature (classical) form of the rotational partition function ($q_r = 8\pi^2 I_k T/\hbar^2$) is not valid at room temperature where physical solubility is expected. The rotational partition function for
this case must be a summation over quantum states including a distinction between the nuclear spin multiplicities for orthohydrogen (even rotational states) and parahydrogen (odd rotational states)\textsuperscript{11} However, the increased complexity of the \( q_r \) in this case does not affect the final results because the rotational motion of the molecule appears in both the free gas and dissolved states producing a cancellation of the \( q_r \) from the final result equation.

D. Polyatomic Gas Solution - Chemical Solubility

The treatment for chemical solubility is basically a simple extension of the physical model just presented. The ideal gas is represented exactly as in the previous section but is assumed to be in equilibrium with a dissociated species in solution. There are two main results of this dissociation. First, the final solubility equations are more lengthy because the \( G(g) \) and \( G(s) \) expressions are more dissimilar.

Second, the solubility, \( n_g \), does not vary with the first power of pressure.

\( G(g) \) is still given by Eq. (1) using the appropriate gas partition function. However, \( G(s) \) is now given by

\[
G(s) = G(Q) + \sum E_i(0) - T \overline{S}_m
\]  

(14)

where \( E_i(0) \) is the binding energy of the \( i \)th dissociated species and \( \overline{S}_m \) is the partial molal entropy of mixing of all the dissociated species among the solubility sites.

The form of the final solubility equation depends greatly upon the specific system involved. Therefore, a simple but representative example
will be developed, viz. the solubility of a homonuclear diatomic gas as
dissociated monatomic species assumed to be localized simple harmonic
oscillators.

The dissociation of the diatomic molecule requires consideration of
the electronic partition function. For non-dissociation, the electronic
terms would have appeared in both \( G(g) \) and \( G(s) \) and would have cancelled.

By choosing the zero of energy as the separated atoms at rest, one can
write

\[
Q_{\text{diatomic}} = \frac{q_{\text{diatomic}}^N}{N!}
\]  

(15)

where

\[
q_{\text{diatomic}} = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} =
\]

\[
= \left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} V \left( \frac{T}{\Theta} \right) \left( \frac{e^{-0_{vi}/2T}}{1 - e^{-\Theta/vi/T}} \right) e^{-\epsilon_e/kT}
\]

(16)

with \( \epsilon_e = -D_e \) and \( D_e \) is the dissociation energy of the diatomic
molecule.

Also,

\[
Q_{\text{mono}} = q_{\text{mono}}^N = \left( q_{\text{vib}} q_{\text{e}} \right)^N = \left[ 2 \left( \frac{e^{-0_{vi}/2T}}{1 - e^{-\Theta/vi/T}} \right)^3 \right]^N
\]

(17)

where the dissolved atom is assumed to be restricted to vibrational
motion. Substitution of Eqs. (16) and (17) into Eqs. (1) and (14)
respectively, gives

$$G(g) = -RT \ln \left[ \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \left( \frac{kT}{2\Theta_r} \right) \left( \frac{e^{-\Theta_{vi}/2T}}{1 - e^{-\Theta_{vi}/T}} \right) e^{-\epsilon_{el}/kT} \right]$$

and

$$G(s) = -2RT \ln \left[ 2 \left( \frac{e^{-\Theta_{vi}/2T}}{1 - e^{-\Theta_{vi}/T}} \right)^3 \frac{N_s}{n_s} \right] + 2E(0).$$

Equating $G(g)$ and $G(s)$ and rearranging terms gives the final solubility equation for the chemical solubility of a homonuclear diatomic gas

$$\frac{n_s}{p^{1/2}} = \left[ \left( \frac{h^2}{2\pi mkT} \right)^{3/2} (kT)^{-1} \left( \frac{2\Theta_r}{T} \right) \left( \frac{1 - e^{-\Theta_{vi}/T}}{e^{-\Theta_{vi}/2T}} \right) \right]^{1/2}$$

$$\times \left[ 2N_s \left( \frac{e^{-\Theta_{vi}/2T}}{1 - e^{-\Theta_{vi}/T}} \right)^3 \right] e^{+\epsilon_{el}/2kT} e^{-E(0)/RT}$$

where $m$ is the mass of the diatomic molecule, $\Theta_r$ is the characteristic temperature for rotation of the diatomic molecule, $\Theta_{vi}$ is the characteristic temperature for internal vibration in the diatomic molecule, $\Theta_v$ is the characteristic temperature for vibration of the monatomic species, $\epsilon_{el}$ is the negative of the dissociation energy of the diatomic molecule, and $E(0)$ is the binding energy between the monatomic species and the glass.

The low temperature complexities of the rotational partition function mentioned in the previous section have been omitted here for
simplicity. This can also be omitted from a practical standpoint as the chemical hydrogen solubility to be discussed later occurs at sufficiently high temperatures that Eq. (20) is valid.
III. EXPERIMENTAL METHOD

The solubility of helium, neon, and hydrogen in fused silica was measured. Care was taken to specifically characterize the thermal history of the fused silica. The measurement of gas solubility was made by two techniques: a modified Seiverts' technique and infrared absorption.

A. Thermal History

Brückner\textsuperscript{15} reported a decrease in the density of fused silica with increased water content where the "water" existed in the glass as hydroxyl units. However, Douglas and Isard\textsuperscript{16} reported an increase of similar magnitude in the density of fused silica with increased fictive temperature. Therefore, in order to have a well characterized fused silica, it was necessary to have a knowledge of the simultaneous effects of both "water" content and fictive temperature on the glass density (which is indicative of the glass structure).

The sample material studied was a standard commercial fused silica* which was the same material used in the solubility experiments to be described in the next section. An emission spectrographic analysis of the types of glass specimens used in this study is summarized in Table I.

For the thermal history study, a hole 1/8 inch in diameter was drilled in a 3/4 inch diameter rod. Disks were sliced from the rod, ground, and then polished to a final thickness of about 0.005 inch. The finished disks were suspended from a fused silica support bar by platinum

\* Amersil CFQ Rod, Standard Quality (T-08); Amersil, Inc., San Francisco, California.
hooks. The support bar assembly was placed in a fused silica envelope approximately 1-3/4 inches in diameter and 27 inches long. The top of the envelope (the specimen end) was located in the hot zone of a Kanthal-wound tube furnace. The bottom of the envelope (the cold finger) contained water and was immersed in a controlled temperature oil bath. After evacuating the envelope, the temperature in the cold finger was brought to a desired temperature which established a given vapor pressure in the system. Runs were made with specimen temperatures of 1000, 1100, and 1200°C and water vapor pressures from 0 atm (evacuated envelope) to 1 atm (cold finger temperature of 100°C). The specimen temperatures were controlled to within ± 10°C. The time for the runs ranged from a few hours at 1200°C to a few weeks at 1000°C in order to obtain equilibrium densities. The runs were ended with air quenches in order to "freeze in" the equilibrium glass structures.

Densities were measured in a graded density column * with a precision of at least ± 0.0002 g/cc. Hydroxyl contents were determined from the 2.7µ absorption peak in the ir spectra of the specimen following the method used by Hetherington and Jack.17 The resulting measurements were obtained with a precision of ± 0.015 weight percent -OH.

Special care was taken in handling any fused silica in order to prevent devitrification. A standard preliminary cleaning procedure involved four steps: (a) 1 minute in xylene, (b) 15 seconds in a 5% HF solution, (c) 1 minute in distilled water, and (d) 1 minute in acetone. By handling the silica only with clean tweezers following this cleaning,

* ASTM: D1505 - 63T: "Density of Plastics by the Density-Gradient Technique."
no devitrification problems occurred.

B. Seiverts' Method of Measuring Solubility

A modification of Seiverts' method\(^{10}\) was the primary technique used to measure gas solubility. A cell containing the sample material (fused silica) was evacuated, filled with the gas of interest to about 1 atm, and then sealed. The pressure of the system dropped slowly as the gas dissolved into the specimen. The total pressure drop indicated the amount of gas dissolved in the known amount of specimen at the final pressure and temperature.

A drawing of the apparatus used for measuring noble gas solubility is shown in Fig. 1. Two cells were used. Each was 1-3/4 inch deep and 3/4 inch diameter and located symmetrically in a nickel block. One cell was filled with fused silica rods of either 1 or 6 mm O.D., and the other was empty. The empty cell served as a control to monitor any pressure fluctuations which were not associated with solubility. The pressure in each cell was monitored by pressure transducers.* Nickel capillary tubing connected each transducer with its respective cell. The cells were heated in a Kanthal wound furnace. The cells and furnace were in a closed chamber which was evacuated and back-filled with argon.

A typical run involved evacuating the cells and heating the system to the experimental temperature. Care was taken to evacuate the experimental cell sufficiently to completely desaturate the fused silica of any dissolved gas. The cells were then back-filled with about one atmosphere of the gas of interest; the individual cell-transducer

* C.E.C. Type 4-312-0002 Pressure Transducer; strain gage type; 0-25 psi A; Consolidated Electrodynamics Corp., Mountain View, Calif.
systems were sealed off; and the pressure of each was monitored. Depending on the system and temperature of operation, a final equilibrium pressure would be established in the experimental cell in from 30 minutes to 24 hours.

The high solubility of hydrogen in nickel required replacing the nickel cells with fused silica cells shown in Fig. 2. Fused silica was then used both as the container and the specimen. This was undesirable but required because fused silica has about as low hydrogen solubility as any conveniently available container material. The amount of gas lost to the container in each experiment was indicated by the control cell, and corrected for.

C. IR Measurement of Solubility

A supplementary method for measuring gas solubility was available for the specific case of chemically dissolved hydrogen in fused silica. It has been noted\(^{18,19}\) that chemically dissolved hydrogen is present as hydroxyl groups, which give an absorption peak at 2.7 \(\mu\) in the ir spectra. This situation is essentially the same as noted for water solubility in section III.A, and the experimental technique is very similar.

Disks of the kind described in section III.A were placed in a Brew furnace and heated to the desired temperature in one atmosphere of flowing hydrogen. The disks were cooled as quickly as possible (at about 300°C/minute) in order to quench in the chemically dissolved hydrogen.

The disks were placed in a Beckman IR-4 infrared spectrometer, and the ir spectrum was monitored from 2 to 5 \(\mu\) to measure the hydroxyl peak.
IV. RESULTS AND DISCUSSION

Equations (8), (13), and (20) express the solubility \( n_s \) of gas atoms or molecules at a given pressure as a function of temperature, fundamental constants, and material parameters.

The temperature range of interest extends from room temperature to near the glass transition temperature (around 1000°C for fused silica). The mass, \( m \), of a given dissolved atom or molecule is known. The number of sites per unit volume, \( N_s \), can be calculated with great accuracy for a crystal, since \( N_s \) is simply the number of most probable (usually largest) openings in the structure which would serve as solubility sites. The disordered structure of glass makes such estimates more difficult. Furthermore, for chemical solubility, the "reactivity" of possible sites is a factor.

For glasses with structures similar to known crystalline forms, a satisfactory estimate should be possible. Values of \( \theta_r \), \( \theta_{vi} \), and \( \varepsilon_1 \) for most common molecules in the gaseous state are readily available. The two parameters for the dissolved species are the vibrational frequency, \( \nu \), and the binding energy, \( E(0) \). Both can be estimated from calculations of the attractive and repulsive potentials acting on the dissolved species in the assumed solubility sites. But even for well-defined sites in a crystalline structure, only approximate values can be obtained because of uncertainty about the exact potentials involved. Consequently, \( \nu \) and \( E(0) \) were chosen (see below) to best fit the experimental solubility data by varying them around values found by others for helium and neon solubility in crystalline oxides.
Following a summary of the characterization of the glass, the experimental solubility results will be correlated with the solubility equations (Eqs. (8), (13), and (20)).

A. Characterization of Fused Silica

Figure 3 shows the dependency of the density of fused silica on both water (or -OH) content and fictive temperature. These data indicated the state of the solubility specimens following a given thermal treatment. The convenient glass transition range for fused silica is 1000 to 1200°C. Below 1000°C, structural relaxation occurs very slowly making equilibrium densities difficult to obtain. Above 1200°C, relaxation is rapid making quenches difficult. Also, devitrification becomes a problem above 1200°C. Most solubility specimens were given a fictive temperature of 1100°C and were nearly water-free. Figure 3(a) indicates the best fit isotherms for the density-hydroxyl content variation. Figure 3(b) shows the density-fictive temperature constant composition curves corresponding to the isotherms of Fig. 3(a).

Figure 3(a) is in general agreement with the results of Brückner in showing a drop in density with increased hydroxyl content. Brückner's values tended to be slightly higher than the 1200°C isotherm as might be expected from the 1300°C annealing step he used prior to measuring the density and water content of his specimens.

Figure 3(b) is in general agreement with the results of Douglas and Isard in showing a rise in density with increasing fictive temperature. Their data agree rather closely with the 0.0 weight percent-OH curve.
B. Physical Solubility – Helium in Fused Silica

The results of a typical experimental run with the Seiverts' type equipment is shown in Fig. 4. The pressure transducer output is in millivolts with the millivoltage linearly proportional to the cell pressure. Figure 5 shows the same data converted to pressure (in the experimental cell) as a function of time. The pressure drop shown in Fig. 5 indicates about 90% of the gas solubility in the glass. However, some gas (about 10% of the total amount dissolved) enters the glass during the brief period of time when the cells are being filled with gas before the cells are sealed (at time = 0 in Fig. 5). Appendix I shows the detailed calculation of the total gas solubility from both of these contributions for the experimental run given in Figs. 4 and 5.

It is also possible to obtain data on the kinetics of gas transport in glass from the shape of the gas uptake curve (e.g., Fig. 5). Relatively crude estimates of diffusivities and permeabilities for all the gas-in-glass systems studied are given in Appendix II for the sake of comparison with more precise and direct measurements from the literature.

The collected solubility data for the helium-fused silica system are shown in Fig. 6. These data are also listed in Table II. Three sets of data are noted. The (1100°C, "dry") set refers to a silica with a fictive temperature of 1100°C and nearly free of chemically dissolved water. The (1200°C, "dry") set refers to a water-free silica with a 1200°C fictive temperature. The (1100°C, "wet") data refers to a silica with 1100°C fictive temperature which was held for 7 days under 1 atm water vapor pressure at 1100°C giving a content of about 0.09 weight percent -OH. Within the scatter of the data, all three sets appear to
follow essentially one curve. A linear least-squares fit to the collected data is shown in Fig. 6.

It should also be noted that 1 mm silica rods were used as specimens for runs below 250°C, and 6 mm rods were used above 250°C because of the increasing diffusivity of helium in fused silica with temperature. Around 250°C, both sizes were used, and the resulting data were generally in good agreement.

One feature of the physical solubility equation, Eq. (8), is the linear dependence of solubility, \( n_s \), on pressure, \( p \). An experimental test of this feature for helium in fused silica at 209°C is shown in Fig. 7.

Figure 8 compares the experimental data for helium in fused silica with a plot of Eq. (8). The mass, \( m = 6.64 \times 10^{-24} \) g, is that for helium. The number of sites, \( N_s = 2.22 \times 10^{22} \) sites per cm\(^3\) of glass, is that calculated for fused silica which has a slightly distorted cristobalite structure.\(^{21}\) The values of \( v ( = 6.9 \times 10^{12} \text{ sec}^{-1}) \) and \( E(0) ( = -1.5 \text{ kcal/mole}) \) were chosen to give the best visual fit between the theoretical curve of Fig. 8 and the linear least squares fit of Fig. 6. The theoretical plot has a slight curvature. Both \( v \) and \( E(0) \) are in good agreement with the range of values found for helium solubility in crystalline oxides including cristobalite.\(^{7,8}\) For instance, Barrer and Vaughan\(^{8}\) calculated \( v \) to be in the range of \( 1.9 - 7.8 \times 10^{12} \text{ sec}^{-1} \) and \( E(0) \) from -2.0 to -3.16 kcal/mole for helium in cristobalite with the variation depending upon the method of calculation. This agreement of experiment and theory using reasonable parameters is considered quite satisfactory. The linear dependence of the solubility, \( n_s \), on pressure,
p, in Fig. 7 further displays this agreement.

It appears that the solubility of helium in fused silica is relatively insensitive to the thermal history of the glass. Some properties such as viscosity and the velocity of sound have been shown to be sensitive to small quantities of OH. However, a property such as physical gas solubility would be expected to be primarily sensitive to the site density, $N_s$, which (along with the bulk density) is varied by much less than one percent by any thermal treatment given to the samples of these experiments. Other parameters such as $\nu$ and $E(0)$ which would depend upon the site geometry would reflect similarly small percentage changes. This insensitivity of solubility to thermal history is in agreement with the findings of Masaryk that helium permeation through fused silica was similarly unaffected by thermal history.

C. Physical Solubility – Neon in Fused Silica

The solubility data for the neon-fused silica system are shown in Fig. 9, and the data is listed in Table III. Only (1100°C, "dry") data are given. A linear least-squares fit to the data is shown in Fig. 9. Figure 10 compares the experimental data for neon in fused silica with a plot of Eq. (8). The mass for neon is $m = 3.55 \times 10^{-23}$ g. The site density, $N_s$, is unchanged from the previous section. The values of $\nu (= 4.38 \times 10^{12}$ sec$^{-1}$) and $E(0) (= -2.8$ kcal/mole) were chosen to give the closest agreement between the theoretical curve and the linear best-fit line of Fig. 9. The $E(0)$ is in the same range found for helium and agrees favorably with the calculations of Barrer and Vaughan for neon in crystalline silica. The lower $\nu$ is expected because the vibrational frequency of a harmonic oscillator is inversely proportional to the square
root of its mass. This observation is discussed further in the next section. As with helium, good agreement is shown in Fig. 10 between the Ne-SiO₂ data and the model.

D. Physical Solubility - Hydrogen in Fused Silica

Data for the physical solubility of hydrogen in fused silica is given in Table IV. Only (1100°C, "dry") data were obtained. Figure 11 gives a plot of the data as a function of temperature along with a linear least-squares fit.

An important test of the hydrogen data is the dependence of solubility on pressure. A linear dependence on pressure indicates molecular solubility, and a dependence on pressure to the one-half indicates dissociative solubility. Figure 12 shows a plot of solubility versus pressure at 147°C indicating linear dependence on pressure which is consistent with molecular solubility.

Figure 13 compares the experimental data for the physical solubility of hydrogen in fused silica with a plot of Eq. (13) which is, as noted before, equivalent to Eq. (8) for the monatomic case. The mass, m, of H₂ is 3.35 x 10⁻²₄ g. The site density, Nₛ, is unchanged from the previous sections. As for the monatomic cases, the values of v (= 1.22 x 10¹³ sec⁻¹) and E(0) (= 3.04 kcal/mole) were chosen to give the closest agreement between the theoretical curve and the linear best-fit of Fig. 11. These values of v and E(0) are in general agreement with those found for the monatomic gases. In the previous section, it was noted that the heavier dissolved species would be expected to have the lower values of v, Table V summarizes the mass and vibrational frequency relationships for the three physically dissolved gases of this study.
The results of Table V are in good qualitative agreement with the expectation noted above although \( v \) is not exactly proportional to the square root of the mass, \( m \). The deviation could result from different force constants for the three oscillators, non-ideality of the oscillation, imprecision of the data, or, more likely, a combination of all these factors. However, the overall agreement between the model and experimental results for physical hydrogen solubility is considered quite satisfactory.

E. Chemical Solubility — Hydrogen in Fused Silica

Lee, et al.\(^18,23-25\) have reported the chemical solubility of hydrogen in fused silica above 500°C. This solubility was in addition to the physical solubility. However, Lee's data had a good deal of scatter and the results varied greatly between different types of fused silica. This lack of reproducibility might be the result of impurity dependence of the chemical hydrogen solubility. Bell, et al.\(^19\) have reported what appears to be the only unambiguous data for chemical hydrogen solubility in fused silica. Using essentially water-free silica,\(^*\) the concentration of chemically dissolved hydrogen (as OH units) was determined after various treatments in hydrogen gas using ir spectroscopy as described in section III.C. Unfortunately, experiments were carried out at only two temperatures. At 800°C under 1 atm of hydrogen gas, a solubility of 0.0018 weight percent OH was obtained. At 1050°C, the hydroxyl content was 0.00165 weight percent. Although

\(^*\) I.R. Vitreosil produced by Thermal Syndicate Ltd., Wallsend, England. This material is produced by the electrical fusing of quartz powder giving a "water" content of about 0.0003 weight percent OH.
only two temperatures were studied, extensive observations of the pressure dependencies of solubility were made at each temperature. The results, shown in Fig. 14, closely follow a $p^{1/2}$ dependency for the solubility indicating dissociative or chemical solubility of the hydrogen.

Attempts were made to reproduce the result of Bell, but all were unsuccessful. No chemical hydrogen solubility was observed in the Amersil fused silica used in this study. The first attempt was to reproduce the experimental technique of Bell as described in section III.C. However, this objective was hindered by two factors. First, the low concentration of chemical hydrogen as reported by Bell would not be sufficient to produce measurable ir absorption for the thin (about 0.005 inch thick) disks. The solubility of water as OH in the silica was about two orders of magnitude higher than the hydrogen-produced OH concentration making the thinner disks acceptable for water solubility measurements but not for chemically dissolved hydrogen. The second problem arose when thicker disks were used in order to obtain a measurable ir absorption. The as-received Amersil had a significant "water" content (about 0.01 weight percent -OH) which would require prohibitively long times to desaturate because the diffusivity of chemically dissolved water is much lower than that for chemically dissolved hydrogen. Consequently, the high "water" absorption peak at 2.7 $\mu$ masked any "hydrogen" absorption peak at the same wavelength in the ir range. Therefore, chemical hydrogen solubility in Amersil could not be measured by ir techniques even though the possibility of solubility still existed.
The second attempt to observe this solubility was with the modified Seiverts' apparatus used in measuring the physical solubility of hydrogen below 500°C. The chemical solubility reported by Bell is on the order of $6 \times 10^{17}$ equivalent molecules of $H_2$ per cm$^3$ at 1 atm $H_2$ pressure at 800°C. Extrapolation of the physical data to this temperature gives a solubility of about $2 \times 10^{17}$ molecules $H_2$ per cm$^3$ atm which means the chemical solubility should be the primary contribution in this temperature range and should be easily measurable with the Seiverts' apparatus. The diffusivities of chemical hydrogen as given by Bell indicated saturation times on the order of one or two hours in this temperature range. However, several experimental runs in the temperature range of 700 to 800°C failed to show any significant solubility above the level expected for physical solubility and solubility increased as $p^1$ indicating non-dissociation. Even considering the additional experimental uncertainty which was introduced by the increasing hydrogen permeation through the walls of the silica cells in this temperature range, it can be concluded that any chemical solubility of hydrogen in Amersil could not be more than a few percent of the values found by Bell in I.R. Vitreosil.

The anomalous results of Lee and the contrasting results of Bell and this study indicate that the chemical solubility of hydrogen in fused silica is highly sensitive to the history of the glass specimens. The most likely hinderence to the chemical solution of hydrogen would seem to be the water dissolved as OH in the glass. Even the relatively dry Amersil used in this study probably contained an OH concentration due to water as great or even greater than the potential OH concentration which could have resulted from hydrogen solution. Consequently,
the Bell data obtained in a material unusually free of water-produced hydroxyls can be considered the most meaningful indication of chemically dissolved hydrogen in fused silica, and it provides the best opportunity for testing Eq. (20).

All of the variables in Eq. (20), except one, are fixed for the given system. The mass, \( m \), of a hydrogen molecule is \( 3.35 \times 10^{-24} \) g. The values of \( \theta_r (= 87.5^\circ K) \), \( \theta_v (= 6350^\circ K) \), and \( \epsilon_e = -7.63 \times 10^{-12} \) ergs/molecule were all obtained from the JANAF Table data for molecular hydrogen. The site density, \( N_s \), was again \( 2.22 \times 10^{22} \) sites per cm\(^3\). The value of \( \theta_v (= 5330^\circ K) \) corresponds to the observed IR absorption peak for hydrogen-produced hydroxyls in fused silica at a wavelength of 2.7 \( \mu \). This leaves only \( E(0) \), the binding energy of the dissociated hydrogen atom to the silica structure, unspecified. A value of \( -63 \) kcal/mole for \( E(0) \) gave general agreement with the solubility values found by Bell over the temperature range of 800 to 1050\( ^\circ \)C. (See Fig. 15.) This value is indicative of a relatively strong chemical bond and contrasts with the values of a few kilocalories found for physical solubility which were indicative of relatively weak van der Waals bonding. At this point, it is difficult to determine the significance of the conflicting slopes of the data and the plot. Bell's data shows a slight decrease of solubility with temperature while the plot rises slightly with temperature. Additional solubility data could provide definite determination of the experimental temperature dependence of solubility. The disagreement could be the result of the idealized assumptions used in deriving Eq. (20). In particular, 1050\( ^\circ \)C is well into the transition range of fused silica so that the assumption of a
rigid structure implicit in the model is less valid. However, Fig. 15 is qualitatively satisfactory since it gives general agreement in the magnitude of solubility over the temperature range using an \( E(0) \) value indicative of chemical bonding of the dissociated hydrogen atom to the silica structure.
V. SUMMARY

The solubility of gases in silica glass below its transition range, i.e., where it is a rigid solid, has been examined. The statistical thermodynamics of the system provided a basic model of the solubility. For equilibrium, the Gibbs free energy of the gas was equated to that of the gas in solution. Expressions for the Gibbs energies were obtained from assumptions of the atomic motion in the free gas and dissolved states. The resulting solubility equations gave the solubility (in atoms or molecules per cubic centimeter of glass) as a function of gas pressure, temperature, fundamental constants, and material parameters. Three main categories of solubility were considered: (a) physical solubility of monatomic gases, (b) physical solubility of polyatomic gases, and (c) chemical solubility of polyatomic gases. The results for (a) and (b) were essentially equivalent. The results for (c) depend upon the specific system involved.

The model was compared with experimental results for a variety of systems. The physical solubility of the monatomic gases for helium and neon in fused silica were measured by a modified Seiverts' technique. Variations in the thermal history of the fused silica did not have a measurable effect on physical solubility as evidenced in the helium data. The physical solubility of polyatomic gases was observed for hydrogen in fused silica, again using the Seiverts' technique. Physical solubility was characterized by a linear dependence on pressure. Binding energies for the physically dissolved species were of the order expected for van der Waal's bonding. Vibrational frequencies of the dissolved species ranged from $4.38 \times 10^{12}$ to $1.22 \times 10^{13}$ sec$^{-1}$ with the
heavier species having the lower frequencies, as expected. Experiments of this study using both Seiverts' method and ir spectroscopy could not observe chemical solubility of hydrogen in the Amersil specimens. However, literature data on I. R. Vitreosil displayed the $p^{1/2}$ dependence indicative of chemical solubility. Comparison of the data with the model gave a binding energy of about 63 kilocalories per mole indicative of a relatively strong chemical bond between the dissolved hydrogen atom and the silica structure. It appears that chemical solubility of hydrogen in fused silica is highly sensitive to specimen history, especially the water-produced hydroxyl concentration.
ACKNOWLEDGMENTS

There are many people to be cited for special thanks. Dr. Richard M. Fulrath was the originator of this program and the research advisor. Dr. David A. Shirley critically reviewed the MODEL section when it was submitted as a class term paper. Drs. Perry L. Studt and David J. Meschi provided most helpful guidance and suggestions throughout the work. Fellow graduate students Robert Atkin and Joseph Masaryk were close colleagues and friends. Dane Anderburg supervised an enormous amount of glass specimen and apparatus fabrication. Jack Borde fabricated the thin glass disks. Countless others have helped to make this work possible.

This work was done under the auspices of the United States Atomic Energy Commission.
APPENDIX I

TYPICAL CALCULATION OF GAS SOLUBILITY FROM SEIVERTS' DATA

The total amount of gas dissolved in the glass sample in an experimental run is the sum of two contributions. The main contribution is the amount indicated by the pressure drop in the sealed cell. A secondary contribution is the amount which diffuses into the glass while the pressure in the cell is steadily increasing before the cell is sealed. The calculation of solubility for the experiment shown in Figs. 4 and 5 is given below.

The first contribution is calculated from the ideal gas law. The initial and final transducer readings were 9.38 and 9.02 millivolts, respectively. These correspond to initial and final pressures of 688.2 and 666.7 mm Hg, respectively. This is a total pressure drop of 21.5 mm Hg or 0.0283 atmosphere. The amount of gas dissolved from the sealed volume at the experimental temperature (209°C) is

\[
(\Delta n)_h = \frac{(2.83 \times 10^{-2} \text{ atm})(2.78 \text{ cc})}{(82.05 \text{ cc-atm/mole-deg})(482^\circ\text{K})} = 1.99 \times 10^{-6} \text{ moles.}
\]

The amount dissolved from the sealed volume at room temperature, i.e. the volume associated with the pressure transducers and external plumbing, is

\[
(\Delta n)_c = \frac{(2.83 \times 10^{-2} \text{ atm})(1.45 \text{ cc})}{(82.05 \text{ cc-atm/mole-deg})(295^\circ\text{K})} = 1.69 \times 10^{-6} \text{ moles.}
\]

The total gas dissolved in the glass during the time the cell is sealed is therefore
\[(\Delta n)_{\text{total}} = 3.68 \times 10^{-6} \text{ moles} = 2.22 \times 10^{18} \text{ atoms.}\]

For a specimen volume of 10.11 cm\(^3\) and a final pressure of 666.7 mm Hg, this gives an initial solubility value of

\[S_{\text{initial}} = \frac{2.22 \times 10^{18} \text{ atoms}}{10.11 \text{ cm}^3} \times \frac{760 \text{ mm Hg/atm}}{666.7 \text{ mm Hg}} = 2.50 \times 10^{17} \text{ atoms/cc-atm}.\]

The additional contribution comes from the brief period before the cell is sealed. During this time (60 seconds in this experiment), the pressure of the system is steadily increasing to the initial value of 688.2 mm Hg. Simultaneously, the surface concentration of gas in the glass is linearly increasing. A good approximation of the surface concentration at a given pressure at a given time is available from the results of the previous calculation. So, basically, one wants to calculate the amount of gas diffusing into a cylinder for which the surface concentration, \(\phi\), increases linearly with time, i.e. \(\phi(t) = kt\). The mathematics of this system have been developed by Crank.\(^{27}\) The amount of gas, \(M_t\), which has entered the rods in time, \(t\), is given as

\[M_t = \pi a^2 t - \frac{\pi ka^4}{8D} + \frac{h\pi k}{D} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{\alpha_n}{\alpha_n^2} \]

where \(D\) is the diffusivity, \(a\) is the cylinder (or rod) radius, and \(\alpha_n\) is the \(n\)th root of a Bessel function of the first kind of order zero. For convenience, this equation is expressed graphically in Fig. Al for
the range useful for the current calculations. The diffusivity, D, was obtained from Swets, et al. For this experiment:

\[ t = 60 \text{ seconds} \]
\[ D = 9.04 \times 10^{-7} \text{ cm}^2/\text{sec} \]
\[ a = 5.73 \times 10^{-2} \text{ cm (avg. rod radius)} \]

This gives

\[ \frac{Dt}{a^2} = 1.65 \times 10^{-2} \]

Figure Al then gives

\[ \frac{MD}{\pi ka^2} = 3.05 \times 10^{-3} \]

The \( \phi_s \) at \( t \) is

\[ \phi_s = 2.50 \times 10^{17} \times \frac{688.2}{760} = 2.26 \times 10^{17} \text{ atoms/cm}^3 \]

giving

\[ k = \frac{\phi_s}{t} = \frac{2.26 \times 10^{17}}{0.6 \times 10^2} = 3.77 \times 10^{15} \text{ atoms/cc-sec.} \]

This gives a value of

\[ M_t = 3.05 \times 10^{-3} \times \frac{\pi \times 3.77 \times 10^{15} \times 1.08 \times 10^{-5}}{9.04 \times 10^{-7}} = 4.31 \times 10^{14} \text{ atoms/cm.} \]
There were 221 rods used of average length of 4.428 cm giving the total absorbed gas during this period of

\[(\Delta N) = 4.428 \times 221 \times 4.31 \times 10^{14} = 4.22 \times 10^{17} \text{ atoms.}\]

Adding this to the gas dissolved after the cell was sealed gives

\[(\Delta N)_{\text{total}} = (2.22 + 0.42) \times 10^{18} = 2.64 \times 10^{18} \text{ atoms}\]

and a final solubility of

\[S = \frac{2.64 \times 10^{18}}{10.11} \times \frac{760}{666.7} = 2.98 \times 10^{17} \text{ atoms/cc-atm.}\]
APPENDIX II

DIFFUSIVITIES AND PERMEABILITIES OF He, Ne, and H2 IN FUSED SILICA

Relatively precise (and direct) measurements of diffusivities, D, and permeabilities, K, for the systems studied in this work are available in the literature. These sources were used whenever values of D were needed in the calculations shown in Appendix I. However, it is also possible to obtain values of D and K from the pressure curves of this work (e.g., Fig. 5). A reasonably simple (but approximate) calculation of D can be made using

\[
\left(\frac{Dt}{a}\right)^{1/2} = 0.245
\]

where \(t\) is the time for an originally gas-free glass cylinder of radius, \(a\), to reach one-half its saturation concentration. For the approximately 1 mm diameter rod specimens used in this study, \(a = 0.0573\) cm, and, for the 6 mm specimens, \(a = 0.266\) cm. The value of \(t\) for each solubility run was obtained from plots such as Fig. 5 by finding the time for the pressure drop in the system to reach one-half the final overall drop. It was then possible to obtain values for K using the relationship \(K = DS\). While both D and K give information about the kinetics of the gas-in-glass systems, they are basically different. D is the coefficient between the flux of diffusing gas atoms (or molecules) and a concentration gradient. K is the coefficient between the flow rate of the gas through a glass membrane under a pressure gradient. In the literature cited above, permeability was measured directly, and diffusivity was obtained from the rate of approach to steady-state permeation.
In this study, diffusivity was obtained from the rate of approach to steady-state solubility and permeability was obtained from the relationship $K = DS$.

Figure A2 shows the values of $D$ obtained for the system helium in fused silica. They are generally slightly lower than those obtained by Swets, et al. Figure A3 shows the values of $K$ for the same system. They are also generally slightly lower than the values found by Masaryk$^{22}$ for helium in the same type of fused silica (standard grade Amersil).

Figure A4 shows the values of $D$ for neon in fused silica, and Fig. A5 gives the permeability, $K$. Both sets of data run generally lower than the literature values given by Frank, et al.$^{29}$

Figures A6 and A7 give the diffusivities and permeabilities, respectively, for hydrogen in fused silica. The diffusivities are generally lower than the values given by Lee, et al.$^{23}$ while the permeabilities tend to be slightly higher than the results of Masaryk$^{22}$ for standard Amersil.

These results are not intended to provide improved $D$ and $K$ values but to illustrate the general agreement between the kinetics of gas transport through fused silica found in these studies and the previously available literature data.
REFERENCES


26. JANAF Thermochemical Tables, August 1965.
Table I. Emission Spectrographic Analysis of Fused Silica Specimens*

Reported as oxides of the elements indicated.

<table>
<thead>
<tr>
<th></th>
<th>0.005 inch thick disk (thermal history specimen)</th>
<th>1 mm dia. rod (solubility specimen)</th>
<th>6 mm dia. rod (solubility specimen)</th>
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<tr>
<td>Si</td>
<td>0.002%</td>
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<td>Al</td>
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<td>&lt;0.001</td>
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<td>Ca</td>
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</tr>
<tr>
<td>Ti</td>
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<td></td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
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* Amersil CFQ Rod, Standard Quality (T-08); Amersil, Inc., San Francisco, California.
Table II. Solubility Data for Helium in Fused Silica

<table>
<thead>
<tr>
<th>$T(°K)$</th>
<th>Solubility (atoms/cc•atm)</th>
<th>$T(°K)$</th>
<th>Solubility (atoms/cc•atm)</th>
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<tr>
<td>325</td>
<td>$4.59 \times 10^{17}$ (C,a)</td>
<td>476</td>
<td>$2.99 \times 10^{17}$ (C,a)</td>
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<td>529</td>
<td>3.03 &quot; (A,b)</td>
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<td>476</td>
<td>2.85 &quot; (C,a)</td>
<td>813</td>
<td>1.94 &quot; (A,b)</td>
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$A - T_F = 1100°C$, "dry"

$B - T_F = 1100°C$, "wet"

$C - T_F = 1200°C$, "dry"

$a - 1 \text{ mm dia. rods}$

$b - 6 \text{ mm dia. rods}$
### Table III. Solubility Data for Neon in Fused Silica

<table>
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<tr>
<th>T(°K)</th>
<th>Solubility (atoms/cc.atm)</th>
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<tr>
<td>670</td>
<td>2.09 x 10^{17} (a)</td>
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<td>1040</td>
<td>1.21 &quot; (b)</td>
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<tr>
<td>1050</td>
<td>1.42 &quot; (b)</td>
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</table>

a - 1 mm dia. rods (T_F = 1100°C, "dry")

b - 6 mm dia. rods (T_F = 1100°C, "dry")
Table IV. Physical Solubility Data for Hydrogen in Fused Silica

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>Solubility (molecules/cc.atm)*</th>
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<tbody>
<tr>
<td>582</td>
<td>4.35 x 10^{17}</td>
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<td>583</td>
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<td>765</td>
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<td>766</td>
<td>2.90</td>
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*All specimens - 1 mm dia. with T_F = 1100°C, "dry"
Table V. Summary of Mass and Vibrational Frequency Relationships for Physically Dissolved Gases

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Mass</th>
<th>Vibrational frequency (ν)</th>
<th>( (m/m_{H_2})^{1/2} )</th>
<th>( ν_{H_2}/ν )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>( 3.35 \times 10^{-24} ) g</td>
<td>( 1.22 \times 10^{13} ) sec(^{-1} )</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>He</td>
<td>( 6.64 \times 10^{-24} ) g</td>
<td>( 6.90 \times 10^{12} )</td>
<td>1.41</td>
<td>1.77</td>
</tr>
<tr>
<td>Ne</td>
<td>( 3.35 \times 10^{-23} )</td>
<td>( 4.38 \times 10^{12} )</td>
<td>3.16</td>
<td>2.79</td>
</tr>
</tbody>
</table>
Figure 1. Schematic of Seiverts' type experimental equipment.
Figure 2. Drawing of a fused silica cell used in hydrogen solubility experiment.
Figure 3. Summary of thermal history experiments for fused silica.
Figure 4. Transducer output versus time for helium-fused silica experiment at 209°C.
Figure 5. Experimental cell pressure versus time for the run of Fig. 4.
Figure 6. Helium-fused silica solubility data with linear least-squares fit.
Figure 7. Solubility versus pressure for helium in fused silica at 209°C.
Figure 8. Helium-fused silica data with plot of Eq. (8).
Figure 9. Neon-fused silica solubility data with linear least-squares fit.
SOLUBILITY OF NEON IN FUSED SILICA (T_F = 1100°C, "DRY")

\[ E(0) = -2.8 \text{ KCAL} \]
\[ \nu = 4.38 \times 10^{12} \text{ SEC}^{-1} \]

Figure 10. Neon-fused silica data with plot of Eq. (8).
Figure 11. Hydrogen-fused silica physical solubility data with linear least-squares fit.
Figure 12. Solubility versus pressure for physically dissolved hydrogen in fused silica at 447°C.
Figure 13. Hydrogen-fused silica data with plot of Eq. (13).
Figure 14. Solubility versus (pressure)\(^{1/2}\) for chemically dissolved hydrogen in fused silica at 800 and 1050°C.\(^{19}\)
Figure 15. Hydrogen-fused silica data with plot of Eq. (20).
The image contains a graph and an equation. The graph is labeled as Figure A-1 and shows the plot of $\frac{M_t D}{\pi k a^4}$ versus $Dt/a^2$. The equation given in the image is:

$$M_t = \pi k a^2 t - \frac{\pi k a^4}{8D} + \frac{4\pi k}{D} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 t}}{\alpha_n^4}$$
Figure A-2. Diffusivities of helium in fused silica.
Figure A-3. Permeabilities of helium in fused silica.
Figure A-4. Diffusivities of neon in fused silica.
Figure A-5. Permeabilities of neon in fused silica.
Figure A-6. Diffusivities of hydrogen in fused silica.
Figure A-7. Permeabilities of hydrogen in fused silica.
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