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October 1971

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SOLUBILITY OF GASES IN GLASS: II.
He, Ne, and H₂ in FUSED SILICA

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ABSTRACT
October 1971

The statistical thermodynamics of the gas-in-glass system provides a basic model of both physical and chemical solubility. The physical solubility result is essentially equivalent to that for monatomic solubility. The chemical solubility result is dependent upon the specific system involved. The model was compared with experiment for a variety of systems. Helium and neon in fused silica were examples of the physical solubility of monatomic gases. 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. Hydrogen in fused silica was an example of the physical solubility of polyatomic gases. 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. Hydrogen in fused
silica was also an example of the chemical solubility of polyatomic
gases. The literature gave data for the chemical solution of hydrogen
in fused silica, but the fused silica of this study did not, 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 solu-
tility (indicative of dissociation) and a binding energy of about 63
kcal/mole (indicative of chemical bonding).
INTRODUCTION

Glasses are used in a wide variety of gas atmospheres. A statistical mechanical model of monatomic gas solubility in glass has recently been developed.¹ The purpose of this paper is to extend the approach used in treating the monatomic gas solution to a general model of polyatomic gas solubility in glasses and, then, to compare the general model with experimental solubility data. New experimental measurements were desirable as most of the literature data was available over a limited temperature range or from indirect measurements (usually from permeation and diffusion experiments).²,³

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' method⁴ 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.

It should be emphasized that the solubility to be discussed is in glasses below their transition temperature 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 use while that in the liquid glass would arise during fabrication.
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.

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.
Physical Solubility

This case has already been treated in the previous paper of this series\(^1\) for monatomic gas solubility. Equilibrium was considered between the gaseous and dissolved states requiring the Gibbs free energy of the gaseous state, \(G(g)\), to be equated to that of the dissolved state, \(G(s)\). Expressions for the Gibbs energies were obtained from the assumed atomic model. Equating these expressions allowed the derivation of a final solubility equation which gave the solubility (in atoms per cubic centimeter of glass) as a function of gas pressure, temperature, fundamental constants, and material parameters (see Eq. (6) of ref. 1).

Actually, this result is quite general for any polyatomic physical solubility in which the internal degrees of freedom (rotation and vibration) are retained and the external translation of the center of mass of the gaseous molecule is transformed to localized vibration for the dissolved molecule. 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. Consequently, the solubility equation for this polyatomic physical solubility is

\[
\frac{n_s}{p} = \left(\frac{\hbar^2}{2\pi mkT}\right)^{3/2} \left(\frac{kT}{\Theta T}\right)^{1/2} N_s \left[\frac{e^{-\Theta/2T}}{1 - e^{-\Theta/2T}}\right] \exp\left[-\frac{E(0)}{RT}\right] (1)
\]

where \(n_s\) is the number of gas molecules dissolved per cubic centimeter of glass, \(p\) is the pressure of the gas atmosphere, \(\hbar\) is Planck's constant, \(m\) is the mass of one molecule, \(k\) is Boltzmann's constant, \(T\) is the absolute temperature, and \(N_s\) is the number of solubility sites available per
cubic centimeter, \( \theta_v (= h \nu / k) \) is the characteristic temperature for vibration of the center of mass of the dissolved molecule with \( \nu \) the frequency of vibration, \( R \) is the gas constant, and \( E(0) \), the binding energy, is the energy of the molecule 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.

Chemical Solubility

The treatment for chemical solubility is basically a simple extension of the physical model. The ideal gas is represented as before 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, \( n_s \), does not vary with the first power of pressure.

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

\[
G(g) = -RT \ln \left\{ \left( \frac{2\pi \hbar^2}{m \tilde{\theta}} \right)^{3/2} \left( \frac{kT}{p} \right)^{T/\left(2\tilde{\theta} \right)} \left[ e^{-\frac{\theta v_1}{2T}} / \left(1-e^{-\frac{\theta v_1}{T}} \right) \right] \right\} \times \exp \left[ -\frac{E_{el}}{kT} \right]
\]

(2)
and

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

(3)

where \( \theta_r \) is the characteristic temperature for rotation (\( \theta_r = \frac{h^2}{8\pi^2Ik} \)) where \( I = \) moment of inertia) of the diatomic molecule, \( \theta_{vi} \) is the characteristic temperature for vibration of the molecule's internal vibrational mode, \( \epsilon_{el} \) is the negative of the dissociation energy of the diatomic molecule, \( \theta_v \) is the characteristic temperature for vibration of the monatomic species, and \( E(0) \) is the binding energy between the monatomic species and the glass. Also, \( n_s \) is now the number of dissolved atoms per cubic centimeter of glass rather than the number of molecules as in the physical solubility case.

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

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

\[ \times 2N_s \left[ \frac{e^{-\theta_v/2T}}{1-e^{-\theta_v/2T}} \right]^3 \exp \left[ \frac{\epsilon_{el}}{2kT} \right] \exp \left[ -\frac{E(0)}{RT} \right]. \] 

(4)

This result will later be compared with the experimental case of \( H_2 \) gas dissociating upon solution to form \( H \) atoms which bond to the oxygen of the fused silica network to form \( Si-OH \) groups.
EXPERIMENTAL METHOD

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

Thermal History

Brückner 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 reported an increase of similar magnitude in the density of fused silica with increased fictive temperature. Therefore, in order to fully characterize fused silica, the simultaneous effects of both "water" content and fictive temperature on the glass density (which is indicative of the glass structure) must be known.

The sample material studied was a standard commercial fused silica in the form of thin (about 0.12 mm thick) disks. An emission spectrographic analysis of the types of glass specimens used in this study is summarized in Table I. Specimens were treated with fictive temperatures of 1000, 1100, and 1200°C and in water vapor pressures from 0 to 1 atm. The treatments were ended with air quenches in order to "freeze in" the equilibrium glass structures. Details of the thermal history experiments are given elsewhere.

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, no devitrification problems occurred.

Seiverts' Method of Measuring Solubility

A modification of Seiverts' method 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.

Each sample cell was 44.5 mm deep and 19.1 mm 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 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. 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 the correction was made.

**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\(^\text{10,11}\) that chemically dissolved hydrogen is present as hydroxyl groups, which give an absorption peak at 2.7 µ in the ir spectra. This situation is essentially the same as noted for water solubility\(^\text{12}\) and the experimental technique is very similar.

Disks of the kind used in the thermal history experiments 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/min.) 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 µ to measure the hydroxyl peak.

**RESULTS AND DISCUSSION**

Solubility model equations are given in the MODEL section. These equations express the solubility (\(n_s\)) of gas atoms or molecules at a given pressure as a function of temperature, fundamental constants, and
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 θ_r, θ_vf, and ε_el for most common molecules in the gaseous state are readily available. The two parameters for the dissolved species are the vibrational frequency, v, 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, v 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.
Characterization of Fused Silica

Figure 1 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 1(a) indicates the best fit isotherms for the density-hydroxyl content variation. Figure 1(b) shows the density-fictive temperature constant composition curves corresponding to the isotherms of Fig. 1(a).

Physical Solubility - Helium in Fused Silica

The results of a typical experimental run with the Seiverts' type equipment is shown in Fig. 2 indicating the specimen cell pressure as a function of time. The pressure drop shown in Fig. 2 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. 2). The solubility data in this paper includes both contributions, i.e., the total solubility.

The collected solubility data for the helium-fused silica system are given 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 as shown in Fig. 3.

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. (1)) 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. 4.

Figure 3 compares the experimental data for helium in fused silica with a plot of the physical solubility equation. The mass, \( m = 6.64 \times 10^{-24} \text{ g} \), is that for helium. The number of sites, \( N_s = 2.22 \times 10^{22} \text{ sites per cm}^3 \) of glass, is that calculated for fused silica which has a slightly distorted cristobalite structure.\(^{13}\) 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. 3 and the linear least squares fit of the data. 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.\(^{14,15}\) For instance, Barrer and Vaughan\(^ {15}\) 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. 4 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.\(^{12}\) 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 1% by any thermal treatment given to the samples of these experiments. Other parameters such as \( v \) 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\(^{16}\) that helium permeation through fused silica was only slightly affected by thermal history.

**Physical Solubility - Neon in Fused Silica**

The solubility data for the neon-fused silica system are given in Table III. Only (1100°C, "dry") data are given.

Figure 5 compares the experimental data for neon in fused silica with a plot of the physical solubility equation. 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 \( v \) (\( = 4.38 \times 10^{12} \) sec\(^{-1}\)) and \( E(0) \) (\( = -2.8 \) kcal/mole) were chosen to give the closest agreement between the theoretical curve and the linear bestfit line of the data. The \( E(0) \) is in the same range found for helium and agrees favorably with the calculations of
Barer and Vaughan\textsuperscript{15} 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. 5 between the Ne-SiO\textsubscript{2} data and the model.

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.

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 6 shows a plot of solubility versus pressure at 447°C indicating linear dependence on pressure which is consistent with molecular solubility.

Figure 7 compares the experimental data for the physical solubility of hydrogen in fused silica with a plot of Eq. (1). The mass, $m$, of $H\textsubscript{2}$ is $3.35 \times 10^{-24}$ g. The site density, $N_\text{s}$, is unchanged from the previous sections. As for the monatomic cases, the values of $\nu (= 1.22 \times 10^{13}$ sec$^{-1}$) and $E(0) (= -3.04$ kcal/mole) were chosen to give the closest agreement between the theoretical curve and the linear bestfit of the data. These values of $\nu$ 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 $\nu$. 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 inversely 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.

Chemical Solubility - Hydrogen in Fused Silica

Lee, et al.\textsuperscript{10,17-19} have reported the chemical solubility of hydrogen in fused silica above 500\(^\circ\)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.\textsuperscript{11} have reported what appears to be the only unambiguous data for chemical hydrogen solubility in fused silica. Using essentially water-free silica,\textsuperscript{20} the concentration of chemically dissolved hydrogen (as OH units) was determined after various treatments in hydrogen gas using ir spectroscopy as described in the Experimental Method Section. Unfortunately, experiments were carried out at only two temperatures. At 800\(^\circ\)C under 1 atm of hydrogen gas, a solubility of 0.0018 weight percent OH was obtained. At 1050\(^\circ\)C, the hydroxyl content was 0.00165 weight percent. Although only two temperatures were studied, extensive observations of the pressure dependencies of solubility were made at each temperature. The results, shown in Fig. 8, 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. Attempts were made using both ir spectroscopy and the Seivert's technique. It was concluded that any chemical solubility of hydrogen in the Amersil material 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 the chemical solubility equation.

All of the variables in Eq. (4), 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°K), $\theta_v$ (= 6350°K), and $\epsilon_{el}$ (= $-\Delta e$ = -7.63 x $10^{12}$ ergs/molecule) were all obtained from the JANAF Table data for molecular hydrogen. The site density, $N_x$, was again $2.22 \times 10^{22}$ sites per cm$^3$. The value of $\theta_v$ (= 5330°K) corresponds to the observed ir absorption peak for hydrogen-produced hydroxyls in fused silica at a wavelength of 2.7 μ. This leaves only $\epsilon(0)$, 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°C. (See Fig. 9.) 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 the equation. In particular, 1050°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. 9 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.

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. The 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 was observed for helium and neon in fused silica and was 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 Waals 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

The authors wish to thank Dr. D. A. Shirley, Dr. David J. Meschi, and Joseph S. Masaryk for many helpful discussions. Dane Anderburg supervised the glass specimen and apparatus fabrication. Jack Borde fabricated the thin glass disks.

This work was supported by the United States Atomic Energy Commission.
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7. Amersil CFQ Rod, Standard Quality (T-08); Amersil, Inc., San Francisco, California.


9. C.E.C. Type 4-312-0002 Pressure Transducer; strain gage type; 0-25 psi A; Consolidated Electrodynamics Corp., Mountain View, Calif.


20. 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.

21. 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>0.12 mm 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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<td>Si</td>
<td>Principal constituent in each sample</td>
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\(^{a}\text{Amersil CFQ Rod, Standard Quality (T-08); Amersil, Inc., San Francisco, California.}\)
### 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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<td>2.98</td>
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<td>327</td>
<td>4.78</td>
<td>486</td>
<td>2.68</td>
</tr>
<tr>
<td>352</td>
<td>4.39</td>
<td>523</td>
<td>2.53</td>
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<tr>
<td>375</td>
<td>3.97</td>
<td>523</td>
<td>2.69</td>
</tr>
<tr>
<td>376</td>
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<td>528</td>
<td>2.79</td>
</tr>
<tr>
<td>379</td>
<td>4.08</td>
<td>529</td>
<td>3.03</td>
</tr>
<tr>
<td>381</td>
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<td>529</td>
<td>2.80</td>
</tr>
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<td>401</td>
<td>3.57</td>
<td>624</td>
<td>2.56</td>
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<td>624</td>
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<td>428</td>
<td>3.80</td>
<td>716</td>
<td>2.20</td>
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<tr>
<td>431</td>
<td>3.34</td>
<td>721</td>
<td>2.20</td>
</tr>
<tr>
<td>450</td>
<td>3.25</td>
<td>811</td>
<td>2.01</td>
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<tr>
<td>476</td>
<td>2.85</td>
<td>813</td>
<td>1.94</td>
</tr>
</tbody>
</table>

A - $T_F = 1100°C$, "dry"
B - $T_F = 1100°C$, "wet"
C - $T_F = 1200°C$, "dry"
a - 1 mm dia. rods
b - 6 mm dia. rods
Table III. Solubility Data for Neon in Fused Silica

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>Solubility (atoms/cc.atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>670</td>
<td>2.09 x 10^{17}</td>
</tr>
<tr>
<td>716</td>
<td>1.91</td>
</tr>
<tr>
<td>762</td>
<td>2.03</td>
</tr>
<tr>
<td>764</td>
<td>1.82</td>
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<tr>
<td>808</td>
<td>1.69</td>
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<tr>
<td>815</td>
<td>1.54</td>
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<td>856</td>
<td>1.52</td>
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<td>859</td>
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<td>902</td>
<td>1.36</td>
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<td>904</td>
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<td>955</td>
<td>1.35</td>
</tr>
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<td>955</td>
<td>1.41</td>
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<td>1040</td>
<td>1.21</td>
</tr>
<tr>
<td>1050</td>
<td>1.42</td>
</tr>
</tbody>
</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)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>582</td>
<td>$4.35 \times 10^{17}$</td>
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<tr>
<td>583</td>
<td>$4.84$</td>
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<tr>
<td>631</td>
<td>$3.67$</td>
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<tr>
<td>631</td>
<td>$3.68$</td>
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<tr>
<td>675</td>
<td>$3.50$</td>
</tr>
<tr>
<td>680</td>
<td>$3.33$</td>
</tr>
<tr>
<td>720</td>
<td>$3.21$</td>
</tr>
<tr>
<td>721</td>
<td>$3.28$</td>
</tr>
<tr>
<td>765</td>
<td>$2.80$</td>
</tr>
<tr>
<td>766</td>
<td>$2.90$</td>
</tr>
</tbody>
</table>

\(^a\)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 (v)</th>
<th>$(m/m_{H_2})^{1/2}$</th>
<th>$(v_{H_2}/v)$</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>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>
<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>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. Summary of thermal history experiments for fused silica (after ref. 8).

Fig. 2. Experimental cell pressure versus time for a typical Seiverts' type solubility experiment.

Fig. 3. Helium-fused silica data with plot of the physical solubility model equation.

Fig. 4. Solubility versus pressure for helium in fused silica at 209°C.

Fig. 5. Neon-fused silica data with plot of the physical solubility model equation.

Fig. 6. Solubility versus pressure for physically dissolved hydrogen.

Fig. 7. Hydrogen-fused silica data with plot of the physical solubility model equation.

Fig. 8. Solubility versus \((\text{pressure})^{1/2}\) for chemically dissolved hydrogen in fused silica at 800 and 1050°C (after ref. 11).

Fig. 9. Hydrogen-fused silica data with plot of the chemical solubility model equation.
FUSED SILICA: \( \rho \leftrightarrow [\text{OH}] \leftrightarrow T_F \)

**A**

- \( \rho \) (g/cc) vs. "Water" Content (\( \% \) OH)
- Lines for different temperatures: 1000°C, 1100°C, 1200°C

**B**

- \( \rho \) (g/cc) vs. Fictive Temperature, \( T_F \) (°C)
- Curves for different OH contents: 0.0, 0.05, 0.10

**Fig. 1**
HELUM IN FUSED SILICA ($T_F = 1100^\circ \text{C}, \text{"DRY"})$

AT $209^\circ \text{C}$
SOLUBILITY OF HELIUM IN FUSED SILICA

\[ E(0) = -1.5 \text{ KCAL} \]
\[ \nu = 6.9 \times 10^{12} \text{ SEC}^{-1} \]

Fig. 3

XBL 7042-7421
SOLUBILITY OF NEON IN FUSED SILICA (T_f = 1100°C, "DRY")

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

Fig. 5
$H_2 - SiO_2 (T_f = 1100^\circ C, "DRY")$ at $447^\circ C$

![Graph showing the solubility of $H_2 - SiO_2$ as a function of pressure. The graph includes a linear relationship and a dashed line indicating a specific solubility value.]

Fig. 6
Physical Solubility of Hydrogen in Fused Silica

$E(0) = -3.04 \text{ Kcal}$

$\nu = 1.22 \times 10^{13} \text{ sec}^{-1}$

Fig. 7
CHEMICAL SOLUBILITY OF HYDROGEN IN FUSED SILICA

○ BELL, ET. AL. DATA

E(0) = -63 KCAL/MOLE

Fig. 9
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