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Perry L. Studt, James F. Shackelford and Richard M. Fulrath

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The Solubility of Gases in Glass - A Monatomic Model

Perry L. Studt

Lawrence Radiation Laboratory, Livermore, California 94550

and

James F. Shackelford and Richard M. Fulrath

Inorganic Materials Research Division, Lawrence Radiation Laboratory,

and Department of Materials Science and Engineering,

College of Engineering, University of California,

Berkeley, California 94720

A statistical mechanical model of gas solubility in glass is presented. For equilibrium, the Gibbs free energy of the free gas is equated to that of the gas in solution. Expressions for the Gibbs energies are obtained from assumptions of the atomic motion in the free gas and dissolved states. The resulting solubility equations express the solubility (in atoms per cm^3 of glass) as a function of gas pressure, temperature, fundamental constants, and material parameters. An initial

evaluation of the model is made by comparison with literature data for helium and neon in fused silica.

INTRODUCTION

The use of glass (and ceramics containing glassy phases) in a variety of gas atmospheres makes this study of practical interest. For the moderate gas atmosphere pressures and dilute solutions usually encountered, one can expect a reasonably idealized model to provide a meaningful representation of the physical system.

A large body of experimental data on gas solubility in glass is available in reviews.[1,2] Adequate quantitative models for this system are lacking. However, statistical models have been proposed for gas solubility in metals.[3-6] These theories have successfully described the solubility of H_2 both with and without the formation of an hydride phase. Monatomic gas solution in crystalline oxides has been treated for UO_2,[7] tridymite,[8] and cristobalite.[8] This paper proposes a statistical mechanical model for gas solution in glass.

The dissolved gas atom in previous statistical models was usually treated as an Einstein oscillator. The model developed in this paper also considers the possibility of translational motion by the dissolved gas atom. However, the oscillator model is shown to be satisfactory in considering the solubility of helium and neon in fused silica.

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. The dissolved state may be considered as a combination of translational (particle-in-a-box) motion and/or vibrational (simple

harmonic oscillator) motion. Such a model is considered reasonable in light of the success of similarly idealized models in treating gaseous equilibria and Langmuir adsorption.[9]

Equilibrium between the gaseous and dissolved states requires

$$G(g) = G(s) \tag{1}$$

where G(g) and G(s) are the Gibbs free energy for the gaseous and dissolved states, respectively. Equation (1) is equivalent to

$$H(g)-TS(g) = H(s)-TS(s) \tag{2}$$

with H, T, and S the enthalpy, absolute temperature, and entropy, respectively.

Expressions for the enthalpy and entropy can be obtained from the assumed atomic model using[9,10]

$$H = kT\left(\frac{\partial \ln Q}{\partial \ln T}\right)_{V,N} + kT\left(\frac{\partial \ln Q}{\partial \ln V}\right)_{T,N} \tag{3}$$

and

$$S = k\left(\frac{\partial \ln Q}{\partial \ln T}\right)_{V,N} + k \ln Q \tag{4}$$

where Q is the canonical ensemble partition function; k is Boltzmann's constant; 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, i.e.

$$Q = \frac{q^N}{N!} = \frac{1}{N!} \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V\right]^N \tag{5}$$

where m is the mass of one atom, h is Planck's constant, V is the volume of the box, and q is the partition function for a single particle. Substituting Eq. (5) into Eqs. (3) and (4) and using the ideal gas law (pV=NkT), one obtains expressions for the enthalpy and entropy which combine to give

$$G(g) = -RT\ln \left[\left(\frac{kT}{p}\right)\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] \tag{6}$$

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

For the dissolved state,[7]

$$H(s) = H(Q) + E(0) \tag{7}$$

and

$$S(s) = S(Q) + \bar{S}_m \quad . \tag{8}$$

H(Q) and S(Q) are given by Eqs. (3) and (4) 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 a 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. E(0) will be discussed further in the next section. $\overline{S}_m$ is the partial molal entropy of mixing for the gas. It is of the form[7]

$$\overline{S}_m = R \ln\left(\frac{N_s}{n_s}\right) \tag{9}$$

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. (9) assumed that N_s and n_s were large numbers and that $N_s \gg n_s$. These assumptions should be valid for all real systems discussed in this paper.

Four cases of solubility will be considered:

(i) The dissolved species is held in a specific solubility site which is large enough to permit three degrees of translational freedom. For this case

$$Q = q^N = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V_s\right]^N \quad . \tag{10}$$

This is essentially the form of Eq. (5) except that the V_s is the volume of a single solubility site and no N! term appears as the species dissolved at specific solubility sites are distinguishable.

(ii) The solubility site is disc-shaped and restricts translation to two directions while adding one degree of vibrational freedom. For

this case

$$Q = q^N = \left[\left(\frac{2\pi mkT}{h^2}\right) A_s \left(\frac{e^{-u/2}}{1-e^{-u}}\right)\right]^N \tag{11}$$

where A_s is the area available for translation and $u = (h\underline{\nu}/kT)$ where $\underline{\nu}$ is the vibrational frequency of a simple harmonic oscillator.

(iii) The solubility site is cylindrical restricting translation to one dimension and yielding two degrees of vibrational freedom. For this case

$$Q = q^N = \left[\left(\frac{2\pi mkT}{h^2}\right)^{1/2} L_s \left(\frac{e^{-u/2}}{1-e^{-u}}\right)^2\right]^N \tag{12}$$

where L_s the length available for translation.

(iv) The solubility site completely restricts the dissolved atom from any translation giving three degrees of vibrational freedom. For this case

$$Q = q^N = \left(\frac{e^{-u/2}}{1-e^{-u}}\right)^{3N} \tag{13}$$

Substituting Eqs. (9) to (13) into Eqs. (3), (4), (7), and (8) give expressions for H(s) and S(a) for each of the four solubility cases. Combining H(s) and S(s) gives G(s). By equating G(s) to the given G(g) in Eq. (6) and rearranging terms, one obtains the final results:

(1) For three degrees of translation in the dissolved state,

$$\frac{n_s}{p} = (kT)^{-1} N_s V_s \exp(-1) \exp[-E(0)/RT]. \tag{14}$$

(ii) For two degrees of translation and one degree of vibration,

$$\frac{n_s}{p} = \left(\frac{h^2}{2\pi mkT}\right)^{1/2} (kT)^{-1} N_s A_s \left(\frac{e^{-u/2}}{1-e^{-u}}\right) \exp\left(-\frac{2}{3}\right) \exp\left[-E(0)/RT\right]. \quad (15)$$

(iii) For one degree of translation and two degrees of vibration,

$$\frac{n_s}{p} = \left(\frac{h^2}{2\pi mkT}\right) (kT)^{-1} N_s L_s \left(\frac{e^{-u/2}}{1-e^{-u}}\right)^2 \exp\left(-\frac{1}{3}\right) \exp\left[-E(0)/RT\right]. \quad (16)$$

(iv) For three degrees of vibration,

$$\frac{n_s}{p} = \left(\frac{h^2}{2\pi mkT}\right)^{3/2} (kT)^{-1} N_s \left(\frac{e^{-u/2}}{1-e^{-u}}\right)^3 \exp\left[-E(0)/RT\right]. \quad (17)$$

The translational motion considered in Eqs. (14), (15), and (16) could actually arise in two ways. First, translation could be in localized sites (e.g., pores) as previously described. Second, translation could be throughout the solid structure, i.e. non-localized with the solid serving as a potential field with the potential being E(0). The final equations are nearly the same for both cases. The factor of exp(-x/3) where x is the number of translational degrees of freedom would be absent from Eqs. (14) to (16) in the case of non-localized translation. The latter case is essentially the approach taken by Fowler and Smithells.[3] In this case, the term $V_s N_s$ (or $A_s N_s$ or $L_s N_s$) becomes the total volume (or area or length) available for translation. However, as long as there is a significant structural barrier between

solubility sites, the assumption of localized vibration rather than non-localized translation is preferable.[6]

The translational motion has been treated classically in all the above cases. This is valid for translational distances down to a few angstroms in the temperature region of room temperature or above. However, for such 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.[7,8] Therefore, small solubility sites are again expected to produce vibrational motion rather than translation.

DISCUSSION

Equations (14) through (17) express the solubility (n_s) of a monatomic species at a given pressure as a function of temperature, fundamental constants, and material parameters. The model considers the possibility of translational motion by the dissolved atoms. Localized translation could occur in relatively large solubility sites such as micropores produced in glass manufacture. Non-localized translation could occur through the silica network. However, for small solubility sites separated by even smaller pathways, the assumption of localized vibration rather than non-localized translation is preferred.

The temperature range of interest extends from room temperature to the glass transition temperature. The mass, m, of a given dissolved species is clearly fixed. The number of sites per unit volume, N_s, can be calculated with great accuracy for a crystal and 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. For glasses with structures similar to known crystalline forms, a satisfactory estimate can be expected. Calculation of the solubility site geometry (L_s, A_s, or V_s) depends upon a similar knowledge of the structure. The vibration frequency, ν, of the dissolved species can be estimated by comparison with literature data for similarly impinged species. The calculation of E(0), the effect of the solid's potential field on the dissolved atom, is made by summing the attractive and repulsive forces acting on the dissolved atom in the assumed solubility site. This is a difficult calculation even for a well defined site in a crystalline structure. Consequently, E(0) was chosen to best fit experimental solubility data by varying it over the range found by others[7,8] for helium and neon in similar crystalline oxides.

While there is a lack of much consistent or precise data on gas solubility in the current literature,[1] an initial evaluation of the model can be made for the systems of helium and neon in fused silica. Data are available which were obtained indirectly from permeation and diffusion measurements.[11,12] Figures 1 and 2 show a comparison of experimental data for these systems with plots of Eq. (17) which assumes the dissolved atom to be a simple harmonic oscillator. For silica with sites approximately 3 Å in diameter, one would expect the dissolved species to be represented by localized Einstein oscillators. This is consistent with the assumption of Barrer and Vaughan for helium and neon in cristobalite.[8]

Figure 1 compares the experimental data for He in fused silica[11] with the plot of Eq. (17). 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.[13] The values of ν($= 6.5 \times 10^{12}$ sec^{-1}) and E(0) (= -1.5 kcal/mole) were chosen to give the best visual fit to the experimental data. Both of these values 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 ν to be in the range of 1.9 to 7.8×10^{12} sec^{-1} and E(0) from -2.0 to -3.16 kcal/mole for He in cristobalite with the variation depending upon the method of calculation. This agreement of experiment and theory using reasonable parameters is considered highly satisfactory.

Figure 2 compares the experimental data for Ne in fused silica[12] with the plot of Eq. (17). All parameters are the same except the mass, m, the binding energy, E(0), and the vibrational frequency, ν. The mass of a neon atom is 3.35×10^{-23}g. The best visual fit to the experimental data was obtained with values of E(0) = -2.9 kcal/mole and $\nu = 2.9 \times 10^{12}$ sec^{-1}. The E(0) is in the same range found for helium and agrees favorably with the calculations of Barrer and Vaughan[8] for neon in crystalline silica. The lower ν is expected as the vibrational frequency of a harmonic oscillator is inversely proportional to the square root of its mass. In fact, the ν_{He}/ν_{Ne} ratio is almost exactly equal to the $\sqrt{m_{Ne}}/\sqrt{m_{He}}$ ratio. As for helium, very good agreement is shown in Fig. 2 between the Ne-SiO_2 data and the model.

Experimental studies are currently planned with the hope of obtaining more direct tests of the various equations developed above. Solubility measurements for glasses with known microporosity would allow a

direct test of the equations containing translational terms.

One can also note the success of a statistical model for solubility in a crystalline oxide. Olander[7] assumed helium dissolves in UO_2 as a simple harmonic oscillator. Consequently, he obtained a solubility equation essentially equivalent to Eq. (17). At 1200°C, his calculated n_s was 2×10^{17} atoms-cm^{-3}-atm^{-1}. The experimental value was $1 - 2 \times 10^{17}$ atoms-cm^{-3}-atm^{-1}.

The model, as presented, might be described as "ideal" solubility in that the dissolved state was assumed to be a combination of independent particle-in-a-box translation and simple-harmonic-oscillator vibration. However, intermediate states might occur. A similar problem in adsorption theory (hindered translation) has been treated.[9] The present data would not warrant such a refinement of the theory, but future data might justify such a treatment.

The current model was limited to monatomic gas solution. Extension of the theory to cases of polyatomic gas solution in which dissociation of the species may or may not occur is planned.

Finally, a brief comment on a recent model of gas solubility in glasses is appropriate. Doremus[14] has proposed a "free volume" model of solubility which considers the free volume or "openness" of the glass structure to determine the magnitude of solubility. The model was proposed while emphasizing that n_s divided by the free gas density, c_g (= p/kT), is constant with temperature for a variety of gases. In terms of our model, this is equivalent to assuming that the dissolved gas atoms retain three degrees of translational freedom. For solution in localized sites, the solubility, n_s, is given by Eq. (14). For non-localized

translation throughout the solid structure, the exp(-1) term is omitted from Eq. (14) as previously discussed in the MODEL section. Dividing n_s by c_g (= p/kT) produces Arrhenius type equation with a temperature independent pre-exponential form. Any temperature dependence is related to the interaction energy, E(0). For E(0) = 0, complete temperature independence is achieved. For localized translation,

$$\frac{n_s}{c_g} = N_s V_s e^{-1}. \tag{18}$$

For non-localized translation,

$$\frac{n_s}{c_g} = N_s V_s. \tag{19}$$

However, this approach is not preferred for two reasons. First, the n_s/c_g plots are only approximately independent of temperature, and any of the four solubility states considered in this paper could produce small temperature dependencies. Second, the reasonableness of the solubility state being considered as three degrees of vibration (the Einstein oscillator) has been previously stated and was then justified by the successful comparison of model and experiment in Figs. (1) and (2). However, the primary objection to the "free volume" model is that it considers the available volume of the structure to be represented by the amount of gas solubility. The more fundamental model of this paper shows that at equilibrium only a small fraction of the available volume is occupied, i.e. $n_s/N_s \ll 1$.

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REFERENCES

1. R. H. Doremus, in Modern Aspects of the Vitreous State, Vol. 2, J. D. MacKenzie Ed. (Butterworths, Washington, 1962), pp. 1-71.
2. H. Scholze, Glass Ind. 47, 546 (1966).
3. R. H. Fowler and C. J. Smithells, Proc. Roy. Soc. (London) 160A, 37 (1937).
4. J. R. Lacher, Proc. Roy. Soc. (London) 161A, 525 (1937).
5. S. Takeuchi and K. Suzuke, Trans. Jap. Inst. Metals 3, 41 (1962).
6. Y. Ebisuzaki and M. O'Keeffe, in Progress in Solid State Chemistry, Vol. 4, H. Reiss Ed. (Pergamon Press, N.Y., 1967) pp. 187-211.
7. D. R. Olander, J. Chem. Phys. 43, 779 (1965).
8. R. M. Barrer and D. E. W. Vaughan, Trans. Faraday Soc. 63, 2275 (1967).
9. T. L. Hill, Introduction to Statistical Thermodynamics (Addison-Wesley Publishing Co., Reading, Mass., 1960), Chap. 1, 7, 10.
10. J. F. Lee, F. W. Sears, and D. L. Turcotte, Statistical Thermodynamics (Addison-Wesley Publishing Co., Reading, Mass., 1963), Chap. 9.
11. D. E. Swets, R. W. Lee, R. C. Frank, J. Chem. Phys. 34, 17 (1961).
12. R. C. Frank, D. E. Swets, and R. W. Lee, J. Chem. Phys. 34, 1451 (1961).
13. J. F. G. Hicks, Science 155, 459 (1967).
14. R. H. Doremus, J. Am. Ceram. Soc. 49, 461 (1966).

FIGURE CAPTIONS

Fig. 1. Comparison of experimental solubility data for helium in fused silica with a plot of Eq. (17) using the parameters $\nu = 6.5 \times 10^{12}$ sec^{-1} and $E(0) = -1.5$ kcal/mole.

Fig. 2. Comparison of experimental solubility data for neon in fused silica with a plot of Eq. (17) using the parameters $\nu = 2.9 \times 10^{12}$ sec^{-1} and $E(0) = -2.9$ kcal/mole.

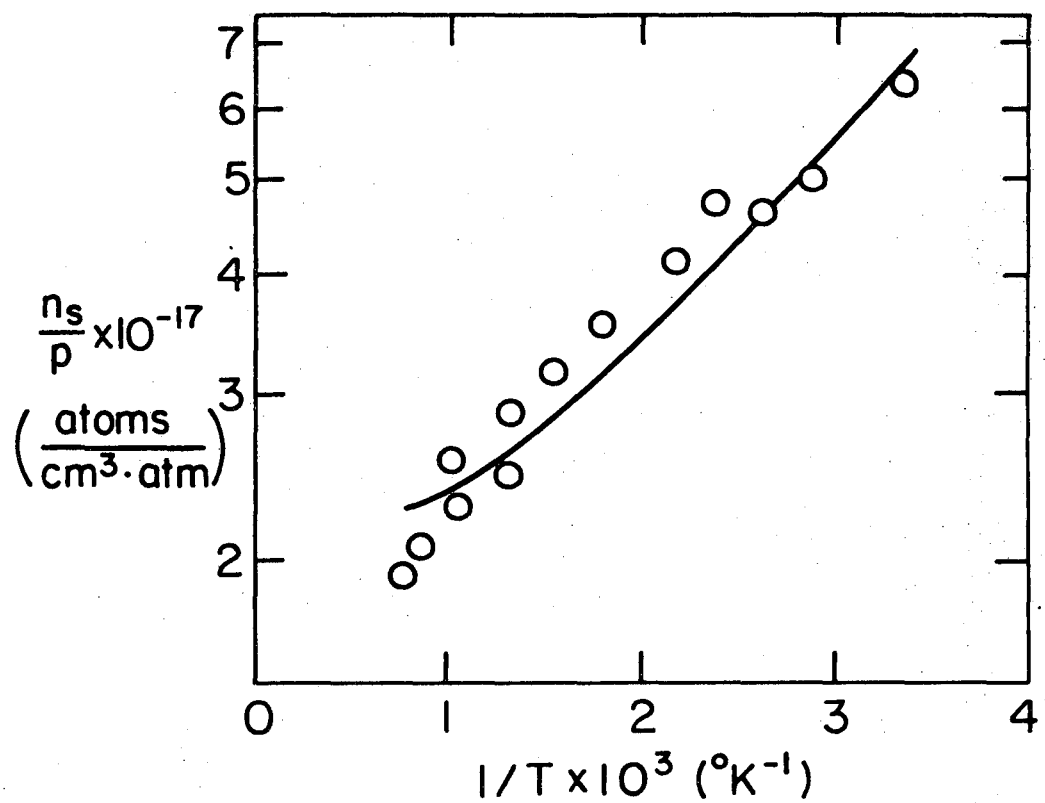

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Fig. 1

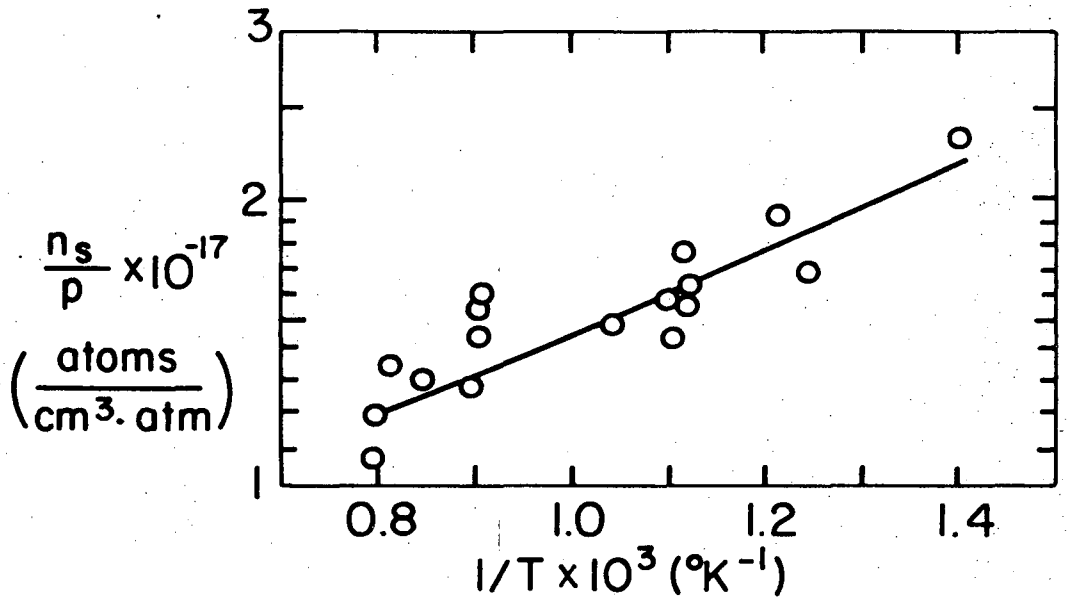

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Fig. 2

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