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# SOLUBILITY OF GASES IN GLASS. II. A POLYATOMIC MODEL

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## ABSTRACT

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The statistical thermodynamics of the gas-in-glass system provides a basic model of the solubility. Equations are derived which give the solubility (in molecules per cubic centimeter of glass) as a function of gas pressure, temperature, fundamental constants, and material parameters. Both physical and chemical solubility are considered. The physical solubility result is essentially equivalent to that for monatomic solubility. The chemical solubility result is dependent upon the specific system involved.

## 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. A comparison of the general model with experimental solubility data will be given in the concluding paper in this series.[2]

It should be emphasized that the solubility to be discussed is in glasses below their glass 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

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[3]

$$G = kT\,(\partial \ln Q/\partial \ln V)_{T,N} - kT \ln Q \qquad (1)$$

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.

For convenience, a specific example will be used, viz. the homonuclear diatomic. Assuming the gas to be ideal, the Q is that for a system of N indistinguishable particles in a three-dimensional box

$$Q=q^N/N!=(1/N!)\left\{\left(2\pi mKT/h^2\right)^{3/2} V\left[T/\left(\sigma\theta_r\right)\right]\left[e^{-\theta_{vi}/2T}/\left(1 - e^{-\theta_{vi}/T}\right)\right]\right\}^N \quad (2)$$

with m the mass of one molecule, h the Planck's constant, q the partition function for a single molecule, $\sigma$ the symmetry number ($\sigma$ = 2 for $H_2$), $\theta_r$ the characteristic temperature for rotation ($\theta_r = h^2/8\pi^2 Ik$ where I = moment of inertia), and $\theta_{vi}$ is the characteristic temperature for vibration ($\theta_{vi} = h\nu/k$). 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. (2) into Eq. (1) and using pV = NkT (the ideal gas law) gives

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

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

For the dissolved state,[4]

$$G(s) = G(Q) + E(0) - T\bar{S}_m \quad (4)$$

with G(Q) given by Eq. (1) where Q is now the partition function associated with the motion of the gas molecule in the dissolved state. E(0), the binding energy, 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. $\bar{S}_m$ is the partial molal entropy of mixing for the gas. It is of the form

$$\bar{S}_m = R \ln \left( N_s / n_s \right) \tag{5}$$

where $N_s$ is the number of solubility sites available per cubic centimeter, and $n_s$ is the number of gas molecules 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.

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 in the next paper ($H_2$ 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

$$q = \left[ T/\left(\sigma\theta_r\right)\right]\left[e^{-\theta_{vi}/2T}/\left(1 - e^{-\theta_{vi}/T}\right)\right]\left[e^{-\theta_v/2T}/\left(1 - e^{-\theta_v/T}\right)\right]^3 \tag{6}$$

where $\theta_v$ is the characteristic temperature for vibration of the center of mass of the dissolved molecule. The resulting G(s) is

$$G(s) = - RT \ln \left[q\left(N_s/n_s\right)\right] + E(0) \tag{7}$$

with q given by Eq. (6). Equating G(g) and G(s) and rearranging terms gives the final solubility equation for homonuclear diatomic physical solubility

$$n_s/p = \left(h^2/2\pi mkT\right)^{3/2}\left(kt\right)^{-1}N_s\left[e^{-\theta_v/2T}/\left(1 - e^{-\theta_v/T}\right)\right]^3 \exp[-E(0)/RT] \tag{8}$$

which is equivalent to the result for the monatomic case.[1]

Actually, Eq. (8) is quite general for any polyatomic physical solubility in which the internal degrees of freedom are retained and the external translation is transformed to localize 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°K) means that the high temperature (classical) form of the rotational partition function ($q_r = 8\pi^2 IkT/\sigma h^2$) 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).[5] 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.

## 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, $n_s$, 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

$$G(s) = G(Q) + \Sigma E_i(0) - T\bar{S}_m \tag{9}$$

where $E_i(0)$ is the binding energy of the ith dissociated species and $\bar{S}_m$ 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

$$Q_{diatomic} = q^{N}_{diatomic}/N! \tag{10}$$

where

$$q_{diatomic} = q_{trans} q_{rot} q_{vib} q_{elec} =$$

$$\left(2\pi mkT/h^2\right)^{3/2} V\left[T/\left(2\theta_r\right)\right]\left[e^{-\theta_{vi}/2T}/\left(1-e^{-\theta_{vi}/T}\right)\right]\exp\left[-\varepsilon_{el}/kT\right] \tag{11}$$

where $\varepsilon_{el} = -D_e$ and $D_e$ is the dissociation energy of the diatomic molecule.

Also,

$$Q_{monatomic} = q^{2N}_{monatomic} = \left(q^{3}_{vib}\ q_{elec}\right)^{2N} = \left\{2\left[e^{-\theta_v/2T}/\left(1-e^{-\theta_v/T}\right)\right]^3\right\}^{2N} \tag{12}$$

where the dissolved atom is assumed to be restricted to vibrational motion. The factor 2N arises from the dissociation of N molecules into 2N atoms. Substitution of Eqs. (11) and (12) into Eqs. (1) and (9)

respectively, gives

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

$$\left. x \exp\left[-\varepsilon_{el}/kT\right]\right\} \tag{13}$$

and

$$G(s) = -2RT \ln\left\{2\left[e^{-\theta_v/2T}/\left(1-e^{-\theta_v/T}\right)\right]^3\left(N_s/n_s\right)\right\} + 2\,E(0). \tag{14}$$

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

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

$$x\left\{2N_s\left[e^{-\theta_v/2T}/\left(1-e^{-\theta_v/T}\right)\right]^3\right\} \exp\left[\varepsilon_{el}/2kT\right]\exp[-\,E(0)/RT] \tag{15}$$

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, $\varepsilon_{el}$ 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. 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.

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 in the next paper[2] occurs at sufficiently high temperatures that Eq. (15) is valid.

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