

Capillary-Wave Model of Gas–Liquid Exchange

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Data leading to the nucleation theory of accommodation of a solute gas by a liquid are reinterpreted in terms of a capillary-wave model, in which the growth of solvent clusters to some critical size is replaced by progressive absorption into a mobile liquid surface, and the cluster-size variable is replaced by an effective coordination number. The new model accounts for the observed linear relationship between the enthalpy and entropy of activation for accommodation of a wide variety of solutes in water on the basis of the statistical mechanics of the absorption process and provides an estimate of the rate of penetration into the liquid on the basis of the calculated capillary-wave spectrum.

Introduction

Molecular-beam studies of the gas–liquid interface^{1,2} show that gas-phase molecules striking the surface of a liquid either can undergo prompt reflection from the rough liquid surface or can become adsorbed momentarily before either re-emission or transfer into the body of the liquid (accommodation or solvation). Molecules actually in the adsorbed state have been identified by surface second-harmonic generation.^{3,4} Measurements by Davidovitz and co-workers of accommodation coefficients for gaseous species into small droplets,^{1,5} for many different solute gases over a range of temperatures, rule out a mechanism in which the rate of solvation of a surface molecule is controlled by the rate of formation of an appropriately sized cavity adjacent to the adsorption site. This has led them to develop a solvation model based on nucleation theory as outlined in ref 1, which also incorporates a useful bibliography of recent work in the field.

According to the solvation model of Davidovitz et al., the interfacial region contains nucleating clusters or “aggregates” of various sizes. Because of the part played by surface tension in this theory, the implication is that these clusters are to be visualized as small droplets of liquid located in the vicinity of the surface. A cluster can incorporate a molecule adsorbed from the gas phase, and there is a critical cluster size such that larger clusters always become incorporated into the bulk liquid, thereby ensuring that the former gas molecule becomes fully solvated. Smaller clusters have the option of dissociating and returning their components to the gas. The existing theory of homogeneous nucleation is then used to calculate the solvation rate. This model is consistent with a plausible free-energy diagram for the gas–liquid transfer process and leads to mathematical expressions which account for the systematic manner in which the measured activation enthalpy and entropy of solvation, as defined in ref 1, vary with the nature of the solute gas. However the model is slightly unphysical, in that a real gas–liquid interface is not usually well-represented by a region of varying density containing clusters of different sizes but instead shows a rather sharp transition in density and other properties.^{6–8} The location of the transition can be so variable, in the presence of capillary waves, as to give the impression of a thick transition zone, but the actual transition at any instant remains well-defined. There is also the weaker objection that a theory of

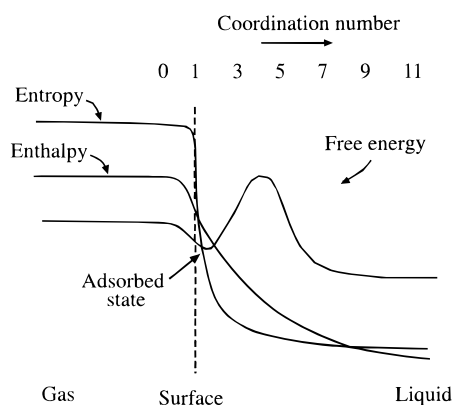


Figure 1. Sketch showing variation of enthalpy, entropy, and free energy of a gas–liquid system with the coordination number of the solute molecule.

gas–liquid exchange must apply as well to transfer of solute gases which are only slightly soluble as to condensation of the bulk liquid itself, and it does not seem likely that molecules of a slightly soluble gas would serve as effective condensation nuclei for the postulated solvent clusters. These objections largely disappear if the cluster idea is regarded as an analogy rather than a physical model,⁹ but that does not seem to have been the original intention of Davidovitz et al.

The aim of the present paper is to show that the free energy diagram upon which the nucleation model, and most of the associated mathematics, are based, is also deducible from a capillary-wave model, and to show that the observed correlation between activation parameters ΔH^\ddagger and ΔS^\ddagger arises naturally from a model in which the cluster-size parameter of Davidovitz et al. is replaced by an effective coordination number for a solute molecule that is in the process of penetrating into and below the liquid surface. Penetration is effected through the random motions of the liquid surface that can be described in terms of capillary waves, and its progress is measured by the increase in coordination number, defined as the number of solvent molecules surrounding and in contact with the solute molecule, to some maximum value which is characteristic of the final solution. The resulting free energy diagram (Figure 1) resembles Figure 12 of ref 1, but the process of solvation now corresponds to an increase of coordination number, rather than cluster size,

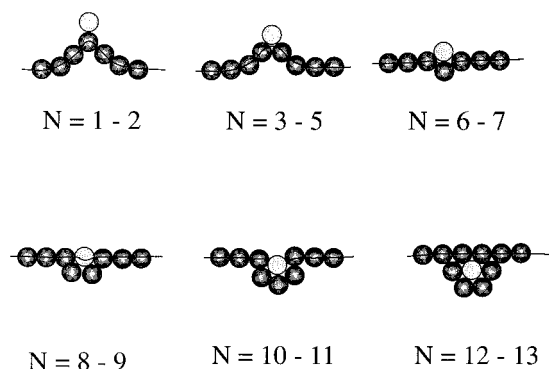


Figure 2. Variation of coordination number N_c during progressive stages of solvation of a solute molecule (light sphere) by solvent molecules (dark spheres).

beyond a critical value at which the free energy passes through a maximum. The characteristic shape of the free energy curve is then mainly the result of differences in the rates of change of the entropy and enthalpy of the system with coordination number.

Capillary waves, also termed “ripples”, are waves for which the restoring force is provided solely by surface tension.¹⁰ Their spectrum extends from macroscopic wavelengths all the way to molecular dimensions, but this is not always evident because at short wavelengths they are very strongly damped by viscosity. Thus the wave amplitude falls by a factor of e in a time shorter than one period of oscillation for wavelengths less than $128^3 \eta^2 \rho / \gamma$ (η = coefficient of viscosity, ρ = density, γ = surface tension), a wavelength which amounts to 0.0054 cm in water at 300 K. It follows that short-wavelength vibrations of the surface membrane are strongly coupled to the heat bath which comprises the bulk liquid and also that, although the normal modes of the membrane can be used as a basis set with which to construct an arbitrary surface displacement, there is no temporal coherence for displacements on a scale much shorter than this distance. The oscillation period of the shortest waves is about 7×10^{-13} s in water at 300 K, which is quite long in comparison with the duration of a collision with the surface for a gas molecule of kinetic energy greater than the average thermal energy at 300 K (assume interaction distance less than 10^{-8} cm, velocity greater than 10^5 cm s⁻¹) so, in molecular beam experiments such as those of ref 1, the liquid surface will usually appear as a frozen landscape and transfer of collisional energy into the capillary-wave spectrum will be very inefficient. However, this will not necessarily be true for low-energy collisions.

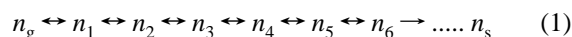
The basis of the present model was established in a previous paper,¹¹ in which the calculated spectrum of thermally excited waves in the membrane formed by surface tension was used to obtain the rms slope and displacement of a liquid water surface, and statistical reaction-rate theory was used to calculate unimolecular rate constants for thermal dissociation of a planar surface membrane in a manner which corresponded to transfer of a molecule into the gas-phase from a point somewhere below the surface. We here extend the model to calculate the rate at which an adsorbed molecule is engulfed by the liquid surface and use elementary statistical mechanics to obtain a relation between the entropy and enthalpy of activation for the accommodation process.

Accommodation as a Function of Coordination Number

The progression from adsorption to solvation is visualized as occurring in the manner shown in Figure 2, where different

stages of the process correspond to different average coordination numbers N_c as indicated approximately on the diagrams. The surface profile shown in the first diagram of Figure 2 is not to be taken as an indication that a wavelet of this particular instantaneous shape is required by the model; it happens that a coordination number of about 1 is easier to illustrate for a sharp-pointed wavelet. Nor is the most stable adsorbed state likely to be associated with a coordination number of 1. As mentioned in the Introduction, the mechanism of solution or evolution is the continual stirring and mixing of the surface layers by thermally excited capillary waves; the driving force is provided by the free energy difference of the solute between gas and solution. Here we consider accommodation of solute into pure solvent, as in the experiments of Davidovitz et al. Both the potential energy per solute molecule and the entropy of the system decrease as the average coordination number of the solute increases, in a manner which depends on the details of the solute-solvent and solvent-solvent potential fields and has been the subject of computer simulations.¹²⁻¹⁴ The simulations invariably show a free energy minimum at the liquid surface, and the free energy of such a system can be made to pass through a maximum value provided the decrease of entropy with increasing N_c is more rapid than the decrease of enthalpy. We return to this point shortly.

We now set up the following kinetic scheme



where the symbol n_g stands for the concentration of gas-phase solute molecules, n_3 similarly stands for the concentration of solute molecules with three nearest neighbors, and so on, n_s stands for the concentration of solvated solute molecules, and double-headed arrows correspond to reversible processes under the conditions of the experiments of Davidovitz et al. The presence of a single-headed arrow after n_6 indicates that the species with seven nearest neighbors is assumed to have passed through the critical configuration for solvation, i.e., is over the crest of the free-energy barrier. We here identify n_6 with the critical configuration for which an alternative label is n^\ddagger . The coordination number corresponding to the critical configuration is expected to depend markedly on the nature of the solvent; for example, a value close to 4 is likely to be more appropriate for water. The rate constants involved in this scheme can be labeled k_{g1} , k_{12} , k_{32} , k_{6s} , and so on, where k_{g1} is the rate constant for the initial adsorption step, k_{32} is the rate constant for the reverse process of transferring an n_3 species to n_2 , the rate constant for direct addition to the population n_5 from the gas-phase would be labeled k_{g5} , and there are assumed to be no rate constants of the type k_{i6} when i is anything but unity. A complete steady-state treatment could be worked out for the concentrations of all the species, but this is not necessary for our present purpose. The quantity that has been measured experimentally is

$$k_{\text{solvation}}/k_{\text{escape}} = \exp(-\Delta G_{\text{obs}}/RT) \quad (2)$$

in the notation of ref 1. The rate of escape from the surface is $k_{1g}n_1$, and the rate of solvation is $k_{6s}n_6$. Hence

$$k_{\text{solvation}} = k_{6s}n_6/(n_1 + n_2 + n_3 + n_4 + n_5 + n_6) \quad (3)$$

and

$$k_{\text{escape}} = k_{1g}n_1/(n_1 + n_2 + n_3 + n_4 + n_5 + n_6) \quad (4)$$

and we have

$$\exp(-\Delta G_{\text{obs}}/RT) = k_{6s}n_6/k_{1g}n_1 \quad (5)$$

We can now put $\exp(-\Delta G_{16}/RT)$ in place of n_6/n_1 , write k_{6s} as $(k_B T/h) \exp(-\Delta G_{67}^\ddagger/RT)$, where ΔG_{67}^\ddagger is the free energy of activation for this process, and write k_{1g} as

$$(k_B T/h)(q_g/q_l) \exp(-\Delta H_{1g}/RT)(k_B T/h) \exp(-\Delta G_{1g}/RT)$$

where we have specifically included partition functions q_g and q_l for the gaseous and adsorbed solute species. Hence $\Delta G_{\text{obs}} = \Delta G_{67}^\ddagger$, or in general

$$\Delta G_{\text{obs}} = \Delta G^\ddagger \quad (6)$$

where the right-hand side of (6) is the free energy difference between the gas phase and the crest of the free energy barrier in Figure 1.

One very striking result from the work of Davidovitz et al. is the linear relationship, amounting to a near-proportionality, which they found between their measured values of ΔH_{obs} and ΔS_{obs} for a wide variety of solutes. Such a result can be predicted for a variety of simple models in the framework of the present theory. For example, suppose that the dependences of enthalpy and entropy on coordination number N_c for all solutes are given by simple power-law expressions, as follows

$$H_N = H_s(N_c/N_H)^{m_H} \quad (7)$$

for $N_c < N_H$, where N_H is the value at which enthalpy ceases to change with N_c , so that for $N_c > N_H$ we have $H = H_s$. Similarly

$$S_N = S_s(N_c/N_S)^{m_S} \quad (8)$$

for $N_c < N_S$; otherwise $S = S_s$. The quantities m_H and m_S are assumed to be characteristic of the solvent, and the state functions are measured relative to the gas-phase values so we can write $H_s = TS_s$. We locate the free-energy extremum by differentiating $G_N = H_N - TS_N$ with respect to N_c , and hence obtain

$$\Delta H_{\text{obs}}/\Delta S_{\text{obs}} = m_S T/m_H \approx \text{constant} \quad (9)$$

From the experimental data for 273 K we find $m_S/m_H \approx 0.85$, which seems not unreasonable. To produce a maximum in G we require $N_S < N_H$. This calculation obviously amounts to a gross oversimplification but does help to demonstrate the plausibility of the model. A more rigorous approach is used in the next section.

Statistical Mechanics of Accommodation

We begin with the standard formula¹⁵ for the entropy of a Boltzmann gas of N indistinguishable particles at temperature T

$$S = Nk_B \ln(q/N) + Nk_B + U/T \quad (10)$$

where q is the molecular partition function, k_B is Boltzmann's constant, and U is internal energy. The entropy change between the gas and the critical configuration is

$$\Delta S^\ddagger = Nk_B \ln(q^\ddagger/q_{\text{gas}}) + (U^\ddagger - U_{\text{gas}})/T \quad (11)$$

which immediately gives

$$\Delta S^\ddagger = \Delta H^\ddagger/T + Nk_B \ln(q^\ddagger/q_{\text{gas}}) - P(V^\ddagger - V_{\text{gas}})/T \quad (12)$$

The second and third terms on the right-hand side of (12) are of opposite sign, and their near-cancellation would lead to the observed near-proportionality of ΔS^\ddagger and ΔH^\ddagger . Alternatively, if there is no near-cancellation, their difference should be small in comparison with ΔS^\ddagger . If we neglect V^\ddagger in comparison with V_{gas} , the third term becomes Nk_B , so the quantity of interest is $Nk_B[\ln(q^\ddagger/q_{\text{gas}}) + 1]$. The ratio of translational partition functions reduces to the ratio of volumes available to a solute molecule, which gives a value of about 1/500 for $q^\ddagger/q_{\text{gas}}$ if we assume that the effective density in the critical configuration is similar to the density of the liquid solute. The ratio of rotational partition functions depends on the extent to which rotation is hindered in the critical configuration. For simplicity we here assume free or only slightly hindered rotation, so this factor is close to unity. Hence the predicted difference between ΔS^\ddagger and $\Delta H^\ddagger/T$ amounts to about 5R per mole. This is not negligible; however, the experimental data (see Figure 11 of ref 1) are compatible with a constant term of this magnitude in the linear relationship between ΔS^\ddagger and ΔH^\ddagger .

Capillary-Wave Calculation of k^\ddagger

The rate constant for the accommodation process can be written as

$$k_{\text{solvation}} = k^\ddagger \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \quad (13)$$

where k^\ddagger is the unimolecular rate constant for motion along the critical coordinate and is normally identified with $k_B T/h$. We now derive an alternative expression for k^\ddagger on the basis of the properties of capillary waves. For a molecule in the process of accommodation, motion along the critical coordinate amounts to motion relative to adjacent molecules in the surface layer. If the vertical displacement of a single capillary wave mode is given by

$$\xi_x = a_x \cos(\omega t - kx) \quad (14)$$

where a_x is the amplitude of the mode characterized by the circular frequency ω and wave vector k , the average vertical velocity v^\ddagger of a molecule at $x = 0$, relative to points on the surface one molecular diameter away along the x -axis, is given by

$$\begin{aligned} v^\ddagger &= \Delta(d\xi_x/dt) \\ &= -a_x \omega \{ \sin \omega t - 1/2(\sin[\omega t - k\sigma] + \sin[\omega t + k\sigma]) \} \\ &= -a_x \omega \sin \omega t [1 - \cos k\sigma] \end{aligned} \quad (15)$$

where σ is the molecular diameter, and a similar expression holds for displacements relative to points on the y -axis due to a mode of the same frequency and wave vector. From here on we drop the x suffix. The energy per unit area in one mode is $1/2 a^2 k^2 \gamma$ where γ is surface tension and the total area involved is $\pi L^2/4$, where the length L can be taken as $\pi\sqrt{(\gamma/\rho g)}$, g being the gravitational acceleration.¹¹ The total number of vertical displacement modes in this area is $\pi L^2/4\sigma^2$, and the degeneracy of mode number m is $\pi m/2$, where $k = \pi m/L$.¹¹ The mean energy per mode is $k_B T$, so the mean value of a^2 is $8k_B T/\pi^3 m^2 \gamma$. The mean value of v^\ddagger for any mode is zero, so the variance of v^\ddagger for one mode is simply equal to its mean-square value, or

$$\langle v^{\ddagger 2} \rangle = 4\omega^2 k_B T (1 - \cos k\sigma)^2 / \pi L^2 \gamma k^2 \quad (16)$$

where we have used $\langle \sin^2 \omega t \rangle = 1/2$. We now apply the central-limit theorem of statistics to the distribution of v^\dagger resulting from superposition of a large number (ca. 10^7) of surface modes, to obtain a Gaussian distribution with variance equal to the variance for a single mode multiplied by the number of modes. Replacing ω^2/k^2 in (16) by $\gamma k/\rho$,¹⁰ multiplying by the degeneracy $\pi m/2$, and using $k = \pi m/L$, gives, for the total variance of v^\dagger for all modes of wave vector k ,

$$\langle v^{\dagger 2} \rangle = 2m^2 k_B T [1 - \cos(\sigma/L)]^2 / L^3 \rho \quad (17)$$

This quantity now has to be integrated over dm between the limits $m = 1$ and $m = L/\sigma$. The integral is greatly simplified by taking the lower limit as zero. The final result is

$$\langle v^{\dagger 2} \rangle = k_B T (8.5 + \pi^2) / \pi \rho \sigma^3 \quad (18)$$

which is independent of any assumptions regarding the value of L . A Gaussian distribution with this variance corresponds to the average absolute value

$$|v^\dagger| = (2k_B T (8.5 + \pi^2) / \pi^2 \rho \sigma^3)^{1/2} \quad (19)$$

and we now define the rate constant for motion along the critical coordinate in this system as $k^\ddagger = |v^\dagger|/\sigma$. With the values $\rho = 1$, $\sigma = 3 \times 10^{-8}$ cm, and $T = 300$ K, this gives $k^\ddagger = 2.6 \times 10^{12}$ s⁻¹. It is interesting that k^\ddagger calculated in this way is only about a factor of 2 smaller than $k_B T/h$. A reduction of k^\ddagger by a further factor of 2 results if we allow for the fact that half of the motions corresponding to v^\dagger are directed out of the surface, and require

ζ_x and ζ_y both to be changing in the same direction. The success of this simple treatment tends to support the view that it is the random superposition of thermally excited capillary waves which transfers an initially adsorbed solute molecule into the body of the liquid.

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