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Review Article

THE KINETICS OF THE TRANSPORT OF MATTER AT THE LIQUID SURFACE

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After a brief summary of the relevant results of irreversible thermodynamics, the simplest example in which the kinetics of evaporation can be formulated is discussed: namely that of a pure ideal gas in contact with the liquid. This is followed by a treatment of transport along a surface, and the kinetics of gas absorption by a liquid. The article concludes with a discussion of transport from the bulk liquid to the surface.

LIST OF SYMBOLS

a	Activity of solute
a_i	Extensive thermodynamic variable
α	Evaporation or condensation coefficient
D	Diffusion coefficient
Δ	Distance from droplet surface beyond which diffusion is rate controlling
erf	Error function
f	Maxwell's velocity distribution function
ϕ	Absorption rate for a gas of a length of liquid jet
G	Volumetric flow rate of a jet
h	Specific enthalpy
J	Flux
k	Boltzmann's constant
L_{ij}	Transport coefficient
λ	Wavelength of jet vibration
M	Molecular weight
m	Mass of a molecule
μ	Coefficient of viscosity or chemical potential
N	Mass per unit area transferred in time t

NTP	Normal temperature and pressure
n	Number of molecules
P	Pressure
r	Radius or radial distance, number of degrees of vibrational or translational freedom of a molecule
ρ	Density
S	Entropy
S_{ij}	Stiffness matrix
σ	Surface tension
T	Absolute temperature
t	Time
Γ	Surface excess concentration
u	Jet velocity
\bar{u}	Mean drift velocity of gas molecules
V	Volume
v	Velocity
W	Mass of droplet
X_i	Thermodynamic force, $\partial S/\partial a_i$
x_i	$\partial \Delta S/\partial \eta_i$
y	Perpendicular distance from the liquid surface
ξ	Velocity components of a particle
η_i	Displacement of extensive variable from equilibrium

I THERMODYNAMICS

Irreversible thermodynamics in the linear approximation has been applied by various authors to the problem of matter transport at the liquid surface.^{1,2} Although in itself thermodynamics provides little information regarding the correctness of the various current theories, e.g., of evaporation, yet it defines certain quantities in which the theories can be expressed and therefore a brief introduction to the classical thermodynamics of non-equilibrium processes is indispensable—it has been employed among others by De Groot³ and was originated by Onsager.⁴

An isolated system is considered which is divided into two subsystems by a partition impermeable to thermal energy. Both the subsystems are in equilibrium and the probability of their not being so is proportional to $\exp(\Delta S/k)$ where ΔS is a small deviation from equilibrium, k is Boltzmann's constant.⁵ A Taylor expansion of ΔS in terms of *extensive* thermodynamic variables, a_i , gives,

$$\Delta S = \sum x_i \eta_i + \sum \frac{1}{2} S_{ij} \eta_i \eta_j + \quad (1)$$

Where $x_i = (\partial S / \partial a_i)_{a_j}$ and S_{ij} consists of differential coefficients of the form, $\partial^2 S / \partial a_i \partial a_j$. The x_i are called *thermodynamic forces*, they are the forces that drive the system towards equilibrium and at equilibrium they are zero in value; the η_i are called *displacements* and they are given by,

$$\eta_i = a_i - a_i^0$$

where the a_i^0 are the equilibrium values of the extensive variables. Being at equilibrium, both subsystems obey Gibbs' equation: $dS = x_i da_i$ or, in particular,

$$T dS = dU + P dV - \mu dM \tag{2}$$

Removal of the partition results in a redistribution of the extensive variables between subsystems 1 and 2 such that,

$$U_1 + U_2 = \text{constant}$$

$$V_1 + V_2 = \text{constant}$$

etc., where U is the internal energy and V is the volume. For the composite system we have,

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 + \tag{3}$$

and therefore when the system as a whole is at equilibrium we have the condition, $\partial S / \partial U_1 = 0$ and, in general, $x_i = 0$; hence the first term in Eq. 1 is zero. Near equilibrium, ignoring the higher terms,

$$x_i = \frac{\partial S}{\partial \eta_i} \simeq \sum \frac{1}{2} S_{ij} \eta_j \tag{4}$$

within this approximation the forces are linear in the displacements. The thermodynamic fluxes are,

$$\dot{\eta}_i = \sum L_{ij} x_j \tag{5}$$

The components of the L_{ij} matrix are called *transport coefficients*. Lavenda⁵ discusses the conditions under which Onsager's relation holds, viz. $L_{ij} = L_{ji}$.

From equation 3 we derive the forces,

$$x_U = \Delta \left(\frac{1}{T} \right) \tag{6}$$

$$x_V = \Delta \left(\frac{P}{T} \right) \tag{7}$$

$$x_M = -\Delta \left(\frac{\mu}{T} \right) \tag{8}$$

where $\Delta(1/T) = 1/T_1 - 1/T_2$, etc. and Eq. 5 can be written, for example,

$$J_M = L_{MM}x_M + L_{MU}x_U \quad (9)$$

$$J_U = L_{UM}x_M + L_{UU}x_U \quad (10)$$

where J_M is the mass flux and J_U is the energy flux. De Groot³ finds that,

$$J_M = -\frac{L_{MM}\Delta P}{\rho T} + (L_{MM}h - L_{MU})\frac{\Delta T}{T^2} \quad (11)$$

$$J_U = -\frac{L_{UM}\Delta P}{\rho T} + (L_{UM}h - L_{UU})\frac{\Delta T}{T^2} \quad (12)$$

where h , the specific enthalpy, is given by,

$$h = \mu + \frac{TS}{M} = \frac{U}{M} + \frac{P}{\rho} \quad (13)$$

II TRANSPORT BETWEEN GAS AND LIQUID

The simplest example of a system in which the kinetics of evaporation can be formulated is that of a pure, ideal gas in contact with the liquid—the surface of liquid helium for example.^{1,6} The simplest—but inadequate—theory is called the Simple Knudsen Gas Model and it expresses the net evaporation or condensation rate, J_N , as the difference between the inward flux coming from the gas and the outward flux going from the liquid,

$$J_N = J_g - J_l \quad (14)$$

It is assumed that $P = nkT$ and that Maxwell's relation holds, i.e. the fraction of molecules having velocities between the limits ξ and $\xi + d\xi$ is,

$$f(\eta) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-m\xi^2}{2kT}\right) d\xi \quad (15)$$

If $\bar{c} = (8kT/\pi m)^{1/2}$ is the mean velocity then the flux of molecules impinging on a plane surface is,

$$J = \frac{1}{4}n\bar{c} = P(2\pi mkT)^{-1/2} \quad (16)$$

The above taken with Eq. 14 gives,

$$J_N = \frac{1}{\sqrt{2\pi mk}} \Delta\left(\frac{P}{\sqrt{T}}\right) \quad (17)$$

TABLE I

Transport coefficients for the Simple Knudsen Gas Model. This and Table II are consistent with Table I of Wiechert,¹ the forces being the same

L_{MM}	$\sqrt{\frac{m}{2\pi kT}} \rho T$
L_{MU}	$2\sqrt{\frac{kT}{2\pi m}} \rho T$

$\Delta P = P_g - P_l$, $\Delta T = T_g - T_l$, the subscripts meaning gas and liquid. Assuming every gas particle carries $2kT$ units of energy and mass m , the mass flux, J_M , and the energy flux, J_U , are given by,

$$J_M = \sqrt{\frac{m}{2\pi kT}} \Delta P - \sqrt{\frac{m}{2\pi kT}} \frac{P}{2T} \Delta T \tag{18}$$

$$J_U = \sqrt{\frac{2kT}{\pi m}} \Delta P + \sqrt{\frac{kT}{2\pi m}} \frac{P}{T} \Delta T \tag{19}$$

Interpreting ΔP and ΔT as the deviations from equilibrium, the above are in the same form as Eq. 5; if the forces are those of Eq. 11 then the transport coefficients correspond with those in Table I.

However the Simple Knudsen Gas Theory is in accordance neither with experiment⁶ nor with other theories¹ and a number of refinements are necessary: the adaption of the Maxwell function to the nonequilibrium condition, the introduction of \bar{u} —the drift velocity—which is proportional to the evaporation rate, the inclusion of the evaporation and condensation coefficients and provision for a variable number of degrees of freedom.

In Eq. 17 the assumption is present that the inward and the outward fluxes are both unchanged by the meeting of the two streams of gas but in fact they become indistinguishable after a period of time exceeding the characteristic collision time, $\pi\mu/4P$, where μ is the viscosity. A correction factor for this can be calculated by the Maxwell Moment Method^{7,8} in which both streams are described by a distribution function like eq. 15 but including simple weighting functions, $\mathbf{n}_f(y, t)$ and $\mathbf{T}_f(y, T)$ where y is the distance from the surface and t is the time,

$$f_1 = \mathbf{n}_1 \left(\frac{m}{2\pi kT_1} \right)^{3/2} \exp\left(\frac{-m\xi^2}{2kT_1} \right) \tag{20}$$

$$f_2 = \mathbf{n}_2 \left(\frac{m}{2\pi kT_2} \right)^{3/2} \exp\left(\frac{-m\xi^2}{2kT_2} \right) \tag{21}$$

The mean value of any function, Q , of the velocity components of the particles can be expressed as a moment of the above distribution functions; the mean value of Q is $\bar{Q} = \int Qf_1 d\xi + \int Qf_2 d\xi$. The four unknown functions \mathbf{n}_1 , \mathbf{n}_2 , \mathbf{T}_1 and \mathbf{T}_2 are found⁸ with four moment equations, $Q = m, m\xi_y, \frac{1}{2}m\xi^2$ and $\frac{1}{2}m\xi^2\xi_y$, the last being an energy flux perpendicular to the surface. Other moments can be used, for example if $Q = \xi_y$ then,

$$\bar{v}_y = \int \xi_y f_1 d\xi + \int \xi_y f_2 d\xi$$

where \bar{v}_y is the mean velocity perpendicular to the surface. With the above four moments the correction factor was found to be⁸ 0.9300 and Eq. 17 becomes,

$$J_N \simeq \frac{0.9300}{\sqrt{2\pi mkT}} \Delta P \tag{22}$$

With six moments the result is $0.8985\Delta P(2\pi mkT)^{-1/2}$.

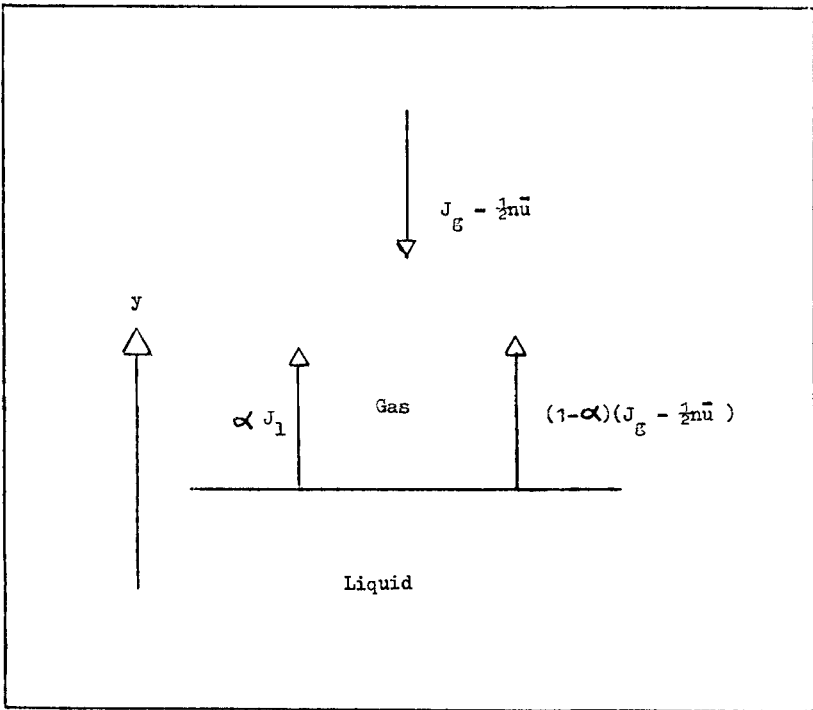


FIGURE 1 The Drifting Knudsen Gas model—inward and outward fluxes.

If there is to be a net flow of matter then the gas must have a finite drift velocity, \bar{u} , with respect to the liquid and it is assumed that $\bar{u} \ll \bar{c}$. If there are r degrees of freedom per gas molecule we get the following fluxes from simple kinetic theory,

$$\text{molecules area}^{-1} \text{ s}^{-1} = \frac{1}{4}n\bar{c} + \frac{1}{2}n\bar{u} \tag{23}$$

$$\text{energy flux} = \frac{1}{4}n\bar{c}(r + 1)(\frac{1}{2}kT) + \frac{1}{2}n\bar{u}(r + 2)(\frac{1}{2}kT) \tag{24}$$

$$\text{momentum flux} = n(\frac{1}{2}kT) + \frac{1}{2}n\bar{u}m\bar{c} \tag{25}$$

The evaporation coefficient, α , is assumed to be equal to the condensation coefficient, i.e. α is the probability that a gas particle will penetrate the surface on impact from either direction; $0 < \alpha < 1$. In the Drifting Knudsen Gas theory, see Figure 1, Eq. 23 rather than 16 is used for J_g in Eq. 14 with the result that,

$$J_N = n\bar{u} = \left(\frac{2\alpha}{2 - \alpha}\right) \frac{1}{\sqrt{2\pi mk}} \Delta\left(\frac{P}{\sqrt{T}}\right) \tag{26}$$

$$J_U = \left(\frac{2\alpha}{2 - \alpha}\right) \left(\frac{r + 1}{2}\right) \frac{kT}{\sqrt{2\pi mk}} \Delta\left(\frac{P}{\sqrt{T}}\right) \tag{27}$$

The transport coefficients resulting are given in Table II under the heading Drifting Knudsen Gas. An alternative treatment given by Cipolla, Lang and Loyalka¹⁰ is free of the ambiguity in the choice of moments inherent in the Maxwell Moment Method—the resulting transport coefficients are given under the heading Theory of Cipolla *et al.* (Table II). Cipolla *et al.* consider only the case with $r = 3$; if $\alpha = 1$ their result is $L_{MU} = 3.792 \times (kT/2\pi m)^{1/2} \rho T$ whereas the Drifting Knudsen Gas Model gives $3.72 \times (kT/2\pi m)^{1/2} \rho T$, if the above-mentioned four moments are used, and $3.59(kT/2\pi mT)^{1/2} \rho T$ for six moments.

In another method of calculation, that of Hunter and Osborne^{6,11}, it is supposed that there exists an intermediate region close to the liquid surface where the gas is in an unknown, intermediate state related to the states in the gas and liquid regions (Figure 2) by conservative equations. This intermediate region is of the order of a mean free path in thickness.¹² Using such a model Marble obtained the result $L_{MU} = 3.64(kT/2\pi m)^{1/2} \rho T$ for $r = 3$, $\alpha = 1$.¹³ Wiechert has discussed the Hunter–Osborne model in some detail¹ and it is only necessary to add that if consideration of the number of degrees of freedom is required his equation A17 for energy conservation becomes,

$$\left(\frac{2n_2\bar{u}}{\alpha}\right) \left(\frac{r + 2}{r + 1}\right) T_3 \sqrt{\frac{\pi m}{2k}} = n_1 T_1^{3/2} - n_2 T_2^{3/2} \tag{28}$$

TABLE II

Transport coefficients with the inclusion of the evaporation coefficient, α , the number of translational plus rotational degrees of freedom, r , and the correction factor, B , obtained by the Maxwell Moment Method. Values of r are—3 (monatomic gas), 5 (diatomic gas) and 6 (polyatomic gas); the value of B is about 0.9⁸ (see text).

	Simple Knudsen gas ¹	Drifting Knudsen gas ¹	Theory of Cipolla <i>et al.</i> ⁹	Hunter-Osborne theory ^{1,11}
L_{MM}	$\alpha B \sqrt{\frac{m}{2\pi kT}} \rho T$	$B \left(\frac{2\alpha}{2-\alpha} \right) \sqrt{\frac{m}{2\pi kT}} \rho T$	$\left(\frac{2.1968\alpha}{2.1968-\alpha} \right) \sqrt{\frac{m}{2\pi kT}} \rho T$	$4 \left(\frac{\alpha}{2-\alpha} \right) \left(\frac{r+1}{2r+3} \right) \sqrt{\frac{m}{2\pi kT}} \rho T$
L_{MV}	$\alpha B \frac{(r+1)}{2} \sqrt{\frac{kT}{2\pi m}} \rho T$	$B \left(\frac{2\alpha}{2-\alpha} \right) \left(\frac{r+1}{2} \right) \sqrt{\frac{kT}{2\pi m}} \rho T$	$\left(\frac{4.5380\alpha}{2.1968-\alpha} \right) \sqrt{\frac{kT}{2\pi m}} \rho T$	$4 \left(\frac{\alpha}{2-\alpha} \right) \left(\frac{r+1}{2r+3} \right) \left(\frac{r+2}{2} \right) \sqrt{\frac{kT}{2\pi m}} \rho T$

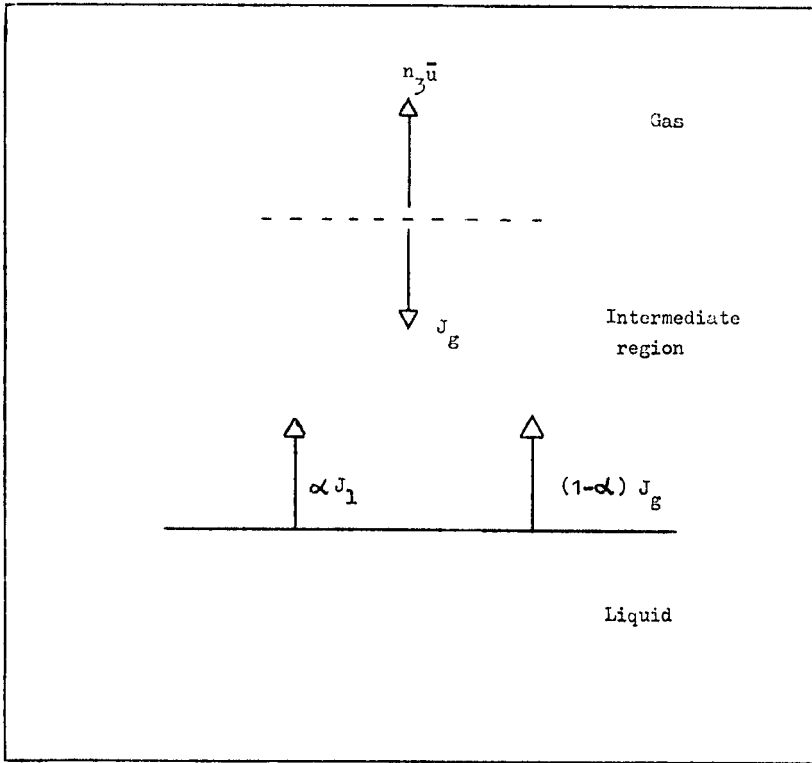


FIGURE 2 The Hunter-Osborne model.

The corresponding equations for momentum and number of particles are,

$$\frac{n_3 \bar{u}}{\alpha} \sqrt{\frac{2\pi m}{k}} = n_1 T_1^{1/2} - n_2 T_2^{1/2} \tag{29}$$

$$\alpha n_1 T_1 + (2 - \alpha) n_2 T_2 = 2 n_3 T_3 \tag{30}$$

and the elimination of the unknown parameters for the intermediate region, i.e. n_2 and T_2 between Eqs. 28, 29 and 30 gives the transport coefficients tabled in 2 under the heading Hunter-Osborne Theory.

Much experimental effort has been put into the determination of evaporation coefficients but the values often differ widely—from 0.04 to unity for water.¹⁴⁻¹⁷ One reason for the discrepancies is surface contamination for small quantities of impurities can either lower^{18,19} or raise²⁰ the value of α and, depending upon the conditions, contamination can arrive at the surface from solution in a matter of milliseconds or travel across the surface of a

pure liquid at velocities of the order of 1 cm s^{-1} . Another experimental uncertainty has been the temperature of the surface (strictly it is as meaningless to write of the temperature of a surface as it is of the temperature of a point²¹ but in practice some surface property such as the tension can be measured to ascertain surface temperature); Hickman¹⁵ emphasises that the rate of evaporation can be limited by the thermal conductivity of the liquid if there is a diminished surface temperature. Contamination can also effect the temperature by bringing about changes in the surface tension or the viscosity.¹⁹ Of value for the continuous provision of a clean, fresh surface is the liquid jet and evaporation coefficients measured with its aid have been reported for organic liquids and water²² but the thermodynamics and hydrodynamics of jets are complicated and corrections²³ to these results give $\alpha = 0.8$ (CCl_4), 0.7 (isopropanol) and values between 1 and 1.5 for water and toluene; another method, based upon Eq. 26, gave $\alpha = 0.94$ (CCl_4) and ≥ 0.7 (water)²⁴ and it might be desirable to add a further correction to the jet results for the effects of surface acceleration as the liquid leaves the orifice.^{25,26} A method capable of high precision is the measurement of the reflectivity of a molecular beam from the surface²⁷—this gave $\alpha = 0.99$ for the condensation of water on ice; the same method gave between 0.65 and 1 for Hg.²⁸ In Paul's compilation of evaporation coefficients many metals, including Hg, take the value of unity but Singhal finds between 0 and 0.74 for Hg by weighing the liquid evaporated in a given time period.²⁹ Since the more obvious experimental difficulties produce low results and the more elaborate experimental methods give values approaching unity it is hard to avoid the conclusion that for most pure liquids an evaporation coefficient of unity is to be expected. Mass spectrometric measurements on a continuously wiped surface *in vacuo*³⁰ gave evaporation coefficients close to unity for dithylene glycol, glycerine, dibutyl phthalate and oleic acid and a similar result for dioctyl phthalate was obtained by studying the kinetics of evaporation of submicron droplets of the liquid in He and N_2 gas.³¹ A measurement of the evaporation coefficient of liquid He puts the value at not less than 0.9 and probably unity.⁶ In a recent compilation Pound³² concludes that most simple liquids have $\alpha = 1$ with the exception of ethanol. It will be impossible to make a judgment between the various theories described in the beginning of this section until reliable evaporation coefficients are available.

If there is a second gas present in any significant amount it is important to provide for the possibility of diffusional control of evaporation—an example is a droplet of water suspended in the atmosphere. Maxwell's equation for the rate of loss of mass of a drop of radius r is,³³

$$\frac{dW}{dt} = -4\pi r D(c_1 - c_g) \quad (31)$$

where D is the diffusion constant, c_1 is the concentration of the evaporating liquid at the surface of the drop and c_g is the concentration in the gas phase. If $P = nkT$, $\Delta P = P_1 - P_g$ and $\Delta T = T_1 - T_g = 0$ the above equation is approximated by,

$$\frac{dW}{dt} = - \frac{4\pi r D m \Delta P}{kT} \tag{32}$$

or

$$J_M = - \frac{Dm}{kTr} \Delta P \tag{33}$$

As a droplet evaporates J_M rises until, when r is sufficiently small, molecular velocity rather than diffusion becomes rate determining and this happens when the ratio of the mean free path in the gas to the droplet radius (the Knudsen number) is large. In the model of Fuchs¹² there is characteristic distance, Δ , of about the length of a mean free path; within the shell between radius $r + \Delta$ and the surface of the droplet mass transport is assumed to be controlled by molecular velocity, as discussed earlier in this section, beyond the shell it is controlled by diffusion. At the surface of the sphere of radius $r + \Delta$, the partial pressure, P' , is obtained by equating the flux coming from the droplet with that leaving by diffusion,

$$16\pi r^2 \left(\frac{\alpha}{2 - \alpha} \right) \left(\frac{r + 1}{2r + 3} \right) \sqrt{\frac{m}{2\pi kT}} (P_1 - P') = \frac{4\pi(r + \Delta) D m P'}{kT} \tag{34}$$

In Eq. 34 the Hunter–Osborne model has been assumed and P_g , the partial pressure of the liquid beyond the sphere is neglected. The unknown pressure, $P' = P_1 r^2 v / \{r^2 v + (r + \Delta) D\}$ is put into Eq. 32 to give,

$$\frac{dW}{dt} = - \frac{4\pi r D c_1}{\left(\frac{r}{r + \Delta} + \frac{D}{rv} \right)} \tag{35}$$

where

$$v = 4 \left(\frac{\alpha}{2 - \alpha} \right) \left(\frac{r + 1}{2r + 3} \right) \sqrt{\frac{kT}{2\pi m}}$$

Equation 35 reduces to diffusion control at low Knudsen number i.e., when $r/(r + \Delta) \rightarrow$ unity ($D/rv \ll$ unity for droplet radius < 1 mm). At high Knudsen numbers, i.e., when $r/(r + \Delta) \rightarrow 0$, Eq. 35 reduces to molecular velocity control and it has been shown to be valid over the intermediate range by experiments with dibutyl phthalate and butyl stearate,³⁴ water,³⁵ lead

and bismuth³⁶ and dioctyl phthalate.³¹ Various attempts have been made to specify Δ ^{34,37,38} but without great success, partly because the value of v depends upon the particular model chosen for the calculation of the evaporation rate and partly because, as Fuchs himself realised, the magnitude of Δ depends on the radius of the drop.

It is noteworthy that ions do not evaporate from a liquid surface unless a large electric field is applied, of about 10^9 V m^{-1} ; even so only univalent ions are to be found in the gas phase above an aqueous solution. This low volatility has been attributed to the solvation energy of the ions³⁹ and the repulsive effect of the image charge existing on the gas side of the surface.⁴⁰

III TRANSPORT ALONG A SURFACE

For a surface, Eq. 5 can be written,

$$T \, dS = dU + \sigma \, dA - \mu \, dM \quad (36)$$

where σ is the surface tension and A is the area; instead of the force of Eq. 7 we now have,

$$x_A = \Delta \left(\frac{\sigma}{T} \right) \quad (37)$$

Crisp⁴¹ distinguished two kinds of transport along a liquid surface: surface diffusion and surface flow. Surface diffusion is the mass flow term resulting from x_M , Eq. 8; it is generally supposed to follow Fick's law but the surface diffusion coefficient is found to depend upon the surface concentration, e.g., in monolayers of myristic, pentadecylenic and oleic acids.^{42,43} By surface flow Crisp meant the term due to x_A , Eq. 37, i.e., flow due to the gradient of surface tension along the surface, $d\sigma/dx$. It is easy to arrange conditions for an experiment in which the surface flow is dominant^{44,45}—say by allowing oleic acid to spread out over a clean water surface—and the velocity of the advancing layer will then be limited only by the viscosity of the underlying liquid with the result that,

$$\frac{d\sigma}{dx} + \mu \frac{dv}{dy} = 0 \quad (38)$$

If the depth, h , of the lower liquid is not too great,

$$v_s = h \frac{dv}{dy} \quad (39)$$

In the above equations μ is the viscosity of the lower layer, v_s is the velocity of the moving layer at the surface and v is the velocity of the layer at height y , $v = dx/dt$. Putting Eq. 38 and 39 together,

$$v_s = - \frac{h}{\mu} \frac{d\sigma}{dx} \quad (40)$$

A further distinction can be made between two separate kinds of experiment: that in which there is a source of surface contaminant which spreads as a layer across a clean surface—the value of $\Delta\sigma$ at the front being the surface pressure—and that in which the surface is covered with a layer at the outset and the area of the surface is varied so that the force-area curve can be obtained. In experiments of the latter type Gibbs' surface elasticity, E , is defined by $x d\sigma/dx$, where x is the length of the surface along which it is extended in a rectangular trough; hence equation 40 can be written,

$$v_s = - \frac{h}{\mu x} E \quad (41)$$

In the other type of experiment we can write,

$$v_s = - \frac{h}{\mu x} \Delta\sigma \quad (42)$$

where x is the distance between the advancing front and the commencement of the layer on the surface. Equation 42 has been verified⁴⁵ for oleic acid on aqueous glycerol and it holds good if $h < 0.2$ cm. If ρ_s is the mass per unit area of the advancing layer the mass flux is,

$$J_M = \rho_s v_s = \frac{-h\rho_s}{\mu x} \Delta\sigma \quad (43)$$

and the transport coefficient is given by $L_{MA} = -h\rho_s T/\mu x$ at constant temperature.

It has been shown⁴⁴ that a layer of water of considerable thickness is carried along beneath a spreading monolayer of oleic acid; experiments with sucrose solutions of varying viscosity revealed that the thickness of the layer increased linearly with viscosity, from 0.027 mm for pure water to 0.096 mm when the viscosity was increased by a factor of 3.92. A number of authors^{46,47} have considered the significance of this in regard to the stability of foams.

IV GAS ABSORPTION BY LIQUIDS

The kinetics of gas absorption by a liquid involves the rate of transport in the gas and the liquid phases and any sufficiently slow process at the surface, the last being called an interfacial resistance.

Within the liquid, well away from the surface, Fick's law is usually valid i.e., $J_M = -D \text{grad } c$; near the surface Fick's law does not generally hold and many substances migrate against the concentration gradient there to produce a surface excess concentration, Γ . At equilibrium Γ might be either positive or negative depending on the rate of change with μ of the surface tension, Gibbs' adsorption isotherm giving, $\Gamma = -d\sigma/d\mu$.

If the flux of gas molecules impinging on a surface is given by the molecular velocity distribution the half-life for the deposition of a complete monolayer is only 10^{-9} s or so at NTP. It is therefore commonly assumed that a fresh liquid surface, of a jet say, is immediately saturated with the gas upon exposure at NTP, the remaining rate controlling stages being diffusion in the liquid bulk and any interfacial resistance there happens to be.

From Fick's law in the form $dc/dt = -D d^2c/dy^2$ and with the surface condition $c = c_s$, c_s being the saturation concentration, the concentration at depth y and time t is given by,

$$c(y) = c_s - c_s \operatorname{erf}\left(\frac{y}{\sqrt{4Dt}}\right) \quad (44)$$

Since $\operatorname{erf}(0.477) = \frac{1}{2}$ we can define a half-life, $t_{1/2}$, at depth y by means of the above equation,

$$\frac{y^2}{4Dt_{1/2}} = 0.477^2 \quad (45)$$

A method used extensively for the measurement of absorption rates of gases in liquids is to flow a jet of the liquid through a chamber containing the gas and to measure the increase in the concentration of the gas in the liquid; since the timescale is about 10 ms the assumption of immediate saturation of the surface by the gas would appear to be reasonable although it has been the subject of some doubt.⁴⁸ For a typical value of D , say $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, there will be half saturation at a depth of about $3 \mu\text{m}$ within 10 ms and the surface can therefore be regarded as planar; from Eq. 44 it follows that the mass absorbed per unit area of surface in unit time is,

$$2(c_s - c_0) \sqrt{\frac{Dt}{\pi}} \quad (46)$$

where c_0 is the concentration of the gas in the liquid before it enters the chamber. The differential equation for diffusion in a jet moving with velocity u in the z direction under conditions of plug flow is,

$$u \frac{dc}{dz} = D \frac{d^2c}{dy^2} \quad (47)$$

and the solution generally used for the jet absorption experiment is,^{49,50}

$$\phi = 4(c_s - c_0)\sqrt{DGl} \quad (48)$$

where ϕ is the absorption rate along a length, l , of the jet and G is the volumetric flow rate.

If the flow in the jet is parabolic we have,

$$u \left\{ 1 - \left(\frac{r}{r_0} \right)^2 \right\} \frac{dc}{dz} = D \frac{d^2c}{dy^2} \quad (49)$$

where r_0 is the radius of the jet and u is the velocity at a distance r from the axis. An approximate solution to Eq. 49, valid near the surface, can be obtained with the substitution,⁵¹

$$\xi = \left(\frac{ur_0^2}{4lD} \right)^{1/3} \left\{ 1 - \left(\frac{r}{r_0} \right)^2 \right\}$$

$$\zeta = \frac{z}{l}$$

Equation 49 then becomes, $\xi dc/d\zeta = d^2c/d\xi^2$. The solution depends upon the boundary conditions, e.g., if $c = 0$ at $\zeta = 0$ and $c = \text{constant}$ at $\zeta = \infty$,

$$c = A \int_0^\zeta \frac{\exp(-\xi^3/9\zeta)}{\zeta^{2/3}} d\zeta \quad (50)$$

where A is a constant.

Although the parabolic velocity distribution relaxes quickly when the jet leaves the orifice, usually within a few milliseconds, the error resulting from the use of Eq. 48 without correction has been assessed at between 15 and a few percent, depending on the experimental conditions.⁵² Diffusivities measured by the jet method with the aid of Eq. 48 for various gases in water are about 80% lower than those measured by the same authors⁵³ using the wetted sphere technique, in which the timescale is around 100 ms—other authors have reported similar findings^{54,55} and although the discrepancy has been attributed both to an unspecified interfacial resistance^{53,54} and to the failure of the surface layer of gas to attain equilibrium at the commencement of the jet's passage across the jet chamber⁴⁸ it appears likely that the failure to correct for the velocity profile is the reason.⁵² There is no acceptable evidence for the existence of interfacial resistance to the absorption of gases through a liquid surface unless it is contaminated. Caskey and Barlage⁴⁹ have developed apparatus in which the jet comes out of a small hole in a plastic film of thickness 0.002 inches so that no velocity profile is formed; they find an interfacial resistance to the absorption of CO_2 by

aqueous solutions of surfactants, the resistance increasing with the length of the hydrocarbon chain.

V TRANSPORT FROM THE BULK LIQUID TO THE SURFACE

It is still true to say that "The study of the kinetics of adsorption and of dynamic surface tension is one of the most complex problems of physical chemistry and one, at the present time, in only the early stages of development."⁵⁵ Historically, the study of the kinetics of the surface adsorption of a solute is almost equivalent to the study of the dynamic surface tension of aqueous solutions; essentially the experiment consists in forming a fresh surface of a solution, either by sweeping a static surface or by a flow method, and then measuring the change with time of the surface tension or some associated property. Much of the work has been done by Rayleigh's vibrating jet method⁵⁶ for which N. Bohr's equation can be written,^{25,57,58}

$$\sigma = \frac{4\rho G^2 \left(1 + \frac{37b^2}{24a^2}\right)}{6r_0 \lambda^2 + 10\pi^2 r_0^3} \quad (51)$$

where ρ is the density of the solution and λ is the wavelength of the vibration of the jet resulting from the use of an elliptically shaped aperture (see Figure 3).

$$b = \frac{1}{2}(r_{\max} - r_{\min})$$

$$r_0 \simeq a = \frac{1}{2}(r_{\max} + r_{\min})$$

According to Defay and Hommelen⁵⁸ Eq. 51 is accurate to 0.2% if the viscosity is less than 0.1 poise but nevertheless they found it gave results for

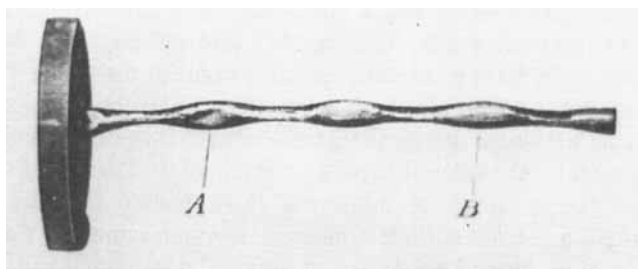


FIGURE 3 The Rayleigh jet method—Rayleigh's original photograph of 1890⁶¹ showing the oscillations set up by the elliptical orifice. There are two wavelengths between points A and B.

water and CCl_4 that were too high. Hansen has given another form.²⁶ Quite soon after Bohr published his equation he discounted P. Lennard's suggestion that pure water possesses a dynamic surface tension i.e., a very high tension existing shortly after the formation of the surface²⁵—even in 1963 this ghost still walked⁵⁹ but recent jet experiments have finally laid it to rest.⁶⁰ However, the phenomenon does exist in the case of solutions, especially surfactant solutions, as Rayleigh proved by showing that the tension of a solution of soap immediately after the formation of the surface was the same as that of pure water;⁶¹ in such a case σ falls over a time span of 10^{-3} to 10^{-1} s—or somewhat longer depending on the conditions—as the result of the formation of a surface layer of excess concentration. There have been various opinions as to whether the process is controlled by diffusion,⁶² by convection,⁶³ by complexation on the surface⁶⁴ or by a combination of processes.^{65,66} Slow changes in surface tension, extending over periods of hours or weeks, have also been reported but such experiments are susceptible to the spurious effect of traces of impurities,⁶⁷ often extremely difficult to remove.

The best model for the calculation of the kinetics of diffusion to the surface is probably that of Ward and Tordai⁶⁸ although they could not verify it for themselves using the data of C. C. Addison. In this model a subsurface layer is considered to exist beneath the surface layer proper; the two layers being always in equilibrium so that immediately upon the formation of the surface the subsurface is stripped of its solute. When sufficient molecules have arrived at the surface by diffusion from the bulk liquid the concentration in the subsurface begins to rise again and back diffusion starts. The mass per unit area transferred to the surface is given by Fick's law and the condition that the subsurface concentration is always zero, the result is $N = 2c\sqrt{Dt/\pi}$, but it is necessary to allow for the eventual rise in the subsurface concentration, $c(t)$, by subtracting for the amount of back diffusion from the subsurface into the bulk liquid—this amounts to $2c(t) \int_0^t \sqrt{Dt/\pi}$. Hence the Ward-Tordai equation for the total,

$$N = 2\sqrt{D/\pi} \left(c\sqrt{t} - \int_0^t c(t) d\sqrt{t} \right) \quad (52)$$

It is necessary to evaluate $c(t)$ experimentally; for this purpose Ward and Tordai used a plot of the bulk concentration, c , against the equilibrium value of the tension, σ . They assumed that dynamic tension measurements, $\sigma(t)$, taken at various short times after the creation of the surface corresponded to values of $c(t)$ equal to those of c when $\sigma = \sigma(t)$ —deriving the latter from their plot. Much of the work done in order to verify the Ward-Tordai equation has been done by the Rayleigh jet method but there are a

number of assumptions in Bohr's equation: namely that—(1) there is no superficial viscosity, implying a clean surface, (2) there is no surface tension gradient along the surface, implying the absence of surface active solutes, (3) the jet radius is constant (4) the velocity components in the liquid are constant apart from small variations of the form $f(x, y)e^{ibz}$. Hansen²⁶ gave a method of correction for the existence of a parabolic velocity profile, then Defay and Pétré⁶⁹ pointed out the existence of the Marangoni effect caused by the presence of a surface tension gradient—in essence this is the surface flow discussed in Section III—attention was also drawn⁶⁹ to the failure in Hansen's treatment to allow for the stretching of the surface as the flow relaxes from parabolic to plug; finally they showed that Bohr's equation can be applied to the fourth or fifth wave onward without any correction at all. Further refinements were added by Hansen⁷⁰ but a vindication of the Ward-Tordai equation by the jet method is awaited yet—possibly the hydrodynamics of the jet is still more complex than has been supposed. However, success has recently been achieved by another method: that of flowing the liquid down an inclined surface and measuring the surface tension at different distances downstream by means of a Wilhemy plate.⁶²

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