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Integrating Eq. (78) for fixed values of $\mathfrak{A}$ and T,

$$A(\mathfrak{A}, N, T) = \int_0^N [\mu^0(T) + kT \log p] dN, \quad (80)$$

since $A(\mathfrak{A}, 0, T) = 0$. Therefore, using Eqs. (79) and (80), and keeping T constant in the following,

$$-\varphi = \int_0^N \frac{\partial}{\partial \mathfrak{A}} [\mu^0(T) + kT \log p] dN, \quad (81)$$

$$= kT \int_0^N \left(\frac{\partial \log p}{\partial \mathfrak{A}} \right)_N dN. \quad (82)$$

Now, since $p = p(\Gamma)$,

$$\left(\frac{\partial \log p}{\partial \mathfrak{A}} \right)_N = \left(\frac{\partial \Gamma}{\partial \mathfrak{A}} \right)_N \frac{d \log p}{d\Gamma} = -\frac{\Gamma}{\mathfrak{A}} \frac{d \log p}{d\Gamma}. \quad (83)$$

Equation (82) becomes

$$\varphi = kT \int_0^\Gamma \Gamma \frac{d \log p}{d\Gamma} d\Gamma \quad (84)$$

or

$$\varphi = kT \int_0^p \Gamma d \log p. \quad (85)$$

In differential form, Eq. (85) is

$$d\varphi = \Gamma kT d \log p. \quad (86)$$

Equations (85) and (86) are the familiar Gibbs equations as applied to this type of adsorption. The derivation given here proves helpful in relating the thermodynamic and statistical aspects of the problem. It will be noted from the derivation that Eqs. (85) and (86) are thermodynamically exact, except for the assumption that the gas phase behaves like a perfect gas. These equations are also general, applying to monomolecular, multimolecular, mobile, and localized adsorption on a solid or liquid. Of course φ is not of much physical interest except for the case of mobile monomolecular adsorption.

The usual procedure in obtaining the equation of state from the experimentally determined adsorption isotherm $\Gamma(p)$ is to evaluate $\varphi(p)$ from Eq. (85), and then, by combining $\Gamma(p)$ and $\varphi(p)$, find $\varphi(\Gamma)$ at the given temperature.

Time-Dependence of Boundary Tensions of Solutions

I. The Role of Diffusion in Time-Effects

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The variation of surface tension of solutions with time has in some cases, where the change is over within a few seconds or less, been explained on the basis of diffusion. This paper attempts a rigorous mathematical analysis of the role that diffusion might play in such time-effects. The limitations of diffusion theories which have been proposed previously are discussed. A general theory of diffusion to the surface is derived, which allows for back-diffusion and which makes no special assumptions of a physical nature. It is possible to use Fick's equation to calculate the total amount of solute which diffuses from a semi-infinite bulk solution into the surface if the concentration immediately under the surface is known at various times throughout the process. It is shown how the latter information may be deduced from the variation of surface tension with time together with final equilibrium values of surface tension. The methods of this theory are applied to analyze recent data on time-effects of short duration. It is concluded that even in cases where the variation of the surface tension is over in less than a second the rate-determining process is not diffusion. Even for these very rapid changes one is therefore led to assume the existence of an activation barrier which determines the rate of adsorption.

INTRODUCTION

MANY instances have been reported of the surface tension of solutions being a function of time. In some cases this has been ascribed to slow chemical changes in the bulk of the solution.[1] But many observed time-variations cannot be explained in this way. The change in surface tension may occur very slowly, over a period of several days.[2,3] On the other hand, variations of an apparently similar kind may be complete in a few hours or within an hour.[4-6] In some cases the time-effect may last only for a

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[2] N. K. Adam and H. L. Shute, Trans. Faraday Soc. **31**, 205 (1935).

[3] N. K. Adam and H. L. Shute, Trans. Faraday Soc. **34**, 758 (1938).

[4] K. S. G. Doss, Kolloid Zeits. **84**, 138 (1938).

[5] K. S. G. Doss, Kolloid Zeits. **86**, 205 (1939).

[6] H. V. Tartar, V. Sivertz, and R. E. Reitmeier, J. Am. Chem. Soc. **62**, 2375 (1940).

few seconds to a few minutes.[7] Finally, time-variations of surface tension have been observed which are complete within a fraction of a second.[8-11] Quite recently, the authors have shown that interfacial tensions may also be time-dependent.[12] The same theory may not explain all these effects; in fact many different explanations have been proposed. A review of these explanations is not contemplated here, but merely an examination of the role that diffusion to the surface may play.

The suggestion that diffusion of the solute to the surface was the cause of the alteration of surface tension with time was first made by Milner,[13] who did not, however, treat the theory quantitatively. Equations to describe the phenomenon in terms of diffusion have been deduced by Bond and Puls,[8] Doss,[5] Ross,[14] and Langmuir and Schaefer.[15] Their treatments involve various approximations and simplifying assumptions. Although no generally exact quantitative treatment of diffusion to the surface has been put forward, it seems clear that many of the observed cases of alteration of boundary tension with time are very much too slow to be explained by diffusion. In general terms, there is some kind of activation barrier, which hinders the establishment of the adsorbed film.[4,12] For those cases where the alteration of surface tension with time is very rapid, diffusion theories so far put forward are insufficiently exact to determine critically whether the variation with time can be entirely attributed to diffusion. The object of the present paper is to develop a general theory of diffusion to the surface which will allow a definite decision to be made in any case as to whether diffusion is a complete explanation of the time-variation or whether some additional effect must be sought.

[7] J. W. McBain and D. A. Wilson, J. Am. Chem. Soc. 58, 379 (1936).
[8] W. N. Bond and H. O. Puls, Phil. Mag. [7] 24, 864 (1937).
[9] C. C. Addison, J. Chem. Soc., p. 252 (1944).
[10] C. C. Addison, J. Chem. Soc., p. 477 (1944).
[11] C. C. Addison, J. Chem. Soc., p. 98 (1945).
[12] A. F. H. Ward and L. Tordai, Nature 154, 146 (1944).
[13] S. R. Milner, Phil. Mag. [6] 13, 96 (1907).
[14] S. Ross, J. Am. Chem. Soc. 67, 990 (1945).
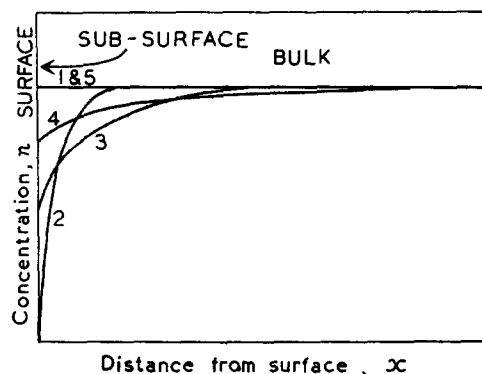[15] I. Langmuir, and V. J. Schaefer, J. Am. Chem. Soc. 59, 2400 (1937).

FIG. 1. Successive stages in concentration gradient from surface into the bulk solution during diffusion to the surface. (1) initial; (2), (3), and (4) intermediate; and (5) final stages.

NATURE OF DIFFUSION PROCESS

Before the diffusion theory is developed, it is convenient to give a physical description of the process. We may suppose that initially there is a solution of uniform concentration and at a certain instant a plane surface (solution/air) is created. At this moment the concentration of solute in the surface is the same as the bulk concentration. If the solute is a substance which is positively adsorbed, its molecules are in a position of lower potential energy in the surface than in the bulk. Although individual molecules move in all directions, the resultant flow of solute molecules is in a direction from the bulk to the surface. The region of the bulk solution, with a thickness of a few molecular diameters only, immediately next to the surface, is referred to here as the "sub-surface." At the initial stage in the formation of the adsorbed layer, solute molecules will diffuse from the bulk to the sub-surface more slowly than they pass from the sub-surface to the surface, on the assumption that equilibrium is established instantaneously between the latter two regions. This is so, because initially the surface is practically empty and every molecule arriving at the surface is likely to arrive at an empty "site" and become adsorbed. For all practical purposes the sub-surface concentration may be regarded as falling from its initial value to zero immediately.

Eventually, as the surface becomes fuller, there is an increased probability that a solute molecule in the sub-surface will arrive at a portion of

the surface already occupied by the adsorbed solute. Such a molecule will, of course, remain in the sub-surface, which will accumulate solute molecules more rapidly than these are passed on to the surface. As soon as the concentration in the sub-surface is sensibly different from zero we must consider the possibility of back-diffusion from the sub-surface to the bulk. The sub-surface concentration will continue to rise until eventually, at equilibrium, it will have a concentration equal to that in the bulk (on the assumption that the bulk region can be regarded as an infinite reservoir of solute molecules). Successive stages in the concentration gradient are shown in Fig. 1.

If the sub-surface concentration at each instant is known throughout this process, the diffusion of molecules from the bulk to the sub-surface might be treated by application of the ordinary diffusion equations. But in fact the sub-surface concentrations cannot be obtained directly. The experimental measurements are the values of the surface tension at various times. Assumptions have to be made relating the surface tension to the sub-surface concentration. It is partly on account of the approximate nature of these assumptions that previous treatments of this problem have been inadequate.

Doss[4, 5] avoided this difficulty in his study of the slow adsorption of benzopurpurin at an air/water surface by measuring directly the surface concentration at various times by compressing the surface film and measuring the area under a definite pressure. However, his theoretical treatment was inaccurate. He neglected back-diffusion from the surface to the bulk. His calculations were based on the Einstein diffusion equation for the mean displacement of a particle, but in the application of this he assumed that the molecules reaching the surface all started from a region where the concentration equalled the bulk concentration. This would only be true at the very beginning and at the end of the diffusion process, and the assumption is equivalent to neglecting the concentration gradient near the sub-surface. This same fundamental inaccuracy is also to be found in the treatment by Ross,[14] who follows Doss's method very closely. Ross compensates for certain deficiencies in the diffusion theory by supposing that the adsorption layer is multi-

molecular. The hypothesis of thick layers on the surface of solutions containing such simple solutes is, however, not acceptable. It has been shown recently[16] that the assumption of monolayers of the solute on the surface of these solutions satisfies the thermodynamical requirement that the activities of the solute in the bulk and surface phases, respectively, shall be proportional to each other. It would therefore appear unjustifiable to postulate the existence of multimolecular layers to explain this new effect.

A diffusion theory was proposed by Bond and Puls[8] based on Fick's diffusion equation. Since this is a statistical equation based on the behavior of all the molecules, it should allow a general solution to be derived, and if appropriate boundary conditions are employed, it should cover both forward- and back-diffusion. However, Bond and Puls made the limiting assumptions that the adsorption layer could be supposed to be almost unoccupied and that the lowering of surface tension was proportional to the concentration. This restricts their treatment to the initial stages only of the diffusion process. In addition, their final integrated equation

$$(\bar{q}-q)/\bar{q}=\exp\left[-(2/\pi^{\frac{1}{2}})(t/\tau)^{\frac{1}{2}}\right],$$

(their Eq. (9)), which has been quoted and used by other workers, is in fact incorrect, presumably because of an erroneous integration procedure.

SIMPLE DIFFUSION THEORY

A simple theory may be developed first for the early stages in the diffusion when the backward movement of solute from the sub-surface to the bulk may be neglected. The surface is then sufficiently empty to take up solute molecules as fast as they arrive and the sub-surface concentration is practically zero. The problem is analogous to that of the diffusion of heat from an infinite conductor, initially at uniform temperature, into a conductor of infinite conductivity placed in contact.

Let $n =$ concentration in the solution at a distance x from the surface at a time t. From the equations for heat flow in the analogous case[17]

[16] A. F. H. Ward and L. Tordai, Trans. Faraday Soc. (in press).
[17] H. S. Carslaw, *Mathematical Theory of Heat Conduction* (MacMillan and Company, London, 1921), p. 34.

we obtain the equation

$$\frac{\partial n}{\partial x} = \frac{n_0}{(\pi Dt)^{\frac{1}{2}}} \exp\left(-\frac{x^2}{4Dt}\right), \qquad (1)$$

where n_0 is the constant bulk concentration and D is the diffusion coefficient defined by Fick's equation

$$\partial n/\partial t = D\partial^2 n/\partial x^2. \qquad (2)$$

At the extreme edge of the bulk solution, i.e., the sub-surface, where $x = 0$, Eq. (1) is simplified to

$$(\partial n/\partial x)_{x=0} = n_0/(\pi Dt)^{\frac{1}{2}}, \qquad (3)$$

and the rate of diffusion across 1 cm^2 of the plane, $x = 0$, is given by

$$(\partial M/\partial t)_{x=0} = -Dn_0/(\pi Dt)^{\frac{1}{2}}. \qquad (4)$$

Hence, the amount of solute which has diffused across this plane into the surface up to the time, t, i.e., the surface concentration at that time, M, is given by

$$M = \int_0^t \left(\frac{\partial M}{\partial t}\right)_{x=0} \cdot dt = 2n_0\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}. \qquad (5)$$

This equation is identical with one used by Langmuir and Schaefer[15] to explain diffusion of ions into monolayers.

GENERAL DIFFUSION THEORY

It is also possible to develop a more general theory which will make allowances for back-diffusion. Such a theory may be derived from Eq. (2) and the treatment is applied to a single phase extending from the bulk (assumed infinite in extent) to the sub-surface, but not including the surface. No assumptions regarding the relation between surface and sub-surface concentrations are introduced at this stage and the solution is therefore quite general.

Consider linear diffusion of solute molecules towards the boundary plane $x = 0$ of a semi-infinite liquid solution. The bulk concentration remains effectively constant (n_0) during the process. The concentration in the sub-surface varies with time and may be expressed as $\phi(t)$. To obtain a solution of the problem it is possible to utilize a mathematically analogous theorem in heat conduction, based on Eq. (2) and the

use of Green's functions[17] (p. 173). The temperature v at a distance x from the surface of the semi-infinite solid of thermal conductivity κ, initially at temperature v_0 with its surface at temperature $\phi(t)$ at time t is given by

$$v = \frac{v_0}{2(\pi\kappa t)^{\frac{1}{2}}} \int_0^\infty \left\{ \exp\left[-\frac{(x-x')^2}{4\kappa t}\right] \right.$$
$$\left. - \exp\left[-\frac{(x+x')^2}{4\kappa t}\right] \right\} dx$$
$$+ \frac{x}{2(\pi\kappa)^{\frac{1}{2}}} \int_0^t \phi(\tau) \frac{\exp\left[-\dfrac{x^2}{4\kappa(t-\tau)}\right]}{(t-\tau)^{\frac{3}{2}}} d\tau, \quad (6)$$

where $\tau (\tau < t)$ is the time at which an instantaneous point source of unit strength, at a distance x' from the surface, generates heat. It is important to note that Eq. (6) is made up of two terms. The first term corresponds to a flow of heat from the bulk region (which is initially at temp. v_0) towards the surface (initially at zero temp.). The second term represents a flow of heat in the opposite direction, from the surface at temp. $\phi(t)$ towards the bulk (initially at zero temp.). In the diffusion nomenclature, we are interested in obtaining

$$(\partial n/\partial x)_{x \to 0},$$

where n, the concentration, replaces v; n_0 and D replace v_0 and κ. D is the diffusion coefficient. To simplify the problem we employ two sets of transformations. In the first term we may write

$$x' = x + 2(Dt)^{\frac{1}{2}}\xi \quad \text{and} \quad x' = -x + 2(Dt)^{\frac{1}{2}}\xi,$$

for the first and second integrals, respectively. In the second term

$$\mu = x/2(D(t-\tau))^{\frac{1}{2}}, \quad \text{that is,} \quad t - \tau = x^2/4D\mu^2.$$

With such a change of variables Eq. (6) reduces to

$$n = \frac{2n_0}{\pi^{\frac{1}{2}}} \int_0^{x/2(Dt)^{\frac{1}{2}}} \exp(-\xi^2) d\xi$$
$$+ \frac{2}{\pi^{\frac{1}{2}}} \int_{x/2(Dt)^{\frac{1}{2}}}^\infty \phi\left(t - \frac{x^2}{4D\mu^2}\right) \exp(-\mu^2) d\mu. \quad (7)$$

It will be convenient to treat the two terms in Eq. (7) separately. It will be assumed that the first term contributes $\partial n_1/\partial x$ and the second $\partial n_2/\partial x$ to give the total $\partial n/\partial x$. Differentiation of the first term with respect to x gives

$$\frac{\partial n_1}{\partial x} = \frac{n_0}{(\pi Dt)^{\frac{1}{2}}} \exp\left(-\frac{x^2}{4Dt}\right). \qquad (8)$$

If x tends to zero in Eq. (8), we obtain Eq. (3) and for the amount of solute, M_1, contributed by this direction of flow, an expression is obtained which is identical with Eq. (5).

Turning our attention to the second term in Eq. (7) and writing $a = x/2(Dt)^{\frac{1}{2}}$, we obtain

$$n_2 \frac{\pi^{\frac{1}{2}}}{2} = \int_a^{\infty} \phi\left(t - \frac{a^2}{\mu^2}t\right) \exp(-\mu^2) d\mu. \qquad (9)$$

The integrand in Eq. (9) may be expanded by Maclaurin's theorem to give

$$n_2 \frac{\pi^{\frac{1}{2}}}{2} = \sum_0^{\infty} \frac{(-1)^r}{r!} a^{2r} t^r \phi(t) \int_0^{\infty} \exp(-\mu^2)\mu^{-2r} d\mu,$$

and by repeated integration by parts we obtain the series

$$n_2 \frac{\pi^{\frac{1}{2}}}{2} = \phi(t) \int_a^{\infty} \exp(-\mu^2) d\mu$$

$$+ \sum_1^{\infty} a \frac{(-1)^r}{r!} t^r \phi^{(r)}(t)$$

$$\times \left[\frac{1}{(2r-1)} - \frac{2a^2}{(2r-1)(2r-3)}\right.$$

$$\left. + \frac{2^2 a^4}{(2r-1)(2r-3)(2r-5)} - \cdots\right]. \qquad (10)$$

Differentiating with respect to a, we have

$$\frac{\pi^{\frac{1}{2}}}{2} \frac{\partial n_2}{\partial a} = -\exp(-a^2)\phi(t)$$

$$+ \sum_1^{\infty} \frac{(-1)^r}{r!(2r-1)} t^r \phi^{(r)}(t) + O(a^2), \qquad (11)$$

and letting $a \to 0$ as $x \to 0$ the final result is

$$\left(\frac{\partial n_2}{\partial x}\right)_{x=0} = -\frac{1}{(\pi Dt)^{\frac{1}{2}}} \sum_0^{\infty} \frac{(-1)^r t^r}{(2r-1)r!} \phi^{(r)}(t), \qquad (12)$$

the first few terms of this series being

$$-\frac{1}{(\pi Dt)^{\frac{1}{2}}}\left\{\phi(t) + t\phi'(t)\right.$$

$$\left. -\frac{1}{6} t^2 \phi''(t) + \frac{1}{30} t^3 \phi'''(t) - \cdots\right\}.$$

It is more convenient to express the series (12) as an integral. It is easily shown that

$$\left(\frac{\partial n_2}{\partial x}\right)_{x=0} = -\frac{1}{2(\pi D)^{\frac{1}{2}}} \int_0^t \frac{\phi(z)}{(t-z)^{\frac{1}{2}}} dz, \qquad (13)$$

where z is a variable; for putting $(t-z) = \theta^2$ we obtain an integral which can be expanded by Maclaurin's theorem to give Eq. (12).

The amount of solute, M_2, which flows from the surface in the direction of the bulk, must next be determined. Starting from Fick's equation

$$(\partial M_2/\partial t)_{x=0} = -D(\partial n_2/\partial x)_{x=0},$$

we are led to consider the integral

$$M_2 = \frac{1}{2}\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int_0^t \int_0^t \frac{\phi(z)}{(t-z)^{\frac{1}{2}}} dz dt. \qquad (14)$$

It can be shown that Eq. (14) reduces to

$$M_2 = -\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int_0^t \frac{\phi(z)}{(t-z)^{\frac{1}{2}}} dz. \qquad (15)$$

To prove the equivalence of Eqs. (14) and (15) use will be made of Cauchy's theorem on n-times repeated integrals. This theorem, together with a process involving differentiation and integration to fractional orders enables us to complete the proof.

If we put

$$F(t) = \frac{1}{\Gamma(n)} \int_0^t (t-z)^{n-1} \phi(z) dz, \qquad (16)$$

then

$$\frac{1}{\Gamma(n)} \int_0^t (t-z)^{n-1} \phi(z) dz$$

$$= \int_0^t \frac{(t-z)^{n-1}}{(n-1)!} \phi(z) dz, \qquad (17)$$

and Cauchy's theorem states

$$\int_0^t \frac{(t-z)^{n-1}}{(n-1)!} \phi(z) dz = D^{-n}\phi(t). \qquad (18)$$

The operator, $\mathbf{D}^{-1}$, stands for $\int_0^t \cdots dz$, whereas $\mathbf{D}^1$ has its usual meaning d/dz. For our particular case we have

$$F(t) = \int_0^t \frac{\phi(z)}{(t-z)^{\frac{1}{2}}} dz.$$

From Eqs. (16)–(18) we obtain

$$F(t) = \Gamma(\tfrac{1}{2}) \mathbf{D}^{-\frac{1}{2}} \phi(t). \tag{19}$$

We are interested in finding the derivative, $F'(t)$, and to show that it gives an integral, such as occurs in Eq. (13). We can write

$$F'(t) = \frac{d}{dt} \int_0^t \frac{\phi(z)}{(t-z)^{\frac{1}{2}}} dz$$

$$= \Gamma(\tfrac{1}{2}) \mathbf{D} \mathbf{D}^{-\frac{1}{2}} \phi(t) = \Gamma(\tfrac{1}{2}) \mathbf{D}^{\frac{1}{2}} \phi(t). \tag{20}$$

From Eqs. (17), (18), and (20) we have

$$F'(t) = \Gamma(\tfrac{1}{2}) \frac{1}{\Gamma(-\tfrac{1}{2})} \int_0^t (t-z)^{-\frac{1}{2}-1} \phi(z) dz$$

$$= -\tfrac{1}{2} \int_0^t \frac{\phi(z)}{(t-z)^{\frac{3}{2}}} dz, \tag{21}$$

which is the result required to prove the equivalence of Eqs. (14) and (15).

For the two opposing processes we now have

$$M = 2 \left(\frac{D}{\pi}\right)^{\frac{1}{2}} \left\{ n_0 t^{\frac{1}{2}} - \int_0^{t^{\frac{1}{2}}} \phi(z) d[(t-z)^{\frac{1}{2}}] \right\}, \tag{22}$$

where the expression for M_2 is written in a slightly different form which has advantages from the point of view of numerical computation.

It is possible to derive the expression for M_2 in a very much simpler but less rigorous way. Consider a semi-infinite liquid solution with zero initial concentration, the surface concentration being kept constant at a value c. After the lapse of time t, the amount which has diffused inward from the surface (taken as the positive direction) is given by

$$M' = 2c \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}. \tag{23}$$

From this system we can reproduce another with a varying surface concentration $\phi(t)$. It is assumed that the surface concentration is changed in a

stepwise manner so that Eq. (23) still applies for a short time, during which the surface concentration is constant and yet the stepwise change is taken to approximate $\phi(t)$, the latter being given by a smooth curve. Such an argument assumes, justifiably, that each portion of the solute which diffuses from the surface during one of the periods with a constant surface concentration, c_n, continues its diffusion independently of any other portions of the solute. This is equivalent to the assumption that the diffusion is an ideal process, that is to say that the diffusion coefficient is independent of concentration.

We have then

Δc_0 on the surface during diffusion from $t=0$ to $t=T$,
Δc_1 on the surface during diffusion from $t=1$ to $t=T$,
....,
Δc_n on the surface during diffusion from $t=n$ to $t=T$,

where $T =$ time needed to reach equilibrium conditions between bulk and surface. The total diffusion inward from the surface in the interval between $t=0$ and $t=T$ is obtained by summation

$$\sum M' = 2 \left(\frac{D}{\pi}\right)^{\frac{1}{2}} \sum_0^T \Delta c_t (T-t)^{\frac{1}{2}}. \tag{24}$$

We can make the approximation as good as we please by decreasing the duration of each step. In the limit, the expression (24) can best be represented by plotting $\phi(t)$ against $(T-t)^{\frac{1}{2}}$ and multiplying the area under the curve by $2(D/\pi)^{\frac{1}{2}}$. This is the integral

$$2 \left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int_0^{T^{\frac{1}{2}}} \phi(t) d[(T-t)^{\frac{1}{2}}], \tag{25}$$

which is identical in form with the corresponding part in Eq. (22) except for the sign. In Eq. (22) M_2 is naturally negative as it represents diffusion away from the surface taken in a negative direction.

CALCULATION OF DIFFUSION COEFFICIENTS

The Eq. (22) enables us in theory to obtain either M or D if one of the two is known. Unfortunately, explicit integration in Eq. (22) is not possible as $\phi(t)$ is not known explicitly. We can, however, employ a physical artifice which makes graphical integration possible and gives M the surface concentration at time t.

If it is assumed that there is no activation barrier between the sub-surface and the surface and that diffusion is the sole reason for the delay in establishing adsorption equilibrium, then the time required for the solute to diffuse from the sub-surface to the surface is very much smaller than the time required for diffusion equilibrium to be established between bulk and sub-surface. At any instant, there is a state of equilibrium between the surface and the sub-surface with respect to the solute.

The observed boundary tension is determined by the concentration of solute in the surface and this is in turn determined by the concentration in the sub-surface, $\phi(t)$. If a certain value of the boundary tension (γ) corresponds to a certain value of $\phi(t)$, say c, at any moment during the diffusion, that particular value of γ would also be obtained under equilibrium conditions when the concentrations in the sub-surface and the bulk were both equal to c. The relationship between γ and $\phi(t)$ can therefore be obtained from observations made under equilibrium conditions when diffusion has ceased. Values of the equilibrium boundary tension are plotted against the corresponding concentrations. In this way, from observed values of γ during the diffusion process, the variation of $\phi(t)$ with time may be found without the necessity of making arbitrary assumptions about the relationship between γ and the surface concentration and between the latter and $\phi(t)$. In this way the integral for M_2 can be evaluated in terms of $D^{\frac{1}{2}}$, for the period of time which is necessary for equilibrium to be established. The values of M ($=$ Gibbs' Γ) at equilibrium may be obtained independently by application of the Gibbs' equation to the observed relationship between the concentration and the equilibrium boundary tension. Since M is known in units of $D^{\frac{1}{2}}$, it is then possible to calculate D.

This method makes it possible to obtain diffusion coefficients from measurements of boundary tensions which vary with time. These will, of course, only be equivalent to the conventional diffusion coefficients if there is nothing in the nature of the physical system to invalidate the assumption of instantaneous equilibrium between the surface and the sub-surface. If this assumption is not true, and there is an activation barrier between the surface and the sub-surface, the value of D calculated from surface tension measurements (which will be referred to as D_s) will be a complex quantity characteristic of both diffusion and the crossing of the barrier. In such a case either of the processes may assume a controlling role. For a calculated value of D_s which is of the same order of magnitude as the conventional D, the normal diffusion process is the slower of the two. In such a case the existence of a small additional barrier at the surface would become a trivial question, as no possible experiment could be devised to investigate the nature of this barrier. For a calculated value of D_s which is smaller than the conventional D it is evidently the barrier at the surface which has the controlling role. If D_s is very small, the diffusion process can be neglected in comparison with the activated adsorption.

Quantitative conclusions cannot, however, be drawn from such very small values of D_s, for it must be borne in mind that in such a case the assumption of instantaneous equilibrium between surface and sub-surface is invalidated and no great significance can be attached to the calculated value of D_s. The theory should therefore give the correct value of the diffusion coefficient (as compared with the conventional value) if the process is purely a diffusion process, but if the calculated value of D_s is smaller than the usual bulk diffusion coefficient, it indicates that diffusion is not the rate-determining process.

A series of short time-effects have been investigated by Addison,[9–11] who measured the surface tensions of freshly formed surfaces of aqueous solutions of fatty alcohols, at intervals of a small fraction of a second. He employed the oscillating jet method and measured changes of surface tension with time, up to about one second, by which time equilibrium had been established after a rapid initial fall. Experimental results were reported for n-amyl, iso-amyl, n-hexyl, n-heptyl, and n-octyl alcohols at 20°C, some of them at several concentrations. The theory developed in this paper was applied to Addison's data and values of D_s were obtained by the graphical integration method. Calculated values of D_s are collected in Table I (column 6).
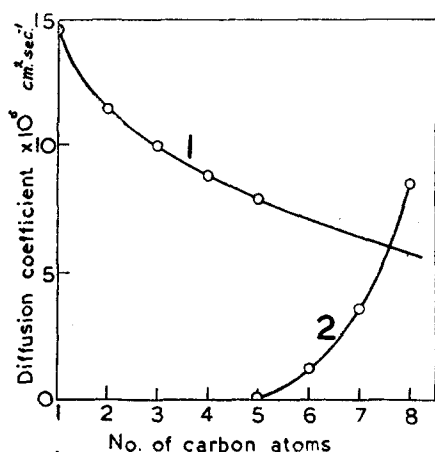
FIG. 2. Variation of calculated and observed diffusion coefficients with chain-length. (1) Observed D. (2) Calculated D_s.

DISCUSSION

Values of Γ have been obtained by the use of the approximate Gibbs' equation (using concentrations) since activity values for solutions of these alcohols were not available. For the lower alcohols at the lowest concentrations this was a sufficiently good approximation. It may be seen from Table I that for the highest concentration of n-hexyl alcohol the calculated value of Γ (8.67×10^{-10}) is obviously too high. This is probably caused by the divergence between concentration and activity. Since a high value of Γ yields a high value of D_s, it appears that if accurate activity data were used the values of D_s in column 6 would at any rate be no higher than those given. They may therefore be taken safely as an upper limit.

The conventional diffusion coefficient (D) for iso-amyl alcohol in water has been obtained by Thovert[18] as 6.9×10^{-6} cm^2 sec.$^{-1}$ at 15°C, corresponding to 7.9×10^{-6} at 20°C. The calculated value of D_s in Table I is 56 times smaller than this. Therefore diffusion is not the rate-determining process here, and a further activation barrier must exist. Experimental values of diffusion coefficients are not available for the higher alcohols. But the probable values may be seen in Fig. 2, where the curve of experimental values of D for the lower alcohols (curve 1) is extrapolated. The decrease in D with increase in the

size of the molecule would be expected from the Stokes-Einstein formula

$$D = kT/6\pi r\eta.$$

Curve 2 shows the values of D_s calculated from Addison's data for the lowest concentrations in each case. Up to heptyl alcohol the values of D_s are all lower than the correct values of D. But the most convincing argument against the process being merely diffusion is not so much the fact that $D_s < D$ as the general trend of D_s to increase with chain-length. This is the opposite of what would be expected for a diffusion coefficient. The fact that D_s for octyl alcohol is of the right order of magnitude for agreement with D is therefore probably fortuitous. Thus the numerical results indicate that the rate of adsorption in these cases is not determined by diffusion.

Some doubt is thrown on the experimental values for the higher alcohols considered in Table I because of the probability that equilibrium was not attained. If $\phi(t)$ is plotted against the time, the curve should flatten when equilibrium is reached. These values are plotted in Fig. 3, for n-amyl alcohol (0.04544 molal) and n-octyl alcohol (0.0007962 molal).

It will be observed that the curve for n-amyl alcohol flattens out satisfactorily within the time of observation. The curve for n-octyl alcohol indicates that equilibrium may not have been attained within 0.11 sec., the time of the final observation.

Available literature seems to indicate that the time required to obtain equilibrium surface tensions increases very rapidly with chain-length for solutions of aliphatic acids. King,[19] using a drop-weight method, found that drop-lives of at

TABLE I.

(1) Solute (alcohols)	(2) Molality	(3) $M_1 \times D^{\frac{1}{2}}$ $\times 10^6$	(4) $M_2 \times D^{\frac{1}{2}}$ $\times 10^6$	(5) $\Gamma \times 10^{10}$ mole/cm^2	(6) $D_s \times 10^6$ cm^2/sec.
n-amyl	0.01136	2.026	1.348	2.93	0.185
n-amyl	0.02272	3.242	2.445	3.98	0.250
n-amyl	0.04544	5.612	3.750	5.92	0.100
iso-amyl	0.01384	2.410	1.620	2.97	0.141
n-hexyl	0.00245	0.895	0.707	2.09	1.28
n-hexyl	0.00735	2.620	2.290	3.77	1.31
n-hexyl	0.01226	4.360	4.070	5.44	3.62
n-hexyl	0.02161	5.975	5.240	8.67	1.39
n-heptyl	0.001724	0.645	0.497	2.83	3.66
n-octyl	0.0007962	0.298	0.127	4.98	8.48

[18] J. Thovert, Ann. d. Physik [9] 2, 369 (1914).

[19] H. H. King, Kansas State Agr. Col., Agr. Exp. Station, Tech. Bull., No. 9 (1922).

least five minutes were required to attain steady values of surface tension with all acids above *n*-butyric acid. For solutions of nonylic acid 30-minute drops had to be used and for decylic acid, the surface tension was still falling after 30 minutes. Addison,[20] working with solutions of decylic acid, found that times of the order of a minute were required to reach a "dynamic equilibrium" and that this was followed by a further slow fall of surface tension. These observations appear to throw more doubt on the existence of a real equilibrium, for solutions of long chain alcohols, after the lapse of a tenth of a second or less. Further experimental information on this point would be valuable.

To explain the apparent increase in "migrational velocity" of the solute molecule with increasing chain-length, Addison has defined this velocity in quantitative terms and assumed that the main factors controlling the rate of adsorption were the free energy change on adsorption and the distance of the solute molecule from the surface. While it is not at all obvious why the velocity of a solute molecule traveling towards the surface should depend on its distance from it, it is even less acceptable to suppose that this velocity should depend on the lowering of the surface tension by the adsorption of the solute molecule. In any physical or chemical change a system may undergo, the velocity of the change depends not on the difference in the free energies between the initial and final states, but on any intermediate activation barriers. The numerical calculations of Addison are further invalidated by his use of the Gibbs' equation for calculating surface excesses at stages prior to the establishment of equilibrium.

The authors have been carrying out experiments on the time-dependence of interfacial tension between water and solutions of long chain compounds in hexane.[12] Full details of this
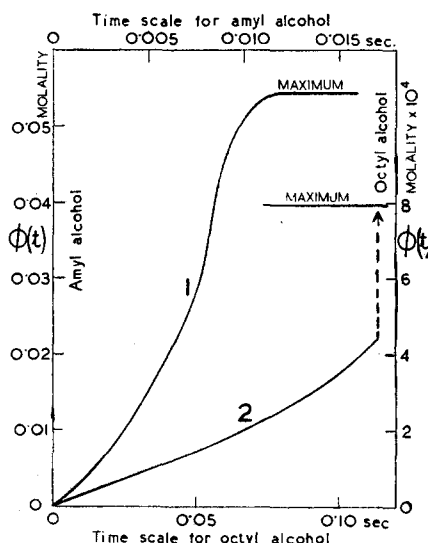

FIG. 3. Change of sub-surface concentration with time. (1) Amyl alcohol. (2) Octyl alcohol.

work will be published shortly, but an example may be given now to support the conclusions reached above. For solutions of palmitic acid in hexane values of $\phi(t)$ were obtained from a complete set of equilibrium interfacial tension data. The surface concentration was obtained by means of an equation of state proposed by Langmuir.[21] For a concentration of 0.04101 molal the calculated value of. D_s so obtained was 5.66×10^{-13}, a value about 10^7 times smaller than the expected magnitude of the diffusion coefficient. It is clear that in this system also there is an activation barrier between the sub-surface and the surface.

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[20] C. C. Addison, Nature **156**, 600 (1945).

[21] I. Langmuir, J. Chem. Phys. **1**, 756 (1933).