

parameters would then be anticipated for each phase.

It is somewhat surprising that cholesteric CM exerts little influence on the kinetics of  $^1\text{P}$  quenching by D and that the quenching process appears to be independent of ground-state conformations. As mentioned, others,<sup>24</sup> employing similar bichromophorics and isotropic, lower-viscosity solvents, have obtained compelling evidence for the intervention of more than one conformer type leading to spectroscopically common excited-state complexes.

Considering the nature of cholesteric CM order, it seems reasonable that the important conformer types be represented crudely by A1, A2, and A3 in Scheme III. P is considered a rectangular plate and D a rod. In the lower energy conformers, A1 and A2, the rod and rectangle lie roughly in one plane. Their interconversion requires that one (or both) rotate out of the plane. Such a motion would seem difficult if A1 and/or A2 lie preferentially parallel to the cholesteric solvent planes, perhaps as difficult as their rotation of A3 (the exciplex geometry in which P and D lie in approximately parallel planes). Yet, the monoexponential decays indicate that no substantial energy barriers separate A1 and A2.

It is conceivable that the interconversions take place via motions which bring P and D into contact with molecules in adjacent solvent "layers". Owing to the somewhat rodlike shape of D and its relatively small size in relation to the solvent molecules, such an interconversion may be

relatively easy, especially if the D interaction is with the chain part of the cholesteric molecules.<sup>33</sup> To test this hypothesis, we are presently investigating the dynamic quenching properties of several  $\alpha,\omega$ -bis(1-pyrenyl)alkanes in CM.

## Conclusions

Dynamic and steady-state fluorescence data indicate that quenching of  $^1\text{P}$  by D in A results in the formation of an intramolecular exciplex in cholesteric and isotropic phases of CM. The efficiency of the process is greatly reduced with respect to that in solvents of low polarity and viscosity. The high viscosity of CM is largely responsible for this change. The geometry of the intramolecular  $^1\text{P}$ -D transition state does not appear to be sensitive to cholesteric solvent order. The activation parameters measured in the cholesteric phase, being slightly larger than those in the corresponding isotropic phase of CM, are reconcilable with the phase viscosity differences.

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(33) A similar argument may apply to previously reported observations concerning the thermal interconversions of vitamin D<sub>3</sub> and previtamin D<sub>3</sub> in a cholesteric phase: Cassis, E. G., Jr.; Weiss, R. G. *Photochem. Photobiol.* 1982, 35, 439.

## Diffusion-Controlled Adsorption Kinetics. General Solution and Some Applications<sup>†</sup>

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If the diffusion coefficient is constant, molecules diffuse independently of each other and so do groups of molecules, and the method of superpositions and reflections is applicable in diffusion calculations. Thus adsorption from a solution of initially uniform concentration  $C_\infty$  can be considered as the difference between the amount diffusing toward the surface—acting as a sink—and the amount diffusing away from the subsurface—acting as a group of sources  $dc_\tau$ , each becoming active at time  $\tau$  when the subsurface concentration  $c_\tau$  is reached. If  $f(t)C_\infty$  is the former, then the latter is  $\int_0^t f(t-\tau) dc_\tau$ , and the difference between the two is  $\Gamma_t$ , the amount adsorbed in time  $t$ .  $t-\tau$  is the lifetime of  $dc_\tau$ . The function  $f(t)$  is generally known or can be obtained without considering time-dependent boundary problems.  $c_\tau$  is defined if it is related to  $\Gamma_\tau$  by an adsorption isotherm, i.e., if there is rapid equilibrium between the surface and subsurface concentrations and diffusion controls the kinetics. This general equation is applied to the plane, yielding a known result, to the sphere, and to stagnant layers on both geometries, as well as to some limiting cases.

Adsorption from solutions is much more frequently studied in its equilibrium than in its kinetic aspects. A probable reason is the paucity of kinetic theories and models available for comparison with experimental data. Yet kinetics can obviously provide information on many points about which equilibrium studies often remain mute. The activation energy for adsorption is the prime example. The question whether minor, analytically undetected components are involved in the process is another one and of special personal interest.<sup>1,5</sup> The nature of the transport processes occurring in a mixture is another question that

may turn out to be of concern.

A relatively simple model involves diffusive transport of the sorbate to the surface which can be further simplified if the activation energy for adsorption is assumed to be zero. The case of adsorption onto a plane from a quiescent liquid has been solved for this model by Ward and Tordai<sup>2</sup> in 1946. Their solution is given below as eq 18. Many surfaces of interest are, however, not planes. Droplets and bubbles are frequently encountered in industrial mass transfer problems as well as in scientific

<sup>†</sup> Presented in part before the Division of Colloid and Surface Chemistry at the 182nd National Meeting of the American Chemical Society, New York, Aug 1981.

(1) K. J. Mysels and A. T. Florence in "Clean Surfaces: Their Preparation and Characterization for Interfacial Studies", G. Goldfinger, Ed., Marcel Dekker, New York, 1970, p 227.

(2) A. F. Ward and L. Tordai, *J. Chem. Phys.*, 14, 453 (1946).

measurements of interfacial tension as by the drop weight or volume, or maximum bubble pressure methods. In such cases a sphere may be a much better approximation than a plane. Furthermore, in many situations the gaseous or liquid mixture cannot be considered as stagnant, especially if the adsorption process extends over a considerable length of time as often happens for dilute systems. Then a stagnant layer separating the adsorbing surface from a well-stirred solution may be a better model.

The purpose of this paper is to generalize the Ward and Tordai solution to any surface for which the much simpler diffusion problem of transport to a sink can be solved, to indicate the relation of this solution to situations in which the activation energy is significant, to consider the spherical and the stagnant layer cases in somewhat greater detail, and to obtain some explicit limiting expressions for ideal and Langmuirian adsorption.

### General Equation

We consider a system consisting of a solution of initially uniform concentration  $C_\infty$  in contact with an initially clean surface of any geometry. Adsorption on the surface begins at zero time and reaches a certain surface concentration  $\Gamma_t$  at time  $t$ . Adsorption involves no activation energy which means that at all times there is equilibrium between  $\Gamma$  and the concentration of the solution in immediate contact with the surface, the subsurface concentration  $c$ . The diffusion coefficient  $D$  is assumed to be constant. The first problem is to express  $\Gamma_t$  as a function of  $C_\infty$  (which is constant with time) and of  $c$  as it changes between times zero and  $t$ . Later we will consider briefly the effect of the adsorption isotherm, i.e., of the equilibrium relation between  $\Gamma$  and  $c$ .

The problem can be formulated in terms of the differential equation of Fick's second law and proper boundary conditions. Their direct solution, especially for the unspecified geometry is certainly difficult and would provide only limited insight into the phenomena occurring. An alternative is based on the method of reflections and superpositions, i.e., on considering the total transport as the sum of simpler ones obeying the same laws and appropriate boundary conditions. This was presented by Ward and Tordai<sup>2</sup> for their special case as "less rigorous". In fact, however, the method is perfectly rigorous where it can be applied. Mathematically it is sound as the sum of solutions of a differential equation is the solution to this equation with the sum of boundary conditions. Physically it corresponds to the fact that a constant diffusion coefficient means that each molecule diffuses independently of the others, and that so does each group of molecules. Hence the overall process can be considered as the appropriate sum of the simpler—and easier to calculate—diffusion of appropriate groups of molecules.

For our purposes the adsorption process can be considered as the superposition of two simpler ones yielding respectively  $\Gamma_1$  the amount reaching a unit surface area in time  $t$  and  $\Gamma_2$  the corresponding amount leaving the surface. The difference between these two amounts is the net amount adsorbed. Thus

$$\Gamma_t = \Gamma_1 - \Gamma_2 \quad (1)$$

$\Gamma_1$  is the amount reaching in time  $t$  a unit area of a perfect sink having the shape of our surface from a solution originally at uniform concentration  $C_\infty$ . We denote it as  $C_\infty f(t)$  where  $f(t)$  does not depend on  $C_\infty$ . That  $\Gamma_1$  is proportional to concentration, though obvious, may be considered as a consequence of the method of superpositions since the total amount due to  $C_\infty$  can be taken as the sum of amounts due to smaller  $C_i$ 's so selected that  $\sum C_i = C_\infty$ .

For this to be true for any selection of the  $C_i$ 's, the total has to be proportional to the  $C_i$ 's and hence to  $C_\infty$ . The function  $f(t)$  depends on the shape of the surface and will be discussed later.

$\Gamma_2$  is the corresponding amount diffusing away from a source having the shape of our surface and a variable concentration  $c_\tau$ . If the concentration were constant at  $C$  then the amount would be given exactly again by  $Cf(t)$ . This follows from considering a solution of constant concentration  $C$  bounded by a nonadsorbing surface. The unchanging concentration can be considered as resulting from equal diffusion to the boundary, considered as a sink, from a solution originally at  $C$  and diffusion from this boundary considered as a source of concentration  $C$  into the solution.

The variable concentration  $c_\tau$  of the source may be considered as the superposition of small sources  $dc_\tau$ , each of which originates in turn at times  $\tau$  as the variable concentration  $c_\tau$  builds up. When the time  $t$  is reached, each of these sources will have acted for its lifetime which is  $t - \tau$ . Hence the contribution of each is  $f(t - \tau) dc_\tau$ , and their total, i.e.,  $\Gamma_2$ , is given by

$$\Gamma_2 = \int_0^t f(t - \tau) dc_\tau = \int_0^t c_\tau df(t - \tau) \quad (2)$$

The second expression is obtained by exchanging the variables, i.e., integrating the same curve along the ordinate instead of the abscissa.<sup>6</sup>

Thus the adsorption  $\Gamma_t$  is given quite generally (using the first expression of (2)) by

$$\Gamma_t = C_\infty f(t) - \int_0^t f(t - \tau) dc_\tau \quad (3)$$

The formal simplicity of this equation is somewhat deceiving, but it does greatly simplify the actual problem of calculating  $\Gamma$  as a function of  $t$ , in addition to providing some insight into the factors that affect it.

As an integral equation eq 3 cannot be solved analytically except in very special cases, but can in principle be solved by numerical iteration in a straightforward way. Any such solution requires, however, a knowledge of the function  $f(t)$  and of the equilibrium relation between  $\Gamma$  and  $c$  so that one of these two unknowns can be eliminated. This last relation, the adsorption isotherm, depends on the chemical nature of the system involved and we will consider briefly two of the simplest forms in the next section.

The main value of eq 3 is that it reduces the original diffusion problem with variable concentration boundary conditions to the much simpler one of finding  $f(t)$ , the law of diffusion, to a sink. This can be obtained by standard methods and, for many interesting cases, is given or implied by expressions in textbooks<sup>3,4</sup> on diffusion or heat conduction. We will consider such cases later.

Another advantage of eq 3 is that because of the simplicity and physical nature of its derivation it can be readily generalized to somewhat more complicated problems, beyond the very limited conditions stated above. Thus clearly the limitation that all the transport be by diffusion, i.e., that the solution be semiinfinite and quiescent as implied in the derivation, is not essential. If the diffusional transport occurs in a stagnant layer bounded on one side by the adsorbing surface and on the other by a well-stirred solution of constant concentration

(3) J. Crank, "The Mathematics of Diffusion", Oxford University Press, London, 1957.

(4) (a) W. Jost, "Diffusion in Solids, Liquids, Gases", Academic Press, New York, 1960; (b) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids", Oxford University Press, London, 1947.

the derivation applies equally well.

A generalization involving an activated adsorption will be briefly examined in the last section.

### Simplified Equations

Equation 3 can readily be solved if  $f(t)$  is a constant, but this does not seem to represent any interesting physical situation. The next simplest expression,  $f(t) = kt$ , can also be solved and may have applications one of which we shall examine in the last section. Differentiating eq 3 with respect to time we obtain, in view of the fact that  $f(t - \tau) = 0$  for  $\tau = t$

$$\frac{d\Gamma_t}{dt} = C_\infty \frac{df(t)}{dt} - \int_0^t \frac{df(t - \tau)}{dt} dc_\tau \quad (4)$$

When  $f(t) = kt$ , this reduces to

$$d\Gamma_t/dt = k(C_\infty - c_t) \quad (5)$$

Integration of this expression requires the knowledge of the adsorption isotherm. The simplest is the ideal one

$$\Gamma = ac \quad (6)$$

which is expected for a minor component forming ideal solutions both in bulk and in the surface.<sup>5</sup> The other interesting isotherm is Langmuir's

$$\Gamma = \frac{ac}{1 + bc} \quad (7)$$

This corresponds to the Szyszkowski equation which seems obeyed by many surfactants.

Equations 5 and 6 can be combined and integrated to give for the ideal case

$$\ln \frac{C_\infty - c_0}{C_\infty - c} = (k/a)(t - t_0) \quad (8)$$

where the subscript 0 indicates corresponding times and subsurface concentrations which may be both zero.

Combining eq 5 and 7 and integrating gives for the Langmuirian case

$$\frac{1}{1 + bC_\infty} \left[ \frac{-1}{1 + bc} + \frac{1}{1 + bC_\infty} \ln \frac{1 + bc}{C_\infty - c} \right] = (k/a)t + \text{constant} \quad (9)$$

For the often interesting case of terminal stages and proximity to saturation adsorption,  $C_\infty - c$  is negligible in comparison with  $C_\infty$  and unity is negligible in comparison to  $bC_\infty$ . Equation 9 then simplifies to

$$\ln (C_\infty - c_1)/(C_\infty - c) = (b^2 C_\infty^2 k/a)(t - t_1) \quad (10)$$

where the subscript 1 denotes corresponding states close to equilibrium.

Neither surface concentration  $\Gamma$  nor the subsurface one,  $c$ , are as easily accessible experimentally as the surface tension  $\sigma$ . The three are related by Gibbs's equation

$$d\sigma = -\Gamma RT(d \ln c + d \ln \gamma) \quad (11)$$

where  $\gamma$  is the activity coefficient. For simplicity we shall neglect the term involving this correction.

Combining eq 11 and 6 and integrating gives for the ideal adsorption isotherm

$$\sigma_e - \sigma = aRT(C_\infty - c) \quad (12)$$

where the subscript e denotes the equilibrium value. Hence eq 8 becomes in terms of surface tension

$$\ln (\sigma_0 - \sigma_e)/(\sigma - \sigma_e) = (k/a)(t - t_0) \quad (13)$$

Similarly from eq 11 and 7 integration gives for the Langmuirian adsorption isotherm

$$\sigma_e - \sigma = (aRT/b) \ln (1 + bC_\infty)/(1 + bc) \quad (14)$$

Making the same approximations, terminal rate and near-saturation, as in deriving eq 10 gives

$$\sigma_e - \sigma = (aRT/bC_\infty)(C_\infty - c) \quad (15)$$

so that eq 10 becomes in terms of surface tension

$$\ln (\sigma_1 - \sigma_e)/(\sigma - \sigma_e) = (b^2 C_\infty^2 k/a)(t - t_1) \quad (16)$$

### Specific Geometries

(1) *Adsorption onto a Plane from a Quiescent Solution.* In this case  $f(t)$  is given directly by Crank's<sup>3</sup> eq 3.15 as

$$f(t) = 2(Dt/\pi)^{1/2} \quad (17)$$

Hence, from (1) and the second form of (3), the adsorption kinetics are given by

$$\Gamma_t = 2(D/\pi)^{1/2}(C_\infty t^{1/2}) - \int_0^t c_\tau d(t - \tau)^{1/2} \quad (18)$$

This is Ward and Tordai's<sup>2</sup> solution. An explicit solution for the ideal adsorption isotherm has been given by Bakker et al.<sup>7</sup> as

$$C_\infty - c = \exp(Dt/a^2) \operatorname{erfc} (Dt/a^2)^{1/2} \quad (19)$$

and Hansen<sup>8</sup> has given a terminal rate expression independent of the adsorption isotherm:

$$C_\infty - c = \Gamma_e/(\pi D\tau)^{1/2} \quad (20)$$

(2) *Adsorption onto a Plane with a Stagnant Layer.* As adsorption times become longer or if the solution is patently not stagnant, a more useful approximation of the real situation may be that of a stagnant layer of thickness  $h$  separating the plane from a well-stirred solution. Here Crank's<sup>3</sup> eq 4.24 is applicable. It can be simplified and written with our symbols as

$$f(t) = \frac{Dt}{h} + \frac{2h}{\pi^2} \left( \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} (1 - \exp(-Dn^2\pi^2 t/h^2)) + 2 \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} (1 - \exp(-D(2m+1)^2\pi^2 t/h^2)) \right) \quad (21)$$

Abbreviating the series terms as  $S(t)$ , we can write on the basis of (3) for the kinetics of adsorption

$$\Gamma_t = (D/h) \left( C_\infty t - \int_0^t (t - \tau) dc_\tau \right) + C_\infty S(t) - \int_0^t S(t - \tau) dc_\tau \quad (22)$$

The first right-hand term of (21) represent the steady-state diffusion through the stagnant layer to the sink and the  $S(t)$  terms give the additional transport due to adjustment of the profile of this layer from the initially uniform concentration to the linear gradient at steady state. These terms are important in the early stages of adsorption, but become negligible for long times resulting

(6) Referees of the original version of this paper pointed out that the above paragraph amounts to a rederivation of a special case of the very powerful theorem of Duhamel (*J. Ec. Polytech. (Paris)*, 14, Cah. 22, 20 (1833)). This theorem well-known in heat conduction (ref 4b, pp 30 and 31) does not seem to be mentioned in books on diffusion.

(7) C. A. P. Bakker, P. M. van Buytenen, and W. J. Beek, *Chem. Eng. Sci.*, 21, 1039 (1960).

(8) R. S. Hansen, *J. Phys. Chem.*, 64, 637 (1960).

(5) K. J. Mysels and A. T. Florence, *J. Colloid Interface Sci.*, 43, 577 (1973).

in a linear  $f(t)$ . When it comes to kinetics of adsorption, eq 22, this is not sufficient to apply the simplified results obtained in the preceding section even to the terminal stages. The reason is that the second integral involves  $t - \tau$  which becomes small for large  $\tau$  bringing out the importance of the  $S$  term.

(3) *Adsorption onto a Sphere in a Quiescent Liquid.* Crank<sup>3</sup> does not give explicit relations for  $f(t)$  for this case, but only a general equation for the concentration as a function of time and position for a region bounded internally by a sphere, his eq 6.60. This can be written for our case of a spherical sink as

$$C_r = C_\infty(1 - (R/r) \operatorname{erfc}((r - R)/2(Dt)^{1/2})) \quad (23)$$

where  $R$  is the radius of the sphere and  $r$  the distance from the center.

Differentiating eq 23 with respect to  $r$  gives the concentration gradient. The limit of this gradient at  $r = R$ , times the diffusion coefficient, gives the flux into the sink as a function of time. Integrating this to time  $t$  gives then the desired  $f(t)$  as

$$f(t) = (D/R)t + 2(D/\pi)^{1/2}t^{1/2} \quad (24)$$

Thus the amount diffusing into a spherical sink (per unit surface) has two components. One component given by the first right-hand term is a constant rate one and is equal to the steady-state diffusion into such a sink. The other component is equal to the amount diffusing to a plane, eq 17, and its rate is rapidly decreasing with time. The rates of the two components are about equal at 1 s for  $R = 0.1$  mm and  $D = 3 \times 10^{-5}$  cm<sup>2</sup>/s. The kinetics of adsorption is now given by

$$\Gamma_t = (D/R)\left(C_\infty t - \int_0^t c_\tau d(t - \tau)\right) + 2(D/\pi)^{1/2}\left(C_\infty t^{1/2} - \int_0^t c_\tau d(t - \tau)^{1/2}\right) \quad (25)$$

At very short times the square root terms dominate and the kinetics of adsorption are similar to those for a plane. As the linear terms becomes significant, adsorption becomes faster. For reasons analogous to those given above, the terminal stages cannot be considered as following from a linear limiting  $f(t)$  alone.

(4) *Adsorption onto a Sphere with a Stagnant Layer.* As for the plane, a useful approximation of the experimental situation is sometimes that of a sphere surrounded by a stagnant layer of thickness  $h$  in a well-stirred bath. Crank's<sup>3</sup> general eq 6.50 for a spherical shell can be simplified when it surrounds a sink to

$$C_r = (C_\infty/r) \left( \left( \frac{(R+h)(r-R)}{h} \right) + (2/\pi) \sum_{n=1}^{\infty} (R/n) \sin \frac{n\pi(r-R)}{h} \exp\left(-\frac{Dn^2\pi^2 t}{h^2}\right) \right) \quad (26)$$

By the same general procedure that led to eq 24, we obtain here for  $f(t)$

$$f(t) = D(t(R+h)/Rh) - (2h/D\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-Dn^2\pi^2 t/h^2) \quad (27)$$

Again, the first right-hand term is a constant rate component corresponding to the steady-state condition and the last term, which we indicate by  $S(t)$ , is the contribution from the adjustment of concentration in the stagnant layer.

The adsorption kinetics are given according to (3) by

$$\Gamma_t = (D(R+h)/Rh)\left(C_\infty t - \int_0^t (t-\tau) dc_\tau\right) - C_\infty S(t) + \int_0^t S(t-\tau) dc_\tau \quad (28)$$

### Activated Adsorption

We consider again the net rate of adsorption  $d\Gamma/dt$  as the difference between the forward rate of elementary adsorption  $d\Gamma_1/dt$  and the reverse one of elementary desorption  $d\Gamma_2/dt$ . In the simplest case these are directly proportional to the concentrations, the subsurface, and the surface one, respectively. Thus

$$d\Gamma_1/dt = k_1 c \quad d\Gamma_2/dt = k_2 \Gamma \quad (29)$$

As a further simplification we assume that diffusional resistance is negligible (or that adsorption is purely activated) so that the subsurface concentration is equal to the bulk one, i.e.,  $c = C_\infty$ . Hence

$$d\Gamma_1/dt = k_1 C_\infty$$

The two equations in (29) correspond to an ideal adsorption isotherm and for any surface concentration  $\Gamma_\tau$ , we can calculate a corresponding hypothetical subsurface concentration  $c_\tau = k_2/k_1 \Gamma_\tau$ . Hence

$$d\Gamma_2/dt = k_1 c_\tau$$

As before we can consider  $c_\tau$  to be composed of a series of  $dc_\tau$  each existing for a time  $t - \tau$ . The net amount adsorbed is equal to the difference between the integrals of the two rates, i.e.

$$\Gamma_t = \int_0^t k_1 C_\infty dt - \int_0^t k_2 \Gamma dt = C_\infty k_1 t - \int_0^t k_1 (t - \tau) dc_\tau$$

which is simply our basic eq 3 with  $f(t) = k_1 t$ , so that the simplified eq 13 and 14 apply in this case at all times as one would expect from elementary kinetics.

Thus the approach developed specifically for a diffusion-controlled adsorption can be readily generalized to some cases where diffusion plays no role.

### Conclusion

The method of superpositions gives insight into the diffusion control of adsorption for arbitrary geometries. It reduces the mathematical problem to the much simpler one of transport to a sink of a given geometry. Known solutions of the latter problems have been used to describe the kinetics for adsorption onto a sphere in a quiescent liquid and for a plane and a sphere with a stagnant layer. A further simple generalization permits the treatment of kinetics of simple ideal activated adsorption.

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