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The Mass-transfer Rate through the Liquid-Liquid Interface. V. Diffusion through an Interface Considering the Variation in the Amount of Adsorption

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The diffusion through an interface has been re-formulated considering the variation in the amount of adsorption on the interface in the case of linear diffusion in a finite composite medium.

In the treatment of the diffusion of a substance through interfaces,[1-4] it has generally been assumed that the flux from one phase to the interface is equal to the flux from the interface to the other phase; this implies that the amount of adsorption on the interface is constant during the diffusion process.

Accordingly, if the concentration in a phase immediately next to the interface, which is in an equilibrium relation with the amount of adsorption, actually varies during the diffusion process, the above treatment may give erroneous results.

In this paper, the diffusion through an interface will be theoretically treated by allowing the amount of adsorption on the interface to vary reasonably during the diffusion process in case of linear diffusion in a finite composite medium.[5]

Theory

Fick's diffusion equation is defined by:

$$\partial c_1/\partial t = D_1(\partial^2 c_1/\partial x^2),\ -a<x<0,\ t>0; \tag{1}$$

$$\partial c_2/\partial t = D_2(\partial^2 c_2/\partial x^2),\ 0<x<a,\ t>0, \tag{2}$$

where c_1 and c_2 are the local concentrations of the solute in Phases 1 and 2 respectively, where D_1 and D_2 are the diffusion coefficients, where x is the diffusion coordinate (the direction from Phase 1 to Phase 2 is selected as positive), and where t is the time.

The boundary conditions are represented by:

$$-D_1(\partial c_1/\partial x) + D_2(\partial c_2/\partial x) = \Gamma_\infty(\mathrm{d}\theta/\mathrm{d}t),\ x=0,\ t>0; \tag{3}$$

$$-D_1(\partial c_1/\partial x) = k_{a1}c_1(1-\theta) - k_{d1}\theta,\ x=0,\ t>0; \tag{4}$$

$$D_2(\partial c_2/\partial x) = k_{a2}c_2(1-\theta) - k_{d2}\theta,\quad x=0,\ t>0; \tag{5}$$

$$\partial c_1/\partial x = 0,\ x = -a,\ t>0; \tag{6}$$

$$\partial c_2/\partial x = 0,\ x = a,\ t>0, \tag{7}$$

where Γ_∞ is the saturated value of the amount of adsorption per unit of area of the interface, where θ is the fraction of the total interface that is occupied by adsorbed molecules, where k_{a1} and k_{a2} are the rate constants of adsorption to the interface from Phase 1 and Phase 2 respectively, and where k_{d1} and k_{d2} are the rate constants of desorption from the interface to Phase 1 and Phase 2 respectively. Equation (3) relates the variation in the amount of adsorption to the fluxes, while Eqs. (4) and (5) give the relation between the adsorption-desorption mechanism and the fluxes. Equations (6) and (7) give the impermeable wall conditions of the solute.

The initial conditions are assumed to be:

$$c_1 = c_{10},\ -a<x<0,\ t = 0; \tag{8}$$

$$c_2 = c_{20},\ 0<x<a,\ t=0; \tag{9}$$

$$\theta = \theta_0,\ x=0,\ t=0, \tag{10}$$

where c_{10}, c_{20}, and θ_0 are constants.

The Laplace transforms of these equations are represented by:

$$\mathrm{d}^2\bar{c}_1/\mathrm{d}x^2 - q_1^2\bar{c}_1 + (c_{10}/D_1) = 0,\ -a<x<0; \tag{1'}$$

$$\mathrm{d}^2\bar{c}_2/\mathrm{d}x^2 - q_2^2\bar{c}_2 + (c_{20}/D_2) = 0,\ 0<x<a; \tag{2'}$$

$$-D_1(\mathrm{d}\bar{c}_1/\mathrm{d}x) + D_2(\mathrm{d}\bar{c}_2/\mathrm{d}x) = \Gamma_\infty(p\bar{\theta}-\theta_0),\ x = 0; \tag{3'}$$

$$\begin{aligned} -D_1(\mathrm{d}\bar{c}_1/\mathrm{d}x) &= k_{a1}\bar{c}_1 - \frac{k_{a1}}{2\pi i} \\ &\times \int_{x_1-i\infty}^{x_1+i\infty}\bar{c}_1(\sigma)\bar{\theta}(p-\sigma)\mathrm{d}\sigma - k_{d1}\bar{\theta},\ x = 0; \end{aligned} \tag{4'}$$

$$\begin{aligned} D_2(\mathrm{d}\bar{c}_2/\mathrm{d}x) &= k_{a2}\bar{c}_2 - \frac{k_{a2}}{2\pi i} \\ &\times \int_{x_2-i\infty}^{x_2+i\infty}\bar{c}_2(\sigma)\bar{\theta}(p-\sigma)\mathrm{d}\sigma - k_{d2}\bar{\theta},\ x = 0; \end{aligned} \tag{5'}$$

$$\mathrm{d}\bar{c}_1/\mathrm{d}x = 0,\ x = -a; \tag{6'}$$

$$\mathrm{d}\bar{c}_2/\mathrm{d}x = 0,\ x = a, \tag{7'}$$

where $\bar{c}_1$, $\bar{c}_2$, and $\bar{\theta}$ are the image functions corresponding to c_1, c_2, and θ respectively, where p is the conversion parameter of the Laplace transformation, and where $q_1=(p/D_1)^{1/2}$ and $q_2=(p/D_2)^{1/2}$.

The general solution of Eqs. (1′) and (2′) may be represented by:

$$\bar{c}_1 = (c_{10}/p) + A_1\sinh(q_1x) + B_1\cosh(q_1x); \tag{11}$$

$$\bar{c}_2 = (c_{20}/p) + A_2\sinh(q_2x) + B_2\cosh(q_2x), \tag{12}$$

where A_1, B_1, A_2, and B_2 are the intergration constants.

These four constants can be solved by virtue of the boundary conditions of Eqs. (4′)—(7′). Equation (3′) is considered to define the mediate variable, $\bar{\theta}$. If we set the non-linear terms in Eqs. (4′) and (5′) at zero for the moment, we obtain a solution for the zero perturbation; by then substituting this solution into the non-linear terms, we obtain the solution for the first perturbation, and so on. The solution for the ith perturbation may be represented as:

$$\bar{c}_{1,i}(p) = (c_{10}/p) - A_{1,i}\cosh[q_1(a+x)]; \tag{13}$$

$$\bar{c}_{2,i}(p) = (c_{20}/p) - A_{2,i}\cosh[q_2(a-x)]; \tag{14}$$

$$\begin{aligned} \bar{\theta}_i(p) = (\theta_0/p) &+ \Gamma_\infty^{-1}[A_{1,i}q_1^{-1}\sinh(q_1a) \\ &+ A_{2,i}q_2^{-1}\sinh(q_2a)]; \end{aligned} \tag{15}$$

$$A_{1,i} \equiv (pD)^{-1}[\alpha_{1,i}\sinh(q_2a) + \beta_{1,i}\cosh(q_2a)];$$

$$A_{2,i} \equiv (pD)^{-1}[\alpha_{2,i}\sinh(q_1a) + \beta_{2,i}\cosh(q_1a)];\ .$$

$$\begin{aligned}\alpha_{1,i} &\equiv \Gamma_\infty D_1 q_1[k_{a1}(c_{10}-pI_{1,i}) - k_{d1}\theta_0]\\ &\quad + q_1^{-1}[k_{a1}k_{d2}(c_{10}-pI_{1,i}) - k_{a2}k_{d1}(c_{20}-pI_{2,i})];\end{aligned}$$

$$\beta_{1,i} \equiv k\Gamma_\infty k_{a2}[k_{a1}(c_{10}-pI_{1,i}) - k_{d1}\theta_0];$$

$$\begin{aligned}\alpha_{2,i} &\equiv k\{\Gamma_\infty D_1 q_1[k_{a2}(c_{20}-pI_{2,i}) - k_{d2}\theta_0]\\ &\quad - q_1^{-1}[k_{a1}k_{d2}(c_{10}-pI_{1,i}) - k_{a2}k_{d1}(c_{20}-pI_{2,i})]\};\end{aligned}$$

$$\beta_{2,i} \equiv k\Gamma_\infty k_{a1}[k_{a2}(c_{20}-pI_{2,i}) - k_{d2}\theta_0];$$

$$\begin{aligned}\boldsymbol{D} &\equiv [a_1 \sinh(q_1 a) + a_2 \cosh(q_1 a)] \sinh(q_2 a)\\ &\quad + [a_3 \sinh(q_1 a) + a_4 \cosh(q_1 a)] \cosh(q_2 a);\end{aligned}$$

$$a_1 \equiv D_1(\Gamma_\infty p + k_{d1} + k_{d2});$$

$$a_2 \equiv k_{a1}(\Gamma_\infty D_1 q_1 + k_{d2} q_1^{-1});$$

$$a_3 \equiv k k_{a2}(\Gamma_\infty D_1 q_1 + k_{d1} q_1^{-1});$$

$$a_4 \equiv k\Gamma_\infty k_{a1}k_{a2};$$

$$k \equiv (D_1/D_2)^{1/2};$$

$$I_{1,i+1} \equiv \frac{1}{2\pi i}\int_{x_1-i\infty}^{x_1+i\infty}[\bar{c}_{1,i}(\sigma)]_{x=0}\bar{\theta}_{,i}(p-\sigma)\mathrm{d}\sigma;$$

$$I_{2,i+1} \equiv \frac{1}{2\pi i}\int_{x_2-i\infty}^{x_2+i\infty}[\bar{c}_{2,i}(\sigma)]_{x=0}\bar{\theta}_{,i}(p-\sigma)\mathrm{d}\sigma,$$

where the subscript i designates the ith perturbation, provided $I_{1,0}=I_{2,0}=0$.

$\bar{c}_{1,i}$, $\bar{c}_{2,i}$, and $\bar{\theta}_{,i}$ are single-valued functions of an arbitrary complex number of p; the inversion to the original functions by the Inversion Theorem, like the integrals of non-linear terms ($I_{1,i}$, $I_{2,i}$), includes only the pole-effects, according to Cauchy's Residue Theorem.

$\bar{c}_{1,i}$, $\bar{c}_{2,i}$, and $\bar{\theta}_{,i}$ have only simple poles at $p=0$ and $p=-D_1\alpha_m^2$, where $\pm\alpha_m$ ($m=1, 2, \cdots$) are the roots (generally complex) of

$$\begin{aligned}&[b_1 \sin(a\alpha) + b_2 \cos(a\alpha)] \sin(ka\alpha)\\ &\quad + [b_3 \sin(a\alpha) + b_4 \cos(a\alpha)] \cos(ka\alpha) = 0,\end{aligned} \tag{16}$$

where:
$$b_1 \equiv D_1(\Gamma_\infty D_1\alpha^2 - k_{d1} - k_{d2});$$
$$b_2 \equiv -k_{a1}(\Gamma_\infty D_1\alpha - k_{d2}\alpha^{-1});$$
$$b_3 \equiv -k k_{a2}(\Gamma_\infty D_1\alpha - k_{d1}\alpha^{-1});$$
$$b_4 \equiv k\Gamma_\infty k_{a1}k_{a2}.$$

Inversion to the original functions gives:

$$\begin{aligned}c_{1,i} &= k_{a2}k_{d1}A + 2\sum_{n=1}^{\infty}[\boldsymbol{D}']^{-1}[\xi_{1,i}\sin(ka\alpha_n)\\ &\quad + \eta_{1,i}\cos(ka\alpha_n)]\cos[(a+x)\alpha_n]\exp(-D_1\alpha_n^2 t);\end{aligned} \tag{17}$$

$$\begin{aligned}c_{2,i} &= k_{a1}k_{d2}A + 2\sum_{n=1}^{\infty}[\boldsymbol{D}']^{-1}[\xi_{2,i}\sin(a\alpha_n)\\ &\quad + \eta_2\cos(a\alpha_n)]\cos[k(a-x)\alpha_n]\exp(-D_1\alpha_n^2 t);\end{aligned} \tag{18}$$

$$\begin{aligned}\theta_{,i} &= k_{a1}k_{a2}A - 2\Gamma_\infty^{-1}\sum_{n=1}^{\infty}[\alpha_n\boldsymbol{D}']^{-1}\{[\xi_{1,i}\sin(ka\alpha_n)\\ &\quad + \eta_{1,i}\cos(ka\alpha_n)]\sin(a\alpha_n) + [\xi_2\sin(a\alpha_n)\\ &\quad + \eta_{2,}\cos(a\alpha_n)]k^{-1}\sin(ka\alpha_n)\}\exp(-D_1\alpha_n^2 t);\end{aligned} \tag{19}$$

$$A \equiv [a(k_{a1}k_{d2}+k_{a2}k_{d1}) + \Gamma_\infty k_{a1}k_{a2}]^{-1}[a(c_{10}+c_{20}) + \Gamma_\infty\theta);$$

$$\begin{aligned}\boldsymbol{D}' &\equiv [\phi_1\sin(a\alpha_n) + \phi_2\cos(a\alpha_n)]\sin(ka\alpha_n)\\ &\quad + [\phi_3\sin(a\alpha_\mathrm{n}) + \phi_4\cos(a\alpha_\mathrm{n})]\cos(ka\alpha_\mathrm{n});\end{aligned}$$

$$\begin{aligned}\phi_1 &\equiv -\Gamma_\infty D_1[2D_1 + a(k_{a1} + k^2{}_{a2})]\\ &\quad + a\alpha_n^{-2}(k_{a1}k_{d2} + k^2 k_{a2}k_{d1});\end{aligned}$$

$$\begin{aligned}\phi_2 &\equiv -\Gamma_\infty D_1^2 a\alpha_n + \alpha_n^{-1}\{a[k^2\Gamma_\infty k_{a1}k_{a2} + D_1(k_{d1}+k_{d2})]\\ &\quad + \Gamma_\infty k_{a1}D_1\} + k_{a1}k_{d2}\alpha_n^{-3};\end{aligned}$$

$$\begin{aligned}\phi_3 &\equiv k(-\Gamma_\infty D_1^2 a\alpha_n + \alpha_n^{-1}a[\Gamma_\infty k_{a1}k_{a2} + D_1(k_{d1}+k_{d2})]\\ &\quad + \Gamma_\infty k_{a2}D_1\} + k_{a2}k_{d1}\alpha_n^{-3});\end{aligned}$$

$$\phi_4 \equiv ka[\Gamma_\infty D_1(k_{a1}+k_{a2}) - \alpha_n^{-2}(k_{a1}k_{d2}+k_{a2}k_{d1})];$$

$$\begin{aligned}\xi_{1,i} &\equiv -\Gamma_\infty D_1\alpha_n^{-1}[k_{a1}(c_{10}+D_1\alpha_n^2 I_{1,i}) - k_{d1}\theta_0\\ &\quad + \alpha_n^{-3}[k_{a1}k_{d2}(c_{10}+D_1\alpha_n^2 I_{1,i})\\ &\quad - k_{a2}k_{d1}(c_{20}+D_1\alpha_n^2 I_{2,i})];\end{aligned}$$

$$\eta_{1,i} \equiv k\Gamma_\infty k_{a2}\alpha_n^{-2}[k_{a1}(c_{10}+D_1\alpha_n^2 I_{1,i}) - k_{d1}\theta_0];$$

$$\begin{aligned}\xi_{2,i} &\equiv -k\{\Gamma_\infty D_1\alpha_n^{-1}[k_{a2}(c_{20}+D_1\alpha_n^2 I_{2,i}) - k_{d2}\theta_0]\\ &\quad + \alpha_n^{-3}[k_{a1}k_{d2}(c_{10}+D_1\alpha_n^2 I_{1,i})\\ &\quad - k_{a2\ d1}(c_{20}+D_1\alpha_n^2 I_{2,i})]\};\end{aligned}$$

$$\eta_{2,i} \equiv k\Gamma_\infty k_{a1}\alpha_n^{-2}[k_{a2}(c_{20}+D_1\alpha_n^2 I_{2,i}) - k_{d2}\theta_0],$$

where $I_{1,i}$ and $I_{2,i}$ are the values[6)] at $p=-D_1\alpha_n^2$.

The amounts of the solute in Phase 1 and Phase 2 per unit of area of the interface are represented as:

$$\begin{aligned}Q_1 &= \int_{-a}^{0} c^*{}_1\mathrm{d}x = k_{a2}k_{d1}aA\\ &\quad + 2\sum_{n=1}^{\infty}[\boldsymbol{D}']^{-1}[\xi^*{}_1\sin(ka\alpha_n) + \eta^*{}_1\cos(ka\alpha_n)]\alpha_n^{-1}\\ &\quad \times \sin(a\alpha_n)\exp(-D_1\alpha_n^2 t);\end{aligned} \tag{20}$$

$$\begin{aligned}Q_2 &= \int_{0}^{a} c^*{}_2\mathrm{d}x = k_{a1}k_{d2}aA\\ &\quad + 2\sum_{n=1}^{\infty}[\boldsymbol{D}']^{-1}[\xi^*{}_2\sin(a\alpha_n) + \eta^*{}_2\cos(a\alpha_n)](k\alpha_n)^{-1}\\ &\quad \times \sin(ka\alpha_n)\exp(-D_1\alpha_n^2 t),\end{aligned} \tag{21}$$

where the superscript $*$ indicates the convergence value.

Remarks on the Application

Figures 1 and 2 show the time-dependences of the transfer amount of the solute and of the coverage of the interface giving hypothetical values to the parameters in Eqs. (21) and (19). Sample 1 corresponds to the case of less interfacial resistance ($\Delta F^{\neq}{}_{di} \sim 4$ kcal/mol), and Samples 2 and 3, to the cases of a distinct interfacial resistance ($\Delta F^{\neq}{}_{di} \sim 16$ kcal/mol), where $\Delta F^{\neq}{}_{di}$ is the activation free energy of desorption from interface into the ith phase.[7)] The dotted curve gives the relation obtained by the usual equation of the semi-infinite composite medium. The equilibrium transfer-amount is computed to be 1.5×10^{-6} mol/cm^2.

The values of the rate constants of adsorption and desorption are given by the following equations:[7)]

$$k_{ai} = \lambda_i\frac{\boldsymbol{k}T}{\boldsymbol{h}}\exp(-\Delta F^{\neq}{}_{ai}/\boldsymbol{R}T);$$

$$k_{di} = \Gamma_\infty\frac{\boldsymbol{h}T}{\boldsymbol{h}}\exp(-\Delta F^{\neq}{}_{di}/\boldsymbol{R}T);$$

$i=1$ and 2, where λ_i ($\sim$10 Å) is the length of the adsorption path from the boundary site of phase i to the interface; $\Delta F^{\neq}{}_{ai}$ is the activation free energy of adsorption from phase i to the interface; $\boldsymbol{k}$ is the Boltzmann constant; $\boldsymbol{h}$ is the Planck constant; $\boldsymbol{R}$ is the gas constant, and T ($\sim$300 K) is the absolute temperature.

The procedure of calculation is as follows.

Assign definite values to k, D_1, Γ_∞, a, k_{a1}, k_{a2}, k_{d1}, and k_{d2} in Eq. (16), and find the positions of the pole on the plane of the complex variable, p. Although the roots of Eq. (16), α_m ($m=1, 2, \cdots$), are generally complex, they are real in our case.

Assign the values to k, D_1, Γ_∞, a, k_{a1}, k_{a2}, k_{d1}, k_{d2}, c_{10}, c_{20}, θ_0, and α_n's ($n \leq 20$ suffices for convergence in our case if $t > 1$ s) in Eqs. (21) and (19), and compute the amount of the solute in Phase 2, Q_2, and the coverage, θ, as functions of the time, t. In our case, $\theta \sim 0.005 \ll 1$, and the Q_2 and the θ were computed approximately by means of the zero perturbation (see Eqs. (4) and (5)).

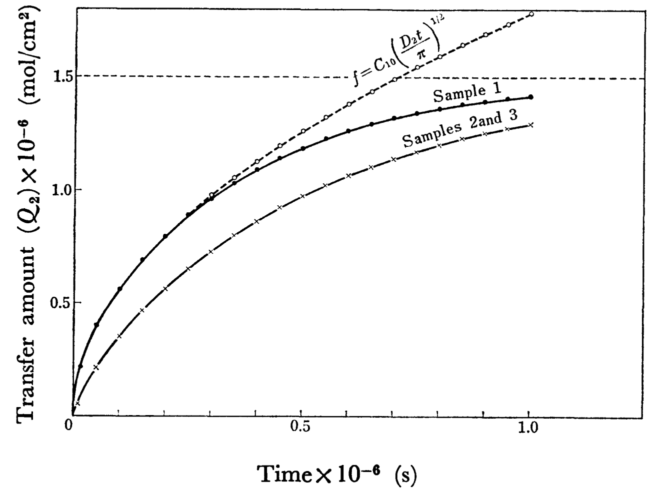

Fig. 1. Time dependences of the transfer amount.

Sample		1	2	3
k	[−]	1	1	1
D_1	[cm²/s]	10^{-5}	10^{-5}	10^{-5}
Γ_∞	[mol/cm²]	7×10^{-10}	7×10^{-10}	7×10^{-10}
a	[cm]	3	3	3
k_{d1}	[mol/(cm²) s]	1	10^{-9}	5×10^{-9}
k_{d2}	[mol/(cm²) s]	1	5×10^{-9}	10^{-9}
k_{a1}	[cm/s]	10^4	10^{-5}	5×10^{-5}
k_{a2}	[cm/s]	10^4	5×10^{-5}	10^{-5}
C_{10}	[mol/cm³]	10^{-6}	10^{-6}	10^{-6}
C_{20}	[mol/cm³]	0	0	0
θ_0	[−]	0	0	0

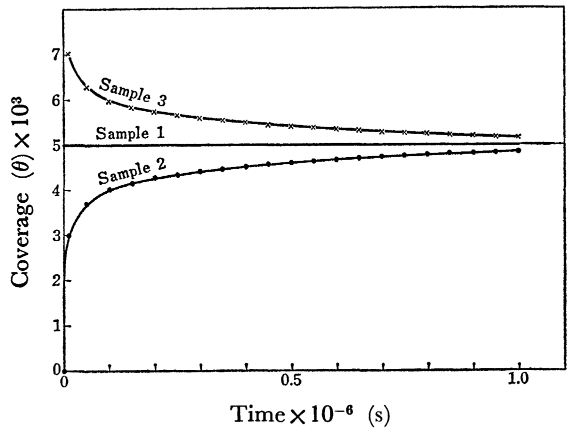

Fig. 2. Time dependences of the coverage of interface.

The curves of Samples 2 and 3 are distinctly below the curve of Sample 1 in Fig. 1, suggesting the possibility of the determination of the interfacial resistances (of this magnitude) by experimental observations of the time-dependence of the transfer amount.

The curves of Samples 2 and 3 are degenerate to a single curve in Fig. 1, indicating the impossibility of the determination of k_{d1} and k_{d2}[8] separately by the same experiment.

On the contrary, the curves of Samples 2 and 3 are greatly separated from each other, and the signs of the tangent differ in a short time in Fig. 2, suggesting the possibility of the determination of the rate-controlling step of desorption by an observation of the interfacial tensions for early stages.

On reflection, the manipulative disturbance on bringing two layers into contact for a transfer experiment may not strictly be avoidable; also, a spontaneous turbulence[9] is likely to occur near the touching time of two layers. These disturbances may generally accelerate the transfer of the solute. We must consider the effect of these disturbances on the analysis of the experimental data.

Suppose that an abnormally swift transfer ceases by $t=\Delta t$, and that the final condition of concentration is approximately given by $c_1=c'_{10}$, $-a<x<0$, $t=\Delta t$; $c_2=c'_{20}$, $0<x<a$, $t=\Delta t$; $\theta=\theta'_0$, $x=0$, $t=\Delta t$, where c'_{10}, c'_{20}, and θ'_0 are constants.

Let the origin of time be transferred to $t=\Delta t$, so that Eq. (21) is applicable.

The rate-controlling step of desorption may be conventionally set up on the side of second phase (for example), by virtue of the exchangeability of the values of k_{d1} and k_{d2}; when k_{d1} is sufficiently greater than k_{d2}, $c'_{10}=c'_{10}(c'_{20})$, and $\theta'_0=\theta'_0(c'_{20})$.

Consequently we may obtain approximate values of k_{di} ($i=1$ or 2), evaluated under the name of k_{d2} in Eq. (21), and c'_{20} by means of experimental determinations of the transfer amount through an interface at each contact time $t(\gg\Delta t)$. The following results of computation show the extent of approximation: $k_{d1}=5\times10^{-9}$ mol/cm² s, $k_{d2}=0.999\times10^{-9}$ mol/cm² s, $c'_{20}=1.001\times10^{-7}$ mol/cm³; $k_{d1}=1$ mol/cm² s, $k_{d2}=0.833\times10^{-9}$ mol/cm² s, $c'_{20}=1.001\times10^{-7}$ mol/cm³ ($k=(D_1/D_2)^{1/2}=1$, $D_1=10^{-5}$ cm²/s, $\Gamma_\infty=7\times10^{-10}$ mol/cm², $a=3$ cm, $K_1=k_{a1}/k_{d1}=10^4$ cm³/mol, $K_2=k_{a2}/k_{d2}=10^4$ cm³/mol, $c_{10}=10^{-6}$ mol/cm³, $c_{20}=\theta_0=0$, $t(1)=5\times10^5$ s, $t(2)=10^5$ s, $Q_2(1)=1.080\times10^{-6}$ mol/cm², $Q_2(2)=5.825\times10^{-7}$ mol/cm²).

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4) T. Shimbashi and T. Shiba, This Bulletin, **38**, 581, 588 (1965).

5) The diffusion in the composite spherical system can also be treated in the same way.

6) The calculation of $I_{1,t}$ and $I_{2,t}$ is easy but somewhat lengthy including the double poles, and so it is omitted here.

7) T. Shimbashi and T. Shiba, This Bulletin, **38**, 572 (1965).

8) k_{a1} and k_{a2} are to be shown as functions of k_{d1} and k_{d2} respectively, provided the equilibrium constants of adsorption are known.

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