A Theoretical Analysis of Some Interrelationships and Mechanisms of Heat and Mass Transfer in Dispersions

BENJAMIN GAL-OR and VERNON WALATKA
Johns Hopkins University, Baltimore, Maryland

Some of the main interrelationships that govern heat and mass transfer in dispersions are considered. Qualitative and quantitative analyses of the effects of holdup, average residence time, surface active agents, viscosity, and average particle size on transfer rates are made for two major domains. In the first domain a convective mass transfer model is formulated for the case of low dispersed phase holdup values and a steady motion of a swarm of bubbles with clean interfaces. A second domain is established for high dispersed phase holdup values and fine dispersions that contain surfactants. A semidynamic model for unsteady state heat (or mass) transfer from a swarm of droplets in a multistage liquid-liquid disperser is demonstrated in this domain by a simultaneous solution of two differential equations (one for each phase).

Most theoretical studies of heat and mass transfer in dispersions have been limited to studies of one phase and to the case of a steady motion of a *single* spherical droplet under the influence of gravity in a clean system. It is clear, however, that *swarms* of suspended droplets which are entrained by turbulent eddies have relative velocities (with respect to the continuous phase) which are different from those derived for the case of a steady rise of a *single* droplet. This is mainly due to the fact that in the case of a swarm of particles, the distributions of velocities, temperatures, and concentrations in the vicinity of one particle are influenced by its neighbors. It is therefore logical to assume that in the case of dispersions, the relative velocities and transfer rates depend on quantities characterizing a swarm of droplets. For the case of uniformly distributed particles, the dispersed phase volume fraction Φ, particle size distribution, and residence time distribution are such quantities.

In this study we first consider the main interrelationships that govern heat and mass transfer in dispersions and then we make qualitative and quantitative analyses of the effects of holdup, contact time, surface active agents, viscosity, and particle size on the transfer rates.

INTERRELATIONSHIPS AND INTERACTIONS IN DISPERSIONS

The pertinent equation in the case of unsteady state diffusion with simultaneous chemical reaction in dilute solutions of one component with constant ρ and D is

$$D_p \nabla^2 c_p = \bar{v} \cdot \nabla c_p + R^*_p + \partial c_p / \partial t \qquad (1)$$

where the subscript P refers to each of the corresponding phases involved. In the case of dispersions, where swarms of particles are moving with different local velocity components relative to an arbitrary moving fluid, the question arises as to the function of $\bar{v}$, the velocity vector relative to an arbitrary moving continuous phase. In general, the magnitude of the local relative velocity of a drop or bubble to a continuous phase in a dispersion may be expressed as (*16, 11*)

$$U_{\text{dispersion}} = \psi(\mu_c, \mu_d, \rho_c, \rho_d, a_\phi, g, t, \Phi, \Gamma, \sigma, P_v, \sum_i \overline{J_i}\, \overline{X_i}) \qquad (2)$$

Coupling effects between, say, a diffusion flux of surfactants and momentum flux may arise since dispersions are nonisotropic media (*1*). Hence, the possibilities of coupling between fluxes that differ from each other by an odd tensorial rank exist (*26*). These effects should depend on the magnitude of J_i, X_i, Γ, and Φ values.

The dispersed phase holdup fraction is responsible also for other important interactions. These are indicated by

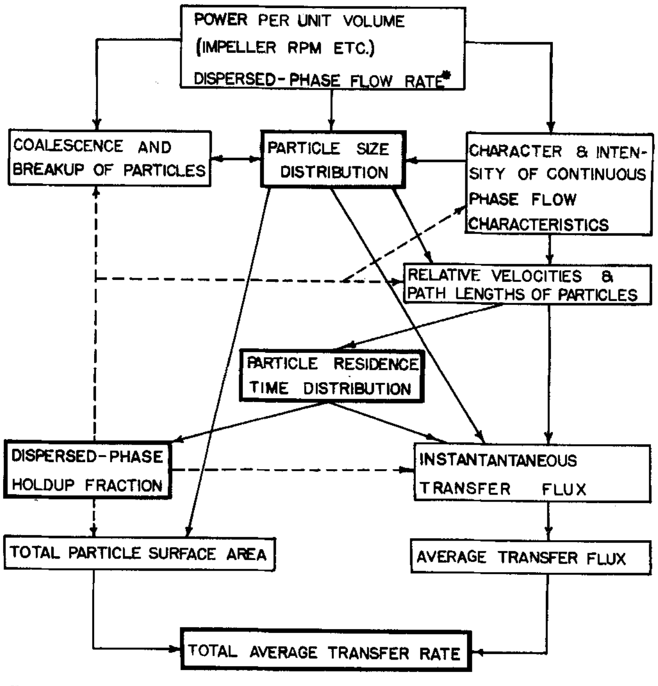

Fig. 1. Qualitative description of the main interrelationships in a given dispersion. Other intermediate phenomena, such as the direct and feedback effects between coalescence and transfer fluxes, are not shown. *In this case Φ increases mainly as a result of higher numbers of produced particles that are proportional to the dispersed-phase flow rate (*6,16*).

Benjamin Gal-Or is at the University of Pittsburgh, Pittsburgh, Pennsylvania.

the dashed lines of Figure 1, which show the main interrelationships that govern the total transfer rate in a given dispersion. Some of these interrelationships have been estimated recently by using mathematical models (*6, 7, 27*).

EFFECT OF HOLDUP ON CONVECTIVE MASS TRANSFER (DOMAIN 1: LOW Φ VALUES AND CLEAN INTERFACES)

The effect of Φ on the steady velocity of a swarm of spherical bubbles has been recently evaluated by Marrucci (9) by using a spherical cell model of radius b, such that

$$b = a\,\Phi^{-1/3} \tag{3}$$

and considering irrotational flow between two concentric spheres exhibiting a relative velocity U as was treated by Lamb (2). Marrucci showed that the effect of dispersed phase holdup can thus be expressed as

$$U_{\text{swarm}} = U_{\text{single}} \cdot (1-\Phi)^2/(1-\Phi^{5/3}) \tag{4}$$

His recent experimental work (*10*) shows that U_{swarm} can be predicted approximately by Equation (4).

Let us now consider the effect of dispersed phase holdup [Equation (4)] on the diffusional flux to a clean bubble surface for a group of bubbles rising steadily under the influence of gravity in a liquid medium. Neglecting the resistance to mass transfer in the gas phase and considering the case of $N_{Re} < 1$ and incompressible axisymmetric flow, Levich (*1*) obtained

$$N_A^* = \left[\frac{D\,\mu_c\,U}{2a(\mu_c+\mu_d)}\right]^{1/2} \cdot \sqrt{\frac{3}{\pi}} \cdot \frac{1+\cos\theta}{\sqrt{2+\cos\theta}}\,(c_o - c_i) \tag{5}$$

The average diffusional flux is obtained by dividing the total mass transfer rate from the entire surface of the bubble by its entire surface:

$$\overline{N}_A = \int_o^{2\pi}\int_o^{\pi} N_A^*\, a^2 \sin\theta\, d\phi\, d\theta/4\pi a^2$$
$$= \frac{2}{\sqrt{6\pi}}\left[\frac{D\,\mu_c\,U}{a(\mu_c+\mu_d)}\right]^{1/2}(c_o - c_i) \tag{6}$$

Substituting Equation (4) in Equation (6) together with Levich's solution for a single bubble velocity (*1*)[†]

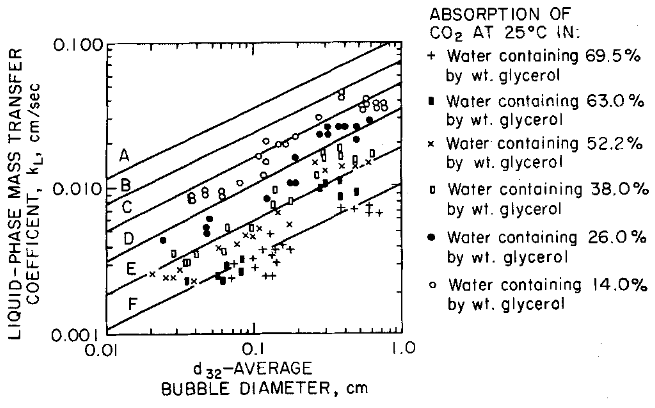

Fig. 2. Comparison of Equation (8) with experimental data of Calderbank and Moo-Young (*4*). Capital letters represent the following concentrations of glycerol: *A*, 14%; *B*, 26.0%; C, 38.0%; *D*, 52.2%; *E*, 63.0%; *F*, 69.5%.

$$U_{\text{single}} = \frac{1}{9}\,\rho_c\,\frac{g\,a^2}{\mu_c} \tag{7}$$

and neglecting gas viscosity, we get

$$(k_L)_{\text{swarm}} = \frac{\overline{N}_A}{c_o - c_i}$$
$$= 0.154\left[\frac{D\,\rho_c\,g}{\mu_c}\right]^{1/2} \cdot \frac{1-\Phi}{\sqrt{1-\Phi^{5/3}}}\sqrt{a_{32}} \tag{8}$$

Here the variable particle size a is replaced by a_{32}. The reason for the replacement is based on a recent study (*7, 8*) on the effect of particle size distribution on mass transfer in dispersions. As a check of Equation (8) the experimental data of Calderbank and Moo-Young (*4*) for mass transfer in dispersions were used (Figure 2). The results of applying their data for D, μ_c, ρ_c, a_{32}, and Φ (*4, 13, 14*) to Equation (8) are shown as solid lines in Figure 2, indicating that their k_L values for large and small bubbles, including what they defined as a *transition region*, are generally predicted by Equation (8). This result is in contradiction with the conclusion of Calderbank and Moo-Young that k_L is not a function of the bubble size. Equation (8), however, predicts some higher values than the observed data, in particular for water-glycerol solutions containing lower concentration of glycerol. The remaining disagreement between Equation (8) and the experimental data can be explained by the presence of minute amounts of surface active impurities in all but the most extraordinarily purified systems.

EFFECT OF SURFACE ACTIVE AGENTS ON DROP VELOCITY (EXTENSION OF DOMAIN 1 TO HIGH-VISCOSITY FLUIDS THAT CONTAIN SURFACTANTS)

The effect of surfactants on the velocity of a drop has been obtained by Levich (*1*) by assuming that surfactants are soluble only in the continuous phase. Neglecting orientation and relaxation processes at the interface, he obtained

$$U_{\text{single}} = \frac{2}{3} \cdot \frac{(\rho_c - \rho_d)\,g\,a^2}{\mu_c} \cdot \frac{\mu_c + \mu_d + \gamma}{2\mu_c + 3\mu_d + 3\gamma} \tag{9}$$

in which γ is the surface retardation coefficient due to interference with surfactants. Equation (9) shows that adventitious surfactant impurities will not influence U (and accordingly the transfer rate will remain unaffected) when

$$\mu_c + \mu_d >> \gamma \tag{10}$$

Therefore, if the effect of molecular blocking (reduction of transfer through the interface due to the *presence* of surfactants) is very small compared with the retardation effect, the experimental data of mass or heat transfer in high viscosity fluids that contain adventitious surfactants should agree with the theories of *clean* interfaces. Consequently, Equation (8) should also apply to this domain, and indeed, better agreement between Equation (8) and the experimental data of Figure 2 is observed with increased glycerol viscosity. Calderbank and Moo-Young's work was probably influenced by very small traces of surfactants that are present, as stated above, in all but the most extraordinarily purified system.

EFFECT OF HOLDUP ON HEAT (OR MASS) TRANSFER IN LIQUID-LIQUID DISPERSER (DOMAIN 2: HIGH Φ VALUES AND PRESENCE OF SURFACTANTS)

Experiments with fluids that have clean interfaces are relatively rare in actual practice. Many unsuspected im-

---

[†] Despite some errors in deriving this equation, his result was later confirmed with some minor improvements (*3, 9*).

purities in a system can be surface active agents and even the equipment *itself* can supply enough to change the results. Hence, much of the experimental data reported in the literature must be used with caution due to an absence of information regarding the purity of the fluid used. The transfer coefficient in the presence of surfactants may be reduced by a factor of 1.5 to 2.2 (*19* to *21*). Adventitious surfactants have also a marked effect on the mechanism of coalescence (*17*). Davies et al. (*20*) found a limit to the reduction of k_L with increased concentration of surfactants. This is in agreement with Lindland and Teriesen (*18*), who found that after a small concentration of surfactant had been used, further additions caused but little change in terminal velocity.

Therefore, for obtaining good reproducibility, the design of the experimental work should be considered under such contamination degree that adventitious fluctuations in surfactant impurities will cause no further change of the transfer coefficient. Protein contamination degree of 1 mg./sq. m. of interface or higher is enough to obtain constant k_L values (*20*). Hence, most laboratory and all industrial operations cannot be analyzed theoretically as if their surfaces were those of pure fluids.

To analyze the effect of surfactants on convective transfer, we rewrite Equation (9) as

$$U_{\text{single}} = 3\, U_{\text{Stokes}} \cdot (\mu_c + \mu_d + \gamma)/(2\mu_c + 3\mu_d + 3\gamma) \tag{11}$$

The retardation coefficient can be expressed as (*1*)

$$\gamma = \left\{ 2\Gamma_O/3a \left[\frac{\partial P^*}{\partial \Gamma} - \frac{\partial Q^*}{\partial \Gamma} \right] \right\} \cdot \frac{\partial \sigma}{\partial \Gamma} \tag{12}$$

when the adsorption on the surface is the controlling rate, or as

$$\gamma = 2\, RT\, \Gamma_O^2 \overline{\delta}/3\, D_S\, a\, c^o \tag{13}$$

when the diffusion of surfactants from the liquid bulk to the surface is the controlling rate.

Equations (11), (12), and (13) show that as a decreases, the quantity of surfactants necessary to make the droplet behave like a *solid* particle becomes smaller. Hence, we assume that most industrial dispersions (small and medium size particles in liquid-liquid and gas-liquid dispersions) behave essentially as a dispersion of solid particles. Under these circumstances, we may estimate ($U_{\text{dispersion}}$) by using Happel's free surface model (*22*) for sedimentation, which predicts

$$U_{\text{swarm}} = U_{\text{Stokes}} \cdot \{3 - 9/2\, \Phi^{1/3} + 9/2\, \Phi^{5/3} - 3\, \Phi^2\}/\{3 + 2\, \Phi^{5/3}\} \tag{14}$$

For equal volumes of dispersed and continuous phases in a dispersion ($\Phi = 0.5$), Equation (14) predicts that the Stokes velocity of the particle (which is already very small for relatively fine dispersions) should be reduced by a factor of 38. Consequently, for the purpose of the analysis of relatively fine dispersions in actual practice, we assume that the particles are *completely entrained* by *eddies of the continuous phase* resulting in a *negligible convective transfer*. However, unsteady state transfer, as well as the effect of a swarm of particles and the resistance of both phases, will be included in the following analysis.

Let us consider now a case of heat (or mass) transfer in a liquid-liquid dispersion with relatively high Φ values and in the presence of adventitious surfactant impurities. The concentration of droplets in the dispersion is given by

$$N_V = \frac{3}{4} \cdot \frac{\Phi}{\pi\, (a_v)^3} \tag{15}$$

in which a_v is the mean volume radius defined by

$$a_v = \left\{ \sum_{i=1}^{N} n_i a_i^3 \Big/ \sum_{i=1}^{N} n_i \right\}^{1/3} \tag{16}$$

To solve this problem we shall use some principles of mathematical models that have been introduced by Gal-Or and Resnick (*6, 15*) and Gal-Or and Hoelscher (*7*). However, for this case the interfacial temperature will not be taken as a constant due to the small heat capacity of the droplet. Consequently, two differential equations should be solved simultaneously (one for each phase) with the appropriate initial and boundary conditions.

Description of Model

The general system to be considered is that in which heat is transferred between small drops and an agitated liquid in a multistage, continuous operation as described in Figure 3. Under constant operating conditions (and after a pseudo steady state has been established) the number of drops in each stage at any instant is time invariant and their total volume (holdup) is equal to $Q^j \overline{\theta}^j$, where $\overline{\theta}^j$ is the average residence time of the drops in the continuous phase of stage j ($j = 1, 2, 3, \ldots.\, r$) and Q^j is the volumetric flow rate of the dispersed phase through this stage. The number of drops in stage j at any instant would then be given by

$$V_v^j N_V^j = N^j = 3\, Q^j \overline{\theta}^j / 4\, \pi\, (a_v^j)^3 \tag{17}$$

and the volume of the continuous phase in each stage by

$$V^j = V_v^j - Q^j \overline{\theta}^j \tag{18}$$

where V_v^j is the dispersion volume in stage j. V^j is now assumed to be subdivided into a number of equal volume eddies V_L^j, equivalent to the number of drops in the stage. Each drop is then considered to be enveloped by a

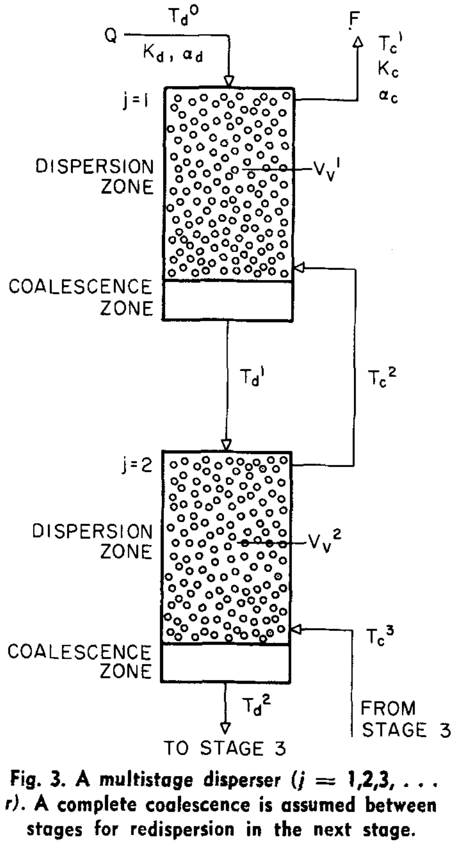

Fig. 3. A multistage disperser ($j = 1,2,3, \ldots r$). A complete coalescence is assumed between stages for redispersion in the next stage.

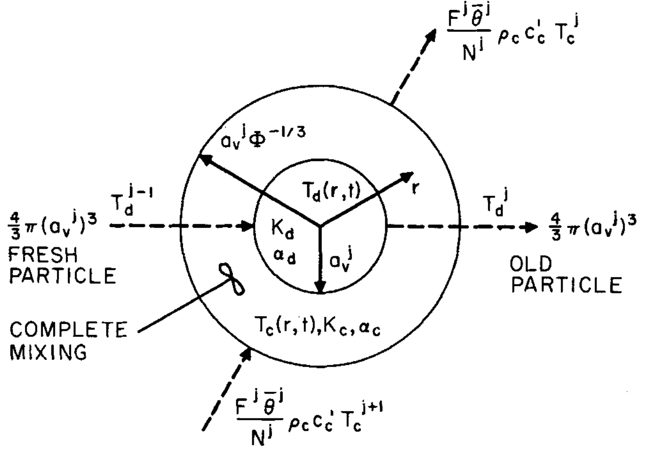

Fig. 4. Mechanism of two-phase spherical model (at $t = \bar{\theta}^j$) for stage j of the multistage disperser described in Figure 3.

spherical shell of volume V_L^j as shown in Figure 4. Thus

$$V_L^j = \frac{4(V_v^j - Q^j\bar{\theta}^j)\pi(a_v^j)^3}{3\,Q^j\bar{\theta}^j} = \frac{4}{3}\pi\,[(b^j)^3 - (a_v^j)^3] \tag{19}$$

where b^j is equal to the outer radius of the shell. From Equation (19)

$$b^j = a_v^j\,(V_v^j/Q^j\bar{\theta}^j)^{1/3} = a_v^j\,(\Phi^j)^{-1/3} \tag{20}$$

Each drop is introduced into each eddy for a retention time equal to $\bar{\theta}^j$. At $t = \bar{\theta}^j$ the drop is removed and a fresh drop is introduced. However, for this continuous operation it is assumed that a volume $F^j\bar{\theta}^j/N^j$ of a continuous phase is also removed and replaced with an equal volume of fresh continuous phase and the entire element is completely mixed (see Figure 4). It is further assumed that the actions of replacing drops and continuous phase elements and the mixing of the continuous phase take place instantaneously. Thus the contact and mixing occur alternately. Consequently each drop is contacted with a continuous phase whose initial temperature is T_c^j which under pseudo steady state conditions is constant. A change in agitation intensity or flow rates will change $\bar{\theta}^j$, Φ^j, and a_v^j and, accordingly b^j, heat transfer per unit drop area, total interfacial area, total heat transfer rate in the stage, and the average temperatures are changed. Thus, the effects of operating and system variables are indirectly interacting in this semidynamic model.

Consider the case in which Q^j, T_d^0, K_d, K_c, α_d, α_c, V_v^j, F^j, T_c^1, a_v^j, and $\bar{\theta}^j$ are known and the estimation of total heat transfer rate in each stage, T_d^j, T_c^{j+1} and number of stages necessary to perform a certain heat exchange are required. The partial differential equations (in spherical coordinates) that should be solved simultaneously according to the mechanisms of the model are

$$\alpha_d\left[\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial T_d}{\partial r}\right)\right] = \frac{\partial T_d}{\partial t};\ \frac{\partial T_d}{\partial \theta} = \frac{\partial T_d}{\partial \phi} = 0$$

$$0 \leq r \leq a_v^j \tag{21}$$

$$\alpha_c\left[\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial T_c}{\partial r}\right)\right] = \frac{\partial T_c}{\partial t};\ \frac{\partial T_c}{\partial \theta} = \frac{\partial T_c}{\partial \phi} = 0$$

$$a_v^j \leq r \leq a_v^j\,(\Phi^j)^{-1/3} \tag{22}$$

Equations (21) and (22) are simplified by the change of variables

$$Z_d = rT_d \tag{23}$$

$$Z_c = rT_c \tag{24}$$

in which T_d is finite at $r = 0$. Thus

$$\alpha_d\frac{\partial^2 Z_d}{\partial r^2} = \partial Z_d/\partial t \qquad 0 \leq r \leq a_v \tag{25}$$

$$\alpha_c\frac{\partial^2 Z_c}{\partial r^2} = \partial Z_c/\partial t \qquad a_v^j \leq r \leq a_v^j\ (\Phi^j)^{-1/3} \tag{26}$$

The continuity conditions are

$$Z_d = Z_c \text{ at } r = a_v^j \text{ for } t > 0 \tag{27}$$

and

$$K_d\left[a_v^j\frac{\partial Z_d}{\partial r} - Z_d\right] = K_c\left[a_v^j\frac{\partial Z_c}{\partial r} - Z_c\right] \tag{28}$$

at $r = a_v^j$ for $t > 0$.

The initial conditions should take into account the effect of mixing under these pseudo steady state conditions, thus

$$Z_d^j = T_d^{j-1}\cdot r \text{ at } t = 0 \text{ for } 0 \leq r < a_v^j \tag{29}$$

By changing the scale of temperature T_c^j, the initial temperature of the agitated continuous phase that each drop is contacted with, is taken as zero, yielding

$$\bar{Z}_c = 0 \text{ at } t = 0 \text{ for } a_v^j < r \leq a_v^j\ (\Phi^j)^{-1/3} \tag{30}$$

and the midway bulk temperature among the eddies

$$\bar{Z}_c = 0 \ \text{ at } \ r = a_v^j(\Phi^j)^{-1/3} \text{ for } \ t \geq 0 \tag{31}$$

where the bar refers to a reduced temperature scale. When the temperature scale in Equations (21) to (29) is readjusted, the solution for Equations (25) and (26) with Equations (27) to (31), and finite $\bar{T}_d$ at $r = 0$ is (23)†

$$\bar{T}_d = \frac{2\,a_v^j\,\bar{T}_d^{j-1}}{r}\sum_{n=1}^{\infty}\frac{\sin^2[\lambda_n a_v^j\{(\Phi^j)^{-1/3} - 1\}]}{f(\Phi^j, a_v^j, \alpha_d, \alpha_c)}\cdot$$

$$\left[\frac{\sin\psi\lambda_n a_v^j}{\psi\lambda_n a_v^j} - \cos\psi\lambda_n a_v^j\right]\cdot$$

$$(\sin\psi\lambda_n r)\exp[-\alpha_c\lambda_n^2 t] \tag{32}$$

in which

$$f(\Phi^j, a_v^j, \alpha_\alpha, \alpha_c) = \psi\lambda_n a_v^j\sin^2\lambda_n a_v^j\,[(\Phi^j)^{-1/3} - 1]$$

$$+\ \gamma^*\lambda_n a_v^j\,[(\Phi^j)^{-1/3} - 1]\cdot\sin^2\psi\lambda_n a_v^j$$

$$+\ \frac{\psi\gamma^* - 1}{\psi\lambda_n a_v^j}\sin^2\psi\lambda_n a_v^j\cdot\sin^2\lambda_n a_v^j\,[(\Phi^j)^{-1/3} - 1] \tag{33}$$

$$\psi = (\alpha_c/\alpha_d)^{1/2},\ \gamma^* = K_c/K_d\,\psi \tag{34}$$

and where λ_n are the nth positive roots of

$$\sin\lambda a_v^j\,[(\Phi^j)^{-1/3} - 1]\{\psi\lambda a_v^j\cos\psi\lambda a_v^j - \sin\psi\lambda a_v^j\}$$

$$+\ \psi\gamma^*\sin\psi\lambda a_v^j\,\{\lambda a_v^j\cos\lambda a_v^j\,[(\Phi^j)^{-1/3} - 1]$$

---

† A minor mistake in the final solution of this reference has been corrected here.

$$+ \sin \lambda\, a_v^j \,[(\Phi^j)^{-1/3} - 1]\} = 0 \quad (35)$$

when $\psi/[(\Phi^j)^{-1/3} - 1]$ is irrational.

A check of Equation (32) and the roots of Equation (35) has been done with an IBM 7094 to prove that at $t = 0$

$$\frac{1}{r} \sum_{n=1}^{\infty} \sin \psi \lambda_n r = \text{constant} \qquad (35a)$$

For the case of water-light oil system, for example, about one hundred-twenty roots are needed to converge these series.

The instantaneous rate of heat transfer per unit surface area is thus given by

$$q^j(t) = -K_d(\partial \overline{T}_d/\partial r)_{r=a_v^j} = 2\,K_d \overline{T}^{j-1}$$

$$\sum_{n=1}^{\infty} \frac{\sin^2 \lambda_n a_v^j \,[(\Phi^j)^{-1/3} - 1]}{f(\Phi^j, a_v^j, \alpha_c, \alpha_d)} \cdot \left\{ \frac{\sin \psi \lambda_n a_v}{\psi \lambda_n a_v^j} - \cos \psi \lambda_n a_v^j \right\}$$

$$\exp[-\lambda_n^2 \alpha_c t] \left[\frac{\sin \psi \lambda_n a_v^j}{a_v^j} - \psi \lambda_n \cos \psi \lambda_n a_v^j \right] \qquad (36)$$

Applying the conclusions of Hanratty (5) in regard to the average residence time of the drops, we can estimate the average rate of heat transfer per unit surface area under the pseudo steady state condition by

$$\overline{q}^j = \int_0^{\overline{\theta}^j} \left[-K_d \left(\frac{\partial \overline{T}_d}{\partial r} \right)_{r=a_v^j} \right] dt \Big/ \int_0^{\overline{\theta}^j} dt \qquad (37)$$

Multiplying $\overline{q}^j$ by the total interfacial area of the drops

$$A^j = 4 N^j \pi (a_v^j)^2 = \frac{3\, Q^j \overline{\theta}^j}{a_v^j} \qquad (38)$$

we obtain the total average rate of heat transfer in stage *j*:

$$\overline{Q}_T^j = \frac{6\, Q^j K_d \overline{T}_d^{\,j-1}}{a_v^j} \sum_{n=1}^{\infty} \frac{\sin^2 \lambda_n a_v^j \,[(\Phi^j)^{-1/3} - 1]}{f(\Phi^j, a_v^j, \alpha_c, \alpha_d)}$$

$$\left\{ \frac{\sin \psi \lambda_n a_v^j}{\psi \lambda_n a_v^j} - \cos \psi \lambda_n a_v^j \right\} \cdot \left\{ \frac{\exp[-\alpha_c \lambda_n^2 \overline{\theta}^j]}{\alpha_c \lambda_n^2} \right\}$$

$$\{\psi \lambda_n \cos \psi \lambda_n a_v^j - (\sin \psi \lambda_n a_v^j)/a_v^j\} \qquad (39)$$

The process of calculating $\overline{Q}_T^j$ should thus proceed until a certain prespecified temperature is reached or until r existing stages are completed. However, to calculate $\overline{T}_d^{j-1}$ we take into account a complete coalescence of drops prior to redispersion in the next stage. A heat balance then gives

$$\int_0^{a_v^j} r^2 \overline{T}_d(r, \overline{\theta}^j)\, dr = \int_0^{a_v^j} r^2\, \overline{T}_d^j\, dr \qquad (40)$$

Integrating and rearranging, we get

$$\overline{T}_d^j = \frac{6\, \overline{T}_d^{j-1}}{(a_v^j)^2} \sum_{n=1}^{\infty} \sin^2 \lambda_n a_v^j \,[(\Phi^j)^{-1/3} - 1]$$

$$\left\{ \frac{\sin \psi \lambda_n a_v}{\psi \lambda_n a_v^j} - \cos \psi \lambda_n a_v^j \right\} \frac{1}{f(\Phi^j, a_v^j, \alpha_c, \alpha_d)} \cdot$$

$$\{(\sin \psi \lambda_n a_v^j)/\psi^2 \lambda_n^2 - (a_v^j \cos \psi \lambda_n a_v^j)/\psi \lambda_n\} \qquad (41)$$

in which $\overline{T}_d^{j-1} = \overline{T}_d^o$ for the first stage.

A heat balance on the continuous phase gives

$$\overline{Q}_T^j = F^j \rho_c c_c' (T_c^j - T_c^{j+1}) \qquad (42)$$

However, in using reduced coordinates we readjust T_c^j to zero for each stage, which results in

$$T_c^{j+1} = -\overline{Q}_T^j / F^j \rho_c c_c' \qquad (43)$$

$\overline{Q}_T^j$ is a positive quantity when heat is transferred from the dispersed phase to the continuous phase and negative when the opposite process is taking place. It is clear that this model is valid also for the case of mass transfer. However, for this case the continuity condition (27) should be $Z_d = mZ_c$, where m is a constant relating the concentrations in both phases.

QUANTITATIVE ANALYSIS OF SOME INTERACTING EFFECTS

An IBM 7094 computer was employed to analyze the equations for $q^j(t)$ and $\overline{Q}_T^j$ for a case of heat transfer between light oil (dispersed phase) and water (continuous

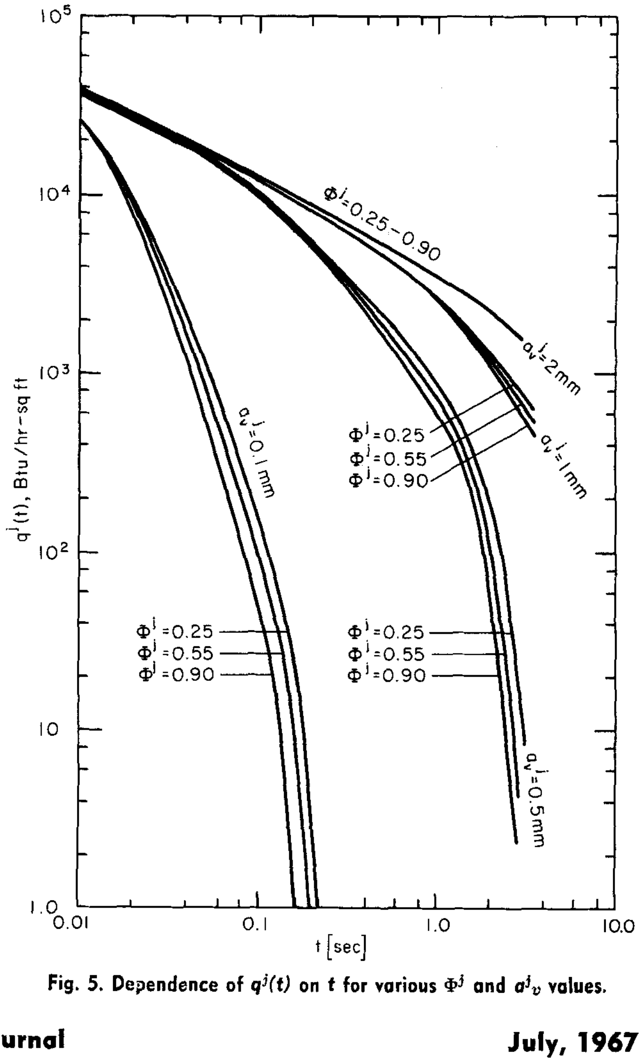

Fig. 5. Dependence of $q^j(t)$ on t for various Φ^j and a_v^j values.

phase). The following values have been used (24): light oil; $K_d = 0.074$ B.t.u./(hr.)(ft.)(°F.), $\alpha_d = 0.00269$ sq.ft./hr. water; $K_c = 0.394$ B.t.u./(hr.)(ft.)(°F.), $\alpha_c = 0.00655$ sq.ft./hr., $V_v^j = 1$ cu. ft., $T_d^o = 100°F$. The behavior of $q^j(t)$ and $\bar{Q}_T^j$ was studied as affected by changes in a_v^j, Φ^j, t, $\bar{\theta}^j$, or Q^j.

Figure 5 shows the effects of contact times and holdup fractions on the instantaneous heat transfer flux for various drop sizes. In general, this model predicts a decrease of instantaneous flux with increasing contact time, but in contradiction with the penetration theory that unrealistically predicts that $q^j(t) \rightarrow \infty$ as $t \rightarrow 0$, this model predicts a finite flux at $t = 0$. The effect of dispersed phase holdup is to decrease the instantaneous flux as Φ^j increases.[†] However, this effect is profound only for small size drops and as a_v^j reaches a value of about 2 mm., the effect of Φ^j for the range of contact times studied vanishes. This phenomenon can be explained in terms of *interaction effects* between adjacent drops in the dispersion. For a given Φ^j value, $2a_v^j\,[(\Phi^j)^{-1/3} - 1]$ (which is a yardstick for the average distance between adjacent particles in the dispersion) decreases as a_v^j decreases, causing changes in profiles of temperature between particles that decrease the flux as $2a_v^j\,[(\Phi^j)^{-1/3} - 1]$ decreases. Consequently the effects of interaction between adjacent particles with drop sizes larger than 2 mm. are negligible for relatively short contact times. However, as the contact time increases, interaction effects become significant as indicated by the instantaneous fluxes for $a_v^j = 0.1$ to 0.5 mm. Thus, mathematical models that do not take into account interaction effects as a function of Φ may introduce a considerable error.

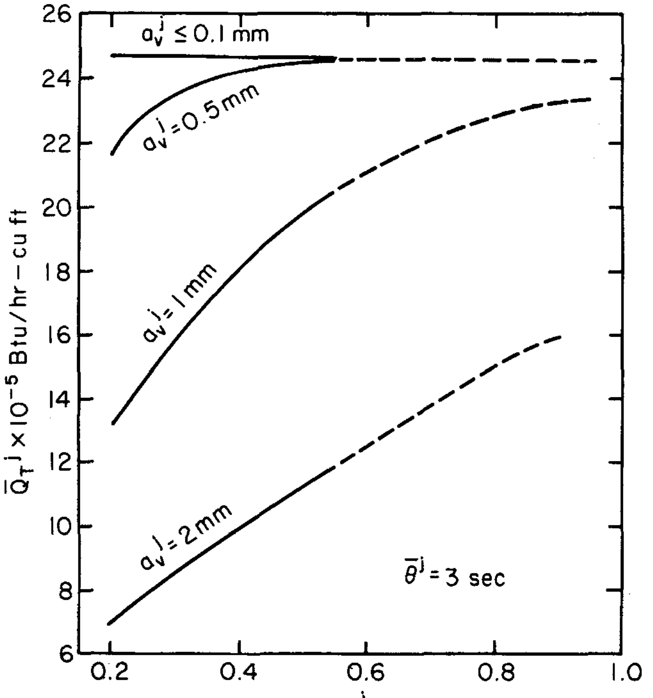

Fig. 6. Dependence of $\bar{Q}_T^j$ on Φ^j for various a_v^j values.

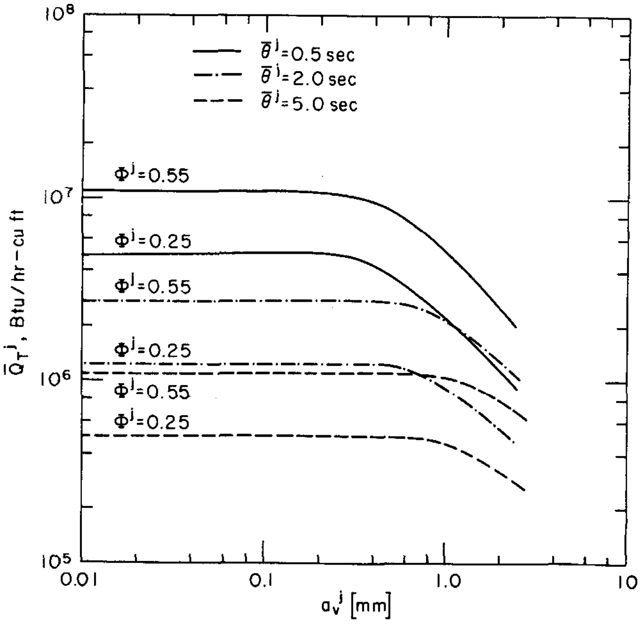

Fig. 7. Dependence of $\bar{Q}_T^j$ on a_v^j for various $\bar{\theta}^j$ and Φ^j values.

The interrelationships between total surface area of the dispersion and average fluxes as a function of the interaction parameters a_v^j, Φ^j, and $\bar{\theta}^j$ were obtained by studying the behavior of $\bar{Q}_T^j$. Figure 6 demonstrates the dependence of $\bar{Q}_T^j$ on Φ^j and a_v^j for constant $\bar{\theta}^j$. A general increase of the total average heat transfer rate in the disperser is observed with increasing Φ values. However, a very significant limit to this increase is observed. This limit corresponds to $a_v^j \leq 0.1$ mm. for $\bar{\theta}^j = 3$ sec. and this particular dispersion, but we might expect similar limits in any dispersed system. The explanation of this phenomenon can be made in terms of two opposing effects. The first is due to a decrease in the transfer flux as a_v^j decreases. Here interaction effects between adjacent particles control the transfer of heat or mass. The second effect is due to the fact that the total interfacial area per stage is inversely proportional to a_v^j and directly proportional to Φ. The second effect is controlling at drop sizes larger than 0.1 mm., while at $a_v^j \leq 0.1$ mm. the two opposing effects became equal in magnitude and no further increase of $\bar{Q}_T^j$ with increasing Φ^j is observed. Thus, for a $a_v^j \leq$ critical size, $\bar{q}^j$ becomes inversely proportional to Φ^j. The critical size in a given system is a function of $\bar{\theta}^j$ as shown in Figure 7.

Experimental tests of the mechanism and predictions of the basic model (*6*) of this kind (but with the gas phase resistance being neglected) were performed recently with gas-liquid dispersions in the cases of mass transfer with (*15*) and without (*25*) simultaneous chemical reactions. In both cases the experimental results were found to be in reasonable agreement with the theoretical predictions. Thus, we may regard these experiments as furnishing justification for confidence in the mechanism of the improved model that is employed here for the case of two-phase resistance to transfer.

SUMMARY

Two major domains were established. In the first one a convective mass transfer model has been formulated for low Φ values and the case of steady motion of a group

---

[†] The maximum theoretical value of Φ for spherical particles is $\pi/6$; consequently the transfer rate for Φ values greater than $\pi/6$ should be regarded as an approximation for deformed particles.

of bubbles with clean interfaces. In contradiction with the conclusions of Calderbank and Moo-Young this model demonstrates that $k_L \alpha (a_{32})^{1/2}$. Reasonable agreement between this model and experimental results is expected for high viscosity fluids even in the presence of surfactants. According to Equation (8) this model predicts a decrease in (k_L) swarm as Φ is increased. A second domain was established for high Φ values and fine dispersions that contain surfactants. A semidynamic model for unsteady state heat (or mass) transfer from a swarm of droplets in a multistage liquid-liquid disperser was established for this domain and relatively short contact times. Quantitative analysis was made on the behavior of the instantaneous heat transfer flux $q^j(t)$ and the total average heat transfer rate $\overline{Q}^j_T$ as affected by changes in a^j_v, Φ^j, t, $\overline{\theta}^j$, or Q^j. It is found that $q^j(t)$ decreases as Φ^j increases and as a^j_v decreases. In contradiction with the penetration theory, which unrealistically predicts that $q^j(t) \to \infty$ as $t \to 0$, this model predicts a finite flux at $t = 0$ which decreases as t increases.

A general increase of $\overline{Q}^j_T$ is predicted as Φ^j increases and a^j_v decreases. However, a limit to this increase is observed, which depends on the average droplet size and the average residence time of the droplets in the dispersion. Hence, efforts to decrease the particle size to increase total heat transfer rates should be restricted to an optimum value. The optimum size depends on the average residence time of the particles as well as on the holdup fraction. For maximizing heat or mass transfer rates the average residence time of the drops per stage should be minimized.

NOTATION

a = particle radius
a_{32} = surface mean radius
a_v = mean volume radius [Equation (16)]
a_ϕ = coordinate(s) describing the size and shape of any particle
A = total interfacial area of the dispersion
b = radius of spherical shell [Equation (20)]
c = concentration
c' = heat capacity
c_i = concentration at the interface
c_o = bulk concentration
c^o = concentration of surfactants in the liquid bulk that correspond to equilibrium concentration Γ_o on the surface
D = diffusion coefficient
D_S = surface diffusion coefficient of surfactants
$f(a^j_v, \Phi^j, \alpha_c, \alpha_d)$ defined in Equation (33)
F = volumetric flow rate of continuous phase
$\underline{g}$ = local acceleration
J_i = flux of transport process i
k_L = mass transfer coefficient, liquid phase
K = thermal conductivity
N = total number of particles
N^*_A = local rate of mass transfer per unit particle surface area
$\overline{N}_A$ = average mass transfer per unit particle surface area
N_V = number of particles per unit volume of dispersion
P^* = flux of desorbed surfactants
P_v = power per unit volume of agitated dispersion
$q(t)$ = instantaneous heat transfer rate per unit particle surface area
$\overline{q}$ = average heat transfer rate per unit particle surface area
Q = volumetric flow rate of dispersed phase
Q^* = flux of adsorbed surfactants
$\overline{Q}_T$ = total average heat transfer rate in the dispersion
r = radius in spherical coordinates
R = gas constant
R^* = chemical reaction rate per unit volume
t = time
T = absolute temperature
$\overline{T}$ = reduced temperature
U = magnitude of particle velocity relative to the fluid
$\overline{v}$ = velocity vector
v_L defined in Equation (19)
V = volume of continuous phase
V_r = radial velocity component
V_v = volume of dispersion
V_θ = tangential velocity component
$\overline{X}_i$ = driving force to flux $\overline{J}_i$
Z = variable defined in Equations (23) and (24)
$\overline{Z}$ = variable based on reduced temperature

Greek Letters

α = thermal diffusivity
γ = retardation coefficient, Equations (12) and (13)
γ^* defined in Equation (34)
Γ = surface concentration of surfactants
Γ_o = equilibrium concentration of surfactants on the surface
λ_n = n^{th} positive roots of Equation (35)
$\overline{\delta}$ = average thickness of diffusion boundary layer
θ = cone angle in spherical coordinates
$\overline{\theta}$ = average residence time of the particles in the dispersion
ρ = density
σ = surface tension
ϕ = polar angle in spherical coordinates
Φ = volumetric dispersed phase holdup fraction
ψ defined in Equation (34)

Subscripts

c = continuous phase
d = dispersed phase

Superscript

j = stage j in a multistage disperser ($j = 1, 2, 3, \ldots r$)

LITERATURE CITED

1. Levich, V. G., "Physiochemical Hydrodynamics," Prentice-Hall, Englewood Cliffs, N. J. (1962).
2. Lamb, H., "Hydrodynamcis," Dover, New York (1945).
3. Astarita, Gianni, and Gennaro Apuzzo, *AIChE J.*, **11**, 815 (1965).
4. Calderbank, P. H., and M. B. Moo-Young, *Chem. Eng. Sci.*, **16**, 39 (1961).
5. Hanratty, T. J., *AIChE J.*, **2**, 359 (1956).
6. Gal-Or, Benjamin, and William Resnick, *Chem. Eng. Sci.*, **19**, 653 (1964).
7. Gal-Or, Benjamin, and H. E. Hoelscher, *AIChE J.*, **12**, 499 (1966).
8. Gal-Or, Benjamin, *ibid.*, **12**, 604 (1966).
9. Marruci, G., *Ind. Eng. Chem. Fundamentals*, **4**, 224 (1965).
10. ———, Univ. Napoli, Italy, personal communication.
11. Gal-Or, Benjamin, and William Resnick, *AIChE J.*, **11**, 740 (1965).
12. Ruckenstein, E., *Chem. Eng. Sci.*, **15**, 131 (1964).
13. Moo-Young, M. B., personal communication, Univ. Western Ontario, Canada.
14. Calderbank, P. H., *Trans. Inst. Chem. Eng.*, **36**, 443 (1958); **37**, 173 (1959).
15. Gal-Or, Benjamin, and William Resnick, *Ind. Eng. Chem.*

Process Design Develop., **5**, 15 (1966).
16. ———, *Advanc. Chem. Eng.*, to be published.
17. Lindblad, N. R., *J. Colloid Sci.*, **19**, 729 (1964).
18. Lindland, K. P., and S. G. Terjesen, *Chem. Eng. Sci.*, **6**, 265 (1956).
19. Davies, J. T., *Advanc. Chem. Eng.*, **4**, 3-49 (1963).
20. ———, A. A. Kilner, and G. A. Ratcliff, *Chem. Eng. Sci.*, **19**, 583 (1964).
21. Timson, W. J., and C. G. Dunn, *Ind. Eng. Chem.*, **52**, 799 (1960).
22. Happel, John, *AIChE J.*, **4**, 197 (1958); **5**, 174 (1959).
23. Bell, B. P., *Proc. Phys. Soc.*, **57**, 45 (1945).
24. Rohsenow, W. M., and H. Y. Choe, "Heat Mass and Momentum Transfer," Prentice-Hall, Englewood Cliffs, N. J. (1961).
25. Gal-Or, Benjamin, H. E. Hoelscher, and J. P. Hauck, to be published.
26. Groot de, S. R., and P. Mazur, "Non-equilibrium Thermodynamics," North-Holland, Amsterdam (1962).
27. Valentaz, K. J., Olegh Bilous, and N. R. Amundson, *Ind. Eng. Chem. Fundamentals*, **5**, 271 (1966).

Manuscript received April 26, 1966; revision received October 11, 1966; paper accepted October 11, 1966. Paper presented at AIChE Detroit meeting.

On a Tracer Method for Evaluating Catalytic Data

JAMES C. W. KUO and JAMES WEI
Mobil Oil Corporation, Princeton, New Jersey

This paper presents theoretical studies of a method of using a radioactive tracer technique to evaluate the kinetic data of heterogeneous catalytic reactions that are coupled with a Knudsen type of pore diffusion. By superimposing a transient radioactive tracer response over the steady state concentration profile in the catalyst particle, one can establish an implicit relation between the total amount of radioactive components diffused out of the particle and the kinetic data of the reaction system. This relation can then be used to evaluate kinetic data of the reaction system. A detailed study of general monomolecular complex systems is given. Use of the method for nonlinear systems is also included.

In 1939 Thiele (*1*) pointed out that the performance of a simple catalytic reaction may be well described by a single dimensionless parameter. Now well known as the Thiele modulus, it is composed of the kinetic rate constant, effective diffusivity of the reactant in the pore of the catalyst, size of the catalyst particle (or size of the pore), and the external concentration of the reactant (for reactions other than first order). In recent years, this modulus has been a major target of the intensive research to determine catalyst activity and the kinetics of the chemical reaction system. To evaluate this modulus, it is necessary to determine both the kinetic rate constant and the effective diffusivity of the reactant in the pore of the catalyst. There are many methods available for this purpose (*2* to *7*).

Recently Brinkley and Peterson (*8*) proposed a new method for measuring the Thiele modulus of a first-order isothermal irreversible catalytic reaction. Basically, their idea was to add a small quantity of radioactively tagged molecules in the reactant stream, which is allowed to reach steady state in the catalytic particle. The tagged reactant stream is then suddenly replaced by a pure nonradioactive reactant stream without affecting the steady state profile of the total (radioactive plus nonradioactive) reactant in the particle. One may then collect the total effluent stream after the tagged reactant stream has been replaced by a nonradioactive reactant stream and measure the ratio of the total amount of radioactive product to radioactive reactant in the collected sample. A functional relation between this ratio and the Thiele modulus is established upon theoretical grounds, and the Thiele modulus can then be evaluated. Brinkley and Peterson also proposed a set of experimental designs for a differential reactor and a sampling device. The advantage of using a differential reactor is that one does not have to worry about the axial diffusion in the bulk fluid, so an analysis for a single catalyst particle is sufficient for obtaining the functional relation.

If one uses the technique for more complicated reaction systems other than the first-order irreversible reaction system, one can use product distribution as well as the isotopic distribution as a double check. There are, however, some possible experimental difficulties. The generation of the step function at the particle boundary is difficult because the radioactive materials in the boundary layer around the catalyst particle will not disappear right away. Furthermore, the method uses a transient effective diffusivity, which may be different from a steady state effective diffusivity if the amount of adsorption on the active surface of the catalyst is extensive and the rate of desorption is slow. It may be that the steady state effective diffusivity is more relevant to the Thiele modulus. The duration of the transience is likely to be short. For a ¼ in. diameter sphere of $D = 10^{-3}$ sq.cm./sec., 92% of the radioactive