Three Phase Slurry Reactors

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This article reviews the major developments in the engineering and design of three-phase slurry catalytic reactors. A general theoretical analysis for predicting the overall rate of reaction in a slurry reactor for various kinetics is presented, incorporating all the transport effects. Modeling of semi-batch reactors is discussed and design procedures are indicated. Some major correlations and methods for determining gas-liquid and liquid-solid mass transfer coefficients and effective diffusivity in liquid filled pores are reviewed. Slurry reactors are compared with other three-phase reactors, such as trickle bed or packed bed reactors, and relative merits are pointed out.

SCOPE

Three-phase reactors have many diverse applications in catalytic reaction engineering. There are two common modes of operation of the three phase reactor: (1) trickle bed or packed bed operation where the catalyst is stationary and the liquid flows as a dispersed phase, the gas being the continuous phase and (2) slurry reactors where the catalyst is suspended in the liquid medium by either mechanical or gas-induced agitation. The slurry is now the continuous phase and the gas is well dispersed in the reactor. Here the liquid medium could either be a reactant or an inert medium for contacting the dissolved gases with the solids. Similarly the gaseous component could be either a reactant or an inert to provide agitation. The solid particles in most cases are catalysts or adsorbents. A number of reviews are available on trickle bed reactors (Satterfield 1975, Goto et al. 1977) and packed bed three-phase reactors (Hofmann 1978), while there is no recent review on the slurry reactors.

Slurry reactors are commonly used in many industrial processes. Some notable examples are hydrogenation of unsaturated oils, Fischer-Tropsch reaction for hydrocarbon synthesis, oxidation of olefins, ethynylation of aldehydes, and polymerization reactions. A recent application of slurry reactors is in the field of pollution control, where a gas or liquid phase contaminant is oxidized in a slurry catalytic reactor. The potential application of slurry reactors is likely to expand with new developments in the field of 'heterogenized' homogeneous catalysts. These catalysts are in the form of polymer bound transition metal complexes, and the reactions are normally carried out in a slurry reactor. (For example, hydroformylation of olefins, carbonylation of methanol to acetic acid, and oxidation of ethylene to vinyl acetate). Slurry operations have many advantages over other modes of three-phase contacting, e.g., in controlling the temperature and reducing the extent of intraparticle diffusion. Since these reactors operate at moderate conditions, higher selectivity can also be envisaged.

It is the purpose of this review to evaluate the major engineering developments and design procedures in this area, and to discuss methods of analyzing slurry reactor systems. The scope of the review is restricted to the cases where the solid is either a catalyst or an adsorbent. The situation where the solid undergoes a reaction in the slurry is not considered.

CONCLUSIONS AND SIGNIFICANCE

Catalytic reactions in slurries involve processes such as gas-liquid mass transfer, liquid-to-particle mass transfer, intraparticle diffusion, adsorption, surface reaction and desorption of products, making it a highly complicated system. In analyzing data in slurry reactors, one must consider carefully all these resistances. In the case of complex reaction systems, additional effects due to non-linear kinetics may be involved. All of these steps can influence the performance of slurry reactors in practice.

In this review, a general theoretical analysis of slurry reactors incorporates all the transport effects and complex kinetics. Equations are presented for calculating the overall rate of reaction, when transport effects are important for various kinetic schemes. A concept of an overall effectiveness factor of a slurry reactor which leads to analytical equations for various non-linear kinetics is introduced. The status of information on consecutive and parallel reaction schemes is also discussed. Several useful criteria are also given, which allow the simplification of complex models for certain situations.

Many industrial slurry reactors are operated in a semi-batch manner (with the liquid phase stationary and continuous gas flow). In such cases, it is necessary to predict the conversion of the liquid phase component as a function of time and in this work, such equations are presented. Further, the influence of some complexities such as change in the solubility and product inhibition are also discussed. Suitable examples illustrate the utility of the theory in some practical situations.

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The status of design information is discussed and some major correlations and methods of experimental determination of gas-liquid and liquid-solid mass transfer coefficients are reviewed. Correlations from different literature sources are compared with suitable examples. The available data on effective diffusivity in liquid filled pores are summarized. We also present a summary of prediction of minimum operating conditions for complete suspension of particles. Methods of analyzing experimental slurry reactor data with a view of evaluating the mass transfer and kinetic parameters are discussed.

The slurry reactors have a number of advantages over other three-phase reactors, such as trickle bed or packed bubble bed reactors. These are:

1. As small particle size of the catalyst can be used in a slurry reactor, the intraparticle diffusional resistance is less in comparison to a trickle or packed bubble bed reactor. The trickle bed reactors normally employ catalyst particle sizes at which the intraparticle diffusion may be significant.
2. The external mass transfer coefficients in slurry reactors are higher than in trickle or packed beds, which leads to better utilization of the catalyst.
3. Slurries have higher heat capacities and higher heat transfer coefficients. Due to this, temperature control of exothermic reactions is better in slurry reactors, and the formation of hot spots can be avoided. Slurry reactors are relatively safer for reactions with temperature runaway. The large liquid volume is also an advantage in maintaining isothermal conditions. The heat recovery, too, in these reactors is better.
4. In trickle bed reactors, partial wetting of catalyst surface may exist for a certain range of liquid flow rates, and in such cases the entire catalyst may not be utilized in certain situations (see, for example, Ramachandran and Smith 1979). In slurry reactors, this problem is not encountered.
5. In view of the pelletizing difficulties and the high cost involved in pelletizing, slurry reactors may prove to be more useful in some cases.

In spite of these several advantages of slurry reactors, they pose some practical problems. A major problem is the difficulty in separating the catalyst and handling of the slurry. Because of this, the application of slurry reactors in continuous processes has been limited.

Two types of slurry reactor operations are normally encountered: mechanically agitated slurry reactors and bubble column slurry reactors. The mechanically agitated reactors have the advantage of high heat and mass transfer efficiency, while they pose problems like catalyst attrition and complete backmixing of the liquid phase. In the bubble column reactors, catalyst is suspended by means of gas induced agitation. They have the advantage of low power consumption. The backmixing can be slightly reduced in this type of reactors. But they have a disadvantage of nonuniform catalyst distribution and lower mass and heat transfer efficiency.

This review considers two aspects of slurry reactors. The first is a mathematical development of the effect of mass transfer on several different intrinsic rate models in a slurry reactor. The second part is a literature review of correlations for predicting design parameters. The information presented here will be useful in selecting suitable reactor type, and experimental evaluation of kinetic parameters and design.

GENERAL THEORETICAL ANALYSIS

A general three-phase slurry system can be represented by the reaction scheme

$$A + \nu B \rightarrow \text{Products} \qquad \text{(i)}$$

The species A is generally a reactant in the gas phase and B is a nonvolatile reactant in the liquid phase. The reaction of A and B is assumed to occur at the interior surface of the catalyst particles, which are suspended in the liquid medium. A number of industrially important reaction systems conform to this scheme. Examples are found in hydrogenation and oxidation reactions. In some industrially important cases, both A and B may be present in the gas phase. Oxidation of SO_2 over activated carbon catalyst is an example which has applications in pollution control. Methanation reaction and Fischer-Tropsch synthesis are other well-known examples.

The intrinsic rate of reaction over the active sites of the catalyst per unit weight of catalyst may be represented by a power-law kinetic model

$$\Omega = k_{(m+n)} A^m B^n \qquad (1)$$

where, Ω is the local rate of reaction at a point within the catalyst where the concentrations are A and B. The analysis of the reaction rate in a slurry system is simplified when one of the reactants (B) is in excess. The variation of B in the reactor is then not significant and concentration of B is uniform throughout the catalyst, hence the kinetic model can be simplified as

$$\Omega = k_m A^m \qquad (2)$$

where, k_m is a pseudo m^{th} order rate constant, equal to $k_{(m+n)}B_1^n$. A criterion for Equation (2) to be valid is discussed later.

An alternate and mechanistically more realistic way of representing the rate is in terms of the Langmuir-Hinshelwood (L-H) model, although the power law model has the advantage of mathematical simplicity. The reaction rate based on this model for single-site mechanism may be expressed as

$$\Omega = \frac{k_2 AB}{(1 + K_A A + K_B B)} \qquad (3)$$

First the analysis of slurry reactors is made for the case when pseudo m^{th} order conditions are satisfied. The effect of transport steps is analyzed in detail for reactions of various orders and for L-H models. A more general case of $(m, n)^{\text{th}}$ order reaction is then analyzed.

The analysis in this section is for differential conditions, so that the conditions in the liquid phase are assumed to change only slightly. This restriction is important because the pseudo-m^{th} order rate constant, k_m, changes with the concentration of liquid phase reactant B. Also, in

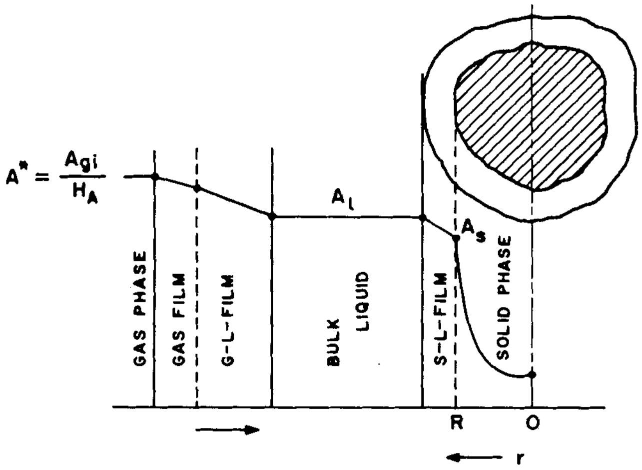


Figure 1. Concentration profile for a slurry catalyzed reaction.

some cases, the solubility of the gas is strongly influenced by changes in liquid concentrations. For example, in the oxidation of SO_2 (Komiyama and Smith 1975) the H_2SO_4 formed decreases the solubility of both O_2 and SO_2 in the medium. A further complicating effect of product inhibition is observed in some systems. These aspects will be briefly discussed later. Thus the analysis is valid for a semi-batch reactor only for a differential increment of time. It is not valid for the entire period of operation. Analysis of semi-batch reactors is attempted in a separate section.

A number of steps have to occur before a species can be converted to products over the active surface of the catalyst in a slurry reactor. For component A present in the gas phase, the steps are

1. Transport of A from the bulk gas phase to the gas-liquid interface.
2. Transport from gas-liquid interface to the bulk liquid.
3. Transport from bulk liquid to the catalyst surface.
4. Intraparticle diffusion in the pores of the catalyst.
5. Adsorption of A on the active sites of the catalyst.
6. Surface reaction of A to yield products.

In the case of reversible reactions, additional steps such as desorption of products, transport of products from the catalyst to bulk liquid and to bulk gas (for volatile products) may also become rate limiting. The concentration profile for an irreversibly reacting species in a slurry system is schematically shown in Figure 1.

Overall Rate of Mass Transfer

The rate of mass transfer of species A from gas phase to the surface of the catalyst, can be derived from the relevant equations for steps 1 to 3. Steady state conditions are assumed, and the mixing pattern of the gas phase in the reactor is assumed to be plug flow. The implication of this assumption is examined later, where the effect of gas backmixing will be discussed.

The mass balance of gas A as a function of height measured from the point of gas inlet is

$$-u_g\left[\frac{dA_g}{dz}\right] = (K_La)_A\left[\frac{A_g}{H_A} - A_l\right] \qquad (4)$$

where $(K_La)_A$ is the overall mass transfer coefficient for transfer of A from bulk gas to bulk liquid. H_A is the Henry's law solubility coefficient of the gas in the liquid medium. The overall mass transfer coefficient $(K_La)_A$ is related to individual gas side and liquid side mass transfer coefficients by

$$\frac{1}{(K_La)_A} = \frac{1}{H_A(k_ga)_A} + \frac{1}{(k_La)_A} \qquad (5)$$

Equation (4) is based on the assumption that the liquid phase is completely mixed. The integrated form of Equation (4) is

$$\frac{A_g - H_AA_l}{A_{gi} - H_AA_l} = \exp(-\alpha_A z) \qquad (6)$$

where

$$\alpha_A = \frac{(K_La)_A}{u_gH_A} \qquad (7)$$

The concentration of gas A leaving the reactor is

$$A_{go} = A_{gi}\exp(-\alpha_AL) + H_AA_l[1 - \exp(-\alpha_AL)] \quad (8)$$

The rate of gas absorbed per unit volume of slurry is

$$R_A = \frac{H_AQ}{V_L}[1 - \exp(-\alpha_AL)]\left[\frac{A_{gi}}{H_A} - A_l\right] \quad (9)$$

The rate of mass transfer from the liquid to the surface of the solid is

$$R_A = (k_sa_p)_A(A_l - A_s) \qquad (10)$$

Combining Equations (9) and (10), the overall rate of transfer of A from the gas phase to the external surface of the catalyst can be expressed as

$$R_A = M_A\left[\frac{A_{gi}}{H_A} - A_s\right] \qquad (11)$$

where

$$M_A = \left[\frac{1}{\frac{H_AQ}{V_L}[1 - \exp(-\alpha_AL)]} + \frac{1}{(k_sa_p)_A}\right]^{-1} \qquad (12)$$

Equation (11) gives total rate of mass transfer from gas phase to the catalyst surface for the reactor. It incorporates gas to liquid mass transfer, liquid to solid mass transfer and also the effects of varying gas phase concentration in the reactor. Note that, for sparingly soluble gases, the term $H_AQ/V_L[1 - \exp(-\alpha_AL)]$ reduces to $(k_La)_A$, indicating that the effects of varying gas phase concentration are negligible. In this situation the overall rate of mass transfer of species A is given by

$$R_A = \left[\frac{1}{(k_La)_A} + \frac{1}{(k_sa_p)_A}\right]^{-1}\left[\frac{A_{gi}}{H_A} - A_s\right] \qquad (13)$$

On the other hand, for highly soluble gases the term $H_AQ/V_L[1 - \exp(-\alpha_AL)]$ reduces to H_AQ/V_L, indicating that the gas to liquid mass transfer resistance has no significance.

Rate of Chemical Reaction

Equations (11) and (12) can be used to predict the rate of mass transfer of A, but the external surface concentration A_s is unknown and has to be determined considering the rate of chemical reaction. The local rate of reaction within the catalyst can be expressed using power law model

$$\Omega = k_mA^m \qquad (14)$$

In this equation, steps of adsorption and surface reaction have not been considered separately. The rate constant k_m and the order m are apparent constants, including the effects of both. When $m = 1$, the value of k_m is a combination of the rate of adsorption and surface reaction steps and is given by

$$\frac{1}{k_1} = \frac{1}{k_a} + \frac{1}{K'k_r} \qquad (15)$$

First, the analysis is given for a case of negligible intraparticle diffusion effects.

mth Order Reaction

For m^{th} order reaction, the rate of reaction of A per unit volume of slurry in the absence of significant intraparticle diffusion gradients can be expressed as

$$R_A = wk_m A_s^m \qquad (16)$$

The intraparticle concentration gradients may be considered to be negligible when the following condition is satisfied

$$\phi_o = \frac{R}{3}\left[\frac{(m+1)}{2}\,\frac{\rho_p k_m (A^*)^{m-1}}{D_{eA}}\right]^{1/2} < 0.2 \qquad (17)$$

Combining Equations (11) and (16) gives the following expression for the rate of m^{th} order reaction in a slurry reactor

$$R_A = M_A\left[\frac{A_{gi}}{H_A} - \left(\frac{R_A}{wk_m}\right)^{1/m}\right] \qquad (18)$$

Equation (18) is an implicit expression for R_A and the rates can be obtained by a trial and error procedure. Also, for specific values of m, such as 1, ½ and 2, explicit relationships could also be obtained. For $m = 1$, the rate of reaction of A is given by

$$R_A = \frac{A_{gi}}{H_A}\left[\frac{1}{\frac{H_A Q}{V_L}[1 - \exp(-\alpha_A L)]} + \frac{1}{k_s a_p} + \frac{1}{wk_1}\right]^{-1} \qquad (19)$$

Equation (19) is similar to those normally used for first order reaction of a single gas in a slurry reactor. See, for example, Satterfield (1970), Sherwood and Farkas (1966), Roberts (1976). The difference between Equation (19) and those presented in earlier works is that Equation (19) is for a reactor and hence is applicable also when the concentration of A in the gas phase is changing significantly along the height measured from the point of gas inlet.

In a number of situations, adsorption plays an important role and the rate of chemical reaction is then better represented by Langmuir-Hinshelwood (L-H) type models. It may be appropriate at this stage to discuss briefly whether the power-law model or L-H model is more suitable for expressing the slurry reactor kinetics. The power-law model is more easy for fitting experimental data but it does not take into account the mechanistic aspects of adsorption and surface reaction. The apparent order of reaction m or n is only an empirical constant and can change with change in concentrations.

Another situation where the power-law kinetics may fail is in reactions proceeding consecutively with the formation of an intermediate. The reactant and intermediate may be competitively adsorbed, and the reaction order may change with the relative concentration of the reactant and the intermediate. The overall rate of reaction

TABLE 1. OVERALL RATE OF REACTION IN A SLURRY REACTOR INCORPORATING EXTERNAL MASS TRANSFER BUT IGNORING INTRAPARTICLE CONCENTRATION GRADIENTS

Reaction type	Kinetic model, Ω = mole/gm/sec	Rate of reaction, R_A, mole/cm³/sec	Equation number
First-order	$k_1 A$	$A^*\left[\frac{1}{M_A} + \frac{1}{wk_1}\right]^{-1}$	T.1.1
Second-order	$k_2 A^2$	$\frac{M_A^2}{2k_2 w}\left[\left(1 + \frac{2wk_2A^*}{M_A}\right) - \left(1 + \frac{4wk_2A^*}{M_A}\right)^{1/2}\right]$	T.1.2
Half-order	$k_{1/2}\sqrt{A}$	$\frac{(wk_{1/2})^2}{2M_A}\left[\left(1 + \frac{4A^*M_A^2}{(wk_{1/2})^2}\right)^{1/2} - 1\right]$	T.1.3
Zero-order	k_0	See text, Equations (35), (36) and (37)	
Langmuir-Hinselwood [single site]	$\frac{k_1 A}{(1 + K_A A)}$	$\frac{M_A}{2K_A}\left\{\left(1 + K_A A^* + \frac{wk_1}{M_A}\right) - \left[\left(1 + K_A A^* + \frac{wk_1}{M_A}\right)^2 - \frac{4wkK_A A^*}{M_A}\right]^{1/2}\right\}$	T.1.4
Second-order [two components]	$k_2 AB$	See Equation (48) in text	—
$A \rightleftharpoons E$	$k_1\left(A - \frac{E}{K_R}\right)$	$[A^* - A_e]\left(\frac{1}{M_A} + \frac{1}{wk_1}\right)^{-1}$	T.1.5
$2A \rightleftharpoons E$	$k_2\left(A^2 - \frac{E}{K_R}\right)$	$M_A\left\{\left(A^* + \frac{M_A}{2wk_2}\right) - \left[\left(A^* + \frac{M_A}{2wk_2}\right)^2 - A^{*2} + A_e^2\right]^{1/2}\right\}$	T.1.6

Note: 1] M_A is defined by Equation (12) in the text.
2] A^* is defined as A_{gi}/H_A.

when Langmuir-Hinshelwood model is applicable can be derived in an analogous manner.

The rate of reaction in a catalytic slurry reactor in the absence of significant intraparticle diffusion has been summarized in Table 1 for various kinetic models. ($m = \frac{1}{2}$, 1, 2, single site L-H model and reversible reactions). More complex models considering the rate of adsorption as an independent step have also been proposed (Zwicky and Gut 1978).

Rate of Reaction Incorporating Intraparticle Diffusion

When the concentration of A is not uniform in the catalyst particle, the above equations are not applicable. It is convenient then to express the rate in terms of a catalytic effectiveness factor

$$R_A = \eta_c w k_m A_s^m \tag{20}$$

The catalytic effectiveness factor η_c can be obtained as an approximation as

$$\eta_c = \frac{1}{\phi}\left[\coth(3\phi) - \frac{1}{3\phi}\right] \tag{21}$$

where, ϕ is the generalized Thiele modulus defined (Bischoff 1965) as

$$\phi = \frac{R}{3}\rho_p\Omega(A_s)\left[\int_0^{A_s} 2D_{eA}\rho_p\Omega(A)\,dA\right]^{-\frac{1}{2}} \tag{22}$$

For m^{th} order reaction, ϕ, is given by

$$\phi = \frac{R}{3}\left[\frac{(m+1)}{2}\frac{\rho_p k_m A_s^{m-1}}{D_{eA}}\right]^{\frac{1}{2}} \tag{23}$$

It is seen that the Thiele modulus ϕ is a function of the concentration A_s, except when $m = 1$. A trial and error calculation is then necessary for calculating R_A for a general case. The calculations are simplified by defining an overall effectiveness factor, as shown by Ramachandran and Chaudhari (1979a).

Overall Effectiveness Factor

An effectiveness factor for a first-order slurry reaction incorporating external and internal mass transfer effects has been defined by Sylvester *et al.* (1975). The concept of an overall effectiveness factor is useful in simplifying the calculation of rate of chemical reaction in a slurry reactor. Ramachandran and Chaudhari (1979a) defined the overall effectiveness factor as actual rate of reaction divided by the rate based on the inlet gas concentration and neglecting all the transport resistances

$$\eta = \frac{R_A}{w\Omega(A^*)} \tag{24}$$

For m^{th} order reaction η is defined as

$$\eta = \frac{R_A}{w k_m (A^*)^m} \tag{25}$$

To obtain an analytical solution for η in terms of known parameters, the surface concentration of $A(A_s)$ has to be eliminated. This can be done by expressing the surface concentration of A in terms of the overall effectiveness factor itself. From Equation (11) we have

$$a_s = 1 - \frac{\eta}{\sigma_A} \tag{26}$$

where

$$\sigma_A = \frac{M_A A^*}{w\Omega(A^*)} \tag{27}$$

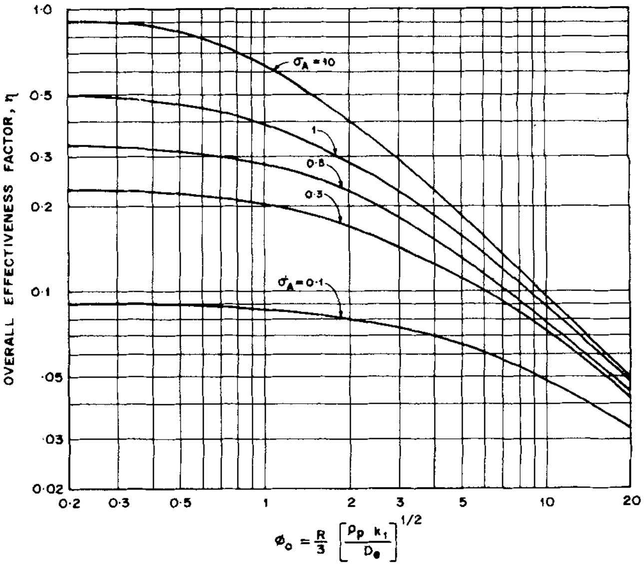


Figure 2. Overall effectiveness factor for a first-order reaction in a slurry reactor.

and

$$a_s = A_s/A^* \tag{28}$$

Incorporating a_s from Equation (26) and rearranging (20), the overall effectiveness factor, η for a m^{th} order reaction in a slurry reactor is given by

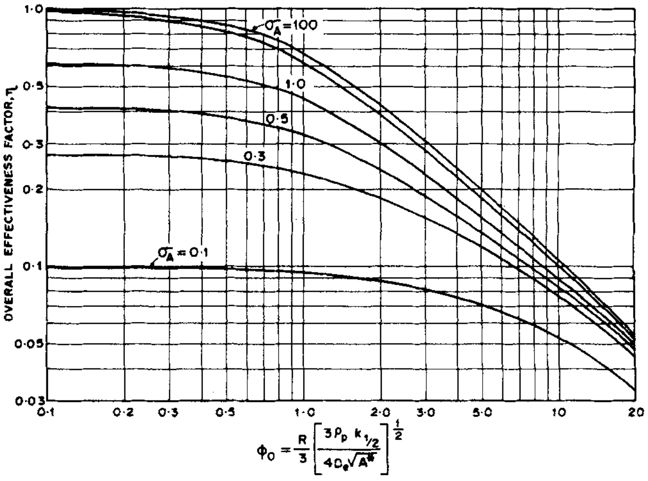


Figure 3. Overall effectiveness factor for a half-order reaction in a slurry reactor.

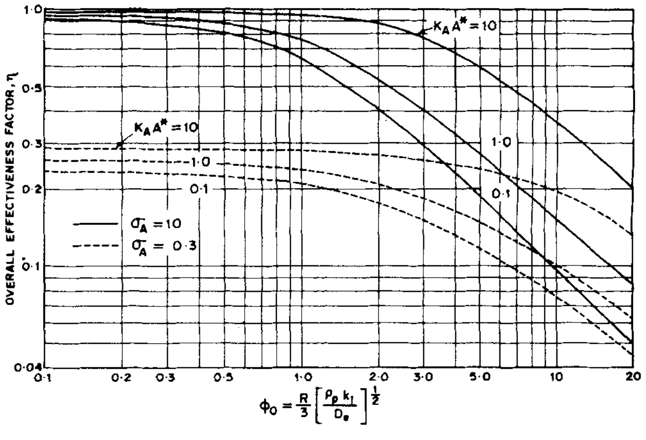


Figure 4. Overall effectiveness factor for L-H type kinetics (single site mechanism).

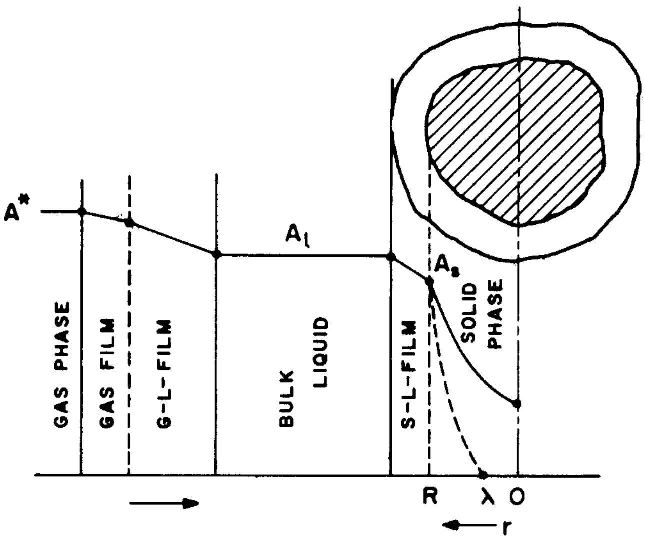


Figure 5. Concentration profile for a zero-order slurry catalyzed reaction. ——— = diffusion effects unimportant. - - - - = diffusion effects important.

$$\eta = \frac{1}{\phi}\left[\coth(3\phi) - \frac{1}{3\phi}\right]\left[1 - \frac{\eta}{\sigma_A}\right]^m \qquad (29)$$

The generalized Thiele modulus ϕ is a function of a_s and a_s is a function of η. Eliminating a_s in Equation (23) for ϕ, using Equation (26), we obtain

$$\phi = \frac{R}{3}\left[\frac{(m+1)}{2}\,\frac{\rho_p k_m A^{*m-1}}{D_{eA}}\left(1 - \frac{\eta}{\sigma_A}\right)^{m-1}\right]^{1/2} \qquad (30)$$

Equation (29) is an implicit expression for η and has to be solved by a trial and error procedure, as ϕ is also a function of η. Having obtained η from Equations (29) and (30), the overall rate for m^{th} order kinetics can be predicted using Equation (24). Thus, the overall effectiveness factor aids in obtaining the rate of reaction in a slurry reactor that incorporates all transport resistances.

For a first order reaction, the Thiele modulus ϕ given by Equation (30) reduces to

$$\phi = \frac{R}{3}\left[\frac{\rho_p k_1}{D_{eA}}\right]^{1/2} \qquad (31)$$

which is independent of a_s. Hence the rate of reaction can be expressed as

$$R_A = \frac{A_{gi}}{H_A}\left\{\frac{1}{\dfrac{H_A Q}{V_L}\,[1 - \exp(-\alpha_A L)]} + \frac{1}{k_s a_p} + \frac{1}{w k_1\left[\dfrac{\coth(3\phi)}{\phi} - \dfrac{1}{3\phi^2}\right]}\right\}^{-1} \qquad (32)$$

For higher values of $\phi(>5)$, the hyperbolic term in Equation (32) can be approximated as unity leading to a simplified equation.

For half-order, second-order and other complex kinetics, such as Langmuir-Hinshelwood kinetics with single site and dual site mechanisms, the equations for the overall effectiveness factor η and the modified Thiele modulus ϕ are summarized in Table 2. Using appropriate equations, the overall effectiveness factor η can be calculated by solving non-linear algebraic equations and then predicting rate using Equation (24). Plots of η as a function of ϕ_o and parameter σ_A have been presented for first-order, half-order and single-site L-H kinetics in Figures 2, 3 and 4, respectively. Such plots can be used to read the rate of reaction in a slurry system directly without resorting to detailed calculations. Such plots are also useful in interpreting laboratory experimental data.

Zero-Order Reaction

Reactions that are intrinsically zero-order with respect to A are common in many cases. For example, the hydrogenation of dinitrotoluene on a Pd-charcoal catalyst (Acres and Cooper 1972), oxidation of cyclohexene on oxide catalysts (Meyer et al. 1965), and ethynylation of formaldehyde on a Cu-acetylide catalyst (Kale and Chaudhari 1978) show zero-order behavior. Zero-order reactions have a certain unique feature, warranting a separate theoretical analysis. This is because the rate of reaction is unaffected by a decrease in concentration, as long as the concentration is finite. The rate of reaction would therefore be independent of concentration and mass transfer rates, provided conditions are such that the concentration of the reactive species is a non-zero quantity everywhere inside the catalyst. If this condition is not satisfied, and the concentration of A drops to zero at some point in the catalyst, the rate of reaction would depend on concentration and on mass transfer rates. Recently Chaudhari and Ramachandran (1980) analyzed this problem and derived conditions under which the rate will be independent of concentration. The condition for concentration of A to be finite inside the catalyst is given by

$$A_{gi} > (A_g)_{\text{critical}} \qquad (33)$$

where

$$(A_g)_{\text{critical}} = \frac{H_A k_o \rho_p R^2}{6 D_{eA}} + w k_o H_A\left[\frac{1}{K_L a} + \frac{1}{k_s a_p}\right] \qquad (34)$$

When condition (33) is satisfied, the rate of reaction is given by

$$R_A = w k_o \qquad (35)$$

If the conditions are such that Equation (33) is not satisfied, and the concentration of A drops to zero at some point λ, as shown in Figure 5, then the rate of reaction can be calculated by a trial and error procedure from the following set of equations

$$R_A = w k_o[1 - (\lambda/R)^3] \qquad (36)$$

and

$$R_A = \left[\frac{1}{K_L a} + \frac{1}{k_s a_p}\right]^{-1}\left[\frac{A_{gi}}{H_A} - \frac{k_o \rho_p R^2}{D_e}\left(1 - 3\left[\frac{\lambda}{R}\right]^2 + 2\left[\frac{\lambda}{R}\right]^3\right)\right] \qquad (37)$$

Equations (36) and (37) can be solved simultaneously to obtain λ/R and R_A. The above theory is applicable to sparingly soluble gases such as hydrogen. The overall effectiveness factor η (see Table 2, Equation T.2.2) as a function of σ_A and ϕ_o for a zero-order slurry reaction is shown in Figure 6. The rate of reaction can be read from this graph without resorting to simultaneous solution of Equations (36) and (37).

There are some implications of this theory for the mode of operation of slurry reactor catalyzing a zero-order reaction. For example, if the concentration of A in the gas phase is greater than the value given by Equation (34), then any further increase in concentration will not

Table 2. Equations for Overall Effectiveness Factor η, and Generalized Thiele Modulus Ø, in a Slurry Reactor for Different Kinetic Models

Kinetic model Ω, mole/gm/sec	Overall effectiveness factor, η	Generalized Thiele modulus definition, Ø	Equation number
$k_m A^m$	$\eta_c \left(1 - \frac{\eta}{\sigma_A}\right)^m$	$\frac{R}{3}\left[\frac{(m+1)}{2}\frac{\rho_p k_m A^{*m-1}}{D_{eA}}\left(1-\frac{\eta}{\sigma_A}\right)^{m-1}\right]^{1/2}$	T.2.1
$k_1 A$	See Equation (32) in text for R_A	$\frac{R}{3}\left(\frac{k_1\rho_p}{D_{eA}}\right)^{1/2}$	
k_0	$\sigma_A\left[1-\frac{\emptyset^2}{6}\{1-3(1-\eta)^{2/3}+2(1-\eta)\}\right]$	$R\left[\frac{\rho_p k_0}{D_{eA}A^*}\right]^{1/2}$	T.2.2
$\frac{k_1 A}{1+K_A A}$	$\eta_c\left[\frac{(1+K_A A^*)(1-\eta/\sigma_A)}{[1+K_A A^*(1-\eta/\sigma_A)]}\right]$	$\frac{R}{3}\left[\frac{\rho_p k_1}{D_{eA}}\right]^{1/2} \frac{K_A A^*(1-\eta/\sigma_A)}{\{1+K_A A^*(1-\eta/\sigma_A)\}\sqrt{2[K_A A^*(1-\eta/\sigma_A)-\ln\{1+K_A A^*(1-\eta/\sigma_A)\}}}$	T.2.3
$\frac{k_1 A}{(1+K_A A)^2}$	$\eta_c\left[\frac{(1+K_A A^*)^2(1-\eta/\sigma_A)}{[1+K_A A^*(1-\eta/\sigma_A)]^2}\right]$	$\frac{R}{3}\left[\frac{\rho_p k_1}{D_{eA}}\right]^{1/2} \frac{K_A A^*(1-\eta/\sigma_A)}{\{1+K_A A^*(1-\eta/\sigma_A)\}^2\sqrt{2\ln\left[\{1+K_A A^*(1-\eta/\sigma_A)\}-\frac{K_A A^*(1-\eta/\sigma_A)}{1+K_A A^*(1-\eta/\sigma_A)}\right]}}$	T.2.4
$k_2 AB$	$\eta_c(1-\eta/\sigma_A)(b_0-\eta/\sigma_B)/b_0$	$\frac{R}{3}\left[\frac{\rho_p k_2 B^*}{D_{eA}b_0}\right]^{1/2}\left(\frac{(b_0-\eta/\sigma_B)}{1-\frac{p}{3}\frac{(1-\eta/\sigma_A)}{(b_0-\eta/\sigma_B)}}\right)^{1/2}$	T.2.5
$k_1(A-E/K)$	$\eta_c\frac{[(1-\eta/\sigma_A)-a_e]}{(1-a_e)}$	$\frac{R}{3}\left[\frac{\rho_p k_1}{D_{eA}}\right]^{1/2}\frac{[(1-\eta/\sigma_A)-a_e]}{\sqrt{(1-\eta/\sigma_A)(1-\eta/\sigma_A-2a_e)}}$	T.2.6

Note: 1] η_c is given as $1/\emptyset\,[\coth 3\emptyset - 1/3\emptyset]$.
2] Parameters σ_A is defined as $M_A A^*/w\Omega(A^*)$.
3] Rate of reaction can be calculated as $nw\Omega(A^*)$.
4] Equation (T.2.5) is applicable when A is the limiting reactant.

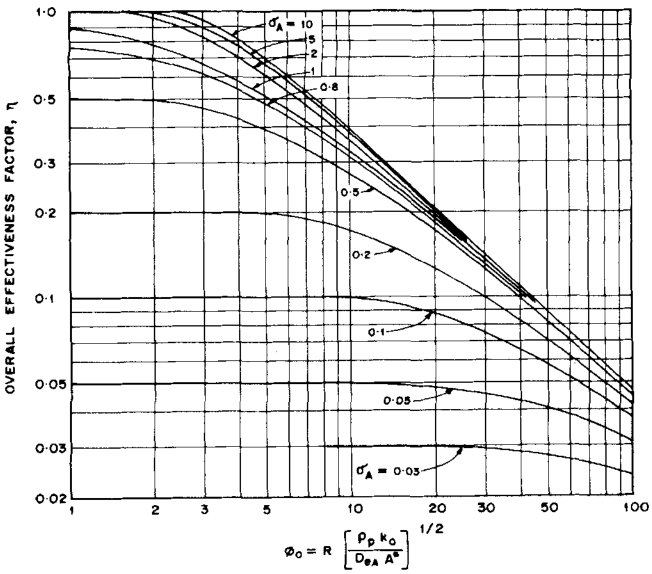


Figure 6. Effectiveness factor for a zero-order reaction in a slurry reactor.

correspondingly improve the reactor performance. If $A_{gi} < (A_g)_{\text{critical}}$, then increasing the mass transfer rate (for instance, by improving agitation) may improve reactor performance. On the other hand, if A_{gi} is greater than $(A_g)_{\text{critical}}$, no further increase in agitation is necessary.

Reversible Reactions

In some cases, the gaseous species react reversibly in a slurry reactor, for example, hydrogenation of fatty acid esters to fatty alcohols (Muttzall and van den Berg 1968). This system is commercially important in the manufacture of fatty alcohols. A simplified case of reversible reaction is examined here, which assumes the following reaction scheme

$$A + B \underset{k_2/K_R}{\overset{k_2}{\rightleftharpoons}} E + F \qquad \text{(ii)}$$

The rate of reaction of A can be expressed as

$$\Omega = k_2(AB - EF/K_R) \qquad (38)$$

If we assume that the concentrations of the liquid phase species B, E and F are in excess (which would generally be the case), the rate is simplified as

$$\Omega = k_1(A - A_e) \qquad (39)$$

where A_e is the equilibrium concentration defined as E_lF_l/B_lK_R and k_1 the pseudo first-order rate constant $= k_2B_l$. (It has been assumed here that the order of reaction with respect to A, B, E and F is unity). The rate of reaction per unit volume of slurry in the absence of significant intraparticle gradients (that is, when the condition given by Equation 17 is satisfied with $m = 1$) is

$$R_A = k_1w(A_s - A_e) \qquad (40)$$

Eliminating A_s using Equation (11) we get an expression for overall rate of reaction

$$R_A = \left[\frac{A_{gi}}{H_A} - A_e\right]\left[\frac{1}{M_A} + \frac{1}{k_1w}\right]^{-1} \qquad (41)$$

In hydrogenation of fatty acid esters to fatty alcohols (Muttzall and van den Berg 1968), the reaction is second-order with respect to hydrogen and alcohol, and first-order with respect to ester. The reaction scheme for this case is

$$2A + B \underset{k_3/K_R}{\overset{k_3}{\rightleftharpoons}} 2E \qquad \text{(iii)}$$

where the kinetics is

$$\Omega = k_3\left[A^2B - \frac{E^2}{K_R}\right] \qquad (42)$$

As a simplification we assume

$$\Omega = k_2(A^2 - A_e^2) \qquad (43)$$

where $k_2 = k_3B_l$ and $A_e^2 = E_l^2/B_lK_R$. The rate of reaction per unit volume of slurry is then

$$R_A = M_A\left[\frac{A_{gi}}{H_A} + \frac{M_A}{2wk_2} - \left\{\left(\frac{A_{gi}}{H_A} + \frac{M_A}{2wk_2}\right)^2 - \left(\frac{A_{gi}}{H_A}\right)^2 + A_e^2\right\}^{1/2}\right] \qquad (44)$$

Equations (41) and (44) are not applicable when intraparticle diffusion is significant. In such cases, the overall effectiveness factor can be used. Equations for this case (reaction scheme ii) are summarized in Table 2.

General $[m,n]^{\text{th}}$ Order Reaction

The pseudo-m^{th} order approximation ceases to be valid when the value of B_l becomes comparable to A^*. This may happen in oxidation of organic pollutants in a slurry reactor where the pollutant concentration B_l would be very small and comparable to A^*. This can also occur when two gases of comparable solubility are reacting in the presence of a suspended catalyst. Some examples falling in this category are: synthesis of hydrocarbons by reaction of CO and H_2 in a slurry phase (Kolbel and Ackermann 1951, Schlesinger et al. 1951), oxidation of CO in a slurry reactor (Ido et al. 1976), hydrogenation of olefins, (Calderbank et al. 1963), oxidation of ethylene to ethylene oxide (Shingu 1961), and oxidation of formic acid (Baldi et al. 1974) and pollutant gases such as SO_2 (Komiyama and Smith, 1975) or H_2S in a slurry reactor.

The concentration profile of two gases A and B which react among themselves in a slurry reactor is shown schematically in Figure 7. When the chemical reaction is

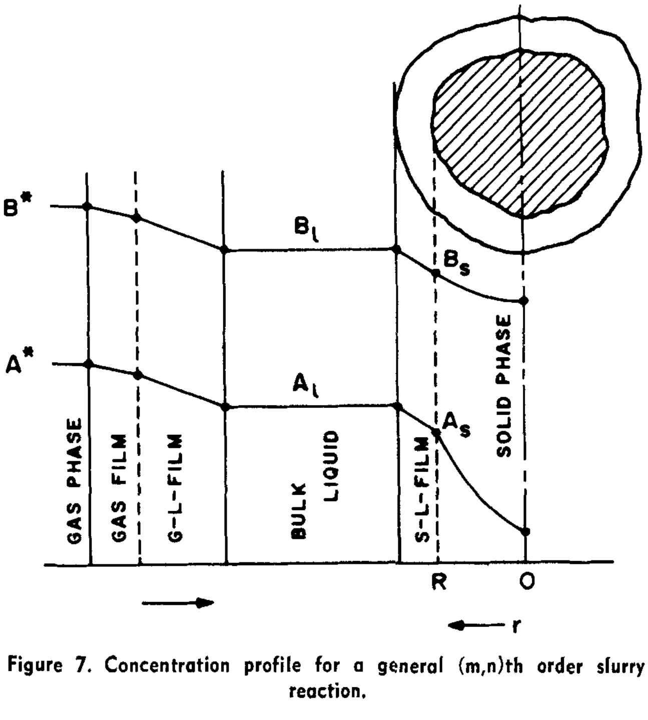


Figure 7. Concentration profile for a general (m,n)th order slurry reaction.

first-order with respect to A and B, the rate of reaction per unit volume of slurry, in the absence of intraparticle diffusion effects, can be expressed as

$$R_A = wk_2A_sB_s \tag{45}$$

The overall rate of mass transfer from gas phase to the surface of catalyst for A is given by Equation (11). Similarly the overall rate of mass transfer of B is given as

$$R_B = \nu R_A = M_B\left[\frac{B_{gi}}{H_B} - B_s\right] \tag{46}$$

where

$$M_B = \left[\frac{1}{\dfrac{H_BQ}{V_L}[1-\exp(-\alpha_BL)]} + \frac{1}{(k_sa_p)_B}\right] \tag{47}$$

and α_B is defined as $(K_La/u_gH)_B$. Substituting for A_s and B_s using Equations (11) and (46) in (45), the overall rate can be expressed as

$$R_A = \frac{M_AM_BA^*B^*}{2}\left[\frac{1}{M_AA^*} + \frac{\nu}{M_BB^*} + \frac{1}{wk_2A^*B^*} - \left\{\left(\frac{1}{M_AA^*} + \frac{\nu}{M_BB^*} + \frac{1}{wk_2A^*B^*}\right)^2 - \frac{4\nu}{A^*B^*M_AM_B}\right\}^{1/2}\right] \tag{48}$$

The conditions for equation (48) to be valid are:

$$\frac{R}{3}\left[\frac{\rho_pk_2B^*}{D_{eA}}\right]^{1/2} < 0.2 \quad \text{when} \quad B^* > A^* \tag{49}$$

and

$$\frac{R}{3}\left[\frac{\rho_pk_2A^*}{D_{eB}}\right]^{1/2} < 0.2 \quad \text{when} \quad A^* > B^* \tag{50}$$

These conditions apply when the solubility coefficients of the two gases H_A and H_B are of comparable magnitude. They do not apply for two gases having widely different solubilities.

For the case when these conditions are not satisfied, Ramachandran and Chaudhari (1979*a*) analyzed the problem in detail and obtained analytical solutions incorporating intraparticle diffusional resistances. Equations for the overall effectiveness factor η and the generalized Thiele modulus ϕ for this case are summarized in Table 2.

Equation (48) discussed in this section and Equation T.2.5 in Table 2 can also be used when B is a liquid phase reactant in small concentrations comparable to A^*. Here, the parameters M_B and B_{gi}/H_B in Equation (46) are modified as $(k_sa_p)_B$ and B_l as the step of gas to liquid mass transfer is not involved for species B. This case is important in industrial reactions where complete conversion is desirable or in oxidation of liquid pollutants.

A situation in which the reaction is first-order with respect to A and zero-order with respect to B has some special features. An example of such a reaction is in oxidizing SO_2 in a slurry of activated carbon, where the reaction is first-order with respect to oxygen and zero-order with respect to SO_2, as shown by Komiyama and Smith (1975). The rate of reaction is independent of the concentration of B, as long as the concentration of B is finite at all points within the catalyst. Equation (19), derived for a pseudo first-order reaction, will then apply. But, if the operating conditions are such that the concentration of B drops to zero at some point λ within the catalyst, then the rate would depend on the concentration of B as well. The reaction between A and B would then occur only in the region λ to R, even though the concentration of A may be finite in the region 0 to λ. Ramachandran and Chaudhari (1979*a*) derived conditions under which the concentration of B would be finite at all points within the catalyst. They also developed equations for calculating the rate of reaction when pseudo first-order conditions are not applicable.

Special Cases: Homogeneous and Heterogeneous Reactions

In some situations, the reaction of A can occur homogeneously in the liquid phase (non-catalytic) and also on the solid catalyst. Some examples are: hydration of propylene oxide to monopropylene glycol (Polyanskii and Poyanskaya 1970), ethylene oxide to monoethylene glycol using ion exchange catalyst; oxidation reactions proceeding through the free radical mechanisms (Sadana and Katzer 1974, Meyer et al. 1965); and chlorination of toluene using $FeCl_3$ catalyst (Tan and Ratcliffe 1974). In such cases, the contribution of homogeneous liquid phase reaction must also be considered to predict the overall rate of reaction. The rate of reaction of A per unit volume of the slurry is then given by

$$R_A = \frac{H_AQ}{V_L}[1-\exp(-\alpha_AL)]\left[\frac{A_{gi}}{H_A} - A_l\right] \tag{51}$$

$$= k_HA_l + k_sa_p(A_l - A_s) \tag{52}$$

and

$$k_sa_p(A_l - A_s) = wk_1A_s\eta_c \tag{53}$$

where k_H is the rate constant for the homogeneous reaction. Both reactions are assumed to be first-order in A. Eliminating A_l and A_s, the following express the overall rate of reaction when both homogeneous and heterogeneous reactions are involved

$$R_A = \frac{A_{gi}}{H_A}\left\{\frac{1}{\dfrac{H_AQ}{V_L}[1-\exp(-\alpha_AL)]} + \frac{1}{k_H + k_sa_p\left\{\dfrac{wk_1\eta_c}{k_sa_p + wk_1\eta_c}\right\}}\right\}^{-1} \tag{54}$$

Here η_c is the catalytic effectiveness factor given by Equation (21), with ϕ defined by Equation (31).

The above theory is valid when there is no appreciable reaction of A in the gas-liquid film. The condition for this to be valid is

$$\frac{\sqrt{Dk_H}}{k_L} < 0.2 \tag{55}$$

Reactions with Very Small Particles

Very small catalyst particles of the order of 5μ are often used in slurry reactors. For particles less than 40μ, the reaction may occur predominantly on the outer surface (Gorokhovatskii 1972). This is because of the proportionately larger external area of the smaller particles, with the internal area. Recently, Varghese et al. (1978) analyzed the effectiveness factor of the catalyst η_c as a function of the external area of the catalyst (as a fraction of total area). This analysis should be incorporated in predicting the rate of reaction for small particles having low porosity and low internal surface area.

Effect of Particle Size Distribution

In a normal slurry operation, a range of particle size will exist in the reactor. This will influence the rate of reaction, as the mass transfer resistances change with particle diameter. Hsu and Ruether (1978) analyzed the influence of particle size distribution on the effectiveness factor in a slurry reactor and proposed equations to incorporate these effects.

Effect of Gas Phase Mixing

In the theoretical analysis of the earlier sections, we assume that the gas phase moves in plug flow. This may be satisfactory for a bubble column slurry reactor. However, in case of a mechanically agitated reactor, the mixing pattern of the gas phase is uncertain. Hence it is necessary to analyze the influence of gas phase mixing, and some work has been done on this aspect. Niiyama and Smith (1976) analyzed the transient response of a three phase slurry adsorber, and found that the mixing pattern of the gas is unimportant for sparingly soluble and for highly soluble gases. Similar effects are predicted by Goto and Smith (1978). Thus the influence of gas phase mixing is likely to be important only for gases in the intermediate solubility range.

When the gas phase is completely backmixed, the mass balance equation for the gas A is

$$Q(A_{gi} - A_{go}) = K_L a V_L \left[\frac{A_{go}}{H_A} - A_1\right] \tag{56}$$

Hence the concentration of the gas leaving the reactor is:

$$A_{go} = A_{gi}\frac{1}{1+\alpha_A L} + H_A A_1\left(1 - \frac{1}{1+\alpha_A L}\right) \tag{57}$$

Comparing Equations (57) and (8), the only difference between the plug flow model and the complete mixing model is that the term $[\exp(-\alpha_A L)]$ is replaced by $1/(1+\alpha_A L)$. All the equations described earlier thus apply also when the gas phase is completely backmixed, provided the above substitution is made. Comparing the terms containing $\alpha_A L$ in parameter M_A for the two extreme cases of plug flow and complete mixing, $[1 - \exp(-\alpha_A L)]$ and $1 - 1/(1+\alpha_A L)$, respectively, both the terms tend to $\alpha_A L$ when $\alpha_A L \rightarrow 0$ (sparingly soluble gas), and 1 when $\alpha_A L \rightarrow \infty$ (highly soluble gas). Thus the influence of gas phase mixing is negligible for these extreme cases of gas solubilities and may be important only when $\alpha_A L$ is in the range of 0.5 to 10 and when gas-liquid mass transfer is important. Similar considerations would apply to other gaseous species, when two gases are reacting in the slurry reactor.

CONSECUTIVE AND PARALLEL REACTIONS

Complex reactions with consecutive or parallel steps are commonly encountered in slurry catalyzed reactors. The types of reactions can be generally classified as

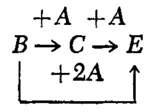
Type I: $A + B \rightarrow C$ (iv)

$A + C \rightarrow E$ (v)

Type II: $A + B \rightarrow C$ (vi)

$B + C \rightarrow E$ (vii)

Type III:



$$B \xrightarrow{+A} C \xrightarrow{+A} E \qquad B \xrightarrow{+2A} E$$

(viii)

In these schemes, A is the gaseous component while B and C are present in the liquid phase. Some examples of slurry reactions of Type I are: hydration of propylene oxide to mono and dipropylene glycol, hydrogenation of chlorobenzene (Kawakami and Kusunoki 1975), hydrogenation of phenylacetylene (Bizhanov et al. 1976, Kawakami and Kusunoki 1976) and butyne-diol (Fukuda and Kusama 1958), hydrogenation of phenolic compounds (Zwicky and Gut 1978).

An example of Type II reaction is found in the ethynylation of formaldehyde to butyne-diol (Kale and Chaudhari 1978). Hydrogenation of unsaturated oils follow Type III reaction scheme (Coenen 1976, Cordova and Harriot 1975, Tsuto et al. 1978, Marangozis et al. 1977).

Kusonoki et al. (1975) analyzed mathematically consecutive reactions Type I in a slurry reactor. Effects of mass transfer resistances, order of reactions, and initial concentrations of reactants on selectivity were studied, using numerical methods.

In simplified analysis of these reactions, we can assume that the concentrations of B and C are in excess, compared to the concentration of A. This will be generally true except in the initial stages of reaction in a semi-batch reactor, starting with no C. The rate of chemical reaction of A in the absence of intraparticle diffusion can be expressed implicitly as

$$R_A = wk_{(m_1+n_1)}B_1^{n_1}\left[A^* - \frac{R_A}{M_A}\right]^{m_1} + wk_{(m_2+n_2)}C_1^{n_2}\left[A^* - \frac{R_A}{M_A}\right]^{m_2} \tag{58}$$

where the reaction orders are (m_1, n_1) and (m_2, n_2) for $A + B$ and $A + C$ reactions respectively.

The selectivity defined as the ratio of the net rate of formation of C to the net rate of formation of E is then given by

$$\beta = \frac{k_{(m_1+n_1)}B_1^{n_1}\left[A^* - \frac{R_A}{M_A}\right]^{m_1}}{k_{(m_2+n_2)}C_1^{n_2}\left[A^* - \frac{R_A}{M_A}\right]^{m_2}} - 1 \tag{59}$$

The influence of the external mass transfer parameter M_A on selectivity can be computed using Equation (59), with R_A calculated from Equation (58). When the order of reactions are different, a drop in the concentration of A due to mass transfer limitations will favor the reaction of lower order. Thus if $m_1 > m_2$ lower mass transfer rates will decrease the selectivity while if $m_1 < m_2$, reduced mass transfer rates will improve the selectivity. If $m_1 = m_2$, the selectivity is independent of external mass transfer parameter M_A. These effects have also been experimentally verified by Kawakami and Kusunoki (1975) for the hydrogenation of chlorobenzene according to the scheme:

$$H_2 + C_6H_5Cl \rightarrow C_6H_6 + HCl \tag{ix}$$

$$3H_2 + C_6H_6 \rightarrow C_6H_{12} \tag{x}$$

The reaction orders with respect to hydrogen in a slurry reactor with 0.5% Pt-carbon catalyst are 0.2 to 0.5 for the first reaction and 0.6 for the second reaction. As in this case $m_1 < m_2$, selectivity would decrease as the stirring speed is increased, also as confirmed by experiments.

The effects of intraparticle diffusion on the rate and selectivity could be incorporated into the mathematical analysis by solving the relevant differential equations. When $m_1 = m_2 = 1$, analytical solutions are possible, following an approach similar to gas-solid catalytic reactions (Wei 1962). The general influence of mass transfer and reaction orders would be similar to that in the absence of intraparticle diffusional gradients, except when B or C is in comparable concentration to A, or when there are significant intraparticle gradients of B or C within the catalyst. Such a case (latter) can arise, for instance, in the hydrogenation of unsaturated oils where D_{eB}/D_{eA} or D_{eC}/D_{eA} values are of the order of 0.01. The selectivity of the intermediate is improved when there are significant intraparticle gradients of B and C. This is because C is formed within the catalyst, and sufficient A may not be available to react with C in the interior of the catalyst. Thus, in hydrogenation of phenyl acetylene Kawakami and Kusunoki (1976) observed that intraparticle diffusion gradients cause an increase of styrene and a decrease of phenyl acetylene in the pellet's interior. This favors the reaction of B in preference to C, and hence improves the selectivity.

Reactions of Type III can occur in the hydrogenation of unsaturated oils containing two or more double bonds (B). Formation of saturated compounds (E) can occur through the intermediate species C, which contains one double bond, or in parallel directly from B to E. A common simplification in the analysis of this reaction is to ignore this step ($B \rightarrow E$). Type III mechanism then reduces to Type I.

Because of the low diffusivity of the oils and products, intraparticle diffusion of the liquid phase reactants can be significant even for particles as small as 3.8μ (van der Planck et al. 1974, Coenen 1976). Tsuto et al. 1978 observed in the hydrogenation of methyl linoleate that until methyl linoleate (B) has almost disappeared, only a small amount of stearate (E) formed. The formation of E increased several-fold when B has almost completely reacted. A possible explanation postulated was that methyl linoleate (B) was strongly adsorbed as compared to methyl oleate (C). An order of magnitude value of K_B/K_C of 10 to 20 appeared to fit the experimental data.

An important general conclusion which can be drawn from this work is that the adsorption equilibrium constants play an important role in selectivity of consecutive slurry reactions. Due to this effect, Langmuir-Hinshelwood type models will be more realistic than power-law models for these systems. In the work of Tsuto et al. (1978) the selectivity to oleate (C) increased with catalyst loading, presumably due to increased mass transfer resistance.

Parallel reactions are also encountered in industrial slurry systems, for example, in hydrogenation of mixed olefins such as ethylene and propylene. Kawakami et al. (1976*a*) studied this reaction in a slurry reactor with 0.5% Pt-carbon catalyst. When hydrogen was in excess as compared to olefins, the reaction was controlled by mass transfer of the olefins, and the selectivity was determined by the mass transfer rates of ethylene and propylene. In the region of excess olefins, selectivity was affected by both external as well as intraparticle diffusion of hydrogen.

ILLUSTRATIVE EXAMPLES

In this section, we illustrate the theory discussed. Reactions following various kinetic orders are presented for completeness.

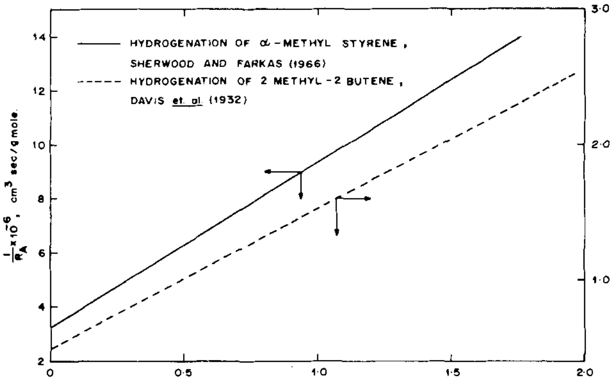


Figure 8. $1/R_A$ vs $1/w$ plots for first-order reactions in a slurry reactor.

First Order Reaction

The hydrogenation of α-methyl styrene on Pd-alumina has been studied by Satterfield et al. (1968). The reaction was pseudo first-order, with respect to hydrogen. The analysis used simplified equations for first order case (Equation 32). Other reactions where first-order kinetics has been observed are: hydrogenation of allyl alcohol (Ruether and Puri 1973), of crotonaldehyde (Kenney and Sedricks 1972) and of 2-methyl-2 butene (Davis et al. 1932).

Using the following relation for solid-liquid mass transfer area

$$a_p = \frac{6w}{\rho_p d_p} \qquad (60)$$

Equation (32) can be rearranged as

$$\frac{A^*}{R_A} = \frac{1}{\dfrac{H_A Q}{V_L}[1 - \exp(-\alpha_A L)]} + \frac{1}{w}\left[\frac{\rho_p d_p}{6k_s} + \frac{1}{\eta_c k_1}\right] \qquad (61)$$

From Equation (61) it is seen that a plot of A^*/R_A vs $1/w$ has an intercept of

$$\left\{ \frac{H_A Q}{V_L}[1 - \exp(-\alpha_A L)] \right\}^{-1}$$

For sparingly soluble gases, the intercept would correspond to $(k_L a)^{-1}$. This method of analyzing slurry reactor data has been conventionally used for obtaining the mass transfer and kinetic parameters. A typical plot of $1/R_A$ vs $1/w$ for a few systems of first order kinetics is shown in Figure 8.

Half Order Reaction: Hydrogenation of Acetone Over Raney Nickel Catalyst

Lemcoff (1977) studied hydrogenation of acetone using Raney nickel catalyst in iso-propanol medium. The reaction was half-order with respect to hydrogen, and the rate constant value obtained at 14°C was 2.35×10^{-3} (cm³, mole)$^{1/2}$/g sec. Based on this rate constant and the following values of other parameters; $\rho_p = 4.5$ g/cm³; $d_p = 0.001$ cm; $k_s = 0.08$ cm/sec; $k_L a = 0.02$ and 0.05 sec^{-1}; $H_A = 15.45$ cm³ (liquid)/cm³ (gas), at 1 atm.; the rates of reaction at different catalyst loadings can be predicted using Equation (T.1.3) in Table 1 for half-order kinetics. The results are shown as a plot of $1/R_A$ vs $1/w$ in Figure 9. Effect of $k_L a$ on the rate was computed. It is important to note that the plot of $1/R_A$

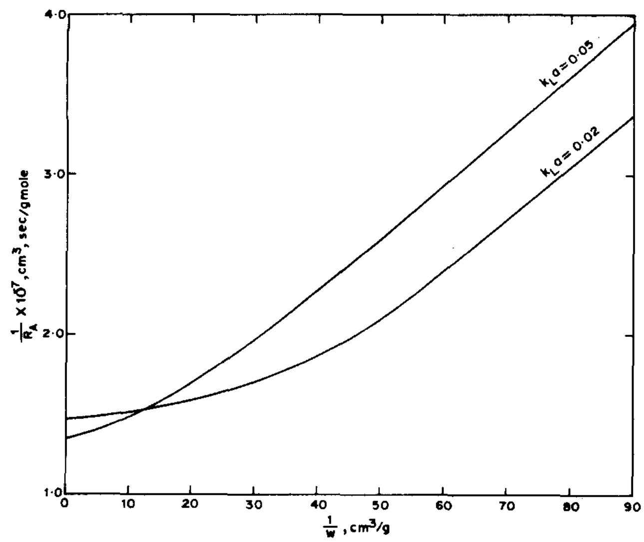


Figure 9. A plot of $1/R_A$ vs $1/w$ for hydrogenation of acetone over Raney nickel catalyst (an example of half-order kinetics).

vs $1/w$ is not a straight line for non-linear kinetics, and evaluating k_La from a linear extrapolation of such graphs can lead to significant errors.

Zero Order Reactions: Hydrogenation of Dinitrotoluene

Acres and Cooper (1972) studied hydrogenation of dinitrotoluene over Pd-charcoal catalyst. The rate of reaction was independent of hydrogen pressure above 8 atm (810 kPa), (indicating a zero-order kinetics) and was a function of hydrogen partial pressure below 8 atm. The rate may depend on H_2 concentration below this pressure because the conditions are such that $A_{gi} < (A_g)_{\text{critical}}$ and concentration of H_2 may be reaching zero at some point, λ, in the interior of the catalyst. Chaudhari and Ramachandran (1979) have demonstrated this, using the theory discussed earlier for zero-order reactions. At 383°K, the value of $[(A_g)_{\text{critical}}/H_A]$ obtained using Equation (34) was 2.36×10^{-5} mole/cm^3. Below this concentration of H_2, the rate would depend on hydrogen concentration. Experimentally, Acres and Cooper (1972) observed that the rate depended on hydrogen concentration below a value of $A^* = (A_{gi}/H_A) = 1.12 \times 10^{-5}$ mole/cm^3, which is in reasonable agreement with the theoretical predictions.

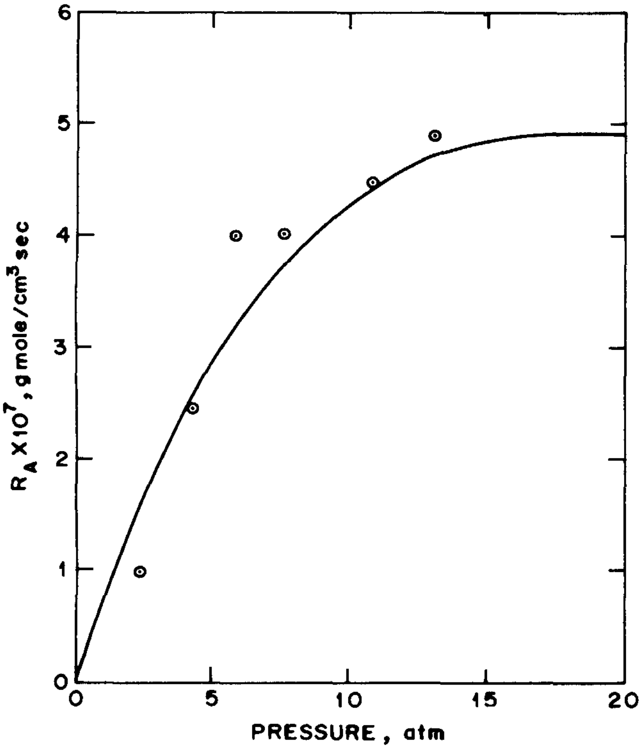


Figure 10. A plot of R_A vs partial pressure of hydrogen for hydrogenation of DNT (zero-order reaction). ——— = theoretical; ⊙ = experimental data of Acres and Cooper, (1972).

The rates of hydrogenation of dinitrotoluene, predicted from theory presented in the section on zero-order reactions and the data of Acres and Cooper are shown in Figure 10 as R_A vs hydrogen partial pressure plot.

The parameters used for this calculation were: temperature = 110°C; pressure = 2-13 atm.; $\rho_p = 0.8$ g/cm^3; $D_{eA} = 1.0 \times 10^{-6}$ cm^2/sec; $H_A = 22.74$ cm^3 (liquid)/cm^3 (gas) at 1 atm (101.32 kPa); $k_La = 0.107$ sec^{-1}; $w = 4 \times 10^{-4}$ g/cm^3; $k_sa_p = 0.18$ sec^{-1}.

Ethynylation of Formaldehyde

The reaction of acetylene with formaldehyde over Cu-acetylide catalyst to give butynediol is an important industrial reaction. Detailed investigation of this reaction has been made by Kale and Chaudhari (1978). The reaction was zero-order with respect to acetylene, above a concentration of 8.5×10^{-6} mole/cm^3. Below this value, the rate depended on the concentration of acetylene. The rate constants estimated from the experimental data were 6.75×10^{-7} mole/g sec at 3M formaldehyde concentration and 9.25×10^{-7} mole/g sec at 4M formaldehyde concentration.

Rate of reaction for this case can be calculated as a function of the acetylene concentration in the feed gas, using the theory for zero order reactions. Figure 11 shows the predicted and experimental results, as a plot of R_A vs partial pressure of acetylene. The theoretical predic-

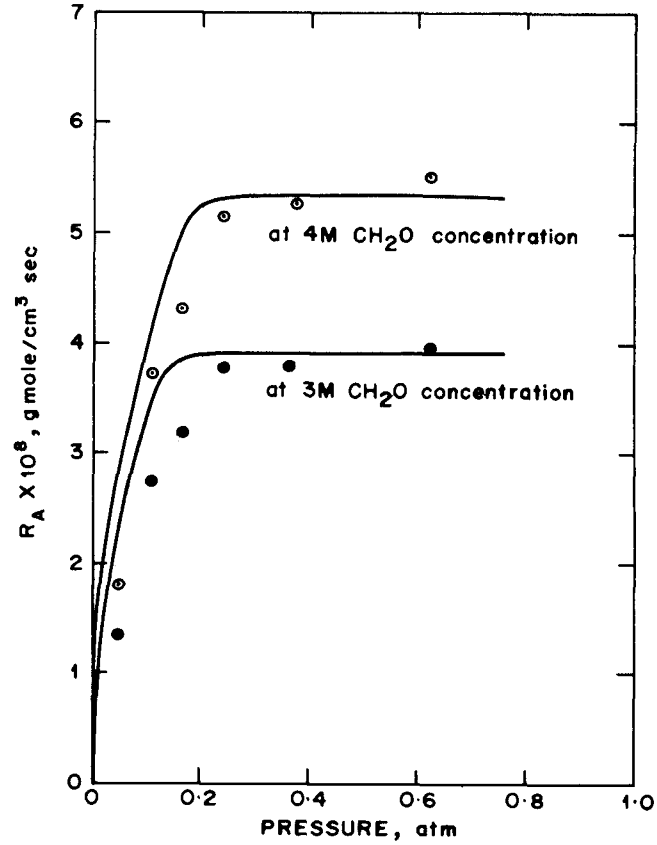


Figure 11. A plot of R_A vs partial pressure of acetylene for ethynylation of formaldehyde over Cu-acetylide catalyst (zero-order reaction). ⊙, ● = experimental data of Kale and Chaudhari (1978).

tions are in good agreement with the experimental results, with a maximum deviation of 23%. The parameter values used for the theoretical predictions were: temperature = 70°C; pressure = 0.2 – 0.6 atm.; $\rho_p = 4.0$ g/cm^3; $D_{eA} = 7.28 \times 10^{-6}$ cm^2/sec; $H_A = 2.53$ cm^3 (liquid)/cm^3 (gas) at 1 atm. (101.32 kPa); $k_La = 0.107$ sec^{-1}; $w = 5.71 \times 10^{-2}$ g/cm^3; $k_sa_p = 0.186$ sec^{-1}.

Reaction of Two Cases: Oxidation of CO Using CoO Catalyst

Reaction of CO and O_2 was studied by Ido et al. (1976) in a slurry reactor, using a CoO catalyst in silicone oil as a medium. This is an example of reaction of two gases in a slurry reactor. Conditions of the experiments were such that the concentration of oxygen was always in excess. A Langmuir-Hinshelwood type model, based on dual site mechanism (see Equation T.2.4 in Table 2) has been proposed for this reaction. For Ido's data, the overall effectiveness factor η can be calculated using Equation (T.2.4) from Table 2.

Oxidation of SO_2 Over Activated-C Catalyst

Oxidation of SO_2 in a slurry of activated carbon was studied by Komiyama and Smith (1975). In the range of concentrations studied ($SO_2\% > 2.3$), the reaction was first-order with respect to O_2 and zero-order with respect to SO_2. This illustrates (1, 0) order kinetics. Ramachandran and Chaudhari (1979) demonstrated that below a critical SO_2 concentration, the rate would depend on SO_2 concentration, even though the intrinsic kinetics is zero-order with respect to SO_2. This is because SO_2 is totally depleted in certain portions of the catalyst. This critical concentration is a function of various parameters and is in the range of 0.2%. Such a region may be of practical importance in air pollution problems since it may be required to remove SO_2 to very low concentration levels.

Homogeneous and Heterogeneous Reaction: Hydration of Propylene Oxide

The hydration of propylene oxide catalyzed by an ion-exchange resin catalyst is an example of a slurry system where Species A (propylene oxide) can react noncatalytically in the liquid phase as well as catalytically on the surface of the ion-exchange resins. The rate constant for the noncatalytic homogeneous reaction k_H is 1.74×10^{-4} sec^{-1} at 90°C. The rate of reaction for a slurry system for this case can be predicted using Equation (54).

The influence of the ratio of the two rate constants $\rho_p k_l/k_H$ on the rate of reaction is shown in Figure 12. We see that the homogeneous reaction contributes significantly to the overall rate of reaction for the range of values assumed in the calculations. Since the catalyst loadings in the slurry are expected to be small, the heterogeneous reaction would predominate only at high values of $\rho_p k_l/k_H$. For a particular case of $w = 0.02$ g/cm^3, a ratio of 10 or more is required for the heterogeneous reaction to contribute to the overall rate. The parameters used for Figure 12 are: $d_p = 0.1$ cm; $\rho_p = 1.2$ g/cm^3; $D_{eA} = 10^{-5}$ cm^2/sec; $w = 2 \times 10^{-2}$ g/cm^3; $k_H = 1.74 \times 10^{-4}$ sec^{-1}; $k_La = 0.1$ sec^{-1}; $k_sa_p = 2 \times 10^{-3}$ sec^{-1}.

MODELING OF SEMI-BATCH SLURRY REACTORS

The general theoretical analysis presented earlier applies to differential operation of a slurry reactor, that is, when the condition of the liquid phase in the reactor changes only slightly. Many industrial slurry reactors are operated in a semi-batch manner (with the liquid phase stationary and continuous gas flow). In such cases, it is often necessary to predict the conversion of liquid phase component (B) as a function of time. Modeling of semi-batch slurry reactors is discussed below for the reaction scheme:

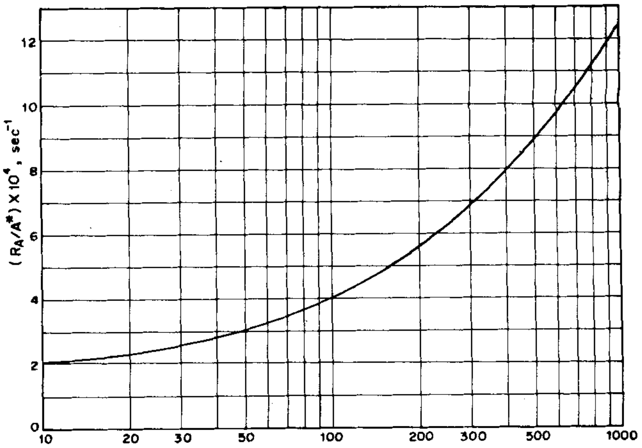


Figure 12. Effect of homogeneous reaction on the hydration rates of propylene oxide in a slurry reactor.

$$A_{(g)} + \nu B_{(l)} \rightarrow \nu_p C_{(l)} \qquad \text{(xi)}$$

It is assumed that B is in excess, so that the pseudo-m^{th} order condition can be assumed throughout the reaction period. This will generally be the case when a sparingly soluble gas is a reactant.

Reactions First Order with Respect to A and B

The rate of reaction for this case can be expressed as

$$\Omega = k_2 A B_l \qquad (62)$$

The rates of reaction of A and B are related by the following stoichiometric equation

$$R_B = \nu R_A \qquad (63)$$

The rate of reaction of B, per unit volume of slurry in the absence of significant intraparticle concentration gradients, is given by

$$-\frac{dB_1}{dt} = R_B = \frac{\nu A_{gi}}{H_A}\left\{\frac{1}{\frac{H_AQ}{V_L}[1-\exp(-\alpha_A L)]} + \frac{1}{k_sa_p} + \frac{1}{wk_2B_1}\right\}^{-1} = \frac{A_{gi}}{H_A}\left[\frac{1}{M_A} + \frac{1}{wk_2B_1}\right]^{-1} \qquad (64)$$

Integration of Equation (64), assuming that the solubility coefficient H_A is not changing significantly, gives an analytical solution for B_1 as a function of time in a semi-batch slurry reactor

$$\frac{B_{lo} - B_{lf}}{M_A} + \frac{1}{wk_2}\ln\frac{B_{lo}}{B_{lf}} = \frac{\nu A_{gi}}{H_A}t \qquad (65)$$

Equation (65) applies only when intraparticle diffusion effects are not significant ($\eta_c \rightarrow 1$). The following criteria must be satisfied for the applicability of Equation (65)

$$\frac{R}{3}\left[\frac{k_2\rho_p B_{lo}}{D_{eA}}\right]^{1/2} < 0.2 \qquad (66)$$

When the condition given by Equation (66) is not satisfied, the intraparticle gradients would be important. Equation (64) would then have to be modified to account for the catalytic effectiveness factor as

$$-\frac{dB_l}{dt}=\frac{\nu A_{gi}}{H_A}\left[\frac{1}{M_A}+\frac{\phi}{\left[\coth(3\phi)-\frac{1}{3\phi}\right]wk_2B_l}\right]^{-1} \tag{67}$$

where

$$\phi=\frac{R}{3}\left[\frac{\rho_p k_2 B_l}{D_{eA}}\right]^{1/2} \tag{68}$$

The integrated form of Equation (67) is

$$\frac{B_{lo}-B_{lf}}{M_A}+\int_{B_{lf}}^{B_{lo}}\frac{dB_l}{\frac{3wD_{eA}}{R^2\rho_p}\left\{R\left[\frac{\rho_p k_2 B_l}{D_{eA}}\right]^{1/2}\coth R\left[\frac{\rho_p k_2 B_l}{D_{eA}}\right]^{1/2}-1\right\}}=\frac{\nu A_{gi}}{H_A}t \tag{69}$$

A method to estimate the batch time is presented by Ramachandran and Chaudhari (1980), where the integral term in Equation (69) is presented graphically.

First-Order with Respect to *A* and Zero-Order for *B*

In a number of situations, the rate is independent of the liquid phase reactant concentration (B). For example, hydrogenation of nitrobenzene on Pd based catalysts (Acres and Cooper 1972, and Tong et al. 1978), of styrene-on 0.5% Pt-Al_2O_3 catalyst (Kawakami et al. 1976*b*) follow zero-order kinetics with respect to B. In this case the rate is given by

$$\Omega=k_1A \tag{70}$$

The rate of reaction of B will then be given by

$$-\frac{dB_l}{dt}=\nu R_A=\frac{\nu A_{gi}}{H_A}\left[\frac{1}{\frac{H_AQ}{V_L}\left[1-\exp(-\alpha_AL)\right]}+\frac{1}{k_sa_p}+\frac{1}{\eta_cwk_1}\right]^{-1} \tag{71}$$

Solving Equation (71) gives an expression for B as a function of t

$$(B_{lo}-B_{lf})\left[\frac{1}{M_A}+\frac{1}{\eta_cwk_1}\right]=\frac{\nu A_{gi}}{H_A}t \tag{72}$$

The effectiveness factor η_c in Equation (72) is given by Equation (21), with the term ϕ defined by Equation (31). In some cases, it has been observed that the rate is independent of concentration of B at higher concentrations but shows first-order dependence when B is less than a critical concentration B_{lc}. To model the reactor performance for such systems, Equation (72) has to be used for B_{lo} to B_{lc}, and then Equation (69) must be used for B_{lc} to B_{lf}.

$[m,n]^{th}$ Order Reaction

The rate of reaction of B per unit volume of slurry is now given by

$$-\frac{dB_l}{dt}=\nu R_A=\nu wk_2\eta\left[\frac{A_{gi}}{H_A}\right]^m B_l^n \tag{73}$$

The effectiveness factor η is a function of B_l, and hence numerical solution will be necessary to obtain B_l vs t relationship. The equation for calculating η at any given time can be obtained from Table 2.

Effect of Solubility Changes

The solubility of the gas phase reactant can be influenced by changes in the concentrations of liquid phase reactants and products. This affects the rate of conversion of B with time in a semi-batch reactor, and the equations given earlier will not apply. The quantity A_{gi}/H_A would be a function of B and concentration of other products formed. Lemcoff (1977) points out that in the hydrogenation of acetone in a slurry reactor, the solubility changes appreciably with changes in acetone and product concentration. Komiyama and Smith (1975) in their study of SO_2 oxidation over activated carbon slurry, report that the solubility of O_2 reduces with increase in H_2SO_4 (product of reaction) concentration.

In a similar context, Satterfield et al. (1968) measured solubility of hydrogen in pure alpha-methyl styrene, pure cumene (the reaction product of hydrogenation) and in a 60:40 volume mixture of the two. They found that solubility changes only slightly with concentration. The following two types of correlations are convenient to quantitatively account for the solubility of A as a function of reactant and/or product concentrations

$$A^*=\frac{A_{gi}}{H_A}=(r_1+r_2B_l+r_3C_l)p_{gA} \tag{74}$$

Or, a power-law type of correlation may be used

$$A^*=\frac{A_{gi}}{H_A}=(r_1+B_l^{r_2}+C_l^{r_3})p_{gA} \tag{75}$$

where p_{gA} is the partial pressure of A in the inlet gas stream, r_1, r_2, r_3 are empirical constants, and B_l and C_l are, respectively, the concentrations of reactant and product, g mole/cm^3.

Concentration of the product C_l can be related to the concentration of reactant B_l by a stoichiometric mass balance

$$C_l=C_{lo}+\frac{\nu_p}{\nu}(B_{lo}-B_l) \tag{76}$$

Substituting Equation (76) in (74), we obtain the following correlation for solubility in terms of B_l

$$A^*=\frac{A_{gi}}{H_A}=\left[r_1+\left[r_2-r_3\frac{\nu_p}{\nu}\right]B_l+r_3\left[C_{lo}+\frac{\nu_p}{\nu}B_{lo}\right]\right]p_{gA} \tag{77}$$

When reaction is first-order with respect to A and B, the rate of change of B_l with time (incorporating the changes in solubility values of A as a function of B_l and ignoring intraparticle diffusion effects) is

$$-\frac{dB_l}{dt}=\nu p_{gA}\left\{r_1+\left[r_2-r_3\frac{\nu_p}{\nu}\right]B_l+r_3\left[C_{lo}+\frac{\nu_p}{\nu}B_{lo}\right]\right.\left[\frac{1}{M_A}+\frac{1}{wk_2B_l}\right]^{-1} \tag{78}$$

Integrating Equation (78), we get an expression for B as a function of time, incorporating the effects of solubility changes

$$\frac{\ln\gamma}{M_A(r_2-r_3\nu_p/\nu)}+\frac{\ln\gamma(B_{lf}/B_{lo})}{wk_2\left[r_1+r_3\left[C_{lo}+\frac{\nu_p}{\nu}B_{lo}\right]\right]}=\nu p_{gA}t \tag{79}$$

where

$$\gamma = \frac{r_1 + r_3[C_{lo} + (\nu_p/\nu)B_{lo}] + B_{lo}[r_2 - r_3(\nu_p/\nu)]}{r_1 + r_3[C_{lo} + (\nu_p/\nu)B_{lo}] + B_{lf}[r_2 - r_3(\nu_p/\nu)]} \tag{80}$$

Similarly, equations for other types of kinetics could be derived. The above equation is valid only when intraparticle diffusion effects are negligible ($\eta_c \rightarrow 1$). When $\eta_c < 1$, more complex equations can be derived to obtain an equation similar to (69), incorporating solubility changes.

Effects of Product Inhibition

In many slurry reaction systems, the product can inhibit the rate of chemical reaction of A. This effect should be incorporated in modeling semi-batch reactors. Product inhibition can be due to any of the following mechanisms: the solubility of gas phase reactant (A) decreases with increase in product concentration; product of the reaction is more strongly adsorbed than the reactants; and the product deactivates the catalyst, either chemically or physically.

The first mechanism is discussed in our section on effects of solubility changes, where some efforts to quantify the effects are presented. The case of product adsorbing more strongly than the reactants is also a common phenomenon. Recently, Kale and Chaudhari (1978) reported such an effect in ethynylation of formaldehyde to butynediol, using Cu-acetylide catalyst. They show that the solubility effects are negligible, and the inhibition is due to strong adsorption capacity of the product butynediol. They propose an empirical rate equation, incorporating the effect of product concentration.

In some systems, product inhibition could be due to both solubility changes and adsorption effects. In the oxidation of SO_2 in activated carbon catalyst Komiyama and Smith (1975) found the retardation of rates was primarily due to reduced solubility in the presence of sulfuric acid. The effect of adsorption of H_2SO_4 was found to be unimportant, as the adsorption isotherm was nearly flat. However, the effect of increase in viscosity would affect external and internal mass transfer rates. For example, at $4NH_2SO_4$ concentration, the rate decreased by a factor of 0.55, while the oxygen solubility decreased by only a factor of 0.67, compared to a system with negligible H_2SO_4 concentration.

An example of the product deactivating the catalyst is in oxidation of H_2S in slurries of activated carbon, where the product sulfur blocks the pores of the catalyst and retards rates. Systematic experimental investigation of this problem does not appear to have been published.

Effect of Temperature

In slurry reactors, the temperature gradients between gas phase and catalyst are generally negligible, due to high heat transfer coefficients. Similarly, the intraparticle temperature gradients can be considered negligible. The intraparticle thermicity parameter, defined as $A^*(-\Delta H)D_{eA}/\lambda_e/T_s$, even for highly exothermic reactions (100 kcal/mole) would be less than 0.01.

Although temperature gradients may be absent, the temperature of the bulk liquid itself may increase due to reaction and go through a maximum as a function of time. This will affect the rate of reaction, due to changes in the kinetic rate constant and the solubility. Simultaneous solution of the transient heat and mass balance would be necessary.

Reaction of Two Gases

Goto and Smith (1978) modeled a slurry reactor in which two gases react catalytically, assuming the reaction to be (1, 0) order. An illustration to SO_2 oxidation has also been presented.

Continuous Slurry Reactors

Some industrial processes use continuous slurry reactors, where liquid and gas phases are continuously flowing in the reactor. Here the conversion of the liquid phase component B is often the quantity of design interest. To predict this, a knowledge of flow pattern of the slurry and gas phase is required. The usual assumption of complete backmixing of the liquid phase is likely to be valid for mechanically agitated reactors and in bubble columns with low L/d_T (<10). This is indicated from the published axial dispersion coefficient data in gas-liquid reactors, reviewed by Shah et al. in 1978.

Analytical equations for conversion of B are possible for various kinetic schemes when the intraparticle diffusional resistances are negligible (Ramachandran and Chaudhari 1979*b*). Complex situations are encountered in bubble columns with large L/d_T ratios, due to change in the total gas flow rate and non-uniform distribution of the catalyst particles etc. More theoretical and experimental work is required in this area.

SUSPENSION OF SOLID PARTICLES

The entire solid mass must be suspended for maximum utilization of the catalyst. The theoretical analysis presented earlier assumes that all solids are in complete suspension and there is no settling of particles. A certain minimum degree of agitation is required to achieve this, and calculating the minimum agitation is required to ensure complete suspension. Zweitering (1958) completed an extensive examination of the conditions for complete suspension. According to him, a suspension can be considered complete if no particle remains at the bottom of the reactor for longer than 1 or 2 sec. He proposed the following correlation

$$N_m = \frac{\beta_2 d_p{}^{0.2} \mu_L{}^{0.1} g^{0.45} (\rho_p - \rho_L)^{0.45} \left[\dfrac{w}{\rho_L}\right]^{0.13}}{\rho_L{}^{0.55} d_I{}^{0.85}} \tag{81}$$

where N_m is the minimum stirrer speed required for complete suspension and β_2 is a constant. He presented the constant β_2 as a graph of β_2 vs d_T/d_I for various agitator arrangements. Nienow (1968, 1975) showed that an approximate value of β_2 for disc turbines is given by

$$\beta_2 = \left[\frac{d_T}{d_I}\right]^{1.33} \tag{82}$$

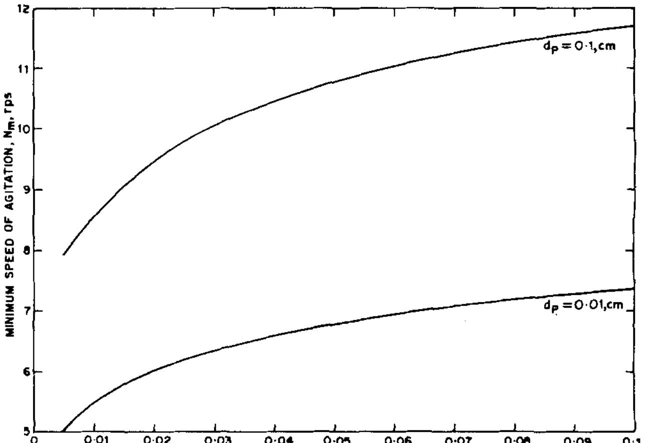


Figure 13. Minimum agitation required for complete suspension for various catalyst loadings.

Baldi et al. (1978) proposed a correlation for N_m which is similar to that of Zwietering.

The minimum speed of agitation for various values of catalyst loadings is shown in Figure 13 for a specific case. The parameters used for the calculation were $d_T = 10$ cm, $d_I = 5$ cm, $\mu_L = 8 \times 10^{-3}$ gm/cm/sec, $l = 1$ g/cm^3, $p = 2$ g/cm^3.

For the bubble column slurry operation, two suspension states may exist: namely, complete suspension in which all particles are in suspension, and homogeneous suspension, in which the particle concentration is uniform throughout the reactor. Roy et al. (1964) derived correlations on the basis of dimensional analysis for critical solid hold-up, defined as the maximum amount of solid that can be kept in complete suspension for a given operating condition. This correlation is

$$w_{\max} = 6.8 \times 10^{-4} \left[\frac{c_\mu d_T u_g \rho_g}{\rho L^\mu g} \right] \left[\frac{S_T \epsilon_g}{u_g \mu_L} \right]^{-0.23} \times \left[\frac{\epsilon_g u_{tp}}{u_g} \right]^{-0.18} (\gamma')^{-3.0} \quad (83)$$

where u_{tp} is the Stoke's terminal settling velocity of the particles given as

$$u_{tp} = \frac{g d_p^2 (\rho_p - \rho_L)}{18\, \mu_L} \quad (84)$$

c_μ is a viscosity correction factor

$$c_\mu = 2.32 \times 10^{-1} - 1.788 \times 10^{-1} \log \mu_L + 1.026 \times 10^{-1} (\log \mu_L)^2 \quad (85)$$

where μ_L is expressed in poise (gm/cm/sec) and γ' is the "wetability" factor, which can be taken as unity for most of the catalysts.

To illustrate this correlation, the minimum gas velocity required to suspend the particles for a given loading is shown in Figure 14 for the following parameters: $d_T = 10$ cm, $\mu_L = 8 \times 10^{-3}$ g/cm/sec, $\mu_g = 1.8 \times 10^{-4}$ g/cm/sec, $s_T = 72$ dyne/cm, $\rho_L = 1$ g/cm^3, $\rho_p = 3$ g/cm^3, $\rho_g = 1.2 \times 10^{-3}$ g/cm^3 (ϵ_g is calculated from Equation 101, discussed later).

Kato et al. (1972) proposed that a solid distribution exists in a bubble column with height. They measured the concentration distribution of solid particles and found an exponential variation with height. This effect may be significant in columns with large L/d_T. Farkas and Leblond (1969) discussed the effect of solid distribution on the rate of reaction in a bubble column.

GAS LIQUID MASS TRANSFER COEFFICIENT

Here, we summarize some correlations for predicting $k_L a$ and some experimental techniques for determination of $k_L a$.

Correlations

Calderbank and Moo-Young (1961) suggest the following correlation for the liquid side mass transfer coefficient

$$k_L = 0.42 \left[\frac{(\rho_L - \rho_g) \mu_L g}{\rho_L^2} \right]^{1/3} \left[\frac{D \rho_L}{\mu_L} \right]^{1/2} \quad (86)$$

This equation applies to bubble swarms of average diameter greater than about 2.5 mm, such as produced when pure liquids are aerated in mixing vessels.

The gas-liquid interfacial area was correlated by Calderbank (1958) as

$$a = 1.44 \frac{\left(\frac{P}{V_L} \right)^{0.4} \rho_L^{0.2}}{S_T^{0.6}} \left(\frac{u_g}{u_t} \right)^{0.5} \quad (87)$$

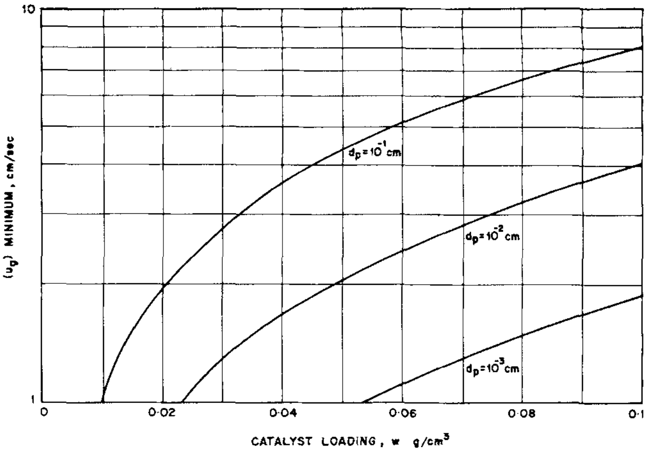


Figure 14. Minimum gas velocity required for complete suspension of catalyst in a bubble column.

where a is in cm^{-1}. The equation applies when

$$\left[\frac{d_I^2 N \rho_L}{\mu_L} \right]^{0.7} \left[\frac{N d_B}{u_g} \right]^{0.3} < 20{,}000 \quad (88)$$

When the value of the above quantity is greater than 20,000, the interfacial area is given as

$$\log_{10} \left[\frac{2.3a}{a_o} \right] = 1.95 \times 10^{-5} \left[\frac{d_I^2 N \rho_L}{\mu_L} \right]^{0.7} \left[\frac{N d_B}{u_g} \right]^{0.3} \quad (89)$$

where a_o is the value of 'a' calculated from Equation (87).

The above equations require a knowledge of the bubble diameter and the terminal gas-bubble velocity in free rise. The latter can be approximated as 26 cm/sec. (Perry and Chilton 1973). The average bubble diameter is given by

$$d_B = 4.15 \frac{(S_T)^{0.6}}{\left[\frac{P}{V_L} \right]^{0.4} \rho_L^{0.2}} \epsilon_g^{1/2} + 0.09 \quad (90)$$

where ϵ_g is the gas hold-up given as

$$\epsilon_g = \left[\frac{u_g \epsilon_g}{u_t} \right]^{1/2} + 0.0216 \frac{\left[\frac{P}{V_L} \right]^{0.4} \rho_L^{0.2}}{S_T^{0.6}} \left[\frac{u_g}{u_t} \right]^{1/2} \quad (91)$$

The power consumption per unit volume can be obtained from the power number N_p defined as

$$\frac{P}{V_L} = \frac{N_p N^3 d_I^5 \psi}{V_L} \quad (92)$$

where ψ is a correction factor for the presence of gas bubbles. The value of N_p has been correlated as a function of $[N d_I^2 \rho_L / \mu_L]$ by Bates et al. (1963).

Prasher and Wills (1973) give the following equation for calculation of P/V_L for gas-liquid systems

$$e = \frac{P}{\rho_L V_L} = \frac{8 N^3 d_I^5 \psi}{d_T^2 L} \quad (93)$$

where the correction factor ψ is given as

$$\psi = 1.0 - 1.26 \left[\frac{Q}{N d_I^3} \right], \quad \text{for} \quad \frac{Q}{N d_I^3} < 3.5 \times 10^{-2} \quad (94)$$

and

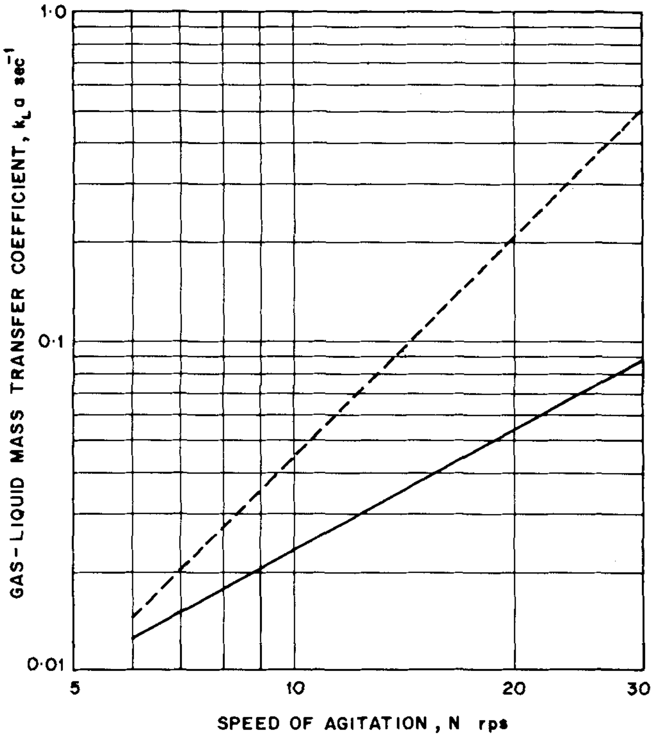


Figure 15. Comparison of correlations for k_L a in an agitated reactor. ---- = Yagi and Yoshida (1975); ——— = Calderbank and Moo-Young (1961).

$$\psi = 0.62 - 1.85\left[\frac{Q}{Nd_I^3}\right], \quad \text{for} \quad \frac{Q}{Nd_I^3} > 3.5 \times 10^{-2} \tag{95}$$

Nagata (1975) indicates that the power consumption in slurries should be taken as $P\rho_s/\rho_L$, where ρ_s is the density of the slurry. This correction factor may not be significant for low catalyst loadings and for catalysts with low densities.

Yagi and Yoshida (1975) proposed a correlation for k_La in an agitated contactor

$$\left[\frac{k_La}{D}\right]d_I^2 = 0.060\left[\frac{d_I^2N\rho_L}{\mu_L}\right]^{1.5}\left[\frac{d_IN^2}{g}\right]^{0.19}\left[\frac{\mu_L}{\rho_LD}\right]^{0.5}\left[\frac{\mu_Lu_g}{S_T}\right]^{0.6}\left[\frac{Nd_I}{u_g}\right]^{0.32} \tag{96}$$

The above equation does not require a knowledge of the power consumption rate and represents the data on CO_2 absorption in glycerol-water at 30°C satisfactorily.

The above two correlations are compared in Figure 15 as a plot of k_La vs N. The parameter values used were $d_T = 10$ cm, $d_I = 5$ cm, $L = 10$ cm, $\rho_L = 1$ g/cm^3, $\mu_L = 8 \times 10^{-3}$ g/cm/sec, $S_T = 72$ dyne/cm, $u_g = 0.2$ cm/sec, $D = 2 \times 10^{-5}$ cm^2/sec, $\rho_g = 1.2 \times 10^{-3}$ g/cm^3.

In a bubble column reactor, the mass transfer coefficient k_L can be estimated using a relationship suggested by Akita and Yoshida (1974)

$$\frac{k_Ld_B}{D} = 0.5\left[\frac{\mu_L}{D\rho_L}\right]^{1/2}\left[\frac{gd_B^3\rho_L^2}{\mu_L^2}\right]^{1/4}\left[\frac{gd_B^2\rho_L}{S_T}\right]^{3/8} \tag{97}$$

Kawagoe et al. (1975) developed the following correlation for k_L in a bubble column

$$\frac{k_Ld_B}{D} = 0.975\left[\frac{\mu_L}{D\rho_L}\right]^{1/2}\frac{gd_B^3\rho_L^2}{\mu_L^2}^{1/4} \tag{98}$$

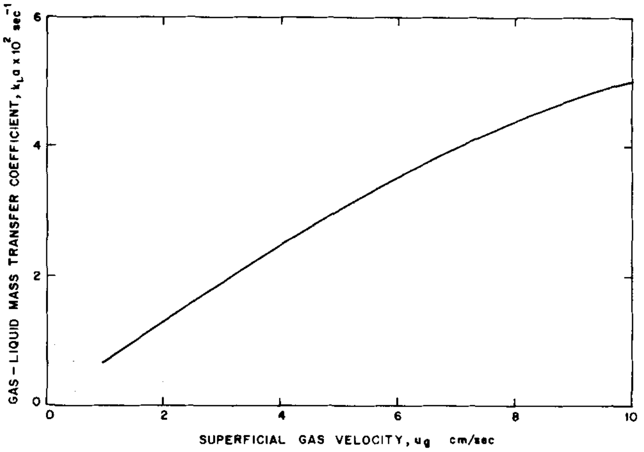


Figure 16. A plot of k_L a vs u_g from Kawagoe *et al.* correlation (1975) for a bubble column.

The gas-liquid interfacial area is given by

$$a = \frac{6\epsilon_g}{d_B} \tag{99}$$

A knowledge of gas hold-up and bubble diameter is necessary to estimate (k_La) in bubble columns. These were correlated by Akita and Yoshida as

$$\frac{d_B}{d_T} = 26\left[\frac{gd_T^2\rho_L}{S_T}\right]^{-0.5}\left[\frac{gd_T^3\rho_L^2}{\mu_L^2}\right]^{-0.12}\left[\frac{u_g}{\sqrt{gd_T}}\right]^{-0.12} \tag{100}$$

$$\frac{\epsilon_g}{(1-\epsilon_g)^4} = 0.20\left[\frac{gd_T^2\rho_L}{S_T}\right]^{1/8}\left[\frac{gd_T^3\rho_L^2}{\mu_L^2}\right]^{1/12}\left[\frac{u_g}{\sqrt{gd_T}}\right] \tag{101}$$

The correlation of Kawagoe et al. is illustrated in Figure 16, where k_La is plotted as a function of the gas velocity u_g. The conditions used for this plot were: $d_T = 10$ cm, $\rho_L = 1$ g/cm^3, $\mu_L = 8 \times 10^{-3}$ gm/cm/sec, $S_T = 72$ dyne/cm, $D = 2 \times 10^{-5}$ cm/sec.

Experimental Methods

Liquid-side mass transfer coefficient, k_La can be determined by measuring the physical absorption rates or bulk concentration of the dissolved gas as a function of time in a batch reactor. For determining the true overall liquid-side mass transfer coefficient, a system with negligible gas-side mass transfer resistance should be used. This can be done by selecting a sparingly soluble gas (such as CO_2) for aqueous systems. Alternately a pure gas can be used.

The concentration time data can be analyzed by well-known methods, to obtain k_La. Techniques based on using a gas which undergoes a slow chemical reaction in the liquid can also be used. The details of this method are discussed by Danckwerts (1970). Absorption with reaction of CO_2 in sodium carbonate-bicarbonate buffer solution is controlled by mass transfer under certain conditions, and this system could be used to evaluate k_La. Mehta and Sharma (1971) used this technique to determine k_La in agitated contactors.

This value could also be obtained from the observed rate of reaction in a slurry system, provided the rate of reaction is controlled by gas-liquid mass transfer. Many hydrogenation reactions on supported Pt catalysts are fairly rapid, so that the rate is controlled by gas-liquid mass transfer. For a first-order slurry reaction, a plot of

$1/R_A$ vs $1/w$ is linear. The intercept of such a plot would represent $H_A/k_La A_{gi}$ for a sparingly soluble gas such as H_2 or when pure gas is used. Hence, experimental rate data from different catalyst loadings can also be used to obtain k_La. Sherwood and Farkas (1966) used this technique for experiments on hydrogenation of α-methyl styrene. It has also been employed by Davis et al. (1932), Lemcoff and Jameson (1975), Komiyama and Smith (1975), and Bern et al. (1976).

A transient method for determining k_La and other rate parameters using an adsorbable gas as a tracer has been proposed by Niiyama and Smith (1976, 1977) and Niiyama et al. (1978). Ramachandran and Smith (1978*b*) discuss the parameter estimation method, using moment analysis of dynamic data.

Influence of Solids on k_La

Most of the correlations for k_La are based on experimental data in the absence of solids, that is, on data obtained for gas-liquid systems. In a slurry system, a solid phase is invariably present, and the extent of influence of the solids on k_La is uncertain. For example, Slesser et al. (1968) indicate that the mass transfer coefficient is affected by the presence of solids for certain range of catalyst loading. Tamhankar and Chaudhari (1979) determined k_La in a magnetically stirred vessel by absorbing acetylene in water containing suspended solid particles. They found that k_La values were unaffected by the presence of solids. In a recent paper, Joosten et al. (1977) also reported that k_La values are not significantly affected by solid particles.

SOLID-LIQUID MASS TRANSFER COEFFICIENT

Correlations

Harriot (1962) and Brian et al. (1969) used Kolmogoroff's theory as a basis for correlating solid-liquid mass transfer. Based on this theory, the solid-liquid mass transfer coefficient is a function of the Reynolds number defined as

$$(Re)_v = \left[\frac{e d_p^4 \rho_L^3}{\mu_L^3} \right]^{1/2}, \quad \text{for} \quad l_e >> d_p \qquad (102)$$

or

$$(Re)_I = \left[\frac{e d_p^4 \rho_L^3}{\mu_L^3} \right]^{1/3}, \quad \text{for} \quad l_e << d_p \qquad (103)$$

where l_e is the eddy size, which is a function of only the energy dissipation rate per unit mass of slurry and the kinematic viscosity

$$l_e = \left[\frac{\mu_L^3}{\rho_L^3 e} \right]^{1/4} \qquad (104)$$

Furusawa and Smith (1973*a*, 1973*b*) obtained the values of k_s for benzene-activated carbon system and confirmed that the above correlation procedure is valid by plotting $k_s d_p/D$ as a function of $(Re_I)^3$. Their results agree with Harriot (1962) and Brian et al. (1969).

Levins and Glastonbury (1972) improved the correlation by including the ratio of impeller to vessel diameter as a correlating term and obtained the following

$$\frac{k_s d_p}{D} = 2 + 0.47 \left[\frac{d_p^{4/3} e^{1/3} \rho_L}{\mu_L} \right]^{0.62} \left[\frac{d_I}{d_T} \right]^{0.17} \left[\frac{\mu_L}{\rho_L D} \right]^{0.36} \qquad (105)$$

The correlation is valid when the density difference between the liquid and solid is not large.

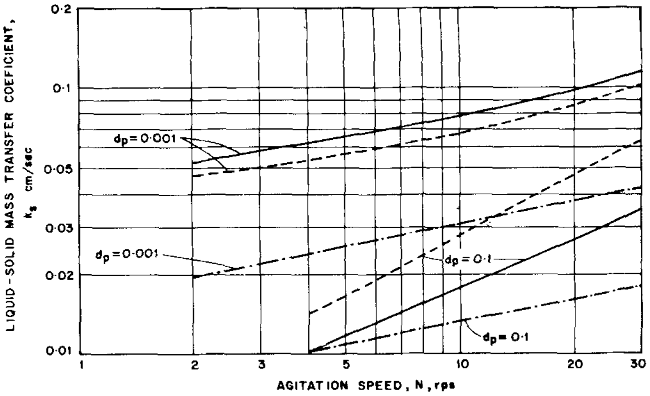


Figure 17. Comparison of correlations for liquid-solid mass transfer coefficient in an agitated reactor. ——— = Levins and Glastonbury (1972); - - - - = Sano *et al.* (1974); —·—·— = Boon-long *et al.* (1978).

Sano et al. (1974) measured solid-liquid mass transfer coefficients in agitated vessels and bubble columns. They cover four sizes of agitated vessels with diameters ranging from 9.5 cm to 40 cm, including fully baffled and nonbaffled conditions and two sizes of bubble columns of diameter 10 and 20 cm. Particle size ranges from 60 to 1100μ including both spherical beads (ion exchange resins) and granules (benzoic acid, $KMnO_4$ and β-naphthol). The data were correlated by the following equation

$$\frac{k_s d_p}{D F_c} = 2 + 0.4 \left[\frac{e d_p^4 \rho_L^3}{\mu_L^3} \right]^{1/4} \left[\frac{\mu_L}{\rho_L D} \right]^{1/3} \qquad (106)$$

where F_c is the shape factor of the particles. The interesting observation of the authors was that the correlation is valid irrespective of the geometry of the equipment and the method of energy input, and hence applies both to a mechanically agitated vessel and a bubble column. The energy supplied to liquid, e, has to be known to use this correlation as well as that of Levins and Glastonbury (1972). This can be calculated from Equation (93) or from the data of Bates et al. (1963).

Recently, Boon-long et al. (1978) proposed the following correlation

$$\frac{k_s d_p}{D} = 0.046 \left[\frac{2 d_p \rho_L d_T \pi^2 N}{\mu_L} \right]^{0.283} \left[\frac{\rho_L^2 g d_p^3}{\mu_L^2} \right]^{0.173} \left[\frac{w V_L}{\rho_L d_p^3} \right]^{-0.011} \left[\frac{d_T}{d_p} \right]^{0.019} \left[\frac{\mu_L}{\rho_L D} \right]^{0.461} \qquad (107)$$

The above three correlations for solid-liquid mass transfer coefficient are compared in Figure 17, where k_s is shown

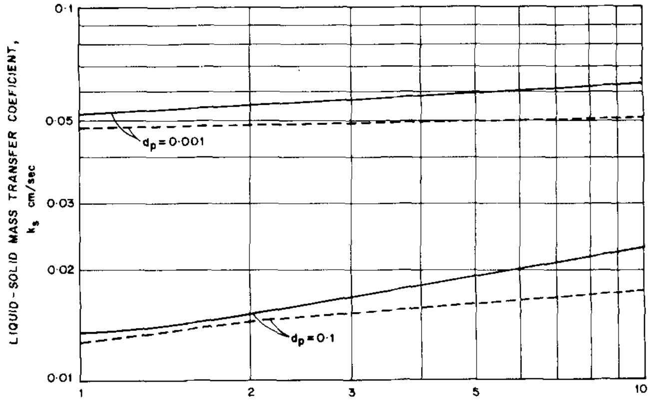


Figure 18. Comparison of correlations for k_s in a bubble column. ——— = Sano *et al.* (1974); - - - - = Kobayashi and Saito (1965).

as a function of stirrer speed for three particle sizes. The reactor data used for the calculations of k_s are the same as reported in the section on gas-liquid mass transfer.

For estimating k_s in bubble columns, Sano et al. (1974) proposed that the correlation given by Equation (106) be used with the energy supplied to the liquid, calculated as

$$e = u_g g \tag{108}$$

Kobayashi and Saito (1965) proposed the following correlation for estimating k_s for bubble columns

$$\frac{k_s d_p}{D} = 2 + 0.212\left[\frac{d_p^3(\rho_p - \rho_L)g}{\mu_L D}\right]^{1/3}\left[\frac{d_p u_g \rho_L}{\mu_L}\right]^{0.112} \tag{109}$$

The two correlations are compared in Figure 18, where k_s is plotted as a function of u_g for various values of d_p. Nienow (1975) critically compared the correlations for k_s, based on the Kolmogoroff theory and the slip velocity theory.

Experimental Methods

The solid-liquid mass transfer coefficient k_s can be experimentally determined by the following four major methods:

1. Dissolution of a sparingly soluble solid in a liquid medium
2. Dissolution accompanied by chemical reaction
3. From slurry reactor data obtained under conditions such that the major controlling resistance is the solid-liquid mass transfer
4. From dynamic methods

In using Method 1, the time of experiments should be very short, as the particle size is changing continuously because of dissolution. This is a simple method, used by many investigators. Systems such as dissolution of β-naphthol or benzoic acid, naphthalene or other sparingly soluble solids can be used to determine k_s by this method (Satterfield et al. 1968, Harriot 1962, Sano et al. 1974, Nienow 1969). Solid dissolution accompanied by reaction has also been used by many investigators (see Nagata, 1975).

Method 3 involves obtaining data on slurry reactors under conditions such that the solid-liquid mass transfer is the controlling mechanism. In many cases, this can be done by using a highly active catalyst, such as palladium or platinum impregnated on carbon. A catalyst coated on the external surface of a non-porous support is also good. For first-order reactions, a plot of A^*/R_A vs $1/w$ gives a straight line with a slope of

$$\left[\frac{\rho_p d_p}{6k_s} + \frac{1}{\eta_c k_1}\right]$$

If the reaction rate constant and D_e are known, the value of k_s can be obtained. Alternately, experiments with different particle sizes can be designed to yield the value of k_s. The transient response of a slurry catalyzed reactor can also be used to estimate k_s although it has not been used experimentally so far.

Method 4 involves the transient response of a slurry adsorber (determining the response to a pulse or step of an adsorbable gas).

EFFECTIVE INTRAPARTICLE DIFFUSIVITY

The effects of intraparticle diffusion are more important in slurry reactors which involve liquid filled pores as compared to gas-solid reactions. This is because of the low order of magnitude of the liquid phase diffusivities. In the absence of complex phenomena such as surface diffusion and restricted diffusion, the problem of predicting effective diffusivity can be reduced to predicting the tortuosity factor, defined by

$$D_e = \frac{D\epsilon_p}{\tau} \tag{110}$$

where D is the molecular diffusivity of the solute in the liquid medium.

The porosity of the catalyst ϵ_p can be determined experimentally, while the molecular diffusivity D can be calculated from well-known estimation methods such as the Wilke-Chang (1955) equation or Reddy-Doraiswamy's (1967) correlation. The value of τ varies somewhat, and is generally in the range of 2 to 3. Experimentally determined values of τ for liquid-filled catalysts for a number of systems are summarized in Table 3.

Surface diffusion effects may be important for solutes which are strongly adsorbed on the catalyst surfaces, for instance, SO_2 and H_2S on activated carbon. The apparent values of tortuosity factors as calculated from Equation (110) using experimentally measured D_e data would be very low, when surface diffusion effects are significant. The effective diffusivity in such system results from a combination of two effects: (a) pore volume diffusion with an effective diffusivity predicted by Equation (110) and (b) the contribution of surface diffusion. When the adsorption follows a linear isotherm, the effective diffusivity can be expressed as

$$D_e = \frac{D\epsilon_p}{\tau} + \frac{\rho_p K' D_s}{\tau} \tag{111}$$

where D_s is the true surface diffusion coefficient.

One method that can be used to isolate the value of D_s from measured D_e data is to obtain the value of τ from independent experimental D_e measurements, using a solute with very low adsorption capacity ($K' \to 0$). With this value of τ and the measured D_e values, D_s can be calculated using Equation (111). Another technique developed by Komiyama and Smith (1974*b*) consists of experimenting with different solvent media. This will effect a change in the value of K' which can be obtained from independent experiments and also D which can be estimated. The true surface diffusivity can then be calculated from

$$D_s = \frac{\epsilon_p D_1}{\rho_p K_2'}\left[\frac{1 - (D_{e1}/D_{e2})(D_2/D_1)}{(D_{e1}/D_{e2}) - (K_1'/K_2')}\right] \tag{112}$$

where the subscripts 1 and 2 denote the values obtained for two different solvents.

As an example, Komiyama and Smith (1974*b*) found that the adsorption equilibrium constant K' for benzaldehyde on Amberlite particles was negligible when methanol was a solvent, but was significant when water was a solvent. Using the experimental values of D_e for these two systems, the surface diffusivity of benzaldehyde on Amberlite particles was obtained 10^{-8}, cm^2/sec. The effective surface diffusivity data for a number of volatile organic compounds on activated carbon were determined by Suzuki and Kawazoe (1975).

Satterfield et al. (1973) show that when the dimensions of the solute molecule were comparable to the average pore diameter, the diffusion rate was considerably restricted. They obtained experimental data on diffusion in silica-alumina catalysts of very fine pore diameter of the order of $3.2 \times 10^{-3}\mu$ for a number of solutes, such that the ratio of the critical molecular diameter of the

Table 3. Intraparticle Diffusivity Data for Liquid Filled Porous

Diffusing species	Solvent/medium	Catalyst	Temperature °C	Pressure (atm.)
1. Oxygen	Water	CuO·ZnO	212 to 240	40
2. Hydrogen	α-methyl styrene	Pd-alumina	70 to 115	1
3. Hydrogen	Crotonaldehyde	Pd-γ-alumina	30 to 70	1
4. Oxygen	Water	Activated carbon	6, 25	1
5. NO	Water	Activated carbon	25	1
6. H_2S	Water	Activated carbon	25	1
7. Hydrogen	Styrene/ethanol	0.5% Pt-Al_2O_3	—5 to 20	0.1 to 1
8. Dodecyl-benzene sulfonate	Water	Activated-carbon	30	
9. Hydrogen	Isopropanol	Raney-nickel	7 to 21	1
10. Benzaldehyde	Methanol and water	XAD4 Amberlite XAD7 Amberlite	25 25	1 1
11. Oxygen	Water	Activated-carbon	25	1
12. Sulfur dioxide	Water	Activated-carbon	25	1
13. Sulfuric acid	Water	Activated-carbon	25	1
14. NaCl, KCl	Water	Activated-carbon	25	1
15. Naphthalene, styrene, p-xylene and ethyl benzene	n-heptane	Cobalt-molybdenum	20	1
16. Hydrogen	α-methyl styrene	1% Pd on alumina	50	1

Metric conversion: 1 atm = 101.321 kPa.

solute to pore diameter varied from 0.088 to 0.506. The experimental data was correlated by

$$\frac{D_{e}\tau}{D\epsilon_p} = 10^{(-2d_s/d_e)} \qquad (113)$$

where d_s is the solute critical diameter, defined as the diameter of the smallest cylinder through which a solute molecule can pass without distortion, and d_e is the pore diameter.

The common experimental methods for measuring effective intraparticle diffusivity are (a) from experimental rate data obtained at various particle sizes, and (b) the dynamic Wicke-Kallenbach method and dynamic tracer experiments, using an adsorbable or nonadsorbable solute as a tracer. When experimental rate data are obtained at different particle sizes, the use of $\eta_c - \phi$ relations gives both the intrinsic rate constant and the intraparticle diffusivity. The external mass transfer resistances (gas-liquid and liquid to solid) have to be accounted for in this method, or experiments have to be planned such that these resistances are not significant.

Satterfield et al. (1968) measured D_e from experimental studies on hydrogenation of α-methyl styrene on Pd-alumina catalyst. Kenney and Sedricks (1972) used this method for hydrogenation of crotonaldehyde on Pd-alumina catalyst. Komiyama and Smith (1975) studied the oxidation of SO_2 in slurries of activated carbon and determined D_e. It is worth noting in this context that the effective diffusivity D_e or the tortuosity factor τ do not depend on the type of reactor. They are function of only the catalyst pore structure. Hence, such data for other three phase reactors such as trickle bed, packed bed etc. also apply to slurry reactors. The intraparticle diffusion effects may be more important in trickle beds or packed beds because of the larger particle sizes. Data may be obtained more easily in these reactors.

A dynamic method for measuring effective diffusivity for liquid-filled pores developed by Shibuya and Uraguchi (1977) is based on the principle of the well known Wicke-Kallenbach method. Other dynamic methods for estimation of D_e are reviewed by Ramachandran and Smith (1978b) (see also Furusawa and Suzuki 1975).

ESTIMATING KINETIC PARAMETERS

The kinetic parameters—reaction orders, rate constant and adsorption equilibrium constants—must be estimated from experimental data only. To obtain the intrinsic kinetics, it is necessary to account for the effects of transport resistances or plan experiments under conditions such that mass transfer resistances are absent. The latter can sometimes be achieved, for instance, by working with sufficiently small particles and at high speeds of agitation. It is also possible to check the contribution of external mass transfer resistances by calculating the surface concentration of the reactive species A_s. This can be calculated provided the external mass transfer coefficients, k_La and k_sa_p in the reactor type used are determined by independent experiments or calculated from suitable correlation. The value of A_s can then be calculated as

$$A_s = \frac{A_{gi}}{H_A} - \frac{R_A}{M_A} = A^* - \frac{R_A}{M_A} \qquad (114)$$

Experimental rate data must be obtained at different concentrations of the reacting species, keeping other conditions constant. This can be done using an inert diluent or changing the total pressure of the reactor. The kinetic parameters are then calculated using the experimental R_A vs A_s data, provided the effects of intraparticle diffusion are accounted for. A knowledge of the effective diffusivity in the catalyst D_e is necessary for this purpose. The effects of intraparticle diffusion for a m^{th} order reaction can be considered negligible, provided the following criteria in terms of known parameters is satisfied

$$\frac{R}{3}\left[\frac{(m+1)\rho_p R_A}{2D_e w A_s}\right]^{1/2} < 0.2 \qquad (115)$$

PARTICLES

Tortuosity factor, τ	Porosity ϵ_p	Reference
1.03	0.56-0.67	Baldi et al. (1974)
3.90	0.59	Satterfield et al. (1968)
1.60	0.54	Kenney and Sedricks (1972)
0.83	0.64	Niiyama and Smith (1977)
0.90	0.64	Niiyama and Smith (1976)
0.72	0.64	Ramachandran and Smith (1978*a*)
2.5 to 3.2	0.56	Kawakami et al (1976*b*)
1.7 to 16	0.65-0.72	Suzuki and Kawazoe (1974)
3.5 to 4.5	0.51	Lemcoff and Jameson (1975)
2.72 1.54	0.51 0.55	Komiyama and Smith (1974*a*)
3.1	0.64	Komiyama and Smith (1975)
1.6	0.64	Komiyama and Smith (1975)
3.2	0.64	Komiyama and Smith (1975)
3.3	0.61	Shibuya and Uraguchi (1977)
2.81, 2.81 3.01, 3.35	—	Midoux and Charpentier (1973)
7.5	0.5	Satterfield et al. (1969)

A rate model has to be assumed to fit a kinetic model to R_A vs A_s data. If the criteria given by Equation (115) are not satisfied, the effect of intraparticle diffusion has to be accounted for. This requires data to be obtained at two or more particle sizes. For the assumed rate model, the value of the generalized Thiele modulus ϕ is obtained from equations such as given in Table 2. The value of η_c can be then calculated, and diffusion-free intrinsic kinetics obtained.

Experimental data from various particle sizes can be analyzed to obtain simultaneously both D_e and the kinetic parameters. To determine the kinetics of the reaction with respect to B, we need the experimental rate data at various concentrations of B. For example, in the hydrogenation of glucose to sorbitol over Raney Nickel catalyst, Brahme and Doraiswamy (1976) obtained experimental rate data at four values of glucose concentrations. Using these data, they successfully distinguished between five postulated kinetic rate models.

For reactions which are first-order with respect to the gaseous component, simple varying of the catalyst loading will yield the rate parameters. For such systems, a plot of $A_{gi}/R_A H_A$ vs $1/w$ should be linear, as indicated by Equation (61). The inherent assumption for the basis of linearity of these plots is that $k_L a$ is independent of w. The intercept of this line would correspond to $V_L/H_A Q [1 - \exp(-\alpha_A L)]^{-1}$ or to $1/k_L a$ for sparingly soluble gases.

The slope of this line gives $[\rho_p d_p/6k_s + 1/n_c k_1]$. To evaluate k_s and k_1 separately, three approaches are possible:

1. The solid-liquid mass transfer coefficient can be estimated from suitable correlations. The value of k_1 can be found from the slope by subtracting the contribution of k_s.

2. Experimental value of the slope can be got at different particle sizes. The term $\rho_p d_p/6k_s$ would change as $d_p^{1.7 \text{ to } 2.0}$, while $1/\eta_c k_1$ would be independent of d_p, provided intraparticle diffusion effects are absent. The term $1/\eta_c k_1$ would change as $d_p^{1.0}$ when the intraparticle diffusion effects are significant. By studying the exponent dependency of the slope on d_p, it is possible to conclude whether solid-liquid mass transfer or chemical reaction is the controlling step. The effect of d_p on the slope of A^*/R_A vs $1/w$ plot for a first-order reaction is illustrated in Figure 19 for different values of the first order rate constant k_1. As can be seen, the dependency of the slope on d_p changes significantly with the change in the controlling regime.

3. The dependency of the slope on the temperature of reaction can be examined. If solid-liquid mass transfer is important, the process would have a low activation energy (1 to 3 kcal/mole). If reaction were controlling, and there are no intraparticle gradients, then the activation energy would be in the higher range.

Proper account of the intraparticle diffusion effects must be taken when the data at various temperatures are analyzed. The intraparticle diffusion limitations may be absent for experiments at lower temperatures, but may become important as temperature is increased. A second limitation is that the adsorption characteristics of the second component (B) may change with temperature, indirectly influencing the rate constant. Detailed experimentation, varying both the concentration of A and B for each temperature under investigation, is necessary for a rational analysis of slurry reactor data.

When the reaction order is nonlinear with respect to A, the plots of $A_{gi}/H_A R_A$ vs $1/w$ are no longer linear as shown in the section on illustrative examples. Care is needed in extrapolating such data to obtain the intercept. For example, Marangozis et al. (1977) show that the data of Bailey et al. (1942) on hydrogenation of cottonseed oil do not follow the linear pattern when plotted as

$$\frac{A_{gi}}{H_A R_A} \text{ vs } \frac{1}{w}$$

If a large number of experimental data are obtained for various operating conditions, search techniques can be used to obtain the kinetic and mass transfer data. An objective function of the type

$$\sum_{1}^{N_T} \left[\frac{R_{A\,\text{exp}} - R_{A\,\text{theory}}}{R_{A\,\text{exp}}} \right]^2$$

can be defined and minimized with respect to the parameter values. Here N_T is the total number of experiments conducted. A number of parameters such as particle size,

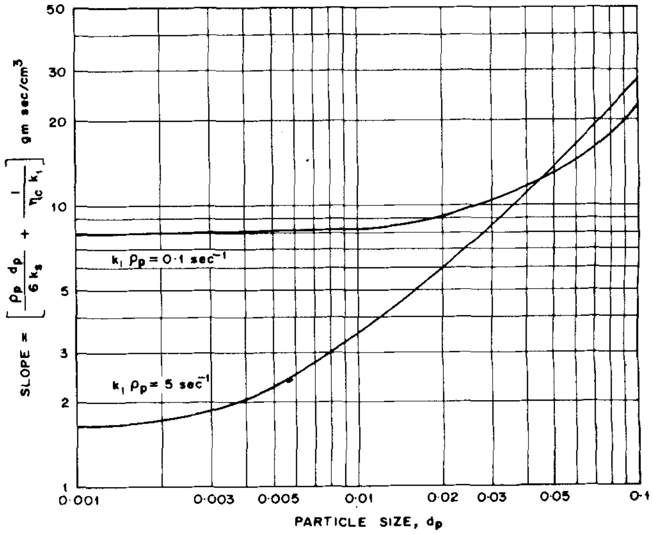


Figure 19. Effect of d_p on the slope of A^*/R_A vs 1/w plot, for a first-order reaction.

catalyst loading, speed of agitation (or gas velocity for bubble columns) and gas phase concentration can be varied, and $R_{A\,\mathrm{exp}}$ data can be taken. The theoretical rate of reaction would depend on the postulated mechanism, and the necessary equations for various cases have been summarized in Tables 1 and 2. A knowledge of how the mass transfer parameters change with operating conditions is necessary in using this method. It is reasonable to assume that $k_L a$ does not depend on d_p or w and varies as $N^{0.85}$ and as $u_g^{0.8}$ for a bubble column. Similarly, the value of k_s would vary as $d_p^{-0.7 \text{ to } -1.0}$ and as $N^{0.2 \text{ to } 0.75}$ in an agitated contactor and as $u_g^{0.25}$ in a bubble column. A multidimensional search is necessary to obtain all the parameters. The search is simplified if some of the parameters are obtained from independent experiments. An order of magnitude value of the adsorption equilibrium constant can be obtained from independent experiments under non-reacting conditions.

DYNAMICS OF SLURRY REACTORS

Knowing the dynamic behavior of slurry reactors is useful in predicting the effect of disturbances in input variables on the reactor performance. Laboratory experimental dynamic data may also help in evaluating the various transport and rate parameters, and in elucidating the reaction mechanism. Ramachandran and Smith (1977) present equations in the Laplace domain for the dynamic behavior of three phase slurry reactor to a step or pulse input for a first-order chemical reaction. A particularly interesting aspect is that the dynamic data offer the possibility of separate evaluation of adsorption and surface reaction rate constants, which is not possible from steady state measurements.

Govindarao (1975) modeled the dynamic behavior of bubble column slurry reactors. The concentration distribution of the catalyst was also considered, and the transient equations are solved by numerical methods.

Experiments on the dynamic behavior of slurry reactors have been limited. The analytical device used for such study must be capable of continuously sensing the concentration of a single component in a multicomponent reaction mixture. Komiyama and Smith (1975) reported data on oxidation of SO_2 in a slurry of activated carbon. The concentration of SO_2 in the outlet gas stream was measured as a function of time with a seven-way sampling valve and a gas chromatograph. The reaction scheme here involves two gases, and theoretical analysis of the dynamic experimental data for such systems has not been published.

Komiyama and Smith (1975) also report some dynamic experimental data on a catalyst which was pretreated with pure oxygen for various intervals of time. These are useful in determining the controlling step of the reaction. Dynamic behavior of a bubble column slurry reactor catalyzing the methanation reaction of CO was studied by Aposporidis and Hammer (1975). Step change of feed gas composition and the gas rate were the input disturbances. If the range of the disturbance is small, simplified linearized models are likely to apply. It is possible to use such simple models in conjunction with the experimental data to find the transport and kinetic parameters and to ascertain the mechanism of the reaction.

NOTATION

a = effective gas-liquid interfacial area per unit volume of slurry, cm^2/cm^3
a_e = dimensionless concentration defined as A_e/A^*
a_p = external area of particles per unit volume of slurry, cm^2/cm^3
a_s = dimensionless concentration of A at the external surface of the catalyst, A_s/A^*
A = concentration of species A at the conditions indicated in the subscript, mole/cm^3
A^* = concentration of A in the liquid in equilibrium with the gas $= A_{gi}/H_A$, mole/cm^3
A_e = chemical reaction equilibrium concentration of A based on the concentrations of the various reactants prevailing in the liquid phase, mole/cm^3
b_o = concentration ratio defined as B^*/A^*
B = concentration of species B at the conditions indicated in the subscript, mole/cm^3
B^* = concentration of B in the liquid in equilibrium with gas B_{gi}/H_B, mole/cm^3
C_l = concentration of C in the bulk liquid, mole/cm^3
c_μ = viscosity correction factor defined by Equation (85)
d_B = average diameter of the gas bubbles in the reactor, cm
d_e = average pore diameter of the catalyst, cm
d_I = diameter of the impeller, cm
d_p = average diameter of the catalyst particles, cm
d_s = critical diameter of the diffusing solute, cm
d_T = diameter of the slurry reactor, cm
D = diffusion coefficient of the diffusing species in the liquid, cm^2/sec
D_e = effective diffusion coefficient in the pores of the catalyst (diffusing species indicated in the subscript), cm^2/sec
D_s = intrinsic surface diffusivity, cm^2/sec
e = energy supplied to the liquid per unit mass, cm^2/sec^3
E_l, F_l = concentration of species E and F in the bulk liquid, mole/cm^3
F_c = shape factor of the catalyst
g = acceleration due to gravity cm/sec^2
H_A = solubility coefficient of gas A, defined as A_g/A_l, cm^3 liquid/cm^3 gas
H_B = solubility coefficient of gas B, cm^3 liquid/cm^3 gas
k_a = adsorption rate constant, cm^3/gm/sec
k_g = gas film mass transfer coefficient, cm/sec
k_H = rate constant for homogeneous reaction of A in the liquid phase, sec^{-1}
k_L = liquid film mass transfer coefficient, cm/sec
k_m = pseudo-m^{th} order rate constant, cm^3/gm (cm^3/mole)$^{m-1}$ sec^{-1} (for example, k_1 = pseudo first order rate constant, cm^3/gm/sec, etc.)
k_{m+n} = rate constant for a (m, n) th order reaction, cm^3/gm (cm^3/mole)$^{m+n-1}$ sec^{-1}
k_r = surface reaction rate constant, sec^{-1}
k_s = liquid to catalyst particle mass transfer coefficient, cm/sec
K' = adsorption equilibrium constant for a linear reversible adsorption $= KS_m$, cm^3/gm
K_A, K_B, K_C = adsorption equilibrium constant of the species indicated in the subscript for the Langmuir-Hinshelwood model, cm^3/mole
K_L = overall gas to liquid mass transfer coefficient, cm/sec
K_R = equilibrium constant for chemical reaction
l_e = eddy size, cm
L = total height of slurry above the entrance of gas bubbles, cm
m, m_1, m_2 = order of reaction with respect to species A
M_A, M_B = parameters defined by Equations (12) and (47) respectively, sec^{-1}
n, n_1 = order of reaction with respect to B

n_2 = order of reaction with respect to intermediate C
N = speed of agitation of slurry, sec^{-1}
N_m = minimum agitation required, sec^{-1}
N_p = power number defined by Equation (92)
N_T = total number of experiments conducted
p_{gA} = partial pressure of reactant A in the inlet gas phase, atm.
p = effective diffusivity ratio defined as $\nu D_{eA}/D_{eB}$
P = power consumption for agitation, $gm/cm^2/sec^3$
Q = volumetric flow rate of gas, cm^3/sec
r_1, r_2, r_3 = empirical constants in Equation (74) or (75)
R = radius of the catalyst particles, cm
R_A, R_B = rate of reaction of A and B respectively per unit volume of slurry, $mole/cm^3/sec$
Re_v, Re_l = Reynolds number defined by Equations (102) and (103) respectively
S_m = total concentration of the active sites of the catalyst, mole/gm
S_T = surface tension of the liquid, gm/sec^2
t = time elapsed since the start of the reaction, sec
T_s = surface temperature of the catalyst, °K
u_g = superficial velocity of the gas in the reactor, cm/sec
u_t = terminal gas bubble velocity, cm/sec
u_{tp} = Stoke's terminal settling velocity of the particles, cm/sec
V_L = total volume of slurry, cm^3
w = mass of catalyst per unit volume of slurry, gm/cm^3
z = vertical distance measured from the entrance of gas bubbles, cm

Greek Letters

α_A = parameter defined by Equation (7) $(k_L a/u_g H)_A$, cm^{-1}
α_B = parameter defined as $(k_L a/u_g H)_B$
β = selectivity defined by Equation (59)
β_2 = constant in Equation (81)
γ = parameter defined by Equation (80)
γ' = wetability parameter in Equation (83)
ΔH = heat of reaction, cal/mole
η = overall effectiveness factor of a slurry reactor
η_c = catalytic effectiveness factor
ϕ = Thiele parameter for reaction
ϕ_o = parameter defined by Equation (17)
ρ_g, ρ_L, ρ_p = density of the gas phase, liquid and catalyst respectively, g/cm^3
ρ_s = density of the slurry, g/cm^3
λ = distance from the center of the catalyst at which the concentration of A becomes zero, cm
λ_e = effective thermal conductivity of the catalyst, cal/cm/sec/°K
σ_A = parameter defined by Equation (27)
Ω = local rate of chemical reaction per unit weight of catalyst, mole/gm/sec
ν, ν_p = stoichiometric coefficient of B and P in the reaction
ϵ_g = gas hold-up
ϵ_p = particle porosity
τ = tortuosity factor of the catalyst
μ_g = viscosity of the gas phase, gm/cm/sec
μ_L = viscosity of the liquid, gm/cm/sec
ψ = correction factor defined by Equation (94) or (95)

Subscripts

g = gas phase
gi = gas entering the reactor
go = gas leaving the reactor
l = liquid phase
lo = liquid at time $t = o$
lf = liquid at time $t = t$
s = external surface of the catalyst

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Intraparticle Mass Transfer in Coal Pyrolysis

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Intraparticle mass transfer in coal pyrolysis is described by ternary diffusion and viscous flow, in conjunction with a simple pore model to predict concentration profiles for gases and tar. At low pressures, product yields depend on particle size only, while at high pressures they depend on pressure and particle size. Limited experimental data from a subbituminous coal confirm these trends. Data from a bituminous coal show different trends, as expected from the drastic changes the pore structure undergoes during pyrolysis.

SCOPE

This study of intraparticle mass transfer in coal pyrolysis concentrates on the effect of pressure and particle size on the product yield. Three ingredients are required for a theoretical description of intraparticle transport: the chemistry of pyrolysis, a pore model of coal, and suitable flux relationships. The probability that a volatile product molecule recombines with the coal matrix before escaping the particle depends on the number of free radical sites

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