

Trickle-Bed Reactors

CHARLES N. SATTERFIELD

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

1. INTRODUCTION

The term *trickle bed* is used here to mean a reactor in which a liquid phase and a gas phase flow concurrently downward through a fixed bed of catalyst particles while reaction takes place. The earliest antecedent probably was the so-called "trickling filter" which has long been used for removal of organic matter from wastewater streams by aerobic bacterial action. Biological growths are allowed to attach themselves to a bed of stone or other support over which the wastewater is allowed to trickle in contact with air. Another antecedent appeared in the 1930s when Duftscheid and co-workers at the I.G. Farbenindustrie used evaporative cooling of an inert oil which flowed upwards through a catalyst bed to remove the heat of reaction in a version of the Fischer-Tropsch process for synthesis of liquid fuels from H_2 and CO and a later version at the U.S. Bureau of Mines operated with concurrent upflow but without evaporative cooling. This was superseded by an ebulliating bed reactor because of difficulties with cementation of the catalyst in the fixed bed, but commercial scale operations of this process in Germany and elsewhere have all utilized completely vapor-phase reaction (Storch et al., 1951; Crowell et al., 1950; Benson et al., 1954; Kastens et al., 1952).

Trickle-bed reactors have been used to a moderate extent in chemical processing, but most of the published information about their industrial applications concerns the processing with hydrogen of various petroleum fractions, in particular the hydrosulfurization or hydrocracking of heavy or residual oil stocks and the hydrofinishing or hydrotreating of lubricating oils. Their commercial development during the 1950s by the Shell Companies and by the British Petroleum Company has been described by van Deemter (1964), Le Nobel and Choufoer (1959), and Lister (1964). The development of hydrocracking and hydrosulfurization processes by Chevron, Esso (Exxon), Gulf, Union Oil, and others has been described in the proceedings of the various World Petroleum Congresses.

Information is fragmentary on uses in chemical processing. A process for synthesis of butynediol ($HOCH_2C \equiv CCH_2OH$) from aqueous formaldehyde and acetylene uses trickle-bed flow over a copper acetylide catalyst and recycle of the product stream for heat removal (Brusie et al., 1963). Other trickle-bed studies of this reaction are given in a thesis by W. Bill, as reported by Bondi (1971), who also cites trickle-bed studies by H. Hofmann on the hydrogenation of glucose to sorbitol. Krönig (1963) describes a trickle-bed process used in one or more commercial plants for selective hydrogenation of acetylene to remove it in the presence of butadiene in C_4 hydrocarbon streams. Operation at 10° to $20^\circ C$ and 1.9 to 5.8 atm pressure allows liquid-phase processing which reportedly gives long catalyst life, unlike gas-phase processing in which polymers rapidly build up on the catalyst. The standard commercial process for manufacture of hydrogen peroxide utilizes a working solution of an alkyl

anthraquinone which is alternately reduced with hydrogen to the hydroquinone and then re-oxidized with air to form hydrogen peroxide and the quinone. In some versions of this process a trickle bed hydrogenator is used. (See also section 2.2)

1.1 Experimental Studies

Considering the widespread use of trickle-bed reactors on a very large scale in the petroleum industry, it is surprising that so little information has been published concerning the development, design, and operation of this type of reactor. A useful general review of gas-liquid-particle operations by Østergaard (1968) gives guidance to the literature up to about 1965-1966 on contacting between a gas and a liquid in fixed beds. Unfortunately for present purposes most of this literature is more relevant to absorption systems than to chemical reactors. Laboratory scale studies of specific chemical reactions in trickle-bed reactors are limited in number. In an early investigation Klassen and Kirk (1955) studied the liquid-phase oxidation of a basic solution of ethanol to acetic acid by oxygen while trickling over a palladium-on-alumina catalyst. Mass transfer resistance through both gas and liquid films was appreciable and mass transfer coefficients derived from their reaction rate data were compared to correlations developed from nonreacting systems. Ware (1959) reported large variations in the rate of hydrogenation of liquid benzene which were attributed to changes in transport resistance depending upon whether catalyst pores were filled with liquid or vapor (Section 3.4). Other studies appear to be mostly of recent origin, as summarized in Table 1 which also includes a recent representative laboratory scale petroleum processing study. Several other laboratory or pilot plant scale studies of petroleum refining reactions are described by Henry and Gilbert (1973), the most pertinent of which are summarized in Table 2. In some trickle-bed studies of chemical reactions, attention was directed primarily to catalytic behavior or chemical kinetics and unless some heat or mass transfer effects or other information relative to reactor behavior were reported, these investigations have been omitted.

1.2 Comparison with Slurry Reactors

The principal alternative to using a fixed bed with two-phase flow, either upwards or downwards, is a slurry reactor or ebulliating bed in which the catalyst particles, which must now be substantially smaller, are in motion. These are also sometimes termed three-phase fluidized-bed reactors or suspended bed reactors. These have the following advantages:

1. A high heat capacity to provide good temperature control
2. A potentially high rate of reaction per unit volume of reactor if the catalyst is highly active
3. Easy heat recovery
4. Adaptability to either batch or flow processing
5. The catalyst may be readily removed and replaced if its working life is relatively short, and

TABLE 1. RECENT LABORATORY-SCALE STUDIES

Reaction	Reference	Superficial flow rate		$Re_L = \frac{d_p L \rho}{\mu}$
		Liquid ^e kg/m ² s	Gas (kg/m ² s) × 10 ³	
A. Oxidation of SO ₂ on wetted C	Hartman and Coughlin ^b (1972)	0.0043 to 0.062	15.4	
B. Hydrogenation of crotonaldehyde	Kenney and Sedricks (1972); Sedricks and Kenney (1973)	0.038	0.47	
C. Isomerization of cyclopropane	Way (1972)	0.26 to 2.1	3 to 28	≈0.04 to 8
D. Hydrogenation of α-CH ₃ styrene	Pelossof ^a (1967)	1.4 to 8.7	—	
E. Hydrogenation of benzene	Satterfield and Özel (1973)	0.9 to 3.0	28 ^d	16 to 55
F. Hydrogenation of α-CH ₃ styrene	Germain et al. ^b (1974)	0.08 to 1.6	0.14 to 3.0	
G. Hydrotreating	Mears ^c (1971)	0.19 to 0.76 ^f	1.65 to 6.61 ^f	2 to 8 ^f

^a Flow over a vertical string of spheres. L calculated for a bed of spheres touching in a square pattern.

^b Countercurrent flow.

^c 100 atm. pressure. All other studies at 1 atm.

^d G for H₂ plus benzene vapor.

^e For $\rho = 1.0$ g/cm³, 1 kg/m² s = 0.1 cm/s.

^f Assumes no vaporization. For 37% vaporization, L is 0.12 to 0.48, G is 70 to 280.

TABLE 2. PERTINENT LABORATORY-SCALE PETROLEUM REFINING STUDIES CITED BY HENRY AND GILBERT (1973)

Reaction	Reference	L , kg/m ² s	% conversion
Hydrocracking of a heavy gas oil	Henry and Gilbert	0.07 to 0.5	61 to 20
Hydrodenitrogenation of various compounds and of a cat. cracked light furnace oil ^(a)	Flinn et al. (1963)	lowest value: 0.07 ^(a) lowest value: 0.035 ^(a)	99.8% (furnace oil reacted at 700°F) 80% (quinoline reacted at 600°F)
Hydrodenitrogenation of a lube oil distillate	Gilbert and Kartzmark (1965)	0.025 to 0.14 ^(b) 0.025 to 0.06 ^(b)	97% to 70% (low temperature reaction) 98.5% to 95% (high temperature reaction)
Hydrogenation of aromatics in a naphthenic lube oil distillate	Henry and Gilbert	0.03 to 0.25 ^(b)	80% to 30% (low pressure) 95% to 40% (high pressure)

^(a) No data points in original reference. Highest flow rates not recorded.

^(b) Taking reactor height as 3 ft. (0.91 m). True height not published.

6. They may permit operation at catalyst effectiveness factors approaching unity, of especial importance if diffusion limitations cause rapid catalyst degradation or poorer selectivity.

Their disadvantages are that:

1. The residence time distribution patterns are close to those of a continuous stirred-tank reactor (CSTR) which makes it difficult to obtain high degrees of conversion except by staging.

2. Catalyst removal by filtration may pose problems with possible plugging difficulties on filters, and the costs of filtering systems may be a substantial portion of the capital investment, and

3. The high ratio of liquid to solid in a slurry reactor allows homogeneous side-reactions to become more important, if any are possible.

In the trickle-bed reactor the catalyst bed is fixed, the flow pattern is much closer to plug flow, and the ratio of liquid to solid present is much less. If heat effects are substantial, they can be controlled by recycle of liquid product stream although this may not be practical if product is not relatively stable under reaction conditions or if a very high percent conversion is desired, as in hydrodesulfurization, since a high recycle rate causes the system to approach the behavior of a CSTR. Even when completely vapor-phase reaction in a fixed catalyst bed may be technically feasible, a trickle-bed reactor may be preferred for the saving in energy costs associated with reactant vaporization.

The most common type of trickle-bed processing by far is hydrogenation and most of the subsequent discussion will refer to this type of reaction. The other reactant may be essentially all in the liquid phase or in both liquid and gas phases and the distribution of reactant and products between gas and liquid phases may vary with conversion. In a few circumstances, as in the version of the Fischer-Tropsch process cited above, the liquid is inert and serves as a heat transfer medium, reaction occurring between reactants in solution and the catalyst.

1.3 Industrial Petroleum Refining

Trickle-bed reactors in the petroleum industry may be operated over a wide variety of conditions, depending upon the properties of the feedstock and the nature of the reaction. Typically the less reactive fractions, which tend to be in the higher boiling range and more viscous at ambient, are processed at the lower liquid flow rates. Representative superficial liquid velocities L are 10 to 100 ft./hr. (0.83 to 8.3 kg/m² s for density of 1 g/cm³) for lubricating oils, heavy gas oils or residual fractions and 100 to 300 ft./hr. (8.3 to 25 kg/m² s) for naphtha fractions, calculated assuming that the feed is entirely in the liquid phase. For lighter fractions this will not generally be the case and much of the feed will actually be present as vapor. Liquid hourly space velocities, LHSV (volume of liquid fed per hour per volume of reactor) may vary from about 0.5 to 10 hr.⁻¹. Some hydrogen is always fed with the hydrocarbon fraction, and the ratio

of hydrogen flow to liquid flow is commonly expressed in terms of volume of H_2 (expressed at standard temperature and pressure) per barrel of feed processed (std.cu.ft./bbl). 1000 std.cu.ft./bbl is equivalent to about 0.02 kg H_2 /kg feedstock. The superficial gas flow rate (at S.T.P.) becomes about

$$G = \frac{(L)(SCF/bbl)}{5.6} \text{ cm/s}$$

where L is likewise expressed in cm/s. Representative values are 2000 to 3000 std.cu.ft./bbl for hydrodesulfurization of a heavy gas oil, 5000 std.cu.ft./bbl for hydrodesulfurization of a heavy residue, and 5000 to 10,000 std.cu.ft./bbl for a hydrocracker. Mild hydrogen treatment, hydrofinishing, may utilize considerably smaller ratios of hydrogen to feedstock. Representative operating conditions over the range of petroleum refining processes are typically total pressures of 500 to 1,500 lb./sq.in. (34 to 102 atm) (substantially higher in a few cases) and temperatures of 650° to 800°F (345° to 425°C). Catalyst particles are typically 1/8 to 1/32 in. (0.32 to 0.08 cm) in diameter. In some systems, for example some hydrodesulfurization reactions, much of the fluid present may be near or above the critical point and phase behavior is uncertain.

In present day units multiple-bed reactors are frequently used. Typically the quantity of catalyst is divided into from 1 to 5 beds, each about 3 to 6 m deep and up to as much as 3 m in diameter. In multiple-bed reactors hydrogen is injected between the beds for temperature control—so-called “cold shot cooling.” In multiple-bed reactors the catalyst beds may be equal in depth, or, more commonly, increase in depth as reaction proceeds, and the quantity of hydrogen injected at each point is adjusted to achieve the desired axial temperature profile, specified so as to limit the adiabatic temperature rise along each bed below some maximum, typically about 30°C or less. The ratio of gas to liquid thus increases with flow through successive beds and the amount of gas injected for cooling can readily exceed that furnished initially. The quantity of H_2 furnished usually far exceeds that needed for stoichiometric reaction and is usually determined primarily by the requirements for temperature control, and perhaps in some cases to help achieve better liquid distribution or to prolong the life of the catalyst. The maximum height of a single catalyst bed is determined by the importance of achieving redistribution of liquid and gas after some limiting bed depth is traversed or by the crushing strength of the catalyst. In present practice this maximum seems to be about 6 to 8 m. In both chemical and petroleum processing, reactors are designed to operate essentially adiabatically. The equivalent of the externally cooled multi-tube reactor commonly utilized in completely gas-phase catalytic processing does not appear to have been applied commercially for trickle-bed flow although there is no basic reason why it could not be used.

Of considerable importance in analyzing data on trickle-bed reactors is the fact that pilot plant work is typically done with reactors 0.5 to 2 m high (and 2.5 to 4 cm in diameter) operated at about the same liquid hourly space velocity (LHSV, volumes of liquid feed per hour per volume of packed reactor) as that utilized commercially. For a specified value of LHSV the true liquid superficial velocity will thus be proportional to reactor length. A large commercial reactor of recent design may have as much as 20 to 25 m total depth of catalyst contained in several beds, for which data for

scale-up may have been obtained in a pilot unit at the same LHSV but therefore at 1/10 or less of the superficial liquid flow rate and correspondingly lower gas rate. Limiting representative conditions for commercial and pilot-plant operation in petroleum refining are shown in Table 3. The fact that the pilot unit and the commercial unit may operate under somewhat different hydrodynamic flow conditions means that the contacting efficiency may be significantly different in the two cases (Section 5). Most of the reports of laboratory studies of any type of reaction are for much lower liquid and gas flow rates than those utilized commercially. Some of the recently reported laboratory-scale studies involved rapid exothermic reactions at low liquid flow rates as a consequence of which heat effects were especially significant. Catalyst pellets were only partially wetted and reactants were relatively volatile so that reaction occurred in both liquid and vapor phases (Section 3.4). The behavior of these systems may be significantly different than those in which the reactant is exclusively in the liquid phase.

Another precaution to take in interpretation stems from the fact that almost all of the information published on performance of industrial trickle-bed reactors has been concerned with petroleum refinery operations such as hydrodesulfurization. The wide spectrum of compounds present, having different reactivities, requires some arbitrariness in describing the intrinsic kinetics. For five fractions of a flashed petroleum distillate, Bondi (1971) reports hydrodesulfurization differential reaction rates over a Co/Mo/Al₂O₃ catalyst varying by as much as a factor of 4 at 40% conversion and 7 or so at 80% conversion. If these are all treated as one compound in reactor analysis, the effect is to increase the apparent order of reaction. A mixture of several species of different reactivities, each exhibiting true first-order kinetics will appear to follow some higher order reaction over a wide range of conversion since the less reactive species will persist longer than the more reactive ones. On the other hand, a group of species of similar reactivity can frequently be adequately treated as following first-order kinetics over a limited range of conversion. The best procedure to follow varies with circumstances. Hutchinson and Luss (1970) and Luss and Hutchinson (1971) analyze methods of lumping mixtures of substances that react in parallel but with a spectrum of rate constants.

2. HYDRODYNAMICS

Caution: In using and comparing correlations, the exact definitions of the dimensionless groups used by each author should be carefully noted. In definitions of the Reynolds number, for example, the liquid flow rate is most commonly the mass rate per unit of superficial area, that is, per unit of empty cross-sectional area of reactor. However, sometimes the liquid rate is instead expressed as true average linear velocity. The length dimension is usually an average particle diameter but is sometimes an average liquid film thickness, a hydraulic radius or ratio of reactor volume to total outside particle area.

2.1 Comparison with Packed Absorption Towers

In its physical form, the trickle-bed reactor is similar to a packed absorption tower and considerable information on such matters as flow patterns, pressure drop, holdup and liquid distribution can be developed from studies directed primarily towards absorbers. The absorption process, however, differs in a number of ways. The process occurs entirely between gas and liquid and the function of the solid is essentially to provide good contact between the two. In applying information about

packed-bed absorbers to trickle-bed reactors, several other differences between the two should be borne in mind.

1. Absorption towers are generally operated at liquid and gas flow rates substantially greater than those used in trickle-bed reactors, under conditions near those of flooding.

2. In order to achieve these high flow rates, absorption towers use larger sizes of packing, a high void fraction and also generally different shapes, such as Berl saddles and Raschig rings, whereas catalysts are generally pellets, extrudates, or spheres.

3. In absorption towers of laboratory size, a considerable portion of the absorption may occur in liquid trickling down the wall. In a packed-bed reactor, the wall contributes nothing to the reaction, but wall flow is a possible mechanism for bypassing.

4. Gas flow is generally concurrent in packed-bed reactors and countercurrent in absorbers.

5. Catalyst pellets are usually porous whereas absorption packings are nonporous. The liquid held in the pores may be a major fraction of the total holdup and may contribute to dispersion. Wetting characteristics may be substantially different.

2.2 Flow Patterns

At sufficiently low liquid and gas flow rates the liquid trickles over the packing in essentially a laminar film or in rivulets, and the gas flows continuously through the voids in the bed. This is sometimes termed the *gas continuous region* or *homogeneous flow* and is the type encountered usually in laboratory and pilot-scale operations. As gas and/or liquid flow rates are increased one encounters behavior described as *rippling*, *slugging* or *pulsing* flow, and this may be characteristic of the higher operating rates encountered in commercial petroleum processing. At high liquid rates and sufficiently low gas rates, the liquid phase becomes continuous and the gas passes in the form of bubbles—sometimes termed *dispersed bubble flow*. This is characteristic of some chemical processing in which liquid flow rates are comparable to the highest encountered in petroleum processing, but where gas/liquid ratios are much less. Flow patterns and the transitions from one form to another as a function of gas and liquid flow rates have been described by several authors including Weekman and Myers (1964) and Charpentier et al. (1969, 1971). Several of these have been recently summarized by Sato et al. (1973).

Figure 1 shows on log-log coordinates the sets of gas

and liquid flow rates utilized in the laboratory and pilot plant scale studies listed in Table 1. The rectangular areas show estimates of the limiting values of L and G used but are not meant to imply that all combinations within the areas are represented. The diagonal parallelo-piped shows the limiting conditions representative of pilot plant and commercial scale operation in the petroleum industry as given in Table 3. These are intended to be indicative rather than definitive.

Little information has been published on trickle-bed hydrogenators as used in the chemical industry but reaction rates are generally higher, allowing the use of relatively high liquid flow rates. The ratios of hydrogen to liquid are typically less than that in petroleum refining. Several patents describe operating aspects of a trickle-bed catalyst hydrogenator used to convert a working solution of an alkyl anthraquinone to the hydroquinone

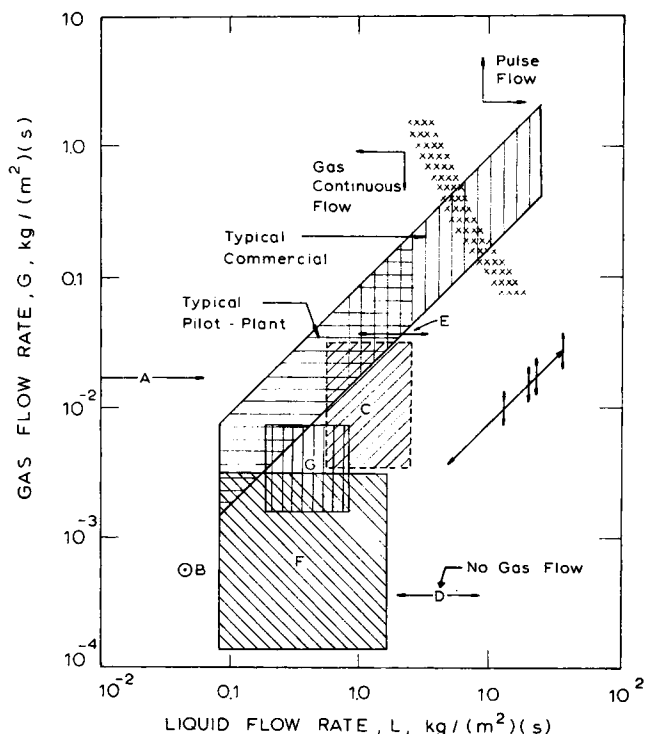


Fig. 1. Ranges of gas and liquid flow rates utilized in laboratory, pilot plant, and industrial trickle-bed reactors. See text (Section 2.2) and Tables 1 and 3.

TABLE 3. REPRESENTATIVE LIMITING FLOW CONDITIONS FOR PETROLEUM PROCESSING

	Superficial liquid velocity		ft./hr. (STP)	Superficial gas velocity ^a	
	ft./hr.	kg/m ² s		cm/s (STP)	kg/m ² s
Commercial reactor	10	0.83	1,780	14.8	0.0132
	300	25.0	8,900	74.2	0.066
Pilot plant ^b	1	0.083	53,500	444	0.395
	30	2.5	266,000	2,220	1.97
	1	0.083	178	1.48	0.0013
	30	2.5	890	7.42	0.0066
	1	0.083	5,350	44.4	0.0395
	30	2.5	26,600	222	0.197

^a Values of G calculated for 1000 and 5000 Std. cu. ft. of H₂/bbl, respectively, and assume all hydrocarbon is in the liquid phase. Although expressed at S.T.P. conditions, operating pressures are usually in the range of 500 to 1500 lb./sq.in., occasionally higher.

^b Length of pilot plant reactor assumed to be 1/10 that of commercial reactor.

^c 1 lb./hr.(ft.²) = 1.36 × 10⁻³ kg/m² s.

form, one step in a commercial process for manufacture of hydrogen peroxide (upon subsequent contact with oxygen, the hydroquinone yields the quinone plus H_2O_2 and the quinone solution is recycled).

Porter (1961) recommended operation of such a hydrogenator at flow rates within the range of 3.6 to 36 $kg/m^2 s$ represented by the diagonal arrow on Figure 1 and patents by Lee and Schrock (1973) and Keith, Cornely, and Lee (1973) have given examples of operation at several liquid flow rates which appear to be representative of commercial practice, shown as vertical flags on the diagonal arrow. No hydrogen flow rates were cited and the ratios of G/L shown correspond to the approximate stoichiometric ratio for hydrogenation to the hydroquinone.

The wide variation in operating conditions that may be used in different trickle-bed reactors should be borne in mind in evaluating specific phenomena reported. The cross-hatched zone indicates the approximate region where the flow pattern shifts from the gas-continuous region to that in which pulsing occurs. The region of transition between continuous two-phase flow and dispersed bubble flow is not well characterized but seems to exist at values of L above approximately 30 $kg/m^2 s$ and G below 1 $kg/m^2 s$ (Charpentier et al., 1971; Sato et al., 1973). Slight amounts of surface-active species or other substances can cause foaming and a major alteration in the hydrodynamic flow pattern. This is also a function of other physical properties of the liquid and of particle size.

2.2a Liquid Distribution and Wall Flow. This has been the subject of a large number of both theoretical and experimental studies, again with particular attention to packed absorber performance. Among published materials available may be cited a study by Jameson (1966) and an extensive investigation, both theoretical and experimental, by Porter and co-workers (1968). Of particular importance in the narrow diameter trickle-bed reactors encountered in laboratory and pilot-scale work is the fact that liquid migrates to the wall and the fraction flowing down the wall increases up to a steady state value typically reached in about 1/3 to 2/3 m. The steady state wall fraction corresponds to as much as 30 to 60% of the total at ratios of reactor diameter to particle diameter of as high as 10, drops with an increase in ratio of column diameter to packing diameter, and is a function of liquid flow rate. Packing shape is particularly important: Acres (1967) has observed that cylinders tend to pack together end-to-end and cause liquid to track through the bed; that spheres are little better than cylinders, tending to channel liquid onto the wall, and that irregular granules performed best. This wall flow is a mechanism for bypassing of the catalyst by liquid reactant, but what is particularly important in trickle-bed reactors is the exchange rate between wall flow and packing flow rather than wall flow as such.

2.3 Pressure Drop

Considerable literature has been published on pressure drop and flow characteristics for concurrent gas-liquid flow down packed beds although much less than for countercurrent flow in beds (see, for example, Reiss, 1967). Unfortunately, the upper range of liquid flow rates under trickle-bed reactor conditions corresponds roughly to the lower limit of much of the literature data. Furthermore, little information has been published on spheres and pellets.

A starting point is the equation developed by Ergun (1952) for single phase flow of fluids through packed beds of granular solids.

$$\frac{\Delta P}{h} \left(\frac{g_c \rho d_p^3}{\mu^2} \right) \left(\frac{\epsilon}{1-\epsilon} \right)^3 = \frac{Re}{(1-\epsilon)} \left[\alpha + \beta \frac{Re}{(1-\epsilon)} \right] \quad (1)$$

where $d_p = 6(1-\epsilon)a$. This is equivalent to the diameter of a sphere of the same volume-surface ratio.

Equation (1) proceeds from the Kozeny-Carman equation, expressing the friction factor in the intermediate region between laminar and turbulent flow as $f_p = \alpha/Re + \beta$, the two terms being the contributions from laminar and turbulent flow, respectively.

For a variety of packed beds and different shapes Ergun reported α and β to be constant and equal to 150 and 1.75, respectively. Values of Re varied from 1 to 2500. However, the frictional pressure drop is a very strong function of the void fraction of the bed which itself may vary by as much as 5 to 10% by the method of packing. Larkins et al. (1961) have also observed that one given material can be packed to give the same void fraction but yield pressure drops varying by as much as 50%, a variable not accounted for in this correlation, but for spheres and cylinders of small aspect ratio as encountered in trickle-bed reactors this effect may be small. Other values of α and β have been reported by other investigators, Larkins' data for example, agreed with Ergun's values for packing of cylinders, but Larkins recommended values of 118 and 1.0 for 0.95 cm ($3/8$ in.) spheres, and 266 and 2.33 for 0.95 cm rings, leading to predicted pressure drops about 20% less for spheres and 75% greater for rings than those predicted by the Ergun constants. The Ergun equation or a similar form can also be used to correlate data on liquid holdup in which the void fraction is now reduced by the amount of liquid present (see, for example, Wijffels et al., 1974).

The principal studies on two-phase concurrent flow in beds of spheres or cylinders seem to be those of Larkins, McIlvried (1956), Weekman and Myers (1964), Turpin and Huntington (1967), and Charpentier et al. (1971). All their correlations are extensions to packed beds of the Lockhart-Martinelli correlations developed for two-phase flow in pipes. That of Larkins is based on a wide variety of conditions and has been used by various subsequent investigators as a basis for correlation and development of similar expressions.

$$\log_{10} \left(\frac{\Delta P_{lg}}{\Delta P_l + \Delta P_g} \right) = \frac{0.416}{(\log_{10} \chi)^2 + 0.666} \quad (2)$$

Here $\chi = (\Delta P_l/\Delta P_g)^{1/2}$, where ΔP_g is the single-phase pressure drop for the gas flowing alone, ΔP_l for the liquid flowing alone, and ΔP_{lg} is the two-phase pressure drop. The same relationship is also given as

$$\log_{10}(\Delta P_{lg}/\Delta P_g)^{1/2} = 0.5 \log_{10}(1 + \chi^2) + \frac{0.208}{(\log_{10} \chi)^2 + 0.666} \quad (3)$$

Larkins defined the two-phase frictional pressure drop as

$$\Delta P_{lg} = - \left(\frac{\Delta P}{\Delta L} \right)_{\text{measured}} + \rho_m$$

where ρ_m is a term added with the assumption that all the liquid holdup contributes a head for downflowing liquid. Subsequent authors have pointed out that this is incorrect in that the flowing liquid was largely supported by the packing and the term ρ_m should be eliminated. Fortunately, for most of Larkins' runs this term was insignificant

TABLE 4. HOLDUP STUDIES ON SPHERES OR CYLINDERS IN PACKED COLUMNS

Reference	L , kg/m ² s	G , kg/m ² s	Notes
Larkins et al. (1961)	0 to 265	0 to 14.7	Air and water or ethylene glycol, 9.6-mm spheres in 5-cm column
Ross (1965)	0.68 to 27.1	0.019	Water in air, 4.8 × 4.8 mm cat. pellets in 5.2 or 200-cm diam. column
Hochman and Effron (1969)	0.8 to 6.7	0 to 0.097	MeOH and N ₂ , 4.8-mm glass beads in 15-cm diam. col.
Charpentier, et al. (1971)	0 to 64	0 to 2.5	Air and water, 3-mm porous alumina or 3-mm nonporous glass spheres in 0.1 m diam. col.
Kolář, Brož and co-workers (1970)	0.2 to 16.7	0 to 0.7	Air and various liquids, counter-current flow, 10, 14.9 or 19.4 mm diam. spheres
Way (1971)	0.25 to 2.07	0 to 0.026	3-mm glass spheres, 1.6 × 8 mm or 3.2 × 3.2 mm cylinders. Hydrocarbons (μ of 1.1 to 40 cP) and air in 2.8-cm diam. col.

See also Davidson et al. (1959) and Pelossof (1967) for holdup studies on a string of spheres. Concurrent flow downwards unless otherwise noted.

and the correction does not affect the above correlations (Way, 1971), but a density term may be significant for studies under different conditions. Slightly different formulations for the frictional energy drop are used by Charpentier et al. (1969, 1971).

The pressure drop is markedly affected by foaming that can occur in some systems at low liquid rates and with high gas solubility, which also causes instabilities. Pressure drop correlations are discussed further by Way (1971) and in the cited references.

In hydroprocessing of residual oils, vanadium, nickel, and iron sulfides, from the metal porphyrins in crude oil and from iron and steel corrosion, can build up in a trickle bed and cause an increase in the pressure drop. A model of bed-plugging caused by this effect has been published by Newson (1972a) and compared to data of Moritz and co-workers on increase in pressure drop with time in a commercial reactor. Newson argues further (1972b) that radial flow reactors should have an advantage over conventional axial flow reactors for trickle-bed operation because of their lower pressure drop which would permit longer time on stream.

2.4 Liquid Holdup

The liquid holdup is a measure, although approximate and incomplete, of the effectiveness of contacting between liquid and solid catalyst. Information on holdup may also be needed to estimate an average residence time or an average film thickness. The liquid holdup is generally expressed as a fractional bed volume, that is, as the volume of liquid present per volume of empty reactor. It comprises liquid held internally in the pores of the catalyst plus that outside the catalyst pellets. The external holdup is frequently divided into (a) free-draining holdup and (b) residual holdup, the fraction of the liquid remaining on the packing after the bed has drained. In small columns, the free-draining liquid holdup can be measured directly as by a system in which inlet and exit liquid shutoff valves are closed quickly and simultaneously and the drained liquid measured. A pulse tracer technique may be employed instead, which provides a residence time distribution as well as the holdup of liquid which is effectively mobile or dynamic. This is not the same as the free-draining holdup although it is tempting to equate the two in the absence of other information.

The size of effectively stagnant zones that may exist in the external liquid is a function of gas and liquid flow rates under operating conditions and differs from the volume of residual lenses of liquid that remain after a column is drained. Charpentier et al. (1971) present a method of analysis of tracer studies to divide the total holdup into its various contributions. Their results show that the application of a gas flow to a flowing liquid reduces the fraction of stagnant zones present. By tracer studies Wijffels and co-workers (1974) measured the fraction of the stagnant holdup in packed beds which is not washed out during trickle flow and have taken this as a measure of the fraction of the bed which is effectively noncontacted during operation. Measurements were made with 1 to 9.5 mm glass beads at superficial liquid velocities of 1 to 7 kg/m² s using primarily water although a few runs were also obtained with cumene. The fraction of the bed freshly contacted with flowing liquid decreased with increasing particle size over the range of 1 to 5 mm.

The maximum internal holdup corresponds to the total pore volume of the catalyst and would typically range from about 0.15 to about 0.40, the latter in the case of very porous catalyst particles. The residual holdup varies typically from about 0.02 to 0.05. The free-draining holdup is a function of the gas and liquid flow rates, the fluid properties, and the catalyst characteristics. A large amount of information on holdup has been published for packing of rings and saddles because of their use in absorption towers. Because of their different shape, the high void fraction of the beds and the operating conditions utilized, the applicability of these studies to trickle-bed reactors is uncertain. Table 4 lists several studies on spheres or cylinders which cover a range of conditions. Charpentier and co-workers (1968, 1969, 1971; Reynier and Charpentier, 1971) have published extensively on holdup and other hydrodynamic characteristics for concurrent downflow through packing of the ring, saddle, etc. types. The cited references to their more recent work give guidance to their earlier studies.

2.4.1 Liquid Holdup in Commercial Reactors. The validity of using residence time distributions obtained by the pulse (tracer) technique for obtaining data on liquid holdup is now well established by the work of Rothfeld and Ralph (1963), who used pulse, step decrease, and step increase methods to obtain the residence time distribution and concluded that the residence time distribu-

tion and the holdup calculated from the average residence time are independent of the method of tracer input. The only holdup data on commercial reactors appear to be those of Ross (1965) who studied 5.1-cm and 10.2-cm diameter columns (water-air), a 5.1-cm diameter pilot hydrotreater reactor, and a 2-m diameter commercial desulfurization reactor. Particularly significant was his observation that under similar operating conditions the commercial reactor holdup was only about 2/3 that of the pilot reactor, and the poorer performance of the commercial unit was attributed to this. (See also Section 5.5.)

The design variable affecting holdup is primarily the liquid flow rate, but other factors can be of considerable importance, including:

1. The liquid inlet distributor (in large columns). Little information has been published on this, although distributors that provide good distribution in absorption columns would presumably be generally applicable here.

2. Shape and size of catalyst particles.

3. Catalyst bed height (perhaps).

4. Wetting characteristics of packing and fluid (Section 5.4).

5. Gas flow rate.

The external holdup is generally correlated as proportional to L^n or Re_L^n , but different investigators report substantially different values for n . For laminar film flow over a column of spheres and with no drag effect by flowing gas, the free-draining holdup H_f is proportional to $L^{1/3}$, both in theory and in actuality (Davidson et al., 1959; Pelossof, 1969). For beds of packing the exponent is larger. Ross reported the dynamic holdup to be proportional to $L^{0.5}$, but at superficial velocities above about 30 m/hr., the exponent became smaller. A brief study by Way indicated an exponent of about 0.4 or a little higher for the dynamic holdup. Hochman and Effron (1969) report H_f to be proportional to $Re_L^{0.76}$ and note fair agreement with a correlation of Mohunta and Laddha (1965) based on countercurrent flow with a variety of packings and liquids, the latter reporting an exponent of 0.75.

In comparing correlations it is important to distinguish between total external and the free-draining holdup and to note that an approximate or assumed value of residual holdup is usually subtracted from the total to arrive at the dynamic holdup. This has the effect of decreasing the value of n . The total holdup data of Hochman and Effron are proportional to about $L^{0.5}$ and that of Ross to about $L^{0.38}$.

Another factor is that the fractional degree of wetting may increase with liquid flow rate to an extent somewhat specific to the system so that the effect of liquid flow rate on holdup may in part be related to wetting or spreading characteristics of the system. Hochman and Effron state that dynamic holdup was independent of gas flow rate under their operating conditions (liquid rates up to 6.7 kg/m² s and gas rates up to about 0.1 kg/m² s). Under conditions in which drag effects by the gas on the liquid are significant, one would expect the liquid holdup to increase with pressure at constant gas mass velocity since, according to Equation (1), ΔP_g will decrease.

3. MASS TRANSFER

3.1 External Mass Transfer—Overall

In the most commonly-encountered situation the mass-transfer limiting reactant is the gaseous species (for example, hydrogen). The gaseous reactant is usually present in substantial stoichiometric excess and in relatively high fractional concentration in the vapor phase as well as

being relatively insoluble in the liquid, as in the case of hydrogen. If this is the case, it is valid to assume that vapor-liquid equilibrium is established between the gas and the gas-liquid interface, that is, that there is no significant mass transfer resistance in the gas phase. If the catalyst is completely surrounded by liquid, dissolved gas must be transported from the gas-liquid interface to the bulk liquid and then to the liquid-solid interface. At steady state the mass flux may be expressed as

$$N = k_l(c_i - c_b) = k_s(c_b - c_s) = k_{ls}(c_i - c_s) \quad (4)$$

The last expression is obtained by eliminating c_b from the previous two equalities and defining

$$\frac{1}{k_{ls}} = \frac{1}{k_l} + \frac{1}{k_s} \quad (5)$$

This assumes that the area for gas-liquid transfer is the same as that for liquid-solid transfer which is reasonable for many situations, especially those at moderate liquid flow rates. For rippling, slugging or bubble-type flow the products $k_l a$ and $k_s a$ should be used instead.

Values of k_{ls} can be determined experimentally or predicted by several different theoretical models. Four presented and discussed by Pelossof (1967) are as follows:

3.1.1 Simple Stagnant Film Model. Taking the average film thickness as Δ and neglecting the velocity gradient across the film,

$$k_{ls} = \frac{D}{\Delta} \quad (6)$$

The film thickness can be estimated as $\Delta = H_0/a$ where H_0 is the external liquid holdup and a is the external catalyst surface per unit bed volume. Equation (6) then becomes

$$k_{ls} = \frac{Da}{H_0} \quad (7)$$

Individual coefficients can also be estimated by arbitrarily assigning one-half of the total resistance to each, giving,

$$k_l = k_s = \frac{2D}{\Delta} = \frac{2Da}{H_0} \quad (8)$$

This assumes that the entire pellet is wetted. If not, a should be based on the fraction of wetted external catalyst surface.

3.1.2 Laminar Flow Over a Vertical String of Spheres, Mixed Model. The following assumptions are made:

1. Liquid flows around a sphere with a parabolic velocity profile,

2. No velocity component exists perpendicular to the surface,

3. The gas exerts no drag on the liquid, and

4. Static holdup consists of lenses at the points of contact of spheres. Mass transfer does not occur through this portion of the film and the size of this zone is taken as being independent of flow rate.

Mass transfer is a combination of two processes, a diffusional process predominating in the direction normal to flow and a convective process predominating in the direction of flow. Mass transfer occurs over most (but not all) of the spherical area. Complete mixing is assumed to occur at each point of contact between successive spheres although in a real bed of spheres with a variety of contact points the concentration profiles may interfere with each other more frequently (Cornish, 1965).

For parabolic flow over a string of spheres, the liquid film thickness Δ caused by the dynamic holdup is

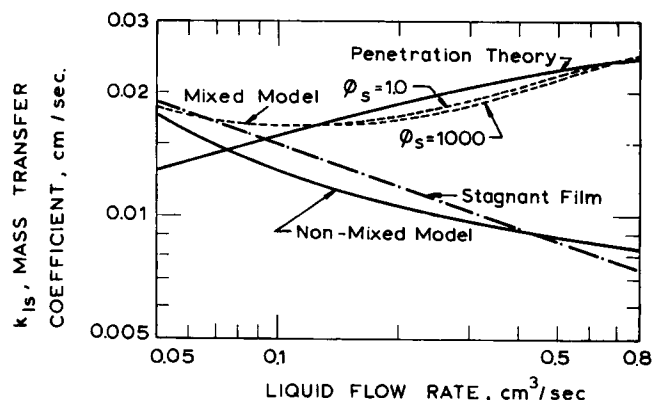


Fig. 2. Comparison of mass transfer coefficients predicted by four models. Hydrogen in α -methyl styrene. A flow rate L of $0.1 \text{ cm}^3/\text{s}$ here is equivalent to about $1.33 \text{ kg}/\text{m}^2 \text{ s}$ for a bed of spheres touching in a square pattern. The calculated film thickness in cm is about $0.09L$.

$$\Delta = \left(\frac{3L\mu}{\pi d \rho g} \right)^{1/3} \sin^{-2/3} \theta \quad (9)$$

In this particular case L = liquid flow rate expressed as cm^3/s . Integration over the solid angle through which mass transfer is taken to occur (assumption 4) yields an average value $\bar{\Delta}$.

3.1.3 Laminar Flow Non-Mixed Model. Mass transfer is modeled as in (3.1.2) above, but the concentration profile at the entry to the next sphere is taken as identical to that leaving the pellet above, that is, this model is analogous to that for a theoretical wetted wall column.

3.1.4 Penetration Theory. The two resistances are calculated by a form of penetration theory as applied to absorption, using Equation (5). The resistance to diffusion on the gas side is taken to be equivalent to the reciprocal of an absorption mass transfer coefficient k_l and that on the solid side to the reciprocal of a mass transfer coefficient for dissolution of a sparingly soluble solid, k_s . Total mixing is assumed to occur often, for example, after each particle length. k_{ls} is then given by Equation (5).

3.1.5 Comparison of Models. The four models are compared in Figure 2, which plots k_{ls} as a function of flow rate for the system of hydrogen in α -methyl styrene ($D = 1.65 \times 10^{-4} \text{ cm}^2/\text{s}$) flowing over a string of spheres 0.825-cm diameter. For a bed of spheres touching in a square pattern, $0.1 \text{ cm}^3/\text{s}$ is equivalent to about $1.33 \text{ kg}/\text{m}^2 \text{ s}$.

Predicted values for the nonmixed model (3.1.3) do not differ greatly from that for the simple stagnant film model (3.1.1), and the latter may be used at low flow rates for first approximation calculations for the value of k_{ls} . The mixed model is a better representation of reality at higher flow rates since the catalyst contact points should act as regions of mixing. The penetration theory model is only valid before the two concentration boundary layers begin to overlap, that is, at the short contact times encountered at high flow rates. For the case shown on Figure 2, this is about $0.7 \text{ cm}^3/\text{s}$, (about $10 \text{ kg}/\text{m}^2 \text{ s}$, but in a packed bed the number of contact points is greater and the length between successive mixings would be less than a particle length. At the high flow rates the penetration theory model and mixed model essentially agree with each other, as they should. The slight difference is caused by slightly different choices of the average outside pellet surface concentration.

A significant conclusion indicated by these models is that even with substantial mass transfer limitation through the liquid film, the observed rate of reaction may change relatively little with a large variation in liquid flow rate, for a fixed average concentration in the bulk liquid. In part this is because the dominating mechanism changes from a stagnant-film model at low flow rates to a mixed model at high, and in part to the fact that for laminar flow over spheres the film thickness is proportional to the cube root of the flow rate. Statements in the literature that a trickle-bed reactor is free of mass-transfer effects if the apparent rate constant is independent of liquid flow rate seem to be based upon a too-facile analogy to single phase flow in which mass transfer is indeed markedly affected by flow rate except at very low velocities.

Hanika, Sporka, and Ruzicka in three related articles make similar analyses to predict conversion for reaction between hydrogen (first order) and a liquid-phase component (zero order). In the first paper (Hanika et al., 1970) they develop a flat plate model with laminar flow of liquid for this system, which is solved for three transverse velocity profiles: plug flow, linear, and parabolic. In a second paper (1971a) a column of spheres is analyzed, in continuation of the analyses of Pelossof. Results are presented for models analogous to the mixed and nonmixed models of Pelossof and also making different assumptions about the role of menisci between spheres. The theoretical analyses are compared to experimental measurements of the hydrogenation of cyclohexene in a solution of methanol or 1-propanol on electrolytic platinum black in a wetted wall column (unfortunately not a trickle-bed reactor) (Hanika, 1971b).

If external mass transfer to catalyst particles is a significant limitation, the particles themselves, if porous, will usually exhibit a low effectiveness factor and the boundary condition at the interface between liquid and solid, which affects the mass transfer through the film, is itself affected by factors determining the effectiveness factor. The appropriate mathematics is outlined by Pelossof and applied to an experimental study of hydrogenation of α -methyl styrene on a string of catalytic spheres. Ermakova and Ziganshin (1970) present a theoretical analysis of a similar situation and show, for example, the effect of both external and internal mass transfer on the distribution of reactant component concentration within the catalyst particle and in the external film. The case is for reactant present only in the liquid in the presence of a large excess of gas, that is, only k_s is involved in the film mass transfer and considers first or zero order kinetics with respect to the liquid. However, some of the combinations of internal and external mass transfer analyzed correspond to external mass transfer coefficients k_s (which they symbolize as β) which appear to be far lower than those physically realizable in trickle-bed reactors.

A limitation to use of these models is evidence that the flowing liquid may not indeed completely surround the catalyst particles in many cases, but instead flows downwards as rivulets, particularly at low liquid rates. This has been reported by a number of investigators. In a study of hydrogenation of benzene to cyclohexane in a trickle-bed reactor, at 1-atm pressure and slightly below the boiling point some reaction apparently occurred directly between benzene vapor and solid even at liquid flow rates as high as $3.5 \text{ kg}/\text{m}^2 \text{ s}$ ($Re = 55$) and in spite of extreme measures taken to provide initial uniform distribution of liquid (Satterfield and Özel, 1973). Nevertheless, values of k_l , k_s , and k_{ls} calculated from the stagnant film model and based on the wetted external

area set minimum values for mass transfer rates through the trickling liquid. Note, however, that the effective film thickness varies with flow rate in a different manner in a bed of pellets than over a string of spheres and that the drag effect of gas flow on liquid film thickness may have to be considered. Mass transfer may be significantly enhanced as the liquid flow rate is increased to cause the flow pattern to change into the pulsing or slugging regime.

3.1.6 Criteria for External Mass Transfer Limitations. If a liquid film indeed surrounds a pellet, mass transfer through it will not be a significant resistance unless the following inequality holds (Satterfield, 1970).

$$\left(\frac{10d_p}{c^*}\right) \tau(1 - \epsilon) > k_{ls} \quad (10)$$

Mass transfer limitations are assumed to be insignificant unless $c_s < 0.95 c_i$. A conservative estimate for k_{ls} is given by Equation (7), or (5) may be used. If no information on H_0 is available, k_{ls} may be conservatively approximated by assuming that 50% of the voids in the reactor are filled with liquid, hence $\bar{\Delta} = \epsilon/2a$.

Then

$$k_{ls} = \frac{D}{\Delta} = \frac{2Da}{\epsilon} \quad (11)$$

For 0.318-cm ($1/8$ -in.) diameter pellets, the film thickness thus calculated is about 0.03 cm.

Mass transfer through the liquid film does not seem to be a significant resistance under typical hydrodesulfurization conditions. The average film thickness is so much less than the radius of the usual catalyst particle that it will not ordinarily be a significant resistance unless the effectiveness factor of the catalyst pellets themselves is quite low. Van Deemter (1964) concluded that under typical industrial conditions (55 atm, 370°C) the effectiveness factor in Co/Mo/Al₂O₃ catalyst particles 0.5 cm in diameter was about 0.36. Adlington and Thompson (1964) concluded from studies at the British Petroleum Co. that at 34 atm and 416°C on 0.318-cm ($1/8$ -in.) pelleted catalyst of the same type the effectiveness factor was about 0.6. Application of the criterion, Equation (10) shows that film resistance is negligible for these conditions.

If the key reactant is a liquid-phase component present in low concentration, mass transfer of this species from the film to the catalyst may become the rate-limiting step instead of transfer of dissolved gas through the film. This could be the case in hydrodesulfurization of a feedstock containing small amounts of organo-sulfur compounds in which case the relevant mass transfer coefficient is k_s , estimated from the stagnant film model as $2D/\Delta = 2Da/H$. At higher flow rates values of k_s as determined experimentally by dissolution of a solid (Section 3.3) may be more applicable.

3.2 Mass Transfer, Gas to Liquid, Experimental Measurements

An early study of concurrent downward gas absorption mass transfer was reported by Dodds et al. (1960), but the most extensive and detailed studies appear to be that of Reiss (1967) who also gives guidance to the earlier literature and that of Gianetto and co-workers (1973). Reiss measured oxygen absorption into water from air at 25°C for concurrent flow down over stacked and dumped 1.25-, 2.54-, and 7-cm rings and recommended the following correlation:

$$k_{la} = 0.12 \cdot E_l^{1/2} \quad (12)$$

where E_l is an energy dissipation term for liquid flow

evaluated as

$$E_l = \left(\frac{\Delta P}{\Delta L}\right)_{ig} \cdot V_l \quad (13)$$

where V_l = superficial liquid velocity, ft./s

$\left(\frac{\Delta P}{\Delta L}\right)_{ig}$ = pressure loss for two-phase flow (lb. force)/(ft.²) (ft.)

E_l = (ft.) (lb. force)/(s) (ft.³)

Reiss also shows that earlier oxygen desorption data of McIlvried (1956) on dumped 0.63-cm rings and on 0.4 and 0.6-cm spheres agree well with this correlation. The range of flow rates covered by Reiss corresponds to superficial liquid velocities up to 300 kg/m² s and superficial gas rates up to about 6.0 kg/m² s. Corresponding values of E_l varied from 2 to 1000 and values of k_{la} varied from about 10⁻¹ to 3 s⁻¹.

The studies of McIlvried on 0.4 and 0.6-cm glass beads were at air rates of about 0.4 to 5.5 kg/m² s and at liquid flow rates of 9.6 to 130 kg/m² s. (The equation which he presents as correlating his data at the lower flow rates seems to be in error by a factor of about ten, but the data as such do agree with those of Reiss.)

Gianetto et al. (1973) studied oxygen desorption with air from a 2N NaOH solution over the range of superficial liquid velocities of 2.7 to 46 kg/m² s for the liquid and 0.5 to 3.0 kg/m² s for the air, using 6-mm glass spheres as well as ring and saddle packing. In terms of energy dissipation, this covers the range studied by Reiss and extends to one order of magnitude lower. Corresponding values of k_{la} varied from about 0.01 to 1 s⁻¹. Data scattered somewhat, but there was no significant effect of the nature of the packing. Values of k_{la} were slightly less than those of Reiss' at high energy dissipation rates and less by a factor of two at the lowest energy dissipation values that Reiss studied. Variations in the degree of wetting of packing or of liquid distribution from one investigator to another would be expected to be the greatest at the lowest flow rates.

For systems other than water-air, k_{la} can be estimated by taking $k \propto D^n$. The value of n will vary somewhat with flow rate and packing type, but a value of 0.5 following penetration theory is reasonable.

Taking the diffusivity of oxygen in water at 25°C as 2.4×10^{-5} cm/s a more general expression for k_{la} based on Reiss' correlation becomes

$$k_{la} = 0.12E_l^{0.5} \left(\frac{D}{2.4 \times 10^{-5}}\right)^{0.5} \quad (14)$$

k_{la} is also proportional to the -0.04 to -0.28 power of the viscosity (Sherwood and Pigford, 1952) and if the viscosity of the liquid differs much from that of water, a further correction must be made.

Values of E_l are preferably obtained from actual reactor pressure drop data or, lacking that, can be calculated from Larkin's equation. However, the accuracy of Larkin's correlation at low flow rates is somewhat questionable.

Mass transfer from gas to liquid was also studied by Sato et al. (1972) who measured desorption of oxygen into nitrogen from water at 15°C, at gas superficial velocities of 0.06 to 1.2 kg/m² s and liquid superficial velocities of 10 to 200 kg/m² s, using glass spheres of from 0.25- to 1.22-cm diameter. Reported values of k_{la} varied from about 0.02 to 3 s⁻¹.

They correlated their data by the following dimensional equation:

$$k_1 a = 31 d_p^{-0.5} U_1^{0.8} U_g^{0.8} \quad (15)$$

where d_p is in mm, U_1 and U_g are in m/s, and $k_1 a$ is in s^{-1} .

Sato et al. also correlated their data as a function of an energy dissipation term, but used a different formulation from that of Reiss. They also determined values of the specific interfacial area a from studies of absorption of CO_2 in aqueous NaOH solution. There was no effect of packing size as such on either $k_1 a$ or a when energy dissipation was used as the means of correlation. Sato et al. state that their results deviate substantially from those of Reiss which they attribute to the lack of use of gas velocity as a correlating variable in the latter's correlation. However, the effect of gas rate that Reiss observed is indirectly included in his correlation in that it affects the energy dissipation function in Equation (12). Ufford and Perona (1973) determined values of $k_1 a$ for absorption of CO_2 into water in concurrent flow at liquid flow rates of 4.5 to 81 kg/m² s and gas rates of about 0.06 to 0.18 kg/m² s over 6-mm to 19-mm saddle and ring packing. The gas rate had a significant effect on mass transfer, but over the range of L and G conditions studied values of $k_1 a$ were lower than those predicted by correlations for countercurrent flow by a factor of as much as 3.

In some trickle-bed operations, gas and liquid flow rates will be below the range to which Equations (12), (14), or (15) apply and in any event a minimum value of $k_1 = 2D/H_0$, established by the stagnant film theory, should be used if it exceeds the value predicted by any of the above correlations. The true minimum may actually be greater than this value since it assumes complete wetting of the external surface.

If gas-liquid mass transfer is an appreciable resistance, as will tend to occur at high reaction rates and correspondingly high liquid flow rates, a higher rate of reaction per unit quantity of catalyst pellets can be obtained by mixing inert material with the catalyst. These zones allow enhanced opportunity for gas to dissolve in the liquid. A recent patent (Lee, 1971) cites improved performance based at least in part on this principle for a trickle-bed reactor for the hydrogenation of an alkyl anthraquinone. The example cited is for a liquid flow rate of 17 kg/m² s. In many cases a minimum concentration of dissolved hydrogen in the liquid in contact with the solid catalyst is needed to avoid the accumulation of partially hydrogenated products adsorbed on the catalyst that can cause accelerated poisoning. The use of inert packing mixed with catalyst pellets may help to minimize this difficulty.

3.2.1 Gas Solubility. For design purposes, or to determine mass transfer effects it will usually be necessary to estimate the solubility of the gas in the liquid. In the absence of desired data useful general references are the two books by Hildebrand and Scott (1950, 1962), a recent paper by Hildebrand and Lamoreaux (1974) and reviews by Battino and Clever (1966) and Prausnitz (1968). For many gases, including hydrogen, the log of the mole fraction gas solubility is inversely proportional to the square of the solubility parameter of the liquid. This squared quantity is defined as the cohesive energy density, the energy of vaporization per unit volume of the liquid. In approximate terms, solubility generally decreases with increasing polarity. The solubility of hydrogen and that of other sparingly soluble gases in organic solvents usually increases moderately with increased temperature. (Between 0 and 40°C the solubility of hydrogen in *n*-heptane increases 30%, in benzene 40%.) The list in the next column gives values of the solubility of hydrogen in representative liquids at 20° to 25°C, taken from several sources and adjusted to 1-atm pressure

using Henry's law.

	g-mole/cm ³
Octane	5×10^{-6}
Cyclohexane	4.5×10^{-6}
Xylene	3.3×10^{-6}
"Naphtha"	3.3×10^{-6}
"Gas oil"	3×10^{-6}
Benzene	2.9×10^{-6}
Aniline	0.8×10^{-6}
Water	0.8×10^{-6}

3.3 Mass Transfer, Liquid to Solid, Experimental Measurements

Van Krevelen and Krekels (1948) studied the rate of dissolution of benzoic acid into water or into aqueous glycerol or sulfur into benzene, using irregular granules with diameters of from 0.29 to 1.45 cm. Data were obtained with liquid flowing through the bed as a single continuous phase and also for film-like flow. However, no forced flow of gas was applied during the film-like flow experiments. Consequently, the bed may actually have been flooded in some cases so some of the data points may be more representative of single phase liquid flow.

The data were represented by

$$Sh' = 1.8(Re')^{1/2} Sc^{1/3} \quad (16)$$

where $Sh' = k_s/aD$ and $Re' = L/a\mu$.

Re' was varied between 0.013 and 12.6; estimating the void fraction ϵ as 0.4, equivalent values of $Re = d_p L/\mu$ are about 0.047 to 45.

Equivalent superficial linear velocities were 0.12 to 3.7 kg/m² s. Sc was varied between 9×10^2 and 2.5×10^6 ; the viscosity was varied from 0.6 to 120 cp.

For comparison, the data for single phase liquid flow were best represented by an equation of the same form but with a constant of 0.8, that is, the effect of adding gas was to slightly more than double the mass transfer coefficient.

The only other known study of solid-liquid mass transfer under two-phase flow conditions is that of Sato et al. (1972) who reported values of k_s from the benzoic acid-water system at air velocities between 0.01 and 1.2 kg/m² s and liquid velocities between 6 and 200 kg/m² s for 12-mm particle diameter material. Results at low gas flow rates (for example, 0.01 to about 0.1 kg/m² s and over the entire liquid flow rate agreed reasonably well with an extrapolation of van Krevelen and Krekels' correlation for film-like flow, [Equation (16)], corresponding values of k_s varied from about 2×10^{-3} to about 1.5×10^{-2} cm/s. The effect of two-phase flow was to increase the mass transfer coefficient over that obtained in single phase flow of liquid alone at the same superficial velocity by an enhancement factor β which in turn was related to the Lockhart-Martinelli parameter $(\Delta P_L/\Delta P_G)^{1/2}$. For gas velocities over the range of 0.01 to 0.1 kg/m² s, β was roughly 2, in agreement with van Krevelen and Krekels.

As with k_1 , a minimum value of k_s is established from the stagnant film model which should be used if it exceeds the value given by the above approaches. For conditions representative of pilot plant work (for example, liquid flow rates up to about 1 kg/m² s, values of k_{1s} calculated by the stagnant film model may equal or exceed those calculated from the experimentally derived correlations (Way, 1971).

3.4 Pore Diffusion Limitations

Internal diffusion limitations are commonly expressed in terms of the catalyst effectiveness factor η defined as

the ratio of the observed rate of reaction to that which would be observed in the absence of any internal concentration or temperature gradients. Methods of estimating η have now been developed in great detail (Petersen, 1965; Satterfield, 1970) and will not be reviewed here.

In summary, for a first-order reaction, internal diffusion will be insignificant if

$$\frac{(d_p/2)^2 \tau (1 - \epsilon)}{D_{eff} c_s} < 1 \quad (17)$$

where c_s is the concentration of the reactant in the liquid at the solid-liquid interface whose diffusion is rate-limiting. This species is usually the dissolved gas, but it may instead be a reactant present in the feed stream in low concentration, as in some hydrodesulfurization processes.

Unless the size of the diffusing molecules is comparable to that of the pores

$$D_{eff} = \frac{D\theta}{\tau} \quad (18)$$

where θ is the catalyst void fraction and τ is the tortuosity factor, usually having a value of about 4, extreme values for the usual catalyst structures being about 2 to 7. This generalization concerning values of τ has been developed primarily from studies of gas-phase bulk diffusion, but there seems to be no reason why τ should be different for diffusion in the liquid phase unless surface diffusion added to the flux or adsorbed species restricted the size of the passageways. In one relatively well-defined case, for dissolved hydrogen diffusing in α -methyl styrene, τ was found to be 3.9, from analysis of the effect of particle size on reaction rate (Ma, 1968). As with vapor-phase transport, surface diffusion of an adsorbed solute would not be expected to make a significant contribution to the total flux except in a solid having very high area, and therefore fine pores, on which the solute is weakly adsorbed. The only quantitative measurements of surface diffusion in liquid-filled pores appear to be those of Komiyama and Smith (1974) who studied the adsorption rates of benzaldehyde in aqueous solution into polystyrene (Amberlite) particles.

Use of these quantitative approaches may be somewhat difficult with the complexities encountered in typical petroleum feedstocks. In these cases, studying the effect of variation of particle size or of viscosity (for example, by dilution of the reactant) may be the best diagnostic tests. As noted in Section 3.1.4, the effectiveness factor for one industrial desulfurizer utilizing 0.5-cm diameter Co/Mo/Al₂O₃ particles was estimated to be about 0.36 (Van Deemter, 1964) and about 0.6 was estimated for another desulfurizer utilizing 0.32 cm pelleted catalyst of the same type (Adlington and Thompson, 1964). Van Zoonen and Douwes (1963), from a study of the effect of particle size, concluded that in their study of hydrodesulfurization the effectiveness factor varied from about 0.5 to 0.8 on 3 × 3 mm pellets of different densities. Quantitative analysis of their results is, however, somewhat uncertain since it is not clear to what extent liquid as opposed to vapor was present in the pores of their catalyst.

When the solute molecular size becomes significant with respect to pore size, the concentration of solute within pores at equilibrium becomes less than that in the bulk by a geometrical exclusion effect and the rate of diffusion becomes less than would otherwise be expected because of the proximity of the pore wall. Little is known of these effects quantitatively, but a study by Pitcher (1973) of the diffusion of a variety of hydrocarbons and

aqueous solutions of salts and sugars in silica-alumina bead catalyst (pore diameter = 32 Å) led to the development of the following empirical relationship to describe this restricted diffusion effect:

$$\log_{10}(D'_{eff}\tau/D) = -2.0\lambda \quad (19)$$

Here λ is the ratio of critical molecular diameter to pore diameter and D'_{eff} is based on the void portion of the porous solid. $D'_{eff} = D_{eff}/\theta$. The relationship is also shown on Figure 3, where $K_r = D'_{eff}\tau/D$ is the factor by which diffusivity is reduced by the proximity of the pore wall. The critical diameter is the diameter of the narrowest cylinder into which the molecule will fit, a dimension relatively easy to establish for small simple molecules. For higher molecular weight substances, molecular conformation becomes increasingly important and a study of diffusion of polystyrene solutes of various molecular weights in porous glass showed no restricted diffusion effect even when the diameter of the molecule expressed as a random coil equalled that of the pore (Colton et al., 1975).

3.4.1 Heat Effects. If reactant is present in both the liquid and vapor phase in a trickle-bed reactor, some unusual effects can develop if heat and/or mass transfer limitations are significant. The maximum steady state temperature difference between center and outside of a catalyst pellet ΔT occurs if diffusion is sufficiently limiting that reactant concentration in the pellet center approaches zero. Then, as shown by Prater (1958)

$$\Delta T = \frac{(-\Delta H) D_{eff} c_s}{\lambda} \quad (20)$$

where λ = thermal conductivity of the porous solid. Even with a highly exothermic reaction, it is unlikely that ΔT will exceed more than a few degrees if the pores remain filled with liquid and unless the gas is much more soluble than is hydrogen in most liquids. An example illustrates: take the enthalpy change on reaction $-\Delta H = 5 \times 10^4$ cal/mole, and a hydrogen solubility of 10^{-4} g-mole/cm³, which would require elevated pressure in typical hydrocarbons. Typical values of the other terms

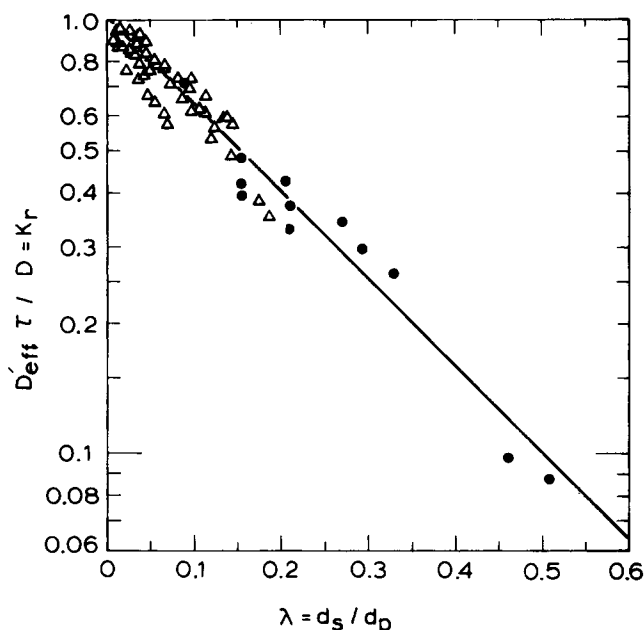


Fig. 3. Effect of ratio of solute critical diameter d_s to pore diameter d_p on effective diffusivity [Satterfield, Colton, and Pitcher, *AIChE J.* 19, 628 (1973)].

are $D_{\text{eff}} = 2 \times 10^{-5} \text{ cm}^2/\text{s}$, $\lambda = 3 \times 10^{-4} \text{ cal/s cm}^\circ\text{K}$. ΔT becomes 0.33°C .

If pores are filled with vapor, however, temperature differences in the hundreds of degrees are quite possible, because values of D_{eff} for vapors are 3 to 4 orders of magnitude greater than for solutes and gas phase concentrations are not lowered by as large a factor. The key limiting component will then usually be vaporized reactant rather than hydrogen. Representative conditions are as follows: $-\Delta H = 5 \times 10^4 \text{ cal/mole}$ (this is now per mole of vaporized reactant), $D_{\text{eff}} = 10^{-2} \text{ cm}^2/\text{s}$, $c_s = 3 \times 10^{-5} \text{ g-mol/cm}^3$, representing vaporized reactant present in small mole fraction but superatmospheric total pressure, and λ as before. ΔT becomes 50°C . This situation will not develop, of course, if the reactant does not have an appreciable vapor pressure.

If a reaction is substantially diffusion-limited when pores are filled with liquid reactant, then circumstances causing the pores to become instead filled with vaporized reactant can cause a marked increase in reaction rate, associated with the marked increase in diffusivity. This, of course, cannot happen if the reactant has insignificant vapor pressure. In an early study by Ware (1959) of the hydrogenation of benzene at 70° to 100°C and 7 to 34-atm pressure the rate varied by a factor of 5 to 10 depending upon the startup conditions. The higher rate was interpreted as a system in which pores were filled with benzene vapor and hydrogen and diffusion limitations were negligible; the lower rate was interpreted as involving diffusional resistance inside liquid-filled pores. More recently the same effect was reported by Sedricks and Kenney (1972, 1973) in a well-defined study of the hydrogenation of crotonaldehyde. In both cases, however, a highly exothermic and rapid reaction was being studied at a low liquid flow rate (about $0.15 \text{ kg/m}^2 \text{ s}$ in Ware's work and $0.045 \text{ kg/m}^2 \text{ s}$ in that of Sedricks and Kenney). Liquid phase reaction could presumably switch to vapor phase reaction at a critical value of the local liquid flow rate below which the heat evolved could no longer be carried away by the flowing liquid. This effect could interact with liquid flow to cause temperature instabilities in various ways. Germain et al. (1974) describe a cyclic and irregular performance of a trickle bed using countercurrent flow of gas against downflowing α -methyl styrene which was hydrogenated to cumene at liquid flow rates of 0.08 to $1.6 \text{ kg/m}^2 \text{ s}$, but here the erratic behavior may have stemmed in substantial degree from the use of countercurrent flow which could have substantially altered the flow and mixing patterns from those obtained with concurrent trickle flow at the same gas and liquid flow rates. Quantitative analysis of coupling effects between heat release on catalyst pellets and dissipation to the flowing fluids might be very helpful in revealing possible causes of instabilities in trickle bed reactors in general.

4. MODELS FOR DESIGN AND ANALYSIS

4.1 The Ideal Trickle Bed Reactor

The analysis of trickle bed performance under ideal circumstances and assuming simple first-order kinetics provides a point of departure for analysis of real cases. We assume the following:

1. Plug flow of liquid, that is, no dispersion in the axial or radial direction.
2. No mass or heat transfer limitations between gas and liquid, between liquid and solid catalyst or inside catalyst particles. The liquid is saturated with gas at all times.

3. First-order isothermal, irreversible reaction with respect to the reactant in the liquid. Gaseous reactant present in great excess.

4. Catalyst pellets are completely bathed with liquid.

5. Reaction occurs only at the liquid-catalyst interface.

6. No vaporization or condensation occurs.

Consider a differential volume element across the reactor and set the rate of reaction in that element equal to the disappearance of reactant as the liquid passes through the element: Then

$$Fc_{\text{in}}dx = r dV \quad (21)$$

where c_{in} = concentration of reactant in entering liquid, moles/ cm^3

x = fractional conversion of reactant

dV = reactor volume in slice under consideration, cm^3

If the reaction is first order,

$$r = k_v c (1 - \epsilon) \quad (22)$$

where $k_v = \frac{\text{cm}^3 \text{ of liquid}}{(\text{cm}^3 \text{ of cat. pellet vol.}) (\text{s})}$

Substituting Equation (22) in (21), we obtain

$$Fc_{\text{in}}dx = k_v (1 - \epsilon) c dV$$

$$c = c_{\text{in}}^{(1-x)}$$

resulting in

$$F \int \frac{dx}{x} = k_v (1 - \epsilon) \int dV$$

or

$$\ln \frac{c_{\text{in}}}{c_{\text{out}}} = \frac{V}{F} k_v (1 - \epsilon) = \frac{k_v (1 - \epsilon)}{L_v/h} = \frac{3600 k_v (1 - \epsilon)}{\text{LHSV}} \quad (23)$$

where V is the volume of the trickle bed packed with catalyst.

4.2 Comparison with Autoclave Measurements

If the same simplifying assumptions again hold, one should be able to obtain the same values of the reaction rate constant k_v from studies in a stirred autoclave. In the autoclave, one measures change in concentration with time, whereas in the trickle-bed reactor we have change in concentration with distance, but the autoclave and the trickle-bed reactor should give the same value of k_v because there is a one-to-one correlation between time in the autoclave and distance traversed in the trickle bed. (For a specified flow rate the distance traversed is inversely proportional to the dynamic liquid holdup, but it is unnecessary to know this in the ideal case—see Section 5.5). In the autoclave,

$$\frac{dc}{dt} = \frac{r(v_{\text{cat}} + v_{\text{liq}})}{v_{\text{liq}}} \quad (24)$$

Here r is moles/(s) (cm^3 of liquid plus cm^3 of catalyst in the autoclave)

v_{cat} = volume of catalyst pellets in autoclave, cm^3

v_{liq} = volume of liquid in autoclave, cm^3

t = time, s

Substituting Equation (22) in Equation (24), where $(1 - \epsilon)$ is now the volume fraction of solid catalyst in the liquid slurry in the autoclave,

$$\frac{dc}{dt} \frac{v_{\text{liq}}}{v_{\text{cat}}} = k_v c$$

$$\ln \frac{c_{\text{init}}}{c_{\text{final}}} = \frac{v_{\text{cat}} k_v t}{v_{\text{liq}}} \quad (25)$$

Although k_v from Equation (25) in principle should equal k_v from Equation (23), in practice that derived from Equation (25) may frequently be greater than that calculated from trickle-bed studies because of a loss of contacting effectiveness in the trickle bed.

Before turning to this concept, however, other possible reasons for differences between the two should be noted. Homogeneous reactions, if they are possible, are more likely to be encountered in an autoclave than in the trickle bed because of the much higher ratio of liquid-to-catalyst volume. This could possibly lead to various unforeseen consequences, such as more formation of side-products, polymers that might block pores, etc. Poisoning of the catalyst would probably also cause the two reactor systems to behave differently. In the autoclave, poisoning would occur uniformly over all the catalyst particles, whereas in the trickle bed, poisons would usually be preferentially adsorbed on the top-most layers of catalyst, leaving most of the bed clean for the main reaction. The net effect could well be to cause a slower drop in reactivity with time in the trickle bed than would be expected from studies in the autoclave. The distribution of poison through an individual catalyst particle may also be a function of particle size as well as of time and the environment.

An upflow (flooded bed) reactor (Section 6), which should give good solid-liquid contacting, could be used instead of an autoclave to obtain information on the intrinsic kinetics.

If reaction is not actually first order, the values of k_v as calculated from Equation (23) and Equation (25) should be the same if the other assumptions hold and if comparison is being made for the same initial and final concentrations. In general, this may not be the case, but for many systems of interest where a high percent of conversion is not required the kinetics of the reaction may be satisfactorily represented as a first-order process even when the true kinetics are substantially different.

Equation (23) is the same expression as one obtains for single phase flow except that k_v is based on catalyst pellet volume and hence a factor $(1 - \epsilon)$ appears. Note that liquid holdup as such or true residence time of liquid in the reactor does not appear in this expression. Neither does the aspect ratio (ratio of length to diameter). The significance of these points will be developed later.

5. CONTACTING EFFECTIVENESS

5.1 Introduction

If data are obtained over a range of linear velocities in a trickle bed, it is usually found that k_v as calculated from Equation (23) increases as liquid flow rate is increased. In different terms, if both h and L_v are doubled (which keeps LHSV constant) the % conversion is increased although Equation (23) predicts there should be no change. Furthermore, in the absence of complications as cited above, the value of k_v at the highest flow rates is found to approach the value obtained in a stirred autoclave where the catalyst is completely surrounded with liquid. Clearly in most trickle-bed reactors there is a loss in what will be termed *contacting effectiveness* below what can be obtained in the ideal reactor, and this loss is greatest at the lowest liquid flow rates.

In the past designers of trickle-bed reactors have gen-

erally used the fact that contacting effectiveness improves with liquid flow rate as a built-in factor of safety by scaling-up from pilot plant to commercial plant size on the basis of equal values of LHSV. Since commercial reactors may be from 5 to 10 times longer than pilot units, this would result in plant units operating at 5 to 10 times the liquid superficial velocity used in the pilot plants, for the same value of LHSV. However, the situation has been confused by the fact that in some cases, as reported by Ross (1965), the commercial unit has performed more poorly than the pilot plant unit in spite of the use of higher linear velocities. This seems to have been caused by poorer liquid distribution and has been characterized by the finding that liquid holdup was poorer in the large unit. (This method of scale-up is unlikely to introduce difficulties from mass transfer limitations unless the catalyst particle size is increased at the same time which, however, the designer may be tempted to do to avoid excessive pressure drop.)

Let us now use the term apparent reaction rate constant k_{app} to refer to the value of the reaction rate constant calculated from Equation (23) or the equivalent, applied to results from a real trickle bed and retain the symbol k_v to refer to the intrinsic (true) value, and consider methods of predicting the effect of liquid flow rate on k_{app} .

5.2 Estimation of k_{app}/k_v

Bondi (1971) developed an empirical relationship of such a form as to cause k_{app} to approach k_v as the superficial liquid velocity approached infinity. His equation, expressed in terms of reaction rate constants, is

$$\frac{1}{k_{\text{app}}} - \frac{1}{k_v} = \frac{A'}{L^b} \quad (26)$$

For a number of systems $0.5 < b < 0.7$ with a median value of about $2/3$. He also reports that an increase in the gas rate moderately increased conversion and suggests multiplying L in his correlation by $(\rho_g G)^\beta$ where for much of his data $0.22 < \beta < 0.5$. However, in a reacting system such as this, changing the gas flow rate also changes the partial pressure of products and reactants such as H_2S and hydrogen. Since H_2S has some inhibiting effect on the reaction rate, the improvement associated with increased gas flow rate was probably partly chemical and partly physical.

The usefulness of this approach is that a contacting effectiveness can be directly defined as k_{app}/k_v . For trickle-phase studies of hydrodesulfurization of a heavy gas oil this ratio was about 0.12 to 0.2 at $L = 0.08 \text{ kg/m}^2 \text{ s}$ and about 0.6 at $0.3 \text{ kg/m}^2 \text{ s}$. At low liquid flow rates, the ratio would be predicted to be proportional to the 0.5 to 0.7 power of the liquid velocity, the power dropping at higher liquid velocities.

5.3 Liquid Holdup

Another approach proceeds from noting that as liquid flow rate is increased, the liquid holdup does also. For the ideal reactor the drop in conversion should follow Equation (23), but with increased holdup it is generally found that c_{out} is lower than predicted. The increased holdup is effective because it has improved contacting or, just possibly, decreased axial dispersion. Regardless of the reason, it is remarkable that a variety of data can be brought into consonance by assuming that the rate of reaction (all other things being equal) is proportional to the holdup H or that

$$k_{app} \propto k_v H \quad (27)$$

For a first-order reaction, one usually plots $\ln c_{out}/c_{in}$ against residence time to obtain the value of k , that is,

$$\ln \frac{c_{out}}{c_{in}} \propto -k_{app} t \quad (28)$$

If $k_{app} \propto k_v H$

$$\ln \frac{c_{out}}{c_{in}} \propto \frac{-k_v H}{(\text{LHSV})} \quad (29)$$

Ross (1965), for example, showed that data on hydrodesulfurization for two commercial reactors and a pilot hydroreactor could be brought into agreement by plotting % sulfur retention versus $(1/\text{LHSV}) H$ on semi-log coordinates. Here the commercial reactors operated more poorly in spite of using higher liquid velocities.

Henry and Gilbert (1973) developed this concept further. For laminar flow down a string of spheres, the free-draining holdup should be proportional to $Re_L^{1/3}$, (Section 2.4.) If one postulates that reaction rate is proportional to free-drainage holdup and that this holdup is proportional to $L_v^{1/3}$, then Equation (23) is replaced by

$$\ln \frac{c_{out}}{c_{in}} \propto \frac{-k_v h^{1/3}}{(\text{LHSV})^{2/3}} \quad (30)$$

It is generally observed that the degree of conversion is increased as bed length is increased at a constant value of LHSV, that is, if liquid velocity is increased in proportion to increase in bed depth. This has been ascribed to decreased axial dispersion, but Equation (30) would predict the same effect, attributed to increased holdup. Henry and Gilbert obtained good correlations of two sets of data on effect of bed length on percent conversion by use of Equation (30) (the flow rates used are not certain) and also showed that for a fixed bed length Equation (30) was followed for several other sets of data (Table 2) on hydrocracking, hydrodenitrogenation, hydrodesulfurization and hydrogenation—all of various petroleum fractions (hydrodenitrogenation included some studies of model compounds). This remarkably good correlation was obtained in spite of two facts:

1. There is no theoretical justification for assuming that the rate of reaction is proportional to holdup.

2. As Henry and Gilbert point out, Equation (30) only applies where $H \propto L^{1/3}$. As the Reynolds number is increased, the dynamic regime changes from gravity-viscosity to gravity-inertia and the exponent on the Reynolds number increases to a value greater than $1/3$.

If reactivity indeed were proportional to holdup, for the laminar film model $H \propto d_p^{-2/3}$ and to $\nu^{1/3}$ where $\nu = \mu/\rho$. Thus the Henry and Gilbert correlation would become

$$\ln \frac{c_{in}}{c_{out}} \propto h^{1/3} (\text{LHSV})^{-2/3} d_p^{-2/3} \nu^{1/3} \quad (31)$$

This predicts that decreasing catalyst size will increase conversion, but the same general effect would be produced by varying catalyst size if diffusion limitations within catalyst particles were significant. Also, a decrease in holdup caused by gas flow would, according to this model, decrease conversion instead of the opposite as found by Bondi.

The Henry and Gilbert correlations were presented in terms of LHSV values and in order to compare them with other work; the range of liquid flow rates used in

each of the most pertinent studies has been estimated as shown in Table 2. Reactor height was not given in some cases, in which event an arbitrary value of one meter has been taken. Although this will result in some error, rough values of liquid superficial velocity can then be calculated. The corresponding % conversions are also cited; in each case the correlating line went through zero % conversion at infinite flow rate.

Certain reservations remain. At very high % conversion, axial dispersion can be a significant factor and it is still uncertain whether the spectrum of compounds present in all cases but one can be properly treated by simple first-order kinetics. Nevertheless Henry and Gilbert's finding of the proportionality of contacting effectiveness to the one-third power of the liquid flow rate seems to hold with flow rates up to $0.5 \text{ kg/m}^2 \text{ s}$, and possibly higher. In contrast Bondi suggested a somewhat higher proportionality in this flow region.

5.3.1 Preliminary Evidence on Contacting Effectiveness. The region in which catalyst contacting approaches 100% effectiveness remains elusive. In analyzing data of Bill on formation of butynediol from C_2H_2 and HCHO and of Hofmann on hydrogenation of glucose to form sorbitol, Bondi noted that contacting effectiveness was still improving with flow rate at velocities as high as $3 \text{ kg/m}^2 \text{ s}$. In hydrodesulfurization studies, a modest further improvement in contacting effectiveness accompanied an increase in the liquid flow rate from about 7 to $10 \text{ kg/m}^2 \text{ s}$. From these and other observations we can begin in a preliminary way to develop a relationship between contacting effectiveness and liquid flow rate as suggested in Figure 4 in which the data point at $L = 0.3$ and vertical flag at $L = 0.08$ are Bondi's findings (Section 5.2).

Still unexplored in any general fashion is the effect of rate of heat release and other heat effects on contacting effectiveness. Germain (1974) in the hydrogenation of α -methyl styrene noted erratic performance at liquid flow rates as high as $1.6 \text{ kg/m}^2 \text{ s}$, but he used upflow of gas and this countercurrent flow pattern may have significantly affected his results. Porter (1961) in a patent on hydrogenation of a working solution of an alkyl anthraquinone, which is involved in a commercial process for manufacture of H_2O_2 , noted a marked increase in reaction rate as liquid flow rate was increased from about 2.4 to $3.6 \text{ kg/m}^2 \text{ s}$. It is not clear whether this reflected a heat effect, but he recommended use of flow rates in the range of 3.6 to $36 \text{ kg/m}^2 \text{ s}$, achieved with a high recycle ratio. Lee and Schrock (1973) at flow rates in the range of 19 to $33 \text{ kg/m}^2 \text{ s}$ and working with a 1.5-m diameter reactor reported an approximately 50% improvement in performance with 2-mm catalyst sphere packing by first filling the reactor with close-packed 10-cm thin wall vertical tubes into which the pellets were placed. The improvement was attributed to controlled channelling of the liquid. The liquid flow rates involved in these various reports are shown on Figure 4 by horizontal arrows, but the vertical location is without significance. It is to be recalled that the hydrodynamic pattern at these high liquid rates may be in the pulse flow or bubble flow region.

From these various studies we may tentatively conclude that for typical trickle-bed reactors in which heat effects are not excessive, nearly complete contacting effectiveness is reached when the liquid rate is increased to a value in the range of about 1 to $5 \text{ kg/m}^2 \text{ s}$. At the low flow rates improved performance would be expected if the reactant has significant vapor pressure. (See Section 7).

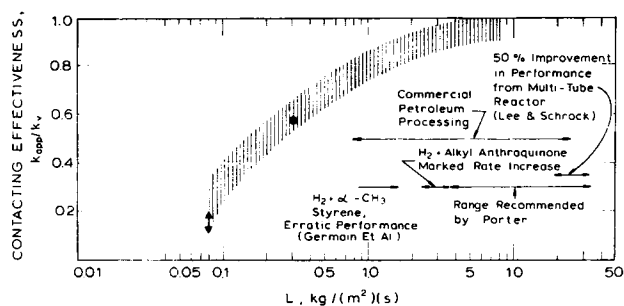


Fig. 4. Preliminary evidence on contacting effectiveness (Section 5.3.1).

Little information has appeared on the effect of gas flow rate other than the suggested correlation of Bondi which predicts a moderate increase in the apparent rate constant with increased gas flow. A study by Charpentier et al. (1971) of liquid residence time distribution and holdup on porous and nonporous spheres showed a decrease in total holdup (at $L = 5 \text{ kg/m}^2 \text{ s}$ as the gas flow rate was increased from 0 to $0.6 \text{ kg/m}^2 \text{ s}$, but an increase in the exchange between mobile holdup and stagnant liquid both external to the packing and inside pores.

5.4 Wetting Characteristics

Mears (1974) has questioned the Henry-Gilbert correlation and suggests that it is more realistic to assume instead that the reaction rate is proportional to the fraction of the outside catalyst surface which is effectively (freshly) wetted by the flowing liquid. Several investigators report that the wetted area of packed beds at moderate liquid flow rates is proportional to the 0.25 to 0.4 power of the mass velocity, and in the very recent correlation of Puranik and Vogelpohl (1974) the wetted area was reported to be proportional to the 0.32 power of the liquid velocity. Applying this correlation for ratio of wetted area to total area, and introducing the effectiveness factor Mears obtains

$$\log \frac{c_{in}}{c_{out}} \propto h^{0.32} (LHSV)^{-0.68} d_p^{0.18} \nu^{-0.05} (\sigma_c/\sigma)^{0.21} \eta \quad (32)$$

The term (σ_c/σ) relates to surface tension properties that are presumably constant for a given combination of liquid and packing.

Mears compares Equations (31) and (32) in various ways with available pilot plant data. Equation (32) would only hold where Puranik and Vogelpohl's proportionality is applicable. Above mass velocities of about $1000 \text{ lb./hr.}(ft.^2)$ (about $1.5 \text{ kg/m}^2 \text{ s}$ or so a different procedure is suggested to allow for the asymptotic approach to complete wetting as liquid flow rate is increased.

The above approach utilizing wetting characteristics has the merit of relating contacting effectiveness to a parameter which can be physically visualized. A film flowing downward uniformly over all the particles in a catalyst bed is not necessarily the most stable configuration since surface tension will tend to reduce the total film area. Observations of a trickle bed during reaction indicate that even with excellent initial distribution, the liquid may gather into rivulets which tend to maintain their position with time. In some portions of the bed, catalyst pellets are bathed continuously with flowing liquid while in other portions the catalyst pellets, although wetted, do not have a liquid film on the surface. It is the active or freshly contacted fraction of the

packed bed that is of principal concern. Although a portion or all of the remainder may be wetted, the stagnant or noncontacted fraction does not contribute to reaction unless other pathways for transport exist. The analogous problem in packed bed absorbers has long been studied to determine the fraction of packing which is effectively wetted, and Hobler (1966) has made a detailed comparison of the correlations developed by various workers through the late 1950s. Recent treatments are referenced by Mears (1974). Some differences between the two systems as listed below should be borne in mind in assessing this approach.

1. Catalyst pellets are almost always porous. Except for operation at low liquid flow rates combined with exothermic reaction, the entire bed will eventually become wetted by capillarity even with rivulet-like flow. Absorption packings are nonporous and a portion of the bed is typically not wetted. Diffusion through the catalyst pores provides a mechanism for contacting between stagnant external holdup and flowing streams. The portion of the reactor bed wetted by capillarity may contribute to reaction with a combination of high diffusion flux and relatively low reaction rate or if vapor pressure of the reactant is substantial.

2. Most of the data are for shapes characteristic of absorber packings such as Berl saddles and Raschig rings rather than for spheres, pellets, and extrudates of concern in trickle-bed reactors, but recent correlations indicate about the same velocity dependence for these various shapes.

3. Quantitative values of the fraction of the bed which is effectively wetted or freshly contacted with flowing liquid will depend upon the method used for their measurement. For example, the effective area for absorption of a gas into a liquid is the total area of that liquid present that is not effectively stagnant.

In this as in other studies, it was found that prewetting of the bed can cause substantially different behavior than that encountered if an initially dry bed is used. At the moderate liquid flow rates characteristic of laboratory-scale trickle beds, the time required to reach steady state with an initially dry bed may be several hours (Sedricks and Kenney, 1973; Satterfield and Özel, 1973), but this may be significantly reduced by pre-flooding. Surrounding catalyst pellets with finer inert material seems to improve wetting (Sedricks and Kenney, 1973) and causes substantially improved conversion at constant liquid flow rate (Mears, 1971). Heat effects can also cause the rate of wetting upon startup to be much slower than that encountered in the absence of reaction. A useful next step in developing these approaches would be to better characterize the contact angles and spreading characteristics of representative organic liquids on porous catalysts.

5.5 Residence Time Distribution (R.T.D.)

Another approach, which is not exclusive of those above, is to determine the extent to which reactor performance suffers by deviations from the ideal plug flow model, as characterized by the residence time distribution of the liquid. Assuming first-order kinetics, if R.T.D. data are available in the form of an exit age distribution function, $E(t)$, and the degree of conversion is known or specified, the two can be related by the expression

$$\frac{c_{out}}{c_{in}} = \int_0^\infty e^{-k \cdot t} E(t) dt \quad (33)$$

Here $E(t)dt$ is the fraction of the exit stream that was present in the reactor for a residence time between t and $t + dt$. For a plug flow reactor the expression is

$$\frac{C_{out}}{C_{in}} = e^{-k't_p} \quad (34)$$

A reactor efficiency \mathcal{E} can then be defined as $\mathcal{E} = (t_p/t_m) 100$ where

$$t_m = \int_0^\infty tE(t)dt \quad (35)$$

t_p is the residence time as calculated from Equation (34) that would produce the same fractional conversion as that found experimentally.

The reactor efficiency can also be defined equivalently as the ratio of the length of an ideal (plug flow) reactor to that of a real reactor required to produce the same specified percent conversion where the true value of k can be calculated from Equation (33). Equations (33) and (34) treat the system as though it were homogeneous and thus $k' = k_p(1 - \epsilon)/H$ s⁻¹ where the holdup H is assumed to be constant with length. The holdup of concern here is the mobile holdup external to catalyst pores but it does not need to be known to determine \mathcal{E} . However, it can be calculated from the $E(t)$ function by Equation (35) and the expression $H = t_m F/V$, if contributions to $E(t)$ from the pores of catalyst pellets can be eliminated.

An example of the use of this method in the analysis of trickle-bed performance is given by Mupferee et al. (1964). For 90% conversion, they found that a small pilot reactor operated at 90% efficiency, a commercial desulfurization reactor under conditions of poor operation operated at 40 to 60% efficiency and under good operating conditions performed at 70 to 80% efficiency. The same method of analysis was also applied by Cecil et al. (1968) in a study of the desulfurization of gas oil or residual fuel oil in a small pilot reactor at liquid rates of 35 to 1500 lb./ (hr.) (ft.²) (about 0.05 to 2.2 kg/m² s). The concept of reactor efficiency as used here may be subject to misinterpretation since \mathcal{E} is very sensitive to the percent conversion chosen for comparison at high degrees of conversion. Thus, a moderate degree of deviation from plug flow behavior can be insignificant at 90% conversion but serious at 99% conversion.

This approach shows the effect of a residence time distribution on reactor performance but does not give direct information on contacting effectiveness as such. The use of Equations (33) and (34) is rigorously correct for a homogeneous system if the reaction is strictly first order. For other than true first-order kinetics, the degree of conversion becomes a function not only of the R.T.D. but also of the degree of mixedness (micromixing) or segregation of fluid elements as they pass through the reactor. The true degree of mixedness in a real reactor cannot be determined, but for a specified R.T.D. the limiting bounds on performance can be calculated for the two extreme cases of maximum mixedness and complete segregation. As emphasized by Schwartz and Roberts (1973), the residence time distribution desired is that of the liquid external to the catalyst pores, but a tracer measurement used to determine the $E(t)$ curve may include some contribution from the internal holdup as well, which exhibits itself in the form of increased tailing.

5.6 Axial Dispersion

As an alternate to the use of a residence time distribution, small deviations from plug flow can instead be described by the axial dispersion model which involves only one parameter, the axial dispersion coefficient, usually expressed as a Peclet number. The dispersion coefficient is obtained by assuming that all the mixing proc-

esses involved follow the same functional relationship as Fick's laws, regardless of the actual mechanism, an assumption that becomes increasingly dubious with large degrees of deviation from plug flow behavior. Residence time distribution measurements in trickle beds may be more realistically represented by a two parameter cross-flow model as used by Hoogendoorn and Lips (1965), Hochman and Effron (1969), and others. These models assume that the holdup consists of liquid in stagnant pockets which exchanges slowly or irregularly with liquid in plug flow and the two adjustable parameters are the fraction of the total liquid in plug flow and an exchange coefficient. Similar models with three or four parameters have also been suggested. Schwartz and Roberts (1973) made a detailed comparison of the effect on predicted reactor performance of various R.T.D. data correlated in terms of the dispersion model versus the cross-flow or an equivalent model. Taking the R.T.D. data of Hochman and Effron, which are provided in both forms, for representative reactor cases corresponding to values of Re_L of 8 and 66, the ratio of required catalyst volume calculated by the dispersion model to that calculated by the cross-flow model was 1.03 to 1.09 at 80% conversion and 1.11 to 1.22 at 90% conversion. This suggests that the axial dispersion model may be the more conservative in general. It is also adequate for making initial estimates as to whether or not deviation from plug flow will be significant in any specific case.

Mears (1971, 1974) presents the following criterion for the minimum h/d_p ratio required to hold the reactor length within 5% of that needed for plug flow.

$$\frac{h}{d_p} > \frac{20m}{Pe_L} \ln \frac{C_{in}}{C_{out}} \quad (36)$$

where $Pe_L = d_p L_v/D_i$ and m is the order of reaction.

The minimum reactor height is seen to increase with the order of reaction and is very sensitive to fractional conversion at high degrees of conversion but the criterion is conservative.

Hochman and Effron (1969) reported dispersion data for concurrent methanol and nitrogen flow in a 15.2-cm column packed with 0.475-cm glass spheres over the range including 600 to 5,000 lb./ (hr.) (ft.²) (0.8 to 7 kg/m² s). Peclet numbers for the liquid varied from about 0.15 at $Re_L = 4$ to about 0.40 at $Re_L = 70$ with considerable scatter. Apparently there were significant, but random, variations in dispersion from point to point and day to day. These values of Pe_L are 1/3 to 1/6 of those for single phase liquid flow at the same Reynolds number and can be compared to $Pe = 2$ for fully developed single-phase turbulent flow in packed beds. Van Swaaij et al. (1969) likewise report values of Pe_L for trickle flow down to an order of magnitude less than that for single phase flow at the same liquid Reynolds number, but with much scatter. Equation (36) shows that for representative laboratory scale trickle-bed reactors of the order of 0.3 m in length, axial dispersion may cause a significant deviation from plug flow behavior when conversions of roughly 90% or more are observed.

Some fifteen or so other studies have been reported of liquid phase axial dispersion but generally for counter-current air-water systems, almost invariably with ring or saddle packing, and sometimes for flow conditions outside the range of interest in trickle bed reactors. A summary listing is given by Michell and Furzer (1972) who present a recommended correlation based on a considerable amount of their own work. This involves a Reynolds number Re_L' based on the interstitial rather than the superficial velocity and therefore must be combined with

an expression for the dynamic holdup H_f to relate superficial and interstitial velocities. The relationships are

$$Pe_L = (Re_L')^{0.70} Ga^{-0.32} \quad (37)$$

$$H_f = (0.68) Re_L^{0.80} Ga^{-0.44} ad_p \quad (38)$$

where Ga is the Galileo number $d_p^3 g \rho^2 / \mu^2$ and the liquid velocity used in the definition of Re_L is the superficial velocity. This represents a refinement over similar correlations developed by Otake and Kunigita (1958) and Otake and Okada (1953). Representative values of Pe_L for countercurrent air-water flow through 2.54-cm or 0.635-cm Raschig rings are 0.25 at $Re_L = 10$ and 0.5 at $Re_L = 100$ which are reasonably close to those reported by Hochman and Effron.

Peclet numbers for the gas phase, as reported by Hochman and Effron, were correlated by the expression:

$$Pe_G = 1.8 Re_G^{-0.71} 10^{-0.005 Re_L} \quad (39)$$

for values of Re_G of 11 and 22 and a range of values of Re_L from 5 to 80. This leads to values of Pe_G one to two orders of magnitude less than those encountered in single phase gas flow, attributed, as earlier suggested by DeMaria and White (1960) to the gas phase seeing agglomerates of particles covered with a bridge of liquid comprising an effectively larger particle diameter. The fact that wet packing in the absence of flowing liquid showed a large increase in dispersion over dry packing and that Pe_G decreased with increased Re_L support this explanation. However, gas-phase dispersion is not ordinarily of concern in trickle-bed processing.

6. UPFLOW (FLOODED BED) VERSUS DOWNFLOW REACTORS

A substantial number of papers have been published on mass transfer, pressure drop, residence times, holdup, etc. for concurrent gas-liquid upflow, but consideration of them is outside the scope of this review.

If the simplifying assumptions leading to Equation (23) indeed held, a concurrent upflow reactor would behave identically to a downflow trickle bed reactor, for the same flow rates, reactor volume, and operating conditions. However, as the discussion in Section 5 indicates, contacting effectiveness in trickle beds is generally poor at low liquid flow rates under which conditions an improved rate of reaction would be anticipated by using an upflow rather than downflow reactor. A comparison of a bench-scale reactor operated in the upflow versus downflow mode for desulfurization of a heavy coker gas oil by Takematsu and Parsons (1972) indeed showed superior performance with the upflow mode. In this system the low-boiling components which are generally more reactive pass into the vapor phase and are swept out more rapidly than the high boiling material which progresses relatively slowly through the bed. Takematsu and Parsons attributed the superior performance of upflow processing to the fact that it maximized the residence time of the heavy liquid fractions, but a more important factor may have been the very low liquid flow rates used, about 0.04 to 0.12 kg/m² s. Figure 4 suggests that the contacting efficiency in the downflow mode may have been rather poor.

The upflow mode may also provide other benefits. If a catalyst gradually becomes deactivated by deposit of polymeric or tarry materials, the upflow reactor may maintain its activity longer by more effectively washing off these deposits. For example, the comparison of upflow and downflow modes by Takematsu and Parsons (1972)

showed over a 25 to 30 hr. operating period no deactivation in the upflow mode in contrast to slow deactivation in the downflow mode. Heat transfer between liquid and solid may also be more effective in upflow than in downflow operation, of particular importance if reaction is rapid and highly exothermic.

The trickle-bed operation, in contrast, has several advantages. Pressure drop through the bed is less which reduces pumping costs and in the downflow mode it also helps keep the bed in place, although with catalysts that are soft or deformable this might hasten undesired cementation. With an upflow reactor some designs may lead to fluidization of the catalyst unless the catalyst were held in place by extra weight or suitable mechanical methods.

As summarized in Section 3.4, mass transfer limitations in catalyst pores are more likely to occur if they are filled with a liquid than with a vapor. Hence if reactant is present in both phases, over a range of operating conditions in which catalyst pellets filled with liquid are diffusion limited, an upflow reactor would be expected to exhibit a lower reaction rate than a partially-wetted trickle bed or one in which the solid catalyst is deliberately designed so as not to be wetted by the liquid phase.

7. REACTANT PRESENT IN BOTH LIQUID AND VAPOR PHASES

If the stoichiometrically limiting reactant is present in equilibrium distribution between liquid and vapor phases, and chemical potential is the driving force for reaction, then thermodynamic reasoning leads to the conclusion that there should be no difference in the reaction rate whether the solid is in contact with liquid or with vapor, provided that no mass or heat transfer gradients exist and that there is no alteration of intrinsic catalytic activity, for example, by preferential adsorption of impurities from one phase causing blockage of catalyst sites. This equivalence indeed was found to be the case in a study of the isomerization of cyclopropane to propylene on a silica-alumina catalyst by comparison of vapor phase reaction and the same reaction carried out in the presence of an inert solvent (Way, 1971) and arguments for it have been advanced by Sedricks and Kenney (1973). However, competitive adsorption on the catalyst between the reactant and other components in the liquid such as impurities, even if these are inert to reaction, can markedly affect catalytic behavior.

Assuming a situation in which the thermodynamic arguments are valid, comparison of the basic kinetic expressions for single phase flow and multiphase flow is revealing. If reactant is present in both liquid and vapor phase and these are in equilibrium with each other, Equation (23) becomes

$$\ln \frac{c_{in}}{c_{out}} = \frac{V k_o (1 - \epsilon)}{\left[F_l + F_g \left(\frac{K V_l}{V_g} \right) \right]} \quad (40)$$

where F_g is the vapor flow rate, F_l is liquid flow rate, both in cm³/s. K is the vapor-liquid equilibrium constant, $K = y/x$ expressed as mole fractions and V_l and V_g are the molar volumes of the liquid phase and gas phase, respectively, at reactor conditions. In effect, the liquid phase feed term F is replaced by a two-phase feed term, $F_l + F_g(KV_l/V_g)$.

An equivalent to Equation (40) can be written in terms of a reaction rate constant defined in terms of vapor phase concentrations k_g and vapor feed rate F_g cm³/s where

$$k_g = \frac{\text{cm}^3 \text{ of gas}}{(\text{cm}^3 \text{ pellet vol.}) (\text{s})}$$

$$\ln \frac{y_{\text{in}}}{y_{\text{out}}} = \frac{V k_g (1 - \epsilon)}{\left[F_l \left(\frac{V_g}{K V_l} \right) + F_g \right]} \quad (41)$$

where

$$\frac{k_v}{k_g} = \frac{K V_l}{V_g}$$

For all gas-phase operation Equation (41) reduces to the familiar first-order expression, as it should.

If an inert liquid phase is introduced into an all gas-phase differential reactor, keeping the inlet gas-phase composition constant and the liquid being saturated with gas, Equation (41) shows that the percent conversion will drop since the rate of reaction expressed as moles per unit time remains the same, but the rate of introduction of reactant has increased. In an integral reactor the overall rate of reaction (for example, as a space-time yield) would increase and the percent conversion decrease. If liquid containing no reactant is added to a gas-phase reactor, this distributes the reactant between the two phases, reducing the chemical potential and decreasing the overall rate of reaction below that occurring in the absence of liquid.

As noted previously (Section 3.4), a two-phase system with catalyst pores filled with liquid is more likely to be diffusion limited than all-gas-phase reaction under similar conditions.

For reversible reactions that approach equilibrium, the introduction of an inert liquid phase may markedly increase conversion if the product is relatively more soluble in the liquid than is reactant. A good example lies in the work of Zabor et al. (1960) who studied the hydration on tungsten oxide of olefins to the corresponding alcohol, in either vapor phase or mixed flow. Calculations showed a substantially higher percent conversion at equilibrium of propylene to isopropanol in the two-phase system than in completely vapor-phase operation and the higher conversion was likewise achieved in practice. The improved performance can be attributed to the difference between the solubility of propylene and isopropanol in the excess water present. Focusing on vapor-phase concentrations, in effect the product is drained away into liquid, thus altering the reactant-product ratio in a favorable direction. The use of an inert liquid in this fashion to alter a vapor-phase reaction would seem to have considerable unexplored potential. Conceivably a liquid-phase reaction might be directed similarly by use of a second immiscible liquid with suitable solubility characteristics.

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NOTATION

A completely consistent set of units cannot readily be provided since some correlations in the literature are dimensional and the units may be either English or metric (SI).

- a = ratio of outside area of catalyst pellets to reactor volume, cm^2/cm^3 ; interfacial area for mass transfer
- c = concentration, g-mole/ cm^3 . c_i for equilibrium concentration at gas-liquid interface, c_b for bulk concentration, c_s for concentration at liquid-solid interface
- D = molecular diffusivity, cm^2/s , D_{eff} for effective diffusivity in porous catalyst, Equation (18); $D'_{\text{eff}} = D_{\text{eff}}/\theta$
- D_l = axial dispersion coefficient, cm^2/s
- d_p = cat. particle diameter, cm
- E_l = energy dissipation, Equation (13)
- F = flow rate, cm^3/s . F_g for gas, F_l for liquid
- G = gas superficial flow rate, $\text{kg}/\text{m}^2 \text{ s}$
- Ga = Galileo number, $d_p^3 g \rho^2 / \mu^2$ [Equations (37) and (38)]
- g_c = conversion constant
- H = holdup, cm^3 liquid/ cm^3 of empty reactor volume. H_i for holdup inside pores, H_0 for external holdup, H_r for residual holdup, H_f for free draining or dynamic holdup. $H_0 = H_r + H_f$
- h = height of reactor, cm; depth of packed bed, cm
- k = first-order reaction rate constant, k_v for first-order reaction rate constant per unit volume of catalyst pellet, cm^3 of liquid/ $(\text{cm}^3$ of cat. pellet vol.) (s)
- k_c = mass transfer coefficient, cm/s , k_l for transfer from gas-liquid interface into liquid, k_s for transfer from liquid to solid; k_{ls} for overall transfer through the liquid [Equations (5), (6), (7), and (11)]. $k_l a$ = mass transfer coefficient on a volumetric basis, s^{-1}
- L = liquid superficial flow rate, $\text{kg}/\text{m}^2 \text{ s}$; L_v in units of cm^3/s
- LHSV = liquid hourly space velocity, volume of liquid fed to reactor per hour per volume of reactor, $= 3600 L_v/h \text{ hr.}^{-1}$
- m = order of reaction
- N = mass flux, g-mole/ s cm^2
- Pe_L = Peclet number for liquid phase, $d_p L_v / D_l$ [Equation (36)]
- ΔP = pressure drop; ΔP_l for single phase liquid, ΔP_g for single phase gas flow, ΔP_{lg} for mixed phase flow
- r = rate of reaction, g-mole/(s) (cm^3 of reactor volume)
- Re_L = Reynolds number for liquid flow $= d_p L_p / \mu$; Re_G for gas flow $= d_p G_p / \mu$
- Re_L' = Reynolds number based on the true average linear liquid velocity through packing
- Sc = Schmidt number $= \mu / \rho D$
- t = time, s

Greek Letters

- Δ = film thickness, cm
- ϵ = void fraction in catalyst bed, same as fraction of reactor volume not occupied by catalyst particles. $(1 - \epsilon)$ = ratio of cat. particle volume to empty reactor volume
- η = effectiveness factor, ratio of actual rate of reaction in a porous catalyst to that which would occur if pellet interior were all exposed to reactants at the same concentration and temperature as that existing at the outside of the pellet
- θ = void fraction in porous catalyst particle
- μ = viscosity, poises
- ν = kinematic viscosity $= \mu / \rho$
- ρ = density, g/cm^3
- τ = tortuosity factor, Equation (18)

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THE AUTHOR

Charles N. Satterfield is a transplanted mid-Westerner who went East to attend Harvard College as one of their early National Scholars and then moved down the Charles River to M.I.T. where he received the Sc. D. degree. A member of the M.I.T. Faculty since 1946, his professional interests center in various aspects of chemical reaction engineering, and in addition to teaching and research, he has been active as a consultant to government and industry.

In his spare time he is a compulsive reader, with interests ranging from the *New York Times* to "Doonesbury" and his outdoor pursuits include landscape gardening and the felling of trees for firewood from his wooded back-acreage. The author or co-author of four books and some 90 technical papers, he admits that he enjoys writing or, more precisely, having written.