120°, 130°, 160°K., the calculated minimum y and associated P agree well with experimental data as shown in Figure 1. Also shown in the figure are curves calculated from the complete form of Equation (2) and the ideal gas values ($y = P_{VP}/P$). Good results were obtained from Equations (3) and (4) with all other binary systems studied. Table 1 lists some of the representative results.

For the calculations shown here, the second virial coefficients were obtained from the Lennard-Jones potentials ϵ/k and σ and Table 1-B of Hirschfelder, Curtiss, and Bird (*5*). For the interaction coefficients, B_{jh}, the same technique was used employing the geometric mean of (ϵ/k) and the arithmetic mean of σ. Other methods of obtaining B_{hh} and B_{jh} were tried (*8, 9*) but the final calculation of $y_{\min}$ did not differ appreciably at the low pressures where the composition minimum was found. In Figure 1, the calculated curve was obtained from Equation (2) with the second virials determined as indicated above. The third virial coefficients were found from Table 1-C (*5*) with

$$(\epsilon/k)_{ijk} = [(\epsilon/k)_i\ (\epsilon/k)_j\ (\epsilon/k)_k]^{1/3}$$

$$\text{and } \sigma_{ijk} = (\sigma_i + \sigma_j + \sigma_k)/3$$

This technique for estimating the third virial coefficient is not satisfactory for estimating solubilities at high pressures; as shown in Figure 1, the agreement between experimental and calculated values of y_{CO_2} begin to differ appreciably at pressures exceeding 80 atm. It is interesting to note that in the system helium-oxygen (He-O_2), the interaction virial B_{O_2-He} is positive at the temperatures used in the experimental work and that Equation (3) would then be inapplicable; the physical significance seems to be that there is no minimum in composition for this system at any reasonable temperatures and pressures.

In summary, it has been shown that Equations (3) and (4) are convenient to use in estimating rapidly both the maximum purification attainable in a freeze-out purification system and the pressure level to be used to attain this purity.

NOTATION

B = second virial coefficient, volume/mole
C = third virial coefficient, (volume/mole)^2
e = natural logarithm base
f = fugacity
P = pressure
R = gas constant
T = temperature
v^s = specific volume of solid
V = specific volume of gas
y = mole fraction
Z = compressibility factor of gas

Subscripts

j = component present in both solid and gas phases
h = solvent component
VP = vapor pressure

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Diffusionally Controlled Surface Reactions in Tube-Wall Reactors

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The problem of obtaining kinetic information for reactions occurring on solid surfaces past which a fluid flows has received increasing attention in recent years. Of particular interest is the extraction of meaningful kinetic data for flow systems in which the observed rate of reaction is essentially the rate of transport to the reaction surface; that is, diffusionally controlled reactions. The literature on this subject has been devoted mainly to the development of mathematical schemes, operating on experimental data, to determine the values of parameters of the surface reaction; for example, surface concentrations.

Because chemical kinetics is largely an experimentally based science, it would seem appropriate to determine whether laboratory measurements of sufficiently high accuracy may be made for use in analytical schemes designed to yield kinetic information. It is the purpose of this note first to estimate surface concentrations in diffusionally controlled reactions of a particular type; and second, to show that simply determined laboratory data in such diffusionally controlled systems cannot be expected to yield estimates of these surface concentrations with any reasonable accuracy.

The simplest analysis of a surface reaction which is dependent upon a diffusional process involves the use of the quasi-stationary method developed by Frank-Kamenetskii (*2*). It is assumed in this method that the conditions of diffusional transport are independent of the course of the surface reaction. The fact that the diffusional and reaction processes are actually coupled by the surface boundary condition means that this method can only serve as an approximate model leading, in some cases, to large errors. These errors generally yield too low a surface concentration compared to more exact methods (*1*). For a first-order reaction, for example, errors of about 10% result which are small compared to other potential sources of error to be examined.

The quasi-stationary method assumes that the rate at which reactant is consumed at the surface equals the rate of diffusion of reactant to the sur-

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face. Thus, for a reaction of arbitrary order n

$$\text{reaction rate} = k\,C_w^n = \beta(C - C_w) \qquad (1)$$

In accordance with Frank-Kamenetskii (2), $\zeta = C_w/C$. Then

$$\text{reaction rate} = kC^n\,\zeta^n = \beta C(1-\zeta) \qquad (2)$$

The dimensionless concentration ratio ζ is found by solving Equation (2)

$$\lambda\,\zeta^n = 1 - \zeta,\ \lambda = \frac{kC^{n-1}}{\beta} \qquad (3)$$

Equations (2) and (3) are easily applied to an experimentally interesting case: a differential tubular reactor with reaction occurring along the tube wall, reactant supplied to the wall by diffusion from fluid passing through the tube. For fully developed laminar flow, $\beta = \gamma N_{Re}^{1/3}$, where γ is a constant for a given diffusing species, fixed tube diameter and length (5). Because a differential reaction is occurring, reactant concentration C is essentially constant along the length of the reactor and may be closely approximated by C_o, the inlet reactant concentration. Then

$$\text{reaction rate} = kC_o^n\zeta^n = \gamma N_{Re}^{1/3}C_o(1-\zeta) \qquad (4)$$

where ζ is given by

$$\lambda\zeta^n = 1 - \zeta,\ \lambda = \frac{kC_o^{n-1}}{\gamma N_{Re}^{1/3}} \qquad (5)$$

The usual differential reactor rate expression, Fx/SAL, where x is reactant conversion, may be cast into a more useful form for our purpose. Because the feed rate is essentially constant everywhere along the tube for a differential reactor (even for the case where reaction stoichiometry indicates a change in total moles), the apparent contact time for fixed L is inversely proportional to N_{Re} (that is, $F/C_oAL = \frac{\mu}{DL\rho} N_{Re}$). Furthermore, reactant conversion for a differential reactor is usually too small to measure experimentally and is best expressed as the measured product concentration at the reactor exit normalized on reactant concentration, C_o (that is, $x = C_{\text{prod}}/\nu C_o$ for $A \rightarrow \nu B$ and product free feed). The net result is a rate of reaction for this differential system of the form $aC_{\text{prod}}\,N_{Re}$ where a is a dimensional constant ($a = \mu/\nu SDL\rho$) incorporating terms resulting from the transformation of the usual rate expression.

Finally

$$aC_{\text{prod}}N_{Re} = kC_o^n\zeta^n = \gamma N_{Re}^{1/3}C_o(1-\zeta) \qquad (6)$$

or

$$\frac{C_{\text{prod}}}{C_o} = \frac{kC_o^{n-1}\,\zeta^n}{aN_{Re}} = \frac{\gamma(1-\zeta)}{aN_{Re}^{2/3}} \qquad (7)$$

and ζ is found from Equation (5) for particular values of $\lambda = kC_o^{n-1}/\gamma N_{Re}^{1/3}$. Equation (7) has two limiting forms:

Complete diffusion control

$$\frac{C_{\text{prod}}}{C_o} = \frac{\gamma}{a} N_{Re}^{-2/3} \text{ for } kC_o^{n-1} >> \gamma N_{Re}^{1/3}$$

Complete activation control

$$\frac{C_{\text{prod}}}{C_o} = \frac{kC_o^{n-1}}{a} N_{Re}^{-1} \text{ for } kC_o^{n-1} << \gamma N_{Re}^{1/3}$$

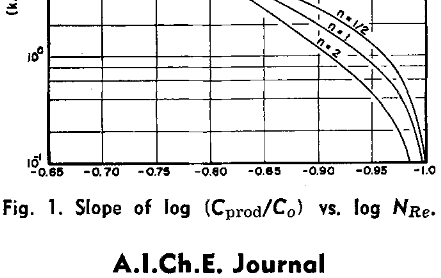

Fig. 1. Slope of log (C_{prod}/C_o) vs. log N_{Re}.

Plots of log (C_{prod}/C_o) vs log N_{Re} will be straight lines of indicated slopes for these two extreme cases. For intermediate control, Equation (7) applies, and a linear relationship between log (C_{prod}/C_o) and log N_{Re} would not be expected. Actually, essentially straight lines do result when Equation (7) is solved for pairs of values of C_{prod}/C_o and N_{Re} at fixed values of kC_o^{n-1}/γ. With a N_{Re} range of 10 to 1,000, deviation from linear behavior is less than 4% for $n = 1/2$, 1, 2, and is certainly within the usual experimental error. The result of measuring the slopes of plots of log (C_{prod}/C_o) vs log N_{Re} for fixed kC_o^{n-1}/γ is shown in Figure 1 for reaction orders, $n = 1/2$, 1, 2. The asymptotic behavior of the slopes for the two limiting cases is evident.

With this method it is possible, for differential tube-wall reactions, to estimate wall reactant concentrations. One need only measure product concentrations at various flow rates for a tube of fixed length and inlet reactant concentration. The slope of a plot of log (C_{prod}/C_o) vs log N_{Re} fixes kC_o^{n-1}/γ and then, provided n is known, ζ or C_w/C_o may be found using Equation (5).

Of particular interest is the accuracy one might expect in estimating C_w/C_o for systems operating under true diffusional control. Although the following analysis may be performed for any reaction order it will be simpler to treat $n = 1$. In any case the conclusions to be drawn will be equally valid for any order reaction simply because

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Chemical Engineers' Handbook, 4th Edition, Edited by R. H. Perry, C. H. Chilton, S. D. Kirkpatrick, McGraw-Hill, New York (1963). 1,915 pages. $29.50.

The first edition of the Chemical Engineers' Handbook, edited by the late John H. Perry, was published in 1934. It was intended to present, in convenient form, many of the equations and data that a practicing engineer needed for the design of chemical-plant equipment. Perry's Handbook, as it became known, was soon regarded as the chemical engineer's "bible."

The rapid growth of chemical engineering literature and changes in design techniques have been evidenced in the subsequent editions of 1941 and 1950 and particularly in the present edition. Although the concept of unit operations is still used for defining the sections of the handbook, emphasis has been shifted toward the more fundamental engineering sciences of thermodynamics, reaction kinetics, solid and fluid mechanics, and mass and energy transfer. There is considerably less in the way of empiricism and more in the use of statistical and mathematical analysis.

Unfortunately, the expansion in the number of topics covered has necessitated an accompanying decrease in detail. In many areas the handbook serves only as a guide to the literature, with a profusion of bibliographical references. In view of the obvious difficulty, or impossibility, of giving adequate coverage to so many topics in one handbook, this reviewer wonders if some of the sections, such as the one on physical and chemical data, should not be published as separate volumes.

Among the new topics presented in the fourth edition are dynamics of falling films and fluidized beds, electromagnetic pumps, jet pulverizers, the use of computers in designing multicomponent distillation units, and unsteady state diffusion.

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INFORMATION RETRIEVAL

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Thermodynamic comparison of large-scale liquefaction of air, hydrogen, and helium, Latimer, R. E., and R. A. Mostello, **A.I.Ch.E. Journal, 10,** No. 3, p. 407 (May, 1964).

Key Words: Liquefaction-8, Refrigeration-8, Air-10, Nitrogen-10, Hydrogen-10, Helium-10, Freon-4, Power-9, Compression-10, Precooling-10, Heat Exchange-10, Cooling-10, Low Temperature-10, Expansion-10, Joule-Thomson-, Conversion-2, Ortho-, Para-, Temperature-6, Pressure-6, Enthalpy-7, Latent Heat-9, Sensible Heat-9, Carnot-, Efficiency-7, Insulation-5, Thermodynamic-, Comparison-9, Cost-9.

Abstract: Comparison is made for air, hydrogen, and helium of Joule-Thomson inversion curves, of pressures and precooling methods used in liquefaction, and of the role of one or more stages of engine expansion in large-scale liquefaction. Carnot efficiencies achievable in large-scale liquefaction are compared. A new thermodynamic function $(\partial \mathbf{H}/\partial \ln \mathbf{P})_T$ is introduced.

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of the asymptotic behavior of the curves shown in the figure.

When Equation (5) is solved for ζ,

$$C_w/C_o = \frac{1}{1 + k/\gamma N_{Re}^{1/3}}, \quad n = 1$$

For the experimental determination of true diffusional control (−2/3 slope) the figure shows that $k/\gamma \geqq 1{,}000$. For $aN_{Re} = 1{,}000$, $C_w/C_o \leqq 0.01$. Suppose an error of only ± 5% results in the measurement of the slope of experimental values of log (C_{prod}/C_o) vs log N_{Re} for a reaction which is truly diffusionally controlled. Instead of a slope $= -0.667$, a plot of log (C_{prod}/C_o) vs log $\mathrm{N_{Re}}$ reveals a slope $= -0.700$. Then k/γ from the figure is 35 instead of 1,000 and $C_w/C_o = 0.22$ at $N_{Re} = 1{,}000$ instead of $C_w/C_o = 0.01$. Thus more than an order of magnitude error results in estimating wall concentration of a reacting species for a nominal 5% error in measuring the slope of a line derived from experimentally measured values.

Katz (*4*) has developed an analytical solution to the tube-wall reaction problem which is of the general form, $C_w/C_o = 1 - F(\theta, h)$, where θ and h are dimensionless contact time and surface rate respectively. Note first that $F(\theta, h)$ contains the experimentally determined reaction rate and physical properties of the system. Assign an experimental accuracy to $F(\theta, h)$ and see what range of values result for C_w/C_o in the diffusionally controlled region. If $C_w/C_o = 0.01$ then $F(\theta, h) = 0.99$. A ± 5% error in $F(\theta, h)$ means that C_w/C_o could be anywhere in the interval 0 to 0.06 (discarding negative values). For a ± 1% accuracy (unusually good for kinetic measurements), C_w/C_o would be found in the range 0 to 0.02. Thus, for reactions under complete diffusion control it would be extremely difficult to determine surface concentrations with sufficient accuracy; for example, to determine reaction mechanisms.

Again using the Katz form of solution, under what conditions could the error in C_w/C_o be reduced? For experimental data accurate to ± 5% and an acceptable error in C_w/C_o of ± 10%, C_w/C_o must be greater than 0.3. At this value of C_w/C_o, $k/\gamma = 23$ for $N_{Re} = 1{,}000$. From the figure it is seen that the slope of log (C_{prod}/C_o) vs log N_{Re} is 0.71 for this value of k/γ. It is to be noted that a slope of this value represents a reaction which is significantly out of the diffusionally controlled region.

The results of these simple computations point up the extraordinary difficulty involved in making laboratory measurements of sufficient accuracy so that meaningful conclusions may be drawn for diffusionally controlled surface reactions. It should be pointed out that this result is not restricted solely to the example presented here of a surface reaction occurring on a tube wall and laminarly flowing fluids. Changes in reactor geometry and flow regime will change the value of the limiting slope of plots of log (C_{prod}/C_o) vs log N_{Re} for diffusionally controlled reactions, but the conclusion that estimating wall concentrations cannot accurately be made will still be valid. Thus, for a turbulently flowing fluid transferring a reactant to a tube wall on which a reaction occurs, the limiting slope of log (C_{prod}/C_o) vs log N_{Re} becomes −0.42 for diffusionally controlled reactions at the mass transfer entry region, since in this case, $\beta = \gamma N_{Re}^{0.58}$ (*6*). For a reaction surface consisting of packed particles the limiting slope in the diffusionally controlled region would be −0.58 because $\beta = \gamma N_{Re}^{0.42}$ for packed-bed transfer processes (*3*). In all cases the limiting slope for surface-controlled reactions remains equal to −1. These results, indicating the extreme difficulty in determining wall concentrations for diffusionally controlled reactions, are independent of the numerical value of the limiting slope of log (C_{prod}/C_o) vs log N_{Re}, but are due to only the asymptotic behavior of the slope as the diffusionally controlled region is approached. It would appear then that only in the region of partial diffusional control may meaningful kinetic data be generated. It is possible to induce some degree of activation control in many nominally diffusionally controlled systems, and perhaps this is the only way in which kinetic parameters for such systems may be determined.

ACKNOWLEDGMENT

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NOTATION

a = dimensional constant
A = reactor cross-sectional area
C = reactant concentration in bulk fluid
C_{prod} = product concentration
D = reactor diameter
F = molar feed rate of reactant
k = rate coefficient for surface reaction
L = reactor length
n = reaction order
N_{Re} = Reynolds number
S = reactor surface area per unit reactor volume
x = reactant conversion

Greek Letters

β = mass transfer coefficient
γ = constant
ζ = concentration ratio, C_w/C_o
ρ = density
μ = viscosity
λ = variable defined by Equations (3) and (5)

Subscripts

o = inlet condition
w = wall condition

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