COMMUNICATIONS TO THE EDITOR

Equilibrium Yield in a Liquid Phase Reactor with High Surface-to-Volume Ratio

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The equilibrium conversion in a chemical reaction depends on the conditions under which the reaction proceeds; if a reaction occurs in the surface of a liquid phase, the conditions for that reaction are different from those prevailing for the same reaction in the bulk liquid. For certain reactions, therefore, the equilibrium yield may be increased by operating the reactor under conditions such that there is a high ratio of surface to volume within the reactor. We report here some brief preliminary studies of the effect of a surface on the equilibrium yield of a liquid phase reactor.

Consider the following reaction occurring in a liquid-gas system:

$$cC + dD \rightleftharpoons eE + fF$$

We consider nonvolatile components; the reaction in the gas phase is therefore negligible. The equilibrium constant for reaction in the bulk liquid region is given by

$$K_a{}^B \equiv \frac{(a_E{}^B)^e (a_F{}^B)^f}{(a_C{}^B)^c (a_D{}^B)^d} \qquad (1)$$

The activities $a_i{}^B$ have as their standard state pure bulk liquid i as is the normal convention. The equilibrium constant for reaction in the surface phase is defined by

$$K_a{}^S \equiv \frac{(a_E{}^S)^e (a_F{}^S)^f}{(a_C{}^S)^c (a_D{}^S)^d} \qquad (2)$$

The standard state for the activities $a_i{}^S$ is chosen as pure component i as a surface phase. This choice of standard state is responsible for the inequality of the equilibrium constants in the bulk and surface regions, even though both regions are at the same temperature. Further discussion regarding this difference in equilibrium constants and the utility of various standard states may be found in the papers of Butler (*1*) and Eriksson (*2*).

If it is assumed that the solution surface is a region of uniform composition located between the bulk liquid and gas phases, we can derive the following relation between the surface tension and the activities of any component i in the bulk phase and in the surface phase (*2, 4*):

$$\sigma^M = \frac{A_i}{\overline{A}_i}\sigma_i + \frac{RT}{\overline{A}_i}\ln\frac{a_i{}^S}{a_i{}^B} \qquad (3)$$

Here σ^M represents the surface tension of the mixture, σ_i the surface tension of pure component i, A_i the molar surface area of component i, and $\overline{A}_i$ the partial molar surface of component i in the surface solution.

In order to obtain an estimate of the surface effect on the equilibrium yield, we assume that the ratio of the equilibrium constants in terms of mole fractions, for the surface and bulk phases, is equal to the ratio of equilibrium constants in terms of activities; that is, we assume

$$\frac{K_x{}^S}{K_x{}^B} = \frac{K_a{}^S}{K_a{}^B} \qquad (4)$$

Our studies of activity coefficients in bulk and surface phases lead us to believe that this assumption leads to errors of less than a factor of two in the calculation of the ratio $K_x{}^S/K_x{}^B$. We make one additional assumption which simplifies the calculation, yet leads to small changes in this ratio, namely, we set $\overline{A}_i = A_i$.

The following relationship may then be obtained from the preceding equations:

$$\ln\frac{K_x{}^S}{K_x{}^B} = \frac{1}{RT}[\sigma^M(eA_E + fA_F - cA_C - dA_D) + cA_C\sigma_C + dA_D\sigma_D - eA_E\sigma_E - fA_F\sigma_F] \qquad (5)$$

We now want to illustrate Equation (5) with a numerical example. Consider the hydrolysis of ethyl acetate proceeding at 20°C.

INFORMATION RETRIEVAL*

Obtaining precise parameter estimates for nonlinear catalytic rate models, Kittrell, J. R., W. G. Hunter, and C. C. Watson, **A.I.Ch.E. Journal, 12,** No. 1, p. 5 (January, 1966).

Key Words: A. Catalysis-8, Heterogeneous-0, Model-Building-4, 8, Estimation-9, Parameters-9, Reactor-10, 9, Design-4, Temperature-6, Partial Pressure-6, Reaction Rate-7, Catalyst-6, Zinc-6, Chromium-6, Nitric Oxide-1, Hydrogen-1, Nitrogen-2, Water-2, Ammonia-3. B. Experimental Design-8, Analysis-8, Data-9, Estimation-9, 2, Parameters-9, Confidence Regions-9, Nonlinear-0, Models-2, 9, Computer-10, Reaction Rate-1, Design-4, Reactor-9.

Abstract: A method is reviewed which allows data points to be chosen in such a fashion that more precise estimates of the parameters in nonlinear reaction rate models can be obtained. This method allows each future data point to be selected such that the confidence region of the estimated parameters is smaller with it than with any other possible data point within the region of experimentation. This procedure is applied for Hougen-Watson models with hypothetical experimental data which were generated with the guidance of an example from the current chemical engineering literature.

Mechanism of dispersed-phase mass transfer in viscous, single-drop extraction systems, Johns, L. E., Jr., and R. B. Beckmann, **A.I.Ch.E. Journal, 12,** No. 1, p. 10 (January, 1966).

Key Words: A. Mass Transfer-8, Extraction-8, Drops-1, Liquids-1, Viscous-0, Dispersed Phase-9, Peclet Number-8, Calculation-8, Nusselt Number-9, Mathematical Model-10.

Abstract: A model is presented for the calculation of the disperse phase Nusselt number in viscous single-drop liquid extraction systems.

Non-Newtonian flow in porous media, McKinley, R. M., H. O. Johns, W. W. Harris, and R. A. Greenkorn, **A.I.Ch.E. Journal, 12,** No. 1, p. 17 (January, 1966).

Key Words: A. Calculation-8, Flow-8, 9, Fluid-9, Non-Newtonian-0, Dextran-9, Water-5, Porous Media-9, Rheology-8, Capillary-9, Darcy's Law-10.

Abstract: This paper describes a preliminary study of the linear flow of a non-Newtonian fluid, a water solution of Dextran (a polysaccharide), in porous media. A modification of Darcy's law, which uses capillary rheology data, is developed to describe non-Newtonian flow in underground reservoirs.

The influence of surface coverage on catalytic effectiveness and selectivity. The isothermal and nonisothermal costs, Hutchings, John, and James J. Carberry, **A.I.Ch.E. Journal, 12,** No. 1, p. 20 (January, 1966).

Key Words: A. Effectiveness-8,7, Selectivity-8,7, Catalyst-9, Nonisothermal-0, Isothermal-0, Heat-6, Mass Diffusion-6, Coverage-6, Surface-9, Reactant-9, Product-9.

Abstract: Both nonisothermal and isothermal catalytic effectiveness factors are computed for kinetic rate laws of the Langmuir-Hinshelwood, Hougen-Watson type, involving surface coverage by reactant and products. Selectivity taxation is also treated and the significant influence of interphase heat and mass gradients surrounding the catalyst is displayed.

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* For details on the use of these Key Words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr.,** Vol. 60, No. 8, p. 88 (August, 1964). A free copy of this article may be obtained by sending a post card, with the words "Key Word Article" and your name and address (please print) to Publications Department, A.I.Ch.E., 345 East 47 St., N. Y. N. Y., 10017. Price quotations for volume quantities on request.

Free tear sheets of the information retrieval entries in this issue may be obtained by writing to the New York office.

(*Continued on page 196*)

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

$$C \quad + D \rightleftharpoons \quad E \quad + F$$

Necessary parameters are

$$c = d = e = f = 1$$

Molar surface areas, Å.^{2} (estimated from surface tension data on the various binary aqueous mixtures, by the technique in reference 2)

$$A_C = 70 \qquad A_E = 44$$
$$A_D = 18 \qquad A_F = 72$$

Surface tensions, dyne/cm.

$$\sigma_C = 24 \qquad \sigma_E = 28$$
$$\sigma_D = 73 \qquad \sigma_F = 22$$

At a particular composition, such that $\sigma^M = 35$ dyne/cm. (low water concentration), using Equation (5), $K_x^S/K_x^B = 17.5$. For a high water concentration, corresponding to $\sigma^M = 65$ dyne/cm., $K_x^S/K_x^B = 140$.

It thus appears that under certain conditions, significantly higher yields may be obtained when carried out in a reactor with a large surface-to-volume ratio. A favorable change in equilibrium yield is usually to be expected in liquid phase reactions where the surface tensions of the reactants are considerably larger than those of the products.

Mechanical processes which produce the dispersion of the liquid mixture as a mist or foam might lead to a ratio of surface phase volume to bulk volume of from 1 to 10%, the higher ratios corresponding to equipment utilizing foaming. Although these volume ratios are not large, creation of as much surface as possible in the reactor might be an attractive procedure for the production of fine chemicals, or else for enhancing the equilibrium yield of those reactions where an increase in temperature leads to the decomposition of the desired product.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for financial support.

NOTATION

A_i = molar surface area of component i
$\bar{A}_i$ = partial molar surface area of component i
a = activity
C, D, E, F = components
c, d, e, f = stoichiometric coefficients
K = equilibrium constant
R = gas constant
T = absolute temperature

Greek Letters

σ = surface tension

Subscripts

a = activity basis
C, D, E, F = components
i = component i
x = mole fraction basis

Superscripts

B = bulk liquid
M = mixture
S = surface

LITERATURE CITED

1. Butler, J. A. V., *Proc. Roy. Soc.* (*London*), A135, 348 (1932).
2. Eriksson, J. C., *Advan. Chem. Phys.*, 6, 145 (1964).
3. Sprow, F. B., Ph.D. dissertation, Univ. California, Berkeley (1965).
4. ———, and J. M. Prausnitz, *Trans. Faraday Soc.*, accepted for publication.

The Second Law. Caratheodory's Principle with Simplified Mathematics

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It is readily apparent that the phenomena of nature are for the most part irreversible. After a change takes place, such as the conduction of heat, diffusion, motion, or flow with friction, it is impossible to restore the initial conditions for both the system and its surroundings. The principle of Caratheodory takes as an axiom in the logical system, what is believed to be a law of nature, that is, the existence of irreversible phenomena. In its formal statement it uses the observed fact that a system can in any state be disturbed, or change spontaneously, in such a way that no adiabatic process can return it to its original condition. For example, a small amount of work performed on the system in the presence of friction produces an irreversible change. The previous state of the system can only be restored by removing heat, thereby effecting a net change of work into heat in the surroundings. The reverse of this process is not possible (the Kelvin statement of the second law). Rather than dwell upon the forbidden process, we choose to examine the original irreversible change. A state has been reached from which the return is impossible by an adiabatic process. The initial state is termed *adiabatically inaccessible* from the final state. Since any system in any state may be adiabatically isolated, and an arbitrarily small irreversible process may be executed, the adiabatically inaccessible states may be arbitrarily close to any state.

[A complete logical exposition would begin by definition of *state*, *process*, and *adiabatic*. Of these the most difficult is *adiabatic*. We will assume that a satisfactory definition has been made, such as *a process is adiabatic if the only external effects are work.*]

FORMAL DEVELOPMENT

Caratheodory's Principle: In the Neighborhood of Every State There are Adiabatically Inaccessible States

This is analogous to a statement which can be made about the real number system: in the neighborhood of every number there is a smaller number. We would like to be able to assign numbers to the states of a system which would rank them by adiabatic accessibility. With real numbers we have the property that if A is less than B, B is not less than A. The corresponding property for states of systems is taken as an auxiliary axiom.

Auxiliary Axiom 1: There are no pairs of states which are mutually inaccessible by adiabatic processes. (If state A is inaccessible from B, then B is not inaccessible from A.)

As a consequence of Caratheodory's principle and the auxiliary axiom, there appears to be a correspondence or similarity between the adiabatic accessibility of states and real numbers. We may define a ranking of states according to adiabatic accessibility in which a larger number is assigned to a more accessible state, starting with an arbitrarily chosen reference state. This ranking is the function called *entropy* in thermodynamics, but we will give it the name *rank* and the symbol R in this context to avoid prejudicing the case. A pair of states which are mutually accessible will have the same value of R. Every state has a rank and the values of R form a continuum. For any possible adiabatic process $dR \geqq 0$. For those processes for which $dR = 0$, the reverse process is possible.

In any physically possible adiabatic process, the sequence of states is always such that each R attained is greater than all previous values of R. This may continue only until a maximum of R is reached. The existence of a constraint on the system such that R has a maximum from which all permissible displacements $dR \leqq 0$, and when R is a continuous function of state variables this means that when R is at the maximum, $dR = 0$. A condition is reached which is called *equilibrium*, from which no change is possible as long as all the external constraints remain unchanged.

Let us examine the properties of R.

Definition: The rank R for a composite system is the sum of the R values of its parts. This has an interesting consequence. Since the only property required of R before this definition was that of order of the points, any monotonically increasing function of R would serve just as well as the original R. The requirement of additivity puts a severe restriction on the acceptable forms for a function of R. In order to display this, we need a mathematical theorem.

Theorem:

If

$$z = x + y \tag{1}$$

and

$$f(z) = f(x) + f(y) \tag{2}$$

Then

$$f(z) = az \tag{3}$$

where a = constant

Proof: Differentiate (2) with respect to x

$$f'(z)\frac{dz}{dx} = f'(x) = \text{independent of } y \tag{4}$$

Differentiate (2) with respect to y

$$f'(z)\frac{dz}{dy} = f'(y) = \text{independent of } x \tag{5}$$