COMMUNICATIONS TO THE EDITOR

A Note on Kinetics Data

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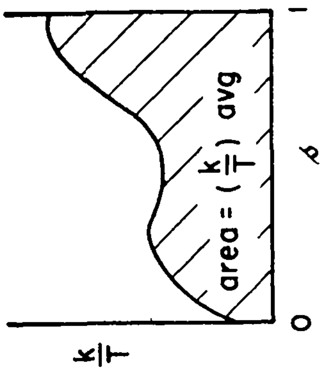

FIG. 3. PROFILE OF K/T IN A REACTOR.

The paper entitled "Equivalent Isothermal Temperatures for Nonisothermal Reactors," written by Mr. Malloy and Dr. Seelig, offers a convenient and excellent method of comparing kinetics data from reactors with widely different temperature profiles. In their method of presentation, the conversion rate is expressed in terms of catalyst volume, which is very convenient because of its simplicity. Nevertheless the conversion rate can also be expressed in terms of residence time. In the case of pure Knudsen flow, the pressure effect on conversion rate is automatically taken care of by the use of residence time, which is directly proportional to the total pressure. If the reaction is partially controlled by diffusion, the pressure effect on diffusivity can be taken care of by the introduction of a pressure factor. In general, diffusivity is inversely proportional to the square root of total pressure. Therefore in many cases the introduction of a factor of $P^{0.5}$ will make a rate equation based on residence time good for any pressure. Otherwise, the total pressure term P may have to be assigned with an exponent lower (or higher) than 0.5 as the case may be. Once kinetics data are obtained for two or more pressures, this correlation with a single equation will enable one to interpolate or extrapolate with considerable confidence and convenience. Of course, the specific reaction rate k expressed in terms of catalyst volume can also be correlated as a function of pressure. But this would need an extra equation or a plot of k vs. P. In this respect it would not be so convenient as the k expressed in terms of residence time.

The residence time of a gas in a differential catalyst bed not only is proportional to the fractional distance through the bed, as mentioned in their paper, but also proportional to the total pressure and inversely proportional to the absolute temperature and the total molal flow rate in that differential bed: i.e.,

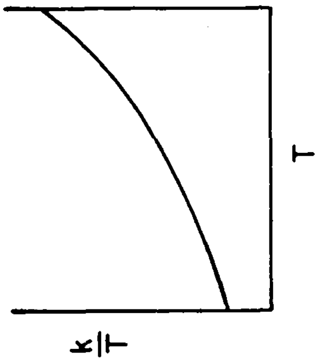

FIG. 2. SPECIFIC REACTION RATE AS A FUNCTION OF TEMPERATURE.

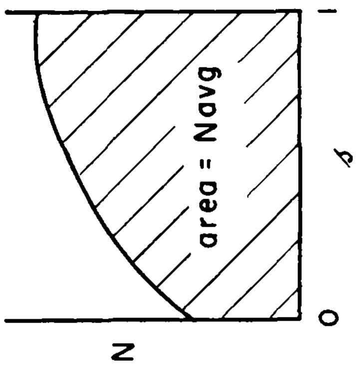

FIG. 5. PROFILE OF MOLAL FLOW RATE IN A REACTOR.

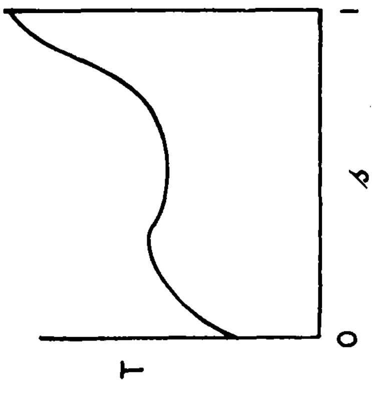

FIG. 1. TEMPERATURE PROFILE IN A REACTOR.

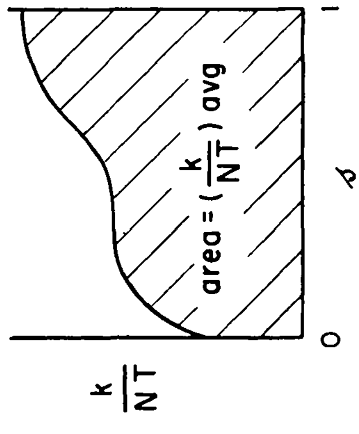

FIG. 4. PROFILE OF K/NT IN A REACTOR.

$$\int k\,d\theta = C\int \frac{kP\,ds}{NT}$$

where C is a constant characteristic of a particular reactor, N the total molal flow rate, P the total pressure, and T the absolute temperature.

Usually the pressure drop through a reactor can be neglected in kinetics studies, and the total pressure becomes a constant. When comparison of reactors is made at the same total pressure, the P term can be dropped, and Equation (4) in their original paper has to be changed to

$$\left(\frac{k}{NT}\right)_{avg} = \int_0^1 \frac{k\,ds}{NT} \qquad (4)$$

Case 1. $\Delta N = 0$. When there is no change in total molal flow rate, such as isomerization or carbon monoxide oxidation,

$$H_2O + CO = H_2 + CO_2$$

the variable N becomes a constant and can be dropped from Equation (4):

$$\left(\frac{k}{T}\right)_{avg} = \int_0^1 \frac{k}{T}\,ds$$

Since T is a function of s, as illustrated in Figure 1, and k/T a function of T, as in Figure 2, k/T is plotted against s as in Figure 3. Since $k = Ae^{-\Delta E/RT}$, and the constants A and ΔE have been determined,

$$(k/T)_{avg} = \frac{Ae^{-\Delta E/RT_{avg}}}{T_{avg}}$$

Hence $(k/T)_{avg}$ is a function of T_{avg} only. From $(k/T)_{avg}$ determined by Gauss's method from Figure 3, a correct equivalent isothermal temperature is obtained from Figure 2 for this case.

Case 2. $\Delta N \neq 0$. When there is a change in the total molal flow rate, such as the reaction of gas cracking or steam-methane reforming,

$$H_2O + CH_4 = 3H_2 + CO$$

the total molal flow rate changes with the distance through the bed. The plot should be made as shown in Figure 4.

Since N is a function of s and T, and since T is a function of s, N is a function of s only (Figure 5).

The total molal flow rate often changes little owing to the presence of a large excess of a reactant or inert gases or to a low conversion.

For practical purposes,

$$(k/T)_{avg} = N_{avg}(k/NT)_{avg}$$

where $(k/NT)_{avg}$ is determined from Figure 4 and N_{avg} from Figure 5. As in case 1, k/T is a function of T. Thus an equivalent isothermal temperature is obtained from Figure 2 in the same manner as in case 1.

The same treatment applies to the determination of radial equivalent isothermal temperature. However, since temperature gradients are approximately linear with respect to radii and usually not high in magnitude compared with longitudinal gradients, and N usually does not change much along the radius, averages with respect to r/R as proposed by the authors are practically as good as averages with respect to r/RNT.

Reply

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Dr. A. P. Ting has called our attention to an error in our paper "Equivalent Isothermal Temperatures for Nonisothermal Reactors" which appeared in the December, 1955 issue of the *Journal.* The error can be corrected if the second sentence under Equivalent Isothermal Temperature on page 528 is replaced by the following:

"Applying this equation to a continuous-flow reactor, one obtains for a differential section of the reactor:

$$dn_A/d\theta = dN_A = k\phi(p_A, p_B, \cdots)\,dC \quad (1a)$$

where

$dn_A/d\theta$ = reaction rate, moles of A/hr.

dN_A = change in molal flow rate of A, moles/hr.

k = rate constant, rate per unit of $\phi(p_A, p_B, \cdots)$ per unit of catalyst

dC = amount of catalyst in the differential section

Separation of variables gives

$$\int \frac{dN_A}{\phi(p_A, p_B, \cdots)} = \int k\,dC$$

$$= C\int k\,ds = Ck_{avg}\int ds \qquad (2)$$

where

s = fractional distance through the catalyst bed."

The error changes only Equation (2); it does not affect the rest of the paper in any way.

We are grateful to Dr. Ting for bringing this error to our attention.

(*Continued from page 245*)

sodium hyposulfite concentration up to some critical value (Case *A*). Beyond this value the rate becomes constant as indicated in the horizontal lines in Figure 3 (Case *B*). The rate of extraction is not affected by the sodium hyposulfite concentration, but by I_2 concentration in the benzene. As in the case of gas absorption, e.g., CO_2 in air and KOH solution, the extraction mechanism is explained in Figure 4. C_B can be called the I_2 concentration in benzene, and C_{Bi} the interfacial concentration. In Case *A* the interfacial concentration of sodium hyposulfite C_{wi} in equilibrium with I_2 is expressed as follows:

$$C_{wi} = mC_{Bi}$$

where m is the distribution coefficient (*4, 1, 8*). The I_2 molecule diffuses through the interface of sodium hyposulfite. The molecule meets and reacts with $S_2O_3^{--}$, thence it becomes I^- and diffuses into the sodium hyposulfite solution. The relation between the bulk concentration of sodium hyposulfite q and the rate of extraction N is given as follows:

$$N = \left(\frac{f}{m/K_B + 1/K_W}\right)^q + \left(\frac{mC_B}{m/K_B + 1/K_W}\right) \qquad (1)$$

where

$$f = D'[I]^-/D'[I]$$

Equation (1) indicates the slope in Figure 3.

When the concentration of sodium hyposulfite is high, i.e., Case *B*, $S_2O_3^{--}$ exists at the interface, reaction takes place rapidly at the interface, thus $C_{Bi} = 0$. The rate of extraction is expressed as follows:

$$N = K_BC_B = \text{constant} \qquad (2)$$

Equation (2) corresponds to the horizontal line in Figure 3.

In order to ascertain the above-mentioned assumptions, experiments using NaI in water were made. The distribution coefficient m was increased considerably by adding I^- to water, as shown in Figure

(*Continued on page 7J*)