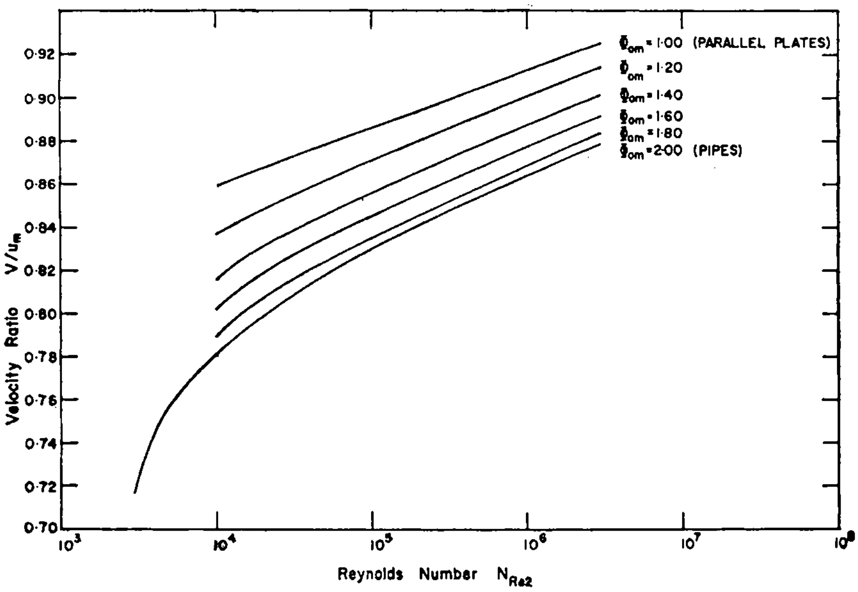

Fig. 6. Ratio of average to maximum velocity in tubes and non circular conduits.

ρ = density of fluid, lb.-mass/cu. ft.

τ = local shearing stress in fluid, lb.-force/sq. ft.; τ_0 = skin friction at wall of conduit, lb.-force/sq. ft.; τ_2 = skin friction at outer wall of annulus, lb.-force/sq. ft.

Φ_0 = geometrical function defined in Equation (19), dimensionless;

Φ_{0m} = maximum value of geometrical function, dimensionless

ψ = function in Equation (35), dimensionless

Subscripts

F = parallel flat plates

p = pipes or tubes

a = annuli

m = association with the point of maximum fluid velocity

Superscript

0 = average taken with respect to the mean local fluid velocity

LITERATURE CITED

1. Corcoran, W. H., F. Page, Jr., W. G. Schlinger, and B. H. Sage, *Ind. Eng. Chem.*, **44**, 410 (1952).
2. Diessler, R. G., *Trans. Am. Soc. Mech. Engrs.*, **73**, 101 (1951).
3. Knudsen, J. G., and D. L. Katz, "Proc. Midwestern Conference on Fluid Dynamics," 1 conf., No. 2, 175 (1950).
4. Lamb, Horace, "Hydrodynamics," 6 ed., p. 586, Cambridge University Press, London (1932).
5. Nikuradse, J., *V. D. I. Forschungsheft*, **356**, 1 (1932).
6. Page, F., Jr., W. H. Corcoran, W. G. Schlinger, and B. H. Sage, *Ind. Eng. Chem.*, **44**, 424 (1952).
7. Page, F., Jr., W. G. Schlinger, D. K. Breaux, and B. H. Sage, *Ind. Eng. Chem.*, **44**, 419 (1952).
8. Rothfus, R. R., and C. C. Monrad, *Ind. Eng. Chem.*, **47**, 1144 (1955).
9. Rothfus, R. R., C. C. Monrad, and V. W. Senecal, *ibid.*, **42**, 2511 (1950).
10. Senecal, V. E., and R. R. Rothfus, *Chem. Eng. Progr.*, **49**, 533 (1953).
11. Stanton, T. E., and J. R. Pannell, *Trans. Roy. Soc. (London)*, **A214**, 199 (1914).

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Liquid-liquid Extraction Accompanied by Chemical Reaction

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From time to time, A.I.Ch.E. Journal is going to present translations of certain technical articles written by our Japanese colleagues in their own language. These translations are to be made by Kenzi Etani, who received his B.S. in chemical engineering in 1953 at the Tokyo Institute of Technology and his M.S. in 1955 at M.I.T. He is associated with Stone & Webster and is an associate member of American Institute of Chemical Engineers. He is also a member of the Society of Chemical Engineers, Japan, and the Japan Oil Chemists' Society. His offer to help break down the language barrier is acknowledged.

The following article (two will follow in the September and December issues, respectively) was published in *Chemical Engineering (Japan)*, volume 21, pages 75-79 (1957). Abstracts, notation, literature cited, tables, and figure captions not published here appear in English in the original paper. No figures will be reproduced in these translations.

Liquid-liquid extraction accompanied by chemical reaction was studied with the use of the following solutes in water and benzene with known interfacial area:

Upper layer		Lower layer		
Solvent	Solute	Solvent	Solute	Transferred material
benzene	iodine	water	sodium hyposulfite	iodine
benzene	iodine	water	sodium hyposulfite + NaI	iodine
benzene	benzoic acid	water	KOH or NaOH	benzoic acid
benzene	monochloro-acetic acid	water	KOH or NaOH	monochloro-acetic acid
benzene	butyric acid	water	KOH or NaOH	butyric acid

EXPERIMENTAL PROCESS

Apparatus used in this experiment is shown in Figure 1. Two known concentration liquids were introduced into the apparatus, then stirred by two mixers, with no break occurring in the surface between the two liquid layers. The stirring speeds of benzene and water were 71 and 78.5 rev./min. respectively, with rotation in the same direction. Benzene was sampled intermittently from the container to determine concentration change. The solute concentration in water was calculated by material balance.

Extraction of I_2 in Benzene by Sodium Hyposulfite Solution

The relation between the rate of extraction and sodium hyposulfite concentration at three I_2 concentrations in benzene is shown in Figure 3. All white points in this figure indicate experimental data (black points will be mentioned later.) At a low concentration of sodium hyposulfite, the rate of extraction increases linearly with the increase of

(Continued on page 6J)

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

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:

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

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*)

(*Continued from page 247*)

2. Other physical characteristics of this system are expected to remain as in previous experiments. In Case *A* at zero sodium hyposulfite concentration, the rate of extraction would be given at a higher point and the slope would decrease. In Case *B* no influence would be expected, as changing m does not affect the rate. Experimental results are shown as black points in Figure 3; the theory, therefore, can be explained by experimentation.

Extraction of Organic Acids in Benzene by Caustic Alkali

Comparison of the extraction rates was made with KOH and NaOH to determine whether these caustic alkali affect the rate in the system of organic acid in benzene and KOH or NaOH in water. KOH and NaOH react differently in gas absorption of CO_2 and caustic alkali solution (*5*, *6*). As one of the experimental results using benzoic acid, Figure 5 shows that there is no difference. Accordingly, the following experiments using NaOH were made. Figure 6 shows the results obtained with benzoic acid, butyric acid, and monochloro-acetic acid. Since acetic acid has a large distribution coefficient m, the first bracket in Equation (1) decreases, and $1/K_W$ in the second bracket is neglected, thus Equation (1) approaches Equation (2). According to experimental results, however, the rate of extraction is increased at low concentration (see Figure 6) but this cannot be explained.

Relation between Diffusivities D and Film Coefficients of Mass Transfer k_B

Figure 7 shows the relation of N vs. C_B. From Equation (2), K_B can be determined by measuring N, a determination revealing that K_B is not affected by C_B and is of constant value. x_B, following Colburn (*2*), is expressed as D/k_B. The effective thickness of benzene film x_B can be calculated by D from Wilke's method (*7*), and k_B from Equation (2) and Figure 7. The calculated x_B is constant as shown in Table 1.

1. Relation between k_B and Temperature

With increasing temperature k_B is increased, as shown in Table 2, such increase probably due to the fact that D is increased and x_B is decreased.

2. Relation between k_B and Stirring Speed

As shown in Table 3, faster stirring has little effect on k_B. When the water is stirred faster, benzene increases accordingly, thus k_B would be increased. (In Table 3, -50 indicates opposite rotating direction.)

3. Relation between k_B and Stirring Speed of Benzene

Results show that k_B increases considerably as shown in Table 4.