Chemical Reaction Processes in Two-Phase

Systems: Theory and Experimental Results for Slow Chemical Reactions in Batch, Column, and Continuous Stirred Tank Reactor Operations

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A theory of design of chemical reactors is developed for two-phase fluid systems where the rates of chemical reaction are low relative to the rates of mass transfer. Equations are presented for batch, column, and continuous stirred tank operations. Experimental data on the continuous hydrolysis of acetic anhydride in a benzene-water system operating countercurrently in a pulsed-flow sieve plate column and in a packed column are analyzed in terms of the theory.

The problem of chemical reaction in two-phase, liquid-liquid, or gas-liquid systems accompanied by mass transfer has only been partially solved to date even though a large number of publications have been devoted to the subject. The present study considers mass transfer between two fluid phases with a relatively slow, simultaneous chemical reaction occurring in one or in both phases and develops design relations for various types of reactors. The treatment is limited to the elementary case of low concentrations of reactants and of products and to reactions of first order. However, as indicated previously, the analysis of extractive reaction processes can be extended to more complex systems (5). The theoretical relations developed in this paper are applied to the analysis of experimental data obtained on a simultaneous transfer and reaction process occurring in countercurrent liquid-liquid extraction columns.

THEORY

Suppose that two phases, 1 and 2, are in contact and that a transfer of component A occurs from phase 1 to phase 2. The concentration of A is a_1 in the main body of phase 1 and a_2 in that of phase 2. In phase 2 a first-order reaction occurs, the rate equation being $-da_2/dt = ka_2$.

In accordance with Hatta (2) and Sherwood and Pigford (4) the fraction η of component A reaching the main

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$$\eta = rac{a_2\cosh\delta\sqrt{rac{k}{D}} + a_{2i}}{a_2 + a_{2i}\cosh\delta\sqrt{rac{k}{D}}}$$

The value of η will be very close to unity; that is $\eta=1$ if

$$\delta\sqrt{\frac{k}{D}} \le 2.10^{-1} \tag{1}$$

When phase 2 is a liquid, then $D \cong 10^{-5}$ sq.cm./sec., and if δ is taken as 10^{-2} cm., then condition (1) requires that

$$k \le 4 \times 10^{-3} \text{ 1/sec.}$$
 (2)

When phase 2 is a gas, $D \approx 0.1$ sq. cm., sec.⁻¹, $\delta \approx 10^{-2}$ cm., and from condition (1)

$$k \leq 40$$
 1/sec.

If the value of k satisfies the inequality, one may consider that essentially all the transferred component A reaches the main body of phase 2 without reacting and that the reaction occurs at a uniform concentration a_2 . Under these conditions the mass transfer and chemical reaction processes are consecutive, and hence the relations describing these can be taken into account separately.

This model will now be used to obtain design relations for batch, tubular, and continuous stirred tank reactor reaction systems.

Batch Operation

The simple case of the first order irreversible reaction $A \xrightarrow{k} B$ is con-

sidered to occur in a batch reactor of volume V.

The rate of mass transfer between the two phases can be written as

$$dn_A = K_A (a_2^* - a_2) V$$

where a_{2}^{\bullet} corresponds to a_{1} ; that is $a_{2}^{\bullet} = \alpha_{A}a_{1}$. In a dilute system α_{A} is constant. K_{A} is the over-all mass transfer coefficient per unit volume of reactor and depends on operating conditions.

Molal balances of A in each phase are

$$-V_1 \frac{da_1}{dt} = K_A(\alpha_A a_1 - a_2) V \quad (3)$$

$$-V_{2}\frac{da_{2}}{dt} = ka_{2}V_{2} - K_{A}(\alpha_{A}a_{1} - a_{2}) V$$
(4)

A combination of (3) and (4) yields

$$\frac{V_{1}}{VK_{A}}\frac{d^{2}a_{1}}{dt^{2}} + \frac{da_{1}}{dt}\left(\alpha_{A} + \frac{kV_{1}}{VK_{A}}\right) + \frac{V_{1}}{V_{0}} + k\alpha_{A}a_{1} = 0$$
 (5)

whose solution is

$$a_1 = G_1 e^{\rho_1 t} + G_2 e^{\rho_2 t} \tag{6}$$

where ρ_1 and ρ_2 are the roots of the characteristic equation .Then

$$a_2 = G_1 \left(\alpha_A + rac{V_1}{V K_A}
ho_1
ight) e^{
ho_1 t} + G_2 \left(lpha_A + rac{V_1}{V K_A}
ho_2
ight) e^{
ho_2 t}$$
 (7

The values of G_1 and G_2 are calculated from the initial conditions

$$egin{align} a_{\mathtt{lo}} &= G_\mathtt{l} + G_\mathtt{l} \ a_{\mathtt{lo}} &= G_\mathtt{l} igg(lpha_\mathtt{A} + rac{V_\mathtt{l}}{V K_\mathtt{d}}
ho_\mathtt{l} igg) \ &+ G_\mathtt{l} igg(lpha_\mathtt{d} + rac{V_\mathtt{l}}{V K_\mathtt{l}}
ho_\mathtt{l} igg) \ \end{aligned}$$

If only the total amount of B formed is needed, this can be readily obtained from the stoichiometric relation

$$b = (a_{10} - a_1) \frac{V_1}{V} + (a_{20} - a_2) \frac{V_2}{V}$$
(8

The concentrations of *B* in each phase are found from molal balances so that

$$\frac{V_1}{VK_B}\frac{d^2b_1}{dt^2} + \left(\frac{V_1}{V_2} + \alpha_B\right)\frac{db_1}{dt} = ka_2$$
(9)

whose solution is

$$b_1 = H_o + H_1 e^{\sigma t} + A_1 e^{\rho_1 t} + A_2 e^{\rho_2 t}$$
(10

where

$$A_{1} = rac{kG_{1}\left(lpha_{A} + rac{
ho_{1}V_{1}}{K_{A}V}
ight)}{
ho_{1}igg(rac{V_{1}}{VK_{B}}
ho_{1} + rac{V_{1}}{V_{2}} + lpha_{B}igg)}$$
 $A_{2} = rac{kG_{2}\left(lpha_{A} + rac{
ho_{1}V_{1}}{K_{A}V}
ight)}{
ho_{1}igg(rac{V_{1}}{VK_{B}}
ho_{1} + rac{V_{1}}{V_{1}} + lpha_{B}igg)}$

and

$$b_{\scriptscriptstyle 2} = lpha_{\scriptscriptstyle B} H_{\scriptscriptstyle o} + H_{\scriptscriptstyle 1} \Big(rac{V_{\scriptscriptstyle 1}\sigma}{V K_{\scriptscriptstyle B}} + lpha_{\scriptscriptstyle B}\,\Big) e^{\sigma t}$$

length L in which two phases are continuously contacted. The reaction

 $A \rightarrow 2B$ occurs in phase 2. The molal balances of A between a section at x and a section at $x + \Delta x$ are

$$(F_{1}a_{1})_{x+\Delta x} - (F_{1}a_{1})_{x} - K_{A}(a_{2}^{\circ} - a_{2})$$

$$S\Delta x = 0 \qquad (12)$$

$$(F_{2}a_{2})_{x} - (F_{2}a_{2})_{x+\Delta x} + K_{A}(a_{2}^{\circ} - a_{2})$$

$$S\Delta x - kra_{\circ}S\Delta x = 0 \qquad (13)$$

For the portion of an equilibrium curve relating the concentrations of the component A distributed between the two phases, which is linear or replaceable by a straight line

$$a_2^* = \alpha_4 a_1 + \beta_4 \tag{14}$$

By substituting (14) into (12) and (13) and letting $\Delta x \rightarrow 0$

$$\frac{F_1}{S} \frac{da_1}{dx} - K_A \beta_A + K_A a_2 - K_A \alpha_A a_1 = 0$$

$$F_2 da_2 + K \beta_A + K \alpha_A A_1 = 0$$
(15)

$$-\frac{F_{2}}{S}\frac{da_{2}}{dx} + K_{A}\beta_{A} - K_{A}a_{2} + K_{A}\alpha_{A}a_{1} - kra_{2} = 0$$
 (16)

From (12) and (13)

$$\frac{F_1 F_2}{K_A S^2 \alpha_A} \frac{d^2 a_2}{dx^2} + \frac{1}{S} \left[\frac{F_1}{\alpha_A} \left(1 + \frac{kr}{K_A} \right) - F_2 \right] \frac{da^2}{dx} - kra_2 = 0$$
 (17)

The general solution of (17) is

$$a_2 = G_1 e^{\rho_1 x} + G_2 e^{\rho_2 x} \qquad (18)$$

$$\rho_{1}, \rho_{2} = \frac{-\left[\frac{F_{1}}{\alpha_{A}}\left(1 + \frac{kr}{K_{A}}\right) - F_{2}\right] \pm \sqrt{\left[\frac{F_{1}}{\alpha_{A}}\left(1 + \frac{kr}{K_{A}}\right) - F_{2}\right]^{2} + \frac{4krF_{1}F_{2}}{K_{A}\alpha_{A}}}}{\frac{2F_{1}F_{2}}{K_{A}S\alpha_{A}}}$$

$$(19)$$

$$egin{align} &+A_1igg(rac{V_1
ho_1}{VK_B}+lpha_Bigg)\,e^{
ho_1 t} \ &+A_2igg(rac{V_1
ho_2}{VK_B}+lpha_Bigg)\,e^{
ho_2 t} \end{array} \eqno(11)$$

 H_o and H_1 are obtained from the initial conditions.

If K_A and K_B have been measured and k is known, the above equations can be used to calculate the conversion for any time t of reaction.

Columnar Operation

Whereas a tubular or column arrangement can be operated in concurrent or countercurrent flow, only the latter more important case will be considered here.

Figure 1 is a schematic representation of a countercurrent column of

From (12)
$$\beta_{A} + \alpha_{A}a_{1} = G_{1} \left(\frac{F_{2}}{K_{A}S} \rho_{1} + \frac{K_{A} + kr}{K_{A}} \right)$$

$$e^{\rho_{1}x} + G_{2} \left(\frac{F_{2}}{K_{A}S} \rho_{2} + \frac{K_{A} + kr}{K_{A}} \right) e^{\rho_{2}x}$$
(20)

The constants G_1 and G_2 are calculated from (18) and (20) written for entrance conditions.

From molal balances of B

$$\frac{F_1}{S} \frac{db_1}{dx} - K_B \beta_B + K_B b_2 - K_B \alpha_B b_1 = 0$$

$$- \frac{F_2}{S} \frac{db_2}{dx} + K_B \beta_B - K_B b_2$$

$$+ K_B \alpha_B b_1 + 2kra_2 = 0 \quad (22)$$

whose solution is

$$b_{2} = H_{o} + H_{1} e^{ax} + A_{1} e^{b_{2}x} + A_{2} e^{b_{2}x}$$
where
$$SK_{B}\alpha_{B} \left(\sum_{i} F_{1} \right)$$

$$\sigma = \frac{SK_{B}\alpha_{B}}{F_{1}F_{2}} \left(F_{2} - \frac{F_{1}}{\alpha_{B}}\right) \quad (24)$$

$$A_{1} = \frac{2krG_{1}}{\rho_{1}}$$

$$F_{1}\rho_{1} - SK_{B}\alpha_{B}$$

$$\frac{F_{1}F_{2}}{S} \rho_{1} + F_{1}K_{B} - F_{2}K_{B}\alpha_{B}$$

$$A_{2} = \frac{2krG_{2}}{\frac{\rho_{2}}{F_{1}\rho_{2} - SK_{B}\alpha_{B}}} = \frac{F_{1}F_{2}}{\frac{F_{1}F_{2}}{S}\rho_{2} + F_{1}K_{B} - F_{2}K_{B}\alpha_{B}}$$

The value of b_1 is obtained by combining (22) and (23):

$$\beta_{B} + \alpha_{B} b_{1} = H_{o} + H_{1} \left(\frac{F_{2}\sigma}{SK_{B}} + 1 \right)$$

$$e^{\sigma x} + A_{1} \left(\frac{F_{2}\rho_{1}}{SK_{D}} + 1 \right) e^{\rho_{1}x}$$

$$+ A_{2} \left(\frac{F_{2}\rho_{2}}{SK_{B}} + 1 \right) e^{\rho_{2}x} - \frac{2kr}{K_{B}}$$

$$(G_{1} e^{\rho_{1}x} + G_{2} e^{\rho_{2}x}) \qquad (25)$$

As before H_o and H_1 are calculated from the feed compositions b_{2o} and b_{1L} .

If K_A , K_B and r are known for a given column, perhaps as functions of the flow rates and nature of the phases, relations (18), (20), or (23) and (25) can be used to calculate the conversion as a function of length.

Since the height of a theoretical plate h in a column is sometimes known, it is useful to find the relation of K to h. In the case of mass transfer without reaction Equation (14) can be applied by letting k = 0. Furthermore the concept of the theoretical plate assumes that the outgoing phase streams at x + h and at x are in equilibrium:

$$a_2(x+h) = \beta_A + \alpha_A a_1(x) \quad (26)$$

Combining (26) with the solution of (17) one obtains

$$K_{A} = \frac{F_{1}F_{2}}{S\alpha_{A} h\left(F_{2} - \frac{F_{1}}{\alpha_{A}}\right)} \ln\left(\alpha_{A} \frac{F_{2}}{F_{1}}\right)$$

$$(27)$$

Continuous stirred tank reactor systems

The concurrent case is treated here; however similar design relations for countercurrent arrangements are likewise obtainable (3). In this development it will be assumed, by way of illustration, that the reaction $A \rightarrow B$ occurs in both phases, the reaction rate constants in each being k_1 and k_2 .

Molal balances for component A around the ith stage of a continuous

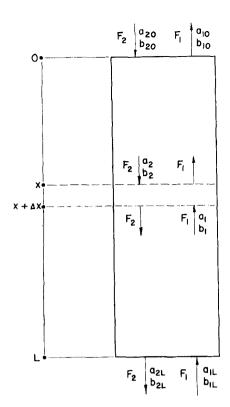


Fig. 1. Schematic representation of a countercurrent column.

stirred tank reactor chain, Figure 2, results in the following difference equations:

$$F_{2}a_{(i-1)2} + K_{A}(a^{*}_{i2} - a_{i2})$$

$$V - F_{2}a_{i2} - k_{2}V_{2}a_{i2} = 0 \qquad (28)$$

$$F_{1}a_{(i-1)1} - K_{A}(a^{*}_{i2} - a_{i2})$$

$$V - F_{1}a_{i1} - k_{1}V_{1}a_{i1} = 0 \qquad (29)$$

where $a^*_{i2} = \alpha_i a_{i1}$ relates the distribution of A between the phases 1 and 2. By combining (28) and (29) a second order difference equation is obtained:

$$a_{i1}[(F_{2} + k_{2}V_{2})(F_{1} + k_{1}V_{1} + K_{A}\alpha_{A}V) + K_{A}V(F_{1} + k_{1}V_{1})] - a_{(i-1)1}(F_{1}F_{2} + k_{1}V_{1}F_{2} + F_{2}K_{A}\alpha_{A}V) + F_{3}F_{2}a_{(i-2)1} = 0$$
(30)

whose solution is

$$a_{i1} = G_1 \rho_1^{i} + G_2 \rho_2^{i} \tag{31}$$

By substituting into (29)

$$a_{i2} = \frac{1}{K_{4}V} \left[\left(\frac{F_{1}}{\rho_{1}} - F_{1} - k_{1}V_{1} - K_{4}\alpha_{4}V \right) G_{1}\rho_{1}^{i} + \left(\frac{F_{1}}{\rho_{2}} - F_{1} - k_{1}V_{1} - K_{4}\alpha_{4}V \right) G_{2}\rho_{2}^{i} \right]$$
(32)

Values of G_1 and G_2 are calculated from the initial conditions a_{10} and a_{20} by letting i = 0 in (31) and (32).

Similarly from molal balances of B around the ith stage

$$A_1b_{i1} + A_2b_{(i-1)1} + A_3b_{(i-2)1}$$

$$= A_ia_{i1} + A_5a_{i2} + A_6a_{(i-1)1}$$
 (33)
ere

$$A_1 = F_1(K_BV + F_2) + K_B\alpha_BF_2V$$
 $A_2 = -[F_2(F_1 + K_B\alpha_BV) + F_1(K_BV + F_2)]$
 $A_3 = F_1F_2$
 $A_4 = k_1V_1(K_BV + F_2)$
 $A_5 = -k_2V_2K_BV$

The solution of (33) is

$$b_{i_1} = G'_1 \sigma_1^i + G'_2 \sigma_2^i + H_1 \rho_1^i + H_2 \rho_2^i$$
(34)

 $A_a = -F_a k_1 V_1$

where σ_1 and σ_2 are the roots of the characteristic equation

$$A_1 \sigma^2 + A_2 \sigma + A_3 = 0$$

 H_1 and H_2 are obtained by substitution of (34) into (33) and identification of the coefficients of ρ_1 and ρ_2 . The equations for reaction occurring in only one phase are readily obtained from the above by equating k_1 or k_2 to zero.

EXPERIMENTAL

A countercurrent liquid-liquid extraction pulsed column was found convenient to experimentally check the above developed relations for mass transfer in the presence of chemical reaction. The pseudo first-order transformation of acetic anhydride to acetic acid was used in the two-solvent system of water and benzene. Experiments were run with twenty-nine perforated

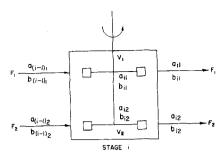


Fig. 2. Continuous stirred tank reactor nomenclature.

plates in the column, and in another series the column was packed with ¼-in. porcelain Berl saddles. The perforated plates were 1/16 in. thick stainless steel, each drilled with 28-1/16-in. diameter holes on concentric circles. In either case the active part of the column had a height of 1 m.

36-mm. diameter glass column, The Figure 3, was temperature controlled by running a stream of water at the desired temperature down the outside wall of the glass tube. The water and benzene streams were fed to the columns by means of bellow pumps from supply bottles placed in a thermostat. Another bellow pump with its check valves removed was employed as a pulsator, and a variable speed transmission was used to vary the pulsations frequency. The flow rates were determined by measuring the time needed to empty calibrated pipettes connected to the supply lines by means of three-way stopcocks.

Distribution of Acetic Anhydride between water and benzene

This determination cannot be very precise, since reaction occurs in the

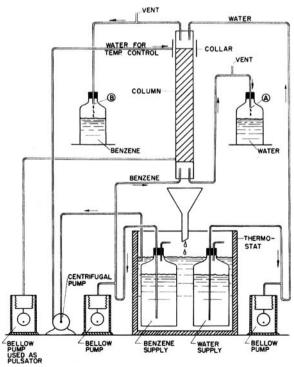


Fig. 3. Experimental assembly.

TABLE I. SUMMARY OF EXPERIMENTAL DATA AND BESILTS.

	Pulsation fre- Col- quency, Temp., F_1 , F_2 ,						Inlet	Inlet	Outlet conc.,		Outlet conc., a_{2L} Theor.		Outlet	Outlet	Total outlet acid, $2a_{2L} + b_{2L}$		Material balance
Run	umn	1/min.	°C.	cc./hr.	cc./hr.	r	a ₁ L	b_{1L}	Exp.	Theor.	Exp.	(corr.)	b_{10}	b_{2L}	Exp.	Theor.	error
1 5 6 7 8 9 10 11 12 14	P* P P P S S S S	81 81 81 81 81 81 36 36 50	20 20 20 20 25 30 25 20 25	2000 1580 2000 1980 1980 1980 2200 2200 2200 2650	1760 1580 1700 3100 3100 3100 900 880 850 730	0.1 0.1 0.1 0.1 0.1 0.1 0.8 0.8 0.8	0.69 1.017 0.760 1.095 0.887 0.710 0.735 0.680 0.481	0.0296 0.098 0.286 0.001 0.159 0.1303 0.152 0.1045 0.0702 0.0492	0.510 0.690 0.550 0.630 0.523 0.564 0.466 0.494 0.450 0.347	0.53 0.66 0.58 0.60 0.52 0.59 0.45 0.49 0.42	0.096 0.117 0.109 0.177 0.123 0.108 0.0664 0.080 0.067	0.095 0.123 0.101 0.179 0.122 0.104 0.061 0.087 0.064 0.037	0.010 0.0049 0.024 0.0138 0.0187 0.0210 0.0078 0.0023 0.0023	0.238 0.52 0.54 0.264 0.262 0.270 1.535 1.26 1.35 1.275	0.43 0.76 0.76 0.62 0.51 0.49 1.48 1.48 1.27	0.45 0.71 0.79 0.57 0.56 0.57 1.51 1.43 1.31	3% 2.2% 10.5% 3% 0.1% 0.1% 0.8%

^{*} P = plate column.
** S = column packed with saddles.

water layer. However approximate equilibrium values were obtained by vigorously shaking water, benzene, and acetic anhydride for a short time (3 min.) in a 2-liter funnel separator and removing the two phases as quickly as possible. Only measurements at 20°C were made. The distribution curve was found to be a straight line and from this $\alpha_A = 0.275$ was obtained. Since at higher temperatures the increased rate of reaction makes the measurements much more imprecise, the values of α_4 for 25° and 30°C, were assumed, after comparison with other systems, to be 0.27 and 0.26 respectively.

Distribution of acetic acid between water and benzene

The results of measurements at 20°C. are represented in Figure 4. Values given in the International Critical Tables were used for 25° and 30°C.

Reaction rate constant

The transformation in a large excess of water of acetic anhydride to acetic acid is a first-order reaction of the type k $A \rightarrow 2B$ whose rate is expressed by $-da/dt = k \ a = 1/2 \ db/dt$. The val-

ues of k used were those of Eldridge and Piret (1) and verified by Cleland and Wilhelm (6):

$$k_{\text{20°C.}} = 1.87 \times 10^{-3} \text{ 1/sec.}$$

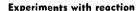
 $k_{\text{25°C.}} = 2.63 \times 10^{-3} \text{ 1/sec.}$
 $k_{\text{30°C.}} = 3.54 \times 10^{-3} \text{ 1/sec.}$

It can be seen that the first two rate constants are within the requirements of Equation (2) and that the last constant is only slightly superior to the limit. The above developed theory may therefore be used for this hydrolysis reaction which occurs almost entirely in the aqueous phase.

Determination of the mass transfer coefficient

Extraction measurements with the benzene-acetic acid-water system were used to determine the number of theoretical plates in the column over the same range of operating conditions employed in the extractive reaction experiments. In the perforated plate assembly experiments, the benzene phase was continuous, while in the packed column the continuous phase was the aqueous, the acetic acid being transferred from benzene to water in

the first case and from water to benzene in the second. The number of theoretical plates were calculated by the usual graphical or analytical techniques (4). For either type of column, when one takes into account the experimental errors, and within the relatively small range of flow rates and pulsations frequencies used, the number of theoretical plates was found not to depend on operating conditions. This number is 2.0 for the perforated plates column and 3.0 for the packed column. The mass transfer coefficient was then calculated by Equation (27), where h = 50 and 33 cm, for each column respectively.



The reaction acetic anhydride to acetic acid was then studied in the extraction column. The anhydride was added to the benzene supply in such quantity that the concentration of anhydride was between 0.5 and 1.0 moles/liter. Distilled water was fed at the top of the column countercurrent to the rising organic phase. For each successive run the same benzene supply was used without intermediate washing out of acid or drying treatment, hence both anhydride and acetic acid were always present in the benzene feed. Anhydride and acid contents were determined by the procedure used by Eldridge and Piret (1). It was established that 3-hr. operation were sufficient to obtain steady state in the column. Samples of the outgoing water and benzene streams were then taken at A and B (Figure 3) and their contents of anhydride and acetic acid determined. The amounts of water and benzene remaining in the column at the end of the run were measured to find the ratio r of the volume occupied by the aqueous phase to the total effective volume of the column.

The results of these experiments are given in Table 1. It can be seen that the material balances effected on the entire column are better for the saddle than for the perforated plate column. This results from the greater stability of the interphase position in the packed column which could therefore be controlled more accurately than in perforated plate apparatus.

The values of a_{10} , that is, the concentration of acetic anhydride in the

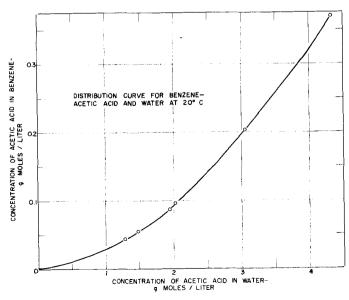


Fig. 4. Acetic acid distribution.

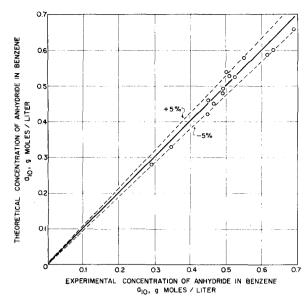


Fig. 5. Experimental and calculated values.

stream of benzene leaving the column, were calculated from relations (18) and (20) with the above determined rate constant, partition, and mass transfer coefficients. These relations are directly applicable, since the distribution curve for anhydride is nearly a straight line going through the origin so that $\beta_A=0$ in Equation (14). The comparison between experimental and calculated values is given in Figure 5; the agreement is good, since most of the experimental values correspond to the theoretical with less than 5% error.

The concentration of acetic anhydride in the stream of water immediately leaving the column, a_{2L} , is calculated from Equation (18). The measured concentrations however are those in a water stream, which has passed through a volume V in the separation section and outlet tubing after leaving the active part of the column. Reaction therefore continued during this passage as well as during the sampling time. From a measure of the volume Vand with an averaged sampling time θ_s the time $\theta = \theta_s + V/F_2$ was estimated, during which transformation of the anhydride continued. The factor $e^{-k\theta}$ was then applied to the calculated values to obtain predicted concentrations at the sampling point. These corrected theoretical values are reported in Table 1 and compared to the experimental. As seen from the table the agreement between theory and experiment is again fairly good, taking into account that the sampling time is only approximate.

For the same reasons the measured values of b_{2L} , that is the acetic acid content of the sampled outgoing aqueous phase, cannot be compared directly to theory. In this case only a comparison of the total acid content of the collected sample, $2a_{2L} + b_{2L}$, with the theoretical given in Table 1. Relations (23) and (25) were used to calculate b_{2L} . Since the partition curve for the acetic acid is not linear, Figure 4, and was approximated by a straight line, the agreement between experiment and theory

cannot be expected to be as good as for the a_{10} values. Furthermore note that in the evaluation of $2a_{2L} + b_{2L}$ the absolute error made in a_{20} is magnified by the factor $2F_1/F_2$. Nevertheless the agreement is satisfactory.

DISCUSSION

Design relations for several types of reactors were derived in the preceding for the case where mass transfer and chemical reaction occur simultaneously. The limiting value of the chemical rate constant was related to the properties of the system. Within this limit the theory was confirmed experimentally. It is seen that the derivations, as illustrated in the case of continuous stirred tank reactor systems, are not complicated when reaction occurs in both phases.

For simplicity the theory was developed with a first-order reaction assumed; however the same considerations can be applied to reactions of higher order. Since the resulting differential equations would be nonlinear, numerical, graphical, or analogue computer techniques will be required in most cases. The limit for chemical rate constants can similarly be found. For example suppose the reaction A + k

 $\stackrel{k}{B} \rightarrow C$ occurs in a phase where B is present, component $\stackrel{k}{A}$ being transferred from another phase to the reactive phase. The limitation for the value of k for this case is given by

$$\delta \sqrt{\frac{k \, b_{\scriptscriptstyle M}}{D_{\scriptscriptstyle A}}} \leq 0.2$$

where $b_{\scriptscriptstyle M}$ is the maximum concentration of B in the reactive phase.

Only the dilute case, that is, the case where reactants and products are pres-

ent in low concentrations in either phase, was considered herein. This condition allows the partition coefficients, flow rates, and phase volumes to be considered constant. If these quantities cannot be assumed constant, complications arise in the derivations and computations, as has been illustrated earlier for extractive reaction processes (5).

ACKNOWLEDGMENT

This investigation was in part supported by a grant of the Graduate School of the University of Minnesota and by an appointment of the International Cooperation Administration under a program administered by the National Academy of Sciences.

NOTATION

A, B = components A, B

a, b = concentrations of A, B

D = diffusivity

F = volumetric flow rate

K = mass transfer coefficient per unit volume of reactor

k = reaction rate constant

n = number of moles

= fraction of the reactor occupied by phase 2

S = cross section

t = time

V = volume of the reactor

= slope of the distribution

eurve
= effective thickness of film

q = fraction of reactant reaching the main body of the reactive phase without reacting

Subscripts

A, B = components A, B $(i-1), i \text{ or } N = i^{\text{th}}, (i-1)^{\text{th}}, \text{ or } N^{th}$ stage in a chain of continuous stirred tank reactors

o, L =end conditions for a column

1, 2 = phases 1 or 2

Superscripts

physical equilibrium

LITERATURE CITED

- Eldridge, J. W., and E. L. Piret, Chem. Eng. Progr., 46, 292 (1950).
- Hatta, S., Technol. Rep. Tohoku Univ., 10, 119 (1932).
- Piret, E. L., W. Penney, and P. J. Trambouze, A.I.Ch.E. Journal, 6, 394 (1960).
- Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," McGraw-Hill, New York (1952).
- 5. Trambouze, P. J., and E. L. Piret, A.I.Ch.E. Journal, 6, 574 (1960).
- Cleland, F. A., and R. H. Wilhelm, ibid., 2, 492 (1956).

Manuscript received April 17, 1959; revision received February 15, 1960; paper accepted February 17, 1960.