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Study on the Pulse Reaction Technique

I. Theoretical Study

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A theoretical investigation of the pulse technique has been carried out using typical reaction models (irreversible, reversible, and consecutive reactions) and the conversion of reactants and the yield of products were compared with those from the continuous flow technique. In the case of linear reactions with no other rate process than first order, even if they are reversible or consecutive, the results from the pulse technique are in agreement with those from the flow technique, while in the case of nonlinear reactions there is a quite remarkable disagreement. In the reversible reactions of $A \rightleftharpoons 2R$ and $A \rightleftharpoons R + S$ the conversion is above that from the flow technique, and in the consecutive reactions such as $A + B \rightarrow R$, $R + B \rightarrow S$, and $A \rightarrow R$, $2R \rightarrow S$, the yield of the intermediate product, R, is larger than that from the flow technique. The results on the nth order irreversible reaction are equivalent to that from the flow technique in the case of a rectangular pulse only. Main factors peculiar to the pulse technique are discussed. The results from the pulse technique vary greatly with the inlet pulse width as well as with the different adsorption strengths of components on a catalyst, but the difference in the results is relatively small for rectangular, triangular, and error function pulses. Furthermore, a method of measurement of kinetic parameters by the pulse technique is proposed for the several reaction models.

The pulse technique, in which small amounts of reactant are injected into a carrier gas stream before the gas enters a reactor packed with a small amount of catalyst, is proving of great use in the study of heterogeneous catalytic reactions. It is easily expected on the analogy of the pulse technique with the gas chromatographic one that components may be separated from others in a catalyst bed according to the different adsorption strengths on the catalyst. Complications arising from the separation of components make fundamental analysis of the reaction kinetics in the pulse technique extremely difficult in contrast to the flow technique.

Some attempts have been made to disclose the kinetic characteristics of the pulse technique. Simple consideration by Bassett and Habgood (*1*) showed that the pulse reaction kinetics for the first order irreversible reaction is in agreement with the continuous flow one, as was confirmed rigidly by Roginskii *et al.* (*2*) and was proved experimentally by Schwab and Watson (*3*) for the dehydrogenation of methanol on a silver catalyst. Gasiev *et al.* (*4*) analyzed theoretically irreversible reactions with zero, first, and second order kinetics in the case of a rectangular or a triangular pulse of reactant and considered that the reverse reaction is negligible because the products are separated from each other, and that reversible reactions can be treated just as irreversible ones. The dehydrogenation of cyclohexane was studied on the basis of such a conception.

The separation of products, however, should be incomplete except in the case of a pulse without width, so the reverse reaction generally may not be negligible. A more practical analysis of the reversible reaction of $A \rightleftharpoons R + S$ was made by Magee (*5*) using an analog computer, the result of which showed that the reaction can proceed beyond its equilibrium conversion on the assumption that the chemical equilibrium is established instantaneously.

In all of these publications, however, the reaction models treated are limited to a few, and the basic assumptions are too simple. In the present work the pulse reaction kinetics of the typical reaction models are analyzed mathematically under more real assumptions either using a digital computer or not. The effects of the shape of inlet pulse, the separation of components in a catalyst bed, and the spreading of product pulses are discussed.

Results demonstrate the applicability of the pluse technique to precise studies of kinetics for the several reaction models. A later study using the pulse technique has been made on the catalytic cracking and disproportionation of cumene and is reported in the following paper (7).

NOMENCLATURE

C_i	Concentration of component i in gas phase (mole/cm^3 of bed)
$C_A{}^0$	Maximum concentration of inlet pulse (mole/cm^3 of bed)
$\overline{C_A{}^0}$	Average initial concentration defined by Eq. (27) (mole/cm^3 of bed)
k	Reaction rate constant
K	Equilibrium constant
K_i	Adsorption equilibrium constant of component i
L	Length of catalyst bed (cm)
r_i	Rate of formation of component i (mole/cm^3 sec)
t	Time (sec)
t_0	Pulse width defined by Eq. (8) (sec)
u	Moving velocity of carrier gas down catalyst bed (cm/sec)
u_i	Characteristic moving velocity of component i down catalyst bed (cm/sec)
v	Ratio of characteristic moving velocity, u_R/u_A
X	Conversion of reactant
X_r, X_t, X_e	Conversion in the case of a rectangular, a triangular, and an error function pulse
X_f	Conversion in the flow technique
Y_i	Yield of component i
z	Distance down catalyst bed (cm)
η_i	Dimensionless concentration of i, $C_i/C_A{}^0$
θ, θ_L	Residence time of carrier gas, z/u, L/u (sec)
θ_i, θ_{iL}	Residence time of Component i, z/u_i, L/u_i (sec)
τ	Dimensionless time, $t(v-1)/\theta_{AL}$
τ_0	Dimensionless pulse width, t_0/θ_{AL}
φ	Dimensionless concentration profiles of inlet pulse

METHOD OF MATHEMATICAL ANALYSIS

The assumptions inherent in the present paper are as follows: (1) All components of reactants and products move as a plug flow of linear velocity u together with a carrier gas. (2) Influence of mass transfer onto catalyst surface is negligible. (3) Linear adsorption equilibrium is established between gas phase and catalyst surface.* (4) The catalyst bed is isothermal.

The differential equation expressing the mass balance within the reactor is

$$\frac{\partial C_i}{\partial t} = -u_i \frac{\partial C_i}{\partial z} + \frac{r_i}{1 + K_i} \qquad (1)$$

where r_i is the rate of formation of component i and u_i is the characteristic moving velocity of component i defined by

$$u_i = u/(1 + K_i) \qquad (2)$$

The boundary conditions at the inlet of catalyst bed ($z = 0$) are as follows: for the reactants,

$$C_i = C_i{}^0\varphi(t) \qquad (3)$$

and for the products,

$$C_i = 0 \qquad (4)$$

where $\varphi(t)$ is a shape of inlet pulse and is given as a function of time. For a rectangular pulse,

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* This assumption is practical under conditions of lower concentration in gas phase. In the later paper the case of Langmuir isotherm will be treated.

$$\text{at} \quad t_0 \geq t \geq 0, \quad \varphi(t) = 1$$
$$\text{and at} \quad t \geq t_0, \quad \varphi(t) = 0 \tag{5}$$

For a triangular pulse,

$$\text{at} \quad t_0 \geq t \geq 0, \quad \varphi(t) = t/t_0$$
$$\text{at} \quad 2t_0 \geq t \geq t_0, \quad \varphi(t) = 2 - (t/t_0)$$
$$\text{and at} \quad t > 2t_0, \quad \varphi(t) = 0 \tag{6}$$

And for an error function pulse,

$$\varphi(t) = \exp\{-\pi(t - t')^2/t_0^2\} \tag{7}$$

Parameter t_0, pulse width, is defined by Eq. (8).

$$t_0 = \int_0^\infty \varphi(t)\, dt \tag{8}$$

It follows that the amount of reactant injected corresponds to $C_A{}^0 t_0$. The initial condition is, at $t = 0$,

$$C_i = 0 \tag{9}$$

Conversion, X, and yield of component i, Y_i, in the pulse technique are obtained by integrating the concentration of reactant A or product i at the outlet of the catalyst bed.

$$X = 1 - \frac{1}{C_A{}^0 t^0} \int_0^\infty C_A(t,L)\, dt \tag{10}$$

$$Y_i = \frac{1}{C_A{}^0 t_0} \int_0^\infty C_i(t,L)\, dt \tag{11}$$

In the case of nonlinear reactions these equations were solved numerically in the following way. Equation (1) means that each component moves down the catalyst bed with its characteristic moving velocity u_i during the reaction. For example, the differential equations expressing the mass balance of reactant A and product R in the reversible reaction are

$$\frac{\partial C_A}{\partial t} = -u_A \frac{\partial C_A}{\partial z} + \frac{r_A}{1 + K_A} \tag{12}$$

$$\frac{\partial C_R}{\partial t} = -u_R \frac{\partial C_R}{\partial z} - \frac{r_R}{1 + K_R} \tag{13}$$

and the transport of A and R predicted from these equations is shown graphically in Fig. 1. Replacing the derivatives in Eqs. (12) and (13) with the simplest difference representations, and rearranging, leads to

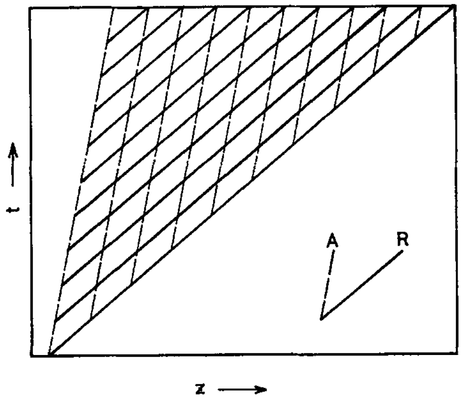

FIG. 1.

$$C_A(n + 1,m) = \left(1 - u_A \frac{\Delta t}{\Delta z}\right) C_A(n,m) + u_A \frac{\Delta t}{\Delta z} C_A(n,m - 1) + \frac{\Delta t}{1 + K_A} r_A(n,m) \tag{14}$$

$$C_R(n + 1,m) = \left(1 - u_R \frac{\Delta t}{\Delta z}\right) C_R(n,m) + u_R \frac{\Delta t}{\Delta z} C_R(n,m - 1) + \frac{\Delta t}{1 + K_R} r_R(n,m) \tag{15}$$

Transport of A and R expected from these equations differs entirely from the actual movement. In contrast the equations obtained in the following way express the actual movement. Equating w to $z - u_A t$, one gets

$$\left(\frac{\partial C}{\partial t}\right)_w = \left(\frac{\partial C}{\partial t}\right)_z + \left(\frac{\partial z}{\partial t}\right)_w \left(\frac{\partial C}{\partial z}\right)_t = \left(\frac{\partial C}{\partial t}\right)_z + u_A \left(\frac{\partial C}{\partial z}\right)_t$$

When this is substituted into Eqs. (12) and (13), they become

$$\left(\frac{\partial C_A}{\partial t}\right)_w = \frac{r_A}{1 + K_A} \tag{16}$$

$$\left(\frac{\partial C_R}{\partial t}\right)_w = -(u_R - u_A)\left(\frac{\partial C_R}{\partial w}\right)_t + \frac{r_R}{1 + K_R} \tag{17}$$

Replacing again the derivatives in the dimensionless form of these equations with the differences and equating $\Delta\tau$ to $\Delta(z/L)$, one gets

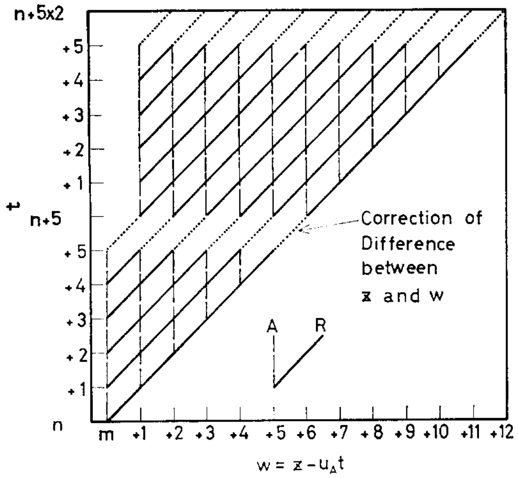

Fig. 2.

$$\eta_A(n+1,m) = \eta_A(n,m) + \frac{1}{v-1}\frac{\Delta\tau\theta_L}{C_A{}^0} r_A(n,m) \quad (18)$$

$$\eta_R(n+1,m+1) = \eta_R(n,m) + \frac{v}{v-1}\frac{\Delta\tau\theta_L}{C_A{}^0} r_R(n,m) \quad (19)$$

Transport of A and R predicted by these equations is shown graphically in Fig. 2, and agrees with the actual behavior shown in Fig. 1 in consideration of the relation between z and w. When the calculation is carried out, the difference between z and w must be corrected by transferring C_i at $w = m$ to $w = m + 1$ when $t = n(v - 1)$, which is represented by the dotted lines at $t = n(v - 1)$ in Fig. 2.

Results

(*A*) *Linear Reaction*

In the previous paper (*6*), theoretical analysis was made on the first order irreversible, reversible, and consecutive reactions. It was found that in these reactions the same result is obtained by the pulse and the flow techniques. In the present paper, analysis was made on a general linear reaction with no other rate process than first order. The linear reactions are characterized by the ability of addition, that is, a rectangular pulse with a pulse width t_0 can be represented as the difference between two step functions, i.e., $\varphi(t) = u(t) - u(t - t_0)$, and the response of a rectangular pulse, η_i, also can be equated to the difference between two indicial responses, i.e., $\eta_i(t) = \psi_i(t) - \psi_i(t - t_0)$. The indicial response $\psi_i(t)$ gets nearer a steady state value Y_{is} with a lapse of time, and agrees with it after a long lapse of time, t_s

$$Y_i = \frac{1}{t_0}\int_0^\infty [\psi_i(t) - \psi_i(t - t_0)]\,dt$$
$$= \frac{1}{t_0}\left[\int_0^{t_s+t_0} \psi_i(t)\,dt - \int_{-t_0}^{t_s} \psi_i(t)\,dt\right] \quad (20)$$

According to the definition of step function, at $t > 0$, $u(t) = 0$ and $\psi_i(t) = 0$. Hence

$$Y_i = \frac{1}{t_0}\left[\int_0^{t_s+t_0} \psi_i(t)\,dt - \int_0^{t_s} \psi_i(t)\,dt\right]$$
$$= \frac{1}{t_0}\int_{t_s}^{t_s+t_0} \psi_i(t)\,dt = Y_{is} \quad (21)$$

This equation suggests that when reactants are fed as a rectangular pulse the conversion of reactants and the yield of products are in agreement with those from the flow technique. Furthermore Eq. (21) keeps its validity in the case of an arbitrary pulse shape because an arbitrary pulse is given as an assemblage of rectangular pulses in the linear reactions.

(*B*) *Nth Order Irreversible Reaction*

In the irreversible reaction the differential equation expressing the mass balance of products is not required, and the continuity equation for reactant is obtained by substitution of the reaction rate expression, $r_A = -kK_A{}^nC_A{}^n$, into Eq. (16),

$$\frac{\partial C_A}{\partial t} = -\frac{kK_A{}^n}{1 + K_A} C_A{}^n \quad (22)$$

Solving this with an initial condition given by Eq. (3) and replacing the term t by contact time θ_A, the concentration profiles of reactant A is obtained (*4*). For $n \neq 1$,

$$C_A = C_A{}^0\varphi(t - \theta_A)[1 + (n - 1)kK_A{}^nC_A{}^{0n-1} \times \{\varphi(t - \theta_A)\}^{n-1}\theta]^{1/1-n} \quad (23)$$

and for $n = 1$,

$$C_A = C_A{}^0\varphi(t - \theta_A)\exp(-kK_A\theta) \quad (24)$$

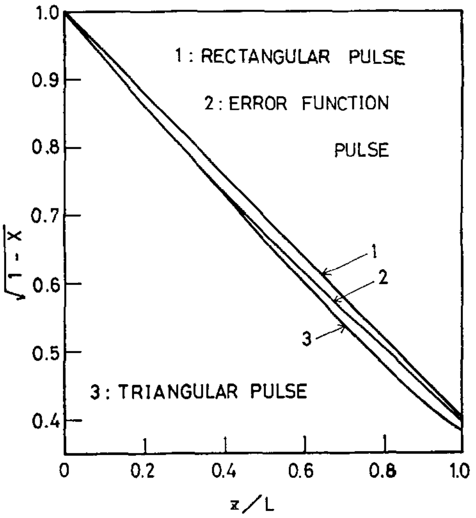

FIG. 3.

Substitution of Eq. (23) into Eq. (10) gives for $n \neq 1$,

$$X = 1 - \frac{1}{t_0}\int_0^\infty \varphi(t) \times [1 + (n-1)kK_A{}^nC_A{}^{0n-1}\theta_L\{\varphi(t)\}^{n-1}]^{1/1-n}\,dt \qquad (25)$$

In the case of the rectangular pulse the conversion X_r is equivalent to that in the flow technique X_f because $\varphi(t) = 1$.

$$X_r = X_f = 1 - [1 + (n-1)kK_A{}^nC_A{}^{0n-1}\theta_L]^{1/1-n} \qquad (26)$$

On the other hand the conversions of the triangular pulse X_t and of the error function pulse X_e differ from X_f. Difference between X_t and X_f or X_e and X_f is mainly due to the difference in the initial concentration. If the average initial concentration defined by Eq. (27) is used instead of the maximum concentration of inlet pulse $C_A{}^0$, X_t, and X_e approximately agree with X_f.

$$\overline{C_A{}^0} = \frac{C_A{}^0}{t_0}\int_0^\infty \{\varphi(t)\}^n\,dt \qquad (27)$$

In Fig. 3 a plot of $(1 - X)^{1/2}$ versus bed length is shown for the half-order reaction. In the case of the rectangular pulse the plot gives a straight line in agreement with that from the flow technique, and in the cases of the triangular and the error function pulses the deviation from the flow technique is only less than 8% and independent of the pulse width. In the first order reaction, as reported previously (*2*), the conversion given by Eq. (28) is independent of pulse shape and is equivalent to that from the flow technique.

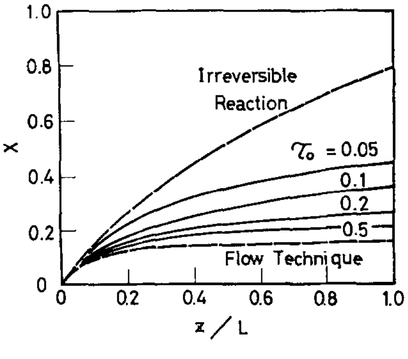

FIG. 4.

$$X = 1 - \exp(-kK_A\theta_L) \qquad (28)$$

(*C*) $A \rightleftharpoons 2R$

On substituting the reaction rate expressions, $r_A = -r_R/2 = -k_1K_AC_A + k_2K_R{}^2C_R{}^2$, into Eqs. (18) and (19), they were solved numerically by a NEAC-2203 digital computer. As can be seen from Fig. 4, the conversions in the pulse technique are over those in the flow technique given by the lower dashed line, although they must be less than that without the reverse reaction

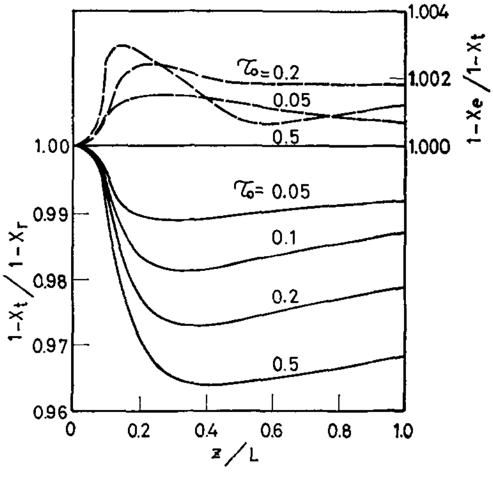

FIG. 5.

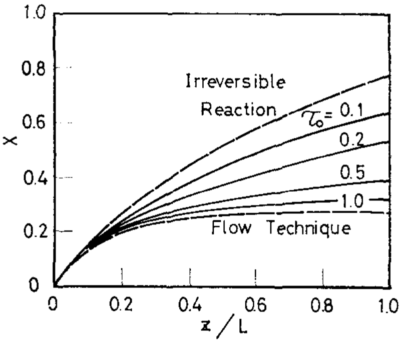

FIG. 6.

given by the upper dotted line. Figure 5 shows that the unconverted fraction of a rectangular pulse is consistent with those of a triangular pulse within 4% and the latter are practically equivalent to those of the error function pulse.

$(D)\ A \rightleftharpoons R + S$

This reaction was analyzed by Magee (*5*) previously, but the situation is restricted because chemical equilibrium is established instantaneously. In this paper the more general case in which the reaction takes place at a finite rate is treated.

On substituting the reaction rate expressions, $r_A = -r_R = -r_S = -k_1K_AC_A + k_2K_RK_SC_RC_S$, into Eqs. (18) and (19), they were solved by the computer for $u_A = u_S$ * and $u_S \neq u_R$. The relation of conversion with the length of catalyst bed is shown in Fig. 6 and the concentration profiles at the outlet of a catalyst bed are shown in Figs. 7 and 8. The conversions in the pulse technique are greater than those in the flow technique as in reaction (C), but the deviation from the flow technique is larger than that in (C). Also the effect of pulse shape is larger than in (C). The ratios of $1 - X_t$ to $1 - X_r$ are in the range of $0.95 \sim 1.00$ and those of $1 - X_e$ to $1 - X_r$ are in the range of $0.994 \sim 1.006$, as shown in Fig. 9.

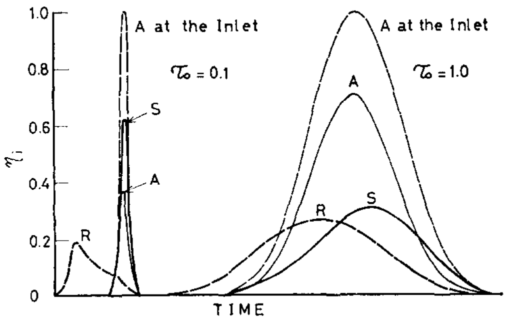

FIG. 7.

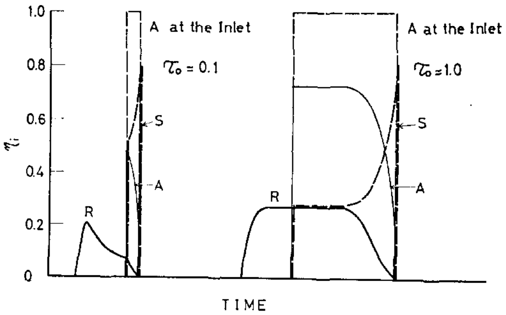

FIG. 8.

$(E)\ A + B \rightarrow R,\ R + B \rightarrow S$

On substituting the reaction rate expressions, $r_A = -k_1K_AK_BC_AC_B$, $r_B = -k_1K_AK_BC_AC_B - k_2K_RK_BC_RC_B$, and $r_R = k_1K_AK_BC_AC_B - k_2K_RK_BC_RC_B$, into Eqs. (18) and (19) they were solved by the computer for $u_A = u_B$, $u_R \neq u_B$, and $C_B{}^0 = 2C_A{}^0$. The relation between the conversion, X, and the yield of R, Y_R, is shown in Fig. 10. Y_R for the pulse technique is larger than that in the flow technique

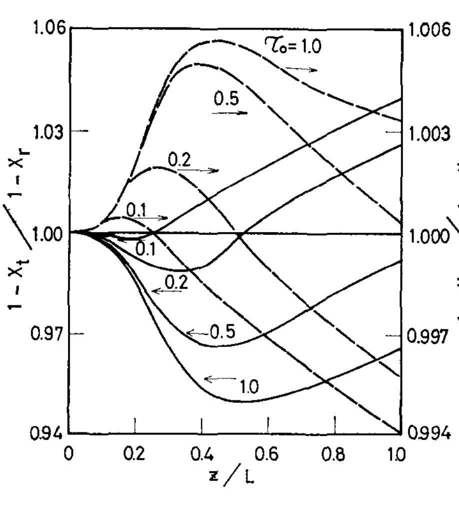

FIG. 9.

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* Assuming $u_A \neq u_S$ the result may remain unchanged.

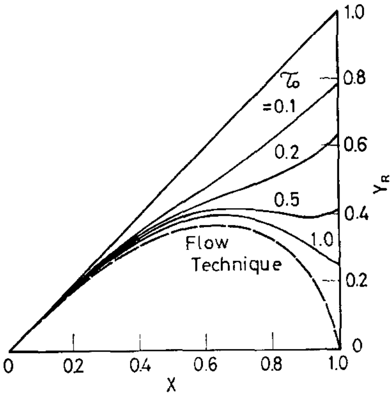

FIG. 10.

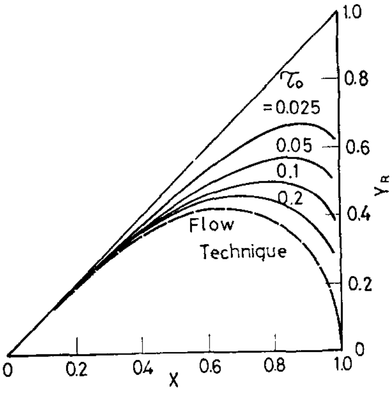

FIG. 11.

illustrated by the lower dotted line, and the deviation from the flow technique increases with decreasing pulse width. The conversion of A is slightly larger and that of B is smaller than in the flow technique, and the differences in the conversions between the techniques also increase with decreasing pulse width.

(*F*) $A \rightarrow R,\ 2R \rightarrow S$

On substituting the rate expressions, $r_A = -k_1K_AC_A$ and $r_R = k_1K_AC_A - k_2K_R{}^2C_R{}^2$, into Eqs. (18) and (19), they were solved by the computer. Figure 11 illustrates that Y_R is larger than that in the flow technique at any total conversion, but the difference between the results for the techniques is less than that in reaction (E). Total conversion of A is equivalent to that in the flow technique.

DISCUSSION OF RESULTS

The results of the present study show that kinetic data from the pulse technique are in agreement with those from the flow technique in any linear reactions which do not involve the rate processes other than first order, although it has been known that this relation holds for the individual reaction models like $A \rightarrow R$ (*1, 2, 6*), $A \rightleftharpoons R$ (*6*) or $A \rightarrow R \rightarrow S$ (*6*).

In the nonlinear reactions, such as (B), (C), (D), (E), and (F), there are remarkable differences in the results from the techniques. That is, the reactions (C) and (D) can proceed over their equilibrium conversions, and in the reactions (E) and (F) the yields of intermediate product R obtained by the pulse technique are much larger than that for the flow technique. The differences are caused mainly by the following three factors: The first is the separation of zones due to the difference of moving velocities and has the largest effect among the three. In the reaction (D) the rate of reverse reaction $R + S \rightarrow A$ falls because R once separated from S is impossible to react any more. The deviation of the conversion increases with the characteristic moving velocity ratio v below 2 and then is settled, as shown in Fig. 12. The effect of pulse width τ_0 on the conversion is remarkable in the range of τ_0 below unity, as shown in Fig. 13. In Figs. 7 and 8, when $\tau_0 = 1$ the separation of zone of R from that of S is so incomplete that the conversion is close to that for the flow technique, but

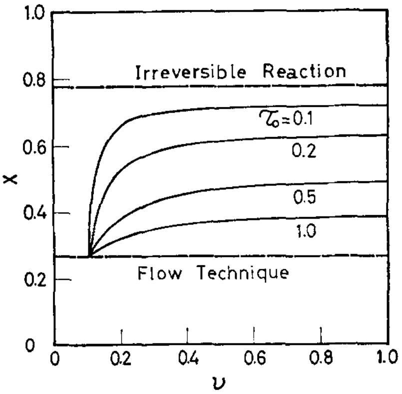

FIG. 12.

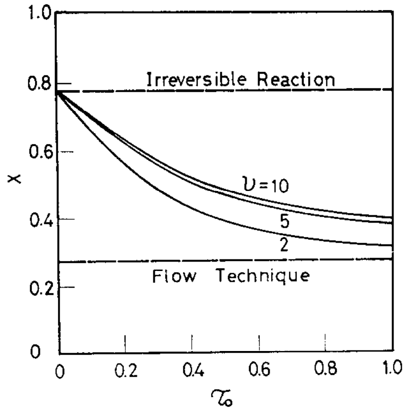

FIG. 13.

when $\tau_0 = 0.1$ the majority of R is separated and the conversion is close to that without the reverse reaction, and if $\tau_0 = 0$, all the molecules of R will be separated from S and the conversion will be equivalent to that in the irreversible reaction. Also in reaction (E), the rate of the second step reaction $R + B \rightarrow S$ falls because of the separation of R from B. It follows therefore that the yield of R is larger and the conversion of B is smaller than in the flow technique. Slightly larger conversion of A is due to the low conversion, in other words, the high concentration of B.

The second is the lowering of the concentration of the products owing to the broadening of zone observed in reactions (C) and (F). Since the product R is formed continuously during the passage of the reactant through the catalyst bed, the zone of R abnormally broadens and the concentration of R lowers, which reduces the rate of the reverse reaction of (C), $2R \rightarrow A$, and of the second step reaction of (F), $2R \rightarrow S$, both with the second order kinetics in respect to R. The deviation of the conversion or the yield from the flow technique increases with the characteristic moving velocity ratio and with decreasing pulse width.

The last factor leading to the disagreement in the results from these techniques is the initial concentration of pulse. In the nth order irreversible reaction the difference by this factor can be reduced by using the average initial concentration of pulse defined by Eq. (27), as mentioned above. In reaction (C), $A \rightleftharpoons 2R$, the initial concentration has a larger effect on the reverse reaction rate than on the forward one because of the difference in kinetic orders. If the pulse width is sufficiently small, the reverse reaction can be neglected and the pulse shape has no effect on the conversion. With increasing pulse width, the role of the reverse reaction grows larger so that the effect of pulse shape becomes larger. But the effect of pulse shape is essentially small in this reaction, as shown in Fig. 5. In reaction (D), the effect of pulse shape is larger than in reaction (C) as shown in Fig. 9. Although the initial concentration has a larger effect on the reverse reaction rate than on the forward one, similarly to reaction (C), the shape of the pulse has an effect on the separation of zone of R from that of S. The triangular and the error function pulses are broader than the rectangular pulse, even if they have the same value of t_0, and the effectiveness of the separation becomes small with spreading inlet pulse, which is the reason why $1 - X_t$ is larger than $1 - X_r$ in the tail part of the catalyst bed, as shown in Fig. 9.

APPLICATION FOR KINETIC MEASUREMENTS

In the linear reactions, as mentioned above, the same results are obtained by both pulse and flow techniques, therefore one can use the pulse technique in place of the flow technique and determine kinetic constants in the usual manner by the pulse technique. Furthermore, if one gets the same conversion or product distribution at the injection of the various amounts of the reactant, the reaction may be regarded as linear. In the nth order irreversible reaction the reaction rate constant can be determined in the following way: Plotting $(1 - X)^{1-n}$ against contact time, the slope of the resulting line is approximately equivalent to $(n - 1)kK_A{}^n\overline{C_A}{}^{0\,n-1}$. If the shape of the pulse at the inlet of catalyst bed is known, the average initial concentration of pulse can be determined by Eq. (27). Dividing the slope of the above-mentioned plot by $(n - 1)\overline{C_A}{}^{0\,n-1}$, one gets an approximate value of the overall reaction rate constant, $kK_A{}^n$.

In these cases kinetic measurement is carried out on the basis of complete or approximate conformity of the results from the pulse and the flow techniques. On the other hand in reactions such as $A \rightleftharpoons 2R$ and $A \rightleftharpoons R + S$, there are remarkable differences between the techniques. But if one makes the best use of the special character of the pulse technique, some new information can be obtained. For example, in the reaction $A \rightleftharpoons R + S$, by extrapolating the pulse width to zero, one can get the conversion without the reverse reaction and the kinetic constants of the forward reaction. In the following paper (*7*), the effect of the pulse width on the catalytic cracking of cumene was studied by the pulse technique with the rectangular pulse, and the activation energy of the forward reaction was determined in such a manner. Further the reaction scheme of diisopropylbenzene formation was studied using the characteristics of the pulse technique.

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