

## Study on the Pulse Reaction Technique

### III. Pulse Reaction Kinetics with Langmuir Isotherm

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A theoretical investigation of the pulse reaction technique has been carried out on several reaction models with the Langmuir adsorption isotherm, and the conversions have been compared with those from the flow technique. In all the reaction models treated the conversions are larger than those from the flow technique and increase with a decrease in the pulse width. It is the lowering of concentrations due to the broadening of peaks that results in the larger conversions than those from the flow technique. In the reaction of  $A \rightleftharpoons R + S$ , the separation between the components has a large effect, too. When an adsorption equilibrium is not established, the deviation from the flow technique is much larger than that when an adsorption equilibrium is established; this is a result of the bare initial surface coverage.

The pulse reaction technique has been widely used to measure catalytic activity mainly because it is more convenient than the continuous flow technique. Recently, however, some attempts have been made to use it in order to get additional information which can be got only with difficulty by the flow technique (1, 2, 3). Such a use of the technique requires sufficient knowledge of the characteristics of the pulse reaction system. In order to ascertain the characteristics of the pulse reaction system, several articles have been devoted to the theoretical analysis of a few reaction models (4, 5, 6). The present authors also made a theoretical analysis of several reaction models and showed that the results from the pulse technique agree with those from the flow technique in the linear reactions, excluding the rate processes other than first order, while in the nonlinear reactions there are sometimes quite remarkable differences between the two techniques (7, 8).

All of these theoretical investigations were made on the basis of the following assumptions: (1) All the components of the reactants and the products in the gas phase move as a plug flow with a linear velocity

$u$  together with a carrier gas. (2) The influence of mass transfer onto the catalyst surface is negligible. (3) There is no change in volume or temperature due to the reaction. (4) A linear adsorption equilibrium is established between the gas and the catalyst surface. Assumptions (1)–(3) can be satisfied by adopting adequate reaction conditions. Assumption (4) may be practical when there are low pressures of reactants and products. However, it can not always be regarded as proper, for sometimes chromatographic peaks are broadened abnormally and asymmetric peaks are obtained.

Real adsorption isotherms are usually classified into five types, four of which are associated with the formation of multilayers and with the capillary condensation of gas (9). Only one type is associated with the isotherms of chemisorption, such as the Langmuir, Freundlich, and Slygin-Frumkin isotherms. The Langmuir isotherm is the most famous and is the most frequently used in kinetic interpretations of heterogeneous catalysis.

In the present study, the pulse reaction kinetics with the Langmuir isotherm, i.e., Langmuir-Hinshelwood kinetics, was

analyzed mathematically in the case of an adsorption equilibrium established ( $A \rightarrow R$ ,  $A \rightleftharpoons R$ , and  $A \rightleftharpoons R + S$ ) and in that of an adsorption equilibrium not established ( $A \rightarrow R$ ).

NOMENCLATURE

- $b_i$  Adsorption equilibrium constant for the Langmuir isotherm (cm<sup>3</sup>/mole)
- $C_i$  Concentration of component  $i$  in the gas phase (mole/cm<sup>3</sup> of bed)
- $C_A^0$  Concentration of inlet pulse (mole/cm<sup>3</sup> of bed)
- $f_i$  Fraction of surface covered by component  $i$
- $k$  Reaction rate constant
- $k_{ai}$  Adsorption rate constant of component  $i$  (sec<sup>-1</sup>)
- $K$  Equilibrium constant
- $K_i$  Adsorption equilibrium constant for the linear isotherm,  $K_i = q^0 b_i$
- $L$  Length of catalyst bed (cm)
- $q^0$  Amount of adsorbed molecules at full coverage (mole/cm<sup>3</sup> of bed)
- $r_i$  Rate of formation of component  $i$  (mole/cm<sup>3</sup> sec)
- $t$  Time (sec)
- $t_0$  Pulse width (sec)
- $u$  Moving velocity of carrier gas (cm/sec)
- $X$  Conversion
- $X_F$  Conversion in the flow technique
- $X_L$  Conversion in the case of the linear isotherm
- $z$  Distance down catalyst bed (cm)
- $\Delta X$  Deviation from the flow technique, defined by Eq. (14)
- $\eta_i$  Dimensionless concentration of  $i$ ,  $C_i/C_A^0$
- $\theta$  Residence time of carrier gas,  $L/u$  (sec)
- $\lambda$  Ratio of  $C_A^0$  to  $q^0$
- $\tau$  Dimensionless time,  $t/\theta$
- $\tau_0$  Dimensionless pulse width,  $t_0/\theta$

Method of Mathematical Analysis

Adsorption equilibrium not established.

The basic equation expressing the mass balance within the catalyst bed is given as follows:

$$\frac{\partial C_i}{\partial t} + q^0 \frac{\partial f_i}{\partial t} = -u \frac{\partial C_i}{\partial z} + r_i \quad (1)$$

The concentration change on the catalyst

surface is equal to the sum of the adsorption rate,  $r_{ai}$ , and the reaction rate,  $r_i$ :

$$q^0 \frac{\partial f_i}{\partial t} = r_{ai} + r_i \quad (2)$$

In the case of the Langmuir isotherm,

$$r_{ai} = k_{ai} \{ (1 - \sum_j f_j) C_i - (f_i/b_i) \} \quad (3)$$

**Adsorption equilibrium established.** When a Langmuir adsorption equilibrium is established there is a well-known relationship between  $C_i$  and  $f_i$ :

$$f_i = b_i C_i / (1 + \sum_j b_j C_j) \quad (4)$$

The substitution of Eq. (4) into Eq (1) gives

$$\left\{ 1 + q^0 b_i \frac{1 + \sum_k b_k C_k}{(1 + \sum_j b_j C_j)^2} \right\} \frac{\partial C_i}{\partial t} - q^0 \frac{b_i C_i}{(1 + \sum_j b_j C_j)^2} \sum_k b_k \frac{\partial C_k}{\partial t} = -u \frac{\partial C_i}{\partial z} + r_i \quad (5)$$

where  $k \neq i$ . Replacing the variables in this equation with dimension less ones results in

$$\sum_j a_{ij} \frac{\partial \eta_i}{\partial \tau} = d_i \quad (6)$$

where

$$a_{ii} = 1 + K_i \frac{1 + \sum_k K_k \lambda \eta_k}{(1 + \sum_j K_j \lambda \eta_j)^2}$$

$$a_{ik} = -K_i \frac{K_k \lambda \eta_i}{(1 + \sum_j K_j \lambda \eta_j)^2}$$

$$d_i = -\frac{\partial \eta_i}{\partial (z/L)} + \bar{r}_i \quad (7)$$

and where  $\bar{r}_i$  is a dimensionless reaction rate. Rearranging Eq. (6) gives

$$\frac{\partial \eta_i}{\partial \tau} = \frac{D_i}{D} \quad (8)$$

where  $D$  is a determinant whose typical element is  $a_{mn}$ , and where  $D_i$  is exactly the same as  $D$  except that the  $i$ th column of  $D$  has been replaced by the column of  $d_i$  to give  $D_i$ .

The initial and the boundary conditions are the same as those in the case of the linear isotherm (7):

$$\text{at } t = 0 \text{ and } L \geq z \geq 0, \quad C_i = f_i = 0 \quad (9)$$

When the reactant, A, is fed as a rectangular pulse with a concentration of  $C_A^0$  and a pulse width of  $t_0$ , the boundary conditions at the inlet are given as follows:

$$\text{at } t_0 \geq t \geq 0, \quad C_A = C_A^0$$

and

$$\text{at } t > t_0, \quad C_A = 0 \quad (10)$$

The sets of Eqs. (1) and (2) or Eq. (8) were solved numerically by a NEAC-2203 digital computer after replacing the derivatives with the simplest difference representations and after rearranging.

### RESULTS AND DISCUSSION

It is well known that the Langmuir isotherm gives two limiting types of behavior. When the adsorption coefficient is sufficiently small ( $K_i\lambda \ll 1$ ), the isotherm is reduced to the linear isotherm

$$f = b_i C_i \quad (11)$$

On the other hand, at a sufficiently large adsorption coefficient ( $K_i\lambda \gg 1$ )

$$f_i = 1 \quad (12)$$

In the present study the adsorption coefficients comparable to unity were adopted for treating the most characteristic situation.\*

The ratio,  $\lambda$ , of  $C_A^0$  to  $q^0$ , would have the value of  $1 \sim 10^{-3}$ , because  $C_A^0$  is about  $10^{-6}$  mole/cm<sup>3</sup> at an atmospheric pressure of 10% and  $q^0$  is between  $10^{-6}$  [the chemisorption of hydrogen on a tungsten powder (10)] and  $10^{-3}$  mole/cm<sup>3</sup> [the number of acidic sites on the silica-alumina catalyst (11)]. In the present study, analysis was made in the case of  $\lambda = 0.1$ . Even at  $\lambda \neq 0.1$ , however, the results remain unchanged if  $K_i\lambda$  is equivalent to that of the analyzed case; the deviations of the conversions at  $K_i = 5$  and  $\lambda = 0.1$  from those at  $K_i = 50$  and  $\lambda = 0.01$  were less than 0.2%.

#### *A → R, Adsorption Equilibrium Established*

On substituting the reaction rate expression (13) into Eq. (8), the continuity equations for A and R were solved by the computer:

\* The case of  $K_i, \lambda \gg 1$  will be treated later.

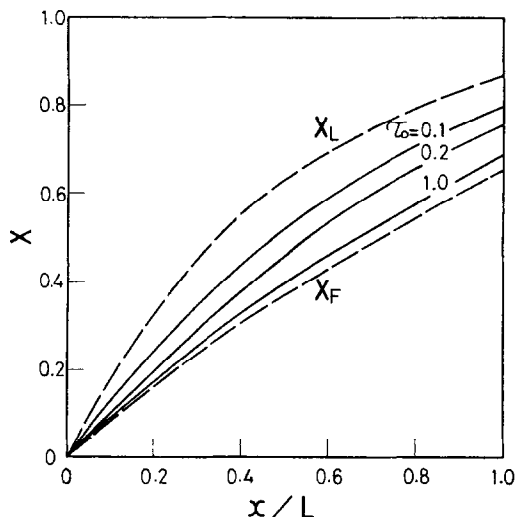


FIG. 1. Conversion as a function of bed length at different pulse widths in  $A \rightarrow R$  (adsorption equilibrium established);  $k_1 K_A \theta = 2$ ,  $K_A = 14$ ,  $K_R = 0.5$ ,  $\lambda = 0.1$ .

$$r_A = -r_R = -k_1 q^0 \frac{b_A C_A}{1 + b_A C_A + b_R C_R} \quad (13)$$

The relation of the conversion to the length of the catalyst bed is shown in Fig. 1, and that of  $\Delta X$  is shown in Fig. 2.  $\Delta X$ , which represents the deviation from the flow

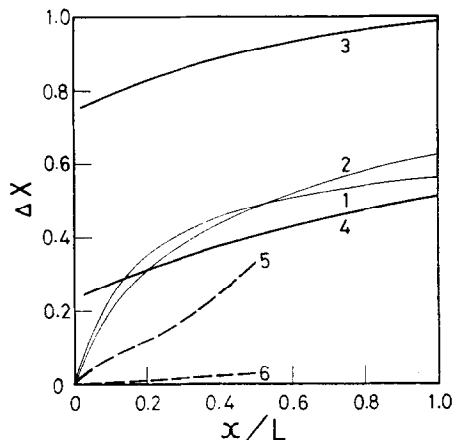


FIG. 2. Deviation from the flow technique;  $\lambda = 0.1$  Fine lines:  $A \rightarrow R$  (adsorption equilibrium established);  $k_1 K_A \theta = 2$ ,  $\tau_0 = 0.1$ ,  $K_A = 5$ , (1)  $K_R = 0.5$ , (2)  $K_R = 5$ . Thick lines:  $A \rightarrow R$  (adsorption equilibrium not established);  $k_1 K_A \theta = 2$ ,  $k_{aA} \theta = k_{aR} \theta = 4$ ,  $K_A = 5$ ,  $K_R = 0.5$ ; (3)  $\tau_0 = 0.1$ ; (4)  $\tau_0 = 0.5$ . Dashed lines:  $A \rightleftharpoons R$  (adsorption equilibrium established);  $k_1 K_A \theta = 2$ ,  $K = 0.5$ ,  $K_A = 50$ ,  $K_R = 5$ ; (5)  $\tau_0 = 0.1$ , (6)  $\tau_0 = 1$ .

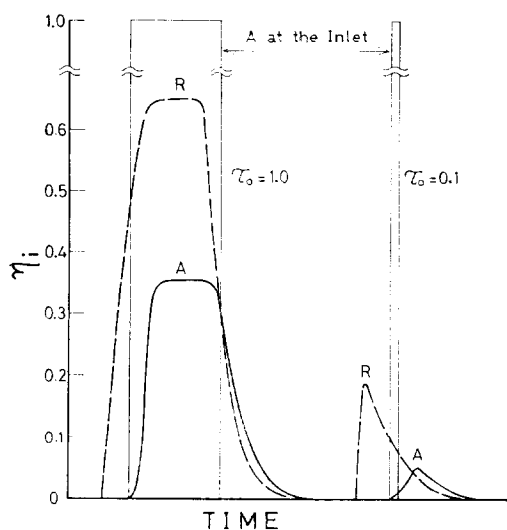


FIG. 3. Concentration profiles at the end of the catalyst bed in  $A \rightarrow R$  (adsorption equilibrium established);  $k_1 K_A \theta = 2$ ,  $K_A = 14$ ,  $K_R = 0.5$ ,  $\lambda = 0.1$ .

technique, is defined by Eq. (14) and is equivalent to zero in the flow technique and to unity in the case of the linear isotherm

$$\Delta X = \frac{X - X_F}{X_L - X_F} \quad (14)$$

where  $X_F$  is the conversion in the Langmuir isotherm obtained by the flow technique and where  $X_L$  is that in the linear isotherm.

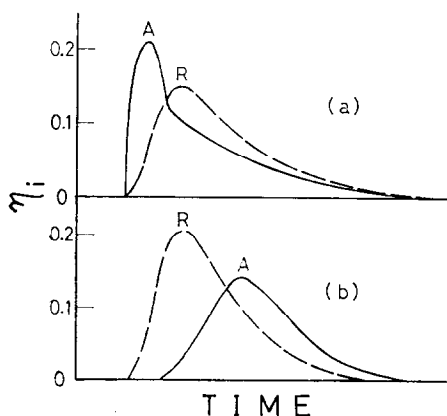


FIG. 4. Concentration profiles at  $z = L/2$  in  $A \rightarrow R$ ;  $k_1 K_A \theta = 2$ ,  $K_A = 5$ ,  $K_R = 0.5$ ,  $\lambda = 0.1$ ,  $\tau_0 = 0.1$ . (a) Adsorption equilibrium is not established.  $k_{aA} \theta = k_{aR} \theta = 4$ . (b) Adsorption equilibrium is established.

Figures 3 and 4b show the concentration profiles at the end of catalyst bed.

As can be seen from Fig. 1, the conversion in the pulse technique lies between that in the flow technique (lower dotted line) and that in the linear isotherm (upper dotted line), and the pulse width, defined by Eq. (15), has a great effect on the conversion

$$\tau_0 = t_0 / \theta (1 + K_A) \quad (15)$$

It was shown in a previous paper (8) that in the case of the linear reactions with no rate processes other than first order, results from the pulse technique are in agreement with those from the flow technique. In the present case, the order of reaction is unity with respect to the concentration of adsorbed molecules, but below unity with respect to the concentration in the gas phase. In the reaction with the order below unity, a lower concentration results in a larger conversion. In the case of a nonlinear isotherm, the zone of each component broadens and the concentration lowers considerably, as can be seen from Figs. 3 and 4b, so a larger conversion than that in the flow technique is obtained in the pulse technique. The effect of the pulse width can be explained in the same way. As is shown in Fig. 3, the zone of A with a smaller pulse width broadens more remarkably than that with a larger pulse width; in other words, the concentration of A with a smaller pulse width is lower than that with a larger one. Therefore a smaller pulse width results in a larger conversion.

The difference between the pulse and the flow techniques is mainly due to the lowering of the concentration, but the separation between the components has little effect. Even when  $K_A = K_R$ , when, that is, the adsorption strength of A is equivalent to that of R, conversion in the pulse technique is larger than that in the flow technique (curve 2 in Fig. 2). Furthermore,  $\Delta X$  in the case of  $K_A = K_R$  (curve 2 in Fig. 2) is approximately equivalent to that in the case of  $K_A = 10K_R$  (curve 1).

$A \rightarrow R$ , Adsorption Equilibrium  
Not Established

After the reaction rate expressions,  $r_A = -r_R = -k_1 q^0 f_A$ , had been substituted into

Eqs. (1) and (2), they were solved by the computer. Much as with reaction (A) the conversion lies between  $X_L$  and  $X_F$ , as is shown by the thick lines in Fig. 2, but the deviation from the flow technique is larger than that in (A) shown by the fine lines in Fig. 2. The difference between the techniques is caused by the following two factors: the lowering of the concentration due to the broadening of the zone mentioned above, and the difference in the initial surface coverage, which results in a larger deviation from the flow technique than that in (A). In the pulse technique, no molecule adsorbs on the catalyst surface before reactants are introduced. Thus the front of the zone is always in contact with the bare surface, where the adsorption rate is equivalent to that in the linear isotherm because the  $(1 - \sum_i f_i)$  term in Eq. (3) is reduced to unity. However, the surface coverage rapidly increases with the lapse of time. For example, when the adsorption of R can be neglected the coverage of A at the top of the catalyst bed increases exponentially, as is shown by the following equation:

$$f_A = \frac{1 - \exp\{-[k_{aA}\lambda + (k_{aA}/K_A) + k_1]t\}}{1 + (1/K_A\lambda) + (k_1/k_{aA})}$$

For that reason, the effect of this factor rapidly decreases with an increase in the pulse width, as can be seen from a comparison of curves 3 and 4 in Fig. 2.

Figure 4a and b show the concentration profiles of A and R at  $z = L/2$  in the case of the adsorption equilibrium not established and established, respectively. The most remarkable difference between Fig. 4a and b is the shape of the A peak. The sharp part at the front of A consists of the molecules flowing through the catalyst bed without any interaction with the catalyst surface, while the gradually declining part consists of the molecules flowing through the catalyst bed with repeated adsorption and desorption.

When the adsorption equilibrium is established, there is no difference between the pulse and the flow techniques at the top of the catalyst bed, as is shown in Fig. 2. It is peculiar to the case of the adsorption equilibrium not established that there is

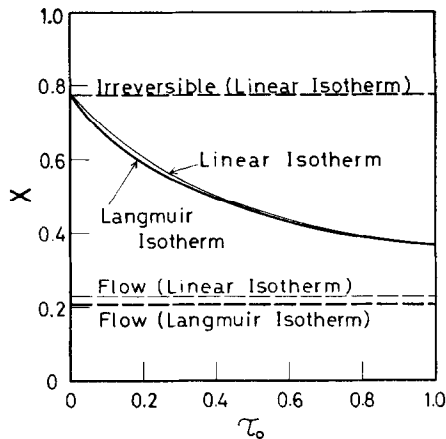


Fig. 5. Effect of the pulse width on the conversion in  $A \rightleftharpoons R + S$  (adsorption equilibrium established);  $k_1K_A\theta = 1.5$ ,  $K/C_A^0 = 0.1$ ,  $K_A = K_B = 4$ ,  $K_R = 0$ ,  $\lambda = 0.1$ .

a remarkable difference between the techniques at the top of the catalyst bed.

#### $A \rightleftharpoons R$ , Adsorption Equilibrium Established

After the reaction rate expression (16) had been substituted into Eq. (8), the

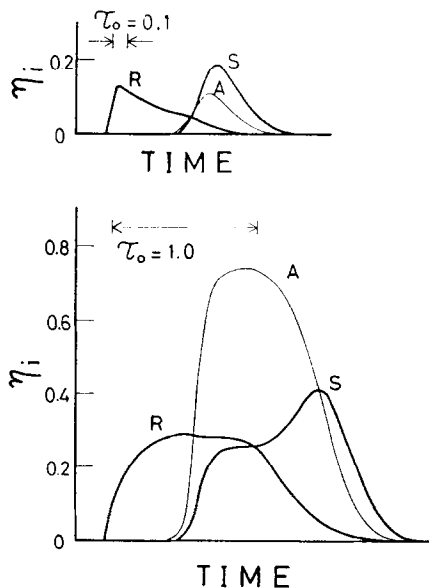


Fig. 6. Concentration profiles at the end of the catalyst bed in  $A \rightleftharpoons R + S$  (adsorption equilibrium established);  $k_1K_A\theta = 1.5$ ,  $K/C_A^0 = 0.1$ ,  $K_A = K_B = 4$ ,  $K_R = 0$ ,  $\lambda = 0.1$ .

continuity equations for A and R were solved by the computer

$$r_A = -r_R = -\frac{k_1q^0b_A C_A - k_2q^0b_R C_R}{1 + b_A C_A + b_R C_R} \quad (16)$$

In this case also a larger conversion than that in the flow technique is obtained, as is shown by the dotted lines in Fig. 2; this is a result of the lowering of the concentration. However, the conversion in the pulse technique can not be more than that in an equilibrium, because the rate of the reverse reaction as well as that of the forward reaction is accelerated.

$A \rightleftharpoons R + S$ , *Adsorption Equilibrium*  
*Established*

After the reaction rate expression (17) had been substituted into Eq. (8), the continuity equations were solved by the computer for the case of  $b_A = b_S$  and  $b_R \approx 0$

$$r_A = -r_R = -r_S = -\frac{k_1q^0b_A C_A - k_2q^0b_R b_S C_R C_S}{(1 + b_A C_A + b_R C_R + b_S C_S)^2} \quad (17)$$

The dependency of the conversion upon the pulse width is shown in Fig. 5, where the fine line shows the dependency for the case of the linear isotherm, while the concentration profiles at the end of the catalyst bed are shown in Fig. 6. As is shown in Fig. 5, the conversion in the pulse technique lies between that in the flow technique and that without the reverse reaction with the linear isotherm, and it increases with a decrease in the pulse width. It is not only the lowering of the concentration but also the separation of the zone of R from that of S that causes the larger conversion than that in the flow technique. The rate of the reverse reaction,  $R + S \rightarrow A$ , falls because R, once separated from S, can no longer react, just as in the case of the linear isotherm (8). The effects of both factors increase with a decrease in the pulse width. As Fig. 6 shows, the concentrations of A, R,

and S lower considerably and the zone of R is separated from S at  $\tau_0 = 0.1$ , while at  $\tau_0 = 1.0$  the concentrations are quite high and the separation is insufficient. However, the difference between the pulse and the flow techniques is not very large considering that there is one more cause of the conversion in the Langmuir kinetics being larger than that in the case of the linear isotherm. In the latter the larger conversion is caused by the separation alone, while in the former it is caused by the two factors mentioned above: the separation and the lowering of the concentration. However, the broadening of the peaks, which results in a lowering of the concentrations, reduces the degree of separation; this is the reason why the conversion in the Langmuir isotherm are not as large as those in the linear isotherm.

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