DETERMINATION OF MECHANISM OF CATALYZED GASEOUS REACTIONS

K. H. YANG and O. A. HOUGEN

University of Wisconsin, Madison, Wisconsin

IN the industrial applications of kinetics a knowledge of the mechanisms of chemical reactions is helpful in establishing the optimum conditions of operation relative to such variables as pressure, temperature, feed composition, space velocity, extent of conversion, and recycling.

This paper is written as a guide in the planning of experimental programs in applied kinetics and as an aid to the selection of the mechanisms of catalytic reactions. It has been observed that much time is lost in failing to pursue an orderly experimental program, and in failing to recognize the important variables. Often it is discovered after years of experimental effort that the important variables were not investigated.

In a previous paper by Hougen and Watson (2) various mechanisms which may be encountered in gaseous reactions when catalyzed by solid surfaces were developed with appropriate mathematical equations for expressing rates.

In a large measure the concepts of chemical kinetics used in this paper also stem from the work of Eyring and associates.

In any given chemical process several reactions may be proceeding consecutively or simultaneously but for each reaction it may be assumed that only one or two chemical steps are rate-controlling. From the standpoint of theoretical kinetics this assumption is not acceptable, but it usually serves as a satisfactory basis for practical purposes.

Where a gaseous reaction is catalyzed by flowing the gas through a bed of solid catalyst pellets, the physical steps involved are the transfer of the component gases up to the catalyst surface, diffusion of reactants into the interior of the pellet, diffusion of products back to the exterior surface, and transfer of the products from the exterior surface to the main stream. These physical steps are usually present. To simplify the interpretation of experimental data

it is desirable to minimize the resistance offered by each of these physical steps and thus to deal only with the chemical aspects of the reaction.

The chemical steps involve activated adsorption of reactants with or without dissociation, surface reactions on active sites, and activated desorption of products. The uncatalyzed reaction also takes place in the main gas stream simultaneously with the surface reaction. This last should be of negligible importance where an effective catalyst is used.

In addition to the above possibilities, fouling and changes in the activity of the catalyst may take place.

It is evident that an experimental study of all these possible effects simultaneously is prohibitive because of complexity. It is desirable, therefore, that experimental procedures be arranged to permit separate determination or separate elimination of these different effects. Resistances to the transfer of mass and heat can be minimized by operating at sufficiently high mass velocities to make the partial pressure and temperature gradients across the gas film negligible. The retarding effect of diffusion of reactants and of products in the interior of the catalyst pellet can be minimized by using pellets of small size. The effect of fouling can be eliminated by extrapolating rate data to the beginning time of catalyst service and the effect of changing activity can be eliminated by continued use of the catalyst until a stable steady state has been attained.

The means of minimizing the various physical steps and the effects of fouling and deactivation will be analyzed separately.

Minimizing Resistances Due to Transfer of Mass and Heat. The general rate of a catalytic reaction in a flow system based upon unit mass of catalyst is given by the relation,

$$r_A dW = F dx_A \qquad (1)$$

where

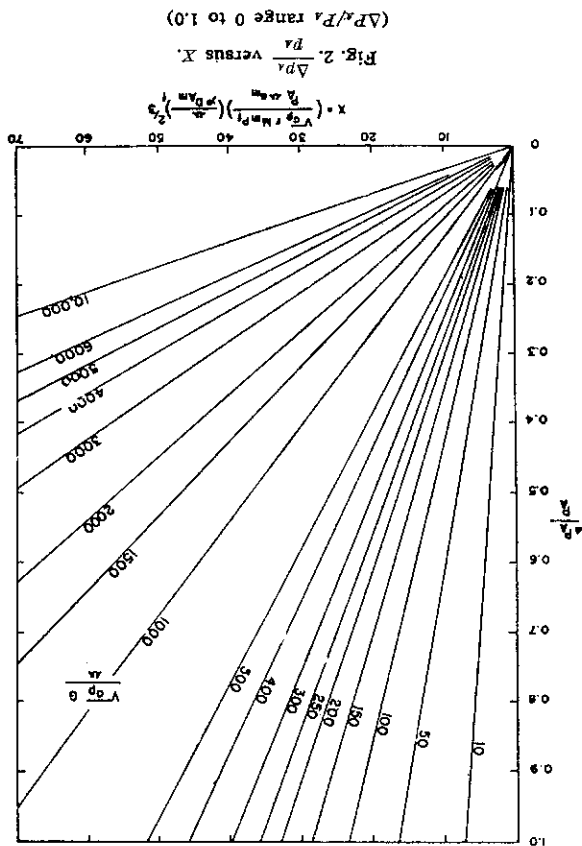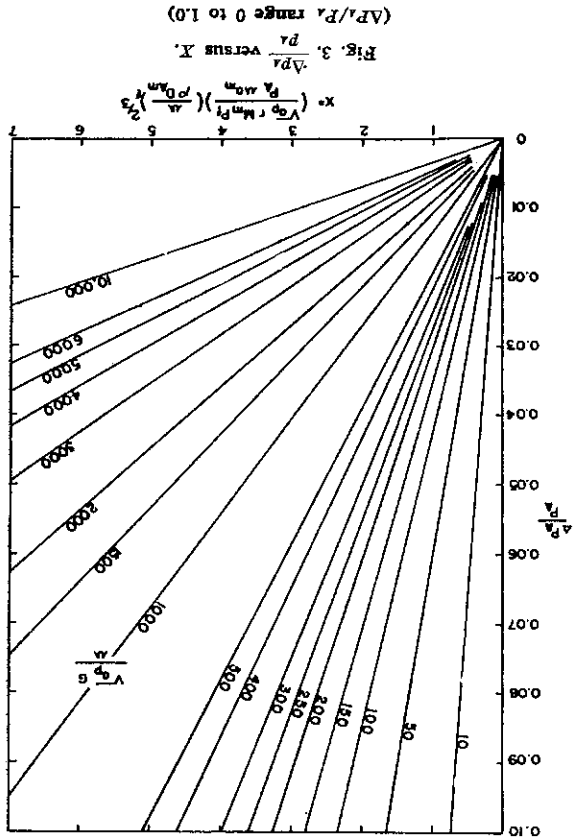r_A = moles of reactant A converted per (unit time) (unit mass of catalyst)

F = flow rate of feed, moles per unit time

W = mass of catalyst

x_A = moles of reactant A converted per mole of feed

Values of the reaction rate r should be correlated against the conditions of composition and temperature which prevail at the surface of the catalyst where the catalytic reaction actually takes place. From equations for mass and heat transfer the film gradients for partial pressures of each component gas and for temperature can be evaluated. However, this correction is troublesome, difficult, and uncertain. In experimental work it is desirable, if possible, to render these gradients insignificant by flowing the gas at high mass velocities. If the rate of a catalytic reaction is plotted against mass velocity the rate increases progressively from a value at zero mass velocity to an asymptotic value at high velocities as shown in Figure 1. It is desirable to operate at sufficiently high velocities so that film gradients become negligible. The value of r at zero mass velocity is the reaction rate obtained in a nonflow system. It is evident from Figure 1 that reaction rates calculated from equal residence times in nonflow and flow systems are not the same. In general catalytic reaction rates obtained in nonflow systems are not applicable directly to flow systems. Indeed it is doubtful if reaction rate data taken in nonflow systems of gases catalyzed by solid surfaces and without agitation in the reactor are of any value in reactor design because of nonsteady state conditions and the uncertainty of concentration gradients due to natural convection within the bed.

The general equation for mass transfer is given as

Experimental data on mass transfer are related to k_G by the relationship:

$$j_d = \left(\frac{k_G M_m p_{bf}}{G}\right)\left(\frac{\mu}{p D_{Am}}\right)^{2/3} \tag{3}$$

Experimental data on values of j_d were obtained for mass transfer in a granular bed by Gamson, Thodos, Wilke, and Hougen (1, 6) and related to a modified Reynolds number, $\frac{\sqrt{a_p G}}{\mu}$ as follows:

$$j_d = a\left(\frac{\sqrt{a_p G}}{\mu}\right)^{-n} \tag{4}$$

where for values of

$\frac{\sqrt{a_p G}}{\mu}$ less than 620, $a = 2.44$ and $n = 0.51$; and for values of $\frac{\sqrt{a_p G}}{\mu}$ greater than 620, $a = 1.25$ and $n = 0.41$.

By a combination of Equations (2), (3), and (4), there results:

$$\frac{\Delta p_A}{p_A} = \frac{1}{a}\left(\frac{\sqrt{a_p}\, r M_m p_{bf}}{p_A u_{a m}}\right)\left(\frac{\mu}{p D_{Am}}\right)^{2/3}\left(\frac{\sqrt{a_p G}}{\mu}\right)^{n-1} \tag{5}$$

In Figure 2 values of $\Delta p_A/P_A$ are plotted against values of a reaction rate number X for different values of $\sqrt{a_p G}/\mu$ where

$$X = \left(\frac{\sqrt{a_p}\, r M_m p_{bf}}{p_A u_{a m}}\right)\left(\frac{\mu}{p D_{Am}}\right)^{2/3}$$

In Figure 3 values of $\Delta p_A/P_A$ over the limited range 0 to 0.1 are similarly plotted. Figure 4 is a cross plot of Figure 3 where X is plotted against values of $\sqrt{a_p G}/\mu$ for values of $\Delta p_A/P_A$ equal to 0.1 and below. If the required experimental accuracy in reaction rates need not be greater than 10%, then the film gradient can be neglected if $\Delta p_A/P_A$ is 0.1 or less; for an accuracy of 1% the film gradient can be neglected if $\Delta p_A/P_A$ is 0.01 or less, and so forth. The film gradients become negligible where surface reactions proceed slowly and also at high partial pressures of the reactants. For example, from Figure 4 the following conditions prevail:

$\frac{\Delta p_A}{p_A}$	X	$\frac{\sqrt{a_p G}}{\mu}$
0.1	5	450
0.1	10	1700
0.01	5	25,000
0.01	10	80,000

Thus, if an accuracy of 10% is tolerated where the rate number X is 5, the modified Reynolds number should not be less than 450, whereas if 1% accuracy is required the modified Reynolds number should not be less than 25,000 for the same rate number.

The rate of mass transfer becomes entirely rate-controlling where $p_{Ai} = 0$ and $\Delta p_A/p_A = 1.0$. This limiting condition is approached with an ideal catalyst where surface reactions are instantaneous. Under these conditions the reac-

where

$$r = k_{G a_m}\Delta p \tag{2}$$

$$\Delta p = p_A - p_{Ai}$$

Fig. 1. Effect of Mass Velocity Upon Reaction Rates.

Fig. 2. $\dfrac{\Delta p_A}{p_A}$ versus X. ($\Delta P_A/P_A$ range 0 to 1.0)

Fig. 3. $\dfrac{\Delta p_A}{p_A}$ versus X. ($\Delta P_A/P_A$ range 0 to 1.0)
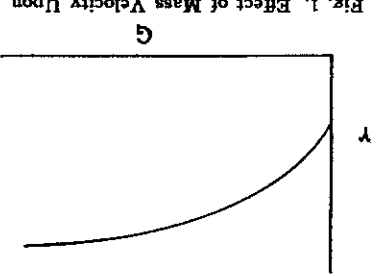
Fig. 4. X versus $\dfrac{\sqrt{a_p}G}{\mu}$ at Various Values of $\Delta P_A/P_A$.

Fig. 5. Limiting Values at X versus $\dfrac{\sqrt{a_p}G}{\mu}$
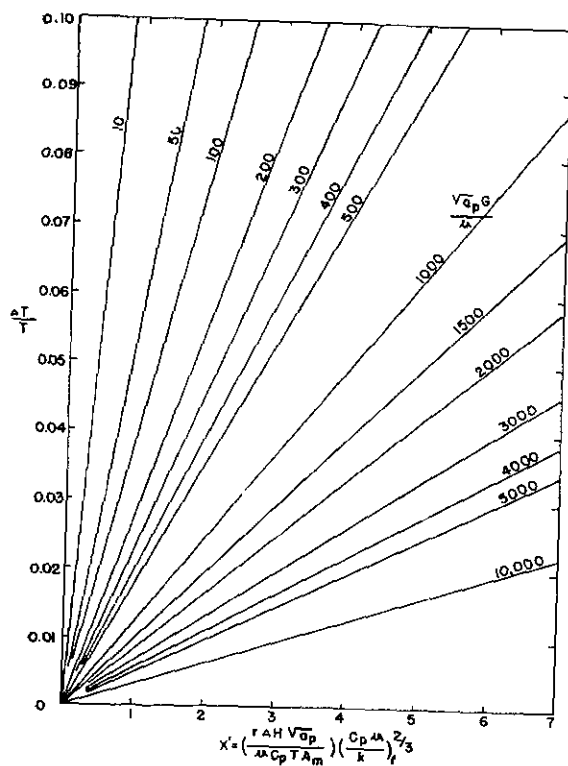
Fig. 6. $\dfrac{\Delta T}{T}$ versus X' at Various Values of $\dfrac{\sqrt{a_p}G}{\mu}$
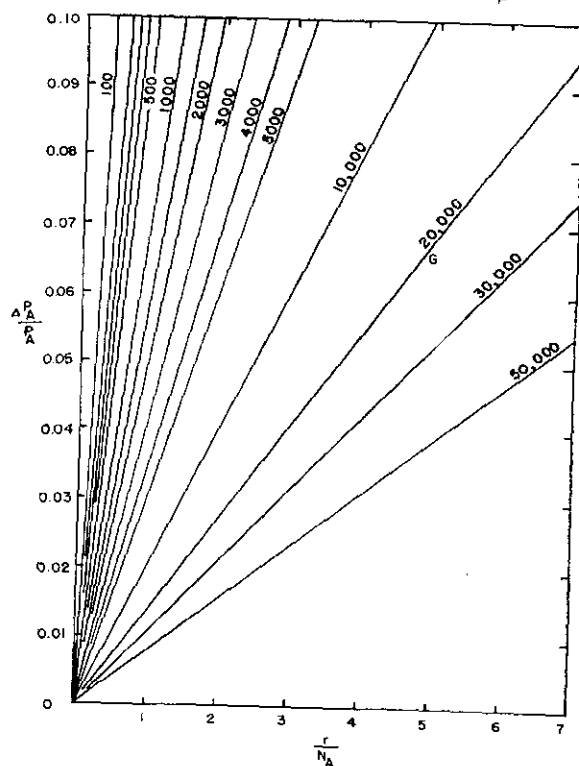
Fig. 7. $\dfrac{\Delta p_A}{p_A}$ versus $\dfrac{r}{N_A}$ at Various Values of G.
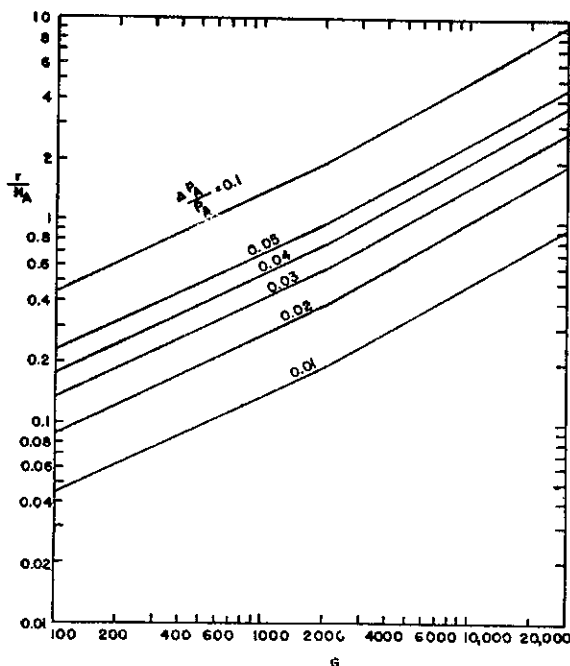
Fig. 8. $\frac{r}{N_A}$ versus G at Various Values of $\Delta P_A/P_A$ for a Specific System.
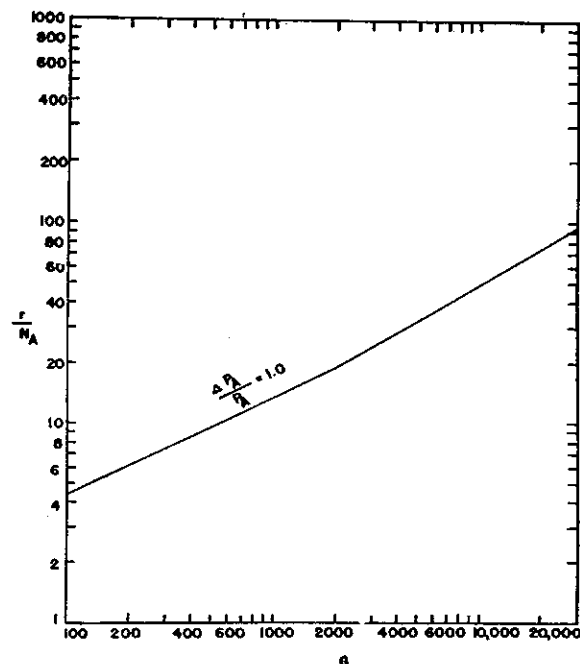
Fig. 9. Limiting $\frac{r}{N_A}$ versus G for a Specific System.

tion rate is controlled entirely by the rate at which the reactants can be brought up to the surface and the products returned. Equilibrium prevails at the interface. This limiting rate is shown by the relationships of Figure 5. Thus from Figure 5 mass transfer becomes entirely controlling and the rate number X cannot exceed the values given for the following modified Reynolds number:
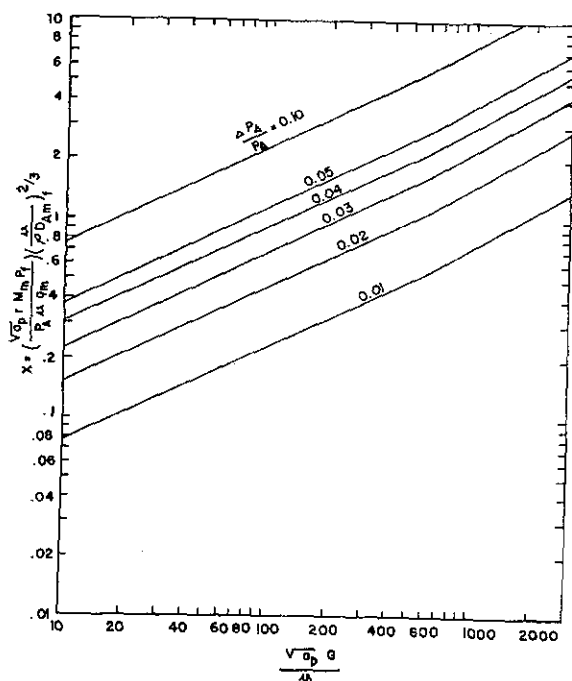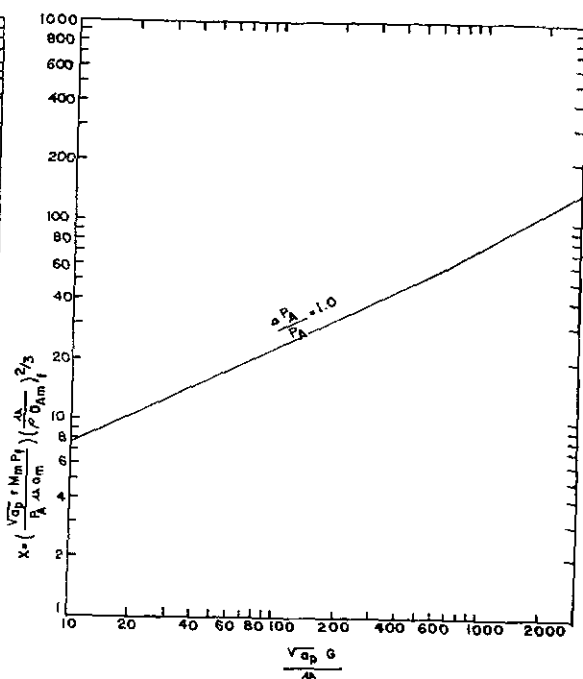
$\frac{\sqrt{a_p G}}{\mu}$	X
10,000	300
1,000	74
100	23
10	7.5

For example, when the modified Reynolds number is 100 the rate number X cannot exceed 23, which condition corresponds to the behavior of an ideal catalyst.

The general equation for heat transfer is given as

$$q = -h_G a_m \Delta t = -\Delta H r \qquad (6)$$

$$\Delta t = t - t_t$$

Experimental data on heat transfer are related to h_G by the relationship,

$$j_h = \left(\frac{h_G}{C_p G}\right)\left(\frac{C_p \mu}{k}\right)_f^{\frac{2}{3}} \qquad (7)$$

Experimental data on j_h were obtained for heat transfer in a granular bed (1, 6) and related as follows:

$$j_h = a'\left(\frac{\sqrt{a_p G}}{\mu}\right)^{-n} \qquad (8)$$

where for values of $\sqrt{a_p G}/\mu$ less than 620, $a' = 2.62$, $n = 0.51$, for values of $\sqrt{a_p G}/\mu$ greater than 620, $a' = 1.35$, $n = 0.41$. By a combination of Equations (6), (7), and (8) the result is

$$\frac{\Delta t}{T} = \frac{1}{a'}\left(\frac{r\Delta H \sqrt{a_p}}{a_m \mu C_p T}\right)\left(\frac{C_p \mu}{k}\right)_f^{\frac{2}{3}}\left(\frac{\sqrt{a_p G}}{\mu}\right)^{n-1} \qquad (9)$$

In Figure 6 values of $\Delta t/T$ are plotted against X' for various values of $\sqrt{a_p G}/\mu$ where

$$X' = \left(\frac{r\Delta H \sqrt{a_p}}{a_m \mu C_p T}\right)'\left(\frac{C_p \mu}{k}\right)_f^{\frac{2}{3}}$$

Film temperature gradients can be neglected if they do not exceed a few degrees Centigrade. If the required accuracy in reaction rates need not be greater than 10% then the film temperature gradient can usually be neglected if ΔT is less than 10° C. These values require verification for specific systems. It should be recognized that the temperature coefficient for reactions catalyzed by solid surfaces is much less than for noncatalytic ones because of the offsetting effects of desorption on the catalytic reactions.

A Hypothetical System. For a hypothetical system the following conditions

were:

Cylindrical pellets $\frac{1}{8} \times \frac{1}{8}$ in.,
$D = \frac{1}{8}$ in.; $D_p = \sqrt{1.5}\, D = 0.0127$ ft.

$a_p = \pi D_p^2 = 0.000507$ sq.ft.
$\mu = 300$ micropoises $= 0.0726$ lb./(hr.)(ft.)

$F_e = 0.40$

$a_v = \frac{6(1-F_e)}{D} = 346$ sq.ft./cu.

$\rho_B = 50$ lb./cu.ft.

$a_m = \frac{a_v}{\rho_B} = 6.92$ sq.ft./lb.

$M_m = 56$

$p_t = \pi$

$\pi = $ total pressure

$\Delta H = -10,000$ B.t.u./lb. mole A converted

$\left(\frac{\mu}{D_{Am}}\right)_f = 1.50$

$\left(\frac{C_p \mu}{k}\right)_f = 0.80$

$C_p = 0.70$ B.t.u./(lb.)(° R.)

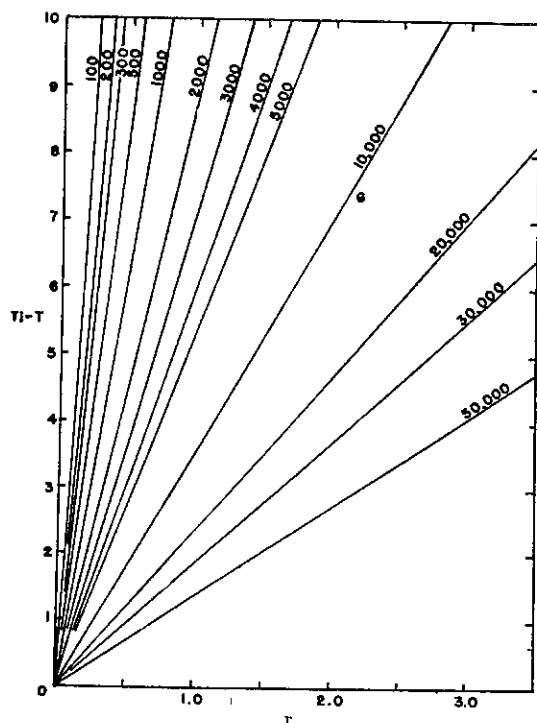at $\frac{\sqrt{a_p G}}{\mu} = 620$; $G = 2,000$ lb./(hr.) (sq.ft.)

Fig. 10 (T_i-T) **Versus** r **at Various Values of** G.

$$N_A = \frac{p_A}{\pi}$$

Then

$$\frac{\Delta p_A}{p_A} = \frac{a''r}{N_A G^{(1-n)}}$$

where

at values of $\sqrt{a_p}G/\mu < 620$;

$$a'' = 2.15; \quad n = 0.51$$

at values of $\sqrt{a_p}G/\mu > 620$;

$$a'' = 4.70; \quad n = 0.41$$

For this system values of $\Delta p_A/p_A$ are plotted against r/N_A for the various parameters of G (Fig. 7) for values of $\Delta p_A/p_A$ ranging from 0 to 0.1 and values of r/N_A are plotted against G for various parameters of $\Delta p_A/p_A$ in Figure 8. From Figure 7 the following values are obtained from this special system:

$\frac{\Delta p_A}{p_A}$	$\frac{r}{N_A}$	G
0.1	5	11,000
0.01	1	35,000

Thus if an error of 10% is tolerated the film gradient for mass transfer can be neglected for a reaction rate r/N_A equal to 5 when the mass velocity G is 11,000 lb./(hr.)(sq.ft.) or greater.

If the reaction at the catalyst surface is instantaneous then the ratio of $\Delta p_A/p_A$ becomes equal to 1.0 and the rate depends upon mass transfer alone.

For this specific system this case is plotted in Figure 9 and values of Δt are plotted against r for various parameters of G in Figure 10.

For this special system mass transfer becomes entirely controlling and the reaction rate r/N_A cannot exceed the following values for the given mass velocities (Fig. 9):

$\frac{\Delta p_A}{p_A}$	G	$\frac{r}{N_A}$
1.0	100	4.46
1.0	1,000	13.7
1.0	10,000	49.2

In order to keep the film temperature drop below 10° C. for this specific system at a reaction rate of $r = 1.0$, the mass velocity G should be 1600 or greater (Fig. 10).

It should be noted that the relationships given in Figures 2-10 are based upon experimental work for water vapor-air mixtures at relatively low temperatures and extrapolated through generally accepted relationships of the transport properties of gases. Extensive experimental work in this field should be encouraged to give greater certainty.

Effect of Size of Catalyst Pellet. The relationship between the effectiveness factor of a catalyst and its modulus are expressed by the relationship of Equation (10) first developed by Thiele [4] for a first-order gaseous reaction neglecting the effects of activated adsorp-

tion and variations in the porosity and permeability within a single pellet.

$$E = \frac{3}{m^2} (m \coth m - 1) \quad (10)$$

The modulus m may be related to pellet size, porosity, and temperature by the following (2):

$$m = \frac{a_1 D'_p e^{b/T}}{\sqrt{F_i}} \quad (11)$$

where

D'_p = diameter of sphere having the same surface area per unit volume as the particle. For a cylinder of height D equal to diameter,

$$D'_p = D = \frac{6}{a_m \rho_p}$$

F_i = interior void fraction of the pellet

ρ_p = density of pellets, mass per unit volume

By using two pellets of identical composition, porosity, and temperature but of different sizes the ratio of moduli is

$$\frac{m_1}{m_2} = \frac{D_1}{D_2} = a \quad (12)$$

By establishing reaction rates for two runs at nearly identical conditions of gas temperature and composition at the surface of the catalyst with these two pellets the following ratio prevails:

$$\frac{r_1}{r_2} = \frac{E_1}{E_2} = b \quad (13)$$

From Equations (10), (12), and (13),

$$am_2 \coth am_2 - 1 = ba^2(m_2 \coth m_2 - 1) \quad (14)$$

From Equations (14), m_2 can be calculated and m_1, E_1, and E_2 from Equations (10), (12), and (13).

The effectiveness factor approaches unity as the particle size is reduced. For establishing rate mechanisms it is desirable to operate with small catalyst pellets in order to minimize the effects of diffusional gradients inside the pellet and to attain effectiveness factors approaching unity. This procedure also minimizes the uncertainties due to time lag in attaining the steady state and to the assumptions made in deriving the relationship of E to m. Cylinders $\frac{1}{8} \times \frac{1}{8}$ in. seem to be the smallest size which can be economically pelleted and used in a stationary bed and at the same time permit high mass velocities without excessive pressure drops and losses by attrition.

Effect of Fouling. Where fouling of a catalyst occurs it is desirable to extrapolate rates to zero time of service and to make all correlations on the fresh catalyst. This introduces an uncertainty

due to the lack of steady conditions in starting a run. Where these difficulties become insurmountable it is necessary to find a temperature range where fouling is negligible.

Effect of Changing Activity of Catalyst. The activity of a catalyst changes due to deactivation caused by employment of excessive temperatures and by poisoning. Where the feed consists of different streams for the separate reactants the poisoning component in each stream can be removed often by passing each stream separately through a special bed of the same catalyst before the reaction takes place. This proves effective if the poison is present in small traces.

C. C. Watson and Stevens (3) have shown in an unpublished thesis that steady-state conditions cannot be attained until the catalyst attains chemical equilibrium with the gas stream; this is in addition to the attainment of physical equilibrium in temperature and concentration gradients through the catalyst. The effect of changing activity can be eliminated by continuous use of the catalyst until complete equilibrium is attained both chemical and physical. This may introduce a serious time lag where composition and temperature of the gas stream are changed from run to run. It may prove impossible with some reactions to eliminate both fouling and lack of equilibrium.

Determination of Rate-Controlling Chemical Step. When effects of heat and mass transfer, diffusion, fouling, and deactivation have been minimized, eliminated, or accounted for, selection of the rate-determining chemical step is in order. Complex chemical processes may be considered as consisting chiefly of a combination of separate bimolecular and unimolecular reactions and for complex reactions the rate equations may not be related to the over-all stoichiometric relations. For gaseous reactions catalyzed by solid surfaces each separate molecular change usually consists of one or two rate-controlling chemical steps such as chemisorption with or without association of one or both reactants; surface reaction between adsorbed reactants and products, and impact of a nonadsorbed component with one that is adsorbed.

Mathematical expressions for rate equations can be derived from the principles given (2). In general these rates may be expressed by a combination of three terms, the kinetics term, the potential term, and the adsorption term, arranged thus,

$$r = \frac{(\text{kinetics term})(\text{potential term})}{(\text{adsorption term})^n}$$

(15)

These terms are summarized herewith for the following four types of reactions:

(I) $A \rightleftharpoons R$; (II) $A \rightleftharpoons R + S$;

(III) $A + B \rightleftharpoons R$; and

(IV) $A + B \rightleftharpoons R + S$

and for the following rate-controlling mechanisms.

Rate-Controlling Mechanisms

A. Reaction between molecularly adsorbed reactants and products without dissociation of any component upon adsorption

  a. Adsorption of A controlling
  b. Adsorption of B controlling
  c. Desorption of R controlling
  d. Surface reaction controlling

B. Reaction between atomically adsorbed A, where B, R, and S are molecularly adsorbed. Upon dissociation A is adsorbed on adjacent sites.

  e. Adsorption of A controlling (with dissociation)
  f. Adsorption of B controlling
  g. Desorption of R controlling (or S)
  h. Surface reaction controlling

C. Reactant B is not adsorbed, A, R, and S are molecularly adsorbed

  i. Adsorption of A controlling
  j. Desorption of R controlling
  k. Surface reaction controlling

D. Reactant B is not adsorbed, A is atomically adsorbed. R and S are molecularly adsorbed. Upon dissociation A is adsorbed on adjacent sites

  l. Adsorption of A controlling
  m. Desorption of R controlling
  n. Surface reaction controlling

E. Reactant A is not adsorbed. B, R, and S are molecularly adsorbed

  o. Impact of A controlling
  p. Desorption of R controlling (or S)
  q. Adsorption of B controlling

F. Uncatalyzed Reaction

  r. Homogeneous gas reaction

As the field of applied kinetics develops it may be found that examples of some of these mechanisms as rate-controlling steps will not be discovered. For example, the assumption of adsorption as a rate-controlling step over the entire composition range for a bimolecular reaction is untenable. Rate of adsorption of A reaches a maximum for the pure gas, but obviously there is no reaction in the absence of B and the adsorption of A will stop when the catalyst becomes saturated with A. Under these circumstances the rate of adsorption diminishes to zero without any reaction. From this it follows that two chemical steps become rate-controlling.

Driving Potential Term. The driving potential in any rate equation fulfills the conditions of becoming zero at conditions of equilibrium where the equilibrium constant K is related to the appropriate activity ratio for the over-all reaction. For example, for the reaction $A + B \rightleftharpoons R + S$ the driving potential is zero where

$$a_A a_B = \frac{a_R a_S}{K} \text{ or } K = \frac{a_R a_S}{a_A a_B}$$

in accordance with the definition of the equilibrium constant for the over-all reaction. These driving potentials are summarized in Table 1 for the four reactions and various mechanisms.

Kinetic Term. The designation, "kin-

TABLE 1. DRIVING POTENTIAL TERMS

Reaction	$A \rightleftharpoons R$	$A \rightleftharpoons R+S$	$A+B \rightleftharpoons R$	$A+B \rightleftharpoons R+S$
Adsorption of A controlling	$a_A - \frac{a_R}{K}$	$a_A - \frac{a_R a_S}{K}$	$a_A - \frac{a_R}{K a_B}$	$a_A - \frac{a_R a_S}{K a_B}$
Adsorption of B controlling	0	0	$a_B - \frac{a_R}{K a_A}$	$a_B - \frac{a_R a_S}{K a_A}$
Desorption of R controlling	$a_A - \frac{a_R}{K}$	$\frac{a_A}{a_S} - \frac{a_R}{K}$	$a_A a_B - \frac{a_R}{K}$	$\frac{a_A a_B}{a_S} - \frac{a_R}{K}$
Surface reaction controlling	$a_A - \frac{a_R}{K}$	$a_A - \frac{a_R a_S}{K}$	$a_A a_B - \frac{a_R}{K}$	$a_A a_B - \frac{a_R a_S}{K}$
Impact of A controlling (A not adsorbed)	0	0	$a_A a_B - \frac{a_R}{K}$	$a_A a_B - \frac{a_R a_S}{K}$
Homogeneous reaction controlling	$a_A - \frac{a_R}{K}$	$a_A - \frac{a_R a_S}{K}$	$a_A a_B - \frac{a_R}{K}$	$a_A a_B - \frac{a_R a_S}{K}$

TABLE 2. KINETIC TERMS.

Multiply each of the terms below by EL except for the homogeneous reaction.	
Adsorption of A controlling	k_A
Adsorption of B controlling	k_B
Desorption of R controlling	$k_R K$
Adsorption of A controlling with dissociation	$\frac{s}{2} k_A$
Impact of A controlling	$k_A K_B$
Homogeneous reaction controlling	k

Surface Reaction Controlling

	$A \rightleftharpoons R$	$A \rightleftharpoons R+S$	$A+B \rightleftharpoons R$	$A+B \rightleftharpoons R+S$
Without dissociation	$k_s K_A$	$k_s s \, K_A$	$k_s s \, K_A K_B$	$k_s s \, K_A K_B$
With dissociation of A	$k_s s \, K_A$	$k_s s \, K_A$	$k_s s (s-1) K_A K_B$	$k_s s (s-1) K_A K_B$
B not adsorbed	$k_s \, K_A$	$k_s s \, K_A$	$k_s \, K_A$	$k_s s \, K_A$
B not adsorbed, A dissociated	$k_s s \, K_A$	$k_s s \, K_A$	$k_s s \, K_A$	$k_s s \, K_A$

etic term," includes all factors which appear in the numerator of the reaction rate equation other than the driving potential such as L, the total number of active sites; the effectiveness factor E; appropriate kinetic constants for adsorption controlling, k_A and k_B; for desorption controlling, k_R and k_S; for surface reactions controlling k_s; and for the homogeneous reaction controlling, k. The factor s represents the number of adjacent active sites. Values of L and s will usually not be known and will be included in a characteristic constant for a specific catalyst. Over-all equilibrium and adsorption equilibrium constants of the reactants A and B may also appear in the kinetic term. Factors in the kinetic term are tabulated in Table 2.

Adsorption Term. Where all reactants, products, and inerts are adsorbed under equilibrium conditions and without dissociation the adsorption term is

$$[1 + K_A a_A + K_B a_B + K_R a_R + K_S a_S + K_I a_I]^n \qquad (16)$$

Under other conditions the replacements shown in Table 3 should be made.

The exponent n of the adsorption term is equal to 1 where the reaction involves only one site, equal to 2 when reaction involves two adjacent sites, and is equal to 3 when the reaction involves three adjacent sites. The exponents take the values shown in Table 4.

Formulation of Rate Equations. From these relations the rate equation for any of the above reactions and rate-controlling mechanisms can be readily formulated. For example,

Where the reaction $A + B \rightleftharpoons R + S$ is

surface-controlling with equilibrium adsorption of all components,

the driving potential term is

$$a_A a_B - \frac{a_R a_S}{K} \qquad \text{(from Table 1)}$$

kinetic term is

$$L s k_s K_A K_B \qquad \text{(from Table 2)}$$

adsorption term is

$$[1 + K_A a_A + K_B a_B + K_R a_R + K_S a_S + K_I a_I]^2$$

the exponent is 2   (Table 4)

and the rate equation becomes

$$r = \frac{L s k_s K_A K_B \left(a_A a_B - \frac{a_R a_S}{K} \right)}{[1 + K_A a_A + K_B a_B + K_R a_R + K_S a_S + K_I a_I]^2} \qquad (17)$$

Where the reaction $A + B \rightleftharpoons R$ proceeds with adsorption of A controlling

and with dissociation of A,
the driving potential term is

$$\left(a_A - \frac{a_R}{K a_B} \right) \qquad \text{(from Table 1)}$$

the adsorption term is

$$\left[1 + \sqrt{\frac{K_A a_R}{K a_B}} + K_B a_B + K_R a_R + K_I a_I \right]^2 \qquad \text{(from Table 3)}$$

the exponent is 2 (Table 4)

and the rate equation becomes

$$r = \frac{L k_s s \left(a_A - \frac{a_R}{K a_B} \right)}{2 \left[1 + \sqrt{\frac{K_A a_R}{K a_B}} + K_B a_B + K_R a_R + K_I a_I \right]^2} \qquad (18)$$

Initial Rates. Initial rates for the pure reactants present in stoichiometric proportions and in the absence of products and inerts can now be readily calculated in terms of total pressure. Thus, for Equation (17), since

$$a_A = a_B = \frac{\pi}{2}$$

and

$$a_R = a_S = 0$$

$$r_0 = \frac{a \pi^2}{(1 + b\pi)^2} \qquad (19)$$

and Equation (18) reduces to

$$r_0 = \frac{a \pi}{(1 + b\pi)^2} \qquad (20)$$

The remainder of this paper will be devoted to an initial selection of the most plausible mechanism from a visual inspection of the shape of rate curves when data are properly obtained to permit such plots. The actual evaluation of the appropriate constants should then be made by statistical methods of fitting data to the selected equation. From the shape of rate curves when plotted against such variables as pressure, feed composition, temperature and conversion, the most plausible mechanism of a simple reaction can be estimated. Examples given herewith are for the four molecular types of gaseous reactions cited assuming only one rate-controlling chemical step. Where several reactions are involved and where more than one chemical step is rate-controlling in each, the analysis becomes complicated. Complexities, however, can be minimized by extrapolating rates to conditions of zero reciprocal space velocity at which condition the complicating effects of several reactions have not begun.

By systematic and separate variations in pressure and feed composition, the mechanism can be fairly well established by visual inspection of the rate curve. When more than one chemical step is rate-controlling the number of constants in the rate equations becomes so numer-

ous and the accuracy of evaluation of each so uncertain that some empirical short cut may prove expedient. The effect of extent of conversion is difficult to generalize and the effect of temperature is of minor value in establishing mechanism.

Effect of Pressure. Pressure is by far the most important variable in determining the mechanism of a gaseous reaction catalyzed by a solid. Unless experiments are set up to operate with pressure as a controlled variable over a wide range it may not be possible to establish with certainty the probable mechanism. Variations in total pressure as well as partial pressures are essential. Partial pressures can be diversified by varying feed composition, but in addition the total pressure must be varied independently. For convenience the effects of total pressure will be illustrated by observing variations in the initial reaction rate with the use of fresh feed with no product present. Under these conditions the reverse reaction is negligible.

In Table 5 effects of pressure upon initial reaction rates are seen to fall into nine types of curves.

In Type *I* the initial rate, $r_o = a$ is independent of pressure. This type indicates that desorption of product R from the catalyst is the rate-controlling step when the reverse reaction is negligible. This situation occurs when all the active sites are saturated with respect to all components except product R and under initial conditions when no products have accumulated in the main gas stream. The same situation is encountered for finite values of the equilibrium constant K where a second product S is formed and adsorbed under equilibrium conditions. As the reaction proceeds with accumulation of product R in the gas stream the reaction rate is no longer constant but progressively diminishes. The value of r at zero pressure is a hypothetical initial rate of desorption. Since there is no supply of reactants at zero pressure, there is no reaction and desorption reaches zero.

Reaction rates of Type I are encountered when catalysts are poisoned.

In Type II the initial rate increases linearly with total pressure, $r_o = a\pi$. This situation applies when the adsorption of reactant A (or B) is rate-controlling where the other reactant B (or A) is not adsorbed or not present as in a unimolecular reaction. This type also holds for the uncatalyzed unimolecular reactions $A \rightleftarrows$.

In Type III the initial reaction rate can be expressed by the relations

$$r_o = \frac{a\pi}{1 + b\pi} \text{ or } r_o = \frac{a\pi}{1 + b\sqrt{\pi} + c\pi}$$

In this type the rate increases with pressure to a maximum asymptotic value. This type is encountered where adsorption of either A or B is controlling in a bimolecular reaction $A + B \rightleftarrows$; also where surface reaction is rate-controlling in a unimolecular reaction $A \rightleftarrows$ with or without dissociation; and where desorption of R is controlling for finite values of the equilibrium constant K in a forward bimolecular reaction $A + B \rightleftarrows R$.

In Type IV,

$$r_o = \frac{a\pi}{1 + b\pi + c\pi^2}$$

the reaction rate starts off linearly with pressure, reaches a maximum value and then diminishes with further increase in total pressure to a constant asymptotic value. This type is characteristic of $A \rightleftarrows R + S$ where the surface reaction is rate-controlling and is also encoun-

tered in the reaction $A + B \rightleftarrows R + S$ where adsorption of A is controlling and proceeds with dissociation on dual sites.

In Type V,

$$r_o = \frac{a\pi}{1 + b\sqrt{\pi}}$$

the rate increases progressively with pressure, starting off linearly and approaches a value proportional to the square root of pressure. This type applies to the reaction $A + B \rightleftarrows$ where adsorption of B is rate-controlling and A is adsorbed with dissociation.
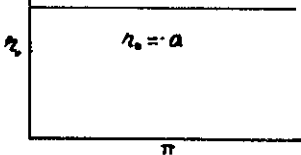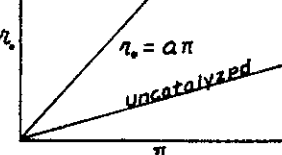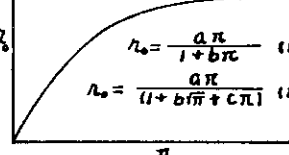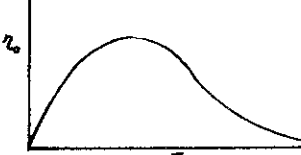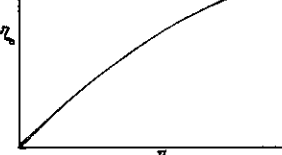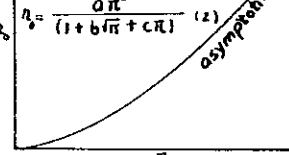
In Type VI,

$$r_o = \frac{a\pi^2}{1 + b\pi} \text{ and } r_o = \frac{a\pi^2}{1 + b\sqrt{\pi} + c\pi}$$

the rate starts off as the square of the pressure and approaches a rate proportional to the first power of pressure.

TABLE 3. REPLACEMENTS IN THE GENERAL ADSORPTION TERMS.

$$\left[1 + K_A a_A + K_B a_B + K_R a_R + K_S a_S + \frac{1}{n_I a_I}\right]^n$$

Reaction	$A \rightleftarrows R$	$A \rightleftarrows R+S$	$A+B \rightleftarrows R$	$A+B \rightleftarrows R+S$
Where adsorption of A is rate controlling replace $K_A a_A$ by	$\dfrac{K_A a_R}{K}$	$\dfrac{K_A a_R a_S}{K}$	$\dfrac{K_A a_R}{K\ a_B}$	$\dfrac{K_A a_R a_S}{K\ a_B}$
Where adsorption of B is rate controlling replace $K_B a_B$ by	0	0	$\dfrac{K_B a_R}{K\ a_A}$	$\dfrac{K_B a_R a_S}{K\ a_A}$
Where desorption of R is rate controlling replace $K_R a_R$ by	$KK_R a_A$	$KK_R \dfrac{A_A}{a_S}$	$KK_R a_A a_B$	$KK_R \dfrac{a_B a_B}{a_A}$
Where adsorption of A is rate controlling with dissociation of A replace $K_A a_A$ by	$\sqrt{\dfrac{K_A a_R}{K}}$	$\sqrt{\dfrac{K_A a_R a_S}{K}}$	$\sqrt{\dfrac{K_A a_R}{K a_B}}$	$\sqrt{\dfrac{K_A a_R a_S}{K\ a_B}}$
Where equilibrium adsorption of A takes place with dissociation				
of A replace $K_A a_A$ by	$\sqrt{K_A a_A}$	$\sqrt{K_A a_A}$	$\sqrt{K_A a_A}$	$\sqrt{K_A a_A}$
and similarly for other components adsorbed with dissociation.				
Where A is not adsorbed replace $K_A a_A$ by	0	0	0	0
and similarly for other components which are not adsorbed.				

TABLE 4. EXPONENTS OF ADSORPTION TERMS

Adsorption of A controlling without dissociation			n = 1
Desorption of R controlling			n = 1
Adsorption of A controlling with dissociation			n = 2
Impact of A without dissociation A + B $\rightleftarrows$ R			n = 1
Impact of A without dissociation A+B $\rightleftarrows$ R+S			n = 2
Homogeneous reaction			n = 0

Surface Reaction Controlling	$A \rightleftarrows R$	$A \rightleftarrows R+S$	$A+B \rightleftarrows R$	$A+B \rightleftarrows R+S$
No dissociation of A	1	2	2	2
Dissociation of A	2	2	3	3
Dissociation of A (B not adsorbed)	2	2	2	2
No dissociation of A (B not adsorbed)	1	2	1	2

TABLE 5. INITIAL REACTION RATES OF SIMPLE GASEOUS REACTIONS.

Effects of Total Pressure.

TYPE I

$r_o = a$

Desorption of One Product Controlling
$(K = \infty)$

Reaction Mechanism	I	II	III	IV
	c	c	c	c
	g	g	g	g
	j	j	j	j
	m	m	m	m
	-	-	p	p

Desorption of One Product Controlling $(K \neq \infty)$
Equilibrium adsorption for S)

Reaction Mechanism	I	II	III	IV
		c		c
		g		g
		j		j
		m		m
				p

TYPE II

$r_o = a\pi$

uncatalyzed

Adsorption of one reactant A (or B) controlling where other reactant B (or A) is not adsorbed or not present

Uncatalyzed Reaction $(A \rightleftharpoons)$

Reaction Mechanism	I	II	III	IV
	a	a		
	e	e		
	i	i	i	i
	l	l	l	l
			q	q

TYPE III

asymptotic

$$r_o = \frac{a\pi}{1 + b\pi} \quad (1)$$

$$r_o = \frac{a\pi}{(1 + b\sqrt{\pi} + c\pi)} \quad (2)$$

Adsorption of A controlling $(A + B \rightleftharpoons)$
Adsorption of B controlling $(A + B \rightleftharpoons)$
Surface reaction controlling $(A \rightleftharpoons R)$
Surface reaction controlling $(A2 \rightleftharpoons)$
Desorption of one Product Controlling $(K \neq \infty)$

Reaction Mechanism	I	II	III	IV	Eq
			a	b	(1)
			a	b	(1)
	c(K=∞)				(1)
	d				(1)
	g(K=∞)				(2)
	h	h			(2)
	j(K=∞)				(1)
	k				(1)
	m(K≠∞)				(2)
	n				(2)

TYPE IV

$$r_o = \frac{a\pi}{(1 + b\pi + c\pi^2)}$$

Surface Reaction Controlling $(A \rightleftharpoons R + S)$
Adsorption of A controlling with dissociation $(A + B \rightleftharpoons R + S)$

Reaction Mechanism	I	II	III	IV
		d		
			e	e
		k		

TYPE V

$$r_o = \frac{a\pi}{1 + b\sqrt{\pi}}$$

Adsorption of B controlling with dissociation of A $(A + B \rightleftharpoons)$

Reaction Mechanism	I	II	III	IV
			f	f

TYPE VI

$$r_o = \frac{a\pi^2}{1 + b\pi} \quad (1)$$

$$r_o = \frac{a\pi^2}{(1 + b\sqrt{\pi} + c\pi)} \quad (2)$$

asymptotic

Surface reaction controlling (B not adsorbed) $(A + B \rightleftharpoons R)$
Impact of A controlling (A not adsorbed) $(A + B \rightleftharpoons R)$
Surface reaction controlling (A dissociated, B not adsorbed) $(A + B \rightleftharpoons)$

Reaction Mechanism	I	II	III	IV	Eq
			k		1
			o		2
			n	n	1

This type is manifest when the surface reaction is controlling for the reaction $A + B \rightleftharpoons R$ where B is not adsorbed; and for reaction $A + B \rightleftharpoons$ where the surface reaction is rate-controlling with A dissociated upon adsorption and with B not adsorbed. It also holds for the reaction $A + B \rightleftharpoons R$ where A is not adsorbed and the controlling step is the impact of A upon reactant B which is held on the cata-

lyst surface by chemisorption on a single site.

Type VII,

$$r_o = \frac{a\pi^2}{1 + b\sqrt{\pi} + c\pi + d\pi^2}$$

is a common type where the reaction starts out as the square of the pressure and then falls off in slope to a zero value reaching a rate of constant asymptotic

value. This case is typified by four cases, (1) by the reaction $A + B \rightleftharpoons$ where the surface reaction is controlling and which proceeds without atomic dissociation; (2) for a surface reaction controlling without adsorption of B; (3) in the reaction $A + B \rightleftharpoons R + S$ where impact of A is controlling or (4) where desorption of product R is controlling for the reaction $A + B \rightleftharpoons R$ and for finite values of K.

TABLE 5. (Continued)
Effects of Total Pressure.

TYPE VII $r_c = \dfrac{a\pi^k}{(1 + b\sqrt{\pi} + c\pi + d\pi^2)}$ asymptote	TYPE VIII $r_o = \dfrac{a\pi^2}{(1 + b\sqrt{\pi} + c\pi)^3}$	TYPE IX $r_o = a\pi^2$

| Surface reaction controlling (no dissociation)(A+B ⇌) Surface reaction controlling (B not adsorbed) Impact of A controlling (A+B ⇌ R+S) Desorption of one product controlling (A+B ⇌ R)(K ≠ ∞) | Surface reaction controlling with dissociation of A (A+B ⇌) | Uncatalyzed reaction controlling (A + B ⇌) |

Reaction Mechanism	I	II	III	IV
			h	h

Reaction Mechanism	I	II	III	IV
			r	r

Reaction Mechanism	I	II	III	IV
			c(K≠∞) d g(K≠∞) j(K≠∞) m p(K≠∞)	d k o

EFFECTS OF TOTAL PRESSURE

In Type VIII,

$$r_o = \frac{a\pi^2}{(1 + b\sqrt{\pi} + c\pi)^3}$$

the rate initially increases as the square of pressure, the slope then falls off to zero at a maximum rate and becomes negative with further increase in pressure. This type applies where surface reaction is rate controlling with dissociation of A in the reaction $A + B \rightleftharpoons$.

Type IX, $r_o = a\pi^2$, represents the behavior of the uncatalyzed bimolecular reaction $A + B \rightleftharpoons$ where the rate increases progressively with the square of pressure.

Effect of Feed Composition upon Initial Rates. The effect of feed composition upon the rate of disappearance of the limiting reactant A falls into six types of rate curves, as shown in Table 6, assuming only one rate-controlling step.

In Type I, $r_{Ao} = aN_A$, the rate increases linearly with the mole fraction of A. This type holds where adsorption of A is the controlling step when B is not adsorbed. The extrapolation of the straight line to $N_A = 1.0$ means that the adsorption rate for A is fastest when there is no B present. However, if there

is no B present there is no over-all reaction, the catalyst soon becomes saturated with A, and adsorption stops. This situation indicates that when the mole fraction of A approaches unity the rate of reaction must be less than the instantaneous rate of adsorption and hence some other mechanism must also be controlling such as the surface reaction or the impact of B upon the adsorbed A. This difficulty can be eliminated by applying adsorption as a rate-controlling step only to the limiting reactant.

In Type II, $r_{Ao} = a(1 - N_A)$, the rate of adsorption of B is controlling where A is not adsorbed. Extrapolation to $N_A = 0$ gives a maximum value corresponding to the rate of adsorption of B in the absence of A. Under this circumstance there is no over-all reaction. The same anomalous situation is encountered as in Type I.

In Type III,

$$r_{Ao} = \frac{aN_A}{1 - bN_A} \quad \text{or} \quad r_o = \frac{aN_A}{(1 - bN_A)^2}$$

the rate curve increases more than linearly with the mole fraction of A and is represented by the adsorption of A controlling with or without dissociation where B attains equilibrium adsorption. The same situation at $N_A = 1.0$ is encountered as in Type I.

In Type IV,

$$r_{Ao} = \frac{a(1 - N_A)}{1 - bN_A} \quad \text{or} \quad \frac{a(1 - N_A)}{1 + b\sqrt{N_A}}$$

the situation corresponds to the adsorption of B as controlling with or without dissociation, when A is at equilibrium adsorption.

In Type V, $r_{Ao} = a$, the rate is independent of feed composition. This means that the desorption of product R is controlling when K is infinite for the reaction $A + B \rightleftharpoons R$. In the extreme ranges of gas composition in the absence of either reactant no product can be formed and hence the rate represents desorption and not reaction. At low concentrations of either A or B desorption of R no longer remains the only rate-controlling step.

In Type VI the reaction rate is zero in the absence of either A or B and attains a maximum value near the middle of the composition range. For catalytic reactions this situation holds (1) for all cases where the surface reaction is controlling; (2) where desorption is controlling and K is finite for the reaction $A + B \rightarrow R$; and (3) where impact of an unabsorbed reactant is controlling. This situation also applies (4) to the homogeneous bimolecular gas reaction.

The following specific equations apply

to Type VI and are not shown in Table 6:

	Rate-Controlling Mechanism	
	III	IV
$r_e = \dfrac{aN_A(1-N_A)}{1 \pm bN_A - cN_A{}^2}$	c, p, j (K ≠ ∞)	
$r_e = \dfrac{aN_A(1-N_A)}{1 + b\sqrt{N_A} + cN_A - N_A{}^2}$	g, m (K ≠ ∞)	
$r_e = \dfrac{aN_A(1-N_A)}{[1 + b\sqrt{N_A} - cN_A]^3}$	h	h
$r_e = \dfrac{aN_A(1-N_A)}{(1 + b\sqrt{N_A})^2}$	n	n
$r_e = \dfrac{aN_A(1-N_A)}{(1 \pm bN_A)^2}$	d	d
$r_e = \dfrac{aN_A(1-N_A)}{1 \pm bN_A}$	k, o	k, o
$r_e = aN_A(1-N_A)$	r	r

Effect of Extent of Conversion Upon Catalytic Reaction Rates. To establish the mechanism of a catalytic reaction by a study of the effect of conversion upon reaction rates is too extensive for detailed examination in this paper. Curves shown in Tables 5 and 6 for the effects of total pressure and feed composition are for zero percentage conversion. To show the effects of conversion each of these curves would be replaced by a family of curves, one for each percentage. Each curve would be of a shape similar to the parent curve at zero conversion but would drop progressively with increase in percentage conversion and reach a zero rate curve at equilibrium. In general where adsorption is controlling, the rate curve plotted against conversion at constant pressure and temperature is concave downwards and where surface reaction is controlling is concave upwards (Fig. 11). For reversible reactions the same relative effects are observed but the falling off in rate is more marked.
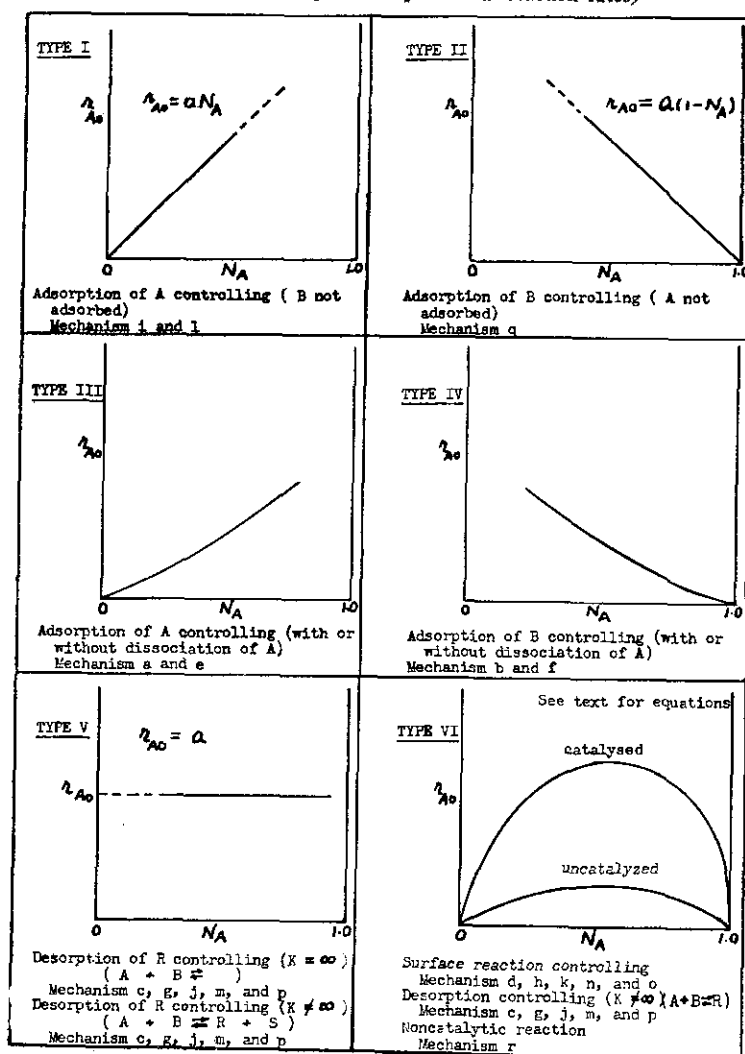
Effect of Temperature. The effect of temperature is of minor importance in the selection of reaction mechanisms of catalytic reactions, contrary to popular notions, but is indispensable in establishing the entropies and enthalpies of formation of the activated complex and of the adsorption compounds of the catalyst with the various reactants and products. This anomalous situation is encountered even where the reverse reaction is negligible. Where adsorption or desorption are rate-controlling steps in irreversible catalytic reactions the rate is accelerated with increase in temperature whether the over-all reaction is exothermic or endothermic (Fig. 12). The same is true for the uncatalyzed irreversible reaction. However, where the surface reaction is rate-controlling the rate increases with temperature to a maximum value and then decreases, as shown by Tschernitz, Bornstein, Beckmann and Hougen (5). This reversal of rate is due to the unfavorable effect of temperature in removing the reactants from the surface which more than offsets the favorable effect of temperature upon the reaction velocity constant.

Summary

In this paper a survey is given of the general procedures in planning and correlating experimental data on gaseous reactions catalyzed by solids. Methods are given for eliminating, minimizing, or evaluating the temperature and concentration gradients in gas films and in catalyst pellets. A summarized procedure is given for setting up the rate equations for many postulated mechanisms of four simple molecular reactions, $A \rightleftharpoons R$; $A \rightleftharpoons R + S$; $A + B \rightleftharpoons R$; and $A + B \rightleftharpoons R + S$. The selection of reaction mechanism from the effects of pressure, feed composition, and extent conversion and temperature is given, especially with reference to the visual appearance of rate curves. After the mechanism of a reaction has been established the various constants in the appropriate rate equations can be obtained from the experimental data by graphical and statistical methods. These methods are not presented in this paper, but are given in (5).

It is recognized that there are shortcomings to the equations presented in this paper, that chemical reactions are not as simple as these imply, that several steps may be rate-controlling, that the adsorption equilibrium constants may be

TABLE 6. INITIAL REACTION RATES OF BIMOLECULAR GASEOUS REACTIONS.
(Effect of feed composition upon initial reaction rates)

TYPE I — $r_{Ao} = aN_A$
Adsorption of A controlling (B not adsorbed)
Mechanism i and l

TYPE II — $r_{Ao} = a(1-N_A)$
Adsorption of B controlling (A not adsorbed)
Mechanism q

TYPE III
Adsorption of A controlling (with or without dissociation of A)
Mechanism a and e

TYPE IV
Adsorption of B controlling (with or without dissociation of A)
Mechanism b and f

TYPE V — $r_{Ao} = a$
Desorption of R controlling ($K = \infty$)
(A + B ⇌)
Mechanism c, g, j, m, and p
Desorption of R controlling ($K \neq \infty$)
(A + B ⇌ R + S)
Mechanism c, g, j, m, and p

TYPE VI
See text for equations
catalysed
uncatalyzed
Surface reaction controlling
Mechanism d, h, k, n, and o
Desorption controlling ($K \neq \infty$)(A+B⇌R)
Mechanism c, g, j, m, and p
Noncatalytic reaction
Mechanism r

adsorption controlling both reactants and products adsorbed

rate

conversion

with reverse reaction

Fig. 11a.

surface reaction controlling also adsorption of one reactant controlling when other is not adsorbed

rate

conversion

with reverse reaction

Fig. 11b.

Fig. 11. Effect of Extent Conversion Upon Catalytic Reaction Rates.

adsorption or desorption controlling irreversible reaction

rate

catalyzed

uncatalyzed

temperature

Fig 12a.

surface reaction controlling

irreversible

exothermic reversible

temperature

Fig. 12b.

Fig. 12. Effect of Temperature Upon Catalytic Reaction Rates.

pressure-dependent as well as temperature-dependent. The present approach represents an attempt to compromise between methods which are so involved in theory as to be beyond the experiences and training of those entrusted to process design, and methods which are so empirical as to be unsafe for extrapolation beyond the range of experimentation.
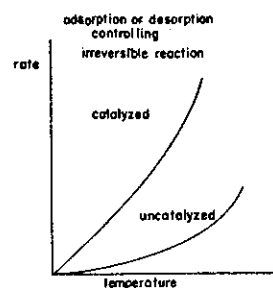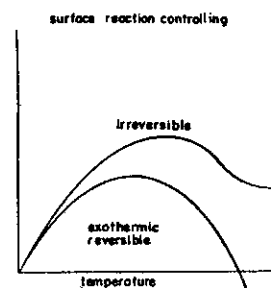
Acknowledgment

Credit is herewith given the Wisconsin Alumni Research Foundation for the support of this project.

Notation

A = component A
a = activity
$a_A, a_B, a_R,$
$\quad a_S, a_I$ = activities of components A, B, R, S, I, respectively
a_p = surface area per single catalyst pellet
a_m = surface area of pellets per unit mass
a = constant
b = constant
B = component B
C_p = specific heat
c = constant
D = diameter
D_{Am} = mean diffusivity of component A in a gas mixture
D_p = effective particle diameter equal to diameter of a sphere having the same surface area as the particle
D_p' = effective particle diameter equal to diameter of a sphere having the same volume as particle
E = effectiveness factor
F = feed rate, moles per unit time
F_e = external void fraction
F_i = internal void fraction

G = mass velocity
ΔH = heat of reaction
h_G = heat transfer coefficient of gas film
I = inert gas
j_d = factor for mass transfer
j_h = factor for heat transfer
K = over-all equilibrium constant
$K_A, K_B, K_R,$
$\quad K_S, K_I$ = adsorption equilibrium constants for components A, B, R, S, I, respectively
k = thermal conductivity
k_G = mass transfer coefficient of gas film
k = reaction velocity constant for the homogeneous reaction
k_A = reaction velocity constant where adsorption of A is controlling
k_B = reaction velocity constant where adsorption of B is controlling
k_R = reaction velocity constant where desorption of R is controlling
k_s = reaction velocity constant where surface reaction is controlling
M_m = mean molecular weight
m = modulus
N_A = mole fraction of component A
n = constant
p = partial pressure
p_f = pressure factor
$p_A, p_B, p_R,$
$\quad p_S, p_I$ = partial pressures of components A, B, R, S, I, respectively
q = rate of heat transmission
r = rate of reaction, moles per unit mass of catalyst
r_o = initial rate of reaction, moles per unit mass of catalyst
R = component R
S = component S

T = temperature, absolute
t = temperature
W = mass of catalyst
$$X = \left(\frac{\sqrt{a_p}\, r M_m p_f}{p_A \mu a_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)_f^{\%}$$
$$X' = \left(\frac{r\Delta H \sqrt{a_p}}{a_m \mu C_p T}\right)\left(\frac{C_p \mu}{k}\right)_f^{\%}$$
X_A = fractional conversion of component A per mole of feed

GREEK LETTERS:

a, a', a'' = constants
μ = viscosity
π = total pressure
ρ = density
ρ_B = density of bed
ρ_p = density of particle

SUBSCRIPTS:

A, B, R, S, I = components A, B, R, S, I, respectively
f = gas film
g = gas film
i = interface
m = mean
m = mass
p = particle
s = surface
v = volume

Literature Cited

1. Gamson, B. W., Thodos, G., and Hougen, O. A., *Trans. Am. Inst. Chem. Engrs.*, **39,** 1 (1943).
2. Hougen, O. A., and Watson, K. M., *Ind. Eng. Chem.*, **35,** 529 (1943).
3. Stevens, William F., and Watson, C. C. Unpublished thesis, Univ. of Wis. (1949).
4. Thiele, E. W., *Ind. Eng. Chem.*, **31,** 916 (1939).
5. Tschernitz, J. L., Bornstein, S., Beckmann, R. B., and Hougen, O. A., *Trans. Am. Inst. Chem. Engrs.*, **42,** 883 (1946).
6. Wilke, C. R., and Hougen, O. A., *Trans. Am. Inst. Chem. Engrs.*, **41,** 445 (1945).