JOURNAL OF CATALYSIS **20**, 132–140 (1971)

Transfer Paths in Kinetics of Heterogeneous Catalysis

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Received February 13, 1970; revised June 22, 1970

Atomic transfer rates are a useful way of characterizing the structure of chemical kinetic equations in heterogeneous catalysis. In general, rate expressions may be developed under actual reaction conditions which involve considerably fewer unknown parameters than techniques involving overall kinetics. Also, by experimentation under various limiting situations valuable information regarding rates of individual mechanistic steps is often obtainable.

INTRODUCTION

It is the purpose of this paper to show that isotopic transfer rates can provide much useful information on the necessary form of the rate equations for an overall reaction. It is then possible to develop rate equations on a less restricted basis than is necessary using the classic approach of Hougen and Watson (*1*). In particular it is not necessary to assume a single slow step in a reaction mechanism. Such an assumption may not always be valid over a wide range of partial pressures of reactants and products.

For pseudomonomolecular kinetics with multiple reactions, the techniques of linear algebra have been elegantly employed by Wei and Prater (*2*). In the present study it is shown that for a single overall reaction which is characterized by a single reaction mechanism, linearization is possible on the basis of the material balances involved without development of the kinetics of individual mechanistic steps. Extension to multiple reactions is in progress but not reported here.

Our study is based on the stoichiometric number concept as applied to reactions where more than one rate-controlling step may exist. This concept was originated by Horiuti (*3*) and has been discussed by Happel (*4*) for cases where a single rate controlling step exists and for more complicated cases, using the concept of reaction paths introduced by Happel (*5*). The stoichiometric number is defined for each elementary step constituting part of an overall reaction. It is the number of times that the step takes place for each occurrence of the latter. When a single rate controlling step exists, it is possible to relate the stoichiometric number of this step to the thermodynamic equilibrium constant and the speed of the forward and reverse reactions. If a reaction occurs in a single path and the stoichiometric number of each rate controlling step is the same, it is still possible to relate forward and reverse reaction rates to thermodynamics in somewhat the same way, as shown by Temkin (*7*).

BASIC RELATIONSHIPS

The concept of forward and reverse reaction rates requires some explanation since they are not uniquely fixed without specifying corresponding reaction paths. The rate of an overall reaction is often reported in terms of disappearance of a key reactant and often this species is taken to have a coefficient of unity in the equation for the reaction so the rate may be taken in terms of occurrences of the overall reaction per unit time. Since in complex reactions different atoms of a reacting molecule may move forward to products at different rates, ambiguity results when it is attempted to carry this concept to the description of forward and backward rates. It is thus convenient to identify the reaction rate with the conversion of the atomic species involved.

Transfer of atomic species proceeds through a network of mechanistic steps which when summed will yield the overall reaction. Sequences beginning at a given reactant and ending at a product characterize these networks. In the sequences each step is related to the previous one by possessing a common molecular species. These sequences can be used for developing rate equations for a given mechanism. However, a sequence which possesses the additional property that a single atomic species is contained in all its steps is more useful from the standpoint of experimental validation by labelled atoms. We have taken the definition of a path (*5*) to be such a sequence in which no break in the chain of atomic transfer occurs. It is possible to define unidirectional velocities in such paths and often to measure them by tracer techniques.

Thus, for the case where an element appears in only two molecular species of a reaction, a reactant and a product, the atoms of the element will pass sequentially from reactant through all the mechanistic steps of an atomic path to the final product. If we assume that a steady state is attained, it is possible to make simple material balances to determine how overall net velocity is related to the velocities of individual mechanistic steps. This approximation is especially suited to heterogeneous catalytic reactions, where steady state concentrations of intermediate can exist on catalytic sites, without any substantial passage of such intermediates to the effluent stream. The forward atomic velocity in such a path is the rate at which atoms introduced into the mechanistic sequence of steps move to product without reverting back to the original reactant molecule. For consistency with usual kinetic nomenclature, in which reaction velocity is expressed in terms of a molecular species A containing an element *e*, we will express the forward velocity V_+ as (the forward atomic velocity of element *e*)/[(the number of atoms of *e* in molecule A) (coefficient of A in the overall chemical equation)]. The forward atomic velocity is proportional to the overall forward velocity for the chosen path expressed in terms of occurrence of the overall reaction as written. If more than one path exists for atomic transfer defined in this manner, each will correspond to a different overall forward velocity. If there is only one path and all rate controlling steps lie in it, the forward velocity corresponds to that discussed by Temkin (*7*). Analogous definitions apply to backward velocities.

Suppose a series of steps in an atomic path is designated by steps 1, 2, . . . , *n* with mechanistic step velocities $v_{\pm 1}$, $v_{\pm 2}$, . . . , $v_{\pm n}$. The overall forward or backward velocity over more than one step will be designated by $V_\pm^{1,2,\ldots,n}$. For the first step, which leads from the reactant to the mechanistic series

$$V_+^1 = v_{+1}/\nu_1 \tag{1}$$

and

$$V_-^1 = v_{-1}/\nu_1, \tag{2}$$

where ν_i's represent the stoichiometric numbers of corresponding steps. For the following step

$$V_+^{1,2} = V_+^1 \text{ (probability of the species going forward through step 2)} \tag{3}$$

and

$$V_+^{1,2} = V_+^1 \left[\frac{v_{+2}/\nu_2}{v_{+2}/\nu_2 + V_-^1}\right] = 1\Big/\left[\frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_2}{v_{+1}v_{+2}}\right]. \tag{4}$$

At the same time

$$V_-^{1,2} = \frac{v_{-2}}{\nu_2} \text{ (probability of the species going backward through step 1)} \tag{5}$$

and

$$V_-^{1,2} = \frac{v_{-2}}{\nu_2}\left[\frac{V_-^1}{V_-^1 + v_{+2}/\nu_2}\right] = 1\Big/\left[\frac{\nu_2}{v_{-2}} + \frac{v_{+2}\nu_1}{v_{-2}v_{-1}}\right]. \tag{6}$$

If this procedure is repeated throughout the *n* steps of the sequence, we will have

$$V_+^{1,2,\ldots,n} = 1 \Big/ \left[\frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_2}{v_{+1}v_{+2}} + \cdots + \frac{v_{-1}v_{-2}\cdots v_{-(n-1)}\nu_n}{v_{+1}v_{+2}\cdots v_{+(n-1)}v_{+n}} \right] \quad (7)$$

and

$$V_-^{1,2,\ldots,n} = 1 \Big/ \left[\frac{\nu_n}{v_{-n}} + \frac{v_{+n}\nu_{(n-1)}}{v_{-n}v_{-(n-1)}} + \cdots + \frac{v_{+n}v_{+(n-1)}\cdots v_{+2}\nu_1}{v_{-n}v_{-(n-1)}\cdots v_{-2}v_{-1}} \right] \quad (8)$$

We will take Eqs. (7) and (8) as a formal definition of the unidirectional rates in a path. If Eq. (7) is divided by Eq. (8), we obtain for a single overall reaction

$$\frac{V_+^{1,2,\ldots,n}}{V_-^{1,2,\ldots,n}} = \frac{v_{+1}v_{+2}\cdots v_{+n}}{v_{-1}v_{-2}\cdots v_{-n}}. \quad (9)$$

A relationship for overall velocity V may be developed similar to Eqs. (7) and (8). Use of it and Eq. (9) gives

$$V = V_+^{1,2,\ldots,n} - V_-^{1,2,\ldots,n}. \quad (10)$$

Thus, for paths which can be identified with the transport of a single atomic species, although the individual unidirectional reaction velocities will vary, the difference in unidirectional rates will always give the overall velocity of the reaction. Even though rates in any path can be so related, it is of course possible that rate-controlling steps will exist in more than a single path. In that case it will not be possible to relate the overall velocity to terminal pressures, compositions, and temperature without taking into account the unidirectional velocities in all paths containing rate controlling steps.

For the case of a single path reaction, the determination of $V_\pm^{(p)}$ by isotopic transfer is simple. Thus, for an element e, if t_e^A is designated as

$$\frac{\text{the net rate of isotope transfer from reactant molecule } A}{(\text{number of atoms of "}e\text{" in a molecule of } A) \times (\text{coefficient of } A \text{ in the overall chemical equation})}$$

and z_e^A is defined as

$$\frac{\text{the concentration of isotope } e \text{ in } A}{\text{total concentration of atoms } e \text{ in } A}$$

it is clear that if we simply marked A, leaving product unmarked

$$t_e^A/z_e^A = V_+^{(p)}, \quad (11)$$

where (p) refers to velocity in a single path. Note that in general t_e^A is observable as a differential both in degree of conversion of A and in degree of transport of labelled isotope with respect to passage through a unit weight of catalyst. It is thus best determined in a differential reactor operating at steady state (10) but can be determined from integral data (14).

It is also possible to show that even where a single product R containing e is also labelled with isotope, the net rate can be related to the unidirectional velocities in a straightforward manner. Thus, if no isotopic kinetic effect exists and the isotope follows only the designated atomic transfer path we would have for a series of mechanistic steps

$$\begin{aligned} t_e^A = t_e^R &= (z_e^A v_{+1} - z_e^{X_1} v_{-1})/\nu_1 \\ &= (z_e^{X_1} v_{+2} - z_e^{X_2} v_{-2})/\nu_2 \\ &= \cdots \\ &= (z_e^{X_{(n-1)}} v_{+n} - z_e^R v_{-n})/\nu_n, \end{aligned} \quad (12)$$

where $X_1, X_2, \ldots, X_{(n-1)}$ are the intermediates of the mechanistic path. If z_e^i is eliminated for each intermediate species X_i, we obtain, from the set of Eqs. (12):

$$\begin{aligned} t_e^A = t_e^R = {} & z_e^A \Big/ \left[\frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_2}{v_{+1}v_{+2}} + \cdots + \frac{v_{-1}v_{-2}\cdots v_{-(n-1)}\nu_n}{v_{+1}v_{+2}\cdots v_{+(n-1)}v_{+n}} \right] \\ & - z_e^R \Big/ \left[\frac{\nu_n}{v_{-n}} + \frac{v_{+n}\nu_{(n-1)}}{v_{-n}v_{-(n-1)}} + \cdots + \frac{v_{+n}\cdots v_{+2}\nu_1}{v_{-n}\cdots v_{-2}v_{-1}} \right] \end{aligned} \quad (13)$$

We may substitute the relationship for $V_\pm^{(p)}$ given by Eqs. (7) and (8) to obtain

$$t_e^A = t_e^R = z_e^A V_+^{AR} - z_e^R V_-^{AR}. \quad (14)$$

Here the superscript AR refers to the sequence of steps leading from reactant A to product R.

Often it will not be possible to find an atomic species or characteristic marked atom in an overall reaction which will follow only a single path. In view of the simplification in kinetics effected by the use of relationships like Eqs. (7) and (8), it seems desirable to establish how velocity terms of mechanistic steps can still be grouped according to this definition of atomic paths.

Suppose that an element e is confined to three terminal species (two paths)—these being designated by a reactant A with products R and S. We will retain the same basic definition $t_e{}^i$ of isotopic transfer rate as previously because net transfer of isotopes from a single reactant to two species is measured simply by the increase of isotope in each of the two product species. In addition, we will assume an effectively uniform surface in which all sites involved in the mechanism behave alike, though they may interact with each other.

It can be demonstrated that to obtain a relationship similar to Eq. (14), it is necessary to take $t_e{}^A = t_e{}^R = t_e{}^S$. In this case the $t_e{}^i$ refer to transfer from reactant A or to products R and S. Such a restriction is possible by adjustment of the concentration of the isotope in the reacting mixture, employing a differential experiment to determine the rates. By conducting an elimination similar to that used for Eq. (12), we again find that (analogous to Eq. (14)

$$\begin{aligned} t_e{}^A = t_e{}^R = t_e{}^S &= z_e{}^A V_+{}^{AR} - z_e{}^R V_-{}^{AR} \\ &= z_e{}^A V_+{}^{AS} - z_e{}^S V_-{}^{AS}. \end{aligned} \qquad (15)$$

Therefore, when an element is contained in more than two paths of a mechanistic system for an overall reaction, it will still often be possible to apply relationships such as Eq. (15) by adjusting experimental conditions so that all $t_e{}^i$ are equal. Under these conditions Eqs. (10) and (15) may be used to relate the unidirectional velocities to quantities that can be determined experimentally.

To utilize these relationships for developing rate equations, it is necessary in a given system to find reaction paths which will encompass all rate controlling steps. Experiments with isotopic tracers will often enable this to be accomplished. Then, it is a straightforward matter to write rate expressions which will provide correlation of data obtained. Csuha and Happel (*6*) have derived expressions similar to those given above and shown how they may be applied to situations where the mechanism involves a single branching step. This limitation is not necessary and complicated mechanisms can be treated if only the necessary tracer paths can be evaluated.

General Rate Equations

We may rewrite Eq. (9) in a form suitable for displaying the fact that any number of paths may be written for a given overall reaction following the individual mechanistic steps in each path without identifying the exact steps involved:

$$\pi\left[\frac{v_{-r}}{v_{+r}}\right] = \frac{V_-{}^{(i)}}{V_+{}^{(i)}}, \qquad (16)$$

where the product is to be taken over *all steps "r" in any given path "i."* We use the superscript i for any path of a multiple path system and p for the only path of a single path system. Equation (16) reduces to the form given by Temkin (*7*) for a single path system. Christiansen (*8*) also derived a similar expression for a single path and restricted it to a specified kinetics for the individual mechanistic steps.

By adding up the contributions of the Gibbs free energy changes of all the mechanistic steps to obtain the total Gibbs free energy change for the overall reaction, the following expression, given by Hollingsworth (*9*), may be obtained

$$\pi\left[\frac{v_{-r}}{v_{+r}}\right]^{\nu_r} = \exp\,(\Delta G/RT), \qquad (17)$$

where ν_r refers to the stoichiometric number of each step in the overall reaction (including all steps in all paths), ΔG is the Gibbs free energy change for the overall reaction, R is the universal gas constant, and T is the absolute temperature. The continuing product is taken over *all steps in the reaction mechanism.*

In order to obtain simple kinetic relationships from Eqs. (16) and (17), we will be confined to mechanisms involving simple substitutions of the continuing product terms. Thus, if all the steps of a mechanism occur in a single path and have a common stoichiometric number, we will obtain

$$\frac{V_-^{(p)}}{V_+^{(p)}} = \exp\left(\Delta G/\nu_{RT}\right). \tag{18}$$

The stoichiometric number, obtained from Eq. (18), will be

$$\nu = \frac{-\Delta G}{kT} \Big/ \ln\frac{V_+^{(p)}}{V_-^{(p)}}. \tag{19}$$

This relationship, due to Horiuti (*3*), enables one to determine whether a reaction mechanism follows a single rate controlling path. In turn, by making use of Eq. (10), we can obtain from Eq. (18), a convenient rate expression:

$$V = V_+^{(p)}\left[1 - \exp\left(\frac{\Delta G}{\nu RT}\right)\right]. \tag{20}$$

It is important to point out that not all mechanistic steps need be included in the above relationships but only those which are rate controlling. A rate-controlling step may be taken as one which has a large Gibbs free energy change. For such a step the velocity ratio (v_{+r}/v_{-r}) must have a value which is significantly higher than unity. Conversely, for a step which is not rate-controlling (*i.e., close to equilibrium*), the Gibbs free energy change approaches zero, and the ratio (v_{+r}/v_{-r}) for the step must be *very close* to unity. Since for each step in a mechanism, $V = (v_{+r} - v_{-r})/\nu_r$ it is necessary for the steps in which $v_{+r}/v_{-r} \simeq 1$ to have large unidirectional velocities. A mechanism may include any number of steps in branching paths with values of $v_{+r}/v_{-r} \simeq 1$ without affecting the relationships given in Eqs. (16)–(20).

Studies of the dehydrogenation of *n*-butane to butenes by Happel and Atkins (*10*) using ^{14}C as a tracer indicate that this system can be treated as a pseudo single overall reaction. The three isomeric butenes produced reach equilibrium very rapidly compared with the rate of dehydrogenation and thus butenes are treated as a single component. Further studies by Happel, Hnatow and Mezaki (*11*) indicate that the form of the prefactor. $V_+^{(p)}$ in Eq. (20), involves more than one term due to the simultaneous reactions occurring, but good correlation is obtained with a separable potential factor i.e., the expression in brackets in Eq. (20). Studies of isobutane dehydrogenation by Kamholz (*12*) indicate that a stoichiometric number of unity is again obtained using ^{14}C. In this case the prefactor is simpler probably because it may be directly identified with a single $V_+^{(p)}$ corresponding to the formation of only one olefin, isobutene.

When rate-controlling steps no longer occur in a single path, the relationships derivable from Eqs. (16) and (17) become more involved. Thus, for a reaction mechanism consisting of two paths of atomic transfer we may expand Eq. (17) to include all rate-controlling steps.

$$\underset{\substack{\text{over all}\\ \text{rate-con-}\\ \text{trolling}\\ \text{steps}}}{\pi}\left[\frac{v_{-r}}{v_{+r}}\right] = \left[\frac{V_-^{(1)}}{V_+^{(1)}}\right]\left[\frac{V_-^{(2)}}{V_+^{(2)}}\right]\left[\frac{V_+^{(1,2)}}{V_-^{(1,2)}}\right], \tag{21}$$

where we have denoted the product of all rate-controlling steps common to both paths (1) and (2) by $V_+^{(1,2)}/V_-^{(1,2)}$.

A number of specific useful developments of Eq. (21) are possible. For example, where all mechanistic steps have the same stoichiometric number,

$$\exp\left[\frac{\Delta G}{\nu RT}\right] = \left[\frac{V_-^{(1)}}{V_+^{(1)}}\right]\left[\frac{V_-^{(2)}}{V_+^{(2)}}\right]\left[\frac{V_+^{(1,2)}}{V_-^{(1,2)}}\right] \tag{22}$$

or

$$\begin{aligned}\exp\left[\frac{\Delta G}{\nu RT}\right] &= 1 - V\left[\frac{1}{V_+^{(1)}} + \frac{1}{V_+^{(2)}} - \frac{1}{V_-^{(1,2)}}\right] \\ &+ V^2\left[\frac{1}{V_+^{(1)}V_+^{(2)}} - \frac{1}{V_+^{(1)}V_-^{(1,2)}} \right.\\ &\left. - \frac{1}{V_+^{(2)}V_-^{(1,2)}}\right] + V^3\left[\frac{1}{V_+^{(1)}V_+^{(2)}V_-^{(1,2)}}\right].\end{aligned} \tag{23}$$

While this equation is not explicit in V, computer solution presents no problem. However, unless a terminal product is produced at the branching step, it will not be possible to measure $V_{\pm}^{(1,2)}$ directly. $V_{-}^{(1,2)}$ is then the only variable in Eq. (23) that cannot be determined directly from an appropriate experiment. Therefore we could use Eq. (23) to determine $V_{-}^{(1,2)}$ provided that there exist only two paths in the reaction mechanism. Note that Eq. (23) will reduce to Eq. (20) if $V_{+}^{(1,2)}$ are the only rate-controlling steps. It will also follow Eq. (20) for a path which includes all rate-controlling steps, and in that case the apparent stoichiometric number, as given by Eq. (19), could be very high for the path which does not include rate-controlling steps. A similar observation was made by Matsuda and Horiuti (*13*). If rate-controlling steps do not occur in $V_{\pm}^{(1,2)}$ but in both $V_{\pm}^{(1)}$ and $V_{\pm}^{(2)}$ Eq. (23) reduces to

$$V^2\left[\frac{1}{V_{+}^{(1)}V_{+}^{(2)}}\right] - V\left[\frac{1}{V_{+}^{(1)}} + \frac{1}{V_{+}^{(2)}}\right] + \left[1 - \exp\frac{\Delta G}{\nu RT}\right] = 0. \quad (24)$$

Studies of Russian data on butane and butene dehydrogenation by Happel, Atkins, and Tanaka (*14*) indicate stoichiometric numbers for ^{14}C transfer greater than unity. If hydrogen chemisorption and desorption are important under the conditions of experiment, a relationship like Eq. (24) may be useful. More data will be needed to establish the applicability of this equation. Another system with a single branching mechanism appears to be the catalytic oxidation of SO_2 to SO_3 over vanadium catalysts. Using ^{35}S as a tracer, Happel, Odanaka, and Rosche (*15*) have found large stoichiometric numbers. In this case since oxygen chemisorption has a different stoichiometric number than the other mechanistic steps, it would be necessary to derive rate relationships from Eqs. (16) and (17), which though more complicated may be useful since they enable the structure of rate equations to be elucidated without reference to any particular kinetic equations for mechanistic steps or any specific adsorption rate theories. The general relations should also be useful for cases where more than one branching step occurs.

In general, the values of $V_{\pm}^{(i)}$ which appear in these equations will be functions of pressure, temperature, and composition of the ambient phase. Since these functions may be complicated, it is interesting to examine the implications of these theories to limiting conditions where they assume simpler forms.

The left side of Eq. (22) includes the experimental conditions of pressure, temperature, and concentration which may be varied in different ways to change $\exp(\Delta G/\nu RT)$. To illustrate, let us consider a simple two path reaction

$$A \rightleftarrows B + C, \quad (25)$$

which is assumed to be governed by the mechanism

$$\begin{array}{lc} (1) & A + l \underset{v_{-1}}{\overset{v_{+1}}{\rightleftarrows}} Al \\ (2) & Al + l \underset{v_{-2}}{\overset{v_{+2}}{\rightleftarrows}} Bl + Cl \\ (3) & Bl \underset{v_{-3}}{\overset{v_{+3}}{\rightleftarrows}} B + l \\ (4) & Cl \underset{v_{-4}}{\overset{v_{+4}}{\rightleftarrows}} C + l, \end{array} \quad (26)$$

where l represents catalyst sites and the individual mechanistic steps have velocities $v_{\pm r}$. In this case, the stoichiometric number ν is taken as unity for all steps. The overall velocity expression, written after the form Eq. (22), will be

$$\exp\left[\frac{\Delta G}{RT}\right] = \frac{p_B p_C}{K p_A} = \left[\frac{v_{-1}v_{-2}v_{-3}}{v_{+1}v_{+2}v_{+3}}\right] \times \left[\frac{v_{-1}v_{-2}v_{-4}}{v_{+1}v_{+2}v_{+4}}\right]\left[\frac{v_{+1}v_{+2}}{v_{-1}v_{-2}}\right]. \quad (27)$$

ABSENCE OF COMPONENTS

An experiment under the terminal conditions of pure reactant, with $p_B = p_C = 0$ implies $v_{-3} = v_{-4} = 0$ with $V_{-}^{(1)} = V_{-}^{(2)} = 0$ and results in the limiting case that $V_{\pm}^{(1)} = V_{\pm}^{(2)} = V$ for both paths (taking $V_{\pm}^{(1)}$ in the path of reaction steps 1, 2, and 3 from A to B and $V_{\pm}^{(2)}$ in the path of reaction steps 1, 2, and 4 from A to C). On the other hand, taking $p_A = 0$ would result in $V_{-}^{(1)} = V_{-}^{(2)} = -V$ so that the reverse unidirectional rates would assume limiting values. Taking either $p_B = 0$ or $p_C = 0$ alone would enable determination of $V_\pm^{(2)}$ or $V_\pm^{(1)}$, respectively. Comparison with V in each case would indicate the relative importance of the paths on reaction rate. In principle a reaction of any degree of complexity could be studied in this fashion by systematic elimination of terminal species.

IRREVERSIBLE REACTIONS

An irreversible reaction is usually taken to mean one in which the final conditions, given sufficient time, correspond to completion of the reaction in either direction. Thermodynamically, when the reaction is considered in the forward direction it corresponds to the case of $K \to \infty$ and hence $\exp(\Delta G/\nu RT) \to 0$. In such a case under conditions where Eq. (20) applies, $V = V_+^{(p)}$ for all concentrations of reactants and products. However, if there is more than one rate-controlling path, there are various ways in which $\exp(\Delta G/\nu RT)$ could approach zero.

Referring again to Eq. (27), we have a case where the left side is always equal to zero; assuming that even if p_A is very small K is still sufficiently large so that an indeterminate form is not obtained.

We see that if any $v_{-r} \ll v_{+r}$ the condition that $\exp(\Delta G/RT) \to 0$ will be met. Thus for Eq. (27), if $v_{-3} \ll v_{+3}$, we would have $V = V_+^{(1)}$. But $V_\pm^{(2)}$ could still each have appreciable values. It is only when $v_{-2} \ll v_{+2}$ or $v_{-1} \ll v_{+1}$ that both $V_-^{(1)}$ and $V_-^{(2)} = 0$, so that $V = V_+^{(1)} = V_+^{(2)}$ as in the case of the terminal condition $p_B = p_C = 0$. If $V_-^{(2)}/V_+^{(2)} \to 1$, the rate $V_+^{(1)}$ would be controlling and a reaction rate expression could be written without involving $V_\pm^{(2)}$.

Irreversible reactions can be studied under conditions where $V = 0$, when all the reactants are not present to form the final product (i.e., a terminal condition with a reactant absent and with K simultaneously very large).

APPROXIMATIONS NEAR EQUILIBRIUM

A number of authors (*9*) have obtained relationships based on expansions of Eq. (17) near equilibrium. Thus, the affinity $A = -\Delta G$ may be written in terms of the overall velocity as

$$\frac{A}{RT} = +\sum_{r=1}^{n} \nu_r \ln\left[\frac{v_{+r}}{v_{-r}}\right] = -\sum_{r=1}^{n} \nu_r \ln\left[1 - \frac{\nu_r V}{v_{+r}}\right]. \quad (28)$$

If V is expanded in a Maclaurin series about the equilibrium point $V = 0$, $A = 0$, we obtain

$$V = \left[\frac{1}{\Sigma\,[\nu_r^2/v_{+r}]}\right]\frac{A}{RT} - \left[\frac{\Sigma\,(\nu_r^3/v_{+r}^2)}{[\Sigma\,(\nu_r^2/v_{+r})]^3}\right]\frac{1}{2!}\left(\frac{A}{RT}\right)^2 + \cdots \quad (29)$$

For a path with a single branching mechanism as represented by Eq. (22), the first term of this expansion becomes

$$V = \frac{A/RT}{\nu\left[\dfrac{1}{V_+^{(1)}} + \dfrac{1}{V_+^{(2)}} - \dfrac{1}{V_+^{(1,2)}}\right]}. \quad (30)$$

Note, in this case we have employed the equilibrium relation that $V_+^{(1,2)} = V_-^{(1,2)}$. The prefactor $1/[\nu(1/V_+^{(1)} + 1/V_+^{(2)} - 1/V_+^{(1,2)})]$ does *not* correspond to a forward reaction velocity constant which can be applied far from equilibrium. Tracer measurements would enable us to establish whether the overall velocity of a given reaction near equilibrium is a linear function of $1/V_+^{(1)}$, $1/V_+^{(2)}$, $1/(1/V_+^{(1)} + 1/V_+^{(2)})$ or the entire denominator of the right hand side of Eq. (30).

Note that $V_+^{(1)}$, $V_+^{(2)}$ and $V_+^{(1,2)}$ will be constants near equilibrium only for given proportions of the three terminal species involved. Prigogine *et al.* (*16*) and Benson (*17*) discuss the case in which one path is involved in Eq. (30) (i.e., $V = V_+^{(1)}\,(A/\nu RT)$ and the rate $V_+^{(1)}$ can be represented by a power law model.

When experiments are conducted precisely at equilibrium with $V = 0$ and $A = 0$, then all $v_{+r} = v_{-r}$. Irreversible reactions in which $V = 0$ have already been noted. It is possible at equilibrium to measure unidirectional rates by isotopic tracers with all terminal species present. Benson (*17*) has reported treatment of the homogeneous reaction

$$2NO + Br_2 \rightleftarrows 2NOBr \qquad (31)$$

at equilibrium, using radioactive bromine as a tracer. This procedure in effect assumes that the bromine transfer path controls the reaction kinetics.

EXCHANGE REACTIONS

An exchange reaction may be defined as one in which no net atomic transfer occurs in the path studied. Such reactions can be studied only by tracer techniques. Examples of their occurrence have been discussed in connection with irreversible reactions and equilibrium reactions, where $V = 0$ because of thermodynamic considerations. Many other systems may also be characterized in this manner, with $V = 0$.

A reaction which is thermodynamically possible will not necessarily proceed at a measurable rate. If the velocities for any one step in a mechanism $v_{\pm r} \rightarrow 0$, the $v_{\pm r}$ for every other appreciably faster step will be approximately equal to each other (i.e., at equilibrium) and path velocities can be determined by tracer techniques. Thus, a reaction which has a step which is slow in one direction, (e.g. the forward direction), can be made to satisfy this requirement by reducing the product of the slow step to zero concentration.

Exchange reactions can also be conducted while a reaction is taking place with $V \neq 0$. Thus in the reaction of an equimolal mixture of hydrogen and butene, no net transfer of hydrogen occurs between these species.

Koehler and Happel (*18*) observed rapid exchange of deuterium in the course of hydrogenation, indicating that reactions involving adsorption and desorption of hydrogen and butenes are rapid and not rate controlling for the formation of butane.

CONCLUSIONS

Employment of the relationships above will facilitate the elucidation of reaction mechanisms and the development of appropriate kinetic equations. The $V_{\pm}^{(i)}$ can generally be determined for all values of the parameters involved so that equations expressing V in terms of them can be used to test the structure of the rate equation for an overall reaction. Once the relationship of V in terms of the $V_{\pm}^{(i)}$ values is determined, specification of reaction and chemisorption kinetics is necessary to calculate the free site concentration on a catalyst. In Eqs. (7) and (8) the intermediate step velocities all involve balancing numerator and denominator factors, so that for every v_{+n} a corresponding $v_{-(n-1)}$ appears, except for terminal mechanistic steps. Thus concentrations of intermediate adsorbed species cancel, if all rate-controlling steps are in a single path. In this case the use of the apparent stoichiometric number is especially useful. These techniques should prove useful in reaction kinetic and mechanistic studies.

ACKNOWLEDGMENTS

This project was supported by the Department of National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, Public Health Service and by the National Science Foundation. Ideas developed at the beginning of the paper were clarified by discussions with Juro Horiuti.

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