Structure of Rate Equations for Heterogeneous Catalysis

RONALD S. CSUHA and JOHN HAPPEL

Chemical Engineering Department
New York University, New York, N.Y. 10453

The structure of the rate equation can be important in the determination of the kinetics of a chemical reaction in that often this structure can be determined much more easily than the rate equation itself. The structure depends, not on the type of kinetics, but on details of the reaction mechanism. Thus, a knowledge or an assumption of a type of kinetics is not needed to determine a structure. However, a structure once determined can frequently be used to elucidate the details of a reaction mechanism. Ultimately, the constants of the rate equation will have to be determined by assuming a specific kinetics and adsorption rate theory, but the process is simplified by a knowledge of the details of the mechanism.

The simplest structure, and generally the most important case, arises when a *potential factor*

$$1 - e^{(\Delta G/\nu RT)} \tag{1}$$

can be factored from the rate equation. This factor contains only thermodynamic variables (the Gibbs free energy change ΔG of the overall reaction and the absolute temperature T) and constants (the base of the natural logarithms e, the universal gas constant R, and the stoichiometric number ν, to be explained later).

Much of the literature concerning rate equations implies the assumption that this potential factor can be factored from the rate equation. However, this assumption may not necessarily be valid. While the existence of a potential factor is a common feature of many rate equations, the conditions under which it can be factored have not always been completely defined. We will attempt to define them in this paper. We will also introduce other forms of the rate equation that will be applicable under certain other conditions.

A simplifying assumption frequently used in the development of rate equations for chemical reaction systems is the existence of a steady state. This assumption seems especially applicable in the case of heterogeneous catalysis, because the solid catalyst phase is usually much smaller than the fluid phase. Thus, the concentration of intermediates, such as adsorbed molecular species, can be expected to rapidly reach a constant value. We therefore employ this assumption in our treatment. Together with a basic transition state theory of chemical reactions, it leads to a general formulation of the equations involved.

A chemical reaction system will usually involve a number of elementary reaction steps. These steps constitute a mechanism whereby the initial reactant species are converted to products. The conversion will be related stoichiometrically by one or more *overall* reactions which do not involve intermediate chemical species. We will restrict the number of overall reactions to a single one and the number of mechanistic steps to that given by the maximum number of *independent* reaction steps that can possibly take place among the specified chemical species (*1*).

If a system is distinguished by a single overall reaction, the overall rate at steady state may be characterized by the appearance or disappearance of any single species appearing in the chemical equation of the overall reaction. The net velocity of an overall reaction can then be determined from the concentration changes taking place, and is generally expressed as a difference of forward and backward velocities. The literature, however, often does not discuss the fact that there may be more than one set of these unidirectional velocities for a given overall reaction. In general, there will be one forward reaction velocity $V_+^{(p)}$ and one backward reaction velocity $V_-^{(p)}$ for each reaction path p, where a reaction path can be defined as a sequence of elementary mechanistic steps, through which an atomic species proceeds from a reactant, through intermediate species, to a single product species. This concept of reaction path was introduced by Happel (*2*). Though there may be more than one set of unidirectional velocities, stoichiometry dictates that the net velocity V of the overall reaction can be written as

$$V = V_+^{(p)} - V_-^{(p)}, \quad p = \text{any reaction path} \tag{2}$$

where the dimension of V may be conveniently expressed as gram-moles per hour per unit mass of catalyst.

In order to illustrate, consider the catalytic oxidation of sulfur dioxide, with a mechanism proposed by Kaneko and Odanaka (*3*), and somewhat modified here:

Reaction Step r	Reaction step	
1	$O_2 + 2l = 2Ol$	
2	$SO_2 + l = SO_2l$	
3	$SO_2l + Ol = SO_3l + l$	
4	$SO_3l = SO_3 + l$	(3)

Correspondence concerning this article should be addressed to Professor John Happel.

Here l represents an active site; Ol, SO_2l, and SO_3l are adsorbed species corresponding to oxygen, SO_2, and SO_3, respectively. The chemical equation of the over-all reaction will be written so that the lowest coefficient will be unity

$$2SO_2 + O_2 = 2SO_3 \tag{4}$$

The reaction system involves two reaction paths:

$p = 1$ over which atomic oxygen can proceed from the reactant O_2, through steps 1, 3, and 4, to the product SO_3, and

$p = 2$ over which either atomic oxygen or atomic sulfur can proceed from the reactant SO_2, through steps 2, 3, and 4, to the product SO_3.

Since an element atom's progress through a path is dependent upon the velocities of the mechanistic steps in the path, and since the steps of one path differ from those of another path, there are two sets of unidirectional velocities ($V_+^{(p)}$, $V_-^{(p)}$, for $p = 1$ and 2). However, since there is only one overall reaction, there is only one net velocity; and the unidirectional velocities have to satisfy Equation (2).

Generally, unidirectional velocities are determined from an experiment which uses isotopic tracers to tag element atoms in the various molecular species present, and subsequently observes the speed of these isotopes through the reaction steps. The easiest way to do this is to employ a differential reactor operating at steady state. However, care must be taken to insure that both the conversion of reactants and the exchange of isotopic (or tagged) atoms are differentially small. For the present analysis, the manner in which element atoms are tagged is not important, as long as we can distinguish between tagged and untagged atoms, and as long as the tagged atoms move through the steps with the same speed as the untagged atoms.

If a specific element e of a reactant (or product) species is tagged, a net tagged atomic velocity t_e^i can be defined as

$$t_e^i = \frac{\text{net rate at which tagged atoms of } e \text{ leave a reactant or enter a product species } i \text{ (g.-atoms per hour per unit mass of catalyst)}}{\begin{array}{c}\text{number of atoms of}\\ e \text{ in a molecule}\\ \text{of the species } i\end{array} \times \begin{array}{c}\text{coefficient of the species}\\ i \text{ in the chemical equa-}\\ \text{tion of the overall reac-}\\ \text{tion}\end{array}} \tag{5}$$

This definition of the tagged velocity is convenient because the mathematical model for the exchange of tagged atoms becomes easier to handle. Also the dimension of the tagged velocity will be consistent with the dimension of the net velocity of Equation (2).

Note that in our previous example, sulfur atoms are confined to path 2 of the reaction system. If the sulfur isotope, ^{35}S, is used to tag sulfur atoms, the two tagged velocities, $t_S^{SO_2}$ and $t_S^{SO_3}$, are both equal. Also, since the amount of isotope leaving the reactant SO_2 is equal to the amount following path 2, the unidirectional velocities for this path may be defined to satisfy the following equation:

$$t_S^{SO_2} = z_S^{SO_2} V_+^{(2)} - z_S^{SO_3} V_-^{(2)} \tag{6}$$

Here z_e^i is the fraction of tagged atoms of the element e in the molecular species i; that is, the number of tagged atoms of the element e in i divided by the total number of atoms of e in i. The subscript S denotes atomic sulfur, and thus replaces the general subscript e in Equation (6). Equations (2) and (6) may then be used to solve for $V_+^{(2)}$ and $V_-^{(2)}$ in terms of variables that can be determined by experimentation. Therefore Equations (2) and (6) are to be considered a definition of the unidirectional rates for path 2 as determined by sulfur transfer.

If ^{18}O were used as a tracer, the situation would not be as simple because there are three tagged velocities. These are restricted by stoichiometry so that

$$t_O^{SO_3} = \frac{1}{3} t_O^{O_2} + \frac{2}{3} t_O^{SO_2} \tag{7}$$

Here the subscript O denotes atomic oxygen. The complication arises because there are two paths governing the exchange of isotopic oxygen.

As for sulfur, we can define unidirectional velocities to be consistent with the following equations:

$$\begin{aligned} t_O^{O_2} &= z_O^{O_2} V_+^{(1)} - z_O^{SO_3} V_-^{(1)} \\ t_O^{SO_2} &= z_O^{SO_2} V_+^{(2)} - z_O^{SO_3} V_-^{(2)} \end{aligned} \tag{8}$$

Since we want the unidirectional velocities of path 2 to be the same whether we use ^{18}O or ^{35}S to trace the path, we have to place an additional restriction on the ^{18}O tracer experiment. This restriction requires the three tagged velocities of Equation (7) to be all equal, and it arises from the consideration of the mathematical model, to be discussed later. The restriction is easily implemented by adjusting the isotopic concentrations in a differential reactor operating at steady state. Then Equations (2) and (8) can be used to solve for the unidirectional velocities of both paths in terms of experimental variables. For ^{18}O tracer experiments, we will take Equations (2) and (8) to be the definitions of the unidirectional velocities, under the restriction that the three tagged velocities of Equation (7) are equal.

Under appropriate restrictions, this technique can be expanded to include reaction systems in which an element atom follows more than two paths. However, due to the complexity of the experimental procedure for such a case, this element should be avoided in the selection of atoms to be tagged. It is possible to avoid this element if there are other elements that follow only one or two paths and if these elements use all the paths of a reaction system. This is a reasonably frequent occurrence, and complicated experiments can often be avoided.

VELOCITY EXPRESSIONS

Since the unidirectional velocities of a path can be determined experimentally, it is advantageous to relate these unidirectional velocities to those of the individual mechanistic steps. These relations may then be used to construct rate equations in terms of experimentally determineable unidirectional velocities.

We can obtain the desired relations by setting up a mathematical model for the transfer of tagged atoms through the elementary steps of a mechanism. We will refer, first, to the exchange of sulfur atoms in the previous example of the oxidation of sulfur dioxide, since this is the simplest situation. If ^{35}S is used to tag the atoms of sulfur in the molecular species SO_2 and SO_3, then the tagged velocities of the isotope through each of steps 2, 3, and 4 can be represented by equations similar to Equation (6). The three equations are

$$\begin{aligned} t_S^{SO_2} = t_S^{SO_3} &= (z_S^{SO_2} v_{+2} - z_S^{SO_2l} v_{-2})/\nu_2 \\ &= (z_S^{SO_2l} v_{+3} - z_S^{SO_3l} v_{-3})/\nu_3 \\ &= (z_S^{SO_3l} v_{+4} - z_S^{SO_3} v_{-4})/\nu_4 \end{aligned} \tag{9}$$

v_{+r} and v_{-r} are the forward and backward rates of step r and are defined consistently so that

$$V = (v_{+r} - v_{-r})/\nu_r \tag{10}$$

The constant ν_r that appears in Equations (9) and (10) is the stoichiometric number of step r and has been defined by Horiuti (*4*) as the number of times step r is needed for each time the overall reaction occurs once. For the reaction system of Equations (3) and (4), $\nu_r = 1, 2, 2,$ and 2 for $r = 1, 2, 3,$ and 4, respectively.

If the tagged fraction $z_e{}^i$ for each intermediate i is eliminated from Equations (9), there will be one resulting equation:

$$t_S{}^{SO_2} = t_S{}^{SO_3} = z_S{}^{SO_2} \Big/ \left[\frac{\nu_2}{v_{+2}} + \frac{v_{-2}\nu_3}{v_{+2}v_{+3}} + \frac{v_{-2}v_{-3}\nu_4}{v_{+2}v_{+3}v_{+4}} \right]$$
$$- z_S{}^{SO_3} \Big/ \left[\frac{\nu_4}{v_{-4}} + \frac{v_{+4}\nu_3}{v_{-4}v_{-3}} + \frac{v_{+4}v_{+3}\nu_2}{v_{-4}v_{-3}v_{-2}} \right] \tag{11}$$

This equation may be combined with Equations (2), (6), and (10) to show that the unidirectional velocities, $V_+{}^{(2)}$ and $V_-{}^{(2)}$, can be represented in terms of the unidirectional velocities of the individual mechanistic steps:

$$V_+{}^{(2)} = 1 \Big/ \left[\frac{\nu_2}{v_{+2}} + \frac{v_{-2}\nu_3}{v_{+2}v_{+3}} + \frac{v_{-2}v_{-3}\nu_4}{v_{+2}v_{+3}v_{+4}} \right]$$
$$V_-{}^{(2)} = 1 \Big/ \left[\frac{\nu_4}{v_{-4}} + \frac{v_{+4}\nu_3}{v_{-4}v_{-3}} + \frac{v_{+4}v_{+3}\nu_2}{v_{-4}v_{-3}v_{-2}} \right] \tag{12}$$

The relations are significant in that $V_+{}^{(2)}$ and $V_-{}^{(2)}$ can be determined experimentally from isotopic exchange data and therefore the groupings of the unidirectional velocities of the mechanistic steps can be related to experimental quantities.

If ^{18}O were used as the tracer, then the only way in which we could describe the exchange of isotope, with a set of equations similar to Equations (9), is to adjust the exchange of isotopic oxygen as discussed previously. Then

$$t_O{}^{SO_3} = t_O{}^{SO_2} = t_O{}^{O_2} \tag{13}$$

Under these conditions, we may write for path 1

$$\begin{aligned} t_O{}^{O_2} = t_O{}^{SO_3} &= (z_O{}^{O_2}\, v_{+1} - z_O{}^{Ol}\, v_{-1})/\nu_1 \\ &= (z_O{}^{Ol}\, v_{+3} - z_O{}^{SO_3l}\, v_{-3})/\nu_3 \\ &= (z_O{}^{SO_3l}\, v_{+4} - z_O{}^{SO_3}\, v_{-4})/\nu_1 \end{aligned} \tag{14}$$

and for path 2:

$$\begin{aligned} t_O{}^{SO_2} = t_O{}^{SO_3} &= (z_O{}^{SO_2}\, v_{+2} - z_O{}^{SO_2l}\, v_{-2})/\nu_2 \\ &= (z_O{}^{SO_2l}\, v_{+3} - z_O{}^{SO_3l}\, v_{-3})/\nu_3 \\ &= (z_O{}^{SO_3l}\, v_{+4} - z_O{}^{SO_3}\, v_{-4})/\nu_4 \end{aligned} \tag{15}$$

Now we can eliminate, from Equations (14) and (15), $z_e{}^i$ for each intermediate i. When the resulting equations are combined with Equations (2), (8), and (10), we are able to show that each of the unidirectional velocities for the paths can be expressed in terms of the unidirectional velocities of the individual mechanistic steps:

$$V_+{}^{(1)} = 1 \Big/ \left[\frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_3}{v_{+1}v_{+3}} + \frac{v_{-1}v_{-3}\nu_4}{v_{+1}v_{+3}v_{+4}} \right]$$
$$V_-{}^{(1)} = 1 \Big/ \left[\frac{\nu_4}{v_{-4}} + \frac{v_{+4}\nu_3}{v_{-4}v_{-3}} + \frac{v_{+4}v_{+3}\nu_1}{v_{-4}v_{-3}v_{-1}} \right]$$
$$V_+{}^{(2)} = 1 \Big/ \left[\frac{\nu_2}{v_{+2}} + \frac{v_{-2}\nu_3}{v_{+2}v_{+3}} + \frac{v_{-2}v_{-3}\nu_4}{v_{+2}v_{+3}v_{+4}} \right]$$
$$V_-{}^{(2)} = 1 \Big/ \left[\frac{\nu_4}{v_{-4}} + \frac{v_{+4}\nu_3}{v_{-4}v_{-3}} + \frac{v_{+4}v_{+3}\nu_2}{v_{-4}v_{-3}v_{-2}} \right] \tag{16}$$

Equations (16) relate, as do Equations (12), groupings of the unidirectional velocities of the mechanistic steps to experimentally determinable unidirectional velocities for the paths. Note that under the restrictions of Equation (13), the unidirectional velocities for path 2, as determined by isotopic oxygen exchange, are identical to those determined by isotopic sulfur exchange and given by Equations (12).

From Equations (16), an important relation can be obtained: the velocity ratio for a path p:

$$V_+{}^{(p)}/V_-{}^{(p)} = \prod_{\substack{\text{over all}\\ \text{steps } r \text{ in}\\ \text{path } p}} (v_{+r}/v_{-r}) \tag{17}$$

This velocity ratio is important because it is in a form that is extremely useful in constructing rate equations. It is also convenient that the velocity ratios can be determined experimentally, even though we may have to place restrictions on the conditions of isotopic exchange. Temkin (*5*) has derived Equation (17) for a single path reaction system, but he has not shown that the unidirectional velocities can be determined experimentally. Christiansen (*6*) also has developed similar expressions involving the net velocity, but he has assumed Langmuir kinetics.

Equation (17) is a rather general result because it can be shown to be valid for paths containing any number of steps, provided that the appropriate restrictions on the isotopic exchange are met. It should therefore be emphasized that the importance of these velocity ratios extends beyond the situations presented here. It can be shown that as long as the atomic element to be tagged is contained in no more than three molecular species of any step of a mechanism, the experimental procedure can be extended to obtain velocity ratios for a general single overall reaction of the type

$$\begin{aligned} &a_1A_1 + a_2A_2 + a_3A_3 + \ldots\ldots \\ &\qquad = b_1B_1 + b_2B_2 + b_3B_3 + \ldots\ldots \end{aligned} \tag{18}$$

where A_i and B_i are a reactant and a product, respectively, and a_i and b_i are the coefficients of A_i and B_i, respectively.

RATE EQUATIONS FOR AN OVERALL REACTION

We will use the velocity ratios of Equation (17) to construct rate equations for a general two-path reaction system—similar to the oxidation of sulfur dioxide. However, we first want to assume that the statistical mechanical transition state theory presented by Horiuti (*4*) applies. Then the unidirectional velocities of a mechanistic step can be related to the Gibbs free energy change of that step by the following equation:

$$\Delta g_r = -RT \ln (v_{+r}/v_{-r}) \tag{19}$$

Here Δg_r is the Gibbs free energy of step r, R is the universal gas constant, and T is the absolute temperature.

By adding the contributions of the free energy changes of the steps to the total free energy change of the overall reaction, the unidirectional velocities of the steps may be used to form an expression for the free energy change of the overall reaction. This expression has been given by Hollingsworth (*7*) and is

$$\prod_{\substack{\text{over all}\\ \text{steps } r \text{ in}\\ \text{the mechanism}}} (v_{-r}/v_{+r})^{\nu_r} = \exp(\Delta G/RT) \qquad (20)$$

In order to simplify Equation (20) and also Equation (17), it will be convenient to introduce the concept of a rate-controlling step. Such a step is one that has a large Gibbs free energy change. Then, from Equation (19), the velocity ratio (v_{+r}/v_{-r}) for the step must have a value that is significantly different from unity. Conversely, for an equilibrium step, the free energy change approaches zero, and the ratio (v_{+r}/v_{-r}) for the step must be very nearly equal to unity. For the velocities to be consistent, the equilibrium steps must have large unidirectional rates and the rate-controlling steps must have small unidirectional rates. Equations (17) and (20) can be simplified by noting that the combined product in these equations actually extends over only the rate-controlling steps.

We can now analyze the possible structures of the rate equation for the previous example of the catalytic oxidation of sulfur dioxide in terms of the forward velocities and the potential factor. There are only three possible structures, and each of these structures depends on the particular steps that are rate controlling. While the three possible structures can be analyzed, the general case, with all four steps rate controlling, cannot be analyzed in the following manner.

The equations used to construct the rate equation are Equation (20) written for this system:

$$\exp(\Delta G/RT) = \left[\frac{v_{-1}}{v_{+1}}\right]\left[\frac{v_{-2}v_{-3}v_{-4}}{v_{+2}v_{+3}v_{+4}}\right]^2 \qquad (21)$$

and the unidirectional velocity ratios for the system as given by Equation (17)

$$\frac{V_+^{(1)}}{V_-^{(1)}} = \frac{v_{+1}v_{+3}v_{+4}}{v_{-1}v_{-3}v_{-4}} \qquad (22)$$

$$\frac{V_+^{(2)}}{V_-^{(2)}} = \frac{v_{+2}v_{+3}v_{+4}}{v_{-2}v_{-3}v_{-4}} \qquad (23)$$

Suppose step 1 is at equilibrium; then all the rate-controlling steps are in path 2, and Equations (21) and (23) may be combined to give

$$\exp(\Delta G/RT) = \left[\frac{V_-^{(2)}}{V_+^{(2)}}\right]^2 \qquad (24)$$

The corresponding rate equation is obtained by applying Equation (2) to eliminate the backward velocities from Equation (24). Then

$$V = V_+^{(2)}\,[1 - \exp(\Delta G/2RT)] \qquad (25)$$

which is the potential form of the rate equation. The factor 2 in the denominator of the exponent arises because the stoichiometric number of each rate-controlling step is 2. Now if the forward velocity for path 2 correlates according to Equation (25), we would know that at least step 1 is at equilibrium and at least one of the steps 2, 3, and 4 is rate controlling. This, of course, assumes that our mechanism is valid.

If steps 1 and 2 were both at equilibrium, the two forward velocities (also the backward velocities) would be equal. Then Equation (21) would be

$$\exp(\Delta G/RT) = \left[\frac{V_-^{(p)}}{V_+^{(p)}}\right]^2 \quad p = 1, 2 \qquad (26)$$

and the corresponding rate equation would be

$$V = V_+^{(p)}\,[1 - \exp(\Delta G/2RT)] \quad p = 1, 2 \qquad (27)$$

Here again all the rate-controlling steps have a stoichiometric number of 2. Therefore if we found that the two forward velocities are equal to each other we would know that the potential form of the rate equation exists, and that steps 1 and 2 have to be at equilibrium.

A more complicated situation exists if step 2 were at equilibrium and at least one of steps 3 and 4 were rate controlling. Then Equation (21) would be

$$\exp(\Delta G/RT) = \left[\frac{V_-^{(1)}}{V_+^{(1)}}\right]\left[\frac{V_-^{(2)}}{V_+^{(2)}}\right] \qquad (28)$$

The corresponding rate equation is now a quadratic in V:

$$V^2 - V(V_+^{(1)} + V_+^{(2)}) + V_+^{(1)}V_+^{(2)}\,[1 - \exp(\Delta G/RT)] = 0 \qquad (29)$$

Note that the potential factor is contained in this expression, even though V cannot be expressed in the ptoential form.

There is only one other form of the rate equation for this system, and that is applicable if steps 1 and 2 are rate controlling, with steps 3 and 4 at equilibrium. Then Equation (21) becomes

$$\exp(\Delta G/RT) = \left[\frac{V_-^{(1)}}{V_+^{(1)}}\right]\left[\frac{V_-^{(2)}}{V_+^{(2)}}\right]^2 \qquad (30)$$

The corresponding rate equation is now a cubic in the velocity:

$$V^3 - V^2\,(V_+^{(1)} + 2V_+^{(2)}) + V\,(V_+^{(2)})\,(V_+^{(2)} + 2V_+^{(1)}) - (V_+^{(1)})(V_+^{(2)})^2\,[1 - \exp(\Delta G/RT)] = 0 \qquad (31)$$

Correlations of the forward velocities can be used to establish whether any one of the rate equations (25), (27), (29), and (31) applies. A knowledge of the form or structure of the rate equation can then lead to some information about the rate-controlling steps. If no correlation is possible, then we would know that one of three possibilities exists: that steps 1, 2, and 4 are rate controlling; or steps 1, 2, and 3 are rate controlling; or all four steps 1, 2, 3, and 4 are rate controlling. Of course, the conclusions obtained rest on the assumption that our proposed mechanism is valid.

It is not always necessary to know the mechanism of the reaction system, because many systems have rate-controlling steps with the same stoichiometric number. For example, it is a rather frequent occurrence for the stoichiometric numbers of the steps of a mechanism to all be equal to unity. Even in our example of the oxidation of sulfur dioxide, three of the four steps have a stoichiometric number of 2, and there is a possibility that these three steps are the rate-controlling steps. If the mechanism is such that all the rate-controlling steps have the same stoichiometric number ν, then Equation (20) may be further simplified:

$$\prod_{\substack{\text{over all rate-}\\ \text{controlling steps } r\\ \text{in the mechanism}}} (v_{-r}/v_{+r}) = \exp(\Delta G/\nu RT) \qquad (32)$$

The rate equations, for the case in which all the rate-controlling steps have the same stoichiometric number, may be constructed from Equations (17) and (32). If we multiply the velocity ratio for path 1 by the ratio for path 2, we will have formed the combined product of the ratio of the unidirectional velocities for each of the steps in the mechanism. In this combined product, each step that is common to both paths is included twice. Since the combined product in Equation (32) includes all the rate-controlling steps only once each, it is convenient to write the following equation:

$$\left\{\begin{array}{l}\Pi\ \ (v_{-r}/v_{+r})\\ \text{over all rate-}\\ \text{controlling}\\ \text{steps } r \text{ in}\\ \text{path 1}\end{array}\right\}\left\{\begin{array}{l}\Pi\ \ (v_{-r}/v_{+r})\\ \text{over all rate-}\\ \text{controlling}\\ \text{steps } r \text{ in}\\ \text{path 2}\end{array}\right\} = \left\{\begin{array}{l}\Pi\ \ (v_{-r}/v_{+r})\\ \text{over all rate-}\\ \text{controlling}\\ \text{steps } r\\ \\ \end{array}\right\}\left\{\begin{array}{l}\Pi\ \ (v_{-r}/v_{+r})\\ \text{over all rate-}\\ \text{controlling}\\ \text{steps } r\\ \text{common to}\\ \text{both paths}\end{array}\right\} \qquad (33)$$

Then Equations (17) and (32) may be substituted into Equation (33) to yield

$$\left[\frac{V_-^{(1)}}{V_+^{(1)}}\right]\left[\frac{V_-^{(2)}}{V_+^{(2)}}\right] = \left[\exp\left(\frac{\Delta G}{\nu RT}\right)\right]\left\{\begin{array}{c}\Pi\ \ (v_{-r}/v_{+r})\\ \text{over all rate-}\\ \text{controlling steps } r\\ \text{common to both paths}\end{array}\right\} \qquad (34)$$

Equation (2) may be used to eliminate the backward velocities from the velocity ratios. Then

$$\left[\frac{V_-^{(1)}}{V_+^{(1)}}\right]\left[\frac{V_-^{(2)}}{V_+^{(2)}}\right] = [1 - (V/V_+^{(1)})]$$
$$[1 - (V/V_+^{(2)})] = 1 - V\,[(1/V_+^{(1)}) + (1/V_+^{(2)})] + V^2\,[1/(V_+^{(1)}\,V_+^{(2)})] \qquad (35)$$

Equation (35) may they be combined with Equation (34) to give

$$V^2\,[1/(V_+^{(1)}\,V_+^{(2)})] - V\,[(1/V_+^{(1)}) + (1/V_+^{(2)})] + 1 - \left[\exp\left(\frac{\Delta G}{\nu RT}\right)\right]\left\{\begin{array}{c}\Pi\ \ (v_{-r}/v_{+r})\\ \text{over all rate-}\\ \text{controlling steps}\\ \text{common to both paths}\end{array}\right\} = 0 \qquad (36)$$

This rate equation is applicable if there are rate-controlling steps in both paths of a two-path reaction system, and if all rate-controlling steps have a stoichiometric number of ν.

It is conceivable that there may exist a reactant and a product that initiate and terminate a third path that comprises only those steps common to both paths 1 and 2. Then it would be possible to determine experimentally the combined product of the velocity ratios of the steps common to both paths. However, usually it is not possible to determine experimentally this combined product so we consider only the situation in which there are no rate-controlling steps common to both paths. Then Equation (36) reduces to

$$V^2 - V\,(V_+^{(1)} + V_+^{(2)}) + V_+^{(1)}\,V_+^{(2)}\,[1 - \exp(\Delta G/\nu RT)] = 0 \qquad (37)$$

and this is a quadratic equation for the velocity in terms of the potential factor. If the two forward velocities are determined experimentally and if they correlate according to Equation (37) so that a constant stoichiometric number ν is obtained, then the structure of the rate equation will be known. Moreover it will be known that there are no rate-controlling steps common to both paths, thus eliminating the necessity of evaluating the rate constants for those steps.

The rate equation is much simpler if all the rate-controlling steps are in a path p. Then Equation (17) may be combined with Equation (32) to yield

$$V_-^{(p)}/V_+^{(p)} = \begin{array}{l}\Pi\ \ (v_{-r}/v_{+r})\\ \text{over all rate-}\\ \text{controlling}\\ \text{steps } r\end{array} = \exp\left(\frac{\Delta G}{\nu RT}\right) \qquad (38)$$

Here, as before, the stoichiometric number of each rate-controlling step equals ν. This equation may also be obtained from the general Equation (36), but this is not as convenient.

Equation (38) may be combined with Equation (2) to eliminate the backward velocity and form the rate equation

$$V = V_+^{(p)}\left[1 - \exp\left(\frac{\Delta G}{\nu RT}\right)\right] \qquad (39)$$

This is the potential form of the rate equation, discussed previously, and is useful in that a unique stoichiometric number ν may be obtained if an experimentally determined forward velocity correlates according to it. Then we can hypothesize that all the rate-controlling steps are in one path, and that they each have the same stoichiometric number. This then is the condition under which a potential form of the rate equation exists. Whether or not this form exists can be verified by experiment, with very little knowledge of the kinetics involved.

Equation (39) also applies to the basic case originally developed by Horiuti (*4*) in which there is only a single rate-controlling step governing the entire system.

As a final example, consider the decomposition reaction discussed by Bischoff and Froment (*8*):

$$A_1 = B_1 + B_2 \qquad (40)$$

with mechanistic steps

Reaction No.	Reaction	Stoichiometric No.
1	$A_1 + l = A_1l$	1
2	$A_1l + l = B_1l + B_2l$	1
3	$B_1l = B_1 + l$	1
4	$B_2l = B_2 + l$	1

(41)

Bishoff and Froment have assumed Langmuir kinetics in order to show that the potential form of the rate equation exists when steps 2 and 3 or steps 2 and 4 are rate controlling. We have shown, without assuming any type of kinetics, that this is true because all the rate-controlling steps will be in one path and the stoichiometric number of each step is unity. We have also shown the less specific result that the potential form exists if either step 3 or step 4 is at equilibrium; that is, if steps 1, 2, and 4 or steps 1, 2, and 3 are rate controlling.

Davidson et al. (*9*) and Bradshaw and Davidson (*10*) have also considered a similar system. They have assumed Langmuir kinetics in order to develop a general rate equation with all the reaction steps rate controlling. If we remove the restriction of Langmuir kinetics from their treatment, we can, by appropriate substitutions into their equation, derive rate equations in terms of the unidirectional velocities of the mechanistic steps. One form of such equations is given by

$$\left[\frac{v_{-1}v_{-2}}{v_{+1}v_{+2}v_{+3}v_{+4}}\right]V^2 + \left[\frac{1}{v_{+1}} + \frac{v_{-1}}{v_{+1}v_{+2}} + \frac{v_{-1}v_{-2}(v_{-3}+v_{-4})}{v_{+1}v_{+2}v_{+3}v_{+4}}\right]V = 1 - \exp\left(\frac{\Delta G}{\nu RT}\right) = 1 - \exp\left(\frac{\Delta G}{RT}\right) \quad (42)$$

This will not be the same rate equation as that given by Davidson et al. because their equation has been specified for Langmuir kinetics. However, their equation is one of the many other forms that may each be obtained from the application of Equation (2) to Equation (42). We can even show that Equation (32) is one of these forms.

Since Equation (42) is equivalent to Equation (32), any conclusions about the mechanism which are drawn from Equation (32) can also be drawn from Equation (42). Both the rate equation derived by Davidson et al. and our equivalent form (42) are inconvenient to use if some of the steps are at equilibrium. This is so because other forms of the rate equation can often be established from a correlation of the forward velocities. These correlations will determine the structure of the rate equation and thus will yield some information about the rate-controlling steps. Once this is known, the general rate equation obtained by the assumption of Langmuir kinetics often can be simplified.

CONCLUSIONS

We have shown that the unidirectional velocities, when measured under certain restrictions of isotopic exchange, can be related to the unidirectional velocities of the individual mechanistic steps. From these relations the structure of a rate equation can be analyzed in terms of experimentally determinable unidirectional velocities and a potential factor. For a general two-path reaction system, the potential factor can be factored from the rate equation if all the rate-controlling steps are in one path, and if they all have the same stoichiometric number. For this case the rate of the overall reaction can be expressed as the product of the potential factor and the forward velocity for the path. If no rate-controlling steps are common to both paths, and if all the rate-controlling steps have the same stoichiometric number, then a quadratic equation in the velocity is obtained. In this form, the potential factor is present, but is not factorable from the rate equation. The overall rate will still be a function of only the potential factor and the experimentally determinable forward velocities of the overall reaction.

The two forms of the rate equation can be used in the correlation of kinetic data to determine the structure of the rate equation. If the data correlate according to either one of these forms of the rate expression, then some important information about the rate-controlling steps of the mechanism can be determined, even with little or no knowledge of the mechanism. In general, it is not necessary to assume a specific adsorption rate theory.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of the Allied Chemical Foundation and the National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, Public Health Service. The doctoral research of Ronald S. Csuha was also aided by a Fellowship from the Petroleum Research Fund administered by the American Chemical Society.

NOTATION

A = general reactant, which may be subscripted to denote a specific species, for example, A_i

a = coefficient of A in the chemical equation of the overall reaction and may be subscripted

B = general product, which can be subscripted to denote a specific species, for example, B_i

b = coefficient of B in the chemical equation of the overall reaction and may be subscripted

g_r, G = Gibbs free energy of a mechanistic step r, and that of the overall reaction

l = active site, and when attached to a molecular species, denotes an adsorbed state of the species

R = universal gas constant

T = absolute temperature

t_e^i = tagged atomic velocity of the element e from or to the molecular species i and is defined by Equation (5)

V = net velocity of an overall reaction

$V_+^{(p)}$, $V_-^{(p)}$ = forward and backward velocities of an overall reaction, and are dependent on the reaction path p

v_{+r}, v_{-r} = forward and backward velocities of the mechanistic step r

z_e^i = fraction of the tagged element e in the species i

Greek Letters

Δ = difference operator used to denote a change in the Gibbs free energy.

ν_r = stoichiometric number of step r, and is defined as the number of times step r occurs for each time the overall reaction occurs once

ν = stoichiometric number of all the rate-controlling steps when it is the same for all rate-controlling steps

Subscripts, Superscripts, and Indices

e = atomic element

i = molecular species

p = reaction path

r = mechanistic reaction step

LITERATURE CITED

1. Aris, Rutherford, and R. H. S. Mah, *Ind. Eng. Chem. Fundamentals Quart.*, **2**, 90 (1963).
2. Happel, John, *J. Res. Inst. Catalysis Hokkaido Univ.*, **16**, 305 (1968).
3. Kaneko, Y., and H. Odanaka, *ibid.*, **13**, 29 (1965); **14**, 213 (1966).
4. Horiuti, Juro, and Takashi Nakamura, *Advan. Catalysis*, **17** (1967).
5. Temkin, M. I., *Nauchn. Osnovy Podbora Proizv. Katalizatorov Akad. Nauk. SSSR, Sibirsk Otel*, 46 (1964).
6. Christiansen, J. A., *Advan. Catalysis*, **5**, 311 (1953).
7. Hollingsworth, C. A., *J. Chem. Phys.*, **27**, 1346 (1957).
8. Bischoff, K. B., and G. F. Froment, *Ind. Eng. Chem. Fundamentals Quart.*, **1**, 195 (1962).
9. Davidson, Burton, R. W. Bradshaw, and F. R. Bernath, paper presented at Second Joint AIChE-IIQPR meeting, Tampa, Fla. (May 1968).
10. Bradshaw, R. W., and Burton Davidson, *Chem. Eng. Sci.*, **24**, 1519 (1969).

Manuscript received July 20, 1969; revision received February 24, 1970; paper accepted March 2, 1970. Paper presented at AIChE Washington meeting.