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## HETEROGENEOUS CATALYSIS WITH A SINGLE OVERALL REACTION

By

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### Abstract

This work was undertaken to establish more exactly the implications of the concept of a rate controlling step in heterogeneous catalytic reactions. Rate expressions are developed for situations with more than one rate controlling step in the mechanistic sequence but, where the system is characterized by a single overall reaction. These relationships are applied to several cases in the literature which have been studied using isotopic tracer techniques to establish forward and backward reaction rates. The results constitute an extension of the stoichiometric number concept originated by HORIUTI.

### Introduction

In developing rate equations for chemical systems a simplifying assumption, which is often made in combining elementary kinetic steps, is the existence of a steady state in which the amount of intermediates in a system does not change with time. This assumption seems especially applicable in the case of heterogeneous catalysis because the solid catalyst phase is usually much smaller than the fluid phase which contains the initial reactants and final products entering into the overall reaction. This assumption is employed in our treatment. Together with the basic transition state theory of chemical reactions, it leads to a general formulation of the kinetic equations involved.

A chemical reaction system will, in general, involve a number of chemical reactions whereby initial reactant species are converted to products. A single overall reaction is defined in terms of a stoichiometric equation which relates a given number of various reactants to a fixed proportion of appropriate products. If a system is characterized 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 overall chemical equation. Changes in temperature, pressure or proportions of reactants will not influence their relative rates of disappearance or that of product formation. It is such systems which are considered in the present paper.

Even with a single overall reaction, it is well known that there will often exist a number of intermediate reactions which constitute the individual mechanistic steps involved in the overall reaction. The problem of distinguishing the number of independent reactions in a complex system has been treated from several viewpoints.<sup>1-3)</sup> For our present purpose, it is sufficient to note that a system which is characterized by a single overall reaction possesses the property that

$$S - I = 1 \quad (1)$$

here  $S$  denotes the number of independent elementary reactions or steps and  $I$  the number of independent intermediate species (species other than reactants and products which enter into mechanistic steps).

An important characteristic of any single overall reaction is the stoichiometric number  $\nu_s$  for each of the elementary steps,  $s$ .  $\nu_s$  for an elementary reaction represents the number of times it occurs for each time the molecular change represented by the overall reaction, as written, occurs once. HORIUTI<sup>4,5)</sup> first introduced this concept. In a rigorous statistical mechanical development, he showed how the stoichiometric number was related to the rates of forward and reverse reactions for the elementary steps in a given overall reaction. These ideas have been further developed and summarized in a recent treatment by HORIUTI and NAKAMURA<sup>1)</sup> which provides a complete theory of heterogeneous catalytic reactions taking into account interaction among adsorbed species on uniform catalyst surfaces.

In the literature the term "path" or "route" is often taken to define a single overall reaction (that is a system governed by Eq. (1)). Since the individual steps may form a complex pattern with branching and recombining of intermediate species, we prefer to use the term path to represent a single unbroken series of mechanistic steps whereby any atomic species can move from initial to final products or the reverse. The transfer of such species can be observed by isotopic tracers and may be much larger than the overall reaction rate, if the path of isotopic transfer does not include a slow step of another path. HORIUTI has shown how experiments with isotopic tracers can provide useful independent information on the exchange rates of atomic species.

It is possible to simplify the overall kinetic expressions by assuming that

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certain individual steps will involve a very small change in free energy as compared with others. HORIUTI<sup>6,7)</sup> has shown that the assumption, that only one mechanistic step involves an appreciable free energy change will lead to the possibility of separating a so called "potential factor" in the overall rate expression, which involves one driving force between reactants and products. This factor contains the overall equilibrium constant together with the partial pressures of reactants and products, and becomes zero as equilibrium is reached. It appears that this relationship will apply in the case of non-uniform as well as uniform surfaces.<sup>8)</sup> TEMKIN<sup>3,9)</sup> extended the theory of steady state reactions and showed that the stoichiometric number and a separable "potential factor" can also be employed to characterize more complicated overall reactions where measurable free energy changes occur in several steps but all along a single reaction path. He introduced the concept of an average stoichiometric number and showed that it will be a constant in the case a single reaction path where there the stoichiometric numbers of all the component steps have the same value. He did not however consider the case for a branching path.

FRUMKIN<sup>10)</sup> employed the stoichiometric number concept in a study of the hydrogen electrode reaction and showed that isotopic transfer may be very high if it by-passes the slow step. In this case an infinite value of the apparent stoichiometric number is obtained even though the overall reaction rate is controlled by the slow step. HORIUTI and MATSUDA<sup>11)</sup> generalized this treatment to include other chemical reactions.

In order to develop detailed overall kinetic equations, it is necessary to assume a form for the individual rates of the mechanistic steps. In addition to assumptions regarding the rate expressions for individual steps (here a step is taken to involve the rates of both forward and backward reactions) it is necessary to assume a model for chemisorption. The LANGMUIR theory, for activated adsorption with a uniform surface composed of a single type of non-interacting active centers, provides the simplest model, although other models have been employed. This chemisorption model, together with the assumption of a single surface chemical reaction, forms the basis for the treatment given in the classic text by HOUGEN and WATSON.<sup>12)</sup> This method of correlation has traditionally been employed in many investigations since its publication. The treatment of HOUGEN and WATSON, later extended by YANG and HOUGEN<sup>13)</sup> employed the further assumption that only one of the sequential steps—adsorption, surface reaction and desorption—is rate controlling.

The present study is aimed at elaboration of the structure of heterogeneous catalysis rate expressions where a single overall reaction is involved, but where more than one slow step exists. Although modern high speed computers

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will enable problems of this type to be solved once the rates of individual steps are given, the experimental determination of appropriate individual rates is not always easy. It is therefore valuable to know when simplifications can be effected in the expressions for determining overall reaction rate.

### General Kinetic Expressions

Consider a uniquely defined overall reaction which takes place in a number of separate mechanistic steps. Let us assume that the reaction starts in a single series of steps, but at some point products of an intermediate step react further in two or more different steps, so that a branching occurs resulting in two (or more) reaction paths. Designate the one series starting with initial species as occurring with velocities  $v_{+1}, v_{+2}, v_{+3}, \dots, v_{+m}$ . The reverse reaction rates of this series will be  $v_{-1}, v_{-2}, v_{-3}, \dots, v_{-m}$ . At an arbitrary point, say the product from step  $i$ , branching occurs. At this point we will have another series of reactions  $v_{+(\delta+1)'}, v_{+(\delta+2)'}, v_{+(\delta+3)'}, \dots, v_{+n'}$ . Corresponding reverse steps  $v_{-(\delta+1)'}, v_{-(\delta+2)'}, v_{-(\delta+3)'}, \dots, v_{-n'}$ . It is assumed that these reactions occur at a steady state. Thus the rates refer to a definite amount of catalyst on which the reactions involved have resulted in the presence of constants of intermediate species. The forward rate of a reaction path can be described<sup>(3,9)</sup> in terms of the probability of forward and backward production at each state in a given series of reactions beginning with initial species and ending with final product. The backward rate is similarly defined except it starts with final products and ends with initial species.

In the example which we have chosen, the forward and backward rates of the initial series will be:

$$V_{+}^{1,2,3,\dots,m} \left( \frac{v_1}{v_{+1}} + \frac{v_{-1}v_2}{v_{+1}v_{+2}} + \frac{v_{-1}v_{-2}v_3}{v_{+1}v_{+2}v_{+3}} + \dots \right) = 1 \quad (2)$$

$$V_{-}^{1,2,3,\dots,m} \left( \frac{v_m}{v_{-m}} + \frac{v_{+m}v_{m-1}}{v_{-m}v_{-(m-1)}} + \frac{v_{-m}v_{+(m-1)}v_{m-2}}{v_{-m}v_{-(m-1)}v_{-(m-2)}} + \dots \right) = 1 \quad (3)$$

Division of equation (2) by equation (3) gives

$$\frac{V_{+}^{1,2,3,\dots,m}}{V_{-}^{1,2,3,\dots,m}} = \frac{v_{+1}v_{+2}v_{+3}\dots v_{+m}}{v_{-1}v_{-2}v_{-3}\dots v_{-m}} \quad (4)$$

Similarly because of the branch in the reaction series a second equation similar to (4), can be derived

$$\frac{V_{+}^{1,2,3,\dots,\delta',(\delta+1)',\dots,n'}}{V_{-}^{1,2,3,\dots,\delta',(\delta+1)',\dots,n'}} = \frac{v_{+1}v_{+2}v_{+3}\dots v_{+\delta'}v_{+(\delta+1)'}\dots v_{n'}}{v_{-1}v_{-2}v_{-3}\dots v_{-\delta'}v_{-(\delta+1)'}\dots v_{n'}} \quad (5)$$

Here  $m$  is the last step of the initial series and  $n'$  is the last step of the

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branch in the initial series.

Either Eq. (4) or (5) satisfies the relationship that the difference between forward and backward rates is equal to the overall rate of the single overall reaction :

$$V = V_{+}^{1,2,3,\dots,m} - V_{-}^{1,2,3,\dots,m} = V_{+}^{1,2,3,\dots,n'} - V_{-}^{1,2,3,\dots,n'} \quad (6)$$

The overall Gibbs Free Energy for the complete reaction is the sum of intermediate free energies for *all* elementary steps multiplied by the stoichiometric number of each step.

$$\Delta G = \nu_1 \Delta g_1 + \nu_2 \Delta g_2 + \nu_3 \Delta g_3 + \dots + \nu_m \Delta g_m + \nu_{(\ell+1)'} \Delta g_{(\ell+1)'} + \dots + \nu_n' \Delta g_{n'} \quad (7)$$

For each individual step, *s*, assuming HORIUTI's statistical mechanical transition state theory,<sup>1)</sup>

$$\Delta g_s = -RT \ln \frac{v_{+s}}{v_{-s}} \quad (8)$$

If we designate the overall chemical reaction by the equation

$$\sum_{j=1}^L \alpha_j A_j = \sum_{j=1}^R \alpha_j A_j \quad (9)$$

where  $\alpha_j$  represents the coefficients which appear in the chemical reaction as written, the overall Gibbs Free Energy may be written<sup>2)</sup> under ideal conditions as

$$\Delta G = -RT \ln K \frac{\prod_{j=1}^L p_j^{\alpha_j}}{\prod_{j=1}^R p_j^{\alpha_j}} \quad (10)$$

The product symbol  $\prod$  denotes the product of factors, *i. e.*  $p_1^{\alpha_1}$ ,  $p_2^{\alpha_2}$ ,  $p_3^{\alpha_3}$ , the partial pressures of reactants and products of the overall reaction. In the non-ideal case the partial pressures are replaced by the partial fugacity.  $K$  is the equilibrium constant.

For the case of a system in which there is a single slow step, the free energy change  $\Delta g$  of all other steps will approach zero. Then, if the slow step occurs in one of the steps  $v_1$ ,  $v_2$ ,  $v_3$ ,  $\dots$   $v_i$  either Eq. (4) or (5) may be used to establish a relationship to obtain the stoichiometric number of the rate controlling step. For example if step  $r$  is rate controlling, we have by dividing Eq. (7) by  $\left(-RT \ln \frac{V_{+}^{1,2,3,\dots,m}}{V_{-}^{1,2,3,\dots,m}}\right)$  and using Eq. (4) to evaluate  $V_{+}/V_{-}$ ,

$$\frac{\Delta G}{-RT \ln \frac{V_{+}^{1,2,3,\dots,m}}{V_{-}^{1,2,3,\dots,m}}} = \frac{\nu_r \Delta g_r}{\Delta g_r} = \nu_r \quad (11)$$

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The use of isotopic tracers will in some instances enable us to determine either  $V_+^{1,2,3,\dots,m}$  or  $V_-^{1,2,3,\dots,m}$  and Eq. (6) relates the determined unidirectional rate to the overall rate of reaction determined by kinetic measurement.

Thus from (11) we may write,

$$V = V_+^{1,2,3,\dots,m} \left( 1 - e^{-\frac{\Delta G}{RT\nu_r}} \right). \quad (12)$$

The familiar form of the kinetic equation for this situation may be obtained by using Eq. (10), whence

$$V = \frac{V_+^{1,2,3,\dots,m}}{\left( \prod_{j=1}^L p_j^{\alpha_j} \right)^{1/\nu_r}} \left[ \left( \prod_{j=1}^L p_j^{\alpha_j} \right)^{1/\nu_r} - \left( \frac{\prod_{j=1}^R p_j^{\alpha_j}}{K} \right)^{1/\nu_r} \right] \quad (13)$$

A relationship using this type of formulation has been presented by HAPPEL.<sup>8)</sup> If we designate the multiplier of the expression in brackets, the "potential factor", by  $\phi$  and use terminology<sup>12)</sup> often employed to designate an overall reaction, we have



and equation (13) may be written

$$V = \phi \left[ (p_A^\alpha p_B^\beta \dots)^{1/\nu_r} - \left( \frac{p_S^\delta p_T^\epsilon \dots}{K} \right)^{1/\nu_r} \right]. \quad (15)$$

The same result would of course be obtained by using Eq. (5) instead of Eq. (4). However, if the rate controlling step occurs after the point where the unidirectional reaction path branches, it would be necessary to choose an isotope tracer which follows the rate controlling step. If this is not done an indefinitely high stoichiometric number will be obtained by application of Eq. (11). Thus suppose the rate controlling step occurred in the series corresponding to Eq. (5) after the branching of reaction series, *i. e.* in one of the steps  $\nu_{(i+1)}, \dots, \nu_n$ , and we choose an isotope which follows the series corresponding to Eq. (4),  $\nu_1 \dots \nu_m$ . By following the procedure shown in Eq. (11), we would obtain

$$\bar{\nu}_r = \frac{\Delta G}{-RT \ln \frac{V_+^{1,2,3,\dots,m}}{V_-^{1,2,3,\dots,m}}} = \frac{\nu_r \Delta g_r}{0} = \infty. \quad (16)$$

This situation has been discussed by FRUMKIN<sup>10)</sup> and by HORIUTI and MATSUDA.<sup>11)</sup>

Aside from the theoretical implications involved in determining the

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stoichiometric number by isotopic tracer experiments, it is seen that the attainment of a constant value for experimentally determined  $\nu_r$  is equivalent to obtaining kinetic rate expressions of the form of Eqs. (12), (13) and (15). Since the separation of a "potential factor" represents a simplification in the mathematical form of the rate expression, it is of interest to define an apparent stoichiometric number  $\bar{\nu}$  determined in the same way from experimental data as if a slow step existed. Thus, we define

$$\bar{\nu} = \frac{-\Delta G}{RT \ln(V_+/V_-)} \quad (17)$$

and analogous to equation (13), we will have

$$V = \frac{V_+}{\left(\prod_{j=1}^L p_j^{\alpha_j}\right)^{1/\bar{\nu}}} \left[ \left(\prod_{j=1}^L p_j^{\alpha_j}\right)^{1/\bar{\nu}} - \left(\frac{\prod_{j=1}^R p_j^{\alpha_j}}{K}\right)^{1/\bar{\nu}} \right] \quad (18)$$

If more than one unidirectional path exists we may obtain different values for  $\bar{\nu}$  for each path. However, if  $\bar{\nu}$  is constant over a range of conditions equations like (18) may be employed to correlate data obtained.

Further development of the general expressions (17) and (18) shows that they have more than purely empirical significance. Thus let us suppose that there exists more than one rate controlling step but that they occur in a single reaction path. For convenience, for example, assume that two slow steps  $\nu_q$  and  $\nu_r$  occur in the series  $\nu_1 \cdots \nu_m$  and that we have chosen an isotopic tracer which also follows this path. If we apply Eq. (17), we have

$$-\bar{\nu} = \frac{\nu_1 \Delta g_1 + \nu_2 \Delta g_2 + \cdots + \nu_q \Delta g_q + \cdots + \nu_r \Delta g_r + \cdots + \nu_m \Delta g_m + \nu_{(\ell+1)} \Delta g_{(\ell+1)'} + \cdots + \nu_n \Delta g_n}{RT \ln \frac{v_{+1}}{v_{-1}} + RT \ln \frac{v_{-2}}{v_{-2}} + \cdots + RT \ln \frac{v_{+q}}{v_{-q}} + \cdots + RT \ln \frac{v_{+r}}{v_{-r}} + \cdots + RT \ln \frac{v_{+m}}{v_{-m}}} \quad (19)$$

If all steps but  $q$  and  $r$  are close to equilibrium, we have  $\Delta g_s = 0$  and correspondingly  $RT \ln \frac{v_{+s}}{v_{-s}} \simeq 0$ , except for  $s = q$  or  $r$ . Now, if in addition,  $\nu_q = \nu_r$ , *i. e.* the slow steps *all* have the same stoichiometric number,

$$\bar{\nu} = \frac{\nu_q \Delta g_q + \nu_r \Delta g_r}{\Delta g_q + \Delta g_r} = \nu_q = \nu_r \quad (20)$$

and Eq. (18) applies exactly. A similar relationship has been given by TEMKIN.<sup>3,9)</sup>



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Note, however, that even if there is a single overall reaction involved, rate controlling steps may occur in *both* branches of the unidirectional series. In that case it is not possible in general to obtain a kinetic expression on which a "potential factor" can be separated, even if the stoichiometric number of all rate controlling steps is the same. This limitation in the use of equation (18) is an important one, not clearly defined in the literature.

More complicated cases can occur involving multiple branching and in such instances it will only be possible to separate a "potential factor" if all slow steps occur on a single path. With multiple branching it may not be possible to find a single atomic species which can be traced through the controlling reaction path because the same terminal reactants or products may occur in more than one path. Such a situation probably exists in the case of the reaction path of hydrogen in the hydrogenation of ethylene.

It should also be noted that, even in the case of a reaction following a single series of steps with the same stoichiometric number, the use of isotopic tracers, in reactants or products which enter or leave the series at intermediate points, will not lead to values of the stoichiometric number applicable in Eq. (18) if a step is skipped which is slow. In that case a high value of  $\bar{\nu}$  will be obtained. This situation can, of course, be used to establish the importance of separate steps in a mechanistic series. The general overall rate equation will not change but it may be possible to use a special form with fewer rate controlling steps.

Very often it will be the case that the stoichiometric numbers involved in plausible reaction sequences will be unity. In that case, a lack of constancy in  $\bar{\nu}$  may be an indication that more than one reaction path exists in which slow reaction steps occur. This can be confirmed by appropriate experiments using different isotopic tracers as demonstrated by KANEKO<sup>14,15)</sup> and his co-workers.

The relationships developed thus far will be applicable to systems involving non-uniform as well as uniform surfaces. They will be valid regardless of the formulation of the kinetic expressions used for individual mechanistic steps because it is only necessary to assume steady state and the applicability of Eq. (8), which is based on HORIUTI's absolute reaction rate theory.

### Formulation of Model Rate Equations

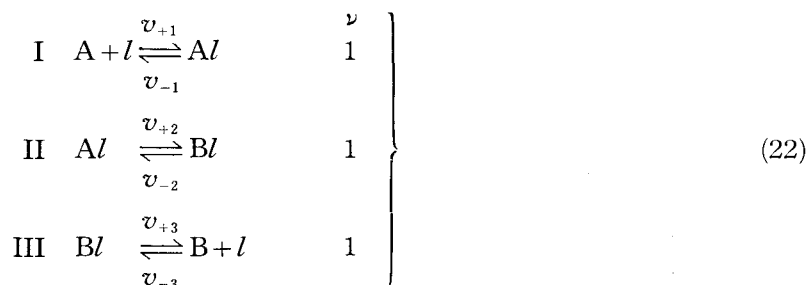
We will apply the expressions developed in the previous section to several basic cases which have appeared in the literature, using simple mass action expressions to obtain rate equations and the LANGMUIR theory for chemisorption.

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Consider first the simple situation treated by ARIS<sup>2)</sup> in which the overall reaction on a catalyst is



The sequence of steps proceeds by a single path with all three steps being slow



where  $l$  is an adsorption site, and the  $\nu$ 's denote reaction rates.

We see immediately that equation (18) applies with  $\nu=1$  and we may write

$$V = \frac{v_{+1}v_{+2}v_{+3}}{p_A(v_{+2}v_{+3} + v_{+3}v_{-1} + v_{-1}v_{-2})} \left[ p_A - \frac{p_B}{K} \right]. \quad (23)$$

Assume that the reaction velocities of individual steps may be expressed as

$$\left. \begin{array}{l} v_{+1} = k_{+1}P_A C_l; \quad v_{-1} = k_{-1}C_{Al} \\ v_{+2} = k_{+2}C_{Al}; \quad v_{-2} = k_{-2}C_{Bl} \\ v_{+3} = k_{+3}C_{Bl}; \quad v_{-3} = k_{-3}C_l P_B \end{array} \right\} \quad (24)$$

where reaction velocity constants are denoted by  $k_i$  and  $C_i$  refers to surface concentrations of appropriate species.

We then obtain

$$V = \frac{k_{+1}k_{+2}k_{+3}C_l}{k_{+2}k_{+3} + k_{+3}k_{-1} + k_{-1}k_{-2}} \left[ p_A - \frac{p_B}{K} \right]. \quad (25)$$

By making use of the relationships for steady state

$$V = v_{+1} - v_{-1} = v_{+2} - v_{-2} = v_{+3} - v_{-3}, \quad (26)$$

we can express  $C_{Al}$  and  $C_{Bl}$  in terms of  $C_l$ . To obtain  $C_l$ , we then use the equation

$$C_l + C_{Bl} + C_{Al} = C_t = 1 \quad (27)$$

The total area is taken as unity without loss of generality and finally we obtain

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$$C_i = \frac{1}{1 + \frac{k_{+1}(k_{-2} + k_{+2} + k_{+3})p_A + k_{-3}(k_{-1} + k_{+2} + k_{-2})p_B}{k_{-1}k_{-2} + k_{-1}k_{+3} + k_{+2}k_{+3}}} \quad (28)$$

We can employ this general relationship to determine the assumptions which are equivalent to employing the concept of a rate controlling step. Suppose, for example, that the adsorption and desorption of A is much slower than the other steps. We then have  $k_{+1}p_A$ ,  $k_{-1} \ll k_{+2}$ ,  $k_{-2}$ ,  $k_{+3}$ ,  $k_{-3}p_B$ . From Eq. (28) for this situation, we find

$$C_i = \frac{1}{1 + \frac{(k_{+2}k_{-3} + k_{-2}k_{-3})p_B}{k_{+2}k_{+3}}} = \frac{1}{1 + \frac{1}{K_3} \left(1 + \frac{1}{K_2}\right) p_B} \quad (29)$$

where  $K_2 = k_{+2}/k_{-2}$  and  $K_3 = k_{+3}/k_{-3}$ . Note also  $K = k_{+1}k_{+2}k_{+3}/k_{-1}k_{-2}k_{-3}$ . From Eq. (25) we have

$$V = \frac{k_{+1} \left[ p_A - \frac{p_B}{K} \right]}{1 + \left(1 + \frac{1}{K_3}\right) \frac{1}{K_3} p_B} \quad (30)$$

Examination of Eqs. (25) and (28) will show that it would not be necessary for  $k_{-3}p_B$  to be included in the inequality relationship. A similar result is obtained by assuming adsorption and desorption of B as the slow step.

If the chemical reaction is assumed to be the slow step, we have  $k_{+2}$ ,  $k_{-2} \ll k_{+1}p_A$ ,  $k_{-1}$ ,  $k_{+3}$ ,  $k_{-3}p_B$ . We then find

$$C_i = \frac{1}{1 + \frac{k_{+1}}{k_{-1}} p_A + \frac{k_{-3}}{k_{+3}} p_B} \quad (31)$$

and

$$V = \frac{K_1 k_{+2} \left[ p_A - \frac{p_B}{K} \right]}{1 + K_1 p_A + \frac{1}{K_3} p_B} \quad (32)$$

which is the usual form obtained using the rate determining step concept as equivalent to attainment of equilibrium in the fast steps. In this case it can be shown that it would not be necessary to include  $k_{+1}p_A$  and  $k_{-3}p_B$  in the inequality to obtain Eq. (32).

When two slow steps exist, it is also possible to simplify Eq. (25), but the form is not as simple as that shown in Eq. (30) and (32). However, in all

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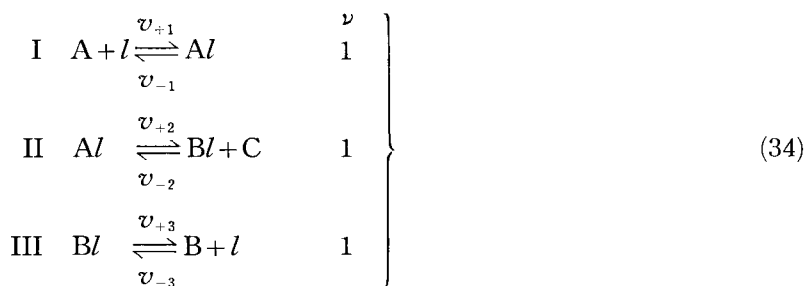
cases it is seen that empirically the same form of expression with a "kinetic term", "driving potential term" and "adsorption term" is obtained.<sup>13)</sup>

Let us next consider a slightly more complicated case which illustrates the problems associated with the assumption of a rate controlling step when we are not dealing with a simple sequence of the type  $A \rightleftharpoons B \rightleftharpoons C$ , etc., where all the product from one step is the reactant for the following sequential step.

Assume the overall reaction,



which follows the sequence



This is similar to the previous example in that we have a single path with no branching and the stoichiometric numbers are all equal to unity,

We may write immediately,

$$V = \frac{k_{+1}k_{+2}k_{+3}C_l}{k_{+2}k_{+3} + k_{+3}k_{-1} + k_{-1}k_{-2}p_C} \left[ p_A - \frac{p_B p_C}{K} \right] \quad (35)$$

and since all rates are the same except  $\nu_{-2} = k_{-2}C_{Bl}p_C$  instead of  $\nu_{-2} = k_{-2}C_{Bl}$  in the previous case  $C_l$  is obtained by replacing  $k_{-2}$  in Eq. (28) by  $k_{-2}p_C$ ,

$$C_l = \frac{1}{1 + \frac{k_{+1}(k_{-2}p_C + k_{+2} + k_{+3})p_A + k_{-3}(k_{-1} + k_{+2} + k_{-2}p_C)p_B}{k_{-1}k_{-2}p_C + k_{-1}k_{+3} + k_{+2}k_{+3}}} \quad (36)$$

In this case if we assume that the adsorption and desorption of A is much slower than the other two steps, we have, analogous to Eq. (30), when  $k_{+1}p_A, k_{-1} \ll k_{+2}, k_{-2}p_C, k_{+3}, k_{-3}p_B$

$$V = \frac{k_{+1} \left[ p_A - \frac{p_B p_C}{K} \right]}{1 + \left( 1 + \frac{p_C}{K_2} \right) \frac{1}{K_3} p_B} \quad (37)$$

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As in the case of equation (30), it would not be necessary to employ  $k_{-3}p_B$  in the inequality.

It is instructive also to consider the case in which the adsorption and desorption of B is rate controlling. Making appropriate substitutions, we find for this case in which  $k_{+3}, k_{-3}p_B \ll k_{-1}p_A, k_{-1}, k_{+2}, k_{-2}p_C$

$$V = \frac{\frac{k_{+3}K_1K_2}{p_C} \left[ p_A - \frac{p_B p_C}{K} \right]}{1 + \left( 1 + \frac{K_2}{p_C} \right) K_1 p_A} \quad (38)$$

In this case, it can be shown that the term  $k_{+1}p_A$  can be omitted from the inequality.

HORIUTI'S<sup>5,6)</sup> conclusion regarding the appearance of partial pressures of species which do not appear in the rate controlling step will be applicable. Thus the appearance of  $1/p_C$  in the numerator of (38) is correctly predicted, when the single step involving adsorption and desorption of B is rate controlling.

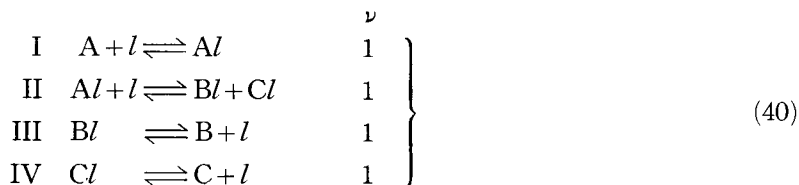
If the rate of chemical reaction is slow, we have  $k_{+2}, k_{-2}p_C \ll k_{+1}p_A, k_{-1}, k_{+3}, k_{-3}p_B$  and, analogous to equation (32),

$$V = \frac{K_1 k_{+2} \left[ p_A - \frac{p_B p_C}{K} \right]}{1 + K_1 p_A + \frac{1}{K_3} p_B} \quad (39)$$

As before it is possible to omit the conditions on  $k_{+1}p_A$  and  $k_{-3}p_B$  in the inequality.

Thus it is seen that the assumption of a single rate controlling step with all other steps at equilibrium will provide sufficient information to allow simplified rate expression to be developed. However, as shown above, all other steps do not need to be at equilibrium to derive these simplified forms.

A more complicated case is considered by BISCHOFF and FROMENT<sup>16)</sup> in which both products are adsorbed with the same basic reaction  $A \rightleftharpoons B + C$  as considered in Eq. (33). The following sequence was studied.



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They assumed that steps II and IV are rate controlling. Since  $\nu_r=1$  in all steps, it is again possible to separate a potential factor. However, it will be noted that this system represents a situation in which a branching path exists. The assumption that II and IV are rate controlling amounts to assuming that the I, II, IV path is rate controlling.

Thus, employing equation (18), we would write

$$V = \frac{V_+^{1,2,4}}{p_A} \left[ p_A - \frac{p_B p_C}{K} \right] \quad (41)$$

$$V_+^{1,2,4} = \frac{\nu_{+1}\nu_{+2}\nu_{+4}}{\nu_{+2}\nu_{+4} + \nu_{+4}\nu_{-1} + \nu_{-1}\nu_{-2}} \quad (42)$$

If we take step I as also being fast so that  $k_{+4}, k_{-4}p_C, k_{+2}, k_{-2} \ll k_{+1}p_A, k_{-1}, k_{+3}, k_{-3}p_B$ , we obtain

$$V = \frac{K_1 k_{+2} C_i^2}{1 + \frac{k_{+2} p_B}{k_{+4} K_2 K_3} C_i} \left[ p_A - \frac{p_B p_C}{K} \right] \quad (43)$$

with

$$C_i = \frac{-\beta + \sqrt{\beta^2 + 4\alpha k_{+4}}}{2\alpha} \quad (44)$$

where

$$\alpha = \frac{k_{-2} p_B}{K_3} + \frac{k_{-2} K_1 p_A p_B}{K_3} + \frac{k_{-2} p_B^2}{K_3^2} + K_1 k_{+2} p_A,$$

$$\beta = k_{+4} + K_1 k_{+4} p_A + \frac{k_{+4} p_B}{K_3} + k_{-4} p_C - \frac{k_{-2} p_B}{K_3}.$$

These equations were derived by assuming steps I and III at equilibrium because the general solution for  $C_i$  is complicated. Derivation of Eq. (43) implies that  $k_{-3}p_B$  is large, but the condition  $k_{+1}p_A$  could probably be omitted from the inequality relationship.

The algebraic form of the solution published by BISCHOFF and FROMENT<sup>16)</sup> differs from that developed in this paper, though numerically the solutions are in agreement. However, the BISCHOFF and FROMENT solution does not clearly indicate how the potential factor separates.

Still considering this example, if we were to assume steps III and IV as being slow, a more complicated rate equation would result because a potential factor could not be separated out.

In that case, if we could determine  $\bar{\nu}$  by an isotopic tracer which followed path I, II, and III alone, we would have

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$$\bar{\nu}^{1,2,3} = \frac{\Delta g_1 + \Delta g_2 + \Delta g_3 + \Delta g_4}{\Delta g_1 + \Delta g_2 + \Delta g_3} = \frac{\Delta G}{\Delta G - \Delta g_4}, \quad (45)$$

$\Delta g_4$  would be a positive quantity.

A second determination of  $\bar{\nu}$  by an isotopic tracer which followed the path I, II, and IV would give

$$\bar{\nu}^{1,2,4} = \frac{\Delta G}{\Delta G - \Delta g_3} \quad (46)$$

Thus it would be possible to assess the relative importance of reactions III and IV, even if I and II were *not fast*. If reactions III and IV were the only slow steps, we would have

$$\bar{\nu}^{1,2,3} = \frac{\Delta g_3 + \Delta g_4}{\Delta g_3} = \frac{\Delta G}{\Delta g_3}, \quad (47)$$

$$\bar{\nu}^{1,2,4} = \frac{\Delta g_3 + \Delta g_4}{\Delta g_4} = \frac{\Delta G}{\Delta g_4}. \quad (48)$$

Since either Eq. (46) or (47) could serve to establish  $\Delta g_3$  and  $\Delta g_4$ , it would be possible to check the hypothesis of two rate controlling steps, *i. e.* III and IV by conducting experiments with two isotopic tracers. The sum of the reciprocals of the two apparent stoichiometric numbers should equal unity in this case.

### Discussion

The above principles may serve to interpret data obtained in experiments with isotopic tracers in which forward and backward rates are determined. Several studies have been reported in the literature in which measurements of this type have been made and we will comment briefly on how the present treatment might be applied in further research using three reactions as examples.

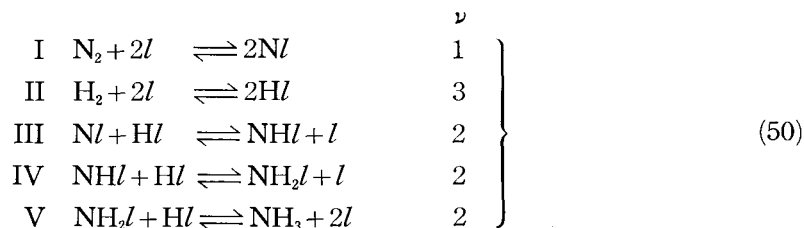
The structure of ammonia synthesis reactions has been widely studied. The overall reaction may be written as



The first studies using the stoichiometric number concept were made by ENOMOTO and HORIUTI<sup>17)</sup> employing <sup>15</sup>N as an isotopic tracer. Assuming that a single rate controlling step exists, these investigators found a stoichiometric number of two for the rate controlling step.

The following mechanistic series of steps was proposed for the ammonia synthesis reactions

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From our previous treatment it is clear that any or all of steps III, IV or V could be rate controlling, since with  $^{15}\text{N}$  we have

$$\bar{\nu}^{1,3,4,5} = \frac{\nu_3 \Delta g_3 + \nu_4 \Delta g_4 + \nu_5 \Delta g_5}{\Delta g_3 + \Delta g_4 + \Delta g_5} = 2. \quad (51)$$

It would also be possible, though unlikely, to obtain an experimental value of  $\bar{\nu}=2$  using  $^{15}\text{N}$  as a tracer, if it is assumed that hydrogen chemisorption does not proceed at a very rapid rate. Thus, suppose  $\Delta g_2 = \Delta g_1/3$  and  $\Delta g_3 = \Delta g_4 = \Delta g_5 = 0$ . We would then have

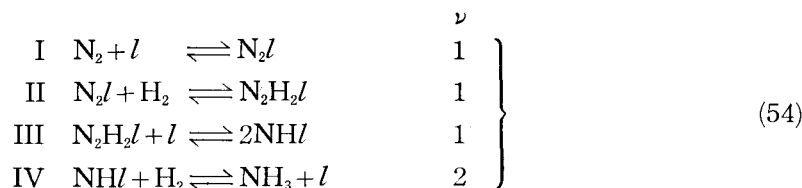
$$\bar{\nu}^{1,3,4,6} = \frac{\nu_1 \Delta g_1 + \nu_2 \Delta g_2}{\Delta g_1} = \frac{\Delta g_1 + \frac{3\Delta g_1}{3}}{\Delta g_1} = 2. \quad (52)$$

Studies by HORIUTI's coworkers more recently<sup>18,19)</sup> seem to point to the conclusion that more than one step may be slow in the ammonia synthesis so that nitrogen adsorption as well as the surface chemical reaction steps might be of importance. If  $^{15}\text{N}$  is employed as a tracer and chemisorption of nitrogen (Step I) were rate controlling, we would have

$$\bar{\nu}^{1,3,4,5} = \frac{\nu_1 \Delta g_1}{\Delta g_1} = \nu_1 = 1 \quad (53)$$

which was in fact found by TANAKA.<sup>18)</sup>

Even the determination of  $\bar{\nu}=1$  does not firmly establish that nitrogen adsorption is rate controlling, because other mechanisms than Eq. (50) may be assumed. Thus TEMKIN<sup>3)</sup> assumes that hydrogen chemisorption does not exist and considers the following sequence to represent the mechanism

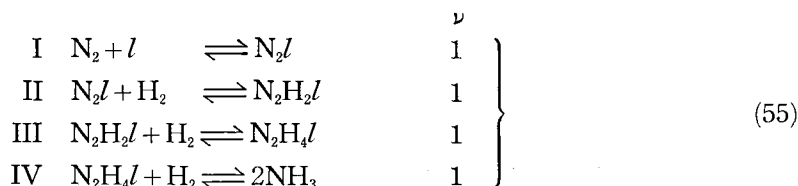




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Temkin did not conduct any isotopic tracer experiments, but it can be seen that if step IV is assumed fast,  $\bar{\nu}=1$  will be obtained with any or all of steps I, II and III being slow.

TEMKIN<sup>20)</sup> also has proposed that the mechanism for ammonia synthesis might be



In this case a stoichiometric number of unity would always be obtained with <sup>15</sup>N. TEMKIN and his coworkers<sup>21)</sup> have continued to develop relationships from overall kinetic data based on the assumption of  $\bar{\nu}=1$  with nitrogen chemisorption and a single surface reaction step as being rate controlling. These equations are complicated because a non-uniform surface rather than Langmuir adsorption is also assumed.

It would seem that additional tracer studies using a hydrogen isotope to follow the exchange between reactant H<sub>2</sub> and product NH<sub>3</sub> would be desirable. In this case if nitrogen chemisorption were rate controlling Eq. (50) would yield,

$$\bar{\nu}^{2,3,4,5} = \frac{\nu_1 \Delta g_1}{0} = \infty \quad (56)$$

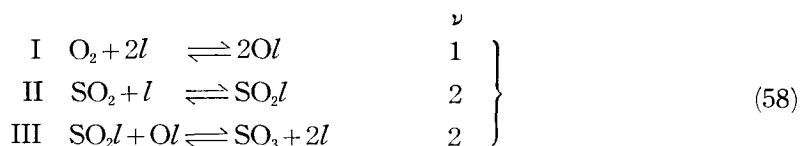
With the mechanism of Eq. (54) or (55), the same result would be obtained. Therefore it should be possible to fix the importance of nitrogen chemisorption as compared with surface reaction rate.

It does not seem possible to establish by isotopic tracer experiments alone whether the surface reaction involves hydrogen adatoms or molecular hydrogen.

Another reaction which has been studied using the isotopic tracer technique is the oxidation of sulfur dioxide, represented by the overall reaction

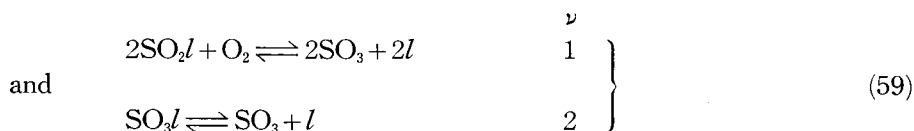


KANEKO and ODANAKA<sup>14)</sup> in studies with platinum catalyst using both <sup>35</sup>S and <sup>18</sup>O as isotopic tracers assume the mechanism



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Although this sequence involves a branching path the use of two tracers enables a decision to be made that only one rate controlling step would exist and that it is Step III. Several investigators have employed rate equations consistent with Eq. (58) with step III rate controlling to correlate overall kinetic data on both platinum and vanadium oxide catalyst. Recent studies by MATHUR and THODOS<sup>22)</sup> include the possibility of such mechanistic steps as



These studies involved overall kinetic data and it would be desirable to supplement them with tracer experiments. If  $\text{SO}_3$  desorption is admitted as a possible rate controlling step, it would be possible with  $\bar{\nu}=2$  to have a mechanism with two rate controlling steps.

A study by ATKINS and HAPPEL<sup>23)</sup> of butane dehydrogenation was conducted recently using  $^{14}\text{C}$  as the tracer. The overall reaction is



A stoichiometric number of one was obtained, which indicates that the reaction is characterized by one or more slow steps in the hydrocarbon skeleton reactions. Earlier overall kinetic studies by HAPPEL, BLANCK and HAMILL<sup>24)</sup> presented problems in selecting a single rate controlling step to characterize the rate expression and further experimental work is in progress to establish whether a mechanism involving two or more rate controlling steps is likely.

The present study indicates that it should be possible to develop somewhat more exact rate expressions for heterogeneous catalysis by taking into account the structure of the combined rate expressions for individual steps. In applying these relationships the use of more than one isotopic tracer will yield valuable information regarding possible rate controlling steps and the resultant form of the overall kinetic equations. Experimental studies discussed above show that it is possible to obtain rather constant stoichiometric numbers over a range of process conditions. The rate expressions presented should be of general value even for situations where non-uniform surfaces or surfaces with interaction between adsorbed species exist. For such studies more involved models will be necessary.

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