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AN IMPROVEMENT OF THE TREATMENT OF STEADY RATES OF CHEMICAL REACTIONS TOWARDS THE SELECTIVITY OF COMPLEX CATALYSIS*

By

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Abstract

The method developed by HORIUTI of treating the steady rate of a chemical reaction in terms of the statistical mechanical expression of unidirectional rates of its constituent, elementary steps has been applied to the mechanistic analysis of catalyzed reactions. The reactions are the modeled "linear and branched sequences of steps" discussed by CHRISTIANSEN and two real, heterogeneous catalysis, *i. e.*, ethylene hydrogenation catalyzed by nickel and ethylene oxidation catalyzed by silver. It was shown that the method is useful in carrying out analysis of the selectivity of complex, heterogeneous catalysis by making us to be able to evaluate affinities and relative rates of constituent steps without the use of currently made assumptions, such as the kinetic mass-action law for the rates of respective steps, the irreversibility of particular steps, near-equilibrium state of the overall reaction, *etc.*

§1 Introduction

A number of methods have been proposed of the mechanistic analysis of chemical reactions as based on the steady state approximation and the kinetic mass-action law assumed for rates of each constituent steps as well as overall reactions.

The kinetic mass-action law assumed as such in those investigations may be effective in most of homogeneous reactions when kinetics of respective steps are known, but not in heterogeneous catalysis which involves reactions among adsorbed entities behaving far differently from those in an ideal mixture. As shown in Appendix I, in the mechanistic analysis of heterogeneous catalysis based on the assumption of kinetic mass-action law, various adsorption isotherms are necessarily assumed for respective, adsorbed entities

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to derive dependences of the steady rates or the selectivity of the catalysis upon the experimental condition, *e.g.*, the reaction temperature and the concentrations of the reactants and products in homogeneous phase. Thus, the conclusions derived as such in the current analysis inevitably confines themselves in the case where such assumptions as mentioned above are probable, whereas we have none of method to prove their reality so far as the currently made mechanistic analysis concerns. And, further, in spite of the conclusions may sometimes be useful for the computation technique, they are possibly far from the real interactions among adsorbed species and the catalyst surface. It is thus desirable to improve the method of the mechanistic analysis so as to be able to clarify the real factors which control the activity and the selectivity of the catalyts.

This has already been essentially solved by HORIUTI¹⁾²⁾³⁾ in the case of the reaction of single route^{*)} and applied successfully to heterogeneous catalysis, *e.g.* hydrogen electrode processes, ammonia synthesis reaction and hydrogenation of ethylene. In more complex reaction, however, one has to consider the case with the reaction routes more than unity and discuss the differences among rates of reactions of these routes, *i.e.*, selectivity. This is usually attributed to different amounts of intermediates, each of which are supposed to be characteristic of respective overall reactions proceeding simultaneously. However, such a view of reaction mechanism is only intuitive, so far as the relative rates of constituent steps are not known.

The principal purpose of the present work is to apply HORIUTI's method to the mechanistic analysis of the complex catalysis, constituent steps of which are known by appropriate methods. Before going into this application, the method will be described by applying it to some simple models of reaction *i.e.*, the sets of steps discussed by CHRISTIANSEN⁴⁾ and real one of ethylene hydrogenation catalyzed by nickel.¹⁾²⁾⁵⁾

§ 2 Steady-state condition of a set of steps and the number of possible overall reactions linearly independent of each other

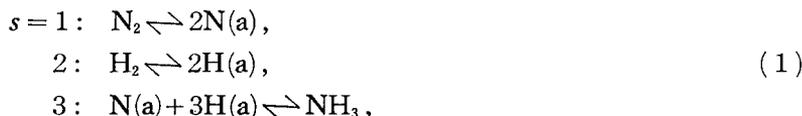
The formation rates of respective products depend, of cause, upon the rates of overall reactions proceeding in the chemical system in question. And, thus, the first problem in the investigation of kinetics of a specified set of steps is to know the sorts of overall reactions able to be caused linearly independently of each other, which are now derived from the steady state condition of these steps as follows.

The set of steps is now exemplified by those of ammonia synthesis

*) Cf. § 2.

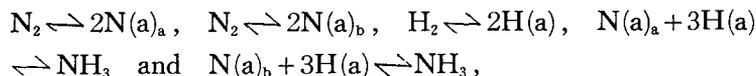
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reaction assumed to be comprised by steps,

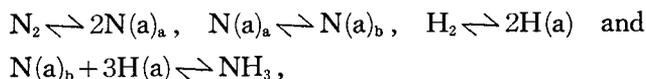


where (a) denotes the adsorbed state.

The catalyst surface is tentatively considered to be uniform with respect to individual adsorbed entities. Such a homogeneity model of the catalyst surface gives, however, not an essential limitation to the kinetic analysis, because of that most of adsorption isotherms or of rate equations of adsorption and desorption have been proved by KEII⁶⁾ and others to be derivable on either bases of the heterogeneity and the homogeneity models of the catalyst surface, taking account in the latter model of the interaction among adsorbed entities of an appropriate type. In a case where adsorbed nitrogen atoms, for instance, adsorbed on two different crystal planes, a and b, of the catalyst surface, are considered as catalytically different from each other, they would be discriminated in scheme (1) as $\text{N}(\text{a})_a$ and $\text{N}(\text{a})_b$, respectively, and five steps as



or four steps as



and so on, to be taken into consideration instead of scheme (1). What set of steps to be adequate is, however, a problem out of the present analysis of the steady state of a given set of steps.

Denoting the intermediates $\text{N}(\text{a})$ and $\text{H}(\text{a})$ by X_1 and X_2 , their concentration by $[X_1]$ and $[X_2]$ and the net rates of steps above by v_1 , v_2 and v_3 , respectively, we have

$$\begin{aligned} d[X_1]/dt &= 2v_1 - v_3 = 0, \\ d[X_2]/dt &= 2v_2 - 3v_3 = 0, \end{aligned} \quad (2)$$

as the steady state condition of the set of steps (1), which is summarized in a matrix equation as

$$\{d[X_i]/dt\} = (a_{is})\{v_s\} = 0, \quad (3)$$

where $\{ \}$ represents a column matrix and

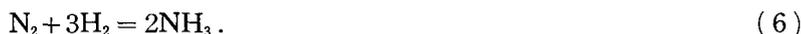
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$$\{a_{is}\} = \begin{pmatrix} 2 & 0 & -1 \\ 0 & 2 & -3 \end{pmatrix} \quad \text{and} \quad \{v_s\} = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}. \quad (4)$$

We have a single, particular solution of Eq. (3) with respect to $\{v_s\}$, from which the general solution is given as

$$\{v_1, v_2, v_3\} = V\{1, 3, 2\}, \quad (5)$$

where V is an arbitrary constant. The overall reaction specified by the solution (5) is given by summing up steps (1), each multiplied by its so-called *stoichiometric number*,³⁾ ν_s , *i. e.*, 1, 3, and 2 respectively, as



The quantity V in Eq. (5) is just the steady rate of this overall reaction.

In a general case of n steps involving m intermediates, it is shown algebraically that the number of particular solutions of Eq. (3) with regard to $\{v_s\}$ is equal to $n - q (= p)$, where q is the rank of $\{a_{is}\}$ ($i = 1, 2, \dots, m$; $s = 1, 2, \dots, n$) and p , called by HORIUTI³⁾ as the number of *independent routes*, represents the number of overall reactions which can take place simultaneously in the steady state of n steps and are linearly independent of each other. We have then, as a general solution of Eq. (3),

$$\{v_s\} = \sum_p V_p \{\nu_s\}_p, \quad (7)$$

where $\{\nu_s\}_p$ is the p -th particular solution of Eq. (3) and V_p is the steady rate of the overall reaction specified by $\{\nu_s\}_p$.

The stoichiometric number, ν_s , of respective steps are very useful in the mechanistic analysis of heterogeneous catalysis of single route as discussed by HORIUTI and others,^{3,6)} but not yet so much for the present in cases of complex heterogeneous catalysis with multi-routes of reaction.

§ 3 Improved expression of the forward and the backward unidirectional rate of a step

We now express the forward and the backward unidirectional rate of any particular step as a product of two characteristic functions. The one is a standard value of the unidirectional rate of the step, defined under the hypothetical condition that all steps preceding or following the step are in equilibrium. The other is the activity of the initial or the final system of the step relative to its standard value also defined under the same hypothetical condition. By the use of these functions we can evaluate relative rates and

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free energy drops, *i. e.*, affinities, of each constituent steps, activities of individual intermediates, *etc.*, without the use of assumptions currently adopted as mentioned in Introduction.

We start our discussions with the statistical mechanical expression³⁾ of the forward and the backward unidirectional rates of *s*-th step respectively as

$$v_{s+} \equiv (kT/h) \exp(-\Delta^*G_{s+}/RT)^* \quad (8. f)$$

and

$$v_{s-} \equiv (kT/h) \exp(-\Delta^*G_{s-}/RT), \quad (8. b)$$

where *k*, *R*, *T* and *h* have their usual significances, and Δ^*G_{s+} and Δ^*G_{s-} are the activation free energies of the forward and the backward act of the step *s*, respectively.

Expressing the initial, critical and final system of step *s* by $I(s)$, $\ddagger(s)$ and $F(s)$, respectively, we have

$$\Delta^*G_{s+} = \mu^{\ddagger(s)} - \mu^{I(s)} \quad (9. f)$$

and

$$\Delta^*G_{s-} = \mu^{\ddagger(s)} - \mu^{F(s)}, \quad (9. b)$$

where $\mu^{I(s)}$ *etc.* are the chemical potentials of $I(s)$ *etc.* and expressed statistical mechanically as

$$\mu^{I(s)} = RT \ln a^{I(s)} \quad (10)$$

etc., where $a^{I(s)}$ is the absolute activity⁸⁾ of $I(s)$. Examples of the particular expression of absolute activity are given in §5 for hydrogen and ethylene molecule in gas phase. We can rewrite Eqs. (8. f) and (8. b) on reference to Eqs. (9) and (10) as

$$v_{s+} = u_s f^{I(s)} \quad \text{and} \quad v_{s-} = u_s f^{F(s)}, \quad (12. v)$$

where

$$u_s \equiv (kT/h) a_e^{I(s)} / a^{\ddagger(s)}, \quad (12. u)$$

$$f^{I(s)} \equiv a^{I(s)} / a_e^{I(s)}, \quad f^{F(s)} \equiv a^{F(s)} / a_e^{I(s)} \quad (12. f)$$

and $a_e^{I(s)}$ is a standard value of $a^{I(s)}$, which would be realized when every

*) Expression (8. f) is quite resembling in its formalism the rate constant given by GLASTONE *et al.*,⁷⁾ however, Δ^*G_{s+} in the present equation are defined³⁾ as shown in Appendix II as function of the activity or the concentration of the initial system of the step in question, hence Eq. (8. f) is the correct expression of the forward unidirectional rate of step *s*, but not the rate constant.

steps but s were in equilibrium. Since the quantity $a_s^{I(s)}$ can be given as the product of the a -functions of reactants and/or products of the overall reactions, from which $I(s)$ is formed by steps in equilibrium, it is uniquely determined by experimental conditions employed. The quantity u_s of Eq. (12. u) is a parameter also characteristic of step s uniquely determined by the experimental conditions. Note that all the quantities given by Eqs. (12) are positive and $f^{I(s)}$ and $f^{F(s)}$ are usually smaller than unity, since not every steps are in equilibrium. We see from Eqs. (10) and (12. f) that

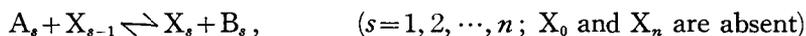
$$RT \ln (f^{I(s)} / f^{F(s)}) = \mu^{I(s)} - \mu^{F(s)} = -\Delta G_s, \quad (12. G)$$

which is the affinity, namely, the free energy drop, of step s .

§ 4 Application to the models of reaction discussed by CHRISTIANSEN

4.1 Reaction of single route

The method described above is applied first to the "open linear sequence of steps" of CHRISTIANSEN,⁴⁾ which is a simple one as



where A_s and B_s are the stable reactant and product of step s , respectively, and X_s is the intermediate formed there by. As a practical example of this set of steps we have the NERNST-chain mechanism⁹⁾ of the hydrogen-chlorine or -bromine reaction.

The steady state of this set of steps is defined by Eq. (3), where $i = 1, 2, \dots, n-1$ and

$$(a_{is}) = \begin{pmatrix} 1 & -1 & 0 & \dots & 0 & 0 & 0 \\ 0 & 1 & -1 & \dots & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & 1 & -1 & 0 \\ 0 & 0 & 0 & \dots & 0 & 1 & -1 \end{pmatrix}.$$

The rank of (a_{is}) is $n-1$ and, accordingly, we have $p = n - (n-1)$, hence a single particular solution of Eq. (3),

$$\{\nu_s\} = \{1, 1, \dots, 1\},$$

which results in the overall reaction,



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The steady rate, V , of this overall reaction is then expressed on reference to Eqs. (12) as

$$\left. \begin{aligned} V &= v_{s+} - v_{s-} && (s=1, 2, \dots, n) \\ &= u_1(1-f_1) = u_2(f_1-f_2) = \dots = u_s(f_{s-1}-f_s) \\ &= \dots = u_n(f_{n-1}-f_n), \end{aligned} \right\} \quad (13. V)$$

where u 's are given similarly to Eq. (12. u) and f 's are

$$\left. \begin{aligned} f^{I(1)} &\equiv a^{I(1)} / a_o^{I(1)} = a^{A_1} / a^{A_1} = 1, \\ f_s &\equiv f^{I(s)} = f^{F(s-1)}, \\ f_n &\equiv f^{I(n)} = \prod_{s=1}^n (a^{B_s} / a^{A_s}). \end{aligned} \right\} \quad (13. f)$$

We see from Eqs. (13. V) that all f 's, which are positive according to their definitions, are smaller than unity so long as $V > 0$. Further, we see from Eqs. (12. G), (13. V) and the last one of Eq. (13. f) that

$$-\sum_{s=1}^n \Delta G_s = RT \ln \left[\frac{1}{f_1} \prod_{s=2}^n (f_{s-1} / f_s) \right] = -RT \ln f_n = -\Delta G, \quad (13. G)$$

where $-\Delta G$ is the affinity of the overall reaction, (13. R).

Solving Eqs. (13. V) with respect to f 's, we have

$$f_s = 1 - V \sum_{s=1}^s (1/u_s) \quad (14. f)$$

or

$$(1-f_s)/V = \sum_{s=1}^s (1/u_s), \quad (14. u)$$

which is reduced to

$$1/V = \sum_{s=1}^n (1/u_s) \quad (14. V)$$

in a case where $s \leq n$ and f_n is negligibly small as compared with unity.

A relation similar to Eq. (14. V) has already been derived by CHRISTIANSEN,⁴⁾ however, he has assumed equilibrium of all steps excepts the last, irreversible one. Such a treatment of CHRISTIANSEN has been improved later¹⁰⁾ by excluding the assumptions mentioned above, but instead, assumption of the first order rate law was newly introduced there not only to the overall rate V but also to the unidirectional rates of each steps. The assump-

tion of the first-order rate law as such is not practical in general, especially in the case of heterogeneous catalysis. In the present analysis, none of these assumptions are used. The particular condition, $f_n \ll 1$, employed in bringing about Eq. (14.V) does not mean the real irreversibility of step n , but that the experimental condition is far different from that in the equilibrium of the overall reaction (13.R), as seen from Eq. (13.G); the irreversibility of step n is strictly given by the condition, $f_n \ll f_{n-1}$, as seen from Eq. (13.V). A case of $f_n \cong f_{n-1} \ll 1$ is possible for $f_n \ll 1$.

Equation (14.V) states that the smallest one among u 's is the upper limit of V and further that $V = u_r$ in a case where $u_r \ll u_s$ ($s \neq r$), that is, step r determines the steady rate of the overall reaction.

If j -th step were irreversible, as often assumed in the current mechanistic analysis, f_j should be negligible as compared with f_{j-1} , hence we have $f_j \ll 1$ on account of $f_{j-1} < 1$ so far as $V > 0$. Thus, Eq. (14.u) is reduced in this case to

$$1/V = \sum_{s=1}^j (1/u_s),$$

which shows that the steady rate V of the overall reaction is independent of the rates of steps following the irreversible one, j .

A discussion is further possible on the relation between $-\Delta G_s$ and u_s . It follows from Eqs. (12.G) and (14.f) that

$$-\Delta G_s = RT \ln \left[\frac{\left(1 - V \sum_{i=1}^{s-1} (1/u_i)\right)}{\left(1 - V \sum_{i=1}^s (1/u_i)\right)} \right], \quad (15)$$

from which we see that $u_{s'}$ of an equilibrium step s' is far larger than V since $-\Delta G_{s'} \cong 0$. Thus, we can evaluate the relative magnitudes of ΔG_l of non-equilibrium step l from those of u_l according to Eq. (15). For instance, in case of $V/u_l = 1/4$ for steps $l = 1, 2, 3$ and 4, it follows from Eq. (15) that

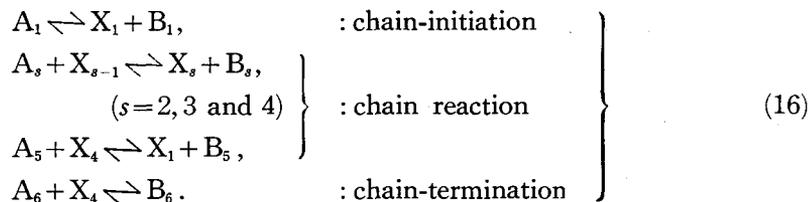
$$\Delta G_2/\Delta G_1 = 1.05, \quad \Delta G_3/\Delta G_1 = 1.50 \quad \text{and} \quad \Delta G_4/\Delta G_1 \gg 1.$$

These results show that in a sequence of non-equilibrium steps with the same value of u_l , the affinity of a step is generally smaller than that of the step that follows, or conversely, that with a common value of affinities of steps, the most preceding step has the smallest value of u .

4.2 Reaction system with two routes; the selectivity

we next discuss the second case of CHRISTIANSEN,⁴⁾ which constitutes a chain reaction accompanied by a chain-initiation and a chain-termination steps as follows.

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We have in this case

$$(a_{is}) = \begin{pmatrix} 1 & -1 & 0 & 0 & 1 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & -1 \end{pmatrix}$$

for (a_{is}) of Eq. (3) and two independent routes according to $p=n-q=6-4$. The general solution, Eq. (7), of Eq. (3) is given as

$$\begin{aligned}
 \{v_s\} &= V_1\{1, 0, 0, 0, -1, 1\} + V_2\{0, 1, 1, 1, 1, 0\} \\
 &= \{V_1, V_2, V_2, V_2, V_2 - V_1, V_1\}.
 \end{aligned} \quad (17. V)$$

The quantities V_1 and V_2 are the steady rates of the overall reactions,

$$A_1 + B_5 + A_6 = B_1 + A_5 + B_6 \quad (17. R_1)$$

and

$$\sum_{s=2}^5 A_s = \sum_{s=2}^5 B_s, \quad (17. R_2)$$

respectively. CHRISTIANSEN⁴⁾ named *a priori* these two reactions as a "side" and "main" reactions, respectively, and obtained rather complicated rate-equation even when steps 2 and 6 are assumed to be irreversible. In the present method, such assumptions are excluded and it is shown below that which of these reactions to be "main" depends upon the relative magnitudes of u 's and accordingly upon the experimental conditions employed.

We have on reference to Eq. (17. V)

$$V_1 = u_1(1-f_1) = u_6(f_5-f_6), \quad (18. a)$$

$$SV_1 = u_2(f_1-f_2) = u_3(f_2-f_3) = u_4(f_3-f_4), \quad (18. b)$$

$$(S-1)V_1 = u_5(f_4-f_1f_5), \quad (18. c)$$

where

$$S \equiv V_2/V_1, \quad (18. S)$$

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$$u_1 \equiv (kT/h)a^{A_1}/a^{*(1)}, \quad u_s \equiv (kT/h)a^{A_s}a_0^{x_s-1}/a^{*(s)}, \quad (s=2, 3, 4 \text{ or } 5)$$

$$u_6 \equiv (kT/h)a^{A_6}a_0^{x_6}/a^{*(6)},$$

$$f_i \equiv a^{x_i}/a_0^{x_i}, \quad (i=1, 2, 3 \text{ or } 4)$$

$$f_5 \equiv \prod_{s=2}^5 (a^{B_s}/a^{A_s}). \quad (18. f_5)$$

$$f_6 \equiv (a^{B_6}a^{A_6}a^{B_6})/(a^{A_6}a^{B_6}a^{A_6}), \quad (18. f_6)$$

and

$$a_0^{x_i} \equiv \prod_{s=1}^i (a^{B_s}/a^{A_s}).$$

Provided that reactants and products in the homogeneous phase behave as those in an ideal mixture, f_5 and f_6 can be recast in the forms of

$$f_5 = \prod_{s=2}^5 ([B_s]/[A_s])/K_2 \quad \text{and} \quad f_6 = ([B_1][A_5][B_6])/([A_1][B_5][A_6])K_1, \quad (18. K)$$

where $[A_1]$ etc. are the concentration of A_1 etc. and K_1 and K_2 the equilibrium constants of the overall reactions (17.R₁) and (17.R₂), respectively.

It follows from Eqs. (18) by elimination of f_1, f_2, f_3 and f_4 that

$$(1-f_6)/V_1 = 1/u_1 + S \sum_{s=2}^4 (1/u_s) + 1/u_6 \quad (19. a)$$

and

$$(1-f_5)/V_1 = (1-f_5)/u_1 + S \sum_{s=2}^5 (1/u_s) - 1/u_5. \quad (19. b)$$

Subtracting Eq. (19.b) from (19.a) side by side, we have

$$S = u_5 [f_5/u_1 + 1/u_6 + (f_6 - f_5)/V_1] + 1. \quad (19. S)$$

Positive or negative value of S respectively represents the directions of two overall reactions (17.R₁) and (17.R₂) being same or opposite to each other, and the absolute value of S larger than unity means that reaction (17.R₂) is the "main" one. We see from Eq. (19.S) that the value of S depends upon the experimental conditions which determine the magnitudes of u 's of three species, 1, 5 and 6 and those of f_5 and f_6 as seen from Eq. (18.K).

In a case where the equilibrium constants K_1 and K_2 of the overall reactions are extremely larger than unity, f_5 and f_6 are negligibly smaller than unity according to Eqs. (18.K), hence Eq. (19.S) is reduced to a simple form of

$$S = u_5/u_6 + 1, \quad \text{that is,} \quad V_2/V_1 = (u_5 + u_6)/u_6,$$

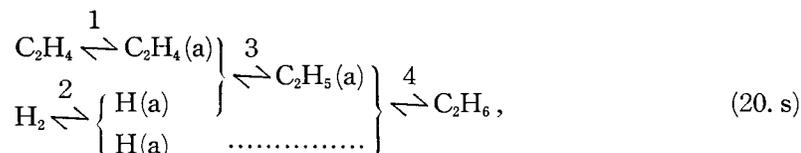
by neglectation of the first and the third terms in the brackets as compared

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with the second one. This relation may be intuitively seen from scheme (16) as the relative rates of two steps which take place by participation of intermediate, X_4 .

§ 5 Hydrogenation of ethylene catalyzed by nickel*

We now discuss hydrogenation of ethylene catalyzed by nickel as a typical example of heterogeneous catalysis with single route, where ν_s are commonly unity for all steps. As shown in Appendix I, the current mechanistic analysis of the present catalysis based on the assumptions of kinetic mass-action law *etc.* arrives at conclusions in disagreements with the experimental results. The present analysis is based on the set of steps



where $\text{H}(\text{a})$, $\text{C}_2\text{H}_4(\text{a})$, $\text{C}_2\text{H}_5(\text{a})$ are hydrogen atom, ethylene and ethyl radical in their adsorbed state, respectively. This scheme was concluded from analysis of the experimental results obtained by infra-red absorption¹¹⁾ and mass-spectrometric analysis of deuteration of light ethylene.^{12)**)} Application of the present method to the set of steps (20.s) easily demonstrates that the possible, overall reaction is single, *i. e.*



according to the values of ν_s being commonly unity for all steps.

It follows in the steady state that

$$\left. \begin{array}{l} V = v_{s+} - v_{s-} \quad (s = 1, 2, 3 \text{ and } 4) \\ = u_1(1 - f_1) = u_2(1 - f_2^2) = u_3(f_1 f_2 - f_3) = u_4(f_2 f_3 - f_4), \end{array} \right\} (20. V)$$

where, if we denote the quantities responsible to C_2H_4 and H_2 in gas phase by the subscripts E and H, respectively,

*) This Section is a short review of our work published in, *e.g.*, a monograph, NSRDS-NBS 13, of National Bureau of Standards (1968).

**) With regard to the observed random distribution of deuterium atoms in ethane some authors are insisting upon the existence of fast elementary reactions between adsorbed hydrocarbons, *e.g.* $2\text{C}_2\text{H}_5(\text{a}) \rightleftharpoons \text{C}_2\text{H}_4(\text{a}) + \text{C}_2\text{H}_6$ *etc.* However, so far as concerning the observed kinetics as such, these elementary reactions cannot be discriminated from the linear combinations of the forward act of step 4 and the backward one of step 3 of scheme (20. s). This scheme includes thus apparently the reactions between adsorbed hydrocarbons as such.

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$$\left. \begin{aligned} u_1 &\equiv (kT/h)a_E/a^{+(1)}, & u_2 &\equiv (kT/h)a_H/a^{+(2)}, \\ u_3 &\equiv (kT/h)a_E a_H^{1/2}/a^{+(3)}, & u_4 &\equiv (kT/h)a_E a_H/a^{+(4)}, \end{aligned} \right\} \quad (20. u)$$

$$\left. \begin{aligned} f_1 &\equiv a^{C_2H_4(a)}/a_E, & f_2 &\equiv a^{H(a)}/a_H^{1/2}, \\ f_3 &\equiv a^{C_2H_4(a)}/a_E a_H^{1/2}, & f_4 &\equiv a^{C_2H_4}/a_E a_H, \end{aligned} \right\} \quad (20. f)$$

As easily seen from Eq. (20.f), $RT \ln f_4 (= -\Delta G)$ is the affinity of overall reaction (20.R) given, similar to Eq. (18.K), as

$$-\Delta G = RT \ln \left[(P_{C_2H_4}/P_E P_H)/K_p \right],$$

where P is the partial pressure and K_p the equilibrium constant of the overall reaction. Hence f_4 is negligibly small as compared with unity under the usual experimental condition because of exceedingly large a value of K_p .

Quantities a_H and a_E are now given statistical mechanically as

$$\begin{aligned} a_H^{-1} &= F_H/C_H \\ &= \frac{kT}{1333 P_H} \cdot \frac{(2\pi m_H kT)^{3/2}}{h^3} \cdot \frac{4\pi I_H kT}{h^2} \\ &\quad \cdot \left[1 - \exp(h\nu_H/kT) \right]^{-1} \cdot \exp(-\mathcal{E}_H/RT) \end{aligned} \quad (21. H)$$

and

$$\begin{aligned} a_E^{-1} &= F_E/C_E \\ &= \frac{kT}{1333 P_E} \cdot \frac{(2\pi m_E kT)^{3/2}}{h^3} \cdot \frac{2\pi^2(2\pi I_E kT)^{3/2}}{h^3} \\ &\quad \cdot \prod_j \left[1 - \exp(h\nu_j/kT) \right]^{-1} \cdot \exp(-\mathcal{E}_E/RT), \end{aligned} \quad (21. E)$$

where F is the complete partition function of the gaseous molecule per unit volume, C is the concentration given as $1333P/kT$ (P in mmHg), m the mass of a molecule, I_H the moment of inertia of H_2 molecule, I_E the geometric mean of the three principal moments of inertia of C_2H_4 molecule, ν_H or ν_j the frequency of the normal vibration of H_2 or C_2H_4 molecule, respectively, and \mathcal{E} is the molar energy in the ground state. The quantities a_H and a_E given above are now rewritten in the form of

$$a_i = (P_i/Q_i) \cdot \exp(\mathcal{E}_i/RT), \quad (i=H_2 \text{ or } C_2H_4)$$

where Q_i is easily seen to be constant at a given temperature. The functions u 's given by Eqs. (20.u) are then recast in the form of

$$\left. \begin{aligned} u_1 &\equiv \rho(P_E/Q_E) \exp(-E_1^*/RT) \equiv U_1 P_E, \\ u_2 &\equiv \rho(P_H/Q_H) \exp(-E_2^*/RT) \equiv U_2 P_H, \end{aligned} \right\} \quad (22)$$

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$$\left. \begin{aligned} u_3 &\equiv \rho(P_E/Q_E)(P_H/Q_H)^{1/2} \exp(-E^*_3/RT) \equiv U_3 P_E P_H^{1/2}, \\ u_4 &\equiv \rho(P_E/Q_E)(P_H/Q_H) \exp(-E^*_4/RT) \equiv U_4 P_E P_H, \end{aligned} \right\}$$

where ρ is a constant approximated to be common to all u 's, E^*_s is the activation energy of the forward act of step s and U 's are constant at a given temperature so far as E^*_1 etc. are practically independent of P_E and P_H .

It follows from Eq. (20. V), similarly to Eq. (14. V), that

$$(1-f_1)/V = f_2^2/u_1 + 1/u_2 + f_2/u_3 + 1/u_4 \quad (23. a)$$

or, on reference to Eqs. (22),

$$P_H/V = f_2^2 P_H / P_E U_1 + 1/U_2 + f_2 P_H^{1/2} / P_E U_3 + 1 / P_E U_4, \quad (23. b)$$

where f_4 is neglected as compared with unity.

ZUR STRASSEN¹³⁾ observed the rate of catalyzed hydrogenation of ethylene in the presence of nickel catalyst under a few hundredths mmHg partial pressures of H_2 and C_2H_4 and found that the steady rate, V , is strictly proportional to P_H at constant P_E and constant temperature throughout his observation from $-7^\circ C$ to $125^\circ C$. Similar kinetics of the reaction has been observed by many investigators.⁵⁾ It follows from this experimental result that P_H/V of Eq. (23.b) at constant P_E must be practically constant independent of the partial pressure of hydrogen. Since terms U_1 etc. in the right-hand side of this equation are constant, f_2 must be either constant or far smaller than unity according to the relation derived from the first equation of (20. V) and u_2 of (22), *i. e.*,

$$V/P_H = U_2(1-f_2^2).$$

In either case of f_2 being constant or far smaller than unity, the first and the third terms of Eq. (23.b) must be negligibly small as compared with the second and the fourth terms, which are both constant. It follows therefore from Eq. (23. a) that

$$1/V = 1/u_2 + 1/u_4. \quad (24)$$

One of the characteristics of the reaction is the presence of an optimum temperature T_x , below and above which the activation heat is positive and negative, respectively. It is found¹²⁾ that T_x is *ca.* $30^\circ C$ in deuteration of light ethylene with equimolar amount of deuterium gas over nickel catalyst at 0.1 mmHg total pressure. Further, light hydrogen in ethylene was never transferred into D_2 gas during the deuteration at $-45^\circ C$ and $-23^\circ C$, but transferred rapidly, yielding isotopically equilibrium mixtures of hydrogen, at temperatures above T_x . The deuterium distribution in ethylene is found

always random independent of the reaction temperature being below or above T_x . Such a random distribution of deuterium in ethylene shows, on reference to scheme (20. s), that steps 1 and 3 must always be in equilibrium. Hence it follows that f_1 of Eq. (20. f) must be unity and further that V/u_1 and V/u_3 are negligibly small, in harmony with the conclusion of Eq. (24). The former fact with regard to the deuterium distribution of hydrogen gas shows that step 2 is rate-determining at temperatures far below T_x but in equilibrium above T_x . Consequently, we see on reference to Eq. (24) that

$$V = \begin{cases} u_2 & \text{at } T < T_x \\ u_4 & \text{at } T > T_x. \end{cases} \quad (25)$$

According to the conclusion above, E_2^* in Eqs. (22) with respect to u_2 can be evaluated by observing V at temperatures far below T_x , identifying V with u_2 there; the value is⁵⁾

$$E_2^* = 4.7 \text{ kcal/mole.} \quad (26. 2)$$

The quantities E_3^* and E_4^* are determined according to the equation derived from Eq. (20. V) with $f_1=1$ and $f_4=0$, *i. e.*,

$$u_2 : u_3 : u_4 = (1-f_2^2)^{-1} : (f_2-f_3)^{-1} : (f_2f_3)^{-1}. \quad (26. f)$$

We can now determine f_2 and f_3 from observed evolution rates of individual deuterio-substituted ethylenes and ethanes at the initial stage of the deuteration of light ethylene, taking the steady state with respect to individual deuter-substituted intermediates into account. It can be shown⁵⁾ according to the experimental results obtained by TURKEVICH *et al.*¹⁴⁾ on the deuteration of 10 mmHg light ethylene by 20 mmHg deuterium over nickel wire at 90°C that the ratio mentioned above take the following values,

$$u_2 : u_3 : u_4 = 1 : 14.7 : 1.84, \quad (26. u)$$

From Eqs. (22), (26. 2) and (26. u), we obtain

$$E_3^* = -12.6 \text{ kcal/mole} \quad (26. 3)$$

and

$$E_4^* = -18.3 \text{ kcal/mole.} \quad (26. 4)$$

Introducing the values of E_2^* *etc.* derived above and those of Q_H and Q_E into Eqs. (22), we have

$$\left. \begin{aligned} \log u_1 &\cong \infty, \\ \log u_2 &= \log \rho(P_H/1.057 \times 10^{10}) - 1027/T, \\ \log u_3 &= \log \rho(P_H/1.057 \times 10^{10})^{1/2}(P_E/3.939 \times 10^{14}) + 2751/T, \\ \log u_4 &= \log \rho(P_H/1.057 \times 10^{10})(P_E/3.939 \times 10^{14}) + 4008/T. \end{aligned} \right\} \quad (27)$$

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Further, according to Eqs, (20.V), we can determine V , f_2 and f_3 , and hence v_{s+} and v_{s-} of steps 2, 3 and 4 individually from the rates u_1 etc. and the values $f_1=1$ and $f_4=0$.

It was found⁽²⁾⁽⁵⁾ that the method described above are very effective in presenting a consistent interpretation of experimental facts obtained on the hydrogenation as well as its related reactions, *e.g.*, equilibration of hydrogen isotopes, $H_2 + D_2 = 2HD$, or parahydrogen conversion, hydrogen exchange between light ethylene and deuterium and evolution rates of individual deuterio-substituted hydrocarbons during deuteration of light ethylene.

From Eq. (24) we see further that

$$u_2 = u_4 \quad \text{at} \quad T = T_x,$$

hence that

$$E_2^* - E_4^* = 2.3RT_x \log(Q_E/P_E),$$

on reference to the expressions of u_2 and u_4 given by Eqs. (22). Comparing this equation with our experimental result⁽¹⁵⁾ that

$$1/T_x = (1/5300)(14.5 - \log P_E),$$

we have

$$E_2^* - E_4^* = 24.2 \text{ kcal/mole} \quad (28. E)$$

and

$$\log Q_E = 14.5. \quad (28. Q)$$

It follows from Eqs. (28.E) and (26.2) that

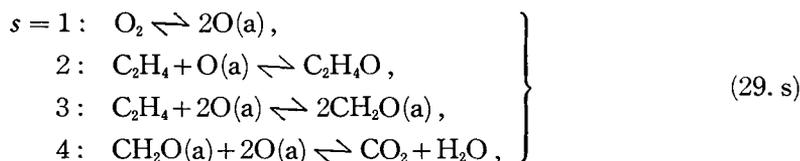
$$E_4^* = -19.5 \text{ kcal/mole},$$

which agrees well with the value given in Eq. (26.4). The value given by Eq. (28.Q) also agrees excellently with the theoretical value, $\log Q_E = 14.596$.

§ 6 Oxidation of ethylene catalyzed by silver catalyst

The present method is finally applied to oxidation of ethylene catalyzed by silver which is one of the typical examples of the selectivity of heterogeneous catalyst. A view currently accepted on the selectivity of ethylene oxide formation is that the adsorbed state of oxygen resulting in ethylene oxide formation differs from that for the complete oxidation of ethylene to CO_2 and H_2O and the selectivity depends upon their amounts. This view is, however, not yet proved experimentally and further wanting in the kinetic analysis of the reaction

We now apply the present method of analysis to the time courses of the amounts of produced ethylene oxide and carbon dioxide. We assume the following set of steps

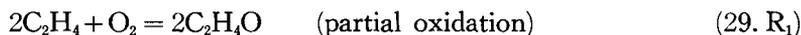


which is a simplified one of that of TWIGG;¹⁶⁾ the steps for the secondary, complete oxidation of ethylene oxide are excluded by limiting our discussion in an early stage of the reaction. Step 2 does not exclude the existence of adsorbed ethylene oxide, $\text{C}_2\text{H}_4\text{O}(\text{a})$, but may be considered as a linear combination of two steps, $\text{C}_2\text{H}_4 + \text{O}(\text{a}) \rightleftharpoons \text{C}_2\text{H}_4\text{O}(\text{a}) \rightleftharpoons \text{C}_2\text{H}_4\text{O}$. Step 4 may be similarly considered with respect to $\text{CO}_2(\text{a})$ and $\text{H}_2\text{O}(\text{a})$.

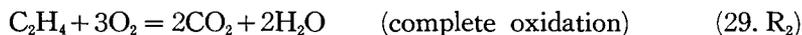
Similar to the foregoing discussions, we have two independent routes, from which the general solution of Eq. (3) is given as

$$\{v_s\} = V_1\{1, 2, 0, 0\} + V_2\{3, 0, 1, 2\}, \quad (29. V)$$

where V_1 and V_2 are, respectively, the steady rates of the overall reactions



and



Denoting O_2 , C_2H_4 , $\text{C}_2\text{H}_4\text{O}$, CO_2 , H_2O , $\text{O}(\text{a})$ and $\text{CH}_2\text{O}(\text{a})$ by A_1 , A_2 , B_1 , B_2 , B_3 , X_1 and X_2 , respectively, we can now recast Eq. (29. V) in the forms of

$$\left. \begin{array}{l} (S+3)V_2 = u_1(1-f_1^2), \\ 2SV_2 = u_2(f_1 - F_1), \\ 2V_2 = 2u_3(f_1^2 - f_2^2) = u_4(f_1^2 f_2 - F_2), \end{array} \right\} \quad (30. V)$$

where

$$S \equiv V_1/V_2, \quad (30. S)$$

$$u_s \equiv (kT/h)a_e^{I(s)}/a^{+(s)}, \quad (s=1, 2, 3 \text{ or } 4) \quad (30. u)$$

$$f_i \equiv a^{X_i}/a_e^{X_i}, \quad (i \equiv 1, 2 \text{ or } 3) \quad (30. f)$$

$$\left. \begin{array}{l} a_e^{I(1)} = a^{A_1}, \quad a_e^{I(2)} = a^{A_1} a_e^{X_1}, \\ a_e^{I(3)} = a^{A_2} (a_e^{X_1})^2, \quad a_e^{I(4)} = (a_e^{X_1})^2 a_e^{X_2}, \end{array} \right\} \quad (30. I)$$

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$$a_e^{X_1} = (a^{A_1})^{1/2}, \quad a_e^{X_2} = (a^{A_1} a^{A_2})^{1/2}, \quad (30. X)$$

and

$$F_1 \equiv a^{B_1} / (a^{A_1})^{1/2} a^{A_2}, \quad F_2 \equiv a^{B_2} a^{B_3} / (a^{A_1})^{3/2} (a^{A_2})^{1/2}. \quad (30. F)$$

We easily see from Eq. (10) that

$$2RT \ln F_1 = 2\mu^{B_1} - (\mu^{A_1} + 2\mu^{A_2})$$

and

$$2RT \ln F_2 = 2\mu^{B_2} + 2\mu^{B_3} - (3\mu^{A_1} + \mu^{A_2}),$$

which are the affinities of overall reactions (20. R₁) and (29. R₂), respectively. Both F_1 and F_2 are negligibly small as compared with unity or with f_i , due to

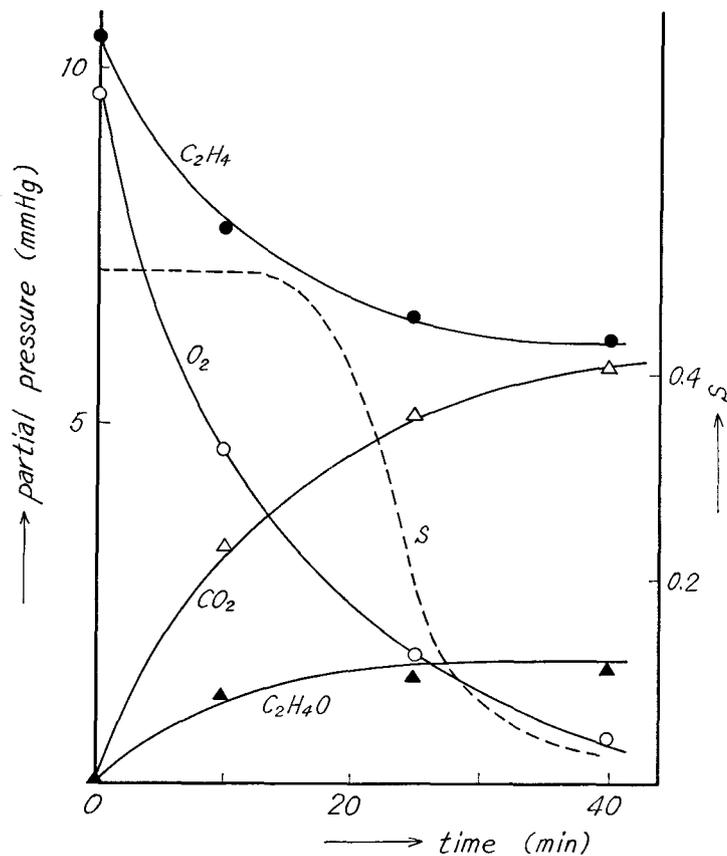


Fig. 1. The time courses of amounts of individual gaseous components and the selectivity $S(\equiv V_1/V_2)$ during oxidation of ethylene over silver catalyst at 300°C.

exceedingly large values of the equilibrium constants of these overall reactions.

We have carried out some experiments on this reaction using a closed reaction apparatus equipped a circulation pump, at temperatures near 300°C. Both V_1 and V_2 are found proportional to $P_{O_2}P_{C_2H_4}$ and their activation heats amounted to 11.0 and 18.5 kcal/mole, respectively, in an early stage of the reaction of equimolar mixture of O_2 and C_2H_4 . A typical example of the time courses of amounts of individual gaseous components and S of Eq. (30.S) at 300°C are shown in Fig. 1. In Fig. 1, S evaluated from the smoothed curves is constant at an early stage of the reaction. Hence we may consider the secondary oxidation of ethylene oxide to be negligible in this stage; this is the reason of the set of steps (29.s) being a probable base of the present analysis.

We discuss first the experimental results on the dependence of V_1 and V_2 upon P_{O_2} and $P_{C_2H_4}$ and their activation heats obtained above. It follows from the first two equations of Eqs. (30.V) and (30.S), neglecting F_1 as compared with f_1 , that

$$1/V_1 = (S+3)/Su_1 + 2f_1/u_2. \quad (31.1)$$

Similarly, neglecting F_2 as compared with $f_1^2f_2$, we have

$$1/V_2 = (S+3)/u_1 + 1/u_3 + 2f_2/f_1^2u_4. \quad (31.2)$$

Analogous to Eqs. (22), we can write u 's, on reference to Eqs. (30.u), (30.I) and (30.X), as

$$u_1 = U_1P_{A_1}, \quad u_2 = U_2P_{A_1}^{1/2}P_{A_2}, \quad u_3 = U_3P_{A_1}P_{A_2}, \quad u_4 = U_4P_{A_1}^{3/2}P_{A_2}. \quad (31.u)$$

The quantities f_1 and f_2 are similarly given as

$$f_1 = a^{X_1}/(U_{A_1}P_{A_1})^{1/2}, \quad f_2 = a^{X_2}/(U_{A_1}U_{A_2}P_{A_1}P_{A_2})^{1/2},$$

where $U_{A_1}P_{A_1}$ and $U_{A_2}P_{A_2}$ are the absolute activity of O_2 and C_2H_4 , respectively, as mentioned already in connection with Eqs. (21) and (22). Consequently, it follows from Eqs. (31.1) and (31.2) that

$$1/V_1 = (S+3)/SU_1P_{A_1} + 2a^{X_1}/U_2U_{A_1}^{1/2}P_{A_1}^{3/2}P_{A_2} \quad (32.1)$$

and

$$1/V_2 = (S+3)/U_1P_{A_1} + 1/U_3P_{A_1}P_{A_2} + 2U_{A_2}^{1/2}a^{X_2}/U_4U_{A_1}^{1/2}(a^{X_1})^{1/2}P_{A_1}^{1/2}P_{A_2}^{3/2}. \quad (32.2)$$

The quantities U_s ($s=1, 3, 3$ and 4), U_{A_1} and U_{A_2} in these equations are constant at a given temperature so far as variations of the partial pressures, P_{A_1} etc., are small, whereas the absolute activities a^{X_1} and a^{X_2} may depend upon the partial pressures. Thus, the observed results that both V_1 and V_2

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are proportional to $P_{O_2}P_{C_2H_4}$, show, at least, that the first term in the right-hand side of Eq. (32.1) or (32.2), where A_1 and A_2 denote respectively O_2 and C_2H_4 , is negligibly small as compared with the other terms so far as S remains constant. Accordingly, it is concluded that the steady rates V_1 and V_2 are mainly controlled by step 2 and 3 (or 4), respectively, in conformity with the activation heats of the overall reactions being different from each other.*) Further, in Eq. (32.1), the absolute activity a^{X_1} of intermediate, $O(a)$, is concluded to be proportional to $P_{O_2}^{1/2}$, which means that step 1 is in equilibrium, in conformity with the negligibly small value of the first term in the right-hand side of this equation.

In addition to the qualitative conclusion derived above, the relative magnitudes of u 's can be evaluated as below on the basis of the observed results of the time courses of the amounts produced of the individual gaseous components as shown in Fig. 1. We have from the first equation of (30.V) that

$$f_1 = [1 - (S+3)V_2/u_2]^{1/2}.$$

It follows from the second one of Eqs. (30.V), by substituting the expression of f_1 given above and further (31.u) for u_1 and u_2 , that

$$2SV_2/U_2P_{A_1}^{1/2}P_{A_2} = [1 - (S+3)V_2/U_1P_{A_1}]^{1/2}. \quad (33.1)$$

Similarly, we have from the third and the fourth ones of Eqs. (30.V) and (31.u), by elimination of f_1 and f_2 ,

$$\begin{aligned} V_2/U_3P_{A_1}P_{A_2} &= 1 - (S+3)V_2/U_1P_{A_1} \\ &\quad - (4V_2^2/U_4^2P_{A_1}P_{A_2})/[1 - (S+3)V_2/U_1P_{A_1}]^2. \end{aligned} \quad (33.2)$$

Provided that U 's remain constant by small variations of P_{O_2} and $P_{C_2H_4}$, we can evaluate U 's and accordingly u 's by Eqs. (31.u) from two sets of values of S , P_{O_2} and $P_{C_2H_4}$, observed at two different times of reaction. The results are shown in Table 1. They show that none of u 's is negative and their values are in conformity with the qualitative conclusion derived above. These facts demonstrate the effectiveness of the present method of analysis.

The results in Table 1 show further that U_1 remains nearly constant, whereas U_2 and U_3 are diminished to *ca.* 0.46 times, with rise of P_{O_2} from

*) In the previous paper¹⁷⁾ of one of the present authors with respect to the coupling of two simultaneous reactions, it was concluded that both the partial and complete oxidations of ethylene catalyzed by silver are rate-determined by step 1, *i.e.*, chemisorption of oxygen. This conclusion is, however, erroneous because of that the discussion on the present catalysis is not confinable to the case of a particular step being extraordinarily slower than the others, as done in the paper.

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TABLE 1. Calculated values of U 's and u 's in the steady oxidation of ethylene at 300°C catalyzed by silver catalyst

Initial partial pressure, mmHg		Mean time of reaction, min.	U_1	U_2	U_3	u_1	u_2	$u_3^{*})$
O ₂	C ₂ H ₄							
30	10	2	0.24	1.82	9.0	6.6	0.9	2.0
		6		$\times 10^{-2}$	$\times 10^{-3}$	6.0	0.8	1.6
50	10	2	0.37	0.86	4.0	18.	0.6	0.7
		6		$\times 10^{-2}$	$\times 10^{-3}$	17.	0.5	0.7

*) The value of u_4 is always infinitely large on account of $1/U_4 \cong 0$.

30 to 50 mmHg. By the same approximation as used in the foregoing section with respect to Eqs. (22), U_2 and U_3 are now given as

$$U_2 = (\rho/Q_{A_1}^{1/2}Q_{A_2}) \exp(-E_2^*/RT) \quad \text{and} \quad U_3 = (\rho/Q_{A_1}Q_{A_2}) \exp(-E_3^*/RT),$$

respectively, where ρ is a constant approximated to be common to all u 's, Q_{A_1} and Q_{A_2} are the constant characteristic of O₂ and C₂H₄ molecule, respectively, and E_s^* is the activation energy of the forward act of step s . It follows then that

$$0.46 = \exp(-\delta E_s^*/RT), \quad (s=2 \text{ and } 3)$$

where δE_s^* is the increment of E_s^* , caused by the increase of P_{O_2} from 30 to 50 mmHg, hence that

$$\delta E_s^* = 0.9 \text{ kcal/mole.}$$

This result suggests the presence of perceptible repulsive interaction between the critical systems, $\neq(2)$ and $\neq(3)$, and their surrounding O(a)'s, which may increase with rise of P_{O_2} and enlarge the values of E_2^* and E_3^* . On the same point of view the interaction among O(a)'s may be concluded to be absent or slightly attractive on account of the value of U_1 increasing slightly with rise of P_{O_2} . This conclusion as well as the value of E_1^* is, however, not certain on account of the strongly divergent values of u_1 from run to run of experiment. This fact probably relates to that the kinetics of the initial rate of the present reactions are not reproducible, strongly depending upon the pretreatment of the catalyst.

The activation energies of steps 2 and 3 are estimated at $P_{O_2} = P_{C_2H_4} = 10$ mmHg as

$$E_2^* = 10.5 \text{ kcal/mole,} \quad E_3^* = 16.5 \text{ kcal/mole,}$$

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which are close, respectively, to those observed with respect to the overall reactions (29.R₁) and (29.R₂).

In addition to the analysis described above, it is noted that f 's of respective intermediates can be evaluated by introduction of the values of u 's into Eqs. (30.V), hence the variations of the activities of respective intermediates or the affinities of respective steps in course of the reaction are essentially to be known.

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Appendix I

Currently-made analysis of the steady rate of heterogeneous catalysis based on the assumption of kinetic mass-action law is now illustrated by that made by SCHWAB¹⁸⁾ with respect to hydrogenation of ethylene catalyzed by nickel.

He assumed that the steady rate of this hydrogenation is controlled by the step of surface reaction, *i. e.*,



and then expressed the steady rate V as

$$V = k\theta_{\text{H}}\theta_{\text{E}} \quad (\text{Assumption 2})$$

according to the extended kinetic mass-action law. Introducing into the coverage fractions θ_{H} and θ_{E} of hydrogen and ethylene, respectively, their expressions of the LANGMUIR adsorption isotherms,

$$\theta_i = b_i P_i / (1 + b_i P_i), \quad b_i = \exp(-\Delta H_i / RT), \quad (\text{Assumption 3})$$

$(i = \text{H}_2 \text{ or } \text{C}_2\text{H}_4)$

where ΔH is the heat of adsorption, he expressed the steady rate as

$$V = kb_{\text{H}}b_{\text{E}}P_{\text{H}}P_{\text{E}}/(1 + b_{\text{E}}P_{\text{E}});$$

in this case $b_{\text{H}}P_{\text{H}}$ was assumed to be negligibly small as compared with unity, that is, hydrogen is scarcely adsorbed on the catalyst.

(Assumption 4)

Referring this expression of V to the observed kinetics that

$$V \propto \begin{cases} P_{\text{H}} & \text{for } T < T_x \\ P_{\text{H}}P_{\text{E}} & \text{for } T > T_x, \end{cases}$$

respectively, as described in the text, he concluded that

$$b_{\text{E}}P_{\text{E}} \begin{cases} \gg 1 & \text{for } T < T_x \\ \ll 1 & \text{for } T > T_x, \end{cases}$$

respectively. This conclusion means with reference to the Assumption 3 that $\theta_{\text{E}} \cong 1$ and $\theta_{\text{E}} \cong 0$ for $T < T_x$ and $T > T_x$, respectively, namely, adsorbed ethylene fully occupied the catalyst surface at temperatures below T_x should evaporate up into gas phase as the temperature rises beyond T_x .

Such an analysis of the steady rate is easy to follow and looks like useful, however, it gives none of informations on the real natures of the

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catalyst surface as easily seen from that the conclusion above is completely responsible upon the assumptions used in the analysis. In fact, the conclusion as well as Assumption 4 has been denied by our direct measurement¹⁵⁾ of the amounts of hydrogen and ethylene adsorbed during the hydrogenation, which were found to be perceptible comparably with each other and scarcely changed as the temperature rose beyond T_x . Furthermore, a relation between T_x and P_E derived on the basis of SCHWAB's theory did not satisfy the observed result given in the text.¹⁵⁾

Appendix II

In this appendix the statistical mechanical formulation done by HORIUTI³⁾ of the unidirectional rate of an elementary reaction is reproduced.

The whole chemical species in the reaction vessel is now treated as a statistical mechanical assembly and its canonical ensemble is investigated as follows. We first distinguish from this assembly a particular system, *i.e.*, a set of particles, which takes place the elementary reaction, $I \rightarrow F$, in question. This particular system assumes in the canonical ensemble all its possible states inclusive of its initial and final states, I and F respectively, while all the other particles in the assembly remain unconverted. We now tentatively extend a hypersurface in the configuration space of the assembly so as to separate the space into two regions, each relevant to the initial and the final states of the particularly distinguished system. The hypersurface should be traversed by the representative points of the assembly in both the directions with equal frequency according to the principle of microscopic reversibility.

We calculate first the number of representative points traversing the hypersurface unidirectionally per unit time. Let q_1 be the coordinate normal to the hypersurface and q_2, \dots, q_N are those along the hypersurface, where N is the number of degrees of freedom of the assembly. The conjugate momenta are represented by p_1, p_2, \dots, p_N , respectively. The number of representative points lying in the intervals,

$$q_i \sim q_i + dq_i; \quad p_i \sim p_i + dp_i, \quad (i=1, 2, \dots, N)$$

is given as

$$\eta \exp \left(-\frac{p_1^2}{2M_1 kT} - \frac{E}{kT} \right) dq_1 dq_2 \cdots dq_N dp_1 dp_2 \cdots dp_N,$$

where η is the proportionality constant, M_1 the reduced mass appropriate to the degree of freedom of q_1 , and E the total energy of the assembly less the kinetic energy $p_1^2/2M_1$. The frequency of the unidirectional traverse of representative points through the hypersurface is obtained by replacing

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dq_i in the above expression by $(p_i/M_i)dt$ and integrating the expression thus obtained with respect to p_i from zero to infinity and with respect to all other variables over the whole regions compatible with the prescribed condition of the assembly, as

$$\eta dt \int (p_i/M_i) \exp(-p_i^2/2M_i kT) dp_i \cdot \int \cdots \int \exp(-E/kT) dq_2 \cdots dp_N dp_L \cdots dp_N \\ = \eta kT J_h dt.$$

The quantity J_h denotes the second factor of the above integrals, which is the phase integral over the hypersurface. Similarly, the number of representative points in the initial region of the configuration space of the assembly is given as J_i , namely, the phase integral over the initial region.

The specific rate of the forward, unidirectional traverse of the representative points in the initial region through the hypersurface is now given as $kT J_h/J_i$, which is the ratio of the number $\eta kT J_h$ of the representative points unidirectionally traversing the hypersurface forward per unit time to that ηJ_i . The specific rate derived as such is that of a particular initial system and should be common to all initial systems which are possible to be composed by any combinations of the particles in the assembly. Let w' be the number of this combinations, then the number of acts of traversing the hypersurface forward per unit time is $w' kT J_h/J_i$.

It is necessary but not always sufficient to traverse the hypersurface for a representative point to transfer from the initial region to the final one. Accordingly, the hypersurface is now shift to adjust J_h to its minimum J_+ ,¹⁹⁾ and then $w' kT J_+/J_i$ is the best upper approximation to the forward, unidirectional rate v_+ of the elementary reaction in question,¹⁹⁾ that is,

$$v_+ = \kappa w' kT J_+/J_i,$$

where κ is the so-called *transmission coefficient* which is smaller than unity. The hypersurface thus fixed is called the *critical surface*; the system with the relevant representative point resting on this surface, the *critical system*; and its state, the critical state.

The forward, unidirectional rate v_+ is now transformed as follows for the application to the practical analysis of the steady rate of reactions. Let Ψ^* or Ψ^I be the partition function of the assembly with its representative point on the critical surface or in the initial region, respectively. The classical approximation to the partition function is the respective phase integral divided by PLANCK constant, h , raised to the power of the number N of the degrees of freedom and by the number of modes of interchange of identical particles. Let w^* or w^I be the number of modes of interchanging

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identical particles in the whole assembly with the particularly distinguished system in the critical or the initial state, respectively. The partition functions mentioned above are thus approximated as

$$\Psi^{\ddagger} = J_{\ddagger} / h^{N-1} \omega^{\ddagger}, \quad \Psi^{\text{I}} = J_{\text{I}} / h^N \omega^{\text{I}},$$

hence we have

$$v_{\ddagger} = \kappa \omega' kT J_{\ddagger} / J_{\text{I}} = \kappa (\omega' \omega^{\ddagger} / \omega^{\text{I}}) (kT/h) (\Psi^{\ddagger} / \Psi^{\text{I}}). \quad (\text{A. 1})$$

The number ω' is that of modes of interchanging identical particles of the critical system derived from the particularly distinguished initial system multiplied by such number of the rest of the assembly; the former number of modes is, further, that of the particular initial system itself, from which the critical system is derived; hence we see that

$$\omega' \omega^{\ddagger} = \omega^{\text{I}}. \quad (\text{A. 2})$$

Let Ψ be the partition function of the assembly which is derived from the assembly relevant to Ψ^{\ddagger} or Ψ^{I} by withdrawing the particularly distinguished system, \ddagger or I, from it. We now define

$$\phi^{\ddagger} \equiv \Psi^{\ddagger} / \Psi \quad \text{and} \quad \phi^{\text{I}} \equiv \Psi^{\text{I}} / \Psi. \quad (\text{A. 3})$$

Then the quantity $-kT \ln \phi^{\delta}$ (δ denotes \ddagger or I) is the chemical potential of the particularly distinguished system δ , hence ϕ^{δ} is just the reciprocal of the absolute activity⁸⁾ a^{δ} of δ .

With reference to Eqs. (A.1), (A.2) and (A.3), the forward, unidirectional rate of s -th elementary step is generally expressed as

$$v_{s\ddagger} = (kT/h) \exp(-\Delta^{\ddagger} G_{s\ddagger} / RT),$$

where

$$\Delta^{\ddagger} G_{s\ddagger} = \mu^{\ddagger(s)} - \mu^{\text{I}(s)} = RT \ln (\phi^{\text{I}(s)} / \phi^{\ddagger(s)}) \equiv RT \ln (a^{\ddagger(s)} / a^{\text{I}(s)})$$

and κ is approximated as unity.