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NUMBER OF SEATS OF HETEROGENEOUS REACTION ON METALLIC CATALYSTS

By

J. HORIUTI, K. MIYAHARA and I. TOYOSHIMA*)

(Received February 5, 1966)

Abstract

A lower limit $N_t^*$ to the number $N^*$ of seats of the critical system of an elementary reaction on a metallic catalyst was determined statistical mechanically by extending previous work2), eliminating some assumptions on which the latter work was based.

The assumption underlying the present work are that of the physical identity of the seats in question and that of existence of a single reaction route for every overall reaction dealt with. The statistical mechanical equation of $N^*$ thus derived enables us to calculate $N_t^*$ from the rate of an overall reaction and its dependence on temperature and on concentrations of reactants and products in gas regardless of its mechanism.

The log $10 N_t^*$ cm$^{-2}$ was thus determined from all presently available data of 66 kinetic observations at a mean value 15.48 with a standard deviation of 0.38 which is attributable to the inaccuracies of the underlying observations. Admitting that the upper limit to $N^*$ is $10^{18}$ cm$^{-2}$ by order of magnitude, it is concluded that the metallic catalysts have, in accordance with the crystal plane model, $10^{15}$ cm$^{-2}$ physically identical seats of the critical system by order of magnitude, and that the transmission coefficient of the rate-determining step is of the order of magnitude of unity.

Introduction

The knowledge of the number $N^*$ of seats on a metallic catalyst for the critical system$^{**1,2}$ of an elementary reaction, termed simply step here, may provide an important criterion for discerning its characteristics; $N^*$ must be of the order of magnitude of $10^{15}$ cm$^{-2}$ if each physically identical seat is provided by a definite set of a few adjacent metal atoms on a lattice plane, but

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*) Research Institute for Catalysis, Hokkaido Univ., Sapporo, Japan.

**) The set of particles involved in a step is called its system and its state prior or posterior to the occurrence of the step the initial or the final state and the system in the respective state the initial or the final system. The critical system is the system at the state which the system has necessarily to pass through in order to transfer from the initial to final state or reversely, and is passed through with least frequency by the canonical ensemble of the assembly in which the step is occurring$^{1,2}$. The critical system is not necessarily an activated complex, which is defined as the system at the saddle point of its potential energy.
must be of smaller order of magnitude if provided by a set of metal atoms of exceptional arrangements, as suggested by the active center theory. The former model will be termed the crystal plane model of catalyst in what follows.

The present authors tried previously to determine the number \( N^* \) by a statistical mechanical analysis of kinetic data; the result obtained was \( \log_{10} N^* = 15.5 \text{ cm}^{-2} \) as an average for 28 kinetic observations\(^3\). This analysis was based on the assumption that the seats are physically identical with each other, and besides that they are either only sparsely or else almost completely occupied by adsorbates of a single kind. The conclusion was hence claimed to hold just in the special case.

The present paper is devoted to developing the previous work\(^3\) by allowing for more than one kinds of adsorbates, with partial coverages of not necessarily close to unity or zero and with interactions among each other and with the critical system\(^1\) of the rate-determining step; the assumptions retained in the present work are that there exists a single reaction route and that sites of adsorption are identical with each other and with the seats of the critical system. The above development has been carried out for the two cases where all the intermediates are independent and where not all of them are independent.

The independence of intermediates and the single reaction route mentioned above\(^1\) are briefly accounted for below. Consider an overall reaction expressed by a stoichiometric equation, which equates a set of reactants with that of products. An overall reaction consists in general of a number of steps. A species which is involved in any of the constituent steps but does not appear in the stoichiometric equation of the overall reaction is called an intermediate. All the intermediates, e.g. \( \text{C}_2\text{H}_4(a) \), \( \text{H}(a) \) and \( \text{C}_2\text{H}_4(a) \) involved in the sequence of steps

\[
\text{C}_2\text{H}_4 \xrightarrow{i} \text{C}_2\text{H}_4(a) \quad \text{iii} \quad \text{H}(a) \xrightarrow{\text{iv}} \text{C}_2\text{H}_4
\]

(1)

of the overall reaction \( \text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_4 \) are called independent\(^5\), inasmuch as none of the expressions for the net number of creation of the respective intermediates, \( i.e. \ n_1 - n_{iii}, 2n_{ii} - n_{iii} - n_{iv} \) and \( n_{iii} - n_{iv} \), is identically derived as a linear combination of others, in other words, they are mathematically independent; \( n_1 \) etc. are numbers of occurrence of steps i etc., and (a) denotes the adsorbed state on the catalyst.

On the other hand, the intermediates \( \text{C}_2\text{H}_4(a) \), \( \text{Br}(a) \) and \( \text{H}(a) \) in the overall reaction \( \text{C}_2\text{H}_2\text{Br} = \text{C}_2\text{H}_4 + \text{HBr} \) consisting of the sequence of steps
are not all independent, inasmuch as the sum of \( n_i - n_{ii} \) (the net number of creation of \( \text{C}_2\text{H}_4(a) \)) and that \( n_{ii} - n_{iii} \) (that of \( \text{H}(a) \)) is identically equal to \( n_i - n_{iii} \) (that of \( \text{Br}(a) \)). In the latter case two of the three net numbers are necessary and sufficient to specify all three, and therefore it is said that there exist two independent intermediates.

The condition of steady state is now given by equating the net numbers of creation of intermediates respectively to zero\(^{18}\). We have three independent homogeneous linear equations in the case of (1), but only two in the case of (2). A theorem of algebra states now that the ratios of various \( n_i \) to each other are uniquely defined by the solution of the simultaneous equations in the case where the number of steps exceeds that of the independent intermediates by one. The excess of number of steps over that of the independent intermediates is called the number of independent reaction routes and the single reaction route is the special case where the latter excess is unity\(^{18}\).

It has now been verified in previous work\(^5\) that in the case where all intermediates involved in an overall reaction are independent, as in sequence (1), the initial or final system of a constituent step is derived from the respective set of reactants and products through constituent steps other than \( s \) without creating or consuming any intermediate other than those comprised in the initial or the final system. The initial system \( \text{C}_2\text{H}_4(a) + \text{H}(a) \) or the final system \( \text{C}_2\text{H}_4(a) \) of step iii of sequence (1) is thus derived, respectively, from the set of reactants \( \text{C}_2\text{H}_4 + \text{H}_2 \) through steps i and ii or from a set \( \text{C}_2\text{H}_4 - (1/2) \text{H}_2 \) of reactant and product through steps ii and iv. This is not secured if not all the intermediates are independent. The initial system of step ii of sequence (2), for instance, is thus derived from reactant \( \text{C}_2\text{H}_4\text{Br} \) through step i, and its final system \( \text{C}_2\text{H}_4 + \text{H}(a) \) from a set \( \text{C}_2\text{H}_4 + \text{HBr} \) of products through step iii,

Premising the presence of \( \ell \) rate-determining step an equation for \( N^* \) is now derived according to the statistical mechanical theory of reaction rate\(^{19}\) for the two cases of complete and incomplete independence of intermediates, as mentioned above. This will enable us to calculate the lower limit, \( N^*_\ell \), of \( N^* \) from the observed dependence of the rate of the overall reaction on temperature and on partial pressures of reactants and products regardless of the mechanism. \( N^*_\ell \) is thus calculated for all presently available data of 66 kinetic observations on metallic catalysts; conclusions are drawn regarding the value
of $N^*$ and the transmission coefficient of the rate-determining step as developed in what follows.

**General Method**

The forward rate $v_+$ of a heterogeneous step is expressed as

$$v_+ = \frac{kT}{h} N^* q^* \theta_0 / \rho_1,$$

where $q^*$ is the Boltzmann factor of the reversible work required to bring a system of the step, from its standard state onto a definite, preliminarily evacuated seat to form a critical system there, $\theta_0$ is the probability of the seat being unoccupied and $\rho_1$ is the Boltzmann factor of chemical potential of the initial system.

The forward unidirectional rate of the overall reaction is obtained by dividing the forward rate $v_+ r$ of the rate-determining step $r$ by its stoichiometric number, but since only the order of magnitude is in question, while the stoichiometric number may be taken of the order of magnitude of unity, $v_+ r$ is directly identified with the observable forward unidirectional rate of the overall reaction. The $v_+$ of (3) new specialized to express $v_+ r$ in what follows.

The right side of (3) has to be multiplied, besides, by the transmission coefficient, which is equal to or less than unity, in order to give $v_+$ exactly. This will be considered later, but till then the effect of this will be disregarded.

The interaction of the critical system with surrounding adsorbates are taken into account by expressing $q^*$ as

$$q^* = q^*_0 \exp \left(- \sum_a u^*_a \theta_a / RT \right),$$

where $\theta_a$ is the probability of the seat being occupied by $a$-th adsorbate, and $u^*_a \theta_a$ is the part of the reversible work due to the interaction of the critical system with the $a$-th adsorbate $\delta_a$, $u^*_a$ being assumed a constant particular to the critical system and $\delta_a$. The probability $\theta_a$ equals the fraction covered by $a$-th adsorbate in case of physically identical sites of adsorption. The $q^*_0$ is the Boltzmann factor of the reversible work in the absence of interaction. The reversible work $-kT \ln q^*_0$ is by definition the increment of free energy of the whole assembly, in which the reaction in question is going on, caused by bringing the system from its standard state onto a definite, preliminarily evacuated seat to form a critical system there in the absence of the interaction. The appropriate increment of entropy of the assembly is quite small, inasmuch

*) The work required in the statistical mechanical equilibrium of the whole assembly concerned kept at a specified composition.
as the critical system is confined in the definite seat of molecular dimension. Since the entropy increment equals the negative temperature coefficient of the appropriate free energy increment, the free energy increment is approximately constant independent of temperature, hence

\[ q^* = \exp\left(-\frac{\varepsilon^*}{RT}\right), \quad \varepsilon^* = \text{constant}. \quad (4. b) \]

We have from (3) and (4)

\[ \frac{\partial \ln v_+}{\partial \ln T} = 1 - \ln q^* - \frac{\partial \ln p^0}{\partial \ln T} + \theta_0 + \sum_{\alpha} (u^*_{\alpha} \theta_0 / RT) \frac{\partial \ln \theta_0}{\partial \ln T} \]

hence

\[ \ln v_+ + \frac{\partial \ln v_+}{\partial \ln T} = \ln N^* - \frac{\partial \ln p^0}{\partial \ln T} + \ln \theta_0 - \frac{\partial \ln \theta_0}{\partial \ln T} - \sum_{\alpha} (u^*_{\alpha} \theta_0 / RT) \frac{\partial \ln \theta_0}{\partial \ln T}. \quad (5) \]

The left side of (5) is directly determined by experiment. The \( N^* \) is thus calculated by evaluating the last five terms on the right side of (5). This is performed for the respective cases of intermediates, where A), all of them are independent, and B) not all of them are, after those fundamental equations of adsorption are reviewed in the next section which are as required for the evaluation.

**Equations of Adsorption**

The fundamental equation of adsorption is \(^3\)

\[ \theta_a = \left(\frac{q^*_{\alpha}}{p^0_{\alpha}}\right) \theta_a, \quad (6. a) \]

where \( \theta_a \) is the probability of a seat being occupied by \( \alpha \)-th adsorbate \( \delta_a \), \( q^*_{\alpha} \) the BOLTZMANN factor of the reversible work required to bring \( \delta_a \) from its standard state onto the definite, preliminarily evacuated site, \( p^0_{\alpha} \) the BOLTZMANN factor of chemical potential of \( \delta_a \) and \( \theta_0 \) the probability of the site being unoccupied. It follows from the definitions of the \( \theta_a \)'s and \( \theta_0 \) that

\[ \sum_a \theta_a + \theta_0 = 1 \quad (6. b) \]

or, with the definition

\[ \theta = \sum_a \theta_a \quad (6. c) \]

that

\[ \theta = 1 - \theta_0 \quad \text{and} \quad \theta_0 \sum_a \left(\frac{q^*_{\alpha}}{p^0_{\alpha}}\right) = 1 - \theta_0. \quad (6. d), (6. e) \]

The \( q^*_{\alpha} \) is formulated, similarly to \( q^* \), as

\[ q^*_{\alpha} = q^* \exp\left(-\sum_{\alpha'} u^*_{\alpha'} \theta_0 / RT\right), \quad (7. a) \]
where

\[ q^*_n = \exp(-\varepsilon_n/RT), \quad \varepsilon_n = \text{constant.} \]  

(7. b)

\( u^{(\alpha)}_n \) is the part of the reversible work due to the interaction of \( \delta_n \) with \( \alpha \)-th adsorbate, \( u^{(\alpha)}_n \) being assumed a constant particular to \( \alpha \) and \( \alpha' \).

If \( \delta_n \) be in partial equilibrium with a set \( \sum_{\alpha} n_\alpha G_\alpha \) of gas molecules, each consisting \( n_\alpha \) particles of \( G_\alpha \), we have

\[ \ln p^* = \sum_{\alpha} n_\alpha \ln p^{(\alpha)} \]  

(8)

where \( p^{(\alpha)} \) is the BOLTZMANN factor of the chemical potential of \( G_\alpha \). The \( p^{(\alpha)} \) is expressed as

\[ p^{(\alpha)} = \frac{Q_\alpha}{N_\alpha}, \]  

(9)

where \( Q_\alpha \) is the partition function of a single \( G_\alpha \) in unit volume and \( N_\alpha \) its concentration. The \( Q_\alpha \) is expressed for a linear \( G_\alpha \) (including of a diatomic one) with good approximation at not very high temperature, as

\[ Q_\alpha = \frac{(2\pi mkT)^{3/2}}{\hbar^3} \frac{8\pi^2 I kT}{s \hbar^3} \]  

(linear),  

(10. a)

where \( m \) is the mass, \( I \) the moment of inertia and \( s \) the symmetry number, approximating its vibrational partition function with unity and referring its energy to the ground state energy. The \( Q_\alpha \) is given similarly, for nonlinear \( G_\alpha \) without internal rotation, as

\[ Q_\alpha = \frac{(2\pi mkT)^{3/2}}{\hbar^3} \frac{8\pi^2 (2\pi I kT)^{3/2}}{s \hbar^3} \]  

(nonlinear),  

(10. b)

where \( I \) is the geometric mean of the three principal moments of inertia.

In the case where adsorbates \( \delta_1 \) and \( \delta_2 \) respectively associated with another adsorbate \( \delta_m \), i.e. \( \delta_1 + \delta_m \) or \( \delta_2 + \delta_m \), are in partial equilibrium with a set \( G_1 \equiv \sum_{\alpha} n_\alpha^{(1)} G_\alpha \) or \( G_2 \equiv \sum_{\alpha} n_\alpha^{(2)} G_\alpha \), respectively we have

\[ p^1 p^m = p^{(\alpha)} = \prod_{\alpha} \frac{(Q_\alpha/N_\alpha)^{n_\alpha}}{(Q/N)^{n_\alpha}} \]  

(11. a)

and

\[ p^1 p^m = p^{(\alpha)} = \prod_{\alpha} \frac{(Q/N)^{n_\alpha}}{(Q/N)^{n_\alpha}} \]  

(11. b)

On the basis of the above development, expressions for \( N^* \) are derived in the respective cases A) and B) of the degree of independence of intermediates.
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**N** in Case A)

The intermediates in question are all independent. The seats of the critical system of the rate-determining step are physically identical with each other, each of them is occupied by the critical system or one of adsorbates \( \delta_a \), \( (a=1,2,\cdots) \) or unoccupied, and \( \delta_a \) is in partial equilibrium with a set \( G_a \) of gas molecules, which consists of \( g \) types of gas molecules \( G_{g} \), each in a number \( \nu_{g}^{(a)} \) \( i.e.G_{a} = \sum_{g} \nu_{g}^{(a)}G_{g} \). It is assumed, as in the case of \( \delta_a \), to be in partial equilibrium with a set \( \sum_{g} \nu_{g}^{(a)}G_{g} \) of gas molecules, \( \ln p^{1} \) on the right of (5) being expressed according to (9) as

\[
\ln p^{1} = \sum_{g} \nu_{g}^{(a)} \ln \left( \frac{Q_{g}}{N_{g}} \right),
\]

hence

\[
\ln p^{1} + \partial \ln p^{1}/\partial \ln T = \sum_{g} \nu_{g}^{(a)} \left\{ \ln \left( \frac{Q_{g}}{N_{g}} \right) + \partial \ln Q_{g}/\partial \ln T \right\}.
\]

The \( \ln \theta_{a} \) on the right side of (5) is given according to (6.e) as

\[
\theta_{a} = \left\{ 1 + \sum_{g} \left( q_{g}^{a}/p_{g}^{a} \right) \right\}^{-1},
\]

so that

\[
-\frac{\partial \ln \theta_{a}}{\partial \ln T} = \sum_{g} \frac{q_{g}^{a}}{p_{g}^{a}} \left( \frac{\partial \ln q_{g}^{a}}{\partial \ln T} - \frac{\partial \ln p_{g}^{a}}{\partial \ln T} \right) \left( 1 + \sum_{g} \frac{q_{g}^{a}}{p_{g}^{a}} \right)
\]
or according to (6.a), (6.b) and (6.c)

\[
-\frac{\partial \ln \theta_{a}}{\partial \ln T} = \sum_{a} \theta_{a} \left( \partial \ln q_{a}^{a}/\partial \ln T - \partial \ln p_{a}^{a}/\partial \ln T \right).
\]

It follows on the other hand from (7) that

\[
\partial \ln q^{a}/\partial \ln T
\]

\[
= \varepsilon_{a}/RT + \sum_{a} u_{a}^{\circ} \theta_{a}/RT - \sum_{a} u_{a}^{\ast} \theta_{a} \left( \partial \ln \theta_{a}/\partial \ln T \right)/RT
\]

\[
= -\ln q^{a} - \sum_{a} u_{a}^{\circ} \theta_{a} \left( \partial \ln \theta_{a}/\partial \ln T \right)/RT.
\]

Substituting \( \partial \ln q^{a}/\partial \ln T \) from the above equation into (13.a), we have

\[
\frac{\partial \ln \theta_{a}}{\partial \ln T} \left[ \sum_{a} \theta_{a} \ln q^{a} + \frac{u_{a}^{\circ} \theta_{a}^{2}}{RT} \right] + \sum_{a} \theta_{a} \frac{\partial \ln p_{a}^{a}}{\partial \ln T},
\]

where

\[
\frac{u_{a}^{\circ} \theta_{a}^{2}}{RT} = \sum_{a} u_{a}^{\circ} \theta_{a}^{2} \theta_{a} \frac{\partial \ln \theta_{a}}{\partial \ln T} / \left( \partial \ln \theta_{a}/\partial \ln T \right).
\]
The left side of (13. b) is written according to (6. d) as
\[
\frac{\partial}{\partial \ln T} \left( \ln \theta_a \right) = \frac{\theta (1/\theta_a + u_\theta/RT)}{\theta (1/\theta_v + u_\theta/RT)} \left( \ln \theta_a \right).
\]

Substituting \( \theta \partial \ln \theta_a / \partial \ln T \) from the above equation and \( q^{*} \) from (6. a) respectively into (13. b) and solving for \( \partial \ln \theta_v / \partial \ln T \), we have with reference to (6. c)
\[
\frac{\partial}{\partial \ln T} \left( \ln \theta_v \right) = \frac{\sum \theta_a \ln \theta_a - \theta \ln \theta_v + \sum \theta_a (\ln p^{*} + \partial \ln p^{*} / \partial \ln T)}{\theta (1/\theta_v + u_\theta/RT)}.
\]

or according to (8) and (9)
\[
\frac{\partial}{\partial \ln T} \left( \ln \theta_v \right) = \frac{\sum \theta_a \ln \theta_a - \theta \ln \theta_v + \sum \theta_a \sum \nu^{(a)} \{ \ln (Q_v/N_v) + \partial \ln Q_v / \partial \ln T \}}{\theta (1/\theta_v + u_\theta/RT)}.
\]

The \( \ln \theta_v + \partial \ln \theta_v / \partial \ln T \) is obtained noting that \( \partial \ln \theta_v / \partial \ln T \) is \( -\theta / \theta_v \) times \( \partial \ln \theta_v / \partial \ln T \) according to (14), as
\[
\ln \theta_v + \partial \ln \theta_v / \partial \ln T = \frac{\theta_v \ln \theta_v (1 + u_\theta/RT) + \sum \theta_a \ln \theta_a + \sum \theta_a \sum \nu^{(a)} \{ \ln (Q_v/N_v) + \partial \ln Q_v / \partial \ln T \}}{1 + u_\theta/RT}.
\]

The last term on the right side of (5) is written as
\[
\sum u_\theta^{(a)} \theta_a \partial \ln \theta_a / \partial \ln T = u_\theta^{(a)} \theta_a \partial \ln \theta_a / \partial \ln T,
\]

thus defining a new quantity \( u_\theta^{(a)} \), or substituting \( \partial \ln \theta_v / \partial \ln T \) from (15), as
\[
\sum u_\theta^{(a)} \theta_a \partial \ln \theta_a / \partial \ln T = \frac{u_\theta^{(a)} \theta_a [\sum \theta_a \ln \theta_a - \theta \ln \theta_v + \sum \theta_a \sum \nu^{(a)} \{ \ln (Q_v/N_v) + \partial \ln Q_v / \partial \ln T \}]}{1 + u_\theta/RT}.
\]

The \( \log_{10} N^* \) is now expressed by substituting the terms in (5) from (12. b), (16) and (17. b), as
\[
\log_{10} N^* = \log_{10} N_v^* + R,
\]

where
\[
\log_{10} N_v^* = \log_{10} v_v + \frac{H_v^*}{2.3 RT} - \log_{10} \frac{ekT}{h} + \sum \nu_v \left( \log_{10} \frac{Q_v}{N_v} + T \frac{\partial \log_{10} Q_v}{\partial T} \right),
\]

\[
H_v^* = RT \partial \ln v_v / \partial T,
\]
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\[ y_{\theta} = v^3_{\theta} - \left\{ \frac{1 + u_x^\theta \theta_s/RT}{1 + u_x^\theta \theta_s}/RT \right\} \sum \theta_x v_{3x}(\theta) \]  
(18. \nu)

and

\[ R = \frac{(1 + u_x^\theta \theta_s/RT) \sum \theta_x \log \theta_s + \{1 + (u_x^\theta - u_x^\theta) \theta_s/RT\} \theta_x \log \theta_s}{1 + u_x^\theta \theta_s/RT}. \]
(18. R)

It is now shown that \( y_{\theta} \) reproduces \( \partial \ln v_{\theta}/\partial \ln N_{\theta} \) with some approximation; we have according to (3), (4), (12. a) and (17. a)

\[ \partial \ln v_{\theta}/\partial \ln N_{\theta} = -(u_x^\theta \theta_s/RT) \partial \ln \theta_s/\partial \ln N_{\theta} + \partial \ln \theta_x/\partial \ln N_{\theta} + v_{3x}^\theta, \]

or according to (6. d)

\[ \partial \ln v_{\theta}/\partial \ln N_{\theta} = -(u_x^\theta \theta_s/RT + \theta_x/\theta_s) \partial \ln \theta_s/\partial \ln N_{\theta} + \partial \ln p_{\theta}^x/\partial \ln N_{\theta} + v_{3x}^\theta, \]  
(19. a)

where

\[ u_x^\theta = \sum \theta_x u_x^\theta_s \left( \partial \ln \theta_s/\partial \ln N_{\theta} \right) \left( \partial \ln \theta_s/\partial \ln N_{\theta} \right). \]
(19. b)

We have on the other hand from (6. a) and (6. c)

\[ \ln \theta_x/\theta_s = \sum (q^x_{\theta}/p_{\theta}^x), \]

or by differentiation with reference to (6. d) and (7. a)

\[ \frac{1}{\theta_x} \partial \ln \theta_x/\partial \ln N_{\theta} = \frac{\sum (q^x_{\theta}/p_{\theta}^x) \left\{ - \sum \theta_x \theta_x^s \theta_x^s \theta_x^s/RT (\partial \ln \theta_s/\partial \ln N_{\theta}) - \partial \ln p_{\theta}^x/\partial \ln N_{\theta} \right\}}{\sum q^x_{\theta}/p_{\theta}^x}. \]

Replacing \( q^x_{\theta}/p_{\theta}^x \) in the above equation with \( \theta_x/\theta_s \) according to (6. a), we have

\[ \frac{\theta}{\theta_x} \frac{\partial \ln \theta_x}{\partial \ln N_{\theta}} = - \frac{u_x^\theta \theta_x^s}{RT} \frac{\partial \ln \theta_x}{\partial \ln N_{\theta}} - \sum \theta_x \frac{\partial \ln p_{\theta}^x}{\partial \ln N_{\theta}}, \]
(20. a)

where

\[ u_x^\theta = \sum \theta_x u_x^\theta_s \theta_x^s \theta_x^s \frac{\partial \ln \theta_x}{\partial \ln N_{\theta}} \left( \frac{\partial \ln \theta_x}{\partial \ln N_{\theta}} \right). \]
(20. b)

Since \( \partial \ln p_{\theta}^x/\partial \ln N_{\theta} \) in (20. a) equals \( -v_{3x}^\theta \) according to (8) and (9), we have

\[ (u_x^\theta \theta_x^s/RT + 1/\theta_s) \theta_x \partial \ln \theta_x/\partial \ln N_{\theta} = \sum \theta_x v_{3x}^\theta. \]
(20. c)

Substituting \( \theta \partial \ln \theta_x/\partial \ln N_{\theta} \) from (20. c) into (19. a), we have

\[ \partial \ln v_{\theta}/\partial \ln N_{\theta} = v_{3x}^\theta - \left\{ \frac{1 + u_x^\theta \theta_x^s/RT}{1 + u_x^\theta \theta_x^s}/RT \right\} \sum \theta_x v_{3x}^\theta, \]  
(21)

which shows with reference to (18. \nu) that \( y_{\theta} \) represents a directly measurable
quantity $\partial \ln v_*/\partial \ln N_\theta$, provided that $u_{\alpha}^* = u_{\alpha N}^*$ and $u_{\tau} = u_{\tau N}$, which holds, conditionally, as seen from the comparison of (17.a) with (19.b) and that of (13.c) with (20.b), if $u_{\alpha}^*$ and $u_{\alpha'}^*$ are respectively constant independent $\alpha$ and $\alpha'$, whereas unconditionally, if there exists only one kind of adsorbate. The $N^*$ is now empirically determinable by (18.v) and (18.N), provided that $R$ be known.

*) If $u_{\alpha}^*$ is a constant $u^*$ independent of $\alpha$, we have from (17.a) with reference to (6.c), $u_{\alpha}^* \sum \theta_\alpha / \partial \ln T = u^* \theta / \partial \ln T = u^* \theta / \partial \ln T = u_{\alpha N}^* \theta / \partial \ln T$, hence $u_{\alpha}^* = u^*$. It follows from (19.b) similarly that $u_{\alpha N}^* = u^*$, hence $u_{\alpha}^* = u_{\alpha N}^*$. It is shown similarly that $u_{\tau} = u_{\tau N}$ from (13.c) and (20.b), if $u_{\alpha'}^*$ is constant independent of $\alpha$ and $\alpha'$.
We see from (18. R) that \( R \) vanishes in any case where every \( \theta_a \) vanishes and in the alternative case where \( \theta_a \) vanishes provided that the seats are then occupied by \( \delta_a \) of a single kind. If occupants are of more than one kind, \( R \) is positive and has a maximum value when all \( \theta_a \)'s are equal to each other, which holds exactly for \( \theta_a = 0 \) and even for \( \theta_a > 0 \), provided that \( u_T \) is approximately identified with \( u_T^* \). Assuming that \( u_T^* = u_T \) and three kinds of adsorbates of equal coverage \( \theta/3 \), \( R \) is calculated as shown in Fig. 1 for different values of total coverage \( \theta \) for \( u_T/RT = u_T^*/RT = 10, 20 \) and 30, and \( N = 3 \).

\( N^* \) in Case B)

We deal with the case, where the formation of the initial system of the rate-determining step is associated with creation of an intermediate \( \delta_m \). It has been shown\(^6\) in case of a single reaction route, as premised here, that the same intermediate is disposed of, together with its final system which is to be reduced to a set of reactants and/or products, through the complete set of steps minus the rate-determining step and the set of steps which has brought about the initial system and \( \delta_m \). Seats of the critical system of the rate-determining step are physically identical with each other and occupied apart from the critical system, either by the initial system or the final system or \( \delta_m \) or unoccupied.

We have in this case by replacing \( p^I \) in (3) with \( p^{m} \) according to (11a)

\[
v_+ = (kT/h)N^* q^* \theta_a p^m \prod_q \left( N_q/|Q_q| \right)^{0(q)}.
\]

hence

\[
\ln v_+ + \delta \ln v_+ / \delta \ln T
= \ln N^* kT/h + \ln \theta_a + \delta \ln \theta_a / \delta \ln T + \ln p^m + \delta \ln p^m / \delta \ln T
- \sum_a (u_a^*/RT) \delta \ln \theta_a / \delta \ln T + \sum_q \left\{ \ln (N_q/|Q_q|) - \delta \ln Q_q / \delta \ln T \right\}.
\]

The \( \theta_a \) is related in this case to \( \theta_i, \theta_m \) and \( \theta_a \), respectively, of adsorbates \( \delta_1 \), \( \delta_m \) and \( \delta_a \) as

\[
\theta_a + \theta_1 + \theta_m + \theta_a = 1 \ ,
\]

where \( \delta_a \) represents the final system of the rate-determining step; we have now\(^8\)

\(\text{\footnotesize *) The net numbers } n_1-n_{11} \text{ and } n_{11}-n_{111} \text{ of creation of intermediates } \text{C}_2\text{H}_2(\text{a}) \text{ and } \text{H(}\text{a}) \text{ in case of sequence } (2) \text{ give their amount respectively present at the steady state, insofar as } n_1 \text{ etc. represent the numbers of occurrence of the respective steps } i \text{ etc. until the steady state is attained. Since the sum of } n_1-n_{11} \text{ and } n_{11}-n_{111} \text{ gives identically } n_1-n_{111}, \text{ i.e. the amount of Br (a) present at the steady state, we have } \theta(\text{C}_2\text{H}_2)+\theta(\text{H})=\theta(Br), \text{ which exemplifies (23 a).}\)
\( \theta_1 + \theta_2 = \theta_m \), \hspace{1cm} (23. a)

hence for \( \theta = \theta_1 + \theta_m + \theta_2 \) from the above two equations

\[ \theta = 1 - \theta \] \hspace{1cm} (23. b)

and

\[ \theta/2 = \theta_m \]. \hspace{1cm} (23. c)

The sum \( \ln \theta_0 + \partial \ln \theta_0/\partial \ln T \) on the right side of (22. b) is expressed according to (23. b), as

\[
\ln \theta_0 + \partial \ln \theta_0/\partial \ln T = \ln \theta_0 - (\theta/\theta_0) \partial \ln \theta/\partial \ln T.
\] \hspace{1cm} (24)

The sum \( \ln \rho^{\text{m}} + \partial \ln \rho^{\text{m}}/\partial \ln T \) in (22. b) is developed by (6. a) referring to (7), (23. b) and (23. c) as

\[
\ln \rho^{\text{m}} + \partial \ln \rho^{\text{m}}/\partial \ln T = \ln \theta_0 + \ln (\theta_0/2) - (1/\theta_0 + u \theta/RT) \partial \ln \theta/\partial \ln T,
\] \hspace{1cm} (25. a)

where

\[
u^{(\text{m})} = \sum_a u_a^{(\text{m})} \theta_a \partial \ln \theta_a/\partial \ln T,
\] \hspace{1cm} (25. b)

\( \alpha \) representing in this case a summation over 1, 2 and \( m \). The next term in (22. b) is written similarly to (17. a) in case A), as

\[
\sum_a u_a^\alpha \theta_a \partial \ln \theta_a/\partial \ln T = u^\alpha \partial \ln \theta/\partial \ln T.
\] \hspace{1cm} (26)

Substituting the terms in (22. b) from (24), (25. a) and (26), we have

\[
\ln \nu + \partial \ln \nu/\partial \ln T = \ln N^* eT/h + 2 \ln \theta_0 - \ln \theta/2
- \{(1 + \theta)/\theta_0 + (u^\alpha) \theta/RT\} \partial \ln \theta/\partial \ln T
+ \sum_q \nu_0^{(\text{e})} \{ \ln (N_0/Q_0) - \partial \ln Q_0/\partial \ln T \},
\] \hspace{1cm} (27)

The differential coefficient \( \partial \ln \theta/\partial \ln T \) is now derived as follows. We have from (6. a) and (11)

\[
\theta_m = (\theta_0)^q^m q^m/\rho^m,
\]

and

\[
\theta_m = (\theta_0)^q^m q^m/\rho^m,
\]

or summing up respective sides of them referring to (23. a) and (23. c),

\[
(\theta/2\theta_0)^q = q^m q^m/\rho^m + q^m q^m/\rho^m.
\] \hspace{1cm} (28)

Differentiation of the logarithms of both the sides gives with reference to (23. b)
Number of Seats of Heterogeneous Reaction on Metallic Catalysts

\[
\frac{1}{\theta_0} \frac{\partial \ln \theta}{\partial \ln T} = - \frac{q^* q^{m*}}{p^{\alpha_i}} \left( \ln q^* q^{m*} + \sum_{a} \frac{u_a^{(1)} + u_a^{(m)}}{RT} \theta_a \frac{\partial \ln \theta_a}{\partial \ln \theta} + \frac{\partial \ln \rho^{\alpha_i}}{\partial \ln T} \right) \nonumber \\
- \frac{q^* q^{m*}}{p^{\alpha_i}} \left( \ln q^* q^{m*} + \sum_{a} \frac{u_a^{(2)} + u_a^{(m)}}{RT} \theta_a \frac{\partial \ln \theta_a}{\partial \ln \theta} + \frac{\partial \ln \rho^{\alpha_i}}{\partial \ln T} \right) \nonumber \\
2(q^* q^{m*} | \rho^{\alpha_i} + q^* q^{m*} | \rho^{\alpha_i}) \quad (29)
\]

Since

\[
(q^* q^{m*} | \rho^{\alpha_i}) = \theta_0/\theta_s \quad (30)
\]

according to (11) and (6. a), (29) is written referring to (23. a) and (23. c) as

\[
(1/\theta + u_\theta/RT) \frac{\partial \ln \theta}{\partial \ln T} = -(\theta/\theta) \ln q^* q^{m*} - (\theta/\theta) \ln \rho^{\alpha_i} \nonumber \\
- (\theta/\theta) \partial \ln \rho^{\alpha_i} / \partial \ln T - (\theta/\theta) \partial \ln \rho^{\alpha_i} / \partial \ln T, \quad (31. a)
\]

where

\[
u_\theta \partial \ln \theta / \partial \ln T = \sum_{a} \{u_a^{(1)}(u_a^{(1)} + u_a^{(m)}) + \theta_a(u_a^{(2)} + u_a^{(m)})\} \theta_a \partial \ln \theta_a / \partial \ln T. \quad (31. b)
\]

Replacing \( q^* \) in (31. a) with \( \theta_0 \rho^{\alpha_i} / \theta_s \) according to (6. a), we have, referring to (11) and (23)

\[
(1/\theta + u_\theta/RT) \frac{\partial \ln \theta}{\partial \ln T} = \ln \theta_s - (1/2) \ln \theta/2 - (\theta/\theta) \ln \theta_s - (\theta/\theta) \ln \theta_s \nonumber \\
- (\theta/\theta) \ln \rho^{\alpha_i} + \partial \ln \rho^{\alpha_i} / \partial \ln T - (\theta/\theta) \ln \rho^{\alpha_i} + \partial \ln \rho^{\alpha_i} / \partial \ln T
\]

or developing \( \ln \rho^{\alpha_i} \) and \( \ln \rho^{\alpha_i} \) according to (11)

\[
\frac{\partial \ln \theta}{\partial \ln T} = \frac{\theta_0 \ln \theta_s - (\theta/\theta) \ln \theta/2 - (\theta/\theta) \ln \theta_s + (\theta_0 \theta_s/RT)}{1 + u_\theta \theta_0/RT} \nonumber \\
+ \frac{\theta_0 \sum \nu_\theta \theta_s / \theta_0}{1 + u_\theta \theta_0/RT} \ln (N_0/Q_0) - \partial \ln Q_0 / \partial \ln T
\]

The \( \log_{\alpha_i} N^* \) is now expressed by substituting \( \partial \ln \theta / \partial \ln T \) from the above equation into (27), as

\[
\log_{\alpha_i} N^* = \log_{\alpha_i} N^* + R, \quad (32. v)
\]

where

\[
\log_{\alpha_i} N^* = \log_{\alpha_i} v_\theta + \frac{H_{\alpha_i}^*}{2.3RT} - \log_{\alpha_i} \frac{ekT}{h} + \sum_\nu \nu_\theta \left( \log_{\alpha_i} Q_\theta \frac{Q_\theta}{N_\theta} + T \frac{\partial \log_{\alpha_i} Q_\theta}{\partial T} \right), \quad (32. N)
\]

\[
H_{\alpha_i}^* = RT^\alpha \partial \ln v_\theta / \partial \ln T, \quad (32. H)
\]
\[
\gamma_{\theta} = \psi_{\theta}^{(1)} - \frac{(\theta_{s}/\theta)\psi_{\phi}^{(1)} + (\theta_{s}/\theta)\psi_{\phi}^{(2)}}{1 + u_{\theta}\theta_{s}/RT}, \quad (32. \nu)
\]

and
\[
R = -\frac{\theta_{s}\log_{10}\theta_{s} + (\theta/2)\log_{10}(\theta/2) + (2u_{\theta} - u_{\theta}^{(m)} - u_{\theta}^{(s)})\{\log_{10}\theta_{s} - (1/2)\log_{10}(\theta/2)\}\theta_{s}/RT}{1 + u_{\theta}\theta_{s}/RT} \nonumber
- \frac{(1 + (u_{\theta}^{(2)} + u_{\theta}^{(s)})\theta_{s}/RT)\{\log_{10}\theta_{s} + \theta_{s}\log_{10}\theta_{s} - (1/2)\log_{10}(\theta/2)\}}{1 + u_{\theta}\theta_{s}/RT}. \quad (32. R)
\]

It is now shown that \( \gamma_{\theta} \) reproduces \( \partial \ln v_{\phi}/\partial \ln N_{\phi} \) with some approximation as in case A. We have from (22.a) referring to (4.a) and (11. a)
\[
\partial \ln v_{\phi}/\partial \ln N_{\phi} = -(u_{\phi}^{(s)} + u_{\phi}^{(m)})/RT \partial \ln \theta_{s}/\partial \ln N_{\phi} + \partial \ln \theta_{s}/\partial \ln N_{\phi} + \partial \ln p^{m}/\partial \ln N_{\phi} + \nu_{\phi}^{(1)}
\]
where
\[
u_{\phi}^{(s)} = \sum_{s} u_{s}^{(s)} \theta_{s} \partial \ln \theta_{s}/\partial \ln N_{\phi}.
\]

or developing \( \partial \ln p^{m}/\partial \ln N_{\phi} \) by (6.a) and \( \partial \ln \theta_{s}/\partial \ln N_{\phi} \) by (23.b),
\[
\partial \ln v_{\phi}/\partial \ln N_{\phi} = \nu_{\phi}^{(s)} - \left\{(1 + \theta_{s}/\theta_{s} + (u_{\phi}^{(s)} + u_{\phi}^{(m)})\theta_{s}/RT\right\} \partial \ln \theta_{s}/\partial \ln N_{\phi}.
\]

where
\[
u_{\phi}^{(s)} = \sum_{s} u_{s}^{(s)} \theta_{s} \partial \ln \theta_{s}/\partial \ln N_{\phi}.
\]

The factor \( \partial \ln \theta_{s}/\partial \ln N_{\phi} \) in (33.b) is derived by differentiating both sides of (28) with respect to \( \ln N_{\phi} \) referring to (7), (11) and (23.b), as
\[
(1/\theta_{s}) \partial \ln \theta_{s}/\partial \ln N_{\phi} = \frac{(q^{m}q^{m}/p^{m})\{\sum_{s} (u_{s}^{(1)} + u_{s}^{(m)})\theta_{s} \partial \ln \theta_{s}/\partial \ln N_{\phi})/RT - \nu_{\phi}^{(1)}\}}{2(q^{m}q^{m}/p^{m}) + q^{m}q^{m}/p^{m}} \nonumber
- \frac{(q^{m}q^{m}/p^{m})\{\sum_{s} (u_{s}^{(2)} + u_{s}^{(m)})\theta_{s} \partial \ln \theta_{s}/\partial \ln N_{\phi})/RT - \nu_{\phi}^{(1)}\}}{2(q^{m}q^{m}/p^{m}) + q^{m}q^{m}/p^{m}}
\]

hence, noting (30)
\[
(1/\theta_{s} + u_{\phi}^{(s)} \theta_{s}/RT)\partial \ln \theta_{s}/\partial \ln N_{\phi} = (\theta_{s}/\theta)\psi_{\phi}^{(1)} + (\theta_{s}/\theta)\psi_{\phi}^{(2)}, \quad (34. a)
\]

where
\[
u_{\phi}^{(s)} = \sum_{s} \left\{(1 + (u_{s}^{(1)} + u_{s}^{(m)}) + \theta_{s}(u_{s}^{(2)} + u_{s}^{(m)}))\right\} \theta_{s} \partial \ln \theta_{s}/\partial \ln N_{\phi}.
\]

The \( \partial \ln v_{\phi}/\partial \ln N_{\phi} \) is obtained by substituting \( \partial \ln \theta_{s}/\partial \ln N_{\phi} \) from (34.a) into (33.b), as
\[
\frac{\partial \ln \nu_s}{\partial \ln N_s} = \nu^{(1)} = \left\{ \frac{[\theta_1][\theta_2] \nu_v^{(1)} + (\theta_1/\theta_2) \nu_v^{(2)}}{1 + \theta + (u_{N_g}^{(m)} + u_{R_0}^{(m)} \theta_0 \theta_2) / RT} \right\}.
\]

Eq. (35) shows, when compared with (32. v), that \( \nu_v \) represents a directly measurable quantity \( \partial \ln \nu_s / \partial \ln N_s \), provided that \( u_{N_1}^{(m)}, u_{N_2}^{(m)} \) and \( u_{R_2} \) are respectively identical with \( u_{R_1}^{(m)}, u_{R_2}^{(m)} \) and \( u_{R} \); the latter proviso holds, as seen from the comparison of (33. a) with (26), (33. c) with (25. b) and (34. b) with (31. b), provided that \( u_{R_1}^{(m)} \) and \( u_{R_2}^{(m)} \) are respectively constant independent of \( \alpha \) and \( \alpha' \) as admitted in the present analysis.

The \( N^* \) is now empirically determinable by (32. v) and (32. N), just as in case A), provided \( R \) there be known. We see readily that the first term of (32. R) vanishes as \( \theta \) tends to 0 or 1. The second term vanishes as \( \theta \) tends to 0, since both \( \theta_1 \) and \( \theta_2 \) are positive and smaller than \( \theta \). The numerator of the third term is transformed according to (23. a) and (23. c) as

\[
- \frac{\theta_1}{\theta \theta_2} \log_{10} \theta_1 \theta_2 - \frac{1}{2} \log_{10} \frac{\theta_1}{\theta_2}.
\]

which is positive and approaches zero as \( \theta_1/(\theta_1 + \theta_2) \) tends zero or unity, but has its maximum value \((1/2) \log_{10} 2\) at \( \theta_1/(\theta_1 + \theta_2) = 1/2 \). The numerator of the third term depends thus only the value of \( \theta_1/(\theta_1 + \theta_2) \) irrespective of the value of \( \theta \).

As \( \theta \) tends to unity, the sum of the second and third terms reduces to

\[
1/2 \log_{10} (1/2) - 2 \theta_1 \log_{10} \theta_1 \theta_2, \text{ when } \theta_1 + \theta_2 \text{ approaches } 1/2 \text{ according to (23. a) and (23. c).}
\]

The sum \( S \) tends now to \(- (1/2) \log_{10} 2 - x \log_{10} x/2 - (1-x) \log_{10} (1-x)/2 \), where \( x = 2 \theta_1 \). Hence we have \( S = (1/2) \log_{10} 2 - x \log_{10} x - (1-x) \log_{10} (1-x) \), which is minimum \((1/2) \log_{10} 2\) as \( x \) equals 0 or 1 and maximum \((3/2) \log_{10} 2\) at \( x = 1/2 \).

We see from (32. R) that every term of \( R \) is positive in case of repulsive interaction, where \( u_{R} \) is positive, provided that \( u_{R}^{(m)} = u_{R} = u_{R}^{(m)} \) which holds according to (26), (31. b) and (25. b), if \( u_{R}^{(m)} \) are constant independent of \( \alpha \) and \( \alpha' \) and equal to \( u_{R}^{(m)} \).

The \( R \)-value for \( \theta_1 = \theta_2 \) is calculated by (32. R) for different values of \( \theta \) between 0 and 1 for \( u_{R}^{(m)} = u_{R} = u_{R}^{(m)} \) and \( u_{R}/RT = 10, 20 \) and 30 as shown in Fig. 2.
Fig. 2. Case B, $\theta_1 = \theta_2 = \theta/4$.

Results and Discussions

We have arrived at formally identical equations (18. N) and (32. N) in the respective cases of the degree of independence of intermediates.

The $\log_{10} N^x_0$ are now calculated as shown in Table 1 for 66 cases of
available kinetic observations, from which we have the mean value \( \log_{10} N_0^* = 15.48 \) with a standard deviation of 0.38. The formally identical equation (18. N) and (32. N) shows now that the main source of error of \( N_0^* \) is \( H_{1^*} \) and \( \nu_0 \), admitting that the observation of \( \nu_+ \) is accurate enough. Standard deviations of 2 Kcal for \( H_1^* \) and of 0.2 for \( \nu_0 \) cause now one that for \( \log_{10} N_0^* \) which amounts to \( \{(2/2.3 \times 0.6)^2 + (0.2 \times 7.1)^2 \times 2\}^{1/2} = 2.5 \) at 300°K, where 7.1 is the value of \( \log_{10} (Q_0/N_0) + T \partial \log_{10} Q_0/\partial T \) for hydrogen and the factor 2 cares for the two species in gas being involved on an average in the observations of Table 1. The above value of the standard deviation of a single observation of \( \log_{10} N_0^* \) is in accordance with that deduced from the actual fluctuation of the data in Table 1, i.e. \( 0.38 \times \sqrt{66} = 3.0 \). The inaccuracy of the mean value of \( \log_{10} N_0^* \) obtained above is thus attributable to those of the basic observations. It is desirable to improve the accuracy of the \( H_{1^*} \)- and \( \nu_0 \)-observations in order to explore the heterogeneous catalysis further.

Conclusions are derived from the above results allowing now for transmission coefficient \( \kappa \). Including the latter, the fundamental equation of \( \nu_+ \) is now

\[
\nu_+ = \kappa \frac{kT}{h} N^* q^* \theta_0 / p^1.
\]

What has so far been treated as \( \nu_+ \) according to (3) is \( \nu_+ / \kappa \) exactly; \( \kappa \) is hence consistently taken into account in evaluating \( \log N^* \) by replacing \( \nu_+ \) in (18) and (32) by \( \nu_+ / \kappa \) as

\[
\log_{10} N^* = \log_{10} N_0^* + \Delta,
\]

where

\[
\Delta = - \log_{10} \kappa - T \partial \log_{10} \kappa / \partial T + R.
\]

The first term \(- \log_{10} \kappa \) in (36. b) is zero or positive, since \( \kappa \) is equal to or less than unity. The temperature coefficient of \( \kappa \) has so far been scarcely explored, but it appears plausibly negative, if not zero, as suggested by the following result. The specific rate of step \( H + H \rightarrow H + H \) has been classically calculated by WALL et al.\(^{18}\) as a function of the kinetic energy of the system which was assumed to be linear throughout as in usual treatments. Their result shows that the specific rate rises rapidly from zero (for the minimum kinetic energy of the system required to complete the step) up to a maximum and then decreases steadily with rise of the energy. This suggests a negative temperature coefficient of \( \kappa \), since otherwise the specific rate should increase with increase of the energy. The \( \Delta \) is then positive, all its constituent terms including \( R \) being positive.
Table 1. Log₁₀ N₀* Derived from Observation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Temperature °K</th>
<th>Total Pressure mmHg</th>
<th>Rate Law</th>
<th>Activation Energy H°F Kcal mol⁻¹</th>
<th>log₁₀ N₀*</th>
<th>Observers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desorption of CO from Pt</td>
<td>2.8 x 10⁹ e⁻ⁿᴴᵗ/RT</td>
<td>600</td>
<td>0</td>
<td>(NCO)⁰</td>
<td>32</td>
<td>16.4</td>
<td>LANGMUIR (1)</td>
</tr>
<tr>
<td>Desorption of O₂ from W</td>
<td>1.3 x 10¹⁰ e⁻ⁿᴴᵗ/RT</td>
<td>2000</td>
<td>0</td>
<td>(NO)⁰</td>
<td>165</td>
<td>16.5</td>
<td>LANGMUIR (2)</td>
</tr>
<tr>
<td>Adsorption of H₂ on Fe (No. 931)</td>
<td>2.7 x 10¹¹ molec. sec⁻¹ cm⁻²</td>
<td>194</td>
<td>760</td>
<td>(NH₄)¹</td>
<td>10.4</td>
<td>17.6</td>
<td>EMMETT &amp; HARKNESS</td>
</tr>
<tr>
<td>Adsorption of H₂ on Cu</td>
<td>&gt; 1.1 x 10¹² molec. sec⁻¹ cm⁻²</td>
<td>673</td>
<td>0.138</td>
<td>(NH₃)¹</td>
<td>20.5</td>
<td>&gt; 14.8</td>
<td>Kwan</td>
</tr>
<tr>
<td>Adsorption of N₂ on W</td>
<td>1.5 x 10¹⁰ molec. sec⁻¹ cm⁻²</td>
<td>473</td>
<td>0.6</td>
<td>(NH₂)¹</td>
<td>10.0</td>
<td>15.2</td>
<td>Davis</td>
</tr>
<tr>
<td>Adsorption of N₂ on W</td>
<td>3.0 x 10¹⁰ molec. sec⁻¹ cm⁻²</td>
<td>673</td>
<td>1.0</td>
<td>(NH₃)¹</td>
<td>23.0</td>
<td>18.5</td>
<td>Davis</td>
</tr>
<tr>
<td>Adsorption of N₂ on W</td>
<td>4.9 x 10⁹ molec. sec⁻¹ cm⁻²</td>
<td>673</td>
<td>25</td>
<td>(NH₂)¹</td>
<td>25.0</td>
<td>17.0</td>
<td>Davis</td>
</tr>
<tr>
<td>Adsorption of N₂ on Fe</td>
<td>9.0 x 10¹⁹ molec. sec⁻¹ cm⁻²</td>
<td>673</td>
<td>760</td>
<td>(NH₃)¹</td>
<td>10.0</td>
<td>16.6</td>
<td>HORIUTI &amp; KITA</td>
</tr>
<tr>
<td>Adsorption of N₂ on Fe (Singly promoted)</td>
<td>1.2 x 10¹⁴ e⁻ⁿᴴᵗ/RT molec. sec⁻¹ cm⁻²</td>
<td>296.9</td>
<td>10</td>
<td>(NH₃)¹</td>
<td>10.7</td>
<td>14.7</td>
<td>SCHOLTEN et al.</td>
</tr>
<tr>
<td>Adsorption of N₂ on Fe (No. 931)</td>
<td>1.1 x 10¹⁰ molec. sec⁻¹ cm⁻²</td>
<td>603</td>
<td>760</td>
<td>(NH₃)¹</td>
<td>14.4</td>
<td>15.3</td>
<td>EMMETT &amp; BRUNAUER</td>
</tr>
<tr>
<td>Decompr. of NH₃ on W</td>
<td>4 x 10⁷ molec. sec⁻¹ cm⁻²</td>
<td>900</td>
<td>50 ~ 200</td>
<td>(N₂H₄)⁰</td>
<td>38.0</td>
<td>13.1</td>
<td>HINSHELWOOD &amp; BURK</td>
</tr>
<tr>
<td>Decompr. of NH₃ on Mo</td>
<td>12.5 x 10⁸ molec. sec⁻¹ cm⁻²</td>
<td>1288</td>
<td>—</td>
<td>(N₂H₄)⁰</td>
<td>53.2</td>
<td>14.7</td>
<td>Burk</td>
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<tr>
<td>Decompr. of NH₃ on W</td>
<td>2 x 10⁹ molec. sec⁻¹ cm⁻²</td>
<td>1316</td>
<td>16 ~ 265</td>
<td>(N₂H₄)⁰</td>
<td>41.5</td>
<td>12.3</td>
<td>KUNSMAH et al.</td>
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<td>Reaction</td>
<td>Rate Constants</td>
<td>Temperature</td>
<td>Logaft R &amp; Kemball</td>
<td>Logan &amp; Kemball</td>
<td>Logan &amp; Kemball</td>
<td>Logan &amp; Kemball</td>
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<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>NH₃ decomposing on Ni</td>
<td>5.0 × 10¹¹</td>
<td>673</td>
<td>12.07</td>
<td>(N⁺ NH₄)²⁺(NH₄)⁻¹.53</td>
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<tr>
<td>NH₃ decomposing on Co</td>
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<td>12.07</td>
<td>(N⁺ NH₄)²⁺(NH₄)⁻¹.42</td>
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<td>NH₃ decomposing on Co</td>
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<tr>
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<td>12.07</td>
<td>(N⁺ NH₄)²⁺(NH₄)⁻².45</td>
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<td>(N⁺ NH₄)²⁺(NH₄)⁻¹.43</td>
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<td>NH₃ decomposing on Ru</td>
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<td>12.07</td>
<td>(N⁺ NH₄)²⁺(NH₄)⁻².8</td>
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<td>NH₃ decomposing on Re</td>
<td>2.5 × 10⁹</td>
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<td>12.07</td>
<td>(N⁺ NH₄)²⁺(NH₄)⁻².6</td>
<td>49.0</td>
<td>11.9</td>
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<td>NH₃ decomposing on Fe</td>
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<td>673</td>
<td>12.07</td>
<td>(N⁺ NH₄)²⁺(NH₄)⁻².7</td>
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<tr>
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<td>2.6 × 10⁶ N⁺NH₄/NH₃</td>
<td>1423</td>
<td>0.25</td>
<td>(N⁺ NH₄)²⁺(NH₄)⁻¹</td>
<td>44.3</td>
<td>18.9</td>
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<tr>
<td>H₂ decomposing on Pt</td>
<td>7.7 × 10¹⁸</td>
<td>693</td>
<td>1.97</td>
<td>(N⁺ PH₃)²⁺</td>
<td>39.3</td>
<td>13.7</td>
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<tr>
<td>HI decomposing on Au</td>
<td>5.2 × 10²⁵</td>
<td>978</td>
<td>100~400</td>
<td>(N⁺ HI)²⁺</td>
<td>25.0</td>
<td>14.4</td>
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<td>HI decomposing on Pt</td>
<td>8.7 × 10¹⁴</td>
<td>836</td>
<td>300</td>
<td>(N⁺ HI)²⁺</td>
<td>13.7</td>
<td>17.1</td>
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<td>NO decomposing on Au</td>
<td>6.1 × 10¹³</td>
<td>1211</td>
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<td>(N⁺ N₂O)²⁺</td>
<td>29.0</td>
<td>18.2</td>
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<tr>
<td>CO₂ + 1/2 O₂ = CO₂</td>
<td>7.1 × 10¹⁴ N₂O/N₂O</td>
<td>572</td>
<td>0~60</td>
<td>(N⁺ NO)²⁺(N⁺ CO)⁻¹</td>
<td>33.3</td>
<td>14.7</td>
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<td>2.2 × 10⁻¹¹ (N⁺ NO₂)²⁺/N₂O</td>
<td>1483</td>
<td>100~500</td>
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Table 1 Continuation (2)

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<th>Reaction</th>
<th>Rate</th>
<th>Temperature °C</th>
<th>Total Pressure mmHg</th>
<th>Rate Law</th>
<th>Activation Energy $H^*$ Kcal mol⁻¹</th>
<th>log₁₀ $N_0^*$</th>
<th>Observers</th>
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</thead>
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<tr>
<td>$\text{ND}_2$, $\text{H}_2$ exchange on Ni</td>
<td>$5.2 \times 10^{16}$ molec. sec⁻¹ cm⁻²</td>
<td>273</td>
<td>805</td>
<td>$(N^{ND}_2)^x (N^{H}_2)^y$</td>
<td>12.0</td>
<td>14.0</td>
<td>Horiuti &amp; Suzuki</td>
</tr>
<tr>
<td>$\text{NH}_3$, $\text{D}_2$ exchange on Pt</td>
<td>$2.5 \times 10^{14}$ molec. sec⁻¹ cm⁻²</td>
<td>235</td>
<td>13.98</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>5.2</td>
<td>17.9</td>
<td>Kemball (1)</td>
</tr>
<tr>
<td>$\text{NH}_3$, $\text{D}_2$ exchange on Rh</td>
<td>$2.0 \times 10^{14}$ molec. sec⁻¹ cm⁻²</td>
<td>286</td>
<td>17.02</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>6.7</td>
<td>18.5</td>
<td>Kemball (1)</td>
</tr>
<tr>
<td>$\text{NH}_3$, $\text{D}_2$ exchange on Pd</td>
<td>$6.3 \times 10^{13}$ molec. sec⁻¹ cm⁻²</td>
<td>302</td>
<td>17.98</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>8.5</td>
<td>19.1</td>
<td>Kemball (1)</td>
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<td>$\text{NH}_3$, $\text{D}_2$ exchange on Ni</td>
<td>$1.3 \times 10^{13}$ molec. sec⁻¹ cm⁻²</td>
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<td>16.02</td>
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<td>$1.0 \times 10^{13}$ molec. sec⁻¹ cm⁻²</td>
<td>393</td>
<td>19.58</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>9.2</td>
<td>17.9</td>
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<td>$\text{NH}_3$, $\text{D}_2$ exchange on W (oxidized)</td>
<td>$5.0 \times 10^{12}$ molec. sec⁻¹ cm⁻²</td>
<td>500</td>
<td>23.60</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>9.6</td>
<td>17.2</td>
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<td>$\text{NH}_3$, $\text{D}_2$ exchange on Fe</td>
<td>$6.3 \times 10^{12}$ molec. sec⁻¹ cm⁻²</td>
<td>408</td>
<td>19.28</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>12.5</td>
<td>19.4</td>
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<tr>
<td>$\text{NH}_3$, $\text{D}_2$ exchange on Cu</td>
<td>$2.0 \times 10^{12}$ molec. sec⁻¹ cm⁻²</td>
<td>485</td>
<td>28.80</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>13.4</td>
<td>19.5</td>
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</tr>
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<td>$\text{NH}_3$, $\text{D}_2$ exchange on Ag</td>
<td>$3.2 \times 10^{12}$ molec. sec⁻¹ cm⁻²</td>
<td>544</td>
<td>25.80</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>14.1</td>
<td>19.6</td>
<td>Kemball (1)</td>
</tr>
<tr>
<td>$\text{NH}_3$, $\text{D}_2$ exchange on Ni (sintered)</td>
<td>$8.15 \times 10^{12}$ molec. sec⁻¹ cm⁻²</td>
<td>365</td>
<td>10.79</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>8.7</td>
<td>18.3</td>
<td>Kemball (2)</td>
</tr>
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<td>$\text{NH}_3$, $\text{D}_2$ exchange on Ni (sintered)</td>
<td>$2.98 \times 10^{13}$ molec. sec⁻¹ cm⁻²</td>
<td>365</td>
<td>17.38</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>8.7</td>
<td>18.9</td>
<td>Kemball (2)</td>
</tr>
<tr>
<td>$\text{NH}_3$, $\text{D}_2$ exchange on Ni (sintered)</td>
<td>$4.39 \times 10^{13}$ molec. sec⁻¹ cm⁻²</td>
<td>365</td>
<td>25.54</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
<td>8.7</td>
<td>18.2</td>
<td>Kemball (2)</td>
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<td>$\text{NH}_3$, $\text{D}_2$ exchange on Ni (sintered)</td>
<td>$1.61 \times 10^{13}$ molec. sec⁻¹ cm⁻²</td>
<td>365</td>
<td>10.79</td>
<td>$(N^{NH}_3)^x (N^{D}_2)^y$</td>
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Table 1 (Continuation 3)

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<th>Reaction</th>
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<th>Temp (K)</th>
<th>Rate</th>
<th>Order</th>
<th>Catalyst</th>
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<td>0.5</td>
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<td>CH₄, D₂ exchange on Ni</td>
<td>1.6 x 10¹¹</td>
<td>473</td>
<td>22.4</td>
<td>0.5</td>
<td>KEMBALL (3)</td>
</tr>
<tr>
<td>CH₄, D₂ exchange on Rh</td>
<td>1.3 x 10¹³</td>
<td>473</td>
<td>22.4</td>
<td>0.5</td>
<td>KEMBALL (3)</td>
</tr>
<tr>
<td>CH₄, D₂ exchange on W</td>
<td>1.6 x 10¹³</td>
<td>473</td>
<td>22.4</td>
<td>0.5</td>
<td>KEMBALL (3)</td>
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<tr>
<td>CH₄, D₂ exchange on Pt</td>
<td>5.0 x 10¹²</td>
<td>473</td>
<td>22.4</td>
<td>0.5</td>
<td>KEMBALL (3)</td>
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<tr>
<td>CH₄, D₂ exchange on Pd</td>
<td>4.0 x 10¹²</td>
<td>473</td>
<td>22.4</td>
<td>0.5</td>
<td>KEMBALL (3)</td>
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<tr>
<td>CH₄, D₂ exchange on Ni</td>
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<td>473</td>
<td>22.4</td>
<td>0.5</td>
<td>KEMBALL (3)</td>
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<tr>
<td>CH₄, D₂ exchange on Rh</td>
<td>1.3 x 10¹⁴</td>
<td>473</td>
<td>22.4</td>
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<td>KEMBALL (3)</td>
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<td>CH₄, D₂ exchange on W</td>
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<td>473</td>
<td>22.4</td>
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<td>CH₄, D₂ exchange on Pt</td>
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<td>22.4</td>
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<td>473</td>
<td>22.4</td>
<td>0.5</td>
<td>KEMBALL (3)</td>
</tr>
<tr>
<td>C₂H₄+H₂=C₄H₆ on Ni</td>
<td>3.2 x 10¹⁵</td>
<td>273</td>
<td>30.0</td>
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<td>MIYAHARA</td>
</tr>
<tr>
<td>C₂H₄+H₂=C₄H₆ on Ni (carbided)</td>
<td>4.2 x 10¹³</td>
<td>273</td>
<td>0.10</td>
<td>0.5</td>
<td>MASUDA</td>
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<td>C₂H₄+H₂=C₄H₆ on Ni (carbided)</td>
<td>2.0 x 10¹²</td>
<td>293</td>
<td>100</td>
<td>0.5</td>
<td>JENKINS &amp; RIDEAL</td>
</tr>
<tr>
<td>C₂H₄+H₂=C₄H₆ on Ni</td>
<td>3.4 x 10¹⁵</td>
<td>273</td>
<td>20</td>
<td>0.5</td>
<td>MIYAHARA</td>
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Number of Sites of Heterogeneous Reaction on Metallic Catalysts
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Temperature °K</th>
<th>Total Pressure mmHg</th>
<th>Rate Law</th>
<th>Activation Energy $H_1$ Kcal mol$^{-1}$</th>
<th>$\log_{10} N_e*</th>
<th>Observers</th>
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</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_4 + \text{D}_2 = \text{C}_2\text{H}_6$ on Ni</td>
<td>$1.2 \times 10^{15}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>273</td>
<td>20</td>
<td>—</td>
<td>6.0</td>
<td>14.3</td>
<td>MIYAHARA</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_4$ on sintered Ni film</td>
<td>$1.3 \times 10^{16}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>273</td>
<td>147</td>
<td>$(\text{NC}_2\text{H}_4)^\circ (\text{H}_2)^\circ$</td>
<td>9.1</td>
<td>18.9</td>
<td>CRAWFORD &amp; et al.</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_4$ on sintered Ni film</td>
<td>$8.5 \times 10^{19}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>273</td>
<td>147</td>
<td>$(\text{NC}_2\text{H}_4)^\circ (\text{H}_2)^\circ$</td>
<td>9.8</td>
<td>19.3</td>
<td>CRAWFORD &amp; et al.</td>
</tr>
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<td>$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_4$ on sintered Ni film</td>
<td>$6.2 \times 10^{19}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>273</td>
<td>147</td>
<td>$(\text{NC}_2\text{H}_4)^\circ (\text{H}_2)^\circ$</td>
<td>10.0</td>
<td>19.3</td>
<td>CRAWFORD &amp; et al.</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_4$ on sintered Ni film</td>
<td>$4.0 \times 10^{19}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>273</td>
<td>147</td>
<td>$(\text{NC}_2\text{H}_4)^\circ (\text{H}_2)^\circ$</td>
<td>9.2</td>
<td>18.6</td>
<td>CRAWFORD &amp; et al.</td>
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<tr>
<td>$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_4$ on sintered Ni film</td>
<td>$1.6 \times 10^{19}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>273</td>
<td>147</td>
<td>$(\text{NC}_2\text{H}_4)^\circ (\text{H}_2)^\circ$</td>
<td>10.3</td>
<td>18.9</td>
<td>CRAWFORD &amp; et al.</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_4$ on Ni-Al$_2$O$_3$</td>
<td>$1.0 \times 10^{15}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>273</td>
<td>75</td>
<td>$(\text{H}_2)^\circ (\text{NC}_2\text{H}_4)^\circ$</td>
<td>11.8</td>
<td>18.9</td>
<td>AMENOMIYA</td>
</tr>
<tr>
<td>$\text{D}_2$ exchange on Pd</td>
<td>$8.0 \times 10^{11}$ molec. sec$^{-1}$ cm$^{-2}$</td>
<td>300</td>
<td>22.51</td>
<td>$(\text{NC}_2\text{H}_4)^\circ (\text{D}_2)^{-1}$</td>
<td>13.0</td>
<td>13.7</td>
<td>ANDERSON &amp; KEMBALL (1)</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + \text{D}_2 = \text{C}_2\text{H}_6$ on Ni</td>
<td>$1.6 \times 10^{12}$ CH$_3$OD molec. sec$^{-1}$ cm$^{-2}$</td>
<td>300</td>
<td>17.74</td>
<td>$(\text{NC}_2\text{H}_4)^\circ (\text{D}_2)^4$</td>
<td>6.6</td>
<td>13.4</td>
<td>ANDERSON &amp; KEMBALL (2)</td>
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Number of Seats of Heterogeneous Reaction on Metallic Catalysts

References for Table

C. H. KUNSMAN, E. S. LAMER and W. E. DENNING, Phil. Mag., 10, 1015 (1930).
T. KWAN, This Journal, 1, 95 (1948-51).
K. MASUDA, This Journal, 12, 57 (1964).
K. MIYAHARA, This Journal, 11, 1 (1963); 13, 20 (1965).

It follows now from (36. a) that \( \log_{10} N_0^* \) in Table 1 is the lower limit to \( \log_{10} N^* \). On the other hand \( \log_{10} N^* \) could never exceed 15 by order of magnitude. It is hence concluded that the surface of metallic catalysts has \( 10^{15} \) seats per unit area by order of magnitude on the one hand and that the transmission coefficient of the rate-determining steps is of the order of magnitude of unity on the other hand.

The first conclusion is against the model of the active centre theory, which is closely connected with the model underlying the distribution function method of adsorption, which has previously been disproved as reviewed below.\(^{(10)}\)
According to this model of adsorption, the energy $E$ of adsorbate depends solely on the site it occupies irrespective of the arrangements of other adsorbates, so that the number of sites with energy of adsorbates lying between $E$ and $E + dE$ is given as $N(E)dE$, where $N(E)$ is the sole function of energy. It has been shown, however, that the observed isotherms led inevitably to $N(E)$ shifting markedly with the temperature of observation from $0^\circ$ to $300^\circ$C, which could hardly be the case unless the surface texture of the adsorbent metal varied "reversibly" with to-and-fro change of temperature.

In contrast with the above model, the crystal plane mode of adsorbent has lattice planes of sufficient extension to secure physically identical sites of adsorption, and the adsorbates on them interact with each other as required by quantum mechanics; the number of physically identical sites is of the same order of magnitude as the number of surface metal atoms, interposed by a relatively small number of sites furnished by lattice imperfections, on which adsorbates have extremely low energies.

It may be pointed out that the crystal plane model of adsorbent has been established by a number of theoretical and experimental results, whereas the present results verify the same model of metallic catalysts.

Acknowledgement: The authors wish to thank Dr. K. Müller for his valuable advices, and also Mr. K. YAMADA for his help in the calculation of the present work.

Glossary of Symbols

$G_g$, the gas molecule

$G_s$, $G_s = \sum G_g$

$N_g$, the concentration of gas molecule per unit volume

$N^*$, the number of states of the critical system of an elementary reaction on a metallic surface

$n_i$, the number of occurrence of step $i$

$p^i$, the Boltzmann factor of the chemical potential of the initial system

$p^\delta, p^\alpha$, the BOLTZMAN factor of chemical potential of $\delta$ or of the $\alpha$-th adsorbate $\delta_a$

$p^*$, the BOLTZMANN factor of the reversible work required to bring a system of the step, from its standard state on to a definite, preliminary seat to form a critical system
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$q^l$, $q^{l'}$, the BOLTZMAN factor of the reversible work required to bring up $\delta$ or $\delta'$ from its standard state to the adsorbed state of $\delta$ (a) or of $\alpha$-th adsorbate $\delta_a$ on a definite, preliminary evacuated site

$q^*_a$, the BOLTZMAN factor of the reversible work in the absence of interaction in the critical system

$V_\alpha$, the forward rate of reaction

$\delta_\alpha$, $\alpha$-th adsorbate

$\delta_m$, species created necessarily in company with initial or the final system from reactants or/and products

$\theta_0$, the probability of the seat being unoccupied

$\theta$, the probability of the seat being occupied by $\alpha$-th adsorbate

$\theta_a$, the probability of the seat being occupied

$u^*_\alpha \theta_a$, repulsive potential of the critical complex due to $\alpha$-th absorbate coverage $\theta_a$

$u^{*\alpha}_a \theta_a'$, repulsive potential of the $\delta_a$ due to $\alpha'$-th adsorbate of coverage $\theta_a'$

$u^*_\alpha$, $u^*_\alpha = \sum_{\alpha} u^*_\alpha \theta_a \frac{\partial \ln \theta_a}{\partial T} \frac{\theta}{\partial \ln \theta}$

$u_T$, $u_T = \sum_{\alpha, \alpha'} u^{\alpha\alpha'} \theta_a \frac{\partial \ln \theta_a}{\partial T} \frac{\theta}{\partial \ln \theta}$

$u^{(m)}_T$, $u^{(m)}_T = \sum_{\alpha} u^{(m)}_\alpha \theta_a \frac{\partial \ln \theta_a}{\partial \ln N_\alpha} \frac{\theta}{\partial \ln \theta}$

$u^{(m)}_m$, $u^{(m)}_m = \sum_{\alpha} u^{(m)}_\alpha \theta_a \frac{\partial \ln \theta_a}{\partial \ln N_\alpha} \frac{\theta}{\partial \ln \theta}$

$u^{*\alpha}_0$, $u^{*\alpha}_0 = \sum_{\alpha} u^{*\alpha}_\alpha \theta_a \frac{\partial \ln \theta_a}{\partial \ln N_\alpha} \frac{\theta}{\partial \ln \theta}$

$u^{*\alpha}_0$, $\psi_\alpha = \frac{\partial \ln v_\alpha}{\partial \ln \theta}$

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