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REMARKS ON THE TREATMENT OF HETEROGENEOUS CATALYSIS

By

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Summary

The mass action law successfully applied to homogeneous elementary reactions (or steps for short) was shown applicable to heterogeneous steps only in unexpectedly limited cases on account of the quantum-mechanically inferable interaction among adsorbed species. In case of an appreciable interaction, especially when it varies, *e.g.* with change of concentrations in question, the rate of step could only be reasonably deduced from the statistical mechanics of the whole mass of interacting species which is usually macroscopic and in thermal equilibrium.7,8) The rate equation thus deduced is called the generalized rate equation, which includes the rate equation of the absolute rate theory,1,2) applicable along with the mass action law, as its special case.

The generalized rate equation was illustrated and the critical state of a step was located for contrasting the generalized rate equation with the absolute rate theory.1,2) The rates of the Langmuir-Hinshelwood and Rideal mechanisms were derived as functions of concentrations of reactants in gas phase by the mass action law, on the one hand, and by the generalized rate equation ignoring the interaction among adsorbates, on the other hand. The functional forms obtained in the respective cases were identical as otherwise generally demonstrated and their comparison revealed the statistical mechanical contents of kinetic constants involved in the former derivation, directing toward the incorporation of interaction.

The incorporation of interaction was exemplified systematically as follows with the catalytic mechanism of hydrogen electrode reaction, where the recombination of hydrogen adatoms determined the rate.

First, the mass action law was applied as usual assuming that (1) the activity of hydrogen adatom, $\underset{*}{\mathrm{H}}$, was proportional to its covered fraction, $\theta(\underset{*}{\mathrm{H}})$, in analogy to the activity of dilute gas proportional to its concentration and that (2) no interaction existed among adsorbates inclusive of hydrogen atoms in the critical state. We then have $\tau \equiv (RT/F)\partial \ln i_{+,1}/\partial \eta = 2$ throughout, where $i_{+,1}$ is the forward unidirectional current density proportional to the rate of recombination and η the overvoltage of hydrogen electrode reaction. This conclusion conflicted with observation of τ around 0.5 which has long been taken the leading ground against the catalytic mechanism.

Second, the assumption (1) was left off on the ground that the activity of $\underset{*}{\mathrm{H}}$ is proportional to $\theta(\underset{*}{\mathrm{H}})/(1-\theta(\underset{*}{\mathrm{H}}))$ rather than to $\theta(\underset{*}{\mathrm{H}})$ in case of exclusive occupation of a site by

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one $\underset{*}{\mathrm{H}}$ as seen from the Langumuir adsorption isotherm derived from the same premise. Staying yet with assumption (2), τ was found 2 at low η but decreased steadily with increase of η down to 0; τ stayed however around 0.5 only for a few tens mV in contrast with for several hundreds mV as observed.

Third, the exchange repulsions among adsorbates were taken into account approximating the repulsive potential as proportional to $\theta(\underset{*}{\mathrm{H}})$ (proportional approximation), thus leaving off both the above assumptions; τ was thus found around 0.5 for about 200 mV.[3)]

Fourth, the proportional approximation was examined as regards the situation that the repulsive potential increased with approach of adsorbates so rapidly that nearest neighbours appeared with far less probability than $\theta(\underset{*}{\mathrm{H}})$ assumed in the proportional approximation. Conclusion was that a sufficient accuracy was securable by treating the repulsions of the first nearest neighbours discretely but those of further neighbours by the proportional approximation.[15)]

Fifth, the repulsive potential was determined as 1.5 times the exchange repulsion[6)] by comparing adsorption isotherms derived by the above procedure with observed ones, in conformity with Toya's theoretical conclusion[4)] that the exchange repulsion was reinforced by the energy elevation of $\underset{*}{\mathrm{H}}$ due to shortage of conduction electrons caused by crowd of $\underset{*}{\mathrm{H}}$'s.[4)] τ calculated on this basis remained a proper fraction for *ca.* 500 mV range of η in accordance with experiment.

$\tau=2$ was deduced from the catalytic mechanism at extremely low η by every approximation mentioned above, whereas $\tau=0$ at extremely high η was inferred by every but the first approximation as seen above. That $\tau=2$ or 0 at the respective extremity was experimentally verified.[16-19)]

Introduction

It is fairly usual to deal with kinetics in terms of the mass action law or of the appropriate rate constant of each constituent elementary reaction of the overall reaction in question; elementary reactions are called steps for short in what follows. The mass action law has thus hitherto been successfully applied to homogeneous steps and extended, perhaps habitually, to heterogeneous steps, which constitute heterogeneous catalyses. The set of particles involved in a step is called its system, the state of the system prior or posterior to the occurrence of step the initial or final state of the system and the system in the respective state the initial or final system respectively.

The mass action law applies and hence the appropriate rate constant is actually constant at constant temperature in case, where the system of the step in question is statistical mechanically independent. The system of heterogeneous step is understood here to include sites on catalyst's surface required by the step and its dynamical state is defined by coordinates and momenta of its constituent particles. A system is termed statistical mechanically independent, if the probability of finding the system in any dynamical state is independent of species of varying population. The interaction of the system, *e.g.* with adsorbate of varying population on the catalyst's surface may vary the probability of dynamical states of the system in question statistically in the neighbourhood of catalyst's surface, disqualifying the system from being statistical mechanically independent, and in consequence the specific rate or the rate constant may vary with the varying population of the adsorbates. The mass action law thus does not apply in case where the appropriate system is not statistical mechanically independent.

A step of statistical mechanically independent system may be dealt with, as if the system existed alone in vacuum or in a definite medium at a constant temperature as done by EYRING *et al.*,[1] and EVANS and POLANYI;[2] a system thus getting into step is likened to a molecule of dilute gas colliding with wall or to a molecule of dilute solute in a definite solvent colliding with semipermeable septum.

It is important to review the statistical mechanical independence of heterogeneous steps which constitute heterogeneous catalyses. A radical effect of the repulsive interaction upon the kinetics of recombination of hydrogen adatoms has been inferred by OKAMOTO, HORIUTI and HIROTA[3] on the basis of assumption that hydrogen adatoms exerted quantum-mechanical exchange repulsion upon each other as well as upon those going to recombine, and of the inference from the observed adsorption heat that there subsisted the population of hydrogen adatoms of the order of magnitude of monolayer. TOYA[4] has developed the quantum-mechanical theory of adatoms on metals from first principles[4] concluding that the repulsion among adatoms was greater than the exchange repulsion on account of the shortage of condution electrons required for forming covalent bonds of $\underset{*}{\mathrm{H}}$'s, when crowded; the shortage gives rise to the decrease of bond energy, which is accounted as the repulsive potential[4] between $\underset{*}{\mathrm{H}}$'s.

The repulsion, if strong, would not, however, affect the probability of dynamical states of systems, were the population of repulsive adsorbates low enough. The population of adsorbates is given often in terms of covered fraction. Consider adsorbates which cover one tenth of $10^{15}\,\mathrm{cm}^{-2}$ physically identical adsorption sites on the surface of catalyst, as one would say of moderate coverage. The thickness of the surfase phase ought to be of the order of magnitude of $10^{-8}\,\mathrm{cm}$ in consistence with the latter two-dimensional concentration of adsorption sites. The three-dimensional concentration of adsorbates in the surface phase is $10^{15}\times 0.1/10^{-8}=10^{22}\,\mathrm{cm}^{-3}$, which is comparable with the concentration of liquid molecules. Adsorbates in the surface phase are thus crowded enough in this measure of population. SWEETT and

RIDEAL[5)] have observed the hydrogen adsorption on Ni at 10^{-3} mmHg partial pressure of hydrogen and room temperature; the adsorption was verified to have attained the practical completion of monoatomic layer of $\underset{*}{\mathrm{H}}$'s or the full occupation of 10^{15} sites cm^{-2} by analyses of the experimental results.[5,6)]

It is in consequence an inevitable conclusion from thess results that systems of heterogeneous steps are subject to pronounced effect of adsorbates, whose populations vary in general along with the activity of the system in question. The rate of step would then only be reasonably derived by applying the statistical mechanics to the whole body of interacting species. The latter body, in which the step of interest is going on, is usually macroscopic and in temperature equilibrium; the body is called the assembly and the rate equation thus derived[7,8)] is called the generalized rate equation.

The present paper is concerned with the illustration of generalized rate equation and with the demonstration of radical difference in kinetics of heterogeneous catalysis derived by the mass action law of constituent steps from that derived by the generalized rate equation with due allowance for the interaction.

1. The Generalized Rate Equation

The generalized rate equations of the forward and backward rates, $v_+(s)$ and $v_-(s)$, of step s are[7,8)]

$$v_+(s) = \kappa(s)(kT/h)p(\neq_s)/p(\mathrm{I}_s)\,, \qquad v_-(s) = \kappa(s)(kT/h)p(\neq_s)/p(\mathrm{F}_s)\,, \tag{1.f), (1.b}$$

where $\kappa(s)$ is the transmission coefficient equal to or less than unity, kT/h of usual meaning and $p(\neq_s)$, $p(\mathrm{I}_s)$ or $p(\mathrm{F}_s)$ is the factor, by which the partition function, $\mathfrak{Q}\mathfrak{A}$, of assembly $\mathfrak{A}$ is multiplied, as the critical, initial or the final system of the step, respectively denoted by $\neq_s$, I_s or F_s, is added to assembly $\mathfrak{A}$. Since $-kT\ln\mathfrak{Q}\mathfrak{A}$ is identified with the Helmholtz energy of $\mathfrak{A}$, $-RT\ln p(\delta)$ gives the chemical potential, $\mu(\delta)$, of species δ representing $\neq_s$, I_s and F_s, *i.e.*

$$\mu(\delta) = -RT\ln p(\delta)\,. \tag{2}$$

The critical system, $\neq_s$, is defined as follows. Consider the configuration space of the whole assembly of a definite composition except for a single system of the step in question, which alone is left free to assume the initial, final and intermediate states. There exist thus two regions in the configuration space relevant to the initial or final state respectively, which do not overlap each other, inasmuch as the configuration of the initial system differs from that of the final system. The region is called the initial or the fianal region according to its relevance to the inintial or final state respectively. A hypersurface is now extended through the configuration space to partition the initial region from the final one. The hypersurface is now varied to minimize the transit rate through it of the representative points of the canonical ensemble of the assembly. The hypersurface thus adjusted is called the critical surface and the system is called the critical system as the appropriate representative point of the assembly is just on the critical surface.

In the particular case, where the system of the step is statistical mechanically independent, the critical surface partitions the partial configuration space of the system into regions relevant to the initial and final states respectively independent of any other coordinates than those of the system and gives the minimum transit rate of representative points of the canonical ensemble of the system among those hypersurfaces which partition the partial configuration space similarly. The hypersurface of the minimum transit rate in the partial configuration space is the intersection of the general critical surface defined above, with the partial configuration space of the system, which will be called the critical surface of the system. The critical system is in this case the system with its representative point situated on the critical surface of the system. In the particular case of a step in dilute gas, $p(\neq_s)$ in Eqs. (1) is reduced to the partition function of the single critical system in the gas phase. The $p(\mathrm{I}_s)$ or $p(\mathrm{F}_s)$ of I_s or F_s consisting of molecules, $\mathrm{I}_{s,i}$ or $\mathrm{F}_{s,f}$, as $\mathrm{I}_s=\sum_i \mathrm{I}_{s,i}$ or $\mathrm{F}_s=\sum_f \mathrm{F}_{s,f}$, is given as $p(\mathrm{I}_s)=\prod_i p(\mathrm{I}_{s,i})$ or $p(\mathrm{F}_s)=\prod_f p(\mathrm{F}_{s,f})$, where $p(\mathrm{I}_{s,i})$ or $p(\mathrm{F}_{s,i})$ is the partition function of a single $\mathrm{I}_{s,i}$ or $\mathrm{F}_{s,f}$ in the gas phase divided by the total number of $\mathrm{I}_{s,i}$ or $\mathrm{F}_{s,f}$ respectively.*) The generalized rate equation is thus reduced to the form identical with the absolute rate equation of EYRING *et al.*,1) although the contents of the partition function of the critical system is not necessarily identical with that of the activated complex of the latter group of authors.1)

In the further particular case, where the critical surface of system passes through the saddle point of its potential energy and the potential energy is maximum along the normal to the critical surface at the saddle point, the partition function of the critical system becomes identical with that of the activated complex, hence the rate equation as well with that of the absolute reaction rate theory.1)

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*) *cf.* Eq. (9) and its derivation, noting that the partition function of a single molecule in dilute gas is proportional to volume of the dilute gas.

2. Location of the Critical System

The location of critical system is illustrated by the simple example of combination of hydrogen and chlorine atoms to form a hydrogen chloride molecule assuming the relevant system statistical mechanically independent in order to show how the critical system contrasts with the activated complex.[1)]

The potential energy of the system, $U(r)$, is given by the Morse function,

$$U(r)=D\{1-e^{-a(r-r_e)}\}^2,$$

as a sole function of the distance r between the constituent atoms, where $D=106.4$ kcal/mole, $a=1.869$ Å^{-1} and $r_e=1.275$ Å are constants spectroscopically determined. The kinetic energy, K. E., is given, in terms of polar coordinates, r, θ and φ for the relative position of hydrogen and chlorine in line with the above expression of potential energy, as

$$\text{K. E.}=\frac{M}{2}(\dot{X}^2+\dot{Y}^2+\dot{Z}^2)+\frac{\mu}{2}(\dot{r}^2+r^2\dot{\theta}^2+r^2\sin^2\theta\dot{\varphi}^2),$$

where $M=m_{\mathrm{H}}+m_{\mathrm{Cl}}$, m_{H} or m_{Cl} is the mass of H or Cl atom respectively, $X=(m_{\mathrm{H}}x_{\mathrm{H}}+m_{\mathrm{Cl}}x_{\mathrm{Cl}})/(m_{\mathrm{H}}+m_{\mathrm{Cl}})$, $Y=(m_{\mathrm{H}}y_{\mathrm{H}}+m_{\mathrm{Cl}}y_{\mathrm{Cl}})/(m_{\mathrm{H}}+m_{\mathrm{Cl}})$ and $Z=(m_{\mathrm{H}}z_{\mathrm{H}}+m_{\mathrm{Cl}}z_{\mathrm{Cl}})/(m_{\mathrm{H}}+m_{\mathrm{Cl}})$ are rectangular coordinates of the centroid derived from those, x_{H}, y_{H} and z_{H}, of H and x_{Cl}, y_{Cl} and z_{Cl} of Cl, and $\mu=m_{\mathrm{H}}m_{\mathrm{Cl}}/(m_{\mathrm{H}}+m_{\mathrm{Cl}})$ is the reduced mass. The K. E. is expressed in terms of momenta, $p_X=\partial(\text{K. E.})/\partial\dot{X}=M\dot{X}$, $p_Y=M\dot{Y}$, $p_Z=M\dot{Z}$, $p_r=\mu\dot{r}$, $p_\theta=\mu r^2\dot{\theta}$ and $p_\varphi=\mu r^2\sin^2\theta\dot{\varphi}$, as

$$\text{K.E.}=\frac{p_X^2+p_Y^2+p_Z^2}{2M}+\frac{p_r^2}{2\mu}+\frac{p_\theta^2}{2\mu r^2}+\frac{p_\varphi^2}{2\mu r^2\sin^2\theta}.$$

Statistical mechanics states now that the number, dN, of representative points of the canonical ensemble of the system in the elementary volume of its phase space, $d\tau\equiv d_X d_Y d_Z dr d\theta d\varphi dp_X dp_Y dp_Z dp_r dp_\theta dp_\varphi$, is given as $dN=C\exp[-(\text{K.E.}+U(r))/kT]d\tau$, where C is the proportional constant. The initial and the final state of the system is described in terms of the polar coordinates as $r\gg r_e$ and $r\simeq r_e$ respectively. The hypersurface, which divides the initial region from the final one, is expressed as $r=r(\theta,\varphi)$, where r remains greater than r_e but about of the same order of magnitude as r_e. The transit rate of representative points of the canonical ensemble of the system through the hypersurface is derived first rewriting the above expression of dN as

$$dN=dG\exp\left(-\frac{p_r^2/2\mu+p_\theta^2/2\mu r^2+p_\varphi^2/2\mu r^2\sin^2\theta+U(r)}{kT}\right)dr d\theta d\varphi dp_r dp_\theta dp_\varphi,$$

where

$$dG = C\exp\left(-\frac{p_X^2+p_Y^2+p_Z^2}{2MkT}\right)dXdYdZdp_Xdp_Ydp_Z\,.$$

The integration of dN over X, Y, Z, p_X, p_Y, p_Z, p_θ and p_φ is

$$CV(2\pi MkT)^{3/2}2\pi\mu kTr^2\sin\theta\exp\left(-\frac{p_r^2/2\mu+U(r)}{kT}\right)drd\theta d\varphi dp_r\,,$$

where V is the volume available for the centroid, *i.e.* the integral of $dXdYdZ$, and the integrations over p_X, p_Y, p_Z, p_θ and p_φ are carried out respectively from $-\infty$ to $+\infty$.

The quotient of the above expression over $r^2dr\sin\theta\,d\theta\,d\varphi$, *i.e.* $CV(2\pi MkT)^{3/2}2\pi\mu kT\exp\left(-\frac{p_r^2/2\mu+U(r)}{kT}\right)dp_r$ is the density of representative points at r, θ and φ in the partial configuration space extended by r, θ and φ with p_r lying between p_r and p_r+dp_r. Let α be the angle between the normal to the surface element over solid angle $d\Omega=\sin\theta\,d\theta\,d\varphi$ and the radius vector to the center of the surface element. Its area is $r^2\sin\theta\,d\theta\,d\varphi/\cos\alpha$ and the transit rate of representative points through it from greater r is given by the product of the velocity of representative points normal to the surface element, *i.e.* $-p_r\cos\alpha/\mu$, the area of the surface element and the density of representative points given above, as

$$-CV(2\pi MkT)^{3/2}2\pi\mu kTr^2\sin\theta d\theta d\varphi(p_r/\mu)\exp\left(-\frac{p_r^2/2\mu+U(r)}{kT}\right)dp_r\,.$$

Integrating the above expression over p_r from $-\infty$ to 0, we have

$$Ad\Omega r^2\exp(-U(r)/kT)\,,\quad\text{where}\quad A=CVkT(2\pi MkT)^{3/2}2\pi\mu kT\,.$$

The coefficient of solid angle $d\Omega\equiv\sin\theta\,d\theta\,d\varphi$, *i.e.* $Ar^2\exp(-U(r)/kT)$ depends only on r and attains the minimum at $r=r_m=5.273$ Å, where $\partial U(r)/\partial r=2kT$ and $U(r)=106.3$ kcal/mole.

The transit rate of representative points through a hypersurface element extending a definite solid angle thus attains the minimum at a common value, r_m, of r irrespective of the orienation of solid angle. It follows that the equation of the critical surface is $r=r_m$, which is a hypersurface in the six dimensional configuration space. The total transit rate of representative points through the critical surface is obtained by integrating the above expression, $Ad\Omega r_m^2\exp(-U(r_m)/kT)$, over Ω as $CVkT(2\pi MkT)^{3/2}8\pi^2\mu r_m^2kT\exp(-U(r_m)/kT)$. The V may be identified with the volume of the container in case, where the pair of atoms at $r=r_m$ is practically regarded as a point in the container.

It may be mentioned that the critical state is located on the basis of the principles presented in **1.** in the utter absence of any saddle point of potential energy.

3. The Effect of "Third Body" on Rates

It is well-known that "third body" accelerates steps, *e.g.* recombination of hydrogen atoms in gas by removing the excess energy over that in the final state. This is the case where the momentum of system in question is exchanged with surroundings through encounter with the "third body". It is now shown that the momentum exchange between the mode of motion orthogonal to the critical surface and other modes of motion can as well decrease the rate, if too frequent, by decreasing $\kappa(s)$.

The $\kappa(s)$ is unity provided that

(i) the momentum exchange is so frequent that the system is stabilized practically with certainty as the representative point enters the final region.

(ii) the momentum exchange is not so frequent that the representative point retains its momentum normal to the critical surface in its neighbourhood until the system is settled down in the final region.

The so-called "third body" serves for realizing point (i). If the momentum exchange is too frequent, representative points transit the critical surface back and forth many times before being settled in the final state. Too frequent a momentum exchange thus reduces $\kappa(s)$, *i.e.* the ratio of the rate of step to the transit rate of representative points through the critical surface; in the case of statistical mechanically independent system of step, the frequency of transit through the critical surface remains unchanged irrespective of "third body", so that the rate of step should decrease. Too frequent a momentum exchange thus reduces the rate along with $\kappa(s)$, giving rise to a "negative catalysis".

The case where $\kappa(s)=1$ or $\kappa(s)\ll 1$ is likened to the flow of dilute gas through an orifice on a thin wall, *i.e.* the molecular effusion, or through a long pore, *i.e.* diffusion respectively as compared with the mean free path of gas molecules. The diffusion is the Poiseuille or Knudsen flow according as the mean free path is sufficiently smaller or greater than the pore diameter respectively.

The decrease of rate due to too frequent a momentum exchange may be the case on application of hydrostatic pressure on an assembly of condensed phase, which is, however, associated with the increase of the work required for increase of partial molar volume of the system against the applied hydrostatic pressure*) from the initial to the critical state; the latter work is

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*) If the partial molar volume decreases from the initial to the critical state, the hydrostatic pressure accelerates the step from this cause.

added to the critical increment of Helmholtz energy of the assembly, *i.e.* $-kT\ln(p(\neq_s)/p(I_s))$, to decrease the rate of step. These two effects of hydrostatic pressure are hardly separable, insofar as we are dealing with steady occurrences of constituent processes of the step, *i.e.* the activation, transit through the critical surface and deactivation.

4. Heterogeneous Step of Statistical-Mechanically Independent System

Heterogeneous step is defined as a step with its critical system situated in a surface phase. The application of mass action law is illustrated by the Langmuir-Hinshelwood and Rideal mechanisms in comparison with that of the generalized rate equation.

4. 1. The Langmuir-Hinshelwood mechanism is based on the tacit assumption of the statistical mechanical independence of the system of step

$$\underset{*}{A}+\underset{*}{B}\longrightarrow C_g+D_g+2*\,, \tag{3}$$

which converts adsorbed species, $\underset{*}{A}$ and $\underset{*}{B}$, *e.g.* $\underset{*}{H_2}$ and $\underset{*}{CO_2}$, into free molecules, C_g and D_g, *e.g.* H_2O_g and CO_g, and a pair of unoccupied adsorption sites, $2*$, which are included in the system. The rate of the step, v_+(LH), is thus expressed as $k_{LH}\theta(\underset{*}{A})\theta(\underset{*}{B})$, where k_{LH} is the rate constant and $\theta(\underset{*}{A})$ or $\theta(\underset{*}{B})$ is the fraction of adsorption sites occupied by A or B respectively. The $\theta(\underset{*}{A})$ and $\theta(\underset{*}{B})$ are developed in terms of concentrations of molecules A_g and B_g in dilute gas, $[A_g]$ and $[B_g]$, assuming partial equilibria of steps,

$$A_g+*\longrightarrow\underset{*}{A}\quad\text{and}\quad B_g+*\longrightarrow\underset{*}{B}\,,$$

as

$$\theta(\underset{*}{A})=K_A[A_g]\theta(0)\,,\qquad\theta(\underset{*}{B})=K_B[B_g]\theta(0)\,,$$

where K_A and K_B are respective equilibrium constants and $\theta(0)$ is the fraction of unoccupied sites. Admitting that $\underset{*}{A}$ and $\underset{*}{B}$ are only adsorbates and that the critical system is rare enough to be ignored as regards the occupation of sites, we have

$$\theta(\underset{*}{A})+\theta(\underset{*}{B})+\theta(0)=1\,, \tag{4.θ}$$

or eliminating $\theta(0)$ from the above three equations

$$\theta(\underset{*}{A})=K_A[A_g]/(1+K_A[A_g]+K_B[B_g])\,, \tag{4. A}$$

$$\theta(\underset{*}{B})=K_B[B_g]/(1+K_A[A_g]+K_B[B_g])\,. \tag{4. B}$$

The rate, $v_+(\mathrm{LH})=k_{\mathrm{LH}}\theta(\underset{*}{\mathrm{A}})\theta(\underset{*}{\mathrm{B}})$, of step (3) is now given as

$$v_+(\mathrm{LH}) = k_{\mathrm{LH}}K_{\mathrm{A}}K_{\mathrm{B}}[\mathrm{A}_g][\mathrm{B}_g]/(1+K_{\mathrm{A}}[\mathrm{A}_g]+K_{\mathrm{R}}[\mathrm{B}_g])^2. \qquad (5.\mathrm{LH})$$

If alternatively the system consisting of A, B and $*$ is statistical mechanically independent, the rate, $v_+(\mathrm{R})=k_{\mathrm{R}}[\mathrm{A}_g][\mathrm{B}_g]\theta(0)$, is given as

$$v_+(\mathrm{R}) = k_{\mathrm{R}}[\mathrm{A}_g][\mathrm{B}_g]/(1+K_{\mathrm{A}}[\mathrm{A}_g]+K_{\mathrm{B}}[\mathrm{B}_g]), \qquad (5.\mathrm{R})$$

whether one of A and B is adsorbed and the other from the dilute gas hits the adsorbed one to form the critical system or the critical system is formed from $\underset{*}{\mathrm{A}}$ and $\underset{*}{\mathrm{B}}$ to liberate one of $*$, insofar as the critical system occupies just one $*$ and the adsorbed species of the initial system is in equilibria with the species in the dilute gas. What is required for the kinetics of Eq. (5.LH) or (5.R) to be realized is that the statistical mechanically independent system consists of A, B and $2*$ or A, B and $*$ respectively and the respective initial system is in equilibrium with species in the dilute gas.

4. 2. Several auxiliary theorems[7)] are introduced for application of the generalized rate equation.

The $p(\delta)$ defined in **1.** is expressed with reference to a small space, σ, which accommodates species δ, as[7)]

$$p(\delta) = q_\sigma(\delta)\theta(0)/\theta(\delta), \qquad (6.\mathrm{a})$$

where $\theta(0)$ or $\theta(\delta)$ is the probability that σ is vacated or occupied by δ respectively and $q_\sigma(\delta)$ is the factor by which the partition function, $\mathfrak{Q}\mathfrak{A}_{\sigma(0)}$, of $\mathfrak{A}_{\sigma(0)}$ is multiplied by addition of one δ to $\mathfrak{A}_{\sigma(0)}$, which has the σ unoccupied with certainty, to make assembly $\mathfrak{A}^{\delta}_{\sigma(\delta)}$, which contains one more δ than $\mathfrak{A}_{\sigma(0)}$ and has the σ occupied by one δ with certainty.

Eq. (6.a) is verified as follows. The $p(\delta)$ is given by definition as

$$p(\delta) = \mathfrak{Q}\mathfrak{A}^{\delta}/\mathfrak{Q}\mathfrak{A}, \qquad (6.\mathrm{b})$$

where $\mathfrak{Q}\mathfrak{A}^{\delta}$ and $\mathfrak{Q}\mathfrak{A}$ are partition functions of assemblies $\mathfrak{A}^{\delta}$ and $\mathfrak{A}$ respectively, $\mathfrak{A}^{\delta}$ being derived from $\mathfrak{A}$ by addition of δ to $\mathfrak{A}$ from outside the assembly.

The $q_\sigma(\delta)$ is similarly by definition

$$q_\sigma(\delta) = \mathfrak{Q}\mathfrak{A}^{\delta}_{\sigma(\delta)}/\mathfrak{Q}\mathfrak{A}_{\sigma(0)}, \qquad (6.\mathrm{c})$$

where $\mathfrak{Q}\mathfrak{A}^{\delta}_{\sigma(\delta)}$ and $\mathfrak{Q}\mathfrak{A}_{\sigma(0)}$ are partition functions of $\mathfrak{A}^{\delta}_{\sigma(\delta)}$ and $\mathfrak{A}_{\sigma(0)}$ respectively. We have from the above two equations

$$p(\delta) = q_\sigma(\delta)(\mathfrak{Q}\mathfrak{A}_{\sigma(0)}/\mathfrak{Q}\mathfrak{A})/(\mathfrak{Q}\mathfrak{A}^{\delta}_{\sigma(\delta)}/\mathfrak{Q}\mathfrak{A}^{\delta}),$$

where $\mathfrak{Q}\mathfrak{A}_{\sigma(0)}/\mathfrak{Q}\mathfrak{A}$ and $\mathfrak{Q}\mathfrak{A}^{\delta}_{\sigma(\delta)}/\mathfrak{Q}\mathfrak{A}^{\delta}$ are identified with probabilities $\theta(0)$ and $\theta(\delta)$ respectively, as

$$\theta(0) = \mathfrak{Q}\mathfrak{A}_{\sigma(0)}/\mathfrak{Q}\mathfrak{A}, \quad \theta(\delta) = \mathfrak{Q}\mathfrak{A}^{\delta}_{\sigma(\delta)}/\mathfrak{Q}\mathfrak{A}^{\delta} \qquad (6.\mathrm{d})\ (6.\mathrm{e})$$

by the property of partition function, which verifies Eq. (6.a).

The $p(\delta)$ of a set of species, $\delta \equiv \sum_i \delta^i$, which are statistical mechanically independent of each other, is given as

$$p(\delta) = \prod_i p(\delta^i) \tag{7}$$

in conformity with the thermodynamic relation, $\mu(\delta) = \sum_i \mu(\delta^i)$, and Eq. (2), where superscript i numbers the constituent parts, δ^i *etc.*, of δ.

If a set of species, δ_a, is in equilibrium with another, δ_b, we have in accordance with thermodynamics by Eq. (2)[7]

$$p(\delta_a) = p(\delta_b), \qquad \delta_a \rightleftharpoons \delta_b. \tag{8}$$

If δ is a molecule, δ_g, in a dilute gas, Eq. (6.a) is reduced to the form[7]*)

$$p(\delta_g) = Q(\delta_g)/[\delta_g], \tag{9}$$

where $Q(\delta_g)$ is the partition function of δ_g per unit volume and $[\delta_g]$ its concentration.

The $p(\neq_s)$ in Eqs. (1) is developed in accordance with Eq. (6.a) as

$$p(\neq_s) = N_s^{\neq} \theta_s^{\neq}(0) q(\neq_s), \tag{10}$$

where $N_s^{\neq}$ is the total number of sites $\sigma_s^{\neq}$'s of critical system $\neq_s$, $\theta_s^{\neq}(0)$ the probability that a $\sigma_s^{\neq}$ is vacated and $q(\neq_s)$ the special case of $q_\sigma(\delta)$, where $\delta \equiv \neq_s$ and $\sigma \equiv \sigma_s^{\neq}$; Eq. (10) follows from Eq. (6.a) by observing that the probability of finding the unique $\neq_s$**) in a particular $\sigma_s^{\neq}$ is the reciprocal of its total number, $N_s^{\neq}$.

4.3. The general rate equation is applied to the same mechanisms for comparison ignoring interactions among adsorbates; the conclusion is the same as that of the mass action law but elucidates the statistical mechanical contents of kinetic constants involved in case of the mass action law.

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*) Molecules in a dilute gas are respectively statistical mechanically independent, so that $\mathfrak{Q}\mathfrak{A}_{\sigma(\delta)}^{\cdot}$ in Eq. (6.c) is factored as $\mathfrak{Q}\mathfrak{A}_{\sigma(0)} Q(\delta_g)|\sigma|$, where $|\sigma|$ is the volume of σ, so that $Q(\delta_g)|\sigma|$ is the partition function of a single δ_g in σ. We have thus $q_\sigma(\delta_g) = Q(\delta_g)|\sigma|$ by Eq. (6.c), hence according to Eq. (6.a), $p(\delta_g) = Q(\delta_g)\theta(0)/(\theta(\delta_g)/|\sigma|)$. The $\theta(\delta_g)$ is the probability of finding one of δ_g's inside σ, while all other δ_g's are outside the σ. Let V be the total volume of the dilute gas and N the total number of gas molecules, δ_g's. The probability of finding a particular δ_g inside or outside σ is $|\sigma|/V$ or $1-|\sigma|/V$ respectively, hence the probability of finding a particular δ_g inside σ and all others outside σ is $(|\sigma|/V)(1-|\sigma|/V)^{N-1}$. The $\theta(\delta_g)$ is obtained by summing up the latter probability over all δ_g's as $\theta(\delta_g) = N|\sigma|(V-|\sigma|)^{N-1}/V^N$, inasmuch as $\theta(\delta_g)$ is relevant to the state with any one of δ_g's inside σ. For infinitesimal $|\sigma|$, $\theta(0)$ is reduced to unity, while $\theta(\delta_g) = N|\sigma|(V-|\sigma|)^{N-1}/V^N$ to $|\sigma|N/V$ or noting that $N/V = [\delta_g]$, to $|\sigma|[\delta_g]$, hence Eq. (9).

**) Eqs. (1) are arrived at in terms of $p(\neq_s)$ defined for the unique critical system in the assembly [Ref. (7)], which is, however, nothing of claiming that there existed physically a unique critical system in the assembly at a time.

The $p(\mathrm{I}_s)$ in Eqs. (1) is given for the Langmuir-Hinshelwood mechanism by Eq. (7) as

$$p(\mathrm{I}_s)=p(\underset{*}{\mathrm{A}})p(\underset{*}{\mathrm{B}}) \tag{11. I$_s$}$$

and $p(\underset{*}{\mathrm{A}})$ and $p(\underset{*}{\mathrm{B}})$ by Eqs. (8) and (9) as

$$p(\underset{*}{\mathrm{A}})=p(\mathrm{A}_g)=Q(\mathrm{A}_g)/[\mathrm{A}_g]\,, \quad p(\underset{*}{\mathrm{B}})=p(\mathrm{B}_g)=Q(\mathrm{B}_g)/[\mathrm{B}_g] \tag*{(11. A), (11. B)}$$

on account of the equilibria between $\underset{*}{\mathrm{A}}$ and A_g, and between $\underset{*}{\mathrm{B}}$ and B_g, hence

$$p(\mathrm{I}_s)=Q(\mathrm{A}_g)Q(\mathrm{B}_g)/[\mathrm{A}_g][\mathrm{B}_g]\,. \tag{12. I$_s$}$$

The $\theta_s^{\neq}(0)$ in Eq. (10) is developed as follows. Eq. (6.a) is written particularly for $\underset{*}{\mathrm{A}}$ and $\underset{*}{\mathrm{B}}$ as

$$p(\underset{*}{\mathrm{A}})=q_\sigma(\underset{*}{\mathrm{A}})\theta(0)/\theta(\underset{*}{\mathrm{A}})\,, \quad p(\underset{*}{\mathrm{B}})=q_\sigma(\underset{*}{\mathrm{B}})\theta(0)/\theta(\underset{*}{\mathrm{B}})\,, \tag*{(12. A), (12. B)}$$

hence by Eqs. (11. A) and (11. B)

$$Q(\mathrm{A}_g)/[\mathrm{A}_g]=q_\sigma(\underset{*}{\mathrm{A}})\theta(0)/\theta(\underset{*}{\mathrm{A}})\,, \quad Q(\mathrm{B}_g)/[\mathrm{B}_g]=q_\sigma(\mathrm{B})\theta(0)/\theta(\underset{*}{\mathrm{B}})\,. \tag*{(13. A), (13. B)}$$

The $\theta(0)$ is obtained by eliminating $\theta(\underset{*}{\mathrm{A}})$ and $\theta(\underset{*}{\mathrm{B}})$ from Eqs. (4.θ), (13.A) and (13.B) as

$$\theta(0)=\left\{1+(q_\sigma(\underset{*}{\mathrm{A}})/Q(\mathrm{A}_g))[\mathrm{A}_g]+(q_\sigma(\underset{*}{\mathrm{B}})/Q(\mathrm{B}_g))[\mathrm{B}_g]\right\}^{-1}. \tag{14}$$

The $\sigma_s^{\neq}$ is identified with one or two σ's according respectively to Rideal or Langmuir-Hinshelwood mechanism. In case of the Rideal mechanism, where $\sigma_s^{\neq}$ is σ itself, the rate is given by Eqs. (1.f), (10) and (12.I$_s$) identifying $\theta_s^{\neq}(0)$ with $\theta(0)$ of Eq. (14). In case of the Langmuir-Hinshelwood mechanism, $\theta_s^{\neq}(0)$ of $\sigma_s^{\neq}$ consisting of two σ's depends on the interaction among adsorbates. There should, however, exist no interaction, insofar as the system is statistically independent as premised, since if existed at all, the system would be subject to interaction with $\underset{*}{\mathrm{A}}$ and $\underset{*}{\mathrm{B}}$, which varies with $\theta(\underset{*}{\mathrm{A}})$ and $\theta(\underset{*}{\mathrm{B}})$ along with change of $[\mathrm{A}_g]$ and $[\mathrm{B}_g]$ according to Eqs. (4), (13.A) and (13.B) to contradict the premised statistical independence of system. The two constituent sites of $\sigma^{\neq}$ are in consequence quite independently vacated, hence $\theta_s^{\neq}(0)=\theta(0)^2$. In a summary, the rate per unit area, $v_{+,1}(s)$, is given as

$$\begin{aligned} v_{+,1}(s)=\kappa(s)(kT/h)N_{s,1}^{\neq}q_s^{\neq}[\mathrm{A}_g][\mathrm{B}_g]/Q(\mathrm{A}_g)Q(\mathrm{B}_g)\Big\{1+(q_\sigma(\underset{*}{\mathrm{A}})/Q(\mathrm{A}_g))[\mathrm{A}_g]+\\ +(q_\sigma(\underset{*}{\mathrm{B}})/Q(\mathrm{B}_g))[\mathrm{B}_g]\Big\}^n, \end{aligned} \tag{15}$$

where n is 1 or 2 for the Rideal and Langmuir-Hinshelwood mechanism respectively and $N^{\neq}_{s,1}$ is $N^{\neq}_{s}$ per unit area. Eq. (15) is identical with Eqs. (5) in functional form but illustrates the statistical mechanical contents of kinetic constants, k_{LH}, k_R, K_A and K_B in Eqs. (5), providing for allowance for the interaction.

The interaction among adsorbates is by no means ignorable as reviewed in the introduction. Kinetics is now allowed for the interaction according to the generalized rate equation with a simple example of the catalytic mechanism of hydrogen electrode reaction in the following sections.

5. Catalytic Mechanism of Hydrogen Electrode Reaction

The rate of hydrogen electrode reaction is determined, according to the catalytic mechanism, by the recombination of hydrogen adatoms, $\underset{*}{\mathrm{H}}$'s, which are in equilibrium with conduction electrons, e^-'s, in the hydrogen electrode and hydrogen ions, H^+'s, in the coexistent solution. Reviews are given first of the usual crude application of mass action law and then of stepwise advanced approximations, thus illustrating the effect of allowance for the interaction among adsorbates inclusive of the critical system in terms of the generalized rate equation.

A basic relation of hydrogen electrode reaction is introduced as follows to proceed with the program. The overvoltage, η, of hydrogen electrode reaction is the excess of potential of a reversible hydrogen electrode in the same environment as that of the hydrogen electrode in question over the potential of the latter, *i.e.*

$$F\eta = \mu(e^-) - \mu(e^-)_{\mathrm{rev}}\,,$$

where F is Faraday and $\mu(e^-)$ or $\mu(e^-)_{\mathrm{rev}}$ is the chemical potential of conduction electron in the hydrogen electrode in question or the reversible one respectively. The $\mu(\underset{*}{\mathrm{H}})$ is given, on account of the equilibrium between $\underset{*}{\mathrm{H}}$ and $H^+ + e^-$, as

$$\mu(\underset{*}{\mathrm{H}}) = \mu(\mathrm{H}^+) + \mu(e^-)\,.$$

The $\mu(e^-)_{\mathrm{rev}}$ is the value of $\mu(e^-)$ in the equilibrium of hydrogen electrode reaction, $2H^+ + 2e^- = H_2$, hence

$$2\mu(\mathrm{H}^+) + 2\mu(e^-)_{\mathrm{rev}} = \mu(\mathrm{H}_2)\,.$$

We have eliminating $\mu(e^-)$ and $\mu(\mathrm{H}^+) + \mu(e^-)_{\mathrm{rev}}$ from the above three equations

$$\mu(\underset{*}{\mathrm{H}}) = F\eta + 1/2 \cdot \mu(\mathrm{H}_2)\,. \tag{16}$$

5. 1. It is usual to apply the mass action law to the recombination, so that the forward unidirectional current density, $i_{+,1}$, of the hydrogen electrode reaction is expressed as proportional to the square of covered fraction of sites by $\underset{*}{\mathrm{H}}$, $\theta(\underset{*}{\mathrm{H}})$, as

$$i_{+,1} \propto \theta(\underset{*}{\mathrm{H}})^2 . \qquad (17.\,i)$$

It is another usual practice to combine $\theta(\underset{*}{\mathrm{H}})$ with overvoltage η of the hydrogen electrode reaction, assuming that

$$\mu(\underset{*}{\mathrm{H}}) = RT \ln \theta(\underset{*}{\mathrm{H}}) + \mathrm{const.} \qquad (17.\,\mu)$$

by analogy to the chemical potential of δ_g in a dilute gas given as $\mu(\delta_g) = RT \ln [\delta_g] + \mathrm{const.}$ The eliminant of $\mu(\underset{*}{\mathrm{H}})$ and $\theta(\underset{*}{\mathrm{H}})$ from Eqs. (16), (17.i) and (17.μ) is

$$\ln i_{+,1} = (2F/RT)\eta + \mathrm{const.},$$

hence

$$\tau \equiv (RT/F)\partial \ln i_{+,1}/\partial\eta = 2 \qquad (18)$$

instead of $\tau = 0.5$ as observed with many hydrogen electrodes.

This has been taken as the leading ground against the catalytic mechanism, paying little attention to the interaction, which renders the mass action law inapplicable as mentioned in the introduction.*)[9]

5. 2. The treatment in **5. 1.** is inexact because of Eq. (17.μ) which does not hold good except for extremely small $\theta(\underset{*}{\mathrm{H}})$, and of Eq. (17.$i$) based on the mass action law which does not apply on account of the interaction. We will first leave off the crude analogy of Eq. (17.μ) but remain for the moment with the neglect of the interaction underlying Eq. (17.i) to see how the conclusion is changed by this step of approximation and by subsequent ones based on the generalized rate equation.

The exact equation of $\mu(\underset{*}{\mathrm{H}})$ is derived from Eqs. (2) and (6.a) reading $\underset{*}{\mathrm{H}}$ for δ and admitting that its adsorption site, σ, is either occupied by $\underset{*}{\mathrm{H}}$ or vacated exclusively, *i. e.*

$$\theta(0) + \theta(\underset{*}{\mathrm{H}}) = 1 \qquad (19)$$

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*) HABER and RUSS suggested [Ref. (9)] that the discrepancy between Eq. (18) and observation would be due to the inapplicability of mass action law in accordance with the discussion in the introduction.

as

$$\mu(\underset{*}{\mathrm{H}}) = -RT \ln p(\underset{*}{\mathrm{H}}) = RT \ln\left[\theta(\underset{*}{\mathrm{H}})/q_\sigma(\underset{*}{\mathrm{H}})(1-\theta(\underset{*}{\mathrm{H}}))\right]. \qquad (20)$$

The $q_\sigma(\underset{*}{\mathrm{H}})$ is constant independent of $\theta(\underset{*}{\mathrm{H}})$ by the premised absence of interaction. We have in consequence from Eqs. (16) and (20)

$$F\eta = RT \ln\left\{\theta(\underset{*}{\mathrm{H}})/(1-\theta(\underset{*}{\mathrm{H}}))\right\} + \mathrm{const.} \qquad (21)$$

The forward unidirectional current density, $i_{+,1}$, of the catalytic mechanism is proportional to $v_{+,1}(s)$ of recombination as given by Eq. (1. f). The $p(\mathrm{I}_s)$ in Eq. (1. f) is developed by Eqs. (7) and (20) as

$$p(\mathrm{I}_s) \equiv p(2\underset{*}{\mathrm{H}}) = p(\underset{*}{\mathrm{H}})^2 = q_\sigma(\underset{*}{\mathrm{H}})^2\left(1-\theta(\underset{*}{\mathrm{H}})\right)^2/\theta(\underset{*}{\mathrm{H}})^2. \qquad (22)$$

The $p(\neq_s)$ in Eq. (1. f) is proportional to $\theta_s^{\neq}(0)$ according to Eq. (10) in the premised absence of interaction, where $q(\neq_s)$ is constant. The $\theta_s^{\neq}(0)$ depends now on the number of constituent sites of $\sigma_s^{\neq}$ as in the case of the Langmuir-Hinshelwood and Rideal mechanism dealt with in **4.3.** The $\sigma_s^{\neq}$ consisting of a single σ renders the activation energy forbiddingly high as seen from a rough survey, while more than two constituent σ's of $\sigma_s^{\neq}$ are improbable on account of the expanse of the electron cloud of hydrogen atom. Admitting that $\sigma_s^{\neq}$ consists of two σ's on this ground, $\theta_s^{\neq}(0)$ is equated to $\theta(0)^2$ or $(1-\theta(\underset{*}{\mathrm{H}}))^2$ by Eq. (19) on account of the premised absence of interaction as in the case of **4.3.**, so that

$$p(\neq_s) \propto \theta(0)^2 = \left(1-\theta(\underset{*}{\mathrm{H}})\right)^2.$$

Substituting $p(\mathrm{I}_s)$ and $p(\neq_s)$ from the above equations into Eq. (1. f) we arrive at Eq. (17. *i*) to establish it as exact in the absence of interaction. Eq. (17. *i*) is the special case of Eq. (15), where $n=2$, $\mathrm{A}_g \equiv \mathrm{B}_g$ and $\underset{*}{\mathrm{A}} \equiv \underset{*}{\mathrm{B}} \equiv \underset{*}{\mathrm{H}}$, as seen from the eliminant of $\theta(0)$, $[\mathrm{A}_g]/Q(\mathrm{A}_g)$ and $[\mathrm{B}_g]/Q(\mathrm{B}_g)$ from Eqs. (13. A), (13. B), (14) and (15) in the special case, *i. e.*

$$i_{+,1} = 2\varepsilon\kappa(s)(kT/h)N_{s,1}^{\neq}\left(q_s^{\neq}/q_\sigma(\underset{*}{\mathrm{H}})^2\right)\theta(\underset{*}{\mathrm{H}})^2, \qquad (23)$$

noting that $i_{+,1}$ equals two elementary charges, 2ε, times $v_{+,1}(s)$.

Eq. (17. *i*) gives, on the other hand, on substitution of $\theta(\underset{*}{\mathrm{H}})$ from Eq. (21),

$$\ln i_{+,1} = -2\ln\left[(1/C)\exp(-F\eta/RT)+1\right] + \mathrm{const.},$$

hence

$$\tau \equiv (RT/F)\partial \ln i_{+,1}/\partial\eta = 2\Big/\left[1+C\exp(F\eta/RT)\right],$$

where $-RT\ln C$ is the const. in Eq. (21). The above equation states that τ decreases with increase of η from 2 to 0 and stays from 0.6 to 0.4 for only 14 mV increase of η[10)], whereas experimentally τ stays in the same interval for several hundreds mV increase of η.

5.3. We review in this and subsequent sections the results of allowance for the interaction in stepwise advanced approximations.

OKAMOTO, HORIUTI and HIROTA[3)] approximated the reversible work,*) $-RT\ln q_\sigma(\underset{*}{\mathrm{H}})$, as

$$-RT\ln q_\sigma(\underset{*}{\mathrm{H}}) = -RT\ln q_\sigma(\underset{*}{\mathrm{H}})_0 + u\theta(\underset{*}{\mathrm{H}})\,, \tag{24}$$

where $q_\sigma(\underset{*}{\mathrm{H}})_0$ is the particular value of $q_\sigma(\underset{*}{\mathrm{H}})$ in the absence of interaction and u the proportional constant of the excess of the reversible work due to repulsion or the sum total of the repulsive potentials of an $\underset{*}{\mathrm{H}}$ due to $\underset{*}{\mathrm{H}}$'s fully occupying its surroundings. Substituting $q_\sigma(\underset{*}{\mathrm{H}})$ from the above equation into Eq. (20) and referring to Eq. (16) we have in place of Eq. (21)

$$F\eta = RT\ln\left[\theta(\underset{*}{\mathrm{H}})\Big/\Big(1-\theta(\underset{*}{\mathrm{H}})\Big)\right] + u\theta(\underset{*}{\mathrm{H}}) + \text{const.} \tag{25}$$

Eq. (25) states that $u\theta(\underset{*}{\mathrm{H}})$ retards the increase of $\theta(\underset{*}{\mathrm{H}})$ with increase of η the more, the greater u is and the remoter $\theta(\underset{*}{\mathrm{H}})$ is from 0 and 1. The $q(\neq_s)_0$ in Eq. (10) is similary allowed for the interaction as

$$-RT\ln q(\neq_s) = -RT\ln q(\neq_s)_0 + u_s^{\neq}\theta(\underset{*}{\mathrm{H}})\,, \tag{26}$$

where $q(\neq_s)_0$ is the value of $q(\neq_s)$ in the absence of interaction and $u_s^{\neq}$ is the proportional constant or the sum total of the repulsive potentials of $\neq_s$ due to $\underset{*}{\mathrm{H}}$'s fully occupying the surroundings. The approximation of Eqs. (25) and (26) is called the proportional approximation in what follows. OKAMOTO, HORIUTI and HIROTA[3)] arrived at the equation,**) substituting $q_\sigma(\underset{*}{\mathrm{H}})$ and $q_s(\neq_s)$

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*) This is the work required, as seen with reference to Eq. (6.c), to derive $\mathfrak{A}^{\delta}_{\sigma(\delta)}$ by addition of δ to $\mathfrak{A}_{\sigma(0)}$ keeping the whole assembly in statistical mechanical equilibrium, per mole addition of δ; this follows from the property of partition function that $-kT\ln\mathfrak{A}^{\delta}_{\sigma(\delta)}$ and $-kT\ln\mathfrak{A}_{\sigma(0)}$ behave as the Helmholtz energies of assemblies $\mathfrak{A}^{\delta}_{\sigma(\delta)}$ and $\mathfrak{A}_{\sigma(0)}$ respectively.

) This equation is not exact because of equation $\theta_s^{\neq}(0)=\theta(0)^2$ derived for the absence of interaction in **4.3., which underlies Eq. (23), since in the presence of interaction a site is vacated not independent of the occupied or vacated state of its adjacent site. This point has later been dealt with consistently [Ref. 11], which approximated the theoretical τ-value to the observed one.

from Eqs. (24) and (26) respectively into Eq. (23),

$$i_{+,1} = 2\varepsilon\kappa(s)(kT/h)N^{\neq}_{s,1}\left(q(\neq_s)_0/q_\sigma(\underset{*}{\mathrm{H}})^2_0\right)\theta(\underset{*}{\mathrm{H}})\exp\left[-(u^{\neq}_s-2u)\theta(\underset{*}{\mathrm{H}})/RT\right], \tag{27}$$

where $N^{\neq}_{s,1}$ is the number of sites of critical system per unit area. Eq. (27) gives $i_{+,1}$ as a function of η with reference to Eq. (25).

The current density has thus been worked out by evaluating constants, $N^{\neq}_{s,1}$, $q(\neq_s)_0$, $q_\sigma(\underset{*}{\mathrm{H}})_0$, $u^{\neq}_s$ and u, assuming the latter two to consist purely of exchange repulsion.[3] The $i_{+,1}$ practically equals its excess over the backward unidirectional current density, $i_{-,1}$, *i.e.* the directly observable current density, $i_{+,1}-i_{-,1}$, for η above 50 mV as follows from Eq. (33), where most of observations are conducted. The range of η, where τ remained a proper fraction was thus calculated to extend to 200 mV,[3] although not as much as observed.

It has been shown on the other hand by analysis of adsorption isotherms[6] that the repulsive potential among hydrogen adatoms was 1.5 times as large as the potential of exchange repulsion estimated by OKAMOTO *et al.*[3] in accordance with the TOYA's conclusion[4] referred to in the introduction. The observed range of η, where τ remained a proper fraction, has been theoretically accounted for by advancing the approximation on the base of the multiplied value of repulsive potential.[12]

5.4. The proportional approximation illustrated in **5.3.** would be justified, provided that $\underset{*}{\mathrm{H}}$ appeared with probability $\theta(\underset{*}{\mathrm{H}})$ even on sites nearest to that occupied by $\underset{*}{\mathrm{H}}$ or $\neq_s$; this cannot be the case in the presence of repulsion, which extraordinarily reduces the probability of appearance of $\underset{*}{\mathrm{H}}$'s on the nearest sites. In order to advance the approximation it needs take account of repulsions of direct neighbours individually instead by the proportional approximation. This is exemplified in the calculations of adsorption isotherm in this section and of current density in the next section with an extremely idealized model on the basis of the statistical mechanical theory introduced in the foregoing sections.

Suppose that each of hydrogen adatoms is situated on one of sites furnished by the atom row in the $[\bar{1}10]$ direction on (110) lattice plane of fcc crystal and that interactions are present only between direct neighbours on the row. Let $\sum$ be a set of three consecutive sites on the row each of which accommodates a critical system or $\underset{*}{\mathrm{H}}$. The partition function, $\mathfrak{Q}\mathfrak{A}_{\sigma_0(0)}$, of assembly $\mathfrak{A}_{\sigma_0(0)}$ in a particular state with the middle site, σ_0, of $\sum$ vacated is developed in terms of the partitition function, $\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}$, of assembly $\mathfrak{A}_{\Sigma(0)}$ with

Σ vacated altogether, as

$$\mathfrak{Q}\mathfrak{A}_{\sigma_0(0)} = \mathfrak{Q}\mathfrak{A}_{\Sigma(0)}\left[1+\left(q_\sigma(\underset{*}{\mathrm{H}})_0\zeta/p(\underset{*}{\mathrm{H}})\right)\right]^2,$$

where $1/p(\underset{*}{\mathrm{H}})$ is the factor by which $\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}$ is multiplied as an $\underset{*}{\mathrm{H}}$ is extracted from somewhere in $\mathfrak{A}_{\Sigma(0)}$ outside Σ. As the extracted $\underset{*}{\mathrm{H}}$ is brought onto one of the two end sites of Σ, the partition function is further multiplied by the factor, $q_\sigma(\underset{*}{\mathrm{H}})_0\zeta$, where ζ is the Boltzmann factor of the extra work due to interaction with $\underset{*}{\mathrm{H}}$ outside Σ. The partition function, $\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}$, is thus multiplied by factor $q_\sigma(\underset{*}{\mathrm{H}})_0\zeta/p(\underset{*}{\mathrm{H}})$, as an $\underset{*}{\mathrm{H}}$ is transferred from somewhere outside Σ onto one of the end sites of Σ. If one of end sites of Σ is left free to be either vacated or occupied by $\underset{*}{\mathrm{H}}$, the appropriate partition function is $1+q_\sigma(\underset{*}{\mathrm{H}})_0\zeta/p(\underset{*}{\mathrm{H}})$ times $\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}$. By leaving the other end site of Σ as well free similarly, the partition function is further multiplied by the same factor, $1+q_\sigma(\underset{*}{\mathrm{H}})_0\zeta/p(\underset{*}{\mathrm{H}})$, on account of the premised absence of interaction between $\underset{*}{\mathrm{H}}$'s on both end sites of Σ, hence the above equation. The above equation is written in terms of

$$\varphi = q_\sigma(\underset{*}{\mathrm{H}})_0/p(\underset{*}{\mathrm{H}}) \tag{28. a}$$

as

$$\mathfrak{Q}\mathfrak{A}_{\sigma_0(0)} = \mathfrak{Q}\mathfrak{A}_{\Sigma(0)}(1+\varphi\zeta)^2. \tag{28. b}$$

The partition function of the assembly with the middle site of Σ occupied by $\underset{*}{\mathrm{H}}$ is developed as

$$\mathfrak{Q}\mathfrak{A}_{\sigma_0(\underset{*}{\mathrm{H}})} = \mathfrak{Q}\mathfrak{A}_{\Sigma(0)}\varphi(1+\varphi\zeta\xi)^2, \tag{28. c}$$

where $\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}\varphi$ is the partition function of the assembly with the middle site alone occupied with certainty by one $\underset{*}{\mathrm{H}}$ brought from somewhere in the assembly outside Σ. By bringing another $\underset{*}{\mathrm{H}}$ in addition from somewhere in the assembly outside Σ to one of the end sites, the partition function is multiplied by the factor, $\varphi\zeta\xi$, where ξ is the Boltzmann factor of the additional work due to the premised interaction with $\underset{*}{\mathrm{H}}$ on the middle site. By leaving one of the end sites free to be occupied by $\underset{*}{\mathrm{H}}$ or vacated, the appropriate partition function is $\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}\varphi$ times $1+\varphi\zeta\xi$ and by leaving the other end site as well similarly free, the partition function gains another same factor $1+\varphi\zeta\xi$ on account of the absence of interaction between $\underset{*}{\mathrm{H}}$'s on the two end sites of $\sum$, hence Eq. (28. c).

$\mathfrak{Q}\mathfrak{A}_{\sigma_0(0)}$ and $\mathfrak{Q}\mathfrak{A}_{\sigma_0(\underset{*}{\mathrm{H}})}$ complete the partition function, $\mathfrak{Q}\mathfrak{A}$, of the microscopically unconstrained assembly, $\mathfrak{A}$, *i.e.*

$$\mathfrak{Q}\mathfrak{A}=\mathfrak{Q}\mathfrak{A}_{\sigma_0(0)}+\mathfrak{Q}\mathfrak{A}_{\sigma_0(\underset{*}{\mathrm{H}})}\,,$$

hence according to Eqs. (28. b) and (28. c)

$$\mathfrak{Q}\mathfrak{A}=\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}\Big[(1+\varphi\zeta)^2+\varphi(1+\varphi\zeta\xi)^2\Big]\,. \tag{29. a}$$

The ratio, $\mathfrak{Q}\mathfrak{A}_{\sigma_0(0)}/\mathfrak{Q}\mathfrak{A}_{\sigma_0(\underset{*}{\mathrm{H}})}$, equals $(1-\theta(\underset{*}{\mathrm{H}}))/\theta(\underset{*}{\mathrm{H}})$, on the other hand, as follows from the property of partition function, hence according to Eqs. (28. b) and (28. c)

$$\theta(\underset{*}{\mathrm{H}})\Big/\Big(1-\theta(\underset{*}{\mathrm{H}})\Big)=\varphi\Big[(1+\varphi\zeta\xi)/(1+\varphi\zeta)\Big]^2\,. \tag{29. b}$$

The partition function, $\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$, of assembly $\mathfrak{A}_{\sigma_1(0)}$ of the same composition as $\mathfrak{A}$, but with one of the end sites, σ_1, of $\sum$ being vacated with certainty is given as

$$\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}=\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}(1+\varphi+\varphi\zeta+\varphi^2\zeta\xi)\,. \tag{30. a}$$

The terms in the parentheses correspond in order respectively to the state of $\sum$ unoccupied altogether, the middle site only occupied, the end site, other than σ_1, only occupied and both sites of $\sum$ other than σ_1 are occupied respectively. The ζ in the above equations is evaluated in accordance with BETHE and PEIERLS[13] equating $\mathfrak{Q}\mathfrak{A}_{\sigma_0(0)}$ with $\mathfrak{Q}\mathfrak{A}_{\sigma_1(0)}$ according to Eqs. (28. b) and (30. a) on the ground of physical identity of σ_0 and σ_1, as

$$\varphi\zeta^2+(1-\varphi\xi)\zeta-1=0\,. \tag{30. b}$$

The $p(\underset{*}{\mathrm{H}})$ of $\underset{*}{\mathrm{H}}$ in equilibrium with $\mathrm{H}_{2,g}$, as denoted by $p(\underset{*}{\mathrm{H}})_e$, is according to Eqs. (7), (8) and (9)

$$p(\underset{*}{\mathrm{H}})_e=\Big\{Q(\mathrm{H}_{2,g})/[\mathrm{H}_{2,g}]\Big\}^{1/2}\,. \tag{31}$$

The φ is evaluated by statistical mechanical calculation of $q_\sigma(\underset{*}{\mathrm{H}})_0$ and $Q(\mathrm{H}_{2,g})$ according to Eq. (28. a) substituting $p(\underset{*}{\mathrm{H}})$ by $p(\underset{*}{\mathrm{H}})_e$ for the isotherm. Calculating further ξ from the repulsive potential between two adjacent $\underset{*}{\mathrm{H}}$'s, $\theta(\underset{*}{\mathrm{H}})$ is determined by Eqs. (28. a), (29. b), (30. b) and (31) as a function of $[\mathrm{H}_{2,g}]$.

5. 5. The current density is now worked out according to the generalized rate equation on the basis of the same $\sum$ used in **5. 4.** for the sake of simplified presentation of the procedure; it is assumed that $\neq_s$ occupies only one of σ's for $\underset{*}{\mathrm{H}}$'s and that $\neq_s$ as well as $\underset{*}{\mathrm{H}}$ repulses only direct neighbours on the atom row in the $[\bar{1}10]$ direction. The $q(\neq_s)\theta_s^{\neq}(0)$ in Eq. (10) is given in terms of partition functions by Eqs. (6.c) and (6.d) as

$$q_s^{\neq}\theta_s^{\neq}(0)=\mathfrak{Q}\mathfrak{A}^{\neq s}_{\sigma_0(\neq_s)}/\mathfrak{Q}\mathfrak{A}\,, \tag{32.a}$$

where $\mathfrak{Q}\mathfrak{A}^{\neq s}_{\sigma_0(\neq_s)}$ is the partition function of the assembly, $\mathfrak{A}^{\neq s}_{\sigma_0(\neq_s)}$, derived from $\mathfrak{A}_{\sigma_0(0)}$ by adding a $\neq_s$ from outside the assembly to the vacated σ_0. $\mathfrak{Q}\mathfrak{A}^{\neq s}_{\sigma_0(\neq_s)}$ is developed according to the premise as

$$\mathfrak{Q}\mathfrak{A}^{\neq s}_{\sigma_0(\neq_s)}=\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}\,q(\neq_s)_0(1+\varphi\zeta\xi^{\neq})^2\,, \tag{32.b}$$

where $\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}\,q(\neq_s)_0$ is the partition function of the assembly derived from $\mathfrak{A}_{\Sigma(0)}$ by adding $\neq_s$ from outside the assembly onto σ_0 with two end sites being vacated with certainty. Transferring further an $\underset{*}{\mathrm{H}}$ from somewhere in the assembly outside Σ onto one of the two end sites of Σ, the partition function is multiplied by $\varphi\zeta\xi^{\neq}$, where $\xi^{\neq}$ is the Boltzmann factor of the additional reversible work due to the interaction with $\neq_s$ on σ_0. Leaving now both the end sites free to be either occupied by $\underset{*}{\mathrm{H}}$ or vacated, the partition function of the assembly gains factor $1+\varphi\zeta\xi^{\neq}$ twice similarly to the case of Eq. (28.b) or (28.c), hence Eq. (32.b).

We have eliminating $\mathfrak{Q}\mathfrak{A}/\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}$ and $\mathfrak{Q}\mathfrak{A}^{\neq s}_{\sigma_0(\neq_s)}/\mathfrak{Q}\mathfrak{A}_{\Sigma(0)}$ from Eqs. (32.a), (32.b) and (29.a)

$$q(\neq_s)\theta_s^{\neq}(0)=q(\neq_s)(1+\varphi\zeta\xi^{\neq})^2\Big/\Big[(1+\varphi\zeta)^2+\varphi(1+\varphi\zeta\xi)^2\Big],$$

hence according to Eqs. (1.f) and (10)

$$v_{+,1}(s)=\kappa(s)(kT/h)N^{\neq}_{s,1}\,q(\neq_s)_0(1+\varphi\zeta\xi^{\neq})^2\Big/\Big\{p(I_s)\Big[(1+\varphi\zeta)^2+\varphi(1+\varphi\zeta\xi)^2\Big]\Big\}.$$

The φ, ζ and ξ are calculated as described in **5.4.** The $p(\mathrm{I}_s)$ is given by Eqs. (22) and (24) for the recombination of $\underset{*}{\mathrm{H}}$'s. The $v_{+,1}(s)$ is thus worked out by evaluating $q^{\neq}_{s,0}$ and $\xi^{\neq}$ further by definition, provided $\kappa(s)$ is reasonably estimated.

5.6. Isotherm and current density have been derived in **5.4.** and **5.5.** respectively, allowing for the interaction of adsorbates with their first nearest neighbours discretely but ignoring that with farther neighbours altogether. This procedure has now been elaborated by taking account of the interaction discretely as far as with the second and third nearest neighbours[14] to work out the isotherm of dissociative adsorption of hydrogen on the (110) lattice plane of fcc Ni catalyst. The result converged with increasing degree of approximation, indicating the necessary radius of the discrete treatment.

The $\sum$ in this case included the site observed, σ_0, and surrounding sites as far as $\underset{*}{\mathrm{H}}$'s on them were premised to exert repulsion upon $\underset{*}{\mathrm{H}}$ on σ_0 as in the idealized case in **5.4.** and **5.5.**; $\sum$ thus included as far as the first, second or third nearest neighbours of σ_0 and the appropriate approximation was called the first, second or third approximation respectively. The first approximation is identical with that illustrated in **5.4.** in case of (110)-lattice plane of fcc crystal.

It has thus been found that the second approximation differed appreciably from the first one but came close to the third approximation. A further investigation has shown[15] that the second approximation was quantitatively reproduced by combining the first approximation with the proportional approximation for the second and third nearest neighbours by replacing $q_\sigma(\underset{*}{\mathrm{H}})_0$ in Eq. (28.a) with $q_\sigma(\underset{*}{\mathrm{H}})_0 \exp(-u_{\mathrm{II\,III}}\theta(\underset{*}{\mathrm{H}})/RT)$, where $u_{\mathrm{II\,III}}$ is the sum total of repulsive potentials due to the second and third nearest neighbours at $\theta(\underset{*}{\mathrm{H}})=1$; the $\theta(\underset{*}{\mathrm{H}})$ was thus worked out by Eqs. (28.a), (29.b) and (30.b) as a function of φ.

5.7. On the basis of the above results the calculation has been extended to the rate of recombination of $\underset{*}{\mathrm{H}}$'s.[12] The rate was worked out with reference to the $\sum$, which includes, besides the two constituent sites of $\sigma_s^{\neq}$, every first nearest site to either of the constituent sites of $\sigma_s^{\neq}$; $\sum$ thus consisted of 6, 8 or 10 adsorption sites of $\underset{*}{\mathrm{H}}$ in the respective case of (110), (100) or (111) lattice plane of fcc crystal.*)[12] Repulsive potentials due to the second nearest and farther neighbours have been taken into account by the proportional approximation after the manner referred to in the foregoing section. The repulsive potential was taken to be 1.5 times the exchange repulsion according to the result referred to in **5.3.**.

It has thus been shown that the adsorption as well as the recombination of hydrogen electrode reaction takes place predominantly on (110)-lattice plane at η below -300 mV, whereas the adsorption attained saturation, while the rate of recombination approached a constant value, as η increased.[12] The recombination proceeded for positive η predominantly on the (111)-lattice plane.[12] The range of η, where τ remained a proper fraction was further extended up to *ca.* 500 mV in accordance with observations.[12]

The τ decreases according to the theoretical conclusion of catalytic

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*) The $\sigma_s^{\neq}$ of every possible distance between its constituent sites has been tried on the rate on every lattice plane; the number of constituent adsorption sites of $\sum$ as mentioned in the text refers to the $\sigma_s^{\neq}$ of the predominant contribution on each lattice plane.

mechanism, from 2 to 0, as η increases from extremely low to high a value irrespective as to whether or how the interaction among $\underset{*}{\mathrm{H}}$'s is taken into account except for the crude analogy to dilute gas of Eq. (17. μ), where τ stays constant at 2 throughout. The allowance for the interaction extends the range of η, where τ remains a proper fraction and the range increases with increase of the magnitude of interaction.

5.8. The values of τ both at the extremities of η have been experimentally verified as follows. We have from Eqs. (1)

$$v_{+,1}(s)/v_{-,1}(s) = p(\mathrm{F}_s)/p(\mathrm{I}_s) .$$

The right side equals $\exp[(2\mu(\underset{*}{\mathrm{H}}) - \mu(\mathrm{H}_2))/RT]$ according to Eq. (2), noting that $\mathrm{I}_s \equiv 2\underset{*}{\mathrm{H}}$ and $\mathrm{F}_s \equiv \mathrm{H}_{2,g}$, hence according to Eq. (16) and the proportionalities, $i_{+,1} \propto v_{+,1}(s)$ and $i_{-,1} \propto v_{-,1}(s)$

$$RT \ln(i_{+,1}/i_{-,1}) = 2F\eta . \qquad (33)$$

In the lower extremity of η, where Eq. (18) applies, we have from Eq. (33) $(RT/F)\partial \ln i_{-,1}/\partial\eta = 0$. This conclusion has been verified by OKAMOTO,[16] who observed the anodic current density, $i_{-,1} - i_{+,1}$, on a hydrogen electrode of Ni; $i_{-,1} - i_{+,1}$ tended to a limiting value with decrease of η, where $i_{-,1}$ predominated over $i_{+,1}$ in accordance with Eq. (33). The limiting value was verified not apparent as that controlled by some transport process on the ground of an appreciable magnitude of its temperature coefficient.

The other extreme value, $\tau = 0$, at the higher extremity of η has been experimentally verified by Kita and his collaborators on hydrogen electrodes of Ni,[17] Ag[18] and Cu.[19]

It might have been seen that the kinetics derived from one and the same mechanism was drastically changed by allowing for the interaction; without allowance the catalytic mechanism led to a conclusion in an explicit discordance with observations but with allowance the same mechanism accounted satisfactorily for experiments.

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