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ON THE LAW OF LAIDLER, GLASSTONE AND EYRING

II. Heterogeneous Reaction of Hydrogen

By

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Summary

The law¹⁾ in the title states originally that $\log_{10} B \equiv \log i_0 + Td \log_{10} i_0/dT$ has approximately common value 3 ± 2 for different hydrogen electrode in aqueous electrolyte, where i_0 is the so-called exchange current density.

HORIUTI, KEII, ENYO and FUKUDA²⁾ have shown previously that the law holds for the hydrogen electrode reaction in non-aqueous solution as well and even for heterogeneous reaction of hydrogen, *i. e.* heterogeneous reaction which involves hydrogen molecule, *e. g.* the catalyzed exchange reaction of hydrogen or the parahydrogen conversion in the presence of metallic catalyst, by formally associating two elementary charges to every hydrogen molecule involved.

The B -value of the heterogeneous reaction of hydrogen which proceeds through the intermediary of hydrogen adatoms on metallic catalysts inclusive of the hydrogen electrode reaction by catalytic mechanism has been theoretically deduced in a previous paper²⁾, which is however exact, as mentioned in Part I⁵⁾, only in case of sparse coverage of the electrode or catalyst surface with the adatoms. In Part I⁵⁾, the theoretical values of B have been determined from those of i at higher coverage, where the TAFEL law holds most closely, by defining i_0 as the latter i extrapolated at zero overvoltage by the TAFEL law in accordance with the practical experimental procedure of determining i_0 .

The present Part is concerned with the theoretical derivation of B -value of other heterogeneous reactions of hydrogen to be compared with the experimental value. The B is theoretically formulated assuming that the number G^* of seats of the critical complex of heterogeneous step is of the order of magnitude of 10^{15} per cm^2 of BET-area of catalyst on the ground of the lattice plane model of catalyst⁷⁾, which is a slight revision of the early one^{8,13)} in accordance with the recent theoretical and experimental results⁷⁾. The above G^* -value is verified by the conformity of the theoretical value of B with experimental one in the simple case of activated adsorption of hydrogen on copper as well as the catalyzed hydrogenation of ethylene on nickel; in the latter case theoretical values are derived on the base of the above G^* -value identically both from the associative mechanism and desorption mechanism³⁵⁾, which attributes the well-known optimum temperature to the desorption of ethylene at the optimum. The associative mechanism accounts for the optimum, on the other hand, as due to the switch of the rate-determining step from the dissociative adsorption of hydrogen at lower temperature to the combination of adsorbed ethyl radical and adsorbed hydrogen

atom at higher temperature. The verified premise $G^* \cong 10^{15}$ provides thus an experimental method to decide between the alternative mechanisms, inasmuch as 10^{15} molecules of ethylene should disappear from the gas phase per unit area of catalyst surface or not at temperatures below or above the optimum respectively according particularly to the desorption mechanism.

With regard to the parahydrogen conversion the BONHOEFFER-FARKAS mechanism leads to a theoretical value of B quite outside the limits of error of its observed value; this disagreement is attributed to either or both of the deficiency of the present approximation in allowing for the interaction between hydrogen adatoms on the catalyst and the alternative operation of the RIDEAL-ELEY mechanism.

Introduction

LAILLER, GLASSTONE and EYRING¹⁾ have found empirically that

$$\log_{10} B \equiv \log_{10} i_0 + Td \log_{10} i_0 / dT \quad (1)$$

has an approximately common value 3 ± 2 for different hydrogen electrodes in aqueous electrode, where i_0 is the so-called exchange current density. HORIUTI, KEII, ENYO and FUKUDA²⁾ have shown that the law applies to hydrogen electrode reaction in nonaqueous electrolyte as well and even to heterogeneous reactions of hydrogen, *i. e.* heterogeneous reactions involving hydrogen molecules, *e. g.* catalyzed exchange reactions of hydrogen $H_2 + D_2 = 2HD$ ³⁾ or of hydrogen with ammonia³⁾ and parahydrogen conversion⁴⁾ in the presence of metallic catalyst, provided that i_0 is expressed in terms of two elementary charges formally associated with each hydrogen molecule involved in the heterogeneous reaction per unit area per unit time.

They²⁾ have shown, on the other hand, that the approximately common value is theoretically deduced in agreement with the empirical law, but their treatment in case of reactions which proceed through the intermediary of hydrogen adatoms as in the catalytic mechanism of hydrogen electrode reaction is only exact for sparse coverage of electrode or catalyst surface by hydrogen adatoms. In Part I⁵⁾ the B of hydrogen electrode reaction of the catalytic mechanism has been deduced from the theoretical value of the cathodic current density i for higher coverage of the electrode surface by hydrogen adatoms, where the TAFEL law is most closely obeyed, by defining i_0 in (1) as the latter i extrapolated at zero overvoltage according to the TAFEL law, in line with the practical experimental procedure of determining i_0 .

The present Part is concerned with the elaboration of the previous treatment²⁾ of the heterogeneous reaction of hydrogen. The i_0 in this case is the rate of hydrogen molecules involved in the heterogeneous reaction in question

formally multiplied by two elementary charges. The theoretical value of the latter rate is deduced according to the generalized theory of reaction rate⁶⁾ on the basis of the lattice plane model of metallic catalyst⁷⁾, which leads to the number G^* of the seats σ^* of the critical complex of the heterogeneous step (elementary reaction) responsible for involving the hydrogen molecules, amounting to 10^{15} per cm^2 of BET-area by order of magnitude as referred to in §3. The comparison of the experimental and the theoretical values of B provides a test of this magnitude for G^* as well as of the underlying mechanism.

The general theory of B is first developed and then applied to a few particular cases of the heterogeneous reactions of hydrogen to draw conclusions on G^* -value and the mechanism. The formal association of two elementary charges to every hydrogen molecule involved is followed as mentioned above in this treatment, although not indispensable, for the sake of ready comparison of the numerical results obtained with previous ones. The quantitative theoretical calculation is conducted in case where the dissociative adsorption or its reverse process is the heterogeneous step involving hydrogen molecules, the requisite fundamental data being provided by previous works^{5,8,9,10)}. The σ^* in the latter case consists of two adjacent sites of physically identical ones of hydrogen adatoms on each lattice plane, as verified by the relevant derivation^{5,8,9)} of the TAFEL law on the basis of the catalytic mechanism allowed for the repulsive interaction between adatoms and between the latter and the critical complex. The repulsive interaction is taken into account in the present work as in Part I⁵⁾ by the proportional approximation¹⁰⁾ according to the recent self-consistent method¹¹⁾.

§ 1. General Theory

The i_0 is expressed according to the generalized theory of reaction rate⁶⁾ as in Part I, as

$$i_0 = 2\varepsilon \frac{kT}{h} \exp\left(\frac{\mu^I - \mu^*}{RT}\right), \quad (2)$$

assuming the transmission coefficient unity, where μ^I or μ^* is the chemical potential of the initial system I or the critical complex *, *i.e.* the set of particles participating the heterogeneous step in question except those of catalyst^{*)} respectively at the initial or the critical state, ε the elementary charge, and k , h and R are of usual meanings. Steps dealt with in this Part

) The participation of constituent particles of catalyst is allowed for through the factor $\theta_{\sigma^(0)}$ in (5).

involve each one hydrogen molecule*) either in the initial or the final system.

We have from (1) and (2)

$$B = 2\varepsilon \frac{kT}{h} \exp\left(1 + \frac{\Delta^*S}{R}\right), \quad (3. a)$$

where

$$\Delta^*S = -(\partial\Delta^*F/\partial T)_P \quad (3. b)$$

and

$$\Delta^*F = \mu^* - \mu^I \quad (3. c)$$

is the increment of the free energy of the whole assembly C, in which the heterogeneous reaction of hydrogen is going on, caused by bringing a set s of particles participating the step (except those constituting the catalyst) from the initial to the critical state per mol of s and P is the pressure of C. The Δ^*S is in consequence the appropriate increment of entropy of C per mol of s .

Laidler *et al.*¹⁾ have shown that B comprises the entropy of activation (standard) besides the surface concentration of the initial system of the rate-determining step. According to the present definition of Δ^*S , B implies as seen in (3. a), solely Δ^*S and absolute temperature besides universal constants; $\log_{10} B$ is thus just a transform of Δ^*S , which implies useful informations on the mechanism.

We have from (3. b) and (3. c)

$$\Delta^*S = -(\partial\Delta^*F/\partial T)_P = \bar{S}^* - \bar{S}^I, \quad (4. a)$$

where

$$\bar{S}^* = -(\partial\mu^*/\partial T)_P \quad (4. b)$$

is by definition the partial molar entropy of the critical complex, called simply its entropy in what follows and

$$\bar{S}^I = -(\partial\mu^I/\partial T)_P \quad (4. c)$$

is such of the initial system referred to hereinafter just as its entropy. The μ^* in (4. b) is developed as^{**),(6)}

*) This does not mean that the set of particles participating the heterogeneous step consists necessarily of two hydrogen atoms; the heterogeneous step $H_2 + H(a) \rightarrow H(a) + H_2$ of the RIDEAL-ELEY mechanism of parahydrogen conversion involves each one hydrogen molecule, while participated by three hydrogen atoms, where $H(a)$ is the adsorbed hydrogen atom.

**) Cf. Eqs. (5.1), (8.12) and §24 of Ref. 6).

$$\mu^* = -RT \ln G^* \theta_{\sigma^*(0)} q^*, \quad (5)$$

where $\theta_{\sigma^*(0)}$ is the probability of a certain σ^* being free to accommodate a critical complex referred to in what follows as evacuated, and q^* is the BOLTZMANN factor of the reversible work required to bring up the constituents of the critical complex from their respective standard states onto a definite, preliminarily evacuated σ^* to compose a critical complex there.

The q^* is expressed for the dissociative adsorption of hydrogen molecule or its reversal by the proportional approximation as in Part I⁵⁾, as

$$q^* = q_0^* \exp\left(-\frac{u^* \theta}{RT}\right), \quad (6. a)$$

where θ is the fraction of catalyst surface covered with hydrogen atom and^{*)}

$$q_0^* = \exp\left(-\frac{E_0^*}{RT}\right) \prod_{i=1}^5 \left\{1 - \exp\left(-\frac{h\nu_i^*}{kT}\right)\right\}^{-1} \quad (6. b)$$

is the particular value of q^* at $\theta=0$, u^* the additional potential of the critical complex due to the repulsion exerted by the surrounding adatoms at $\theta=1$, E_0^* the ground state energy of the critical complex and ν_i^* the frequency of its i -th normal mode of vibration.

The entropy of the critical complex is developed according to (4. b), (5) and (6. a) as

$$\bar{S}^* = R \ln G^* + R \frac{dT \ln q_0^*}{dT} + R \left(\frac{\partial T \ln \theta_{\sigma^*(0)}}{\partial T} \right)_P - u^* \left(\frac{\partial \theta}{\partial T} \right)_P. \quad (7. a)$$

The first term of the above equation is the entropy due to the manifoldness of the seats of the critical complex. The next term is the entropy of a critical complex fixed in its definite seat, which contributes just a little to $\log_{10} B$ as seen from (6. b), insofar as the temperature is not very high. The third term is the increment of entropy due to the evacuation per mol of σ^* , inasmuch as $-RT \ln \theta_{\sigma^*(0)}$ is the increment of free energy^{**)} caused by the evacuation per mol of σ^* ; this term is negative, if adsorbate is simply compressed on the catalyst surface by the evacuation, but positive, if the evacuation results in the

) The q_0^ here is identical with q_p^{*d} given by Eq. (23) of Ref. 8) and E_0^* here equals $\epsilon_{H_2} + 1/2 \sum_i h\nu_i$ there multiplied by the AVOGADRO number.

***) The $\theta_{\sigma^*(0)}$ is expressed in terms of the partition function ΩC of the whole assembly C as $\theta_{\sigma^*(0)} = \Omega C_{\sigma^*(0)} / \Omega C$,

where $\Omega C_{\sigma^*(0)}$ is the partition function of $C_{\sigma^*(0)}$, which is the C subject to the particular condition that a certain definite σ^* is kept evacuated with certainty. Since $-kT \ln \Omega C_{\sigma^*(0)}$ or $-kT \ln \Omega C$ is the free energy of $C_{\sigma^*(0)}$ or C respectively, $-RT \ln \theta_{\sigma^*(0)}$ is the reversible work required to evacuate σ^* per mol, i. e. the appropriate increment of free energy.

expulsion of adatoms as molecules in gas, where they acquire a large amount of entropy. The last term $-u^*(\partial\theta/\partial T)_P$ in (7.a) is the negative temperature derivative of the free energy increase $u^*\theta$ due to the interaction between the critical complex and the surrounding adatoms, hence is the appropriate entropy increase of C.

In the extreme case of bare catalyst surface, both the last two terms of (7.a) vanish, inasmuch as $\Theta_{\sigma^*(0)}$ is then unity, while θ is zero. If, on the other hand, every σ^* is practically occupied by chemical species A, which has to be inevitably expelled into gas phase in order to evacuate a σ^* , the term $R(\partial T \ln \Theta_{\sigma^*(0)}/\partial T)_P$ is the entropy increase caused by transferring adsorbed A in σ^* into the gas phase, or the excess of partial molar entropy \bar{S}^A of A in gas over its entropy in the σ^* , *i.e.*

$$R\left(\frac{\partial T \ln \Theta_{\sigma^*(0)}}{\partial T}\right)_P = \bar{S}^A - R\left(\frac{\partial T \ln q^A}{\partial T}\right)_P, \quad \Theta_{\sigma^*(0)} \ll 1, \quad (7. b)$$

since then $\Theta_{\sigma^*(0)} = p^A/q^A$ for $\Theta_{\sigma^*(A)} = 1$, according to the general relation*), $\Theta_{\sigma^*(0)}/\Theta_{\sigma^*(A)} = p^A/q^A$, where $-RT \ln p^A$ is the chemical potential of A and q^A the BOLTZMANN factor of the reversible work required to bring up A from its standard state onto a definite, preliminarily evacuated σ^* , hence the second term $R(\partial T \ln q^A/\partial T)_P$ is the appropriate entropy increase. In this case the last term $-u^*(\partial\theta/\partial T)_P$ in (7.a) may be taken to vanish, insofar as θ is kept practically zero or constant on account of the full occupation of σ^* by A. The second term on the right of (7.b) nearly vanishes similarly as $R(\partial T \ln q^*/\partial T)_P$ does according to (6), so that $R(\partial T \ln \Theta_{\sigma^*(0)}/\partial T)_P$ equals \bar{S}^A approximately.

The μ^I in (4.c) is expressed in accordance with the scope of the present paper, as

$$\mu^I = n\mu^{H_2}, \quad (8. a)$$

where n is the number of hydrogen molecules which make as they are or through conversion the initial system of the heterogeneous step in question and μ^{H_2} the chemical potential of hydrogen in C. The initial system I of the IDEAL-ELEY mechanism of parahydrogen conversion is $H_2 + H(a)$, hence $n = 3/2$, insofar as hydrogen adatom H(a) is in equilibrium with $1/2 \cdot H_2$ or $\mu^{H(a)} = 1/2 \cdot \mu^{H_2}$. We have thus

$$\bar{S}^I = n\bar{S}^{H_2}, \quad (8. b)$$

where \bar{S}^{H_2} is the entropy of hydrogen or the entropy of 1 mol pure hydrogen under the pressure equal to its partial pressure and the temperature in C.

We have now from (3.a), (4.a), (7.a) and (8.b) in case where hydrogen

*) Cf. footnote *) on p. 33 or Eq. (5.1) of Ref. 6).

adatoms are sole adsorbate

$$\log_{10} B = \log_{10} 2\varepsilon \frac{kT}{h} G^* e + \frac{dT \log_{10} q_o^*}{dT} - \frac{n\bar{S}^{H_2}}{2.3R} + \left(\frac{\partial T \log_{10} \Theta_{\sigma^{*(0)}}}{\partial T} \right)_P - \frac{u^*}{2.3R} \left(\frac{\partial \theta}{\partial T} \right)_P. \quad (9. a)$$

If θ is constant particularly, the last two terms of the above equation, *i. e.* those of (7. a) vanish as mentioned above, hence

$$\log_{10} B = \log_{10} 2\varepsilon \frac{kT}{h} G^* e - \frac{n\bar{S}^{H_2}}{2.3R} + \frac{dT \log_{10} q_o^*}{dT}. \quad (9. b)$$

In the other case where σ^* 's are occupied by A practically with certainty, the last term of (9. a) vanishes as mentioned above, whereas the second last term assumes the form of (7. b), so that

$$\log_{10} B = \log_{10} 2\varepsilon \frac{kT}{h} G^* e + \frac{\bar{S}^A - nS^{H_2}}{2.3R} + \frac{dT \log_{10} q^*/q^A}{dT}. \quad (9. c)$$

These theoretical expressions of B are applied to a few cases of the heterogeneous reaction of hydrogen after the approximations and fundamental data used, and the crystal plane model of catalyst basic to the present applications are summarized in the next two sections.

§ 2. Approximations and Fundamental Data

Repulsive interactions exerted by hydrogen adatoms are allowed for by the expressions of $\Theta_{\sigma^{*(0)}}$ and θ , which are derived consistent with each other in accordance with the proportional approximation^{5,11)}, as

$$\Theta_{\sigma^{*(0)}} = (1 + 2\beta + \xi\beta^2)^{-1} \quad (10. a)$$

and

$$\theta/(1 - \theta) = \beta(1 + \xi\beta)/(1 + \beta), \quad (10. b)$$

where

$$\beta = \gamma \exp \{ (u - u_1) \theta / RT \}, \quad (11. a)$$

$$\xi = \exp (-u_1 / RT), \quad (11. b)$$

$$\gamma = \sqrt{\frac{1.360 \times 980.5 h^5 P^{H_2} \text{ mmHg}}{(2\pi m^{H_2} kT)^{3/2} 4\pi^2 I^{H_2} (kT)^2}} q^{H(a)}, \quad (12. a)$$

and

$$q_o^{H(a)} = \prod_{j=1}^3 \left\{ 1 - \exp\left(-\frac{h\nu_j}{kT}\right) \right\}^{-1} \exp\left(-\frac{E_o^H}{RT}\right); \quad (12. b)$$

above equations are applicable in case of dissociative adsorption of hydrogen or its reversal, where hydrogen adatoms are sole adsorbate and σ^* consists of two sites of hydrogen adatoms; u is the additional potential of hydrogen adatom per mol due to the repulsion exerted by surrounding ones at $\theta=1$, u_1 the repulsive potential between two hydrogen adatoms per mol respectively occupying the two constituent sites of σ^* , $q_o^{H(a)}$ the BOLTZMANN factor of the reversible work required to bring up a hydrogen atom from its standard state onto a definite, preliminarily evacuated site of adsorption in the absence of surrounding ones, E_o^H the ground state energy of adatom per mol in the absence of surrounding ones as referred to the ground state energy of hydrogen molecule, ν_j the frequency of j -th normal vibration of the adatom and m^{H_2} or I^{H_2} is the mass or the moment of inertia of hydrogen molecule respectively. E_o^H was determined in a previous work¹⁰⁾ from measurement of the heat of adsorption at extremely low coverage, as

$$E_o^H = -12.3 \text{ Kcal/mol.} \quad (13)$$

The γ is expressed as (12), in case where hydrogen adatoms are in equilibrium with hydrogen gas of P^{H_2} mmHg pressure^{*,5,10)}.

The G^* in (5) or in (9) is taken to be 10^{15} on the basis of the crystal plane model of catalyst specified in the next section. The numerical values used for the calculation of $\Theta_{\sigma^*(0)}$ and q_o^* are

$$u^* = 8.04, \quad u = 6.78, \quad u_1 = 0.372, \quad \text{Kcal/mol,} \quad (14. a), (14. b), (14. c)$$

$$\nu_i^*/c = 936, 687, 1704, 368, 626 \text{ cm}^{-1} \text{ } ^8), \quad (15. a)$$

and

$$\nu_j/c = 417, 479, 1900 \text{ cm}^{-1} \text{ } ^8), \quad (15. b)$$

where c is the light velocity in vacuum. The values of u and u_1 are 1.2 times as large as those calculated in a previous paper⁸⁾ as the exchange repulsions between unbonded hydrogen atoms. The values of u and u_1 given above have been found, as parameters in the theoretical isotherms of a higher approximation⁷⁾, to fit in with observed ones over pressures below 1 atm. and temperatures below 200°C in accordance with the conclusion from quantum-mechanical

*) Eq. (12) is identical with Eq. (23. γ) of Ref. 10), E_o^H in the former being identical with -4ϵ in the latter multiplied by the AVOGADRO number, or with Eq. (24. a) in Part I⁹⁾ for $\eta=0$, in which particular case adatoms are in equilibrium with gaseous hydrogen.

theory of adatoms¹²⁾ that the repulsion among them is greater than the exchange repulsion mentioned above. The u^* in (14. a) is that obtained in the previous work⁸⁾ multiplied by the same factor 1.2 in line with u and u_1 .

§ 3. Crystal Plane Model

The crystal plane model has been formerly advanced in order to explain the phenomena of adsorption¹³⁾ and those of hydrogen electrode reaction⁸⁾ and recently evidenced⁷⁾ in the main by observations with slow electron diffraction¹⁴⁾ and field emission microscope¹⁵⁾. The f.c.c. polycrystalline surface of nickel, for instance, consists, according to the model originally advanced^{13,8)}, of perfect (110), (100) and (111) lattice planes, each of which provides above it another lattice plane of sites of hydrogen adatoms congruent to it, which sites are practically physically identical with each other.

It has recently been concluded from the quantum-mechanical theory of adsorption advanced by TOYA¹²⁾, that there exist two kinds of adatoms on metallic adsorbents, *i.e.* the r-adatoms and s-adatoms; r-atom is just that of usual sense, while s-atom is a sort of dissolved atom in the metal but situated close to the electronic surface of the metal. It is on the other hand experimentally confirmed that the lattice plane of each kind is associated with lattice imperfections, *i.e.* steps, kinks and defects, which provide such "abnormal" sites as occupied, as deduced theoretically¹²⁾, by s-adatoms of extraordinary low energy, but presumably hardly by any r-atom. The "abnormal" sites amount, as estimated experimentally^{7,15,17)} to around a few percent of the whole sites. It is also theoretically^{8,12,18)} and experimentally confirmed^{14,15,17)} that the energy of r-atom on "normal" sites, *i.e.* physically identical ones mentioned above of the respective lattice planes on nickel increases, apart from the additional potential due to interaction with surrounding adatoms, distinctly stepwise in the order of (110), (100) and (111) and the energy of s-adatoms is fairly high as compared with that of r-adatoms on the respective lattice plane in case of nickel. It follows that hydrogen adatoms block the "abnormal" sites due to lattice imperfections at the very beginning of adsorption and then are accommodated as r-adatoms on (110)-lattice plane. The r-adatoms repulse each other much stronger than s-adatoms do each other and r-adatoms¹²⁾. With increase of population of r-adatoms, its thermodynamic activity increases rapidly due to the repulsion, so that the further increase of population may consist in the increase of s-adatoms as well as that of r-adatoms on other lattice planes of higher energy.

At extremely high activity of adatoms the lattice plane of the lowest energy

of adatoms would be fully occupied by r-adatoms as well as by s-adatoms and the increase of population with increase of activity would practically occur on lattice planes of higher energy of adatoms. It is now concluded in a forthcoming paper¹⁹⁾ that the number of "normal" sites on (110)-lattice plane of reduced nickel powder amounts to $0.4 \times 10^{15} \text{ cm}^{-2}$, *i.e.* about one third of that of the surface metal atoms per cm^2 of BET area, from the comparison of the theoretical adsorption isotherm $\theta(P^{\text{H}_2})$ on (110)-lattice plane with parameters specified by (14. b), (14. c) and (15. b), with the observed adsorption isotherm, *i.e.* adsorbed amount $a(P^{\text{H}_2})$ observed as a function of equilibrium pressure P^{H_2} of hydrogen lower than 1 atm and at temperatures below 200°C. We may safely attribute the number of "normal" sites of the same order of magnitude to (100)- and (111)-lattice planes, which are thermodynamically more stable than (110).

Our lattice plane model of metallic adsorbent is thus a slight revision of the earlier one in the following two points; the physically identical sites on each lattice plane are associated with the "abnormal" sites due to the lattice imperfections and adatoms of usual sense, *i.e.* r-adatoms are accompanied by s-adatoms. The B is calculated theoretically on the basis of this model as that of metallic catalyst with the following two postulates. The s-adatoms are excluded from participating the heterogeneous step in question, inasmuch as they are inbedded in the electron cloud of the catalyst metal and in consequence the hydrogen molecule involved would give rise to inhibitive high an activation energy, insofar as it is situated in the same nuclear position as required for participating the heterogeneous step in question. Another postulate is that the seat σ^* of the critical complex of the dissociative adsorption or its reversal consists of adjacent pair of physically identical sites of adatoms, which has effectively accounted for experimental results in previous works^{5,8,9)}. It follows that number of σ^* on each lattice plane amounts to 10^{15} per cm^2 of BET area by order of magnitude. This conclusion that the number of σ^* 's amounts to 10^{15} per cm^2 of BET area by order of magnitude is extended to the other heterogeneous steps dealt with in the present paper.

On this ground it may be understood that the magnitudes of u^* , u and u_1 required for deducing the TAFEL law of hydrogen electrode reaction from the catalytic mechanism by the proportional approximation amount to more than three times as large as those of (14). It is readily shown that the thermodynamic activity of hydrogen adatoms amounts to that in adsorption equilibrium with hydrogen of 10^{16} mmHg pressure at 400 mV overvoltage, around which the TAFEL law is most closely obeyed as observed²⁰⁾ in accordance with theoretical calculation^{5,9,11)}. It follows that the increase of current density is effected by that of adatoms on (100) or (111) lattice plane of higher energy of adatoms

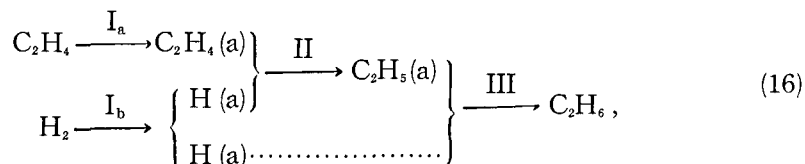
along with the increase of their activity, hence of the overvoltage, while the (110)-lattice plane of the lowest energy of adatom, which plays alternatively the leading part at lower activity of adatoms as in case of the adsorption isotherm mentioned above, is practically fully occupied, thus contributing just a constant amount to the current density.

The repulsive potentials u^* , u and u_1 depend now on the geometry of the lattice plane. An adatom on (110)-lattice plane has only two nearest neighbours at $\theta=1$, which contribute more than 80% of u , while an adatom on (100)- or (111)-lattice plane has four or six such neighbours respectively. It is hence reasonable that more than three times as large an amount of u etc. in (14) reproduces the TAFEL law at the above magnitude of overvoltage, whereas the latter amount of u etc. fits in with the adsorption isotherm observed below 1 atm. of hydrogen pressure.

A theoretical calculation of higher approximation than the proportional one is going on in this laboratory on the contribution of (100) and (111)-lattice plane to the cathodic current density.

§ 4. Mechanism of Catalyzed Hydrogenation of Ethylenic Linkage

It is well-known that the rate of catalyzed hydrogenation of ethylenic linkage in the presence of metallic catalyst reveals an optimum temperature, *e. g.* in cases of ethylene²¹⁾, crotonic and maleic acids²²⁾ and different isomers of butylene²³⁾. HORIUTI and POLANYI²⁴⁾ have advanced the associative mechanism, as expressed with special reference to ethylene, as



where (a) signifies the adsorbed state. HORIUTI and POLANYI²⁴⁾ suggested that the last step III was rate-determining. HORIUTI and others²⁵⁻³⁰⁾ have later developed a statistical mechanical theory of the catalyzed hydrogenation on the basis of the sequence (16) of steps without *a priori* specifying the rate-determining step and concluded by fitting the parameters implied to the experimental results that the rate-determining step switches over from I_b to III as temperature is raised from below to above the optimum temperature. With the parameters thus adjusted the statistical mechanical theory²⁵⁻³⁰⁾ has accounted for the kinetics of the hydrogenation observed as well as different

phenomena associated with it, *e.g.* those of the exchange reaction between hydrogen and ethylene, the equilibration $H_2 + D_2 = 2HD^{25}$, parahydrogen conversion²⁵⁾ and the formation²⁶⁾ of different deuterioethylenes and deuterioethanes. They^{25,27)} have thus semiquantitatively explained the correlation between the degree of equilibration and deuterium content of hydrogen in course of the catalyzed deuteration of ethylene in the presence of nickel as observed by TWIGG and RIDEAL²⁸⁾ over the range of temperature from 84°C to 207°C and predicted quite a different correlation at lower temperatures^{25,29)}, which has been experimentally verified by MATSUZAKI³¹⁾.

The scheme (16) so far verified will be referred to as the associative mechanism in what follows. It follows from the latter mechanism that at temperatures below the optimum the rate of the catalyzed hydrogenation equals the unidirectional rate of $I_b^{25,27)}$, *i.e.* the dissociative adsorption of hydrogen. The B is hence given by (9. b) with $n=1$, provided that θ is constant.

MIYAHARA³²⁾ has recently secured the experimental condition for essentially reproducible observations of the hydrogenation rate on evaporated nickel film. We have from his result³²⁾ of observation at temperatures below the optimum

$$\log_{10} B_{\text{exp.}} = 1.5, \quad \text{at } 0^\circ\text{C}, \quad P^{H_2} = P^{C_2H_4} = 15 \text{ mmHg}, \quad (17. E)$$

where P^{H_2} or $P^{C_2H_4}$ is the partial pressure of hydrogen or ethylene respectively.

Theoretically on the other hand, we have from (9. b) for the same condition

$$\log_{10} B_{\text{theor.}} = 1.6, \quad (17. T)$$

which agrees excellently with the observed value of (17. E). The respective terms of (9. b) are evaluated as

$$\log_{10} 2\varepsilon \frac{kT}{h} G^* e = 9.70, \quad \frac{dT \log_{10} q_0^*}{dT} = 0.35,$$

$$\frac{\bar{S}^{H_2}}{2.3R} = 8.40, \quad 0^\circ\text{C}, \quad P^{H_2} = 15 \text{ mmHg}.$$

The $dT \log_{10} q_0^*/dT$ is calculated according to (6. b) by the ν_i^* -values of (15. a). The $\bar{S}^{H_2}/2.3R$ is calculated on the base of the value $\bar{S}^{H_2} = 31.211$ cal/deg. mol at 25°C and 760 mmHg from the "Selected Values"³⁴⁾ by the equation

$$\bar{S}^{H_2} = 31.211 + \frac{7}{2} R \ln \frac{T}{298.16} + R \ln \frac{760}{P^{H_2}} \text{ cal/deg. mol}, \quad (18)$$

which is derived as below.

The chemical potential μ^{H_2} of hydrogen of concentration N^{H_2} molecules cm^{-3} in gas, *i.e.* the GIBBS free energy of 1 mol pure hydrogen gas at the same concentration and temperature

is expressed statistical mechanically as*)

$$\mu^{\text{H}_2} = -RT \ln Q^{\text{H}_2}/N^{\text{H}_2}, \quad (19. a)$$

where Q^{H_2} is the partition function of a single hydrogen molecule in unit volume in gas, which is expressed approximately as

$$Q^{\text{H}_2} = \frac{(2\pi m^{\text{H}_2} kT)^{3/2}}{h^3} \frac{4\pi^2 I^{\text{H}_2} kT}{h^2}, \quad (19. b)$$

identifying its vibrational partition function with unity, expressing the rotational partition function classically as $4\pi^2 I kT/h^2$, ignoring vibration-rotation interaction and referring the energy to its ground state. Substituting N^{H_2} from the gas law $P^{\text{H}_2} = kTN^{\text{H}_2}$ into (19. a), we have

$$\mu^{\text{H}_2} = -RT \ln \frac{(2\pi m^{\text{H}_2} kT)^{3/2} 4\pi^2 I^{\text{H}_2} (kT)^2}{h^5 P^{\text{H}_2}}.$$

We have from the above equation

$$\bar{S}^{\text{H}_2} = - \left(\frac{\partial \mu^{\text{H}_2}}{\partial T} \right)_P = R \ln \frac{(2\pi m^{\text{H}_2} kT)^{3/2} 4\pi^2 I^{\text{H}_2} (kT)^2}{h^5 P^{\text{H}_2}} + \frac{7}{2} R,$$

hence

$$\bar{S}^{\text{H}_2} = \bar{S}^{\text{H}_2}(25^\circ\text{C}, 760 \text{ mmHg}) + \frac{7}{2} R \ln \frac{T}{298.16} + R \ln \frac{760}{P^{\text{H}_2}_{\text{mmHg}}} \text{ cal/deg. mol}$$

or (18) above, noting that the partial molar entropy of hydrogen at 25°C and 760 mmHg partial pressure equals the entropy 31.211 cal/deg. mol³⁴⁾ of pure hydrogen at the same temperature and the pressure equal to the partial pressure.

§ 5. Alternative Mechanism of Catalyzed Hydrogenation of Ethylene

The catalyzed hydrogenation of ethylene in the presence of metallic catalyst is sometimes attributed to the LANGMUIR-HINSHELWOOD mechanism³³⁾ or RIDEAL mechanism³⁵⁾ assuming that the optimum is due to the desorption there of ethylene³⁵⁾³⁶⁾, from which it follows that the catalyst surface is practically completely covered by ethylene at temperatures below the optimum.

We might first pick out from these alternative mechanisms such ones as fit in with the experimental results that, at temperatures below the optimum, the rate of catalyzed hydrogenation on nickel is proportional to the hydrogen partial pressure but practically independent of ethylene partial pressure²¹⁾.

According to the LANGMUIR-HINSHELWOOD mechanism the unidirectional forward rate of the hydrogenation is represented, in terms of the current density i_0 , formally associating 2ε with every hydrogen molecule involved, as

$$i_0 = 2\varepsilon \frac{kT}{h} G^* q^* \frac{N^{\text{H}_2} N^{\text{C}_2\text{H}_4} / Q^{\text{H}_2} Q^{\text{C}_2\text{H}_4}}{(1 + q^{\text{H}_2} N^{\text{H}_2} / Q^{\text{H}_2} + q^{\text{C}_2\text{H}_4} N^{\text{C}_2\text{H}_4} / Q^{\text{C}_2\text{H}_4})^2} \quad (20. L. I)$$

*) Cf. e. g. Eq. (5.5) and (8. 12) of Ref. 6).

in case where σ^* consists of two adjacent sites σ 's of adsorption, each of which is competitively occupied by H_2 and C_2H_4 or as

$$i_0 = 2\varepsilon \frac{kT}{h} G^* q^* \frac{N^{H_2} N^{C_2H_4} / Q^{H_2} Q^{C_2H_4}}{(1 + q_{\sigma_1}^{H_2} N^{H_2} / Q^{H_2})(1 + q_{\sigma_2}^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4})} \quad (20. L. II)$$

in case where σ^* is the adjacent pair of sites σ_1 and σ_2 , which are respectively exclusively occupied by H_2 and C_2H_4 ; Q^{H_2} or $Q^{C_2H_4}$ is the partition function of single H_2 or C_2H_4 molecule respectively in unit volume in gas, N^{H_2} or $N^{C_2H_4}$ the concentration of the respective molecule in gas, $q_{\sigma_i}^{H_2}$ or $q_{\sigma_i}^{C_2H_4}$ the BOLTZMANN factor of the reversible work required to bring up H_2 molecule from its standard state onto a definite, preliminarily evacuated site σ or σ_1 respectively and $q_{\sigma_i}^{C_2H_4}$ or $q_{\sigma_i}^{H_2}$ the similar one for C_2H_4 molecule. According to the RIDEAL mechanism³⁵⁾, we have

$$i_0 = 2\varepsilon \frac{kT}{h} G^* q^* \frac{N^{H_2} N^{C_2H_4} / Q^{H_2} Q^{C_2H_4}}{1 + q^{H_2} N^{H_2} / Q^{H_2} + q^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4}}, \quad (20. R)$$

which implies that a σ^* is identical with an adsorption site σ , which is competitively occupied by H_2 and C_2H_4 . The above three expressions are derived as below neglecting the interaction among adsorbates and the critical complex.

The i_0 is expressed by (2) referring to (5) as

$$i_0 = 2\varepsilon \frac{kT}{h} G^* q^* \Theta_{\sigma^*(0)} \exp(\mu^1 / RT). \quad (21)$$

The factor q^* is constant at constant temperature independent of the coverage on account of the premised absence of interactions. It is tacitly assumed with the LANGMUIR-HINSHELWOOD mechanism that σ^* consists of two sites of adsorption for H_2 and C_2H_4 ; for, the proportionality of the rate to the covered fraction of H_2 and that of C_2H_4 as implied in the mechanism is alternatively stated that the reaction is the quadrimolecular one of H_2 , C_2H_4 and two vacant sites. Hence, the two adjacent vacant sites together constitute a vacant σ^* . This mechanism contrasts, in this respect, with the RIDEAL mechanism, which is alternatively stated that the reaction is termolecular one of H_2 , C_2H_4 and one vacant site.

The $\Theta_{\sigma^*(0)}$ is developed on this basis as follows. Let σ be one of the two constituent sites of σ^* , each of which is competitively occupied by H_2 and C_2H_4 . The occupied or unoccupied state of one constituent σ of σ^* should occur independent of that of the other constituent σ , because of the premised absence of interaction of adsorbates. Hence, $\Theta_{\sigma^*(0)}$ equals the square of probability $\Theta_{\sigma(0)}$ of one of the constituent sites being unoccupied. Let now $\Omega C_{\sigma(0)}$ be the partition function of the whole assembly C at a particular state, *i.e.* $C_{\sigma(0)}$, where a definite σ is unoccupied with certainty. The partition function ΩC of the same assembly without such restriction is expressed as

$$\Omega C = \Omega C_{\sigma(0)} (1 + q_{\sigma}^{H_2} N^{H_2} / Q^{H_2} + q_{\sigma}^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4}),$$

inasmuch as ΩC is the sum of the partition functions of the three different possible states of C with regard to σ , *i.e.* the state with the σ unoccupied, that with the σ occupied by H_2 and

that with the σ occupied by C_2H_4 . The partition function of C at the first state is $\Omega C_{\sigma(0)}$ itself; C at the second state is derived from $C_{\sigma(0)}$ by removing a hydrogen molecule from it and by adding the hydrogen molecule removed onto the σ , hence its partition function $\Omega C_{\sigma(0)} q^{H_2} N^{H_2} / Q^{H_2}$, which is the BOLTZMANN factor of the appropriate free energy, *i. e.*

$$-kT \ln \Omega C_{\sigma(0)} - (-kT \ln Q^{H_2} / N^{H_2}) + (-kT \ln q^{H_2}),$$

where $-kT \ln Q^{H_2} / N^{H_2}$ is the loss of free energy of $C_{\sigma(0)}$ caused by the above mentioned removal as seen from (19. a) and $-kT \ln q^{H_2}$ is the gain of its free energy by the addition of the removed H_2 onto the σ . The partition function $\Omega C_{\sigma(0)} q^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4}$ of C at the third state with the σ occupied by C_2H_4 is similarly derived. The probability $\theta_{\sigma(0)}$ is now the ratio $\Omega C_{\sigma(0)} / \Omega C$, *i. e.*

$$\theta_{\sigma(0)} = \Omega C_{\sigma(0)} / \Omega C = (1 + q^{H_2} N^{H_2} / Q^{H_2} + q^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4})^{-1}, \quad (22. a)$$

hence

$$\theta_{\sigma^*(0)} = (1 + q^{H_2} N^{H_2} / Q^{H_2} + q^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4})^{-2}. \quad (22. b)$$

Since I consists of H_2 and C_2H_4 insofar as these mechanisms are concerned, we have

$$\mu^I = \mu^{H_2} + \mu^{C_2H_4}, \quad (23)$$

where μ^{H_2} is expressed by (19. a) and $\mu^{C_2H_4}$ similarly as

$$\mu^{C_2H_4} = -RT \ln Q^{C_2H_4} / N^{C_2H_4}. \quad (24)$$

Eq. (20. L. I) is obtained from (19. a), (21), (22. b), (23) and (24).

The only difference among (20. L. I), (20. L. II) and (20. R) is that in $\theta_{\sigma^*(0)}$, the initial system I and in consequence μ^I in (21) being common to all of them. Let σ_1 and σ_2 be the constituent sites of σ^* , which are respectively exclusively occupied by H_2 and C_2H_4 . The $\theta_{\sigma^*(0)}$ of (20. L. II) is now

$$\theta_{\sigma^*(0)} = \theta_{\sigma_1(0)} \theta_{\sigma_2(0)},$$

where $\theta_{\sigma_1(0)}$ or $\theta_{\sigma_2(0)}$ is the probability of σ_1 or σ_2 being respectively kept unoccupied. Since σ_1 does not accommodate C_2H_4 , the last term $q^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4}$ in the parentheses of the third member of (22. a) vanishes in case of $\theta_{\sigma_1(0)}$, so that

$$\theta_{\sigma_1(0)} = (1 + q_{\sigma_1}^{H_2} N^{H_2} / Q^{H_2})^{-1}.$$

We have similarly

$$\theta_{\sigma_2(0)} = (1 + q_{\sigma_2}^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4})^{-1}.$$

The $\theta_{\sigma^*(0)}$ in this case is expressed by the last three equations, hence (20. L. II).

In case of the RIDEAL mechanism, σ^* is σ itself, so that we have (20. R), equating $\theta_{\sigma^*(0)}$ in (21) to $\theta_{\sigma(0)}$ of (22. a) and expressing μ^I identically with in the case of (20. L. I). Eq. (20. R) thus obtained holds, as it should, irrespective as to whether H_2 or C_2H_4 is first adsorbed, insofar as the configuration of the critical complex is identical.

Eqs. (20) are of course kinetically identical with usual equations derived by mass action law in the respective cases, except that the constants comprised are statistical mechanically defined in this case.

We now impose upon (20) the condition mentioned above that the catalyst surface is fully occupied by C_2H_4 . It is readily seen from the derivation of

(22. a) that the last term in the parentheses, which is proportional to the probability of σ being occupied by C_2H_4 outweighs the former two at the specified condition. Similarly the term $q_{\sigma_1}^{C_2H_4} N^{C_2H_4} / Q^{C_2H_4}$ in (20. L. II) outweighs unity. We have thus from (20)

$$i_0 = 2\varepsilon \frac{kT}{h} G^* \frac{q^*}{(q^{C_2H_4})^2} \frac{N^{H_2}}{Q^{H_2}} \frac{Q^{C_2H_4}}{N^{C_2H_4}}, \quad (25. L. I)$$

$$i_0 = 2\varepsilon \frac{kT}{h} G^* \frac{q^*}{q_{\sigma_2}^{C_2H_4}} \frac{N^{H_2}}{Q^{H_2}} \left/ (1 + q_{\sigma_1}^{H_2} N^{H_2} / Q^{H_2}) \right. \quad (25. L. II)$$

and

$$i_0 = 2\varepsilon \frac{kT}{h} G^* \frac{q^*}{q^{C_2H_4}} \frac{N^{H_2}}{Q^{H_2}}. \quad (25. R)$$

Eq. (25. L. I) states that i_0 is proportional to N^{H_2} but inversely proportional to $N^{C_2H_4}$, which contradicts the experimental results mentioned above and (25. L. II) does as well, unless the adsorption of hydrogen is weak enough or $q_{\sigma_1}^{H_2} N^{H_2} / Q^{H_2}$ is negligible. If then, (25. L. II) is kinetically identical with (25. R), which fits in with the observed kinetics in question. We have, by substituting i_0 from the latter equation into (1) with reference to (4. c) and (19. a)

$$\log_{10} B = \log_{10} 2\varepsilon \frac{kT}{h} G^* e^{-\frac{\bar{S}^{H_2}}{2.3R}} + \frac{dT \log_{10} q^*}{dT} - \frac{dT \log_{10} q^{C_2H_4}}{dT}. \quad (26)$$

The mechanism premised to (25. R) or (26) will be called the desorption mechanism*). Eq. (26) is identical with (9. b) for $n=1$, from which the theoretical value of (17. T) is deduced, except the term $dT \log_{10} q^{C_2H_4} / dT$. The latter term being expected small as $dT \log_{10} q_{\sigma}^* / dT$ or $dT \log_{10} q_{\sigma}^{(a)} / dT$ is, we would have practically no distinction between the associative mechanism and the desorption mechanism as regards the value of B .

However, the coincidence of the theoretical value of (17. T) with the experimental one of (17. E) requires, with reference to (9. b) or (26), that the number G^* of σ^* amounts to 10^{15} per cm^2 BET area by order of magnitude, which are fully occupied at temperatures below the optimum but evacuated

*) JENKINS and RIDEAL³⁷⁾ have revised the earlier theory of RIDEAL *et al.*³⁵⁾³⁶⁾ that ethylene molecule hits adsorbed hydrogen, instead of being adsorbed, to complete the hydrogenation, which step is denoted by (H). They³⁷⁾ accounts for the optimum by assuming that $k_3 P^{C_2H_4} \gg k_2$ or $k_3 P^{C_2H_4} \ll k_2$ respectively below or above the optimum, where $k_3 P^{C_2H_4}$ or k_2 is the specific rate of adsorbed hydrogen being involved in step (H) or desorbed. It follows from the latter assumption that the rate-determining step is the adsorption of hydrogen or step (H) respectively at temperatures below or above the optimum, which is common with the associative mechanism introduced in the foregoing section.

at higher temperature according to the desorption mechanism*). It follows that *ca.* 0.3 mmHg ethylene should disappear from the gas phase of 100 cc volume or not at all respectively above or below the optimum in the presence of catalyst of 1000 cm² BET area before the steady state of hydrogenation is reached according to the desorption mechanism but no such effect could be produced by the associative mechanism. We could appeal to experiment for the decision.

§ 6. Adsorption Rate of Hydrogen on Copper

KWAN³⁸⁾ observed the rate of adsorption of hydrogen on reduced copper at hydrogen pressure around 0.1 mmHg at 300°, 350° and 400°C and found that the extremely slow adsorption was first order with respect to hydrogen pressure, the appropriate activation energy amounting to *ca.* 20 Kcal/mol. These experimental results indicate that the rate observed is the unidirectional one of activated adsorption. The area of the adsorbent was so small as measured by the BET-method that only its upper bound could be estimated from the limits of error of the method, hence the lower bound of the rate of adsorption per unit area and that of *B* as

$$\log_{10} B > -1.49 \pm 0.34. \quad (27. E)$$

The first order rate**) $k_+ = (2.303/t) \log_{10} P_0^{H_2}/P^{H_2}$ calculated from the observation, given in the original paper³⁸⁾, of hydrogen pressure $P_0^{H_2}$ or P^{H_2} at time $t=0$ or t is 0.00686, 0.0302, and 0.0879 hr⁻¹ at 300, 350 and 400°C respectively, each being a simple mean of observed values of $k_+ = (2.303/t) \log_{10} P_0^{H_2}/P^{H_2}$ at different time t . It requires, besides the surface area of the adsorbent, the volume of the space containing hydrogen to be adsorbed, to calculate i_0 , hence *B*.

The upper bound of the surface area A_1 per gm adsorbent is reversely calculated from the description in the paper³⁸⁾ that the lower bound of the covered fraction by 0.1 cc NTP hydrogen per gm adsorbent was 0.2 as calculated from the latter upper bound of the BET-area under the assumption that each hydrogen molecule occupies, when adsorbed, two copper atoms on the surface, which count 10¹⁵ per cm² of BET-area; the lower bound 0.2 of the covered fraction relates thus to A_1 , as

$$0.2 < \frac{0.1}{22400} \times 6.0 \times 10^{23} \times 2/10^{15} A_1$$

or

$$A_1 < 2.7 \times 10^4 \text{ cm}^2.$$

We have in consequence for the total area *A* of the reduced copper prepared from 2 gm

) It is possible for σ^ 's of such number to exist in the case of L. II-mechanism, where each σ^* consists of a pair of σ_1 and σ_2 , if σ_1 's and σ_2 's are arrayed in a checkered pattern each σ_1 being surrounded by σ_2 's and vice versa.

**) The values of k_+ given in Table 1 of Ref. 38) are not used, being erroneously calculated.

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copper oxide

$$A = 2 \times \frac{63.5}{79.5} A_1 < 4.3 \times 10^4 \text{ cm}^2,$$

where the factor by which A_1 is multiplied is the weight of reduced copper from 2 gm CuO.

No description is found in the paper³⁸⁾ on the volume V of the space containing hydrogen to be adsorbed except that the decrease of hydrogen pressure by 0.139 mmHg corresponds to the amount of adsorption of 0.1 cc NTP per gm adsorbent. The V is determined from the latter description for the adsorbent from 2 gm copper oxide, by the equation

$$760 \times \left(\frac{0.1 \times 2 \times 63.5 / 79.5}{V} \right) \times \frac{298}{273} = 0.139$$

as

$$V = 955 \text{ cc},$$

where the numerator of the fraction in the parentheses is the NTP volume of hydrogen adsorbed and the space containing hydrogen to be adsorbed is assumed to be at 25°C.

The "current density" i_0 at 300°C and 0.138 mmHg pressure of hydrogen is now given formally associating two elementary charges with every hydrogen molecule adsorbed, as

$$i_0 = 2Fk_+ \frac{V \times (273/T) \times (P/760)}{22400} / 3600A \text{ Amp cm}^{-2}.$$

Substituting for A its upper bound $4.3 \times 10^4 \text{ cm}^2$ and introducing the above value of V , we have the lower bound of i_0 , hence the lower bound of B according to (1) as given by (27. E).

The theoretical value of $\log_{10} B$ is calculated for the same conditions by (9. b) for a bare adsorbent surface, taking $n=1$ for the simple dissociative adsorption, as

$$\log_{10} B = -0.34, \quad 300^\circ\text{C}, \quad P^{\text{H}_2} = 0.138 \text{ mmHg}, \quad (27. T)$$

which conforms with the experimental lower bound of (27. E).

The first term of (9. b) counts for $G^* = 10^{15}$

$$\log_{10} 2\varepsilon \frac{kT}{h} G^* e = 10.02.$$

The second term is obtained for $n=1$ by (18) as

$$\frac{\bar{S}}{2.3R} = 11.56, \quad 300^\circ\text{C}, \quad P^{\text{H}_2} = 0.138 \text{ mmHg},$$

which exceeds the first term in magnitude at the specified condition. The last term $dT \log_{10} q_0^* / dT$ is calculated by (6. b) on the base of the values of ν_i^* / c of (15. a), assuming that it equals approximately that in case of nickel adsorbent, as

$$dT \log_{10} q_0^* / dT = 1.20, \quad 300^\circ\text{C}.$$

The last three equations give (27. T) according (9. b) for $n=1$. We see that

the increase of entropy with rise of temperature and decrease of hydrogen pressure renders $\log_{10} B$ negative as seen in (27. T) in conformity with the observed result of (27. E).

§ 7. Parahydrogen Conversion

The B -value is worked out from the classical work of FARKAS³⁹⁾ on catalyzed parahydrogen conversion at 125°C and 100 mmHg hydrogen pressure in the presence of nickel wire of 0.5 cm² area in a reaction vessel of about 500 cc volume, as

$$\log_{10} B = 3.13 \pm 0.75, \quad (28)$$

where 0.75 is the mean error.

The first order rate of parahydrogen conversion is given as $k_c = \frac{2.3}{t} \log_{10} \frac{u_0}{u_t}$, where u_t or u_0 is the excess fraction of parahydrogen over that in equilibrium at time t or $t=0$ respectively. The specific rate k_c is as well-known the sum of the specific rate k_+ of the conversion of para- to orthohydrogen and that k_- of the reverse one.

It is shown first, there could be no difference at such high a temperature as in question in the specific rate of parahydrogen being involved in the heterogeneous step of BONHOEFFER-FARKAS mechanism, *i.e.* the dissociative adsorption or that of RIDEAL-ELEY mechanism⁴⁰⁾, from that of orthohydrogen. Eq. (2) is written, removing the formal annex 2ε in conformity with the concept of specific rate, as

$$v_+ = \frac{kT}{h} \exp\left(\frac{\mu^I - \mu^*}{RT}\right),$$

where v_+ is the number of the unidirectional forward act of the heterogeneous step per unit time. The above equation is developed according to (5) and (8. a), as

$$v_+ = \frac{kT}{h} G^* q^* \theta_{\sigma^*(0)} \exp(n\mu^{H_2}/RT), \quad (29)$$

where $n=1$ for the dissociative adsorption or $n=3/2$ for the heterogeneous step of the RIDEAL-ELEY mechanism^{40)*}. The v_+ gives the rate per cm², if G^* is allotted to the same area. Substituting μ^{H_2} from (19. a), we have for the dissociative adsorption

$$v_+ = \frac{kT}{h} G^* q^* \theta_{\sigma^*(0)} N^{H_2} / Q^{H_2}.$$

The difference in the specific rate v_+/N^{H_2} is caused, if at all, by q^*/Q^{H_2} , other factors being common to para- and orthohydrogen. There exists no difference in the potential energy of the critical complex, hence in q^* according to (6) which is defined by the relevant potential energy, besides by the state of adsorption on the catalyst surface, which is of course common to both the kinds of hydrogen molecule. Neither is there any difference in Q^{H_2} , insofar as the rotational partition function is describable classically as in (19. b) at the high temperature in question. The specific rate v_+/N^{H_2} has thus no difference in this case.

*) *cf.* p. 19.

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The v_+ is expressed in case of RIDEAL-ELEY mechanism by (29) for $n=3/2$ and (19. a), as

$$v_+ = \frac{kT}{h} G^* q^* \theta_{\sigma^*(0)} \left(\frac{N_{H_2}}{Q_{H_2}} \right)^{\frac{3}{2}}, \quad (30)$$

which is transformed as below with particular reference to the specific rate of hydrogen molecule being involved in the heterogeneous step in this case. The $\theta_{\sigma^*(0)}$ is expressed as*

$$\theta_{\sigma^*(0)} = \theta_{\sigma^*(H)} \frac{\rho^{H(a)}}{q_{\sigma^*(H)}^{H(a)}}, \quad (31. a)$$

where $\theta_{\sigma^*(H)}$ is the probability of the seat σ^* of the critical complex of the heterogeneous step in question being occupied by one hydrogen adatom ready to form the appropriate critical complex there with a hydrogen molecule, $q_{\sigma^*(H)}^{H(a)}$ the BOLTZMANN factor of the reversible work required to bring up a hydrogen atom from its standard state onto σ^* and $\rho^{H(a)}$ is the BOLTZMANN factor of the chemical potential $\mu^{H(a)}$ of hydrogen adatom H(a) allotted to a single H(a), *i. e.*

$$\rho^{H(a)} = \exp(-\mu^{H(a)}/RT).$$

Because of the adsorption equilibrium prevailing, we have $2\mu^{H(a)} = \mu^{H_2}$, hence

$$\rho^{H(a)} = \exp(-\mu^{H_2}/2RT). \quad (31. b)$$

Eq. (30) is transformed by (31) and (19. a) as

$$v_+ = \frac{kT}{h} G^* \frac{q^*}{q_{\sigma^*(H)}^{H(a)}} \theta_{\sigma^*(H)} \frac{N_{H_2}}{Q_{H_2}},$$

from which it is similarly concluded that the specific rate v_+/N_{H_2} of hydrogen molecule being involved in the heterogeneous step is common to para- and orthohydrogen.

Let now k' be the common specific rate with which para- and orthohydrogen are involved in the heterogeneous step. The para- or orthohydrogen thus involved should be given back to gas phase at equilibrium ratio, *i. e.* 1 : 3, since otherwise the catalyst would shift the equilibrium. It follows that $k_+ = 3/4 \cdot k'$ and $k_- = 1/4 \cdot k'$ so that

$$k_c = k_+ + k_- = k'$$

or in other words k_c is the specific rate of the heterogeneous step, with which it involves para- and orthohydrogen equally.

) This sort of relations is generally formulated in Eq. (5.1) of Ref. 6), and in particular derived as follows. The $\theta_{\sigma^(0)}$ defined as $\partial C_{\sigma^*(0)} / \partial C$ (*cf.* footnote**) on p. 18) is identically expressed as

$$\theta_{\sigma^*(0)} = \frac{\partial C_{\sigma^*(0)}}{\partial C_{\sigma^*(H)}^{H(a)}} \frac{\partial C_{\sigma^*(H)}^{H(a)}}{\partial C^{H(a)}} \frac{\partial C^{H(a)}}{\partial C},$$

where $C^{H(a)}$ is the assembly derived from C by addition of one H(a) to C and $C_{\sigma^*(H)}^{H(a)}$ is $C^{H(a)}$ at the particular state that H(a) alone is seated in a definite σ^* with certainty and $\partial C^{H(a)}$ or $\partial C_{\sigma^*(H)}^{H(a)}$ is the partition function of $C^{H(a)}$ or $C_{\sigma^*(H)}^{H(a)}$ respectively. We have $\theta_{\sigma^*(H)} = \partial C_{\sigma^*(H)}^{H(a)} / \partial C^{H(a)}$ according to the property of partition function, that it is proportional to the probability of the appropriate state; we have on the other hand $q_{\sigma^*(H)}^{H(a)} = \partial C_{\sigma^*(H)}^{H(a)} / \partial C_{\sigma^*(0)}$ and $\rho^{H(a)} = \partial C^{H(a)} / \partial C$ according to the another property of the partition function that it is the BOLTZMANN factor of the appropriate free energy, where $q_{\sigma^*(H)}^{H(a)}$ or $\rho^{H(a)}$ is the BOLTZMANN factor of the respectively appropriate reversible work or increment of the free energy. Hence we have (31. a).

The i_0 is now calculated as the rate of the heterogeneous step similar to those in the other cases, as

$$i_0 = 2Fk_e \frac{V \times (273/T) \times (100/760)}{22400 A},$$

where $V = 500$ cc, $A = 0.5$ cm² and $T = 273 + 125$ according to the specified condition of the experiment; the numerator of the quotient is NTP volume of hydrogen present in the space of volume V . The B -value of (28) is obtained from i_0 determined as above from the observations³⁹⁾ of k_e at 50, 125, 150 and 200°C according to (1) by the method of least squares.

Theoretically $\log_{10} B$ is calculated according to the BONHOEFFER-FARKAS mechanism by (9.a) on the base of fundamental data given in §2 for the experimental condition of (28) (125°C, 100 mmHg hydrogen pressure) as detailed below, as

$$\log_{10} B = 6.89, \quad (32)$$

which is quite outside the limits of error of the experimental value of (28).

The experimental value may be smaller than the theoretical one, if the catalyst is poisoned to decrease G^* in (9.a) by *ca.* 10^4 factor, which appears, however, to be hardly the case, inasmuch as the catalyst is carefully protected from poison in the classic work³⁹⁾ underlying the experimental value (28) of B . A possible cause of this discrepancy is the deficiency of the proportional approximation resorted to in allowing for repulsions exerted by hydrogen adatoms; the B -value is free from this cause, if any, in case of the treatment of §4 and 6, where the repulsive interactions are taken constant or absent. Another cause might consist in the RIDEAL-ELEY mechanism⁴⁰⁾ being operative instead; if at all, n in (9.a) increases to $3/2$ to decrease $\log_{10} B$ to 2.89 in fair agreement with the experimental value of (28), provided that σ^* is identical with that in the BONHOEFFER-FARKAS mechanism and $-(u^*/2.3R) (\partial\theta/\partial T)_P$ as well as $dT \log_{10} q_0^*/dT$ does not so much increase by the increase of constituent hydrogen adatoms of the critical complex by one, as to upset the above agreement.

It would require a further refinement of the theoretical calculation of B in case of the presence of hydrogen adatoms in order to settle the underlying mechanism.

The value of $\log_{10} B$ in (32) is arrived at on the basis of the BONHOEFFER-FARKAS mechanism as follows. The first term of (9.a) is calculated for $G^* = 10^{15}$, the second term by (6. b) on the base of the numerical values of (15. a) and the third term for $n=1$ by (18) respectively as

$$\log_{10} 2\varepsilon \frac{kT}{h} G^* e = 9.86, \quad \frac{dT \log_{10} q_0^*}{dT} = 0.71, \quad \frac{\bar{S}^{\text{H}_2}}{2.3R} = 8.15. \quad (33. a), (33. b), (33. c)$$

The fourth term $(\partial T \log_{10} \theta_{\sigma^*(0)} / \partial T)_P$ of (9. a) is calculated by developing it according to (10. a), as

On the Law of Laidler, Glasstone and Eyring II.

$$\left(\frac{\partial T \log_{10} \theta \sigma^{*(0)}}{\partial T}\right)_P = \log_{10} \theta \sigma^{*(0)} - \theta \sigma^{*(0)} \left\{ 2\beta(1+\xi\beta) T \left(\frac{\partial \log_{10} \beta}{\partial T}\right)_P + \xi\beta^2 T \frac{d \log_{10} \xi}{dT} \right\}. \quad (34)$$

The factor $d \log_{10} \xi / dT$ implied is readily determined by (11. b) and (14. c) as $u_1/2.3RT$; β and $(\partial \log_{10} \beta / \partial T)_P$ in (34) are evaluated as follows. The β implies θ and τ as seen in (11). In the foregoing paper⁵⁾, the values of θ have been prescribed and the appropriate values of β and of overvoltage η included in τ in that case determined. In the present case, the θ - and β -values are determined for the adsorption equilibrium, which corresponds to the particular case of the foregoing paper⁵⁾, where $\eta=0$. The τ is calculated by (12) on the base of the numerical values of (13) and (15. b), taking $I=4.664 \times 10^{-11}$ *) as in the previous work⁵⁾.

The θ and β are now determined by trial and error according to (10. b) and (11) on the base of the numerical values of (14. b) and (14. c); practically, a trial value of θ is put into (11. a) and the β -value thus obtained is substituted into (10. b) to calculate θ , the trial value of θ being varied until the trial and the resultant values coincide with each other. The values thus obtained are

$$\tau = 4.381 \times 10^3, \quad \theta = 0.8089, \quad \beta = 6.255. \quad (35. \tau), (35. \theta), (35. \beta)$$

The $(\partial \log_{10} \beta / \partial T)_P$ implied in (34) as well as $(\partial \theta / \partial T)_P$ in the last term of (9. a) is obtained by solving the two simultaneous equations of them, which are derived by differentiating (10. b) and (11. a) with respect to T , as

$$T \left(\frac{\partial \log_{10} \beta}{\partial T}\right)_P = \frac{\frac{d(T \ln \tau)}{2.3 dT} - \log_{10} \beta - \frac{(u-u_1)u_1}{2.3(RT)^2} - \frac{\xi\beta}{1+\xi\beta} \theta(1-\theta)}{1 + \frac{u-u_1}{RT} \theta(1-\theta)\varphi}. \quad (36. a)$$

and

$$\left(\frac{\partial \theta}{\partial T}\right)_P = \frac{(-\ln \beta/T + dT \ln \tau / T dT)\varphi + \xi\beta u_1 / (1+\xi\beta) RT^2}{1/\theta(1-\theta) + (u-u_1)\varphi / RT}, \quad (36. b)$$

where

$$\varphi = \left(\frac{1}{1+\beta} + \frac{\xi\beta}{1+\xi\beta}\right). \quad (36. c)$$

The differential coefficient $dT \ln \tau / dT$ comprised both in (36. a) and (36. b) is determined from (12) similarly as in Part I, as

$$\frac{dT \ln \tau}{dT} = \frac{1}{2} \ln \frac{1.360 \times 980.5 Ph^5}{(2\pi m k T)^{3/2} 4\pi^2 I (kT)^2} - \frac{7}{4} - \sum_{j=1}^3 \left[\ln \left\{ 1 - \exp\left(-\frac{h\nu_j}{kT}\right) \right\} - (h\nu_j/kT) \left\{ \exp(h\nu_j/kT) - 1 \right\}^{-1} \right]. \quad (37)$$

The $\theta \sigma^{*(0)}$ and the last two terms of (9. a) are computed by (11. a), (11. b), (34) and (36) on the base of numerical values of (14) and (35), as

$$\theta \sigma^{*(0)} = 0.0263$$

and

$$(\partial T \log_{10} \theta \sigma^{*(0)} / \partial T)_P = 1.66, \quad -\frac{u^*}{2.3R} \left(\frac{\partial \theta}{\partial T}\right)_P = 2.80. \quad (38. a), (38. b)$$

*) Landolt "Tabellen" 5, Erg. III c, p. 2349 (1936).

The numerical results of (33) and (38) complete the value of $\log_{10} B$ of (32) according to (9. a) for the BONHOEFFER-FARKAS mechanism.

§ 8. Conclusive Remark

The present work is an extension of the previous ones^{2,5)} on the theoretical interpretation of the law of LAIDER, GLASSTONE and EYRING that $\log_{10} B$ has approximately common value 3 ± 2 for different hydrogen electrode reaction. The $\log_{10} B$ is defined for any heterogeneous step, which involves hydrogen molecule by associating formally two elementary charges with every hydrogen molecule involved in the step. It is thus shown that $\log_{10} B$ is a sole function of the activation entropy Δ^*S and temperature, where Δ^*S is defined as the increment of entropy of the whole assembly concerned as caused by raising the system of particles participating the heterogeneous step in question from its initial state to the critical state. The $\log_{10} B$ is thus regarded as an alternative expression of Δ^*S , which implies useful informations on the underlying mechanism.

Since Δ^*S depends among others upon the entropy of hydrogen gas, which varies with the temperature and its pressure, $\log_{10} B$ is in general a function of the latter variables rather than a constant. The theoretical value of $\log_{10} B$ is thus found even negative in conformity with the experimental one in case of adsorption of hydrogen on copper at high temperature and low hydrogen pressure as shown in § 6. Rather definite value of B in case of hydrogen electrode reaction might be due to the definite temperature and hydrogen pressure, to which the experimental condition appears to be technically restricted.

The important basis of the theoretical calculation of B is that G^* is of the order of magnitude of 10^{15} per cm^2 of BET area, as based on the crystal plane model of metallic catalyst as reviewed in § 3. This basis is regarded as confirmed by the agreement of the observed value of $\log_{10} B$ for the catalyzed hydrogenation of ethylene in the presence of nickel with the theoretical value as deduced according to either the associative mechanism or the desorption mechanism^{*)} which fits in with observed kinetics of the hydrogenation and further by the result on the adsorption rate of hydrogen on copper described in § 6, which is alternatively stated that the lower bound of G^* is 10^{14} per cm^2 BET-area. The G^* -value thus confirmed provides an experimental method, referred to in § 5, of deciding the alternative mechanisms mentioned above of the catalyzed hydrogenation of ethylene.

It is suspected, however, that the proportional approximation resorted to

*) Cf. § 5.

in Part I and in the present work in accounting for the effect of hydrogen adatoms on B is not precise enough in case of their high population. The calculation of the latter effect by higher approximations is going on in this laboratory. Settlement of this problem would render B or Δ^*S a useful criterion for deciding the mechanism.

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