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THEORY OF HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

II. Quantitative Determination of Characteristic Rate Functions $\{\tilde{\kappa}(s)\}$'s of Constituent Steps s 's of the Associative Mechanism

By

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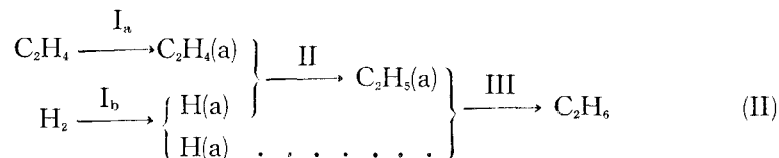
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Introduction

It has been shown in Part I¹⁾ that experimental data of the catalyzed hydrogenation of ethylene



in the presence of metallic catalyst and associated reactions are semiquantitatively reproduced on the basis of the associative mechanism^{2)**)}



in terms of statistical-mechanical function $\{\tilde{\kappa}(s)\}$'s each characteristic of step s involved, *i. e.* I_a , I_b , II or III , where (a) denotes adsorbed states. The associated reactions are deuterium exchange, parahydrogen conversion, equilibration



and so on in the course of hydrogenation, where P denotes protium. P and D will be represented by H and called hydrogen in what follows as in Part I¹⁾. It was shown¹⁾ that the rate of deuterium exchange of ethylene or hydrogen respectively defined as

$$E^E = n^E \dot{X} / (Y - X), \quad E^H = n^H \dot{Y} / (X - Y) \quad (\text{IV. E}) (\text{IV. H})$$

is not necessarily identical with but possibly different from each other during

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^{**)} Associative mechanism means here simply the sequence of steps indicated by (II), without the rate-determining step being specified as in the original presentation (Ref. 2).

the progress of the catalyzed hydrogenation, unless there exists particularly a relation $n^E \dot{X} + n^H \dot{Y} = 0$ as in cases of simple exchange, when neither the amounts of the exchange partners nor the total amounts of isotopes are changed, where n^E or n^H is the number of hydrogen atoms and X or Y the deuterium atomic fraction respectively in ethylene **E** or hydrogen **H** in gas. The rate of parahydrogen conversion E^p or that E^i of equilibration is defined as

$$E^p = n^H/2 \cdot \dot{x}^p / (x_\infty^p - x^p), \quad E^i = n^H/2 \cdot \dot{u},$$

where x^p is the mol fraction of parahydrogen, x_∞^p its value at equilibrium of parahydrogen conversion of the hydrogen present and $u = n^{PD}/n_\infty^{PD}$ is the fraction of the number n^{PD} of PD molecules over its particular value n_∞^{PD} at equilibrium of $P_2 + D_2 = 2PD$ of the hydrogen present.

The experimental data were reproduced by expressing the steady rate V_s of the catalyzed hydrogenation as well as E^E , E^H , E^p and E^i by $\mathfrak{K}(s)$'s, which are each the forward rate of step s at the steady state of the overall reaction (I) multiplied by a factor $a_e^{I(s)}/a^{I(s)}$ of increase of the activity of the initial complex $I(s)$ of step s from that $a^{I(s)}$ at the steady state to that $a_e^{I(s)}$ at equilibria of all steps but s . Under the assumption of bare and homogeneous catalyst's surface, $\mathfrak{K}(s)$ was statistical-mechanically expressed as a function of partial pressures of **E** and **H** and temperature, which function comprized the appropriate activation energy $\mathcal{A}^* \varepsilon(s)$ as a unique adjustable parameter. By fitting $\mathcal{A}^* \varepsilon(s)$ to experiments or estimating it theoretically, the following experimental data were semiquantitatively reproduced¹⁾.

1. Optimum temperature of the catalyzed hydrogenation and its variation with partial pressures³⁾⁴⁾⁵⁾⁶⁾.
2. The excess activation energy $RT^2 \partial \ln E^H / \partial T$ of the associated hydrogen exchange⁷⁾⁸⁾ over that $RT^2 \partial \ln V_s / \partial T$ of the catalyzed hydrogenation.
3. The predominance of C_2P_6 in the initial product of catalyzed interaction of C_2P_4 with D_2 ⁹⁾¹⁰⁾.
4. Inhibition of the catalyzed equilibration $P_2 + D_2 = 2PD$ by ethylene.
5. Increase of the initial value of u with increase of temperature in the catalyzed interaction of C_2P_4 with D_2 ⁸⁾.

The above theory has led on the other hand to the following predictions¹⁾.

- a. Kinetics of V_s , E^H , E^E , E^p and E^i at different temperatures.
- b. Relation that

$$V_s = E^E/2 > E^H/2 = E^p > (E_0^i)_{Y=1/2} \quad \text{or} \quad E^p = (E_0^i)_{Y=1/2} > E^E/2 = E^H/2 > V_s$$

respectively at temperature below or above the optimum referred to in 1. above, where E_0^i is E^i at $u=0$. E^E thus diverges from E^H at lower temperatures below

the optimum but coincides with E^h above.

c. No inhibition of equilibration by ethylene at temperatures above the optimum.

It is the purpose of the present paper to fit the functions $\mathfrak{K}(s)$ closer in with experiments by allowing for adsorption for a precise verification of the associative mechanism in terms of these functions.

§ 1 General Procedure

The general procedure developed in Part I^D of deriving observable quantities in terms of $\mathfrak{K}(s)$'s will first be reviewed below, so far as necessary for the present developments.

The steady condition of the catalyzed hydrogenation is stated in accordance with Scheme (II) as

$$V_s = \bar{v}(s) - \bar{v}(s), \quad s = I_a, I_b, II, III, \quad (1.1)$$

where $\bar{v}(s)$ and $\bar{v}(s)$ are the forward and backward rates of step s . The $\bar{v}(s)$ and $\bar{v}(s)$ are expressed generally as¹⁸⁾¹⁸⁾¹⁹⁾

$$\bar{v}(s) = \kappa(s) \frac{kT}{h} p^{*(s)}/p^{I(s)}, \quad \bar{v}(s) = \kappa(s) \frac{kT}{h} p^{*(s)}/p^{F(s)}, \quad (1.2. I), (1.2. F)$$

where $\kappa(s)$ is the transmission coefficient, k or h the BOLTZMANN or PLANCK constant and T the absolute temperature; p^δ is the BOLTZMANN factor of the chemical potential μ^δ or the reciprocal of the absolute activity a^δ of a group δ of particles inclusive of the initial complex $I(s)$, the critical complex $*(s)$ and the final complex $F(s)$ of step s , *i. e.*

$$p^\delta = \exp(-\mu^\delta/RT), \quad (1.3)$$

where R is the gas constant.

$\mathfrak{K}(s)$'s are now introduced in accordance with (1.2) as

$$\bar{v}(s) = \mathfrak{K}(s) p_e^{I(s)}/p_e^{I(s)}, \quad \bar{v}(s) = \mathfrak{K}(s) p_e^{F(s)}/p_e^{F(s)} \quad (1.4. \bar{v}) (1.4. \bar{v})$$

or defined as

$$\mathfrak{K}(s) = \kappa(s) \frac{kT}{h} p^{*(s)}/p_e^{I(s)}, \quad (1.4. \mathfrak{K})$$

where $p_e^{I(s)}$ is the particular value of $p^{I(s)}$ at equilibria of all steps but s . $\mathfrak{K}(s)$ differs from $\bar{v}(s)$ as seen from (1.4) only by the factor $p^{I(s)}/p_e^{I(s)}$ or $a_e^{I(s)}/a^{I(s)}$ as mentioned in the introduction but reserves $p^{*(s)}$ appropriate to the steady state.

It has been shown¹⁾ on the basis of the above definitions that¹⁾

$$p_e^{I(a)} = p^E, \quad p_e^{I(b)} = p^H, \quad p_e^{I(II)} = p^E (p^H)^{1/2}, \quad p_e^{I(III)} = p^E p^H, \\ (1.5. I_a), (1.5. I_b), (1.5. II), (1.5. III)$$

$$\bar{v}(I_a) = \mathfrak{K}(I_a), \quad \bar{v}(I_a) = \gamma(C_2H_4) \mathfrak{K}(I_a), \quad (1.6. I_a)$$

$$\bar{v}(I_b) = \mathfrak{K}(I_b), \quad \bar{v}(I_b) = \gamma(H)^2 \mathfrak{K}(I_b), \quad (1.6. I_b)$$

$$\bar{v}(II) = \gamma(H) \gamma(C_2H_4) \mathfrak{K}(II), \quad \bar{v}(II) = \gamma(C_2H_5) \mathfrak{K}(II), \quad (1.6. II)$$

$$\bar{v}(III) = \gamma(H) \gamma(C_2H_5) \mathfrak{K}(III), \quad \bar{v}(III) = \Gamma \mathfrak{K}(III), \quad (1.6. III)$$

where

$$\gamma(C_2H_4) = \frac{p^E}{p^{C_2H_4(a)}}, \quad \gamma(H) = \frac{(p^H)^{1/2}}{p^{H(a)}}, \quad \gamma(C_2H_5) = \frac{p^E (p^H)^{1/2}}{p^{C_2H_5(a)}}, \\ (1.7. C_2H_4), (1.7. H), (1.7. C_2H_5)$$

$$\Gamma = P^A / K_P P^E P^H, \quad (1.8. \Gamma)$$

$$K_P = P_e^A / P_e^E P_e^H. \quad (1.8. K)$$

P^E , P^H and P^A are partial pressures of E, H and A respectively and those with suffix e their particular values at equilibrium of the reaction $C_2H_4 + H_2 = C_2H_6$.

The steady condition (1.1) is now developed according to (1.6), as

$$V_s = \mathfrak{K}(I_a)(1 - \gamma(C_2H_4)) = \mathfrak{K}(I_b)(1 - \gamma(H)^2) = \mathfrak{K}(II)(\gamma(H)\gamma(C_2H_4) - \gamma(C_2H_5)) \\ = \mathfrak{K}(III)(\gamma(H)\gamma(C_2H_5) - \Gamma). \quad (1.9)$$

Γ is positive by definition and has the values 5×10^{-26} at 200°K and 2.7×10^{-6} at 500°K for $P^E = P^H = P^A = 10$ mmHg, monotonously increasing with temperature. It follows in general from (1.9)¹⁾ for Γ less than unity that V_s is positive and that $\gamma(C_2H_4)$, $\gamma(H)$ and $\gamma(C_2H_5)$ are all positive and less than unity, *i. e.*

$$0 < \gamma(C_2H_4), \gamma(H), \gamma(C_2H_5) < 1, \quad (1.10)$$

$$\frac{V_s}{1 - \Gamma} < \mathfrak{K}(s), \quad s = I_a, I_b, II, III, \quad (1.11)$$

and that $V_s/(1 - \Gamma)$ approaches $\mathfrak{K}(r)$, if one $\mathfrak{K}(r)$ of $\mathfrak{K}(s)$'s gets smaller than all other $\mathfrak{K}(s)$'s and inverse.(1.12)

Step r is called the rate-determining step, when $\mathfrak{K}(r)$ is sufficiently smaller than all other $\mathfrak{K}(s)$'s. $\mathfrak{K}(s)$'s defined above are written, according to (1.4), in the form

$$\mathfrak{K}(s) = k(s)/p_e^{I(s)} = k(s)a_e^{I(s)}, \quad (1.13. \mathfrak{K})$$

where

$$k(s) = \kappa(s) \frac{kT}{h} p^{*(s)} \quad (1.13. k)$$

and

$$a_e^{I(s)} = (p_e^{I(s)})^{-1}. \quad (1.13. a)$$

The $k(s)$ might be termed the appropriate rate constant, although not necessarily a constant, which is developed¹⁾¹³⁾ as

$$k(s) = \kappa(s) \frac{kT}{h} G^* q^{*(s)} \Theta_{\sigma_s^*(0)}, \quad (1.14)$$

where $\Theta_{\sigma_s^*(0)}$ is the probability of a site σ_s^* for the critical complex $*(s)$ of step s being unoccupied or ready to accept $*(s)$, $q^{*(s)}$ is the BOLTZMANN factor of the work $\varepsilon^{*(s)}$ required to bring up the constituents of $*(s)$ from their respective standard states onto a definite site σ_s^* preliminarily evacuated, at the statistical-mechanical equilibrium of the whole system of a definite composition, *i. e.*

$$q^{*(s)} = \exp(-\varepsilon^{*(s)}/RT) \quad (1.15)$$

and G^* is the total number of σ_s^* 's present^{*}.

The $\gamma(C_2H_4)$, $\gamma(H)$ and $\gamma(C_2H_5)$ are according to (1.7) the respective relative activities of $C_2H_4(a)$, $H(a)$ and $C_2H_5(a)$ referred to the state at equilibria of $C_2H_4(a) \rightleftharpoons E$, $H(a) \rightleftharpoons \frac{1}{2} H$ and $C_2H_5(a) \rightleftharpoons E + \frac{1}{2} H$ ^{**}.

The following two points will be remarked in connection with the above summary for the sake of the present application.

(A) Eq. (1.9) states that the relative values of $\mathfrak{K}(s)$'s fix $\gamma(C_2H_4)$, $\gamma(H)$ and $\gamma(C_2H_5)$, hence those of $\bar{v}(s)$'s and $\bar{v}(s)$'s according to (1.6). The relative values of $\bar{v}(s)$'s and $\bar{v}(s)$'s determine now those of V_s , E^E , E^H , E^p and E^q as seen from Eqs. (2.2), (4.5), (4.8), (5.8) and (6.2) of Part I¹⁾. The relative values of the rates of evolution of different deuterostitution products of **E**, **H** and **A** are also fixed by those of $\mathfrak{K}(s)$'s as shown in §7.

Conversely, the relative magnitudes of $\mathfrak{K}(s)$ are determined purely experimentally from those of any four of the above observable quantities, which are

*) The expression $p^{*(s)} = G^* q^{*(s)} \Theta_{\sigma_s^*(0)}$ or (1.14) of $k(s)$ is valid in the case when all σ_s^* 's are physically identical with each other; otherwise $p^{*(s)}$ or $k(s)$ must be the sum of contributions of the groups each of physically identical σ_s^* 's. If the catalyst's surface consists of lattice planes (Ref. 15), these groups are discrete in their properties and one of them may be predominant in contribution to $p^{*(s)}$, as if it were the sole one existing. We will call such catalyst's surface as providing every adsorptive inclusive of $*(s)$ practically with physically identical sites of adsorption, simply homogeneous. The $\varepsilon^{*(s)}$ in (1.15) will be taken constant independent of temperature in the absence of interaction between $*(s)$ and surrounding adsorptives, neglecting the excited states on account of appreciably high vibrational frequencies due to a narrow space of molecular dimension, in which $*(s)$ is confined.

**) Note that $p^{I(s)} = p^{F(s)}$ for every step in equilibrium according to (1.3).

given as independent functions of $\mathfrak{K}(s)$'s. Absolute values of the four decide $\mathfrak{K}(s)$'s absolutely of course.

(B) $\mathfrak{K}(s)$'s are in general affected by adsorption and in consequence vary with the relative activities $\gamma(\text{C}_2\text{H}_4)$, $\gamma(\text{H})$ and $\gamma(\text{C}_2\text{H}_6)$ of the adsorbed intermediates at the steady state in accordance with (1.13. \mathfrak{K}), (1.14) and (1.15), inasmuch as $\Theta_{\sigma_s^*(0)}$ varies with the activities of adsorbed intermediates and $\varepsilon^{*(s)}$'s, too, through the interaction of $* (s)$ with them. Systematic data of V_s , E^E etc. provide, according to (A) above, the knowledge of $\mathfrak{K}(s)$'s as functions of $\gamma(\text{C}_2\text{H}_4)$ etc. besides of partial pressures and temperature, which might lead us to the laws governing the individual constituents s 's of the overall reaction, although our present experimental knowledges are far from sufficient in this regard.

§ 2. Approximate Form of $\mathfrak{K}(s)$'s in the Absence of Adsorption

$\mathfrak{K}(s)$'s in the absence of adsorption have been recasted¹⁾ into a form $A \cdot \exp(-B/RT) \cdot P$, where A and B are constants and P the product of powers of P^E and P^H in mmHg, for the sake of an expedient analysis, as

$$\mathfrak{K}(\text{I}_a) = \rho(\text{I}_a) \frac{P^E}{Q_P^E} \exp\left(-\frac{\Delta^* \varepsilon(\text{I}_a)}{RT}\right), \quad (2.1. \text{I}_a)$$

$$\mathfrak{K}(\text{I}_b) = \rho(\text{I}_b) \frac{P^H}{Q_P^H} \exp\left(-\frac{\Delta^* \varepsilon(\text{I}_b)}{RT}\right), \quad (2.1. \text{I}_b)$$

$$\mathfrak{K}(\text{II}) = \rho(\text{II}) \frac{P^E}{Q_P^E} \left(\frac{P^H}{Q_P^H}\right)^{1/2} \exp\left(-\frac{\Delta^* \varepsilon(\text{II})}{RT}\right), \quad (2.1. \text{II})$$

$$\mathfrak{K}(\text{III}) = \rho(\text{III}) \frac{P^E}{Q_P^E} \frac{P^H}{Q_P^H} \exp\left(-\frac{\Delta^* \varepsilon(\text{III})}{RT}\right), \quad (2.1. \text{III})$$

where

$$\rho(s) = \kappa(s) \frac{kT_N}{h} e^{G^{*(s)}} \Theta_{\sigma_s^*(0)}, \quad (2.2)$$

$$\Delta^* \varepsilon(\text{I}_a) = \varepsilon^{*(\text{I}_a)} + RT_N - \varepsilon^E, \quad \Delta^* \varepsilon(\text{I}_b) = \varepsilon^{*(\text{I}_b)} + RT_N - \varepsilon^H, \quad (2.3. \text{I}_a), (2.3. \text{I}_b)$$

$$\Delta^* \varepsilon(\text{II}) = \varepsilon^{*(\text{II})} + RT_N - \varepsilon^E - 1/2 \cdot \varepsilon^H, \quad (2.3. \text{II})$$

$$\Delta^* \varepsilon(\text{III}) = \varepsilon^{*(\text{III})} + RT_N - \varepsilon^E - \varepsilon^H, \quad (2.3. \text{III})$$

$$\varepsilon^E := \varepsilon_0^E + 4RT_N, \quad \varepsilon^H := \varepsilon_0^H + 7/2 \cdot RT_N, \quad (2.4. \text{E}), (2.4. \text{H})$$

ε_0^E or ε_0^H is the energy of the ground state per mol of the respective gas, ε^E or ε^H its partial molar enthalpy by definition at T_N i.e. a certain medium temperature over the range of temperature in question. $\Theta_{\sigma_s^*(0)}$ in (2.2) is unity

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in the absence of adsorption. The $\rho(s)$'s are common to all s 's, provided that $G^{*(s)}$'s, $\theta_{\sigma_s^*(s)}$'s and $\kappa(s)$'s are so respectively. Q_P^E or Q_P^H is defined as

$$Q_P^E = \frac{kT_N}{1333} e^{\epsilon} Q_0^E(T_N), \quad Q_P^H = \frac{kT_N}{1333} e^{7/2} Q_0^H(T_N) \quad (2.5. E), (2.5. H)$$

in mmHg, where $Q_0^E(T_N)$ or $Q_0^H(T_N)$ is the particular value at $T = T_N$ of Q_0^E or Q_0^H defined as^{*}

$$Q_0^E = \frac{(2\pi m^E kT)^{3/2}}{h^3} \frac{8\pi^2 (2\pi I^E kT)^{3/2}}{s^E h^3} \prod_{j=1}^{12} \left\{ 1 - \exp\left(-\frac{h\nu_j}{RT}\right) \right\}^{-1}, \quad (2.6. E)$$

$$Q_0^H = \frac{(2\pi m^H kT)^{3/2}}{h^3} \frac{8\pi^2 I^H kT}{s^H h^2}, \quad (2.6. H)$$

m^E or m^H and s^E or s^H are the mass and the symmetry number of the molecule **E** or **H**, I^H the moment of inertia of **H**, I^E the geometric mean of the three principal moments of inertia I_A^E , I_B^E and I_C^E of **E** and ν_j the frequency of j -th normal vibration of **E**.

The p^E and p^H of (1.3) are given¹⁾¹³⁾ as

$$p^E = Q^E/N^E, \quad p^H = Q^H/N^H, \quad (2.7. E), (2.7. H)$$

where N^E or N^H is the concentration of **E** or **H** and

$$Q^E = Q_0^E \exp(-\epsilon_0^E/RT), \quad Q^H = Q_0^H \exp(-\epsilon_0^H/RT), \quad (2.8. E), (2.8. H)$$

or approximately as

$$p^E = Q_P^E \exp(-\epsilon^E/RT)/P^E, \quad p^H = Q_P^H \exp(-\epsilon^H/RT)/P^H, \quad (2.9. E), (2.9. H)$$

which are of the form $A \exp(-B/RT) \cdot P$, too, and exactly reproduce (2.7) at T_N . Numerical values of Q_P^E and Q_P^H are worked out according to (2.5) and (2.6) for T_N of 100°C as^{**)}

$$Q_P^E = 3.939 \times 10^{14} \text{ mmHg}, \quad Q_P^H = 1.057 \times 10^{10} \text{ mmHg}. \quad (2.10. E), (2.10. H)$$

The $\ln \mathfrak{F}(s)$'s are respectively linear functions of $1/T$ according to (2.1), which intercept the height $\ln \rho(I_s) P^E/Q_P^E$ etc. at the ordinate $1/T = 0$. It has been concluded on their basis in Part I¹⁾ from the strict proportionality of V_s to

^{*}) The vibrational partition function makes a slight difference in the case of ethylene but none practically in the case of hydrogen. The vibrational partition function of ethylene was left out by mistake in Eqs. (11.4.E), (13.2.E) and (13.7.E) of Part I (Ref. 1), whereas correctly included in the numerical values of Eq. (13.7.E) there.

^{***)} Basic data are $h = 6.6252 \times 10^{-27}$ erg. sec., $k = 1.3804 \times 10^{-16}$ erg/deg, $T(0^\circ\text{C}) = 273.15^\circ\text{K}$, $I^H = 0.4602 \times 10^{-40}$ cm²gm (Ref. 16), $I_A^E = 33.85 \times 10^{-40}$ cm²gm (ib.), $I_B^E = 28.08 \times 10^{-40}$ cm²gm (ib.), $I_C^E = 5.752 \times 10^{-40}$ cm²gm (ib.) and vibrational frequencies given in Ref. 17.

P^H at $P^E=0.03$ mmHg as observed by ZUR STRASSEN³⁾ that either I_b or III must be the rate-determining step in accordance with the equation^{*)}

$$\frac{1-\Gamma}{V_s} = \frac{1}{\mathfrak{K}(I_b)} + \frac{1}{\mathfrak{K}(III)} . \quad (2.11)$$

The observed $\ln V_s$ increases or decreases with increases of $1/T$ approximately linearly at higher or lower temperatures of observation attaining a maximum intermediately. It follows that, noting negligibly small Γ compared with unity^{**)}, either of $\mathfrak{K}(I_b)$ and $\mathfrak{K}(III)$ is alternatively smaller than the other, so that the reciprocal of the smaller one is predominant on the right of (2.11), hence the straight lines of $\ln \mathfrak{K}(I_b)$ and $\ln \mathfrak{K}(III)$ versus $1/T$ intersect each other in the neighbourhood of the optimum. Putting $\mathfrak{K}(I_b)$ and $\mathfrak{K}(III)$ equal to each other at the temperature T_x of the intersection, we have from (2.1) and (2.10. E)

$$\Delta^* \varepsilon(I_b) - \Delta^* \varepsilon(III) = RT_x \ln Q_p^E/P^E = 24.6 \text{ kcal} , \quad (2.12)$$

identifying T_x with the optimum temperature *ca.* 60°C of the zur Starssen's experiment, where $P^E=0.03$ mmHg.

This amounts more than twice as large as the corresponding experimental value *ca.* 10 kcal deduced, in accordance with (2.11), as the excess of the inclination of $\ln V_s$ against $-1/RT$ at lower temperature over that at higher temperature. This discrepancy indicates that the linear form (2.1) of $\ln \mathfrak{K}(s)$ against $1/T$ based on the assumption of absence of adsorption is too crude quantitatively to account for the experimental results.

We proceed in subsequent sections to determine $\mathfrak{K}(s)$'s allowing for the adsorption.

§ 3. The Effect of Adsorption

The linear form (2.1) of $\ln \mathfrak{K}(s)$'s versus $1/T$ rests upon the assumption of absence of adsorption besides those of homogeneous catalyst's surface^{***)} and of negligible probability of excited states of the critical complex as mentioned in the foregoing section.

Adsorption varies the rate constant $k(s)$ according to (1.14) by diminishing $\Theta_{\sigma^*(s)}$ and by changing $\varepsilon^{*(s)}$ or $q^{*(s)}$ in accordance with (1.15) through the interaction of adsorptives with $*(s)$. It may be noted with regard to the latter effect of adsorption that the coverage of hydrogen at adsorption equilibrium, even appreciably lower than unity, varies extraordinarily slowly with hydrogen pressure¹¹⁾¹⁴⁾ and temperature¹²⁾¹⁴⁾ compared especially with in the case of ethylene.

*) Cf. (1.12).

***) Cf. § 1.

***) Cf. footnote *) on p. 167.

The latter result is only explicable, under the assumption of homogeneous catalyst's surface^{*}), by admitting an extraordinarily strong repulsive interactions between adsorbed hydrogen atoms¹³⁾.

Coverage θ of dissociative adsorption of hydrogen is expressed statistical-mechanically as^{***)}

$$\frac{\theta}{1-\theta} = q^{\text{H(a)}} / p^{\text{H(a)}}, \quad (3.1)$$

where $q^{\text{H(a)}}$ is, similarly as $q^{*(a)}$ defined by (1.15), the BOLTZMANN factor of the work $\varepsilon^{\text{H(a)}}$ required to bring up H(a) onto a definite, preliminarily evacuated site σ at the statistical-mechanical equilibrium of the whole system of a definite composition^{***)}, *i. e.*

$$q^{\text{H(a)}} = \exp(-\varepsilon^{\text{H(a)}}/RT). \quad (3.2)$$

Eliminating p^{H} , $p^{\text{H(a)}}$ and $q^{\text{H(a)}}$ from (1.7.H), (2.9.H), (3.1) and (3.2), we have

$$RT \ln \frac{\theta}{1-\theta} + \varepsilon^{\text{H(a)}} - \frac{1}{2} \varepsilon^{\text{H}} = \frac{RT}{2} \ln \frac{P^{\text{H}}}{Q_P^{\text{H}}} + RT \ln r(\text{H}), \quad (3.3)$$

where the second term on the right vanishes at equilibrium of chemisorption of H, when $r(\text{H})=1$ by (1.3) and (1.7.H).

Differentiating the above equation with respect to T or P' , *i. e.*

$$P' \equiv r(\text{H})^2 P^{\text{H}}, \quad (3.4)$$

assuming that $\varepsilon^{\text{H(a)}}$ is a function solely of θ , we have

$$\left(\frac{\partial \theta}{\partial \ln T} \right)_{P'} = - \left\{ \ln \frac{\theta}{1-\theta} + \frac{1}{2} \ln \frac{Q_P^{\text{H}}}{P'} \right\} \left\{ \frac{1}{\theta(1-\theta)} + \frac{d\varepsilon^{\text{H(a)}}}{d\theta} / RT \right\} \quad (3.5.T)$$

or

$$\left(\frac{\partial \theta}{\partial \ln P'} \right)_T = \frac{1}{2} \left\{ \frac{1}{\theta(1-\theta)} + \frac{d\varepsilon^{\text{H(a)}}}{d\theta} / RT \right\}^{-1}. \quad (3.5.P)$$

The differential coefficients $(\partial\theta/\partial \ln T)_{P'}$ and $(\partial\theta/\partial \ln P')_T$ are determined severally from adsorption isotherms of hydrogen on evaporated tungsten film¹⁴⁾ observed at different temperatures, where $P' = P^{\text{H}}$ by (3.4), as $(\partial\theta/\partial \ln T)_{P'} = -0.235$ and $(\partial\theta/\partial \ln P')_T = 1.26 \times 10^{-2}$ at 0°C , $P' = P^{\text{H}} = 5 \times 10^{-3}$ mmHg and $\theta = 0.725$, from which we have according to (3.5.T) and (3.5.P) respectively

$$d\varepsilon^{\text{H(a)}}/d\theta = 59 RT \quad \text{and} \quad d\varepsilon^{\text{H(a)}}/d\theta = 35 RT.$$

These values are of the same order of magnitude, unanimously showing an extraordinarily strong repulsive interactions, which diminishes both $(\partial\theta/\partial \ln T)_{P'}$ and $(\partial\theta/\partial \ln P')_T$ *ca.* tenfold from those in its absence as seen from (3.5).

The strong repulsive interaction between H(a)'s should necessarily accompany the increase of $\varepsilon^{*(\text{I}_b)}$ with increase of their coverage, since the potential of $*(\text{I}_b)$ due to interactions with surrounding H(a)'s is, in zeroth order approximation,

*) Cf. footnote *) on p. 167.

**) Cf. Eq. (5.1) of Ref. 13.

***) Cf. §2 of Ref. 13.

the sum of those of individual constituent hydrogen atoms of $\ast(I_b)^{\ast 15}$. This effect may vary $\Delta^\ast\epsilon(I_b) - \Delta^\ast\epsilon(III)$ along with the change of θ in accordance with (2.3), provided that H(a)'s affect $\epsilon_0^{\ast(III)}$ differently from $\epsilon_0^{\ast(I_b)}$, which is quite probable because of a good deal of compensation of the repulsion by VAN DER WAALS' attraction expected in the former case from a larger polarizability of a larger critical complex of $\ast(III)$ composed of $C_2H_5(a)$ and H(a).

The effect of H(a) upon the difference $\Delta^\ast\epsilon(I_b) - \Delta^\ast\epsilon(III)$ of the activation energy through $\Theta_{\sigma_s^{\ast(o)}}$ may be neglected, since $\Theta_{\sigma_s^{\ast(o)}}$ of I_b and that of III cancel each other in the expression $RT^2\partial\{\ln \widehat{\mathfrak{K}}(I_b)/\widehat{\mathfrak{K}}(III)\}/\partial T$ of the difference of the activation energies, if σ_s^{\ast} 's both for $\ast(I_b)$ and $\ast(III)$ are identical with each other, or even different, contribute to the difference only insignificantly, provided that θ is not very near unity ** .

§ 4. Explanation of Experimental Results

We have seen in §2 that $\Delta^\ast\epsilon(I_b) - \Delta^\ast\epsilon(III)$ deduced from the experimental result $^{3)}$ is appreciably lower than that expected from the simple theory not allowed for adsorption and in §3 that H(a) could increase $\Delta^\ast\epsilon(I_b)$ preferentially by repulsive interactions. We will show below that the above experimental result is accounted for by considering the latter preferential repulsive interactions alone, irrespective of other effects of adsorptives.

The $\ln \widehat{\mathfrak{K}}(I_b)_0$ in Fig. 1 shows the value of $\ln \widehat{\mathfrak{K}}(I_b)$, which would be observed in the absence of H(a), by an almost horizontal straight line in accordance with the experimental results $^{20)21)}$ referred to in Part I $^{1)}$, that the activation energy of hydrogen adsorption on a bare nickel surface is almost zero. The broken line $\ln \widehat{\mathfrak{K}}(I_b)_x$ shows that in the case of constant $\epsilon^{\ast(I_b)}$, hence of constant $\Delta^\ast\epsilon(I_b)$, which intersects the straight line of $\ln \widehat{\mathfrak{K}}(III)$ at $T = T_x$. The $\ln \widehat{\mathfrak{K}}(I_b)_x$ is a straight line because of constant $\Delta^\ast\epsilon(I_b)$ and passes through the same point at $1/T \rightarrow 0$ as $\ln \widehat{\mathfrak{K}}(I_b)_0$ does. The constant value of $\Delta^\ast\epsilon(I_b) - \Delta^\ast\epsilon(III)$ is necessarily that given by (2.12).

The $\epsilon^{\ast(I_b)}$ or $\Delta^\ast\epsilon(I_b)$ may however increase with increase of temperature, in so far as the rate-determining step switches from I_b to III ***). For, $\gamma(H)^2$ approaches I' or unity by (1.9) and (1.12) according as I_b or III governs the

*) See, for instance, H. EYRING, J. WALTER and G. E. KIMBALL, "Quantum Chemistry" New York (1949), p. 232 or L. PAULING and E. B. WILSON, Jr. "Introduction to Quantum Mechanics" New York (1935), p. 366.

**) The $\Theta_{\sigma_s^{\ast(o)}}$'s are given approximately by $(1-\theta)^n$, where n is the number of sites σ 's of adsorption of H(a)'s constituting σ_s^{\ast} 's, provided that H(a)'s are the only adsorptives.

***) Cf. § 2.

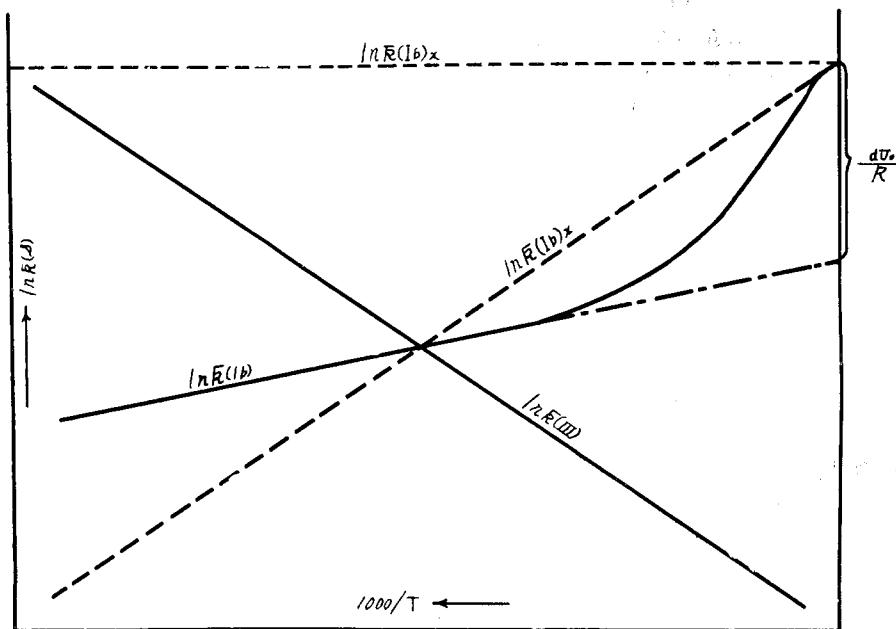


Fig. 1. Effect of repulsive interaction of H(a)'s with $\ast(I_b)$ on $\mathfrak{K}(I_b)$.

rate, so that it increases with temperature across the switch to increase θ according to (3.4) and (3.5. P) possibly overcoming the decreasing effect on θ of temperature^{*}).

The full line $\ln \mathfrak{K}(I_b)$ shows now the course of variation of $\mathfrak{K}(I_b)$ with $1/T$ in the case when $\varepsilon^{\ast(I_b)}$ or $\Delta^{\ast}\varepsilon(I_b)$ increases with increase of temperature in accordance with the above consideration to depress $\mathfrak{K}(I_b)$ by (2.1. I_b) more and more with increase of temperature, resulting in a lower rate of temperature increase of $\mathfrak{K}(I_b)$ compared with that in the case of constant $\Delta^{\ast}\varepsilon(I_b)$ of $\mathfrak{K}(I_b)_x$. The production of the tangent to $\ln \mathfrak{K}(I_b)$ at the intersection, shown by a chain line in Fig. 1, should pass through a point on the ordinate $1/T=0$ lower than that of $\ln \mathfrak{K}(I_b)_0$ or of $\ln \mathfrak{K}(I_b)_x$.

The coverage of H(a)'s and in consequence $\Delta^{\ast}\varepsilon(I_b)$ can not however increase with temperature without limit. Since P^H/Q_P^H is extremely small compared with unity^{**}), θ should ultimately vanish practically at higher temperature by (3.3) even for $\gamma(H)=1$. The $\ln \mathfrak{K}(I_b)$ should in consequence deviate upwards from

^{*}) The $(\partial\theta/\partial \ln T)_{P'}$ is negative by (3.5. T') on account of a huge number of Q_P^H/P' as seen from (2.10. H), (3.4) and (1.10), in so far as θ is as large as to affect $\varepsilon^{\ast(I_b)}$ or $\Delta^{\ast}\varepsilon(I_b)$.

^{**}) P^H/Q_P^H is of the order of magnitude of 10^{-12} for $P^H=0.03$ mmHg by (2.10. H).

the production toward $\ln \mathfrak{K}(\text{I}_b)_0$ and pass through the same point at $1/T=0$ as $\ln \mathfrak{K}(\text{I}_b)_0$ or $\ln \mathfrak{K}(\text{I}_b)_x$ as shown in Fig.1.

This situation is allowed for in the first approximation by an additional potential U , which increases with increase of temperature in the neighbourhood of the intersection, as

$$U = U_0(1 + \alpha T), \quad (4.1. U)$$

where both U_0 and α are positive constants. We have now according to (2.1. I_b)

$$\mathfrak{K}(\text{I}_b) = \rho(\text{I}_b) \exp\left(-\frac{\alpha U_0}{R}\right) \frac{P^{\text{H}}}{Q_p^{\text{H}}} \exp\left(-\frac{\Delta^*\varepsilon(\text{I}_b)_0 + U_0}{RT}\right), \quad (4.1. \mathfrak{K})$$

where $\Delta^*\varepsilon(\text{I}_b)_0$ is the particular value of $\Delta^*\varepsilon(\text{I}_b)$ in the absence of adsorptives *i. e.* that relevant to $\mathfrak{K}(\text{I}_b)_0$. Eq.(4.1. \mathfrak{K}) shows that the intersection of $\ln \mathfrak{K}(\text{I}_b)$ with the ordinate $1/T=0$ is lowered by $\alpha U_0/R$ from that of $\ln \mathfrak{K}(\text{I}_b)_0$ or of $\ln \mathfrak{K}(\text{I}_b)_x$.

The low value of $\Delta^*\varepsilon(\text{I}_b) - \Delta^*\varepsilon(\text{III})$ as deduced from experiment is now accounted for by expressing the similar increment U' of $\varepsilon^*(\text{III})$ or of $\Delta^*\varepsilon(\text{III})$ due to the interactions as

$$U' = U'_0(1 + \alpha T) \quad (4.2. U)$$

in accordance with a plausible assumption that U/U' remains constant irrespective of the amount of coverage, hence of temperature, where U'_0 is a constant specific to $\varepsilon^*(\text{III})$. Eq. (2.1. III) is now

$$\mathfrak{K}(\text{III}) = \rho(\text{III}) \exp\left(-\frac{\alpha U'_0}{R}\right) \frac{P^{\text{E}}}{Q_p^{\text{E}}} \frac{P^{\text{H}}}{Q_p^{\text{H}}} \exp\left(-\frac{\Delta^*\varepsilon(\text{III})_0 + U'_0}{RT}\right), \quad (4.2. \mathfrak{K})$$

where $\Delta^*\varepsilon(\text{III})_0$ is a particular value of $\Delta^*\varepsilon(\text{III})$ in the absence of adsorptives. Equating $\mathfrak{K}(\text{I}_b)$ to $\mathfrak{K}(\text{III})$ at $T=T_x$ and $\rho(\text{I}_b)$ to $\rho(\text{III})$, we have from (4.1. \mathfrak{K}) and (4.2. \mathfrak{K})

$$RT_x \ln Q_p^{\text{E}}/P^{\text{E}} - \alpha T_x(U_0 - U'_0) = (\Delta^*\varepsilon(\text{I}_b)_0 + U_0) - (\Delta^*\varepsilon(\text{III})_0 + U'_0). \quad (4.3)$$

We see from (4.1. \mathfrak{K}), (4.2. \mathfrak{K}) and (4.3) that the excess of the activation energy $RT^2 \partial \ln \mathfrak{K}(\text{I}_b)/\partial T = \Delta^*\varepsilon(\text{I}_b)_0 + U_0$ of I_b over that $RT^2 \partial \ln \mathfrak{K}(\text{III})/\partial T = \Delta^*\varepsilon(\text{III})_0 + U'_0$ of III is given, if $\alpha=0$ or $U_0=U'_0$, *i. e.* if the additional critical energy increments do not vary with temperature or identical with each other, by $RT_x \ln Q_p^{\text{E}}/P^{\text{E}}$ or 24.6 kcal in accordance with (2.12). Since the right-hand side of (4.3) is only *ca.* 10 kcal by experiment as mentioned in §2, the second term on the left should amount to *ca.* 15 kcal or, according to (4.1. U) and (4.2. U), U must be considerably greater than U' .

§ 5. General Procedure of Adjusting $\mathfrak{K}(s)$'s

Experimental results were shown in § 4 to be in accordance with what was expected in § 3 from an appreciable repulsive interaction, which is compensated to a greater extent in the case of $\ast(\text{III})$ on account of its larger polarizability than that of $\ast(\text{I}_b)$. On the same ground we might expect that U of $\ast(\text{I}_b)$ outweighs those of $\ast(\text{I}_a)$ and $\ast(\text{II})$, which are respectively composed of $\text{I}(\text{I}_a) \equiv \text{E}$ and $\text{I}(\text{II}) \equiv \text{C}_2\text{H}_4(a) + \text{H}(a)$. We see further from (4.1) and (4.2) that the relative magnitude of $\mathfrak{K}(\text{I}_b)$ and $\mathfrak{K}(\text{III})$ affected by $\text{H}(a)$'s are correctly given by increasing $\Delta^*\varepsilon(\text{I}_b)$ alone by $U-U'$, treating $\Delta^*\varepsilon(\text{III})$ as if unaffected. The relative magnitudes of $\mathfrak{K}(s)$'s, which fix those of V_s , E^e , E^a , E^b , E^c and of rates of evolution of different deuterioethylenes and deuterioethanes according to § 1, (A) and § 7, are now correctly obtained by increasing $\Delta^*\varepsilon(\text{I}_b)$ alone properly, provided that the differences between U' and the corresponding ones of $\mathfrak{K}(\text{I}_a)$ and $\mathfrak{K}(\text{II})$ as well as the effects of other adsorptives are negligible.

We proceed now in accordance with the above consideration, a step further from the previous approximation of neglecting the effect of adsorptives altogether, to allow for the repulsive interactions of $\ast(\text{I}_b)$ with $\text{H}(a)$'s alone. The $\Delta^*\varepsilon(\text{I}_b)_0 + U_0$ will be denoted simply by U_0 or U_0 taken to include $\Delta^*\varepsilon(\text{I}_b)_0$, α being appropriately changed, and $\rho(s)$'s will be identified with a common value ρ . Eq. (4.1. \mathfrak{K}) is thus rewritten as

$$\mathfrak{K}(\text{I}_b) = \rho \frac{P^{\mu}}{Q_P^{\text{H}}} \exp\left(-\frac{U_0(1+\alpha T)}{RT}\right). \quad (5.1)$$

The values of U_0 , α and $\Delta^*\varepsilon(\text{III})$ are thus adjusted to the experimental results of ZUR STRASSEN in § 6 in accordance with (2.11), (5.1) and (2.1. III). The experimental results are found very closely fitted in with by respectively constant values of U , α and $\Delta^*\varepsilon(\text{III})$ over the whole ranges of temperature and of hydrogen partial pressure of a few hundredths mmHg at a constant partial pressure 0.03 mmHg of ethylene of the experiment.

The value of U_0 thus determined may be more or less different from its value appropriate to the range of partial pressures around 10 mmHg, which we will be later mainly concerned with, on account of a difference in the activity of $\text{H}(a)$. Since there exist no sufficient experimental data to decide the relevant value in the latter case, we proceed to reserve the value U_0 determined as above and to fit α alone to the relative values of $\mathfrak{K}(s)$'s deduced from the experiments of TURKEVICH, SCHISLER and IRSA⁹⁾ in the latter range of partial pressures.

The $\bar{v}(\text{III})$ will be neglected throughout compared with $\bar{v}(\text{II})$, as shown valid later in § 8 and the isotopic difference of rates ignored throughout.

§ 6. Adjusting of $\mathfrak{R}(I_b)$

Substituting $\mathfrak{R}(I_b)$ from (5. 1) and $\mathfrak{R}(III)$ from (2. 1. III) into (2. 11) identifying $\rho(III)$ with ρ and neglecting Γ compared with unity, we have

$$\frac{1}{V_s} = \frac{Q_P^H}{\rho f P^H} \exp\left(\frac{U_0}{RT}\right) + \frac{Q_P^H Q_P^E}{\rho P^H P^E} \left(\frac{\Delta^* \varepsilon(III)}{RT}\right), \quad (6. 1. \mathfrak{R})$$

where

$$f = \exp(-\alpha U_0/R). \quad (6. 1. f)$$

Rewriting the above equation as

$$\log \left\{ \frac{P^H}{V_s} - \frac{Q_P^E Q_P^H}{\rho P^E} \exp\left(\frac{\Delta^* \varepsilon(III)}{RT}\right) \right\} = \log \frac{Q_P^H}{\rho f} + \frac{U_0}{2.30 RT} \quad (6. 2)$$

and substituting $(-d \ln P^H/dt)^{-1}$ observed by ZUR STRASSEN³⁾ for P^H/V_s in the

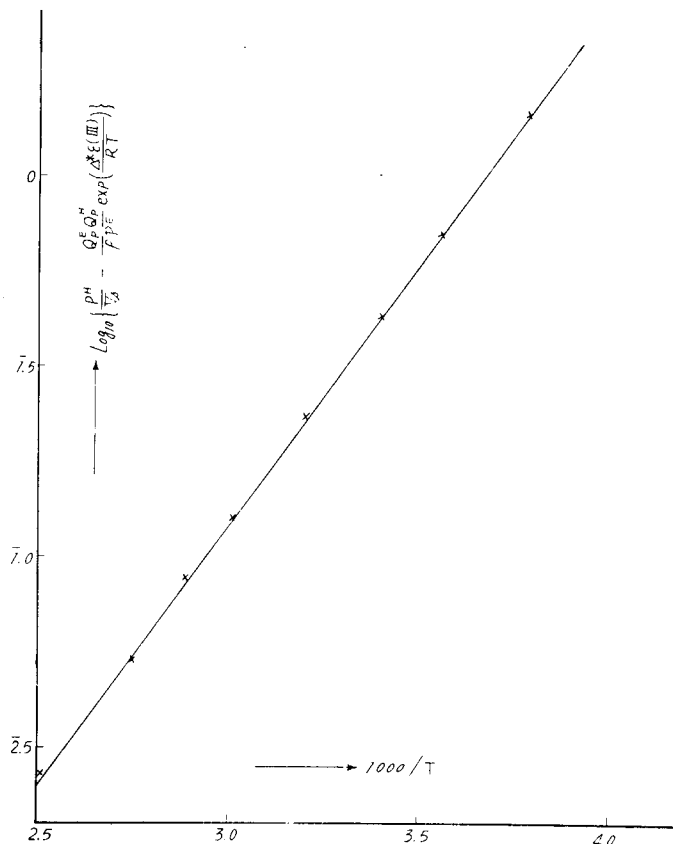


Fig. 2. The linear relation of Eq.(6.2) fitted to the experimental result of ZUR STRASSEN³⁾.

above equation regarding ρ as an appropriate constant, where t is time, $Q_p^E Q_p^H / \rho P^H$ and $\Delta^* \epsilon$ (III) were varied until a linear relation was attained between its left-hand side and $1/T$ as shown in Fig. 2. Constants are thus determined as^{*)}

$$U_0 = 6.21 \text{ kcal}, \quad (6.3. I_b)$$

$$\Delta^* \epsilon \text{ (III)} = -5.00 \text{ kcal}, \quad (6.3. III)$$

$$\alpha U_0 = 39.6 \text{ cal deg}^{-1}, \quad (6.4. a)$$

$$T_X = 329^\circ \text{K}. \quad (6.4. T)$$

§ 7. Adjusting of $\mathfrak{R}(s)$'s to Evolution Rates of Deuterocompounds

The method of adjusting $\mathfrak{R}(s)$'s to observed evolution rates of deuterio-substitution products will be discussed in general in this section before applied particularly in § 8 to the observation of TURKEVICH *et al.*⁹⁾

Unidirectional evolution rates V^{E_l} , V^{H_m} and V^{A_n} respectively of l -, m - and n -deuterio-substitution products, *i. e.* **E**, **H_m** and **A_n** of **E**, **H** and **A** are given in accordance with Scheme (II) and the assumption of neglecting isotopic difference of rates^{**)} as

$$V^{E_l} = x_l \bar{v}(\text{I}_a), \quad l = 0, 1, 2, 3, 4, \quad (7.1. E)$$

$$V^{H_m} = \frac{2!}{(2-m)! m!} y_0^{2-m} y_1^m \bar{v}(\text{I}_b), \quad m = 0, 1, 2, \quad (7.1. H)$$

$$V^{A_n} = (y_1 z_{n-1} + y_0 z_n) \bar{v}(\text{III}), \quad n = 0, \dots, 6, \quad (7.1. A)$$

where x_l is the fraction of $\text{C}_2\text{P}_{4-l}\text{D}_l(\text{a})$ over whole $\text{C}_2\text{H}_4(\text{a})$, y_0 or y_1 the atomic fraction of P (a) or D (a) in H (a) and z_n that of $\text{C}_2\text{P}_{5-n}\text{D}_n(\text{a})$ over whole $\text{C}_2\text{H}_5(\text{a})$. It follows from the definitions that

$$x_{l(<0)} = x_{l(>4)} = 0, \quad z_{n(<0)} = z_{n(>5)} = 0, \quad (7.2. x), (7.2. z)$$

$$\sum_{l=0}^4 x_l = 1, \quad y_0 + y_1 = 1, \quad \sum_{n=0}^5 z_n = 1. \quad (7.3. x), (7.3. y), (7.3. z)$$

The unidirectional evolution rates V^{E_l} for $l = 1, 2, 3, 4$, V^{H_m} for $m = 0, 1$ and V^{A_n} for $n = 0, \dots, 6$ are directly observable at the initial stage of catalyzed reaction of C_2P_4 and D_2 .

It is shown below that fractions x_l 's, y_m 's and z_n 's at the steady state are

*) T_X is obtained by putting first and second term of (6.1. \mathfrak{R}), which express $1/\mathfrak{R}(\text{I}_b)$ and $1/\mathfrak{R}(\text{III})$ respectively, equal to each other at $T = T_X$ and $P^E = 0.03 \text{ mmHg}$ in accordance with the experimental condition of ZUR STRASSEN (Ref. 3) with reference to (6.3), (6.4. a), (6.1. f) and (2.10. E).

***) Cf. § 5.

fixed by the relative values of $\bar{v}(s)$'s and $\bar{v}(s)$'s, hence according to (7.1) and § 1, (A), the relative values of evolution rates are determined by those of $\mathfrak{R}(s)$'s and conversely that the latter are decided from four observations of relative evolution rates of deuterocompounds, which are independent functions of $\mathfrak{R}(s)$'s.

The steady condition for adsorptives $C_2P_{4-l}D_l(a)$, $D(a)$, $P(a)$ and $C_2P_{5-n}D_n(a)$ are respectively stated as below according to (II), admitting that deuterium atoms in $C_2H_4(a)$ are distributed with equal chance over the four hydrogen atoms comprised as warranted in the present case, where **E** implies initially no deuterium.

$$X_l\bar{v}(I_a) - x_l\bar{v}(I_a) - x_l\bar{v}(II) + \left[\left(1 - \frac{l-1}{4}\right) \times \frac{2}{3} y_1 x_{l-1} + \left(1 - \frac{l}{6}\right) y_0 x_l \right. \\ \left. + \left(\frac{1}{3} + \frac{l}{6}\right) y_1 x_l + \frac{l+1}{6} y_0 x_{l+1} \right] \bar{v}(II) = 0, \quad l = 0, \dots, 4, \quad (7.4.E)$$

$$2Y\bar{v}(I_b) - 2y_1\bar{v}(I_b) - y_1\bar{v}(II) + \frac{2x+y_1}{3}\bar{v}(II) - y_1\bar{v}(III) = 0, \quad (7.4.D)$$

*) Eq. (7.4.E) is derived as follows. The first or the fourth term gives the rate of supply of $C_2P_{4-l}D_l(a)$ by the forward act of I_a or the backward one of II and the second or the third term its loss by the backward act of I_a or the forward one of II respectively. $C_2P_{4-l}D_l(a)$ is now supplied by the backward act of II either from $C_2P_{5-l}D_l(a)$ by releasing $P(a)$ (case A) or from $C_2P_{5-(l+1)}D_{l+1}(a)$ by giving off $D(a)$ (case B).

$C_2P_{5-l}D_l(a)$ in case A is now formed, in accordance with the neglect of $\bar{v}(III)$, exclusively either by the combination of $D(a)$ and $C_2P_{4-(l-1)}D_{l-1}(a)$ (case A_D) or by that of $P(a)$ and $C_2P_{4-l}D_l(a)$ (case A_P) in the forward act of II . The fractions of $C_2P_{5-l}D_l$ respectively of cases A_D and A_P over whole $C_2H_5(a)$ are $y_1 x_{l-1}$ and $y_0 x_l$ respectively. The overall rate of $C_2P_{5-l}D_l(a)$ of case A_D releasing $H(a)$ is hence $y_1 x_{l-1} \bar{v}(II)$, of which the part of giving off $P(a)$ is now alone in question. Since one of the three hydrogen atoms on the methyl group is deuterium picked up in the forward act of II in this case, the $P(a)$ must be released from the other two hydrogen atoms originating from $C_2P_{4-(l-1)}D_{l-1}(a)$. The probability of one of the two being protium is $1 - \frac{l-1}{4}$, while that of either of the two being released in the backward act of II is $2/3$. It follows that the rate of $C_2P_{5-l}D_l(a)$ of case A_D releasing $P(a)$ in the backward act of II is $\left(1 - \frac{l-1}{4}\right) \cdot 2/3 \cdot y_1 x_{l-1} \bar{v}(II)$ as given by the first term in the brace of (7.4.E).

In case A_P one of the three hydrogen atoms on the methyl group of $C_2P_{5-l}D_l(a)$ is originating from $P(a)$ and two others are from $C_2P_{4-l}D_l(a)$, hence of deuterium atomic fraction $l/4$. The rate of $C_2P_{5-l}D_l(a)$ in this case releasing $P(a)$ by the backward act of II is in consequence $\{1/3 + (1-l/4) \cdot 2/3\} y_0 x_l \bar{v}(II)$, the first or the second term in the parentheses $\{ \}$ corresponding to the rate of $P(a)$ being released from the one originating in $P(a)$ or from the other two in $C_2P_{4-l}D_l(a)$.

Similar consideration gives for case B the rates $(1/3 + l/4 \cdot 2/3) y_1 x_l \bar{v}(II)$ and $(l+1)/4 \cdot 2/3 \cdot y_0 x_{l+1} \bar{v}(II)$ of $C_2P_{5-(l+1)}D_{l+1}(a)$ respectively originating from $D(a) + C_2P_{4-l}D_l(a)$ and $P(a) + C_2P_{4-(l+1)}D_{l+1}(a)$ to yield $C_2P_{5-l}D_l(a)$ by releasing $D(a)$.

$$2(1-Y)\bar{v}(\text{I}_b) - 2y_0\bar{v}(\text{I}_b) - y_0\bar{v}(\text{II}) + \frac{2(1-x) + y_0}{3}\bar{v}(\text{II}) - y_0\bar{v}(\text{III}) = 0, \quad (7.4. \text{P})$$

$$\{y_1x_{n-1} + y_0x_n\}\bar{v}(\text{II}) - z_n\bar{v}(\text{II}) - z_n\bar{v}(\text{III}) = 0, \quad n=0, \dots, 5, \quad (7.4. \text{A})$$

where X_l is the fraction of E_l over whole E and x the atomic fraction of deuterium in $\text{C}_2\text{H}_4(a)$, which satisfy the equations by definition

$$\sum_{l=0}^4 X_l = 1, \quad X = \sum_{l=1}^4 lX_l/4, \quad x = \sum_{l=1}^4 lx_l/4. \quad (7.5. \text{E}), (7.5. \text{X}), (7.5. x)$$

We have by summing up five equations of (7.4. E) respectively for $l=0, \dots, 4$, referring to (7.2. x), (7.3. x), (7.3. y) and (7.5. E),

$$\bar{v}(\text{I}_a) - \bar{v}(\text{I}_b) - \bar{v}(\text{II}) + \bar{v}(\text{III}) = 0, \quad (7.6. \text{E})$$

which states the overall steady condition for $\text{C}_2\text{H}_4(a)$. Similar overall steady condition is derived for $\text{H}(a)$ by adding (7.4. D) to (7.4. P) referring to (7.3. y) or for $\text{C}_2\text{H}_5(a)$ by summing up (7.4. A) for $n=0, \dots, 5$, remembering (7.2. x) and (7.3), as

$$2\bar{v}(\text{I}_b) - 2\bar{v}(\text{I}_a) - \bar{v}(\text{II}) + \bar{v}(\text{III}) - \bar{v}(\text{III}) = 0 \quad (7.6. \text{H})$$

or

$$\bar{v}(\text{II}) - \bar{v}(\text{II}) - \bar{v}(\text{III}) = 0. \quad (7.6. \text{A})$$

Eqs. (7.6) are however direct conclusions of the steady condition (1.1), to which $\bar{v}(s)$'s and $\bar{v}(s)$'s are essentially subject*).

It follows that only 13 equations out of 16 ones of (7.3) and (7.4) are independent on account of (7.6), for 13 unknowns, *i. e.* x_l 's ($l=0, \dots, 4$), y_0 , y_1 and z_n 's ($n=0, \dots, 5$). These unknowns are decided by the relative magnitudes of $\bar{v}(s)$'s and $\bar{v}(s)$'s, inasmuch as the above independent equations are homogeneous with respect to the latters. The relative magnitudes of $\bar{v}(s)$'s and $\bar{v}(s)$'s fix in consequence those of V^{E_l} 's, V^{H_n} 's and V^{A_n} 's according to (7.1) on the one hand and are themselves fixed by the relative magnitudes of $\mathfrak{K}(s)$'s as stated in § 1, (A) on the other hand. Consequently, observable relative magnitudes of four evolution rates of deuterocompounds are sufficient to decide those of four $\mathfrak{K}(s)$'s as exemplified in the next section.

§ 8. Adjusting of $\mathfrak{K}(s)$'s to the Experimental Results of TURKEVICH *et al.*⁹⁾

TURKEVICH *et al.*⁹⁾ allowed light ethylene and pure deuterium gas respectively

*) Eq. (1.1) is developed, $\bar{v}(\text{III})$ being neglected, as

$$\bar{v}(\text{I}_a) - \bar{v}(\text{I}_a) = \bar{v}(\text{I}_b) - \bar{v}(\text{I}_b) = \bar{v}(\text{II}) - \bar{v}(\text{II}) = \bar{v}(\text{III})$$

from which (7.6) readily follows.

of initial pressures of 10 and 20 mmHg to react at 90°C in the presence of nickel wire as catalyst and followed the relative amounts of evolution of different deuterioethylenes and deuterioethanes, and of the overall hydrogenation simultaneously with time. The relative initial evolution rates of deuterocompounds and overall hydrogenation are determined from their results as

$$V^{A_0} : V^{A_1} : V^{A_2} : V^{A_{n(>2)}} = 1 : 0.94 : 0.22 : 0 \quad (8.1. A)$$

and

$$V_s : V^{E_1} : V^{E_{l(>1)}} = 1 : 2.50 : 0, \quad (8.1. E)$$

where

$$V_s = \sum_{n=1}^6 V^{A_n}. \quad (8.1. V)$$

It is deduced from the above data according to §7 that

$$\mathfrak{K}(I_a) : \mathfrak{K}(I_b) : \mathfrak{K}(II) : \mathfrak{K}(III) = \infty : 1 : 10.26 : 1.295, \quad (8.2)$$

from which αU_0 and $\Delta^* \varepsilon(II)$ are evaluated by (5.1), (2.1. II), (2.1. III) and (2.10. H), identifying $\rho(s)$'s with ρ , as

$$\alpha U_0 = 31.8 \text{ cal deg}^{-1}, \quad \Delta^* \varepsilon(II) = 0.757 \text{ kcal}. \quad (8.3. \alpha), (8.3. II)$$

We have, multiplying (7.4. E) by l , summing up the product from $l=1$ to $l=4$ and referring to (7.3. x), (7.3. y) and (7.5. x), $-4x\bar{v}(I_a) - 4x\bar{v}(II) + \left\{ \frac{2}{3}y_1 + \frac{10}{3}x \right\} \bar{v}(II) = 0$, noting that $X_0=1$ and $X_1=X_2=X_3=X_4=0$ at the initial experimental condition of TURKEVICH *et al.*⁹⁾ or eliminating $\bar{v}(I_a) + \bar{v}(II)$ from the above equation and (7.6. E)

$$6x\bar{v}(II) + (x-y_1)\bar{v}(II) = 0. \quad (8.4. E)$$

Eqs. (7.4. D) and (7.6. H) give, on the other hand, on elimination of $2\bar{v}(I_b) + \bar{v}(II) + \bar{v}(III)$ from them noting that $Y=1$ at the experimental condition in question,

$$3(1-y_1)\bar{v}(I_b) + (x-y_1)\bar{v}(II) = 0. \quad (8.4. H)$$

We have further eliminating $\bar{v}(II) + \bar{v}(III)$ from (7.4. A) and (7.6. A),

$$y_1x_{n-1} + y_0x_n = z_n, \quad (8.4. A)$$

noting that $\bar{v}(II) > 0$, in so far as the steady reaction of the rate $\bar{v}(II) - \bar{v}(II)$ should proceed at all in accordance with (1.1).

The relative magnitudes of $\bar{v}(s)$'s and $\bar{v}(s)$'s, and hence those of $\mathfrak{K}(s)$'s are now deduced below from the experimental results (8.1) by (8.4). V^{A_0} and V^{A_3} are expressed by (7.1. A) and (7.2. z) respectively as

$$V^{A_0} = y_0z_0\bar{v}(III), \quad V^{A_3} = (y_1z_2 + y_0z_3)\bar{v}(III),$$

which is respectively different from or equal to zero according to (8.1. A). It follows that neither y_0 nor z_0 should vanish, while both y_1z_2 and y_0z_3 must be zero, hence either or both of y_1 and z_2 must be zero. If $y_1=0$, we have on the one hand from (8.4. E)

$$x(6\bar{v}(I_a) + \bar{v}(II)) = 0$$

or by (7.5. x)

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$$x = x_1 = x_2 = x_3 = x_4 = 0$$

and on the other hand from (8.4. A) and (7.3. y)

$$x_n = z_n, \quad n = 0, \dots, 4.$$

It follows from the above two equations that $z_n (n=1, 2, 3, 4)$ should individually vanish and in consequence, according to (7.1. A) that V^{A_1} and V^{A_2} must be zero, which is contradictory to the experimental result (8.1. A).

The y_i as well as y_0 must in consequence be different from zero. It follows now from (7.1. A) for $n=3, 4, 5$ and the experimental result (8.1. A), that

$$z_2 = z_3 = z_4 = z_5 = 0, \quad (8.5. z)$$

hence from (8.4. A)

$$x_1 = x_2 = x_3 = x_4 = 0 \quad (8.5. x)$$

or according to (7.3. x) and (7.5. x)

$$x_0 = 1, \quad x = 0. \quad (8.6. a), (8.6. b)$$

We have now from (7.2. x), (8.4. A), (8.5. x) and (8.6. a)

$$y_0 = z_0, \quad y_1 = z_1,$$

hence from (7.1. A) with reference to (7.2. z) and (8.5. z)

$$V^{A_0} = y_0^2 \bar{v} \text{ (III)}, \quad V^{A_1} = 2y_0 y_1 \bar{v} \text{ (III)}, \quad V^{A_2} = y_1^2 \bar{v} \text{ (III)}, \quad (8.7)$$

which give, by comparison with the experimental result (8.1. A), remembering (7.3. y),

$$y_1 = 0.320. \quad (8.8)$$

The relative magnitude of $\hat{v} \text{ (II)}$ to $\bar{v} \text{ (Ib)}$ is determined by (8.4. H), (8.6. b) and (8.8) as

$$\hat{v} \text{ (II)} = \frac{3(1-y_1)}{y_1} \bar{v} \text{ (Ib)} = 6.38 \bar{v} \text{ (Ib)}. \quad (8.9)$$

We have on the other hand from (7.4. E) for $l=1$, noting that $X_1=0$ at the initial condition and neglecting all terms in the coefficient of $\hat{v} \text{ (II)}$ except the first one according to (8.5. x)

$$x_1 \hat{v} \text{ (Ia)} = \frac{2}{3} y_1 x_0 \hat{v} \text{ (II)} - x_1 \bar{v} \text{ (II)}.$$

The second term on the right is negligible compared with the first one by (8.5. x), (8.6. a) and (8.8), inasmuch as $\hat{v} \text{ (II)} > 0.86 \bar{v} \text{ (II)}$, as follows from (8.9) and the relation $\bar{v} \text{ (II)} - \hat{v} \text{ (II)} < \bar{v} \text{ (Ib)}$ due to (1.1), hence $x_1 \hat{v} \text{ (Ia)}$ is finite or $\hat{v} \text{ (Ia)}$ is practically infinite. We have thus

$$\hat{v} \text{ (Ia)} / \hat{v} \text{ (II)} \longrightarrow \infty \quad (8.10. I)$$

and by (7.1. E) and (8.1. E)*

$$V^{E_1} = \frac{2}{3} y_1 x_0 \hat{v} \text{ (II)} = 2.50 V_s$$

or by (8.8) and (8.6. a)

$$\hat{v} \text{ (II)} = \frac{3 \times 2.50}{2 \times 0.320} V_s = 11.72 V_s. \quad (8.10. II)$$

The relative magnitudes of $\hat{v} \text{ (Ia)}$, $\bar{v} \text{ (Ib)}$, $\hat{v} \text{ (II)}$ and V_s are now given by (8.9) and (8.10),

* We see from (7.4. E) that the coefficient of $\hat{v} \text{ (II)}$ there vanishes for $l > 1$ according to (8.5. x), so that $x_l \hat{v} \text{ (Ia)}$ or V^{E_l} for $l > 1$ is zero in distinction from V^{E_1} in accordance with the experimental result (8.1. E). V^{A_n} for $n > 2$ should also vanish by (7.1. A) and (8.5. z), while those for $n=0, 1, 2$ are finite, in agreement with the experimental result (8.1. A).

from which those of $\mathfrak{K}(s)$'s are worked out as follows. It follows from (1.1) and (8.10. I) that $\bar{v}(\text{I}_a)/V_s \rightarrow \infty$ or according to (1.6. I_a), $\mathfrak{K}(\text{I}_a)/V_s \rightarrow \infty$, hence by (1.9)

$$\tau(\text{C}_2\text{H}_4) = 1. \quad (8.11. \text{C}_2\text{H}_4)$$

We have on the other hand from (8.9), (8.10. II), (1.6. I_b) and (1.9)

$$\tau(\text{H}) = 0.675. \quad (8.11. \text{H})$$

Substituting now $\bar{v}(\text{II})$ and $\bar{v}(\text{I}_b)$ from (1.6) into (8.9) and eliminating $\mathfrak{K}(\text{I}_b)/\mathfrak{K}(\text{II})$ from the resulting equation and the equation of the third and fourth member of (1.9), we have

$$\tau(\text{C}_2\text{H}_5)(1 - \tau(\text{H})^2) = 6.38(\tau(\text{H})\tau(\text{C}_2\text{H}_4) - \tau(\text{C}_2\text{H}_5))$$

or by (8.11)

$$\tau(\text{C}_2\text{H}_5) = 0.622. \quad (8.11. \text{C}_2\text{H}_5)$$

The relative values of $\mathfrak{K}(s)$'s are now determined by (1.9) and (8.11) as

$$\mathfrak{K}(\text{I}_a)/\mathfrak{K}(\text{I}_b) \rightarrow \infty, \quad \mathfrak{K}(\text{II})/\mathfrak{K}(\text{I}_b) = \frac{1 - \tau(\text{H})^2}{\tau(\text{H}) - \tau(\text{C}_2\text{H}_5)} = 10.26,$$

$$\mathfrak{K}(\text{III})/\mathfrak{K}(\text{I}_b) = \frac{1 - \tau(\text{H})^2}{\tau(\text{H})\tau(\text{C}_2\text{H}_5)} = 1.295,$$

which are summarized in (8.2).

We have from the above results according to (1.6. III) and (8.11) that

$$\bar{v}(\text{III})/\bar{v}(\text{III}) = \Gamma/0.675 \times 0.622$$

or that $\bar{v}(\text{III})$ is completely negligible as compared with $\bar{v}(\text{III})$ as preliminarily assumed in §5, inasmuch as Γ is extremely small as inferred from (1.8. Γ) and data given in §1.

§9. $\mathfrak{K}(s)$'s Allowed for the Effect of H(a)'s

All $\mathfrak{K}(s)$'s but $\mathfrak{K}(\text{I}_b)$ may be expressed by (2.1) according to §5, in so far as their relative magnitudes are concerned; $\mathfrak{K}(\text{I}_b)$ fitted particularly to the experiments of ZUR STRASSEN³⁾ and of TURKEVICH *et al.*⁹⁾ in §6 and §8 respectively is now formulated as a function of varying experimental condition in what follows.

We presuppose as in §5 that U_0 is constant independent of the experimental condition. Writing $\mathfrak{K}(\text{III})$ of (2.1. III) as

$$\ln \mathfrak{K}(\text{III}) = \ln \rho \frac{P^H}{Q_P^H} \frac{P^E}{Q_P^E} - \frac{\Delta^* \epsilon(\text{III})}{RT}, \quad (9.1)$$

identifying $\rho(\text{III})$ with a common factor ρ , we have

$$T_x = 369^\circ\text{K} \quad (9.2)$$

by equating $\mathfrak{K}(\text{I}_b)$ of (5.1) with $\mathfrak{K}(\text{III})$ of (9.1) on the base of data given by (2.10. E), (6.3) and (8.3. α) at T_x and $P^E = 10$ mmHg for the experimental condition of TURKEVICH *et al.*⁹⁾, hence

$$\alpha U_0 T_x = 11.7 \text{ kcal}, \quad (9.3. T)$$

which agrees with that from (6. 4)

$$aU_0T_x = 13.0 \text{ kcal} \quad (9. 3. S)$$

appropriate to the experiment of ZUR STRASSEN³⁾ within errors expected from those of basic data especially of (8. 2).

Values of (9. 3) lead now to a constant value U_x of U at $T=T_x$ or of $U_x - \Delta^*\epsilon(\text{III})$ according to (4. 1. U) and (6. 3); we have from (9. 3. T) or (9. 3. S) respectively

$$U_x - \Delta^*\epsilon(\text{III}) = 22.9 \text{ kcal} \quad (9. 4. T)$$

or

$$U_x - \Delta^*\epsilon(\text{III}) = 24.2 \text{ kcal} . \quad (9. 4. S)$$

It follows from the constant value of U_x on the one hand that the value $\mathfrak{K}(\text{I}_b)_x$ of $\mathfrak{K}(\text{I}_b)$ at T_x lies on a straight line

$$\ln \mathfrak{K}(\text{I}_b)_x = \ln \rho \frac{P^H}{Q_P^H} - \frac{U_x}{RT} \quad (9. 5)$$

on the chart of $\ln \mathfrak{K}(s)$ versus $1/T$ as shown in Fig. 1 according to (4. 1. U) and (5. 1) and on the other hand from the above constant value of $U_x - \Delta^*\epsilon(\text{III})$ that the equation of T_x , as derived from (5. 1), (9. 1) and (4. 1. U) by equating $\mathfrak{K}(\text{I}_b)$ to $\mathfrak{K}(\text{III})$ at $T=T_x$, *i. e.*

$$T_x = \frac{U_x - \Delta^*\epsilon(\text{III})}{R \ln Q_P^E/P^E} \quad (9. 6)$$

is practically identical with (2. 12), which has reasonably reproduced the observed optimum temperatures of the catalyzed hydrogenation by different authors at various conditions^{*)}.

The above presupposition thus fits in sufficiently with the constancy of $U_x - \Delta^*\epsilon(\text{III})$ of (9. 4), verified by experiment but not conversely deduced from the latter practically^{**)}. We will be contented with the sufficient presupposition at the present stage of our experimental knowledge and formulate the function of $\mathfrak{K}(\text{I}_b)$ as

*) Cf. § 18 of Part I. (Ref. 1).

**) The value of $\mathfrak{K}(\text{III})/\mathfrak{K}(\text{I}_b)$ given by (8. 2) fixes $U_0 + aU_0T$ in accordance with (5. 1), (9. 1), (6. 3. III) and (2. 10. E), where T is the temperature of experiment, whereas the constant value of $U_x = U_0 + aU_0T_x$ experimentally confirmed gives another relation between unknowns U_0 and aU_0 , which may be determined in principle by solving these simultaneous equations. But $T=363^\circ\text{K}$ of the experiment of TURKEVICH *et al.* (Ref. 9) lies too close to $T_x=369^\circ\text{K}$ by (9. 6) to determine U_0 and aU_0 with sufficient accuracy.

$$\ln \mathfrak{K}(I_b) = \ln \rho \frac{P^H}{Q_p^H} + \frac{U_x - U_0}{U_x - \Delta^* \varepsilon(\text{III})} \ln \frac{P^E}{Q_p^E} - \frac{U_0}{RT} \quad (9.7)$$

by the condition*) that $\mathfrak{K}(I_b)$, $\mathfrak{K}(\text{III})$ and $\mathfrak{K}(I_b)_x$ pass through a common point. The above determination of $\mathfrak{K}(I_b)$ is equivalent to drawing a straight line of the inclination U_0/R for $\ln \mathfrak{K}(I_b)$ through the intersection of straight lines of $\ln \mathfrak{K}(I_b)_x$ and $\ln \mathfrak{K}(\text{III})$ on the chart of $\ln \mathfrak{K}(s)$ versus $1/T$ as shown in Fig. 1.

The coefficient [a] of $\ln P^E/Q_p^E$ on the right of (9.7) is given according to (4.1. U) as

$$[a] \equiv \frac{U_x - U_0}{U_x - \Delta^* \varepsilon(\text{III})} = \frac{\alpha U_0 T_x}{U_x - \Delta^* \varepsilon(\text{III})},$$

which is evaluated at [a]=0.512 by (9.3. T) and (9.4. T) from the experiment of TURKEVICH *et al.*⁹⁾ or at [a]=0.538 by (9.3. S) and (9.4. S) from that of ZUR STRASSEN³⁾. The average of these two values, *i. e.*

$$[a] \equiv \frac{U_x - U_0}{U_x - \Delta^* \varepsilon(\text{III})} = 0.525 \quad (9.8)$$

is adopted as the probable value of the coefficient, so that $\mathfrak{K}(I_b)$ is given numerically with reference to (9.7), (2.10) and (6.3. I_b) as

$$\log \mathfrak{K}(I_b) = \log \rho \frac{P^H \text{ mmHg}}{1.057 \times 10^{10}} + 0.525 \log \frac{P^E \text{ mmHg}}{3.939 \times 10^{10}} - \frac{6210 \text{ cal}}{2.30 RT}. \quad (9.9. I_b)$$

$\mathfrak{K}(\text{II})$ and $\mathfrak{K}(\text{III})$ are given similarly by (2.1. II), (9.1), (8.3. II), (6.3. III) and (2.10), identifying $\rho(\text{II})$ with ρ , as

$$\log \mathfrak{K}(\text{II}) = \frac{1}{2} \log \frac{P_H \text{ mmHg}}{1.057 \times 10^{10}} + \log \rho \frac{P^E \text{ mmHg}}{3.939 \times 10^{14}} - \frac{757 \text{ cal}}{2.30 RT}, \quad (9.9. \text{II})$$

$$\log \mathfrak{K}(\text{III}) = \log \rho \frac{P^H \text{ mmHg}}{1.057 \times 10^{10}} + \log \frac{P^E \text{ mmHg}}{3.939 \times 10^{14}} + \frac{5000 \text{ cal}}{2.30 RT}, \quad (9.9. \text{III})$$

whereas $\mathfrak{K}(I_a)$ is left indeterminate, being practically infinite compared with all other $\mathfrak{K}(s)$'s as deduced from experimental results either of ZUR STRASSEN³⁾ or of TURKEVICH *et al.*⁹⁾.

It may be noted that $\mathfrak{K}(I_b)$ depends on the partial pressure of ethylene as well as on P^H , even if I_b is rate-determining and that (9.7) or (9.9. I_b) is valid only for the case considered in § 4, when the rate is determined alternately by I_b and III over the range in question as is the case with the analyzed results of

*) We have from the condition according to (5.1), (9.1) and (9.5)

$$\frac{\alpha U_0}{R} + \frac{U_0}{RT_x} = -\ln \frac{P^E}{Q_p^E} + \frac{\Delta^* \varepsilon(\text{III})}{RT_x} = \frac{U_x}{RT_x}, \text{ hence } \frac{\alpha U_0}{R} = \frac{U_x - U_0}{U_x - \Delta^* \varepsilon(\text{III})} \ln \frac{P^E}{Q_p^E}$$

by eliminating T_x , and further (9.7) in the text by (5.1).

ZUR STRASSEN's^{*)3)} and TURKEVICH *et al.*'s^{**)9)} experiments.

$\mathfrak{K}(s)$'s given by (9.9) will be applied to the explanation of experimental results and to the predictions of yet unobserved facts in subsequent Parts of this series.

Summary

1. A brief review was given of the theory developed in Part I¹⁾, which led to derive the rate at the steady state of catalyzed hydrogenation in the presence of metallic catalysts and the rates of associated reactions, *i. e.* exchange reactions, equilibration of hydrogen, parahydrogen conversion, evolution of different deuterocompounds of ethylene, hydrogen and ethane semiquantitatively in accordance with experiments on the basis of the associative mechanism as respective functions of statistical-mechanical functions $\mathfrak{K}(s)$'s of partial pressures of reactants and temperature respectively relevant to the steps s 's of the mechanism; $\mathfrak{K}(s)$ is the forward rate of step s multiplied by a factor $a_e^{I(s)}/a^{I(s)}$ of increase of the activity of the initial complex I(s) of s from that $a^{I(s)}$ at the latter steady state to that $a_e^{I(s)}$ at equilibria of all steps but s , which was determined in Part I under the assumption of bare and homogeneous catalyst's surface.

2. The cause of quantitative discrepancies between the observation and the theoretical conclusion derived from the $\mathfrak{K}(s)$'s determined in Part I was discussed and attributed principally to the repulsive interaction of adsorbed hydrogen atoms with the critical complexes of s 's, which was altogether neglected in Part I.

3. Functions $\mathfrak{K}(s)$'s were revised allowing for the effect of the adsorbed hydrogen atoms, by fitting them quantitatively to the experimental results of ZUR STRASSEN³⁾ and of TURKEVICH, SCHISLER and IRSA⁹⁾

References

- 1) J. HORIUTI, this Journal **6**, 250 (1958).
- 2) J. HORIUTI and M. POLANYI, Trans. Faraday Soc. **30**, 1164 (1934).
- 3) H. ZUR STRASSEN, Z. physik. Chem. **A 169**, 81 (1934).
- 4) E. K. RIDEAL, J. Chem. Soc. London, 309 (1922).
- 5) T. TUCHOLSKI and E. K. RIDEAL, *ibid.* 1701 (1935).
- 6) G. I. JENKINS and E. K. RIDEAL, *ibid.* 2490 (1955).
- 7) A. FARKAS, L. FARKAS and E. K. RIDEAL, Proc. Roy. Soc. London **A 146**, 630 (1934).
- 8) G. H. TWIGG and E. K. RIDEAL, *ibid.* **A 171**, 55 (1939).
- 9) J. TURKEVICH, D. O. SCHISLER and P. IRSA, J. Phys. Coll. Chem. **55**, 1078 (1951).

*) Cf. § 12 of Part I.

**) Cf. § 8 of this Part.

- 10) T. KEIL, this Journal **3**, 36 (1953-5).
- 11) O. BEECK, A. E. SMITH and A. WHEELER, Proc. Roy. Soc. A **177**, 62 (1940).
- 12) H. S. TAYLOR and R. M. BURNS, J. Am. Chem. Soc. **43**, 1273 (1921).
- 13) J. HORIUTI, this Journal **1**, 8 (1948-51).
- 14) E. K. RIDEAL and E. M. W. TRAPNELL, Discussions Faraday Soc. **8**, 114 (1950).
- 15) G. OKAMOTO, J. HORIUTI and K. HIROTA, Sci. Papers Inst. Phys. Chem. Research, Tokyo, **29**, 223 (1936).
- 16) G. HERZBERG, *Molecular Spectra and Molecular Structure I*, New York (1951), Table 39; II, New York (1949), Table 132.
- 17) B. L. CRAWFORD, Jr., J. E. LANCASTER and R. G. INSKEEP, J. Chem. Phys. **21**, 678 (1953).
- 18) J. HORIUTI, *The Theory of Reaction Rate*, Iwanami Book Co. Tokyo, (1940) (in Japanese).
- 19) J. HORIUTI, Bull. Chem. Soc. Japan **13**, 210 (1938).
K. HIROTA and J. HORIUTI, Sci. Papers Inst. Phys. Chem. Research, Tokyo **34**, 1174 (1938).
- 20) P. M. GUNDRY and F. C. TOMPKINS, Trans. Faraday Soc. London A **177**, 62 (1956).
- 21) A. MATSUDA, this Journal **5**, 71 (1957).