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STATISTICAL MECHANICAL RESEARCH ON THE HETEROGENEOUS REACTION

(Abstract)

PART I. HETEROGENEOUS REACTION IN GENERAL

By Juro HORIUTI

Statistical mechanical theory presented in a previous paper^(*) is now further developed with special reference to heterogeneous reaction.

In the first place heterogeneous elementary reaction, which constitutes the heterogeneous reaction, and the adsorption which conditions the heterogeneous reaction are investigated with following specifications.

(A) The elementary reaction proceeds on the surface of a metallic catalyst surrounded by a gas consisting of the reactant, δ^G and resultant δ^D of the heterogeneous reaction. (discriminated from the initial δ^I and the final complex δ^F of the individual elementary reaction).

(B) The boundary surface of the metallic catalyst consists in segments of principal lattice planes and a certain set σ^A of a few metal atoms on either of them is taken to be the seat σ^A of adsorbed system δ^A . Any lattice plane has sufficient number of metal atoms so that geometrically congruent σ^A 's may be taken as physically identical.

(C) Seat σ^* of critical complex δ^* is a set of metal atoms of the similar description as σ^A . The σ^* and σ^A are not generally identical but may partially or totally include each other.

Adsorption equilibrium $\delta^A(a) \rightleftharpoons \delta^A(g)$ is expressed according to (1), MSM as that,

$$\theta_{\sigma^A(\delta^A)} / \theta_{\sigma^A(0)} = q_{\sigma^A}^{\delta^A(a)} / p^{\delta^A(g)} \quad (1)$$

where $\delta^A(g)$ is the system in gas which may consist in general each ν_a^A pieces of δ_a^A 's i.e. $\delta^A(g) = \sum_a \nu_a^A \delta_a^A$.

(*) Horiuti: "A Method of Statistical Mechanical Treatment of Equilibrium and Chemical Reactions", submitted to the Institute for Physical and Chemical Research, Tokio in Sept. 1944. Its abstract which will be printed in third series of the "Catalyst" is quoted here with the abbreviation MSM.

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The rate \vec{v} and the reverse one \overleftarrow{v} of the heterogeneous elementary reaction which proceeds in G equivalent σ^* 's is given by Eq. (17) of MSM as that,

$$\vec{v} = K a^{\delta^I}, \quad \overleftarrow{v} = K a^{\delta^R} \quad (2. \vec{v}), \quad (2. \overleftarrow{v})$$

where
$$K = \kappa \frac{kT}{h} G q_{\sigma^*}^{\delta^*} \Theta_{\sigma^*(G)}, \quad a^{\delta^*} = (p^{\delta^*})^{-1} \quad (3. K), \quad (3. a)$$

The $q_{\sigma^*}^{\delta^*}$ is $q_{\sigma^*}^{\delta^*}$ of the critical complex δ^* , $\Theta_{\sigma^*(G)}$ the probability that σ^* is clear and a^{δ^*} or-reciprocal p^{δ^*} is the activity.

For our purpose of investigating the adsorption and the heterogeneous elementary reaction $p^{\delta(g)}$ and $q_{\sigma^*}^{\delta(g)}$ are developed as follows: $p^{\delta(g)}$ is expressed as that $p^{\delta(g)} = \frac{Q_{\delta}^{\delta(g)}}{N^{\delta}}$ [MSM, Eq. (2. b)] where N^{δ} is the concentration of $\delta(g)$ and $Q_{\delta}^{\delta(g)}$ the partition function (abbreviated to PF) of $\delta(g)$ moving in unit volume. The latter is the product of the constant statistical weight of nuclear spin and electronic state, which is a constant, the translational partition function Q_T proportional to $T^{\frac{3}{2}}$ the rotational PF , K_R proportional to T or $T^{\frac{3}{2}}$ according as $\delta(g)$ is linear or non-linear, vibrational PF and an Boltzmann factor $e^{-\frac{\epsilon_0^{\delta(g)} + \sum_j h\nu_j^{\delta(g)}/2}{kT}}$ of the minimum potential energy $\epsilon_0^{\delta(g)}$ plus the zero point energy $\sum_j h\nu_j^{\delta(g)}/2$ where $\nu_j^{\delta(g)}$ is the frequency of j -th normal vibration. Assuming that the vibrations are "hard" enough so that vibrational PF sufficiently approximates unity, the product of first four factors $Q_{\delta}^{\delta(g)}$ is expressed as that $Q_{\delta}^{\delta(g)} = \text{constant} \times T^{n(\delta)}$ where $n(\delta)$ is $5/2$ for a linear and $6/2$ for a non-linear $\delta(g)$ or half the number of translational and rotational degree of freedom. Replacing N^{δ} by p^{δ}/kT and T there as well as in $Q_{\delta}^{\delta(g)}$ by $T_m e^{1-\frac{T_m}{T}}$ which is correct in its value and its first derivative at the medium T_m of the temperature range in question, we obtain,

$$p^{\delta(g)} = \frac{Q_{\delta}^{\delta(g)}}{p^{\delta}} e^{-\frac{\epsilon_0^{\delta(g)}}{kT}} \quad (4)$$

where

$$Q_p^\delta = \frac{kT_m}{\Gamma} Q_0^\delta(T_m) e^{n(\delta)+1}, \quad \epsilon^{\delta(g)} = \epsilon_0^{\delta(g)} + \sum_j h\nu_j^{\delta(g)}/2 + \{n(\delta)+1\}kT_m, \quad (5), (6)$$

P^δ is the pressure of $\delta(g)$ in mmHg, $\Gamma = 1333$ the conversion factor from mmHg into c.g.s. unit, $Q_0^\delta(T_m)$ the value of Q_0^δ at T_m . If $\delta(g)$ consists each Z_i pieces of $\delta(g)$'s or $\delta'(g) = \sum_i Z_i \delta_i(g)$, we have for Eq. (4),

$$P^\delta = \prod_i (P^{\delta_i})^{Z_i}, \quad Q_p^\delta = \prod_i (Q_p^{\delta_i})^{Z_i}, \quad \epsilon^{\delta(g)} = \sum_i Z_i \epsilon^{\delta_i(g)} \quad (7. P), (7. Q), (7. \epsilon)$$

q_σ^δ is on the other hand approximately expressed in the form,

$$q_\sigma^{\delta(a)} = q_{\sigma,0}^{\delta(a)} e^{-\frac{\epsilon^{\delta(a)}}{kT}},$$

where

$$\epsilon^{\delta(a)} = \epsilon_0^{\delta(a)} + \sum_j h\nu_j^{\delta(a)}/2 \quad (8)$$

and $q_{\sigma,0}^{\delta(a)}$ is the vibrational *PF* of $\delta(a)$ moving in the average potential field of σ . Identifying $q_{\sigma,0}^{\delta(a)}$ with unity along with the approximation for $p^{\delta(g)}$, we have,

$$q_\sigma^{\delta(a)} = e^{-\frac{\epsilon^{\delta(a)}}{kT}} \quad (9)$$

Similarly for $q_{\sigma^*}^{\delta^*}$ we have,

$$q_{\sigma^*}^{\delta^*} = e^{-\frac{\epsilon^{\delta^*}}{kT}}, \quad \epsilon^{\delta^*} = \epsilon_0^{\delta^*} + \sum_k h\nu_k^{\delta^*}/2 \quad (10), (11)$$

It is shown with $\epsilon^{\delta(g)}$ and $\epsilon^{\delta(a)}$ that,

$$\bar{X}_p^{\delta(g)} = N_A \epsilon^{\delta(g)}, \quad \text{and} \quad \bar{X}_p^{\delta(a)} = N_A \epsilon^{\delta(a)} \quad (12.g), (12.a)$$

where $\bar{X}_p^{\delta(g)}$ or $\bar{X}_p^{\delta(a)}$ is the partial molal enthalpy of $\delta(g)$ or $\delta(a)$ respectively and N_A the Avogadro's number so that

$$\chi = N_A (\epsilon^{\delta(g)} - \epsilon^{\delta(a)}) \quad (13)$$

is the heat of adsorption at constant pressure.

Catalyst

$p^{\delta(g)}$ and $q_{\sigma^A}^{\delta^A(a)}$ thus being developed Eq. (1) assumes now the form,

$$\frac{\theta_{\sigma^A(\epsilon^A)}}{\theta_{\sigma^A(0)}} = e^{-\frac{\epsilon^{\delta^A(a)}}{kT}} \bigg/ p^{\delta^A(g)} = e^{-\frac{\epsilon^{\delta^A(a)}}{kT}} \alpha^{\delta^A(g)} = \frac{P^{\delta^A}}{Q^{\delta^A}} e^{-\frac{\Delta\epsilon(\delta^A)}{kT}}, \quad (14.\theta)$$

where $\Delta\epsilon(\delta^A) = \epsilon^{\delta^A(g)} - \epsilon^{\delta^A(a)} = \chi^{\delta^A}/N_A$ (14.\epsilon)

and in general in accordance with Eq. (7),

$$P^{\delta^A} = \prod_a (P^{\delta_a^A})^{\nu_a^A}, \quad Q^{\delta^A} = \prod_a (Q^{\delta_a^A})^{\nu_a^A} \quad \text{and} \quad \epsilon^{\delta^A(g)} = \sum_a \nu_a^A \epsilon^{\delta_a^A(g)} \quad (15.P), (15.Q), (15.\epsilon)$$

Therefrom it is deduced that (I) adsorption is perceptible at ordinary temperature only when $N_A \Delta\epsilon(\delta^A)$ amounts to the magnitude of 10 Kcal [such δ^A 's only are dealt with in this work], that (II) if δ^A is of only one kind, $\theta_{\sigma(0)}$ or $\theta_{\sigma^A(\delta^A)}$ tends to unity at the higher or the lower temperatures respectively, [Greatest possible value of $\theta_{\sigma^A(\delta^A)}$ attained at the lower extremity of temperature is not necessarily exactly unity because of possible overlapping of σ^A . cf. (B)] and that (III) if several such δ^A 's exist $\theta_{\sigma(0)}$ tends to unity at the higher temperatures as before but at lower temperatures $\theta_{\sigma^A(\delta^A)}$ tends to unity for that δ^A , for which $\theta_{\sigma^A(\delta^A)}/\theta_{\sigma^A(0)}$ is very large compared with unity and with that of any other δ^A 's.

On the other hand Eq. (2) for the rate assumes the form by introducing the expressions for $p^{\delta(g)}$ and $q_{\sigma^A}^{\delta^A(a)}$,

$$\vec{v} = K a^{\delta} = \gamma^{\delta^I} K_P^I P^{\delta}, \quad \vec{v} = K a^{\delta^F} = \gamma^{\delta^F} K_P^F P^{\delta^F} \quad (16.\vec{v}), (16.\vec{v})$$

where $\gamma^{\delta^I} = \alpha^{\delta^I} / \alpha^{\delta^I(g)}$, $\gamma^{\delta^F} = \alpha^{\delta^F} / \alpha^{\delta^F(g)}$ (17.I), (17.F)

and $\delta^I(g)$ or $\delta^F(g)$ is a gaseous system which converts mutually with δ^I or δ^F respectively, p^{δ^I} , K_P^I and p^{δ^F} , K_P^F being relevant to $\delta^I(g)$ and $\delta^F(g)$ respectively. K_P^I is given by

$$K_P^I = \frac{\rho}{Q_P^{\delta^I}} e^{-\frac{\Delta^*\epsilon}{kT}} \theta_{\sigma^*(0)} \quad (18.K)$$

where $\rho = \frac{kT_m}{h} eG$ and $\Delta^*\epsilon = \epsilon^{\delta^*} + kT_m - \epsilon^{\delta^I(g)}$ (18.\rho), (18.\epsilon)

and K_p^F similarly. $\Theta_{\sigma^*(0)}$ is expressed in the case of the presence of different kinds of δ^A 's as that,

$$\Theta_{\sigma^*(0)} = \left\{ \Theta_{\sigma^A(\delta^A)} Q_P^{\delta^A} e^{-\frac{\Delta \epsilon(\delta^A)}{kT}} / P^{\delta^A} \right\}^{\alpha(\delta^A)} \quad (19)$$

where δ^A is one of adsorbed systems and $\alpha(\delta^A)$ the ratio of the number of lattice points belonging to δ^* over that to σ^A .

Heterogeneous elementary reaction and adsorption thus being investigated the heterogeneous reaction of the following specification is now discussed.

(α) The reactant δ^G of the reaction (as expressed by relevant chemical equation with numerical coefficients normalized to least possible integers) is completely transferred into the resultant δ^D by respective finite number $n(r)$ [stoichiometrical number of the reaction. cf. (i), MSM] of operations of each constituent elementary reactions r 's.

(β) The initial (final) complex of the elementary reaction which consumes the reactant (produces the resultant) consists of the reactant (resultant) or its part but neither of the intermediates (δ^L or δ^F or a part of either of any elementary reaction which belongs neither to δ^G nor to δ^D).

(γ) Every constituent elementary reaction is necessary to complete Operation (I).

Hydrogenation of ethylene $C_2H_4 + H_2 = C_2H_6$ consisting of the elementary reactions, $C_2H_4 \rightarrow C_2H_4(a)$, $H_2 \rightarrow 2H(a)$, $C_2H_4(a) + H(a) = C_2H_5(a)$, $C_2H_5(a) + H(a) = C_2H_6$, satisfies the conditions but the Nernst chain $Cl_2 \rightarrow 2Cl$, $H_2 + Cl \rightarrow HCl + H$, $Cl_2 + H \rightarrow HCl + Cl$ for the reaction $H_2 + Cl_2 = 2HCl$ does not. Followings are deduced from the specification.

(δ) The rate of the steady reaction \mathfrak{R} or the number of the reactant transferred per unit time into the resultant is given by

$$\mathfrak{R} = m(r) \{ \vec{v}(r) - \overleftarrow{v}(r) \} \quad r = 1, \dots, t \quad (20)$$

where $m(r)$ is $1/n(r)$ or the number of the reaction completed per one elementary reaction r at the steady state.

$$(V) \quad \omega(r) = \frac{a_e^{\delta^F(r)}}{a_e^{\delta^L(r)}} = \frac{p^{\delta^L(r)}}{p^{\delta^F(r)}} = \left(\frac{p^{\delta^D}}{p^{\delta^G}} \right)^{m(r)} = \left(\frac{p^{\delta^G}}{p^{\delta^D}} \right)^{m(r)} = e^{\frac{m(r)(\mu^{\delta^D} - \mu^{\delta^G})}{kT}} \quad (21)$$

Catalyst

where suffix e denotes the particular value of $a^{\delta^I(r)}(p^{\delta^I(r)})$ or $a^{\delta^F(r)}(p^{\delta^F(r)})$ assumed when $\gamma^{\delta^I(r)} = 1$ or $\gamma^{\delta^F(r)} = 1$ respectively provided that $\delta^I(g)$ or $\delta^F(g)$ in Eq. (17) respectively converts with $\delta^I(r)$ or $\delta^F(r)$ from each other via any elementary reaction but r . $\gamma^{\delta^I(r)}$ and $\gamma^{\delta^F(r)}$ will be used hereafter in this restricted sense. $\mu^\delta = RT \log a^\delta = -RT \log p^\delta$ is the chemical potential of δ . (cf. MSM)

For the further deduction following quantities are defined.

$$\mathfrak{R}(r) = m(r)K(r)(a_e^{\delta^I(r)} - a_e^{\delta^F(r)}) \quad (22)$$

$$\mathfrak{R}(r, H) = m(r)K(r, H)(a_e^{\delta^I(r)} - a_e^{\delta^F(r)}) \quad (23)$$

$$\mathfrak{R}(r, L, \delta^A) = m(r)K(r, L, \delta^A)(a_e^{\delta^I(r)} - a_e^{\delta^F(r)}) \quad (24)$$

$K(r, H)$ is the value of $\mathfrak{R}(r)$ obtained by replacing $\theta_{\sigma^*(0)}$ in Eq. (18. K) with unity and $\mathfrak{R}(r, L, \delta^A)$ that obtained by substituting the latter $\theta_{\sigma^*(0)}$ from Eq. (19) and putting $\theta_{\sigma^A(\delta^A)} = 1$.

$\mathfrak{R}(r)$ thus defined is according to Eqs. (16), (17) and (20) the rate of the reaction which would be realized if all elementary reactions but r happened to satisfy the equilibrium condition $p^{\delta^I} = p^{\delta^F}$ or $a^{\delta^I} = a^{\delta^F}$ and $\mathfrak{R}(r, H)$ or $\mathfrak{R}(r, L, \delta^A)$ that realized if $\theta_{\sigma^*(0)}$ or $\theta_{\sigma^A(\delta^A)}$ further happened to be unity. Hence it is deduced further as follows.

(VI) $\mathfrak{R}(r) \leq \mathfrak{R}$ i.e. every $\mathfrak{R}(r)$ is an upper limit to \mathfrak{R} .

(VII) When one of $\mathfrak{R}(r)$'s, $\mathfrak{R}(r')$, becomes smaller compared with any others, $\mathfrak{R}(r')$ approximates \mathfrak{R} without limit and all r but r' tends to equilibrium. The elementary reaction of such small $\mathfrak{R}(r)$ may be called the rate-determining step.

(VIII) $\mathfrak{R}(r) = \mathfrak{R}(r, H) \theta_{\sigma^*(0)} = \mathfrak{R}(r, L, \delta^A)(\theta_{\sigma^A(\delta^A)})^{\alpha(\delta^A)}$ i.e. $\mathfrak{R}(r, H)$ and $\mathfrak{R}(r, L, \delta^A)$ are upper limits to $\mathfrak{R}(r)$ and hence to \mathfrak{R} , since $\theta_{\sigma^*(0)} < 1$ and $\theta_{\sigma^A(\delta^A)} < 1$.

(IX) When $\theta_{\sigma^A(\delta^A)} = \theta_{\sigma^A(0)}$, $\mathfrak{R}(r, H)$ and $\mathfrak{R}(r, L, \delta^A)$ coincides. The temperature of the coincidence is particular to δ^A but independent of r .

(X) In the case when the interaction between δ^* and δ^A 's is small so that $q_{\sigma^*}^{\delta^*}$ and $q_{\sigma^A}^{\delta^A}$'s are independent of $\theta_{\sigma^A(\delta^A)}$'s, and $\omega(r) \ll 1$ or according to (V) $\mu^{\delta^D} \ll \mu^{\delta^G}$ for all r 's,

(a) $\log \mathfrak{R}(r, H)$ and $\log \mathfrak{R}(r, L, \delta^A)$ are respectively linear functions of $1/T$ at constant $p^{\delta^I(r)}$,

(b) $\mathfrak{R}(r, L, \delta^A)$ straight line inclines against $1/T$ axis steeper than $\mathfrak{R}(r, H)$'s does, and,

(c) $\mathfrak{R}(r)$ line tends to $\mathfrak{R}(r, H)$ or $\mathfrak{R}(r, L, \delta^A)$ straight line at higher or lower temperatures respectively. The ratio of $\mathfrak{R}(r, H)$ or $\mathfrak{R}(r, L, \delta^A)$ at the intersection over $\mathfrak{R}(r)$ is 2.

(XI) If $\theta_{\sigma A(\delta^A)}/\theta_{\sigma A(0)} \ll 1$ for all r 's [cf. Eq. (14. θ)] the steady state is unique for which $\theta_{\sigma^*(0)} = 1$. If $\theta_{\sigma A(\delta^A)}/\theta_{\sigma A(0)} \gg 1$ for several δ^A 's, one of them may have $\theta_{\sigma A(\delta^A)}$ unity in accordance with (III) and with equilibrium relations determined by the prevailing rate-determining step, which is reciprocally conditioned by $\theta_{\sigma A(\delta^A)}$'s. The steady state which is self-consistent in this respect, as it should be for being realizable, is in general no more unique.

Assuming that $q_{\sigma^*}^{\delta^A}$ and $q_{\sigma A}^{\delta^A}$ are independent of $\theta_{\sigma A(\delta^A)}$'s as in (X) it is shown that such steady state among these as rendering $\mathfrak{R}(r)$ of certain r smallest has the greatest PF of the assembly or is most stable and hence realizable.

The consistency of the theorem is assured by auxiliary one stating that the order in magnitude of $\mathfrak{R}(r)$ is the same for every r .

On the basis of these theorems following rule for graphycal construction of \mathfrak{R} from $\mathfrak{R}(r, H)$ and $\mathfrak{R}(r, L, \delta^A)$ is obtained, which give, general features of the rate and the mechanism of the reaction varying with temperature at constant p^{δ^G} and p^{δ^D} .

Plot $\log \mathfrak{R}(r, H)$ and $\log \mathfrak{R}(r, L, \delta^A)$ for all r 's and δ^A 's against $1/T$ on one diagram. Straight lines are obtained in the special case of (X). At temperatures above the highest temperature of coincidence [cf. (IX)] or intersection, the lowest line gives simply the best upper limit to \mathfrak{R} of the unique realizable steady state, [cf. (XI)] which is generally coincident with but deviating from \mathfrak{R} in the neighbourhood of intersection. [cf. (X. c).]

For the temperature range below the highest intersection following procedure is followed.

Compare at any given temperature $\mathfrak{R}(r, H)$'s with each other or $\mathfrak{R}(r, L, \delta^A)$'s for each δ^A with each other. Examine whether r giving the lowest $\mathfrak{R}(r, H)$ or $\mathfrak{R}(r, L, \delta^A)$ for a certain δ^A and hence determining the rate fits according to (XI) the steady state specified by $\theta_{\sigma A(0)} = 1$ or by $\theta_{\sigma A(\delta^A)} = 1$. The lowest line of the self-consistent sets thus selected gives the best upper limit of the similar description as that above [this is justified in the special case of (XI) whereas in general case the steady state of greatest PF should be determined by detailed calculation.]

Simple example of the construction is given showing the possibility of sudden fall of the steady reaction rate not experimentally observed as yet.

STATISTICAL MECHANICAL RESEARCH ON THE HETEROGENEOUS REACTION

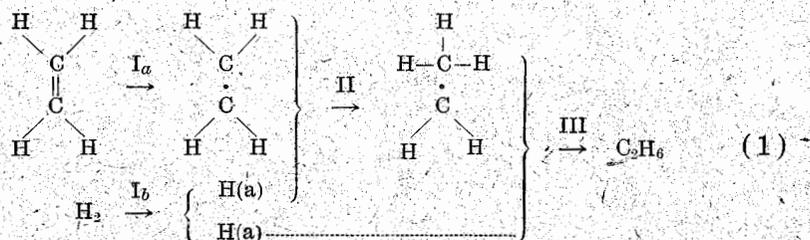
(Abstract)

PART II. MECHANISM OF THE HYDROGENATION OF ETHYLENE IN THE PRESENCE OF NICKEL CATALYST

By Juro HORIUTI

The statistical method developed in Part I [equations and theorems there are quoted with additional figure I] is applied to the enunciated reaction for establishing the mechanism or its structure with respect to $\mathfrak{R}(r)$'s of the constituent elementary reaction r 's. Experimental results are first investigated, finding zur Strassen's results⁽¹⁾ most reliable, any possible transport process being practically in equilibrium.

On the basis of this result as well as of those on the hydrogen electrode process and the hydrogenation of carbonyl group appropriate set of r 's is concluded as that



where $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$, $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array}$ and H(a) denote ethylene, ethyl group and hydrogen atom adsorbed on the catalyst respectively. The first two are denoted $\text{C}_2\text{H}_4(\text{a})$ and $\text{C}_2\text{H}_5(\text{a})$ in what follows. This set of r 's with step III as the

(1) Zur Strassen; Z. physik. Chem. **169** (1934), 81.

rate-determining is the associative mechanism due to Horiuti and Polanyi⁽²⁾.

Before dealing with $\theta(r)$'s, δ^A 's involved in the scheme i.e. $C_2H_4(a)$, $C_2H_5(a)$ and $H(a)$ are investigated for their adsorption according to Eq. (I. 14. θ),

$$\tau = \frac{\theta_{\sigma^A} \delta^A}{\theta_{\sigma^A(o)}} = \gamma(\delta^A) \frac{P^{\delta^A}}{Q_P^{\delta^A}} e^{\frac{\Delta \epsilon: \delta^A}{kT}}, \quad \gamma(\delta^A) = 1 \quad \text{at equilibrium} \quad (2)$$

Estimating heat of adsorption of ethylene $N_A \Delta \epsilon(\delta^A)$ at 16 Kcal and evaluating $Q_P^{\delta^A}$ from spectroscopic data it is found for the equilibrium, $C_2H_4(g) \rightleftharpoons C_2H_4(a)$, $\tau < 2 \times 10^{-3}$ over the range of zur Strassen's experimental condition, $p_{H_2} = p_{C_2H_4} = 0.03$ mmHg, $-10^\circ \sim 125^\circ C$, much less for all other possible equilibrium, for instance $C_2H_6 = C_2H_4(a) + H_2$ corresponding to the rate-determining step of I_a and for the case of existence of other δ^A 's or of equilibrium not being attained when $\gamma(\delta^A) < 1$.

Heat of adsorption for the adsorption $C_2H_4 + 1/2 H_2 \rightleftharpoons C_2H_5(a)$ is estimated at 23.3 Kcal from the above value for $N_A \Delta \epsilon(C_2H_4)$ assuming the additivity of the bond energy. It is similarly found $\tau < 5 \times 10^{-3}$ over the range of zur Strassen's condition with due regards to all other possible adsorption reactions.

Heat of adsorption of hydrogen is found by Fryling⁽³⁾ at $0^\circ C$ varying appreciably with adsorbed quantity. It is concluded that we are thereby dealing with the activated adsorption and hence that $\theta_{\sigma H(o)} = 1 - \theta_{\sigma H(H)}$ on the ground that this and other experimental facts are adequately accounted for by the picture taking the repulsive potential between $H(a)$'s, each on one lattice point, into consideration. Substituting $\theta_{\sigma H(o)}$ therefrom into Eq. (2) and combining the relation between $\theta_{\sigma H(H)}$, p_{H_2} and $\Delta \epsilon(H)$ thus obtained with the experimentally observed dependence of p_{H_2} and $\Delta \epsilon(H)$ on adsorbed quantity we have $\Delta \epsilon(H)$ as a function of $\theta_{\sigma H(H)}$. This function allows us to calculate $\theta_{\sigma H(H)}$ by Eq. (2) at every T and p_{H_2} . The result obtained for zur Strassen's experimental conditions is as follows:

$t^\circ C$	-10°	0°	60°	120°	$(p_{H_2} = 0.03 \text{ mmHg})$
$\theta_{\sigma H(H)}$	0.28	0.24	0.12	0.07	

It is seen that $\theta_{\sigma H(H)}$ varies extremely slowly with temperature

(2) Horiuti & Polanyi; Trans. Faraday Soc. 30 (1934), 1164.

(3) Fryling. J. Phys. Chem, 30 (1926), 818.

Catalyst

which is accounted for by taking exceptionally far reaching exchange repulsion between H(a)'s into consideration and is hence taken rather exceptional.

Summarizing these results it is concluded that the adsorption of C₂H₄(a) and C₂H₅(a) are negligible over the range of Zur Strassen's experimental condition, and that H(a) is the only δ⁴ which affects θ_{σ*(0)} and Δ*ε(r) [cf. Eqs. (I, 2) and (I, 3)], whereby such part played by saturated system H₂ and C₂H₆ being neglected.

The theory of steady reaction developed in Part I is now specified to the scheme (1). Noting m(r) = 1 for every elementary reaction in this case [cf. Eq. (I, 20)], Eqs. (I, 21), (I, 16), (I, 17), (I, 22) and (I, 20) are written in the forms,

$$\omega(r) = \omega = e^{-\frac{\mu_{C_2H_4} + \mu_{H_2} - \mu_{C_2H_6}}{kT}} \quad (3)$$

$$\vec{v}(I_a) = \frac{\mathfrak{R}(I_a)}{1 - \omega}, \quad \vec{v}(I_b) = \frac{\mathfrak{R}(I_b)}{1 - \omega} \quad (4. I_a) \quad (4. I_b)$$

$$\vec{v}(II) = \gamma(H)\gamma(C_2H_4) \frac{\mathfrak{R}(II)}{1 - \omega}, \quad \vec{v}(III) = \gamma(H)\gamma(C_2H_5) \frac{\mathfrak{R}(III)}{1 - \omega} \quad (4. II) \quad (4. III)$$

$$\vec{v}(I_a) = \gamma(C_2H_4) \frac{\mathfrak{R}(I_a)}{1 - \omega}, \quad \vec{v}(I_b) = \gamma(H)^2 \frac{\mathfrak{R}(I_b)}{1 - \omega}, \quad (5. I_a), \quad (5. I_b)$$

$$\vec{v}(II) = \gamma(C_2H_5) \frac{\mathfrak{R}(II)}{1 - \omega}, \quad \vec{v}(III) = \omega \frac{\mathfrak{R}(III)}{1 - \omega}, \quad (5. II), \quad (5. III)$$

$$\gamma(H)^2 = \frac{(\alpha_{H(a)})}{\alpha_{H_2}}, \quad \gamma(C_2H_4) = \frac{\alpha_{C_2H_4(a)}}{\alpha_{C_2H_4}}, \quad \gamma(C_2H_5) = \frac{\alpha_{C_2H_5(a)}}{(\alpha_{H_2})^{\frac{1}{2}} \alpha_{C_2H_4}}$$

(6. H₂), (6. C₂H₄), (6. C₂H₅),

$$\mathfrak{R}(I_a) = \rho \frac{P_{C_2H_4}}{Q_{C_2H_4}} e^{-\frac{\Delta^* \epsilon(I_a)}{kT}} \theta_{\sigma^*(0)} (1 - \omega), \quad (7. I_a)$$

$$\mathfrak{R}(I_b) = \rho \frac{P_{H_2}}{Q_{H_2}} e^{-\frac{\Delta^* \epsilon(I_b)}{kT}} \theta_{\sigma^*(0)} (1 - \omega), \quad (7. I_b)$$

$$\mathfrak{R}(II) = \rho \left(\frac{P_{H_2}}{Q_{H_2}} \right)^{\frac{1}{2}} \frac{P_{C_2H_4}}{Q_{C_2H_4}} e^{-\frac{\Delta^* \epsilon(II)}{kT}} \theta_{\sigma^*(0)} (1 - \omega), \quad (7. II)$$

$$\mathfrak{R}(\text{III}) = \rho \frac{P_{\text{H}_2}}{Q_P^{\text{H}_2}} \frac{P_{\text{C}_2\text{H}_4}}{Q_P^{\text{C}_2\text{H}_4}} e^{-\frac{A^* \epsilon \cdot \text{III}}{kT}} \theta_{\sigma^*(\text{H})} (1-\omega), \quad (7. \text{III})$$

$$\begin{aligned} \mathfrak{R} &= \frac{\mathfrak{R}(\text{I}_a)(1-\gamma(\text{C}_2\text{H}_4))}{1-\omega} = \frac{\mathfrak{R}(\text{I}_b)(1-\gamma(\text{H})^2)}{1-\omega} = \frac{\mathfrak{R}(\text{II})(\gamma(\text{H})\gamma(\text{C}_2\text{H}_4)-\gamma(\text{C}_2\text{H}_5))}{1-\omega} \\ &= \frac{\mathfrak{R}(\text{III})(\gamma(\text{H})\gamma(\text{C}_2\text{H}_5)-\omega)}{1-\omega} \end{aligned} \quad (8)$$

From Eq. (8) we have further,

$$\frac{1}{\mathfrak{R}} = \frac{\gamma(\text{H})^2}{\mathfrak{R}(\text{I}_a)} + \frac{1}{\mathfrak{R}(\text{I}_b)} + \frac{\gamma(\text{H})}{\mathfrak{R}(\text{II})} + \frac{1}{\mathfrak{R}(\text{III})} \quad (9)$$

The ω is calculated at Zur Strassen's experimental condition according to Eq. (3) and to that $\mu^\delta = \mu_1^\delta + RT \log P^\delta$ from known data of μ_1^δ as that,

$$\omega < 10^{-6} \quad (10)$$

Eq. (9) is now compared, with due regard to the state of adsorption concluded above, with Zur Strassen's experimental results, i.e. (1) \mathfrak{R} has an optimum temperature at ca 60°C (2) \mathfrak{R} is strictly proportional to PH_2 over the whole range of experimental condition (3) \mathfrak{R} is almost independent of PC_2H_4 at lower temperatures below the optimum and (4) at the higher extremity of temperature (120°) \mathfrak{R} is nearly proportional to PC_2H_4 . Followings are concluded therefrom. (a) The first and the third term on the right of Eq. (9) is negligible compared with the sum of the second and the fourth term, i.e.

$$\frac{1}{\mathfrak{R}} = \frac{1}{\mathfrak{R}(\text{I}_b)} + \frac{1}{\mathfrak{R}(\text{III})}$$

(b) $\mathfrak{R}(\text{III}) \doteq \mathfrak{R}(\text{III}, \text{H})$ over the whole range. (c) At the lower temperatures $\gamma(\text{H}) \ll 1$ and $\mathfrak{R}(\text{I}_b) \ll \mathfrak{R}(\text{III})$, I_b being rate-determining. (d) At higher temperatures $\gamma(\text{H}) \doteq 1$ and $\mathfrak{R}(\text{I}_b) \gg \mathfrak{R}(\text{III})$, III being the rate-determining. It follows further from (c) that H(a) vanishes according to Eq. (6) at lower temperatures so that $\mathfrak{R}(\text{I}_b) \doteq \mathfrak{R}(\text{I}_b, \text{H})$ there, whereas this can not be the case at higher temperatures on account of (d) and of the far-reaching repulsion and that according to (a), (b), (c) and (d) \mathfrak{R} is expressed by

$$\frac{1}{\mathfrak{R}} = \frac{1}{\mathfrak{R}(\text{I}_b, \text{H})} + \frac{1}{\mathfrak{R}(\text{III}, \text{H})} \quad (11. a)$$

Catalyst

apart from the transient region in the neighbourhood of the optimum whereas exactly by,

$$\frac{1}{\mathfrak{R}} = \frac{1}{\mathfrak{R}(I_b)} + \frac{1}{\mathfrak{R}(III, H)} \quad (11. b)$$

where

$$\mathfrak{R}(I_b, H) = \rho \frac{PH_2}{Q_P^{H_2}} e^{-\frac{\Delta^* \epsilon(I_b, H)}{kT}}, \quad \mathfrak{R}(III, H) = \rho \frac{PH_2}{Q_P^{H_2}} \frac{PC_2H_4}{Q_P^{C_2H_4}} e^{-\frac{\Delta^* \epsilon(III, H)}{kT}} \quad (12. I), (12. III)$$

putting $\theta_{\sigma^*}(0) = 1$ in Eq. (7) according to Part I and neglecting ω .

Eq. (11. a) is fitted now numerically to zur Strassen's result for general features of the structure on one hand while Eq. (11. b) for accurate structure in the transient region assuming that $\log \mathfrak{R}(I_b)$ varies there locally linearly with $1/T$.

The former procedure with spectroscopic data $Q_P^{H_2} = 1.09 \times 10^{10} \text{ cc}^{-1} \text{ mmHg}^{-1}$, $Q_P^{C_2H_4} = 3.89 \times 10^{14} \text{ cc}^{-1} \text{ mmHg}^{-1}$, at $PH_2 = PC_2H_4 = 0.03 \text{ mmHg}$ gives $N_A \Delta^* \epsilon(I_b, H) = 12 \text{ Kcal}$ and $N_A \Delta^* \epsilon(III, H) = -12 \text{ Kcal}$ [N_A : -Avogadro's number] whereas the second, denoting the coefficients of the linearity,

$$\log \mathfrak{R}(I_b) = \log \rho \frac{PH_2}{Q_P^{H_2}} - \frac{\Delta^* \epsilon(I_b)}{kT}$$

with prime, that $Q_P^{H_2'} = 2.6 \times 10^{18}$, $N_A \Delta^* \epsilon(I_b)' = 5 \text{ Kcal}$ and $N_A \Delta^* \epsilon(III, H) = -7 \text{ Kcal}$.

For $\mathfrak{R}(I_a)$ and $\mathfrak{R}(II)$ it is concluded that, $\Delta^* \epsilon(I_a) < 3 \text{ Kcal}$ and that $N_A(\Delta^* \epsilon(II) - \Delta^* \epsilon(III)) = 7 \text{ Kcal}$ by virtue of the theoretical results, $\mathfrak{R}(I_a) = \mathfrak{R}(I_a, H)$ and $\mathfrak{R}(II) = \mathfrak{R}(II, H)$ as inferred from (b). $\Delta^* \epsilon(II)$ thus depends of course on the alternative value of $\Delta^* \epsilon(III, H)$.

The results of the first procedure are shown in the Fig. I_a and III alternatively determines the rate there according to the construction rule in Part I at temperatures respectively below or above the intersection, at which the synthesized steady reaction rate is maximum. The calculated value according to Eq. (11. a) deviates considerably from the observed as expected, each being shown respectively by the broken or the full line under the intersection in the figure. Figure at lower temperatures is constructed assuming the absence of interaction between δ^* and δ^{**} 's and hence that $\Delta^* \epsilon(r) = \Delta^* \epsilon(r, H) = \Delta^* \epsilon(r, L, \delta^A)$. Vertical

chain lines denoted by respective δ^A show the desorption temperature relevant to respective δ^A [cf. I, (IX)], superfix 1 to the latter denoting respectively the appropriate adsorption reactions, $H_2 \rightleftharpoons 2H(a)$, $C_2H_4 \rightleftharpoons C_2H_4(a)$ and $1/2H_2 + C_2H_4 = C_2H_5(a)$.

The desorption temperature of H(a) is conventionally calculated assuming $\Delta\epsilon(r, H)$ at $\theta_{\sigma H(H)}/\theta_{\sigma H(0)} = 1$ is kept constant throughout [cf. I, (IX)]. $\mathfrak{R}(r, H)$ or $\mathfrak{R}(r, L, \delta^A)$ shown in the figure below the highest intersection temperature is that belonging to the self-consistent steady state [cf. I].

The results of the second procedure is used in Part III where the limited region is quantitatively investigated.

The conclusion is the same in the both cases as regards the alternative rate-determining step, which deviates from the current theory⁽⁴⁾ of the reaction which attributes the optimum to the ethylene desorption there. The correctness of the present conclusion is verified below and in Part III.

It is seen from the figure that the similar diagram for nickel catalyst at any other set of values of PH_2 and PC_2H_4 is immediately obtained by shifting the straight lines parallel respectively by appropriate amounts. It is thus shown in general that $\mathfrak{R}(r, H)$ straight lines become more close to each other in the neighbourhood of I, III intersection if PH_2 alone increased, reverse is the case if PC_2H_4 alone increased and the effect of PH_2 outweighs if both PH_2 and PC_2H_4 are increased by the same factor, the intersection temperature being unshifted by PH_2 -increase whereas shifted toward higher temperature by PC_2H_4 -increase.

The conclusion of the above procedure is compared with experiments as follows. Rideal⁽⁵⁾ finds at $PH_2 + PC_2H_4 = 760$ mmHg, $PC_2H_4 =$ ca. 30 mmHg the rate is proportional to PC_2H_4 and attains maximum at 137°C, whereas at $PH_2 + PC_2H_4 = 760$ mmHg, $PH_2 =$ ca. 30 mmHg the rate is proportional to PH_2 , attains no maximum up to 190°C and gains upon the former's there first. Investigation of the experiment as in zur Strassen's case shows the result qualitatively reliable, diffusion being possibly not quite in equilibrium especially in the former case. The diagram constructed for the experimental condition reserves the structure of zur Strassen's case qualitatively, I, III intersection shifting to 120°C for the former or to 180°C for the latter case respectively, the latter's rate gaining upon the former's just at 180°C. It is shown that the approximation implied in the

(4) Schwab; Z. physik. Chem. **A171** (1934), 421.

(5) Rideal; J. Chem. Soc. London, **121** (1922), 309.

first procedure makes the shift of the optimum too small, which is in accordance with experiments. Experimental findings for the proportionality between \mathfrak{R} and PC_2H_4 at lower temperatures, which is the only deviation from the theory, is attributed to the diffusion for controlling the rate making the latter apparently proportional to PC_2H_4 .

The result obtained by Toyama⁽⁶⁾ at $\text{PH}_2 = 45 \text{ mmHg}$ and $\text{PC}_2\text{H}_4 = 50 \text{ mmHg}$ between 99°C and 165°C that $\mathfrak{R} = \frac{\text{PH}_2\text{PC}_2\text{H}_4}{1 + k_2\text{PC}_2\text{H}_4}$, [k_2, k_4 ; const] with optimum in the neighbourhood of 140°C , is proved quantitatively reliable whereas that of the same author⁽⁷⁾ at -78°C to 0°C being suspected of diffusion through the liquid film formed by capillary condensation for being controlling. The constructed diagram again reserves qualitatively zur Strassen's structure with an optimum at 134°C and hence reproduces the above dependency of \mathfrak{R} according to Eqs. (11. a) and (12).

Farkas, Farkas and Rideal's result⁽⁸⁾ at $\text{PH}_2 = \text{PC}_2\text{H}_4 = \text{ca. } 10 \text{ mmHg}$ with ca. 30% shifted hydrogen, proved similarly quantitatively reliable, shows that the shift appreciably decreases in the course of hydrogenation at 120°C and 150°C whereas slightly increases at 20°C . Analysing their data it is found at 20°C that \mathfrak{R} is proportional to PH_2 but independent of PC_2H_4 . The appropriate diagram is again qualitatively reserves zur Strassen's structure with the optimum lying at 115°C . It follows from the latter that at 20°C where I_b is rate-determining the kinetics must be such as observed and the deuterium content is practically conditioned by the relative rate of consumption of H and D by step I_b , thus remaining almost constant or rather slightly increasing and that at 120° and 150° where III is rate-determining C_2H_4 and H_2 are free to exchange hydrogen atoms as inferred from scheme (1), thus accounting for the experiment. The observed variation of the shift cannot however be explained by the current theory which attributes the optimum to the ethylene desorption.

(6) Toyama; Rev. Phys. Chem. Japan, VII (1938), 115.

(7) Toyama; Rev. Phys. Chem. Japan, VI (1937), 353.

(8) Farkas, Farkas & Rideal; Proc. Roy. Soc. London, **A146** (1934), 63.

STATISTICAL MECHANICAL RESEARCH ON THE HETEROGENEOUS REACTION

(Abstract)

PART III. ISOTOPIC EXCHANGE, EQUILIBRATION AND PARA HYDROGEN CONVERSION ACCOMPANIED BY THE HYDROGENATION OF ETHYLENE IN THE PRESENCE OF NICKEL CATALYST.

By Juro HORIUTI

On the basis of the "structure" of the hydrogenation reaction determined in Part II (equation and theorems in Part I and II are denoted by additional figures I and II respectively) expressions in terms of $\mathfrak{R}(r)$'s are derived here for the rate of change in isotopic content, para-hydrogen conversion and equilibration reaction (according to Twigg and Rideal's⁽¹⁾ terminology),

$$P_2 + D_2 = 2PD$$

where P or D denotes protium or deuterium while H represents them; the expressions are now checked by experiments for a further confirmation of the "structure". In this treatment the isotopic shift of the rate and hence of the equilibrium is neglected throughout and $\mathfrak{R}(r)$'s are referred to constants adjusted quantitatively for the limited region in the neighbourhood of the optimum temperature according to the second procedure in Part II.

With the notations,

$x^H(a)$, $x^{C_2H_4}(a)$;—atomic fraction of D in $H(a)$ and $C_2H_4(a)$
 DH_2 , DC_2H_4 , DC_2H_6 ;—total number of D atoms forming H_2 , C_2H_4 and C_2H_6
 $\mathfrak{N}H_2$, $\mathfrak{N}C_2H_4$, $\mathfrak{N}C_2H_6$;—total number of molecules of " " "
 x^{H_2} , $x^{C_2H_4}$, $x^{C_2H_6}$;—atomic fraction of D in " " "

the rate E^H of change in deuterium content of H_2 and that E^E of C_2H_4 , or those of the "exchange reaction" are defined and expressed with regard to the "structure" as that,

(1) Twigg & Rideal; Proc. Roy. Soc. London, **A171** (1939), 55.

Catalyst

$$E^H = -\mathfrak{R}_{H_2} \dot{x}_{H_2} = (x^{H_2} - x^{H(a)}) \dot{v}(I_a) \quad (I. H)$$

$$E^E = \mathfrak{R}_{C_2H_4} \dot{x}_{C_2H_4} = (x^{C_2H_4(a)} - x^{C_2H_4}) \dot{v}(I_a) \quad (I. E)$$

Stating the steady state condition with respect to D in the form,

$$\begin{aligned} 2x^{H_2} \dot{v}(I_b) + \frac{1}{3} (x^{H(a)} + 2x^{C_2H_4(a)}) \dot{v}(II) + x^{C_2H_6} \dot{v}(III) \\ = 2x^{H(a)} \dot{v}(I_b) + x^{H(a)} \dot{v}(II) + x^{H(a)} \dot{v}(III) \end{aligned} \quad (2. H)$$

or

$$\begin{aligned} 4x^{C_2H_4} \dot{v}(I_a) + \left\{ 2x^{C_2H_4(a)} + \frac{2}{3} (2x^{C_2H_4(a)} + x^{H(a)}) \right\} \dot{v}(II) \\ = 4x^{C_2H_4(a)} \dot{v}(I_a) + 4x^{C_2H_4(a)} \dot{v}(II) \end{aligned} \quad (2. E)$$

which equals the time rate of supply of D to $H(a)$ or $C_2H_4(a)$ in accordance with scheme (II, 1) on the left with that of loss on the right, respectively, it is obtained, eliminating x^{H_2} and $x^{C_2H_4(a)}$ from Eqs. (1), (2) and the overall steady state condition,

$$\dot{v}(I_a) - \dot{v}(I_a) = \dot{v}(I_b) - \dot{v}(I_b) = \dot{v}(II) - \dot{v}(II) = \dot{v}(III) - \dot{v}(III),$$

as that,

$$E^H = \frac{\dot{v}(I_a) \dot{v}(II) (x^{H_2} - x^{C_2H_4}) + \dot{v}(III) (x^{H_2} - x^{C_2H_6})}{\dot{v}(I_b) + \frac{4\dot{v}(I_a) \dot{v}(II)}{6\dot{v}(I_a) + \dot{v}(II)} + \dot{v}(II)} \quad (3. H)$$

$$E^E = \dot{v}(I_a) \frac{\dot{v}(II)}{6\dot{v}(I_a) + \dot{v}(II)} \left\{ \frac{2\dot{v}(I_b) (x^{H_2} - x^{C_2H_4}) + \dot{v}(III) (x^{C_2H_6} - x^{C_2H_4})}{2\dot{v}(I_b) + \frac{4\dot{v}(I_a) \dot{v}(II)}{6\dot{v}(I_a) + \dot{v}(II)} + \dot{v}(III)} \right\} \quad (3. E)$$

The general expression is now simplified with due regard to the special situation common to structure diagrams in Part II that,

$$\mathfrak{R}(I_a) \gg \mathfrak{R}(r), \quad r = I_b, \quad II \quad \text{or} \quad III \quad (4. \mathfrak{R}')$$

or according to Eqs. (II, 8) and (II, 9),

$$\gamma(C_2H_4) = 1 \quad (4. \gamma)$$

and that $w < 10^{-8}$ in the form,

$$E^H = -\mathfrak{R}_{H_2} x_{H_2} = (x_{H_2} - x_{C_2H_4}) F \overset{\leftarrow}{v}(I_b), \quad (5. H)$$

$$E^E = \mathfrak{R}_{C_2H_4} x_{C_2H_4} = \frac{1}{2} (x_{H_2} - x_{C_2H_4}) F \vec{v}(I_b) \quad (5. E)$$

where

$$x^H(a) = \frac{3 \vec{v}(I_b) x_{H_2} + \overset{\leftarrow}{v}(II) x_{C_2H_4}}{3 \vec{v}(I_b) + \overset{\leftarrow}{v}(II)}, \quad x_{C_2H_4}(a) = x_{C_2H_4} \quad (5. x^H), (5. x^E)$$

and $F = \overset{\leftarrow}{v}(II) / 3 \vec{v}(I_b) + \overset{\leftarrow}{v}(II) \quad (5. F)$

Conclusions are drawn from Eqs. (5) as below.

(1) With regard to the change of D content accompanied by the hydrogenation, we are not in general dealing with simple "exchange reaction" for which $x_{H_2} + \frac{2\mathfrak{R}_{C_2H_4}}{\mathfrak{R}_{H_2}} x_{C_2H_4}$ is conserved, as generally accepted to be. For instance in the case when $\mathfrak{R}_{H_2} = \mathfrak{R}_{C_2H_4}$ and $x_0^{H_2} > x_0^{C_2H_4}$ (suffix 0 denotes initial values) we have $x_0^{H_2} - x_{H_2} = 2 \int_{x_0^{C_2H_4}}^{x_{C_2H_4}} \gamma(H)^2 dx_{C_2H_4}$ or $x_0^H + 2x_0^{C_2H_4} \leq x_{H_2} + 2x_{C_2H_4}$ where $\gamma(H)^2 = \frac{\overset{\leftarrow}{v}(I_b)}{\vec{v}(I_b)} \leq 1$ [cf. Eqs. (II. 4. I_b) and (II. 5.

I_b)]. In the further extreme case when $x_0^{C_2H_2} = 1$, $x_0^{C_2H_4} = 0$ and $\gamma(H) \ll 1$ or I_b is the rate-determining step, $x_{H_2} + 2x_{C_2H_4}$ would be conserved if C₂H₄ paid out just twice as much P for hydrogenation as H₂ did D for the rate-determining step; but since $D(a)$ thus formed readily mix up with P 's of C₂H₄ [cf. (2. a) below] giving out P in its place for hydrogenation P is consumed more than twice as much as D is and hence $x_0^{H_2} + x_0^{C_2H_4} < x_{H_2} + x_{C_2H_4}$.

(2) In the case when $x_0^{H_2} = 1$ and $x_0^{C_2H_4} = 0$, Eqs. (5) assume the forms according to Eqs. (II. 4. I_b), (II. 5. I_b) neglecting w ,

$$E_0^H = F \overset{\leftarrow}{v}(I_b) = F \gamma(H)^2 \mathfrak{R}(I_b), \quad E_0^E = F \vec{v}(I_b) = F \mathfrak{R}(I_b), \quad (6. H), (6. E)$$

and $F = \frac{\gamma(C_2H_5) \mathfrak{R}(II)}{3 \mathfrak{R}(I_b) + \gamma(C_2H_5) \mathfrak{R}(II)} \quad (6. F)$

Eqs. (6) when solved simultaneously with the equations,

Catalyst

$$\mathfrak{R} = (1 - \gamma(\text{H})^2)\mathfrak{R}(\text{I}_b) = (\gamma(\text{H}) - \gamma(\text{C}_2\text{H}_5))\mathfrak{R}(\text{II}), \quad \frac{1}{\mathfrak{R}} = \frac{1}{\mathfrak{R}(\text{I}_b)} + \frac{\gamma(\text{H})}{\mathfrak{R}(\text{II})} + \frac{1}{\mathfrak{R}(\text{III})}, \quad (7), (8)$$

derived from Eqs. (II. 8), (II. 9) and (4) determine E_0^{H} and E_0^{E} as well as \mathfrak{R} , $\gamma(\text{H})$, $\gamma(\text{C}_2\text{H}_5)$ for a given set of values of $\mathfrak{R}(\text{I}_b)$, $\mathfrak{R}(\text{II})$ and $\mathfrak{R}(\text{III})$. Fig. 1 shows values of E_0^{H} and E_0^{E} thus worked out at $P_{\text{H}_2} = P_{\text{C}_2\text{H}_4} = 10$ mmHg. E_0^{H} increases with temperature, as shown in Fig. 1, much steeper at lower temperatures than $\mathfrak{R}(\text{I}_b) = \mathfrak{R}$ does while E_0^{E} runs almost parallel to the latter, the both tending to run parallel to $\mathfrak{R}(\text{II})$ at higher temperatures.

(2 a) At lower temperatures where I_b is the rate-determining or $\mathfrak{R} = \mathfrak{R}(\text{I}_b)$ [cf. Part I] it is deduced from Eq. (7) and Fig. 1 that,

$$\gamma(\text{H}) = \gamma(\text{C}_2\text{H}_5) = \sqrt{\frac{\mathfrak{R}(\text{I}_b)}{\mathfrak{R}(\text{III})}} \ll 1 \quad \text{and} \quad \mathfrak{R}(\text{II}) \gg \sqrt{\mathfrak{R}(\text{I}_b)\mathfrak{R}(\text{III})}$$

and henceforth that $\vec{v}(\text{I}_b) = \mathfrak{R}(\text{I}_b) \gg \overleftarrow{v}(\text{I}_b)$ and H(a) mix up with P's of C_2H_4 much more readily than is consumed by III. Taking the above relations into account we have from Eq. (6) for the case $x_{\text{H}_2} = 1$ and $x_{\text{C}_2\text{H}_4} = 0$ that

$$E_0^{\text{H}} = \overleftarrow{v}(\text{I}_b) = \mathfrak{R}(\text{I}_b)^2/\mathfrak{R}(\text{III}), \quad E_0^{\text{E}} = \frac{1}{2}\vec{v}(\text{I}_b) = \frac{1}{2}\mathfrak{R}(\text{I}_b), \quad F = 1 \quad (9. \text{H}), (9. \text{E}), (9. \text{F})$$

(2 b) At higher temperatures where,

$$\mathfrak{R}(\text{I}_b) \gg \mathfrak{R}(\text{II}) \gg \mathfrak{R}(\text{III}), \quad (10. \mathfrak{R})$$

it is according to Eqs. (7), (8), (II. 4) and (II. 5) that,

$$\gamma(\text{H}) = \gamma(\text{C}_2\text{H}_5) = 1, \quad \vec{v}(\text{I}_b) = \overleftarrow{v}(\text{I}_b) = \mathfrak{R}(\text{I}_b) \quad (10. \gamma), (10. \text{I}_b)$$

$$\vec{v}(\text{II}) = \overleftarrow{v}(\text{II}) = \mathfrak{R}(\text{II}), \quad \vec{v}(\text{III}) = \mathfrak{r}(\text{III}) \quad (10. \text{II}), (10. \text{III})$$

Taking Eqs. (10) into account Eqs. (6) for the case $x_{\text{H}_2} = 1$ and $x_{\text{C}_2\text{H}_4} = 0$ assumes the form,

$$E^H = \frac{1}{3}\mathfrak{R}(\text{II}), \quad E_0^E = \frac{1}{3}\mathfrak{R}(\text{II}), \quad F = \mathfrak{R}(\text{II})/3\mathfrak{R}(\text{I}_b)$$

(11. H), (11. E), (11. F)

Conclusions (2), (2a) and (2b) show that the "activation energy of the exchange reaction" $RT^2 \frac{d \log E_0^H}{dT}$ varies from its constant value,

$NA(2\Delta^*\epsilon(\text{I}_b, \text{H}) - \Delta^*\epsilon(\text{III}, \text{H}))$ [cf. Eqs. (9. H) and (II. 12)] at lower temperatures gradually through the region in the neighbourhood of the optimum temperature to settle at another constant value $\Delta^*\epsilon(\text{II}, \text{H})$ at higher temperatures. The constant value is 17 or zero Kcal respectively which contrasts with $RT^2 \frac{d \log \mathfrak{R}}{dT}$ at respective region $\Delta^*\epsilon(\text{I}_b, \text{H}) = 5$ Kcal or $\Delta^*\epsilon(\text{III}, \text{H}) = -7$ Kcal [cf. II].

Twigg and Rideal⁽¹⁾ observes with the hydrogenation of ethylene with D_2 at $P_{H_2} = P_{C_2H_4} = \text{ca } 10$ mmHg in the presence of nickel catalyst that $RT^2 \frac{d \log E_0^H}{dT}$ is 19 Kcal at 70°C which decreases as temperature rises down to 4 Kcal at 200°C whereas $RT^2 \frac{d \log E_0^H}{dT} - RT^2 \frac{d \log \mathfrak{R}}{dT}$ is about 4~5 Kcal at higher temperatures but seems appreciably to increase at lower temperatures.

The results (certified for being quantitatively reliable at least so far as isotopic effect is concerned as in the case of experimental materials in Part II) are compared with the theoretical results derived from Fig. 1 that $RT^2 \frac{d \log E_0^H}{dT} = 17$ or 4 Kcal at 70°C or 200°C respectively. The satisfactory agreement thus verifies the underlying "structure" of the reaction.

The steeper rise of E_0^H as compared with that of \mathfrak{R} , which led Twigg and Rideal to the conclusion of a higher energy barrier for the "exchange reaction" compared with that for the hydrogenation proper is accounted for by the following procedure rather intuitive but assured by the present exact theory. Noting first that $E_0^H = -\mathfrak{R}_{H_2} x_{H_2}$ is given at $x_{H_2} = 1$, $x_{C_2H_4} = 0$ simply by $v(\text{I}_b)$ when I_b is the rate-determining step or by the rate of coming back of P from $\text{H}(a)$ for which practically $x^{\text{H}(a)} = 0$, [cf. (2a)] E_0^H is given as the product of $v(\text{I}_b) = \mathfrak{R}(\text{I}_b)$ and the fraction of coming back of $\text{H}(a)$. The first factor is proportional to

Catalyst

$e^{-\frac{\Delta^*\epsilon(I_b, H)}{kT}}$ [cf. Part II] whereas the second is $e^{-\frac{\Delta^*\epsilon(I_b, H)}{kT}} / e^{-\frac{\Delta^*\epsilon(III, H)}{kT}}$
 $= e^{-\frac{\Delta^*\epsilon(I_b, H) - \Delta^*\epsilon(III, H)}{kT}}$ or the Boltzmann factor of the relative height of the energy barrier of I_b above that of III, which latter controls the consumption of $H(a)$ as readily inferred from (2a). The result is that $E_0^H \propto e^{-\frac{2\Delta^*\epsilon(I_b, H) - \Delta^*\epsilon(III, H)}{kT}}$ or that $RT^2 \frac{d \log E_0^H}{dT} = 2\Delta^*\epsilon(I_b, H) - \Delta^*\epsilon(III, H)$, in accordance with the exact theory. The reason why $RT^2 \frac{d \log E_0^H}{dT}$

$> RT^2 \frac{d \log f}{dT}$ is that the height of the energy barrier of I_b is measured twice from the both sides, along with the situation that the "exchange reaction" consists in the reverse step of I_b which sends back a small fraction of $H(a)$ poured from H_2 at a rate equal to the forward rate $\vec{v}(I_b) = \mathfrak{R}(I_b)$ of I_b . It is true in the case of an independent steady reaction that the height of the energy barrier of the rate-determining step is simply measured by the temperature variation but not with a palastic phenomenon as the "exchange reaction".

(3) The simultaneous differential equation (5) is now integrated with the initial condition, $\mathfrak{N}_{H_2} = \mathfrak{N}_{C_2H_4} = \mathfrak{N}_0$, $x_{H_2} = 1$ and $x_{C_2H_4} = 0$. with the results,

$$E^H = -\mathfrak{N}_0 x_{H_2} = \vec{v}(I_b) F e^{\int_P^{P_0} \left(\frac{1}{2} \vec{v}(I_b) + \overleftarrow{v}(I_b) \right) \frac{F}{\mathfrak{R}} d \log P} \quad (12)$$

$$1 - x_{H_2} = \int_P^{P_0} \frac{\vec{v}(I_b) F}{\mathfrak{R}} e^{-\int_P^{P_0} \left(\frac{1}{2} \vec{v}(I_b) + \overleftarrow{v}(I_b) \right) \frac{F}{\mathfrak{R}} d \log P} d \log P \quad (13)$$

where P is the partial pressure of H_2 and C_2H_4 corresponding to $\mathfrak{N}_{H_2} = \mathfrak{N}_{C_2H_4}$. E^H , $x^{H(a)}$ and x_{H_2} are calculated according to Eqs. (1. H), (11) and (12) with various value of P ranging from 10 to 10^{-3} mmHg.

In the next place the rate of equilibration, accompanied by the hydrogenation, $E^u = \mathfrak{N}_{H_2} u$ [$u = \mathfrak{N}^{PD} / \mathfrak{N}_{Eq}^{PD}$; $\mathfrak{N}_{Eq}^{PD} : -\mathfrak{N}^{PD}$ which would be realized at the equilibration equilibrium of the H_2 gas present] is expressed with regard to the "structure" of the hydrogenation as that;

$$E^u = \mathfrak{N}_{H_2} u = \left(\frac{x^{H(a)}(1 - x^{H(a)})}{x_{H_2}(1 - x_{H_2})} - u \right) \overleftarrow{v}(I_b) - \left(\frac{1}{x_{H_2}} - \frac{1}{1 - x_{H_2}} \right) x_{H_2} \mathfrak{N}_{H_2} u, \quad (14)$$

assuming in accordance with the present neglect of isotopic shift that,

$$\mathfrak{N}_{E_0^D}^D / \mathfrak{N}_{E_0^P}^P \cdot \mathfrak{N}_{E_0^D}^D = 4$$

Eq. (14) is specialized to the condition, $x_{C_2H_4} = u = 0$, on one hand as that,

$$E_0^D = \frac{x^{H(a)}(1-x^{H(a)})}{x^{H_2}(1-x^{H_2})} v(I_b) \quad (15)$$

or is solved simultaneously with Eq. (1. H) for the initial conditions, $\mathfrak{N}_0^{H_2} = \mathfrak{N}_0^{C_2H_4} = \mathfrak{N}_0$, $x_0^{H_2} = 1$ and $x_0^{C_2H_4} = 0$ on the other hand, with the result,

$$u = \frac{1}{x^{H_2}(1-x^{H_2})} e^{-\int_{x^{H_2}}^1 \frac{dx}{x^{H_2} x^{H_2-x^{H(a)}}}} \int_{x^{H_2}}^1 \frac{x^{H(a)}(1-x^{H(a)})}{x^{H_2-x^{H(a)}}} e^{\int_{x^{H_2}}^1 \frac{dx}{x^{H_2} x^{H_2-x^{H(a)}}}} dx^{H_2} \quad (16)$$

$$\lim_{x^{H_2} \rightarrow 1} u = x_0^{H(a)} \quad (17)$$

E_0^D calculated according to Eq. (15) and (5. x^{H_2}) at $x^{H_2} = \frac{1}{2}$ approaches E_0^H at lower temperatures as seen from Fig. 1. This is however rather fortuitous due to the particular values of $\Delta^* \varepsilon(r, H)$'s, as shown by the expression, $E_0^D = 3\{\mathfrak{R}(I_b)\}^{\frac{5}{2}} / \mathfrak{R}(II) \{\mathfrak{R}(III)\}^{\frac{1}{2}} (1-x^{H_2})$ which is derived specially for the case similarly as in the case of E_0^H and E_0^P . The expression valid specially at higher temperatures, $E_0^D = \mathfrak{R}(I_b)$, on the other hand shows that $\mathfrak{R}(I_b)$ necessarily traces out, in accordance with Fig. 1, the "structure" hidden to the observation of the steady rate \mathfrak{R} , just as E_0^P or E_0^D does there with $\mathfrak{R}(II)$, apart from the respective constant factor.

The quantity u is calculated on the other hand as a function of x^{H_2} varying in the course of hydrogenation by Eq. (16) using data of $x^{H(a)}$ and x^{H_2} calculated by Eqs. (12), (13) and (1. H). Plot of $1-u$ thus obtained against x^{H_2} is shown in Fig. 2, in comparison with Twigg and Rideal's experimental results. The theoretical curve at 207°C runs close to a straight line. It runs higher and varies in form at temperatures between 156°C and 84°C but somewhat stationarily about another straight line lying higher than that at 207°C.

This reproduces at least qualitatively the Twigg and Rideal's experimental conclusion, not very accurate as they state, that the line is

Catalyst

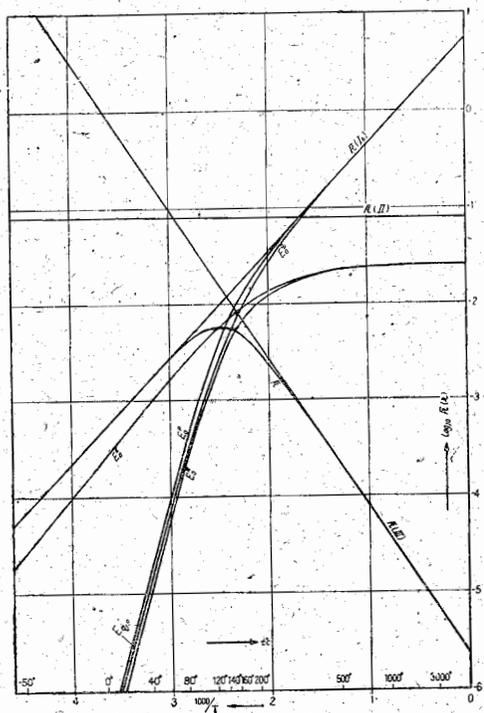
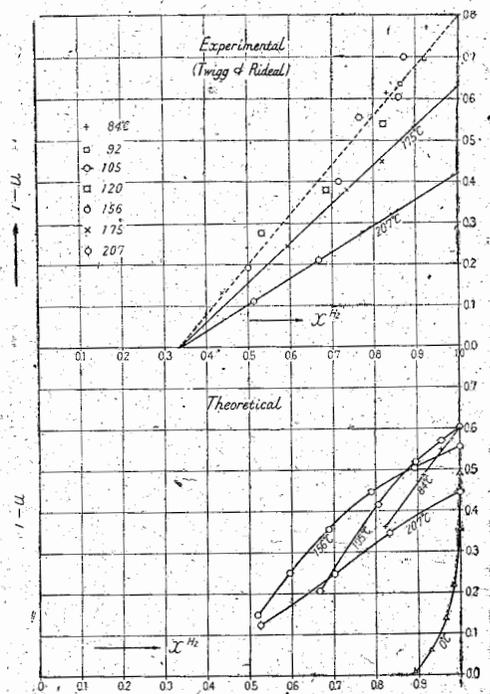


Fig. 2.
The Relation between
 u and x_{H_2}

Fig. 1.
Synthesis of The Rate of
The Hydrogenation
 $PH_2 = PC_2H_4 = 10\text{mm Hg}$,
Ni-Catalyst.



straight at any temperature, which gets higher as temperature is lowered from 207° to 156°C, whence it remains stationary down to 80°C. The theory predicts however that at 0°C the curve badly deviates from the "stationary straight line".

Another finding of Twigg and Rideal that at $x_{C_2H_4} = u = 0$ the rate of equilibration is much slower in the existence of C_2H_4 than in the absence is reproduced directly in Fig. 1 at lower temperatures since $E_0^g = \mathfrak{f}(I_b)$ in the absence, as derived from Eq. (15) with regard to the particular condition, $\vec{v}(I_b) = \overleftarrow{v}(I_b) = \mathfrak{R}(I_b)$ and $x_{H_2} = x_{H(a)}$ prevailing there [cf. (2b)]. In the presence E_0^g falls appreciably below $\mathfrak{R}(I_b)$ at lower temperatures as shown in Fig. 1. This holds true whenever x_{H_2} is not very close to 1 according to (2a), $\vec{v}(I_b) = \mathfrak{R}(I_b) \gg \overleftarrow{v}(I_b)$ and $x_{H(a)} = 0$ there. [(2a)] or in words E_0^g is reduced below that in the absence due to the consumption of $H(a)$ which makes $\overleftarrow{v}(I_b)$ much less than $\mathfrak{R}(I_b)$ and to the dilution of $D(a)$ by P 's of C_2H_4 rather than to the "poisoning" of C_2H_4 as stated by Twigg and Rideal. The theory predicts that at higher temperatures the absence or the presence of C_2H_4 makes no difference although the consumption and dilution of $H(a)$, which are responsible for "poisoning" is still prevailing.

Finally the rate E^p of para-hydrogen conversion defined by

$$E^p = -\mathfrak{N}H_2 \frac{x^p}{x^p - x_\infty^p}, \quad [x^p; -\mathfrak{N}PH_2/\mathfrak{N}H_2; x_\infty^p; -x^p \text{ at equilibrium}]$$

is expressed with regard to the "structure" as that, $E^p = v(I_b)$. E^p calculated therefrom approximates E_0^H at lower temperatures whereas traces out $\mathfrak{R}(I_b)$ at higher temperatures just as E_0^g does as shown analytically as well as in Fig. 1. No experimental material is found to check the theoretical conclusion.

Summarizing the above results it is pointed out that four out of five rates i.e. \mathfrak{R} , E^H , E^E , E^a and E^p provide so many independent functions of the fundamental quantities $\mathfrak{R}(r)$'s [E^H and E^E may be independent of each other as shown above] and henceforth that therein consists at least in principle a general method for determining $\mathfrak{R}(r)$'s and hence the "structure" from experimental data without any approximations provided that the scheme like (II, 1) is settled which implies r 's not exceeding in number that of these observable functions.

STATISTICAL MECHANICAL RESEARCH ON THE HETEROGENEOUS REACTION

(Abstract)

PART IV. RATE OF ETHYLENE HYDROGENATION IN THE PRESENCE OF METALLIC CATALYSTS

By Juro HORIUTI

The "structure" theory of ethylene hydrogenation in the presence of nickel catalyst verified in Part II and III is extended here to different metallic catalysts semi-quantitatively for the general survey of the relative catalytic capacity of them.

The elements $\mathfrak{R}(r, H)$ and $\mathfrak{R}(r, L, \delta^A)$ for synthesis of the "structure" theory are given according to I and II as that,

$$\log \mathfrak{R}(r, H) = \log \rho \frac{P\delta^I}{Q\delta^I} - \frac{\Delta^* \epsilon(r, H)}{kT} \quad (1. H)$$

$$\log \mathfrak{R}(r, L, \delta^A) = \log \rho \frac{P\delta^I}{Q_P\delta^I} \left(\frac{Q\delta^A}{P\delta^A} \right)^{a(r, \delta^A)} - \frac{\Delta^* \epsilon(r, L, \delta^A) + a(r, \delta^A) \Delta \epsilon(\delta^A)}{kT} \quad (1. L)$$

Assuming with our end in view that $\Delta^* \epsilon(r, H) = \Delta^* \epsilon(r, L, \delta^A)$ and that $a(r, \delta^A)$ [cf. Eq. (I. 19)] is independent of kind of metals it follows that $\mathfrak{R}(r, H)$ and $\mathfrak{R}(r, L, \delta^A)$ are fully determined by appropriate $\Delta^* \epsilon(r)$ and $\Delta \epsilon(\delta^A)$. Denoting the excess of latter and other quantity relevant to a catalyst Me over those of nickel by $\delta \Delta^* \epsilon(r)$, $\delta \Delta \epsilon(\delta^A)$ etc., the former is expressed as that

$$\delta \Delta^* \epsilon(r) = a \delta \epsilon^{\delta^I(a)} + (1-a) \delta \epsilon^{\delta^F(a)} \quad (2)$$

where $\delta \Delta^* \epsilon(r) = \delta \epsilon^{\delta^*(r)}$ according to Eq. (I, 18. ϵ). Eq. (2) expresses the frequently observed rule⁽¹⁾⁽²⁾ that $\delta \epsilon^{\delta^*(r)}$ is the fraction of $\delta \epsilon^{\delta^I(r)}$ or $\delta \epsilon^{\delta^F(r)}$

- (1) Brønsted; Chem. Rev. **5** (1928), 231.
Horiuti & Polanyi; Acta. Physicochim. URSS. **2** (1935), 595.
Horiuti & Okamoto; Sc. Pap. Inst. Phys. Chem. Res. Tokio; **28** (1936), 231,
Okamoto, Horiuti & Hirota; Sc. Pap. I.P.C.R. Tokio; **29** (1936), 223.
Evans & Polanyi; Trans. Faraday Soc., **33** (1937), 448.
- (2) Bowden & Agar; Annual Report, Chem. Soc. London, **35** (1939), 90.

if $\delta^I(r)$ or $\delta^F(r)$ is subject to the same influence of varying condition as $\delta^*(r)$ is. $\delta\varepsilon^{\delta^I(r)}$ or $\delta\varepsilon^{\delta^F(r)}$ is different from zero in our case only when $\delta^I(r)$ or $\delta^F(r)$ implies adsorbed system $\delta^A(a)$, which is subject to the same influence as $\delta^*(r)$ is of the varying condition, i.e. that of different adsorbent metals; it vanishes of course when $\delta^I(r)$ or $\delta^F(r)$ consists only of systems in gas. Coefficients α and $1-\alpha$ are thus respectively proper fraction, they being fitted to the plausible requirement that $\delta\varepsilon^{\delta^*} = \delta\varepsilon^{\delta^I(r)} = \delta\varepsilon^{\delta^F(r)}$, if $\delta\varepsilon^{\delta^I(r)} = \delta\varepsilon^{\delta^F(r)}$.

Since further $\delta\Delta\varepsilon(\delta^A) = -\delta\varepsilon^{\delta^A}$ according to Eq. (I. 14. e), the present procedure is reduced to the evaluation of three possible components of $\delta^A(a)$ i.e. H(a), C₂H₄(a) and C₂H₅(a), or assuming the additivity of bond energy, to evaluate,

$$\delta D(\text{Me-H}) = -\delta\varepsilon^{\text{H(a)}}, \quad \delta D(\text{Me-C}) = -\frac{1}{2}\delta\varepsilon^{\text{C}_2\text{H}_4\text{(a)}} = -\delta\varepsilon^{\text{C}_2\text{H}_5\text{(a)}} \quad (3. \text{H}), \quad (3. \text{C})$$

where D(Me-H) or D(Me-C) is the bond energy between a metal atom Me and H or Me and C respectively and C₂H₄(a) is taken as linked to the metal by two (Me-C) bonds whereas C₂H₅(a) by one.

D(Me-H) being combined with the heat of adsorption, $\chi_{\text{Me}}^{\text{H}_2}$ as that,

$$\chi_{\text{Me}}^{\text{H}_2} = 2D(\text{Me-H}) - D(\text{H-H}) \quad (5)$$

the latter is given below as taken directly from thermal or spectroscopic data,

METAL	Zn	Ag	Pt	Ni	W	Al	Cu	Au	
$\chi_{\text{Me}}^{\text{H}_2}$	-54	5	16	26	40	41	47	79	Kcal.

D(Me-C) in Eq. (3. c) is determined from D(C-Ni) estimated in Part II and above data of D(Me-H) according to a relation,

$$\frac{D(\text{C-Me})}{D(\text{C-Ni})} = \frac{D(\text{H-Me})}{D(\text{H-Ni})} \quad (6)$$

which follows from the Pauling's rule of geometrical mean⁽³⁾ expressed as that,

(3) Pauling; "Nature of Chemical Bonds", New York 1940, § 2.

Catalyst

$$D(C-Me) = \{D(C-C)D(Me-Me)\}^{\frac{1}{2}},$$

$$D(H-Me) = \{D(H-H)D(Me-Me)\}^{\frac{1}{2}}$$

$$D(C-Ni) = \{D(C-C)D(Ni-Ni)\}^{\frac{1}{2}},$$

$$D(H-Ni) = \{D(H-H)D(Ni-Ni)\}^{\frac{1}{2}}$$

Assuming further that $\alpha = \frac{1}{2}$ as supported by close agreement in the case of hydrogen electrode, $\mathfrak{R}(r)$ or $\mathfrak{R}(r, L, \delta^A)$ and hence the "structure" of the reaction is now determined according to the theory developed in Part I by a single parameter $\chi_{Me}^{H_2}$ or $\beta = 1 + \chi_{Me}^{H_2}/\chi_{Ni}^{H_2}$. Values of $\Delta^*\epsilon(r)$ of Ni used thereby is referred to the second procedure of Part II for the general features of $\mathfrak{R}(r)$'s.

The "structure" diagram is first drawn for Pt at $P^{H_2} = 40$ mmHg $P^{C_2H_4} = 20$ mmHg to compare with experimental results of Farkas and Farkas⁽⁴⁾ at the same condition. The diagram is qualitatively the same as that of Fig. (II. 1) or (III. 1) for Ni except that $\mathfrak{R}(II)$ is the lowest over a small range in the neighbourhood of the $\mathfrak{R}(I_b)$, $\mathfrak{R}(III)$ intersection. $\mathfrak{R}(I_b)$ is steeper here than in Fig. (II. 1) referred to the first procedure of Part II. \mathfrak{R} synthesized from $\mathfrak{R}(r)$'s according to Eq. (II. 8) and (II. 10) has maximum at 150°C and the behavior of calculated E_0^H according to Eq. (III. 6. H) as referred to that of \mathfrak{R} are of much the same features as that shown in Fig. (III. 1). These theoretical results are found in satisfactory agreement with Farkas and Farkas's experimental results.

The "structure" diagram is now drawn at $P^{H_2} = P^{C_2H_4} = 10$ mmHg for cases when $\beta = -8, -2, -1, -1/2, 0(Ni), 0.385(Pt), 1, 2$ and 3. The desorption temperature of H(a) is conventionally calculated [cf. Part II] as in the case of Fig. (II. 1) for Ni by taking $N_A \Delta\epsilon(H) = \frac{1}{2}\chi_{Me}^{H_2} - 7$ Kcal where 7 Kcal is the excess in the case of Ni of $N_A \Delta\epsilon(H) = \frac{1}{2}\chi_{Me}^{H_2}$ at $\theta_{\sigma H(H)} = 0$ as extrapolated from Fryling's data⁽⁵⁾ over that at $\theta_{\sigma H(H)} = \frac{1}{2}$.

Consideration of repulsive potential between H(a), to which the difference of 7 Kcal is attributed shows that the latter is too large in the

(4) Farkas & Farkas; J. Am. Chem. Soc. **60** (1938), 22.

(5) Fryling; J. Phys. Chem. **30** (1926), 818.

case of other metals so that the "desorption temperature" shows according to: Eq. (I. 14. θ) the lower limit of temperature at which $\theta_{\sigma H(H)} = \frac{1}{2}$.

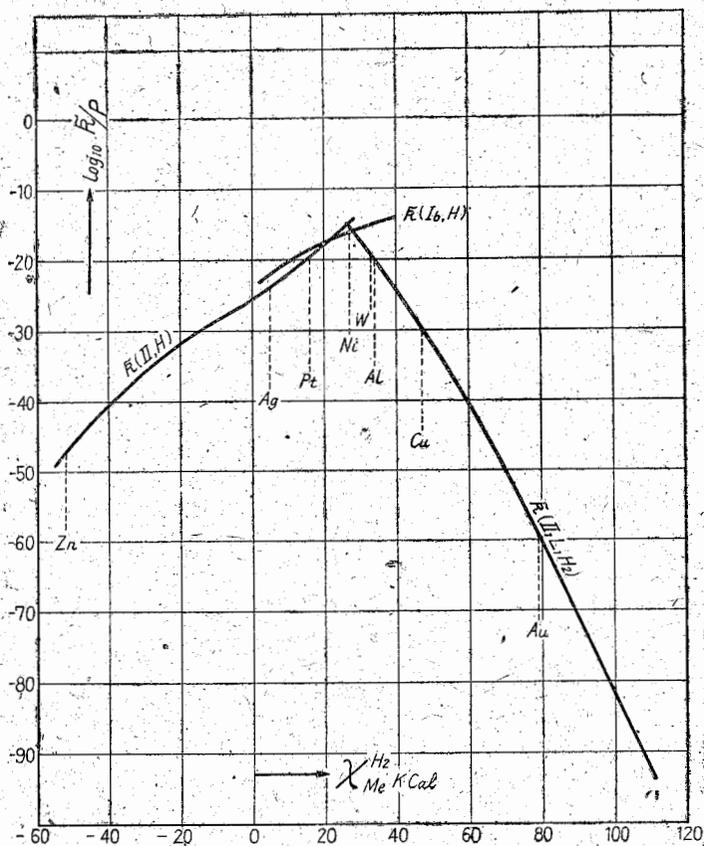


Fig. 3.

The Relation between Synthesized Rate, \mathfrak{R} and the Heat of Adsorption of H_2 , $\chi_{Me}^{H_2}$ 100 °C, $P_{H_2} = P_{C_2H_4} = 10$ mm Hg.

The resulting "structure" diagram looks quite different at different β . The optimum point of \mathfrak{R} falls in the finite temperature range first at $\beta = 1$ as β decreases from 3, then shifts toward lower T and higher \mathfrak{R} until β becomes zero (Ni) whence back again toward higher T and smaller \mathfrak{R} .

Catalyst

$\log \mathfrak{R}$ at 100°C given by respective diagram plotted against $\chi_{\text{Me}}^{\text{H}_2}$ is shown in Fig. 1. The curves denoted by either r shows $\log \mathfrak{R}(r)$ at 100°C which happen to be the lowest and hence to give $\log \mathfrak{R}$. Vertical dotted lines show real values of $\chi_{\text{Me}}^{\text{H}_2}$ of respective metals. Fig. 1 is interpreted that as $\chi_{\text{Me}}^{\text{H}_2}$ increases from a smaller value or β decreases from greater value, $\Delta^*\varepsilon(r)$'s decreases as inferred from Eq. (2) and hence \mathfrak{R} increases but since $\Delta\varepsilon(\delta^A)$ increases along with $\chi_{\text{Me}}^{\text{H}_2}$ even quicker than $\Delta^*\varepsilon(r)$ decreases, the adsorption sooner or later sets in which poisons the reaction more and more strongly.

Fig. 1 shows that a pure metallic catalyst better than Ni can hardly be found at least so far as the present particular condition of 100°C and $P^{\text{H}_2} = P^{\text{C}_2\text{H}_4} = 10 \text{ mmHg}$ is concerned and the scheme (II. 1) is followed. So that other scheme is practically followed, the appropriate rate must exceed that of Fig. 1 or generally the latter gives the lower limit to the rate of hydrogenation. Theoretical and experimental grounds are advanced however with Au, Ag, Cu, Fe and Pt [in the absence of H_2O or other polar molecules], apart from the above evidence for Pt, therefor that hydrogenation in their presence actually proceeds according to the scheme (II. 1) or that Fig. 1 gives the rate within the accuracy of the present method at least in these cases. Fig. 1 suggest further that the hydrogenation proceeds with Al or W according to the scheme at least as good as with Cu. That they are rarely employed as catalysts is plausibly attributed to the rigid oxide film coating the surface.