



Title	THEORY OF HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS : . Fundamentals of Analysis
Author(s)	HORIUTI, Juro
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 6(3), 250-307
Issue Date	1958-12
Doc URL	<a href="http://hdl.handle.net/2115/24685">http://hdl.handle.net/2115/24685</a>
Type	bulletin (article)
File Information	6(3)_P250-307.pdf



[Instructions for use](#)

# THEORY OF HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

## I. Fundamentals of Analysis

By

JURO HORIUTI<sup>\*)</sup>

(Received December 31, 1958)

### Contents

Introduction . . . . .	251
Chapter 1. Fundamental Theory . . . . .	254
§ 1. Outlines . . . . .	254
§ 2. Theory of Steady Reaction . . . . .	255
§ 3. Interrelations among $V_s$ , $\bar{r}(s)$ 's, $F$ , $r(C_2H_4)$ etc. . . . .	258
§ 4. Rates of Exchange Reaction between Hydrogen and Ethylene during Hydrogenation . . . . .	260
§ 5. Rate of Equilibration $P_2 + D_2 = 2PD$ . . . . .	262
§ 6. Rate of Parahydrogen Conversion . . . . .	264
§ 7. Kinetics of Scheme (3) . . . . .	264
§ 8. Kinetics of Scheme (4) . . . . .	267
§ 9. $r(H)$ and $r(C_2H_5)$ of Schemes (3) and (4) . . . . .	268
§ 10. Kinetic Difference between Schemes (3) and (4) . . . . .	271
Chapter 2. Determination of $\bar{r}(s)$ 's . . . . .	275
§ 11. Statistical-Mechanical Expressions of $\bar{r}(s)$ 's . . . . .	275
§ 12. Rate-Determining Step. . . . .	276
§ 13. Reduction of $\bar{r}(s)$ 's for Evaluation . . . . .	278
§ 14. Determination of $\bar{r}(I_b)$ and $\bar{r}(III)$ . . . . .	280
§ 15. Estimation of $A^{*c}(II)$ . . . . .	281
§ 16. Estimation of $A^{*c}(I_a)$ . . . . .	282
§ 17. Structure Diagram . . . . .	284
Chapter 3. Explanation of Experimental Results . . . . .	284
§ 18. Optimum Temperatures . . . . .	284
§ 19. Kinetics of Catalyzed Hydrogenation . . . . .	287
§ 20. Experiments of FARKAS, FARKAS and RIDEAL . . . . .	290
§ 21. Activation Energy of Hydrogen Exchange . . . . .	292
§ 22. Formation of Different Deuteroethanes in the Catalyzed Deuteration of Light Ethylene . . . . .	294
§ 23. Equilibration Reaction . . . . .	295

<sup>\*)</sup> Research Institute for Catalysis, Hokkaido University.

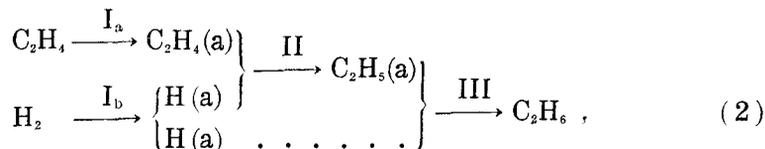
Chapter 4. Discussions and Remarks . . . . .	298
§ 24. General Results . . . . .	298
§ 25. Allowance for Diffusion . . . . .	298
§ 26. Explanation of Experimental Results of WAGNER <i>et al.</i> . . . . .	301
§ 27. Discrimination between Schemes (2), (3) and (4) . . . . .	303
Summary . . . . .	304

### Introduction

POLANYI has put forward in conjunction with the present author<sup>1)2)</sup> the mechanism of catalyzed hydrogenation of ethylene



in the presence of metallic catalyst that the reaction follows the scheme

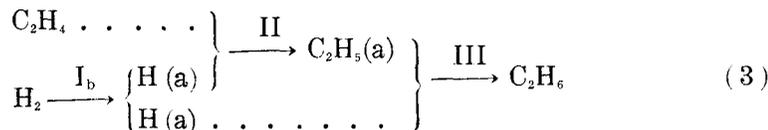


with the rate-determining step of III, where (a) denotes the adsorbed state of atoms or atom groups.

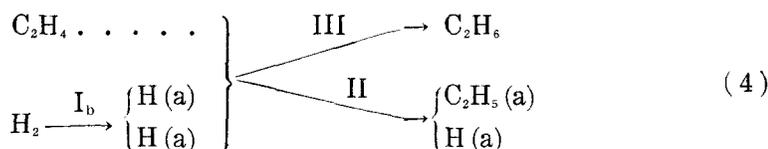
The present author has later developed a general theory of the steady reaction (1)<sup>3)</sup>, without however specializing the rate-determining step to III, thus accounting for the existing data at that time of hydrogenation and associated reactions, e. g. the exchange reaction between hydrogen and ethylene, the equilibration of H<sub>2</sub>+D<sub>2</sub> and the parahydrogen conversion. KER<sup>4)</sup> has deduced on the basis of the above theory the distributions of deuterioethylenes and deuterioethanes resulting from the catalyzed deuteration of ethylene, accounting, on the one hand, for the experimental results of TURKEVICH, SCHISSLER and IRSA<sup>5)</sup>, especially the predominance of light ethane over the initial products and predicting, on the other hand, the alternative abundance of dideuterioethane at higher temperatures.

JENKINS and RIDEAL<sup>6)</sup> have recently concluded from their experimental results that gaseous ethylene reacts, without being preliminarily adsorbed as in Scheme (2), directly with a pair of adsorbed hydrogen atoms to complete the hydrogenation in one act as well as with a single adsorbed hydrogen atom to form C<sub>2</sub>H<sub>5</sub>(a) resulting in the exchange reaction on reversion. Their experimental results do not however necessarily exclude, if not positively evidence, the existence of the

intermediate  $C_2H_4(a)$  at the very steady state of hydrogenation. Scheme (2) is on the other hand kinetically identical with the scheme without  $C_2H_4(a)$ , *i. e.*



in its special case when  $I_a$  is extremely rapid as shown in §7, although kinetically not identical, even in the latter extreme case, with the scheme proposed by JENKINS and RIDEAL,<sup>6)</sup> in accordance with the above conclusion



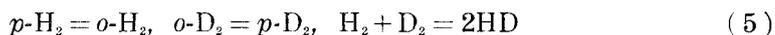
as shown in §8-§10.

Scheme (2) might, besides, be in question with regard to the possibility left open of any constituent step governing the rate<sup>7)</sup>, since it is recently frequently argued that both the associative adsorption  $I_a$  of ethylene and the dissociative adsorption  $I_b$  of hydrogen cannot be the rate-determining step of hydrogenation on the ground of instantaneous adsorption observed on freshly evaporated nickel film<sup>7,8)</sup>.

Catalyst's surface is, however, by no means bare at the steady state of hydrogenation like that of freshly evaporated film but more or less covered. Coverage decreases now the heat of adsorption, as well-known<sup>7-11)</sup>, or raises the energy of the final state of adsorption and in consequence the energy of the critical state or the critical energy increment of the elementary act of adsorption to a definite available site, as illustrated by potential surfaces respectively of the initial and the final states which locates the critical state at their intersection<sup>12)</sup>; the increase of critical energy increment reduces the rate of the above elementary act of adsorption, but raises the relative or logarithmic increase of the rate with temperature. The coverage has on the other hand just the same effect on the abundance of the available sites of adsorption, inasmuch as coverage is more or less reduced with rise of temperature. Since now the rate or the rate constant of adsorption is proportional to the product of the rate of the individual elementary act of adsorption at a definite available site and the number of available

sites, the coverage should doubly depress the rate of adsorption and similarly raise its logarithmic increase with temperature or the relevant activation energy.

Experimentally it is known that the rate of hydrogen adsorption on freshly evaporated nickel films is, besides extremely large as mentioned above, almost independent of temperature, the activation energy amounting a few tenths kilocalorie at most<sup>13)</sup>. MATSUDA<sup>14)</sup> has obtained a similar result with a carefully degassed nickel wire. It has been observed on the other hand that the rates of reactions



at a finite hydrogen or deuterium pressure are moderately slow to be measured and associated with an appreciable amount of activation energy. FARKAS and FARKAS<sup>15)</sup> thus observed the rates of (5) on platinum at 18 mmHg hydrogen or deuterium pressure, finding the activation energy of the amount from 10 to 11 Kcal<sup>15)</sup> and BONHOEFFER, BACH and FAJANS<sup>16)</sup> found on nickel at 0.004 mmHg pressure, beside measurably slow rate of the first and last reaction of (5), the appropriate activation energy amounting to 7~8 Kcal. These experimental results verify the above theoretical inference that the adsorption of ethylene or hydrogen may possibly be slow enough at the steady state of hydrogenation, even if extremely rapid and associated with minute amount of activation energy on a bare surface, provided that reactions (5) proceed through the BONHOEFFER-FARKAS mechanism<sup>16)</sup> as admitted recently by RIDEAL and others<sup>10)18)</sup>. Further evidence for the BONHOEFFER-FARKAS mechanism<sup>17)</sup> has been brought about by HORIUTI, KEI, EN'YO and FUKUDA<sup>19)</sup>, who have shown by a statistical-mechanical reasoning that the critical complex of the rate-determining step of (5) consists of two hydrogen atoms in accordance with BONHOEFFER-FARKAS mechanism rather than of three ones as implied in the mechanism previously suggested by RIDEAL<sup>20)</sup> and ELEY<sup>21)</sup>.

The above consideration indicates that Scheme (2) without any specification of the rate-determining step is still a quite sound and general basis of the analysis of the catalyzed hydrogenation even in view of modern experimental results. The previous work<sup>3)</sup> written in Japanese, as well as its English abstract is, however, rather unintelligible mainly because of the difficulties in printing directly after the last War. These situations have urged the present author to restate here, with reference to recent experimental data, its essential lines,

which underlie several works published<sup>4)</sup> or going on in this laboratory.

Theory of steady reaction has been developed in the previous work<sup>3)</sup> formulating the steady rates, *i.e.* the rates at the steady state of hydrogenation and associated reactions mentioned above as functions of characteristic quantities  $\mathfrak{K}(s)$ 's each to one of the constituent steps  $s$ 's. Determining  $\mathfrak{K}(s)$ 's by fitting them to experimental results or by theoretical estimation, first ignoring the effect of adsorption on rates, the whole series of experimental results existing at that time have been semiquantitatively explained and adjusting them then taking the effect of adsorption into account, particular experimental results of interest have been quantitatively accounted for. The first part of the above treatment in the previous work<sup>3)</sup> only will be reproduced here as mentioned above in this part of the present series.

The fundamental theory is developed in Chapter 1 to formulate the steady rates as respective functions of  $\mathfrak{K}(s)$ 's on the base of Scheme (2) in comparison with those of other schemes,  $\mathfrak{K}(s)$ 's determined by fitting them to experimental results or by theoretical estimation in Chapter 2, conclusions derived from  $\mathfrak{K}(s)$ 's thus determined were shown semiquantitatively to account for experimental results in Chapter 3 and the present method was extended to discuss peculiar experimental results obtained by WAGNER *et al.*<sup>22)23)</sup> and the experimental methods for discriminating between underlying schemes in Chapter 4.

In what follows protium or deuterium will be denoted respectively by P or D, which are collectively signified by H and called hydrogen.

## Chapter 1. Fundamental Theory

### § 1. Outlines

The steady rate  $V_s$  of hydrogenation and the forward and backward rates  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's of the respective steps  $s$ 's of Scheme (2) are given as functions of characteristic quantities  $\mathfrak{K}(s)$ 's on the basis of the general theory of steady reaction (§2), several lemmas are derived with regard to  $\mathfrak{K}(s)$ 's and activities of intermediates, *i.e.*  $C_2H_4(a)$ ,  $H(a)$  and  $C_2H_5(a)$  as the basis of further developments (§3) and then steady rates of associated reactions referred to in the introduction, *i.e.* those of exchange reaction between hydrogen and ethylene, equilibration  $P_2 + D_2 = 2PD$  and paraphydrogen conversion during hydrogenation are derived as respective functions of  $\mathfrak{K}(s)$ 's (§4-§6).

The kinetic identity of Scheme (2) in its special case of extremely rapid  $I_a$  with Scheme (3) is shown (§7), kinetics on the base of Scheme (4) similarly developed (§8) and the kinetic difference between Schemes (2) or (3) and (4) illustrated (§9, §10). It is shown in §4 that the steady rates of exchange reaction or the rate of change of isotopic fraction of ethylene and that of hydrogen during the catalyzed hydrogenation are not necessarily equal to each other as in the ordinary case of exchange reaction, when overall amounts of participant molecules and isotopes are kept respectively constant, but are independent functions of  $\mathfrak{R}(s)$ 's.

The isotopic difference of rates as well as the effect of adsorption on rates is ignored whole throughout the present treatment as mentioned in the introduction and three hydrogen atoms on the methyl group of  $C_2H_5(a)$  are taken chemically equivalent or, in particular, any of the three, whether it be protium or deuterium, converts into one of hydrogen atoms in a methylene group of  $C_2H_4(a)$  or into  $H(a)$  with equal chance by the reversal of II.

## § 2. Theory of Steady Reaction

The rate  $V_s$  of a steady reaction is expressed in terms of the forward and backward rates,  $\bar{v}(s)$  and  $\tilde{v}(s)$ , of the constituent Steps  $s$ 's generally as

$$V_s = \frac{\bar{v}(s) - \tilde{v}(s)}{\nu_s}, \quad (2.1)$$

where  $\nu_s$  is the stoichiometric number of Step  $s$ <sup>24)-29)\*)</sup> *i.e.* the number of acts of the step to occur for every overall reaction specified by a definite chemical equation through a single reaction route<sup>\*\*)</sup>. The  $\nu_s$  being particularly unity for every step of Scheme (2) with regard to

---

\*) The similar concept the "molecularity" of a reaction has been independently introduced by BORESKOW (cf. Ref. 29).

\*\*\*) There are in general  $P=S-I$  reaction routes or independent modes of assigning stoichiometric numbers to each step of a given set of  $S$  steps for completing overall reactions without afterall consuming or creating any intermediates involved, *i.e.* of composing steady reactions (cf. Ref. 27);  $I$  is the number of independent intermediates, *i.e.* such intermediates as their increments given respectively as the linear homogeneous functions of numbers of acts of steps are linearly independent from each other and the simultaneous increments of every other intermediates are given as the linear combination of them. There exists only a single reaction route or  $P=1$  in the case of Scheme (2), when  $S=4$  and  $I=3$ , in accordance with the above equation.

the appropriate chemical equation (1), (2.1) reduces in this case to the equation

$$V_s = \bar{v}(s) - \tilde{v}(s), \quad s = I_a, I_b, II, III. \quad (2.2)$$

The forward and backward rates,  $\bar{v}$  and  $\tilde{v}$  of any thermal step are given as<sup>(25)(26)(30)\*)</sup>

$$\bar{v} = \kappa \frac{kT}{h} p^*/p^I, \quad \tilde{v} = \kappa \frac{kT}{h} p^*/p^F, \quad (2.3. \bar{v}) (2.3. \tilde{v})$$

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

$$p^\delta = \exp(-\mu^\delta/RT), \quad (2.4)$$

where  $R$  is the gas constant.

The  $\bar{v}(s)$  and  $\tilde{v}(s)$  of Scheme (2) are expressed in accordance with (2.3), denoting by  $(s)$  the relevance of  $\kappa$ , \*, I and F to Step  $s$ , as

$$\bar{v}(s) = \mathfrak{K}(s) \frac{p_e^{I(s)}}{p^{I(s)}}, \quad \tilde{v}(s) = \mathfrak{K}(s) \frac{p_e^{F(s)}}{p^{F(s)}} \quad (2.5. \bar{v}), (2.5. \tilde{v})$$

where

$$\mathfrak{K}(s) = \kappa(s) \frac{kT}{h} p^{*(s)}/p_e^{I(s)} \quad (2.5. \mathfrak{K})$$

and  $p_e^{I(s)}$  is the particular value of  $p^{I(s)}$ , which would be realized, if every step but  $s$  were in equilibrium<sup>(25)(26)</sup>. Eq. (2.5.  $\bar{v}$ ) shows that  $\mathfrak{K}(s)$  gives the forward unidirectional rate of hydrogenation in the special case when all steps but  $s$  are in equilibrium and in consequence  $p^{I(s)} = p_e^{I(s)}$ .

Our program is now, as stated in the introduction, to derive the steady rates of hydrogenation and associated reactions as functions of the characteristic quantities  $\mathfrak{K}(s)$ 's to the respective steps, by expressing  $\bar{v}(s)$ 's and  $\tilde{v}(s)$ 's in terms of  $\mathfrak{K}(s)$ 's and the steady rates in turn by  $\bar{v}(s)$ 's and  $\tilde{v}(s)$ 's.

Noting that

$$p^I = p^F \quad (2.6. e)$$

for steps in equilibrium<sup>(25)(26)</sup>, as readily follows from (2.4) or (2.5), and that<sup>(25)(26)</sup>

\*) Cf. Eq. (24.1), Ref. 26.

$$p^{\delta} = \prod (p^{\delta_i}) \quad (2.6. i)$$

for  $\delta$  consisting of statistically independent parts  $\delta_i$ 's,  $p_e^{I(s)}$  defined above is expressed as

$$p_e^{I(I_a)} = p^E, \quad p_e^{I(I_b)} = p^H, \quad p_e^{I(II)} = p^E(p^H)^{1/2}, \quad p_e^{I(III)} = p^E p^H, \quad (2.7. I_a), (2.7. I_b), (2.7. II), (2.7. III)$$

where H and E refer to gaseous hydrogen and ethylene respectively, and hence we have

$$\frac{p_e^{I(I_a)}}{p^{I(I_a)}} = 1, \quad \frac{p_e^{I(I_b)}}{p^{I(I_b)}} = 1, \quad \frac{p_e^{I(II)}}{p^{I(II)}} = \gamma(C_2H_4)\gamma(H), \quad \frac{p_e^{I(III)}}{p^{I(III)}} = \gamma(C_2H_5)\gamma(H), \quad (2.8. I_a), (2.8. I_b), (2.8. II), (2.8. III)$$

$$\frac{p_e^{I(I_a)}}{p^{F(I_a)}} = \gamma(C_2H_4), \quad \frac{p_e^{I(I_b)}}{p^{F(I_b)}} = \gamma(H)^2, \quad \frac{p_e^{I(II)}}{p^{F(II)}} = \gamma(C_2H_5), \quad \frac{p_e^{I(III)}}{p^{F(III)}} = \frac{p^E p^H}{p^{C_2H_5}} \equiv \Gamma, \quad (2.9. I_a), (2.9. I_b), (2.9. II), (2.9. III)$$

where

$$\gamma(C_2H_4) = \frac{p^E}{p^{C_2H_4(a)}}, \quad \gamma(H) = \frac{(p^H)^{1/2}}{p^{H(a)}}, \quad \gamma(C_2H_5) = \frac{p^E(p^H)^{1/2}}{p^{C_2H_5(a)}} \quad (2.10. E), (2.10. H), (2.10. C_2H_5)$$

are relative activities, in accordance with the definition (2.10), of intermediates,  $C_2H_4(a)$ ,  $H(a)$  and  $C_2H_5(a)$  at the steady state, each referred to the absolute activity of the intermediate at the particular state, where all steps in Scheme (2) which derive the intermediate from the reactant  $C_2H_4 + H_2$  of (1) are respectively in equilibrium.

The  $p^{\delta_i}$  of gaseous components, e.g.  $H_2$ ,  $C_2H_4$  and  $C_2H_6$ , is given as<sup>25)26)</sup>

$$p^{\delta_i} = Q^{\delta_i} / N^{\delta_i} \quad (2.11)$$

where  $Q^{\delta_i}$  is the partition function of a single gaseous molecule  $\delta_i$  in unit volume, which is a function solely of temperature, and  $N^{\delta_i}$  is concentration of  $\delta_i$  in gas. The  $\bar{v}(s)$  and  $\bar{v}(s)$  are now expressed according to (2.5), (2.8) and (2.9) as

$$\bar{v}(I_a) = \mathfrak{K}(I_a), \quad \bar{v}(I_a) = \gamma(C_2H_4) \mathfrak{K}(I_a), \quad (2.12. I_a)$$

$$\bar{v}(I_b) = \mathfrak{K}(I_b), \quad \bar{v}(I_b) = \gamma(H)^2 \mathfrak{K}(I_b), \quad (2.12. I_b)$$

$$\bar{v}(II) = \gamma(H)\gamma(C_2H_4)\mathfrak{K}(II), \quad \bar{v}(II) = \gamma(C_2H_5)\mathfrak{K}(II), \quad (2.12. II)$$

$$\bar{v}(III) = \gamma(H)\gamma(C_2H_5)\mathfrak{K}(III), \quad \bar{v}(III) = \Gamma \mathfrak{K}(III), \quad (2.12. III)$$

and hence we have according to (2.2)

$$\begin{aligned} V_s &= \mathfrak{K}(I_a)(1-\gamma(C_2H_4)) = \mathfrak{K}(I_b)(1-\gamma(H)^2) \\ &= \mathfrak{K}(II)(\gamma(H)\gamma(C_2H_4) - \gamma(C_2H_6)) = \mathfrak{K}(III)(\gamma(H)\gamma(C_2H_6) - \Gamma) \end{aligned} \quad (2.13)$$

or eliminating  $\gamma(C_2H_4)$ ,  $\gamma(H)$  and  $\gamma(C_2H_6)$ ,

$$\Gamma = (1 - V_s/\mathfrak{K}(I_a))(1 - V_s/\mathfrak{K}(I_b)) - \frac{V_s}{\mathfrak{K}(II)} \sqrt{1 - \frac{V_s}{\mathfrak{K}(I_b)}} - \frac{V_s}{\mathfrak{K}(III)}. \quad (2.14)$$

Four equations of (2.13) determine  $V_s$  and the three relative activities and hence  $\bar{v}(s)$  and  $\bar{v}(s)$  by (2.12) as functions of four  $\mathfrak{K}(s)$ 's for any known  $\Gamma$  determined from the experimental condition by (2.9.III) and (2.4), as

$$\Gamma = \exp\left(\frac{\mu^{C_2H_6} - \mu^E - \mu^H}{RT}\right). \quad (2.15)$$

The values of  $\bar{v}(s)$  and  $\bar{v}(s)$  determine now the steady rates, besides that of hydrogenation by (2.2), of different associated reactions as shown in the subsequent sections, so that the steady rates are given as functions of  $\mathfrak{K}(s)$ 's particular to the sequence of steps defined by Scheme (2). The mode of the characteristic quantities  $\mathfrak{K}(s)$ 's constituting these steady rates has been called<sup>3)</sup> the "structure" of the reaction.

### § 3. Interrelations among $V_s$ , $\mathfrak{K}(s)$ 's, $\Gamma$ , $\gamma(C_2H_4)$ etc.

We have from (2.14) and (2.13) noting  $\gamma(C_2H_4) > 0$  and  $\gamma(H) > 0$  by definition that

$$\Gamma \leq 1 \text{ according as } V_s \geq 0 \quad (3.1)$$

and vice versa, which states that the steady reaction proceeds in such a direction as  $\Gamma < 1$ , *i.e.* as the free energy of the whole system decreases by (2.15) in accordance with the requirement of thermodynamics. We will deal in what follows exclusively with the case, when

$$\Gamma < 1 \quad (3.2. I')$$

and hence

$$V_s > 0. \quad (3.2. V)$$

It is deduced from the definitions (2.10) and (2.9.III) that  $\gamma(C_2H_6)$  and  $\Gamma$ , besides  $\gamma(C_2H_4)$  and  $\gamma(H)$ , are all positive on the one hand and from (3.2), (2.13) and the same definitions that they are respectively less than unity, noting that  $\mathfrak{K}(s)$ 's are all positive by their definition, on the other hand, *i.e.* that

$$1 > \gamma(C_2H_4), \gamma(H), \gamma(C_2H_6), \Gamma > 0. \quad (3.3)$$

It is further shown from (2.13), (3.2) and (3.3) that<sup>\*)</sup>

$$\frac{V_s}{1-\Gamma} < \mathfrak{K}(s), \quad s=I_a, I_b, H, III, \quad (3.4)$$

that

$$V_s/(1-\Gamma) \text{ approaches } \mathfrak{K}(r), \text{ as } \mathfrak{K}(r) \text{ gets smaller than all other } \mathfrak{K}(s)'s^{**)} \quad (3.5. a)$$

and conversely that

\*) We have from (2.13) and (3.3) on account of positive  $\mathfrak{K}(s)'s$

$$1 - V_s/\mathfrak{K}(I_a) = r(C_2H_4) > 0, \quad 1 - V_s/\mathfrak{K}(I_b) = r(H)^2 > 0$$

and hence according to (2.14) and (3.2)

$$\Gamma < 1 - V_s/\mathfrak{K}(I_a), \quad \Gamma < 1 - V_s/\mathfrak{K}(I_b)$$

$$\Gamma < 1 - V_s/\mathfrak{K}(I_b) - \sqrt{1 - V_s/\mathfrak{K}(I_b)} \cdot V_s/\mathfrak{K}(II) = \sqrt{1 - V_s/\mathfrak{K}(I_b)} (\sqrt{1 - V_s/\mathfrak{K}(I_b)} - V_s/\mathfrak{K}(II)) < 1 - V_s/\mathfrak{K}(II) \quad \text{and} \quad \Gamma < 1 - V_s/\mathfrak{K}(III),$$

which are summarised in accordance with (3.2.  $\Gamma$ ) in (3.4).

\*\*\*) We have from (2.14) by transposition

$$1 - \frac{V_s}{\mathfrak{K}(I_a)} = \Gamma + \frac{V_s}{\mathfrak{K}(I_b)} \left(1 - \frac{V_s}{\mathfrak{K}(I_a)}\right) + \frac{V_s}{\mathfrak{K}(II)} \sqrt{1 - \frac{V_s}{\mathfrak{K}(I_b)}} + \frac{V_s}{\mathfrak{K}(III)}, \quad (i)$$

which states that  $1 - V_s/\mathfrak{K}(I_a)$  on the left-hand side approaches  $\Gamma$ , as  $\mathfrak{K}(I_a)$  gets smaller than all other  $\mathfrak{K}(s)'s$ , since all addends to  $\Gamma$  on the right are positive and then near zero, inasmuch as  $V_s$  is, by (3.4) and (3.3), even smaller than the smallest  $\mathfrak{K}(s)$ , *i. e.*  $\mathfrak{K}(I_a)$ . This is the content of (3.5. a) specially referred to  $\mathfrak{K}(I_a)$ . It is similarly shown that (3.5. a) holds true for  $I_b$  taken as  $r$ . Eq. (2.14) may be alternatively written as

$$1 - \frac{V_s}{\mathfrak{K}(II)} = \Gamma / \sqrt{1 - \frac{V_s}{\mathfrak{K}(I_b)}} + 1 - \left(1 - \frac{V_s}{\mathfrak{K}(I_a)}\right) \sqrt{1 - \frac{V_s}{\mathfrak{K}(I_b)}} + \frac{V_s}{\mathfrak{K}(III) \sqrt{1 - V_s/\mathfrak{K}(I_b)}} \quad (ii)$$

or as

$$1 - \frac{V_s}{\mathfrak{K}(III)} = \Gamma + \frac{V_s}{\mathfrak{K}(I_a)} + \frac{V_s}{\mathfrak{K}(I_b)} \left(1 - \frac{V_s}{\mathfrak{K}(I_a)}\right) + \frac{V_s}{\mathfrak{K}(II)} \sqrt{1 - \frac{V_s}{\mathfrak{K}(I_b)}}, \quad (iii)$$

which states that  $1 - V_s/\mathfrak{K}(II)$  or  $1 - V_s/\mathfrak{K}(III)$  similarly tends to  $\Gamma$ , as  $\mathfrak{K}(II)$  or  $\mathfrak{K}(III)$  gets respectively smaller than all other  $\mathfrak{K}(s)'s$ , because of  $V_s$  being even smaller than the smallest  $\mathfrak{K}(s)$ . Proposition (3.5. a) holds thus in every case of  $s$ .

The converse (3.5. b) of (3.5. a) is shown as follows. As  $\mathfrak{K}(I_a)$  tends to  $V_s/(1-\Gamma)$ , *i. e.*  $1 - V_s/\mathfrak{K}(I_a)$  to  $\Gamma$ , the positive addends to  $\Gamma$  on the right of (i) must individually vanish. Multipliers  $1 - V_s/\mathfrak{K}(I_a)$  and  $\sqrt{1 - V_s/\mathfrak{K}(I_b)}$  respectively of  $V_s/\mathfrak{K}(I_b)$  and  $V_s/\mathfrak{K}(II)$  being  $\Gamma$  or  $\Gamma^{1/2}$  at least by (3.4),  $V_s/\mathfrak{K}(I_b)$ ,  $V_s/\mathfrak{K}(II)$  and  $V_s/\mathfrak{K}(III)$  must individually approach zero or  $\mathfrak{K}(I_b)$ ,  $\mathfrak{K}(II)$  and  $\mathfrak{K}(III)$  tend respectively to infinity as  $\mathfrak{K}(I_a)$  approaches  $V_s/(1-\Gamma)$ . It is similarly shown that (3.5. b) holds true for  $I_b$  taken as  $r$ .

Rewriting (ii) in the form

$$1 - \frac{V_s}{\mathfrak{K}(II)} - \Gamma = \Gamma \left( \frac{1}{\sqrt{1 - V_s/\mathfrak{K}(I_b)}} - 1 \right) + \left\{ 1 - \left(1 - \frac{V_s}{\mathfrak{K}(I_a)}\right) \sqrt{1 - \frac{V_s}{\mathfrak{K}(I_b)}} \right\} + \frac{V_s}{\mathfrak{K}(III) \sqrt{1 - V_s/\mathfrak{K}(I_b)}},$$

we see that positive terms on the right should individually vanish and hence  $\mathfrak{K}(s)$  other than  $\mathfrak{K}(II)$  should grow without limit, as  $\mathfrak{K}(II)$  tends to  $V_s/(1-\Gamma)$  or  $1 - V_s/\mathfrak{K}(II)$  to  $\Gamma$ . The similar is the case with  $\mathfrak{K}(III)$ , as readily be shown by (iii).

The proposition (3.5. b) is thus verified.

$\mathfrak{K}(s)$ 's of Steps  $s$ 's other than  $r$  get infinitely larger than  $\mathfrak{K}(r)$ , as  $\mathfrak{K}(r)$  approaches  $V_s/(1-\Gamma)^{**}$ . (3. 5. b)

Step  $r$  will be called the rate-determining step as  $\mathfrak{K}(r)$  is sufficiently small compared with all other  $\mathfrak{K}(s)$ 's.

#### § 4. Rates of Exchange Reaction between Hydrogen and Ethylene during Hydrogenation

Rates of the exchange reaction are developed here as respective functions of  $\bar{v}(s)$ 's and  $\tilde{v}(s)$ 's, and hence of  $\mathfrak{K}(s)$ 's in accordance with §2.

It is originally meant by "exchange reaction" the isotopic replacement between chemical species, whose overall amounts and the total amounts of the respective isotopes are individually kept constant meanwhile. If for instance ethylene and hydrogen exchange deuterium under such condition, we have

$$n^H \dot{x}^H + n^E \dot{x}^E = 0, \quad (4.1)$$

where  $n^H$  or  $n^E$  is the total amount of hydrogen atoms in hydrogen or ethylene respectively and  $\dot{x}^H$  or  $\dot{x}^E$  the time derivative of the respective deuterium atomic fraction  $x^H$  or  $x^E$ . Defining the rate of exchange reaction between hydrogen and ethylene individually with respect to the participants as <sup>\*\*\*)</sup>

$$E^H \equiv n^H \dot{x}^H / (x^E - x^H), \quad E^E \equiv n^E \dot{x}^E / (x^H - x^E), \quad (4.2.H), (4.2.E)$$

we have immediately from (4.1)

$$E^H = E^E. \quad (4.3)$$

There exists however no such simple relation in the general case of hydrogenation, when (4.1) does not necessarily hold.  $E^H$  and  $E^E$  defined by (4.2) are developed separately as functions of  $\tilde{v}(s)$ 's and  $\bar{v}(s)$ 's as follows. The atomic fractions  $x^H$  and  $x^E$  in hydrogen and ethylene are expressed as

$$x^H = D^H/n^H, \quad x^E = D^E/n^E,$$

where  $D^H$  and  $D^E$  are amounts of deuterium atoms comprised in hydrogen and ethylene respectively. Differentiating above equations with respect

\*) see footnote \*\*) on p. 259.

\*\*) These expressions for exchange rates have been adopted for the sake of simplicity and uniformity of presentation as seen later instead of those  $E^H = -\frac{1}{2} n^H \dot{x}^H$  and  $E^E = \frac{1}{4} n^E \dot{x}^E$  in the previous work (Ref. 3).

to time, we have

$$\dot{x}^H = \dot{D}^H/n^H - x^H \dot{n}^H/n^H, \quad \dot{x}^E = \dot{D}^E/n^E - x^E \dot{n}^E/n^E. \quad (4.4. H), (4.4. E)$$

Time derivatives  $\dot{D}^H$ ,  $\dot{D}^E$ ,  $\dot{n}^H$  and  $\dot{n}^E$  are expressed in terms of  $\bar{v}(s)$  and  $\check{v}(s)$  as

$$\begin{aligned} \dot{D}^H &= 2\bar{v}(I_b)x^{H(a)} - 2\check{v}(I_b)x^H, & \dot{D}^E &= 4x^{C_2H_4(a)}\bar{v}(I_a) - 4x^E\check{v}(I_a) \\ \dot{n}^H &= 2\bar{v}(I_b) - 2\check{v}(I_b), & \dot{n}^E &= 4\bar{v}(I_a) - 4\check{v}(I_a), \end{aligned}$$

where  $x^{H(a)}$  and  $x^{C_2H_4(a)}$  are the atomic fractions of deuterium in adsorbed hydrogen atom and adsorbed ethylene molecule respectively. Eliminating  $\dot{D}^H$ ,  $\dot{D}^E$ ,  $\dot{n}^H$  and  $\dot{n}^E$  from above six equations, we have according to (4.2)

$$E^H = \frac{n^H \dot{x}^H}{x^E - x^H} = 2 \frac{x^{H(a)} - x^H}{x^E - x^H} \bar{v}(I_b), \quad E^E = \frac{n^E \dot{x}^E}{x^H - x^E} = 4 \frac{x^{C_2H_4(a)} - x^E}{x^H - x^E} \bar{v}(I_a) \quad (4.5. H), (4.5. E)$$

The  $x^{H(a)}$  and  $x^{C_2H_4(a)}$  in the above equations are expressed as functions of  $\bar{v}(s)$ 's,  $\check{v}(s)$ 's,  $x^H$ ,  $x^E$  and  $x^{C_2H_6}$  according to the steady state conditions; that for D(a) is

$$\begin{aligned} 2x^H\bar{v}(I_b) + \frac{1}{3}(x^{H(a)} + 2x^{C_2H_4(a)})\bar{v}(II) + x^{C_2H_6}\bar{v}(III) \\ = x^{H(a)}\{2\bar{v}(I_b) + \bar{v}(II) + \bar{v}(III)\}, \end{aligned} \quad (4.6. H)$$

which equates the rate of consumption of deuterium on the right to that of its supply on the left; the coefficient  $(x^{H(a)} + 2x^{C_2H_4(a)})/3$  of the second term on the left gives the probability of one of three hydrogen atoms on the methyl group of  $C_2H_5(a)$  given out as H(a) being deuterium in accordance with the postulate of chemical equivalence of the three hydrogen atoms\*). The steady state condition for deuterium in  $C_2H_4(a)$  is given similarly as

$$\begin{aligned} 4x^E\check{v}(I_a) + \left\{2x^{C_2H_4(a)} + \frac{2}{3}(2x^{C_2H_4(a)} + x^{H(a)})\right\}\check{v}(II) \\ = 4x^{C_2H_4(a)}(\check{v}(I_a) + \check{v}(II)) \end{aligned} \quad (4.6. E)$$

by equating the rate of supply of deuterium in  $C_2H_4(a)$  on the left to that of its consumption on the right. We have, on the other hand, the steady state conditions implied in (2.2)

$$\bar{v}(I_b) + \bar{v}(III) = \bar{v}(I_b) + \bar{v}(III), \quad \bar{v}(I_b) + \bar{v}(II) = \check{v}(I_b) + \check{v}(II)$$

\*) Cf. § 1.

and hence

$$2\bar{v}(\text{I}_b) + \bar{v}(\text{II}) + \bar{v}(\text{III}) = 2\bar{v}(\text{I}_b) + \bar{v}(\text{II}) + \bar{v}(\text{III})$$

or, substituting the coefficient of  $x^{\text{H}(\text{a})}$  on the left of (4.6.H) from the above equation,

$$(x^{\text{H}} - x^{\text{H}(\text{a})}) \bar{v}(\text{I}_b) + \frac{1}{3}(x^{\text{C}_2\text{H}_4(\text{a})} - x^{\text{H}(\text{a})}) \bar{v}(\text{II}) + \frac{1}{2}(x^{\text{C}_2\text{H}_6} - x^{\text{H}(\text{a})}) \bar{v}(\text{III}) = 0. \quad (4.7. H)$$

Eq. (4.6.E) is similarly rewritten, according to another steady state condition  $\bar{v}(\text{I}_a) + \bar{v}(\text{II}) = \bar{v}(\text{I}_a) + \bar{v}(\text{II})$  derived from (2.2), as

$$(x^{\text{E}} - x^{\text{C}_2\text{H}_4(\text{a})}) \bar{v}(\text{I}_a) + \frac{1}{6}(x^{\text{H}(\text{a})} - x^{\text{C}_2\text{H}_4(\text{a})}) \bar{v}(\text{II}) = 0 \quad (4.7. E)$$

Solving (4.7) for  $x^{\text{H}(\text{a})}$  and  $x^{\text{C}_2\text{H}_4(\text{a})}$ , we have

$$x^{\text{H}(\text{a})} = \frac{2x^{\text{H}}\bar{v}(\text{I}_b) + x^{\text{E}} \frac{4\bar{v}(\text{I}_a)\bar{v}(\text{II})}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})} + x^{\text{C}_2\text{H}_6}\bar{v}(\text{III})}{2\bar{v}(\text{I}_b) + \frac{4\bar{v}(\text{I}_a)\bar{v}(\text{II})}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})} + \bar{v}(\text{III})} \quad (4.8. H)$$

and

$$x^{\text{C}_2\text{H}_4(\text{a})} = \frac{6x^{\text{E}}\bar{v}(\text{I}_a)}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})} + \frac{x^{\text{H}(\text{a})}\bar{v}(\text{II})}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})}. \quad (4.8. E)$$

Since  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's are functions of  $\mathfrak{K}(s)$ 's according to (2.12) and (2.13),  $E^{\text{H}}$  and  $E^{\text{E}}$  are given as respective functions of  $\mathfrak{K}(s)$ 's by (4.5) and (4.8). They equal each other in such particular case as mentioned above, whereas not in general in course of hydrogenation but independent functions of  $\mathfrak{K}(s)$ 's as shown in §10.

### § 5. Rate of Equilibration $\text{P}_2 + \text{D}_2 = 2\text{PD}$

The rate  $E^q$  of equilibration



is defined as

$$E^q = n^{\text{H}}\dot{u}/2, \quad u = n^{\text{PD}}/n_e^{\text{PD}}, \quad (5.2. E), (5.2. u)$$

where  $n^{\text{PD}}$  is the amount of PD molecules existing and  $n_e^{\text{PD}}$  the particular value of  $n^{\text{PD}}$ , which would be realized when the existent hydrogen attained the equilibrium of (5.1).  $E^q$  defined by (5.2) is given as

a function of  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's as follows. The atomic fraction  $x^H$  of deuterium in gas and  $n^H$  are respectively expressed by amounts  $n^{D_2}$ ,  $n^{PD}$  and  $n^{P_2}$  of  $D_2$ ,  $PD$ , and  $P_2$  molecules existing as

$$x^H = (2n^{D_2} + n^{PD})/n^H \quad (5.3.x)$$

and

$$n^H/2 = n^{P_2} + n^{PD} + n^{D_2}, \quad (5.3.n)$$

which hold irrespective as to whether the equilibrium of (5.1) is attained or not. Denoting  $n^{P_2}$ ,  $n^{PD}$  and  $n^{D_2}$  at equilibrium by  $n_e^{P_2}$ , etc. and putting

$$(n_e^{PD})^2 / n_e^{P_2} n_e^{D_2} = 4 \quad (5.4)$$

in accordance with our present approximation of ignoring the kinetic difference between P and D, we have

$$n_e^{PD} = x^H (1 - x^H) n^H \quad (5.5)$$

by eliminating  $n_e^{P_2}$  and  $n_e^{D_2}$  from (5.3) and (5.4) written particularly for  $n_e^{P_2}$ , etc. Substituting  $n_e^{PD}$  from (5.5) into (5.2.u), we have

$$u = \frac{n^{PD}}{x^H (1 - x^H) n^H} \quad (5.6)$$

The  $\dot{u}$  in (5.2.E) is given now by the logarithmic differentiation of the above equation as

$$\frac{\dot{u}}{u} = \frac{\dot{n}^{PD}}{n^{PD}} - \frac{\dot{n}^H}{n^H} - \frac{\dot{x}^H}{x^H} + \frac{\dot{x}^H}{1 - x^H} \quad (5.7)$$

The  $\dot{n}^{PD}$  in the above equation is given as

$$\dot{n}^{PD} = 2x^{H(a)}(1 - x^{H(a)})\bar{v}(I_b) - \frac{2n^{PD}}{n^H}\bar{v}(I_b),$$

from which we have for the first term of (5.7) referring to (5.6)

$$\frac{\dot{n}^{PD}}{n^{PD}} = \frac{2}{n^H} \left\{ \frac{x^{H(a)}(1 - x^{H(a)})}{x^H(1 - x^H)u} \bar{v}(I_b) - \bar{v}(I_b) \right\},$$

while for  $\dot{n}^H$  of the same equation

$$\dot{n}^H = 2\bar{v}(I_b) - 2\bar{v}(I_b).$$

Substituting  $\dot{n}^{PD}/n^{PD}$  and  $\dot{n}^H$  from the above two equations into (5.7), we have according to (5.2.E)

$$E^a = n^H \dot{u}/2 = \left\{ \frac{x^{H(a)}(1 - x^{H(a)})}{x^H(1 - x^H)} - u \right\} \bar{v}(I_b) - \left( \frac{1}{x^H} - \frac{1}{1 - x^H} \right) \dot{x}^H u n^H/2. \quad (5.8)$$

The particular value  $E_0^q$  of  $E^q$ , when  $u=0$  and  $x^E=0$ , is given as

$$E_0^q = \frac{x_0^{H(a)}(1-x_0^{H(a)})}{x^H(1-x^H)} \bar{v}(I_b), \quad (5.9)$$

where  $x_0^{H(a)}$  is the particular value of  $x^{H(a)}$  at  $x^E=0$ .

Eqs. (5.8) or (5.9) gives  $E^q$  or  $E_0^q$  as a function of  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's according to (4.8.H) at given  $u$ ,  $x^H$ ,  $x^E$  and  $x^{O_2H_2}$  and hence as a function of  $\bar{\omega}(s)$ 's according to (2.12) and (2.13).

### § 6. Rate of Parahydrogen Conversion

The rate  $E^p$  of parahydrogen conversion is defined as

$$E^p = - \frac{n^H}{2} \frac{\dot{x}^p}{x^p - x_\infty^p}, \quad (6.1)$$

where  $x^p$  is the fraction of the amount  $n^{p-H_2}$  of parahydrogen present over the total amount  $n^H/2$  of hydrogen molecules existing, *i.e.*

$$x^p = 2n^{p-H_2}/n^H$$

and  $x_\infty^p$  is the value of  $x^p$  at the equilibrium of parahydrogen conversion.  $E^p$  thus defined is expressed by  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's as follows. Differentiating  $x^p$  of the above equation with respect to time as

$$\dot{x}^p = 2\dot{n}^{p-H_2}/n^H - x^p\dot{n}^H/n^H$$

and expressing  $\dot{n}^{p-H_2}$  and  $\dot{n}^H$  as

$$\dot{n}^{p-H_2} = x_\infty^p\dot{v}(I_b) - x^p\dot{v}(I_b),$$

$$\dot{n}^H = 2\dot{v}(I_b) - 2\dot{v}(I_b),$$

we have from the above three equations, according to (6.1),

$$E^p = \bar{v}(I_b). \quad (6.2)$$

It is admitted in this derivation that desorbed hydrogen is at equilibrium of parahydrogen conversion as implied in the term  $x_\infty^p\dot{v}(I_b)$  in the expression of  $\dot{n}^{p-H_2}$  above. This is equivalent, with reference to the thermodynamical condition of the indifference of equilibrium to catalysts, to the identical chance of para- and ortho-hydrogen to react in the reverse direction, *i.e.* to be chemisorbed as implied in the second term in the same expression.

### § 7. Kinetics of Scheme (3)

The steady state condition of Scheme (3) is

$$V_s = \bar{v}(I_b) - \check{v}(I_b) = \bar{v}(II) - \check{v}(II) = \bar{v}(III) - \check{v}(III) \quad (7.1)$$

in place of (2.2). Forward and backward rates  $\bar{v}(s)$  and  $\check{v}(s)$  are expressed by a similar reasoning to that in § 2, as

$$\bar{v}(I_b) = \mathfrak{K}(I_b), \quad \check{v}(I_b) = r(H)^2 \mathfrak{K}(I_b), \quad (7.2. I_b)$$

$$\bar{v}(II) = r(H) \mathfrak{K}(II), \quad \check{v}(II) = r(C_2H_5) \mathfrak{K}(II), \quad (7.2. II)$$

$$\bar{v}(III) = r(H) r(C_2H_5) \mathfrak{K}(III), \quad \check{v}(III) = \Gamma \mathfrak{K}(III), \quad (7.2. III)$$

where  $r(H)$  and  $r(C_2H_5)$  are defined identically by (2.10),  $\Gamma$  by (2.9. III) and  $\mathfrak{K}(s)$ 's by (2.5.  $\mathfrak{K}$ ) and (2.7). We have from (7.1) and (7.2)

$$\begin{aligned} V_s &= \mathfrak{K}(I_b)(1 - r(H)^2) = \mathfrak{K}(II)(r(H) - r(C_2H_5)) \\ &= \mathfrak{K}(III)(r(H) r(C_2H_5) - \Gamma) \end{aligned} \quad (7.3)$$

or eliminating  $r(H)$  and  $r(C_2H_5)$ ,

$$\frac{1 - \Gamma}{V_s} = \frac{1}{\mathfrak{K}(I_b)} + \frac{1}{\mathfrak{K}(II)} \sqrt{1 - \frac{V_s}{\mathfrak{K}(I_b)}} + \frac{1}{\mathfrak{K}(III)}. \quad (7.4)$$

$E^H$  defined by (4.2.H) is given by quite the similar reasoning identically by (4.5.H), *i. e.* as

$$E^H = 2 \frac{x^{H(a)} - x^H}{x^E - x^H} \bar{v}(I_b). \quad (7.5. H)$$

As regards  $E^E$ , we have to go back to general equations (4.2.E) and (4.4.E), because of lack of the Step  $I_a$  in this case.  $\dot{D}^E$  and  $\dot{n}^E$  in (4.4.E) is given in accordance with Scheme (3) as

$$\dot{D}^E = \left\{ 2x^E + \frac{2}{3} (2x^E + x^{H(a)}) \right\} \bar{v}(II) - 4x^E \check{v}(II)$$

and

$$\dot{n}^E = 4\bar{v}(II) - 4\check{v}(II),$$

and hence we have by (4.2.E) and (4.4.E)

$$E^E = \frac{2}{3} \frac{x^{H(a)} - x^E}{x^H - x^E} \bar{v}(II). \quad (7.5. E)$$

We obtain exactly the same expressions for  $E^a$ ,  $E^q$  and  $E^p$ , with which Step  $I_a$  has nothing directly to do, as those respectively given by (5.8), (5.9) and (6.2), *i. e.*

$$E^a = \left\{ \frac{x^{H(a)}(1 - x^{H(a)})}{x^H(1 - x^H)} - u \right\} \bar{v}(I_b) - \left( \frac{1}{x^H} - \frac{1}{1 - x^H} \right) \dot{x}^{H(a)} u^H / 2, \quad (7.5. q)$$

$$E^q = \frac{x_0^{H(a)}(1-x_0^{H(a)})}{x^H(1-x^H)} \bar{v}(I_b), \quad (7.5.q_0)$$

and

$$E^p = \bar{v}(I_b). \quad (7.5.p)$$

The  $x^{H(a)}$  comprised in the above expressions is determined in accordance with the present scheme by the steady state condition for D(a), which state is just the same as (4.7.H) except that  $x^{C_2H_4(a)}$  is replaced by  $x^E$ , as

$$x^{H(a)} = \frac{2x^H\bar{v}(I_b) + \frac{2}{3}x^E\bar{v}(II) + x^{C_2H_4}\bar{v}(III)}{2\bar{v}(I_b) + \frac{2}{3}\bar{v}(II) + \bar{v}(III)}. \quad (7.6)$$

It is now shown that  $V_s$ ,  $E^H$ ,  $E^E$ ,  $E^q$  and  $E^p$  in this case are identical functions of  $\mathfrak{R}(I_b)$ ,  $\mathfrak{R}(II)$  and  $\mathfrak{R}(III)$  respectively with those of Scheme (2) in its special case, when  $I_a$  is rapid enough, so that

$$\mathfrak{R}(I_a) \gg V_s \quad \text{and} \quad 6\bar{v}(I_a) \gg \bar{v}(II). \quad (7.7.a), (7.7.b)$$

It follows from (7.7.a) and (2.13) that  $1-\gamma(C_2H_4)$  is extremely small compared with unity, *i.e.* practically

$$\gamma(C_2H_4) = 1. \quad (7.8)$$

Eqs. (2.12) and (2.13), which determine  $\bar{v}(s')$  and  $\bar{v}(s')$ , where  $s'=I_b$ , II and III, are now quite identical with (7.2) and (7.3) respectively, so that  $\bar{v}(s')$  and  $\bar{v}(s')$  in the special case of Scheme (2) are identical functions of  $\mathfrak{R}(s')$ 's respectively with those of Scheme (3).

Steady rates  $V_s$ ,  $E^H$  *etc.* on the basis of Scheme (2) are now given as functions of  $\bar{v}(s)$  and  $\bar{v}(s)$  besides of  $x^{H(a)}$  and  $x^{C_2H_4(a)}$ . The  $x^{H(a)}$  or  $x^{C_2H_4(a)}$  there, is, as given by (4.8), respectively identical, in the special case according to (7.7.b), with that of (7.6) or  $x^E$ .  $E^E$  of Scheme (2) written according to (4.5.E) and (4.7.E) as

$$E^E = \frac{2}{3} \frac{x^{H(a)} - x^{C_2H_4(a)}}{x^H - x^E} \bar{v}(II), \quad (7.9)$$

is now identical with  $E^E$  of Scheme (3) given by (7.5.E) on account of  $x^{C_2H_4(a)}$  being equal to  $x^E$ . Other rates  $E^H$ ,  $E^q$  and  $E^p$ , besides  $V_s$ , of Scheme (2) are given as functions of  $\bar{v}(s')$ ,  $\bar{v}(s')$  and  $x^{H(a)}$  quite identically with those of (7.5). It follows that the steady rates  $V_s$ ,  $E^H$  *etc.* are identical functions of  $\mathfrak{R}(s')$ 's and hence kinetically identical in both the cases as detailed in §9 and §10.

§ 8. Kinetics of Scheme (4)

According to Scheme (4) we have the steady state condition

$$V_s = \bar{v}(I_b) - \dot{v}(I_b) = \bar{v}(III) - \dot{v}(III) \quad (8.1.H)$$

and

$$\bar{v}(II) = \dot{v}(II) . \quad (8.1.E)$$

The  $\bar{v}(s)$ 's and  $\dot{v}(s)$ 's involved are given by a similar reasoning to that in §2, as

$$\bar{v}(I_b) = \mathfrak{K}(I_b), \quad \dot{v}(I_b) = r(H)^2 \mathfrak{K}(I_b), \quad (8.2.I)$$

$$\bar{v}(II) = \dot{v}(II) = r(H) \mathfrak{K}(II), \quad (8.2.II)$$

$$\bar{v}(III) = r(H)^2 \mathfrak{K}(III), \quad \dot{v}(III) = \Gamma \mathfrak{K}(III), \quad (8.2.III)$$

where  $\mathfrak{K}(I_b)$ ,  $\mathfrak{K}(II)$ ,  $\mathfrak{K}(III)$ ,  $r(H)$  and  $\Gamma$  are defined identically with those defined by (2.5.℔), (2.7), (2.10.H) and (2.9.III).

We have from (8.1) and (8.2) for the steady state of hydrogenation

$$V_s = \mathfrak{K}(I_b)(1 - r(H)^2) = \mathfrak{K}(III)(r(H)^2 - \Gamma) \quad (8.3.V)$$

instead of (7.3) and eliminating  $r(H)^2$

$$\frac{1 - \Gamma}{V_s} = \frac{1}{\mathfrak{K}(I_b)} + \frac{1}{\mathfrak{K}(III)} . \quad (8.3.r)$$

$E^H$  defined by (4.2.H) is expressed on the base of Scheme (4) identically by (4.5.H), *i.e.* as

$$E^H = 2 \frac{x^{H(a)} - x^H}{x^E - x^H} \dot{v}(I_b) . \quad (8.4.H)$$

$E^E$  is expressed generally by (4.2.E) and (4.4.E) as

$$E^E = \frac{n \dot{x}^E}{x^H - x^E} = \frac{\dot{D}^E - x^E \dot{n}^E}{x^H - x^E} ,$$

where  $\dot{D}^E$  is given, noting that deuterium is transferred into ethylene by two routes, *i.e.* II and III, according to Scheme (4), as

$$\dot{D}^E = \left\{ 2x^E + \frac{2}{3}(x^{H(a)} + 2x^E) \right\} \dot{v}(II) - 4x^E \dot{v}(II) + 4x^{C_2H_4} \dot{v}(III) - 4x^E \dot{v}(III)$$

or according to (8.1.E) as

$$\dot{D}^E = \frac{2}{3}(x^{H(a)} - x^E) \dot{v}(II) + 4x^{C_2H_4} \dot{v}(III) - 4x^E \dot{v}(III) ,$$

while  $\dot{n}^E$  as

$$\dot{n}^E = 4\bar{v}(\text{III}) - 4\bar{v}(\text{II}),$$

so that we have

$$E^E = \frac{2}{3} \frac{x^{\text{H(a)}} - x^E}{x^{\text{H}} - x^E} \bar{v}(\text{II}) + 4 \frac{x^{\text{C}_2\text{H}_6} - x^E}{x^{\text{H}} - x^E} \bar{v}(\text{III}). \quad (8.4. E)$$

$E^q$ ,  $E_0^q$  and  $E^p$  are given, as readily be shown, identically by (7.5) as

$$E^q = \left\{ \frac{x^{\text{H(a)}}(1 - x^{\text{H(a)}})}{x^{\text{H}}(1 - x^{\text{H}})} - u \right\} \bar{v}(\text{I}_b) - \left( \frac{1}{x^{\text{H}}} - \frac{1}{1 - x^{\text{H}}} \right) x^{\text{H}} u n^{\text{H}} / 2, \quad (8.4. q)$$

$$E_0^q = \frac{x_0^{\text{H(a)}}(1 - x_0^{\text{H(a)}})}{x^{\text{H}}(1 - x^{\text{H}})} \bar{v}(\text{I}_b), \quad (8.4. q_0)$$

and

$$E^p = \bar{v}(\text{I}_b), \quad (8.4. p)$$

while  $x^{\text{H(a)}}$  is determined by the steady state condition for D(a), *i.e.*

$$2x^{\text{H}} \bar{v}(\text{I}_b) + \frac{1}{3} (x^{\text{H(a)}} + 2x^E) \bar{v}(\text{II}) + 2x^{\text{C}_2\text{H}_6} \bar{v}(\text{III}) = x^{\text{H(a)}} \{ 2\bar{v}(\text{I}_b) + \bar{v}(\text{II}) + 2\bar{v}(\text{III}) \},$$

which equates the rate of supply of D(a) on the left to that of consumption on the right, in accordance with (8.1), as

$$x^{\text{H(a)}} = \frac{x^{\text{H}} \bar{v}(\text{I}_b) + 1/3 \cdot x^E \bar{v}(\text{II}) + x^{\text{C}_2\text{H}_6} \bar{v}(\text{III})}{\bar{v}(\text{I}_b) + 1/3 \cdot \bar{v}(\text{II}) + \bar{v}(\text{III})}. \quad (8.5)$$

In our practical cases of interest, when  $x^{\text{H}}$  or  $x^E$  is appreciably greater than the natural abundance, terms including  $\bar{v}(\text{III})$  in (7.6), (8.4) and (8.5) are practically completely negligible.  $V_s$ ,  $E^{\text{H}}$ ,  $E^E$ ,  $E^q$ ,  $E_0^q$  and  $E^p$  are then respectively identical functions of  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's common to both Schemes (3) and (4) as seen above. The  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's are however not in general identical functions respectively of  $\hat{\mathfrak{K}}(s)$ 's, and hence the dependence of steady rates  $V_s$  *etc.* on  $\hat{\mathfrak{K}}(s)$ 's are in general different as developed in the subsequent sections.

### § 9. $r(\text{H})$ and $r(\text{C}_2\text{H}_6)$ of Schemes (3) and (4)

Scheme (2) is kinetically identical with Scheme (3) under the condition (7.7), which is practically satisfied in most of cases dealt with in this paper as seen later. We might compare the kinetics of Scheme (3), accessible to a simpler treatment, as an approximation to that of Scheme (2), with that of Scheme (4). The  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's depend gen-

erally differently on  $\mathfrak{R}(s)$ 's as seen from (7.2) for Scheme (3) and (8.2) for Scheme (4) except when  $r(H)=r(C_2H_5)$  in the former case and  $r(H)$  happens to be an identical function in both the cases.  $\mathfrak{R}(s)$ 's are on the other hand definite functions of concentrations  $N^{\delta}$ 's of hydrogen, ethylene and ethane or of corresponding partial pressures at constant temperature and if the change of adsorption accompanied by the variation of partial pressures affects the rates or  $p^*$  in (2.5.  $\mathfrak{R}$ ) only insignificantly in accordance with Chapter 2,  $\mathfrak{R}(I_b)$ ,  $\mathfrak{R}(II)$  and  $\mathfrak{R}(III)$  are respectively simply proportional to  $P^H$ ,  $(P^H)^{1/2}P^E$  and  $P^H P^E$  respectively, as follows from (2.5.  $\mathfrak{R}$ ), (2.7) and (2.11), *i.e.*

$$\mathfrak{R}(I_b) \propto P^H, \quad \mathfrak{R}(II) \propto (P^H)^{1/2}P^E, \quad \mathfrak{R}(III) \propto P^H P^E, \quad (9.1. I), (9.1. II), (9.1. III)$$

where  $P^H$  and  $P^E$  are partial pressures of hydrogen and ethylene. It follows that steady rates  $V_s$  *etc.* of Schemes (3) and (4) are, although identical functions of  $\bar{v}(s)$ 's and  $\tilde{v}(s)$ 's as seen in the foregoing section, in general different functions of partial pressures depending on the underlying scheme which modulates  $r(H)$  and  $r(C_2H_5)$  particularly.

We might first investigate in this section  $r(H)$  and  $r(C_2H_5)$  as functions of  $\mathfrak{R}(s)$ 's on the base of Scheme (3) in the three typical cases ( $I_b$ ), (II) and (III), when Steps  $I_b$ , II and III respectively govern the rate and compare them with those of Scheme (4).

( $I_b$ )  $V_s = \mathfrak{R}(I_b)$ . We have from (7.3)

$$\mathfrak{R}(I_b)/\mathfrak{R}(II) = r(H) - r(C_2H_5), \quad (9.2. a)$$

$$\mathfrak{R}(I_b)/\mathfrak{R}(III) = r(H)r(C_2H_5), \quad (9.2. b)$$

neglecting  $\Gamma$  and hence

$$r(H) = \frac{\mathfrak{R}(I_b)}{2\mathfrak{R}(II)} \left( 1 + \sqrt{1 + 4\mathfrak{R}(II)^2/\mathfrak{R}(I_b)\mathfrak{R}(III)} \right), \quad (9.3)$$

which gives in conjunction with (9.2) two sets of values of  $r(H)$  and  $r(C_2H_5)$  according as

$$\kappa^2 = \mathfrak{R}(II)^2/\mathfrak{R}(I_b)\mathfrak{R}(III) \quad (9.4)$$

is far greater or less than unity, *i.e.*

$$r(H) = r(C_2H_5) = \sqrt{\mathfrak{R}(I_b)/\mathfrak{R}(III)}, \quad \kappa^2 \gg 1, \quad (9.5. a)$$

and

$$r(H) = \mathfrak{R}(I_b)/\mathfrak{R}(II), \quad r(C_2H_5) = \mathfrak{R}(II)/\mathfrak{R}(III), \quad \kappa^2 \ll 1. \quad (9.5. b)$$

Similarly we have from (7.3)

$$(II) \quad V_s = \mathfrak{K}(II), \quad r(H) = 1, \quad r(C_2H_5) = \mathfrak{K}(II)/\mathfrak{K}(III) \quad (9.6)$$

and

$$(III) \quad V_s = \mathfrak{K}(III), \quad r(H) = r(C_2H_5) = 1. \quad (9.7)$$

We see that (2.12) and (2.13) for Scheme (2) provide, under the condition (7.8) which follows from (7.7.a), equations identical with (7.2) and (7.3) for Scheme (3), which determine  $r(H)$  and  $r(C_2H_5)$  and hence  $\bar{v}(s')$  and  $\bar{v}(s')$  ( $s' = I_b, II, III$ ) identically as functions of  $\mathfrak{K}(s')$ 's. It follows that the above conclusions hold for Scheme (2) by virtue of (7.7.a), which is comprised in the above specifications of the rate-determining step as  $I_b, II$  and  $III$ , irrespective of (7.7.b). These conclusions are summarized in Table 1.

TABLE 1.  $r(H)$  and  $r(C_2H_5)$  of Scheme (3)

$r$	$I_b$		II	III
	$\kappa^2 \gg 1$	$\kappa^2 \ll 1$		
$r(H)$	$\sqrt{\frac{\mathfrak{K}(I_b)}{\mathfrak{K}(III)}}$	$\frac{\mathfrak{K}(I_b)}{\mathfrak{K}(II)}$	1	1
$r(C_2H_5)$	$\sqrt{\frac{\mathfrak{K}(I_b)}{\mathfrak{K}(III)}}$	$\frac{\mathfrak{K}(II)}{\mathfrak{K}(III)}$	$\frac{\mathfrak{K}(II)}{\mathfrak{K}(III)}$	1

In the case of Scheme (4) we have from (8.3.V) neglecting  $I'$

$$r(H) = \sqrt{\mathfrak{K}(I_b)/(\mathfrak{K}(I_b) + \mathfrak{K}(III))},$$

or for the respective cases of the rate-determining step

$$(I_b) \quad r(H) = \sqrt{\mathfrak{K}(I_b)/\mathfrak{K}(III)}, \quad (9.8.I_b)$$

$$(III) \quad r(H) = 1, \quad (9.8.III)$$

irrespective of  $II$ , which is constantly at equilibrium by (8.1.E), in no case governing the rate.

We see from the comparison of Table 1 and (9.8) that both in the cases ( $I_b$ ),  $\kappa^2 \gg 1$  and (III) of Scheme (3), functions  $r(H)$  and  $r(C_2H_5)$  are identical with each other as well as with  $r(H)$  of Scheme (4) in the respective cases of ( $I_b$ ) and (III). It follows now from (7.2) and (8.2) that  $\bar{v}(s')$ 's and  $\bar{v}(s')$ 's are identical functions of  $\mathfrak{K}(s')$ 's in the respective

cases. Steady rates  $V_s$ ,  $E^H$  etc. of Scheme (3) in the case of (I<sub>b</sub>),  $\kappa^2 \gg 1$  or (III) are in consequence respectively kinetically identical with those of Scheme (4) in the case of (I<sub>b</sub>) or (III). Only in the cases of (I<sub>b</sub>),  $\kappa^2 \ll 1$  and (II) of Scheme (3), when  $r(H)$  and  $r(C_2H_4)$  are neither identical functions with each other nor with  $r(H)$  of Scheme (4), steady rates  $V_s$  etc. are generally different functions of  $\mathfrak{K}(s)$ 's from those of Scheme (4).

### § 10. Kinetic Difference of Schemes (3) and (4)

We investigate below the kinetics, *i.e.* the dependence of rates on partial pressures in the respective cases of Scheme (3) mentioned in the foregoing section, when it is either identical with that of Scheme (4) or not.

(I<sub>b</sub>),  $\kappa^2 \gg 1$ . We have beside

$$V_s = \mathfrak{K}(I_b), \quad (10.1.V)$$

the relation

$$x^{H(a)} = \frac{x^H + \kappa/3 \cdot x^E}{1 + \kappa/3} \quad (10.1.x)$$

according to (7.6), (7.2), (9.4) and Table 1, neglecting terms including  $\bar{v}(III)$ . Substituting  $x^{H(a)}$  from (10.1.x), and  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's from (7.2) into (7.5), we have by (9.4) and Table 1, neglecting unity,  $1-x^H$  and  $x^H$  against  $\kappa/3$ ,

$$E^H = 2\mathfrak{K}(I_b)^2 / \mathfrak{K}(III), \quad E^E = 2\mathfrak{K}(I_b) \quad (10.2.H), (10.2.E)$$

$$E_0^q = 3\mathfrak{K}(I_b)^{5/2} / (1-x^H)\mathfrak{K}(II) \mathfrak{K}(III)^{1/2}, \quad E^p = \mathfrak{K}(I_b)^2 / \mathfrak{K}(III) \quad (10.2.q), (10.2.p)$$

(III) We have similarly as in (I<sub>b</sub>),  $\kappa^2 \gg 1$

$$V_s = \mathfrak{K}(III), \quad x^{H(a)} = \frac{x^H + 1/3 \cdot x^E \mathfrak{K}(II) / \mathfrak{K}(I_b)}{1 + 1/3 \cdot \mathfrak{K}(II) / \mathfrak{K}(I_b)} \quad (10.3.V), (10.3.x)$$

from (7.6), (7.2) and Table 1 or substituting  $x^{H(a)}$  from (10.3.x) into (7.5)

$$E^H = E^E = \frac{2\mathfrak{K}(I_b) \mathfrak{K}(II)}{3\mathfrak{K}(I_b) + \mathfrak{K}(II)} \quad (10.3.HE)$$

$$E_0^q = 3 \frac{3(1-x^H) \mathfrak{K}(I_b) + \mathfrak{K}(II)}{(1-x^H)(3\mathfrak{K}(I_b) + \mathfrak{K}(II))^2} \mathfrak{K}(I_b)^2, \quad E^p = \mathfrak{K}(I_b). \quad (10.3.q), (10.3.p)$$

In the extreme cases when  $\mathfrak{K}(I_b) \gg \mathfrak{K}(II)$ , (10.3) leads to the equations

$$E^H = E^E = \frac{2}{3} \mathfrak{K}(\text{II}), \quad E_0^q = E^p = \mathfrak{K}(\text{I}_b), \quad (10.4. \text{HE}), (10.4. pq)$$

provided that  $x^H$  is not very near 1, and when  $\mathfrak{K}(\text{I}_b) \ll \mathfrak{K}(\text{II})$  to those

$$E^H = E^E = 2\mathfrak{K}(\text{I}_b), \quad E_0^q = \frac{3}{1-x^H} \frac{\mathfrak{K}(\text{I}_b)^2}{\mathfrak{K}(\text{II})}, \quad E^p = \mathfrak{K}(\text{I}_b). \quad (10.5. \text{HE}), (10.5. q), (10.5. p)$$

( $\text{I}_b$ ),  $\kappa^2 \ll 1$ . We have similarly as in the case of ( $\text{I}_b$ ),  $\kappa^2 \gg 1$

$$V_s = \mathfrak{K}(\text{I}_b), \quad x^{H(a)} = \frac{x^H + \kappa^2/3 \cdot x^E}{1 + \kappa^2/3} \quad (10.6. V), (10.6. x)$$

or substituting  $x^{H(a)}$  from (10.6.x) into (7.5) and neglecting  $2/3 \mathfrak{K}(\text{II})^2/\mathfrak{K}(\text{III})$  against  $\mathfrak{K}(\text{I}_b)$  according to the premiss  $\kappa^2 \equiv \mathfrak{K}(\text{II})^2/\mathfrak{K}(\text{I}_b)\mathfrak{K}(\text{III}) \ll 1$ ,

$$E^H = \frac{2}{3} \frac{\mathfrak{K}(\text{I}_b)^2}{\mathfrak{K}(\text{III})}, \quad E^E = \frac{2}{3} \frac{\mathfrak{K}(\text{II})^2}{\mathfrak{K}(\text{III})}, \quad (10.6. \text{HE})$$

$$E_0^q = E^p = \mathfrak{K}(\text{I}_b)^3/\mathfrak{K}(\text{II})^2, \quad (10.6. qp)$$

provided that  $1-x^H$  is sufficiently greater than  $1/3 \cdot \kappa^2$ .

(II) Similarly as above, we have

$$V_s = \mathfrak{K}(\text{II}), \quad x^{H(a)} = \frac{x^H + \kappa^2/3 \cdot x^E}{1 + \kappa^2/3} \quad (10.7. V), (10.7. x)$$

and henceforth

$$E^H = E^E = \frac{2}{3} \frac{\mathfrak{K}(\text{II})^2}{\mathfrak{K}(\text{III})} \quad (10.7. \text{HE})$$

and

$$E_0^q = E^p = \mathfrak{K}(\text{I}_b), \quad (10.7. pq)$$

substituting  $x^{H(a)}$  from (10.7.x) into (7.5) and neglecting  $1/3 \cdot \kappa^2$  against unity in accordance with the premiss  $r = \text{II}$ .

The above results are summarized in Table 2.

The validity of Table 2 for Scheme (2) depends on the condition (7.7.a), which is however implied in the above specification of the rate-determining steps, *i.e.* of those except  $\text{I}_a$ ; it rests besides upon (7.7.b), with which  $x^{H(a)}$  given by (4.8) for Scheme (2) reduces to that by (7.6) of Scheme (3) and  $x^{C_2H(a)}$  to  $x^E$  respectively. By these  $x^{H(a)}$  and  $x^{C_2H(a)}$  steady rates  $V_s$ , *etc.* of Scheme (2) become identical functions of  $\bar{v}(s)$ 's and  $\bar{v}(s)$  and henceforth identical functions of  $\mathfrak{K}(s)$ 's respectively with those of Scheme (3), since  $\bar{v}(s)$ 's and  $\hat{v}(s)$ 's are given respectively as

TABLE 2. Steady Rates  $V_s$  etc. as Functions of  $\mathfrak{K}(s)$ 's on the Basis of Scheme (3)

Rate-Det. Step Steady Rates	I <sub>b</sub>		II	III	
	$\kappa^2 \gg 1$	$\kappa^2 \ll 1$		$\mathfrak{K}(I_b) \ll \mathfrak{K}(II)$	$\mathfrak{K}(I_b) \gg \mathfrak{K}(II)$
$V_s$	$\mathfrak{K}(I_b)$	$\mathfrak{K}(I_b)$	$\mathfrak{K}(II)$	$\mathfrak{K}(III)$	$\mathfrak{K}(III)$
$E^H$	$2\mathfrak{K}(I_b)^2/\mathfrak{K}(III)$	$\frac{2}{3}\mathfrak{K}(I_b)^2/\mathfrak{K}(III)$	$\frac{2}{3}\mathfrak{K}(II)^2/\mathfrak{K}(III)$	$2\mathfrak{K}(I_b)$	$\frac{2}{3}\mathfrak{K}(II)$
$E^E$	$2\mathfrak{K}(I_b)$	$\frac{2}{3}\mathfrak{K}(II)^2/\mathfrak{K}(III)$	$\frac{2}{3}\mathfrak{K}(II)^2/\mathfrak{K}(III)$	$2\mathfrak{K}(I_b)$	$\frac{2}{3}\mathfrak{K}(II)$
$E_0^q$	$\frac{3\mathfrak{K}(I_b)^{5/2}}{(1-x^H)\mathfrak{K}(II)\mathfrak{K}(III)^{1/2}}$	$\mathfrak{K}(I_b)^3/\mathfrak{K}(II)^2$	$\mathfrak{K}(I_b)$	$\frac{3}{1-x^H} \frac{\mathfrak{K}(I_b)^2}{\mathfrak{K}(II)}$	$\mathfrak{K}(I_b)$
$E^p$	$\mathfrak{K}(I_b)^2/\mathfrak{K}(III)$	$\mathfrak{K}(I_b)^3/\mathfrak{K}(II)^2$	$\mathfrak{K}(I_b)$	$\mathfrak{K}(I_b)$	$\mathfrak{K}(I_b)$

identical functions of  $\mathfrak{K}(s)$ 's in both cases of the Schemes by virtue of (7.7.a) as mentioned in §7. Steady rates of Scheme (2) in some other cases e.g. when (7.7.a) holds but  $6\bar{v}(I_a) \ll \bar{v}(II)$  on the contrary to (7.7.b) may be similarly derived, although not given here because of apparently less importance. The case when (7.7.a) does not hold but  $I_a$  governs the rate will be dealt with in Chapter 4.

It might be noted that steady rates are independent functions of  $\mathfrak{K}(s)$ 's as seen from Table 2. It follows that the set of  $\mathfrak{K}(s)$ 's or the structure are determined from knowledge of any four of these steady rates, which fixes the fifth steady rate as well, although at present we have to rely upon rather crude estimation as seen from the next Chapter to arrive at the structure because of lack of sufficient knowledge of steady rates.

Dependence of steady rates  $V_s$  etc. on partial pressures at constant temperature is derived from Table 2 and (9.1) as shown in Table 3, where each pair of numbers denotes the exponents to  $P^H$  and  $P^E$  of the product of their powers, to which the relevant steady rate is proportional.

The dependence in the case of  $(I_b)$ ,  $\kappa^2 \gg 1$  and  $(III)$  for Scheme (3) is, as already stated, identical with that in the cases  $(I_b)$  and  $(III)$  of Scheme (4) respectively. Sets of exponents peculiar to Scheme (3), not shared by Scheme (4) should in consequence be found, if any, in columns of  $(I_b)$ ,  $\kappa^2 \ll 1$  and  $(II)$ , although some of sets in the latter may happen to coincide with those in the columns of  $(I_b)$ ,  $\kappa^2 \gg 1$  and  $(III)$ . Such sets are, as seen from Table 3, those surrounded by bold lines. Herein we have an experimental method of discriminating Scheme (3) from (4) by ob-

servicing the dependence on partial pressures of steady rates  $V_s$ , etc.

TABLE 3. Exponents  $x$ ,  $y$  of the Product  $(P^H)^x (P^E)^y$  Proportional to Steady Rates  $V_s$ , etc. of Scheme (3)

Rate-Det. Step Steady Rates	I <sub>b</sub>		II	III	
	$\kappa^2 \gg 1$	$\kappa^2 \ll 1$		$\mathfrak{R}(I_b) \ll \mathfrak{R}(II)$	$\mathfrak{R}(I_b) \gg \mathfrak{R}(II)$
$V_s$	1, 0	1, 0	$\frac{1}{2}$ , 1	1, 1	1, 1
$E^H$	1, -1	1, -1	0, 1	1, 0	$\frac{1}{2}$ , 1
$E^E$	1, 0	0, 1	0, 1	1, 0	$\frac{1}{2}$ , 1
$E_0^q$	$\frac{3}{2}$ , $-\frac{3}{2}$	2, -2	1, 0	$\frac{3}{2}$ , -1	1, 0
$E^p$	1, -1	2, -2	1, 0	1, 0	1, 0

TAYLOR states that the associative mechanism leads to the conclusion\*) that  $E^H/V_s \propto (P^H)^{-1/2}$ . This mechanism was originally put forward as Scheme (2) with the rate-determining step of III as mentioned in the introduction. We see from Table 3, which holds for Scheme (2) under the condition (7.7), that the above conclusion of TAYLOR is valid for the rate-determining step of III, only when  $\mathfrak{R}(I_b) \gg \mathfrak{R}(II)$  but not when  $\mathfrak{R}(I_b) \ll \mathfrak{R}(II)$ . TAYLOR\*) has taken for granted in arriving at the above conclusion that  $V_s \propto \bar{v}(III)$  and  $E^H \propto \bar{v}(II)$ . The first of these is generally assured by (2.2) or (7.1), in so far as  $\bar{v}(III)$  is negligible compared with  $\bar{v}(II)$ , but the second not necessarily even in the case of (III) as seen from the equation

$$E^H = 2\bar{v}(I_b) \bar{v}(II) / (3\bar{v}(I_b) + \bar{v}(II)), \quad (10.10)$$

which follows from (10.3.HE) and (7.2) according to (9.7). We have from (10.10) that  $E^H = 2/3 \cdot \bar{v}(II)$ , when  $\bar{v}(I_b) \gg \bar{v}(II)$ . This means that every act of II in the reverse direction results in an exchange of hydrogen atom with 2/3 probability, once in three times being just a return of H(a) to the starting point, provided that H(a) originating from ethylene has a good chance of arriving at the state of gaseous hydrogen before going back home again, *i.e.*  $\bar{v}(I_b) \gg \bar{v}(II)$ , which is satisfied by the above condition  $\bar{v}(I_b) \gg \bar{v}(II)$ , since  $\bar{v}(I_b) = \bar{v}(II)$  by (9.7) and (7.2). If on the contrary  $\bar{v}(I_b) \ll \bar{v}(II)$ , the "rate-determining step" of the exchange reaction is no more the reversal of II but that of I<sub>b</sub>, *i.e.* the recombination. Since then H(a) are almost certainly originating from ethylene,

\*) Cf. p. 282, Ref. 18.

every act of the reversal of  $I_b$  successfully transposes two hydrogen atoms from ethylene into hydrogen at a rate  $E^H = 2\bar{v}(I_b)$  as deduced directly from the above equation for the specified condition. This illustrates that the above conclusion of TAYLOR is of only limited validity.

## Chapter 2. Determination of $\mathfrak{K}(s)$ 's

### § 11. Statistical-Mechanical Expressions of $\mathfrak{K}(s)$ 's

$\mathfrak{K}(s)$ 's will now be statistical-mechanically developed for determining them with some simplifications by experimental results and theoretical estimations.

The  $p^{*(s)}$  in (2.5.  $\mathfrak{K}$ ) for a heterogeneous step is expressed as<sup>\*</sup>

$$p^{*(s)} = G^{*(s)} q^{*(s)} \theta_{\sigma_s^{*(s)}}^{*(s)}, \quad (11. 1)$$

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

$$q^{*(s)} = \exp(-\varepsilon^{*(s)}/RT), \quad (11. 2)$$

where  $\varepsilon^{*(s)}$  is taken practically independent of temperature, neglecting the probability of the excited states of  $*(s)$  confined in a space  $\sigma_s^*$  of molecular dimension.

The  $p_e^{*(s)}$  in (2.5.  $\mathfrak{K}$ ) is expressed according to (2.7) by  $p^H$  and  $p^E$ , which are given by (2.11) as

$$p^H = Q^H/N^H, \quad p^E = Q^E/N^E \quad (11. 3. E), (11. 3. H)$$

and the partition function  $Q^H$  or  $Q^E$  of a single gas molecule  $H_2$  or  $C_2H_4$  in unit volume is expressed with a close approximation as

$$Q^H = \frac{(2\pi m^H kT)^{3/2}}{h^3} \cdot \frac{4\pi^2 I^H kT}{h^2} \exp(-\varepsilon_0^H/RT), \quad (11. 4. H)$$

$$Q^E = \frac{(2\pi m^E kT)^{3/2}}{h^3} \cdot \frac{2\pi^2 (2\pi I^E kT)^{3/2}}{h^3} \exp(-\varepsilon_0^E/RT), \quad (11. 4. E)$$

\* ) Cf. § 24, Ref. 25.

neglecting the probability of excited vibrational levels, where  $m^H$  or  $m^E$  is the mass of the respective molecule,  $I^H$  the moment of inertia of  $H_2$ ,  $I^E$  the geometric mean of three principal moments of inertia of  $C_2H_4$  and  $\epsilon_0^H$  or  $\epsilon_0^E$  the energy of the ground state of the respective molecule.

Substituting  $p^{*(s)}$  and  $p^{I(s)}$  from (11.1) and (2.7) into (2.5.8) and expressing  $p^H$  and  $p^E$  there by (11.3), we have

$$\mathfrak{K}(I_a) = K_N(I_a) N^E / Q^E, \quad \mathfrak{K}(I_b) = K_N(I_b) N^H / Q^H, \quad (11.5. I_a), (11.5. I_b)$$

$$\mathfrak{K}(II) = K_N(II) N^E (N^H)^{1/2} / Q^E (Q^H)^{1/2}, \quad \mathfrak{K}(III) = K_N(III) N^E N^H / Q^E Q^H, \quad (11.5. II), (11.5. III)$$

where

$$K_N(s) = \kappa(s) \frac{kT}{h} G^{*(s)} q^{*(s)} \theta_{\sigma_s^*(s)}. \quad (11.5. K)$$

We have now from (11.5) and (2.13)

$$V_s / N^H = K_N(I_b) (1 - \gamma(H)^2) / Q^H, \quad (11.6)$$

$$\begin{aligned} V_s &= \frac{\gamma(H)^2 (1 - \gamma(C_2H_4))}{\gamma(H)^2 / \mathfrak{K}(I_a)} = \frac{1 - \gamma(H)^2}{1 / \mathfrak{K}(I_b)} = \frac{\gamma(H)^2 \gamma(C_2H_4) - \gamma(C_2H_5) \gamma(H)}{\gamma(H) / \mathfrak{K}(II)} \\ &= \frac{\gamma(H) \gamma(C_2H_5) - \Gamma}{1 / \mathfrak{K}(III)} = \frac{1 - \Gamma}{\frac{\gamma(H)^2}{\mathfrak{K}(I_a)} + \frac{1}{\mathfrak{K}(I_b)} + \frac{\gamma(H)}{\mathfrak{K}(II)} + \frac{1}{\mathfrak{K}(III)}}, \end{aligned}$$

and

$$(11.7. a)$$

$$\frac{1 - \Gamma}{V_s} = \frac{\gamma(H)^2}{\mathfrak{K}(I_a)} + \frac{1}{\mathfrak{K}(I_b)} + \frac{\gamma(H)}{\mathfrak{K}(II)} + \frac{1}{\mathfrak{K}(III)} \quad (11.7. b)$$

or

$$\frac{N^H (1 - \Gamma)}{V_s} = \frac{\gamma(H)^2 Q^E N^H}{K_N(I_a) N^E} + \frac{Q^H}{K_N(I_b)} + \frac{\gamma(H) (Q^H)^{1/2} Q^E (N^H)^{1/2}}{K_N(II) N^E} + \frac{Q^H Q^E}{K_N(III) N^E}. \quad (11.7. c)$$

## § 12. Rate-Determining Step

ZUR STRASSEN<sup>31)</sup> has observed the rate of catalyzed hydrogenation of ethylene in the presence of nickel catalyst under a few hundredths mmHg partial pressure of hydrogen and ethylene.  $\mathfrak{K}(s)$ 's are adjusted to this experiment as below, since the low pressures used are expected favorable to the present analysis without allowance for adsorption.

ZUR STRASSEN has found that the steady rate  $V_s$  of hydrogenation is strictly proportional to the hydrogen partial pressure at constant temperature and constant ethylene partial pressure throughout his observation from  $-7^\circ\text{C}$  to  $125^\circ\text{C}$ . Both  $q^{*(s)}$  and  $\theta_{\sigma^*(s)}$  in (11.5.K) and hence  $K_N(s)$ 's are respectively constant at constant temperature<sup>\*)</sup>, in so far as the effect of the variation of adsorption is negligible. It follows on the other hand from the strict proportionality of  $V_s$  to the hydrogen partial pressure at constant temperature and constant ethylene partial pressure, that the left  $V_s/N^H$  of (11.6) is constant throughout. Since  $I'$  is of the order of magnitude of  $10^{-7}$  at most at the condition of the ZUR STRASSEN's experiment as calculated by (2.15)<sup>\*\*)</sup>, the left of (11.7.c) is also practically constant. Since further  $Q^H$  and  $Q^E$  are respectively functions solely of temperature as seen from (11.4),  $\gamma(H)$  must be constant or far smaller than unity according to (11.6) at constant temperature and  $N^E$ . If  $\gamma(H)$  is constant, the first and third terms of (11.7.c) are respectively proportional to  $N^H$  and its square root, whereas the second and fourth terms are constant at the specified condition and in consequence that the former two must be negligibly small compared with other constant terms, since all terms involved are positive. Neglecting thus the first and the third terms, we have referring to (11.5)

\*) The  $\varepsilon^{*(s)}$  of (11.2) and hence  $q^{*(s)}$  is affected by adsorptives, if the latter exert force upon the critical complex  $\Sigma^*(s)$ , while they may as well reduce  $\theta_{\sigma^*(s)}$  by occupying  $\sigma^*$ .

\*\*) Expressing  $\mu^{\delta i}$  in (2.15) as  $\mu^{\delta i} = \mu^{\delta i} + RT \ln P^{\delta i}$  and noting that  $\mu^{C_2H_4} = \mu^E + \mu^H$  at equilibrium, we have  $\Gamma = P^{C_2H_4} / K_p P^E P^H$  where  $P^{\delta i}$  is the partial pressure of  $\delta$  representing  $C_2H_6$ ,  $E \equiv C_2H_4$ , and  $H \equiv H_2$ ,  $\mu^{\delta i}$  the values of  $\mu^{\delta i}$  at  $P^{\delta i} = 1$ ,  $K_p = P^{C_2H_4} / P^E P^H$  the equilibrium constant and  $P_e^{\delta i}$  the value of  $P^{\delta i}$  at equilibrium.

The  $K_p$  is calculated from spectroscopic data as

$T^\circ K$	200	300	400	500
$K_{P \text{ mmHg}}$	$2.0 \times 10^{24}$	$4.2 \times 10^{13}$	$1.7 \times 10^8$	$3.7 \times 10^4$

which data have been converted from the original data [Landolt "Tabellen" Erg. III c, p. 2622] given in  $\text{atm}^{-1}$  by dividing them by 760.

The  $\Gamma$ -values are obtained from the above values of  $K_p$  as below :

$\Gamma$ -Values

$T^\circ K$		200	300	400	500
$P^H = P^E$	10	$5.0 \times 10^{-26}$	$2.4 \times 10^{-15}$	$5.9 \times 10^{-10}$	$2.7 \times 10^{-6}$
$= P^{C_2H_4}$	0.03	$1.7 \times 10^{-23}$	$8 \times 10^{-13}$	$2.0 \times 10^{-7}$	$9.0 \times 10^{-4}$

$$\frac{1-\Gamma}{V_s} = \frac{1}{\mathfrak{K}(I_b)} + \frac{1}{\mathfrak{K}(III)}, \quad (12.1)$$

which states that either  $I_b$  or III may be the rate-determining step but neither  $I_a$  nor II, so far as the experimental condition of ZUR STRASSEN is concerned\*).

If  $r(H) \ll 1$ , alternatively,  $I_b$  determines the rate according to (2.13) and (3.5.b), which is the special case of the above conclusion.

### § 13. Reduction of $\mathfrak{K}(s)$ 's for Evaluation

Before  $\mathfrak{K}(s)$ 's are adjusted to the experimental result in accordance with (12.1), they will be reduced to a form ready for numerical evaluation.

We have from (11.5), (11.2) and (11.4), assuming  $\kappa(s)=1$

$$\mathfrak{K}(I_a) = \frac{kT}{h} G^{*(I_a)} \theta_{\sigma_{I_a}^{*(o)}} \frac{N^E}{Q_0^E} \exp\left(-\frac{\epsilon^{*(I_a)} - \epsilon_0^E}{RT}\right), \quad (13.1. I_a)$$

$$\mathfrak{K}(I_b) = \frac{kT}{h} G^{*(I_b)} \theta_{\sigma_{I_b}^{*(o)}} \frac{N^H}{Q_0^H} \exp\left(-\frac{\epsilon^{*(I_b)} - \epsilon_0^H}{RT}\right), \quad (13.1. I_b)$$

$$\mathfrak{K}(II) = \frac{kT}{h} G^{*(II)} \theta_{\sigma_{II}^{*(o)}} \frac{N^E}{Q_0^E} \left(\frac{N^H}{Q_0^H}\right)^{1/2} \exp\left(-\frac{\epsilon^{*(II)} - \epsilon_0^E - \frac{1}{2}\epsilon_0^H}{RT}\right), \quad (13.1. II)$$

and

$$\mathfrak{K}(III) = \frac{kT}{h} G^{*(III)} \theta_{\sigma_{III}^{*(o)}} \frac{N^E}{Q_0^E} \frac{N^H}{Q_0^H} \exp\left(-\frac{\epsilon^{*(III)} - \epsilon_0^E - \epsilon_0^H}{RT}\right), \quad (13.1. III)$$

where

$$Q_0^H = \frac{(2\pi m^H kT)^{3/2}}{h^3} \frac{4\pi^2 I^H kT}{h^2} \quad (13.2. H)$$

and

$$Q_0^E = \frac{(2\pi m^E kT)^{3/2}}{h^3} \frac{2\pi^2 (2\pi I^E kT)^{3/2}}{h^2}. \quad (13.2. E)$$

The  $G^{*(s)} \theta_{\sigma_s^{*(o)}}$ 's or the numbers of free sites for critical complexes of the respective steps are identified with each other, which must at least

\*) If  $\mathfrak{K}(I_a)$  be so small compared with all other  $\mathfrak{K}(s)$ 's, as determining the rate in accordance with (3.5.a), it follows from the second and third members of (2.13) that  $1-r(H)^2$  must be appreciably smaller than unity or that  $r(H)$  are nearly unity, since  $1-r(C_2H_4)$  is less than unity according to (3.3). The first term on the right of (11.7.b) must then be important instead of being negligible as concluded from experimental results. The rate-determining step of II leads to the similar contradiction.

be of the same order of magnitude for a homogeneous catalyst's surface.

The  $N^H$  and  $N^E$  in (13.1) are expressed by partial pressures  $P^H$  and  $P^E$  in mmHg as

$$N^H = 1333 P^H / kT \quad \text{and} \quad N^E = 1333 P^E / kT. \quad (13.3.H), (13.3.E)$$

The factor  $T$  in non-exponential factor in the expression of  $\mathfrak{R}(s)$  obtained by substituting  $N^H$  and  $N^E$  from (13.3) is replaced with reference to the average temperature  $T_N$  over the temperature range in question, as

$$T \rightarrow T_N \exp(1 - T_N/T), \quad (13.4)$$

where  $T_N \exp(1 - T_N/T)$  reproduces  $T$  by reserving its expansion with respect to  $(T - T_N)/T_N$  up to the first order term. The result is

$$\mathfrak{R}(I_a) = \rho \frac{P^E}{Q_P^E} \exp(-\Delta^* \epsilon(I_a) / RT), \quad (13.5.I_a)$$

$$\mathfrak{R}(I_b) = \rho \frac{P^H}{Q_P^H} \exp(-\Delta^* \epsilon(I_b) / RT), \quad (13.5.I_b)$$

$$\mathfrak{R}(II) = \rho \frac{P^E}{Q_P^E} \left( \frac{P^H}{Q_P^H} \right)^{1/2} \exp(-\Delta^* \epsilon(II) / RT), \quad (13.5.II)$$

$$\mathfrak{R}(III) = \rho \frac{P^E}{Q_P^E} \frac{P^H}{Q_P^H} \exp(-\Delta^* \epsilon(III) / RT), \quad (13.5.III)$$

where

$$\Delta^* \epsilon(I_a) = \epsilon^{*(I_a)} + RT_N - (\epsilon_0^E + 4RT_N), \quad (13.6.I_a)$$

$$\Delta^* \epsilon(I_b) = \epsilon^{*(I_b)} + RT_N - (\epsilon_0^H + 7/2 \cdot RT_N), \quad (13.6.I_b)$$

$$\Delta^* \epsilon(II) = \epsilon^{*(II)} + RT_N - (\epsilon_0^E + 1/2 \cdot \epsilon_0^H + 4RT_N + 7/4 \cdot RT_N), \quad (13.6.II)$$

$$\Delta^* \epsilon(III) = \epsilon^{*(III)} + RT_N - (\epsilon_0^E + \epsilon_0^H + 4RT_N + 7/2 \cdot RT_N), \quad (13.6.III)$$

$$Q_P^H = \frac{kT_N}{1333} \frac{(2\pi m^H kT_N)^{3/2}}{h^3} \frac{4\pi^2 I^H kT_N}{h^2} e^{7/2} = 1.057 \times 10^{10}, \quad T_N = 373.2^\circ \text{K}, \quad (13.7.H)$$

$$Q_P^E = \frac{kT_N}{1333} \frac{(2\pi m^E kT_N)^{3/2}}{h^3} \frac{2\pi^2 (2\pi I^E kT_N)^{3/2}}{h^3} e^4 = 3.939 \times 10^{14}, \quad T_N = 373.2^\circ \text{K}, \quad (13.7.E)$$

and

$$\rho = \frac{kT_N}{h} e^{G^{*(s)}} \theta_{s^*(s)} \quad (13.8)$$

is the factor taken common to all  $s$ 's .

We have on the other hand from (2.11), (13.3), (13.4) and (13.7) by a similar transformation

$$p^H = Q_P^H \exp(\varepsilon^H/RT)/P^H, \quad p^E = Q_P^E \exp(\varepsilon^E/RT)/P^E, \quad (13.9. H), (13.9. E)$$

where

$$\varepsilon^H = \varepsilon_0^H + 7/2 \cdot RT_N, \quad \varepsilon^E = \varepsilon_0^E + 4RT_N. \quad (13.10. H), (13.10. E)$$

The  $Q_P^E$ ,  $Q_P^H$ ,  $\rho$  and  $\Delta^*\varepsilon(s)$ 's are respectively constant for a constant  $T_N$ , in so far as the excited states involved in  $\varepsilon^{*(s)}$ ,  $\varepsilon_0^E$  and  $\varepsilon_0^H$  as well as the effect on them of variation of adsorption are negligible, so that the relative values of  $\mathfrak{K}(s)$ 's are fixed with known values of  $Q_P^E$  and  $Q_P^H$  of (13.7) by a single constant  $\Delta^*\varepsilon(s)$  for each  $\mathfrak{K}(s)$  according to (13.5). The constants  $\Delta^*\varepsilon(s)$ 's will be evaluated in the subsequent sections to determine  $\mathfrak{K}(s)$ 's as functions of temperature and partial pressures  $P^E$  and  $P^H$ .

It might be noted that  $\varepsilon^{*(s)} + RT_N$  is the average energy or the enthalpy at  $T=T_N$  of the critical complex transiting the critical state. The  $(\varepsilon_0^E + 4RT_N)$  etc. on the right of (13.6) are, on the other hand, each the enthalpy of the set of reactant molecules<sup>\*)</sup>, each of which is kept in equilibrium with the appropriate initial complex by equilibria of steps other than the appropriate one, inasmuch as  $\varepsilon_0^H + 7/2 \cdot RT_N$  and  $\varepsilon_0^E + 4RT_N$ , *i.e.*  $\varepsilon^H$  and  $\varepsilon^E$  according to (13.10), are enthalpies (partial molar) at  $T=T_N$  respectively of hydrogen and ethylene as deduced from the thermodynamical expression  $\mu^\delta - T(\partial\mu^\delta/\partial T)_P$  of enthalpy, (2.4) and (13.9). The  $\Delta^*\varepsilon(I_a)$  etc. are in consequence the activation enthalpies, *i.e.* the critical increments of enthalpy referred to the states of the above sets of reactant molecules.

#### § 14. Determination of $\mathfrak{K}(I_b)$ and $\mathfrak{K}(III)$

Substituting  $\mathfrak{K}(I_b)$  and  $\mathfrak{K}(III)$  from (13.5) into (12.1), we have

$$\frac{\rho}{V_s} = \frac{Q_P^H}{P^H} e^{\frac{\Delta^*\varepsilon(I_b)}{kT}} + \frac{Q_P^H}{P^H} \frac{Q_P^E}{P^E} e^{\frac{\Delta^*\varepsilon(III)}{kT}},$$

neglecting  $\Gamma$ , or

$$\ln \frac{V_s}{P^H} \left( \frac{Q_P^E}{P^E} e^{\frac{\Delta^*\varepsilon(III) - \Delta^*\varepsilon(I_b)}{kT}} + 1 \right) = - \frac{\Delta^*\varepsilon(I_b)}{kT} - \ln \frac{Q_P^H}{\rho}, \quad (14.1)$$

<sup>\*)</sup> Such sets are  $C_2H_4$ ,  $H_2$ ,  $C_2H_4 + 1/2 \cdot H_2$  and  $C_2H_4 + H_2$  respectively for Steps  $I_a$ ,  $I_b$ , II and III.

which states that the quantity on the left is a linear function of  $1/T$ . Substituting  $V_s/P^H$  and  $P^E$  observed by ZUR STRASSEN<sup>31)</sup> and  $Q_P^E$  from (13.7.E) into the left-hand side of the above equation and adjusting  $\Delta^*\epsilon(\text{III}) - \Delta^*\epsilon(\text{I}_b)$  for the linear relation,  $\Delta^*\epsilon(\text{I}_b)$  and  $\Delta^*\epsilon(\text{III})$  are determined individually as

$$\Delta^*\epsilon(\text{I}_b) = 12 \text{ Kcal}, \quad \Delta^*\epsilon(\text{III}) = -12 \text{ Kcal}, \quad (14.2.1), (14.2.3)$$

which fix  $\mathfrak{K}(\text{I}_b)$  and  $\mathfrak{K}(\text{III})$  numerically as functions of  $T$ ,  $P^H$  and  $P^E$  by (13.5) aside from the common factor  $\rho$ .

### § 15. Estimation of $\Delta^*\epsilon(\text{II})$

The  $\Delta^*\epsilon(\text{II})$  is estimated, assuming that

$$\epsilon^{*\text{I(II)}} - \epsilon^{\text{I(II)}} = \epsilon^{*\text{I(III)}} - \epsilon^{\text{I(III)}}, \quad (15.1)$$

where  $\epsilon^{\text{I(II)}}$  or  $\epsilon^{\text{I(III)}}$  is the enthalpy identified with the energy of the initial complex  $\text{C}_2\text{H}_4(\text{a}) + \text{H}(\text{a})$  of II or  $\text{C}_2\text{H}_5(\text{a}) + \text{H}(\text{a})$  of III respectively, on the ground that both processes of II and III consist in leaping of  $\text{H}(\text{a})$  at the adsorbed hydrocarbon  $\text{C}_2\text{H}_4(\text{a})$  or  $\text{C}_2\text{H}_5(\text{a})$ . Expressing  $\epsilon^{\text{I(II)}}$  and  $\epsilon^{\text{I(III)}}$  as

$$\epsilon^{\text{I(II)}} = \epsilon^{\text{C}_2\text{H}_4(\text{a})} + \epsilon^{\text{H}(\text{a})}, \quad \epsilon^{\text{I(III)}} = \epsilon^{\text{C}_2\text{H}_5(\text{a})} + \epsilon^{\text{H}(\text{a})},$$

where  $\epsilon^{\text{C}_2\text{H}_4(\text{a})}$ ,  $\epsilon^{\text{C}_2\text{H}_5(\text{a})}$  and  $\epsilon^{\text{H}(\text{a})}$  are energies of  $\text{C}_2\text{H}_4(\text{a})$ ,  $\text{C}_2\text{H}_5(\text{a})$  and  $\text{H}(\text{a})$  respectively, we have from the above three equations, (13.6) and (13.10.H)

$$\begin{aligned} \Delta^*\epsilon(\text{II}) &= \Delta^*\epsilon(\text{III}) + \epsilon^{*\text{I(II)}} - \epsilon^{*\text{I(III)}} + \frac{1}{2} \epsilon^{\text{II}} \\ &= \Delta^*\epsilon(\text{III}) + \epsilon^{\text{C}_2\text{H}_4(\text{a})} + \frac{1}{2} \epsilon^{\text{H}} - \epsilon^{\text{C}_2\text{H}_5(\text{a})} \end{aligned} \quad (15.2)$$

The energy difference  $\epsilon^{\text{C}_2\text{H}_4(\text{a})} + \frac{1}{2} \epsilon^{\text{H}} - \epsilon^{\text{C}_2\text{H}_5(\text{a})}$  in the above equation is expressed relying upon the additivity of bond energies as

$$\epsilon^{\text{C}_2\text{H}_4(\text{a})} + \frac{1}{2} \epsilon^{\text{H}} - \epsilon^{\text{C}_2\text{H}_5(\text{a})} = -D(\text{C}-\text{Ni}) - \frac{1}{2} D(\text{H}-\text{H}) + D(\text{C}-\text{H}),$$

where  $D(\text{C}-\text{Ni})$ ,  $D(\text{H}-\text{H})$  and  $D(\text{C}-\text{H})$  are the respective bond energies, *i.e.* the energy required to dissociate the respective single bonds. It is deduced on the same basis that  $D(\text{Ni}-\text{C})$  is combined with the heat  $H^E$  of adsorption of ethylene as

$$H^E = 2D(\text{C}-\text{Ni}) + D(\text{C}-\text{C}) - D(\text{C}=\text{C}), \quad (15.3)$$

where  $D(\text{C}-\text{C})$  and  $D(\text{C}=\text{C})$  are single and double bond energies between carbon atoms. From the above two equations, we have

$$\begin{aligned} \epsilon^{\text{C}_2\text{H}_4(\text{a})} + \frac{1}{2} \epsilon^{\text{H}} - \epsilon^{\text{C}_2\text{H}_2(\text{a})} = \frac{1}{2} \{ D(\text{C}-\text{C}) - D(\text{C}=\text{C}) - D(\text{H}-\text{H}) \} \\ + D(\text{C}-\text{H}) - \frac{1}{2} H^E. \end{aligned} \quad (15.4)$$

The  $H^E$  on freshly evaporated nickel film decreases rapidly from its initial value 58 Kcal/mol with increase of coverage according to BEECK et al.<sup>7)</sup>. We might adopt the value

$$H^E = 27.3 \text{ Kcal}, \quad 130^\circ \sim 140^\circ \text{C}, \quad (15.5. H)$$

which kept constant as observed by MATSUSHITA<sup>32)</sup> on reduced nickel, over a hydrogen pressure range from  $10^{-6}$  to  $10^{-2}$  mmHg, in accordance with the fact that coverage appreciably reduces the heat of adsorption admitting that the catalyst's surface is more or less covered in course of hydrogenation instead of being bare as freshly evaporated film as referred to in the introduction. Bond energies  $D(\text{C}-\text{C})$  etc. are given as<sup>\*)</sup>

$$D(\text{C}-\text{C}) = 59.6 \text{ Kcal}, \quad D(\text{C}=\text{C}) = 102.1 \text{ Kcal}, \quad (15.5. S), (15.5. D)$$

$$D(\text{H}-\text{H}) = 104.2 \text{ Kcal}, \quad D(\text{C}-\text{H}) = 88.2 \text{ Kcal}. \quad (15.5. H), (15.5. CH)$$

We have now from (15.2), (15.4) and (15.5)

$$\Delta^* \epsilon(\text{II}) - \Delta^* \epsilon(\text{III}) = 1.2 \text{ Kcal},$$

which decides  $\Delta^* \epsilon(\text{II})$  by (14.2.III) as

$$\Delta^* \epsilon(\text{II}) = -10.8 \text{ Kcal}. \quad (15.6)$$

#### § 16. Estimation of $\Delta^* \epsilon(\text{I}_a)$ ,

KFEL<sup>33)</sup> has calculated the critical increment  $\epsilon^{*(\text{I}_a)} - \epsilon_0^E$  of energy similarly as SHERMAN, SUN and EYRING<sup>34)</sup> did with the adsorption of benzene on nickel, for different values of  $D(\text{C}-\text{Ni})$  (from 38.2 to 60 Kcal) and of Ni-Ni distances (from 3.52 Å to 2.49 Å), whereas  $D(\text{C}-\text{Ni})$  amounts in accordance with (15.3) and (15.5) to  $\frac{1}{2} H^E + \frac{1}{2} D(\text{C}=\text{C}) - \frac{1}{2} D(\text{C}-\text{C}) = 34.9 \text{ Kcal}$ . He has thus found<sup>33)</sup> that the critical increment  $\epsilon^{*(\text{I}_a)} - \epsilon_0^E$  varies only slightly around 2.9 Kcal with the  $D(\text{C}-\text{Ni})$ -value

\*) Landolt "Tabellen" I, 2 (1951), p. 24.

*Theory of Hydrogenation of Ethylene on Metallic Catalysts I.*

as well as with the Ni-Ni distance. Since the VAN DER WAALS' attraction potential is not included in the LONDON'S approximation formula used and is nearly of the same magnitude to the latter value of  $\epsilon^{*(I_a)}$   $-\epsilon_0^{E*}$ , we might assume approximately

$$\epsilon^{*(I_a)} - \epsilon_0^E \simeq 0$$

and hence by (13.6.I<sub>a</sub>) as

$$\Delta^* \epsilon(I_a) \simeq -3RT_N \simeq -2.2 \text{ Kcal}, \quad T_N = 373.2^\circ \text{K}. \quad (16.1)$$

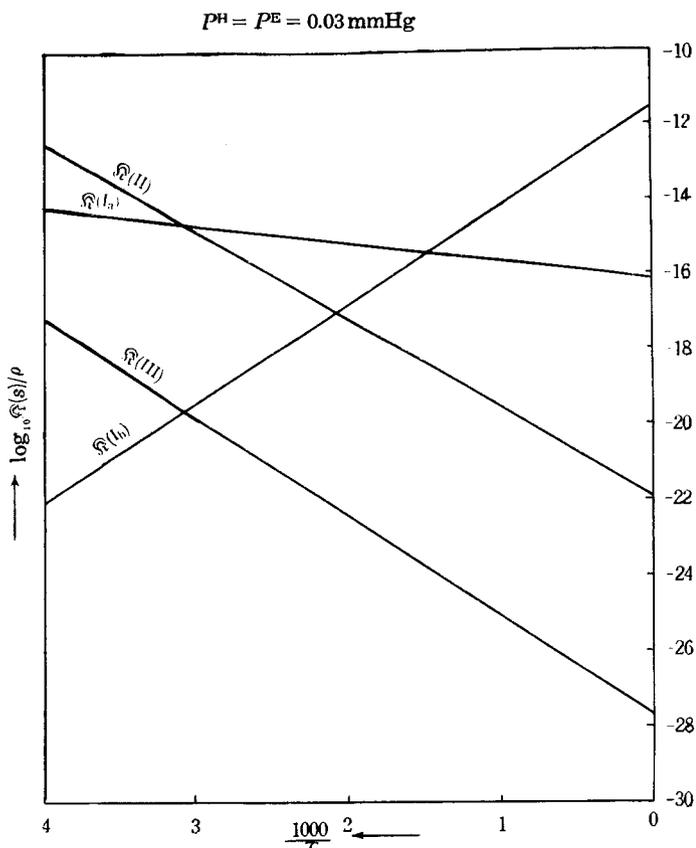


Fig. 1.

\*) The VAN DER WAALS' potential amounts to 2.6 Kcal according to BARDEEN'S formula [Phys. Rev. 58, 727 (1940)] on the base of the distance  $D=2.85 \text{ \AA}$  [Ref. 33] from the molecule at the critical state to the surface, the polarisability of ethylene  $\alpha=42.6 \times 10^{-25} \text{ cm}^3$  [Landolt "Tabellen" I, 3 (1951), p. 511], the mean excited energy of ethylene  $\Delta_A=8.91 \text{ e.v.}$  [ibid. p. 61] and the radius  $r_s=1.16 \text{ \AA}$  of a sphere of the volume per free electron, as worked out by Prof. T. TOYA of this Institute, to whom the best thanks of the present author are due.

### § 17. Structure Diagram

The structure diagram or the plot of  $\log_{10} \mathfrak{R}(s)/\rho$  against  $1/T$  is given in Fig. 1 for the condition of ZUR STRASSEN'S experiment<sup>31)</sup>, *i.e.*  $P^H = P^E = 0.03$  mm Hg by substituting the values of  $\Delta^* \epsilon(s)$  from (14.2), (15.6) and (16.1) into (13.5).

We see that both  $\mathfrak{R}(I_a)$  and  $\mathfrak{R}(II)$  of the above rather crude estimation run above the lower of  $\mathfrak{R}(I_b)$  and  $\mathfrak{R}(III)$  over the temperature range from  $-7^\circ$  to  $125^\circ\text{C}$  of ZUR STRASSEN'S experiment in accordance with the conclusion in §12. Fig. 1 shows in accordance with §3 that  $I_b$  or III alternatively determines the rate respectively at lower or higher temperature, giving rise to the well-known optimum of catalyzed hydrogenation around the intersection of  $\mathfrak{R}(I_b)$  and  $\mathfrak{R}(III)$  owing to different signs of  $\Delta \epsilon^*(I_b)$  and  $\Delta \epsilon^*(III)$  as given by (14.2).

The structure diagram at other partial pressures of ethylene and hydrogen is readily obtained by shifting  $\mathfrak{R}(s)$ 's parallel from those of Fig. 1 in accordance with (13.5).  $\mathfrak{R}(I_a)$  or  $\mathfrak{R}(I_b)$  is thus lowered relative to other  $\mathfrak{R}(s)$ 's by increasing the partial pressure respectively of hydrogen or ethylene.

Based on the structure arrived at, various experimental results are now accounted for in the subsequent chapter.

## Chapter 3. Explanation of Experimental Results

### § 18. Optimum Temperatures

Structure diagrams are drawn in Fig. 2 for other experimental conditions than that of Fig. 1 in accordance with the foregoing section to show how the optimum temperatures are determined in the respective cases. We see that  $\mathfrak{R}(I_b)$  or  $\mathfrak{R}(III)$  is the lowest throughout, so that optimum temperature is situated around their intersection just as in the case of Fig. 1 according to (3.5.a). The absolute temperature  $T_x$  of the intersection is determined from the condition  $\mathfrak{R}(I_b) = \mathfrak{R}(III)$  according to (13.5) as

$$T_x = (\Delta^* \epsilon(I_b) - \Delta^* \epsilon(III)) / R \ln(Q_P^E / P^E). \quad (18.1)$$

Table 4 compares the temperature  $t_x^\circ$  of intersection calculated by (18.1) with the optimum temperature  $t_{\text{opt.}}^\circ$  observed. Observed optimum temperatures are as shown in the Table semiquantitatively reproduced by the structure.

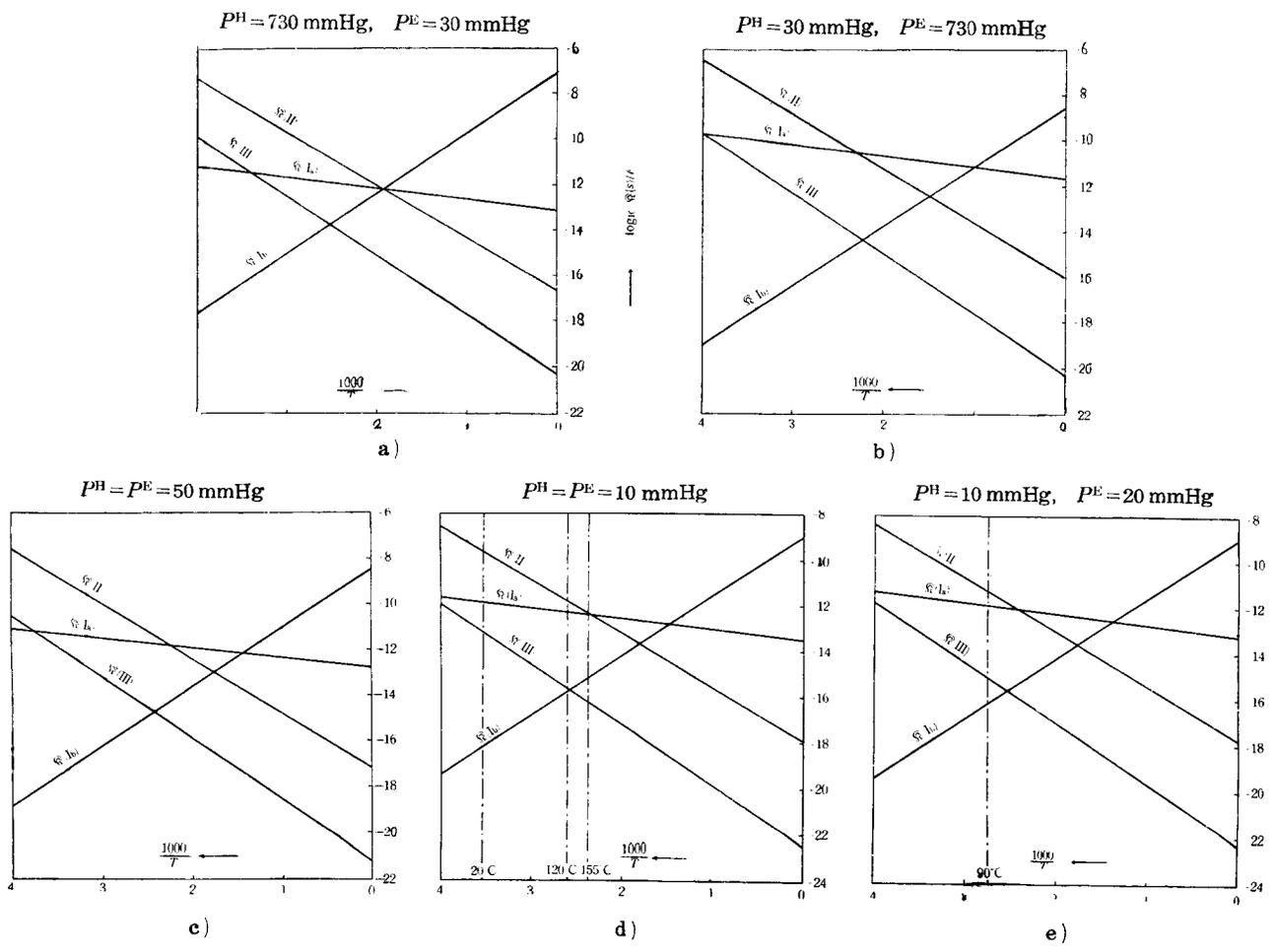


Fig. 2.

TABLE 4. Optimum Temperatures

Observers	ZUR STRASSEN <sup>31)</sup>	TUCHOLSKI & RIDEAL <sup>35)</sup>	RIDEAL <sup>36)</sup>	JENKINS & RIDEAL <sup>6)</sup>	RIDEAL <sup>36)</sup>
$P^E$ mmHg	0.03	3	30	50	730
$P^H$ mmHg	0.03	5	730	50	30
$t_{opt.}$ °C	~60	139	137	160~165	≥ 190
$t_X$ °C	53	100	128	134	175

The structure accounts further for the experimental results observed by RIDEAL<sup>36)</sup> that at  $P^H=730$  mmHg and  $P^E=30$  mmHg the optimum temperature was observed at 137°C but not at  $P^H=30$  mmHg and  $P^E=730$  mmHg up to 190°C, and that the rate of hydrogenation was smaller in the latter case attaining that in the former case first at 190°C. The  $\mathcal{R}$ (III) stands at the same height both in Fig. 2, a) and b) because of the same magnitude of  $P^H P^E$  according to (13.5.III), whereas  $\mathcal{R}$ (I<sub>b</sub>) is depressed from Fig. 2, a) to b) by the factor 30/730 according to (13.5.I<sub>b</sub>). The intersection must be shifted to higher temperature, and the hydrogenation rate lower in b) at lower temperatures, overtaking that in a) at the optimum semiquantitatively in accordance with observation.

RIDEAL<sup>36)</sup> has observed however in the case of Fig. 2, a) that the rate of hydrogenation varied approximately proportional to  $P^E$  at constant temperature but appreciably slowly with temperature at constant  $P^E$ . The proportionality to  $P^E$  does not follow from a), which requires instead that the rate is governed by I<sub>b</sub> and hence according to (13.5.I<sub>b</sub>) proportional to  $P^H$  but independent of  $P^E$ . This result might be attributed to the situation that the rate, which would be increased 730/30-fold from b) to a), if governed by I<sub>b</sub>, is controlled instead by the diffusion of ethylene with a rate approximately proportional to  $P^E$  and in consequence increasing only slowly with temperature. The diffusion control of the hydrogenation rate may be effective at higher total pressure, because of the following reason. The diffusion rate is proportional to the concentration gradient in the neighbourhood of the catalyst and to the mean free path there, which are respectively proportional and inversely proportional to the total pressure, so that the diffusion rate is constant at constant temperature independent of the total pressure. The rate of the surface reaction increases on the

other hand at equilibrium of diffusion with increase of the lowest  $\mathfrak{K}(s)$  by (3.5.a), which increases as seen from (13.5) with partial pressures increasing along with the total pressure, until at last the overall rate is governed by diffusion. There exists a similar situation as seen later in the experiments of WAGNER *et al.*<sup>22,23</sup>, which might give rise to the diffusion control.

### § 19. Kinetics of the Catalyzed Hydrogenation

ZUR STRASSEN has observed that the ratio of the hydrogenation rate to hydrogen partial pressure was approximately independent of ethylene partial pressure at 45°C, slightly increases with it at 67°C and appreciably at 120°C but not quite proportional to it. Eq. (12.1) is written according to (13.5) as

$$\frac{V_s}{1-\Gamma} = \frac{\rho P^H}{Q_p^H e^{\Delta^* \epsilon(I_b)/RT}} \cdot \frac{P^E}{P^E + Q_p^E e^{(\Delta^* \epsilon(III) - \Delta^* \epsilon(I_b))/RT}}, \quad (19.1)$$

and hence the apparent order  $\partial \ln V_s / \partial \ln P^E$  of reaction with respect to  $P^E$  is given with reference to (18.1) as

$$\frac{\partial \ln V_s}{\partial \ln P^E} = \left[ \exp \left\{ \frac{\Delta^* \epsilon(I_b) - \Delta^* \epsilon(III)}{R} \left( \frac{1}{T} - \frac{1}{T_x} \right) \right\} + 1 \right]^{-1}, \quad (19.2)$$

where  $\Delta^* \epsilon(I_b) - \Delta^* \epsilon(III)$  is positive according to (14.2). Eq. (19.2) states that the order is zero or unity at temperature sufficiently below or above  $T_x$  and 1/2 just at  $T_x$ . This conclusion is in accordance with the above observation as referred to the value  $t_x = 53^\circ\text{C}$  derived from the structure.

TOYAMA<sup>37</sup> has observed the catalyzed hydrogenation in the presence of nickel wire under several ten mmHg partial pressures of hydrogen and ethylene over the temperature range from 99° to 165°C with the result that its rate  $V_s$  is given as a function of partial pressures

$$V_s = k \frac{P^H P^E}{1 + k' P^E}, \quad (k, k': \text{constants}).$$

Since either  $\mathfrak{K}(I_b)$  or  $\mathfrak{K}(III)$  is the lowest also at this condition as shown by Fig. 2, c), (19.1) remains valid accounting for the above empirical relation.

FARKAS, FARKAS and RIDEAL<sup>38</sup> have observed the rate of catalyzed hydrogenation of ethylene in the presence of nickel as well as the simultaneous change of deuterium content in hydrogen. Table 5 shows

TABLE 5. Hydrogenation Rate and Simultaneous Change of Deuterium Atomic Fraction in Hydrogen, 20°C<sup>38)</sup>

Time of Reaction <i>t</i> min.	$P^H$ mmHg	$P^E$ mmHg	First Order Rate $\frac{1}{t} \ln \frac{P_0^H}{P^H} \text{ min}^{-1}$	Deuterium Atomic Fraction in Hydrogen %
0	32.5 (= $P_0^H$ )	21.5	—	30.6
10	24.5	13.5	0.028	30.0
25	16.5	5.5	0.027	33.2
34	12.0	1.0	0.029	33.8

the first order rate  $t^{-1} \ln P_0^H/P^H$  of hydrogenation calculated from their results of observation at 20°C, where  $t$  is the time of reaction and  $P_0^H$  the initial value of  $P^H$ . The first order rate keeps fairly constant irrespective of  $P^E$  decreasing more than by 20 factor as shown in the Table.

Fig. 2, c) or d) indicates on the other hand that Step I<sub>b</sub> determines, at 20°C, the rate of hydrogenation at § (I<sub>b</sub>) to keep the first order rate  $t^{-1} \ln P_0^H/P^H$  constant by (13.5.I<sub>b</sub>) independent of  $P^E$  as observed. As the hydrogenation proceeds, both  $P^E$  and  $P^H$  decrease without however affecting Step I<sub>b</sub> governing the rate as readily been inferred<sup>\*)</sup>.

TUCHOLSKI and RIDEAL<sup>35)</sup> reported later that the hydrogenation rate was zeroth order with respect to the total pressure at 0°,  $P^H=8$  and  $P^E=5$  mmHg<sup>\*\*)</sup>, and at 17°,  $P^H=2$  and  $P^E=1.3$  mmHg<sup>\*\*)</sup>. Similar kinetics was observed at higher temperatures as they report, although the data are not given explicitly<sup>35)</sup>. This conclusion is in conflict with that derived from the observation of FARKAS, FARKAS and RIDEAL<sup>38)</sup>,

\*) By increasing  $P^H$  and  $P^E$  respectively by factors  $10^2$  and  $10^6$ , straight lines of I<sub>a</sub>, I<sub>b</sub>, II and III in the structure diagrams shift parallel upwards respectively by  $e$ ,  $h$ ,  $e+h/2$  and  $e+h$  according to (13.5). It follows that those of I<sub>a</sub> and II remain above that of III by any decrease of  $P^H$  and  $P^E$  from those of Fig. 2, c) or d) throughout the whole range of temperature of interest, so that both I<sub>a</sub> and II can never govern the rate by the decrease according to §3. The rate-determining step is thus either I<sub>b</sub> or III irrespective of the decrease according as the temperature is below or above  $t_x$ , which descends now according to (18.1) and (14.2) monotonously from 123°C to 87°C with decrease of  $P^E$  from 21.5 to 1 mmHg. It follows that I<sub>b</sub> governs the rate throughout at the condition of the experiment of Table 5.

\*\*\*) The  $P$  given in the paper of TUCHOLSKI and RIDEAL<sup>35)</sup> without definition was taken equal to the pressure decrease  $\Delta P$  by hydrogenation on the ground of its numerical coincidence with the product of  $\Delta P/t$  and  $t$  as given by them except in a few cases of discrepancy seemingly due to misprint.

*Theory of Hydrogenation of Ethylene on Metallic Catalysts I.*

inasmuch as the rate cannot be of zeroth order with respect to the total pressure, in so far as it is first and zeroth order with respect to hydrogen and ethylene partial pressures in accordance with the latter conclusion. Table 6 and 7 show however that the latter conclusion fits in with above experimental results much the same as the former.

TABLE 6. Order of Catalyzed Hydrogenation of Ethylene  
by Nickel,  $(P^H)^1 (P^E)^0$  or  $P^0$

$P$ : total pressure,  $P_0$ : initial value of  $P$ ,  
Temperature:  $0^\circ\text{C}$ ,  $P_0^H \equiv P^H(\text{initial}) = 8 \text{ mmHg}$ ,  $P^E(\text{initial}) = 5.2 \text{ mmHg}$

Time of Reaction $t$ min.	$P_0 - P$ <sup>35) *)</sup> mmHg	$P^H = P_0^H - (P_0 - P)$ mmHg	$(P^H)(P^E)^0$ $1/t \log_{10} P_0^H/P^H$	$P^0$ $(P_0 - P)/t$ <sup>35)</sup>
2	1.05	6.95	0.031	0.53
3	1.37	6.63	0.027	0.46
5	2.10	5.90	0.026	0.42
8	2.95	5.05	0.025	0.37
10	3.00	5.00	0.020	0.30
13	4.42	3.58	0.027	0.34

TABLE 7. Order of Catalyzed Hydrogenation of Ethylene  
by Nickel,  $(P^H)^1 (P^E)^0$  or  $P^0$

$P$ : total pressure,  $P_0$ : initial value of  $P$ ,  
Temperature:  $17^\circ\text{C}$ ,  $P_0^H \equiv P^H(\text{initial}) = 2.1 \text{ mmHg}$ ,  $P^E(\text{initial}) = 1.37 \text{ mmHg}$ .

Time of Reaction $t$ min.	$P_0 - P$ <sup>35) *)</sup> mmHg	$P^H = P_0^H - (P_0 - P)$ mmHg	$(P^H)^1 (P^E)^0$ $1/t \log_{10} P_0^H/P^H$	$P^0$ $(P_0 - P)/t$ <sup>35)</sup>
3	0.21	1.89	0.015	0.070
7	0.50	1.60	0.017	0.071
9	0.71	1.39	0.020	0.079
12	0.92	1.18	0.021	0.077
15	1.13	0.97	0.022	0.075
17	1.24	0.86	0.023	0.073
19	1.37	0.73	0.024	0.072

The third column of the Tables shows the momentary partial pressure of hydrogen derived from the initial value  $P_0^H$  of  $P^H$  and the decrease  $P_0 - P$  of total pressure observed by TUCHOLSKI and RIDEAL <sup>35)</sup>.

\*) See footnote \*\*) on p. 288.

The fourth and fifth columns give  $\frac{1}{t} \log_{10} P_0^H/P^H$  and  $(P_0 - P)/t$ , which must be respectively constant as readily be shown, according as the order of reaction is first and zeroth with respect to  $P^H$  and  $P^E$  as denoted by  $(P^H)^1 (P^E)^0$  or zeroth with respect to  $P$  as signified by  $P^0$ . We see that both in the cases of Tables 6 and 7 the former kinetics fits in with the experimental results equally as the latter, so that the kinetics derived from the structure is in accordance, if not exclusively, with the experiment.

JENKINS and RIDEAL<sup>6)</sup> observed recently the rate of hydrogenation on carbided nickel film in accordance with (19.1) with an optimum around 160–165°C at 50 mmHg each hydrogen and ethylene partial pressure, finding in particular the kinetics of  $(P^H)^1 (P^E)^0$  at temperatures sufficiently below the optimum.

#### § 20. Experiments of FARKAS, FARKAS and RIDEAL<sup>38)</sup>

FARKAS, FARKAS and RIDEAL<sup>38)</sup> found in their experiment cited in Table 5 that the deuterium content in hydrogen hardly decreases at 20°C in course of hydrogenation, while it does appreciably at 120° and 155°C under the partial pressures of ethylene and deuterium around 10 mmHg respectively. These results are deduced as follows from the structure of Fig. 2, d) appropriate to the condition of the experiment.

Vertical chain lines at 20°, 120° and 155°C show that at 20° and 155°C, I<sub>b</sub> and III are respectively rate-determining, while both the states cross at 120°C. In Fig. 3 are drawn at the same condition common logarithms of  $V_s$ ,  $E^H/2$ ,  $E^E/2$ ,  $(E_0^q)_{xH=1/2}$  and  $E^p$  worked out on the basis of Scheme (2) side by side with those of  $\mathfrak{R}(s)$ 's against  $1/T$ . We see that  $E^H$  and  $E^E$  diverge at lower temperature but join at higher temperature to trace out  $\mathfrak{R}(I_b)$  and then  $\mathfrak{R}(II)$  both hidden from the measurement of hydrogenation rate above  $\mathfrak{R}(III)$  of the rate-determining step III apart from the constant factor 2 and 2/3 respectively.  $E^p$  on the other hand lies high above  $(E_0^q)_{xH=1/2}$  in coincidence with  $E^H/2$  at lower temperatures, but at high temperature they jointly trace out  $\mathfrak{R}(I_b)$  hidden, similarly as  $\mathfrak{R}(II)$ , above  $\mathfrak{R}(III)$ . Dotted line drawn close to the curve of  $(E_0^q)_{xH=1/2}$  shows its value calculated according to Scheme (3), which is the only case when a steady rate so calculated deviates perceptively on Fig. 3 from the corresponding value on the basis of Scheme (2).

At 20°C the exchange rate  $E^H$  is smaller than the hydrogenation rate

*Theory of Hydrogenation of Ethylene on Metallic Catalysts I.*

by a factor more than  $10^4$ , so that the exchange could hardly be observed, even if a good fraction of hydrogen be consumed meanwhile. The deuterium fraction in hydrogen should then remain practically constant during the hydrogenation, provided that protium and deuterium react with equal chance as assumed here. If protium reacts preferentially as is usually the case, deuterium must be left back in hydrogen to increase more or less  $x^H$  as actually seen from the result of FARKAS, FARKAS and RIDEAL<sup>38)</sup> quoted in Table 5. TWIGG and RIDEAL<sup>39)</sup> have also observed a slight increase of deuterium fraction in hydrogen with the progress of the nickel catalyzed hydrogenation.

With rise of temperature  $E^H$  increases more rapidly than  $V_s$  appreciably to exceed the latter at  $155^\circ\text{C}$  as seen from Fig. 3. This explains that a considerable fraction of deuterium is exchanged before consumed by hydrogenation as observed by the former group of authors<sup>38)</sup> at the temperature.

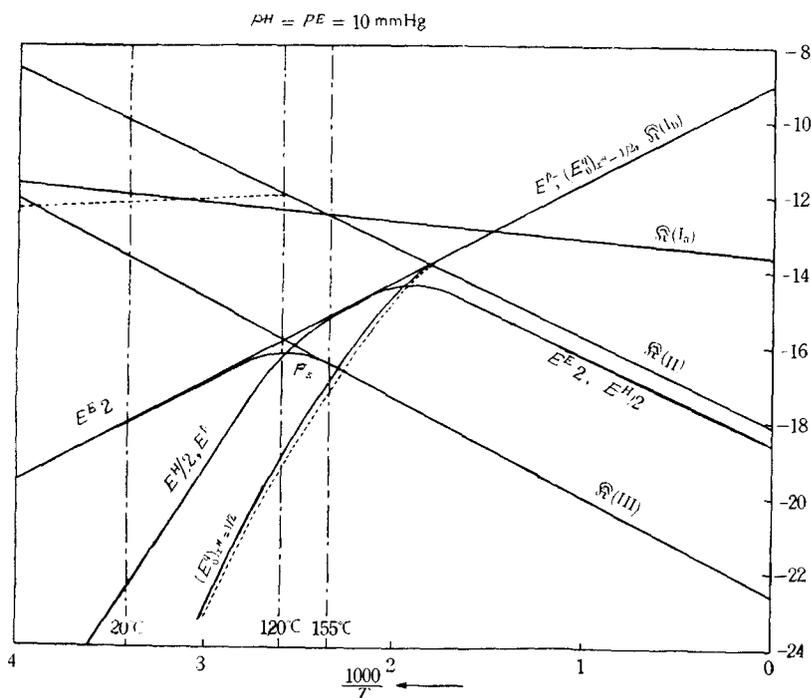


Fig. 3.

§ 21. Activation Energy of Hydrogen Exchange

Fig. 3 illustrates moreover the results obtained by TWIGG and RIDEAL.<sup>39)</sup> nearly at the same condition that the rate  $-dx^H/dt$  at  $x^H=1$  and  $x^E=0$  during hydrogenation catalyzed by nickel has a greater activation energy than the hydrogenation rate, being constant at 18.6 Kcal below 100°C decreasing gradually above 100°C down to 4 Kcal at 207°C. From this result they concluded that the exchange reaction could not follow the sequence of steps for hydrogenation as Scheme (2) with an excess activation energy over that of the latter but some separate sequence not comprised in that of hydrogenation. Scheme (4) is designed in accordance with this conclusion. Fig. 3 shows however that Sequence (2) or (3) does give rise to an excess activation energy of exchange reaction over that of hydrogenation as well as to its gradual decrease with rise of temperature, disproving their argument.

We might alternatively explain below how the activation energy of exchange reaction could exceed that of hydrogenation on the basis of the single sequence of Scheme (2). We have from (4.8.H) referring to the condition  $x^E=0$  of the above experiment and neglecting terms including  $\bar{v}$ (III)

$$x_0^{H(a)} = x^H(1 + F/6\bar{v}(I_b))^{-1} \quad (21.1.H)$$

and

$$x_0^{C_2H_4(a)} = \frac{Fx^{H(a)}}{12\bar{v}(I_a)}, \quad (21.1.E)$$

where  $x_0^{C_2H_4(a)}$  is the value of  $x^{C_2H_4(a)}$  at  $x^E=0$  and

$$F \equiv 12\bar{v}(I_a)\bar{v}(II)/(6\bar{v}(I_a)+\bar{v}(II)) \quad (21.1.F)$$

lies between  $6\bar{v}(I_a)$  and  $\bar{v}(II)$ , *i. e.*

$$6\bar{v}(I_a) > F > \bar{v}(II) \quad (21.2.a)$$

or

$$6\bar{v}(I_a) < F < \bar{v}(II). \quad (21.2.b)$$

We see now from Fig. 3 immediately that (7.7.a) is satisfied, hence (7.8) holds and in consequence  $r(H)$  and  $r(C_2H_4)$  are determined identically with the case of Scheme (3)\*. Fig. 3 shows further that  $\kappa^2 \gg 1$  at lower temperatures, where  $I_b$  determines the rate and hence (9.5.a) applies;

\*) Cf. § 7.

it follows that  $\bar{i}(\text{II})$  and  $\bar{v}(\text{II})$  are given according to (2.12) as

$$\bar{i}(\text{II}) = \bar{v}(\text{II}) = \sqrt{\frac{\mathfrak{K}(\text{I}_b)}{\mathfrak{K}(\text{III})}} \mathfrak{K}(\text{II}), \quad (21.3. \text{II})$$

which is indicated in the Figure by a dotted line annexed to the full line of  $\mathfrak{K}(\text{II})$ . The  $\bar{v}(\text{II})$  is thus smaller than but nearly of the same order of magnitude as  $6\mathfrak{K}(\text{I}_a)$  or  $6\bar{i}(\text{I}_a)$  according to (2.12), so that  $F$  is of the same order of magnitude as  $\bar{v}(\text{II})$  according to (21.2). It follows now from (21.1) that both  $x^{\text{H(a)}}$  and  $x^{\text{C}_2\text{H}_4(\text{a})}$  are very small compared with unity, since  $\bar{v}(\text{II})$  as given by (21.3.II) is, as seen from the Figure, far greater than  $\mathfrak{K}(\text{I}_b)$  which equals  $\bar{v}(\text{I}_b)$  according to (2.12), *i. e.*

$$\bar{i}(\text{II}) = \bar{v}(\text{II}) \gg \mathfrak{K}(\text{I}_b) = \bar{v}(\text{I}_b) \quad (21.3. \text{I}_b)$$

$E^{\text{H}}$  is now given according to (4.5.H),  $x^{\text{E}}=0$  and  $x^{\text{H(a)}} \ll 1$  as  $2\bar{v}(\text{I}_b)$ , or as (10.2.H) by (2.12) and (9.5.a). The activation energy  $RT^2 d \ln E^{\text{H}}/dT$  of exchange reaction\*) must be in consequence greater than the activation energy of hydrogenation  $\mathcal{J}^* \epsilon(\text{I}_b)$  by  $\mathcal{J}^* \epsilon(\text{I}_b) - \mathcal{J}^* \epsilon(\text{III})$  which is positive as observed according to (14.2), although not numerically in coincidence.

This aspect might further be illustrated as follows. We have

$$\bar{i}(\text{I}_a) = \bar{v}(\text{I}_a) \gg V_s \quad (21.3. \text{I}_a)$$

from (7.8) shown valid above, (2.12) and Fig. 3. Consecutive steps  $\text{I}_a$  and  $\text{II}$  are thus according to (21.3) occurring back and forth far quicker than hydrogenation and are respectively practically in equilibrium. It follows that deuterium in  $\text{H(a)}$  given out from hydrogen of  $x^{\text{H}}=1$  at a rate  $V_s$  is completely washed away by protium from ethylene of  $x^{\text{E}}=0$  by the rapid consecutive steps of  $\text{I}_a$  and  $\text{II}$ , so that  $x^{\text{H(a)}}$  is kept practically at zero.  $E^{\text{H}}$  is given at this condition simply by the rate of backward flow by recombination of  $\text{H(a)}$  originating from ethylene, *i. e.* by  $E^{\text{H}}=2\bar{v}(\text{I}_b)$  according to (4.5.H). The backward flow  $2\bar{v}(\text{I}_b)$  is now given as the product of the rate  $2\mathfrak{K}(\text{I}_b)$  of hydrogen atoms poured out by the forward act of  $\text{I}_b$  and the fraction  $\bar{v}(\text{I}_b)/(\bar{v}(\text{I}_b) + \bar{i}(\text{III}))$  of hydrogen atoms going back home. We have thus according to (2.5) and (2.7)

$$E^{\text{H}} = 2\mathfrak{K}(\text{I}_b) \frac{\mathfrak{K}(\text{I}_b)p^{\text{H}}/(p^{\text{H(a)}})^2}{\mathfrak{K}(\text{I}_b)p^{\text{H}}/(p^{\text{H(a)}})^2 + \mathfrak{K}(\text{III})p^{\text{E}}p^{\text{H}}/p^{\text{C}_2\text{H}_4(\text{a})}p^{\text{H(a)}}$$

\*)  $E^{\text{H}}$  is identical with the exchange rate  $-dx^{\text{H}}/dt$  at  $x^{\text{H}}=1$  and  $x^{\text{E}}=0$  of TWIGG and RIDEAL<sup>39)</sup> according to (4.2.H) except a factor  $n^{\text{H}}$ , which or the corresponding pressure has to be kept constant in differentiation with respect to  $T$ , although not explicitly remarked in the original paper.

Because of equilibrium of I<sub>a</sub> and II deduced above, we have according to (2.6)

$$p^E = p^{C_2H_4(a)}, \quad p^{C_2H_4(a)} p^{H(a)} = p^{C_2H_6(a)}$$

and hence from the above three equations

$$E^H = 2\mathfrak{R}(I_b) \cdot \mathfrak{R}(I_b) / (\mathfrak{R}(I_b) + \mathfrak{R}(III)).$$

But since  $\mathfrak{R}(I_b) \ll \mathfrak{R}(III)$  in the region in question, we have practically the expression (10.2.H).

This illustration might have realized that, for the rate of exchange reaction or of H(a) returning back to the starting point, the critical energy of Step I<sub>b</sub> is twice effective, forwards and backwards, in exerting inertia, whereas only once for the hydrogenation thus providing an excess activation energy to the former reaction even in this case of single sequence of steps.

## § 22. Formation of Different Deuteroethanes in the Catalyzed Deuteration of Light Ethylene

TURKEVICH, SCHISLER and IRSA<sup>5)</sup> have observed at 90°C the relative rates of formation of different deuteroethanes as well as of deuteroethylenes in the catalyzed deuteration of 10 mmHg light ethylene with 20 mmHg deuterium in the presence of evaporated nickel film. The conspicuous result they obtained is the predominance of light ethane in the initial products.

It is deduced from Fig. 2, e) which corresponds to this condition of experiment that there holds the similar situation as that of (21.3), so that both  $x^{H(a)}$  and  $x^{C_2H_4(a)}$  are considerably smaller than unity. Deuterium content in ethane evolved must in consequence be very small in accordance with Scheme (2) or light ethane predominantly produced as observed.

At higher temperatures above the optimum, where III determines the rate, we have in accordance with (9.7)

$$r(C_2H_4) = r(H) = r(C_2H_6) = 1 \quad (22.1. \gamma)$$

and hence according to (2.12)

$$\bar{v}(s') = \bar{v}(s') = \mathfrak{R}(s'), \quad s' = I_a, I_b, II. \quad (22.1. \nu)$$

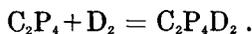
At relatively lower temperatures of this region,  $F \gg \bar{v}(I_b)$  similarly as in the region below the optimum as seen from Fig. 2, e), since  $F$  lies

between  $6\bar{v}(I_a)$  and  $\bar{v}(II)$  by (21.2). The  $x^{H(a)}$  must hence be very small compared with unity according to (21.1.H) and  $x^{C_2H_4(a)}$  is nearly of the same order of magnitude as  $x^{H(a)}$  by (21.1.E), inasmuch as the same is true with  $6\mathfrak{R}(I_a)$  and  $\mathfrak{R}(II)$  in this region as seen from Fig. 2, e). Both  $x^{H(a)}$  and  $x^{C_2H_4(a)}$  thus being very small, the same conclusion is arrived at as below the optimum on the distribution of deuterioethanes.

Noting that  $F$  approaches the lower of  $12\bar{v}(I_a)$  and  $2\bar{v}(II)$  as they become apart from each other according to (21.1.F), we see from Fig. 2, e) in accordance with (22.1.7) and (2.12) that  $2\bar{v}(II) = F \ll \bar{v}(I_b)$  at temperatures sufficiently high above the optimum, so that we have from (21.1)

$$x^{H(a)} = x^H, \quad x^{C_2H_4(a)} = x^H \bar{v}(II) / 6\bar{v}(I_a). \quad (22.2.H), (22.2.E)$$

Since  $\mathfrak{R}(I_a)$  is fairly greater than  $\mathfrak{R}(II)$ , which equals  $\bar{v}(II)$  by (22.1.v), at higher temperatures as seen from Fig. 2, e),  $x^{C_2H_4(a)}$  is so much smaller than  $x^H$  by (22.2.E). It follows that dideuterioethane is predominant in this case according to Scheme (2), as might be expected from the chemical equation



The latter conclusion is yet to be experimentally verified.

КЕИИ<sup>4)</sup> has derived expressions for the distribution of deuterioethylenes and deuterioethanes formed as functions of parameters, which depend on the relative magnitudes of  $\bar{v}(s)$ 's and  $\bar{v}(s)$ 's, arriving at a conclusion consistent with the above one deduced directly from the structure.

### § 23. Equilibration Reaction

TWIGG and RIDEAL<sup>39)</sup> have found further that

A) ethylene "inhibits" the equilibration, *i. e.* the reaction  $P_2 + D_2 = 2PD$  catalyzed by nickel is much slower in the presence of ethylene than in the absence, and that

B) when *ca.* 10 mmHg ethylene is catalytically hydrogenated in the presence of nickel catalyst with equimolecular deuterium at different constant temperatures ranging from 84° to 207°C, "the non-equilibrium fraction" in hydrogen, *i. e.*  $1-u$  in accordance with (5.2.u) varies at a constant temperature linearly with  $x^H$ , which decreases from unity along with the progress of hydrogenation and the appropriate straight lines pass through a common point  $1-u=0$ ,  $x^H=1/3$ ;  $1-u$  at  $x=1$  is, as extrapolated by the straight line, *ca.* 0.4 at 207°C but gradually increases

with decreasing temperature up to 0.8 at 156°C and stayed there down to 84°C.

The experimental condition of A) is not specified but if it be that of B) at temperature below the optimum illustrated in Fig. 3, where  $I_b$  governs the rate, we have according to Table 2

$$E_0^q = \frac{3}{1-x^H} \frac{\mathfrak{R}(I_b)}{\mathfrak{R}(II)} \left( \frac{\mathfrak{R}(I_b)}{\mathfrak{R}(III)} \right)^{1/2} \mathfrak{R}(I_b) \quad (23.1)$$

for Scheme (2) provided that the condition (7.7) holds<sup>\*)</sup>. The  $E_0^q$  in the absence of ethylene is given on the other hand as

$$E_0^q = \mathfrak{R}(I_b) \quad (23.2)$$

according to (5.9) observing that  $x_0^{H(a)} = x^H$  and  $\bar{v}(I_b) = \mathfrak{R}(I_b)$  in this case.

The second and third factors on the right of (23.1) are both far less than unity in the specified case, when  $I_b$  governs the rate, as seen from Fig. 3, while the first factor may be taken of order of magnitude of unity, for  $x^H$  must be selected remote either from zero or unity in order to secure a sufficient accuracy of  $E^q$ -measurement in accordance with (5.2) and (5.5). Eqs. (23.1) and (23.2) thus explain that  $E^q$  in the presence of ethylene is considerably smaller than that given by (23.2) in its absence.

At temperatures sufficiently high above the optimum, where Step III governs the rate and both the conditions of (7.7) are satisfied according to (22.1.v) and Fig. 3, we have according to Table 2 for the case  $\mathfrak{R}(I_b) \gg \mathfrak{R}(II)$

$$E_0^q = \mathfrak{R}(I_b)$$

in coincidence with (23.2) in the absence, *i.e.* the presence of ethylene makes no difference. This conclusion is yet to be experimentally verified.

\*) Condition (7.7.a) holds, in so far as  $I_b$  determines the rate. The validity of (7.7.b) is not very decisive as mentioned in §21, but the error committed by admitting it is that of replacing  $F$  of (21.1.F) with  $2\bar{v}(II)$ , which amounts to a multiplication by an extra factor between 1 and 2, inasmuch as  $F$  lies between  $2\bar{v}(II)$  and  $\bar{v}(II)$ , so long as  $6\bar{v}(I_b) > \bar{v}(II)$ , as readily be deduced from (21.1.F). Noting that (21.3.I<sub>b</sub>) is similarly valid in this case,  $x_0^{H(a)}$  is given according to (21.1.H) as  $x_0^{H(a)} = x^H \cdot 6\bar{v}(I_b)/F$ ; with which  $E_0^q$  is expressed by (5.9) as  $E_0^q = 6\bar{v}(I_b) \cdot \bar{v}(I_b)/F(1-x^H)$ , neglecting  $x^H \cdot 6\bar{v}(I_b)/F$  compared with unity according to (21.3.I<sub>b</sub>) or as (23.1) replacing  $F$  in the above expression with  $2\bar{v}(II)$  referring to (21.3.II) and  $\bar{v}(I_b)$  by  $\mathfrak{R}(I_b)^2/\mathfrak{R}(III)$  according to (2.12.I<sub>b</sub>) and Table 1.  $E_0^q$  as given by (23.1) is thus too small for Scheme (2) by a factor within 2.  $(E_0^q)_{x^H=1/2}$  by (23.1) is shown by a dotted line in Fig. 3, which lies close to the curve  $(E_0^q)_{x^H=1/2}$  derived from Scheme (2); cf. §20.

The experimental result B) above is accounted for as follows. Eq. (5.8) is written substituting  $\tilde{v}(I_b)$  from (4.5.H) in the form

$$\frac{du}{dx^H} = \frac{x^{H(a)}(1-x^{H(a)})}{x^H(1-x^H)(x^{H(a)}-x^H)} - \left( \frac{1}{x^{H(a)}-x^H} + \frac{1}{x^H} - \frac{1}{1-x^H} \right) u \quad (23.3)$$

or by integration as

$$u = \frac{\exp(-X)}{x^H(1-x^H)} \left\{ \int_{x^H}^1 \frac{x^{H(a)}(1-x^{H(a)})}{x^H-x^{H(a)}} \exp(X) dx^H + C \right\}, \quad (23.4.X)$$

where

$$X = \int_{x^H}^1 \frac{dx^H}{x^H-x^{H(a)}}$$

and  $C$  is the integration constant.  $C$  is determined at zero by comparison of (23.4.X) with (5.6), which leads to the equation

$$n^{PD} = n^H \exp(-X) \left\{ \int_{x^H}^1 \frac{x^{H(a)}(1-x^{H(a)})}{x^H-x^{H(a)}} \exp(X) dx^H + C \right\},$$

noting that  $n^{PD}=0$  at  $x^H=1$ . We have hence

$$u = \frac{\exp(-X)}{x^H(1-x^H)} \int_{x^H}^1 \frac{x^{H(a)}(1-x^{H(a)})}{x^H-x^{H(a)}} \exp(X) dx^H \quad (23.4.u)$$

which gives

$$\lim_{x^H \rightarrow 1} u = x^{H(a)}. \quad (22.5)$$

Similar conclusion has been previously arrived at by TWIGG and RIDEAL.<sup>39)</sup> by different consideration.

Result B) is now stated in terms of  $x^{H(a)}$  that  $1-x^{H(a)}$  increases from 0.4 up to 0.8 as temperature decreases from 207°C to 156°C but stays there down to 84°C.

It has been shown in foregoing sections for the similar conditions that  $x^{H(a)}$  at  $x^H=1$  and  $x^E=0$  is very small compared with unity at lower temperature but approximates unity at higher temperature. It is hence expected that  $1-x^{H(a)}$  or  $1-u$  at the latter condition will gradually decrease from lower to higher temperatures in accordance with the above observation. Calculations at the condition of Fig. 3 according to (4.8.H) give the following results semiquantitatively in agreement with the observation.

$x^{\text{H(a)}}$ -Values Calculated from the Structure

$$P^{\text{C}_2\text{H}_4} = P^{\text{H}} = 10 \text{ mmHg}, \quad x^{\text{H}} = 1, \quad x^{\text{E}} = 0$$

$t^{\circ}\text{C}$	84	144	223	285	439
$1-x^{\text{H(a)}}$	1.00	1.00	0.72	0.23	0

## Chapter 4. Discussions and Remarks

### § 24. General Results

So far we have shown that the rates of the catalyzed hydrogenation of ethylene, and those reactions associated with it, *i. e.* the exchange reaction between hydrogen and ethylene *etc.* are given as respective functions, which depend on the scheme of constituent elementary steps, of a set of fundamental quantities  $\mathfrak{R}(s)$ 's each characteristic to a constituent step  $s$ ;  $\mathfrak{R}(s)$ 's were shown determinable from sufficient knowledge of rates of the hydrogenation and the associated reactions. Because of the lack of the latter, the present author proceeded to determine the set of  $\mathfrak{R}(s)$ 's from available measurements supplemented by theoretical estimations on the basis of Scheme (2) put forward by HORIUTI and POLANYI<sup>1)2)3)</sup>. A number of experimental results on the hydrogenation and the associated reactions have been semiquantitatively accounted for in terms of  $\mathfrak{R}(s)$ 's thus determined.

Two other schemes of steps composing the catalyzed hydrogenation of ethylene have been comparatively dealt with, *i. e.* Scheme (3) which is kinetically comprised in Scheme (2) as its special case when one of its constituent steps  $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4(\text{a})$  is rapid enough and Scheme (4) advanced by JENKINS and RIDEAL<sup>6)</sup>, which is in some points common to Scheme (3). Different sets of functions of  $\mathfrak{R}(s)$ 's have been derived each appropriate to the above schemes and hence different kinetics accessible to experimental discrimination.

In subsequent sections of this Chapter we will extend the present method to discuss some peculiar experimental aspects<sup>22)23)</sup> not so far dealt with in connection with experimental procedures of discriminating between Schemes (2), (3) and (4).

### § 25. Allowance for Diffusion

WAGNER, WILSON, OTVOS and STEVENSON<sup>22)23)</sup> have circulated 10 m mol

hydrogen and 1 m mol ethylene in 300 ml volume over reduced nickel catalyst (Harshaw No. 78) at  $-50^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  with the result that no deuterioethylene was formed, while all possible deuterioethanes were produced with an appreciable abundance around  $\text{C}_2\text{P}_4\text{D}_2$ .

Partial pressures of hydrogen and ethylene are *ca.* 600 and 60 mmHg respectively as calculated from the above data. Since the increase of hydrogen partial pressure raises  $\mathfrak{K}(\text{I}_b)$  and  $\mathfrak{K}(\text{III})$  relative to  $\mathfrak{K}(\text{II})$  and  $\mathfrak{K}(\text{I}_a)$ , while the decrease of ethylene partial pressure lowers the last three  $\mathfrak{K}(s)$ 's relative to the first as seen from (13.5),  $\mathfrak{K}(\text{I}_a)$  must be situated lower in this case relative to  $\mathfrak{K}(\text{I}_b)$  compared with in the cases of Fig. 2 or 3 especially at later stage of hydrogenation, where ethylene is decreased by a larger factor than hydrogen is. The larger total pressure in this case leaves, on the other hand, the rate of diffusion of reactants toward the catalyst's surface approximately unchanged from that at lower total pressure but gives rise to larger  $\mathfrak{K}(s)$ 's at equilibrium of the diffusion process similarly as in the case of RIDEAL's experiment<sup>36)</sup> discussed in §18. The diffusion might have further been retarded compared with in other cases *e.g.* that of evaporated film or wire by narrow pores of pellets of the catalyst used.

The effect of retarded diffusion on the kinetics is allowed for in accordance with Scheme (2) by the steady state equation

$$\begin{aligned} V_s &= D^{\text{H}}(C_g^{\text{H}} - C_s^{\text{H}}) = D^{\text{E}}(C_g^{\text{E}} - C_s^{\text{E}}) \\ &= \mathfrak{K}(\text{I}_a)(r(\text{C}_2\text{H}_4)_s - r(\text{C}_2\text{H}_4)) = \mathfrak{K}(\text{I}_b)(r(\text{H}_2)_s - r(\text{H})^2) \\ &= \mathfrak{K}(\text{II})(r(\text{H})r(\text{C}_2\text{H}_4) - r(\text{C}_2\text{H}_5)) = \mathfrak{K}(\text{III})(r(\text{H})r(\text{C}_2\text{H}_5) - \Gamma) \quad (25.1) \end{aligned}$$

in place of (2.13), where  $D^{\text{H}}$  or  $D^{\text{E}}$  is the diffusion rate of hydrogen or ethylene respectively at the unit concentration difference between in the bulk of gas and at the catalyst's surface,  $C_g^{\text{H}}$  and  $C_s^{\text{H}}$  or  $C_g^{\text{E}}$  and  $C_s^{\text{E}}$  concentrations in gas and at catalyst's surface respectively of hydrogen or ethylene, and  $r(\text{H}_2)_s$  or  $r(\text{C}_2\text{H}_4)_s$  is the activity of hydrogen or ethylene gas at the catalyst's surface referred to that in the bulk of gas.  $D^{\text{H}}$  and  $D^{\text{E}}$  are now respectively proportional to the diffusion coefficients of hydrogen and ethylene, which are in the ratio of *ca.* 4 : 1, ignoring the difference in their mean free paths in the same gas mixture. Writing now the first three members of (25.1) in the form

$$V_s = D^{\text{H}}C_g^{\text{H}}(1 - C_s^{\text{H}}/C_g^{\text{H}}) = D^{\text{E}}C_g^{\text{E}}(1 - C_s^{\text{E}}/C_g^{\text{E}}),$$

we see that  $D^{\text{H}}C_g^{\text{H}}$  is at least *ca.* 40 times as large as  $D^{\text{E}}C_g^{\text{E}}$ , since  $C_g^{\text{H}}/C_g^{\text{E}}$  is at least ten, so that  $1 - C_s^{\text{H}}/C_g^{\text{H}}$  is at most *ca.* one fortieth of  $1 - C_s^{\text{E}}/C_g^{\text{E}}$ .

As  $1 - C_s^E/C_g^E$  is unity at most,  $C_s^H/C_g^H$  may be equated to unity with an error of a few percents at most.

The ratio  $C_s^H/C_g^H$  or  $C_s^E/C_g^E$  is however respectively the activity  $\gamma(H_2)_s$  or  $\gamma(C_2H_4)_s$  of hydrogen or ethylene at the catalyst's surface referred to that in the bulk. Identifying  $\gamma(H_2)_s$  with unity according to the above consideration, we have from (25.1)

$$\begin{aligned} V_s &= \mathfrak{K}(I_a)(1 - \gamma(C_2H_4)) = \mathfrak{K}(I_b)(1 - \gamma(H)^2) \\ &= \mathfrak{K}(II)(\gamma(H)\gamma(C_2H_4) - \gamma(C_2H_5)) = \mathfrak{K}(III)(\gamma(C_2H_5)\gamma(H) - \Gamma), \end{aligned} \quad (25.2.V)$$

where

$$1/\mathfrak{K}(I'_a) = 1/\mathfrak{K}(I_a) + 1/D^E C_g^E. \quad (25.2.\mathfrak{K})$$

Eq. (25.2) is identical with (2.13) except that  $\mathfrak{K}(I_a)$  in the latter is replaced by that  $\mathfrak{K}(I'_a)$  of a "step"  $I'_a$ , which formally represents the cooperation of  $I_a$  and the diffusion in accordance with (25.2. $\mathfrak{K}$ ).  $\mathfrak{K}(I'_a)$  is, as seen from (25.2. $\mathfrak{K}$ ) more or less smaller than  $\mathfrak{K}(I_a)$  depending on the rate of diffusion. It is readily shown\*) that the unidirectional rate  $\bar{v}(I'_a)$  of gaseous ethylene arriving at the state of  $C_2H_4(a)$  is given by  $\mathfrak{K}(I'_a)$  and the similar rate  $\bar{v}(I'_a)$  of  $C_2H_4(a)$  transferred reversely to gaseous ethylene by  $\mathfrak{K}(I'_a)\gamma(C_2H_4)$ , while  $\bar{v}(s)$  and  $\bar{v}(s)$  of other steps, *i.e.*  $I_b$ , II and III are invariably presented by (2.12.I<sub>b</sub>), (2.12.II) and (2.12.III) respectively. Lemmas and equations derived on the basis of (2.13) in §3-§6 hold now by replacing  $I_a$  formally with  $I'_a$ . We will use these lemmas and equations in what follows just reading  $I'_a$  for  $I_a$ . The effect of diffusion thus consists formally in the depression of  $\mathfrak{K}(I'_a)$  in the structure diagram, being modulated by that of lean ethylene in accordance with (25.2. $\mathfrak{K}$ ).

It is thus quite possible that  $I'_a$  governs the rate in this case in accordance with §3, *i.e.*  $V_s$  is practically equal to  $\mathfrak{K}(I'_a)$  according to (3.5.a). If then,  $V_s$  is at least approximately proportional to the partial pressure of ethylene according to (25.2. $\mathfrak{K}$ ) and (13.5.I<sub>a</sub>), inasmuch as

\*) The unidirectional rate of gaseous ethylene arriving at the catalyst's surface is given by  $D^E C^E$ . Ethylene at the catalyst's surface goes back toward gas unidirectionally with the rate  $D^E C^E \gamma(C_2H_4)_s$  or forward to the state of  $C_2H_4(a)$  with the rate  $\mathfrak{K}(I_a) \gamma(C_2H_4)_s$ , so that the fraction of ethylene at the catalyst's surface going forward is  $\mathfrak{K}(I_a) \{D^E C^E + \mathfrak{K}(I_a)\}^{-1}$  or the rate of ethylene going straightforwards through from gas to the state of  $C_2H_4(a)$  is  $D^E C^E \mathfrak{K}(I_a) \{D^E C^E + \mathfrak{K}(I_a)\}^{-1}$ , *i.e.*  $\mathfrak{K}(I_a)$  according to (25.2. $\mathfrak{K}$ ). Similarly it is shown that the reverse unidirectional rate  $\bar{v}(I'_a)$  from  $C_2H_4(a)$  to gaseous ethylene is given by  $\mathfrak{K}(I'_a) \gamma(C_2H_4)$ .

$C_9^{15}$  is proportional to ethylene partial pressure, while  $D^E$  is approximately constant. WILSON, OTVOS, STEVENSON and WAGNER<sup>22)23)</sup> have observed at quite the similar condition to that of the present reaction in question, the rate of catalyzed hydrogenation of cis-2-butene approximately proportional to the partial pressure of the olefine, and suggested on this ground that the rate of hydrogenation of cis-2-butene might be governed by the diffusion, although no description is found in their same paper<sup>22)23)</sup> on the kinetics of ethylene hydrogenation at the latter condition.

### § 26. Explanation of Experimental Results of WAGNER et al.

Experimental results of WAGNER *et al.*<sup>22)23)</sup> referred to in the foregoing section is accounted for below assuming the rate-determining step of  $I_a'$ . It then follows from (3.5.a) and (25.2.V)

$$V_s = \mathfrak{K}(I_a'), \quad (26.1)$$

$$r(H) = 1, \quad r(C_2H_5) = \mathfrak{K}(I_a')/\mathfrak{K}(III) \quad (26.2.H), (26.2.C_2H_5)$$

and

$$r(C_2H_4) = \mathfrak{K}(I_a')(\mathfrak{K}(II)^{-1} + \mathfrak{K}(III)^{-1}) \quad (26.2.E)$$

neglecting  $\Gamma\mathfrak{K}(III)$  similarly as in the previous cases. Rates  $\bar{r}(I_a')$  etc. are given by (26.2) and (2.12), as

$$\bar{r}(I_a') = \mathfrak{K}(I_a'), \quad \bar{v}(I_a') = \mathfrak{K}(I_a')^2(\mathfrak{K}(II)^{-1} + \mathfrak{K}(III)^{-1}) \quad (26.3.a), (26.3.b)$$

$$\bar{r}(I_b) = \mathfrak{K}(I_b), \quad \bar{v}(II) = \mathfrak{K}(I_a')\mathfrak{K}(II)/\mathfrak{K}(III), \quad (26.4.I), (26.4.II)$$

with which  $x^{H(a)}$  and  $x^{C_2H_4(a)}$  are expressed by (4.8) for the condition  $x^H=1$  and  $x^E=0$  of the experiment in question as

$$x^{H(a)} = (1 + 2\varphi\mathfrak{K}(I_a')/\mathfrak{K}(I_b))^{-1}, \quad x^{C_2H_4(a)} = \varphi x^{H(a)}, \quad (26.5.H), (26.5.E)$$

$$\varphi = \mathfrak{K}(II)(6\mathfrak{K}(III) + \mathfrak{K}(II))^{-1}, \quad (26.5.\varphi)$$

neglecting terms including  $\bar{v}(III)$ . The  $x^{H(a)}$  is close to unity by (26.5.H), as  $\mathfrak{K}(I_a')$  is sufficiently small compared with  $\mathfrak{K}(I_b)$  in accordance with the premiss and  $\varphi$  is by (26.5. $\varphi$ ) smaller than unity;  $x^{C_2H_4(a)}$  is smaller than  $x^{H(a)}$  according to (26.5.E) by the factor  $\varphi$ .

Deuteroethanes are formed from H(a) and C<sub>2</sub>H<sub>4</sub>(a) of the above deuterium content in accordance with Scheme (2) at a rate  $\mathfrak{K}(I_a')$  according to (26.1), while C<sub>2</sub>H<sub>4</sub>(a) is carried back to gaseous ethylene at a rate  $\bar{v}(I_a')$ , which is far smaller than  $\mathfrak{K}(I_a')$  by (26.3.b) or the for-

mation of deuterioethylenes of any kind is practically suppressed. Different deuteriosubstitution products of  $C_2H_4(a)$  must however be of the so-called random distribution, because of the equal chance of deuterium being substituted for its four chemically equivalent hydrogen atoms by the reversal of II, so that all deuterioethanes are formed possibly with the distribution maximum around dideuterioethane on account of  $x^{H(a)}$  close to 1 and of lower  $x^{C_2H_4(a)}$  as shown below.

The probability of N-deuterioethane evolved is given in accordance with the above conclusion, as

$$\sum_{n=N-2}^N \binom{2}{N-n} (x^{H(a)})^{N-n} (1-x^{H(a)})^{2-N+n} \times \binom{4}{n} (x^{C_2H_4(a)})^n (1-x^{C_2H_4(a)})^{4-n}, \quad (26.6)$$

which is shown by a full line in Fig. 4 with arbitrary unit as calculated for the particular values

$$x^{H(a)} = 0.95, \quad x^{C_2H_4(a)} = 0.15 \quad (26.7)$$

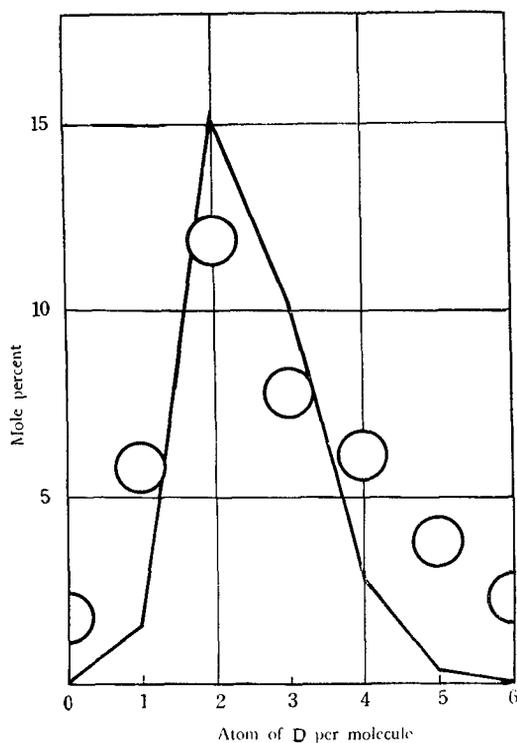


Fig. 4.

and compared with the experimental results of WAGNER *et al.*<sup>22)23)</sup> shown

by circles in the Figure. Appropriate relative values of  $\mathfrak{K}(s)$ 's are deduced from (26.7) by (26.5), as

$$\mathfrak{K}(I'_a) = 0.17 \mathfrak{K}(I_b), \quad \mathfrak{K}(II) = 1.1 \mathfrak{K}(III). \quad (26.8. a), (26.8. b)$$

While (26.8.a) conforms with the present assumption of  $I'_a$  being the rate-determining step, (26.8.b) does not numerically with the structure for the experimental condition in question in which  $\mathfrak{K}(II)$  lies appreciably high above  $\mathfrak{K}(III)$  similarly as in the case of Fig. 2 or Fig. 3. It might be noted that  $\mathfrak{K}(II)$  is much lower, when adjusted quantitatively to experimental results, even than  $\mathfrak{K}(III)$  at lower temperatures in question as developed in later parts of this series. Experimental results of WAGNER *et al.*<sup>22)23)</sup> are thus semiquantitatively explained on the basis of Scheme (2) with the rate-determining step of  $I'_a$ .

It is now shown below that no other rate-determining step than that of  $I'_a$  is capable of accounting for the latter experimental results on the basis of Scheme (2). Let  $r$  be the step other than  $I'_a$  which determines the rate. We have then in accordance with § 3

$$\mathfrak{K}(I'_a) \gg \mathfrak{K}(r), \quad r = I_b, II, III, \quad (26.9)$$

hence by (25.2.V), (3.2.V) and (3.3)

$$r(C_2H_4) \simeq 1,$$

and in consequence according to (2.12.I<sub>a</sub>)

$$\mathfrak{K}(I'_a) = \bar{v}(I_a) \simeq \bar{v}(I_a). \quad (26.10)$$

It follows from (26.9), (26.10) and (3.4) that  $C_2H_4(a)$  is desorbing at much higher rate than  $V_s$ , with which rate deuterioethanes are formed. Since practically no deuterioethylene is evolved,  $x^{C_2H_4(a)}$  must be zero and in consequence no deuterioethane higher than  $C_2P_4D_2$  should be evolved. Since this conflicts with the experimental results of WAGNER *et al.*, no step other than  $I'_a$  could ever determine the rate.

### § 27. Discrimination between Scheme (2), (3) and (4)

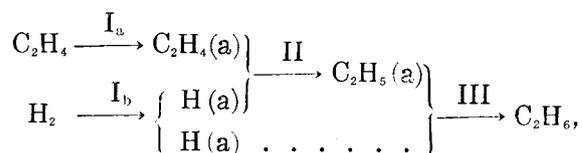
Schemes (2) would be discriminated from (3) and (4) as the exclusively valid one, if one could verify that the experimental results of WAGNER *et al.*<sup>22)23)</sup> were due to genuin chemical reaction at the catalyst's surface but not effected by diffusion, since then the observed absence of deuterioethylene should necessarily lead in accordance with Scheme (3) as well as (4) to the absence of deuterioethanes higher than  $C_2P_4D_2$  contradicting

the experimental results.

If not and it would have turned out by removing the inertia of diffusion either that deuterioethanes produced were those not higher than  $C_2P_4D_2$  only or that deuterioethylenes were appreciably evolved instead, Schemes (3) and (4) are not excluded with this cause. None the less we are able to depress  $\mathfrak{K}(I_a)$  relatively to other  $\mathfrak{K}(s)$ 's by increasing  $P^H$  or by decreasing  $P^E$ . It is thus possible in principle to verify the existence of Step  $I_a$  or Scheme (2), if at all, excluding (3) and (4). Scheme (4) may be invalidated besides, if one could find out the kinetics of the cases ( $I_b$ ),  $\kappa^2 \ll 1$  and (II) in Table 3, which are not shared by Scheme (4). The former case does appear under the condition of Fig. 3 at accessibly lower temperature by a closer adjustment of  $\mathfrak{K}(II)$  referred to above although scarcely in the present case of crude estimation. The latter case (II) may be realized even at ordinary temperature according to Fig. 2 or Fig. 3 and (13.5) by increasing  $P^H$ .

### Summary

1. It was shown with special reference to the catalyzed hydrogenation of ethylene that the rate  $V_s$  of steady reaction of hydrogenation and those of associated reactions, *i.e.* that of the associated increase of deuterium content  $E^H$  in hydrogen, that  $E^E$  in ethylene, the rate  $E^q$  of equilibration  $P_2 + D_2 = 2PD$  ( $P$ : protium) and that  $E^p$  of parahydrogen conversion are expressed as respective functions of quantities  $\mathfrak{K}(s)$ 's each characteristic to a constituent step  $s$  of the scheme advanced by HORIUTI and POLANYI (Refs. 1 and 2), *i.e.*



where (a) denotes the adsorbed states and  $I_a$  *etc.* signify  $s$ 's individually.  $\mathfrak{K}(s)$  was shown to be the forward unidirectional rate of hydrogenation, which would be realized when all steps but the appropriate  $s$  are in equilibrium.

2. It was shown that  $\mathfrak{K}(r)$  of a certain step  $r$  among  $s$ 's approaches  $V_s/(1-\Gamma)$  as  $\mathfrak{K}(r)$  becomes lower than  $\mathfrak{K}(s)$  of any other constituent step and conversely that the latter becomes infinitely higher than  $\mathfrak{K}(r)$ , as  $\mathfrak{K}(r)$  approaches  $V_s/(1-\Gamma)$ , where  $\Gamma$  is the BOLTZMANN factor of the

free energy increment  $\mu^{C_2H_6} - \mu^E - \mu^H$  of the reaction  $C_2H_4 + H_2 = C_2H_6$  in terms of the chemical potentials  $\mu^{C_2H_6}$ ,  $\mu^E$  and  $\mu^H$  of  $C_2H_6$ ,  $C_2H_4$  and  $H_2$  respectively.

3. Forms of functions  $V_s$  etc. of  $\mathfrak{K}(s)$  were shown to depend on the underlying scheme, the alternative functions being derived from other ones inclusive of the JENKINS and RIDEAL's scheme (Ref. 6).

4.  $\mathfrak{K}(s)$ 's were statistical-mechanically developed to a form by which relative magnitudes of  $\mathfrak{K}(s)$  are fixed by a single constant  $\Delta^*\epsilon(s)$  for each, which is the activation energy  $RT^2 d \ln V_s/dT$  of hydrogenation realized when all constituent steps but  $s$  are kept in equilibrium.

5.  $\mathfrak{K}(I_b)$  and  $\mathfrak{K}(III)$  were determined by fitting them to the hydrogenation rate observed by zur STRASSEN (Ref. 31), while  $\mathfrak{K}(I_a)$  and  $\mathfrak{K}(II)$  theoretically estimated.

6. On the basis of  $\mathfrak{K}(s)$  thus determined, the well-known optimum temperatures of hydrogenation in different cases were calculated semi-quantitatively in agreement with experimental results, observed kinetics of catalyzed hydrogenation explained, the exchange reaction accompanied by hydrogenation as observed by FARKAS, FARKAS and FIDEAL (Ref. 38) accounted for, the excess of activation energy of hydrogen exchange reaction over that of hydrogenation as observed by TWIGG and RIDEAL (Ref. 39) was derived as a necessary conclusion of the above scheme, the predominance of light ethane in the products of deuteration of light ethylene observed by TURKEVICH, SCHISLER and IRSA (Ref. 5) demonstrated, the relation between the degree of equilibration and deuterium content of hydrogen observed by TWIGG and RIDEAL (Ref. 39) in the course of catalyzed deuteration of ethylene elucidated and several unobserved facts predicted.

7. Experimental results of WAGNER, WILSON, OTVOS and STEVENSON (Refs. 22 and 23), that ethylene hardly exchanges, while all possible deuterioethanes are produced, were concluded as due to either or both of diffusion and  $I_a$  governing the rate. It was pointed out that this experimental result would exclude the scheme proposed by JENKINS and RIDEAL (Ref. 6), if it survived the governing effect of diffusion. Other experimental procedures were noted for discriminating between the schemes as derived from the present method just developed.

### References

- 1) J. HORIUTI and M. POLANYI, *Trans. Faraday Soc.* **30**, 663 (1934).
- 2) J. HORIUTI and M. POLANYI, *Trans. Faraday Soc.* **30**, 1164 (1934).
- 3) J. HORIUTI, "Shokubai" (*Catalyst*) **2**, 1 (1947).
- 4) T. KEII, *this Journal* **3**, 36 (1953-5).
- 5) J. TURKEVICH, D. O. SCHISSLER and P. IRSA, *J. Coll. Phys. Chem.* **55**, 1078 (1951).
- 6) G. I. JENKINS and E. K. RIDEAL, *J. Chem. Soc.* **1955**, 2490.
- 7) O. BEECK, A. E. SMITH and A. WHEELER, *Proc. Roy. Soc. London, A* **177**, 62 (1942).
- 8) O. BEECK, *Discussions Faraday Soc.* **8**, 118 (1950).
- 9) W. G. FRANKENBURG, *J. Am. Chem. Soc.* **66**, 1827, 1838 (1944).
- 10) E. K. RIDEAL and B. M. W. TRAPNELL, *Discussions Faraday Soc.* **8**, 114 (1950); *Proc. Roy. Soc. A* **205**, 409 (1951). B. M. W. TRAPNELL, *Proc. Roy. Soc. A* **206**, 39 (1951).
- 11) O. BEECK, "Advance in Catalysis" Vol. II, p. 151, New York, Academic Press, 1950. O. BEECK, W. A. COLE and A. WHEELER, *Discussions Faraday Soc.* **8**, 314 (1950).
- 12) J. HORIUTI and M. POLANYI, *Acta Physicochim. URSS* **2**, 505 (1935). J. HORIUTI and G. OKAMOTO, *Sci. Papers Inst. Phys. Chem. Research, Tokio* **28**, 203 (1936). J. HORIUTI, T. KEII and K. HIROTA, *this Journal* **2**, 1 (1951-3).
- 13) P. M. GUNDRY and F. C. TOMPKINS, *Trans. Faraday Soc. London A* **177**, **62** (1956).
- 14) A. MATSUDA, *this Journal* **5**, 71 (1957).
- 15) A. FARKAS and L. FARKAS, *J. Am. Chem. Soc.* **60**, 22 (1938).
- 16) K. F. BONHOEFFER, F. BACH and E. FAJANS, *Z. physik. Chem. A* **168**, 313 (1934). E. FAJANS, *Z. physik. Chem.* **28**, 239 (1935).
- 17) A. FARKAS, "Orthohydrogen, Parahydrogen and Heavy Hydrogen", Cambridge University Press, Cambridge, England, 1935; *Trans. Faraday Soc.* **35**, 906 (1939).
- 18) T. I. TAYLER, "Catalysis" P. H. EMMETT, Vol. 5, New York, 1957, p. 257-403.
- 19) J. HORIUTI, T. KEII, M. EN'YO and M. FUKUDA, *this Journal* **5**, 40 (1957).
- 20) E. K. RIDEAL, *Proc. Cambridge Phil. Soc.* **35**, 130 (1939); *Chemistry and Industry* **62**, 335 (1943).
- 21) D. D. ELEY, *Proc. Roy. Soc., A* **178**, 452 (1941); *J. Phys. and Coll. Chem.* **55**, 1017 (1951).
- 22) C. D. WAGNER, J. N. WILSON, J. W. OTVOS and D. P. STEVENSON, *J. Chem. Phys.* **20**, 338, 1331 (1952).
- 23) J. N. WILSON, J. W. OTVOS, D. P. STEVENSON and C. D. WAGNER, *Ind. Eng. Chem.*, **45**, 1480 (1953).
- 24) J. HORIUTI and M. IKUSIMA, *Proc. Imp. Acad. Tokio*, **15**, 39 (1939).
- 25) J. HORIUTI, "The Theory of Reaction Rate", Iwanami Book Co., Tokio, 1940.
- 26) J. HORIUTI, *this Journal* **1**, 8 (1948-51).
- 27) J. HORIUTI and T. NAKAMURA, *Z. physik. Chem. (Neue Folge)* **11**, 358 (1957).
- 28) J. HORIUTI, *this Journal* **5**, 1 (1957). J. HORIUTI, "Advance in Catalysis", Academic Press, Inc. New York IX, 339 (1957). J. HORIUTI, *Z. physik. Chem. (Neue Folge)* **12**, 321 (1957). T. NAKAMURA and H. YAMAZAKI, *this Journal* **5**, 98 (1957). T. NANAMURA, *this Journal* **6**, 20 (1958).

*Theory of Hydrogenation of Ethylene on Metallic Catalysts I.*

- 29) G. K. BORESKOW, *J. Phys. Chem. URSS* **19**, 92 (1945).
- 30) J. HORIUTI, *Bull. Chem. Soc. Japan* **13**, 210 (1938). K. HIROTA and J. HORIUTI, *Sci. Papers Inst. Phys. Chem. Research, Tokio* **34**, 1174 (1938).
- 31) ZUR STRASSEN, *Z. physik. Chem. A* **169**, 81 (1934).
- 32) S. MATSUSHITA, *this Journal* **4**, 160 (1956-7).
- 33) T. KEII, "Shokubai" (Catalyst) **3**, 47 (1948).
- 34) A. SHERMAN, C. E. SUN and H. EYRING, *J. Chem. Phys.* **3**, 49 (1935).
- 35) T. TUCHOLSKI and E. K. RIDEAL, *J. Chem. Soc. London* **1935**, 1701.
- 36) E. K. RIDEAL, *J. Chem. Soc. London* **1922**, 309.
- 37) O. TOYAMA, *Rev. Phys. Chem. Japan* **12**, 115 (1938).
- 38) A. FARKAS, L. FARKAS and E. K. RIDEAL, *Proc. Roy. Soc. London A* **146**, 630 (1934).
- 39) G. H. TWIGG and E. K. RIDEAL, *Proc. Roy. Soc. London A* **171**, 55 (1939).