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# ACTIVATION FREE ENERGY AND ACTIVATION ENERGY AS DETERMINING FACTORS OF CHEMICAL REACTION RATE

By

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## Summary

It was pointed out that the rate of elementary reaction or step is best approximated by that of passage of the relevant reaction complex through the state of the highest free energy intermediate between the initial and the final state rather than that of the highest energy conventionally and traditionally accepted instead since ARRHENIUS and that the discrepancy between the results both of the above procedures may be enhanced in the case of heterogeneous steps, where the pronounced decrease of entropy of the reaction complex from the state of free molecules to that fixed to a site on surface may possibly result in the state of highest free energy associated with negative increment of energy.

The above consideration was extended to the case of a steady reaction consisting of several steps with special reference to the associative mechanism of the catalyzed hydrogenation of ethylenic linkage in the presence of metallic catalyst, *e.g.*  $C_2H_4 \xrightarrow{I_a} C_2H_4(a)$ ,  $H_2 \xrightarrow{I_b} 2H(a)$ ,  $C_2H_4(a) + H(a) \xrightarrow{II} C_2H_5(a)$  and  $C_2H_5(a) + H(a) \xrightarrow{III} C_2H_6$  for ethylene, where (a) signifies the adsorbed state; it was thus shown that the rate of the steady reaction is controlled, if at all, by a step of the highest activation free energy rather than that of the highest activation energy. The activation free energy  $\Delta^*F(s)$  or activation energy  $\Delta^*H(s)$  is here the increment of free energy or energy accompanied by bringing an appropriate set  $I_e(s)$  of chemical species each at the state on the left-hand side of the chemical equation of the steady reaction to the activated complex of a step  $s (= I_a, I_b, II, III)$  in question, which are combined with the relevant increment of entropy, *i.e.* the activation entropy  $\Delta^*S(s)$ , as  $\Delta^*F(s) = \Delta^*H(s) - T\Delta^*S(s)$ .

The activation entropy  $\Delta^*S(s)$  of the heterogeneous step was now shown to be given approximately as  $\Delta^*S(s) = R \ln G^{*(s)} - S^{I_e(s)}$ , where  $G^{*(s)}$  is the total number of sites for the activated complex of step  $s$  and  $S^{I_e(s)}$  is the partial molal entropy of  $I_e(s)$ .  $G^{*(s)}$  being identical for every step at least in order of magnitude,  $\Delta^*S(s)$  makes difference of  $\Delta^*F(s)$  through the term  $TS^{I_e(s)}$ . It was shown in the case of the catalyzed hydrogenation of ethylene that  $I_e(III) = C_2H_4 + H_2$  of step III comprizes gaseous ethylene molecule  $C_2H_4$  in excess over  $I_e(I_b) \equiv H_2$  of step  $I_b$ , which increases  $\Delta^*F(III)$  relative to  $\Delta^*F(I_b)$  by  $TS^E$ , where  $S^E$  is the partial molal entropy of ethylene. The excess  $TS^E$  amounts to 18 Kcal/mol or more at the usual experimental condition. Hence it was demonstrated, as based on the evidenced fact that

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I<sub>b</sub> governs the rate of the catalyzed hydrogenation of ethylene over a certain temperature range, that the rate-determining step should necessarily switch over to that of III resulting in the negative activation energy of the steady reaction at higher temperature, hence an optimum at the switch.

It was shown that the set of the values of  $\Delta^*F(s)$ 's at different temperatures, a version of "structure" of steady reaction advanced in previous works<sup>14)15)16)</sup>, accounts for the remarkably low optimum temperature and the kinetics of the double bond migration of 1-butylene in the presence of nickel catalyst, and the excess of the activation energy of the exchange reaction over that of the catalyzed hydrogenation of ethylene, besides a number of versatile experimental results associated with the latter reaction.

It was emphasized that the principle of the step of the highest activation energy to govern the rate of steady reaction could not be even approximately relied upon especially in the case of heterogeneous steps constituting the steady reaction and that it should be replaced by that of the highest activation free energy to control the rate.

### Introduction

The activated complex of an elementary reaction is assigned according to the theory of absolute reaction rates of EYRING *et al.*<sup>17)</sup>, at the maximum of the potential energy along the reaction coordinate, *i. e.* the saddle point. The specific rate  $k$  of the elementary reaction, termed simply the step in what follows, is expressed, with reference to the activated complex thus defined, as

$$k = \kappa \frac{kT}{h} \exp(-\Delta F_{\ddagger}^{\dagger}/RT), \quad (1)$$

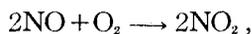
where  $\Delta F_{\ddagger}^{\dagger}$  is the free energy of activation,  $\kappa$  the transmission coefficient equal to or less than unity and  $k$ ,  $R$ ,  $h$  and  $T$  are of usual meanings. The factor  $(kT/h) \exp(-\Delta F_{\ddagger}^{\dagger}/RT)$  is hence the upper bound to  $k$ . It follows, anticipating alternative assignments of the activated state, that the best assignment should be that which renders the upper bound  $(kT/h) \exp(-\Delta F_{\ddagger}^{\dagger}/RT)$  minimum or  $\Delta F_{\ddagger}^{\dagger}$  maximum.

The  $\Delta F_{\ddagger}^{\dagger}$  is expressed in terms of the heat  $\Delta H_{\ddagger}^{\dagger}$  of activation and the entropy  $\Delta S_{\ddagger}^{\dagger}$  of activation, as

$$\Delta F_{\ddagger}^{\dagger} = \Delta H_{\ddagger}^{\dagger} - T\Delta S_{\ddagger}^{\dagger}.$$

Since  $\Delta H_{\ddagger}^{\dagger}$  is closely reproduced by the appropriate increment of potential energy, the above assignment of activated state is relevant to the maximum  $\Delta H_{\ddagger}^{\dagger}$  rather than to the maximum  $\Delta F_{\ddagger}^{\dagger}$ .

Suppose that the activated state is chosen at maximum  $\Delta F_{\ddagger}^{\dagger}$ .  $\Delta H_{\ddagger}^{\dagger}$  may then be negative, even though  $\Delta F_{\ddagger}^{\dagger}$  is maximum provided they are associated with a sufficient loss  $-\Delta S_{\ddagger}^{\dagger}$  of entropy. Such a situation might have revealed itself in the case of a homogeneous step, *e. g.*



where the entropy must have considerably decreased by gathering three free molecules to an activated complex to result in an appropriate amount of  $\Delta F^\ddagger$  despite the negative  $\Delta H^\ddagger$ . The entropy loss of this sort must be pronounced in the case of heterogeneous step, where the initial complex of free molecules is confined to a site on the boundary surface without translation or rotation as a whole.

UHARA<sup>2)</sup> has found negative temperature coefficient  $RT^2 d \ln \alpha / dT = -4.3 \sim -8.0$  Kcal of the fraction  $\alpha$  of the molecules  $\text{I}_2$  etc. dissolved into a jet of liquid  $\text{H}_2\text{O}$  etc. over those striking its surface<sup>\*</sup>). The negative  $\Delta H^\ddagger$  of the considerable absolute amount must have been overcompensated by an appreciable loss  $-\Delta S^\ddagger$  of entropy to result in the observed value of  $\alpha$  of the order of magnitude of  $10^{-4**}$ ).

It appears traditionally taken for granted since ARRHENIUS to attribute the inertia of rate processes to the activation energy rather than to the activation free energy. Closely connected with this conception, the rate-determining step of an overall reaction composed of several steps is unconcernedly assigned to that of the highest activation energy. TWIGG and RIDEAL<sup>3)</sup> inferred that the catalyzed hydrogenation of ethylene in the presence of nickel catalyst could not imply the rate-determining step of the exchange reaction giving rise to its activation energy higher than that of the simultaneous hydrogenation. This inference holds only, if the steady rate of hydrogenation is governed exclusively by a step of the highest activation energy. This is not assured at all, since any other step of lower activation energy may have the highest activation free energy to govern the rate on account of an appropriate negative activation entropy.

It is eloquent of the latter situation that the activation energy of catalyzed hydrogenation of ethylenic linkage, *i. e.* that of ethylene<sup>4)-6)</sup>, butylene<sup>8)</sup>, maleic

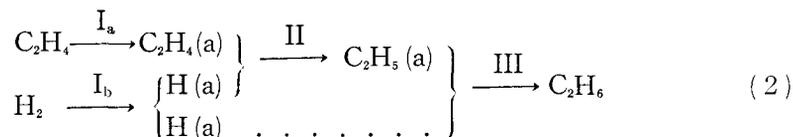
\*) The  $\alpha$  is in general the fraction of the rate of the unidirectional dissolution minus that of the unidirectional evaporation from the layer of liquid at the surface over the gas kinetic rate of the solute molecule striking the liquid surface. The unidirectional rate of evaporation will increase with the concentration of the solute in the surface liquid layer hence with the contact time of the liquid with solute gas. The observed  $\alpha$  (Ref. 2) may correspond practically to the unidirectional rate of dissolution, since it did not vary (Ref. 2) with the contact time ( $5 \sim 8 \times 10^{-3}$  sec) of the jet with the solute gas and greater by a factor of *ca.* 10 than its value observed with a vigorously stirred liquid in steady contact with the solute gas (Ref. 2).

\*\*\*) The  $\alpha$  is expressed as the BOLTZMANN factor of  $\Delta F^\ddagger$ , which denotes here the excess of the standard free energy of solute molecules at the activated state over that of solute molecules just on the liquid surface.  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  denote here the corresponding excesses of enthalpy and entropy, so that  $\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ .

acid<sup>10)</sup> and crotonic acid<sup>10)</sup> is generally negative at higher temperatures revealing an optimum temperature, provided that any other step of positive activation energy is yet comprized in the sequence of steps responsible for the reaction.

The present paper is concerned with the demonstration of this point.

The present authors previously generalized the theory of absolute reaction rate in two directions<sup>11)12)13)</sup>, which rendered its exact application to any type of step inclusive of heterogeneous one practicable; the activated state was fitted to the maximum free energy of activation and the rate equation was formulated in unified form allowing for the interaction of reaction complex with surroundings. Theory of steady reaction composed of several steps was now developed on the basis of the unified theory with special reference to the associative mechanism<sup>14)15)16)</sup>



of the catalyzed hydrogenation of ethylene in the presence of nickel catalyst, where suffix (a) signifies the adsorbed state. The associative mechanism will mean here just the sequence of steps (2) rather than the latter associated with the rate-determining step of III as originally presented<sup>17)</sup>.

Points of the latter theory will first be reviewed so far as necessary for the present application, showing that the theory leads to the principle that the step of the highest activation free energy controls the rate of the steady reaction. It is now demonstrated on the basis of the theory that the optimum temperature associated with the negative activation energy and versatile experimental aspects involved are necessary conclusions from the associative mechanism.

### § 1. Rate Equation

Rate of a thermal step was formulated with reference to the state of the highest free energy of activation as follows. The set of particles involved in a step in question is called the reaction complex and the latter at the state before or after the occurrence of the step the initial or final complex respectively. Consider the configuration space of a macroscopic system of a definite constituents at constant temperature, in which the step in question goes on. The reaction complex in question is in general under more or less mechanical influence of other particles constituting the macroscopic system. We have two regions of the configuration space exclusive of each other, which correspond respectively to the different configurations of the initial and final state of a particular reaction

complex of the step, where any other reaction complex is supposed to be fixed either to its initial or the final state. A hypersurface through the configuration space is now supposed to be extended to separate the regions respectively appropriate to the initial and the final state of the reaction complex on its both sides.

The hypersurface is not thus precisely defined. This is now fixed so as to minimize the fraction of the number of the representative points of the canonical ensemble of the macroscopic system passing the surface from its side of the initial complex toward that of the final complex per unit time over the number of the representative points on the side of the initial complex. The passage of the representative points in this direction will be called forward and the reverse one backward. The surface thus fitted was called the critical surface and the reaction complex in question with the relevant representative point situated on the critical surface the critical complex.

The rate of the single reaction complex completing the step in question is given by the above fraction multiplied by the transmission coefficient, *i. e.* the ratio of the number of the representative points transferring from the initial to the final region over the number of them just transiting the critical surface forward. The total sum of the rates of the initial complexes of the same kind over the whole macroscopic system is the forward rate  $\bar{v}$  of the appropriate step occurring in the macroscopic system; this rate and the corresponding backward rate  $\bar{v}$  are expressed as<sup>(11)(12)(13)</sup>

$$\bar{v} = \kappa \frac{kT}{h} p^* / p^I, \quad \bar{v} = \kappa \frac{kT}{h} p^* / p^F, \quad (3. a), (3. b)$$

where  $p^*$  is the factor of increase of the partition function of the macroscopic system caused by adding a single critical complex existing in the system\*),  $p^I$  or  $p^F$  the factor of increase of the partition function caused by addition of the initial or the final complex and  $\kappa$  the transmission coefficient. Such factor will be denoted by  $p^\delta$ , where  $\delta$  represents \*, I and F as well as any other set of chemical species. It may be noted that  $\kappa$  and  $p^*$  are respectively common to the forward and the backward rate of the same step<sup>(12)(13)</sup>.

The factor  $(kT/h)p^*/p^I$  or  $(kT/h)p^*/p^F$  respectively of (3. a) or (3. b) gives the minimum rate of the reaction complexes transiting the state defined by the hypersurface, which separates the initial and the final region of the configuration space on its both sides, from the side of the initial or the final region respectively.

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\*) It is not meant that there existed *physically* a single critical complex constantly throughout the system, but that the function thus defined gives the rate  $\bar{v}$  or  $\bar{v}$  in accordance with (3); *cf.* Refs. 12 and 13.

We will deal with the case, in what follows, where  $\kappa$  appropriate to the critical surface is unity, so that (3) is written as

$$\bar{v} = \frac{kT}{h} p^*/p^I, \quad \bar{v} = \frac{kT}{h} p^*/p^F. \quad (4. a), (4. b)$$

Eq. (3) reduces to (1) in the particular case<sup>12)13)</sup> where the reaction complex is practically dynamically independent and the critical surface implies the saddle point of potential energy of the reaction complex and is orthogonal to the reaction coordinate.

## § 2. Steady Reaction of Catalyzed Hydrogenation

We have

$$V = \bar{v}(s) - \bar{v}(s), \quad s = I_a, I_b, II, III \quad (5)$$

at the steady state of the catalyzed hydrogenation  $C_2H_4 + H_2 = C_2H_6$  in accordance with Scheme (2), where  $s$  denotes a constituent step and  $V$  the rate of the steady reaction. The forward and backward rates,  $\bar{v}(s)$  and  $\bar{v}(s)$ , of step  $s$  is expressed according to (4) as

$$\bar{v}(s) = \mathfrak{K}(s) p_e^{I(s)} / p^{I(s)}, \quad \bar{v}(s) = \mathfrak{K}(s) p_e^{I(s)} / p^{F(s)}, \quad (6. \bar{v}), (6. \bar{v})$$

where

$$\mathfrak{K}(s) = \frac{kT}{h} p^{*(s)} / p_e^{I(s)} \quad (7)$$

and  $p_e^{I(s)}$  is the particular value of  $p^{I(s)}$ , which would be realized, if all steps other than  $s$  were in equilibrium, hence\*

$$p_e^{I(I_a)} = p^E, \quad p_e^{I(I_b)} = p^H, \quad p_e^{I(II)} = p^E (p^H)^{1/2}, \quad p_e^{I(III)} = p^E p^H, \quad (8. I_a), (8. I_b), (8. II), (8. III)$$

where  $p^E$  or  $p^H$  denotes ethylene or hydrogen molecule in gas. Noting that

$$I(I_a) \equiv C_2H_4, \quad I(I_b) \equiv H_2, \quad I(II) \equiv C_2H_4(a) + H(a)$$

and

$$I(III) \equiv C_2H_6(a) + H(a),$$

\*) Eqs. (8) and (9) are obtained by the following two theorems demonstrated in Refs. 13 and 14. Let  $p^A$  and  $p^B$  be the factor of increase of the partition function of the macroscopic system caused by adding to it the sets of particles A and B, which are in equilibrium with each other. We have then  $p^A = p^B$ . Let now  $\delta$  consist of statistically independent particles or groups of particles,  $\varepsilon_i$ 's, *i. e.*  $\delta = \sum_i \varepsilon_i$ . The factor  $p^\delta$  of increase of the partition function of the macroscopic system is now  $p^\delta = \prod_i p^{\delta_i}$ , where  $p^{\delta_i}$  is the similar factor appropriate to  $\varepsilon_i$ .

(6) is written according to (8) for the individual steps as

$$\left. \begin{aligned} \bar{v}(\text{I}_a) &= \mathfrak{K}(\text{I}_a), \quad \bar{v}(\text{I}_b) = \mathfrak{K}(\text{I}_b), \quad \bar{v}(\text{II}) = \mathfrak{K}(\text{II})\gamma(\text{C}_2\text{H}_4)\gamma(\text{H}), \\ \bar{v}(\text{III}) &= \mathfrak{K}(\text{III})\gamma(\text{C}_2\text{H}_5)\gamma(\text{H}) \\ \bar{v}(\text{I}_a) &= \mathfrak{K}(\text{I}_a)\gamma(\text{C}_2\text{H}_4), \quad \bar{v}(\text{I}_b) = \mathfrak{K}(\text{I}_b)\gamma(\text{H})^2, \\ \bar{v}(\text{II}) &= \mathfrak{K}(\text{II})\gamma(\text{C}_2\text{H}_5), \quad \bar{v}(\text{III}) = \mathfrak{K}(\text{III})\Gamma. \end{aligned} \right\} \quad (9)$$

where

$$\left. \begin{aligned} \gamma(\text{C}_2\text{H}_4) &= p^E/p^{C_2H_4(a)}, \quad \gamma(\text{H}) = (p^H)^{1/2}/p^{H(a)} \\ \gamma(\text{C}_2\text{H}_5) &= p^E(p^H)^{1/2}/p^{C_2H_5(a)}, \quad \Gamma = p^E p^H/p^{C_2H_6}. \end{aligned} \right\} \quad (10)$$

Eq. (5) is now developed according to (9) as

$$\begin{aligned} V &= \mathfrak{K}(\text{I}_a) \{1 - \gamma(\text{C}_2\text{H}_4)\} = \mathfrak{K}(\text{I}_b) \{1 - \gamma(\text{H})^2\} \\ &= \mathfrak{K}(\text{II}) \{\gamma(\text{C}_2\text{H}_4)\gamma(\text{H}) - \gamma(\text{C}_2\text{H}_5)\} = \mathfrak{K}(\text{III}) \{\gamma(\text{C}_2\text{H}_5)\gamma(\text{H}) - \Gamma\}. \end{aligned} \quad (11)$$

Since  $\mathfrak{K}(s)$ 's are positive by definition (7) and every term in the parentheses  $\{ \}$  of (11) is positive by (10),  $V$  and the contents of the parentheses  $\{ \}$  are simultaneously positive or zero or negative. We see, on the other hand, that the product of the four first terms in the parentheses bears a ratio  $1/\Gamma$  to the product of the four second terms. This ratio must be greater than or equal to or less than unity according as  $V$  is positive or zero or negative respectively, hence the converse is also true. The  $\Gamma$  is now extremely small compared with unity<sup>14,15)</sup> at the usual experimental condition in question. It follows that

$$V > 0, \quad (12. V)$$

hence according to (11), that

$$0 < \gamma(\text{C}_2\text{H}_4), \quad \gamma(\text{H}), \quad \gamma(\text{C}_2\text{H}_5) < 1, \quad (12. \gamma)$$

and

$$\begin{aligned} \gamma(\text{H})^2 < 1, \quad \gamma(\text{C}_2\text{H}_5) < \gamma(\text{C}_2\text{H}_4)\gamma(\text{H}), \quad \Gamma < \gamma(\text{C}_2\text{H}_5)\gamma(\text{H}). \end{aligned} \quad (12. a), (12. b), (12. c).$$

It is now readily shown by (12.  $\gamma$ ), (12. a), (12. b) and (12. c) that every content of the parentheses  $\{ \}$  of (11) is less than  $1 - \Gamma$ , so that

$$V < \mathfrak{K}(s)(1 - \Gamma), \quad s = \text{I}_a, \text{I}_b, \text{II}, \text{III}. \quad (13)$$

*i. e.*  $\mathfrak{K}(s)(1 - \Gamma)$  is the upper bound to  $V$ .

Let one  $\mathfrak{K}(r)$  of  $\mathfrak{K}(s)$ 's tend to decrease relative to all other  $\mathfrak{K}(s)$ 's. The coefficients of  $\mathfrak{K}(s)$ 's in (11) other than  $\mathfrak{K}(r)$  approach then zero, hence it is shown that the coefficient of  $\mathfrak{K}(r)$  does  $1 - \Gamma$ , *i. e.*

$$V \rightarrow \mathfrak{K}(r)(1-\Gamma), \quad (14)$$

in which case  $r$  is the rate-determining step of the overall reaction.  $\mathfrak{K}(r)$  or  $\mathfrak{K}(r)\Gamma$  is the forward or the backward rate of the step  $r$  at equilibria of all steps except  $r$  as deduced from (9), so that the right-hand side of (14) is the net rate of  $r$  at the limiting condition.

### § 3. Thermodynamic Presentation of $\mathfrak{K}(s)$

$\mathfrak{K}(s)$ 's introduced in the preceding section are now transcribed into thermodynamic terminology in order to demonstrate the points raised in the introduction.

Since a partition function behaves as the BOLTZMANN factor of the appropriate free energy, the  $p^{*(s)}$ ,  $p^{I(s)}$  and  $p^{F(s)}$  relate with the respective chemical potentials  $\mu^{*(s)}$ ,  $\mu^{I(s)}$  and  $\mu^{F(s)}$  as<sup>13)</sup>

$$-RT \ln p^{\delta} = \mu^{\delta}. \quad (15)$$

$\mathfrak{K}(s)$  is now expressed according to (7) and (15), as

$$\mathfrak{K}(s) = (kT/h) \exp(-\Delta^*F(s)/RT), \quad (16. \mathfrak{K})$$

where

$$\Delta^*F(s) = \mu^{*(s)} - \mu_e^{I(s)}, \quad (16. F)$$

and  $\mu_e^{I(s)}$  is the particular value of  $\mu^{I(s)}$  appropriate to  $p_e^{I(s)}$  in accordance with (15). The  $\mu_e^{I(s)}$  is expressed by (8) and (15) for the individual  $s$ , as

$$\left. \begin{aligned} \mu_e^{I(I_a)} &= \mu^E, & \mu_e^{I(I_b)} &= \mu^H, & \mu_e^{I(II)} &= \mu^E + 1/2 \cdot \mu^H, \\ \mu_e^{I(III)} &= \mu^E + \mu^H. \end{aligned} \right\} \quad (17)$$

The rate of the steady reaction is, as shown in the preceding section, governed by the step  $r$  of sufficiently low  $\mathfrak{K}(r)$  as compared with all other  $\mathfrak{K}(s)$ 's. The thermodynamic version of this proposition is now according to (16.  $\mathfrak{K}$ ) that *the rate is governed by a step of sufficiently high activation free energy as compared with those of all other constituent steps.*

### § 4. Thermodynamics of Activation Free Energy

$\Delta^*F(s)$  is expressed as<sup>13)</sup>

$$\Delta^*F(s) = \Delta^*H(s) - T\Delta^*S(s), \quad (18. F)$$

where

$$\Delta^*S(s) = -\partial\Delta^*F(s)/\partial T; \quad (18. S)$$

$\Delta^*H(s)$  is the increment of enthalpy and  $\Delta^*S(s)$  that of entropy respectively of

the macroscopic system accompanied with the increment  $\Delta^*F(s)$  at constant pressure, to which the partial differential coefficients are referred to throughout the present paper\*).  $\Delta^*H(s)$  and  $\Delta^*S(s)$  will be called the activation energy and the activation entropy in what follows.

It should be noted that  $\Delta^*F(s)$ ,  $\Delta^*H(s)$  and  $\Delta^*S(s)$  are respective increments due to transfer of the reaction complex to the critical complex from the state  $I_0(s)$  consisting of ethylene and hydrogen in gas, *i. e.*  $C_2H_4$ ,  $H_2$ ,  $C_2H_4 + 1/2 \cdot H_2$  or  $C_2H_4 + H_2$  respectively in the case of  $I_a$ ,  $I_b$ , II or III;  $I_0(I_a)$  and  $I_0(I_b)$  happen to be identical with the respective initial complexes  $C_2H_4$  and  $H_2$ , whereas  $I_0(II)$  and  $I_0(III)$  are different from  $I(II) \equiv C_2H_4(a) + H(a)$  and  $I(III) \equiv C_2H_5(a) + H(a)$  respectively.

### § 5. Statistical Mechanical Expression of Thermodynamic Quantities

The statistical mechanical expression of  $\mu^{*(s)}$  is developed by (15) and the equation

$$p^{*(s)} = G^{*(s)} \theta_0^{*(s)} q^{*(s)} \quad (19)$$

previously deduced<sup>13)</sup>, where  $G^{*(s)}$  is the number of sites  $\sigma^{*(s)}$ 's of the critical complex,  $\theta_0^{*(s)}$  the probability of  $\sigma^{*(s)}$  being unoccupied or ready for accommodating the critical complex and  $q^{*(s)}$  is the factor of increase of the partition function of the macroscopic system caused by adding the critical complex  $*(s)$  from outside onto a definite, unoccupied site  $\sigma^{*(s)}$ , which is expressed assuming that the critical complex localized to  $\sigma^{*(s)}$  is exercising harmonic vibrations, as<sup>13)18)</sup>

$$q^{*(s)} = q_0^{*(s)} \exp(-\epsilon_0^{*(s)}/RT), \quad (20. q)$$

where

\*) Let the macroscopic system be kept at constant volume instead. The increment  $\Delta^*F(s)$  of the free energy due to the relevant process remains unchanged and relates with the associate increments of energy  $\Delta^*U(s)$  and entropy  $\Delta^*S_p(s)$  of the macroscopic system, (Ref. 13) as

$$\Delta^*F(s) = \Delta^*U(s) - T\Delta^*S_p(s);$$

$\Delta^*S_p(s)$  differs from  $\Delta^*S(s)$  as (Ref. 13)

$$\Delta^*S(s) = \Delta^*S_p(s) + (a/b) \Delta^*V(s),$$

hence  $\Delta^*U(s)$  does from  $\Delta^*H(s)$  according to (18. F) and the above two equations, as

$$\Delta^*H(s) = \Delta^*U(s) + T(a/b) \Delta^*V(s),$$

where  $a$  is the expansion coefficient,  $b$  the isothermal compressibility and  $\Delta^*V(s)$  the volume increment at constant pressure accompanying the process, respectively of the macroscopic system. The term  $T(a/b) \Delta^*V(s)$  in the above equation is reduced to  $\Delta^*n(s) RT$  in the particular case of the macroscopic system of an ideal gas mixture (Ref. 13), where  $\Delta^*n(s)$  is the increment of the number of mols relevant to the process.

$$q_0^{*(s)} = \prod_{j=1}^{3m(s)-1} \{1 - \exp(-h\nu_j(s)/kT)\}^{-1}, \quad (20. II)$$

$m(s)$  is the number of atoms constituting the critical complex,  $\nu_j(s)$  the frequency of  $j$ -th normal vibration and  $\epsilon_0^{*(s)}$  the energy of  $*(s)$  at the ground state. In the case of bare catalyst's surface,  $p^{*(s)}$  is constant at constant temperature according (19) and (20), since then  $\theta_0^{*(s)}$  is unity and  $q^{*(s)}$  is constant because of the absence of interactions of  $*(s)$  with surrounding adsorbates. The  $\mu^{*(s)}$  is now developed according to (15), (19) and (20.  $q$ ), as

$$\mu^{*(s)} = -RT \ln G^{*(s)} \theta_0^{*(s)} q_0^{*(s)} + \epsilon_0^{*(s)}. \quad (21)$$

The statistical mechanical expression of  $\mu_e^{I(s)}$  in (16.  $F$ ) is derived according to (17) as follows. The factors  $p^E$  or  $p^H$  relevant to  $\mu^E$  or  $\mu^H$  according to (15) is expressed statistical mechanically as<sup>(13)(14)(15)</sup>

$$p^E = Q_P^E \exp(-\epsilon^E/RT)/P^E, \quad p^H = Q_P^H \exp(-\epsilon^H/RT)/P^H, \quad (22. E), (22. H)$$

where

$$Q_P^E = \frac{(2\pi m^E kT)^{3/2}}{h^3} \frac{2\pi^2 (2\pi I^E kT)^{3/2}}{h^3} \Pi^E kT e^{\epsilon^E}, \quad (23. E)$$

$$Q_P^H = \frac{(2\pi m^H kT)^{3/2}}{h^3} \frac{4\pi^2 I^H kT}{h^2} \Pi^H kT e^{\epsilon^H/2}, \quad (23. H)$$

$$\epsilon^E = \epsilon_0^E + 4RT, \quad \epsilon^H = \epsilon_0^H + 7/2 \cdot RT, \quad (24. E), (24. H)$$

$$\Pi^E = \prod_{j=1}^{12} \{1 - \exp(-h\nu_j^E/kT)\}^{-1}, \quad \Pi^H = \{1 - \exp(-h\nu^H/kT)\}^{-1}, \quad (25. E), (25. H)$$

$\epsilon_0^E$  or  $\epsilon_0^H$  is the ground state energy per mol of the respective gas,  $m^E$  or  $m^H$  the mass of ethylene or hydrogen molecule,  $I^E$  the geometric mean of the three principal moments of inertia of ethylene molecule,  $I^H$  the moment of inertia of hydrogen molecule,  $\nu_j^E$  the frequency of  $j$ -th normal vibration of ethylene molecule and  $\nu^H$  the vibrational frequency of hydrogen molecule. We have hence by (15) and (22)

$$\mu^E = RT \ln P^E/Q_P^E + \epsilon^E, \quad \mu^H = RT \ln P^H/Q_P^H + \epsilon^H. \quad (26. E), (26. H)$$

The statistical mechanical expression of  $\Delta^*F(s)$  is now completed by (16.  $F$ ), (17), (21) and (26).

## § 6. Activation Entropy

The activation entropy  $\Delta^*S(s)$  is given by (16.  $F$ ) and (18.  $S$ ) as

$$A^*S(s) = S^{*(s)} - S^{I(s)}, \quad (27. a)$$

where

$$S^{*(s)} = -\partial\mu^{*(s)}/\partial T, \quad S^{I(s)} = -\partial\mu_e^{I(s)}/\partial T. \quad (27. b), (27. c)$$

$S^{*(s)}$  is developed according to (21) and (27. b) as

$$\begin{aligned} S^{*(s)} = & R \ln G^{*(s)} + R \ln \theta_0^{*(s)} + RT \frac{\partial \ln \theta_0^{*(s)}}{\partial T} - \frac{\partial \varepsilon_0^{*(s)}}{\partial T} \\ & + R \ln q_0^{*(s)} + RT \frac{\partial \ln q_0^{*(s)}}{\partial T}. \end{aligned} \quad (28)$$

The first term of (28) contributes 68.6 e. u. for 1 cm<sup>2</sup> surface area of catalyst, assuming that  $G^{*(s)} = 10^{15}$ . The second, third and fourth terms vanish in case of bare catalyst's surface, since then  $\theta_0^{*(s)}$  is unity and  $\varepsilon_0^{*(s)}$  is constant. If not bare,  $\theta_0^*$  is less than unity and varies with temperature, and  $\varepsilon_0^{*(s)}$  may change as well because of the variation of the interaction potential of the critical complex with the surrounding adsorbate along with change of their population.

The magnitude of the last two terms of (28) is exemplified in Table 1 with the critical complex of chemisorption of hydrogen molecule, *i.e.* I<sub>b</sub> on (110)-lattice plane of nickel, for which  $\nu_j$ 's are calculated at 936, 687, 1704, 368 and 626 cm<sup>-1</sup> in wave numbers<sup>18)</sup>.

TABLE 1.

Temp °K	$\ln q_0^*$	$T \frac{\partial \ln q_0^*}{\partial T}$	$R \ln q_0^* + RT \frac{\partial \ln q_0^*}{\partial T}$
298.16	0.283	0.694	1.94 e. u.
400.00	0.546	1.108	3.28 e. u.

Even if the catalyst's surface is not completely bare, the absolute magnitudes of the second, third and fourth terms of (28) are of small absolute magnitudes, insofar as  $\theta_0^*$  is not very small and varies slowly with temperature on account of the repulsive interactions of adsorbates as in the case of hydrogen electrode<sup>18)19)</sup>; the last two terms of (28) being very small as exemplified in Table 1, the predominant first term alone may be retained to calculate the activation entropy almost quantitatively as verified<sup>20)</sup> with various cases involving the chemisorption of hydrogen molecule. The last two terms may be somewhat larger for a critical complex of more degrees of freedom, but we might safely assume that the first term alone of (28) would give the relative order of magnitudes of  $\mathfrak{F}(s)$ 's correctly.

The  $S^{I(s)}$  is developed according to (27.c) and (17) in the respective cases of  $s$ , as

$$S^{I(a)} = S^E, \quad S^{I(b)} = S^H, \quad (29. I_a), (29. I_b)$$

$$S^{I(II)} = S^E + 1/2 \cdot S^H, \quad S^{I(III)} = S^E + S^H, \quad (29. II), (29. III)$$

where

$$S^E = -\partial\mu^E/\partial T, \quad S^H = -\partial\mu^H/\partial T \quad (30. E), (30. H)$$

are the partial molal entropy of ethylene and hydrogen, which will be called simply the entropy of the respective molecule in what follows. Eqs. (30), (26), (23) and (24) lead to the statistical mechanical expression of  $S^E$  and  $S^H$ , *i. e.*

$$S^E = S_1^E - R \ln P^E, \quad S^H = S_1^H - R \ln P^H, \quad (31. E), (31. H)$$

where

$$S_1^E = R \ln Q_p^E + RT \partial \ln \Pi^E / \partial T \quad (32. E)$$

and

$$S_1^H = R \ln Q_p^H + RT \partial \ln \Pi^H / \partial T \quad (32. H)$$

are standard entropies, which are, as seen from (23), (24) and (25), respective functions solely of temperature.  $S_1^E$  is calculated by (23. E), (25. E) and (32. E) as\*)

$$S_1^E = 52.44 \text{ e. u. } (25^\circ\text{C}), \quad S_1^E = 55.85 \text{ e. u. } (400^\circ\text{K}). \quad (33)$$

The second term of (32. E) contributes to  $S_1^E$  only 0.53 or 1.34 e. u. at  $25^\circ\text{C}$  or  $400^\circ\text{K}$  respectively, whereas that of (32. H) does practically completely negligible an amount to  $S_1^H$ .

## § 7. Activation Energy

The activation energy  $\Delta^*H(s)$  is developed according (18. F), (16. F) and (27. a) as

$$\Delta^*H(s) = H^{*(s)} - H^{I(s)}, \quad (34. A)$$

where

$$H^{*(s)} = \mu^{*(s)} + TS^{*(s)} \quad (34. *)$$

and

$$H^{I(s)} = \mu_c^{I(s)} + TS^{I(s)} \quad (34. I)$$

are the partial molal enthalpy of the critical complex and that of the initial complex;  $H^{*(s)}$  is given by (21), (28) and (34. \*) as

\*) Molecular constants were taken from Landolt "Tabellen" 1. Band, 2. Teil, p. 273 (1951).

$$H^{*(s)} = \varepsilon_0^{*(s)} + RT^2 \partial \ln q_0^{*(s)} / \partial T + RT^2 \partial \ln \theta_0^{*(s)} / \partial T - T \partial \varepsilon^{*(s)} / \partial T. \quad (35)$$

$H^{(s)}$  is expressed by (17), (29) and (34. I), as

$$H^{(I_a)} = H^E, \quad H^{(I_b)} = H^H, \quad H^{(II)} = H^E + 1/2 \cdot H^H, \quad H^{(III)} = H^E + H^H, \quad (36)$$

where

$$H^E = \mu^E + TS^E, \quad H^H = \mu^H + TS^H$$

or according to (26), (31) and (32)

$$H^E = \varepsilon^E + RT^2 \partial \ln II^E / \partial T, \quad H^H = \varepsilon^H + RT^2 \partial \ln II^H / \partial T. \quad (37)$$

We have hence from (36), (37) and (24), neglecting the second terms of (37),

$$H^{(I_a)} = \varepsilon_0^E + 4RT, \quad H^{(I_b)} = \varepsilon_0^H + 7/2 \cdot RT, \quad (38. I_a), (38. I_b)$$

$$H^{(II)} = \varepsilon_0^E + 23/4 \cdot RT, \quad H^{(III)} = \varepsilon_0^E + \varepsilon_0^H + 15/2 \cdot RT. \quad (38. II), (38. III)$$

The activation energy  $\Delta^*H(s)$  is now expressed by substituting  $H^{*(s)}$  from (35) and  $H^{(s)}$  from (38) into (34. A); in case of bare catalyst's surface, where the last two terms of (35) vanishes, we have

$$\Delta^*H(I_a) = \varepsilon_0^{*(I_a)} - \varepsilon_0^E - 4RT + RT^2 \frac{\partial \ln q_0^*}{\partial T}, \quad \text{etc.}, \quad (39)$$

which show with reference to Table 1 that  $\Delta^*H(s)$ 's vary only slowly with temperature.

### § 8. Rate-Determining Step

The rate-determining step of the catalyzed hydrogenation of ethylene is now discussed on the basis of Scheme (2) and the theory of reaction reviewed in the foregoing sections. Present arguments will be based on the assumption that the catalyst's surface is practically bare for the sake of a simple presentation of the points raised; the conclusion on the mechanism of the reaction is not qualitatively altered by allowing for the coverage<sup>15)16)</sup>.

$\mathfrak{R}(s)$  is expressed according to (7), (8) and (22) as

$$\mathfrak{R}(I_a) = k(I_a)P^E, \quad \mathfrak{R}(I_b) = k(I_b)P^H, \quad (40. I_a), (40. I_b)$$

$$\mathfrak{R}(II) = k(II)P^E(P^H)^{1/2}, \quad \mathfrak{R}(III) = k(III)P^E P^H, \quad (40. II), (40. III)$$

where

$$k(I_a) = \frac{kT}{h} p^{*(I_a)} / Q_P^E \exp\left(-\frac{\varepsilon^E}{RT}\right), \quad k(I_b) = \frac{kT}{h} p^{*(I_b)} / Q_P^H \exp\left(-\frac{\varepsilon^H}{RT}\right), \quad (41. I_a), (41. I_b)$$

$$k(\text{II}) = \frac{kT}{h} p^{*(\text{II})} / Q_P^E (Q_P^H)^{1/2} \exp\left(-\frac{\varepsilon^E + 1/2 \cdot \varepsilon^H}{RT}\right), \quad (41. \text{ II})$$

and

$$k(\text{III}) = \frac{kT}{h} p^{*(\text{III})} / Q_P^E Q_P^H \exp\left(-\frac{\varepsilon^E + \varepsilon^H}{RT}\right) \quad (41. \text{ III})$$

are respectively constant at constant temperature, inasmuch as the same is the case with  $Q_P^E$  and  $Q_P^H$  according to the foregoing section and with  $p^{*(s)}$  as well on a bare surface.

We have on the other hand from (11)

$$V = \mathfrak{K}(\text{I}_b)(1 - \gamma(\text{H})^2) \quad (42. \text{ a})$$

and

$$\begin{aligned} V &= \frac{\gamma(\text{H})^2 - \gamma(\text{H})^2 \gamma(\text{C}_2\text{H}_4)}{\gamma(\text{H})^2 / \mathfrak{K}(\text{I}_a)} = \frac{1 - \gamma(\text{H})^2}{1 / \mathfrak{K}(\text{I}_b)} \\ &= \frac{\gamma(\text{C}_2\text{H}_4) \gamma(\text{H})^2 - \gamma(\text{H}) \gamma(\text{C}_2\text{H}_5)}{\gamma(\text{H}) / \mathfrak{K}(\text{II})} = \frac{\gamma(\text{H}) \gamma(\text{C}_2\text{H}_5) - \Gamma}{1 / \mathfrak{K}(\text{III})} \end{aligned} \quad (42. \text{ b})$$

or adding numerators and denominators respectively

$$\frac{1 - \Gamma}{V} = \frac{\gamma(\text{H})^2}{\mathfrak{K}(\text{I}_a)} + \frac{1}{\mathfrak{K}(\text{I}_b)} + \frac{\gamma(\text{H})}{\mathfrak{K}(\text{II})} + \frac{1}{\mathfrak{K}(\text{III})}. \quad (42. \text{ c})$$

Substituting  $\mathfrak{K}(s)$ 's from (40) into (42), we have

$$V/P^H = k(\text{I}_b)(1 - \gamma(\text{H})^2), \quad (43. \text{ a})$$

$$\frac{P^H(1 - \Gamma)}{V} = \frac{\gamma(\text{H})^2 P^H}{k(\text{I}_a) P^E} + \frac{1}{k(\text{I}_b)} + \frac{\gamma(\text{H})(P^H)^{1/2}}{k(\text{II}) P^E} + \frac{1}{k(\text{III}) P^E}. \quad (43. \text{ b})$$

Since  $V$  is strictly proportional<sup>(3), (6), (8)</sup> to  $P^H$  as observed, the left-hand side both of the above equations is respectively constant,  $\Gamma$  being quite negligible compared with unity<sup>(14), (15)</sup>. It follows from (43. a), that  $\gamma(\text{H})^2$  is constant, hence the first and the third terms of (43. b), which are positive and increase with increase of  $P^H$ , must be negligible compared with the sum of the other two positive terms. We have in consequence by (40. I<sub>b</sub>) and (40. III)

$$\frac{1 - \Gamma}{V} = \frac{1}{\mathfrak{K}(\text{I}_b)} + \frac{1}{\mathfrak{K}(\text{III})}. \quad (44)$$

It follows from (44) that, as  $\mathfrak{K}(\text{I}_b)$  gets small compared with  $\mathfrak{K}(\text{III})$ ,  $\mathfrak{K}(\text{I}_b)$  tends to  $V/(1 - \Gamma)$ , hence that terms on the right-hand side of (42. c) other than  $1/\mathfrak{K}(\text{I}_b)$ , which are all positive, should then approach zero or that the numerators of the second, fourth and fifth member of (42. b) tend to vanish.

The conclusion is, with reference to (9), that the steps other than  $I_b$  approach equilibrium or  $I_b$  becomes the rate-determining step in accordance with §2.

It is shown similarly that  $\mathfrak{K}(III)$  tends to  $V/(1-I')$  as it gets smaller than  $\mathfrak{K}(I_b)$ , hence III becomes the rate-determining step.

$V$  should in consequence be proportional either to  $P^H$  or to  $P^E P^H$  by (40.  $I_b$ ) or (40. III), according as  $I_b$  or III determines the rate. Since the former alternative fits in with the observation at temperatures below the optimum,  $I_b$  must govern the rate there. On this basis it will be shown in the next section, that the rate-determining step should necessarily switch over to III at the optimum, beyond which  $V$  has a negative temperature coefficient.

### §9. Negative Activation Energy

The rate-determining step is concluded to be  $I_b$  in the preceding section from the experimental results<sup>(3)-(6), (8)</sup> on the catalyzed hydrogenation of ethylene in the presence of nickel catalyst over the temperatures below the optimum;  $\mathfrak{K}(I_a)$ ,  $\mathfrak{K}(II)$  and  $\mathfrak{K}(III)$  should then lie sufficiently high above  $\mathfrak{K}(I_b)$  there. The factor  $kT/h$  of (16.  $\mathfrak{K}$ ) being common to all the steps, we have then

$$\Delta^*F(I_b)/T \gg \Delta^*F(III)/T.$$

Let  $\Delta^*F(s)/T$  be plotted against  $1/T$ . The inclination  $\partial(\Delta^*F(s)/T)/\partial(1/T)$  of the curve equals  $\Delta^*H(s)$  according to (18), which varies very slowly with temperature as concluded in §7. The tangent to the curve of  $\Delta^*F(s)/T$  at a certain temperature  $T_N$  intersects the ordinate at the point

$$\Delta^*F(s)/T - \partial(\Delta^*F(s)/T)/\partial(1/T) \cdot (1/T) = \partial\Delta^*F(s)/\partial T,$$

which equals  $-\Delta^*S(s)$  at  $T_N$  according to (18.  $S$ ). The negative activation entropy  $-\Delta^*S(s)$  is now given according to (27. a) and (28), neglecting small terms in (28) as

$$-\Delta^*S(s) = S^{I(s)} - R \ln G^{*(s)} \quad (45. s)$$

or in particular by (29), as

$$-\Delta^*S(I_b) = S^H - R \ln G^{*(I_b)}, \quad (45. I_b)$$

$$-\Delta^*S(III) = S^H + S^E - R \ln G^{*(III)}, \quad (45. III)$$

where both  $G^{*(I_b)}$  and  $G^{*(III)}$  are taken to be of the order of magnitude of  $10^{15}$ . It follows from the above two equations that the tangent to the curve of  $\Delta^*F(III)/T$  intersects the ordinate at a higher point than that, where the tangent to curve of  $\Delta^*F(I_b)/T$  at the same temperature intersects the ordinate, by  $S^E$ . These two curves should intersect each other at a higher temperature, provided

that the appropriate activation energies vary slowly enough for the tangents approximately to reproduce the respective curves. Beyond the intersection, step III governs then the rate according to §3, so that the rate is proportional to  $P^E P^H$  according to §8 in conformity with the experimental results<sup>(4)(5)(6)</sup>.

At the intersection we have  $\Delta^*F(I_b) = \Delta^*F(III)$ , so that by (18.F)

$$\Delta^*H(I_b) - \Delta^*H(III) = T_x \{ \Delta^*S(I_b) - \Delta^*S(III) \}$$

or by (45)

$$\Delta^*H(I_b) - \Delta^*H(III) = T_x S_{T=T_x}^E. \quad (46)$$

It is deduced on the other hand from (23.E), (25.E) and (32.E) that  $S_1^E$  increases steadily although slowly with increase of temperature as exemplified by (33). We have thus by (31.E) and (33) at the condition that  $P^E = 10 \text{ mmHg}$  and  $T = 273.16 + 25^\circ\text{K}$ , where  $I_b$  governs the rate, hence  $T_x > T$ ,

$$S_{T=T_x}^E > 52.44 + R \ln \frac{760}{10} = 61.04 \text{ e. u.} \quad (47)$$

or according to (46)

$$\Delta^*H(I_b) - \Delta^*H(III) > 18.2 \text{ Kcal.} \quad (48)$$

The activation energy  $RT^2 \partial \ln V / \partial T$  of the overall reaction has been observed around  $25^\circ\text{C}$  with results varying from  $5^5$  to  $11^{(21)(22)}$  Kcal, which equals  $\Delta^*H(I_b) + RT$  by (16.⊗) and (18) because of the rate-determining step of  $I_b$ . The  $\Delta^*H(III)$  should in consequence inevitably be negative, *i.e.* the temperature coefficient of  $V$  should be negative over the temperature above  $T_x$ , revealing an optimum at  $T_x$ .

This analysis exemplifies that the rate of a steady reaction is not even approximately determined by a step of *the highest activation energy* but by that of *the highest activation free energy* as established in §3 and that a step of negative activation energy may have the highest activation free energy to govern the rate, despite the presence of steps of higher activation energy, on account of the negative activation entropy of the sufficiently large absolute amount, which is brought about, as seen in (45), by an addition to the reaction complex.

The entropy of the critical complex is approximately identically  $R \ln G^{*(s)}$ , whether the critical complex is formed from  $\text{H}_2$  or  $\text{C}_2\text{H}_4 + \text{H}_2$  in the respective case of  $I_b$  or III, so that  $-\Delta^*S(III)$  exceeds  $-\Delta^*S(I_b)$  by a net amount of  $S^E$  as seen from (45). Such could not, however, be the case with a homogeneous reaction, where the entropy of the critical complex should appreciably increase by such an addition through increase of its molecular weight and pronouncedly

through that of the moments of inertia.

It might be noted that the simple procedure of attributing the rate-determining step to that of the highest activation energy would be valid, if the tangents at every temperature concentrate at a point on the ordinate, *i. e.* every step has the same activation entropy, which may be far from truth particularly in the case of heterogeneous reaction, as so far exemplified.

### § 10. Explanation of Experimental Results on the Base of the Structure

Fig. 1 shows  $\Delta^*F(s)/T$  plotted against  $1/T$  according to the equation

$$\Delta^*F(s)/T = -\Delta^*S(s) + \Delta^*H(s)/T \quad (49)$$

under the simplifying assumption that  $\Delta^*H(s)$  is constant at its value at  $T=T_N$ , hence  $\Delta^*S(s)$  constant similarly<sup>\*</sup>), where  $T_N$  is arbitrarily assigned at 100°C. Fig. 1 is the thermodynamic version of the structure<sup>\*\*</sup>) of the steady reaction put forward in previous papers<sup>14)15)</sup>, which version will be called the structure here.

These straight lines are hinged on the point of  $-\Delta^*S(s)$  height on the ordinate, each of them thus being fixed by a single parameter  $\Delta^*H(s)$ ;  $\Delta^*H(I_b)$  and  $\Delta^*H(III)$  were fitted to the experimental results of ZUR STRASSEN<sup>5)</sup>, whereas  $\Delta^*H(I_a)$  and  $\Delta^*H(II)$  theoretically estimated along with the previous presentation<sup>15)</sup> as shown in Fig. 1.

On the basis of the structure a number of versatile experimental results

<sup>\*</sup>) It is readily shown by (18), that if  $\Delta^*H(s)$  is constant,  $\Delta^*S(s)$  must also be constant.

<sup>\*\*</sup>) In the previous case of the "structure" (Ref. 14, 15) the relative values of  $\mathfrak{F}(s)$ 's at different temperatures were illustrated by plotting  $\log \mathfrak{F}(s)/\rho$  against  $1000/T$ , where

$$\rho = \frac{kT_N}{h} e^{G^{*(s)}\theta_0^{*(s)}},$$

and  $\theta_0^{*(s)}$  signifies its particular value at  $T=T_N$ . We have from (16.  $\mathfrak{F}$ ) and (18)

$$\partial \ln \mathfrak{F}(s) / \partial (1/T) = -(\Delta^*H(s) + RT)/R.$$

The equation of tangent to the curve of  $\log \mathfrak{F}(s)/\rho$  versus  $1/T$  at  $T=T_N$  is, according to (16.  $\mathfrak{F}$ ), (18) and the above two equations

$$\log \mathfrak{F}(s)/\rho = \frac{\Delta^*S(s)}{2.3 R} - \frac{\Delta^*H(s) + RT_N}{2.3 RT} - \log G^{*(s)}\theta_0^{*(s)},$$

where  $\Delta^*S(s)$  and  $\Delta^*H(s)$  express their particular values at  $T=T_N$ .

The tangent to the curve of  $\Delta^*F(s)/T$  versus  $1/T$  at  $T=T_N$  in the present case is given, on the other hand, by (49) with the similar specification of  $\Delta^*H(s)$  and  $\Delta^*S(s)$ . Since the addition of  $RT_N$  to  $\Delta^*H(s)$  makes just a trifling difference, the relative magnitudes of  $\Delta^*F(s)$ 's in accordance with (49) is closely reproduced from the previous structure, where  $1/T$  was graduated from right to left, by reversing the ordinate as well as the abscissa, apart from unimportant additive constant and constant factor.

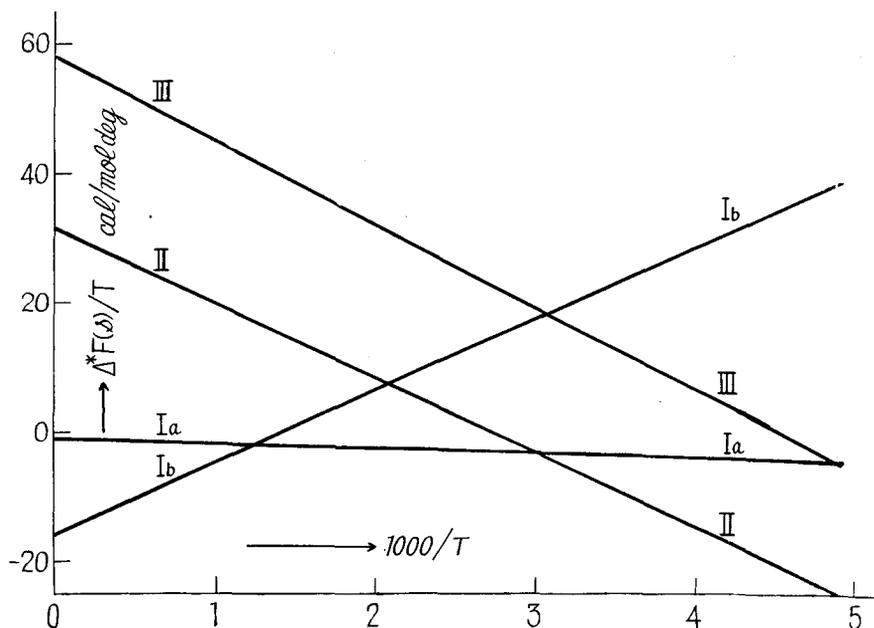


Fig. 1. Structure of Catalyzed Hydrogenation of Ethylene.

associated with the catalyzed hydrogenation in question are semi-quantitatively accounted for<sup>14)15)23)24)</sup>. They are (1) the shift of optimum temperature with change of partial pressures of hydrogen and ethylene<sup>15)</sup> as well as with substitution of other olefine for ethylene<sup>9)</sup>, (2) the excess activation energy<sup>3)</sup> of the exchange reaction associated with the catalyzed hydrogenation over the activation energy of the latter reaction<sup>15)</sup>, (3) the inhibition<sup>3)</sup> of catalyzed equilibration  $H_2 + D_2 = 2HD$  by ethylene in the presence of nickel catalyst<sup>15)23)</sup>, (4) the relation between the simultaneous equilibration and exchange<sup>3)15)23)24)</sup> and (5) the predominance<sup>23)</sup> of light ethane in the initial product of the catalyzed deuteration of ethylene<sup>15)23)26)</sup>.

Two among these will be commented upon below, which might be of particular interest with regard to the point raised in the present paper.

TWIGG and RIDEAL<sup>3)</sup> and TWIGG<sup>27)</sup> inferred that the step giving rise to the activation energy of the exchange reaction in excess over that of the simultaneous catalyzed hydrogenation could not be included in the sequence of steps appropriate to the latter reaction. It has already been shown contradicting the above inference that this excess activation energy of exchange reaction results from the single sequence of step of the associative mechanism<sup>14)15)</sup>, as alternatively reviewed below.

The exchange in question is observed with light ethylene and pure deuterium as the increasing rate of protium fraction in the heavy hydrogen gas. It is deduced on the other hand from the structure<sup>14)15)</sup>, over the temperature range below the optimum, where  $I_b$  governs the rate, that

$$\bar{v}(I_a) \doteq \bar{v}(I_a) \gg \bar{v}(II) \doteq \bar{v}(II) \gg \bar{v}(I_b) \doteq \bar{v}(III) \gg \bar{v}(I_b). \quad (50)$$

Deuterium molecules are adsorbed by  $I_b$  with the rate  $\bar{v}(I_b)$  to form adsorbed deuterium atoms  $D(a)$ 's, which are rapidly washed away by  $H(a)$ 's originating from the light ethylene through the steps  $I_a$  and  $II$  occurring rapidly back and forth according to (50). The rate of the "exchange" is now given approximately by  $\bar{v}(I_b)$  as shown analytically in previous papers<sup>14)15)</sup>, which is developed in terms of  $\mathfrak{K}(I_b)$  and  $\mathfrak{K}(III)$  as follows.

We have from (9) and (50)

$$\gamma(C_2H_4) \doteq 1, \quad \gamma(C_2H_6) \doteq \gamma(H),$$

hence

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

so that

$$\bar{v}(I_b) = \bar{v}(I_b) \bar{v}(I_b) / \bar{v}(III) = \bar{v}(I_b) \mathfrak{K}(I_b) / \mathfrak{K}(III).$$

The activation energy of the exchange reaction, *i.e.*  $RT^2 d \ln \bar{v}(I_b) / dT$  is in consequence greater than that  $RT^2 d \ln \bar{v}(I_b) / dT$  of the hydrogenation by  $RT^2 d \ln \mathfrak{K}(I_b) / dT - RT^2 d \ln \mathfrak{K}(III) / dT$ , which equals  $\Delta^*H(I_b) - \Delta^*H(III)$  according to (16.  $\mathfrak{K}$ ) and (18). Since  $\Delta^*H(I_b)$  is positive, while  $\Delta^*H(III)$  negative, the activation energy of the exchange should necessarily exceed that of the hydrogenation, although none of single step of so high an activation energy governs the rate of the exchange reaction.

It was shown<sup>14)15)</sup> on the same basis that the activation energy of the exchange reaction decreases as observed<sup>9)</sup> with increase of temperature along with that of the catalyzed hydrogenation.

Admitting that the ethylenic linkage of other olefines undergoes the catalyzed hydrogenation through similar sequence of steps to (2), it may be assumed that the activation energy of each step on the same catalyst is approximately the same as that of the corresponding one of ethylene. All the change in the structure is then that due to the change in entropy of olefine in accordance with (49). We see from (49), (45.s) and (29), that the lines of  $\Delta^*F(I_a)/T$ ,  $\Delta^*F(II)/T$  and  $\Delta^*F(III)/T$  are shifted parallel upwards by the excess of the entropy of the other olefine over that of ethylene.

AMENOMIYA<sup>9)</sup> found the optimum temperature of the catalyzed hydrogenation

of 1-butylene in the presence of nickel catalyst at 31°C for the partial pressures 40 and 35 mmHg respectively of hydrogen and 1-butylene. This value of the optimum temperature is much lower than that 137°C found with the hydrogenation of ethylene at approximately the same partial pressure, *i.e.* 30 mmHg of ethylene<sup>9)</sup>.

The function  $Q_p^B$  of 1-butylene similar to  $Q_p^E$  is calculated<sup>9)</sup> at  $7.46 \times 10^{16}$  at 100°C, *i.e. ca.* 200 times  $Q_p^E$ , ignoring the deviation from unity of the vibrational partition function. It follows that  $S^B$  of 1-butylene is so much greater than  $S^E$  at the same partial pressure, hence the optimum temperature of 1-butylene should be lower than that of ethylene at the same pressure as seen in Fig. 1 in accordance with the experimental result.

AMENOMIYA<sup>9)</sup> determined the structure of the catalyzed hydrogenation of 1-butylene similar to those of ethylene hydrogenation by fitting the appropriate  $\Delta^*H(s)$ 's to the observed optimum point and the observed activation energies of the catalyzed hydrogenation and the double bond migration. The structure thus determined was found to be approximately in agreement with that derived from the structure of ethylene hydrogenation simply by taking account of the ratio  $Q_p^B/Q_p^E$  and to reproduce the kinetics of the catalyzed hydrogenation and the associated double bond migration closely.

It is usual to attribute the optimum to the desorption of olefine<sup>5)27)28)</sup>. This hypothesis could hardly account for the lower optimum temperature of 1-butylene than that of ethylene, besides it being incapable of accounting for a number of phenomena associated with the catalyzed hydrogenation mentioned above.

## § 11. Conclusion

Rate of a step is best approximated by that of its passage through the critical state of the maximum free energy rather than by that through the so-called activated state of the maximum potential energy of the system involved. Appropriate activation energy may even be negative, provided the negative of the relevant activation entropy is large enough.

Similarly the rate of a steady reaction consisting of several steps is controlled, if at all, by a step of the highest activation free energy rather than by that of the highest activation energy, both being referred to a set  $I_e$  of chemical species on the left-hand side of the chemical equation of the steady reaction, from which the initial complex of the step in question is derived by other steps.

Particularly in the case of a heterogeneous steps constituting a steady reaction, the activation entropy consists approximately in the common value  $R \ln G^{*(s)}$  of the critical complex less the partial molal entropy of  $I_e$ . It follows

that the negative of activation entropy is considerably increased by addition to the constituents of  $I_0$ . It has thus been shown that the increase of  $I_0$  from that  $H_2$  of  $I_0$  to that  $H_2 + C_2H_4$  of III causes a pronounced decrease of activation entropy, which contributes to the activation free energy more than 18 Kcal, hence that the rate-determining step of  $I_0$  should necessarily switch over with rise of temperature to that of III resulting in the negative activation energy of the steady reaction.

We could not even approximately rely upon the principle that a step of the highest activation energy governs the rate of steady reaction as usually accepted, particularly in the case of steady reaction composed of heterogeneous steps of unequal  $I_0$ 's.

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