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THEORY OF HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

III. Theoretical Relations between Equilibrium Fraction, Deuterium Atomic Fraction and Partial Pressure of Hydrogen in Course of Catalyzed Hydrogenation of Ethylene in the Presence of Nickel Catalyst

By

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Introduction

It has been shown in Part I¹⁾ of this series that the rate of the catalyzed hydrogenation**¹⁾



in the presence of metallic catalysts and those of associated reactions***²⁾ are given as functions of characteristic rate functions $\mathfrak{R}(s)$'s respectively relevant to constituent steps s 's of the overall reaction (1). $\mathfrak{R}(s)$ is the forward rate of step s at the steady state of the overall reaction (1) multiplied by a factor $a_e^{I(s)}/a^{I(s)}$ of increase of the activity of the initial complex I(s) from that $a^{I(s)}$ at the latter steady state to that $a_e^{I(s)}$ at equilibria of all constituent steps but s .

Assuming a bare and homogeneous catalyst's surface, $\mathfrak{R}(s)$'s were statistical-mechanically formulated in Part I¹⁾ particularly for the associative mechanism, *i. e.*

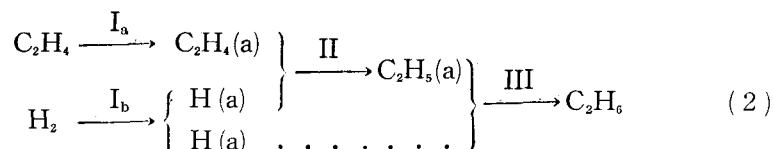
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**²⁾ Protium and deuterium atoms are denoted by P and D respectively, they together represented by H and called hydrogen atoms as in Parts I and II.

***³⁾ They are exchange reaction of ethylene, that of hydrogen, equilibration of hydrogen ($\text{P}_2 + \text{D}_2 = 2\text{PD}$), parahydrogen conversion and evolution of different deuterocompounds of ethylene, hydrogen and ethane in course of the catalyzed hydrogenation. The rate of exchange E^E of ethylene (E) and that E^H of hydrogen (H) respectively defined as

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

are not necessarily identical with each other as shown in Part I (Ref. 1), where n^E or n^H is number of hydrogen atoms implied in E or H, X or Y the deuterium atomic fraction of E or H and \dot{X} or \dot{Y} its time derivative, unless there exists such a relation $n^E \dot{X} + n^H \dot{Y} = 0$ as in simple cases of exchange reaction, when n^E , n^H and the total amounts of isotopes involved remain respectively unchanged.



as functions of partial pressures P^E and P^H of E and H, each including the appropriate activation energy as a unique adjustable parameter; the latter being fitted to experiment or estimated theoretically, a number of experimental results were accounted for and several experimentally verifiable conclusions derived on the basis of the associative mechanism (2)¹⁾. Among others the following result of TWIGG and RIDEAL²⁾ was semiquantitatively explained on their basis.

TWIGG and RIDEAL²⁾ have observed that in the catalyzed interaction of 10 mmHg ethylene with equimolecular deuterium at different temperatures ranging from 84 to 207°C in the presence of Ni-catalyst, the non-equilibrium fraction*³⁾ $1-u$ varied linearly with the deuterium atomic fraction Y of hydrogen, and that the linear relation stayed constant from 84°C to 156°C, extrapolating $1-u=0.8$ at $Y=1$ but deviated from the constant one with rise of temperature above 156°C, $1-u$ extrapolated at $Y=1$ decreasing down to 0.4 at 207°C. TWIGG and RIDEAL²⁾ based their mechanisms proposed against the associative mechanism on the above experimental fact of the constant linear relation being kept up between 84°C and 156°C, disregarding the deviation from it at higher temperatures. It was shown in terms of the above simplified functions of $\mathfrak{K}(s)$'s in Part I¹⁾, that the limiting value of $1-u$ for $Y \rightarrow 1$ stays constant at lower temperature but decreases at higher temperature in accordance with their experimental result²⁾.

The simplifying assumption of bare catalyst's surface was now examined in Part II³⁾, with a conclusion that adsorbed hydrogen atoms exert an appreciable effect upon $\mathfrak{K}(s)$'s; with allowance for the latter, the $\mathfrak{K}(s)$'s were determined by fitting them to the experimental results of ZUR STRASSEN⁴⁾ and TURKEVICH, SCHISLER and IRSA⁵⁾. The present Part is devoted to derive the relation between u and Y and that between Y and P^H from the revised $\mathfrak{K}(s)$'s over an extended temperature range, inclusive of that of the above experiment of TWIGG and RIDEAL in order to explain the observations quantitatively on the one hand and to find some criterion for discriminating between the mechanisms on the other hand.

*) The equilibrium fraction u is defined as $u = n^{PD} / n_{\infty}^{PD}$, where n^{PD} is the amount of PD molecules present and n_{∞}^{PD} is the particular value of n^{PD} at equilibrium of the reaction $\text{P}_2 + \text{D}_2 = 2\text{PD}$ of the hydrogen existing.

Derivation of the Relations

The relation between u and Y has been given by Eq.(23.4. u) of Part I¹⁾ on the basis of the associative mechanism ignoring the isotopic difference of rates as

$$u = \frac{\exp\left(-\int_Y^1 \frac{dY}{Y-y_1}\right)}{Y(1-Y)} \int_Y^1 \frac{y_1(1-y_1)}{Y-y_1} \exp\left(\int_Y^1 \frac{dY}{Y-y_1}\right) dY \quad (3)$$

for the initial condition $Y=1$, where y_1 is the atomic fraction of deuterium of adsorbed hydrogen atoms.

The y_1 in (3) must be given as a function of Y for arriving at the relation between u and Y in question. We have from Eqs. (7.9) and (4.5) of Part I¹⁾

$$n^E \dot{X} = 2/3 \cdot (y_1 - x) \bar{v}(\text{II}), \quad n^H \dot{Y} = 2(y_1 - Y) \bar{v}(\text{I}_b) \quad (4. \text{E}), (4. \text{H})$$

and by Eqs. (4.8) there for the deuterium atomic fraction x in $\text{CH}_4(\text{a})$ and y_1 ,

$$x = \frac{6X\bar{v}(\text{I}_a)}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})} + \frac{y_1\bar{v}(\text{II})}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})}, \quad (5. \text{E})$$

$$y_1 = \frac{X \frac{4\bar{v}(\text{I}_a)\bar{v}(\text{II})}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})} + 2Y\bar{v}(\text{I}_b) + Z\bar{v}(\text{III})}{\frac{4\bar{v}(\text{I}_a)\bar{v}(\text{II})}{6\bar{v}(\text{I}_a) + \bar{v}(\text{II})} + 2\bar{v}(\text{I}_b) + \bar{v}(\text{III})}}, \quad (5. \text{H})$$

where X or Z is the deuterium atomic fraction in ethylene or ethane, $\bar{v}(s)$'s or $\bar{v}(s)$'s are the forward or backward rates of steps s 's ($s=\text{I}_a, \text{I}_b, \text{II}, \text{III}$) of the associative mechanism (2) subject to the steady condition^{*})

$$V_s = \bar{v}(s) - \bar{v}(s), \quad s = \text{I}_a, \text{I}_b, \text{II}, \text{III}, \quad (6)$$

and V_s is the steady rate of the catalyzed hydrogenation. The $\bar{v}(s)$'s and $\bar{v}(s)$'s are expressed in terms of $\mathfrak{K}(s)$'s by Eq.(2.12) of Part I, as

$$\bar{v}(\text{I}_a) = \mathfrak{K}(\text{I}_a), \quad \bar{v}(\text{I}_a) = \gamma(\text{C}_2\text{H}_4) \mathfrak{K}(\text{I}_a), \quad (7. \text{I}_a)$$

$$\bar{v}(\text{I}_b) = \mathfrak{K}(\text{I}_b), \quad \bar{v}(\text{I}_b) = \gamma(\text{H})^2 \mathfrak{K}(\text{I}_b), \quad (7. \text{I}_b)$$

$$\bar{v}(\text{II}) = \gamma(\text{H})\gamma(\text{C}_2\text{H}_4) \mathfrak{K}(\text{II}), \quad \bar{v}(\text{II}) = \gamma(\text{C}_2\text{H}_5) \mathfrak{K}(\text{II}), \quad (7. \text{II})$$

$$\bar{v}(\text{III}) = \gamma(\text{H})\gamma(\text{C}_2\text{H}_5) \mathfrak{K}(\text{III}), \quad \bar{v}(\text{III}) = \Gamma \mathfrak{K}(\text{III}), \quad (7. \text{III})$$

where Γ is the BOLTZMANN factor of the affinity of the hydrogenation and $\gamma(\text{H})$, $\gamma(\text{C}_2\text{H}_4)$ or $\gamma(\text{C}_2\text{H}_5)$ is the relative activity respectively of the intermediate $\text{H}(\text{a})$, $\text{C}_2\text{H}_4(\text{a})$ or $\text{C}_2\text{H}_5(\text{a})$ involved in (1), referred to its activity at its equilibrium^{**)}

^{*}) Eq. (2.2) of Part I (Ref. 1).

^{**)} The equilibrium of $\text{C}_2\text{H}_5(\text{a})$ for instance is that $\text{C}_2\text{H}_5(\text{a}) = \text{C}_2\text{H}_4 + 1/2 \cdot \text{H}_2$.

with the reactants, *i.e.* ethylene and hydrogen. We have from (6) and (7)

$$\begin{aligned} V_s &= \mathfrak{K}(I_a)(1-\gamma(C_2H_4)) = \mathfrak{K}(I_b)(1-\gamma(H)^2) \\ &= \mathfrak{K}(II)(\gamma(H)\gamma(C_2H_4) - \gamma(C_2H_6)) = \mathfrak{K}(III)(\gamma(H)\gamma(C_2H_6) - \Gamma). \end{aligned} \quad (8)$$

It has been shown in Part I¹⁾ that Γ is extremely small compared with unity at the experimental conditions in question and that it follows from Γ less than unity in general that

$$V_s > 0$$

and

$$1 > \gamma(C_2H_4), \gamma(H), \gamma(C_2H_6) > 0. \quad (9)$$

It has further been shown on the basis of the revised $\mathfrak{K}(s)$ 's³⁾ with reference to the experimental condition of TWIGG and RIDEAL²⁾, that⁶⁾ $\mathfrak{K}(I_a)$ is practically infinite compared with other $\mathfrak{K}(s)$'s, hence with V_s according to (8) and (9), and that³⁾ $\Gamma\mathfrak{K}(III)$ or $\bar{v}(III)$ according to (7. III) is completely negligible compared with all other $\bar{v}(s)$'s and $\bar{v}(s')$'s, *i.e.*

$$\mathfrak{K}(I_a) \gg \mathfrak{K}(s'), \quad s' = I_b, II, III; \quad \mathfrak{K}(I_a) \gg V_s; \quad (10. \mathfrak{K}), (10. V)$$

$$\bar{v}(III) \ll \bar{v}(II), \quad \bar{v}(III) \ll \bar{v}(s''), \quad \bar{v}(s''), \quad s'' = I_a, I_b, II. \quad (10. III)$$

It follows now from (10. \mathfrak{K}), (7) and (9), that $\bar{v}(I_a)$ is infinitely greater than all $\bar{v}(s')$'s and $\bar{v}(s'')$'s, hence (5) is simplified, besides by ignoring $\bar{v}(III)$ according to (10. III), as

$$x = X, \quad (11. x)$$

$$y_1 = \frac{X\bar{v}(II) + 3Y\bar{v}(I_b)}{\bar{v}(II) + 3\bar{v}(I_b)}. \quad (11. y)$$

Substituting x and y_1 from (11) into (4), we have

$$n^E \dot{X} = 2(Y - X)F\bar{v}(I_b), \quad n^H \dot{Y} = 2(X - Y)F\bar{v}(I_b), \quad (12. X), (12. Y)$$

where

$$F = \bar{v}(II)/(\bar{v}(II) + 3\bar{v}(I_b)), \quad (12. F)$$

hence

$$Y - X = \exp \left\{ - \int_0^t 2F \left(\bar{v}(I_b) \frac{n^H}{n^E} + \bar{v}(I_b) \right) \frac{dt}{n^H} \right\} \quad (13)$$

for the initial condition $X=0$ and $Y=1$ at $t=0$, where t is the time. The n^H/n^E there keeps constant at 1/2 throughout for the catalyzed interaction of equimolecular ethylene and deuterium in this case. Substituting $Y-X$ from (13) into (12. Y), we have

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$$n^H \dot{Y} = -2F \bar{v}(I_b) \exp \left\{ - \int_0^t 2F \left(\bar{v}(I_b) \frac{n^H}{n^E} + \bar{v}(I_b) \right) \frac{dt}{n^H} \right\}, \quad (14. x)$$

which gives on integration with reference to the above initial condition

$$1 - Y = 2 \int_0^t F \bar{v}(I_b) \exp \left\{ - \int_0^t 2F \left(\bar{v}(I_b) \frac{n^H}{n^E} + \bar{v}(I_b) \right) \frac{dt}{n^H} \right\} \frac{dt}{n^H} \quad (15. a)$$

or on substitution of $n^H \dot{Y}$ from (4. H)

$$y_1 - Y = -F \exp \left\{ - \int_0^t 2F \left(\bar{v}(I_b) \frac{n^H}{n^E} + \bar{v}(I_b) \right) \frac{dt}{n^H} \right\}. \quad (15. b)$$

The variable of integration is now changed for the sake of an expedient numerical calculation, noting that n^H is proportional to P^H and that $2V_s = -dn^H/dt$ by definition *i. e.*

$$- \frac{d \ln n^H}{dt} \equiv \frac{2V_s}{n^H} = - \frac{d \ln P^H}{dt},$$

hence

$$2dt/n^H = -d \ln P^H / V_s. \quad (16)$$

Substituting dt/n^H from (16) into (15), we have

$$1 - Y = \int_{P^H}^{P_0^H} \frac{F \bar{v}(I_b)}{V_s} \exp \left\{ - \int_{P^H}^{P_0^H} \frac{F}{V_s} \left(\bar{v}(I_b) \frac{n^H}{n^E} + \bar{v}(I_b) \right) d \ln P^H \right\} d \ln P^H, \quad (17. a)$$

$$y_1 - Y = -F \exp \left\{ - \int_{P^H}^{P_0^H} \frac{F}{V_s} \left(\bar{v}(I_b) \frac{n^H}{n^E} + \bar{v}(I_b) \right) d \ln P^H \right\}, \quad (17. b)$$

where P_0^H is the initial value of P^H .

Eqs.(17) enable us to compute the correlative values of Y , y_1 and P^H varying with the progress of hydrogenation and these values decide the relation between u and Y , when substituted into (3). The rates $\bar{v}(I_b)$, $\bar{v}(I_b)$, $\bar{v}(II)$, $\bar{v}(II)$ and V_s in (17) are given as functions of P^H as follows. We have $\gamma(C_2H_4) \simeq 1$ by (10. V) and (8), so that (8) is reduced, by (10. III) and (7), to the form

$$V_s = \mathfrak{K}(I_b)(1 - \gamma(H)^2) = \mathfrak{K}(II)(\gamma(H) - \gamma(C_2H_5)) = \mathfrak{K}(III)\gamma(H)\gamma(C_2H_5). \quad (18)$$

V_s , $\gamma(H)$ and $\gamma(C_2H_5)$ are calculated by (18) from $\mathfrak{K}(s)$'s revised in Part II³⁾ as^{*}

$$\mathfrak{K}(I_b) = 2.0573 \times 10^{-18} \times 10^{\frac{-1356.6}{T}} \times P^H (P^E)^{0.525} \rho,$$

$$\mathfrak{K}(II) = 2.4687 \times 10^{-20} \times 10^{\frac{-220.12}{T}} (P^H)^{1.2} P^E \rho,$$

^{*}) The present calculation is based on the value $-220.12/T$ in the expression of $\mathfrak{K}(II)$, which is to be replaced by somewhat a larger value $-165.4/T$. The result from the latter corrected value will be reported in a later paper, although the conclusion is essentially unchanged as expected from the similar variation — added at the proof.

$$\mathfrak{K}(\text{III}) = 2.4012 \times 10^{-25} \times 10^{\frac{1092.3}{T}} \times P^H P^E \rho,$$

hence $\bar{v}(s)$'s and $\tilde{v}(s)$'s by (7) as functions of T and P^H , where ρ is a common factor, which is of less importance in the present calculation of the quantities, which depend solely on the relative magnitudes of $\tilde{v}(s)$, $\bar{v}(s)$ and V_s as seen from (17) and (3), hence on those of $\mathfrak{K}(s)$'s as shown in Part II³⁾.

Results

The values of Y and y_1 calculated as above at different $P^H = P^E$ decreasing

TABLE 1. Correlative variation of Y , y_1 and $P^H = P^E$ during the catalyzed interaction of C_2P_4 with D_2 in the presence of Ni-catalyst.

$P^H = P^E$ mmHg	t °C Y, y_1	300	150	100	80	50	0	-25
		10	Y y_1	1 0.7355	1 0.3830	1 0.2738	1 0.2519	1 0.2419
9	Y y_1	0.3681 0.3529	0.8770 0.3827	0.9721 0.2847	0.9875 0.2620	0.9971 0.2506		
8	Y y_1		0.7607 0.3800	0.9414 0.2980	0.9733 0.2731	0.9937 0.2603	0.9997 0.2730	
6	Y y_1		0.5643 0.3757	0.8680 0.3245	0.9377 0.3007	0.9849 0.2845	0.9994 0.2936	
4	Y y_1		0.4323 0.3736	0.7372 0.3264	0.8859 0.3390	0.9712 0.3195	0.9988 0.3240	
2	Y y_1			0.5934 0.3747	0.7907 0.3944	0.9442 0.3802	0.9976 0.3783	
1	Y y_1			0.5039 0.4055	0.7049 0.4458	0.9125 0.4392	0.9961 0.4338	0.9995 0.4366
0.1	Y y_1				0.5429 0.5266	0.7286 0.4019	0.9881 0.6068	0.9985 0.6052
0.03	Y y_1					0.6268 0.4904	0.9814 0.6825	0.9976 0.6806
0.01	Y y_1						0.9732 0.7407	0.9965 0.7397
0.003	Y y_1						0.9615 0.7927	0.9948 0.7936
0.001	Y y_1						0.9485 0.8302	0.9928 0.8381

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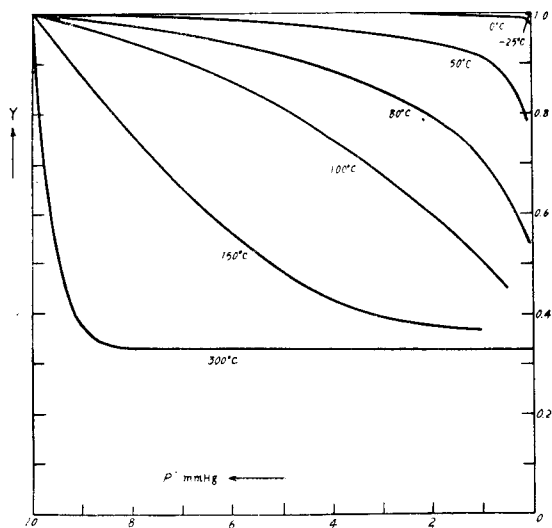
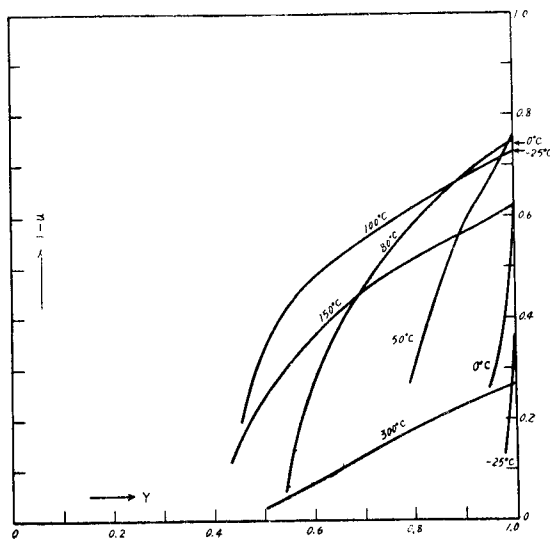


Fig. 1.
The Y, P^H -relation in course of catalyzed interaction of C_2P_4 with D_2 in the presence of Ni-catalyst.

Fig. 2.
The $1-u, Y$ -relation in course of catalyzed interaction of C_2P_4 with D_2 in the presence of Ni-catalyst.



Note: Horizontal arrows on the right indicate the starting points on the ordinate $Y=1$ of the curves of 0°C and -25°C .

TABLE 2. The $1-u, Y$ -relation in course of catalyzed interaction of C_2P_4 with D_2 in the presence of Ni-catalyst.

$P^M = P^E$ mmHg	$t^\circ C$ Y $1-u$	300	150	100	80	50	0	-25
		10	Y $1-u$	1 0.2645	1 0.6170	1 0.7262	1 0.7481	1 0.7581
9	Y $1-u$		0.8770 0.5522	0.9721 0.7115	0.9875 0.7397	0.9971 0.7572		
8	Y $1-u$		0.7607 0.4895	0.9414 0.6944	0.9733 0.7301	0.9937 0.7484	0.9997 0.7343	
6	Y $1-u$		0.5643 0.3186	0.8680 0.6519	0.9377 0.7041	0.9849 0.7300	0.9994 0.7222	
4	Y $1-u$		0.4323 0.1094	0.7372 0.5765	0.8859 0.6617	0.9712 0.7077	0.9988 0.7073	
2	Y $1-u$			0.5984 0.4760	0.7907 0.5717	0.9442 0.6636	0.9976 0.6776	
1	Y $1-u$			0.5039 0.3414	0.7049 0.4648	0.9125 0.6106	0.9961 0.6439	0.9995 0.6470
0.1	Y $1-u$				0.5429 0.05137	0.7286 0.4199	0.9881 0.5194	0.9985 0.5258
0.03	Y $1-u$					0.6268 0.3221	0.9814 0.4500	0.9976 0.4616
0.01	Y $1-u$						0.9732 0.3863	0.9965 0.4049
0.003	Y $1-u$						0.9615 0.3175	0.9948 0.3456
0.001	Y $1-u$						0.9485 0.2566	0.9928 0.2961

from its initial value 10 mmHg at different temperatures are given in Table 1 and the Y, P^M -relation is shown in Fig. 1.

Table 2 and Fig. 2 show the $1-u, Y$ -relation derived from the result of Table 1 by (3). We see from Fig. 2 that the curves of $1-u$ versus Y , not quite linear as in the experiment of TWIGG and RIDEAL, rise with decrease of temperature upwards, increasing the height $1-u$ at $Y=1$ up to ca. $50^\circ C$ and then, approximately fixing the latter height, draws the point on the abscissa toward the ordinate $Y=1$, adhering to it at lower temperatures.

The above behavior of the theoretical curve with temperature is approximately in agreement with the experimental results of TWIGG and RIDEAL²⁾ in

the respects that it remains more or less stationary between *ca.* 50 C and 150 C and that it turns down with increase of temperature above *ca.* 150 C, which was disregarded by these authors²⁾ as the basis of their mechanisms. The theoretical curve runs thus quite differently at temperatures below 50 C from the constant straight line, which is required by the mechanisms proposed by these authors²⁾.

The above theoretical predictions are thrown to experimental tests by one of the present authors (I.M.)⁷⁾.

Summary

Theoretical procedure developed in Part I¹⁾ and II³⁾ of deriving rates of the catalyzed hydrogenation of ethylene and of reactions associated with it in terms of the characteristic rate functions $\mathfrak{K}(s)$'s relevant respectively to the constituent steps s 's of the associative mechanism of the catalyzed hydrogenation was applied to follow the correlative variation of the equilibrium fraction u (the fraction of PD present over that at equilibrium of the reaction $P_2 + D_2 \rightleftharpoons 2PD$, where P is protium), the deuterium atomic fraction Y and the partial pressure of hydrogen in course of the catalyzed interaction of C_2P_4 with D_2 for the experimental condition of TWIGG and RIDEAL²⁾, where the initial partial pressures both of C_2P_4 and D_2 were 10 mmHg. The appropriate calculation was based on $\mathfrak{K}(s)$'s revised in Part II³⁾ with allowance for the effect of adsorbed hydrogen atoms.

The theoretical conclusion from the associative mechanism thus derived on the relation between u and Y was found in concordance with the experimental results of TWIGG and RIDEAL²⁾ over the temperature range of their observation but to deviate distinctly at lower temperatures from that expected from their mechanisms²⁾, thus providing a criterion for experimentally discriminating the associative mechanism from their mechanisms.

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