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# MECHANISM OF CATALYZED HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

## Verification of Theoretical Conclusion from Associative Mechanism

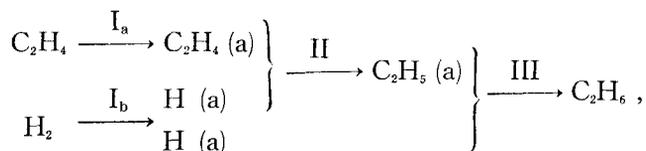
By

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(Received December 15, 1959)

### § 1. Introduction

On the basis of the statistical mechanical theory of the HORIUTI and POLANYI's Associative Mechanism<sup>1)</sup> for the catalyzed hydrogenation of ethylene on metallic catalysts



((a) denotes the adsorbed state)

reasonable explanations<sup>2)-6)</sup> and theoretical predictions<sup>4)6)</sup> have hitherto been deduced on various existing and yet unexplored phenomena involved in the catalyzed hydrogenation of ethylene inclusive of associated exchange, equilibration  $\text{P}_2 + \text{D}_2 = 2\text{PD}$  (P: protium) *etc.*, *i. e.* the well-known existence of optimum temperature of the catalyzed hydrogenation<sup>7)-10);2)3)</sup>, the excess activation energy of hydrogen exchange over that of hydrogenation<sup>11);2)3)</sup>, the inhibition of equilibration by ethylene<sup>11);2)3)</sup>, the simultaneous changes of the deuterium atomic fraction in hydrogen<sup>\*\*)</sup> and the equilibrium fraction of hydrogen<sup>11);2)3)</sup> and of the deuterium atomic fraction in hydrogen and the hydrogen partial pressure<sup>4)</sup> during deuteration of ethylene, the formation of deuterioethylenes and deuterioethanes during deuteration<sup>12)13);5)6)</sup>, the "redistribution" of deuterium<sup>14);3)</sup> during deuteration and the evolution of  $\text{P}_2$  or  $\text{PD}$ <sup>5)</sup> during deuteration. This paper is concerned with experimental examination of some of the theoretical predictions.

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<sup>\*\*)</sup> In this paper protium or deuterium is denoted respectively by P or D, which are collectively signified by H and called hydrogen.

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HORIUTI and the present author<sup>4)</sup> have recently revised the previous theoretical calculation of HORIUTI<sup>2)</sup> on the correlation among the simultaneous changes<sup>11)15)</sup> of the hydrogen partial pressure  $P^H$ , the deuterium atomic fraction  $Y$  in hydrogen and the non-equilibrium fraction<sup>\*)</sup>  $(1-u)$  of hydrogen during the progress of the interaction in the presence of nickel catalyst between light ethylene  $C_2P_4$  and deuterium  $D_2$  each of 10 mmHg initial partial pressure. The revised result is reproduced<sup>\*\*)</sup> in Fig. 1 by the plot of  $P^H$  or  $(1-u)$  versus  $Y$

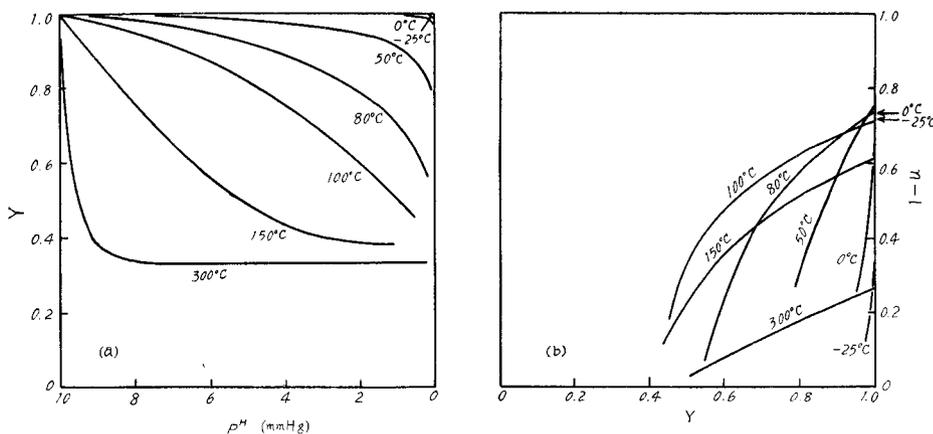


Fig. 1. The theoretical result on the simultaneous changes of  $P^H$ ,  $Y$  and  $(1-u)$  in the reaction in the presence of nickel catalyst between  $C_2P_4$  and  $D_2$  each of 10mmHg initial partial pressure. (Horizontal arrows on the right indicate the starting points on the ordinate  $Y=1$  of the curves of  $0^\circ C$  and  $-25^\circ C$ .)

- Note 1.  $P^H$ : Partial pressure of hydrogen  
 $Y$ : Deuterium atomic fraction in hydrogen  
 $(1-u)$ : Non-equilibrium fraction of hydrogen  
 2. The temperatures in the figure represent the reaction temperature.

simultaneously varying during the progress of the above-specified reaction for the sake of comparison with experimental results described below.

TWIGG and RIDEAL<sup>11)</sup> previously observed the  $Y$ ,  $(1-u)$ -relation over the temperature range of  $84\sim 207^\circ C$ , finding a constant linear relation over  $84\sim 156^\circ C$  as shown by the dotted line in Fig. 2, and suggested on its ground their two mechanisms<sup>11)16)</sup> which attribute a common course of reaction to both the

\*) It is defined that  $u \equiv N^{PD}/N_\infty^{PD}$ , where  $N^{PD}$  is the molecular fraction of PD molecule over the total hydrogen molecules present and  $N_\infty^{PD}$  the particular value of  $N^{PD}$  at the equilibrium of the reaction  $P_2 + D_2 = 2PD$  of the hydrogen.

\*\*\*) The result of Fig. 1 is for the value  $-220.12/T$  in the expression of  $\mathcal{R}$  (II). (See the footnote on p. 191, this volume).

exchange and the equilibration as responsible for the constant relation. As seen by comparison between Fig. 1 (b) and Fig. 2, the theoretical  $Y, (1-u)$ -relation approximately reproduces the experimental result of TWIGG and RIDEAL inclusive of the observed deviation from the constant linear  $Y, (1-u)$ -relation at higher temperatures above  $156^{\circ}\text{C}$ , while it predicts another marked deviation from the same relation at lower temperatures outside the range of their measurements. As for the  $P^H, Y$ -relation, the theoretical one shown in Fig. 1 (a) is quite in conformity with the abrupt decrease of the relative rate of hydrogen exchange to hydrogenation with decreasing temperature observed over the range of about  $60\sim 207^{\circ}\text{C}$  by TWIGG and RIDEAL<sup>11)</sup> and at  $20$  and  $120^{\circ}\text{C}$  by FARKAS, FARKAS and RIDEAL<sup>15)</sup>, but requires a thorough investigation for quantitative verification.

The purpose of the present research is to appeal the theoretical conclusion on the  $P^H, Y$ - and  $Y, (1-u)$ -relations to experimental test.

## § 2. Experimental

The method employed for the purpose of following the simultaneous changes of  $P^H, Y$  and  $(1-u)$  was designed on the model of the experiment of TWIGG and RIDEAL<sup>11)</sup> where the same quantities had been measured under similar reaction conditions.

### 1) Materials.

The ethylene was prepared by dehydration of ethyl alcohol with phosphorus pentoxide and purified by repeated distillation in vacuo. The cylinder deuterium of over 99.5% purity from Stuart Oxygen Co. (San Francisco, U. S. A.) was used after purification by passage through a heated palladium thimble. The protium used together with deuterium to calibrate the thermal conductivity gauge for the  $Y$ - and  $(1-u)$ -determination was prepared by electrolysis of ordinary water and purified by passage through heated platinized asbestos.

### 2) Apparatus.

The apparatus was essentially composed, as shown in Fig.3, of gas

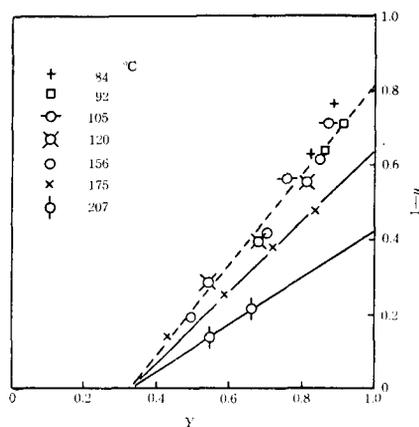
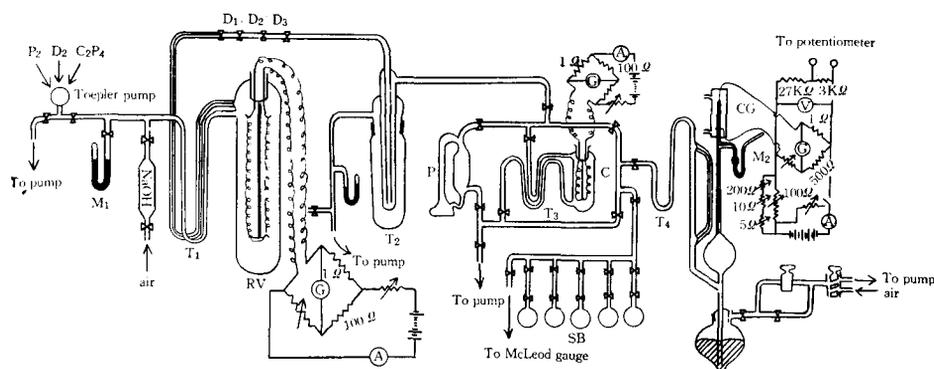


Fig. 2. TWIGG and RIDEAL's experimental result on the simultaneous changes of  $Y$  and  $(1-u)$  in the same reaction as in Fig. 1.

Note: See the notes of Fig. 1.

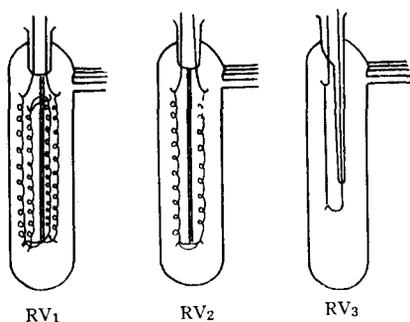
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**Fig. 3.** The apparatus.

reservoirs, a reaction vessel (RV), a pumped-out liquid nitrogen trap ( $T_2$ ), sampling bulbs (SB) and an analytical system consisting of a micro-thermal conductivity gauge (CG), a mercury diffusion pump (P) and a vessel (C) containing a nickel wire catalyst. The whole apparatus was evacuated to less than  $10^{-6}$  mmHg

pressure measured on a McLeod gauge by means of an oil diffusion pump backed by a rotary oil pump.



**Fig. 4.** Structure of the reaction vessels.

Three reaction vessels ( $RV_1$ ), ( $RV_2$ ) and ( $RV_3$ ) shown in Fig. 4 were preliminarily constructed by sealing 6 m (0.45 g), 60 cm and 6 cm respectively of nickel wire of 0.1 mm diameter and about 99.9% purity in vessels of about 150 cc capacity, and used respectively depending on the reaction temperature so as to allow the reaction to proceed at practicably measurable speed. The catalyst in (RV) was

protected against contact with tap grease and mercury vapor by immersing the trap ( $T_1$ ) in either liquid nitrogen or alcohol cooled at about  $-80^\circ\text{C}$  by mixing it with dry ice or liquid nitrogen. The capillary tubing at ( $T_1$ ) was of 1 mm bore and 50 cm length, serving for appropriate samples to be taken out of the reaction vessel without waiting for diffusion by rejecting the first sample in it.

The liquid nitrogen trap ( $T_2$ ) was pumped-out at a pressure of 5–10 mmHg, insuring complete removal of ethylene and ethane from hydrogen to be analyzed.

The mercury diffusion pump (P) and the vessel (C) containing nickel wire 3 m in length of 0.1 mm diameter as catalyst for bringing the hydrogen to

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$P_2 + D_2 = 2PD$  equilibrium were arranged as shown in Fig. 3, so that the set of measurements by thermal conductivity gauge for  $Y$  and  $(1-u)$  could be made with one and the same sample to minimize the amount of the reactant gas mixture extracted from the reaction vessel. The catalyst in (C) was prevented from contact with tap grease and mercury vapor by immersing the trap ( $T_3$ ) in liquid nitrogen and could be maintained at a constant temperature near 500 C by means of the Wheatstone-bridge shown there.

The micro-thermal conductivity gauge (CG) was of the MELVILLE and BOLLAND's<sup>17)</sup> type, consisting of tungsten wire of 0.02 mm diameter and 5 cm length sealed in a thin-walled tubing of 1 mm bore and connected to a Wheatstone-bridge. The gauge was operated at constant voltage (6.200 V) across the bridge adjusted by means of a potentiometer, 50 mmHg of the sample pressure and 28°C of the jacket-water temperature. The adjustment of the sample pressure to 50 mmHg was facilitated by the use of a remodeled U-tube manometer ( $M_2$ ) of small dead space and high sensitivity attached close to the gauge. Contamination of sample gas with tap grease vapor was avoided by immersing the trap ( $T_4$ ) in liquid nitrogen. The gauge was preliminarily calibrated for  $Y$  and  $(1-u)$  according to the method described by TWIGG<sup>18)</sup>.

In runs at  $-25$ ,  $0$  and  $25^\circ\text{C}$  where much catalyst was used in contrast with those in runs at higher temperatures, the reaction vessels were immersed in alcohol-dry ice mixture to fix the reaction during sampling and measuring the gas pressure as well as to keep the reaction vessel at constant temperature during the pressure measurement.

### **3) Procedure.**

The catalyst was subjected for the first use to twice the activation treatment (I), consisting of oxidation at  $600^\circ\text{C}$  for 30 min. in atmospheric air and subsequent reduction at  $300^\circ\text{C}$  for 30 min. in deuterium of 30~50 mmHg, and then to once the activation treatment (II), consisting of oxidation at  $600^\circ\text{C}$  for 1 hr. in atmospheric air and subsequent reduction at  $300^\circ\text{C}$  for 10~15 hrs. in deuterium of 30~50 mmHg. The catalyst was reused after once the treatment (I) followed by the treatment (II). Homogeneous heating of the catalyst was effected by heating the reaction vessel at  $280^\circ\text{C}$  in an electric furnace and supplying additional heat electrically through the bridge.

The electric resistance of the activated catalyst was measured at room temperature in vacuo by passing through the Wheatstone-bridge just a small electric current, *e.g. ca.* 3 mA, to avoid the Joule's heat virtually raising the temperature of the catalyst. The electric resistance of the catalyst at a reaction temperature was calculated from the above observation at room temperature

and the temperature coefficient of the electric resistance of nickel ( $=6.7 \times 10^{-3}/^{\circ}\text{C}$ ). The bridge was preliminarily adjusted so as to be balanced at the calculated resistance of the catalyst. The reactant gases were now introduced as follows into the reaction vessel immersed in ice-water except in runs at  $-25$ ,  $0$  and  $25^{\circ}\text{C}$  mentioned in 2);  $\text{C}_2\text{P}_4$  was first introduced through the trap ( $\text{T}_1$ ) immersed in alcohol cooled at  $-80^{\circ}\text{C}$  to the amount slightly exceeding 10 mmHg, and its pressure adjusted exactly to 10 mmHg by extracting small portions of the gas stepwise by means of the pipettes ( $\text{D}_1$ ), ( $\text{D}_2$ ) and ( $\text{D}_3$ ) respectively of 0.5, 1 and 2 cc capacity under careful observation of the manometer ( $\text{M}_1$ ) by a traveling microscope; then, after condensing  $\text{C}_2\text{P}_4$  in ( $\text{T}_1$ ) by replacing the cooled alcohol by liquid nitrogen,  $\text{D}_2$  was introduced and adjusted exactly to 10 mmHg\* similarly to  $\text{C}_2\text{P}_4$ . After replacing the liquid nitrogen again by the cooled alcohol, thereby allowing the two gases to mix, the catalyst was maintained for a recorded time at a specified reaction temperature by balancing the bridge, and then a small amount of the reactant gas extracted by means of the pump ( $\text{P}$ ) into the sampling bulb ( $\text{SB}$ ) via the pumped-out trap ( $\text{T}_2$ ). The pressure of the reactant gas was measured before and after the sample extraction. This series of procedures of balancing the bridge, measuring the pressure and extracting a sample gas was repeated on one reactant gas mixture until several samples were taken into the sampling bulbs.

By means of the pump ( $\text{P}$ ) the sample gas once stored in ( $\text{SB}$ ) was first pumped directly into the gauge and subjected to the measurement by the gauge; then, after brought to the  $\text{P}_2 + \text{D}_2 = 2\text{PD}$  equilibrium by circulating it over the catalyst in ( $\text{C}$ ) heated near  $500^{\circ}\text{C}$ , the sample was again subjected to the similar measurement. The  $Y$  and  $(1-u)$  of the sample were readily obtained by referring the above measurements to the calibration curve preliminarily constructed.

### § 3. Result

As the catalyst is inevitably poisoned<sup>(1)(19)(20)</sup> through hydrogenation of ethylene, the effect of poisoning was investigated in the first series of the present experiment by conducting several successive runs of simultaneous measurements of  $P^{\text{H}}$ ,  $Y$  and  $Y(1-u)$ -relations, without subjecting the catalyst inbetween to any treatment except evacuation at room temperature for 1 hr., respectively at  $-25$ ,  $0$ ,  $25$ ,  $50$ ,  $100$ ,  $150$ ,  $200$  and  $300^{\circ}\text{C}$  using as much catalyst as applicable to minimize the catalyst poisoning in the first run. The result of this series

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\* ) The total pressure after evaporation was observed to exceed 20 mmHg by *ca.* 0.2 mmHg because of the low temperature of the trap during the introduction of  $\text{D}_2$ . The reaction was started with this slight excess of hydrogen.

revealed that the catalyst poisoning was so appreciable especially at higher temperatures that the rate was perceptibly depressed even from the first to the second run. In the second series several successive runs were carried out with reduced quantities of the catalyst to one tenth of the first at some of the temperatures of the first one in order to distinguish the effect of the catalyst poisoning upon the  $P^H, Y, (1-u)$ -correlation. It was thus confirmed that the catalyst poisoning resulted in an appreciable change in the  $P^H, Y$ -curves, whereas but little in the  $Y, (1-u)$ -curves.

In Tab. 1 are summarized the reaction conditions of the individual runs conducted, where each pair of figures in the first column represents a run, the former figure signifying a group of successive runs numbered by the latter figure for each group which were conducted with the same catalyst at the same temperature. The last two columns show the relative activity  $a_n$  and the degree of poisoning  $b_n$  defined as

$$a_n = - \left( \frac{dP^H}{dt} \right)_{0,n} / w$$

$$b_n = \frac{a_1 - a_n}{a_1},$$

where

$-\left(\frac{dP^H}{dt}\right)_{0,n}$  : Initial rate of hydrogenation of the  $n$ -th run,

$w$  : Weight of catalyst.

The  $a_n$  is the initial rate of hydrogenation of the  $n$ -th run per unit quantity of catalyst used, and  $b_n$  the ratio of decrease  $a_1 - a_n$  caused by  $(n-1)$  times use to  $a_1$ .

Fig. 5 (a)~(d), 6 (a)~(d) and 7 (a)~(h) show respectively the plots of  $P^H$  against the reaction time  $t$  for some representative series, those of  $P^H$  against

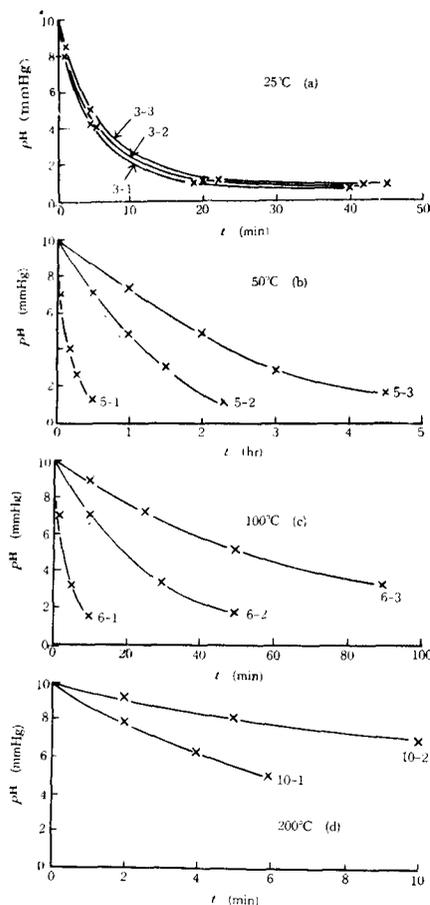


Fig. 5. The observed change of the reaction time  $t, P^H$ -relation with repeated use of the catalyst in the same reaction as in Fig. 1.

Note 1. See the notes of Fig. 1.

2. Each pair of numbers in the figure represents the run number shown in Tab. 1.

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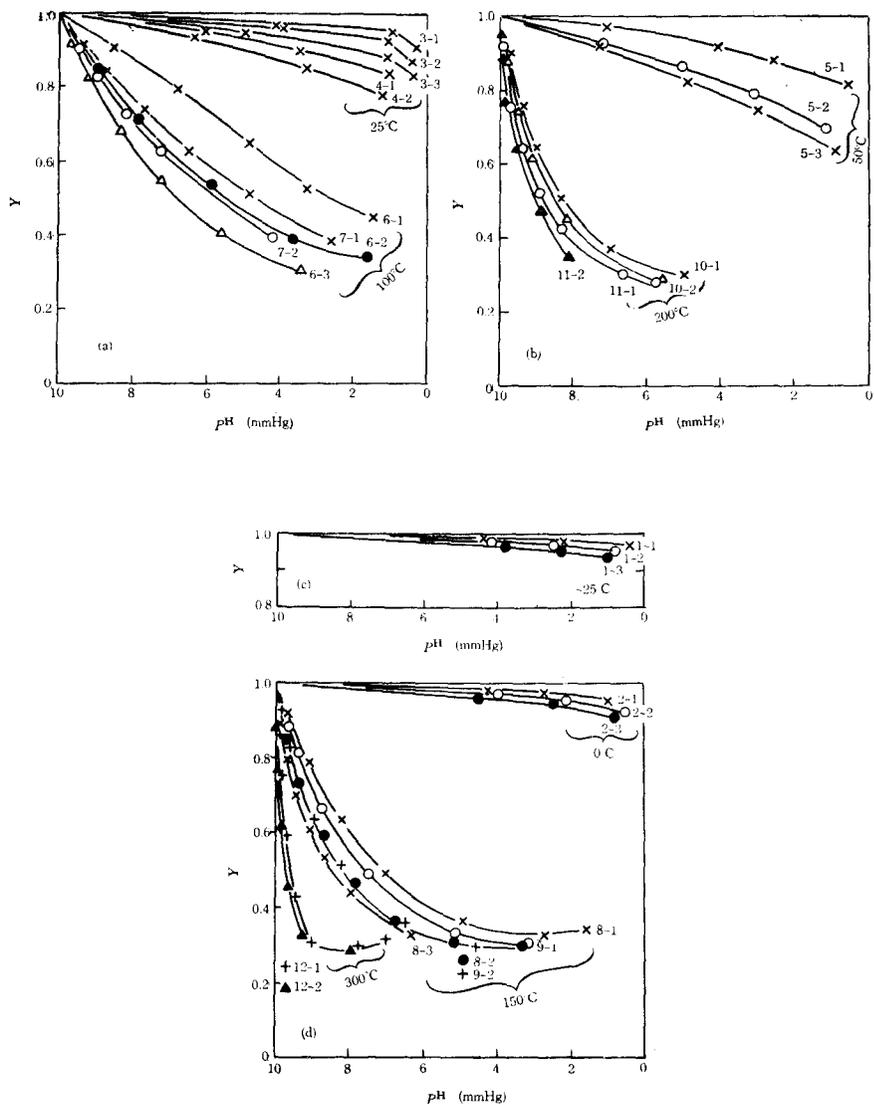


Fig. 6. The observed change of the  $P^H, Y$ -relation with repeated use of the catalyst in the same reaction as in Fig. 1.

- Note 1. See the notes of Fig. 1.  
 Note 2. See the note 2 of Fig. 5.

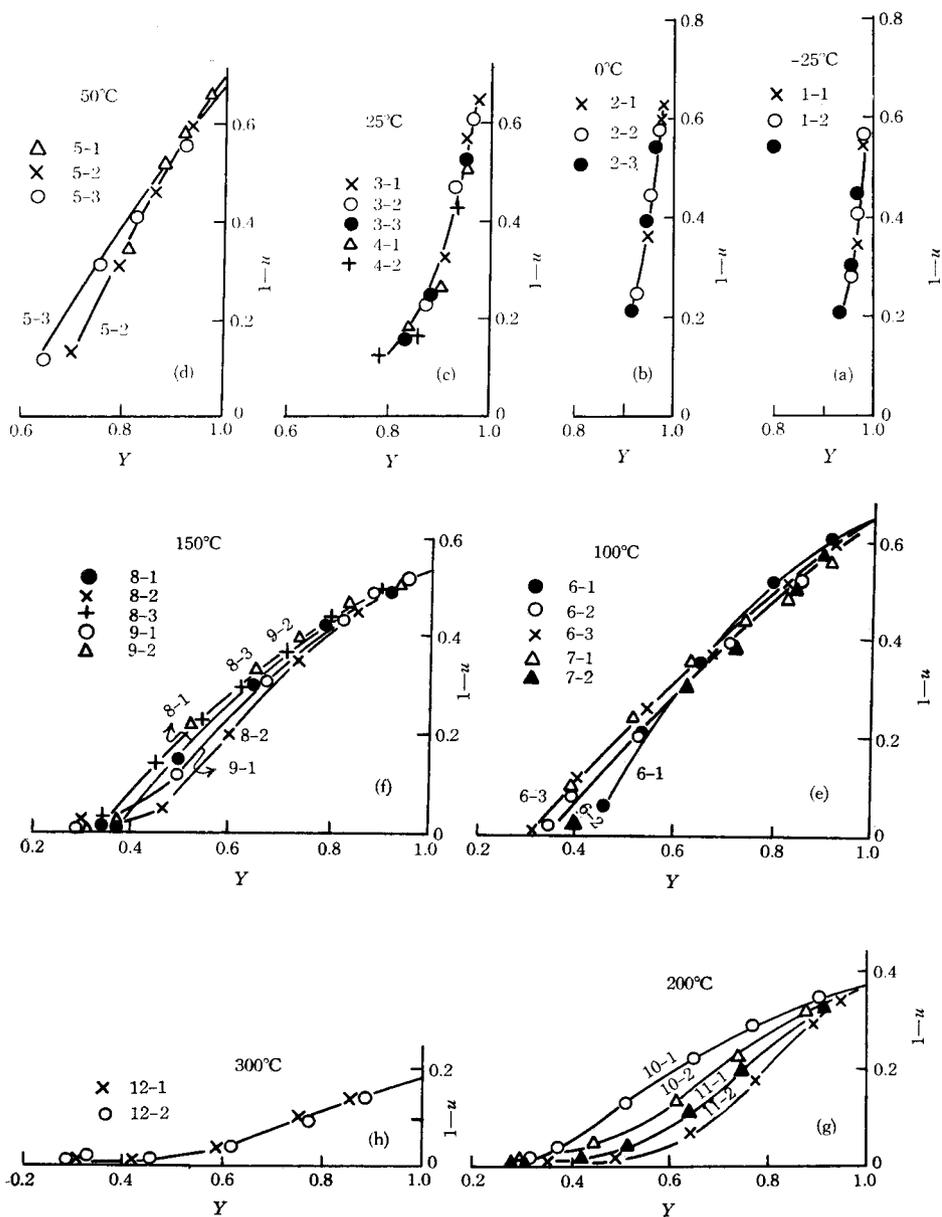


Fig. 7. The observed change of the  $Y$ ,  $(1-u)$ -relation with repeated use of the catalyst in the same reaction as in Fig. 1.

Note 1. See the notes of Fig. 1.  
 Note 2. See the note 2 of Fig. 5.

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TABLE 1. Relative activity of catalyst  $a_n$  and degree of poisoning  $b_n$  for each run conducted.

Run no.	React. temp. (°C)	React. vessel used	Catalyst used (g)	$a_n$ (mmHg/min/g)	$b_n$
1-1	-25	RV <sub>1</sub>	0.45	0.30	
1-2	"	"	"	0.264	0.12
1-3	"	"	"	0.24	0.20
2-1	0	RV <sub>1</sub>	0.45	1.67	
2-2	"	"	"	1.54	0.08
2-3	"	"	"	1.42	0.15
3-1	25	RV <sub>1</sub>	0.45	5.5	
3-2	"	"	"	5.22	0.06
3-3	"	"	"	5.0	0.10
4-1	"	RV <sub>2</sub>	0.045	4.0	
4-2	"	"	"	2.2	0.44
5-1	50	RV <sub>2</sub>	0.045	31.0	
5-2	"	"	"	2.4	0.92
5-3	"	"	"	1.1	0.96
6-1	100	RV <sub>2</sub>	0.045	49.0	
6-2	"	"	"	7.8	0.84
6-3	"	"	"	2.4	0.95
7-1	"	RV <sub>3</sub>	0.0045	14.5	
7-2	"	"	"	4.7	0.68
8-1	150	RV <sub>2</sub>	0.045	67.0	
8-2	"	"	"	22.0	0.67
8-3	"	"	"	16.0	0.76
9-1	"	RV <sub>3</sub>	0.0045	27.0	
9-2	"	"	"	11.0	0.59
10-1	200	RV <sub>2</sub>	0.045	51.0	
10-2	"	"	"	19.0	0.63
11-1	"	RV <sub>3</sub>	0.0045	15.5	
11-2	"	"	"	6.7	0.57
12-1	300	RV <sub>3</sub>	0.0045	19.1	
12-2	"	"	"	9.2	0.52

$Y$  and  $(1-u)$  against  $Y$  for all series of successive runs conducted<sup>\*</sup>).

These results are commented upon with regard to the catalyst poisoning as follows:

1) The catalyst is poisoned as seen from the change of the  $t, P^H$ -curves with repeated use of the catalyst shown in Fig. 5. The values of  $a_n$  and  $b_n$  summarized in Tab. 1, however, show that the poisoning takes place appreciably slowly at lower temperatures compared with at higher temperatures.

2) As seen from Tab. 1 and Fig. 6, the  $P^H, Y$ -curves descend appreciably with increase of poisoning over the whole temperature range of investigation, whereas the  $Y, (1-u)$ -curves not, as seen from Tab. 1 and Fig. 7, except at 200°C. These results indicate a preferential poisoning of the hydrogenation to the hydrogen exchange but none of such poisoning of the hydrogen exchange to the equilibration except at 200°C.

#### § 4. Discussion

The theoretical conclusion<sup>4)</sup> has been derived by formulating the rate of reactions of hydrogenation, hydrogen exchange and equilibration on the basis of the Associative Mechanism in terms of four characteristic functions each appropriate to a constituent elementary step of the mechanism, which implies, besides partial pressures of reactants, the relevant activation energy as a unique adjustable parameter. The numerical conclusion have thus been deduced by adjusting each activation energy of the four constituent elementary steps to the experimental results of ZUR STRASSEN<sup>8)</sup> and of TURKEVICH, SCHISLER and IRSA<sup>12)</sup>. The experimental results of ZUR STRASSEN may be taken free from poisoning to a considerable extent because of extremely low partial pressure (0.03 mmHg)

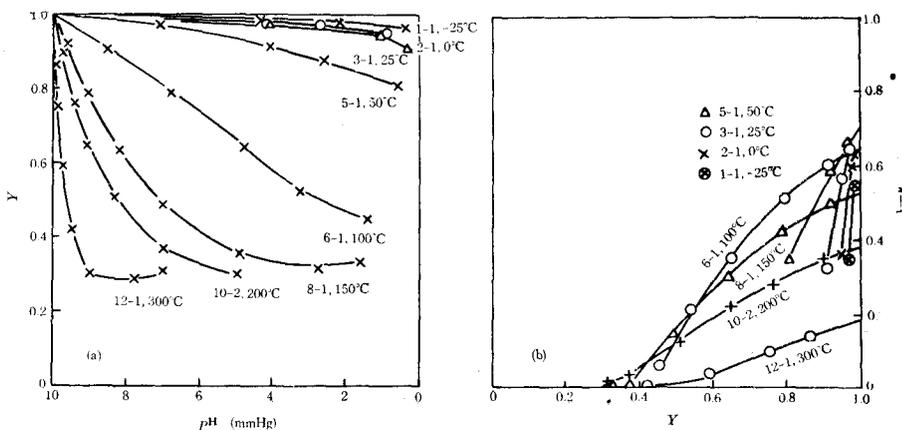
<sup>\*</sup>) Each extraction of sample gas caused a pressure depression of the reactant gas corresponding to 0.3~0.5 mmHg hydrogen partial pressure, which could not be neglected compared with the hydrogen initial pressure of 10 mmHg. The  $Y, (1-u)$ - and  $P^H, Y$ -relations unaffected by the sampling were determined as follows. It was confirmed by a series of measurements that  $t, \alpha, t, Y$ - and  $t, (1-u)$ -relations remain unchanged irrespective of samplings, where  $\alpha$  is the fraction of initial amount of hydrogen converted into ethane and  $t$  the integrated time of reaction either intermitted by samplings or not, *i.e.* by allowing  $C_2P_4$  and  $D_2$  each of 10 mmHg initial pressure to react in several runs with varying time of reaction and number of sampling in the presence of catalyst of the same initial activity. The invariant  $t, Y$ - and  $t, (1-u)$ -relations determined directly the  $Y, (1-u)$ -relation unaffected by sampling. The  $t, P^H$ -relation in the absence of sampling was now deduced from the invariant  $t, \alpha$ -relation in accordance with the relation  $\alpha = (P_0^H - P^H) / P_0^H$ , where  $P_0^H$  is the initial partial pressure of hydrogen and  $P^H$  the hydrogen pressure in the absence of sampling. The  $P^H, Y$ -relation in question was now determined from the  $t, P^H$ -relation thus obtained and the above  $t, Y$ -relation.

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of ethylene, while those of TURKEVICH *et al.* similarly in effect because of the initial relative rates of evolution of deuterioethylenes and deuterioethanes particularly availed for the adjustment. The theoretical conclusion must in consequence duly be compared with the experimental results free from catalyst poisoning.

The observed  $Y, (1-u)$ -relation has been found remarkably insensitive to poison as stated in 2) above, which may in consequence be taken a suitable material for comparison except 200°C. At any rate, the result with the catalyst of the highest activity may reasonably be taken the material free from poison at its best.

Fig. 8 shows those curves observed at the highest activity of catalyst each at the temperature of investigation. Nearly quantitative coincidence of the curves in Fig. 8 with those in Fig. 1 provides a further verification of the Associative Mechanism. The present result of experiment disproves besides the other two mechanisms, *i. e.* the TWIGG and RIDEAL'S<sup>11)</sup> and the TWIGG'S<sup>16)</sup>, contradicting the constant linear relation between  $Y$  and  $(1-u)$ , on which they are based.



**Fig. 8.** The  $P^H, Y$ - and  $Y, (1-u)$ -curves obtained at the highest activity of catalyst at each reaction temperature of investigation.

- Note 1. See the notes of Fig. 1.  
2. See the note 2 of Fig. 5.

It is remarkable that the catalyst poisoning exerts different effects on the rate of hydrogenation on the one hand and on that of exchange and equilibration on the other hand or there exists some sort of selective poisoning even in this apparently simple case of catalyzed interaction between ethylene and deuterium, which requires further investigation for elucidation.

### Summary

Experimental examination has been made of a theoretical conclusion<sup>4)</sup> from the statistical mechanical theory of the HORIUTI and POLANYI's Associative Mechanism<sup>1)</sup> on the simultaneous changes of the hydrogen partial pressure  $P^H$ , the deuterium atomic fraction  $Y$  in hydrogen and the non-equilibrium fraction  $(1-u)$  of the hydrogen during the progress of the interaction in the presence of nickel catalyst between light ethylene and deuterium each of 10 mmHg initial partial pressure.

Simultaneous measurements were conducted of  $P^H$ ,  $Y$  and  $(1-u)$  as well as of the catalyst activity during the progress of the above-mentioned reaction over the temperature range of  $-25\sim 300^\circ\text{C}$  on a highly active nickel wire catalyst obtained by repetition of oxidation at  $600^\circ\text{C}$  and reduction at  $300^\circ\text{C}$ .

The result was that the  $Y$ ,  $(1-u)$ -relation was observed nearly in quantitative agreement with the theoretical conclusion almost irrespective of the catalyst poisoning, while the  $P^H$ ,  $Y$ -relation, more or less affected by the catalyst poisoning, approached semiquantitatively to the theoretical conclusion with decreasing extent of the catalyst poisoning.

Thus the theoretical conclusion from the Associative Mechanism has on the one hand been verified, and on the other hand both the mechanism of TWIGG and RIDEAL<sup>11)</sup> and that of TWIGG<sup>10)</sup> disproved by the observed non-fulfillment of the constant linear relation independent of temperature between  $Y$  and  $(1-u)$ , on which they are based.

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