THE KINETICS OF THE CATALYTIC HYDROGENATION OF ETHYLENE WITH NICKEL. [1]*

By Osamu Toyama.

The kinetics of the catalytic combination of ethylene and hydrogen has long been a subject of investigation for the elucidation of the mechanism of the catalytic hydrogenation of an unsaturated organic compound, and various results have been obtained. The results gained at high temperatures are relatively in good agreement; and this may be attributed to the fact that the expression of the kinetics at high temperatures resembles that of a homogeneous reaction. Therefore, it is at low temperatures that various characteristics of heterogeneous reactions manifest themselves. From this point of view, the author investigated the reaction kinetics under various experimental conditions below 0°C., using reduced nickel.

Experimental.

Materials.

Ethylene was prepared from ethyl alcohol and pyrophosphoric acid principally by the method of Moser and Lindinger,[1] but with some improvement, and it was condensed with liquid air, and then fractionated several times before use.

Ethane was obtained by the hydrogenation of ethylene with nickel in excess of hydrogen, and condensed with liquid air, and then purified by fractional distillation.

Hydrogen was obtained from cylinder supply of electrolytic hydrogen and purified with heated platinum-asbestos as usual.

The catalyst used was prepared by the reduction of the oxide obtained by the calcination at 400°C. of pure nitrate. The reduction was performed for about ten hours in such a high temperature range from 450° to 500°C. to stabilize the catalytic activity.

Apparatus and procedure.

The rate of reaction was measured statically, first at constant volume, and then at constant pressure of one reactant. The reaction chamber, the volume of which was about 65 c.c. including the capillary side tubes, was attached to a spring manometer as shown in Fig. 1. The measurements at constant pressure of one reactant were carried out by keeping the total pressure always constant by continuous supply of the reactant, the rate of reaction being measured

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* This paper is the revised English translation of the same article in *Rev. Phys. Chem. Japan*, 9, 119 (1935).

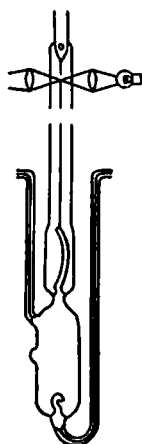1) Moser and Lindinger, *Monatsh.*, 44, 141 (1923).

Fig. 1.
The reaction
chamber with
a spring
manometer.

in the volume of the gas supplied, which was stored in a gas burette in a thermostat.

The catalyst was prepared in the reaction chamber by reduction of the required quantity of the oxide. A few milligrams of nickel oxide were sufficient for the measurement at $0°C.$, but it required more than ten-fold quantity to obtain a suitable reaction rate at $-78°C.$ The pressure change due to the adsorption on the catalyst was confirmed to be small enough compared with that due to the reaction. It was found that the final pressure of the reaction always coincided with the theoretical value within the experimental error[2].

The reaction temperatures were $0°$, $-33°$ and $-78°C.$, using ice, liquid ammonia, and dry ice respectively. For the reduction and degassing of the catalyst, an electric furnace was used. As the activity of the catalyst was decreased by heating in the presence of ethylene, the reaction chamber was washed with hydrogen after each measurement and evacuated at $100°C.$ for three or four hours. The catalyst was protected from any poisonous vapour, such as water or grease vapour, by means of a trap immersed in dry ice and alcohol.

Experimental Results.

The stability of the catalytic activity.—The catalyst which was prepared by prolonged reduction of the oxide at lower temperatures than $300°C.$ was found to be very active, but was so unstable that reproducible results were not obtained with such a catalyst. When the reduction was carried out at higher temperatures $(450°—500°C.)$, far better reproducibility were found except directly after the reduction. Some examples are shown in Table I, in which t_{50} means the time of half-change.

Table I.

Reac. temp.$=0°C.$　　Catalyst I. (0.005g., reduced at $490°C.$)

Expt. no.	Initial partial press. (mm.)		Final total press.(mm.)	t_{50} (min.)	Expt. no.	Initial partial press. (mm.)		Final total press.(mm.)	t_{50} (min.)
	H_2	C_2H_4				H_2	C_2H_4		
1	102.8	103.5	104.1	42.1	5	101.3	100.1	101.1	43.2
2	102.0	101.3	103.2	41.9	6	101.1	102.5	103.3	43.4
3	104.7	104.0	105.0	42.5	7	103.5	101.9	104.2	44.0
4	101.5	100.8	101.9	43.0					

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2) The product of the reaction was not analysed, for it has been generally recognized since Sabatier reported that ethylene was completely hydrogenated to ethane without any side reaction at low temperatures. Taylor and his coworkers (*J. Am. Chem. So*., **59**, 1103 (1937)) have lately reported that ethylene is slowly polymerized by nickel at room temperature, but hydrogenated entirely to ethane in the presence of hydrogen.

The effect of pretreatment of the catalyst.—The catalyst was kept in contact with ethylene or hydrogen for some time; after this pretreatment the reaction chamber was evacuated rapidly for a short time and a mixture of the reactants admitted and then the rate of reaction measured. The results obtained were compared with those of the standard reaction obtained after full evacuation. When a small quantity of the catalyst was used and so the reaction was not rapid, no great influence of the pretreatment upon the reaction observed. But in case a large quantity of the catalyst was used and so the reaction was rapid, some appreciable influence of the pretreatment was noticed in the initial stage of the reaction as shown in Fig. 2. The pretreatment with ethylene reduced the initial rate of reaction; while that with hydrogen increased it; that with-ethane had, in practice, no influence.

The concentration of the reactants and the reaction rate.— The results of the experiments carried out at constant volume at 0°C. are given in Table II, and Figs. 3 and 4, an example of the pressure reading in Table III.
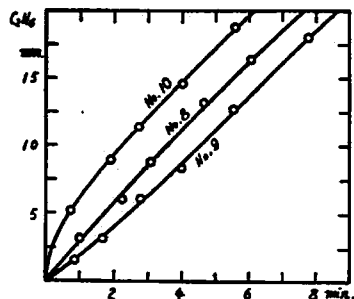

Fig. 2.

The effect of the pretreatment of the catalyst: no. 8, without any pretreatment; no. 9, pretreated with ethylene; no. 10, pretreated with hydrogen. Composition of gas mixture, 5 cm. H_2 + 5 cm. C_2H_4. Catalyst II (0.01 g., reduced at 450°C.). Reac. temp., 0°C.

Table II.

Reac. temp.=0°C.   Catalyst III. (0.003g., reduced at 480°C.)

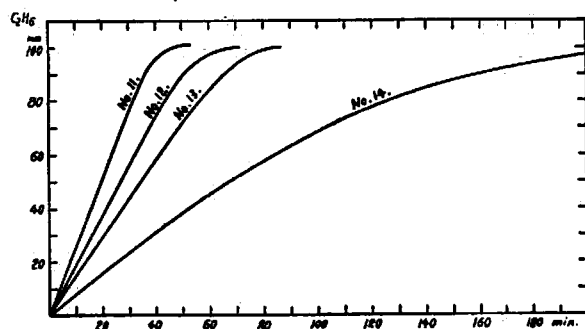| Expt. no.	Intial Partial press. (mm.)		Final total press.(mm.)	t_{50} (min.)	Expt. no.	Initial partial press. (mm.)		Final total press.(mm.)	t_{50} (min.)
	H_2	C_2H_4				H_2	C_2H_4		
11	397.5	101.4	398.0	19.8	15	101.1	203.3	204.5	81.9
12	301.3	100.8	302.0	27.2	16	102.0	299.8	300.5	99.9
13	209.1	99.9	208.9	34.0	17	100.5	401.2	401.9	124.1
14	105.6	107.3	108.4	71.5					

Fig. 3.

Expts. at constant volume, initial pressure of hydrogen being varied; reac. temp., 0°C.
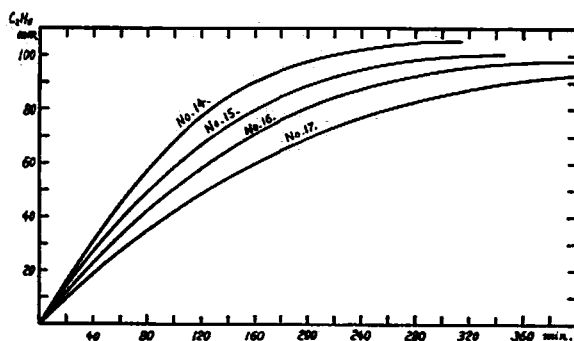
Fig. 4.

Expts. at constant volume, initial pressure of ethylene
being varied; reac. temp., 0°C.

Table III.

Expt. No. 14.

Time (min.)	Press. (mm.)	C$_2$H$_6$ (mm.)	Time (min.)	Press. (mm.)	C$_2$H$_6$ (mm.)
0	212.9	0	107.3	140.5	72.4
4.3	209.4	3.5	120.9	134.8	78.1
6.1	207.9	5.0	125.4	133.1	79.8
10.4	204.6	8.3	134.0	130.1	82.8
16.4	199.8	13.1	140.5	126.9	86.0
19.7	197.1	15.8	146.1	126.2	86.7
23.9	193.9	19.0	150.2	125.0	87.9
30.4	188.9	24.0	156.9	123.7	89.2
33.7	186.5	26.4	167.6	120.8	92.1
39.5	182.0	30.9	182.8	118.0	94.9
47.3	176.8	36.1	199.4	115.4	97.5
53.1	172.2	40.7	211	113.8	99.1
64.5	164.7	48.2	224	112.0	100.9
77.2	156.7	56.2	241.5	110.9	102.0
83.4	153.0	59.9	250	110.0	102.9
98.0	144.9	68.0	final	108.4	104.5

These curves in Figs. 3 and 4 clearly indicate that the reaction rate is
influenced mainly by the pressure change of hydrogen and accelerated considerably
when hydrogen pressure is raised, while
the pressure increase of ethylene retards
the reaction to some extent. The reaction
is nearly of the zero order when hydro-
gen is in excess and tends to be of the
first order with respect to hydrogen when
ethylene is in excess, although an exact
first order relation does not exist even in
Expt. 17, as shown in Table IV.

Table IV.

Expt. No. 17.

t (min.)	x (mm.)	k_m ×0.4343×10^4
20	9.5	21.6
40	18.8	22.5
60	27.2	22.8
100	42.0	23.5
200	69.3	25.4
300	85.2	27.2
400	92.9	28.0

From the general picture of the above obtained relation between the rate of the reaction and the pressures of the reactants, it is apparent that the course of the reaction at constant volume is determined by the difference of two contrary effects, i. e., the velocity decrease due to the pressure decrease of hydrogen and the velocity increase due to the pressure decrease of ethylene.   This fact gives rise to complexity in the reaction curves.   This complexity resulting from simultaneous change of the pressures of both reactants, however, could be avoided when the pressure of either reactant is kept constant during the reaction

A typical result obtained at constant hydrogen pressure is given in Table V

Table V.

Expt. No. 23. Catalyst V. (0.006g., reduced at 500°C.)

Time (min.)	H_2 in the burette (cc.)	C_2H_6 (cc.)
0	48.64 (calcd.)	0
3.3	46.73	1.91
5.9	45.29	3.35
8.3	43.72	4.92
11.1	41.95	6.69
15.3	39.41	9.23
19.6	36.30	12.34
21.2	35.32	13.32
24.1	33.08	15.56
27.9	30.45	18.19
31.0	28.27	20.37
34.3	25.70	22.94
38.9	22.32	26.32
43.3	18.92	29.72
49.7	14.95	33.69
52.1	14.24	34.40
55.5	13.86	34.78·
58.8	13.81	34.83
61.4	13.64	35.00
final	13.54	35.10

and Fig. 5, and one at constant ethylene pressure in Fig. 6. As expected, at constant hydrogen pressure the reaction is always slightly accelerated as it proceeds, while at constant ethylene pressure the rate is only reduced as hydrogen is consumed.   In the latter, the reaction rate becomes nearly proportional to hydrogen pressure when ethylene pressure is high, as given in Table VI.
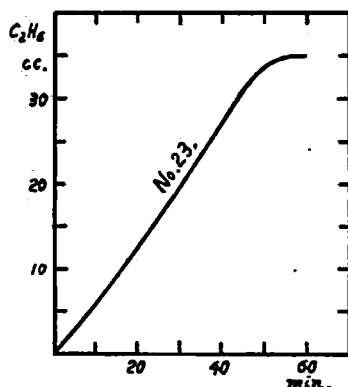
Fig. 5.

Expt. at constant pressure of hydrogen;
reac. temp., 0°C.; catalyst V (0.006 g.,
reduced at 500°C.); H_2, 101.4 mm.; C_2H_4,
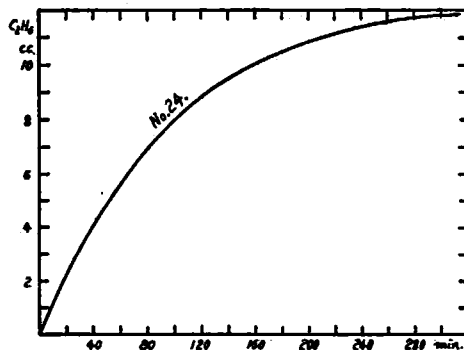113.9 mm.; gas vol. in c.c. at 10.5°C.
(temp. of gas burette).

Fig. 6.

Expt. at constant pressure of ethylene; reac.
temp., 0°C.; catalyst V; H_2, 102.3 mm; C_2H_4,
467.6 mm; gas vol. in c.c. at 10.5°C.

Table VI.

Exp. No. 24.

t (min.)	x′ (cc.)	k′$_m$ ×0.4343×10^4
10	1.13	43.2
20	2.22	44.6
40	4.00	44.3
60	5.60	45.8
80	6.89	46.4
100	7.95	47.6
150	9.77	49.4
200	10.82	51.4

The effect of the reaction product.—
Ethane was initially added to the mixture
of the reactants and the rate of reaction
measured was compared with that without
ethane. The results obtained are given in
Table VII, from which one may conclude
that ethane has practically no influence on
the rate of reaction.

The effect of temperature.— The
measurement was carried out at −78°C.,
and the nature of the reaction, as a whole, proved to be unaltered as shown in

Table VII.

Reac. temp.=0°C.   Catalyst IV (0.0035g., reduced at 480°C.)

Expt. no.	Initial partial press. (mm.)			Final total press. (mm.)	t$_{50}$ (min.)
	H_2	C_2H_4	C_2H_6		
18	121.3	122.1	——	122.5	53.3
19	123.4	123.9	20.6	124.3	54.1
20	120.9	122.1	106.3	122.8	54.5
21	124.0	123.2	193.8	124.5	55.2
22	120.4	121.0	——	121.1	54.3

Fig. 7. But the maximum rate of the reaction at constant hydrogen pressure
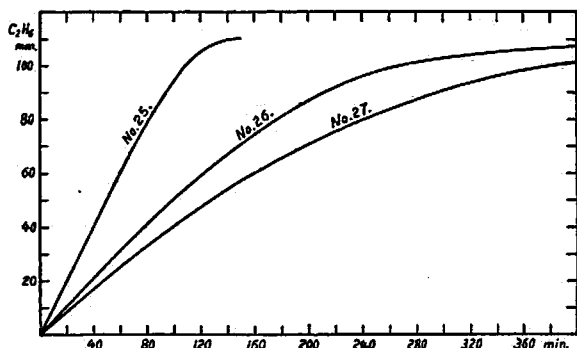now manifests itself clearer as shown in Fig. 8,

Fig. 7.

Expts. at constant volume at —78°C.: no. 25, 3 H₂:
1C₂H₄; no. 26, 1 H₂: 1 C₂H₄; no. 27, 1 H₂: 3 C₂H₄;
catalyst VI (0.041g., reduced at 480°C.)
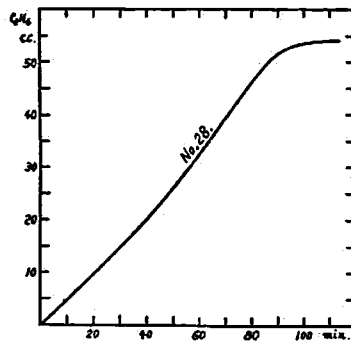
Fig. 8.

Expt. at constant pressure of
hydrogen at —78°C.: H₂, 95.0
mm.; C₂H₄, 122.2 mm.; gas
vol. in c.c. at 19.9°C.

The temperature coefficient of the reaction rate was calculated from the initial linear part of the reaction curve obtained at constant volume and the heat of activation was about 6 kcal. The results obtained are given in Table VIII.

Table VIII.

Catalyst	Reac. temp. (°K.)	Initial press. (mm., 0°C.)		Reac. vel. $\left(\dfrac{mm.}{min.}, \ 0°C.\right)$	Heat of activation (Kcal.)
		H₂	C₂H₄		
IV. (0.0035g., reduced at 480°C.)	273	361.5	120.3	2.55	6.1
	240	366.2	128.1	0.53	
VII. (0.021g., reduced at 490°C.)	240	413.1	136.5	2.16	6.5
	195	429.8	140.1	0.43	

Discussion.

The mechanism of the reaction. —Taylor and his coworkers[3] explained the photochemical combination of hydrogen and ethylene sensitized with mercury vapour by a chain mechanism. Bennewitz and Neumann[4] assumed the same mechanism in the catalytic combination with platinum. But such a mechanism seems inapplicable to a catalytic reaction below 0°C. since the chain length may be short and the desorption of the hydrogen atom from a metallic catalyst should require energy greater than 40 kcal[5]. Foresti,[6] on the other hand, succeeded to obtain

3) Taylor and Marshall, *J. Phys. Chem.*, 29, 1140 (1925); Taylor and Hill, *J. Am. Chem. Soc.*, 51, 2922 (1929).

4) Bennewitz and Neumann, *Z. physik. Chem.* (B), 7, 273 (1930); 17, 457 (1932).

5) Polanyi, *Z. Elektrochem.*, 35, 526 (1929); Lennard-Jones, *Trans. Farad. Soc.*, 28, 343 (1932).

6) Foresti, *Ateneo Parmense*, 4, 401 (1932); *Chem. Abstract*, 28, 3292 (1934).

the majority of the reaction heat directly on the surface of a catalyst, so that any chain mechanism in the gas phase seems to be inappropriate.

Treating the reaction as one of the ordinary adsorption catalysis, there are still two alternative mechanisms; (A) both reactants adsorbed on the catalyst react, and (B) one reactant adsorbed reacts on the other in the gas phase colliding with it. The retarding effect of ethylene observed experimentally must be due to the fact that the adsorption of ethylene disturbs that of hydrogen. Consequently, it is apparent that both ethylene and hydrogen are adsorbed on the active surface of the catalyst. Therefore, the mechanism (B) will be improbable since there is no evidence that adsorbed ethylene cannot react. In fact Schüster[7] reported that as to active carbon the adsorbed ethylene reacted on the adsorbed hydrogen. It is, therefore, supposed that the reaction takes place according to the mechanism (A). Accordingly, the whole reaction proceeds consecutively as follows: (1) Supply of the reactants in the gas phase to the catalyst surface, (2) adsorption of the reactants, (3) combination of the adsorbed reactants on the surface, (4) desorption of the product, (5) transport of the product away from the catalyst. The rate of reaction should be determined by the slowest of these processes. The last two can not be regarded as the slowest processes, for the reaction is not retarded by the product. The rate of the first process can be neglected from the following consideration. If the supply of one reactant in the gas phase to the catalyst is the slowest process, the rate of reaction will be proportional to the pressure of the reactant and to the area of the active surface left free on the catalyst. When the pressure of the other reactant is constant, the area left free will increase or be constant according as the adsorption equilibrium is disturbed by the reaction or not. Hence, it may be expected that the apparent order of reaction $\geq$ 1. It is evident, however, from the experimental results that these relation do not exist. Finally there remain the rate of the surface reaction and that of the adsorption. If the so-called activated adsorption is concerned with the catalytic reaction as suggested by H. S. Taylor, it may be possible that the adsorption process becomes slower, since it has been frequently reported that the activation energy of such an adsorption is considerably high. The experimental results in Fig. 2, however, show that the pretreatment of the catalyst with reactants affects only the initial rate of the reaction.

Hence, it may be concluded that the rate of reaction is slower than that of adsorption, that is, (3), the surface reaction, is the rate-determining step of the whole reaction. Therefore, the rate of reaction is proportional to the product of

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7) Schuster, Z. *Physik. Chem.* (B), 14, 249 (1931).

the concentrations of both reactants adsorbed. The experimentally observed facts that the rate of reaction is chiefly controlled by the concentration of the adsorbed hydrogen, so that it is accelerated by the pressure increase of hydrogen and retarded by that of ethylene indicate that the adsorption of hydrogen is weak and depressed more in the presence of ethylene which is strongly adsorbed. No influence of ethane, the product, upon the rate of reaction shows that the life of ethane on the active surface of the catalyst is negligibly short.

The rate of reaction.—From the above consideration, the observed rate of reaction is given by the equation :

$$\frac{dx}{dt} = k\, c_H c_E, \tag{1}$$

where c_H and c_E are the surface concentrations of hydrogen and ethylene respectively. Assuming that the adsorption equilibria are not so disturbed by the reaction, the surface concentrations of the adsorbed reactants may be represented by Langmuir's isotherm whose applicability to catalysis has generally been recognised. Since the adsorption of the reaction product is negligible, only the adsorptions of two reactants are to be considered, provided that they repel each other on the active surface of the catalyst. The resulting expressions for the surface cencentrations are

$$c_H \infty \frac{P_H}{1 + a P_H + \beta P_E}, \qquad c_E \infty \frac{P_E}{1 + a P_H + \beta P_E}, \tag{2}$$

where P_H and P_E are the pressures of hydrogen and ethylene in the gas phase, a and β the adsorption coefficients respectively. Hence, the rate of reaction is given by

$$\frac{dx}{dt} = k \frac{P_H P_E}{(1 + a P_H + \beta P_E)^2}\ ^{[8]}. \tag{3}$$

It is easy to show that equation (3) is able to represent the general nature of the reaction satisfactorily : if v_0 reperesents the initial rate at constant volume,

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[8] This equation is further simplified to

$$\frac{dx}{dt} = k_1 \frac{P_H}{P_E}$$

when $\beta P_H \gg 1 + a P_H$, and to

$$\frac{dx}{dt} = k_2 P_H$$

when $a P_H \ll 1 + \beta P_E$ and $P_E = $const. These simplified forms, however, do not agree with the results obtained, and so such approximations must be given up.

and a and b the initial pressures of hydrogen and ethylene respectively, then it follows from equation (3) that

$$v_0 = k\frac{ab}{(1+\alpha a+\beta b)^2}.$$

Therefore

$$\frac{\partial v_0}{\partial a} = k\frac{b(1-2a+\beta b)}{(1+\alpha a+\beta b)^3}.$$

Thus $\partial v_0/\partial a \gtrless 0$ according to $1+\beta b \gtrless \alpha a$.

Similarily,

$$\frac{\partial v_0}{\partial b} = k\frac{a(1+\alpha a-\beta b)}{(1+\alpha a+\beta b)^3},$$

so that $\partial v_0/\partial b \gtrless 0$ according to $1+\alpha a \gtrless \beta b$. Now it may be assumed that the relation $1+\alpha a < \beta b$ holds inasmuch as the adsorption of ethylene is far stronger. Then we have

$$\frac{\partial v_0}{\partial a} > 0 \quad \text{and} \quad \frac{\partial v_0}{\partial b} < 0.$$

These relation are what were experimentally obtained.

At constant pressure of hydrogen, equation (3) becomes

$$\frac{dx}{dt} = v = k\frac{ap_E}{(1+\alpha a+\beta b)^2}.$$

Therefore

$$\frac{dv}{dP_E} = k\frac{a(1+\alpha a-\beta P_E)}{(1+\alpha a+\beta b)^3}.$$

If $1+\alpha a < \beta b$ again, the rate of reaction increases as the reaction proceeds, until the maximum rate is attained at $p_E = \dfrac{1+\alpha a}{\beta}$.

Similarily at constant pressure of ethylene the rate is given by

$$\frac{dx}{dt} = v = k\frac{bp_H}{(1+\alpha a+\beta b)^2}.$$

Accordingly

$$\frac{dv}{dP_H} = k\frac{b(1-\alpha P_H+\beta b)}{(1+\alpha a+\beta b)^3}.$$

The rate only decreases to the end when $1+\alpha a < \beta b$, and approximately does in proportion to hydrogen pressure in case ethylene pressure is high. All the characteristics of the reaction can be thus satisfactorily explained.

It is, however, difficult to analyse each reaction curve precisely by equation (3), because it holds more or less approximately. Therefore the applicability of the equation was examined as follows: at constant volume equation (3) may be written as

$$v = k \frac{(a-x)(b-x)}{\{1 + \alpha(a-x) + \beta(b-x)\}^2}. \tag{3'}$$

Putting

$$C = \frac{1 + \alpha a + \beta b}{\alpha + \beta},$$

$$K = \frac{\sqrt{k}}{\alpha + \beta},$$

and

$$y = \sqrt{\frac{(a-x)(b-x)}{v}},$$

the equation becomes

$$C - x = Ky. \tag{4}$$

Further, the linear relation between x and y was examined. The values of the tangents for the reaction curves were plotted for x, and v corresponding to any value of x was interpolated. As shown in Fig. 9 the linear relation is on the whole satisfactory and the curves run nearly parallel with each other as required by the formula. But the adsorption coefficients calculated from these curves were not constant.

The relation analogous to equation (4) was also examined for the reaction at
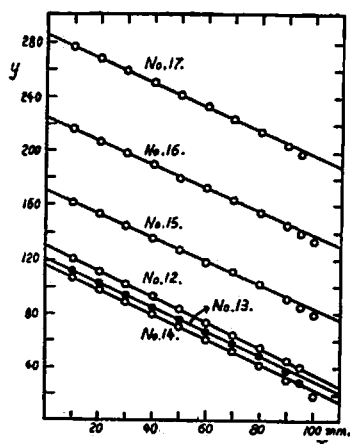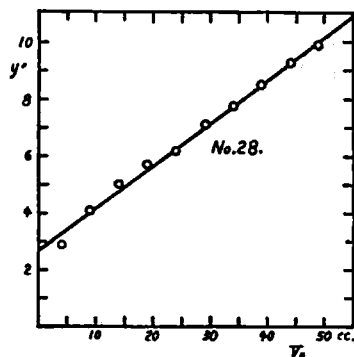

Fig. 9.

Expts. at constant volume at 0°C.

Fig. 10.

Expt. at constant pressure of hydrogen at −78°C. $V_{\rm E}$, vol. of C_2H_4 in reac. vessel at any instant, measured in c.c. at temp. of gas burette; $y' = \sqrt{V_{\rm E}/v}$, v being measured in c.c. similarily.

constant pressure with similar results, one of which being shown in Fig. 10.

Comparison with other experimental results.— It has been often reported that the reaction at low temperatures was simply of the zero or first order with

respect to hydrogen. The results obtained in the present work, however, show that the matter is not so simple.

Of the experiments carried out with nickel catalyst, that of zur Strassen[9] is the most analogous to the present work. The results obtained, however, do not evidently coincide : zur Strassen observed that the rate of reaction was proportional only to the pressure of hydrogen, being uninfluenced by ethylene in the temperature range from $-9°$ to $45°C$. Although from what this difference results is not clear at present, it may be pointed out that the experimental conditions were not the same in both cases, i.e. zur Strassen worked at far lower pressures, using a wire catalyst.

The work by Pease[10] with copper catalyst appears rather comparable with the present one, inasmuch as he found that ethylene in excess inhibited the reaction to some extent at low temperatures ($0°\sim20°C.$).

Some investigators have lately discussed the reaction mechanism from the comparison between the reaction rate with deuterium and that with hydrogen. For example, Farkas, Farkas and Rideal[11] have observed that the reaction is of the zero order at low temperature ($20°C.$), the reaction rate being the same both with deuterium and with hydrogen, and concluded that the rate of evaporation of ethylene determines that of reaction. It can not be mentioned, however, that their experimental results are decisive for the conclusion. For the fact that hydrogen reacts faster than deuterium in the similar temperature range has been observed by Tucholsky and Rideal[12] with a nickel catalyst, and by Wheeler and Pease[13] with copper catalyst.

Summary.

1) The kinetics of the catalytic hydrogenation of ethylene has been investigated statically in the low temperature range ($-73°\sim0°C.$) in the presence of nickel catalyst reduced from the oxide. The rate of reaction has been measured first at constant volume and then at constant pressure of one of the reactants.

2) The initial rate of reaction is accelerated by the hydrogen adsorbed on the catalyst prior to the reaction, while it is retarded by the ethylene similarily adsorbed ; and it is unaffected by the ethane similarily adsorbed.

9) zur Strassen, Z. physik. Chem., (A), 169, 81 (1934).
10) Pease, J. Am. Chem. Soc., 45, 1196, (1923).
11) Farkas, Farkas and Rideal, Proc. Roy. Soc., (A), 146, 630 (1934).
12) Tucholsky and Rideal, J. Chem. Soc., 1701. (1935)
13) Wheeler and Pease, J. Am. Chem. Soc., 58, 1665 (1936).

3) The course of the reaction is mainly controlled by the hydrogen pressure, while ethylene retards the reaction to some extent. Ethane, not only produced in the reaction but also added to the mixture of reactants, has no influence on the reaction rate.

4) The general nature of the reaction remains unchanged when the temperature of reaction has been varied from $0°$ to $-78°C$. The apparent energy of activation has been found to be about 6 kcal.

5) As to the reaction mechanism, the reaction takes place between both reactants adsorbed on the active surface of the catalyst; the surface combination of the reactants is the rate-determining step of all the processes involved; hence the reaction rate is proportional to the product of the concentrations of the reactants adsorbed, but chiefly controlled by that of hydrogen, inasmuch as its adsorption is small and diminished by the presence of ethylene which is more strongly adsorbed. Ethane leaves the active surface as soon as it is produced, and does not disturb the reaction.

6) Langmuir's isotherm applied to the concentrations of the reactants adsorbed leads to an expression for the rate of reaction which explains the experimental results satisfactorily well.

7) The results in the present work have been compared with those of other investigators and discussed.

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