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ADSORPTION AND DECOMPOSITION OF ETHYLENE ON NICKEL*)

By

Sanjuro MATSUSHITA**)

(Received Jan. 8, 1962)

To a vacuum system of 600 cc capacity which contained about 0.4 g reduced nickel kept at
140°C a small amount of ethylene was admitted, the subsequent pressure change being followed
by a McLeod gauge. The fact was found that the gas of the initial pressure below 0.35 mm Hg
always exhibits a monotonic decrease of pressure to attain a constant value, but that, when
the gas is admitted in an amount of about 0.5-mm Hg initial pressure, the pressure once de-
creased increases again remarkably to give a pressure-time curve having a sharp minimum
within the first 10 minutes. A combustion analysis indicated that the increased pressure was
due to ethane. Based on an assumption that ethane is produced from adsorbed ethylene
molecules forming a group on the catalyst surface (consisting of molecules of the order of 15
in number), the differential equations expressing the pressure change then to be resulted were
set up. The initial gas pressure actually employed being given as the initial condition, solution
of the equations produced the two types of pressure-time curves in good agreement with the
observed ones. It was inferred from the equations that the gas of an initial pressure as high
as 10 mm Hg should show again a monotonic decrease of pressure under occurrence of ethane
formation, which was verified by the experiment. From the rate constants used in the equations
the reaction rates are discussed.

INTRODUCTION

The adsorption of ethylene on nickel has been a puzzling problem. Hitherto,
many workers made observations on this system, but in the region higher than
0°C in temperature and higher than $10^{-1}$ mm Hg in pressure reliable adsorption
equilibria have never been attained1-9. JENKINS and RIDEAL5 worked at 20°C
and reported that when the gas amount supplied was small the gas was completely
adsorbed and when the amount was increased to a certain extent only ethane
was detected in the gas phase.

The present author observed this adsorption on reduced nickel at 140°C by
following the pressure variation due to its progress in a system of constant
volume. It was found that remarkably different types of pressure vs. time
curves are obtained only by changing the gas amount to employ within a narrow
range. These curves seem to give a suggestion as to the behavior of ethylene

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on nickel. The observed facts and the results of attempted analysis of them will be reported in this paper.

I. EXPERIMENT

Experimental

The apparatus used is shown in Fig. 1. The reaction bulb R contained nickel catalyst, which was prepared in this place by reducing 0.5 g of nickel oxide with hydrogen. The bulb was kept at a constant temperature by an autoregulated electric furnace, with an accuracy of ±1°C during the catalyst reduction and, with special care, of almost ±0.2°C during the measurement. The trap T was cooled directly with liquid air or at ca. −120°C according as the gas to be admitted was hydrogen or ethylene, the latter temperature being obtained by means of indirect cooling using a copper jacket*); once the reduction was begun, the catalyst had never been exposed to the vapors of cock grease and mercury throughout all the period of experiment. Pressure was read by the McLeod gauge M or by the manometer M'. The sample gas and hydrogen for reduction were reserved in the flasks E and H. The volume of the vacuum system from the reaction bulb R to the cock b, including the McLeod gauge, was ca. 600 cc. The right-hand part of the system from the cock d was added for gas analysis, of which the description will be given later.

The reduction of the catalyst was carried out at 350°C, in which the statical method was used but the hydrogen was frequently pumped off and renewed. It was continued for some twenty days until resulting moisture became

* The trap temperature was continually watched with a thermocouple attached to the wall.
no more detectable in the "test with liquid air"*). When the reduction was complete, the bulb was evacuated at the same temperature for several hours to attain the vacuum of $10^{-4}$ mm Hg.

In beginning the measurement, first an amount of ethylene was taken in the part of the system confined by the cocks a and b, and its pressure was read. By turning the cock a the gas was allowed to expand to the catalyst bulb, and the subsequent pressure variation was followed by the McLeod gauge (by the manometer in a few cases). Correct values of pressure near the Knudsen range were determined by the use of a calibration curve which was prepared through preliminary blank tests.

When a run of the observation was finished, the catalyst was evacuated at the same temperature $140^\circ$C, and then hydrogen was temporarily introduced in order to wash out adhering ethylene, final evacuation being made under elevating the temperature to $250^\circ$C. Since ethylene on nickel is possible to decompose and to leave some residue, for the purpose of cleaning, the catalyst was again subjected to the reduction with hydrogen, which was continued for some days at $250^\circ$C**).

**Materials.** Nickel: From nickel oxide as described above; the oxide was prepared by calcining basic carbonate at 500°C in air.

Ethylene: Pure ethyl alcohol was dehydrated with concentrated sulphuric acid; evolving ethylene was, through washing bottles of sulphuric acid and of a caustic soda solution, led to a vacuum system and trapped in a trap cooled with liquid air under continuous pumping. In a complete vacuum system, pumping of the condensed ethylene and distillation using liquid air and a $-80^\circ$C bath were repeated several times, finally about one third of the initial amount being reserved.

Hydrogen for reduction: Electrolytic hydrogen filtered through a heated palladium thimble.

**Gas analysis.** In the course of the adsorption experiment arose the necessity of examining a change in the gaseous composition of the system from pure ethylene. As a means, the gas was burnt with oxygen added and the amounts of resulting water and carbon dioxide were measured; the procedure then adopted is as follows. In every case the test was made on the portion of gas that was present in the compartment between the cocks a and b. Six times as much oxygen as the sample is taken using the manometer P (capable of small adjustment of the pressure) in the lock L which has an accurately determined volume

* When any spot on the glass wall near the bulb is cooled with liquid air, even a trace of moisture certainly gives a white cloud on the wall due to its condensation.

** Carbon deposited on nickel is reduced to methane by hydrogen at 250°C (e.g., see the ref. (13)).
and serves as a gas pipette. With the cocks c and f closed and by opening the cocks b, d and e, the sample and oxygen are allowed to expand to the combustion bulb B, previously evacuated, to mix together. The filament of the bulb, which is similar in construction to an electric lamp, is heated at ca. 1200°C for 30 minutes. Finally, the partial pressures of carbon dioxide and remaining oxygen are measured separately by making use of the trap C and appropriate refrigerants. The amount of produced water was determined from the difference of consumed oxygen and produced carbon dioxide, because water vapor is notably adsorbed by a glass wall. These procedures and the conditions of combustion were determined after making preliminary tests using gases of known composition*).

In certain special cases, in which there were sufficient amounts of the sample gas, the analysis was made chemically by using a solution of mercuric nitrate as absorbent of ethylene. In such cases, a “water vessel” containing the solution, outgassed exhaustively, had been attached to the system beforehand (in place of the flask H). First, the sample present in the vacuum line is gathered into the vessel with liquid air. Gas uncondensed, if any, is regarded as hydrogen and/or methane. The vessel is detached from the system and shaken at room temperature to let ethylene to be absorbed quickly; after it is restored to the system and immersed in a -80°C bath, gas remaining in it is examined on the pressure gauge, which is regarded as ethane.

Results

As regards the pressure variation after the contact of the gas and catalyst, the following facts were observed. When the amount of gas initially taken is sufficiently small, the pressure decreases monotonically as in ordinary adsorptions and tends to a constant value, where most of the pressure drop occurs within several minutes and the \( p-t \) (pressure vs. time) curve becomes L-shaped. When the initial gas amount is increased to exceed a certain value, the shape of the observed \( p-t \) curve changes, that is, a remarkable rise in pressure following the initial steep drop gives a curve having a sharp minimum. Two curves obtained with gas amounts lying in the boundary zone are shown in Fig. 2. The fact should be noted that a difference in the initial pressure as small as between 0.4 and 0.5 mmHg yielded this divergence. The “initial pressure” is the pressure that ethylene would have when it was expanded to

*) It was found that the cock grease vapor gave an error in the result of combustion, but that it could be cancelled by corrections. The correction values were obtained in a blank test in which the filament was heated with oxygen alone admitted but under otherwise identical conditions.
the catalyst bulb but were not adsorbed at all, and in this paper the amount of ethylene initially taken will often be represented by this pressure. (This pressure was determined by computation through known volumes of vacuum lines). The curves shown in Fig. 2 were reproducibly obtained either with the catalyst cleaned by the hydrogen reduction or with one prepared freshly.

As a trial, it was done that small amounts of ethylene were successively admitted to the catalyst bulb each after the pre-admitted gas showed a constant pressure (which was always sufficiently small compared with the pressure of the gas to be admitted); it was found that the curve with a pronounced minimum appears when the total amount of the gas admitted reaches the equivalent of about 0.5 mmHg of the initial pressure, even if the last addition is below that of 0.4 mmHg.

The fact that the pressure once decreased increases again can be explained only by concurrence of some other reaction with the adsorption. It is well-known that ethylene decomposes on nickel above 200°C\textsuperscript{13}. Also below this temperature, the possibility of self-hydrogenation of ethylene has often been suggested\textsuperscript{17}-\textsuperscript{19}. Therefore, it seemed almost certain that the pressure rise in this experiment is due to production of ethane from adsorbed ethylene; to confirm this, however, the gas remaining in the gas phase was subjected to the combustion test mentioned in the previous section, in either case of Fig. 2(a) and 2(b) each after being followed in pressure for 1 hour.
Adsorption and Decomposition of Ethylene on Nickel

TABLE 1.

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<tr>
<th>Case</th>
<th>Fig. 2 (a)</th>
<th>Fig. 2 (b)</th>
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<tr>
<td>Amount of sample</td>
<td>16.6</td>
<td>36.0 *</td>
</tr>
<tr>
<td>&quot; of CO₂ yielded</td>
<td>33</td>
<td>61</td>
</tr>
<tr>
<td>&quot; of H₂O &quot;</td>
<td>35</td>
<td>81</td>
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* mmHg·cc

The results are shown in Table 1. Although the accuracy of these values are not high (since they were determined as differences between larger quantities), the figures evidently shows that the second sample contained in a considerable proportion a species richer in the hydrogen-atom content than ethylene, whereas the first sample remained almost pure ethylene. The somewhat too low value for CO₂ in the above results will probably be due to the presence of a small amount of hydrogen in the sample (hydrogen is, of course, less than ethylene in the content of hydrogen atoms).

II. INTERPRETATION OF OBSERVED CURVES

Discussion

In view of the fact observed in the above experiment that the pressure shows an increase after the initial decrease, it is clear that ethane is produced from ethylene in the adsorbed state. Further, for that adsorbed state, it appears reasonable to assume, as has generally been done, that ethylene is adsorbed on nickel with its double bond opened and the two carbon atoms individually linked with adjacent two of surface nickel atoms.

The most remarkable in the observed facts is that the decomposition of ethylene sets in suddenly on increasing the gas amount and hence increasing the surface concentration of adsorbed gas. We consider first, therefore, the question of what may occur among adsorbed ethylene molecules on the surface as the concentration of the molecules is increased. Suppose a uniform net plane of nickel crystal. It has already been shown that, when an ethylene molecule is adsorbed on two adjacent nickel atoms in the way mentioned above, no serious steric hindrance can occur if two or more molecules are adsorbed to as many successively adjacent pairs of nickel atoms on the plane. Consequently, it will actually happen that a certain number of adsorbed molecules fully cover a portion of the surface which contains just twice the number of
When the concentration of adsorbed molecules is low, such an area on the surface will be small and rare, but as the concentration increases it will become greater in number as well as in size.

A group of ethylene molecules which are adsorbed on a continuity of nickel atoms is schematically represented in Fig. 3 (a), in one dimension for convenience. If, however, this group is sufficiently large, the state of bonds between atoms as shown in Fig. 3 (a) will no longer exist near the center of the group.

In this figure, any carbon atom having two carbon atoms as immediate neighbors forms a perfect single bond with one and none at all with the other; but, in reality, when these atoms are situated sufficiently distant from either end of the row, there is no reason for the central atom to distinguish one neighbor from the other (because they are in physically identical conditions), and hence bonds of equal strength should be formed between the central atom and both the neighbors. Thus, the true state of bonds in the group must be like that represented symbolically in Fig. 3 (b). Such an electronic state occurring in the system will well be explained in terms of the quantum mechanical resonance as well as by the molecular orbital theory. It is certain that near the end of the row there exists the end effect due to the end atom which has only one neighbor, that is, the alternation strong and weak linkages between successive carbon atoms remains there. In consequence, it is clear that a state of bonds as above described can fully be realized within a group only when the group consists of molecules more than a certain number. (The number of molecules

*) The measurement of BET area of the catalyst used was made using nitrogen and using ethylene\(^1\), both giving a well-agreed value of 12 m\(^2\). The necessary quantity of ethylene to fill up that surface was \(7 \times 10^{19}\) molecules. These numbers indicate that, if the surface atom density is of the (110) plane, in the physical adsorption an ethylene molecule covers just two surface nickel atoms, though for (100) or (111) the correspondence becomes 1 to about 3. It appears true that (110) planes predominate at the surface of this catalyst\(^2\). (1) L. A. Wooten & C. Brown, J. Am. Chem. Soc., 65, 113 (1943). (2) S. Yamaguchi & T. Katsurai, J. Colloid Sci., 3, 257 (1948).
in Fig. 3 was determined simply for convenience of drawing.\)

Although the illustration has now been made on a group of one dimension, an analogous situation will occur also in a group consisting of a two-dimensional array of molecules. In the interior of these groups the electronic state existing between atoms must be different from that of a singly adsorbed molecule. It is very probable that under such conditions there be an increased chance for a recombination of atoms. Now, we assume that, when such a group is formed on the surface, decomposition of ethylene initiates within it.

We have no direct information as to the minimum number of molecules for a group to satisfy the above condition. Of hydrocarbon molecules with conjugated double bonds, however, the nature of the successive bonds has been well studied\(^6\); COULSON's calculation shows that, in the case of a long chain molecule, alternation in the "bond order" is appreciable up to about the tenth from each end. Indeed, the wave patterns of electrons in the above two systems will be considerably different from each other, but the similar features found in them are essentially of the same nature (arise from a general property of electrons). Hence, we may obtain a rough idea of the magnitude of such resonance systems from the latter example. The author presumes the number of molecules in question to be of the order of 10 or 20.

**Mathematical Formulation and Representation of Pressure Curves**

Based on the assumption discussed so far, we shall below set up the equations which represent the variation of pressure occurring in a system as we studied. The purpose is to examine whether or not the characteristic features of the observed pressure curves are reasonably derived and explained. Since the present author has observed a perfectly reversible adsorption in this system in the pressure region lower than 10\(^{-3}\) mmHg (at 140°C)\(^9\), it is presupposed in the following treatment that adsorption and desorption of ethylene take place simultaneously with formation of ethane.

First, to represent the adsorption reaction we employ a rate equation of Langmuir's type
\[ \frac{dp_e}{dt} = k\theta_e - k'p_e (1 - \theta), \]  

where \( p_e \) is the (partial) pressure of ethylene, and \( k \) and \( k' \) are constants. Unlike Langmuir's original form, \( \theta_e \) and \( \theta \) in this expression are not the same, being defined as

\[ \theta_e = \frac{\text{no. of adsorbed ethylene molecules}}{\text{total no. of surface nickel atoms}} \]  
\[ (\text{due to the two-point adsorption of ethylene, } 0 \leq \theta_e \leq \frac{1}{2}), \]  

\[ \theta = \frac{\text{no. of nickel atoms occupied by any}}{\text{total no. of surface nickel atoms}} \]  
\[ (0 \leq \theta \leq 1). \]

The distinction is needed because we assume a species other than ethylene also to cover the surface.

In expressing the pressure variation due to decomposition of ethylene, we shall treat the reaction product arising in gas as being all ethane. (It is true that a small amount of by-product, probably hydrogen, was detected in the experiment, but in the light of our present purpose this treatment can be admitted.) The assumption laid in the previous section is used in a developed form that the rate of ethane formation is proportional to the number of the adsorbed ethylene groups, each having the sufficient magnitude, present on the catalyst surface; we do not specify in this work any detailed mechanism of the formation of products.

The above number can be substituted with the probability that one of such groups is present at one particular site (for a group) on the surface, which, when \( \theta_e \) is sufficiently small, is proportional to \( \theta_e^n \) whatever arrangement of molecules in forming the group is concerned,\(^*) \) \( n \) being the number of the molecules. Since in the experiment of which the results are shown in Fig. 2 \( \theta_e \) is around 0.05, we employ this relation as an approximation. As for \( n \), from the review made in the preceding section, the author arbitrarily adopt a number 15. Thus, we can write the rate equation as

\[ \frac{dp_a}{dt} = k''\theta_e^n, \]

where \( p_a \) denotes the partial pressure of ethane and \( k'' \) is the third constant.

\(^*) \) The probability that two ethylene molecules are present on four successively adjacent (in various ways) nickel atoms has been formulated as functions of \( \theta_e \) [S. Matsushita, Catalyst, 3, 55 (1948)]. By generalizing the method it can be proved that, the probability considered in the text \( \rightarrow \text{const} \cdot \theta_e^n \) as \( \theta_e \rightarrow 0 \), in every case.
Adsorption and Decomposition of Ethylene on Nickel

Since ethane is known to be adsorbed not appreciably by nickel, the terms relating to adsorption have been omitted.

For the self-hydrogenation of ethylene on the catalyst, the reasonable and widely accepted equation is

\[ 2\text{C}_2\text{H}_4 = \text{C}_2\text{H}_6 + \text{C}_2\text{H}_2 , \]

where it is understood that the acetylene remains on the catalyst surface in some form. (Generation of gaseous acetylene cannot be accepted from the equilibrium consideration.) We assume this decomposition residue still to remain occupying two nickel atoms; to express its coverage, \( \theta_r \), is defined in the same way as in \( \theta_e \). The total coverage of the surface is given by

\[ \theta = 2(\theta_e + \theta_r) . \quad (4) \]

Further change of this residue that might take place in a long period of time is ignored; under this condition the residue present and the ethane produced must be equal in the number of mol. This equality is expressed as

\[ p_e = \kappa \theta_r , \quad (5) \]

where \( \kappa \) is a constant. The proportionality constant of \( p_e \) to the number of mol is \( RT/V \) and that of \( \theta_r \) is, by the definition (2), \( 1/S \), if we denote by \( V \) the available volume in the apparatus and by \( S \) the total number of surface nickel atoms given in mol. Hence, we know that

\[ \kappa = \frac{RT}{V} S . \quad (6) \]

Of the total ethylene initially taken the material balance is considered and we have one more relation. If each quantity is expressed in pressure and the initial ethylene pressure \( \left(p_e \right)_{t=0} \) denoted by \( m \), the relation becomes

\[ m = p_e + \kappa \theta_e + 2p_n . \quad (7) \]

The total pressure to be observed is

\[ p = p_e + p_n , \quad (8) \]

and its time variation is given by the equations (1) and (3). \( \theta \) and \( \theta_e \) in those equations are eliminated by using the relations (4), (5) and (7), with \( \kappa \) and \( m \) entered. Finally, the equations become

\[ \frac{dx}{dt} = ma - (a + \kappa b + 2mb)x - 2axy - 2bx^2 - 2bxy \quad (9) \]

and
\[
d\frac{dy}{dt} = k^{-11}(m-x-2y)^{18},
\]

where the following short symbols are used:

\[
x = p_e, \quad y = p_n, \quad a = k/k, \quad b = k'/k, \quad l = k''/k.
\]

In order to draw actually \(p\sim t\) curves by these differential equations, the numerical values of constants in the equations must be determined, which were made as follows.

The determinations of three rate constants \(k, k'\) and \(k''\) were essentially arbitrary as described below, but this does not mean that the best values were chosen for making the theoretical curves approach to the observed ones. The rate constant of adsorption \(k'\) was determined from the initial pressure drop in an observed \(p\sim t\) curve on the assumption that the initial velocity is simply proportional to the pressure. In the \(p\sim t\) curve shown in Fig. 2(a), the adsorption equilibrium that would be realized in the absence of decomposition reaction was assumed to exist near the minimum of the curve. This equilibrium pressure, on being combined with the above value of \(k'\), gave the desorption rate constant in the Langmuir-type adsorption, \(k\). The maximum inclination on the curve shown in Fig. 2(b) was again arbitrarily assumed to be almost purely due to formation of ethane, thereby the decomposition rate constant \(k''\) being calculated.
Amsorption and Decomposition of Ethylene on Nickel

\( \kappa \), the parameter relating to the apparatus and the quantity of the catalyst, was determined by the formula (6), in which \( V \) was known through a direct measurement and \( S \) obtained by multiplying the BET area of the catalyst by the surface atom density. The atom density was taken as \( 1.3 \times 10^{15} / \text{cm}^2 \), considering the (110) plane of nickel but with partial coexistence of denser planes taken into account.

The final values which were adopted for solving the equations were

\[
\begin{align*}
  a &= 0.15, \\
  b &= 0.25, \\
  \kappa^{-1} l &= 170, \text{ and } \kappa = 8. \quad \text{(unit: min, mmHg)}
\end{align*}
\]

The initial condition \( m \) being taken as 0.4 or 0.5 (mmHg), the equations were numerically solved, which gave the curves shown in Fig. 5(a) and (b). Since the initial conditions correspond, these curves are to be compared with the observed curves given in Fig. 2(a) and (b), respectively. In each pair of the observed and calculated curves the coincidence seems satisfactory. The same calculations showed that at \( t = 60 \text{ min} \) the fractions of ethylene in the remaining gas are 93% for \( m = 0.4 \) and 47% for 0.5, which are also in harmony with the results of the combustion tests.

III. APPLICATIONS OF THE EQUATIONS

Application to Other Cases

We shall below examine the validity of the equations for other \( p-t \) curves which have been obtained under different experimental conditions.

It has been mentioned before that the observed curves shown in Fig. 2 are reproducible, but there is a fact that many times repeated use of the same
sample effects a gradual change in the shape and in the position of the minimum of the $p\sim t$ curve. An extreme example of such changed curves is shown in Fig. 6(a). Possible changes in a catalyst by such treatments will be contamination of the surface in addition to a decrease of the surface area due to sintering. By inserting $\kappa$, the parameter proportional to the surface area, and $b$, the rate constant of adsorption, with their values reduced to 70% and 40%, respectively, of the original ones, the equations gave the curve shown in Fig. 6(b) resembling the observed curve. It is well-known that, in general, the rate of adsorption becomes small by contaminating the surface, though the reason is not fully clear. It seems difficult to explain the curve in Fig. 6(a) only by a decrease of the surface area, because solution of the equations with $\kappa$ only reduced by a factor 1/2 has given the curve shown in Fig. 6(c).

Next, let us remember that in data hitherto reported on the ethylene—nickel system near 140°C$^{5,6}$ the adsorption rate curve always shows a monotonic decrease of pressure without a minimum. Those experiments were carried out in the pressure region above 1 cm Hg, and it appears that the adsorption was accompanied by decomposition of ethylene. Accordingly, it is of interest to examine the possibility of the above equations to show that when the gas amount to use becomes sufficiently large the total pressure decreases again monotonically with time notwithstanding the decomposition reaction concurring. First, we shall investigate the limit of $m$ below which the $p\sim t$ curve has a minimum. Unfortunately, it is difficult to solve these differential equations analytically, and hence to know the condition of existence of the minimum by simple differentiation. This condition was determined, however, by employing a sequence of mathematical reasoning, though in the course of the reasoning it had to be assumed that no maximum occurs on the curve.

The condition under which a minimum appears. The mathematical derivation of this condition will be described below.

The equation (8) may be rewritten here:

$$p(t) = x(t) + y(t),$$

where $p$ is the total pressure and $x$ and $y$ are the partial pressures of ethylene and ethane, respectively. The initial condition is that $t=0$, $x=m$, and $y=0$. If the content of the equations (9) and (10) is considered physically, it is seen that $x\rightarrow0$ and $y\rightarrow m/2$ as $t\rightarrow\infty$. (This final condition is now stated only as a property of the function and its actual realization is not being discussed.) Consider the function $y(x)$, which would be obtained by eliminating $t$ from $x(t)$ and $y(t)$. The curve representing this function runs from $(m, 0)$ to $(0, m/2)$. 

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Adsorption and Decomposition of Ethylene on Nickel

At an extremum on the curve \( p(t) \), \( dp/dt = 0 \) holds. This point corresponds to a point where \( dy/dx = -1 \) on the curve \( y(x) \), because, from (i), \( dp/dt = dx/dt + dy/dt \). The \( dy/dx \) can be expressed from the equations (9) and (10) as

\[
\frac{dy}{dx} = \frac{k \cdot (m-x-2y)^2}{ma-(a+k^2-2mb)x-2ay-2bx^2-2bxy} .
\] (ii)

At \((m, 0)\), this derivative is zero, which is easily checked by inserting the values into (ii). Therefore, if the derivative \( dy/dx \) is smaller than \(-1\) at \((0, m/2)\), at least one point where \( dy/dx = -1 \) must exist between \((0, m/2)\) and \((m, 0)\), so long as the \( dy/dx \) is a continuous function.

Here it is assumed that the maximum never occurs on the curve \( p(t) \). Then, the extrema that can occur are only one minimum, and the condition of its occurring is

\[
\left( \frac{dy}{dx} \right)_{x=m/2} < -1 .
\] (iii)

The value of \( dy/dx \) at \((0, m/2)\), however, cannot be determined by direct insertion into \( x \) and \( y \) in (ii), because this makes the function an indeterminate form. Accordingly, we first eliminate \( y \) from (ii) by inserting \( y \) expanded as

\[y = m/2 + k_1x + k_2x^2 + \ldots \ldots .\]

The expression (ii) then takes the form,

\[
\frac{dy}{dx} = \frac{O(x^n)}{O(x^n) - (a + kb - mb + 2ak_1)x} ,
\]

where \( O(x^n) \) signifies a function not involving lower order terms than \( x^n \). Now, individual differentiation of denominator and numerator by \( x \) can be performed. Thus,

\[
\left( \frac{dy}{dx} \right)_{x=m/2} = \left[ \frac{O(x^n)}{O(x^n) - (a + kb - mb + 2ak_1)x} \right]_{x=m/2} .
\] (iv)

If the second term in denominator on the right-hand side is not zero, clearly the expression (iv) becomes equal to zero. In the other case that the second term in denominator is zero, the very relation directly gives what we want:

\[
- \frac{a + kb - mb}{2a} = k_1 = \left( \frac{dy}{dx} \right)_{x=m/2} .
\] (v)

Of these two alternatives, the first cannot be accepted by the following reason and the second must be the case. One molecule of ethane is produced from two molecules of adsorbed ethylene, so that \( y \) is not greater than \((m-x)/2\)
at any point on the curve $y(x)$. In other words, the curve lies within the region confined by the two co-ordinate axes and a straight line passing through the points $(0, m/2)$ and $(m, 0)$; this conflicts with that $dy/dx = 0$ at $(0, m/2)$.

Putting the expression (v) in (iii) and simplifying, we obtain the formula showing the range of $m$ giving the minimum on the $p \sim t$ curve, that

$$m < \kappa - a/b.$$  

The right-hand side of this inequality may be expressed by using the "equilibrium constant of adsorption" as $\kappa - k/k'$.

When values of constants given in (12) are inserted, this critical pressure $\kappa - a/b$ becomes 7.4 mmHg. In fact, by putting 10 larger than 7.4 into $m$ and solving the equations (for the other constants the values given in (12) were not altered), a curve without a minimum as shown in Fig. 7(a) was obtained. On the other hand, an experiment using the initial pressure of 10 mm Hg was actually carried out, giving the $p \sim t$ curve shown in Fig. 7(b). In this case, permitted by sufficient quantity of sample, chemical analysis was made on the gas remaining in gas phase after following the pressure change for 1.5 hour.

![Graphs](image-url)

It was proved that a greater part of the sample was ethylene and the rest was ethane. The solid circle in the figure indicates the partial pressure of ethylene determined through the above analysis. Probably because the present treatment based on the assumption that $\theta$, is small is too simple, a close resemblance is not seen between the two $p \sim t$ curves, but it should be noted
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that the theoretical curve correctly shows a monotonic decrease of pressure under ethane formation.

Also in the case of \( m = 100 \), there was found a qualitative agreement between the observed and calculated curves, as seen in Fig. 8.

Discussions on Reaction Rates

First, let us reconsider the meanings of the constants \( a, b \) and \( l \). These constants were defined by the relations (11) initially for the sake of simplicity of expressions, but it will be found that they are more fundamental quantities representing the reaction rates than \( k, k' \) and \( k'' \).

The left and right sides of the equation (1) are divided by the respective sides of \( RT/V = \epsilon/S \) [the relation (6)] and the definitions (2) and (11) are remembered; it can then easily be seen that \( a \) and \( b \) have the following meanings.

\( a \): the number*) of ethylene molecules desorbing during unit time from one nickel atom pair on which an ethylene molecule is adsorbed.

\( b \): the number*) of ethylene molecules to be adsorbed during unit time under unit ethylene pressure by one bare surface nickel atom (it is assumed that a nickel atom adsorbs 0.5 molecule of ethylene at one time).

The same operation on the equation (3) shows that the number of ethane molecules generating from the whole surface during unit time equals \( l \theta_{c}^{15} \) times the number of surface nickel atoms. On the other hand, the number of groups of adsorbed ethylene as discussed before existing on the whole surface is equal to the probability of a group being present at one particular site on the surface, multiplied by the total number of such sites**). The site for the group, mentioned here, is such that to one different site corresponds each of different ways of putting fifteen ethylene molecules on a completely bare surface so as to form one satisfactory group. The number of such sites must be comparable with the number of surface nickel atoms. Let us now assume that these two numbers are the same**). Then, since the probability in question also becomes equal (not only proportional) to \( \theta_{c}^{15} \), we can regard \( \theta_{c}^{15} \) times the number of surface atoms as the number of groups on the whole surface. The relation obtained initially, therefore, leads to the interpretation that

\( l \) is the number*) of ethane molecules to be produced during unit time from one adsorbed ethylene group.

Thus, it is seen that the constants \( a, b \) and \( l \) do not contain factors such

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*) The number averaged or integrated for unit time.

**) Reasoning is being advanced on the assumption that \( \theta_{c} \) is sufficiently small.

***) This will be exactly correct if the molecule is adsorbed only on a pair of nickel atoms having a given distance on (110) planes.
as the quantity of catalyst or the volume of apparatus; in the equations (9) and (10) these factors are all represented in $\kappa$.

Values given in (12) show that $l$ is $10^{13}$ sec$^{-1}$, which is of the magnitude of $kT/h$ at the reaction temperature, the upper limit of elementary reaction rates in general. Considering that the number of molecules assumed for the group, 15, is not so significant to its second figure, the true rate of ethane formation from an adsorbed ethylene group is, in fact, not identical to the above value of $l$, probably some orders of magnitude smaller than the value. However, the fact that the rate is near the limit value implies a great probability of the reaction consisting of a single elementary reaction.

Next, we investigate the problem of which reaction is rate-determining in the formation of ethane in the present system, assuming that the reaction represented by $l$ is an elementary reaction. Although the rate-determining step

![Diagram showing pressure (mmHg) against time (hr) for three cases: a, b, c.](image)

is properly defined for reactions in the steady state, it is similarly significant in a system varying with time when we limit the time length to consider short enough to permit the variations in concentrations of reactants to be ignored. In the present discussion, we shall mark the region on the $p\sim t$ curve in which a pronounced pressure rise is exhibited.

For the above purpose, the equations (9) and (10) were solved using the values of constants $a$, $b$ and $l$ one (or two) of which was intentionally changed from its true value; if the reaction whose rate constant was thus changed is, in a period during the process, acting as the rate-determining step, the $p\sim t$ curve given by this calculation should show a remarkably changed overall reaction rate in that period.
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In Fig. 9, the curve in (a) is the same as shown in Fig. 5(b), corresponding to the actually observed one, while the curve in (b) is the solution of the equations obtained with $l$, only, reduced to one-fifth of its true value, and the curve in (c) is that obtained with both $a$ and $b$, and only them, reduced equally (for no change in equilibrium of the adsorption) also by the factor 1/5. These results show that the rate-determining step in this case is the reaction represented by $l$, despite the fact that the rate constant $l$ is extremely large; and this means that the adsorption reaction, the preceding step of the rate-determining one, is almost in equilibrium.

Needless to say, the rate-determining step of a reaction (complex) is changeable according to the conditions on which the reaction proceeds. In the case of a small $\kappa$ as shown in Fig. 6(c), similar calculations indicated that the pressure increase was determined chiefly by $a$ and $b$ and not by $l$, as is seen in Fig. 10. This is the case in which the decomposition occurs when the adsorption has not yet arrived at the equilibrium and that process is controlling the formation of ethane.

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