

THE ACTIVATED ADSORPTION OF METHANE ON REDUCED NICKEL *

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The activated adsorption plays an important part in catalysis and it has been the subject of many studies. It is well known that nickel is highly active as a catalyst for the decomposition of methane,¹⁾ but the adsorption of methane on nickel has not been studied so much. According to O. Schmidt,²⁾ methane is adsorbed little on nickel and seems to make no activated adsorption from a monotonous isobar in the temperature range between room temperature and 230°C. H. S. Taylor and his co-workers,³⁾ however, assumed that methane might make such an activated adsorption as breaks the C-H bond from the exchange reaction of methane with CD₄ or D₂ at more than 138°C. The present research is to ascertain the existence of the activated adsorption directly from experiments on adsorption performed by using the nickel carefully prepared, and elucidate the nature of the adsorption in question.

Experimental.

Apparatus and Method.

Experiments were carried out under low pressures 10^{-3} ~5 mm., using a large quantity of active nickel catalyst because it adsorbs little methane. The main part of the apparatus is shown in Fig. 1. The volume of the adsorption space was measured by the standard volume V. The specific gravity of nickel was taken as 8.90. Before the experiment is carried out, the catalyst in S is fully desorbed and a required quantity of methane filled in the right-hand side of c₁. The initial pressure shown at the moment the gas was introduced into S through c₁ was calculated from the volume of the adsorption space and its temperature. The pressure measured at any time being deduced from it, the adsorption amount was obtained.

The temperature of the electric furnace used was kept within $\pm 0.5^\circ\text{C}$. during the experiment by means of a regulator of chopper bar type.⁴⁾ In the experiment at low temperatures ether cooled by liquid air (-112°C .), solid carbonic acid (-78°C .) and liquid ammonia (-33°C .) were used.

* This is the detailed report which appeared in *Proc. Imp. Acad. Tokyo*, 14, 61~66 (1938).

1) e.g. Slater, *J. Chem. Soc.*, 109, 101 (1916); Cantelo, *J. Phys. Chem.*, 28, 1036 (1924); 30, 899, 1941 (1926); 31, 124 (1927).

2) Schmidt, *Z. physik. Chem.*, 118, 211 (1925); 135, 295 (1928).

3) Morikawa, Benedict and Taylor, *J. Am. Chem. Soc.*, 58, 1445 (1936).

4) Kubokawa, *Rev. Phys. Chem. Japan*, 12, 90 (1938).

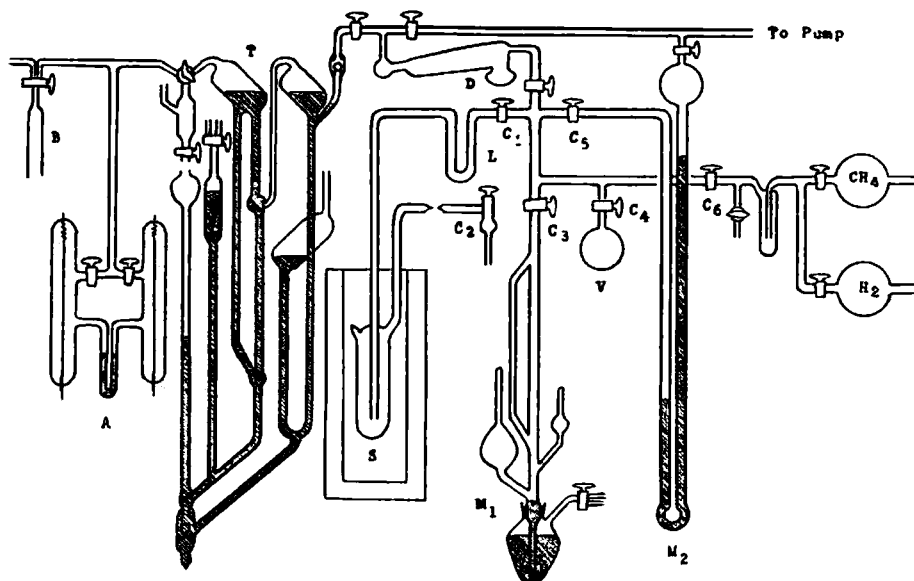
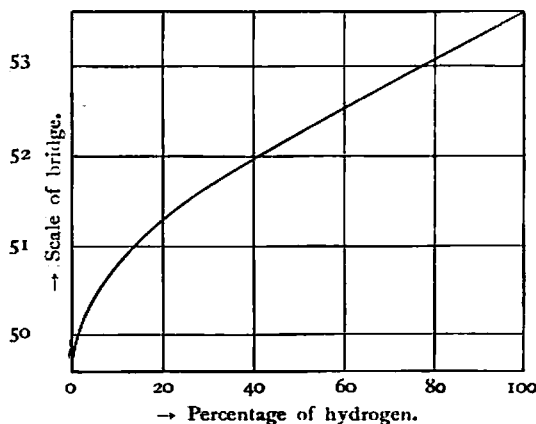


Fig. 1.—Apparatus.

- | | |
|------------------------------------|--|
| S Sorption vessel. | A Apparatus for gas analysis by thermal conductivity method. |
| T Automatic Töpler pump. | B Gas burette for ordinary gas analysis. |
| D Diffusion pump. | V Standard volume of 220 c.c. |
| M ₁ McLeod manometer. | |
| M ₂ Ordinary manometer. | |

In the case of analysis of the desorbed gas, the gas was introduced into A by means of an automatic Töpler pump T.⁵⁾ A consists of two chambers connected with a U tube holding sulphuric acid. In each chamber a platinum wire 0.1 mm. in diameter and 30 cm. in length is stretched. These two wires are set as the arms of Wheatstone bridge, on which a given

Fig. 2.—Calibration curve for gas analysis of CH_4 and H_2 mixture.

low electric current is transmitted. If one of the chambers holds a gas of good thermal conductivity such as hydrogen, the temperature of the wire does not rise and the wire shows smaller resistance than the other. Therefore, in one of the chambers pure methane being put under a low pressure (2mm. Hg) and in the other a hydrogen-methane mixture of known percentage under the same pressure, the reading of the bridge was made. The calibration curve thus obtained is shown in Fig.

2.

5) Weaver and Shepherd, *J. Am. Chem. Soc.*, 50, 1829 (1928).

From this curve the amount of hydrogen contained in 0.01 c.c. of methane (at N.T.P.) could be detected within the accuracy of $\pm 0.2\%$.

For fear of the vapour of grease and mercury, the part L was cooled with solid carbonic acid. The grease used was Apiezon grease L.

Materials.

Methane which was prepared by the reaction between aluminium carbide and water was carefully refined and distilled several times with liquid air.⁶⁾

Nickel was prepared thus: nickel oxide prepared by decomposing completely nickel nitrate of Kahlbaum free from cobalt at 350°C . was reduced with hydrogen. In every experiment 15 g. of nickel oxide was reduced in S in Fig. 1. Hydrogen was passed over the oxide at a speed of 1 l. an hour and let it out through c_2 . The conditions of the reduction are as follows:

Ni(I)Reduced at 350°C . for 3 days.

Ni(II).....Reduced at 250°C . for 5 days.

Hydrogen was prepared by the electrolysis of potassium hydroxide solution and dried with phosphorus pentoxide after passing it over heated platinum black.

Results.

Adsorption at low temperatures.

In the temperature range $-110^{\circ}\sim 20^{\circ}\text{C}$. adsorption equilibrium was established within several minutes after the introduction of the gas. The adsorbed gas being easily removed, reproducible results were obtained. It is considered from these results that methane makes only van der Waals' adsorption on nickel at these temperatures. The isotherms for Ni(I) is shown in Fig. 3.

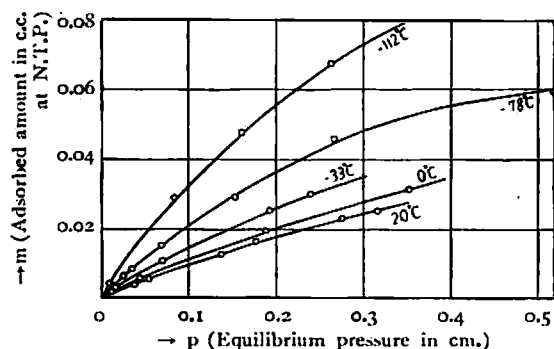


Fig. 3.—Adsorption isotherms of methane.

As shown in Fig. 4, the adsorption isotherms coincide well with Langmuir's equation, which is expressed thus:

$$m = abp / (1 + bp),$$

or
$$p/m = 1/ab + p/a,$$

where m is the adsorbed amount, p equilibrium pressure, a and b constants.

From the assumption of the monomolecular adsorption the amount of methane required for surface saturation becomes 0.115 c.c. (N.T.P.) using the value of a obtained from Fig. 4. The heat of adsorption Q is calculated by

6) Kubokawa, *Rev. Phys. Chem. Japan*, 11, 82 (1937).

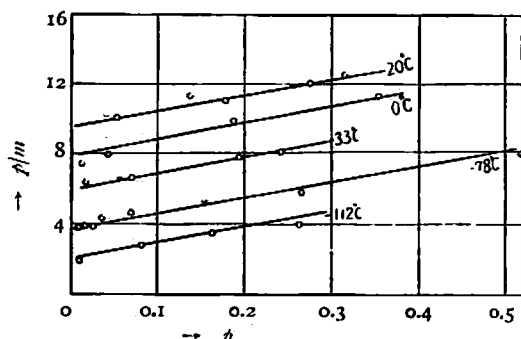


Fig. 4.

Adsorption above room temperature.

It is evident from Fig. 3 that van der Waals' adsorption is decreased with the rise of temperature, especially above room temperature. At temperatures a little higher than room temperature, however, another type of a slow adsorption was observed. This adsorption is considered to be what is called activated adsorption as the velocity of the adsorption increases with rising temperature. In the case of Ni(I) at 100°C. this type of adsorption proceeded at measurable rate, while in the case of Ni(II), which is more active than Ni(I) being reduced

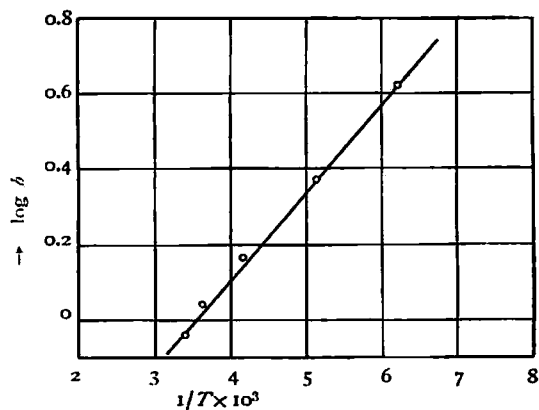


Fig. 5.

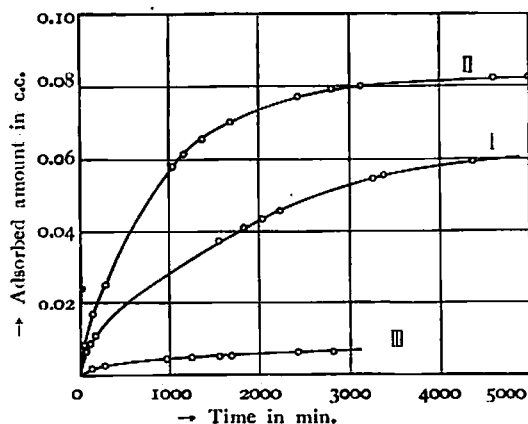


Fig. 6.—Velocity curve of activated adsorption of methane on Ni (I).

- I. Expt. at 100°C, $p_0=0.01173$ cm.
- II. " " 130°C, $p_0=0.01032$ cm.
- III. " " 150°C, $p_0=0.00858$ cm.

$b=b_0 e^{\frac{Q}{RT}}$, or $\log b = Q/4.57 T + \text{const.}$
The relation between $1/T$ and the logarithm of b calculated from Fig. 4 is linear as shown in Fig. 5. As the value of the heat of adsorption 1 kcal/g. mol was obtained, which is a reasonable value for the heat of van der Waals' adsorption.

at lower temperatures, the adsorption was observed even at 40°C. But at such a low temperature as this adsorption equilibrium is not so rapidly established: it is established in more than 5 days at 100°C., in 3 days at 130°C., and in 1 hour at 170°C.

One of the curves of the adsorption velocity of Ni(I) is shown in Fig. 6 and that of Ni(II) in Fig. 7. The ordinates of Figs. 6 and 7 denote the amount of adsorption and the

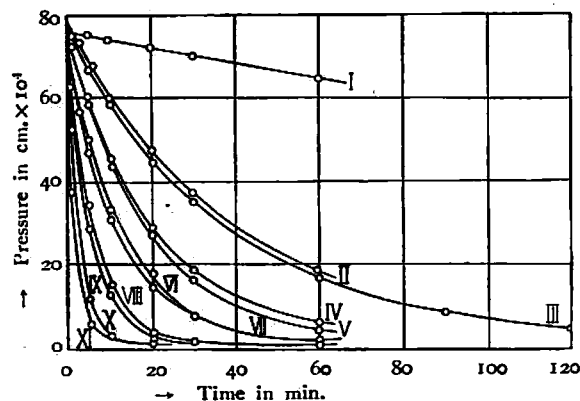


Fig. 7.—Velocity curve for activated adsorption of methane on Ni(II).

I.	Expt. at 40°C,	$p_0=0.00897$ cm.
II.	" 80°C,	0.00930 cm.
III.	" 80°C,	0.00902 cm.
IV.	" 100°C,	0.00909 cm.
V.	" 100°C,	0.00900 cm.
VI.	" 120°C,	0.00915 cm.
VII.	" 120°C,	0.00873 cm.
VIII.	" 150°C,	0.00910 cm.
IX.	" 170°C,	0.00913 cm.
X.	" 200°C,	0.00913 cm.
XI.	" 250°C,	0.00911 cm.

pressure of the system respectively.

To obtain the adsorption isobar a number of experiments must be carried

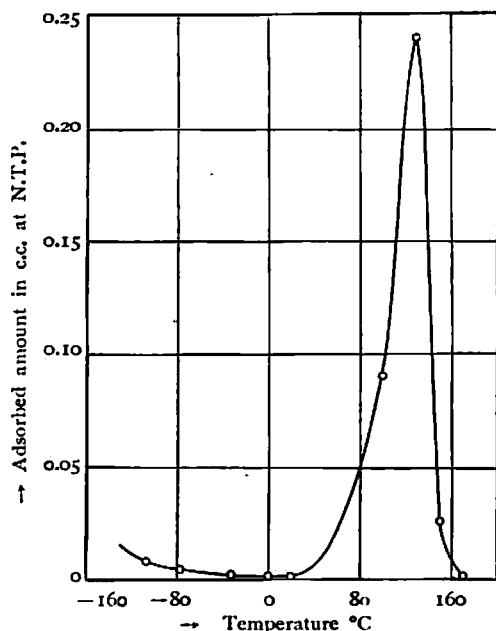


Fig. 8.—Adsorption isobar of methane at 0.01 c.c. for Ni(I).

out at different temperatures and pressures. Therefore, the isotherms obtained as many as possible were interpolated and the isobar for an equilibrium pressure obtained. The isobars of Ni(I) and Ni(II) are shown in Figs. 8 (0.01 cm.) and 9 (0.0001 cm.) respectively.

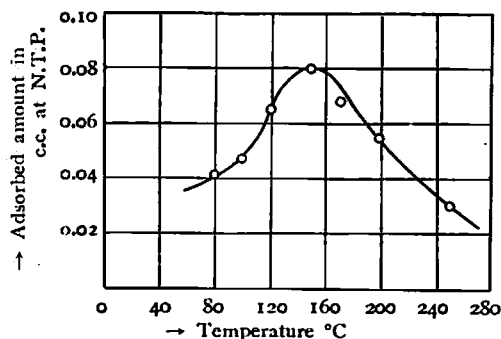


Fig. 9.—Adsorption isobar of methane at 0.0001 cm. for Ni(II).

The isobar of Fig. 8 covers a wide range—from van der Waals' adsorption to the activated one.

In both figures, the maximum particular to the activated adsorption is seen. The maximum temperature is about 120°~150°C. The isobar below these temperatures is apparent one, for measurement has been done in 24 hours in the case of Ni(I) and in 10 hours in the case of Ni(II).

On the reproducibility of the results.

The methane adsorbed above room temperature can not easily desorbed merely by evacuation. But when evacuated at 200°C. for an hour, it is completely desorbed. Therefore this previous evacuation was made before each experiment. If methane is adsorbed above 250°C., the adsorbability of nickel falls. This may be due to the formation of nickel carbide⁷⁾ taking place above the temperature, since the activity of nickel is recovered by passing hydrogen over it at the temperature for 24 hours.⁸⁾ At such a low temperature as 170°C. the activated adsorption could be reproduced only by evacuation.

The examination of van der Waals' adsorption at -78°C. on the nickel which had made activated adsorption showed the decrease in the amount of adsorption. The desorption at 200°C. before the experiment on van der Waals' adsorption, however, produced no influence on the adsorption.

Allmand and Chaplin⁹⁾ have shown that the activated adsorption can be interpreted by the phenomena of the displacement of surface impurity such as unreduced oxide or adsorbed oxygen. Their interpretation must be denied in the present research. For nickel was fully reduced; much attention was paid to the poisoning by leakage of the atmospheric gas. The fact that methane was not adsorbed at 120°C. when poisoned by introducing a small quantity of air to the system and the reproducibility of the present experiment show that the measurement was made on true activated adsorption. What is, then, the activated adsorption of methane? Is it nothing but the activation of the C-H bond or is it so dissociative an activation as will cut the bond? To solve these questions, the following experiment was performed.

The detection of hydrogen in the desorbed gas.

The methane which had made activated adsorption was taken out by means of Töpler pump and the content of hydrogen contained in it was examined as already mentioned. After the hydrogen which had adsorbed on Ni(I) was fully desorbed by evacuating at 350°C. for six hours, methane was introduced. One of the experiments carried out is thus: methane was left in the vessel under the initial pressure of 1.37 cm. at 150°C. and five days later, when equilibrium was established, the gas to be desorbed at the same temperature was analysed. The gas coming out for the first 1 minute was pure methane; the gas taken out for

7) Scheffer, Dokkum and Al, *Rec. trav.*, 45, 803 (1926).

8) This fact is interpreted according to the equation: $\text{Ni}_x\text{C} + 2\text{H}_2 \rightarrow x\text{Ni} + \text{CH}_4$.

9) Allmand and Chaplin, *Trans. Farad. Soc.*, 28, 223 (1932).

the next 30 minutes contained 14% of hydrogen; the gas desorbed hereafter became rich in hydrogen. This result shows that the methane which had made activated adsorption has been dissociated and that the dissociated hydrogen can not easily come out into the gaseous phase because of its strong adsorption on nickel.

Both the adsorbability of the hydrogen dissociated by activated adsorption and the velocity of adsorption can not be neglected in the present research, because they must be taken into consideration in calculating the heat of activated adsorption of methane and the activation energy.

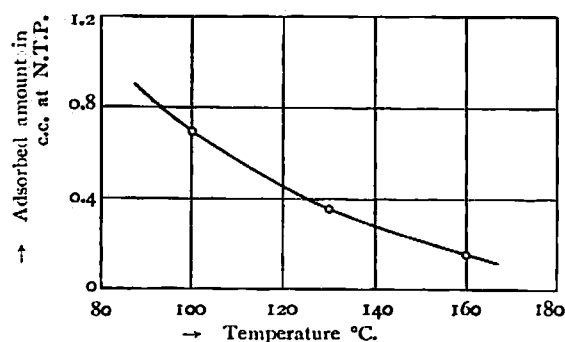


Fig. 10.—Adsorption isobar of hydrogen at 0.0001 cm. for Ni(I).

The isobar of hydrogen for nickel at 0.0001 cm. is shown in Fig. 10.¹⁰⁾ From the comparison of Fig. 10 with Fig. 8 under the assumption that the adsorption is in Henry's region, it is seen that hydrogen is adsorbed on Ni(I) about 100 times as methane at 130°C. The amount of adsorption of hydrogen is thus large, so that the heat

of adsorption calculated from the isobar of the activated adsorption of methane is not reliable at all. For example, the heats of adsorption for Ni(I) and Ni(II) calculated from Figs. 8 and 9 are 40 and 6 kcal./g. mol respectively.

Kinetics of the activated adsorption.

Whether the measured velocity of the activated adsorption of methane is the velocity of the surface reaction which means the dissociation of the C-H bond or that of the sorption of the dissociated hydrogen into the interior of nickel¹¹⁾ which follows the surface reaction must be determined. The velocity of the activated adsorption of hydrogen is exceedingly large as compared with that of methane. For instance, in the case of Ni(I) 0.134 c.c. of hydrogen was adsorbed for 15 minutes at $p_0=0.01588$ cm. Comparing this result with Fig. 6 it is seen how rapidly hydrogen is adsorbed.¹²⁾ The diffusion laws¹¹⁾¹³⁾ which are applicable to the activated adsorption of hydrogen can not be applied to that of methane. These

10) Cf. Benton and White, *J. Am. Chem. Soc.*, 52, 2325 (1930).

11) Ward, *Proc. Roy. Soc. [A]*, 133, 506 (1931), *Trans. Farad. Soc.*, 28, 444 (1932).

12) Cf. Iijima, *Rev. Phys. Chem. Japan*, 7, 3, 24, 36 (1933); 8, 44 (1934); 12, 1 (1938).

13) Williams and Cady, *Chem. Rev.*, 14, 171 (1934).

facts lead to the conclusion that the observed velocity is the velocity of the surface reaction including the activation of the C-H bond of methane.

From the reversibility of the surface reaction the rate of sorption is expressed thus:¹⁴⁾

$$-\frac{dp}{dt} = k_1 p(1-\theta) - k_2 \theta,$$

where p is the pressure of methane, k_1 and k_2 constants, and θ the fraction of the surface covered with adsorbed methane. For small amount adsorbed, $(1-\theta)$ may be taken as unity, and the above equation reduces to

$$-\frac{dp}{dt} = k(p-p_e),$$

where p_e denotes the equilibrium

pressure, as a limiting expression of both adsorption and desorption. Integrating this equation, it becomes

$$\log(p-p_e) = \log(p_0-p_e) - 0.4343 kt,$$

where p_0 is the initial pressure of methane. The linear relation between $\log(p-p_e)$ and t required by this equation holds well as shown in Fig. 11 for Ni(I) and Fig. 12 for Ni(II).

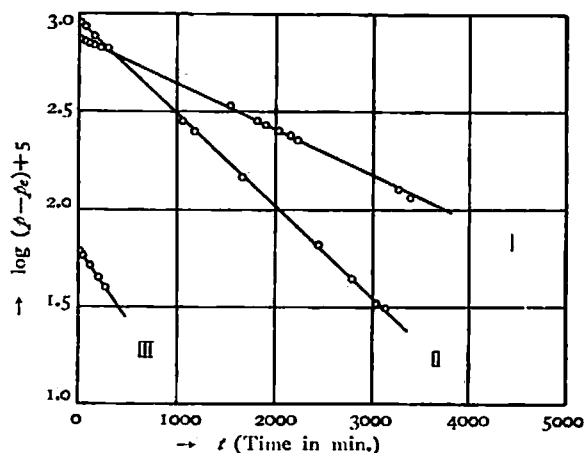


Fig. 11.

- I. Expt. at 100°C, $p_0 = 0.01173$ cm.
 II. " 130°C, $p_0 = 0.01032$ cm.
 III. " 150°C, $p_0 = 0.00858$ cm.

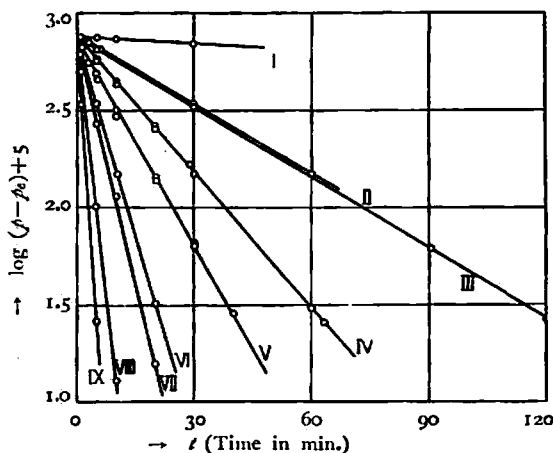


Fig. 12.

- I. Expt. at 40°C, $p_0 = 0.00768$ cm.
 II. " 60°C, 0.00801 cm.
 III. " 80°C, 0.00777 cm.
 IV. " 100°C, 0.00784 cm.
 V. " 120°C, 0.00791 cm.
 VI. " 150°C, 0.00790 cm.
 VII. " 170°C, 0.00794 cm.
 VIII. " 200°C, 0.00796 cm.
 IX. " 250°C, 0.00797 cm.

14) Barrer, *Proc. Roy. Soc. [A]*, 149, 253 (1935).

The heat of activation E is given by Arrhenius' equation, a being a constant.

$$k = ae^{\frac{-E}{RT}}.$$

This relation holds as shown in Figs. 13 and 14.

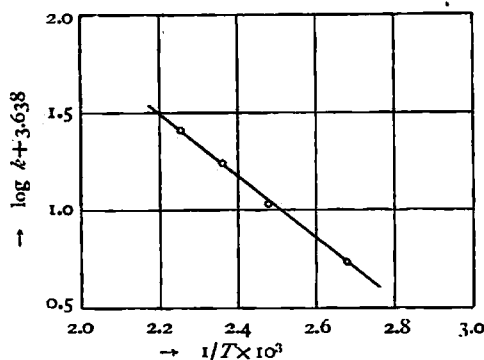


Fig. 13.

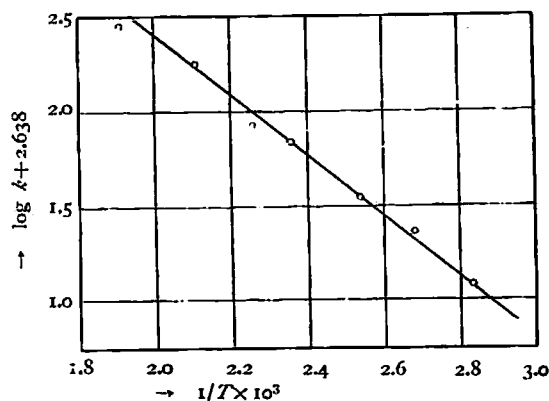


Fig. 14.

As the heat of activation, $E = 7$ kcal./g. mol was obtained, which was the same for both Ni(I) and Ni(II).

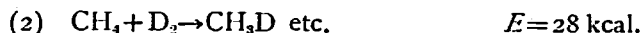
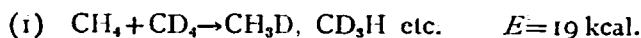
Discussion of Results.

It is very interesting to mention that the C-H bond of so stable a saturated hydrocarbon as methane is activated on the surface of nickel at a low temperature, such as 40°C . The process of the dissociation which follows the activation is considered to be successive dehydrogenation of the surface free radicals; $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \rightarrow \text{CH}_2 + 2\text{H} \rightarrow \text{CH} + 3\text{H} \rightarrow \text{C} + 4\text{H}$. The process of the desorption is reverse: the surface free radicals are successively hydrogenated and desorbed as methane.

It seems probable, therefore, that various C-H fragments exist on the nickel surface in equilibrium. This equilibrium will be affected by temperature, pressure and the nature of surface. The formation of carbon (graphite) during the course of the activated adsorption is evident from the fact that the amount of the activated adsorption is considerably large as compared with the saturation value of van der Waals' adsorption of methane. It is also clear from the reproducibility of the present experiment that the adsorption by separated graphite is negligible.

The observed value of the activation energy, 7 kcal., is the one obtained for the initial part of the reaction, so that it is probably the value for the first stage, $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$. Therefore, let us compare the value with that of Taylor and

others.¹⁵⁾ According to their report, it was ascertained that in the presence of nickel CH_4 makes exchange reaction with CD_4 , D_2 or D_2O above 138°C ., and from this fact it was assumed that above the temperature the dissociation of the C-H bond of methane would take place. Their values of the activation energy are as follows:



The velocity of reaction (1) is regarded as that of the process of desorption of the radicals $-\text{CH}_3$, CD_3 , etc.—as methane by their recombination with D or H. Q , the heat of activated adsorption of methane on nickel can be calculated from the data of the present experiment thus:¹⁶⁾

$$Q = 19 - 7 = 12 \text{ kcal./g. mol.}$$

As to the activation energy for reaction (2), it is considered to include the energy of desorption of deuterium from the fact that the reaction is retarded by strong adsorption of deuterium. Therefore it is not suitable to discuss here.

It has been found that the activation energy of the reaction $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$, which is the first stage of the homogeneous decomposition of methane, is so high as 100 kcal.¹⁷⁾ It is to be noted that such a high energy is reduced only to 7 kcal. in the case of methane adsorbing on the surface of nickel, for this fact indicates a remarkable action of the catalyst.

Summary.

1) The adsorption of methane on reduced nickel has been measured under $10^{-3} \sim 5$ mm. pressures in the temperature range $-112^\circ \sim 250^\circ\text{C}$.

2) Only van der Waals' adsorption being measured below room temperature, the heat of adsorption has been found to be 1 kcal. In the presence of active nickel catalyst, activated adsorption has been measured even above 40°C .

3) It has been ascertained from the analysis of the desorbed gas that the activated adsorption of methane is a dissociative adsorption including the activation of the C-H bond.

4) The activation energy calculated from the velocity of the activated adsorption is 7 kcal.

15) *Loc. cit.*

16) There is a little difference between the activation energy of C-H and that of C-D caused by difference between their zero point energies, which has been neglected in the calculation.

17) Rice and Dooley, *J. Am. Chem. Soc.*, 56, 2747 (1934).

5) Considering the observed value of the activation energy to be that of the process, $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$, and calculating the heat of activated adsorption to be 12 kcal., the energy relation to the initial stage of the catalytic decomposition has been elucidated.

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