Title	THE RATE LAW FOR THE ADSORPTION OF GASES ON CATALYSTS
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 3(1), 16-27
Issue Date	1953-11
Doc URL	https://hdl.handle.net/2115/24622
Type	departmental bulletin paper
File Information	3(1)_P16-27.pdf

THE RATE LAW FOR THE ADSORPTION OF GASES ON CATALYSTS

By

Takao KWAN

Introduction

There are a number of kinetic data for the adsorption of gases on catalysts in which various types of rate equation have been put forward to describe the experimental data. Generally speaking, these formulae appear to fall into two groups, —those based on the Langmuir equation in character and those not. The rate equation, however, seems in most cases to be valid only to one particular instance although there exists such a relatively simple rate equation as ZELDOWITSH and ROGINSKY's[1] one applicable in several instances to the experiment as claimed by these workers and also recently by TAYLOR and THON.[2]

In studying the adsorption of nitrogen on a carefully reduced iron synthetic ammonia catalyst, we have found a new adsorption rate equation applicable to this system. This equation includes the Langmuir adsorption rate equation as the special case. Moreover, there are numerous other instances of rate data which have been shown to follow satisfactorily the equation. The results of these studies are here communicated.

Form of Adsorption Rate Equation

Experimental.—A 10,4 g. sample of iron synthetic ammonia catalyst containing 1.06% K_2O, 1.82% of Al_2O_3, 0,41% of SiO_2 and traces of MgO and CaO supplied by *Toa Synthesis Co.* was reduced at 500–550°C in a stream of hydrogen at pressure of *ca.* 600 mm. Hg which was circulated through the catalyst bed by means of electromagnetic pump in a closed system. The reduction was allowed to continue in an exhaustive manner

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[1] J. ZELDOWITSH, S. ROGINSKY, Acta Physicochim., U. R. S. S., 1, 554 (1934).
S. ROGINSKY, Nature, 134, 925 (1934).

[2] H. A. TAYLOR, N. THON, J. Am. Chem. Soc., 74, 4169 (1952).

until hydrogen consumption becomes as small as less than 0.01 mg. per hour. The catalyst was then outgassed at the same temperature for three hours before brought into contact with nitrogen. The catalyst was kept from any mercury or grease vapor which might pass in by means of liquid air trap which was attached just to either side of the U-type catalyst vessel throughout the experiment.

Nitrogen was prepared by igniting sodium azide in high vacuum. Hydrogen, used for the reduction of catalyst, was prepared electrolytically and purified by passing it over calcium chloride, *Pt*-asbestos and then liquid air trap.

The apparatus and technique employed in making the measurements of adsorption are in most respects identical with those described in the previous paper.[3]

Results.—A known quantity of nitrogen was introduced on the catalyst which was beforehand outgassed with a mercury diffusion pump and brought to a definite temperature. The decrease in pressure due to adsorption was measured by means of McLeod gauge at suitable

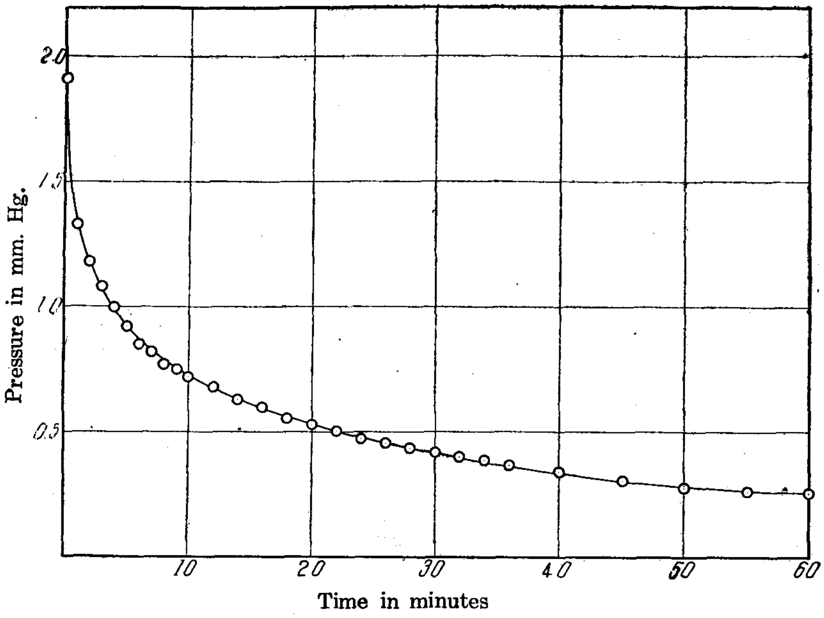

Fig. 1.

Typical Adsorption Rate Curve of Nitrogen on an Iron Synthetic Ammonia Catalyst at 400°C. $P_0=1.91$ mm. Hg.

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[3] T. Kwan, This Journal. **1**, 81 (1949).

time intervals. A typical adsorption rate curve, *i. e.*, pressure-time relation obtained at 400°C is illustrated in Fig. 1.

If we evaluate the adsorption rate or $-dp/dt$ graphically and plot the values of logarithm of $(1/p.dp/dt)$ as ordinate and logarithm of (p_0-p) as abscissa a linear relation can hold between them over the nearly whole range of adsorption. Here, p_0 is the pressure of nitrogen at time zero, (p_0-p) hence being proportional to the adsorbed quantity of nitrogen at time t. These data are arranged in Table I below.

TABLE I.

The Dependence of the Adsorption Rate upon the Surface Coverage. $p_0=1.91$ mm. Hg.

t min.	p mm. Hg	$-\frac{1}{p}\frac{dp}{dt}$	$\log\left(-\frac{1}{p}\frac{dp}{dt}\right)$	p_0-p mm. Hg	$\log(p_0-p)$
2	1.18	9.02×10^{-2}	− 1.05	0.73	− 0.136
4	0.98	7.73	− 1.11	0.93	− 0.032
6	0.85	5.75	− 1.24	1.06	0.026
8	0.78	4.24	− 1.37	1.13	0.054
11	0.69	3.42	− 1.46	1.22	0.087
20	0.53	2.56	− 1.59	1.38	0.140
30	0.42	2.22	− 1.65	1.49	0.174
50	0.28	1.59	− 1.80	1.63	0.213

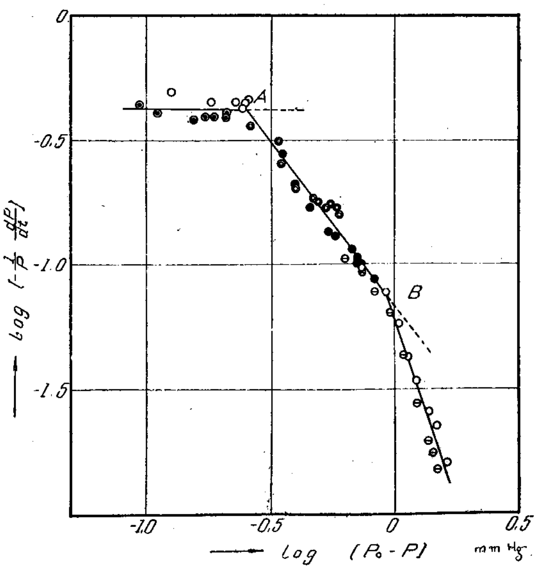

Fig. 2.

Adsorption Rate of Nitrogen on an Iron Catalyst at 400°C as a Function of Coverage.

○, ◎ etc. indicate different adsorption runs made at varying initial nitrogen pressure.

Passing hydrogen over the catalyst and outgassing similarly as before, a series of experiment with varying initial pressure of nitrogen has been performed with the purpose of establishing the dependence of the adsorption rate upon the fraction of surface covered.

Plotting $\log(1/p.dp/dt)$ against $\log(p_0-p)$ in every case of runs, it was found that they give three straight lines over the course of the adsorption investigated as shown in Fig. 2. As can be seen from the figure the inclination of the straight line is zero within a certain region of lower surface coverage, that is, the adsorption rate is independent of the coverage. The slope then becomes discontinuously steeper with increasing adsorption.

Such a relation may now be represented by

$$\log\left(-\frac{1}{p}\frac{dp}{dt}\right)=-\alpha\log\theta+\log k_a \qquad (1)$$

where α and k_a are "constants" characteristic of some intervals of the surface coverage. Removing logarithm from eq. (1) we have

$$-\frac{dp}{dt}=k_a p\,\theta^{-\alpha} \qquad (2)$$

Examination of the Kinetic Data,—The process of adsorption or $-dp/dt$ is in general expressed as[4)]

$$-\frac{dp}{dt}=\vec{v}\left(1-e^{\Delta\mu/RT}\right) \qquad (3)$$

where $\vec{v}$ is the forward rate and $\Delta\mu$ the difference of chemical potential between gas and adsorbed one. Using the thermodynamical relation of μ to activity a, $\mu=RT\ \ln a$, and assuming that the activity of gas is proportional to the gas pressure, we have from eq. (3)

$$-\frac{dp}{dt}=\vec{v}\left(1-\frac{p_e}{p}\right) \qquad (4)$$

where p_e is the pressure of the gas which would be in equilibrium with adsorbed quantity at time t, and obtainable from the data of adsorption isotherm. An examination of the adsorption isotherm data shows that the p_e amounts to *ca.* 3×10^{-3} mm. Hg at the highest degree of adsorption (*i.e.*, at the lowest pressure of nitrogen) in the specified run illustrated

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4) J. HORIUTI, This Journal. **1**, 1 (1948).

in Fig. 1. Since any p_e should be less than the above value during the period of the run and p is on the other hand, at the lowest, 2.8×10^{-1} mm.Hg, p_e/p in eq. (4) is considerably small compared with unity, in other words, the reverse process may be practically ignored. It was confirmed further that such conditions can be fulfilled in any adsorption run observed at 400°C. On the basis of these facts eq. (2) possesses merit as the forward rate formula.

Adsorption Isotherms.—Adsorption isotherms of nitrogen were determined in the main at 450°C and 500°C and by a few points at 400°C where two or three days were required to reach equilibria and at pressures ranging from 10^{-3} to 20 mm. Hg. It was found that any of isotherms obeys FREUNDLICH's equation

$$\log \theta = \frac{1}{n} \log p + \log K \qquad (5)$$

The logarithmic isotherms bear some resemblance to those of W-H_2 obtained by FRANKENBURG[5] or W-N_2 by DAVIS,[6] that is, the isotherms conform to a fan-like convergence, the point of a common intersection in the region of high equilibrium pressures amounting to 8×10^{14} molecules per sq. centimeter of the catalyst surface. It was found that the value of n changes discontinuously at that coverage corresponding to the second break B in Fig. 2. The existence of another discontinuity corresponding to A, if any, could not be made clear on account of too small equilibrium pressures.*)

The Form of Rate Equation.—From both the forward rate and equilibrium formulae determined above we can find an expression, $k_d \theta^{\beta}$, for the reverse rate with the relation of

$$K = \left(\frac{k_a}{k_d}\right)^{\frac{1}{\alpha+\beta}}, \ n = \alpha + \beta \qquad (6)$$

Consequently we have the following expression:

$$-\frac{dp}{dt} = k_a p \theta^{-\alpha} - k_d \theta^{\beta} \qquad (7)$$

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*) In this connection, we may refer to the work by MATSUSITA of this institute who obtained a log-log adsorption isotherm accompanying two breaks for the adsorption of ethylene on reduced nickel. To be published.

5) W. G. FRANKENBURG, J Am. Chem. Soc., **66**, 1827, (1944).

6) R. T. DAVIS, J. Am. Chem. Soc., **68**, 1395 (1946).

for the net rate. It is now obvious that the eq. (7) is the "component" of the FREUNDLICH's adsorption isotherm equation. To check the experimental data in which the reverse rate is significant it is required to use, in place of eq. (7), an expression

$$\log\left(-\frac{1}{p}\,\frac{dp}{dt}\Big/1-\frac{p_e}{p}\right)=-\alpha\log\theta+\log k_a \qquad (8)$$

It is readily shown also that we may use an equation of the form

$$\log\left(\frac{d\theta}{dt}\Big/1-\frac{p_e}{p_c}\right)=-\alpha\log\theta+\log k_a \qquad (9)$$

in cases where the data on adsorption rates are given at constant pressure p_c.

Tests of the Rate Equation

i. We shall first confine ourselves to the adsorption in the region of low surface coverage. If we assume that $n=1$ (HENRY's law) and $\alpha=0$ and consequently $\beta=n-\alpha=1$, eq. (7) leads to its particular form as

$$-\frac{dp}{dt}=k'_a p-k_d\theta \qquad (10)$$

This equation is of the Langmuir type in character and has been used by BARRER[7] and KUBOKAWA[8] respectively for the adsorption of hydrogen on carbon and methane on reduced nickel with success. Further instance where equation (10) was successfully applied is the adsorption of C_2H_4 on V_2O_3 obtained by TARAMA and his co-workers.[9]

ii. According to our previous work[10] the adsorption rate of hydrogen on reduced copper is proportional to hydrogen pressure in the region far removed from equilibrium. The surface coverages were less than 0.1 during the course of the adsorption process. This is evidently fulfilled by the special case of eq. (10) where $k_d\theta$ is ignored.

iii. Assuming that the reverse process may be negligible, KINGMAN[11] and IIJIMA[12] attempted to apply the equation

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[7] R. M. BARRER, J. Chem. Soc. London 1256, 1261 (1936).

[8] M. KUBOKAWA, Rev. Phys. Chem. Japan 12, 157 (1938).

[9] K. TARAMA, S. TERANISHI, K. HATTORI, K. MIYAZAKI, J. Ind. Chem. Soc. Japan 55, 216 (1952).

[10] T. KWAN, This Journal, 1, 95 (1949).

[11] F. E. T. KINGMAN, Trans. Far. Soc., 28, 269 (1932).

[12] S. IIJIMA, Rev. Phys. Chem. Japan 12, I (1938).

$$-\frac{dp}{dt} = k_a p\,(1-\theta) \tag{11}$$

to their data of hydrogen on carbon and hydrogen or ethylene on reduced nickel respectively.

IIJIMA extended the measurement of adsorption for Ni-H_2 at $-78°C$ up to 14500 minutes, thus the adsorption apparently reaching a saturation. He deduced from eq. (11) an expression

$$\log \frac{p}{p-p_g} = Kt + C \tag{12}$$

where p_g is the pressure at the time when the adsorption has reached an equilibrium, and K and C are constants. The $\log p/p-p_g$ *versus* t diagram reveals however that a linear relation holds between them only within some limited range of adsorption, deviations from the straight line occurring at both the beginning and end of the run. KINGMAN has led to the result that eq. (11) is satisfactorily applicable to the experiment except for the first few minutes.

Let us assume with these workers that the reverse process may be neglected, or that $1-\frac{p_e}{p}$ in eq..(8) is approximately equal to unity.

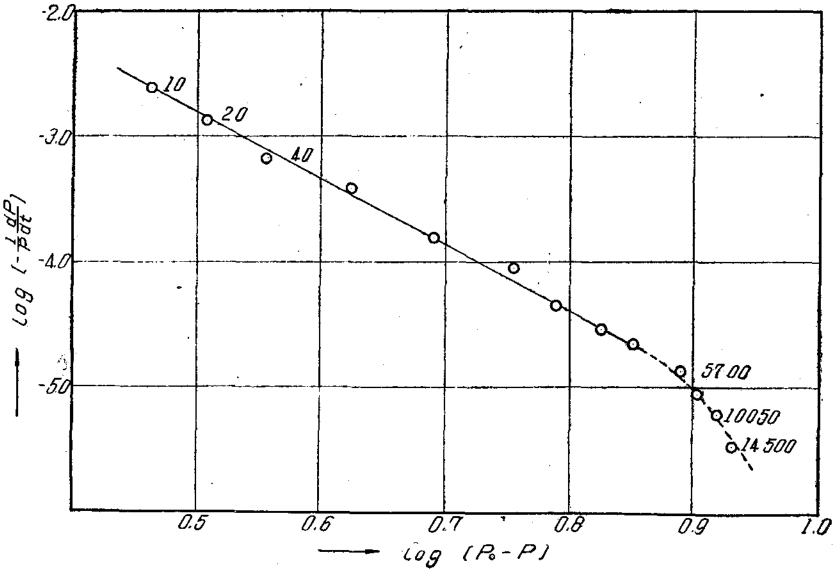

Fig. 3.

Adsorption Rate of Hydrogen on Reduced Nickel at $-78°C$ (IIJIMA).

KINGMAN's data at temperature of 482°C give thus a straight line, when $\log(1/p.dp/dt)$ *versus* $\log(p_0-p)$ is plotted , the slope of which was found to be 1.2. A similar examination of IIJIMA's data for Ni-H_2 at −78°C indicated that eq. (8) can hold over almost the whole range of adsorption with the value $\alpha=5.2$, as shown in Fig. 3, where the annexed figures on the plot represent the elapsed time in minutes. Although a deviation occurs from the straight line near the end of the log-log plot, this may probably be ascribed to the fact that the reverse process can not be neglected.

iv. EMMETT and BRUNAUER[13] and DAVIS[6] determined both the rates and equilibria for the adsorption of nitrogen on a promoted iron catalyst and reduced tungsten respectively. The application of eq. (9) to their data at temperatures of 397 and 500°C where the reverse process seems respectively to be significant has led to satisfactory result. The plot of $\log(dx/dt/1-p_e/p_c)$ against $\log x$, for instance with respect to the former, yields a linear relation within the limits of experimental accuracy as shown in Fig. 4 where θ is replaced by the adsorbed quantity of nitrogen x in cc. N.T.P. The values of α evaluated from

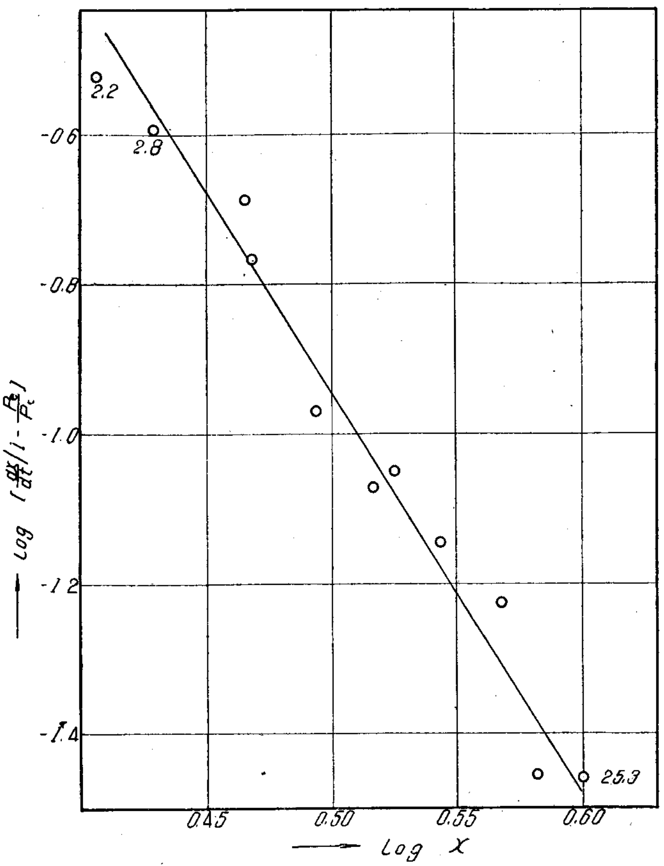

Fig. 4.

Adsorption Rate of Nitrogen on an Iron Catalyst at 397°C (EMMETT, BRUNAUER).

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[13] P. H. EMMETT, S. BRUNAUER, J. Am. Chem. Soc., **56**, 35 (1934).

the slope of the log-log straight line are shown in column 4 of Table II.

TABLE II.
Values of n, α and β

System	Temperature °C	n	α	β
Fe—N_2	397	7.7	5.2	2.5
W—N_2	500	18	15	3

TEMKIN and PYZHEV[14] and also BRUNAUER, LOVE and KEENAN[15] made use of the adsorption rate equation expressed by

$$-\frac{dp}{dt} = k_a p\, e^{-\alpha\theta} - k_d e^{\beta\theta} \tag{13}$$

and the corresponding adsorption isotherm equation as

$$\theta = \frac{1}{\alpha+\beta} \ln a_0 p \tag{14}$$

where a_0 is a constant equal to k_a/k_d and have shown these equations to fit satisfactorily the adsorption data of Fe-N_2 obtained by EMMETT and BRUNAUER. An examination of EMMETT and BRUNAUER's isotherm data, for instance, at temperature of 396°C, however, does in fact reveal that θ *versus* $\ln p$ plot yields by no means a linear relationship which is a requirement of eq. (14) while the logarithmic plot affords an excellent straight line over the whole range of their measurements as demanded by eq. (5). The slope of the log-log straight line or the value of n at 396°C*) was determined therefrom and β was calculated by means of eq. (6). As regards DAVIS' data, the value of n was evaluated from his linear logarithmic isotherm at 500°C, from which β being similarly determined. These values are presented in columns 3 and 5 of Table II.

According to BRUNAUER *et al.*[15] eq. (13) fails to account for the data of TAYLOR and SICKMAN[16] obtained for the adsorption of hydrogen on zinc oxide and those of FRAZER and HEARD[17] for the adsorption of oxygen

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*) The temperature at which adsorption isotherm has been determined was 1° lower than that of the rate measurement but this difference was disregarded in calculations.

[14] M. TEMKIN, V. PYZHEV, Acta Physicochim., U.R.S.S., 12, 327 (1940).

[15] S. BRUNAUER, K. S. LOVE, R. G. KEENAN, J. Am. Chem. Soc., 64, 751 (1942).

[16] H. S. TAYLOR, D. V. SICKMAN, J. Am. Chem. Soc., 54, 602 (1932).

[17] J.C. W. FRAZER, L. J. HEARD, J. Phys. Chem., 42, 855 (1938).

on chromite catalysts. Tests of eq. (8) or (9) were made successfully to these data as will be mentioned next.

v. Finally we shall refer to ZELDOWITSH-ROGINSKY's adsorption rate equation which has been expressed as

$$\frac{d\theta}{dt} = ae^{-\alpha\theta} \tag{15}$$

where a and α are constants. TAYLOR and THON[2] recently demonstrated that this equation fits in with the data of BURWELL and TAYLOR[18] for the adsorption of hydrogen on chromium oxide and also those of numerous other systems. As is apparent from the study of TAYLOR and THON, eq. (15) breaks down in most cases toward the start of adsorption. For instance, the datum of TAYLOR and SICKMAN for the adsorption of hydrogen on zinc oxide at temperature of 184°C indicated that the adsorption is preceded by an "initial massive adsorption" – 0.06 cc per g.– which is not described by the "exponential" law.

If we assume that the reverse process is neglected eq. (8) proves to satisfy the nearly whole range of adsorption with the value $\alpha=3.4$ as shown in Fig. 5. The experimental data deviate apparently from the straight line at the early stage of adsorption but we might presume

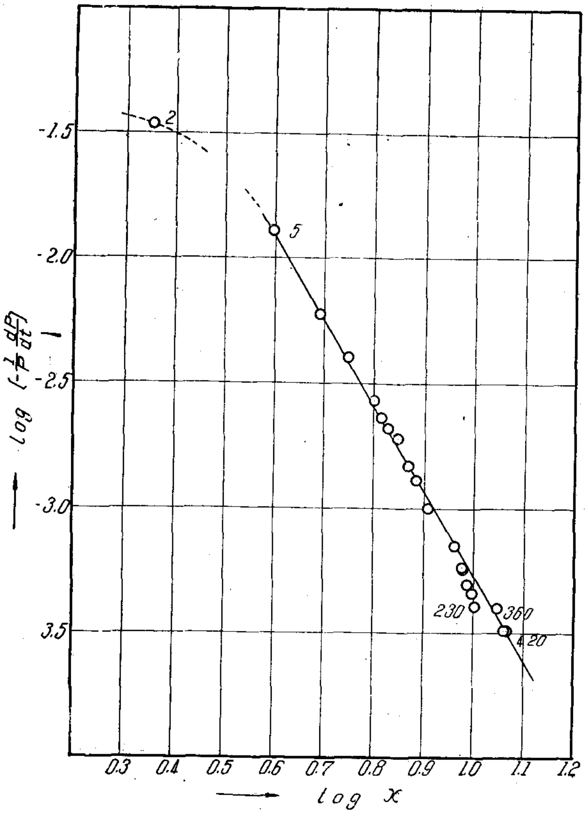

Fig. 5.

Adsorption Rate of Hydrogen on Zinc Oxide at 184°C (TAYLOR and SICKMAN).

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[18] R. L. BURWELL, H. S. TAYLOR, J. Am. Chem. Soc., 58, 697 (1936).

a certain smaller value of α, even near zero, there similarly as in the cases of Fe-N_2 and others. The lacking of adsorption rate data at lower degree of adsorption in question, however, does not enable us to evaluate a definite value for α.

Using eq. (9) and assuming that $p_e/p_c \ll 1$, an attempt was made to FRAZER and HEARD's data for the adsorption of oxygen on copper chromite at 200°C with success. The plot of $\log dx/dt$ *versus* $\log x$ gives a straight line, the slope of which or α being found to be 2.4. A similar plot was taken also from BURWELL and TAYLOR's data for the adsorption of hydrogen on chromium oxide at 154°C and assured the validity of eq. (9) with the value $\alpha=0.8$, as shown in Fig. 6.

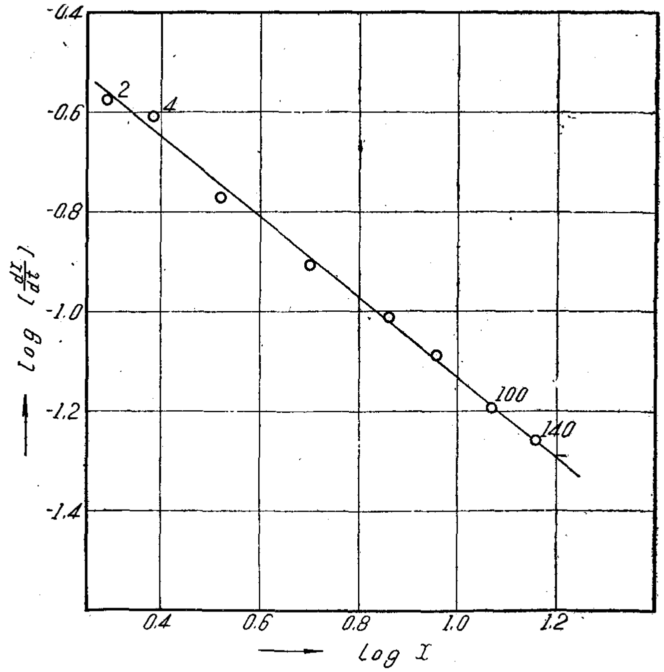

Fig. 6.

Adsorption Rate of Hydrogen on Chromium Oxide at 154°C (BURWELL and TAYLOR).

Parenthetically, the ZELDOWITSH-ROGINSKY's plot in terms of log dx/dt *versus* x does not yield a linear relation toward the data for Fe-N_2 due to the present author.

Conclusion

From the above investigations it is now evident that the adsorption rate equation of the general form (7) can be valid for various adsorption rate data differing in chemical nature and over a sufficiently wide range of surface coverage. However, because of the scarcity of adsorption rate data accompanied with those of equilibria for a given system the value of β in the equation was estimated only for a few cases. It is hoped that the latter should be determined directly on the basis of desorption data. Most of the examinations of eq. (7) have been carried out by assuming that the desorption rate can be neglected and led to the result that the term α is given as a single value, if not entirely, over the surface coverage investigated except for the ZnO-H_2 system. As regards the temperature dependency of α no account has been made in the present paper. An examination of the adsorption rate data on the system Fe-N_2 at different temperatures indicated however that α varies linearly with the reciprocal of absolute temperature. This affords promise of the activation energy for adsorption process to be a linear function of log θ. Detailed accounts along these lines will be given separately in the near future.

Acknowledgments.—Thanks are especially due to Professor J. HORIUTI for his interest and important advice and also to the Grant in Aid for Scientific Research of the Ministry of Education. I wish to express my gratitude to Mr. YAMAMORI and Mr. ÔKOSHI for their active participation in this investigation.

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