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SORPTION OF HYDROGEN BY NICKEL WIRE

By

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The kinetics of the sorption of hydrogen by nickel wire have been studied. The endothermic or exothermic sorption found respectively above or below 250°C was attributed to the absorption or chemisorption.

The rate of the absorption was found as expressed by the equation $\dot{n} = k_s \left(\sqrt{P} - \frac{n}{n_e} \sqrt{P_e} \right)$ throughout the observation, whereas the chemisorption obeyed the modified ROGINSKY-ZELOVICH's type equation $\dot{n} = k_a \sqrt{P} \exp(-bn/RT)$, where n is the quantity of hydrogen sorbed, P the hydrogen pressure, suffix e signifying the value at sorption equilibrium and k_s or k_a is a constant at a constant temperature. The b was found appreciably constant throughout the temperature range from 250°C to the temperature of liquid nitrogen.

The activation energy $RT^2(d\ln k_a/dT)$ of adsorption was found 0.87 kcal/mol or 5.5 kcal/mol respectively below or above 120°C.

The entropy of activation $R(dT \ln k/dT)$ of the sorption was found to vary linearly with the relevant activation energy $RT^2(d\ln k/dT)$, throughout the absorption and the adsorption, where k stands for k_s and k_a .

Introduction

Despite the increasing knowledge of sorption of hydrogen on metals, rather few informations have been provided with regard to its kinetics.

This appears to be due to the difficulties of measuring the rapid rate of sorption on evaporated metal films although obtainable extremely in pure states, while in the case of wires and plates, of securing their pure states and of separating the adsorption on the surface from the absorption into the bulk of metals which possibly predominates in this case. In the case of evaporated films even the absorption has recently been reported by several authors^{1,2)}.

It is the purpose of the present work to observe adsorption and absorption in comparison with each other, discriminating between them by observing isotherms of the respective sorption. Nickel wire was adopted as the sorbent of being possibly afforded with suitable capaci-

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ties for both the sorts of sorptions and used at a pure state as far as possible.

§ 1. Experimental

The rate measurements were carried out at constant volume over a temperature range from 400°C to -195°C and a pressure range from 5×10^{-4} to 5×10^{-3} mmHg.

Nickel wire used was of 0.1 mm diameter and 197 m long as selected to have appropriate capacities for adsorption and absorption. The wire was treated in hydrogen at 420°C for a few days and evacuated at the same temperature for several hours repeatedly until the sorption rate at a certain definite temperature, which increases along with the repetition of the treatments, attains a constant value. It was shown by the similar treatments at higher temperatures up to 820°C that the sorption rate did no more vary from that ultimately attained at 420°C.

Hydrogen was prepared by electrolysis of water, and purified by passing over Pt-black at 300°C, calcium chloride and finally through a palladium thimble.

The pressure change was followed by a Pirani-gauge with tungsten wire of 20μ diameter and 40 cm long, and had the sensitivity of about 5×10^{-5} mmHg. The rapid change of pressure was followed by means of electromagnetic oscillograph.

Fig. 1 shows the apparatus used and the associated electric circuit; A is the reaction chamber containing nickel wire, B the Pirani-gauge immersed in the mixture of ice and water, C the U-tube dipped in liquid nitrogen, D the hydrogen storage vessel, E₁ or E₂ stopcocks, F the wheatstone bridge circuit and G the oscillograph.

After the treatment of wire described above, a definite quantity of hydrogen dosed between the stopcocks E₁ and E₂ from D was expanded into the combined space of A, B and C and the change of pressure with time was photographically recorded by the oscillograph. The observed pressure P_b at Pirani-gauge, falling in the Knudsen region over the whole range, was corrected for that P_a in the reaction chamber according to the Knudsen law, i.e., $P_c/\sqrt{T_c} = P_b/\sqrt{T_b} = P_a/\sqrt{T_a}$, where P_c or T_c is the pressure in the U-tube C immersed in liquid nitrogen or the absolute temperature there and T_b or T_a the temperature in the Pirani-gauge identified with that at room temperature for the correction or in the reaction chamber A.

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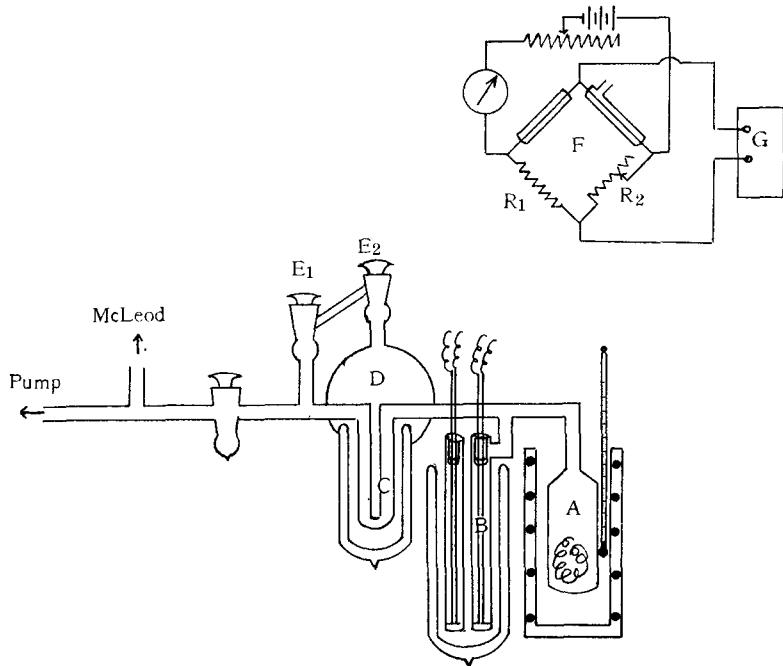


Fig. 1 The reaction apparatus and electric circuit.

The pressure observed by the Pirani-gauge was found to attain a maximum *ca.* two seconds after the opening of E_1 to expand the dosed gas into the combined space of A, B and C. A control experiment without the sorbent in A has shown that the final constant pressure is attained likewise *ca.* two seconds after the expansion.

It was concluded that this time lag was due to the slow diffusion of gas through the tube of the combined space from the facts that the time lag was reduced from 2 to 0.3 seconds by increasing the inner diameter of the tube from 1 cm to 1.5 cm and that G shows an appropriate constants current instantaneously without any observable time lag at the variation of the resistance R_1 and R_2 in the case when the combined space was evacuated or occupied statically by a definite amount of gas.

Assuming the rate dP/dt of pressure increase in the Pirani-gauge is proportional to the excess $P_\infty - P$ of the pressure P attained at the diffusion equilibrium over the momentary pressure P as

$$dP/dt = k(P_\infty - P), \quad (1)$$

the proportionality constant k was determined from the $P-t$ diagram of the above control experiment.

It is expected that k in the above equation when applied to the case of the actual sorption measurements, is even larger than that in the mere expansion, inasmuch as the gas is supplied into A in the former case partially from vicinal spaces, or at least that the difference between dP_{∞}/dt and dP/dt , i. e., $(1/k)d^2P/dt^2$ according to the equation

$$(1/k)d^2P/dt^2 = dP_{\infty}/dt - dP/dt \quad (2)$$

obtained by differentiating (1), is of the same order of the magnitude as that between the rate dP_a/dt of sorption and dP/dt , where P_a is the pressure in A. The $(1/k)d^2P/dt^2$ was thus calculated for every series of measurements to screen out those for which the magnitude of $(1/k)d^2P/dt^2$ remains within the limit of errors ca. 3% of dP/dt -determination.

The equilibrium of sorption was nearly established within thirty

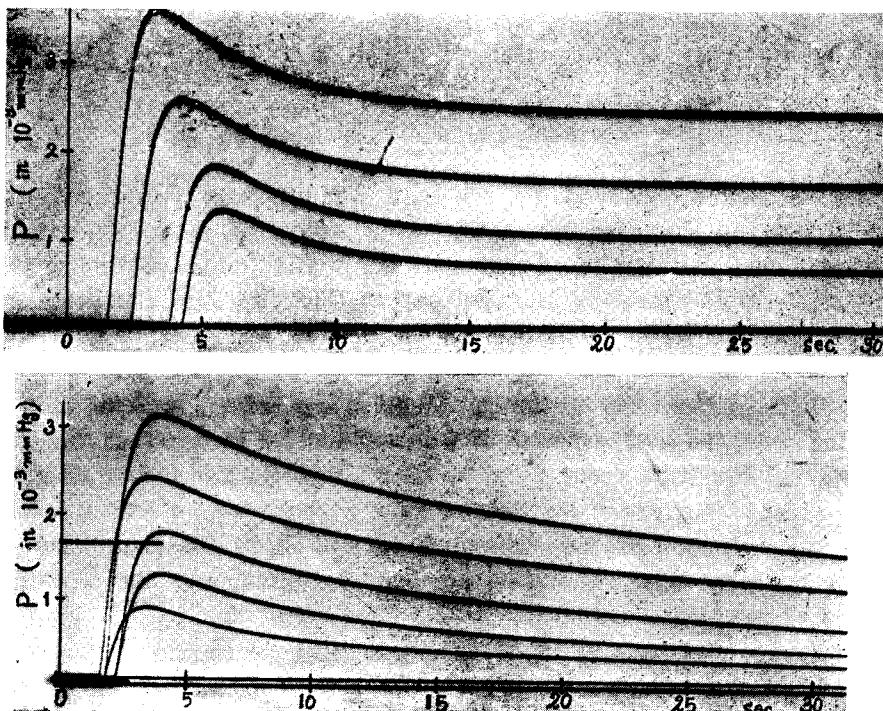


Fig. 2 Typical examples of oscillograms, at
288°C and 151°C.

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seconds at high temperatures above 280°C and several minutes over the temperature range from 250°C to 120°C but not attained within one hour below 120°C.

Typical examples of $P-t$ diagrams are shown in Fig. 2.

§ 2. Sorption Equilibrium

It is well-known that adsorption of hydrogen on nickel is exothermic, whereas its absorption endothermic; it is hence thermodynamically expected that either adsorption or absorption predominates at lower or higher temperature respectively and is observed practically as the sole effect by a proper selection of the volume and the surface area of nickel wire. This situation has been realized with nickel wire of the size described above, as shown by the following observation of isotherms of sorption over the temperature range from 150°C to 800°C.

The sorbed quantity at equilibrium was taken as that 30 minutes after the admission of hydrogen into the reaction vessel, it being attained practically within a few minutes after the admission and the resistance of the Pirani-gauge being ascertained sensibly constant over a much longer period of time, as the combined space is evacuated or charged with a definite quantity of gas.

Fig. 3 shows typical isotherms of hydrogen sorption on nickel wire

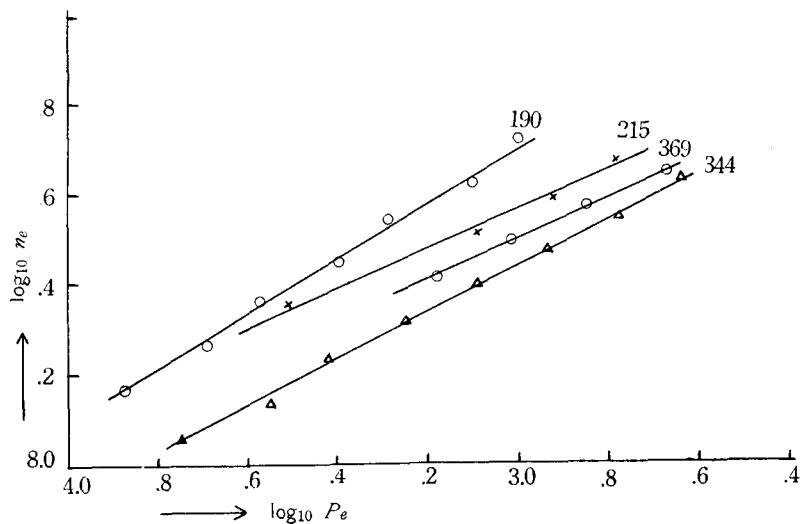


Fig. 3 The sorption isotherms.

with the logarithm of sorbed quantity n_e in moles plotted against of the logarithm of the equilibrium hydrogen pressure P_e . $\log_{10} n_e$ varies, as shown in the Figure, linearly with $\log_{10} P_e$, the slope being ca. $x = 1/2$ at various temperatures as seen from Table I; their average 0.51 states that n_e is very nearly proportional to $\sqrt{P_e}$.

TABLE I. The slope x of $\log_{10} n_e$ against $\log_{10} P_e$.

Temp. °C	190	262	347	344	369	381	397	215
x	0.59	0.58	0.51	0.52	0.46	0.46	0.61	0.43

Average $x = 0.51 (\pm 0.08)$

The plot of n_e against $\sqrt{P_e}$ is shown in Fig. 4. The equilibrium constant $K \equiv n_e/\sqrt{P_e}$ of sorption is determined from this linear relation and $\log_{10} K - 1/T$ plots are shown in Fig. 5.

The $\log_{10} K - 1/T$ diagram consists of two branches developed respectively below or above 250°C as seen from Fig. 5, each being

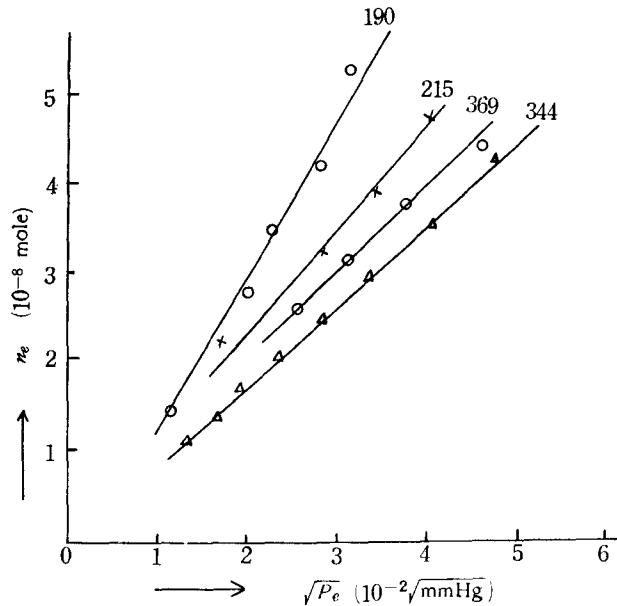


Fig. 4 The $n_e - \sqrt{P_e}$ plots.

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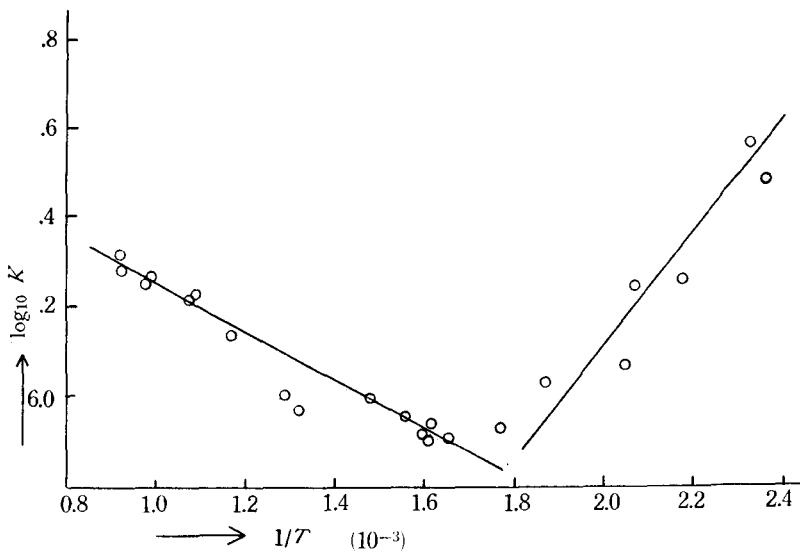


Fig. 5 The $\log_{10} K - 1/T$ plots.

approximately a straight line of the slope or the heat toning $RT^2(d\ln K/dT)$ of -5 kcal/mole or 14 kcal/mole. The negative heat toning above 250°C is in accord with the heat of solution of hydrogen for nickel reported in literatures³⁾, whereas the positive one 14 kcal/mole below 250°C is appreciably lower than the heat of chemisorption 31 kcal/mole observed with evaporated films⁴⁾ or 26 kcal/mole with reduced nickel powders⁵⁾.

The above result might be attributed to the situation that the sorption equilibrium in the present experiment has been virtually attained at higher temperatures, while not completely at lower temperatures, apparently reducing the heat toning, inasmuch as the sorption equilibrium is attained the less completely, the lower the temperatures thus apparently reducing the temperature difference of the sorbed quantity.

It is inferred on this ground that we are dealing with endothermic or exothermic sorption respectively above or below 250°C and hence with the absorption or adsorption predominantly in the respective temperature region.

§ 3. Kinetics of Sorption

The sorption rate \dot{n} of hydrogen was determined from the negative

inclination $-dP/dt$ of $P-t$ diagrams, screened out as described in §1, as $\dot{n} = -(V/RT) dP/dt$ in the temperature range from 400°C to -195°C.

3 a. The initial rates of sorption

The initial rates \dot{n}_i 's are found to be proportional to the square root of initial pressures as shown in Fig. 6 which shows the relation

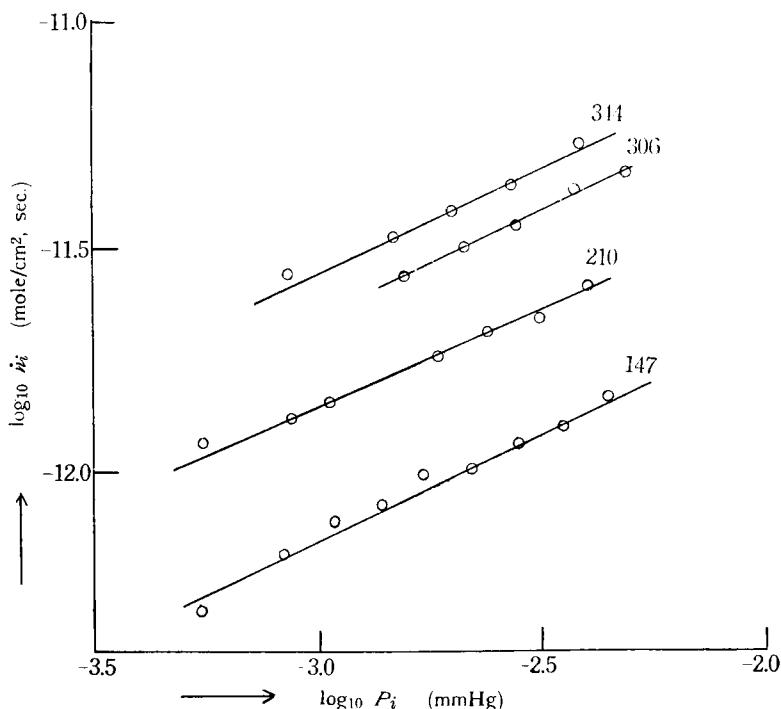


Fig. 6 The $\log_{10} \dot{n}_i - \log_{10} P_i$ plots.

TABLE II. The slope of $\log_{10} \dot{n}_i$ against $\log_{10} P_i$.

Temp. °C	344	306	306	369	331	288	147	147
The slope	0.45	0.46	0.50	0.47	0.31	0.40	0.50	0.50
Temp. °C	251	251	151	190	262	0	210	
The slope	0.45	0.47	0.40	0.53	0.54	0.60	0.45	

The average of the slope = 0.47

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between $\log_{10} \dot{n}_e$ and $\log_{10} P_e$ in the temperature range above described, i.e., both in absorption and adsorption regions $\log_{10} \dot{n}_e$ varies linearly as $\log_{10} P_e$ with the slope of mean value 0.47.

The values of slopes at various temperatures are listed in Table II.

3 b. The rates of absorption

It is now ascertained that \dot{n} determined as above described is proportional to $X \equiv (\sqrt{P} - \frac{n}{n_e} \sqrt{P_e})$ over the whole course of every run up to equilibrium, the proportionality constant k_s being definite at definite temperature irrespective of the initial pressure as shown in Fig. 7, i.e., $\dot{n} - X$ plots of different runs at a definite temperature fall on a common straight line through the origin, as

$$\dot{n} = k_s \left(\sqrt{P} - \frac{n}{n_e} \sqrt{P_e} \right). \quad (3)$$

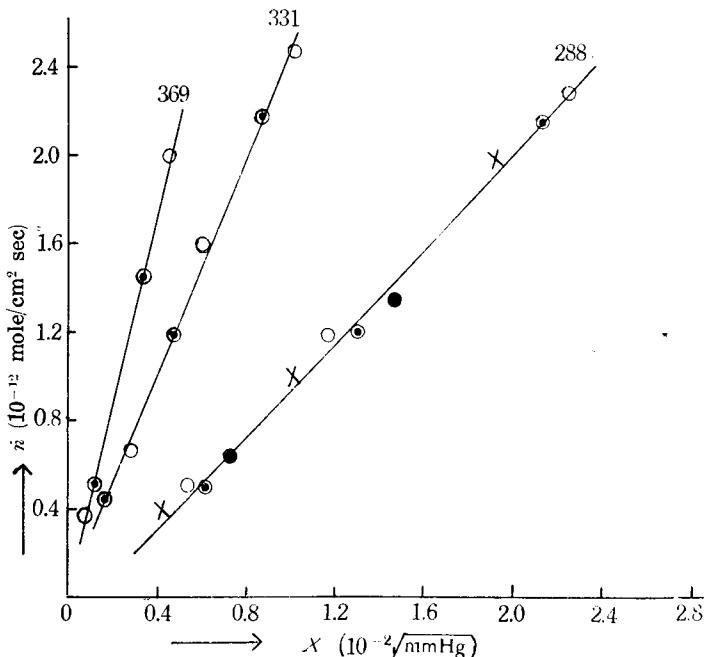


Fig. 7 The $\dot{n} - X$ plots.

$$X \equiv \sqrt{P} - \frac{n}{n_e} \sqrt{P_e}$$

TABLE III. The absorption rate constants k_s .

(mol/sec cm² √mmHg)

Temp. °C	369	331	280	306	288	344	306
$k_s \times 10^{10}$	4.40	2.52	1.03	1.45	1.05	3.00	1.89

Table III shows the values of the rate constant k_s at different temperatures. The plot of $\log_{10} k_s$ vs. $1/T$ is linear as shown in Fig. 8 giving the activation energy 25 kcal/mole which nearly equals to that of diffusion process of hydrogen through nickel⁶.

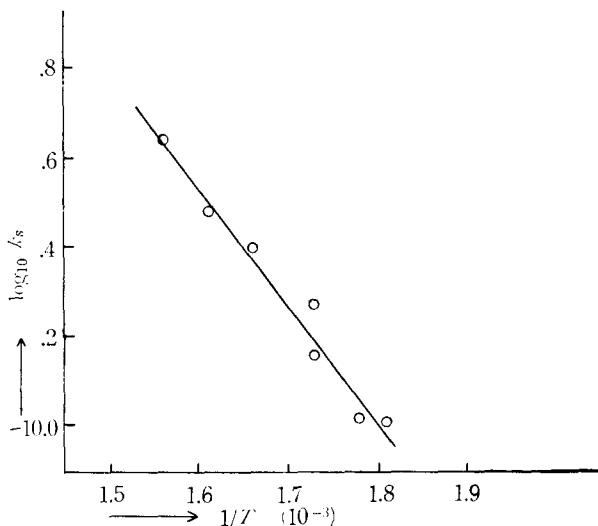


Fig. 8 The temperature dependence of the absorption rate constant k_s (mole/sec cm² √mmHg).

3 c. The rates of adsorption

The rate of adsorption on nickel wire was determined similarly as in the case of absorption from $P-t$ diagrams over the temperature range from 250°C to -195°C.

The adsorption rate \dot{n} thus obtained was found to obey the equation of ROGINSKY-ZELDOVICH type⁷ $\dot{n} = a \exp(-cn)$ except in the later stage of runs as exemplified in Fig. 9 by the plot of $\log_{10} \dot{n}$ against n at different initial pressures at 0°C.

It has further been found that the plots of $\log_{10} \dot{n}/\sqrt{P}$ against n fall

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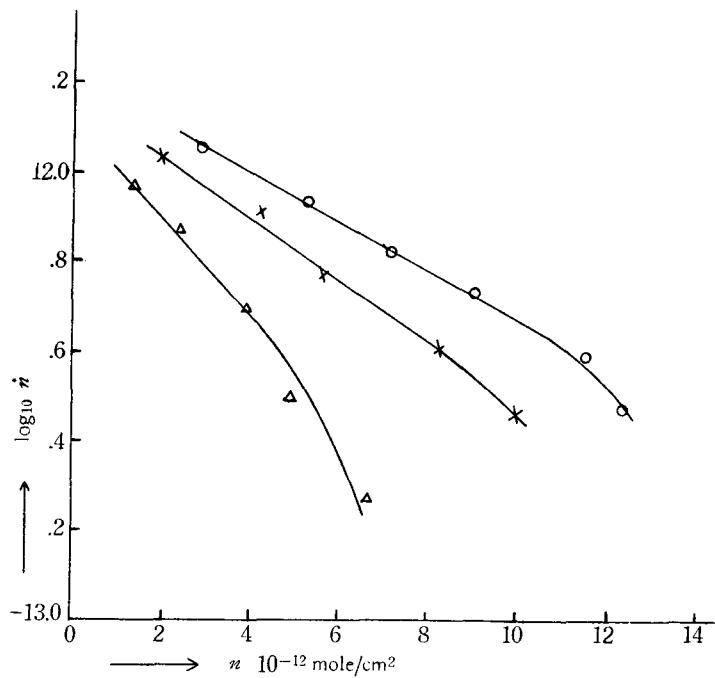


Fig. 9 Variation of adsorption rate with amount adsorbed at various initial pressures at 0°C.

on a common straight line at constant temperature irrespective of the initial pressure as shown in Fig. 10 except in the later stage of runs, i.e., that there exists a relation

$$\dot{n} = k_a \sqrt{P} \exp(-c'n), \quad (4)$$

where k_a and $c' = (\partial \ln \dot{n} / \partial n)_T$ are constants independent of initial pressures and further that the constant c' is proportional to $1/T$ as shown in Fig. 11. The rate of the adsorption is thus ultimately expressed as

$$\dot{n} = k_a \sqrt{P} \exp(-bn/RT), \quad (5)$$

where b is a constant independent of pressures and temperatures over the temperature range from -195°C to 250°C and calculated at $4.4 \times 10^{13} \text{ cal (mole/cm²)}^{-1}$.

The validity of (5) shows that the initial rate is proportional to the square root of pressure similarly as in the case of absorption,

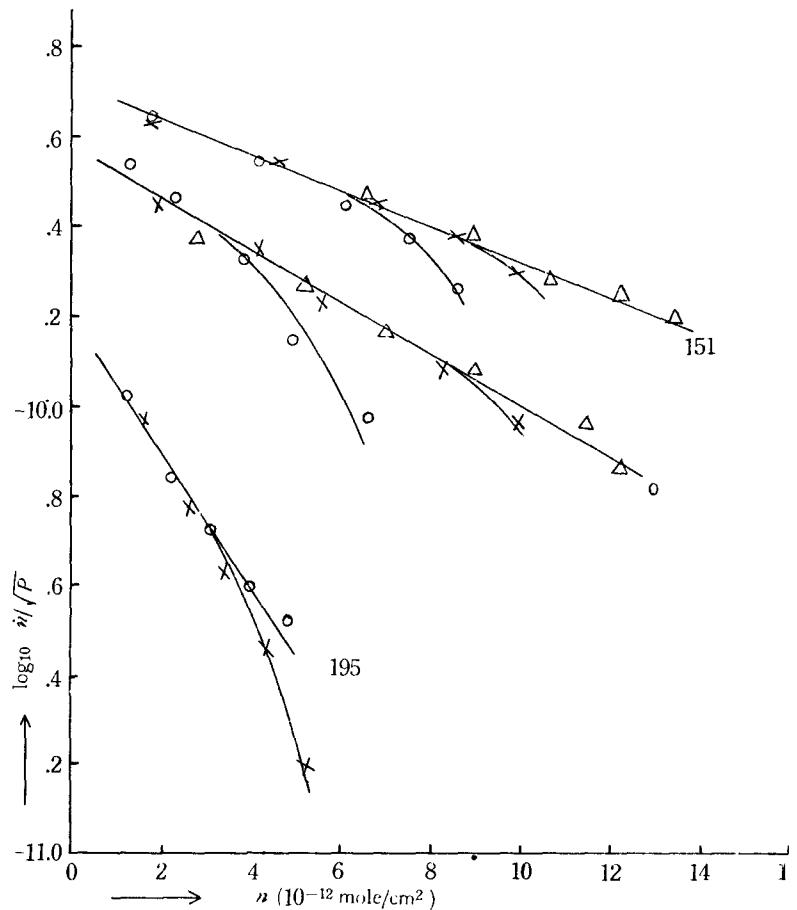


Fig. 10 Variation of n/vP with amount adsorbed
at various temperatures.

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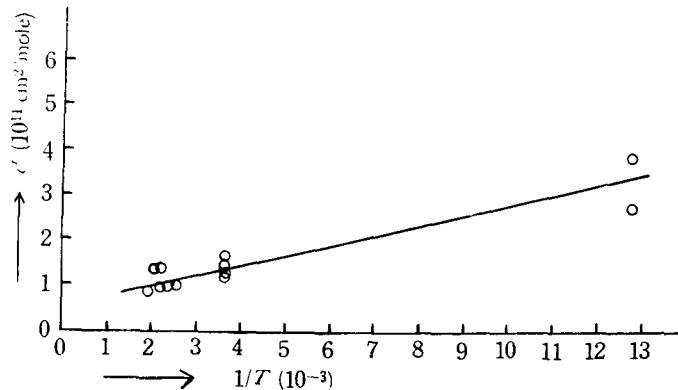


Fig. 11 The relation between
 $c' = \left(\frac{\partial \log_{10} i}{\partial n} / \sqrt{P} \right)_T$ and $1/T$.

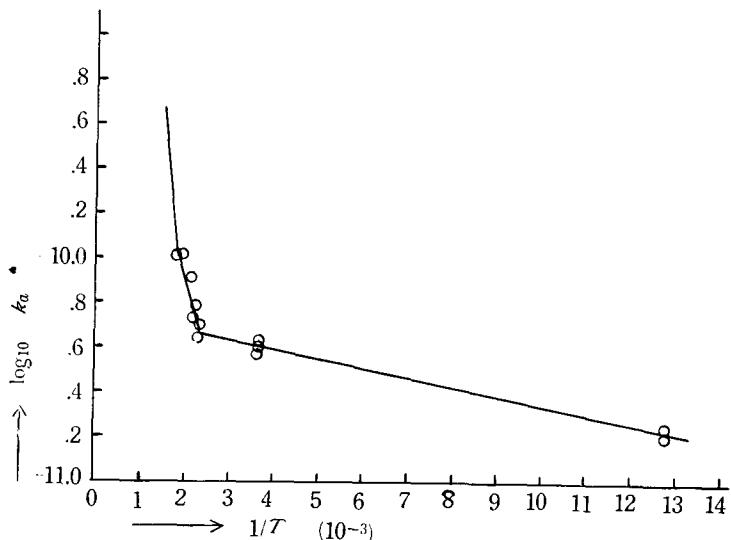


Fig. 12 The temperature dependence of the
 adsorption rate constant k_a
 (mole/sec $\text{cm}^2 \sqrt{\text{mmHg}}$).

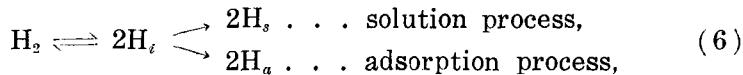
as was verified in §3 a. The deviation from (5) at the later stage bears, on the other hand, closely on the adsorption equilibrium incompletely attained as mentioned in §2 or on the difficulty of empirically formulating the reverse reaction rate in the present experiments in contrast to the case of absorption.

The temperature dependence of constant k_a determined by (5) is shown in Fig. 12. The appropriate activation energy $RT^2(d \ln k_a/dT)$ is found at 5.5 kcal/mole or 0.37 kcal/mole respectively above or below 120°C.

§ 4. Discussion

It was found that the sorption of hydrogen by nickel wire takes place in either of two types, i.e., the absorption into the interior of metal or the adsorption on the surface of metal respectively predominant above or below 250°C, whereas the initial rate of hydrogen uptake varies as the square root of the pressure throughout.

These results are accounted for by the mechanism with the rate-determining step of the transition of intermediate adatoms H_i into the state of absorbed atoms H_s or stable adatoms H_a , i.e., as



where the first step is assumed to be in partial equilibrium.

Assuming the classical kinetics applicable for such a low hydrogen pressure as in the present experiment, it follows from the above mechanism that the forward rate \vec{V}_s of absorption is proportional to the surface concentration of H_i or to the square root \sqrt{P} of the pressure of hydrogen gas, which is in partial equilibrium with H_i by the first step, i.e., as $\vec{V}_s = \vec{k}_s \sqrt{P}$. Assuming the backward rate \vec{V}_s of absorption similarly proportional to the concentration n of H_s , as $\vec{V}_s = \vec{k}_s n$, we have $V_s = \vec{k}_s \sqrt{P} - \vec{k}_s n$ for the overall rate $V_s = \vec{V}_s - \vec{V}_s$ of absorption. At the absorption equilibrium we have, however, $\vec{k}_s / \vec{k}_s = n_e / \sqrt{P_e}$ and hence

$$V_s = \vec{k}_s \left(\sqrt{P} - \frac{n}{n_e} \sqrt{P_e} \right), \quad (7)$$

which is identical with (3) aside from the notation of the rate constant. It may be noted that the mechanism advanced is confirmed by the value of the activation energy $RT^2(d \ln k_e/dT)$ 25 kcal/mole nearly coinci-

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dent with that of diffusion process of hydrogen through nickel as mentioned above.

It follows from the mechanism advanced for the adsorption similarly that the forward rate is proportional to the square root of hydrogen pressure in accordance with the experimental results (5) valid over the temperature range from 250°C to -195°C, which gives the forward rate at the initial stage as the initial rate $k_a\sqrt{P}$ itself. The constant b in Eq. (5) is determined from the experimental results at 4.4×10^{13} cal (mole/cm²)⁻¹, which is compared with the value 1.0×10^{13} cal (mole/cm²) recalculated from the results of the "slow sorption" by GUNDRY and TOMPKINS obtained with evaporated films⁸⁾.

The same kinetics (5) as that observed by the latter authors as well as the same order of magnitude of the b -values might suggest that we are dealing with a physically the same process in the adsorption by wires as in the slow sorption on evaporated films observed by them.

The activation energy $RT^2(d \ln k_a/dT)$ of the initial adsorption shows moreover an abrupt change at 120°C from 5.5 kcal/mole above to 0.37 kcal/mole below the latter temperature, while b remains constant

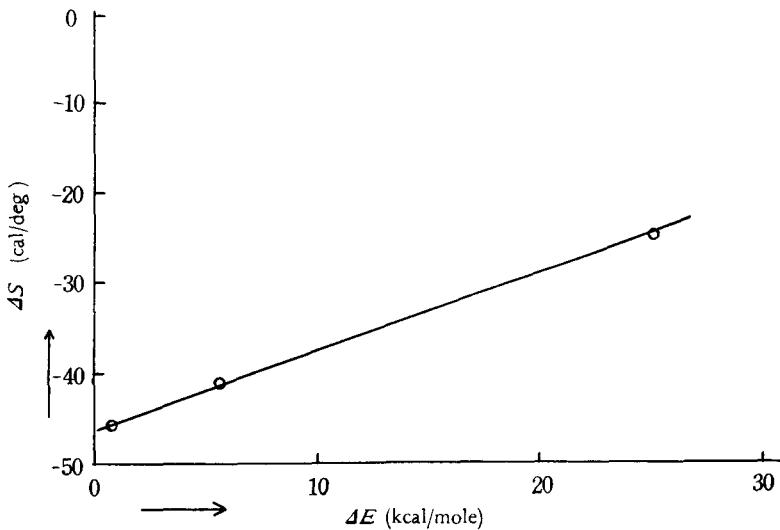


Fig. 13 The relation between the activation energy and the activation entropy of sorption.

throughout from 250°C to -195°C as shown in Fig. 11. This result might suggest that there exists two sorts of adsorption.

It is finally pointed that there exists a so-called compensation effect between the activation energy $RT^2(d \ln k/dT)$ and the activation entropy $R(dT \ln k/dT)$ among three sorts of sorption as shown in Fig. 13, where k stands for k_s , and two values of k_a respectively relevant to the two kinds of adsorption.

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