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# DETERMINATION OF DIFFUSION COEFFICIENT OF HYDROGEN THROUGH NICKEL FOIL

By

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## Abstract

The diffusion coefficient of electrolytically charged hydrogen through nickel foil around room temperature was determined by observing the permeation rate of hydrogen through nickel foils of thickness 4.9, 7.4 and 9.3 $\mu$. The value of the diffusion coefficient $D$ obtained was $D\,(\mathrm{cm^2/sec}) = D_0 \exp(-E/RT) = 4.1 \cdot 10^{-2} \cdot \exp(-13.5\ \mathrm{kcal}/RT)$. The reported works on the absorption of hydrogen in nickel and those on the desorption were examined; and by using the above $D$-value they were semi-quantitatively elucidated as the phenomena of diffusion control processes.

## Introduction

EURINGER[1], HILL and JOHNSON[2], and EDWARDS[3] obtained the values of diffusion coefficient $D$ observing thermally charged hydrogen evolution from nickel specimens. BARANOWSKI, SMIALOWSKA and SMIALOWSKI[4] obtained it by observing the rate of hydrogen desorption from electrolytically hydrogen-charged nickel wires. They also stated that the non-uniformity of hydrogen distribution in electrolytically surcharged nickel is an important problem requiring further studies. Following this work they reported many phemomena related to those which might be explained in terms of "diffusion control" in making use of the $D$-value of $6 \cdot 10^{-10}\,\mathrm{cm^2\,sec^{-1}}$ which they obtained. Thus BARANOWSKI and SMIALOWSKI[5] suggested the existence of the limited depth of penetration of electrolytically charged hydrgen into nickel films on the basis of the observed $D$-value. Although they reported many works afterwards, the determination of the $D$-value was not followed further.

The present authors observed the rate of permeation of electrolytically charged hydrogen through several Ni foils of different thickness and obtained the $D$-value as $6.3 \cdot 10^{-12}\,\mathrm{cm^2\,sec^{-1}}$ at 25°C with $D_0 = 4.1 \cdot 10^{-2}$, and $\mathrm{E} = 13.5$ kcal.

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## Experimental

Nickel foils of different thickness stated as 4.9, 7.4 and 9.3 $\mu$ respectively were cut in 30 mm × 30 mm square pieces and weighed to determine their thick- nesses precisely. They were treated in boiling 10% KOH solution for 10 minutes and then thoroughly washed with redistilled hot water and mounted in the cell. The electrolytic cell used is shown in Fig. 1. The volume of hydrogen permeated was measured by micro burette. The electrolyte solution used was 250 cc of 1 N-$H_2SO_4$ containing $(NH_2)_2$ CS or $SeO_2$ or $As_2O_3$ as an additive. Most of the experiments were carried out in a solution containing

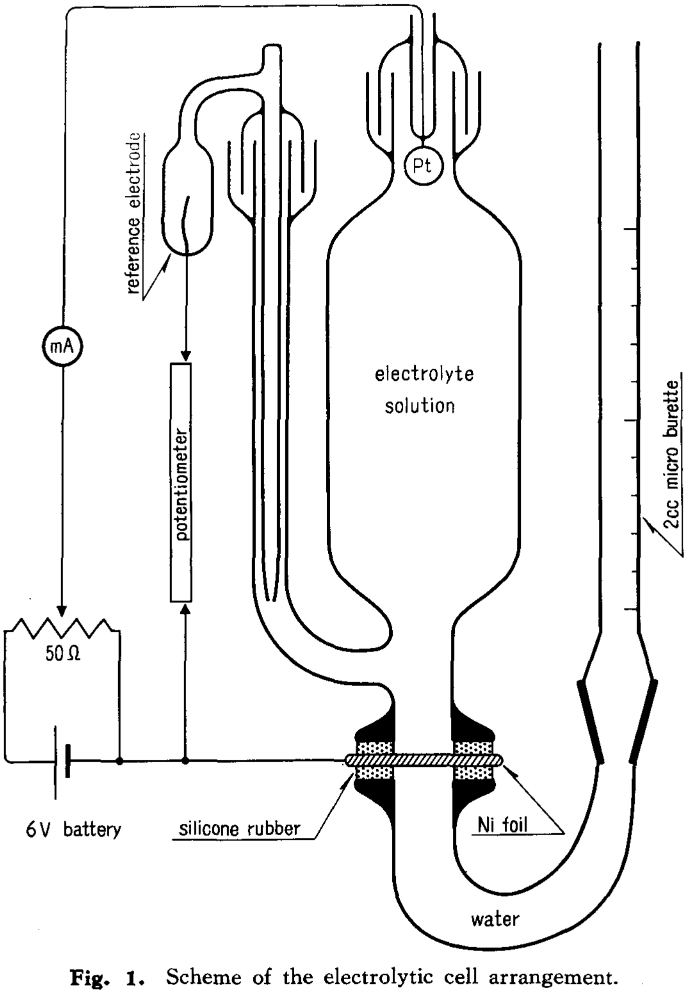

**Fig. 1.** Scheme of the electrolytic cell arrangement.

$(NH_2)_2CS$ at 25.0°C in a thermostat. The geometrical area of the nickel electrode was 1.78 cm$^2$. The nickel electrode potential during electrolysis was measured referring to the quinhydrone electrode and recorded. The specimens were used only once to avoid trouble from pin-holes which sometimes occurred during electrolysis.

## Results

### 1. Effects of the additives on the hydrogen electrode reaction on platinum and nickel electrodes

In Fig. 2, the change of the electrode potential of the platinum electrodes in an open circuit, which in pure sulfuric acid solution without any additives rest at the equilibrium potential of the hydrogen electrode, is plotted as a function of amount of the additives. Thiourea does not change the electrode potential at all. But the addition of minute amounts of $As_2O_3$ makes a distinct change in the electrode potential by about +0.3 volt. However, the double layer capacity*) of the electrodes remained with the same value before and after the addition of these 3 sorts of additives. Once arsenic oxide is added, it is very difficult to remove it from the electrode surface and from the cell.

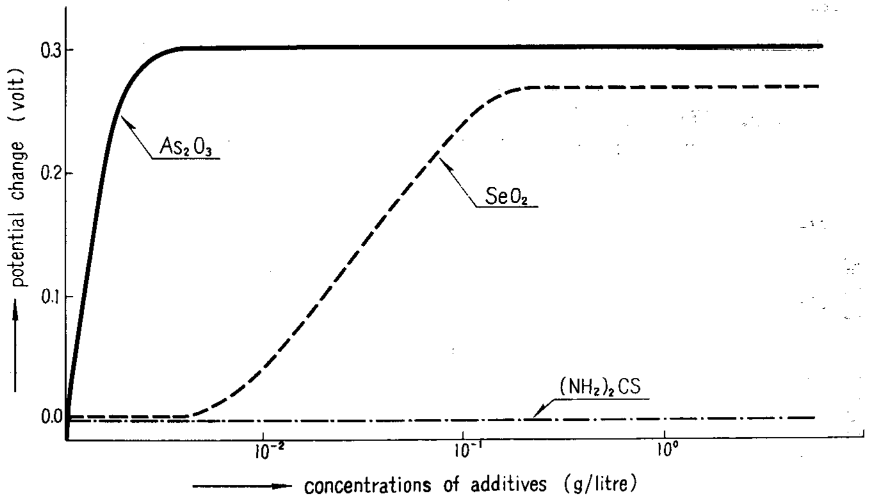

**Fig. 2.** Effects of the additives on the platinum hydrogen electrode rest at equilibrium potential.

Fig. 3 shows the potential *vs.* current density relationship of the nickel electrode in the presence of the additives. It is noticed from the figure that

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*) The electrode capacity was measured by the galvano-static transient method proposed by MATSUDA[6].

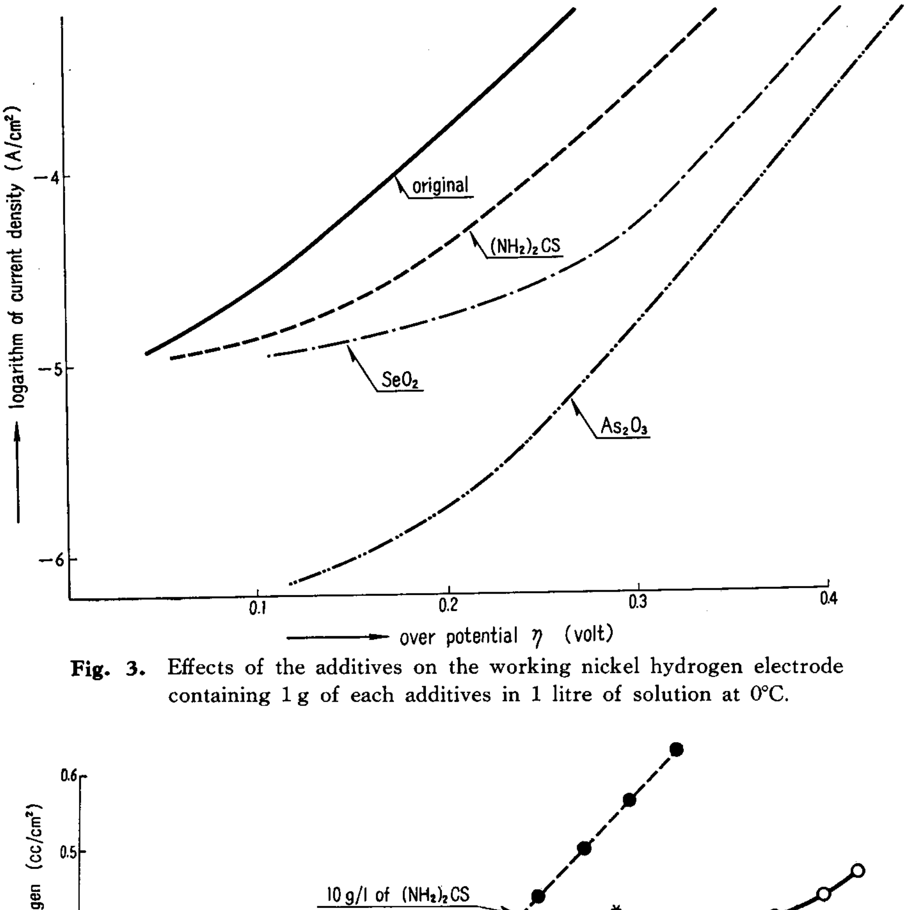

**Fig. 3.** Effects of the additives on the working nickel hydrogen electrode containing 1 g of each additives in 1 litre of solution at 0°C.

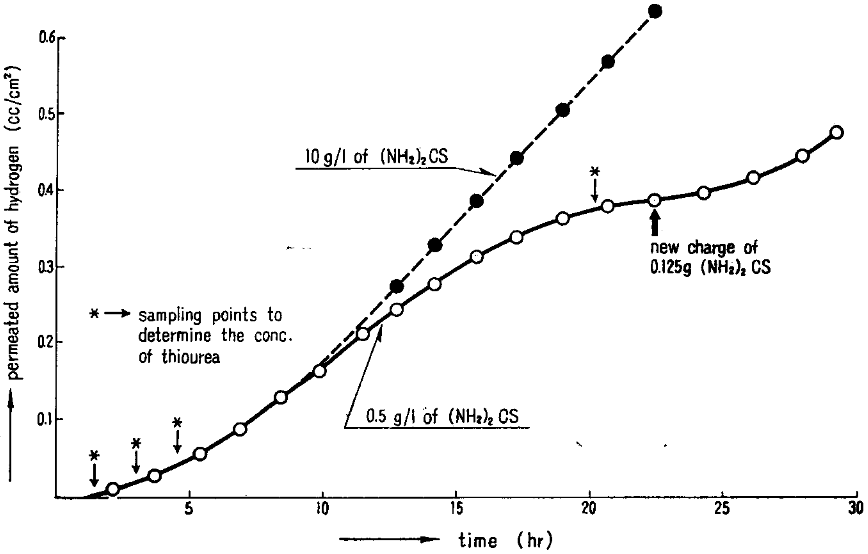

**Fig. 4.** The relation between the amount of permeated hydrogen and time under different concentration of thiourea: (9.3 $\mu$ of thickness 25 mA/cm² of current density at 25°C).

only arsenic oxide acts to prevent nickel from dissolving.

### 2. Effects of the amount of thiourea on the rate of hydrogen permeation

Fig. 4 illustrates the relation between the amount of permeated hydrogen (cc/cm$^2$) and time. When 10 g of $(NH_2)_2CS$ is added to 1 litre of 1 N–$H_2SO_4$, the permeation rate given by the slope of curve approaches to a constant value after the elapse of 7 hrs as seen from the broken line which extends up to 30 hrs or more, while the addition of 0.5 g of $(NH_2)_2CS$ (per litre of 1 N–$H_2SO_4$) is not sufficient to maintain the permeation rate at a constant value as seen from the full curve in the figure. A supplemental addition of 0.125 g of $(NH_2)_2CS$ into the cell containing 250 cc of solution accelerates the permeation rate. These results indicate that, during the electrolysis, thiourea can be consumed by evolving hydrogen, and its concentration on the surface of the Ni electrode becomes low. Fig. 5 shows the absorption spectra of the electrolyte solution at 1.5, 3, 4.5 and 20 hrs after the initiation of electrolysis under the same conditions with that shown by the full curve in Fig. 4. The decrease of peak height at the 236 mμ with the progress of electrolysis due to $>C\overset{-}{\rightarrow}S$ transition moment confirms the consumption of thiourea as mentioned above.

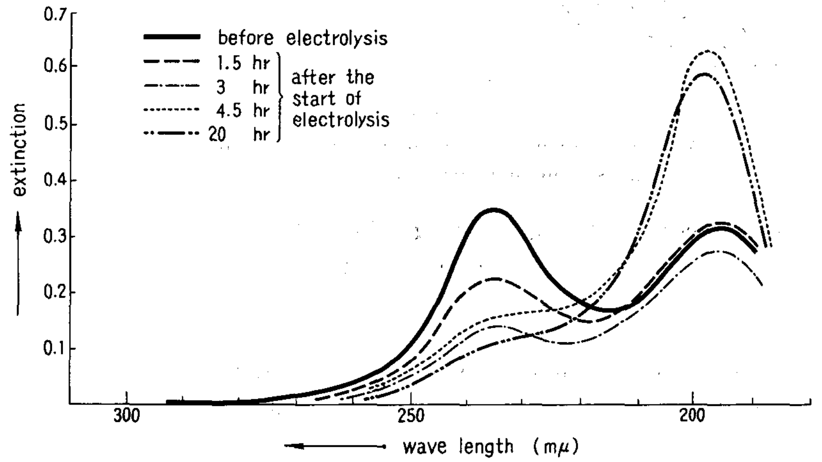

**Fig. 5.** The change of the absorption spectra of thiourea with time during electrolysis.

### 3. The relations between the lag-time τ or the constant rate of permeation $V_p$ and the thickness $d$ of the nickel foil

Varying the thickess $d$ of the nickel foils, the amount of permeated hydrogen *vs.* time relations are observed under a current density of 25 mA/cm$^2$ in 1 N–$H_2SO_4$ containing 10 g/litre of $(NH_2)_2CS$ at 25°C. Results are shown in

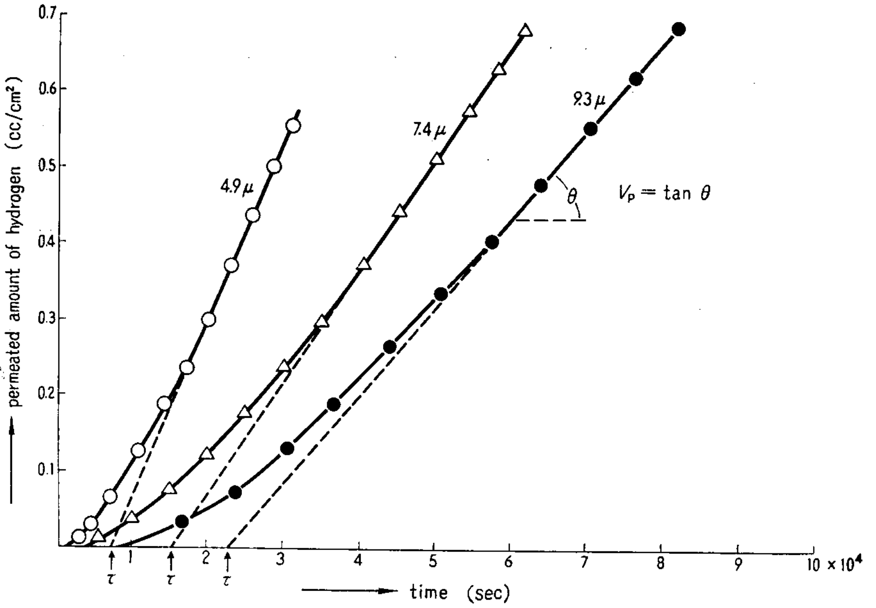

**Fig. 6.** The relation between the amount of permeated hydrogen against time and thickness $d$ of the foil

Fig. 6. If diffusion of hydrogen through the nickel foil is the rate-determining process of the permeation, the $D$ value is given by the relation,

$$\tau/d^2 = 1/6D \tag{1}$$

using the set of value$d$'s and $r$'s where $\tau$ is the lag-time of permeation. The constant rate of permeation, $V_p$ (cc/sec·cm²), is given by FICK's law as

$$V_p = D\cdot(C_i - C_0)/d \tag{2}$$

where $C_i$ and $C_0$ is the concentration of hydrogen in nickel (ccH/ccNi) at the inlet side (polarization side) and the outlet side (diffusion side) of the foil respectively. As the maximum value of $C_0$ in equilibrium with 1 atm $H_2$ gas is estimated as about $10^{-4}$ (H/Ni in atomic ratio) which is negligible as compared with $C_i$, we have

$$V_p = D\cdot C_i/d\,. \tag{3}$$

In Fig. 7 and 8, $\tau$ *vs.* $1/d^2$ and $V_p$ *vs.* $1/d$ relations are shown, from which we have (as the mean value) $D = 6.3\cdot10^{-12}$ (cm²/sec) and $C_i = 0.91$ (H/Ni) under the present experimental conditions.

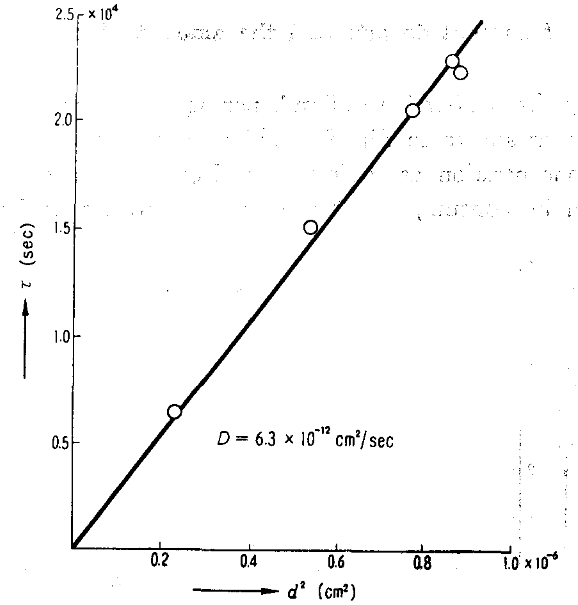

**Fig. 7.** The relations between the lag-time $\tau$ and the thickness $d$ of the foil.

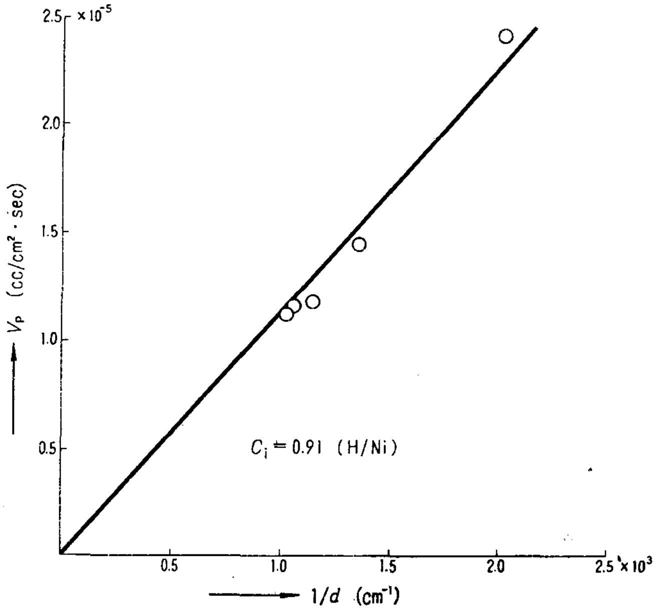

**Fig. 8.** The relations between the constant rate of permeation $V_p$ and the thickness $d$ of the foil.

### 4. The effects of current density and the amount of $(NH_2)_2CS$ on the $D$ value

In the range from 10 mA to 25 mA per sq·cm², current density does not alter the $D$-value as shown in Fig. 9. Thiourea shows some effect on the $D$-value at low concentration as indicated in Fig. 10, which is understood in conjunction with its consumption during the electrolysis as already described.

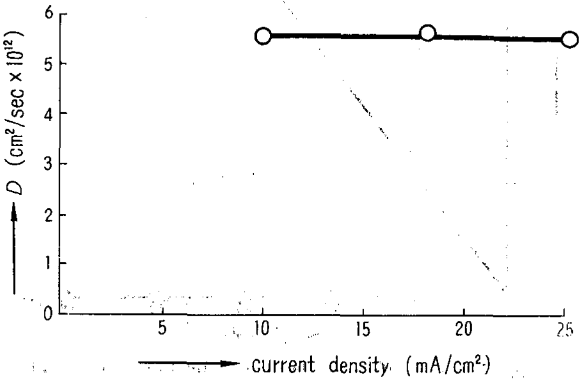

**Fig. 9.** The influence of current density on the $D$-value

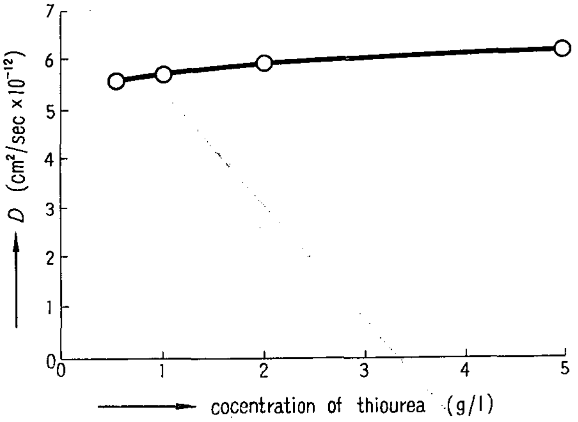

**Fig. 10.** The influence of the concentration of thiourea on the $D$-value

### 5. Heat of activation of diffusion

From the $D$-values obtained at 30°C, 25°C, 20°C and 15°C, the heat of activation $E$ was estimated accordingly by the equation $D = D_0 \exp(-E/RT)$. Fig. 11 shows the plots of $\log_{10} D$ against $1/T$ for the case of $d = 4.9\,\mu$ and

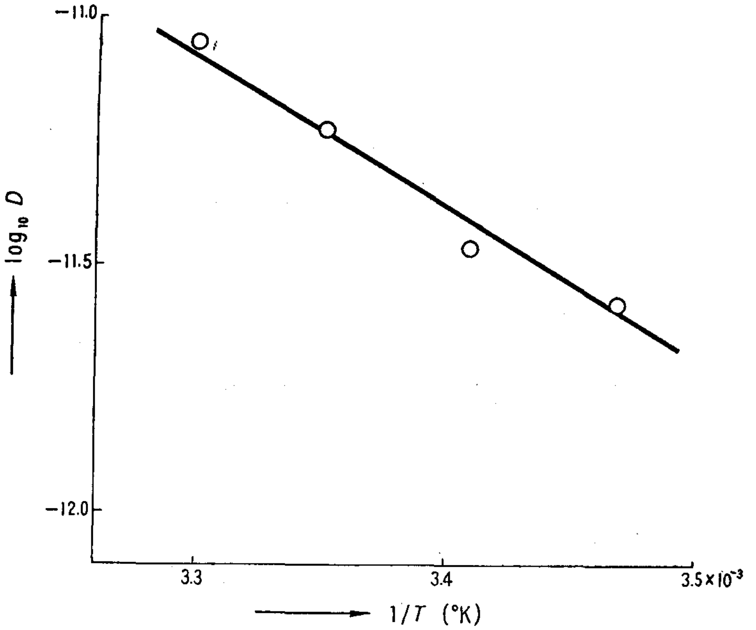

**Fig. 11.** $\log_{10} D$ *vs.* $1/T$ relation.

the current density of 25 mA/cm$^2$. Thus, we have $D=4.1\cdot 10^{-2}\exp(-13.5\ \text{kcal}/RT)$.

## 6. Effect of pH on the permeation of hydrogen

Fig. 12 shows the relationships between the amount of permeated hydrogen

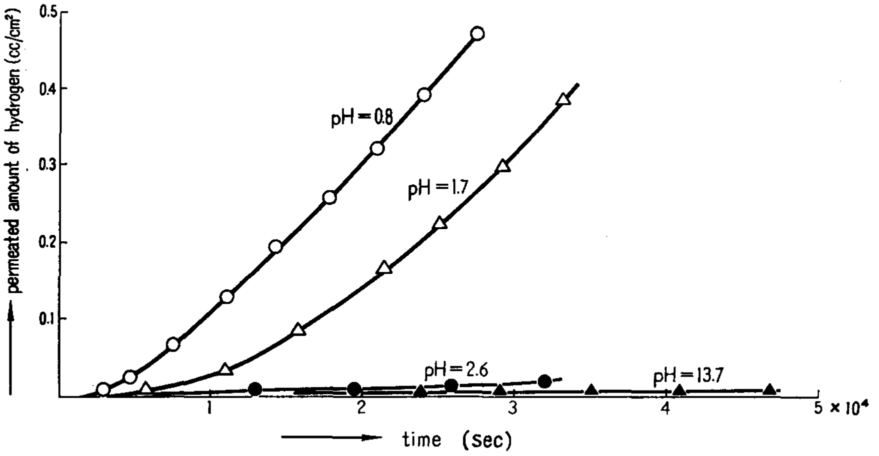

**Fig. 12.** The effect of pH on the permeation of hydrogen ($d=4.9\ \mu$, $i=25$ mA/cm$^2$, 10 g/l of thiourea, 25°C)

and time observed at different *pH*-values of the electrolyte solution. In neutral and alkaline solution, the permeation of hydrogen through nickel foil was not detectable.

## Discussion

It is obvious from the present results that the rate of permeation of hydrogen through nickel is controlled by the diffusion process. Present value of $D$, however, differs by a factor of $10^2$ from those in the literature[1-4]. Following calculation of absorption and desorption of hydrogen in and from nickel respectively may suggest that our $D$-value will be more probable than those reported. BARANOWSKI[7] repoted that the hydrogen desorption from nickel obeys the equation for the first order reaction:

$$dV/dt = -kV, \qquad (4)$$

where $V$ is the volume of hydrogen comprised by the given sample at the time $t$, and $k$ is the rate constant. He obtained the value of $k$ at 25°C for nickel foil of a thickness around 9 $\mu$ as $10^{-4}$ sec$^{-1}$ in the order of magnitude, and the value of heat of activation of desorption process as $E = 13.7$ kcal/mol. Now we assume that:

1) the rate determining process of desorption of hydrogen from nickel is the diffusion process;
2) the hydrogen concentration $C_{0,0}$ in nickel, before the desorption process occurs, is the same throughout the foil;
3) the hydrogen desorbs from both sides of the foil;
4) the hydrogen concentration at the surface of the nickel foil, when desorption occurs, is zero.

With these assumptions, the hydrogen concentration $C_{t,x}$ at time $t$ from the commencement of desorption and at a distance $x$ from the surface of the specimen is given by the equation (5) as:

$$C_{t,x} = \frac{4C_{0,0}}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \sin \frac{(2m+1)\pi x}{d} \exp \left\{ \frac{-D(2m+1)^2\pi^2 t}{d^2} \right\} \qquad (5)$$

where $m$ is the integer, $d$ is the thickness of the foil. We can now evaluate the value of $C_{t,x}/C_{0,0}$ with the use of known values of $d = 9\,\mu$, $D = 6.3 \cdot 10^{-12}$ (cm$^2$/sec) as functions of $x$ and $t$. The results are plotted in Fig. 13. According to the assumption 3, the limit of $x$ is $d/2 = 4.5\,\mu$. The area below the curves gives the total amount of hydrogen $C$ in nickel at time $t$. Fig. 14 shows the log $(C/C_0)$ *vs.* time relationship at 25°C, where $C_0$ is the initial

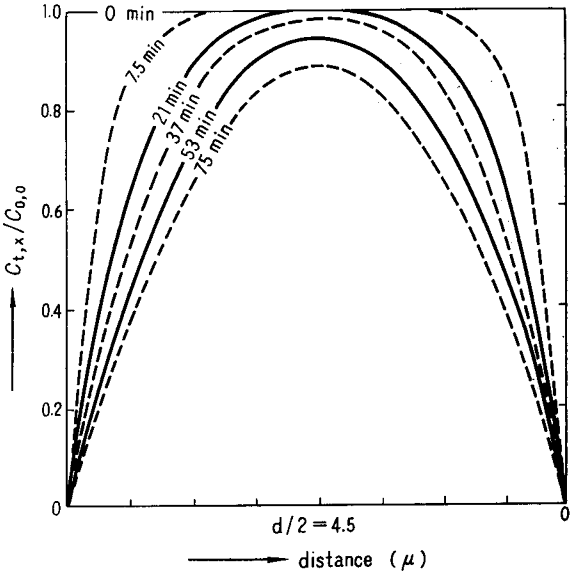

**Fig. 13.** $C_{t,x}/C_{0,0}$ against $x$ and $t$ relationship for the nickel foil of $d=9\,\mu$ at 25°C.

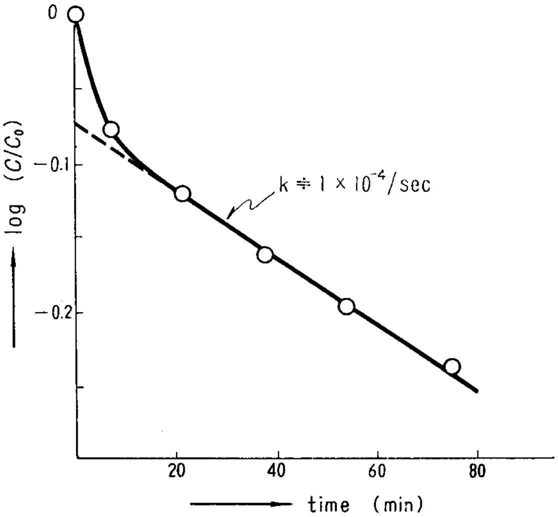

**Fig. 14.** log $(C/C_0)$ versus time relation-ship for the nickel foil of $d=9\,\mu$ at 25°C.

hydrogen content. From Fig. 14, we obtain the value of the rate constant of the hydrogen desorption process as $k \fallingdotseq 1\cdot 10^{-4}$ ($\mathrm{sec}^{-1}$). From the assumption 1 the heat of activation of desorption process should be the same with that of diffusion process. Our observed value of heat of activation of diffusion is $E=13.5$ kcal. Both of these are in quite good agreement with the reported values for the desorption process by BARANOWSKI[7].

We now treat the absorption process with the assumptions given below:

1) the hydrogen can be taken up into nickel foil from both sides;
2) there is no hydrogen in nickel at $t=0$;
3) during electrolysis the hydrogen concentration at both surfaces remains at a constant value of $C_{0,0}$;
4) the rate determining process of the absorption of hydrogen is the diffusion of hydrogen through nickel.

$C_{t,x}$ is now given similarly as the case of Eq. (5) as follows.

$$C_{t,x}=C_{0,0}\left[1-\frac{4}{\pi}\sum_{m=0}^{\infty}\frac{1}{(2m+1)}\sin\frac{(2m+1)\pi x}{d}\exp\left\{\frac{-D(2m+1)^2\pi^2 t}{d^2}\right\}\right] \qquad (6)$$

When $d$ is large, $C_{t,x}$ can be expressed as:

$$C_{t,x}=C_{0,0}\left(1-\frac{2}{\sqrt{\pi}}\int_0^{x/2\sqrt{Dt}}e^{-y^2}dy\right) \qquad (7)$$

Using $C_{0,0}=0.91$ (H/Ni) and $D=4.3\cdot 10^{-12}$ ($\mathrm{cm}^2/\mathrm{sec}$) at 21.5°C from our experiment, the amount of hydrogen absorbed in nickel during electrolysis is calculated.

In Fig. 15, we show the comparison of experimental data by MOON and CLEGG[9] with our calculated values in two cases, *i.e.*, in one case $d=12.4\,\mu$ and in the other $d$ is very large, where of Eq. (7) is valid.

The good agreement of calculated values with those of experiments shows the reliability of both the $D$ and $E$ value obtained. MOON and CLEGG[9] doubt BARANOWSKI's suggestion that there is a limited depth of hydrogen penetration into nickel. The coincidence of the above calculated results of the absorption of hydrogen by very thick nickel foil with the experimental one of MOON and CLEGG shows that there is but one rate determining diffusion process and no limited depth of penetration. This divergence of views might be caused by the use of uncertain values of $D$ and $E$ in conjunction with the use of insufficient amount of additives such as $(NH_2)_2CS$. It is obvious that additives are consumed during electrolysis and when consumption occurs, it retards the rate of absorption. Thus, we are afraid that less stable conditions for the absorption

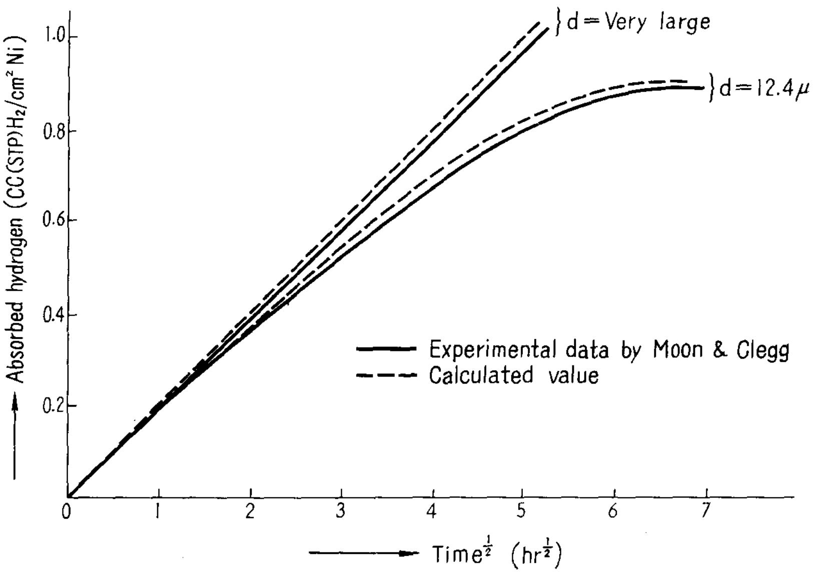

**Fig. 15.**

of hydrogen were maintained in those works quoted above. When $d$ is large enough, say $30\,\mu$, the value of lag-time $\tau$ should be from Eq. (1) about 70 hrs. During that time thiourea will be consumed to a considerable extent and the rate of uptake of hydrogen greatly retarded; and some of the hydrogen absorbed can escape from the nickel specimen, leading to the uneven distribution of hydrogen in nickel.

## Conclusion

The present authors observed a constant rate of permeation of electrolytically charged hydrogen through nickel foils of the thickness 4.9, 7.4 and $9.3\,\mu$, and determined the values of the diffusion coefficient $D$ and the heat of activation of diffusion $E$ as $D = 4.1 \cdot 10^{-2} \exp(-E/RT)$ and $E = 13.5$ kcal respectively. Although the $D$-value of the present work differs by a factor of $10^2$ from those reported[1-4], the rates of absorption and desorption calculated on the basis of our observation shows quite good agreement with experimental results reported, suggesting the reliability of the present value of $D$ and $E$.

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