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RATES OF PERMEATION AND DIFFUSION COEFFICIENTS OF HYDROGEN AND DEUTERIUM THROUGH PALLADIUM

By

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Summary

The rates of permeation of hydrogen and deuterium through palladium wire fused in glass, along its axis from its one end in the respective gas of pressure P toward the other end in vacuum were measured. The permeation rate of hydrogen $V_{P^2}^H$ and its ratio to that $V_{P^2}^D$ of deuterium were determined as

$$V_{P^2}^H = \frac{1.41 \times 10^{-2}}{l} \sqrt{P} \exp\left\{-\frac{3220}{RT}\right\} \text{ cc (NTP)/sec cm}^2, \text{ mm thick,}$$

and

$$V_{P^2}^H/V_{P^2}^D = 1.8 \exp\left\{-\frac{80}{RT}\right\},$$

where l is the length of the palladium wire fused in glass (mm), and T the absolute temperature; the observation ranged from 3.6 to 63 cmHg of P or from 14 to 53 cmHg of P respectively in case of hydrogen or deuterium and from 443° to 563°K of T . Under these experimental conditions it was verified that the permeation is controlled by diffusion through palladium metal, the diffusion coefficient of hydrogen D^H and its ratio D^H/D^D to that D^D of deuterium were determined as

$$D^H = 5.96 \times 10^{-3} \exp\left\{-\frac{5650}{RT}\right\} \text{ cm}^2/\text{sec},$$

and

$$D^H/D^D = 2.45 \exp\left\{-\frac{850}{RT}\right\},$$

with reference to the known solubility data of hydrogen and of deuterium in palladium.

The diffusion coefficients of hydrogen and deuterium in palladium were theoretically calculated, on the other hand, on the basis of a model that the diffusion consists in the transition of proton or deuteron from a position of the lowest potential energy to the nearest similar one through the path of the least potential energy, where the potential energy is the total sum of the screened coulombic repulsive potential energy, *i.e.* $V = \frac{Ze^2}{r} e^{-\lambda r}$ due to each a palladium ion; r is the distance from the proton or the deuteron to the palladium ion, Z

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the effective charge of palladium ion and λ the coefficient of shielding effect of proton or deuteron by electron cloud. Calculated values of the diffusion coefficients of hydrogen and deuterium were found in accordance with the observed ones for $Z=1$ and $\lambda = \frac{1}{0.34} \sim \frac{1}{0.42} \text{ \AA}^{-1}$, which are theoretically reasonable values.

Introduction

The present author¹⁾ has previously observed the permeation of hydrogen through palladium wire fused in glass for 11.5 mm length from one end exposed to hydrogen atmosphere toward its other end in vacuum. The rate of permeation of hydrogen mentioned above was concluded to be controlled by the diffusion of hydrogen through the metal from the following experimental results :

1) The rate of permeation was proportional to the square root of the pressure of hydrogen atmosphere to which one end (inlet end) of the palladium wire was exposed with the other end (outlet end) in vacuum.

2) The rate of permeation was not affected by exposing the inlet end of the wire preliminarily to 1 atm air at 260°C, or by addition of 0.2% carbon monoxide to hydrogen gas.

3) The diffusion coefficient derived from the observed permeation rate assuming solution equilibria at both inlet and outlet ends was found concordant with that determined by the "time lag" method.

The present paper is concerned with the observation of the permeation rate of deuterium through palladium wire from which result the diffusion coefficient D^D of deuterium is similarly determined on the one hand and with the theoretical calculation of D^H as well as D^H/D^D on the basis of a pertinent model to be compared with the experimental results on the other hand. The diffusion control of the permeation rate of hydrogen is further confirmed in the present work by varying the length of palladium wire fused in glass.

The sorption rate of hydrogen and deuterium by palladium ball was previously observed by JOST and WIDMANN²⁾. They deduced from the experimental result the isotope effect on the diffusion coefficient, admitting that the observed sorption rate was controlled by the inner diffusion without satisfactory evidence.

Experimental

The apparatus and experimental methods are the same as that reported previously for hydrogen¹⁾. Fig. 1 shows the schematic diagram of the apparatus used and Fig. 2 the cell. Number of cells which differ in the length of palladium wire fused in glass are used in case of hydrogen in order to confirm

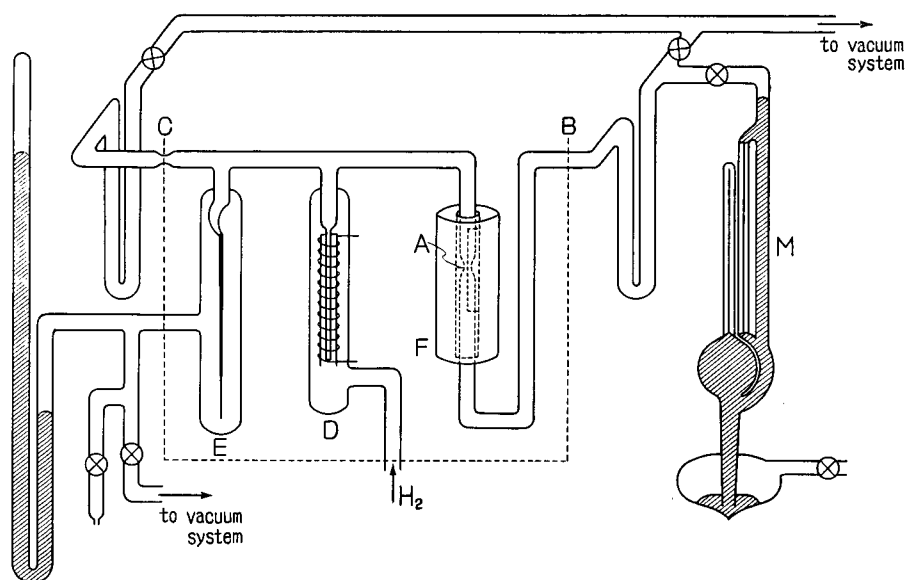


Fig. 1. Apparatus for measuring permeation rate.

A permeation cell	F electrical furnace
D palladium thimble	M McLeod gauge
E Bourdon gauge	

the previous conclusion that the permeation is controlled by diffusion.

Deuterium supplied by Stuard Oxygen Co. in U.S.A. was introduced into the cell for measurements after being passed through a palladium thimble.

Results

(1) Rate of permeation of hydrogen

The rate of permeation of hydrogen are observed for different length l of palladium wire fused in glass. A series of experiments was conducted for each cell to confirm the linear relation between the rate of permeation and the square root of hydrogen pressure \sqrt{P} , as exemplified by Fig. 3. The permeation rate reduced to 55.3 cmHg hydrogen pressure from the latter relation varied now inversely proportional to l as shown

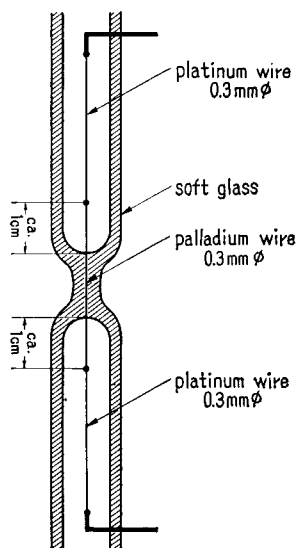


Fig. 2. Permeation cell.

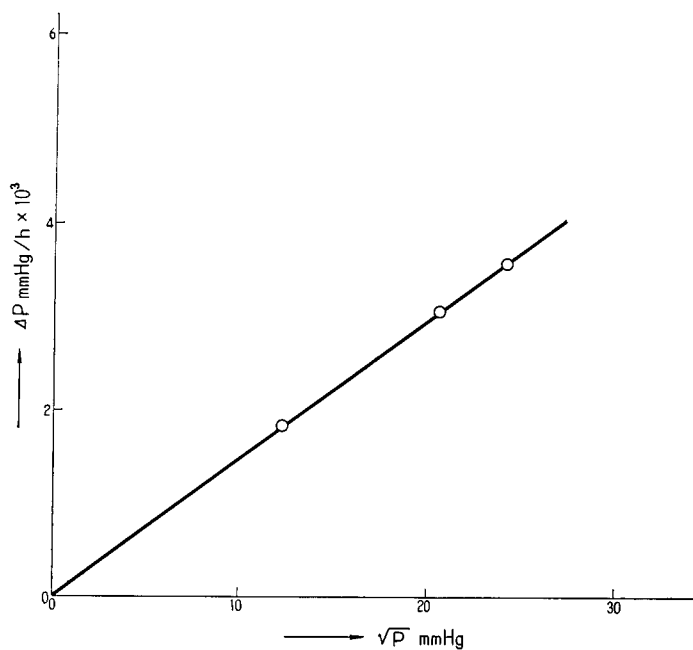


Fig. 3. Dependence of permeation rate, *i.e.* increase of pressure at the outlet space per hour, of hydrogen upon length of permeation path.

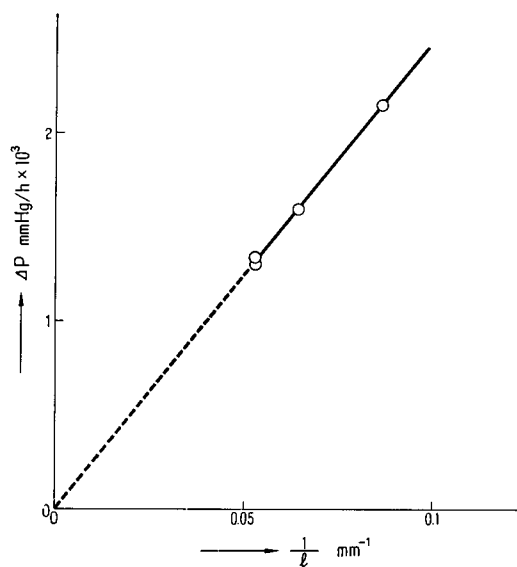


Fig. 4. Dependence of permeation rate, *i.e.* increase of pressure at the outlet space per hour, of deuterium upon pressure.

in Fig. 4. The result of Fig. 4 confirms the assumption in the previous paper¹⁾ and is expressed as

$$V_P^{H_2} = \frac{1.41 \times 10^{-2}}{l_{(mm)}} \sqrt{P_{(cmHg)}} e^{-\frac{3220}{RT}} \text{ cc (NTP)/sec cm}^2, \text{ mm thick.} \quad (1)$$

(2) Rate of permeation of deuterium

The rates of permeation of deuterium $V_P^{D_2}$ through palladium wire fused in glass for 15.5 mm length were observed at temperatures from 443° to 563°K and deuterium pressures from 14 to 53 cmHg. Fig. 3 shows the rate of permeation *vs.* the square root of deuterium pressure; Fig. 5 shows $\log V_P^{H_2}$ and $\log V_P^{D_2}$ plotted against reciprocal absolute temperature, where $P=58.3$ cmHg.

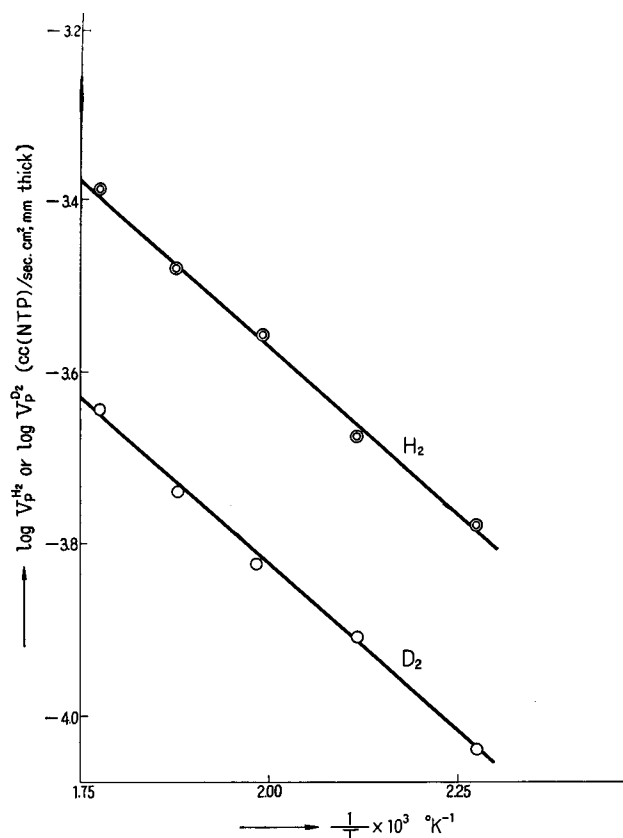


Fig. 5. Dependence of permeation rate $V_P^{H_2}$ of hydrogen and that $V_P^{D_2}$ of deuterium upon temperature. $P=58.3$ cmHg.

It follows from the result shown in Fig. 3 and Eq. (1) that the ratio of the rate of permeation of hydrogen to that of deuterium at the same pressure is independent of the pressure and is expressed as

$$V_P^{H_2}/V_P^{D_2} = 1.8e^{-\frac{80}{RT}}. \quad (2)$$

(3) "Time lag" observation

"Time lag" L of hydrogen was observed at temperatures 443°, 488° and 533°K in order to determine the diffusion coefficient D^H according to the relation³⁾

$$L = \frac{l}{6D^H}.$$

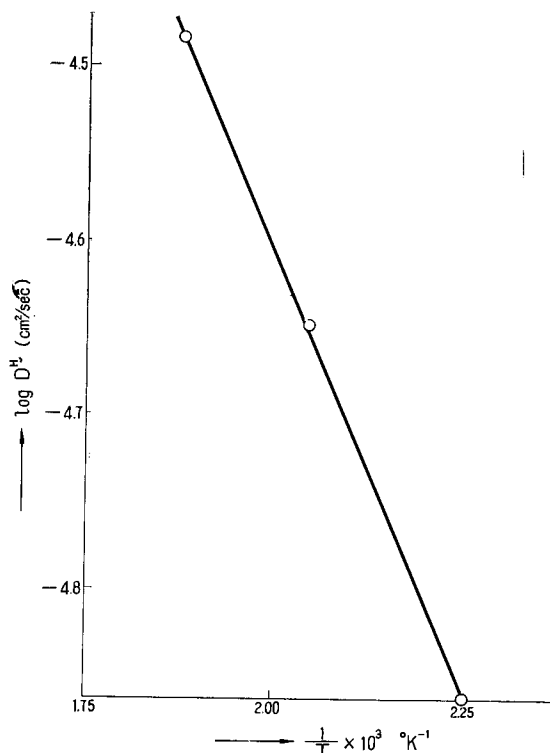


Fig. 6. Dependence of diffusion coefficient of hydrogen measured by "time lag" method upon temperature.

The diffusion coefficient thus determined is plotted against temperature in Fig. 6, which is expressed analytically as

$$D^H = 4.22 \times 10^{-3} e^{-\frac{5330}{RT}} \text{ cm}^2/\text{sec}. \quad (3)$$

Discussion

Experimental results in Fig. 4 confirms further the previous conclusion that the permeation rate is governed by diffusion, inasmuch as the steady rate of permeation V_P^H of hydrogen through palladium is inversely proportional to l in accordance with the relation

$$V_P^H = -D^H \frac{c_0^H - c_l^H}{l}, \quad (4)$$

where D^H is the diffusion coefficient and c_l^H and c_0^H are the concentration of dissolved hydrogen in palladium (cc (NTP)/cc Pd) respectively at the inlet and the outlet ends, which are respectively kept practically constant under the assumption of sorption equilibrium maintained at both the ends. The c_l^H and c_0^H are calculated from the known sorption equilibrium of hydrogen shown in Figs. 7 and 8, which are analytically expressed with special reference to the temperature range from 180° to 290°C of the present observation as

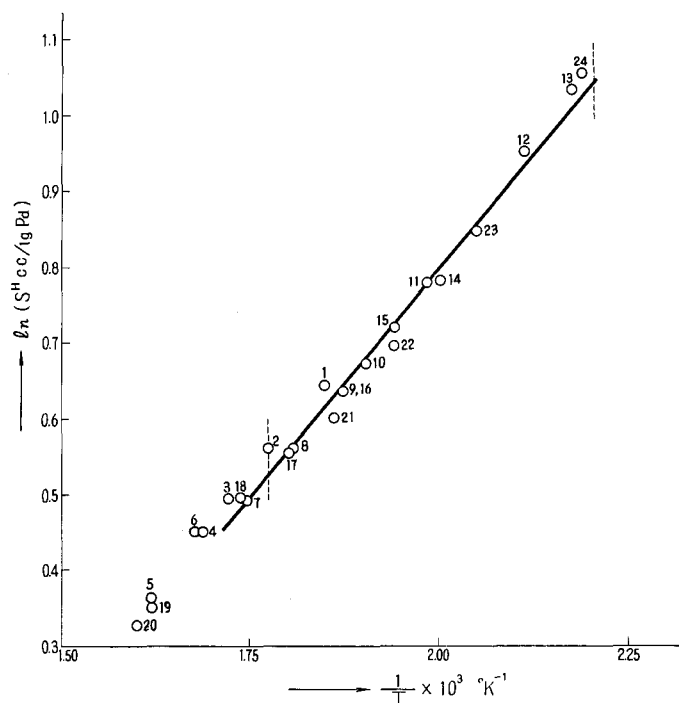


Fig. 7. Dependence of equilibrium amount of hydrogen dissolved in palladium upon temperature at 74 cmHg. Numbers indicate the order of experiments. (SIEVERTS and DANZ⁴⁾)

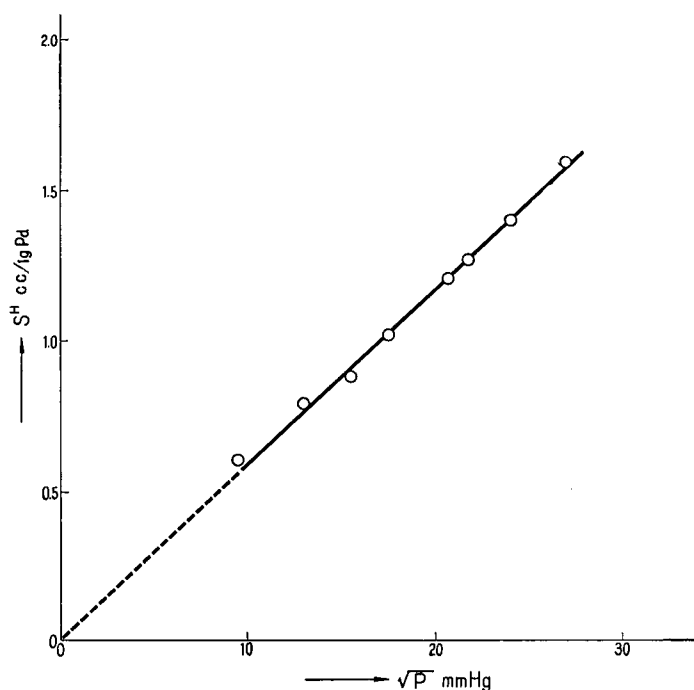


Fig. 8. Dependence of equilibrium amount of hydrogen dissolved in palladium upon pressure at 300°C. (SIEVERTS and DANZ¹⁰)

$$S^H = 2.26 \times 10^{-2} \sqrt{P} e^{\frac{2430}{RT}} \text{ cc (NTP)/gm Pd},$$

where S^H is the NTP volume in cc of hydrogen sorbed by 1 gm palladium, or as

$$c^H = 2.72 \times 10^{-1} \sqrt{P} e^{\frac{2430}{RT}} \text{ cc (NTP)/cc Pd}. \quad (5)$$

The c_0^H may be neglected as compared with c_i^H , inasmuch as the pressure around the outlet end has not exceeded 10^{-1} mmHg during the present observation, hence from Eqs. (1), (4) and (5)

$$D^H = 5.96 \times 10^{-3} e^{-\frac{5650}{RT}} \text{ cm}^2/\text{sec}. \quad (6)$$

The diffusion coefficient of deuterium is similarly determined from the steady permeation rate as

$$D^D = 2.43 \times 10^{-3} e^{-\frac{4800}{RT}} \text{ cm}^2/\text{sec}, \quad (7)$$

on the base of the observed sorption equilibrium of deuterium in palladium

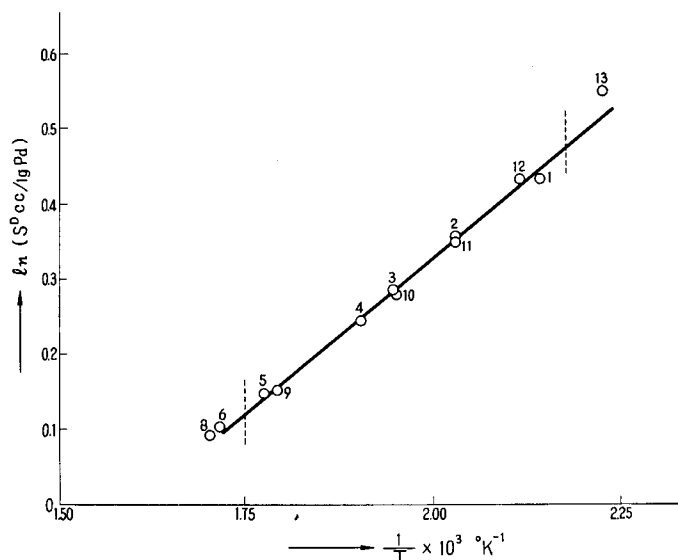


Fig. 9. Dependence of equilibrium amount of deuterium dissolved in palladium upon temperature at 74 cmHg. Numbers indicate the order of experiments. (SIEVERTS and DANZ⁴⁾)

shown in Fig. 9⁴⁾, expressed as

$$S^D = 3.07 \times 10^{-2} \sqrt{P} e^{\frac{1660}{RT}} \text{ cc (NTP)/gm Pd,}$$

or

$$c^D = 3.69 \times 10^{-1} \sqrt{P} e^{\frac{1660}{RT}} \text{ cc (NTP)/cc Pd.} \quad (8)$$

We have from Eqs. (6) and (7)

$$D^H/D^D = 2.45 e^{-\frac{850}{RT}}. \quad (9)$$

The D^H given by Eq. (6) agrees fairly well with that of Eq. (3) determined by "time lag" method, and excellently with the previous determination of JOST and WIDMANN²⁾ by palladium ball, *i.e.*

$$D^H = 5.95 \times 10^{-3} e^{-\frac{5720}{RT}} \text{ cm}^2/\text{sec}.$$

The ratio V_P^H/V_P^D decreased from 2.4 to 2.05 with rise of temperature from 200° to 300°C, as observed by FARKAS and FARKAS³⁾, and from 1.9 to 1.6 over the same temperature range according to MELVILLE and RIDEAL⁶⁾, whereas it increases with rise of temperature according to the present result given by Eq. (2).

The present result on D^H/D^D as given by Eq. (9) is in concordance with

the result of JOST and WIDMANN²⁾, *i.e.* 1.31 at 302.5°C and 1.25 at 192.5°C as observed with palladium ball of 15 mm diameter, as regards the dependency of the ratio upon temperature.

Theoretical calculation of diffusion coefficient

The diffusion coefficients of hydrogen isotopes in palladium are theoretically calculated on the basis of a model described below, and are compared with the experimental results.

Palladium metal has a face-centred cubic lattice of 3.88 Å lattice constant. Fig. 10 shows its unit cell. Hydrogen atom dissolved in palladium is dissoci-

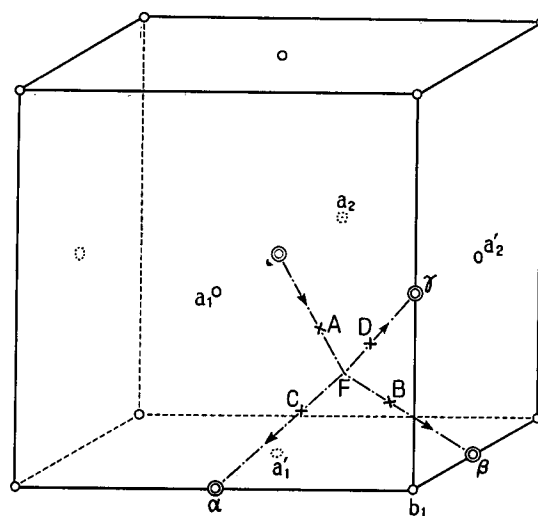


Fig. 10. Unit cell of palladium metal and diffusion path of proton.

ated into proton and electron. The electron thus formed behaves as metal electron, while the proton more or less shielded by electron cloud has the coulombic repulsive potential V^n , *i.e.*

$$V = \frac{Ze^2}{r} e^{-\lambda r} \quad (10)$$

due to each palladium ion, where r is the distance from the proton to the palladium ion, Z the effective charge of palladium ion, and λ the coefficient of shielding effect of proton with electron. A proton has thus equilibrium positions, where sum of V over all palladium ions is minimum, each of which coincides with a centre of a unit cell signified by \odot in Fig. 10.

Diffusion of proton is now the transition from one to the next equilibrium

position denoted by α , β or γ , called the initial and the final state respectively, through the path of least potential energy. This path, called the diffusion path, is determined by calculating the potential field according to the Eq. (10) with $Z=1$ and $\lambda=\frac{1}{0.34}\text{\AA}^{-1*}$, as shown by chained lines in Fig. 10. The potential of proton along the diffusion path is shown in Fig. 11, where A and

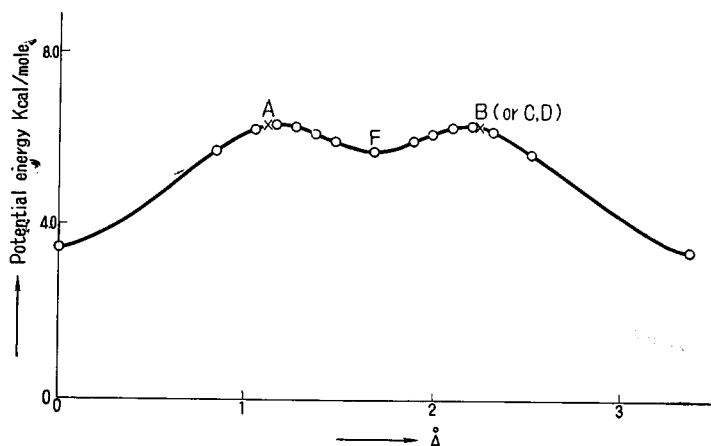


Fig. 11. Potential of proton along diffusion path.

B (or C and D) are the saddle points and F the minimum between A and B. Proton passes from the initial state, *i.e.* the centre of unit cell shown in Fig. 10, to F *via* A and then proceeds along one of arrows, *via* B or C or D.

The second maximum of potential energy at the latter point may drive back the proton over A. In case where the momentum with which the proton got over A persists no more at F, the proton reaches the four nearest equilibrium positions with equal chance; the proton arrives at one of equilibrium positions other than that from which it started with the probability of 3/4. The probability increases toward unity in case where the momentum more or less persists. Since the probability is sufficiently near unity at the least, a proton, if once gets over A, will be taken to reach one of the three equilibrium position, and in consequence, A may be taken the activated state.

Consider a plane 1 through the initial state in Fig. 10 parallel to the plane 2 of the regular triangle $\alpha\beta\gamma$. The forward and the backward rates of transition of proton from plane 1 to 2 are given according to the generalized theory of reaction rate⁸⁾ respectively as

*) See p. 55.

$$v_+ = \frac{kT}{h} \frac{p^*}{p^I}, \quad v_- = \frac{kT}{h} \frac{p^*}{p^F}, \quad (11. a), (11. b)$$

assuming the transmission coefficient unity, where p^* is the BOLTZMANN factor of the increment of the free energy F of the whole assembly M caused by addition of an activated complex, denoted by $*$, of the elementary reaction in question, *i.e.* the transition from an equilibrium position on plane 1 to one of those on plane 2, in the preliminary absence of activated complex in M, p^I or p^F the BOLTZMANN factor of the increment of F caused by addition to M of a proton at the initial or the final state respectively and k , h and T are of usual meaning.

The above equations are transformed in order to derive a statistical mechanical expression of diffusion coefficient according to the theorem⁸⁾,

$$p^\delta = \frac{\Theta_{\sigma(0)}}{\Theta_{\sigma(\delta)}} q^\delta$$

where δ represents $*$, I and F, σ is a site of δ , $\Theta_{\sigma(0)}$ or $\Theta_{\sigma(\delta)}$ the probability that σ is vacant or occupied by δ respectively and q^δ is the BOLTZMANN factor of the increment of F caused by addition of δ onto a definite, preliminarily evacuated site σ .

We have from the above equation for the critical complex and the initial system

$$p^* = \frac{\Theta_{\sigma^*(0)}}{\Theta_{\sigma^*(*)}} q^*, \quad p^I = \frac{1-\theta}{\theta} q^I, \quad (12. a), (12. b)$$

where σ^* is the site of the activated complex and θ is the covered fraction of sites of initial system I or the probability that a site of I being occupied.

We have now from Eqs. (11.a) and (12)

$$v_+ = \frac{kT}{h} \frac{\Theta_{\sigma^*(0)}}{\Theta_{\sigma^*(*)}} \frac{q^*}{q^I} \frac{\theta}{1-\theta}.$$

The probability $\Theta_{\sigma^*(*)}$ of a σ^* being occupied by a single activated complex added is the reciprocal of the number G of the sites σ^* 's existing, while the probability $\Theta_{\sigma^*(0)}$ of a σ^* being unoccupied may taken practically unity. We have now, assuming further that covered fraction θ is sufficiently small as compared with unity, from the above equation

$$v_+ = \frac{kT}{h} \frac{q^*}{q^I} n, \quad (13. a)$$

where

$$n = G\theta. \quad (13. b)$$

Let now G be allotted to cm^2 on the plane through the point A parallel to the plane 1 and 2. We see readily from the geometry of the initial and the activated state that G equals the number of equilibrium positions or the sites of I and in consequence n is, according to Eq. (13.b), the number of protons per cm^2 on plane 1. The concentration c of protons in three dimensional space corresponding to n is now obtained by multiplying n by the number of planes parallel to planes 1 and 2 per cm, *i.e.* the reciprocal of the distance d between the adjacent planes, *i.e.*

$$c = \frac{n}{d}. \quad (14)$$

The reverse rate per cm^2 of transition of proton from plane 2 to plane 1 is similarly derived from Eq. (11.b) as

$$v_- = \frac{kT}{h} \frac{q^*}{q^F} (n - \Delta n), \quad (15)$$

where Δn is the excess of n over the number of proton per cm^2 on plane 2.

The factors q^* , q^I and q^F are expressed as in the previous papers for heterogeneous reactions³⁾ in terms of the appropriate ground state energies and frequencies of normal vibrations as

$$q^* = e^{-\frac{E_0^{H^*} + \sum_{j=1}^2 \frac{N_A h \nu_j^{H^*}}{2}}{RT}} \prod_{j=1}^2 (1 - e^{-h \nu_j^{H^*}/kT})^{-1} \quad (16. a)$$

$$q^I = q^F = e^{-\frac{\sum_{\ell=1}^3 \frac{N_A h \nu_{\ell}^{H,I}}{2}}{RT}} \prod_{\ell=1}^3 (1 - e^{-h \nu_{\ell}^{H,I}/kT})^{-1}, \quad (16. b)$$

where $E_0^{H^*}$ is the potential energy per mole of proton at point A in Fig. 10 as referred to its potential energy in the equilibrium position on plane 1 and N_A the Avogadro number; the identity of q^I with q^F stated by Eq. (16.b) holds under the assumption that the potential energy of proton on a equilibrium position on plane 1 or plane 2 is independent of n or $(n - \Delta n)$ on the respective plane, which is consistent with the above assumption that θ is sufficiently small as compared with unity.

We have now from Eqs. (13.a), (15) and the above identity of q^I with q^F for the net rate $v_+ - v_-$ of transition from plane 1 to plane 2

$$v_+ - v_- = \frac{kT}{h} \frac{q^*}{q^I} \Delta n.$$

The above net rate is alternatively expressed at the steady state of diffusion as

$D^H \frac{\Delta c}{d}$, where Δc is the decrease of the three dimensional concentration from plane 1 to plane 2, hence $\Delta c/d$ is the negative gradient of the concentration. Equating the alternative expressions with each other, we have

$$D^H \frac{\Delta c}{d} = \frac{kT}{h} \frac{q^*}{q^I} \Delta n$$

where Δc is given, in accordance with Eq. (14) as

$$\Delta c = n/d - (n - \Delta n)/d = \Delta n/d,$$

hence

$$D^H = \frac{kT}{h} \frac{q^*}{q^I} d^2,$$

or according to Eq. (16)

$$D^H = D_0^H e^{-\frac{E^{H*}}{RT}} \quad (17. H)$$

where

$$D_0^H \equiv \frac{kT}{h} d^2 \frac{\prod_{j=1}^2 (1 - e^{-\frac{h\nu_j^{H*}}{kT}})^{-1}}{\prod_{\ell=1}^3 (1 - e^{-\frac{h\nu_{\ell}^{H,I}}{kT}})^{-1}},$$

$$E^{H*} \equiv E_0^{H*} + \sum_{j=1}^2 \frac{N_A h \nu_j^{H*}}{2} - \sum_{\ell=1}^3 \frac{N_A h \nu_{\ell}^{H,I}}{2}.$$

The activation energy A^H of diffusion is defined as

$$A^H = RT^2 \frac{\partial \ln D^H}{\partial T} = RT - \sum_{\ell=1}^3 h \nu_{\ell}^{H,I} N_A (e^{\frac{h\nu_{\ell}^{H,I}}{kT}} - 1)^{-1}$$

$$+ \sum_{j=1}^2 h \nu_j^{H*} N_A (e^{\frac{h\nu_j^{H*}}{kT}} - 1)^{-1} + E^{H*}. \quad (18. H)$$

The diffusion coefficient of deuterium is similarly expressed as

$$D^D = D_0^D e^{-\frac{E^{D*}}{RT}}$$

by replacing deuterium for hydrogen in the above derivation, where

$$D_0^D \equiv \frac{kT}{h} d^2 \frac{\prod_{j=1}^2 (1 - e^{-\frac{h\nu_j^{D*}}{kT}})^{-1}}{\prod_{\ell=1}^3 (1 - e^{-\frac{h\nu_{\ell}^{D,I}}{kT}})^{-1}},$$

$$E^{D^*} \equiv E_0^{D^*} + \sum_{j=1}^2 \frac{N_A h \nu_j^{D^*}}{2} - \sum_{i=1}^3 \frac{N_A h \nu_i^{D, I}}{2}$$

and

$$E_0^{H^*} = E_0^{D^*} \equiv E_0^*,$$

in accordance with UREY's postulate⁹⁾, which has been extensively verified.

The activation energy of diffusion of deuterium A^D is defined similarly as

$$A^D = RT - \sum_{i=1}^3 h \nu_i^{D, I} N_A (e^{\frac{h \nu_i^{D, I}}{kT}} - 1)^{-1} + \sum_{j=1}^2 h \nu_j^{D^*} N_A (e^{\frac{h \nu_j^{D^*}}{kT}} - 1)^{-1} + E^{D^*}. \quad (18. D)$$

The normal vibrational frequencies of proton in the initial state or in the activated state are calculated as follows. Let x , y and z be the rectangular coordinates of proton at the initial state with origin at the equilibrium position.

Second differential coefficient of V_i of Eq. (10) with respect to x is given as

$$\left(\frac{\partial^2 V_i}{\partial x^2} \right)_{x=0} = \frac{ze^2}{r_i} e^{-\lambda r_i} \left\{ - \left(\frac{1}{r_i^2} + \frac{\lambda}{r_i} \right) + \left(\frac{3}{r_i^2} + \frac{3\lambda}{r_i} + \lambda^2 \right) \frac{x_i^2}{r_i^2} \right\},$$

where V_i is the coulombic repulsive potential of proton due to a palladium ion in a position (x_i, y_i, z_i) and $r_i = \sqrt{x_i^2 + y_i^2 + z_i^2}$. The force constant of vibration along x -direction $k_x^{H, I}$ is given as

$$k_x^{H, I} = \left(\frac{\partial^2 \sum_i V_i}{\partial x^2} \right)_{x=0},$$

where the summation is taken over all the palladium ions, hence the frequency $\nu_x^{H, I}$ of normal vibration in x -direction, *i.e.*

$$\nu_x^{H, I} = \frac{1}{2\pi} \sqrt{\frac{k_x^{H, I}}{m^{H^+}}}, \quad (19)$$

where m^{H^+} is the mass of proton. Those $\nu_y^{H, I}$ and $\nu_z^{H, I}$ respectively in y - and z -directions are found coincident with $\nu_x^{H, I}$.

The frequencies $\nu_1^{H^*}$, $\nu_2^{H^*}$ of the two normal vibrations perpendicular to the reaction coordinate of diffusion are similarly determined, which are coincident with each other as well.

The force constants remain unaltered by the isotopic replacement, insofar as the potential energy does as mentioned above. The normal vibrational frequencies $\nu_x^{D, I}$, $\nu_y^{D, I}$, $\nu_z^{D, I}$ of deuteron in the initial state, and $\nu_1^{D^*}$, $\nu_2^{D^*}$ of deuteron in the activated state are determined on the base of the same values of the respectively appropriate force constants, just replacing m^{H^+} by the mass

TABLE 1. Theoretical Values of Quantities Associated with Diffusion of Hydrogen and Deuterium Through Palladium.

λ (\AA^{-1})	E^* (cal)	Normal vibrational frequency $\times 10^{13}$				$\sum_{j=1}^2 \frac{N_A h \nu_j^{H^*}}{2}$ $-\sum_{i=1}^3 \frac{N_A h \nu_i^{H \cdot I}}{2}$ (cal)	E^{H^*} (cal)	$E^{H^*} - E^{D^*}$ (cal)	$D_0^H \times 10^{-3}$		$D_0^D \times 10^{-3}$		$\frac{D_0^H}{D_0^D}$	A^H (cal)	$A^H - A^D$ (cal)
		Initial state		Activated state					200°C	300°C	200°C	300°C			
		$\nu_i^{H \cdot I}$	$\nu_i^{D \cdot I}$	$\nu_j^{H^*}$	$\nu_j^{D^*}$										
$\frac{1}{0.34}$	2860	1.02	0.73	1.84	1.30	320	3180	95	1.81	1.79	1.26	1.24	1.44	3140	135
$\frac{1}{0.40}$	4840	1.34	0.95	2.26	1.60	260	5100	75	2.44	2.47	1.75	1.75	1.40	5180	155
$\frac{1}{0.42}$	5520	1.44	1.02	2.38	1.68	180	5700	55	2.61	2.66	1.90	1.91	1.38	5820	145

m^{D+} of deuteron.

Theoretical values mentioned above depend upon those of Z and λ in Eq. (10). TOYA¹⁰⁾ has recently derived theoretically that $Z=1$, and $\lambda = \frac{1}{0.34} \text{ \AA}^{-1}$ for proton in platinum, on which bases he has calculated the heat of dissolution of hydrogen in platinum in good agreement with experimental values. He has derived on the other hand from observed electric conductivity that $\lambda = \frac{1}{0.40} \sim \frac{1}{0.42} \text{ \AA}^{-1}$. These values of Z and λ for platinum are used plausibly for palladium in calculating the theoretical values of above mentioned quantities as shown in Table 1.

We see from the Table that D_0^H or D_0^D remains practically constant independent of temperature as it should.

These theoretical values are to be compared with the experimental values $D_0^H = 5.95 \times 10^{-3} \text{ cm}^2/\text{sec}$, $D_0^D = 2.43 \times 10^{-3} \text{ cm}^2/\text{sec}$, $D_0^H/D_0^D = 2.45$, $A^H = 5650 \text{ cal}$ and $A^H - A^D = 850 \text{ cal}$. The theoretical values of D_0^H and A^H for hydrogen in Table 1 are in good agreement with the above experimental values. The theoretical values of $(A^H - A^D)$ for these three values of λ are always positive in agreement with the experimental result.

It is expected theoretically that the effective charge of palladium ion in the activated state is larger than that in the initial state, because proton penetrate deeper into the ionic shell of palladium in the activated state than in case of the initial state. It is expected that the theoretical values will come closer to experimental values by taking this effect into account.

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