

## Diffusion of Hydrogen Through Platinum and Nickel and Through Double Layers of These Metals

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**Measured energy in Japan**

David von Seggern  
(vonneg@seismo.unr.edu) University of Nevada  
July 2012, page 10

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The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy release of a 100-megaton explosion and the damage potential of nuclear bombs. The authors use the relation for seismic energy release rather than total strain energy release. I believe the authors underestimate the total strain energy release by a variable that depends on friction on the fault plane. Accounting for total strain energy release would increase the earthquake energy number by orders of magnitude.

Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

The article does not have any references.

**Comment on this article**

By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.

Written by Edgar McCarroll, 14 July 2012 19:59

## Diffusion of Hydrogen Through Platinum and Nickel and Through Double Layers of These Metals

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(Received April 15, 1933)

Flow of hydrogen through single sheets of Ni and Pt with atmospheric pressure on ingoing side and pressure of 0.1/mm on outgoing side follows the empirical equation

$$R = A \cdot ((p_0^{\frac{1}{2}} - p_i^{\frac{1}{2}})/x) \cdot T^{-\frac{1}{2}} \cdot e^{-b_1/T}$$

similar to that given by Borelius, where  $p_i$  is small compared with  $p_0$  but apparently proportional to  $p_0$ ; with double layers of these two metals the  $b_1$  of the exponential

is dependent *only on the metal at the outgoing surface*, and is the difference between the work of escape from the outgoing surface and the heat of solution of hydrogen in that metal. The kinetic theory flow equation is sufficient to explain the  $p_i$ , and the variation of  $p_i$  with temperature may be used to compute the work function at the outgoing surface, and also to obtain values of  $m/k$  where  $m$  is the mass of the hydrogen atom and  $k$  the Boltzmann constant.

### EXPERIMENTAL PROCEDURE

A SHEET of platinum was placed between two heavy steel tubes with integral flanged ends ground flat and smooth and put under pressure by means of bolts through heavy steel rings on either side of the flanges. It was not found necessary to make grooves in the ground ends in order to prevent leakage.

A moderate vacuum of about  $10^{-2}$  cm Hg was maintained on one side and  $H_2$  at atmospheric pressure allowed to flow to the other side, the excess burning in a small flame kept at constant height.

Rates were measured both with McLeod gauges of quite different volumes and also by a manometer, the scheme being quite similar to that used by Richardson, Nicol and Parnell,<sup>1</sup> with the minor addition of a tungsten point inserted in one arm of the manometer about 2 mm above the mercury level and connecting with a neon lamp. These arrangements are shown schematically in Fig. 1.

The steel tubes with a sheet of the material to be tested between were placed in a resistance furnace with Chromel Alumel thermocouples in contact (a) with the sheet on the  $H_2$  side, (b) with the steel container outside the platinum and (c) about half way along the tubes and (d) next the water cooler as shown in the diagram. The

temperatures indicated by (a), (b) and (c) couples were nearly the same and could be kept sufficiently constant without difficulty. The area of a sheet exposed to  $H_2$  was very sharply defined by the marks of the steel holder. The rates were computed in the usual way by measuring rate of change of pressure in a given time for a known volume, and also by using a neon lamp arrangement by measuring the times for a given change of pressure also for a known volume.

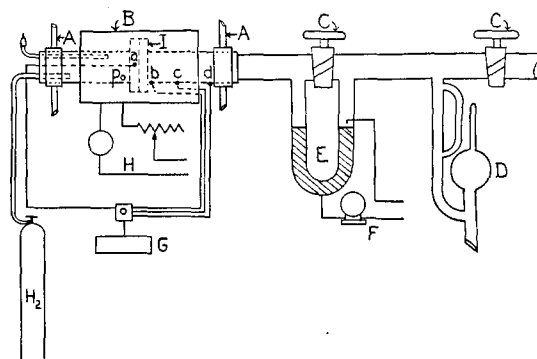


FIG. 1. Diagram of apparatus.

*a, b, c and d*, thermocouples *F*, neon light circuit  
*A*, water coolers *H*, heater circuit  
*B*, electric furnace *I*, adaptor  
*C*, stopcocks *G*, potentiometer  
*D*, McLeod gauge *H<sub>2</sub>*, commercial tank hydrogen  
*E*, mercury manometer *p<sub>0</sub>*, pressure ingoing surface

<sup>1</sup> O. W. Richardson, J. Nicol and T. Parnell, *Phil. Mag.* **8**, 1-29 (1904).

It is desirable to keep the pressure low on the outgoing side, otherwise the sorption of the inside surface of the steel exit tube will diminish the

measured rate. Plating the inside of this part of the apparatus with gold would have avoided error from this source, since tests made with gold sheets in this same apparatus show that the transmission of hydrogen through gold over the range of temperatures used is undetectable.

After sufficient data had been obtained on Pt, a Ni disk was substituted for it and the work repeated. This nickel, not supposed to be particularly pure, contained 2.5 percent Fe by analysis and was from the G. E. Company.

A disk of platinum, supposedly pure as furnished by Baker and Company, was then placed in contact with a disk of the above mentioned

nickel in the holders, the platinum being on the high pressure side, with the expectation that when heated the sheets would weld together, which was found to be the case; the runs were repeated with this double layer, the direction of flow then reversed and the observations taken again.

It is to be noted that with a large McLeod gauge no corrections for heated gas are necessary in computing rates, and with the small McLeod gauge such corrections are trivial, but with the manometer, which was found convenient, at the higher temperatures, a small correction was made following usual lines for the heated gas in that

TABLE I. Observed rate of diffusion of hydrogen through Ni, Pt-Ni, Ni-Pt, and Pt.

(a)		(b)		(c)		(d)	
Nickel		Platinum-Nickel		Nickel-Platinum		Platinum	
Area 3.6 sq. cm		Area 3.14 sq. cm		Area 3.14 sq. cm		Area 3.14 sq. cm	
Thickness 0.0127 cm		Thickness		Thickness		Thickness 0.0133 cm	
Volume system 50 cc		Pt = 0.0102 cm Ni = 0.0133 cm		Ni = 0.0133 cm Pt = 0.0102 cm		Volume system 237 cc	
T°K	Rate μ/min.	T°K	Rate μ/min.	T°K	Rate μ/min.	T°K	Rate μ/min.
649	244	620	8.5	711	5.25	705	3.95
664	309	633	8.4	753	10.5	720	5.5
718	590	634	8.2	769	13.2	723	5.8
737	807	667	18.0	770	14.0	725	5.9
788	1310	689	28.3	827	29.6	746	8.35
829	2380	690	28.0	888	66.8	754	9.9
855	2800	704	30.0	829	32.0	755	9.85
873	3410	707	26.5			757	10.75
		751	49.5			781	14.7
		799	82.3			802	20.7
		803	82.6			807	21.3
		841	134.0			827	30.0
		853	158.0				
Slope $b_1 = 6700 \pm 100$		Slope $b_1 = 6690 \pm 40$		Slope $b_1 = 9005 \pm 30$		Slope $b_1 = 9000 \pm 40$	

Slopes are given for these data substituted in the equation  $R = Ae^{-b_1/T}$ .

Rate (R) is expressed in change of pressure in microns per minute for the particular volume of the system used.

TABLE II. Computed rate of diffusion of hydrogen through Ni, Pt-Ni, Ni-Pt, and Pt on the assumption that slopes in Fig. 2 of Ni and Pt-Ni, also Pt and Ni-Pt are identical.

Temp.	Nickel	Platinum-Nickel	Nickel-Platinum	Platinum
600°	$303 \times 10^{-11}$ g/cm <sup>2</sup> sec.	$74.8 \times 10^{-11}$	$6.8 \times 10^{-11}$	$6.36 \times 10^{-11}$
700°	$1484 \times 10^{-11}$	$367 \times 10^{-11}$	$58.1 \times 10^{-11}$	$54.3 \times 10^{-11}$
800°	$4890 \times 10^{-11}$	$1209 \times 10^{-11}$	$290 \times 10^{-11}$	$271 \times 10^{-11}$
Slope	6690°	6690°	9005°	9905°

A conservative estimate of the relative consistency of the values of these slopes is P.E. =  $\pm 100$  for all.

The rates above are in grams per sec. per sq. cm for the particular thicknesses used. Said thicknesses may be found at the top of Table I.

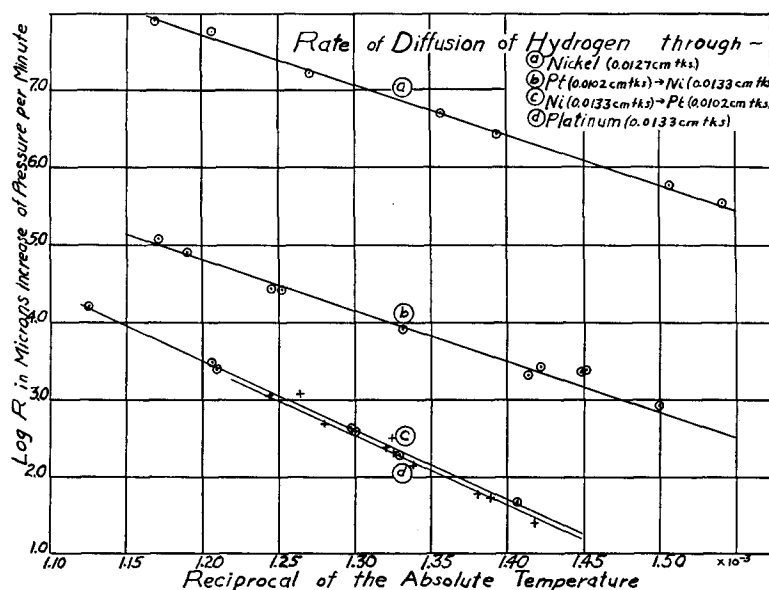


FIG. 2. Observed rate of diffusion of hydrogen through Ni, Pt-Ni, Ni-Pt and Pt

part of the apparatus in the furnace.

Four original sets of data including all rates as taken are given in Table I, a, b, c, and d and shown graphically on Fig. 2 which fits Table I. All the slopes in Fig. 2 were computed by least square methods, the lines drawn and the points then inserted. Table II shows results for 600 and 700°K computed on the basis of the experimental rates at 800°K and on the assumption that the  $b$  values for Ni and Pt-Ni are identical and also that the  $b$  of Pt and Ni-Pt is the same. Table II is inserted for use in calculations in order to avoid experimental errors as far as possible.

#### DISCUSSION OF RESULTS

It is immediately apparent that the work of Borelius<sup>2</sup> and others is checked quite completely for single sheets, but the data on double layers make it clear that the emergent surface is the controlling factor so far as the temperature coefficient of the rate is concerned, since the curve of hydrogen through Pt-Ni is parallel to the curve of hydrogen through Ni and the hydrogen through Ni-Pt curve is parallel to the hydrogen through Pt curve.

<sup>2</sup> Borelius and Sven Lindblom, Ann. d. Physik **82**, 201 (1927).

#### THEORY

Since the results of the experiments on double layers of nickel and platinum emphasize the importance of the outgoing surface, in discussing the theory of the passage of gas through a sheet of metal, it seems reasonable to ascertain whether the simple kinetic theory of flow through a surface does or does not apply. In the following Eqs. (1), (2) and (3), the symbols are defined as follows:

$dm/dt$  = rate of diffusion of hydrogen in  $\text{g cm}^{-2} \text{sec}^{-1}$

$p_i$  = pressure, in dynes, of hydrogen just inside the outgoing surface

$m$  = mass in grams of hydrogen ion (or atom)

$k$  = Boltzmann constant

$T$  = absolute temperature

$b_2$  = surface work function expressed in equivalent degrees

$p_0$  = impressed pressure

$A$  = a constant characteristic of material

$x$  = thickness

$b_1$  = net apparent work function for flow, often erroneously associated with heat of dissociation, but really the sum of two work functions (as later appears).

Kinetic theory gives for flow of hydrogen through a surface,

$$dm/dt = p_i \cdot (m/2\pi k)^{1/2} \cdot T^{-1/2} \cdot \epsilon^{-b_2/T}. \quad (1)$$

But this same rate of flow of hydrogen through a metal sheet is empirically,

$$dm/dt = A(p_0^{1/2} - p_i^{1/2})/x \cdot \epsilon^{-b_1/T} \quad (2)$$

as given by Borelius,<sup>2</sup> who seems the most careful of recent investigators and who has thus modified the original equation of Richardson<sup>1</sup>; e.g.,

$$dm/dt = A \cdot (p_0^{1/2}/x) \cdot \epsilon^{-b_1/T} \quad (3)$$

by the subtraction of the quantity  $p_i^{1/2}$  from the square root of the impressed pressure. He does this because, in plotting rate of flow  $dm/dt$  against the square root of the impressed pressure ( $p_0^{1/2}$ ), he finds for any particular temperature an approximately linear relation between the impressed pressure and the rate of flow, that is, for the larger pressures. When this straight line is extended to the  $p_0^{1/2}$ -axis, it does not pass through the origin, but has a  $p_0^{1/2}$  intercept which he calls  $p_i$ . We wish to define further this quantity,  $p_i$ , by association with the pressure  $p$  that appears in the kinetic theory. Eq. (1).

However, before we substitute numerical data we must introduce a relation (which also may be regarded for the present as empirical) between  $p_i$ , the equivalent inside pressure on the outgoing side, and  $p_1$  the corresponding pressure on the incoming side. This is necessary in order to derive and extend Borelius' (or Richardson's) empirical flow equation from the flow equation of the kinetic theory. Such an empirical relation may be written as follows:

$$p_i = p_1(1 - \epsilon^{-a/x}). \quad (4)$$

If we assume equilibrium to be reached in the reaction represented by  $\frac{1}{2}H_2 \rightleftharpoons H + e^-$  at the ingoing side we may write  $p_1^2/p_0 = M$  and the equation becomes

$$p_i = Mp_0^{1/2}(1 - \epsilon^{-a/x}),$$

and since

$$M = M_0 \epsilon^{-\Delta w/T}$$

(derivable from fundamental thermodynamics)

$$p_i = M_0 \epsilon^{-\Delta w/T} \cdot p_0^{1/2} \cdot (1 - \epsilon^{-a/x}),$$

where the quantities involved are

$p_0$  = impressed pressure

$a$  = a constant of the material

$x$  = thickness

$M_0$  = mass action constant

$\Delta w$  = the heat of solution per gram atom divided by  $R$

$T$  = absolute temperature.

Substituting (4) in (1) gives

$$\begin{aligned} \frac{dm}{dt} &= a M_0 \left( \frac{m}{2\pi k} \right)^{1/2} \cdot \frac{p_0^{1/2} - p_0^{1/2}(a/2x)}{x} \cdot T^{-1/2} \cdot \frac{-b_2 - \Delta w}{T} \\ &= A \left( \frac{p_0^{1/2} - p_i^{1/2}}{x} \right) \cdot T^{-1/2} \cdot \epsilon^{-b_1/T} \end{aligned} \quad (5)$$

this latter being identical with the Borelius (or Richardson) formula except for the  $T^{-1/2}$  which could not have been detected.

We shall, therefore, introduce this  $T^{-1/2}$  in both Richardson's and Borelius' equations for handling numerical data.

Since  $p_i$  in general is small compared with  $p_0$ , to a close approximation Eq. (5) may be written

$$dm/dt = (A p_0^{1/2}/x) \cdot T^{-1/2} \cdot \epsilon^{(-b_2 - \Delta w)/T}. \quad (6)$$

And comparing with Eq. (1) and solving for  $P_i$ ,

$$p_i = A p_0^{1/2}/x(2\pi k/m)^{1/2} \cdot \epsilon^{-\Delta w/T}. \quad (7)$$

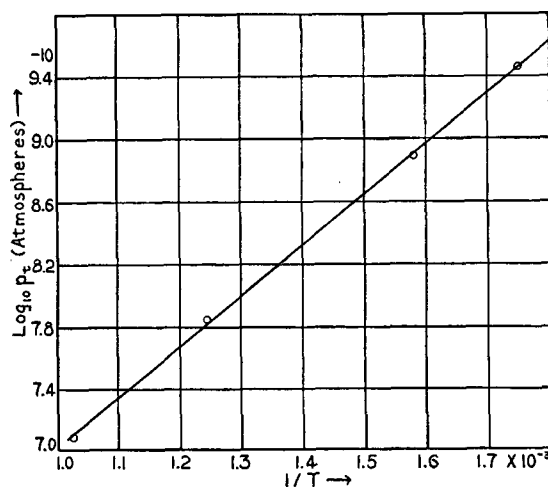


FIG. 3. Relation between back pressure in iron ( $p_i'$ ) and absolute temperature ( $T$ ) from Table III. (Data of Borelius and Lindblom.)

Taking logs for a case where  $p_0$  and  $x$  is constant

$$\log p_t = \log (\text{const.}) - \Delta w/T.$$

Borelius' data for  $p_t$  and  $T$  are tabulated in Table III which also includes  $p_t'$  found as indicated in footnote of tabulation and involving a small graphic correction, chiefly of theoretical importance. The relation between  $p_t'$  and  $T$  is shown graphically in Fig. 3. We note from the slope that  $\Delta w = 7500^\circ$  approximately, and is positive, hence may be associated with energy released.

TABLE III. Data of Borelius and Lindblom on internal pressures in iron at various temperatures with calculated values of  $(m/k)^{1/2}$  and calculated internal pressure from kinetic theory equation of flow.

From Borelius Data			Calculated		
(a)	(b)	(c)	(d)	(e)	(f)
$T^\circ\text{K}$	$dm/dt$ $\times 10^3$ g/sec.	$p_t$ (atmos.)	$p_t'$ (atmos.) (corrected)	$p_t$ calculated (atmos.)	$(m/k)^{1/2}$
975	3.	0.0012	0.0012	0.001	$0.9 \times 10^{-4}$
805	1.	.007	.007	.005	$.8 \times 10^{-4}$
633	0.2	.07	.08	.06	$.7 \times 10^{-4}$
571	0.09	.25	.30	.23	$.8 \times 10^{-4}$

#### Accepted Values

$$m_H = 1.66 \times 10^{-24} \text{ grams} \quad (m/k)^{1/2} = 1.09 \times 10^{-4}$$

$$k = 1.372 \times 10^{-16} \text{ ergs/degree}$$

Final value of work function at outgoing surface for hydrogen through iron;  $-b_2 = 5200^\circ + 7500^\circ = 12,700^\circ$ .

Note:  $p_t'$  differs from  $p_t$  in that it is taken from the  $p_0^{1/2}$  intercept of the tangent to Borelius curves at the tabulated values of  $dm/dt$  instead of from the  $p_0^{1/2}$  intercept of the lines drawn as in Borelius' paper.

Using Eq. (5) and Borelius' data for the same iron, we find  $b_2 + \Delta w = -5200^\circ$  approximately.

Hence  $b_2$ , which may be defined as the work function at the back surface from the kinetic theory, (Eq. (1)), is given by

$$b_2 = -5200^\circ - 7500^\circ = -12,700^\circ.$$

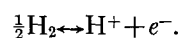
Having found this back surface work function we may test Eq. (1) directly by substitution of numerical values. The author has chosen to regard  $(m/k)^{1/2}$  as the unknown. The various values of  $(m/k)^{1/2}$  thus obtained as shown in Table III

and are of the same order of magnitude as found in any handbook that has universal physical constants. The variation does not seem beyond experimental error.

This seems very significant, since, considering the magnitude of the various quantities involved, the chance for such a check being accidental is very remote.

To summarize: The application of two principles and one empirical relation seems to give the equation of flow of hydrogen through Fe, Ni, and Pt; these are:

(a) A mass action formula associated with a reaction



(b) An empirical relation between inside pressure of hydrogen (or concentration) at back surface and inside pressure at front surface, previously given as (Eq. (4)).

(c) The kinetic theory equation for flow of a gas across a potential barrier.

That is, starting with (c) substituting (b) and then (a) gives a form of Richardson's equation; namely,

$$dm/dt = (A p_0^{1/2}/x) \cdot T^{-3/2} \cdot e^{-b_1/T}.$$

Direct experiments on double layers of platinum and nickel show that the temperature coefficient of flow is *wholly dependent on the outgoing surface*, as would follow from (a), (b) and (c), and in general with metals behaving as do platinum, nickel and iron toward hydrogen, the *exit surface* largely determines the rate of diffusion, at least for such temperatures as are usually employed in diffusion experiments.

Note: Equations of flow of hydrogen through Ni and Pt and through double layers of these two metals are also sufficient for an approximate determination of  $(m/k)^{1/2}$ . Solution of such simultaneous equations takes much space and, therefore, has not been included. In both methods of approach one would expect a variation with temperature of the viscosity coefficient (associated with "a" of Eq. (4)); apparently the effect is small since the computed values of  $(m/k)^{1/2}$  from either method are not much more different from accepted values than could be attributed to experimental error.

The experimental work connected with this

paper has largely been done by Mr. J. D. Sauter and assistants, and much aid in the calculations has been furnished by Messrs. M. A. Jeppesen and K. D. Larsen, all of the Physics Department of The Pennsylvania State College. Suggestions

have also been offered by Dr. E. P. Barrett of the School of Mineral Industries, and by Dr. W. P. Davey and Dr. J. G. Aston of the School of Chemistry and Physics of The Pennsylvania State College.