[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

THE PERMEABILITY OF HOT METALS TO HYDROGEN[1]

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A paper[2] which appeared in December, 1923, reported a preliminary study of the diffusion of hydrogen through hot metals. In July of that year Lombard[3] published the results of a study of the diffusion of hydrogen through nickel and the following year Johnson and Larose[4] presented their work upon the diffusion of oxygen through silver. A second paper from Johnson and Larose[5] gives both improved apparatus and a changed interpretation. Lombard has published two papers[6] upon diffusion since his first. The first of these makes a comprehensive analytical study of the available data upon hydrogen diffusion through nickel. The second deals with experiments with other gases including argon, nitrogen and helium, and with other metals such as copper, iron and platinum. In his last paper he also attempts to formulate a generalization for all such diffusion.

It is proposed in this paper to give a restudy of copper and zinc as diffusion diaphragms for hydrogen and to measure diffusions through nickel under varying temperatures and pressures of the gas. The results obtained, as well as those of other students of diffusion, are to be studied for the relation of diffusion values to the different conditioning factors.

This work, while using essentially the same apparatus as that already described,[2] has introduced certain modifications of that practice. By introducing Swartz tubes filled with phosphorus pentoxide, in addition to soda-lime tubes used in the former research, "blank values" have been reduced from 1.5 mg. per hour to 0.4 mg. per hour or less. By permitting the outlet[2] from the hydrogen chamber to terminate in a pipet dipping beneath the surface of a carefully graduated cylinder of mercury, the hydrogen pressure has been regulated and maintained at the desired value in spite of fluctuations of the atmospheric pressure and changes in other variable influences in the train.

Varying pressures of the diffusing gas, hydrogen, have been secured by mixing hydrogen and nitrogen in varying proportions. The gasometer used was calibrated and read within an accuracy of 0.5%. Lom-

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[1] Read before the Physical and Inorganic Division of the American Chemical Society at Columbus, Ohio, April, 1929.

[2] Deming and Hendricks, THIS JOURNAL, **45**, 2857–2864 (1923).

[3] Lombard, *Compt. rend.*, **177**, 116 (1923).

[4] Johnson and Larose, THIS JOURNAL, **46**, 1377 (1924).

[5] Johnson and Larose, *ibid.*, **49**, 312 (1927).

[6] Lombard, *J. chim. phys.*, **25**, 501, 587 (1928).

bard[7] found by experiments with similar mixtures that the diffusion rate of the hydrogen was independent of the presence of the nitrogen in the mixtures. He[8] also found that the diffusion rate of hydrogen through nickel varied inversely with the thickness of the metal. Thus Fick's law correctly describes the diffusion of hydrogen through nickel. By the aid of Fick's law the specific diffusion of hydrogen through hot metals is here expressed as the number of milligrams of hydrogen diffusing per square meter of surface per millimeter thickness of metal per hour. In arriving at this specific diffusion for different temperatures, corrections were made, in every instance, for the increase of both the diaphragm area and thickness due to thermal expansion. This increase varied both with the kind of metal used and with the temperature change.

The temperatures were measured by a chromel–alumel thermocouple calibrated for the melting points of Mallinckrodt C. P. tin and zinc and General Chemical Company aluminum. The millivoltmeter for the thermocouple was read to 0.1 millivolt, which corresponded to less than 3°. The cold junction of the couple was kept in an ice pack in a Dewar container.

The gases used were secured and purified as described in the previous paper except for the before-mentioned drying.

The diffused hydrogen, as in the former work, was oxidized to water by hot copper oxide and collected by absorption in phosphorus pentoxide-filled U-tubes. These were always weighed counterbalanced by a U-tube of equal volume kept in the balance case. The tube to be weighed was always cooled and filled with dry air before weighing.

Zinc.—The sample of zinc[9] used in this study contained not more than 0.1% of lead, 0.005% of cadmium and 0.008% of iron. Its purity was the same as that of the sample used in the work[2] previously reported. The disk used had a thickness of 0.515 mm., while 1.643 mm. was the thickness of the sample tested in the earlier work. Its diffusion area at the temperatures of the experimental work was 1.7% greater than at room temperature. Table I exhibits the summarized results of over twenty hours of work with this metal. The temperature deviation from the

TABLE I

RESULTS WITH ZINC

Thickness, 0.515 mm.; area, 47.78 sq. cm. at 20°; average "blank" for three runs, 0.3 mg. per hour; hydrogen partial pressure, 1.000 ± 0.007 atm.

Mean temperature, °C.	305	373
Water collected, mg. per hour	0.9 ± 0.2	3.0 ± 0.4
Sp. diff. of hydrogen through zinc	8.0 ± 4.0	32.2 ± 4.8

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[7] Lombard, *J. chim. phys.*, **25**, 519 (1928).

[8] Lombard, *ibid.*, **25**, 527 (1928).

[9] Generously supplied by the New Jersey Zinc Company.

mean value was in all cases, in this and in the following tables, less than the precision of the thermocouple.

These values leave no doubt that zinc is hydrogen permeable and that it becomes increasingly so with higher temperatures. A study of the plate before and after the diffusion experiments showed a decrease in crystal size as a result of its exposure to hydrogen at these temperatures near its melting point.

Copper.—Sieverts,[10] after a series of tests, concluded that pure copper was permeable to hydrogen above 640° with no effect upon the copper. However, he found that commercial copper tubes changed, "became brittle and fissured," in an atmosphere of hydrogen. A similar result was reported by Deming and Hendricks in a previous paper.[2] Lombard[11] states that a trial with copper resulted in "a rapid and progressive increase in the diffusion value even when the temperature and pressure were held constant."

The copper used in the present work had been carefully deoxidized by phosphorus.[12] It was 99.900% pure before this phosphorus reduction. Even though pure and oxygen-free, some difficulty was experienced in getting the limited data presented in Table II.

TABLE II

RESULTS WITH COPPER

Thickness, 0.385 mm.; area, 46.56 sq. cm. at 20°; average "blank" for two runs, 0.2 mg. per hour; hydrogen pressure, 1.000 ± 0.007 atm.

Mean temperature, °C.	497	568	632
Water collected, mg. per hour	2.2 ± 0.3	3.35 ± 0.5	6.5 ± 0.7
Sp. diff. of hydrogen through copper	17.3 ± 1.8	28.9 ± 0.4	57.7 ± 6.5

Microscopic examination of this sample, after the diffusion tests, showed a decided increase in crystal size. A similar change was reported in the previous paper[2] though the intercrystalline cracks were there attributed to the reducing action of hydrogen upon inclusions of cuprous oxide. The previous treatment of the copper samples, here used, would make that explanation untenable. A more plausible hypothesis might well be that increased crystal size gives rise to larger crystalline planes of cleavage. These planes, as they more and more nearly extend through the thin plate, presently become mechanical openings or fissures, rendering the copper more permeable as well as more brittle.

The above results, it should be noted, do not agree with Sievert's either in regard to the lowest temperature at which diffusion through copper takes place or in the effect of diffusion upon the pure copper metal.

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[10] Sieverts, *Z. physik. Chem.*, **60**, 188–201 (1907).

[11] Lombard, *J. chim. phys.*, **25**, 590 (1928).

[12] These samples were generously prepared and furnished by the American Brass Company.

Nickel.—The nickel used[13] was electrolytically refined. After 100 or more hours of exposure to hydrogen gas at high temperatures, this metal showed no change either in crystal size or in diffusion rate. Such consistency was very advantageous to work which sought both the effect of temperature variations upon diffusion rate and the influence of pressure changes upon that phenomenon. Results for three different pressures of the diffusing hydrogen through nickel are presented in Table III A, B and C.

TABLE III

RESULTS WITH NICKEL

Thickness, 0.423 mm.; diffusion area, 46.56 sq. cm. at 20°; average "blank" for four runs, 0.4 mg. per hour.

Mean temp., °C.	Water coll., mg. per hour	Sp. diff. of hydrogen through nickel	Mean temp., °C.	Water coll., mg. per hour	Sp. diff. of hydrogen through nickel
Part A			Part B		
Hydrogen pressure, 1.000 ±0.007 atm.			Hydrogen partial press., 0.514 ±0.009 atm.		
478	3.8 ±0.7	34.2 ± 7.0	471	3.3 ±0.7	28.7 ± 6.5
503	5.45 ±0.05	50.6 ± 0.7	532	5.9 ±0.3	54.8 ± 3.5
553	9.0 ±1.3	82.3 ± 9.0	597	8.6 ±1.3	81.7 ±13.5
570	9.2 ±1.6	88.6 ±16.3	619	11.3 ±0.2	109.4 ± 2.0
640	14.9 ±0.9	144.7 ± 8.5	665	12.6 ±1.1	122.4 ±10.1
678	18.0 ±0.5	176.7 ± 4.5	677	14.2 ±1.7	133.4 ±21.3
703	20.7 ±1.7	202.4 ±16.9	Part C		
747	24.9 ±2.0	238.6 ±14.4	Hydrogen partial press., 0.150 ±0.01 atm.		
798	37.7 ±0.9	369.2 ± 8.8			
			498	2.7 ±0.8	23.1 ± 8.0
			577	4.4 ±0.2	39.7 ± 2.4
			658	7.0 ±0.3	65.4 ± 3.5
			719	10.4 ±1.0	94.2 ± 4.4

Diffusion and Pressure.—In order to study the relation of diffusion rate to pressure at constant temperatures, the data presented in Table III A, B and C above were put in graphic form as in Fig. 2 in the first paper.[2] From these curves the values tabulated in the first horizontal line, for each temperature, in Table IV were obtained.

Richardson, Nicol and Parnell,[14] Lombard[15] and Johnson and Larose[16] have all intrepreted their experimental data for pressure variation by a relationship expressed by $D = K\sqrt{P}$, in which D is the specific diffusion, P is the partial pressure of the diffusing gas and K is a constant varying with the temperature. For this paper this constant was determined for each of the four temperatures by the graphic method. The values found were: 76.2 for 550°, 116.0 for 600°, 152.2 for 650° and 190.0 for 700°. The second horizontal line under each temperature of Table IV records specific diffusion values calculated by use of this constant in

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[13] The samples were generously furnished by the International Nickel Co.

[14] Richardson, Nicol and Parnell, *Phil. Mag.*, [6] **8**, 1 (1904).

[15] Lombard, *J. chim. phys.*, **25**, 518, 593 (1928).

[16] Johnson and Larose, THIS JOURNAL, **49**, 317 (1927).

TABLE IV

RELATION OF SPECIFIC DIFFUSION TO PRESSURE

Temp., °C.			Specific diffusion values in atmospheres for the pressures 1.000	0.514	0.150
550	1	From graphs	80.0	60.0	35.0
	2	Calculated	76.2	54.6	29.5
	3	Observed (553°)	82.3 ± 9.0		
600	1		110.0	85.0	47.5
	2		116.0	83.1	44.9
	3	(597°)		81.7 ± 13.5	
650	1		150.0	115.0	65.0
	2		152.2	109.1	58.9
	3	(658°)			65.4 ± 3.4
700	1		197.5	147.5	85.0
	2		190.0	136.2	73.5
	3	(703°)	202.4 ± 16.9		

the equation above. The third horizontal line in the table exhibits specific diffusion values, with their deviations from the mean, obtained directly by experiment for the temperatures shown in parentheses. The calculated values, it should be noted, show no greater deviation from the observed values than do the observed from their own mean.

Diffusion and Temperature.—Three different expressions have been put forth for the correct relation of diffusion rate to temperature: $D = KT^b$; $D = K \times 10^{at}$ and $D = KT^{1/2}e^{-q/4T}$.

The first was proposed by Ryder[17] and was used by Johnson and Larose[4] in 1924 in connection with their study of the diffusion of oxygen through silver. The expression may be put in the form $\log D = \log K + b \log T$, which lends itself to graphic representation. The authors find that when their data for the diffusion of hydrogen through nickel are so plotted, the result is not a first-order curve. Johnson and Larose in their second paper,[5] for the same reason, decided against this expression for the temperature–diffusion relationship. In other words, this formulation is inadequate either for the diffusion of oxygen through silver or the diffusion of hydrogen through nickel.

The second equation, $D = K \times 10^{at}$, is that which Lombard[18] claims to represent acceptably the relation of diffusion to temperature for his study of hydrogen and nickel as well as for other gases through other metals. His evidence for his conclusion is that when $\log D$ is plotted against T, the curve resulting is of the first order. A critical examination of Lombard's curves does not lead the authors to his conclusions. Neither does such graphic treatment of their own data lead to his generalization. In fact they have found that whether Lombard's work with hydrogen and nickel, their own work with hydrogen and nickel, Johnson and

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[17] Ryder, *Elect. J.*, **17**, 161 (1920).

[18] Lombard, *J. chim. phys.*, **25**, 597 (1928).

Larose's work with oxygen and silver or Richardson, Nicol and Parnell's work with hydrogen and platinum, is given this graphic form, the curve is invariably concave toward the temperature axis and convex toward the diffusion axis.

Johnson and Larose in their second paper[5] show that $D = KT^{1/2}e^{-q/4T}$ gives a much more satisfactory generalization for the diffusion of oxygen through silver than did the Ryder formulation, $D = KT^b$, which they first used. The expression is a derivation from the more general form: $D = K/dP^{1/2}T^{1/2}e^{-q/4T}$, when P and d are assumed as constants. This general equation was set up from thermodynamic considerations[19] and connects specific diffusion, D, with absolute temperature, T, diaphragm thickness, d, and pressure, P. In it "e" is the base for the natural system of logarithms, q is a constant representing the heat of dissociation of the gas within the metal and K is a general constant. A simple method of applying this relationship to a set of data is to plot the reciprocal of the temperature, $1/T$, against $\log D - {}^1/_2 \log T$. The authors show the graph resulting for data from their Table III A in Curve H and in Fig. 1. For comparison purposes they have also included curves for hydrogen through platinum, R, oxygen through silver, J, and hydrogen through

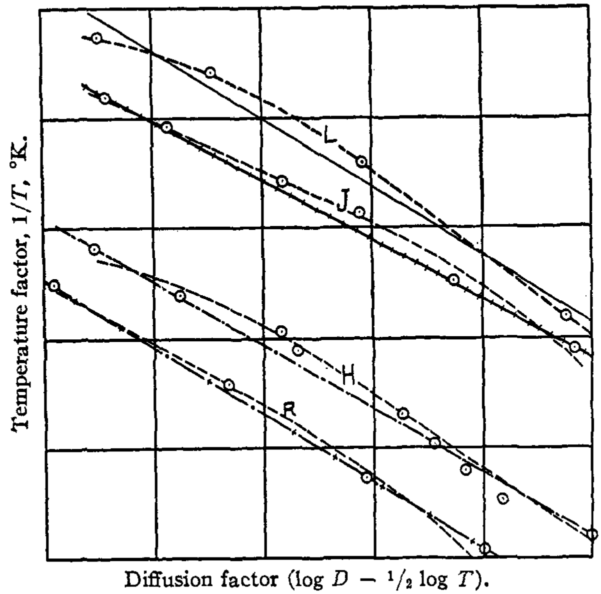

Fig. 1.—Relation of diffusion rate to temperature for: R, Richardson's hydrogen through platinum; J, Johnson's oxygen through silver; H, authors' hydrogen through nickel; L, Lombard's hydrogen through nickel.

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[19] Richardson, *Phil. Mag.*, [6] 7, 266 (1904).

nickel, L, in the same figure.[20] The essential point sought in the figure is to show that, within the limits of experimental error, Richardson's equation represents the temperature–diffusion relationship for the diffusion of hydrogen through platinum and nickel and of oxygen through silver.

The authors cannot refrain, however, from pointing out that the broken-line curves, as drawn in Fig. 1, are not an undue distortion of the points as located. The graph, L, of Lombard's data especially makes evident the concavity of these curves toward the origin. For work so far reported, experimental values probably deviate from their means by amounts sufficient to "iron out" such concavity. Yet why do all four of these curves consistently show curvature in the same direction? Probability can hardly account for such regularity.

In order to check the applicability of the Richardson equation to data under study in a more precise manner, constants q and K have been determined for the diffusion of hydrogen through nickel and the specific diffusions calculated for all data exhibited in Table III A, B and C. The results are presented in Table V.

TABLE V

COMPARISON OF CALCULATED RATES OF DIFFUSION WITH THOSE OBSERVED

Temp.,	Diffusion		Dev. of calcd.	Temp.,	Diffusion		Dev. of calcd
°C.	Observed	Calcd.	from obs.	°C.	Observed	Calcd.	from obs.
Hydrogen pressure, 760 mm.				Hydrogen pressure, 390.6 mm.			
478	34.2 ± 7.0	38.1	+ 3.9	471	28.7 ± 6.5	25.6	− 3.1
503	50.6 ± 0.7	48.6	− 2.0	532	54.8 ± 3.5	45.2	− 9.6
553	82.3 ± 9.0	75.3	− 7.0	597	81.7 ± 13.5	76.2	− 5.5
570	88.6 ± 16.3	86.3	− 2.3	619	109.4 ± 2.0	89.4	−20.0
640	144.7 ± 8.5	144.3	− 0.4	665	122.4 ± 10.0	122.1	− 0.3
678	176.7 ± 4.5	185.0	+ 8.3	677	133.4 ± 21.3	131.8	+ 2.4
703	202.4 ± 16.9	215.6	+13.2	Hydrogen pressure, 115 mm.			
747	238.6 ± 14.4	277.5	+38.9				
798	369.2 ± 8.8	362.6	− 6.6	498	23.1 ± 8.0	18.0	− 5.1
				577	39.7 ± 2.4	35.3	− 4.4
				658	65.4 ± 3.5	63.0	− 2.4
				719	94.2 ± 4.4	91.8	− 2.4

Table V tabulates, in the third column, not only the average observed specific diffusion but the deviation of other observed values, for that temperature, from the average. A comparison of the values in the fifth column with these deviations is the essential purpose of the table. As a summary of this comparison, the average deviation of specific diffusion values from their means in Table III A, B and C is 9.8%, while the average deviation of the calculated values from the observed as exhibited in Table V is 7.9%. The calculated results check the observed to within the experimental error.

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[20] The reader should bear in mind that Curves L, R and J are not drawn to the same scale as H.

The Heat of Hydrogen Dissociation.—The constant, q, represents the heat of dissociation of the gas within the metal. For hydrogen in nickel this quantity (average for ten different determinations) is 20.8 ± 2.2 kilogram calories. Using data from Lombard's first paper,[3] an average of 29.7 ± 14.1 kilogram calories was found. These values are surprisingly low.

Richardson, Nicol and Parnell's value for the heat of dissociation of hydrogen in platinum was found to be 36.5 kilogram calories. The energy of molecular hydrogen's dissociation is commonly given as 100.0 kilogram calories. Richardson's lower value can be reconciled with this by assuming that platinum's energy of hydrogen-adsorption has reduced hydrogen's energy of dissociation within the metal. Johnson and Larose also found a lower value, 43.2 kilogram calories, for oxygen's dissociation within silver than the usual 160.0 kilogram calories, the heat of dissociation for molecular oxygen. This can be accounted for as was hydrogen's value in platinum.

Extending the same reasoning to the heat of dissociation of hydrogen in nickel requires that nickel's energy of adsorption for hydrogen be greater than that of platinum. The fact that nickel's coefficient of thermal expansion is one and one-half times that of platinum might aid in an explanation if greater expansion could be interpreted to mean greater internal surface for adsorption and so greater activation. This would mean that this heat of dissociation should become less at higher temperatures. A preliminary examination of the data for the diffusion of hydrogen through nickel indicates that this last statement is roughly true. A more thorough study of this might prove profitable.

Conclusions

1. Zinc has been shown to be permeable to hydrogen at temperatures between 305° and its melting point.
2. Pure copper, or at least oxygen-free copper, has been shown to be permeable to hydrogen from 500° and above. The hypothesis is advanced that its tendency to become brittle and fissured is due to the development of larger planes of cleavage as the crystal size increases rather than to the reducing action of the diffusing gas.
3. Within the limits of experimental error the diffusion of gases through metals is best related to temperature and pressure by $D = KP^{1/2}T^{1/2}e^{-q/4T}$.
4. It is suggested that more precise technique in this field may lead to a modification of the preceding generalization.
5. The heat of dissociation of hydrogen gas within nickel has been determined as 20.8 ± 2.2 kilogram calories. The "constancy" of this constant has been questioned.

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