Summary

1. The electromotive forces of cells of the type, $H_2 \mid HI\ (c),\ AgI \mid Ag$, have been measured at 25° for various concentrations of hydrogen iodide.

2. The free-energy decrease and the heat-content decrease attending the cell reaction have been calculated.

3. The free-energy decrease accompanying the transfer of one mole of hydrogen iodide from the various concentrations to a concentration exactly 0.005 M has been computed. From these values we have calculated the geometric mean activity coefficients of the ions of hydrogen iodide, and we have found that for concentrations up to 0.05 M these coefficients are practically equal to the corresponding coefficients for hydrogen chloride at the same concentrations. Obviously, the activities of the iodide and chloride ions are equal when in equivalent concentrations of their salts.

Iowa City, Iowa

[Contribution from the Department of Chemistry, University of Nebraska]

THE DIFFUSION OF HYDROGEN THROUGH METALS[1]

By Horace G. Deming and B. Clifford Hendricks

Received August 29, 1923

Deville and Troost,[2] Graham,[3] Sieverts,[4] and Charpy and Bonnerot[5] have studied the diffusion of hydrogen through platinum, iron, palladium, copper and nickel. The rate of diffusion, found to be very different for different metals, was shown to increase rapidly with increasing temperature, but the results obtained were hardly more than qualitative, and were not expressed in terms that may be compared with recent work. More accurate data have been obtained by Schmidt[6] and by Holt[7] on palladium, by Richardson and coworkers[8] on platinum, and by Edwards and Pickering[9] on rubber, the rate of diffusion of hydrogen through these substances at different temperatures being shown graphically. In the work described in the present paper a method has been developed that permits the rate of diffusion of gases through metals to be determined under more precisely controlled conditions than has previously been possible; and preliminary

[1] Abstract of a thesis presented by B. Clifford Hendricks to the Graduate College of the University of Nebraska in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Deville and Troost, *Compt. rend.*, **56**, 977 (1865); **57**, 965 (1863).

[3] Graham, *Phil. Mag.*, [4] **32**, 503 (1866).

[4] Sieverts, *Z. physik. Chem.*, **60**, 129 (1907).

[5] Charpy and Bonnerot, *Compt. rend.*, **156**, 394 (1913).

[6] Schmidt, *Ann. Physik*, [IV] **13**, 767 (1904).

[7] Holt, *Proc. Roy. Soc.*, **91A**, 148 (1915).

[8] Richardson and others, *Phil. Mag.*, [6] **8**, 1 (1904).

[9] Edwards and Pickering, *Bur. Standards Sci. Paper*, **387**, 346 (1920).

results have been obtained for the rate of diffusion of hydrogen through nickel, copper, lead, zinc and aluminum.

Apparatus

In designing the apparatus to be used in this work it seemed desirable: (1) that the metal to be tested should be in the form of flat sheets or discs; (2) that one metal should be easily interchangeable for another at the end of a series of tests; (3) that diffusion should be limited to a definitely measurable area; (4) that the temperature over this area should be as uniform as possible; (5) that the apparatus should be usable up to temperatures of at least 1000°. The method finally developed met these five requirements quite perfectly, the essential parts of the "diffusion-unit" being as shown in Fig. 1.

The metal to be tested was a disk D, about 9.5 cm. in diameter, of any desired thickness. This was clamped between two cylindrical steel blocks XY, each delimited by two concentric circular knife-edges AB, and centered by a steel ring C. Bolts MM′, passing through insulating soapstone blocks S and an asbestos ring V, served to draw the circular knife-edges against the metallic disk, but not necessarily tight enough to make a gas-tight joint.

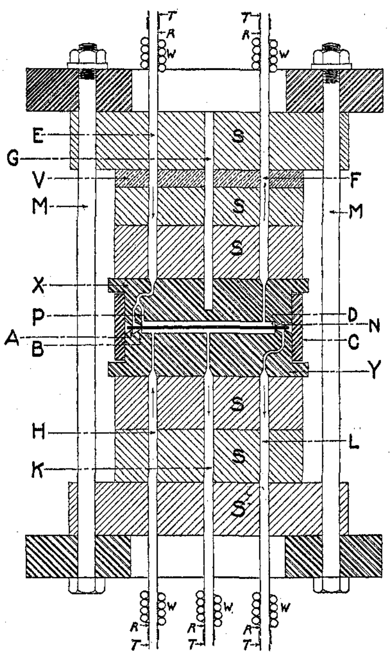

Fig. 1

Each steel block was tapped to receive three threaded steel tubes, joints being made gas-tight with metaphosphoric acid. Through one of these tubes, H, hydrogen, purified as described hereafter, was admitted to the shallow cavity in the upper surface of the lower steel block Y. The annular channel between the two knife-edges of this block was connected, through L with a vacuum pump, in order that any hydrogen leaking outward past the inner knife-edge might be immediately removed. The area of metal exposed to diffusion was thus definitely restricted to that circumscribed by the inner knife-edge of the lower block. This was 46.03 sq. cm. at 20°, becoming greater by about 0.2% at 100°, 1.2% at 500°, and 2.6% at 750°, on account of the expansion of the steel.

Any hydrogen diffusing through the given area of the metallic disk D was immediately swept out through F by a current of nitrogen which was admitted to the upper block through the tube E and the capillary opening P. This nitrogen also had direct access to the annular space N between the two knife-edges of the upper block and, being there maintained under a slight pressure, served to prevent the loss by leakage outward under the knife-edges of the upper block. of any hydrogen that might have diffused through the disk. By maintaining a brisk current of nitrogen through the upper portion of the apparatus it was possible to keep the hydrogen there at a very low concentration, and thus make sure that no appreciable part of the hydrogen diffusing through the disc should afterward be lost by being absorbed by the steel of the upper block or outlet tube.

The opening G served to admit a Chromel-Alumel thermocouple; K served as an outlet, when the chamber in the lower block was swept out with nitrogen, in preparing for a "blank determination." Connections were made outside the furnace in which the steel "diffusion unit" was heated, by tinning the steel tubes, and soft-soldering to platinized Pyrex glass.[10] The soldered joints were water-cooled at higher temperatures.

Surrounding the steel blocks of the "diffusion unit" was a heating unit. The thermocouples, calibrated at the freezing points of tin, zinc, antimony and sodium chloride,[11] showed the temperature within the two steel blocks to be uniform, within 5°.

Connected to the tube F, Fig. 1, was a small electrically-heated furnace, containing copper oxide. This was kept at a dull red heat; and the water vapor, produced by oxidation of the hydrogen which had diffused through the metallic disk, was absorbed in phosphorus pentoxide and weighed.

Manipulation

In beginning each experiment, the "diffusion unit" was first heated slowly to the desired temperature, with the shallow chambers above and below the metallic disk filled with nitrogen, to prevent oxidation. Then a "blank determination" was made, to determine whether there was any change in the weight of the U-tubes containing phosphorus pentoxide when no hydrogen was being admitted to the "diffusion unit." In practice, an increase in weight of 1 or 2 mg. was obtained in the blank test, in several hours' run.[12] Hydrogen was admitted to the lower chamber after preliminary blanks were secured, and measurements were then made at various temperatures which gradually approached the melting point of the sample under examination. Finally, the hydrogen in the lower chamber was displaced by nitrogen, in order that the series of measurements might be concluded with a second "blank determination."

The hydrogen was generated in a Kipp apparatus from zinc and dil. sulfuric acid, and purified by being passed successively through an alkaline potassium permanganate solution, a 5% silver nitrate solution, concd. sulfuric acid, a small electric furnace charged with copper turnings and heated to about 350°, and U-tubes containing soda-lime and calcium chloride. The nitrogen was obtained from a commercial cylinder, and was purified by being passed through an apparatus containing ammoniacal ammonium chloride solution to absorb oxygen.[13] From this it entered a gasometer, displacing dil. sulfuric acid, and was subsequently purified by being passed through concd. sulfuric acid, a furnace containing copper oxide and copper

[10] McKelvy and Taylor, THIS JOURNAL, **42**, 1366 (1920).

[11] *Bur. Standards Circ.*, **35** (1919).

[12] In the results submitted, these "blank" values, which are probably due to moisture from the copper oxide and from hydrogen adsorbed by the steel blocks of the diffusion units, are not satisfactory. This is one procedure of this research which the junior author hopes to refine in work now under way.

[13] Badger, *J. Ind. Eng. Chem.*, **11**, 1052 (1919); **12**, 161 (1920).

turnings heated to about 350°, and finally through U-tubes containing soda-lime and calcium chloride.

Experimental Results

Aluminum.—The aluminum used was a disk of commercial sheet metal, 0.637 mm. thick. After a few preliminary determinations, to standardize the manipulation, the data given in Table I were obtained. The water collected in the blank determinations, expressed in milligrams per hour was, on the average, practically the same as when hydrogen was admitted to the lower chamber of the "diffusion unit." Thus, aluminum appears to be totally impermeable to hydrogen at temperatures as high as 550°. The hydrogen appeared to produce no great alteration in the physical properties of the aluminum, except that minute blisters appeared, forming parallel streaks across the surface of the metal, doubtless due to bubbles of gas trapped just beneath the surface, and elongated during rolling.

Table I

Diffusion of Hydrogen through Aluminum

Disk, 0.637 mm. thick. Area exposed to diffusion, 46.7 sq. cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	
5.9	510	8.2	1.4	Blank
2.4	540	1.8	0.7	Determination
4.4	540	4.1	0.9	Determination
1.03	575	0.6	0.6	Determination
2.3	550	4.9	2.1	Blank
1.01	570	0.7	0.7	Blank

Average blank, 1.4 mg. of water per hour. No detectable diffusion at temperatures around 550°.

Zinc.—The zinc used was a sample of Horse Head Brand, supplied by the New Jersey Zinc Company, stated to be about 99.5% pure, and containing at most 0.5% of lead and 0.011% of iron. The disc had an average

Table II

Diffusion of Hydrogen through Zinc

Disk, 1.643 mm. thick. Area exposed to diffusion, 46.7 cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
3.7	260	1.7	0.46	Blank
2.0	255	1.4	.70	0.0008
2.0	262	1.0	.50	.0004
4.5	310	3.8	.84	.0012
3.05	375	2.0	.66	.0008
6.1	380	4.1	.67	.0008
2.0	385	0.5	.25	Blank

Average blank, 0.35 mg. of water per hour.

thickness of 1.643 mm. Discarding a few experiments in which the time of diffusion was only two hours or less, the data obtained are given in Table II. The figures in the last column are obtained by correcting the data in the fourth column for the average rate of collection of water in the two blanks. The area exposed to diffusion in the temperature range studied was taken as 46.7 sq. cm.

Assuming the rate of diffusion to be inversely proportional to the thickness of the metal disk (Fick's law) we may calculate the specific diffusion rate of hydrogen through zinc, expressed in mg. per hour per sq. cm. area per mm. thickness, to be about 0.0012 at 375°.

Lead.—A disk of commercial soft lead was used, with an average thickness of 0.862 mm. The data obtained are given in Table III. The two preliminary blanks were unusually high, presumably due to incomplete drying of the copper oxide in the combustion furnace. If we assume that the first few determinations are vitiated by the same cause, we nevertheless have evidence from the remaining data of an extremely slight permeability of lead to hydrogen. We may calculate the specific diffusion rate of hydrogen through lead (mg. per hour per sq. cm. per mm. of thickness) to be not more than 0.001.

Table III

Diffusion of Hydrogen through Lead

Disk, 0.862 mm. thick. Area exposed to diffusion, 46.7 sq. cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
1.5	185	1.4	0.9	Blank
1.5	210	1.2	.8	Blank
2.5	250	1.0	.4	Rejected
2.6	270	1.3	.05	Rejected
1.5	255	0.6	.4	0.0005
1.5	265	.9	.6	.0009
1.5	280	1.1	.7	.0014
1.25	295	0.3	.2	Blank
1.0	300	.0	.0	Blank

Blank correction in this series taken as 0.2 mg. of water per hour. Average rate of diffusion in three final determinations, 0.0009 mg. of hydrogen per sq. cm. per hour at temperatures around 265°.

Copper.—The data obtained with copper at first were very erratic. The metal appeared to be much more permeable to hydrogen than any of those previously examined. But after the metal had been exposed in the furnace to alternate heating and cooling for a number of hours, the rate of diffusion suddenly seemed to increase enormously. Microscopic examination showed a decided increase in the size of the metallic crystals, and the development of intra-crystalline cracks, as a result of the heating. In addition, the disk was perforated by several minute holes immediately above the hydrogen inlet.

It was presumed that a part of the difficulty might have been due to the reduction, by the hydrogen, of the cuprous oxide which is an impurity in ordinary copper. For this reason subsequent tests were made on sheet copper[14] which had been made by cold-rolling cathode copper. Care was also taken to begin the observations at a high temperature, and to make successive determinations at lower and lower temperatures, without permitting the furnace to cool until the end of the series. In this way the alternate contraction and expansion of the copper disk, caused by repeated

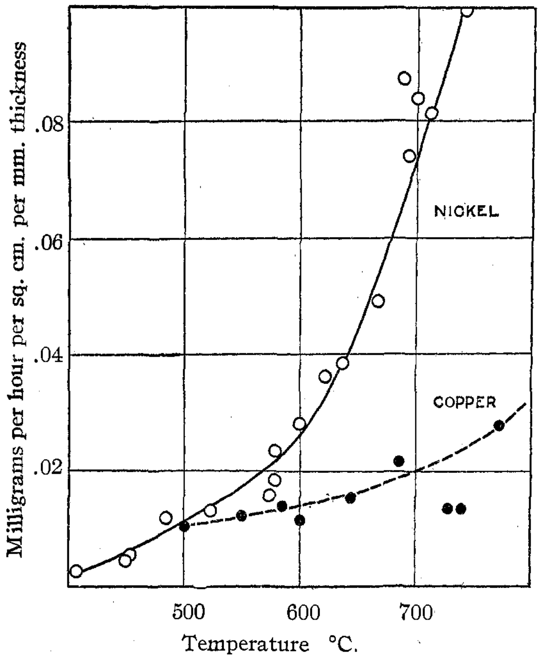

Fig. 2

heating and cooling, were avoided, and the tendency to form intra-crystalline cracks was minimized.[15] Under these conditions the data given in Table IV were obtained. A rapid increase in permeability with increasing temperature is indicated, as shown graphically in Fig. 2. The specific diffusion rate of hydrogen through copper (mg. per hour per sq. cm. per mm. of thickness) may be calculated to be about 0.028 at 770° and about 0.011 at 500°.

Nickel.—Of the five metals studied, nickel was the easiest with which to work. The sample was of electrolytically refined nickel,[16] and had an aver-

[14] Furnished by the American Brass Company.

[15] A similar precaution was found to be necessary in work done by Richardson and coworkers (Ref. 8) on platinum.

[16] Furnished by the International Nickel Company.

TABLE IV

DIFFUSION OF HYDROGEN THROUGH COPPER

Disk, 0.391 mm. thick. Area exposed to diffusion, 46.7 sq. cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
1.0	730	0.6	0.6	Blank
.5	730	7.2	14.4	0.034
.8	737	11.4	14.3	.034
.6	770	19.3	32.2	.072
.5	687	11.8	23.6	.056
.5	645	8.7	17.4	.042
.7	605	8.4	12.0	.028
.5	585	7.6	15.2	.036
.6	550	8.2	13.7	.032
.5	500	5.6	11.2	.027
1.9	538	0.2	0.1	Blank
1.25	475	.2	.2	Blank

Average blank, 0.3 mg. of water per hour.

age thickness of 0.653 mm. This was under observation for a total of more than 90 hours, and was repeatedly heated and cooled, without showing any of the tendency to crack that appeared in the case of copper. A few of the

TABLE V

DIFFUSION OF HYDROGEN THROUGH NICKEL

Disk, 0.653 mm. thick. Area exposed to diffusion, 46.7 sq. cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
3.5	613	1.3	0.4	Blank
2.5	595	3.0	1.2	Blank
1.0	580	16.1	16.1	0.036
0.7	580	9.3	13.3	.029
3.17	575	34.8	11.0	.024
2.0	625	48.1	24.0	.056
1.5	665	47.6	31.7	.074
2.9	695	138.3	47.6	.114
1.07	710	56.4	52.7	.124
0.8	690	45.2	56.5	.133
3.0	403	8.4	2.8	.004
3.0	405	7.4	2.5	.004
1.5	450	6.2	4.1	.007
1.5	452	6.3	4.2	.008
1.6	487	10.5	8.6	.018
1.6	527	15.0	9.4	.020
2.0	600	38.6	19.3	.044
1.0	637	25.6	25.6	.060
1.5	700	81.3	54.0	.128
3.9	745	250.7	64.4	.153
2.0	570	2.8	1.4	Blank
2.9	570	3.6	1.2	Blank

Average blank, 1.0 mg. of water per hour.

results obtained, selected impartially from a much larger number of determinations, are given in Table V. Here again a rapidly increasing rate of diffusion with increasing temperature is evident, as shown graphically in Fig. 2. The curves here given for copper and nickel have the same general appearance as those obtained by other workers[6,8,9] for palladium, platinum and rubber. The specific diffusion rate of hydrogen through nickel may be calculated to be about 0.100 at 750° and about 0.012 at 500°. Thus, hydrogen diffuses through nickel at temperatures around 750° about four times as fast as it does through copper, and 80 to 100 times as fast as it does through lead and zinc at temperatures just below the melting points of the latter metals.

Summary

An apparatus has been described for studying the rate of diffusion of gases through definitely measurable areas of sheet metal at definite, uniform temperatures. The specific diffusion rate of hydrogen through several common metals, expressed in milligrams per hour per square centimeter area per millimeter thickness has been found to be:

Metal	Specific diffusion rate	°C.	Metal	Specific diffusion rate	°C.
Aluminum....	Not detectable[a]	555	Copper.......	0.028	770
Zinc.........	0.0012	375	Nickel........	.012	500
Lead.........	.001	265	Nickel........	.100	750
Copper.......	.011	500			

[a] Namely, less than about 0.0005.

In addition, the specific diffusion rate of hydrogen through copper and through nickel has been determined over a considerable range of temperature, and the results have been shown graphically.

Further work is in progress, by the junior author, extending this investigation over a wider range of temperature, metal-thickness and pressure variation.

LINCOLN, NEBRASKA