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UNITED STATES ATOMIC ENERGY COMMISSION

PERMEATION OF HYDROGEN THROUGH MATERIALS AND HYDROGENOUS SYSTEMS FOR SHIELDING. Quarterly Status Report No. 1 [for] July 1, 1956 through September 30, 1956.

By
Edward A. Sullivan
Sidney Johnson

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METAL HYDRIDES INCORPORATED

FROM THE Chemical Research Laboratory

Quarterly Status Report No. 1

PERMEATION OF HYDROGEN THROUGH MATERIALS

and

HYDROGENOUS SYSTEMS FOR SHIELDING

by

Edward A. Sullivan, Chemist
and

Sidney Johnson, Group Leader
Research and Development Laboratories

Subcontract No. 390 under Contract No. W-7405-eng-26

Metal Hydrogen Systems

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Beverly, Massachusetts

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A. PERMEATION OF HYDROGEN THROUGH MATERIALS

1. Permeation of Hydrogen through molten Sodium hydroxide

Tentative values have been determined for the rate of hydrogen permeation through molten sodium hydroxide. This was done by causing hydrogen to permeate through the system consisting of a layer of molten sodium hydroxide and the nickel diaphragm on which it was placed. The rate of hydrogen permeation, $D_{OH8+Ni,*}$ in $\text{cm}^3/\text{hr.}$ was determined. The reciprocal of this value, tabulated as R_{OH8+Ni} , may be considered as the total resistance of sodium hydroxide plus nickel to permeation of hydrogen through the system. Since the rate of permeation of hydrogen through nickel alone has been previously measured, the resistance of the nickel diaphragm is known; and with the basic assumption that the total resistance of the system is equal to the sum of the resistances of the sodium hydroxide and the nickel, it is possible to determine the resistance, and therefore the permeability, of the molten sodium hydroxide layer. The data are summarized in Tables 1-1 and 1-2, and depicted graphically in Figure 1-1; values of individual runs given in Tables 1-3, 1-4, and 1-5.

Below 500°C. , the rate of hydrogen permeation through molten sodium hydroxide is too small to be measured by the techniques being used. The small amount of hydrogen which is collected is much larger than the quantity to be expected on the basis of equations derived from data obtained at higher temperatures. This may reasonably be ascribed to "leakage" around the hydroxide by permeation through the metal walls. Under the conditions employed, the rate of hydrogen permeation through sodium hydroxide approaches, within an order of magnitude, the rate of hydrogen permeation through the nickel diaphragm at about 500°C. , and it is at and above this temperature where the data are reliable. The logarithm of the rate of hydrogen permeation through molten sodium hydroxide is a linear function of the reciprocal of the absolute temperature. The energy of activation of the diffusion pro-

* The number following the OH in the subscript is the approximate thickness of the sodium hydroxide layer in sixteenths of an inch.

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cess through molten sodium hydroxide is 42 kcal./mole H_2 .

While a linear relationship is found for data taken at successively higher temperatures, the rate of hydrogen permeation does not return to its original value if the temperature is reduced. The last 20 runs of Table 1-5 may be compared to previous data in the same Table to illustrate this point. The same result has been observed previously. The reason is not known, but it is believed that as the temperature is increased an increasing concentration of nickel corrosion product is contained in the molten sodium hydroxide. The effect, if any, which this has on the rate of hydrogen permeation is definite and reproducible from run to run. When the temperature is reduced, however, very finely divided nickel is produced by a reversal of the corrosion reaction, and, in some way, perhaps by being dispersed throughout the melt, this increases the rate of hydrogen permeation through the system. After the sodium hydroxide has been cooled and thoroughly removed from the nickel diaphragm by washing with water, the rate of hydrogen permeation through the nickel diaphragm alone is found to be identical to its original value.

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TABLE 1-1

SUMMARY OF HYDROGEN PERMEATION DATA THROUGH SODIUM HYDROXIDE + NICKEL

Diaphragm 2 (Thickness, 0.129 inch; diameter 0.998 inch; OH8, 10.960g. NaOH; OH16 21.920 g. NaOH)

t (°C.)	$10^3/T$ (°K ⁻¹)	D_{Ni} (cm. ³ / hr.)	R_{Ni} (hr./ cm. ³)	D_{OH8+Ni} (cm. ³ / hr.)	R_{OH8+Ni} (hr./ cm. ³)	R_{OH8} (hr./ cm. ³)	D_{OH8} (cm. ³ / hr.)	$D_{OH16+Ni}$ (cm. ³ / hr.)	$R_{OH16+Ni}$ (hr./ cm. ³)	R_{OH16} (hr./ cm. ³)	D_{OH16} (cm. ³ / hr.)	$\frac{R_{OH8}}{R_{OH16}}$
400	1.486	0.1822	5.488	0.1347 0.04745	7.424 21.07	1.935 15.59	0.5167 0.6416	0.09354	10.69	5.202	0.1922	
450	1.383	0.3558	2.811	0.2094	4.776	1.965	0.5089	0.1641	6.094	3.283	0.3046	
500	1.293	0.6519	1.534	0.3026 0.1508	3.305 6.631	1.771 5.097	0.5648 0.1962	0.2321	4.308	2.775	0.3604	
550	1.215	1.049	0.9531	0.5055 0.4994	1.978 2.002	1.025 1.049	0.9755 0.9530					
600	1.145	1.667	0.5999	1.097 1.079	0.9117 0.9271	0.3118 0.3272	3.207 3.056	0.7912	1.264	0.6640	1.507	0.470 0.493
650	1.083	2.434	0.4108	1.876 1.883	0.5331 0.5311	0.1223 0.1203	8.178 8.313	1.560	0.6411	0.2308	4.333	0.530 0.521
700	1.027	3.477	0.2876	3.157	0.3168	0.02920	34.25	2.892	0.3458	0.05820	17.18	0.502
750	0.977	4.888	0.2046	4.662	0.2145	0.009939	100.6	4.442	0.2251	0.02050	48.78	0.485

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TABLE 1-2

SUMMARY OF HYDROGEN PERMEATION DATA THROUGH SODIUM HYDROXIDE

10.960 Grams Sodium hydroxide

First series

<u>t(°C.)</u>	<u>10³/T(°K⁻¹)</u>	<u>D_{OH8}(cm.³/hr.)</u>	<u>log D_{OH8}</u>
400	1.486	0.5167	-0.2868
450	1.383	0.5089	-0.2934
500	1.293	0.5648	-0.2481
550	1.215*	0.9755	-0.0108*
600	1.145*	3.207	0.5061*
650	1.083*	8.178	0.9126*
700	1.027*°	34.25	1.5345*°
750	0.977*°	100.6	2.0022*°

Second series

400	1.486	0.6416	-1.1927
500	1.293*	0.1962	-0.7073*
550	1.215*	0.9530	-0.0209*
600	1.145*°	3.056	0.4852*°
650	1.083*°	8.313	0.9197*°

* Points least squared to give equation:

$$\log D_{OH8} = \frac{-8283.6}{T} + 9.997$$

° Points least squared to give equation:

$$\log D_{OH8} = \frac{-9197.2}{T} + 10.966$$

21.920 Grams Sodium hydroxide

400	1.486	0.1922	-0.7162
450	1.383	0.3046	-0.5163
500	1.293	0.3604	-0.4432
600	1.145*	1.507	0.1782*
650	1.083*	4.333	0.6368*
700	1.027*	17.18	1.2351*
750	0.977*	48.78	1.6882*

* Points least squared to give equation:

$$\log D_{OH16} = \frac{-9137.7}{T} + 10.598$$

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TABLE 1-3
(Continuation of Table 57-3)

RATE OF HYDROGEN PERMEATION THROUGH NaOH + NICKEL

Diaphragm 2 (Thickness, 0.129 inch;
diameter, 0.998 inch;
21.920 g. NaOH)

Run No.	Temp. (°C.)	Pressure (atm.)	Rate (cm. ³ /hr.)	Specific Rate (cm. ³ mm./ cm. ² hr.)
282-2-OH16	550	3.000	0.9846	
283-2-OH16	550	3.000	0.9981	
284-2-OH16	550	3.000	0.9860	
	550	3.000	0.9895*	

* Indicates average value taken by combining results of all runs at the indicated temperature and pressure. Since all runs were not of the same time duration, the rate is a weighted average.

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TABLE 1-4

RATE OF HYDROGEN PERMEATION THROUGH NICKELDiaphragm 2 (Thickness, 0.129 inch; diameter, 0.998 inch)

Run No.	Temp. (°C.)	Pressure (atm.)	Rate (cm. ³ /hr.)	Specific Rate (cm. ³ mm./cm. ² hr.)
286-2	600	3.000	1.673	
287-2	600	3.000	1.668	
288-2	600	3.000	1.667	
	600	3.000	1.669*	

* Indicates average value taken by combining results of all runs at the indicated temperature and pressure. Since all runs were not of the same time duration, the rate is a weighted average.

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TABLE 1-5

RATE OF HYDROGEN PERMEATION THROUGH NaOH + NICKEL

Diaphragm 2 (Thickness, 0.129 inch;
diameter 0.998 inch;
10.960 g. NaOH)

Run No.	Temp. (°C.)	Pressure (atm.)	Rate (cm. ³ /hr.)	Specific Rate (cm. ³ mm./cm. ² hr.)
295-2-OH8	400	3.000	0.04729	
296-2-OH8	400	3.000	0.04799	
297-2-OH8	400	3.000	0.04712	
	400	3.000	0.04745*	
298-2-OH8	400	4.500	0.05789*	
300-2-OH8	500	3.000	0.1506	
301-2-OH8	500	3.000	0.1509	
	500	3.000	0.1508*	
305-2-OH8	550	3.000	0.4992	
306-2-OH8	550	3.000	0.4996	
	550	3.000	0.4994*	
309-2-OH8	600	3.000	1.075	
310-2-OH8	600	3.000	1.080	
	600	3.000	1.079*	
314-2-OH8	650	3.000	1.879	
315-2-OH8	650	3.000	1.885	
	650	3.000	1.883*	
316-2-OH8	650	4.500	2.300	
317-2-OH8	650	4.500	2.300	
	650	4.500	2.300*	

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Table 1-5 (Continued)

Run No.	Temp. (°C.)	Pressure (atm.)	Rate (cm. ³ /hr.)	Specific Rate (cm. ³ mm./cm. ² hr.)
319-2-OH8	500	3.000	0.4878	
320-2-OH8	500	3.000	0.4912	
321-2-OH8	500	3.000	0.4841	
	500	3.000	0.4872*	
322-2-OH8	650	3.000	2.075	
323-2-OH8	650	3.000	2.095	
324-2-OH8	650	3.000	2.116	
325-2-OH8	650	3.000	2.129	
326-2-OH8	650	3.000	2.151	
327-2-OH8	650	3.000	2.157	
328-2-OH8	650	3.000	2.172	
329-2-OH8	650	3.000	2.178	
330-2-OH8	650	3.000	2.206	
331-2-OH8	650	3.000	2.205	
332-2-OH8	650	3.000	2.178	
333-2-OH8	650	3.000	2.224	
334-2-OH8	650	3.000	2.202	
336-2-OH8	600	3.000	1.665	
337-2-OH8	600	3.000	1.666	

* Indicates average value taken by combining results of all runs at the indicated temperature and pressure. Since all runs were not of the same time duration, the rate is a weighted average.

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Log D_{OH} vs. $10^3/T$ 3 atmosphere isobar data for hydrogen permeation through molten sodium hydroxide

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2. Permeation of Hydrogen through Copper

The first attempts to determine the rate of hydrogen permeation through copper were unsuccessful, because, after exposure to hydrogen at 500°C., the copper diaphragms became permeable to hydrogen even at room temperature. In some cases, hydrogen permeability at room temperature could be detected even before the diaphragm was heated. Figure 1-2 shows a microphotograph of the copper in question. The nearly linear arrangement of dark spots represents the presence of an oxide phase at the grain boundaries. Figures 1-3a and 1-3b show another sample of the same metal after treatment with hydrogen at 500°C. Fissures caused by steam, which is formed from the oxide and hydrogen, are very pronounced.

Microphotograph of Copper before Hydrogen Treatment
Magnification ~100x

Figure 1-2

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Microphotograph of Copper after Hydrogen Treatment at 500°C.
Magnification $\sim 100\times$

Figure 1-3a

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Microphotograph of Copper after Hydrogen Treatment at 500°C.
Magnification $\sim 100\times$

Figure 1-3b

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Figure 1-4 shows a microphotograph of vacuum cast copper, and the complete absence of any oxide phase is immediately apparent. Diaphragms machined from this vacuum cast copper have been sent to Oak Ridge National Laboratory for welding, and permeation studies will start immediately when they are returned to Metal Hydrides Incorporated.

Microphotograph of Vacuum Cast Copper
before Hydrogen Treatment
Magnification $\sim 100\times$

Figure 1-4

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B. HYDROGENOUS SYSTEMS FOR SHIELDING

1. Lithium borohydride-Ammonia System

Lithium borohydride forms a number of stable adducts with ammonia. These have been described previously. It also has been shown that a very slow ammonolysis reaction takes place. The first step of this reaction is undoubtedly represented by the equation

The H_3BNH_2^- ion may then react either with ammonia or with borohydride ion in the first step of a polymerization process, according to the scheme outlined below

In order to more clearly define the actual course of the ammonolysis, 2.013 millimoles of ammonia were added to 4.904 millimoles of lithium borohydride. After heating to 100°C. for 200 hours, the product was cooled; 0.260 mmoles of hydrogen had been evolved. The product was then allowed to warm, and 1.865 millimoles of ammonia were recovered, indicating that 0.148 millimoles of ammonia had reacted to liberate 0.260 millimoles of hydrogen. This indicates that the H_3BNH_2^- ion reacts further with the borohydride ion, presumably according to the equation

This would be the expected course of reaction under these conditions, since the borohydride ion, rather than ammonia, is present in excess. At higher tempera-

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ture and with longer reaction times, the product probably tends toward a $(-NHBH_2-)_x$ polymer, similar to the $(-NH_2BH_2-)_x$ polymer believed to be formed from a closely related reaction (G. W. Schaeffer, M. D. Adams, and F. J. Koenig, J. Am. Chem. Soc., 78, 725 (1956)).

Studies of the ammonolysis of lithium borohydride show that the rate:

1. decreases with time,
2. increases with temperature,
3. decreases with increasing ammonia content.

Ammonolysis studies were carried out at 50, 60, 80, and 100°C. The amount of hydrogen evolved from the lithium borohydride-ammoniates during a two-hour period was measured. The ammonia to lithium borohydride mole ratio was then increased and additional two hour heating cycles carried out. In this way, data were obtained correlating the ammonolysis rate to the ammonia concentration and the temperature.

When a sample had been at temperature for exactly two hours, the heating bath was removed and the sample cooled with liquid nitrogen. The evolved hydrogen was transferred to a standard volume by means of a Toepler pump. For each mole of hydrogen gas evolved, it was assumed that one mole of lithium borohydride was consumed, in accordance with Equations 1 and 2.

The amount of lithium borohydride consumed was deducted from the original quantity in calculating molar ratios for subsequent runs on a given sample. Results are given in Table 1-6 and depicted graphically in Figures 1-5, 1-6, and 1-7. Figures 1-6 and 1-7 suggest the ammonolysis rate of lithium borohydride to be an exponential function of composition at a given temperature, and an exponential function of the reciprocal of the absolute temperature at a given composition, respectively.

A sample of composition $LiBH_4 \cdot 0.390NH_3$ was heated at 100°C. for 95 hours, and the increase in pressure as a function of time noted. The sample was cooled to -196°C., and the hydrogen gas pumped off. A second increment of ammonia was added to bring the composition to $LiBH_4 \cdot 0.816NH_3$ and the sample again held at 100°C. for 184 hours. The slower rate of ammonolysis during the second heating is due to the previous treatment,

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and to the increased ammonia concentration. Data are given in Table 1-7 and shown graphically in Figure 1-8.

2. Lithium borohydride-trimethylamine system

Attainment of equilibrium in this system is so slow as to seriously impair any practical value the system may have as a shield. The equilibrium $\text{LiBH}_4 \cdot \text{N}(\text{CH}_3)_3(\text{s}) \rightleftharpoons \text{LiBH}_4(\text{s}) + \text{N}(\text{CH}_3)_3(\text{g})$ exhibits a pressure of 7 mm. at 20°C., but the system requires more than 100 hours to equilibrate. Also, trace quantities of trimethylamine-borane were found to have sublimed above all of the samples. This was completely unexpected since the constituents have been reported not to interact (H. I. Schlesinger and H. C. Brown, J. Am. Chem. Soc., 62, 3429 (1940)). This may be due to trace impurities in the lithium borohydride, but more probably is due to the reaction

This was partially confirmed by the detection of lithium hydride in the sample by means of x-ray diffraction.

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TABLE 1-6

EFFECT OF TEMPERATURE AND CONCENTRATION
ON AMMONOLYSIS RATE OF LITHIUM BOROHYDRIDE

Mole % Lithium borohydride reacted in two hours

$\frac{n_{\text{NH}_3}}{n_{\text{LiBH}_4}}$	$t(^{\circ}\text{C.})$			
	50	60	80	100
0.5	0.060 0.065	0.296	0.495	1.382
1.0	0.060 0.078	0.139 0.163	0.510	0.585
1.5	0.042 0.045	0.070 0.118	0.213	0.434
2.0	0.074 0.033	0.051	0.069	0.257
2.5	0.041	0.057	0.069	
3.0	0.025	0.028		
3.5	0.029			

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TABLE 1-7

AMMONOLYSIS RATE OF LITHIUM BOROHYDRIDE AT 100°C.

First NH ₃ addition LiBH ₄ ·0.390 NH ₃		Second NH ₃ addition LiBH ₄ ·0.816 NH ₃	
Time (hours)	Pressure (mm.)	Time (hours)	Pressure (mm.)
18.0	159	1.0	40
19.0	165	16.5	73
19.5	168	18.0	85
20.0	171	19.5	86
20.5	175	21.0	88
21.5	180	21.5	92
22.5	186	22.5	94
23.5	190	23.5	96
24.5	195	24.5	95
26.0	202	25.0	96
42.5	261	40.0	108
44.5	267	42.0	109
67.5	322	43.0	109
90.0	360	45.0	114
92.0	360	46.0	111
93.0	361	47.5	111
95.0	361	48.5	112
		64.0	119
		67.5	123
		70.0	129
		94.0	143
		114	149
		136	155
		141	155
		160	163
		184	169

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AMMONOLYSIS OF LITHIUM BOROHYDRIDE: RATE vs. CONCENTRATION

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AMMONOLYSIS OF LITHIUM BOROHYDRIDE: RATE vs. COMPOSITION

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AMMONOLYSIS OF LITHIUM BOROHYDRIDE: RATE vs. RECIPROCAL TEMPERATURE

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Total Pressure (Hydrogen + Ammonia) (mm.)

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AMMONOLYSIS RATE OF LITHIUM BOROHYDRIDE AT 100°C.