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APPENDICES

Appendix A Thermodynamic Equilibrium Calculations

The reaction between water and iron produces magnetite was considered.

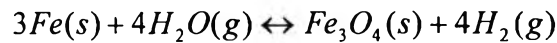


Table A.1 shows the thermodynamics properties of every species that is involved in this reaction.

Table A.1 Thermodynamics properties (Perry's Handbook)

Components	ΔG_{298}^f (kcal/mole)	ΔH_{298}^f (kcal/mole)	C_p (cal/deg/mole)
Fe ₃ O ₄ (s)	-242.3	-266.9	41.17+0.01882T-979500(T ⁻²)
H ₂ O (g)	-54.6351	-57.7979	8.22+0.00015T+1.34×10 ⁻⁶ (T ²)
H ₂ (g)	0	0	6.62+0.00081T
Fe (s)	0	0	4.13+0.00638T

Consider at room temperature, 25 °C (298 K)

$$\begin{aligned} \sum v_i \Delta G_i^f &= \Delta G_{Fe_3O_4}^f + 4\Delta G_{H_2}^f - 3\Delta G_{Fe}^f - 4\Delta G_{H_2O}^f \\ &= (-242.3) - 4(-54.6351) \\ &= -23.7596 \text{ kcal/mole} = -23759.6 \text{ cal/mole} \end{aligned}$$

$$\Delta G^0 = -RT \ln K = \sum v_i \Delta G_i^f$$

$$-(1.9859 \text{ cal/mol/K})(298 \text{ K}) \ln K = -23756.6 \text{ cal/mole}$$

$$\ln K = 40.15$$

$$K = 2.73 \times 10^{17}$$

since,

$$K = \frac{(P_{H_2})^4}{(P_{H_2O})^4}$$

$$\text{at } 25 \text{ }^\circ\text{C}, \quad \frac{(P_{H_2O})}{(P_{H_2})} = 4.38 \times 10^{-5}$$

Consider at various temperatures

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^T (C_{P(\text{Fe}_3\text{O}_4)} + 4C_{P(\text{H}_2)} - 4C_{P(\text{H}_2\text{O})} - 3C_{P(\text{Fe})}) dT$$

$$\begin{aligned} \Delta H_{298}^0 &= (-266.9) - 4(-57.7979) \\ &= -35.7084 \text{ kcal/mole} = -35708.4 \text{ cal/mol (endothermic reaction)} \end{aligned}$$

$$\begin{aligned} \Delta H_T^0 &= -35708.4 + \int_{298}^T [(41.17 + 0.01882T - 979500 \times 1/T^2) + 4(6.62 + 0.00081T) \\ &\quad - 4(8.22 + 0.00015T + 1.34 \times 10^{-6} T^2 - 3(4.13 + 0.00638T))] dT \end{aligned}$$

$$\Delta H_T^0 = -35708.4 + \int_{298}^T [22.38 + 2.32 \times 10^{-3} T - 979500 T^{-2} - 1.34 \times 10^{-6} T^2]$$

$$\Delta H_T^0 = -45755.74 + 22.38T + 1.16 \times 10^{-3} T^2 + 979500 T^{-1} - 0.447 \times 10^{-6} T^3$$

$$R \int_{298}^T d(\ln K) = \int_{298}^T \left(\frac{\Delta H_T^0}{T^2} \right) dT$$

$$R \int_{298}^T d(\ln K) =$$

$$\int_{298}^T \left(\frac{-45755.74 + 22.38T + 1.16 \times 10^{-3} T^2 + 979500 T^{-1} - 0.447 \times 10^{-6} T^3}{T^2} \right) dT$$

$$1.9859 (\ln K_T - \ln K_{298}) = -275.75 - 489750 T^{-2} + 45755.74 T^{-1} + 22.38 \ln T + 1.16 \times 10^{-3} T - 0.2235 \times 10^{-6} T^2$$

$$\begin{aligned} \ln K &= -98.71 - 246614 T^{-2} + 23040.3 T^{-1} + 11.27 \ln T + 5.84 \times 10^{-4} T \\ &\quad - 1.125 \times 10^{-7} T^2 \end{aligned}$$

The relationship between the equilibrium constant (K) and temperatures can be plotted using the equation above.

Appendix B Diffusion Coefficient by Time-Lag Method

The HEP Pressure (Pa)

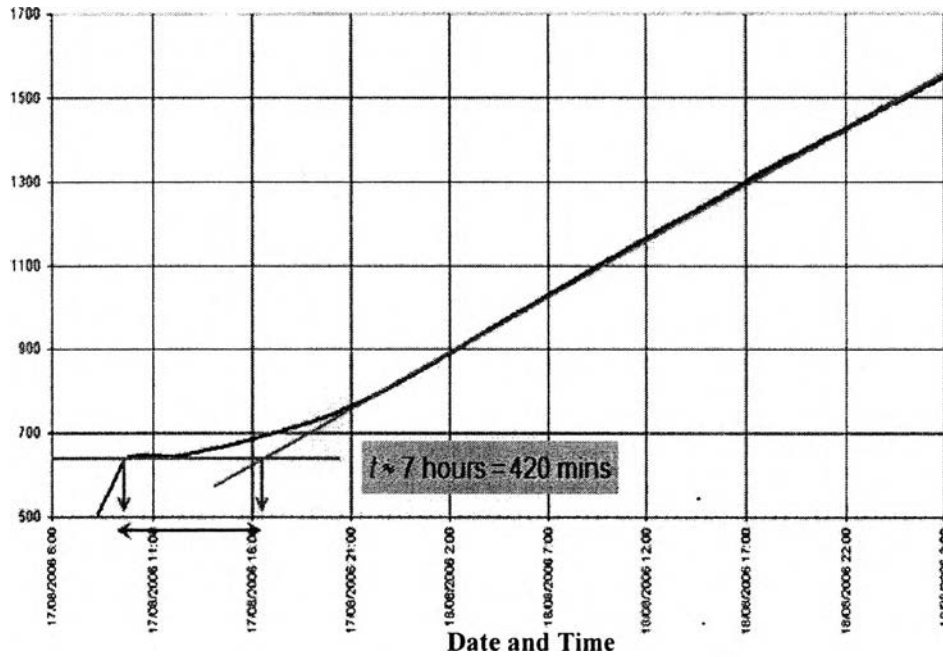


Figure B.1 The hydrogen diffusivity of the carbon steel pipe at PLGS calculated by using the Time-Lag method.

In the Time-Lag method, the diffusion coefficient can be calculated by using the Equation below,

$$L = \frac{l^2}{6D} \quad \text{or} \quad D = \frac{l^2}{6L}$$

Where L = time (s)

D = diffusion coefficient (m^2/s)

l = pipe thickness (m)

For this case, the average thickness of the pipe is 6 mm. The value of L can be read from Figure B.1. Therefore the diffusion coefficient is,

$$D = \frac{l^2}{6L} = \frac{(6 \times 10^{-3} \text{ m})^2}{6(420 \times 60 \text{ sec})} = 2.38 \times 10^{-10} \text{ m}^2/\text{s}$$

Appendix C Hydrogen Diffusion Through the Pressure Transducer Diaphragm

C.1 Using Fick's Equation

$$\text{Fick's first law: } J = D \frac{(c_1 - c_2)}{l}$$

Since the hydrogen pressure is low (i.e. 2000 Pa), it is assumed that the concentration of hydrogen at the surface of metal is equal to the concentration of hydrogen gas inside the pressure chamber for the simplicity of calculation. The ideal gas law is applied to estimation of the hydrogen concentration.

$$\frac{n}{V} = \frac{P}{RT} = \frac{(2000Pa)}{\left(8.314 \frac{Pa \cdot m^3}{mol \cdot K}\right)(45 + 273.15K)} = 0.756 \frac{mol}{m^3}$$

The hydrogen diffusivity of Inconel at 45 °C is $7.016 \times 10^{-15} \text{ m}^2/\text{s}$. Substitution into Fick's First Law gives,

$$J = D \frac{(c_1 - c_2)}{l} = 7.016 \times 10^{-15} \left(\frac{m^2}{s}\right) \times \frac{(0.756 - 0) \left(\frac{mol}{m^3}\right)}{5.08 \times 10^{-5} (m)} = 1.04 \times 10^{-10} \left(\frac{mol}{m^2 s}\right)$$

The rate of hydrogen diffusion through the diaphragm = diffusion flux (J) \times area.

$$\begin{aligned} &= \left(1.04 \times 10^{-10} \frac{mol}{m^2 s}\right) \times \left(2.2 \times 10^{-4} m^2\right) \\ &= 2.3 \times 10^{-14} \frac{mol}{s} \end{aligned}$$

The ideal gas law is used to convert the rate of hydrogen transfer to a unit of hydrogen pressure. Total volume of the HEP is 9.714 cm^3 .

$$P = \frac{nRT}{V} = \frac{\left(2.3 \times 10^{-14} \frac{mol}{s}\right) \left(8.314 \frac{Pa \cdot m^3}{mol \cdot K}\right) (45 + 273.15K)}{(9.714 \times 10^{-6} m^3)} = 6.26 \times 10^{-6} \frac{Pa}{s}$$

$$P = \left(6.26 \times 10^{-6} \frac{Pa}{s}\right) \times \left(\frac{60 \times 60 \times 24 s}{day}\right) = 0.54 \frac{Pa}{day}$$

C.2 Using the Permeability Equation

$$\text{Permeability equation: } J_{H_2} = \frac{\phi(p_{H_2(1)}^{0.5} - p_{H_2(2)}^{0.5})}{l}$$

The hydrogen permeability at 45 °C is $5.562 \times 10^{-12} \text{ cm}^3(\text{NTP})/\text{cm} \cdot \text{s} \cdot \text{atm}^{1/2}$. The hydrogen pressure is 0.0197 atm (2000 Pa) at operating temperature.

$$J_{H_2} = \frac{\left(5.562 \times 10^{-12} \frac{\text{cm}^3(\text{NTP})}{\text{cm} \cdot \text{s} \cdot \text{atm}^{1/2}} \right) (0.0197^{1/2} \text{ atm}^{1/2} - 0)}{0.00508 \text{ cm}} = 1.537 \times 10^{-10} \frac{\text{cm}^3(\text{NTP})}{\text{cm}^2 \cdot \text{s}}$$

$$= 6.39 \times 10^{-11} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

The rate of hydrogen diffusion through the diaphragm = diffusion flux (J) × area.

$$= \left(6.39 \times 10^{-11} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right) \times (2.2 \times 10^{-4} \text{ m}^2)$$

$$= 1.41 \times 10^{-14} \frac{\text{mol}}{\text{s}}$$

The ideal gas law is used to convert the rate of hydrogen transfer to a unit of hydrogen pressure. Total volume of the HEP is 9.714 cm^3 .

$$P = \frac{nRT}{V} = \frac{\left(1.41 \times 10^{-14} \frac{\text{mol}}{\text{s}} \right) \left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}} \right) (45 + 273.15 \text{ K})}{(9.714 \times 10^{-6} \text{ m}^3)} = 3.96 \times 10^{-6} \frac{\text{Pa}}{\text{s}}$$

$$P = \left(3.96 \times 10^{-6} \frac{\text{Pa}}{\text{s}} \right) \times \left(\frac{60 \times 60 \times 24 \text{ s}}{\text{day}} \right) = 0.34 \frac{\text{Pa}}{\text{day}}$$

The calculated rates of hydrogen diffusion through the diaphragm from the two equations above are in good agreement.

Appendix D Average Hydrogen Diffusion Coefficient of α -Iron

T(°C)	m ² /s	T(°C)	m ² /s	T(°C)	m ² /s	T(°C)	m ² /s	T(°C)	m ² /s	T(°C)	m ² /s	T(°C)	m ² /s
1	3.85E-09	51	6.37E-09	101	9.24E-09	151	1.23E-08	201	1.55E-08	251	1.87E-08	301	2.18E-08
2	3.90E-09	52	6.42E-09	102	9.30E-09	152	1.24E-08	202	1.55E-08	252	1.87E-08	302	2.18E-08
3	3.95E-09	53	6.48E-09	103	9.36E-09	153	1.24E-08	203	1.56E-08	253	1.88E-08	303	2.19E-08
4	3.99E-09	54	6.53E-09	104	9.42E-09	154	1.25E-08	204	1.57E-08	254	1.88E-08	304	2.20E-08
5	4.04E-09	55	6.59E-09	105	9.48E-09	155	1.26E-08	205	1.57E-08	255	1.89E-08	305	2.20E-08
6	4.08E-09	56	6.64E-09	106	9.54E-09	156	1.26E-08	206	1.58E-08	256	1.90E-08	306	2.21E-08
7	4.13E-09	57	6.70E-09	107	9.60E-09	157	1.27E-08	207	1.59E-08	257	1.90E-08	307	2.22E-08
8	4.18E-09	58	6.75E-09	108	9.66E-09	158	1.28E-08	208	1.59E-08	258	1.91E-08	308	2.22E-08
9	4.22E-09	59	6.81E-09	109	9.72E-09	159	1.28E-08	209	1.60E-08	259	1.92E-08	309	2.23E-08
10	4.27E-09	60	6.86E-09	110	9.78E-09	160	1.29E-08	210	1.61E-08	260	1.92E-08	310	2.23E-08
11	4.32E-09	61	6.92E-09	111	9.84E-09	161	1.29E-08	211	1.61E-08	261	1.93E-08	311	2.24E-08
12	4.37E-09	62	6.97E-09	112	9.90E-09	162	1.30E-08	212	1.62E-08	262	1.93E-08	312	2.25E-08
13	4.41E-09	63	7.03E-09	113	9.96E-09	163	1.31E-08	213	1.62E-08	263	1.94E-08	313	2.25E-08
14	4.46E-09	64	7.09E-09	114	1.00E-08	164	1.31E-08	214	1.63E-08	264	1.95E-08	314	2.26E-08
15	4.51E-09	65	7.14E-09	115	1.01E-08	165	1.32E-08	215	1.64E-08	265	1.95E-08	315	2.26E-08
16	4.56E-09	66	7.20E-09	116	1.01E-08	166	1.33E-08	216	1.64E-08	266	1.96E-08	316	2.27E-08
17	4.61E-09	67	7.25E-09	117	1.02E-08	167	1.33E-08	217	1.65E-08	267	1.97E-08	317	2.28E-08
18	4.66E-09	68	7.31E-09	118	1.03E-08	168	1.34E-08	218	1.66E-08	268	1.97E-08	318	2.28E-08
19	4.71E-09	69	7.37E-09	119	1.03E-08	169	1.34E-08	219	1.66E-08	269	1.98E-08	319	2.29E-08
20	4.75E-09	70	7.42E-09	120	1.04E-08	170	1.35E-08	220	1.67E-08	270	1.99E-08	320	2.29E-08
21	4.80E-09	71	7.48E-09	121	1.05E-08	171	1.36E-08	221	1.68E-08	271	1.99E-08	321	2.30E-08
22	4.85E-09	72	7.54E-09	122	1.05E-08	172	1.36E-08	222	1.68E-08	272	2.00E-08	322	2.31E-08
23	4.90E-09	73	7.60E-09	123	1.06E-08	173	1.37E-08	223	1.69E-08	273	2.00E-08	323	2.31E-08
24	4.95E-09	74	7.65E-09	124	1.06E-08	174	1.38E-08	224	1.69E-08	274	2.01E-08	324	2.32E-08
25	5.00E-09	75	7.71E-09	125	1.07E-08	175	1.38E-08	225	1.70E-08	275	2.02E-08	325	2.33E-08
26	5.05E-09	76	7.77E-09	126	1.08E-08	176	1.39E-08	226	1.71E-08	276	2.02E-08	326	2.33E-08
27	5.10E-09	77	7.83E-09	127	1.08E-08	177	1.40E-08	227	1.71E-08	277	2.03E-08	327	2.34E-08
28	5.16E-09	78	7.88E-09	128	1.09E-08	178	1.40E-08	228	1.72E-08	278	2.04E-08	328	2.34E-08
29	5.21E-09	79	7.94E-09	129	1.09E-08	179	1.41E-08	229	1.73E-08	279	2.04E-08	329	2.35E-08
30	5.26E-09	80	8.00E-09	130	1.10E-08	180	1.41E-08	230	1.73E-08	280	2.05E-08	330	2.36E-08
31	5.31E-09	81	8.06E-09	131	1.11E-08	181	1.42E-08	231	1.74E-08	281	2.05E-08	331	2.36E-08
32	5.36E-09	82	8.12E-09	132	1.11E-08	182	1.43E-08	232	1.75E-08	282	2.06E-08	332	2.37E-08
33	5.41E-09	83	8.17E-09	133	1.12E-08	183	1.43E-08	233	1.75E-08	283	2.07E-08	333	2.37E-08
34	5.46E-09	84	8.23E-09	134	1.13E-08	184	1.44E-08	234	1.76E-08	284	2.07E-08	334	2.38E-08
35	5.51E-09	85	8.29E-09	135	1.13E-08	185	1.45E-08	235	1.76E-08	285	2.08E-08	335	2.39E-08
36	5.57E-09	86	8.35E-09	136	1.14E-08	186	1.45E-08	236	1.77E-08	286	2.09E-08	336	2.39E-08
37	5.62E-09	87	8.41E-09	137	1.14E-08	187	1.46E-08	237	1.78E-08	287	2.09E-08	337	2.40E-08
38	5.67E-09	88	8.47E-09	138	1.15E-08	188	1.47E-08	238	1.78E-08	288	2.10E-08	338	2.40E-08
39	5.72E-09	89	8.53E-09	139	1.16E-08	189	1.47E-08	239	1.79E-08	289	2.10E-08	339	2.41E-08
40	5.78E-09	90	8.58E-09	140	1.16E-08	190	1.48E-08	240	1.80E-08	290	2.11E-08	340	2.42E-08
41	5.83E-09	91	8.64E-09	141	1.17E-08	191	1.48E-08	241	1.80E-08	291	2.12E-08	341	2.42E-08
42	5.88E-09	92	8.70E-09	142	1.18E-08	192	1.49E-08	242	1.81E-08	292	2.12E-08	342	2.43E-08
43	5.94E-09	93	8.76E-09	143	1.18E-08	193	1.50E-08	243	1.81E-08	293	2.13E-08	343	2.43E-08
44	5.99E-09	94	8.82E-09	144	1.19E-08	194	1.50E-08	244	1.82E-08	294	2.13E-08	344	2.44E-08
45	6.04E-09	95	8.88E-09	145	1.19E-08	195	1.51E-08	245	1.83E-08	295	2.14E-08	345	2.45E-08
46	6.10E-09	96	8.94E-09	146	1.20E-08	196	1.52E-08	246	1.83E-08	296	2.15E-08	346	2.45E-08
47	6.15E-09	97	9.00E-09	147	1.21E-08	197	1.52E-08	247	1.84E-08	297	2.15E-08	347	2.46E-08
48	6.20E-09	98	9.06E-09	148	1.21E-08	198	1.53E-08	248	1.85E-08	298	2.16E-08	348	2.46E-08
49	6.26E-09	99	9.12E-09	149	1.22E-08	199	1.54E-08	249	1.85E-08	299	2.17E-08	349	2.47E-08
50	6.31E-09	100	9.18E-09	150	1.23E-08	200	1.54E-08	250	1.86E-08	300	2.17E-08	350	2.48E-08

Appendix E Solubility of Oxygen in the Solution

Henry's Law Constant vs temperatures can be calculated from the equation below (Fernández-Prini *et. al*, 2003 and Watanabe *et. al*, 2004),

$$\ln\left(\frac{k_H}{p_1^*}\right) = \frac{-9.448}{T_R} + \frac{(4.438) \cdot \tau^{0.355}}{T_R} + 11.420(T_R)^{-0.41} \exp(\tau) \quad (\text{E.1})$$

where $\tau = 1 - T_R$, $T_R = T/T_{Cl}$, T_{Cl} is the critical temperature of the solvent which is 647.096 K for H₂O, and p_1^* is the vapor pressure of the solvent at the temperature of interest.

The temperature of the solution reservoir is 20 °C or 293.15 K. The vapor pressure of water at this temperature is 2340 Pa.

$$T_R = \frac{293.15K}{647.096K} = 0.453K$$

$$\tau = 1 - 0.453K = 0.547K$$

Substituting p_1^* , T_R and τ in the equation (E.1),

$$\ln\left(\frac{K_{O_2}}{2334Pa}\right) = \frac{-9.448}{0.453} + \frac{(4.438) \cdot 0.547^{0.355}}{0.453} + 11.420(0.453)^{-0.41} \exp(0.547)$$

Thus, $K_{O_2(20^\circ C)} = 3957 \text{ MPa}$

Henry's Law is given by

$$p_{O_2} = y_{O_2} \Pi = K_{O_2} \cdot x_{O_2} \quad (\text{E.2})$$

where p_{O_2} is the partial pressure of oxygen, y_{O_2} is mole fraction of oxygen in the gas phase, Π is total pressure of the system which is atmospheric pressure, x_{O_2} is the mole fraction of oxygen in oxygen-saturated water, and K_{O_2} is the Henry's Law Constant for oxygen in water.

The argon from the cylinder contains less than 2 ppm of oxygen. Thus mole fraction of oxygen equal to 2 ppm was used in this calculation.

$$p_{O_2} = (2 \times 10^{-6})(101325Pa) = (3957 \times 10^6 Pa)x_{O_2}$$

$$x_{O_2} = 5.1 \times 10^{-11}$$

Mole fraction of dissolved oxygen in the solution could be as high as 51 pmol O₂/mol solution. The concentration of oxygen can be calculated as follows (the density of water at 20°C is 0.998 g/cm³).

$$\frac{\text{Concentration(ppb)}}{10^9} = \frac{\text{Amount of solute}}{\text{Amount of solvent}}$$

$$\text{Concentration(ppb)} = \left(\frac{5.1 \times 10^{-11} \text{ mol O}_2}{1 \text{ mol H}_2\text{O}} \right) \left(\frac{32 \text{ g O}_2}{1 \text{ mol O}_2} \right) \left(\frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \right) \left(\frac{0.998 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \right) \times 10^9$$

$$\text{Oxygen concentration} = 0.09 \text{ ppb}$$

In this experiment, the solution flow rate is 840 mL/min. Thus the amount of dissolved oxygen flowing in the solution is 2.37×10^{-9} mol/min or 3.94×10^{-11} mol/s.

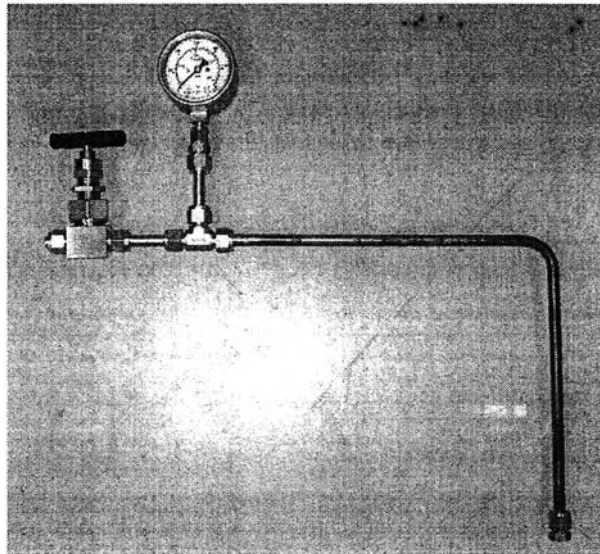
Appendix F Hydrogen Permeation

A carbon steel tube, ASTM A179, was used in this experiment to determine hydrogen permeation through steel. The tube had a 90° bend and was capped at one end by a Swagelok fitting. Another end of the tube was connected to a pressure gauge and a valve as shown in Figure F.1. The composition of carbon steel, ASTM A179, and carbon steel, ASME SA106 Grade B, that was used in the experiment in Loop 1 is shown in Table F.1.

The carbon steel, ASTM A179, was cleaned before being used in order to eliminate the oxide film that formed on the steel surface both inside and outside. First, the tube was polished by 600 grids sandpaper on the outside surface. Chemical cleaning or pickling was done on the inside surface. After cleaning and bending, the tube was annealed at 600 °C for 1 hour to release the stress from the bending. The tube was pickling again after annealing. Then all fittings were assembled on the tube.

Table F.1 Composition of carbon steel ASME SA106 and ASTM A179

Element	ASME SA106 Grade B	ASTM A179
	Mass fraction (%)	Mass fraction (%)
Fe	Balance	Balance
C	0.30	0.06-0.18
Mn	0.29	0.27-0.63
Si	0.10	-
P	0.04	0.048
S	0.04	0.058
Cr	0.03	-

**Figure F.2** Carbon steel tube used in the hydrogen permeation experiment.

The tube was checked for leakage by charging with 100 psig of argon gas and monitoring the reduction in pressure at room temperature. After testing for leakage, the tube was filled with 100 psig of hydrogen gas, and placed in an oven. The temperature of the oven was gradually increased from room temperature to 310 °C. The change in pressure inside the tube was recorded for 5 days. Next the tube was

filled with 90 psig helium gas. The same procedure was carried out in order to compare the results from the two different gases.

Table F.2 The change of pressure inside the tube

Hydrogen				Helium			
Date	Time	Temperature (°C)	Pressure (psig)	Date	Time	Temperature (°C)	Pressure (psig)
3/4/2008	9.17	100	100	8/4/2008	11.30	100	90
	10.47	100	100		12.30	100	90
	10.47	200	110		13.00	200	100
	11.47	200	120		14.00	200	110
	12.47	310	140		15.30	310	120
	13.47	310	140		16.30	310	120
	14.47	310	140		17.00	310	120
	15.47	310	140		17.30	310	120
	16.47	310	140		18.00	310	120
	17.47	310	140		18.30	310	120
4/4/2008	9.10	310	130	9/4/2008	10.00	310	120
7/4/2008	10.00	310	120	10/4/2008	15.00	310	120
	17.30	310	120		16.00	310	120

The results show that the pressure inside the tube decreased with time when the tube was filled with hydrogen. The pressure inside the tube was constant when filled with helium.

It is believed that the hydrogen gas diffused through the steel which proves that hydrogen can dissociate and diffuse out of the carbon steel at 310 °C under a pressure of 100 psig. The rate of the pressure reduction was low and presumably was controlled by the surface reaction or dissociation of hydrogen at the inside tube surface.

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