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TMED-4 Interim Report Pure Zr Equilibrium Test Results
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Summary

A series of experiments were conducted to determine equilibrium pressures and isotherm data for the zirconium – protium and zirconium – deuterium systems. The data match the published literature data reasonably well with the plateau extending to loadings of about 1.4. There is a significant pressure rise for loadings greater than 1.7.

Background

Due to higher than expected permeation rates in the production of tritium in the TVA, a development and testing program was implemented to develop the understanding of why the higher rates were occurring. In addition, improved data are needed for both the design as well as the predictive models. One part of the program was to determine the equilibrium pressure of hydrogen and tritium over NPZ (1). During the course of this testing, some curious results were discovered (2) compared to the published literature data (3). Due to these apparently results, a follow-on task was undertaken to determine the equilibrium pressure of protium and deuterium over pure zirconium.

Experimental

The experiments reported here were performed on a stainless steel manifold test station equipped with an Alcatel Drytel 31 vacuum pump as well as a series of calibrated volumes. Instrumentation on the system included a MKS 0-10K torr Baratron and a MKS 100 mtorr Baratron. Several thermocouples were attached via stainless steel shim stock which was spot welded to the sample vessel at various points along the vessel to monitor the temperature gradient. Since this work is considered to be a scoping study the use of calibrated M&TE was not required, however the Baratrons, the associated readouts, and the thermocouples (Type K) were all M&TE with current calibrations. Two dual element thermocouples were welded to the bottom of the sample vessel. The sample and vessel preparations were consistent with that used previously (4).

In summary, strips of zirconium foil weighing a total of one gram were mechanically abraded using P1200 grit grinding paper on the flat surfaces of the sample. The strips were mechanically abraded to remove any potential surface oxide layer that may have been present on the zirconium strips. Previous efforts showed that this oxide would inhibit the hydriding of the sample. The samples were cleaned, loaded into the vessel, and evacuated. A room temperature rate of rise was conducted prior to incrementally heating to the loading temperature. The samples were incrementally loaded starting at Q/M of 0.2 by 0.3 increments to 2.0. After loading, the sample temperature was reduced to room temperature. Desorption data were collected by reheating from 370°C to 550°C in 30°C increments and absorption data were collected by cooling using the same increments. Equilibrium data were recorded at each temperature when the pressure changed by less than 0.5 mtorr. All of the testing was conducted using detailed R&D Directions (5).

Results

The absorption and desorption equilibrium pressure data for protium from 370 to 550°C are listed in Table 1 and are graphically presented in Figures 1 and 2. These data are linear above about 430°C based on the van't Hoff plots shown in the figures. The data for T > 430°C were modeled using an exponential equation of the form

$$P = A_o e^{M/T}$$

Where M = -Q/R and A_o = a pre-exponential constant.

The curve fit data are presented in Table 2 for the protium equilibrium data. The higher temperature data (T > 430°C) were used for these curve fits. The fit, as indicated by the "R" ratio, is very good for the higher temperature data. In addition, the slope or activation energy is nominally 45,000 cal/mol/K, for both adsorption and desorption when the 0.2 and 0.5 Q/M desorption data and both the absorption and desorption at Q/M of 2.0 are discarded. The Q/M 2.0 can legitimately be deleted from the average analysis since the physics of the process changes once the plateau pressure is exceeded. The low desorption pressures were not included since they appear to be from a different population. The slope and energy data of the selected sets are consistent with the Zr-4 data generated previously.

An isotherm type plot was generated from both the absorption and desorption protium data. The plateau for protium and pure Zr extends to H/Zr of 1.4 before increasing rapidly. The data at a loading of Q/M 2 was between 100 to 1000 times that of 1.7 which was only about four times that at 1.4.

Table 1. Protium equilibrium pressure data.

Nominal Temp (C)	0.2 H/M	0.5 H/M	0.8 H/M	1.1 H/M	1.4 H/M	1.7 H/M	2.0 H/M
							Desorption Data (mTorr)
370	0.04	0.00	0.00	0.01	0.00	0.08	242.75
400	0.18	0.00	0.04	0.08	0.04	0.31	1126.00
430	0.73	0.13	0.25	0.38	0.26	1.37	3289.00
460	2.50	0.33	0.88	1.42	2.07	5.37	7377.00
490	3.23	0.81	2.89	4.89	7.54	20.01	13358.00
520	9.01	2.31	8.57	15.19	24.10	70.51	21560.00
550		6.33	23.05	43.75	63.29	231.67	31170.00
							Absorption Data (mTorr)
550	8.58	6.33	23.05	43.75	63.29	231.67	31170.00
520	2.83	2.22	7.50	14.48	21.79	70.50	21539.00
490	0.96	0.74	2.38	4.53	6.88	20.70	13838.00
460	0.29	0.23	0.70	1.35	2.09	5.79	7797.00
430	0.03	0.04	0.20	0.35	0.56	1.54	3512.00
400	0.03	0.02	0.06	0.07	0.13	0.37	1249.00
370	0.00		0.00	0.00	0.00	0.07	357.06

Table 2. Protium absorption and desorption curve fit data.

Absorption				
Q/M	Ao	M (K^{-1})	Q (cal/mol/K)	R
0.2	4.15E+12	-22040	43639	0.9998
0.5	2.94E+12	-21920	43402	0.9996
0.8	2.49E+13	-22700	44946	0.9995
1.1	7.34E+13	-23040	45619	0.9999
1.4	2.30E+14	-24030	47579	0.9991
1.7	5.73E+14	-23570	46669	0.9994
2	3.20E+11	-13080	25898	0.9779
Desorption				
Q/M	Ao	M (K^{-1})	Q (cal/mol/K)	R
0.2	9.05E+08	-14510	28730	0.9514
0.5	4.84E+10	-18650	36927	0.9945
0.8	6.98E+12	-21640	42847	0.9977
1.1	5.48E+13	-22790	45124	1.0000
1.4	1.57E+14	-23660	46847	0.9998
1.7	1.95E+15	-24540	48589	0.9996
2	8.85E+11	-13880	27482	0.9705

The deuterium zirconium equilibrium pressure data are presented in Table 3 and Figures 5 and 6 for both adsorption and desorption, respectively. The data were curve fit using the best four to five data points. The results of the curve fit are listed in Table 4. The data appear to be linear on the van't Hoff plots for data at temperatures greater than 430°C. The isotherm data are presented in Figures 7 and 8.

Table 3. Absorption and desorption data for deuterium and pure Zr.

	0.2 D/M	0.5 D/M	0.8 D/M	1.1 D/M	1.4 D/M	1.7 D/M	2.0 D/M
Desoprtion							
370	0.01	0.05	0.06	0.07	0.04	0.70	441.3
400	0.08	0.12	0.12	0.14	0.12	3.06	1913.0
430	0.33	0.43	0.37	0.47	0.44	12.79	5093.0
460	1.24	1.42	1.19	1.75	1.62	51.37	10855.0
490	3.60	4.50	3.95	5.80	5.61	194.78	19208.0
520	10.01	13.33	12.90	18.39	18.60	615.54	29762.0
550	27.03	37.91	37.16	53.24	59.92	1891.00	42637.0
Absorption							
550	29.38	37.91	37.16	53.24	59.92	1891.00	42637.0
520	11.27	13.15	12.90	17.31	18.50	611.02	29500.0
490	4.07	4.46	4.21	5.58	5.59	192.35	18903.0
460	1.48	1.43	1.31	1.70	1.76	53.77	10685.0
430	0.51	0.42	0.41	0.48	0.47	13.49	4938.0
400	0.16	0.14	0.13	0.14	0.12	3.43	1733.0
370	0.06	0.04	0.04	0.06	0.04	0.88	360.6

Table 4. Curve fit data from van't Hoff Plots deuterium over zirconium

Absorption				
Q/M	Ao	M (K^{-1})	Q (cal/mol/K)	R
0.2	6.76E+14	-25480	50450	0.9797
0.5	1.57E+16	-27880	55202	0.9801
0.8	1.65E+13	-22200	43956	0.9977
1.1	3.64E+13	-22638	44823	0.9977
1.4	9.47E+13	-23340	46213	0.9992
1.7	8.23E+13	-24270	48055	0.9998
2	8.53E+11	-13710	27146	0.9659
Desorption				
Q/M	Ao	M (K^{-1})	Q (cal/mol/K)	R
0.2	1.87E+12	-20670	40927	0.9995
0.5	2.05E+15	-26130	51737	0.9806
0.8	2.13E+13	-22420	44392	0.9988
1.1	1.52E+13	-21900	43362	0.9912
1.4	1.42E+14	-23670	46867	0.9993
1.7	6.88E+15	-24102	47722	0.9999
2	9.09E+09	-10150	20097	0.9903

Conclusions

The pure zirconium and hydrogen isotope data are consistent with the literature data and show the plateau extending to about 1.4 prior to significant increases in pressure.

The activation energy for both deuterium and protium desorption and absorption is nominally 45 Kcal/mol/K.

References

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4. SRNL-L2100-2008-00003, Results of the Zircaloy-4 Pressure Scoping Tests with Protium, G.A. Morgan and P.S. Korinko, Sept. 2008.
5. SRNL-L2100-2010-00029, Desorption and Absorption of Hydrogen Isotopes on NPZ – Method B, P :Korinko & G. Morgan

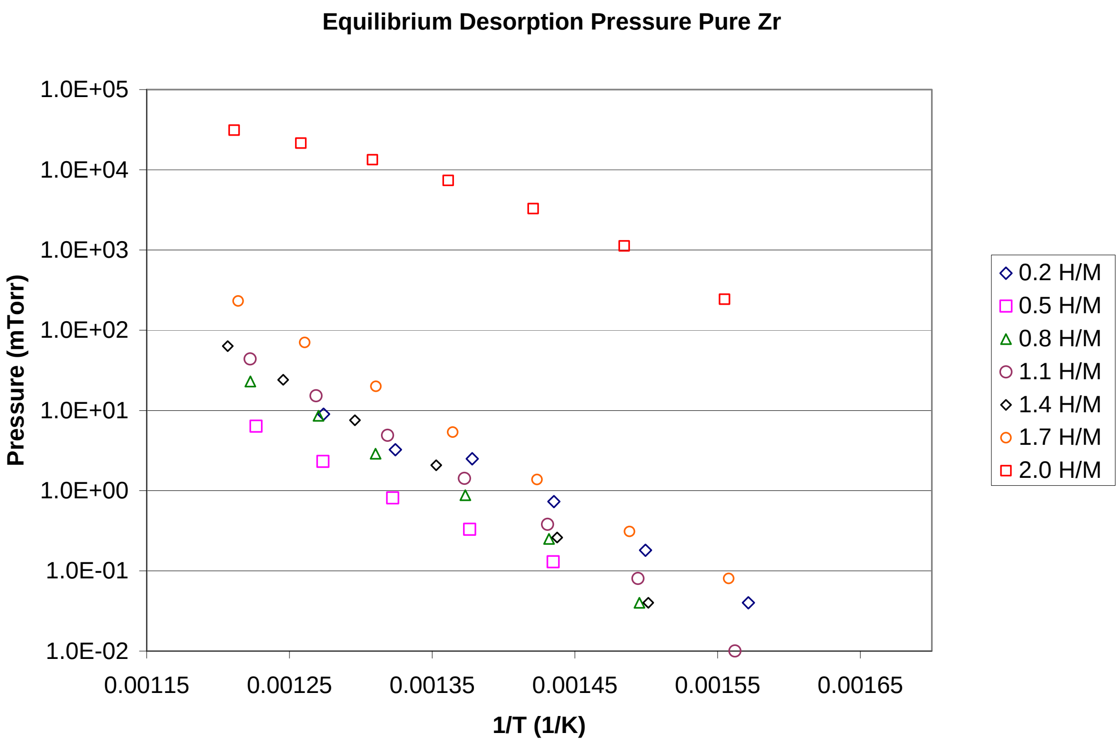

Figure 1. Desorption protium equilibrium pressures for zirconium.

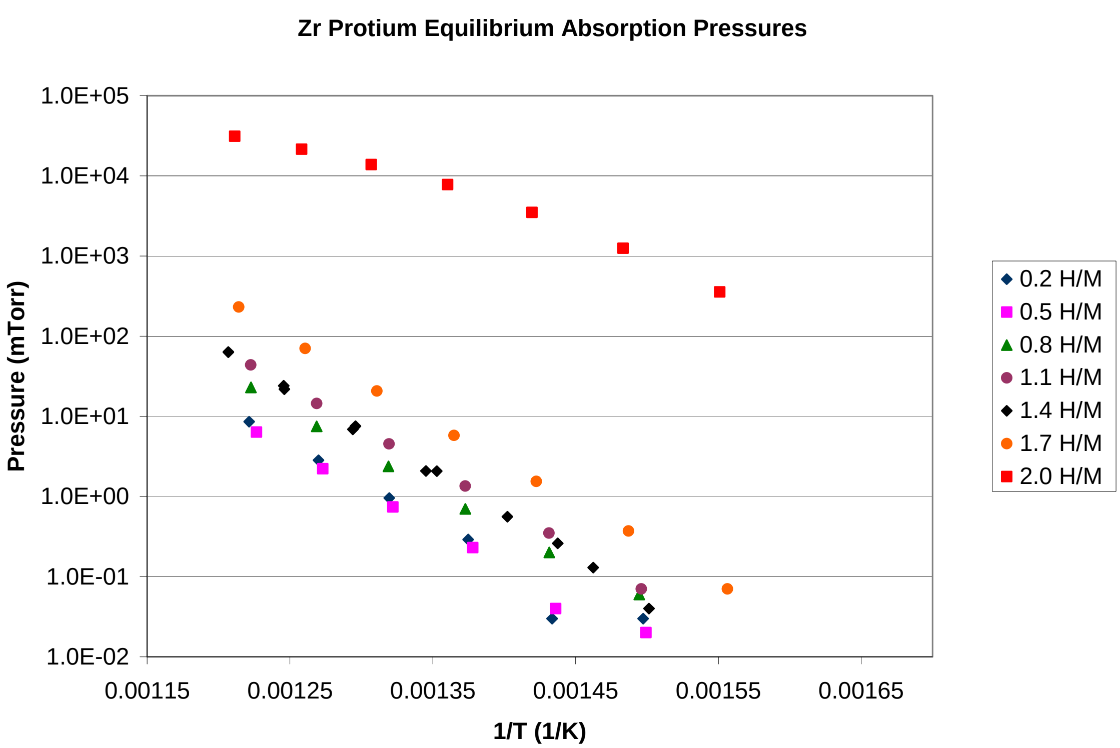

Figure 2. Absorption protium equilibrium pressures for zirconium.

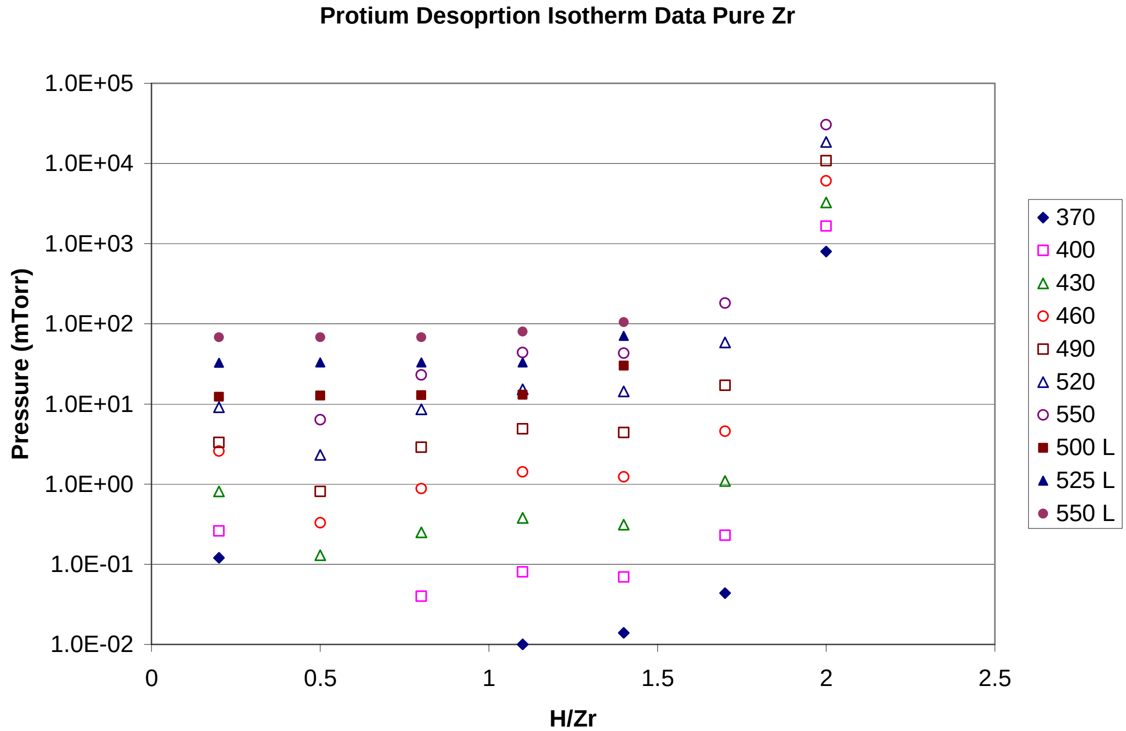

Figure 3. Desorption Isotherm for zirconium (solid points are from Ref.3)

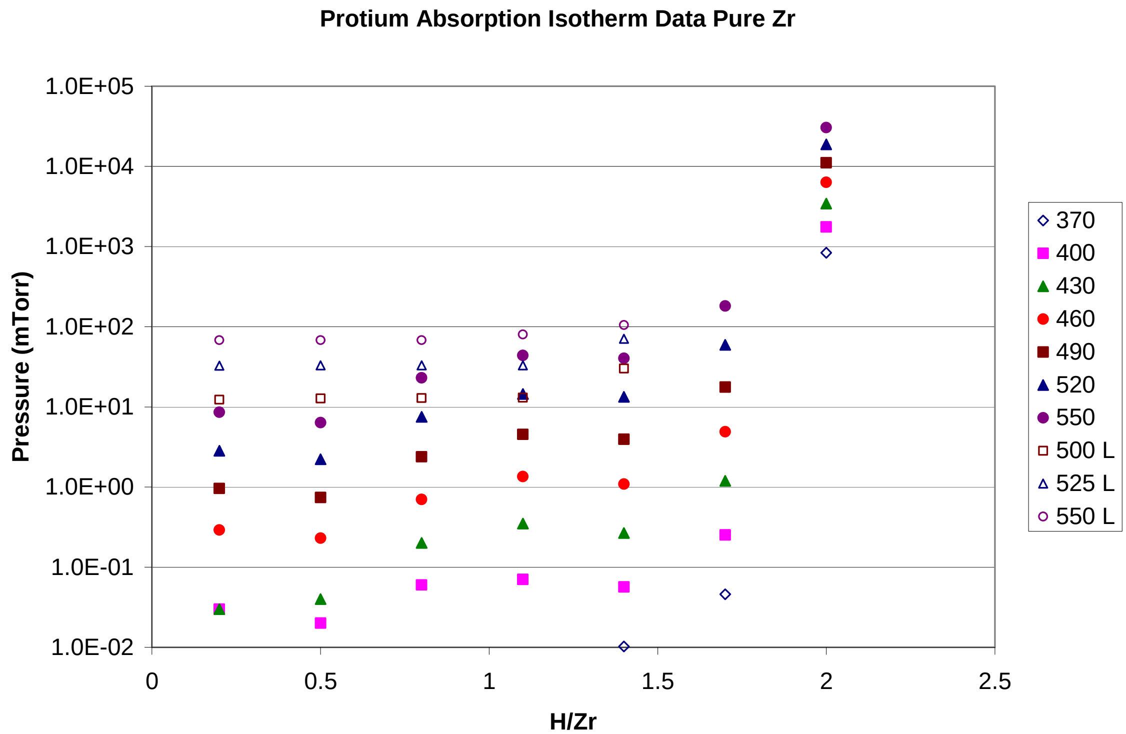

Figure 4. Protium absorption isotherm for zirconium (hollow points are from Ref.3)

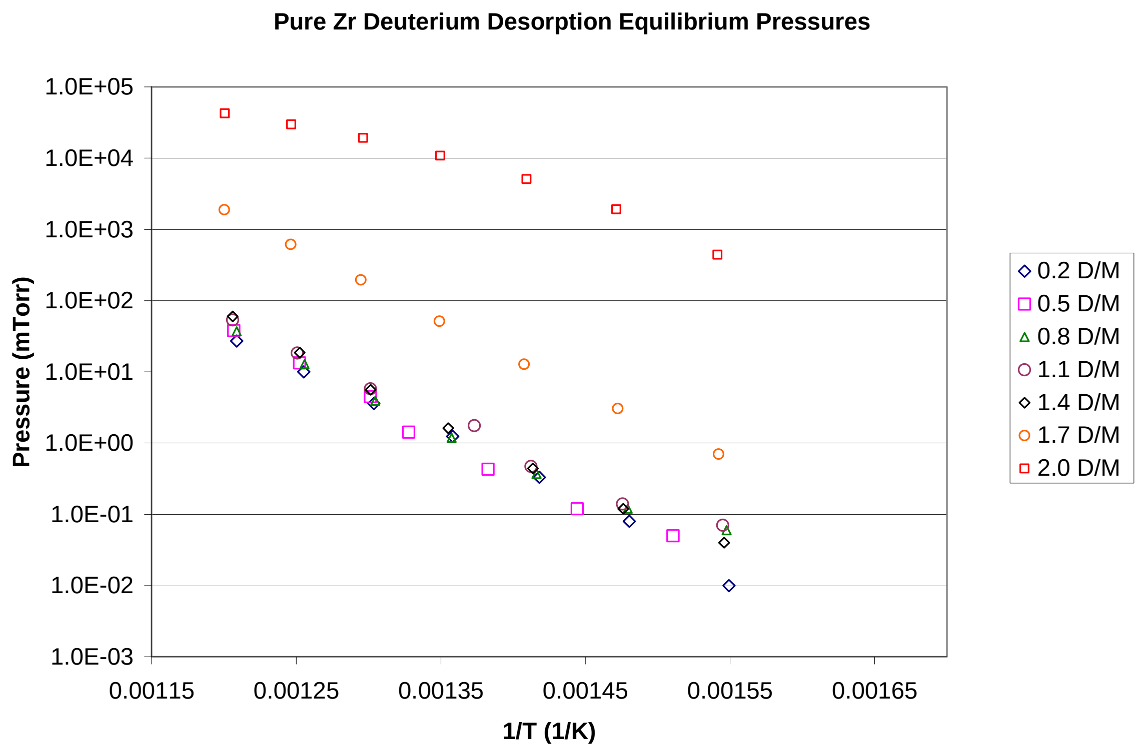

Figure 5. Deuterium desorption equilibrium data for pure Zr.

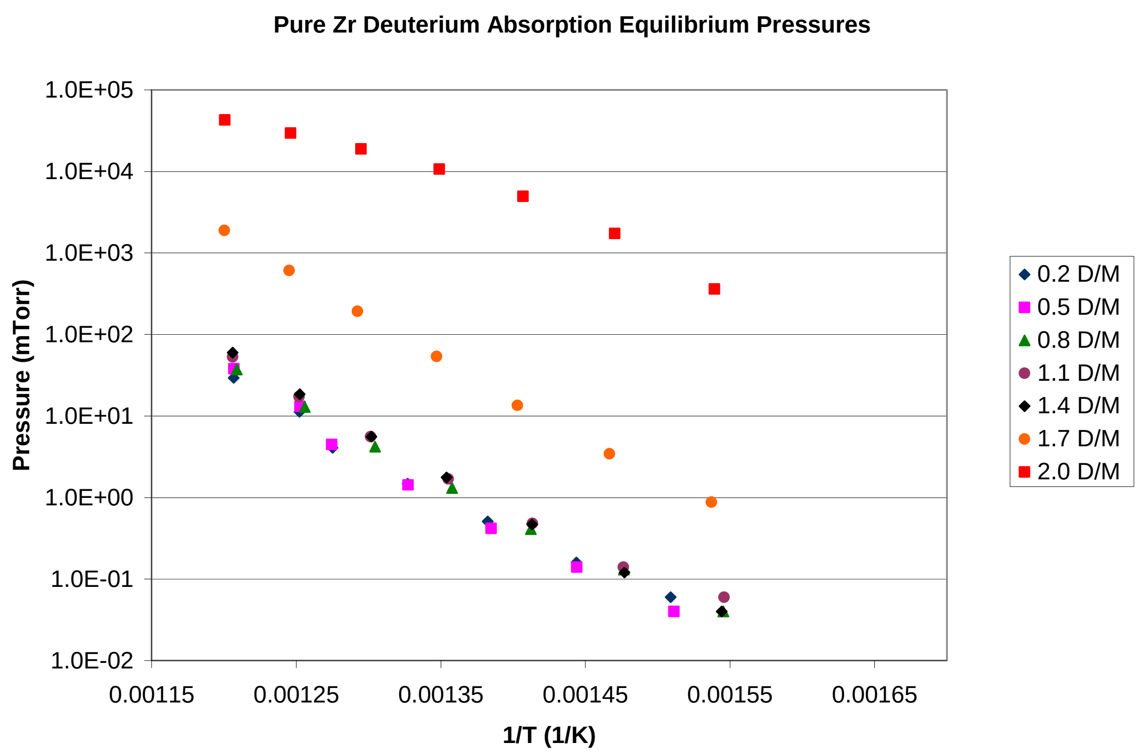

Figure 6. Deuterium absorption equilibrium data for pure Zr

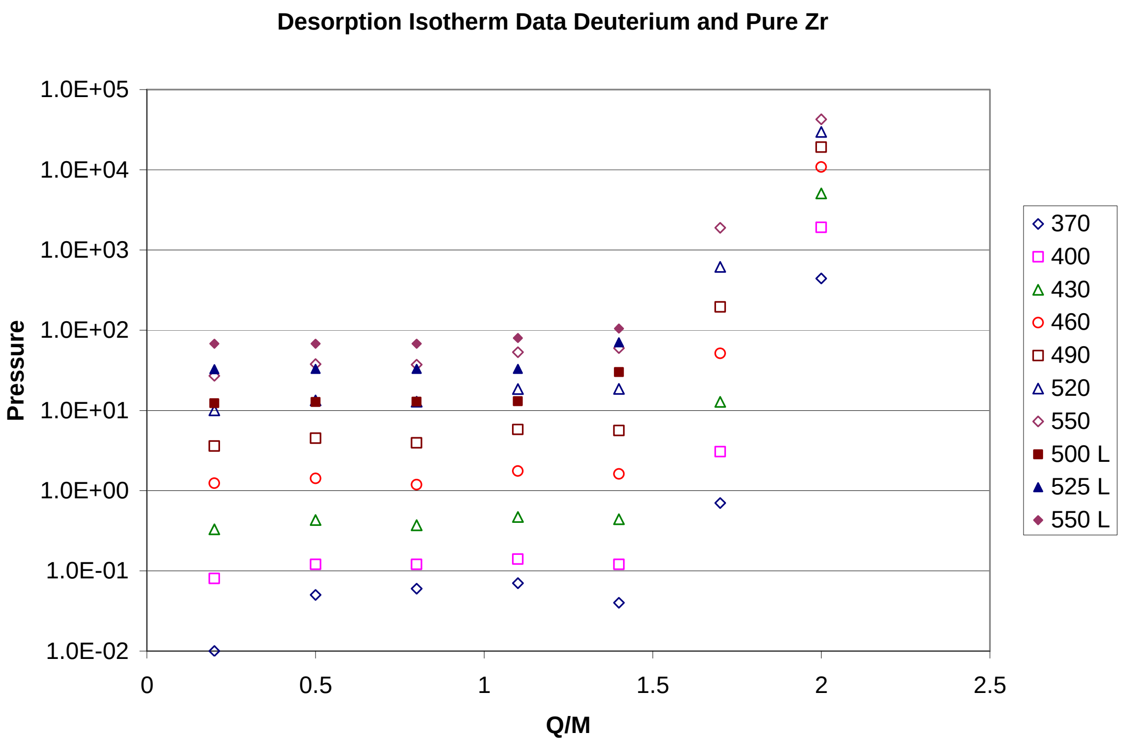

Figure 7. Desorption isotherm for deuterium and zirconium (solid points are from Ref.3)

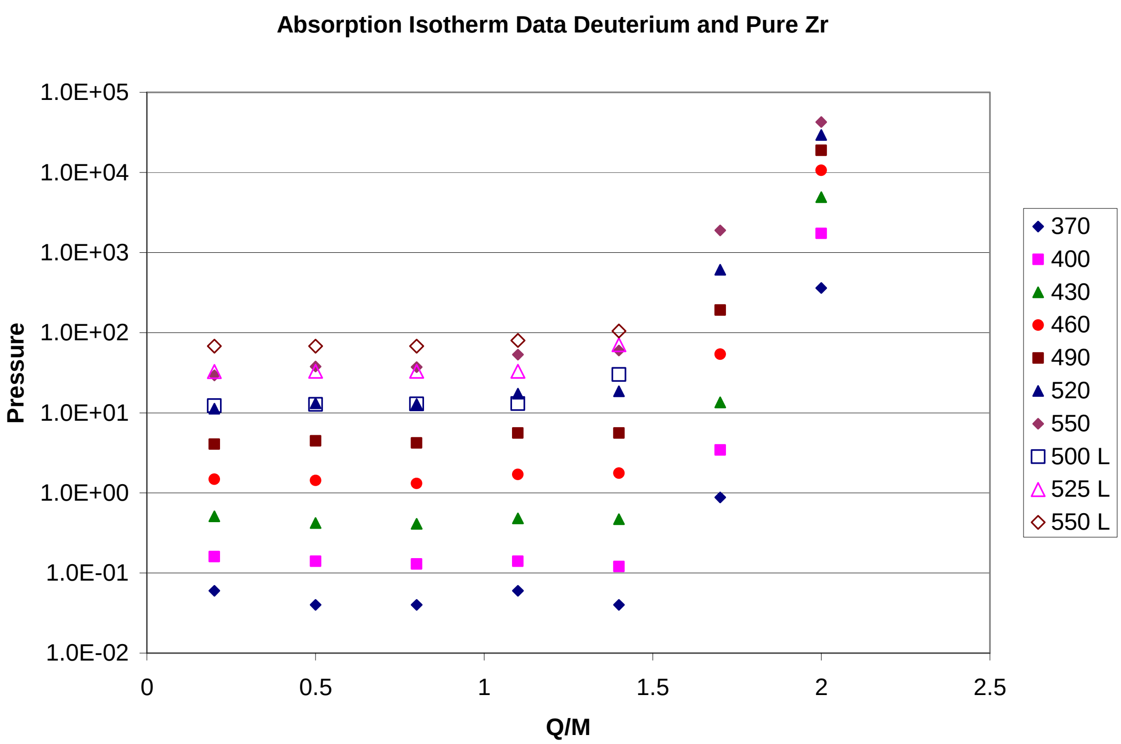

Figure 8. Absorption Isotherm for deuterium and zirconium (hollow points are from Ref.3)