

Search for Anomalous Effects Involving Excess Power and Helium during D₂O Electrolysis Using Palladium Cathodes

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ABSTRACT

Eight electrolysis gas samples collected during episodes of excess power production in two identical cells showed the presence of ⁴He. Six control samples gave no evidence for helium. Various studies of helium diffusion into our Pyrex glass sample flasks established a minimum helium detection limit of 3×10^{13} ⁴He/500 mL (3 ppb) for our experiments. This places our rate of ⁴He production at 10^{11} - 10^{12} ⁴He/s•W which is the correct magnitude for typical fusion reactions that yield helium as a product. Simultaneous evidence for excess power, helium production, and anomalous radiation was present in these experiments. Progress relating to helium measurements have been hindered by difficulties in obtaining large excess power effects.

1. Introduction

The low intensity of neutrons in cold fusion experiments has prompted proposals of nuclear processes that yield only heat and helium as products. We report here the results of electrochemical calorimetric experiments designed to detect helium in the effluent gases while rigorously excluding possible helium contamination from other sources. However, the diffusion of atmospheric helium into our Pyrex glass flasks during the time period between sample collection and analyses (22-61 days) could be significant. We have therefore investigated the atmospheric helium diffusion rate for our flasks when filled with either nitrogen, hydrogen, or deuterium-oxygen electrolysis gases. These studies yield revised helium detection limits that place our rate of ⁴He production in the range of 10^{11} - 10^{12} atoms/s per watt of excess power.

2. Methods

The eight round-bottom Schlenk flasks (500 mL Pyrex) used for the collection of electrolysis gas samples were vacuum leak tested prior to use. All

glass joints were carefully lapped for a concentric fit and lubricated with silicon grease (Dow Corning, High Vacuum). The average glass wall thickness determined volumetrically was $d = 1.8$ mm. The electrolysis gas samples collected at China Lake were sent to the University of Texas for analysis by mass spectrometry. Details of the electrochemical experiments and helium analyses are reported elsewhere by B. F. Bush et. al. and by M. H. Miles et. al. Two commercial laboratories (Helium Field Operations, Department of the Interior, Amarillo, Texas, and Rockwell International, Canoga Park, California) were used for studies of the rate of atmospheric helium diffusion into these flasks.

The detection of anomalous radiation involved the use of a thin end window Geiger-Mueller (GM) alpha-beta-gamma detector (Ludlum, Model 44-7) positioned about 20 cm from the tops of the electrochemical cells and connected to a scalar rate meter (Ludlum, Model 2200 and printer (Casio HR-8A). Dental X-ray film (Kodak Ultra-Speed, DF-58) placed near the outside surface of the electrochemical cell was also used for the detection of any radiation. There was no direct contact of the film with the electrolysis gases (D_2 , O_2) which exited the system through an oil bubbler about 1 meter from the cell.

3. Results

Table 1 presents results from two different laboratories relating to atmospheric helium diffusion into three of our flasks when filled with nitrogen. These measurements yield a mean diffusion rate of $3.2 \pm 0.6 \times 10^{12}$ atoms/day that is in good agreement with the theoretical value as defined by S. Dushman

$$q = \frac{K \cdot P}{d} = 2.6 \times 10^{12} \text{ atoms/day} \quad (1)$$

for Pyrex flasks with $A = 314 \text{ cm}^2$ and $d = 1.8$ mm. This experimental agreement indicates that these three flasks were quite uniform. Measurements by the two laboratories were done several months after our helium measurements were completed, hence any effects due to deuterium or hydrogen saturation of the glass would have likely dissipated.

Table 1. Experimental Helium Diffusion Rates in Nitrogen-Filled Flasks (500 mL Pyrex, $A = 314 \text{ cm}^2$, $d = 1.8$ mm).

Time (days)	Measured ^4He (atoms)	Diffusion rate (atoms/day)
14 ^a	47×10^{12}	3.4×10^{12}
44.6 ^b	167×10^{12}	3.7×10^{12}
65 ^a	170×10^{12}	2.6×10^{12}

^a Helium Field Operations, Amarillo, Texas.

^b Rockwell International, Canoga Park, California.

Measurements of atmospheric helium diffusion into our flasks when filled with hydrogen or deuterium-oxygen electrolysis gases are shown in Figures 1 and 2. These four flasks yield a mean helium diffusion rate of $1.9 \pm 0.3 \times 10^{12}$ atoms/day suggesting that the inward diffusion of atmospheric helium is somewhat slower for flasks containing hydrogen or deuterium as postulated by Miles et. al. Flask uniformity is again indicated by the good agreement of helium diffusion rates for these four flasks. A total of eight flasks were used in our heat/helium studies, but one flask was broken during shipment, hence Table 1 and Figures 1 and 2 present helium diffusion results for all seven remaining flasks. A very important result from these helium diffusion studies is that there is absolutely no evidence for any leakage of air into our flask in any of these experiments. Additional studies by the Amarillo, Texas laboratory indicated that the rate of atmospheric helium diffusion into our flasks is 2-3 times slower for flasks that contain deuterium instead of nitrogen.

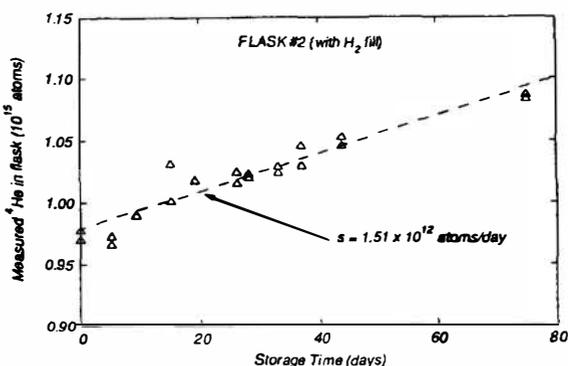


Figure 1. Experimental rate of atmospheric helium diffusion into one of our Pyrex flasks when filled with hydrogen.

The excellent agreement between experimental and theoretical rates for the diffusion of atmospheric helium into our nitrogen-filled flasks allows us to determine a minimum value for our ^4He detection limit. As reported by M. H. Miles and R. A. Hollins et. al. four of our flasks filled with nitrogen were analyzed for helium by our usual procedures after 9 days of storage. One flask showed the presence of ^4He at the detection limit while no helium could be detected in the other three flasks. Based on the mean helium diffusion rate of 3.2×10^{12} atoms/day established experimentally in Table 1, our helium analyses for the nitrogen-filled flasks yields a minimum ^4He detection limit of 3×10^{13} atoms/500 mL or 3 ppb. This detection limit compares favorably with the ± 1 ppb error range reported by a commercial laboratory (Amarillo, Texas) for the analysis of our gas samples. Helium detection limits of 1000 ppb (1 ppm) reported by N. S. Lewis et. al. and D. Albagli et. al. are far too insensitive to detect any ^4He fusion product in the effluent gases of Pd/D₂O electrolysis cells.

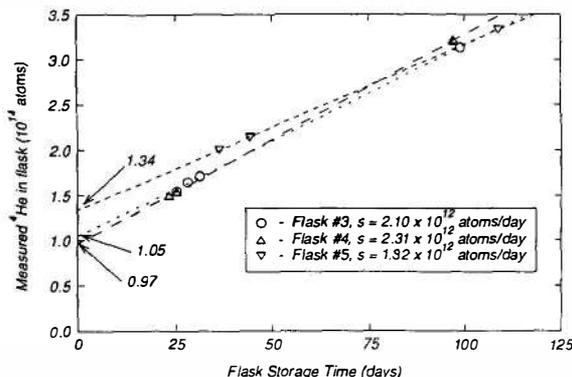


Figure 2. Experimental rate of atmospheric helium diffusion into three of our Pyrex flasks when filled with D_2O_2 from Pd/ D_2O electrolysis.

Table 2 presents results for the calorimetric measurements of excess power that were time-correlated with the collection of electrolysis gas samples for helium analysis. Since $X = P_{OUT}/P_{IN}$, the input power (P_{IN}) can be calculated from $P_{IN} = P_{EX}/(X-1)$. The numerical values for 4He are based on the revised detection limit of approximately 10^{13} atoms/500 mL. The time

Table 2. Helium Production During D_2O Electrolysis: Revised Detection Limits.

Sample	P_{EX} (W)	X	4He Atoms/500 mL ^a
12/14/90-A	0.52b	1.20b	10^{15} (large peak)
10/21/90-B	0.46	1.27	10^{15} (large peak)
12/17/90-A	0.40b	1.19b	10^{14} (medium peak)
11/25/90-B	0.36	1.15	10^{15} (large peak)
11/20/90-A	0.24	1.10	10^{14} (medium peak)
11/27/90-A	0.22	1.09	10^{15} (large peak)
10/30/90-B	0.17	1.12	10^{13} (small peak)
10/30/90-A	0.14	1.08	10^{13} (small peak)
10/17/90-A	0.07	1.03	$< 10^{13}$ (no peak)
12/17/90-B	0.29 ^{b,c}	1.11 ^{b,c}	$< 10^{13}$ (no peak)

^a No 3He was detected. Mass spectrometer always at highest sensitivity.

^b $I = 250$ mA/cm². All other experiments used $I = 200$ mA/cm².

^c Possible calorimetric errors due to low D_2O solution levels.

required to generate 500 mL of electrolysis gas is 4440 seconds at 200 mA/cm² for our electrode area ($A = 2.6$ cm²), laboratory temperature (23°C), and pressure (700 torr). For the experiments yielding 10^{15} 4He atoms per 500 mL of

electrolysis gas, the rate of helium production is 10^{11} - 10^{12} $^4\text{He}/\text{s}\cdot\text{W}$. This is the correct magnitude for typical fusion reactions listed in Table 3 that yield ^4He as a product.

Table 3. Low-Energy Deuteron Fusion Reactions Producing Helium.

Reaction	Energy (MeV)	Reactions/second/1 W output
$^2\text{H} + ^2\text{H} \rightarrow ^4\text{He} + \gamma$	23.8	2.6×10^{11}
$^2\text{H} + ^3\text{H} \rightarrow ^4\text{He} + \text{n}$	17.6	3.6×10^{11}
$^2\text{H} + ^6\text{Li} \rightarrow 2\ ^4\text{He}$	22.4	2.8×10^{11}
$^2\text{H} + ^7\text{Li} \rightarrow 2\ ^4\text{He} + \text{n}$	15.1	4.1×10^{11}

The amount of helium observed versus the flask storage time for each electrolysis gas sample is shown in Figure 3. Results for the four nitrogen-filled flasks are also included. Since Table 1 and Figures 1 and 2 show that the flasks are reasonably homogeneous with respect to helium diffusion, any significant diffusion of atmospheric helium into our flasks should yield helium levels that increase linearly with the flask storage time. No such effect exists in Figure 3. For the D_2O -LiOD experiments, high and low helium levels occur at both short and long storage times that ranged from 22 to 61 days. In fact, linear regression

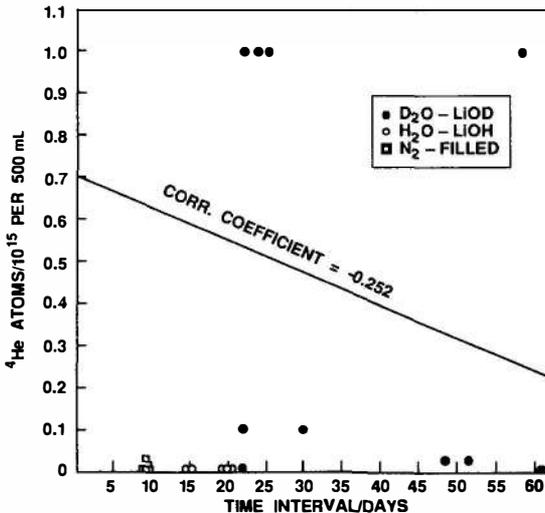


Figure 3. Amount of helium observed versus the flask storage time interval between gas collection and helium analysis. The results for the N_2 -filled flasks establish a minimum helium detection limit for our experiments of 10^{13} atoms/500 mL.

shows a negative correlation if any exists at all. Ignoring the heat/helium relationship (Table 2), the simple yes or no detection of helium in 8 out of 8

experiments producing excess power and the absence of helium in 6 out of 6 control experiments (1 in D₂O and 5 in H₂O) implies a chance probability of only $(1/2)^{14} = 1/16,384$ or 0.0061%. Atmospheric helium contamination, therefore, does not provide a likely explanation for our ⁴He measurements.

The exposure of dental films during episodes of excess power has been reported elsewhere by Miles et. al. During this same time period our GM-detector recorded anomalous high radiation count rates as shown in Figure 4. Several following experiments involving Pd/D₂O + LiOD electrolysis and using new Pd cathodes yielded near-normal radiation counts as shown in Figure 5. These electrolysis experiments also failed to produce significant excess power and showed no exposure of dental films. Furthermore, the passing of the electrolysis gases directly into our GM-detector did not yield anomalous radiation count rates. Several later electrolysis experiments also failed to produce any anomalous radiation counts as shown in Figure 6. This series of studies were used to establish a mean and standard deviation of $31,296 \pm 275$ counts per 12-hours for our GM-detector. Radiation monitoring continued as shown in Figure 7 for periods of electrolysis studies as well as for time periods with no experiments in operation. Normal radiation counts were always observed, and no excess power was detected. The anomalous radiation counts shown in Figure 4 have proven to be nearly as elusive as the excess power effect.

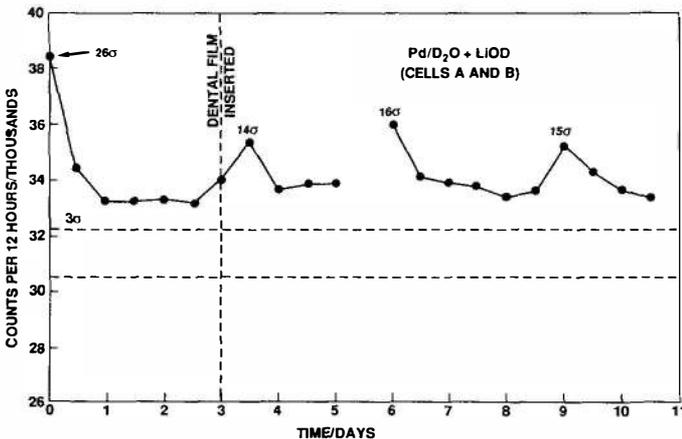


Figure 4. Anomalous radiation counts observed with the GM-detector during the time period December 15-25, 1990. During this same time period, gas sample 12/17/90-A showed the production of helium (Table 2) and dental films in cells A and B became blackened.

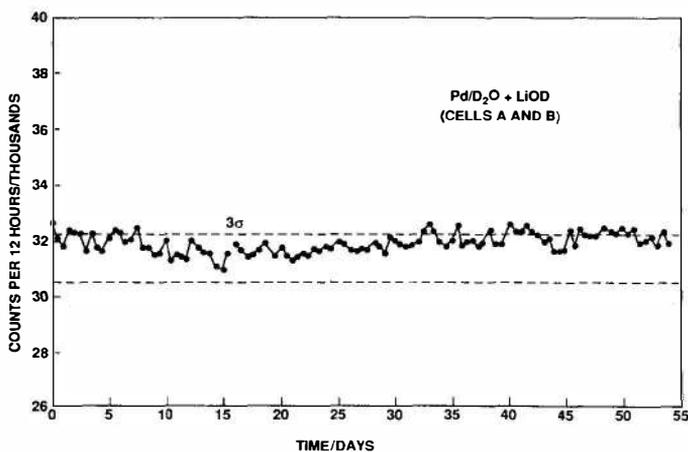


Figure 5. Radiation counts observed with the GM-detector during Pd/D₂O + LiOD electrolysis for the time period March 14-May 6, 1991. The electrolysis experiment began on February 25, 1991.

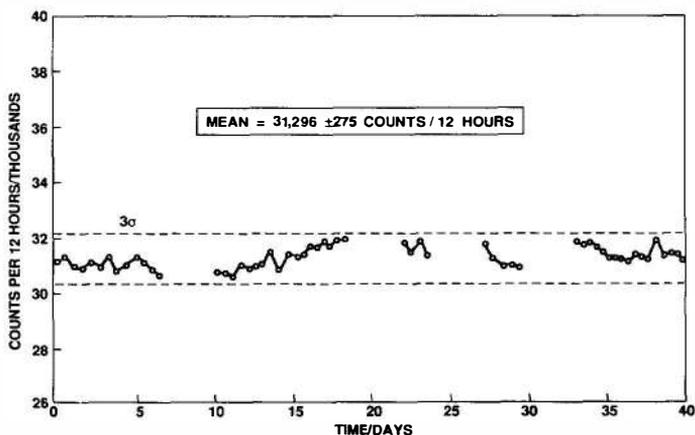


Figure 6. Radiation counts observed with the GM-detector for the time period July-September 1991. Various Pd/D₂O experiments were conducted but no significant excess power was detected. These radiation counts were used to establish the mean background of $31,296 \pm 275$ counts per 12 hours.

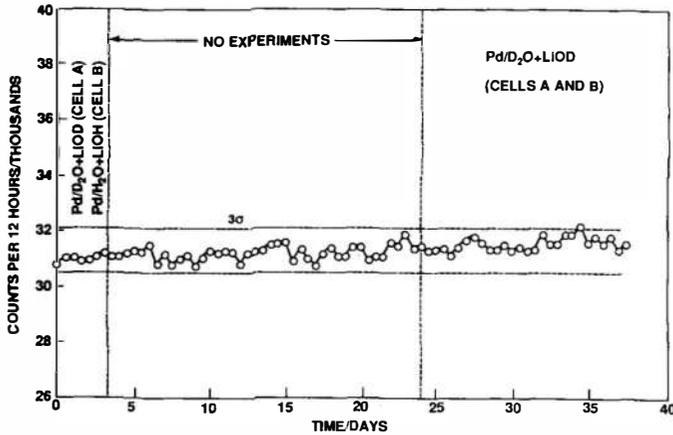


Figure 7. Radiation counts observed with the GM-detector for the time period October 15-November 21, 1991. Periods of Pd/D₂O + LiOD and Pd/H₂O + LiOH electrolysis as well as a period of no experiments are shown.

The plateau determination for our GM-detector is shown in Figure 8 for our normal background as well as for ⁵⁵Fe and ¹³⁷Cs sources. No unusual

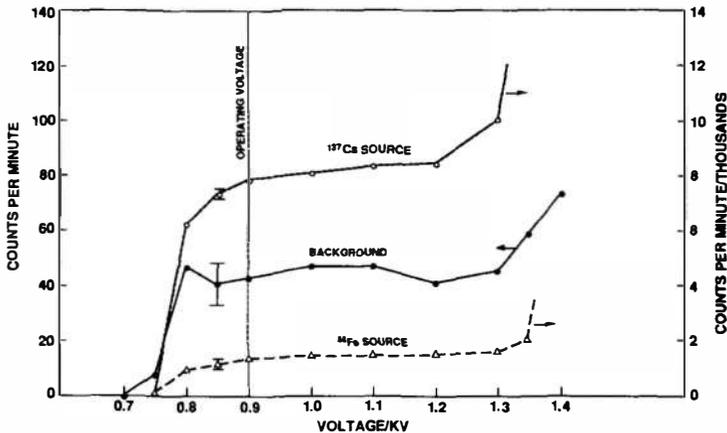


Figure 8. Plateau determinations for our GM-detector using ¹³⁷Cs and ⁵⁵Fe sources as well as the background counts. Normal behavior is observed.

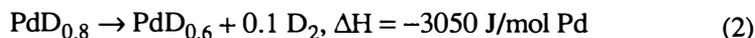
behavior was observed. At the instrument setting of 0.9 kV suggested by the manufacturer, small voltage changes would not produce high count rates for this detector. The problem of reproducibility has hindered further studies of this anomalous radiation effect. However, several more recent experiments with the

GM-detector placed closer to the Pd/D₂O + LiOD cells (5 cm) have shown sporadic periods of elevated counts as reported by M. H. Miles, R. A. Hollins et. al. Furthermore, the variation of the distance between the cell and detector traces the radiation source back to the electrolysis cell. Similar detections of radioactive emissions have been reported by H. Uchida et. al.

4. Discussion

Factors that may affect the reproducibility of the excess power effect during Pd/D₂O + LiOD electrolysis include the palladium metallurgy, the handling or conditioning of the palladium, the extent of deuterium loading, the cell configuration and symmetry, the current density profile, the electrolyte; impurities in the cell components, palladium, D₂O or lithium; atmospheric contaminations such as H₂O or CO₂ as well as the time span of the experiments. Our experience suggests palladium metallurgy as a possible critical factor for excess power. Two of our palladium rods have given excess power in seven of eight experiments. Experiments using eight new palladium rods have all failed to give any large excess power effect. Our results suggest that palladium rods that yield excess power may be used repeatedly.

Experimental processes that could yield excess power effects include the exothermic formation of PdD_n where $n \leq 0.6$ and the exothermic deloading of the palladium for $n \geq 0.6$ as reported by J. Balej and J. Divisek. The exothermic formation of PdD_{0.6} in our experiments would yield an excess power less than the detection limit of our calorimeter (± 0.020 W) as reported by M. H. Miles, R. A. Hollins et. al. The exothermic deloading of the palladium cathode represented by



yields an excess power effect of 0.012 W for our experiments (0.0416 mol Pd) when averaged over a 3-hour period required by our calorimetry (time constant ≈ 25 minutes). This exothermic deloading effect for our cells, therefore, yields an excess power that is again less than the detection limit of our calorimeter.

Another possible explanation for the excess power observed is the Joule-Thomson effect for deuterium compressed into the palladium. The Joule-Thomson coefficient is expressed thermodynamically as

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T(\partial V / \partial T)_{P-V}}{C_P} \quad (3)$$

From the Van der Waals' equation of state, the Joule-Thomson coefficient for hydrogen is

$$\mu = \frac{2a/RT - b}{C_P} = -0.02331 \text{ K/atm} \quad (4)$$

A similar value would be expected for deuterium. Thus for 1 cm³ of Pd containing PdH_{1.0} (0.0565 mol H₂), a pressure change for hydrogen of -10⁵ atm averaged over a 3-hour time period would yield an excess power effect of 0.35 W. This is approximately the excess power that we have observed as seen in Table 2. However, there are several major problems with this Joule-Thomson explanation for excess power. Since a net enthalpy balance is required by the First Law of Thermodynamics, periods of excess power due to the release of deuterium under pressure must be balanced by periods of power shortfalls when deuterium is compressed into the palladium. Furthermore, the Joule-Thomson effect could not sustain excess power over long time periods as observed experimentally. In addition, excess power based on the Joule-Thomson effect would be expected for both H₂O and D₂O experiments. Finally, any Joule-Thomson derived excess power would not correlate experimentally with any helium production as reported in Table 2.

Progress relating to helium measurements at our laboratory has been hindered by experimental difficulties in obtaining large excess power effects. However, small excess power as well as anomalous radiation was detected when the electrolysis samples shown in Figure 2 were collected. Flasks 3 and 5 were collected at the same time from cells A and B, respectively. An anomalous radiation count of 38,668 per 12 hours (27 σ) was observed during this time period. Flask 4 was collected 4 days later from cell B during a time period of normal radiation (31,240 counts per 12 hours). The experimental excess power was 0.08 W for flask 5 and about 0.02 W for both flasks 3 and 4. As seen from Figure 2, the extrapolated amount of helium initially present is largest for flask 5 (1.34×10^{14} atoms/500 mL) that showed the largest excess power effect. Smaller amounts of helium that are nearly identical were measured for the other two flasks (1.05×10^{14} and 0.97×10^{14} atoms/500 mL) where the excess power was near the detection limit of our calorimeter. Although these excess power measurements are marginal, the differences in detected helium and observed power for flasks 3 and 5 or for flasks 4 and 5, nevertheless, yields 10^{11} - 10^{12} atoms/s•W. This is in good agreement with our previous studies. Furthermore, these were double blind experiments since neither Rockwell International nor our laboratory knew the correlation of excess power and helium measurements until after all results were reported to a third party.

5. Conclusions

Simultaneous evidence for excess power, helium production, and anomalous radiation suggests that nuclear reactions do in fact occur in Pd/D₂O + LiOD electrolysis experiments. Reproducibility remains a major problem in defining these effects.

6. Acknowledgments

We thank David L. Miles for computer assistance in the analysis and display of the experimental data. We also thank Dr. Brian M. Oliver (Rockwell International) and Tom Davidson (Helium Field Operations, Department of the Interior) for measurements relating to helium diffusion into our flasks.

7. List of Symbols/Nomenclature

a	=	Van der Waal's gas constant, $L^2 \text{ atm mol}^{-2}$
b	=	Van der Waal's gas constant, $L \text{ mol}^{-1}$
C_p	=	Heat capacity at constant pressure, $\text{JK}^{-1} \text{ mol}^{-1}$
d	=	Average thickness of glass, mm
H	=	Thermodynamic enthalpy, J
K	=	Permeability for helium diffusion through glass
P	=	Thermodynamic pressure, atm
ppm	=	Parts per million
ppb	=	Parts per billion
T	=	Thermodynamic temperature, K
V	=	Volume, liters (L)

8. References

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