Deuterium analysis issues

Paul E Reimer
With help and comments from
Andrew Chen, Markus Diefenthaler, Grass Wang

Abstract: There has been a lot of confusion about the content of our deuterium target. Specifically, we need to know what the ratio of ^1H to ^2H in the liquid $^2H_2$ target. An analysis of the $^2H_2$ gas that was either in the target flask or in the bottle from which the flask was filled was done by Los Alamos. This note attempts to document what we know about the target gas.

The SeaQuest deuterium target was emptied and filled several times while we were recording data. At each of these times, a sample was taken from either the deuterium gas from the target as it warmed up or from the deuterium gas cylinder that was used to fill the target. These samples were sent to Los Alamos for isotopic analysis[1]. Each sample was analyzed twice. The results of this analysis are shown in Table 1. For each sample, the two analyses are in agreement. Upon examination of the table, some problems are immediately clear. Specifically, the ratios of $^1H_2$, $^1H^2H$ and $^2H_2$ are different between the different samples that were analyzed, but the bottles were supposed to have been filled from the same source many years ago. Second, the some of samples had a significant contribution of other gases, including $^{14}N_2$ and $^{16}O_2$. This indicates an additional contamination of air. In addition, a sample of the first $^1H_2$ target was analyzed. Those results are show in Table 2.

Table 1 The results of the gas analysis at Los Alamos expressed in mole percent for the deuterium samples. Each sample was analyzed twice (on the same day) and each sample was internally very consistent. There is, however, significant variation between the different samples. Note that the total is greater than 100% because those components marked with a “<” sign represent upper limits, but the sum assumed that they were at these limits. For runs after 14653, commercial $^2H_2$ was used. This gas came with an analysis showing it was 99.9999% pure.

Sample ID:	W1F0521(?)		D2 Run II 9-6-2014		D2 Run III 2-9-2015		D2 Run III 3-25-2015	
Date:			12/03/13		11/08/14		02/10/15	
Runs:			3230-11143		11144-11477		11478-14652	
Analysis Number:	1	2	1	2	1	2	1	2
Species:								
H_2	0.784	0.788	1.23	1.225	0.25	0.251	4.603	4.591
HD	12.7	12.703	16.187	16.171	8.393	8.391	6.983	6.982
D_2	85.183	85.164	79.78	79.729	90.871	90.808	80.504	80.443
He	1.253	1.273	2.2	2.188	0.018	0.014	< 0.01	< 0.01
CH_4	< 0.004	< 0.004	< 0.009	< 0.009	< 0.007	< 0.007	< 0.008	< 0.008
H_2O	< 0.004	0.011	< 0.009	0.073	0.038	0.099	0.033	0.061
HDO	0.004	0.009	0.015	0.026	0.024	0.033	0.021	0.04
D_2O			< 0.007	< 0.009	< 0.007	< 0.008	< 0.009	0.012
Ne	0.049	0.029	0.07	0.065	< 0.027	< 0.027	< 0.03	< 0.03
N_2	0.018	0.016	0.428	0.419	0.323	0.323	6.395	6.382
C_2H_4	0.008	0.007						
C_2H_6	< 0.005	< 0.005	< 0.006	< 0.006	< 0.005	< 0.005	< 0.006	< 0.006
O_2	< 0.003	< 0.003	0.085	0.098	0.068	0.068	1.389	1.416
Ar	< 0.001	< 0.001	0.005	0.006	0.004	0.003	0.063	0.064
CO_2	< 0.001	< 0.001	< 0.002	< 0.002	0.011	0.009	0.01	0.01
C_3H_8	< 0.003	< 0.003	< 0.006	< 0.006	< 0.005	< 0.005	< 0.006	< 0.006
Total	100.02	100.017	100.039	100.032	100.051	100.051	100.07	100.061

[1] https://seaquest-docdb.fnal.gov/cgi-bin/ShowDocument?docid=1462

Table 2 The results of the gas analysis at Los Alamos expressed in mole percent for the hydrogen sample.

Sample ID:		W1C8637(020)		
Date:				
Runs:		1-3229		
Analysis Number:		1		2
Species:				
H_2		98.051		97.992
HD		0.033		0.026
D_2	<	0.002	<	0.002
He	<	0.008	<	0.008
CH_4	<	0.003	<	0.003
H_2O		0.028		0.035
HDO		0.005		0.003
D_2O				
Ne	<	0.008	<	0.008
N_2		1.455		1.475
C_2H_4	<	0.001	<	0.001
C_2H_6	<	0.003	<	0.003
O_2		0.405		0.444
Ar		0.019		0.02
CO_2		0.004		0.005
C_3H_8	<	0.002	<	0.002
Total		100.027		100.027

1. History of the $^2H_2$ and possible contamination

The deuterium that was obtained from Fermilab was initially used in bubble chamber experiments. At some time in the past, the contents of the bubble chamber were transferred into a tube trailer for storage. At a later time, the $^2H_2$ was transferred into cylinders for storage. Discussions with Jim Kilmer indicate that there was probably no special treatment of the cylinders other than being evacuated when they were filled with $^2H_2$ (*i.e.* the cylinders were probably not baked)[2]. When we requested deuterium, the cylinders we received were taken from this stock. Since run 11478, we have been using commercial deuterium gas that has an analyzed purity of >99.9999%.

Contamination from air in the sample gases is unlikely to have come from the targets. Prior to filling, the targets under several cycles of evacuation and refilling with deuterium before the final fill is done. This should remove all residual air from the target flask. If there were air in the gas being filled into the target, all but the lowest temperature gases should have been removed by the liquid nitrogen cold trap. The hypothesis is that the gases that should have been removed by the cold trap were introduced during the sampling process. The hypothesis of heavier gases being introduced during the filling of the sample bottles is not completely consistent, however, since the ratio of O_2/N_2 is consistently smaller than that for air. An explanation for this would be to assume that some of the O_2 form H_2O in the nearly pure deuterium/hydrogen environment. Aside from hydrogen isotopes, helium is the only other component found in the samples. The target temperature was about 23K so any helium would have been in a gas state and not in the

[2] Based on a discussion with Jim Kilmer about the cylinder's history; although, no written procedures from that time have been found.

bulk liquid in the flask[3]. Thus, the gases from the analysis show in Table 1can be renormalized to have only the hydrogen isotopes. This is shown in Table 3.

The $^1H_2$ contamination in the deuterium samples is more troublesome. We expected some contamination of the deuterium samples with $^1H_2$, but we expected it to be the same for all samples, since every cylinder can be traced back to the same source. One possible explanation is lies in the history of the cylinders themselves. Hydrogen is known to have a tendency to diffuse into metal surfaces. Typically, metal containers are baked under vacuum to remove this contamination. The cylinders, target flasks and sample bottles were *not* baked out before they were filled with deuterium. In one case, the target flask was filled with liquid hydrogen and immediately before being purged and filled with deuterium. Countering the argument[4] of diffused hydrogen entering the sample is the extremely small diffusion constant, especially at room temperature or cryogenic temperatures[5]. These two augments leave the source of the difference in hydrogen/deuterium ratios in the samples a mystery.

2. Recommendation for interim publications

We recommend that the analysis groups use the atomic percentages provided by the Los Alamos analysis as shown in Table 4. While we hope that we will have a better understanding of the deuterium target gas in the future, this represents what we know now. To assign a systematic uncertainty to these numbers, we propose using asymmetric uncertainties, assuming that one the extreme values for h and d. Note that there is a complete inverse correlation between hydrogen and deuterium (and hence I don't bother specifying the uncertainty for h).

Table 3 Mole percent ratios for the low temperature gases in the samples analyzed by Los Alamos. The two analyses were done for each sample and the average was taken after normalizing to only these gases.

Sample ID:	W1F0521(?)	D2 Run II 9-6-2014	D2 Run III 2-9-2015	D2 Run III 3-25-2015
Applicable Runs:	Jan-29	3230-11143	11144-11477	11478-14652
H_2	0.80%	1.26%	0.25%	4.99%
HD	12.87%	16.65%	8.44%	7.59%
D_2	86.33%	82.08%	91.31%	87.42%

Table 4 The deuterium target composition in terms of atomic percentages and a suggested (extreme and asymmetric) systematic uncertainty on the deuterium percentage. Note that aside from the small (ignorable at this point) helium contamination, the hydrogen and deuterium are completely anti-correlated.

Sample ID:	W1F0521(?)	D2 Run II 9-6-2014	D2 Run III 2-9-2015	D2 Run III 3-25-2015	D2 Run III Commercial
Runs:	1-3229	3230-11143	11144-11477	11478-14652	14652-16077
h	7.2%	9.6%	4.5%	8.8%	0.0%
d	$92.8\%^{+3\%}_{-2\%}$	$90.4\%^{+5\%}_{0\%}$	$95.5\%^{+0\%}_{-5\%}$	$91.2\%^{+4\%}_{-1\%}$	$100.0\%^{+0\%}_{0\%}$

---

[3] Thanks to Bryan Kerns for pointing this out to me.
[4] Thanks to Roy Holt for pointing this out to me.
[5] Chris San Marchi, et al. *Permeability, Solubility and Diffusivity of Hydrogen Isotopes in Stainless Steels at High Gas Pressures,* Sandia National Laboratory, report WSRC-STI-2007-00579, 12 September 2005.