Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

We put science to work.™

Savannah River National Laboratory®

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Estimation of the Tritium Isotope Effect in the SAS Compressor Bed 1 Material (LANA10)

Kirk L. Shanahan

July 2020

SRNL-STI-2020-00257

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2020-00257
Revision 1

Keywords: *SAS, Tritium, hydride*

Retention: *Permanent*

Estimation of the Tritium Isotope Effect in the SAS Compressor Bed 1 Material (LANA10)

Kirk L. Shanahan

July 5, 2020

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory®

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy under contract number DE-AC09-08SR22470.

EXECUTIVE SUMMARY

A recent report presented a method to estimate the SAS Compressor Bed 1 (SAS CB1) loading level, in Q/M units, based on measured equilibrium pressure and temperature where the material was clearly loaded into the β-phase. This method requires the use of the equilibrium desorption isotherm plateau pressure, but no data exists to specify that value at this time. This report details a previously unreported investigation into tritium isotope effects on plateau pressure of a closely related material, herein called LANA05, conducted in the 1989-to-1993 time frame by then-SRL (Savannah River Laboratory) researchers. Data from that investigation is used to estimate the tritium isotope effect on plateau pressure in the SAS CB1 virgin LANA10 material by constructing a tritium van't Hoff plot for LANA10 that mimics the isotope behavior in LANA05.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
TF	Tritium Facilities
SAS	Sample Assay System
LANA	La-Ni-Al Alloy
CB	Compressor Bed
H	Hydrogen Isotope Protium
D	Hydrogen Isotope Deuterium
T	Hydrogen Isotope Tritium
Q	All Hydrogen Isotopes (H + D + T)
M	Metal Atom
Q/M	Hydrogen (all isotopes) Concentration in solid hydride material
Peq	Equilibrium Pressure (in Torr)
P_{plat}	Equilibrium Plateau Pressure (in Torr)
SS	Stainless Steel

1.0 Introduction

The SAS Compressor Bed (CB) is to be included in the physical inventory reconciliation performed once every 2 years in the Tritium Facilities (TF). Recently, a report[1] was issued that used a mathematical model of the β-phase region of the reduced pressure desorption isotherms to compute a loading Q/M (Q = H + D + T, M = metal atoms) value given a set of equilibrium conditions (temperature, pressure). The 'reduced' pressure is computed by dividing the measured pressure for each point in an isotherm by the desorption plateau pressure for that material at that temperature. This collapses the temperature-dependent isotherms on top of each other and allows the Q/M value to be computed from a single equation. However, tritium (T or T_2) isotherm data were not available for the SAS CB1 material, a La-Ni-Al alloy $LaNi_{4.9}Al_{0.1}$ (herein called LANA10). In that report it was recommended that the tritium data be measured during the accountability procedure, but an alternative to this would be to somehow provide a van't Hoff equation to use to compute the tritium plateau pressure at a given temperature. This report produces just such an equation by comparing tritium isotope effect data from a closely related compound, $LaNi_{4.95}Al_{0.05}$ (herein called LANA05) to LANA10 isotope effect data for protium (H) and deuterium (D). This approach was necessitated by the fact that no actual T data exists for the LANA10 material.

2.0 Experimental Procedure

Two materials were purchased from Ergenics, Inc sometime in the 1980's with the specification for both calling for a LANA05 ($LaNi_{4.95}Al_{0.05}$) composition. The SAS CB material (lot designation 1500-V-2) was found to be a LANA11 ($LaNi_{4.89}Al_{0.11}$) material by the X-ray Diffraction (XRD) techniques used by Dr. W. C. Moseley. The second lot of material (lot designation no. 1164-V-2) was similarly declared to be of composition LANA05 by XRD. The designations of these materials in the old laboratory notebooks was LANA0.05 and LANA0.11.

For the recent report[1], the SAS CB1 material, called LANA10 there, was studied at and below room temperature, and the data added to a prior study[2] conducted at slightly higher temperatures, primarily with protium but with some limited deuterium data. Chemical analysis of it showed that it was actually closer to a $LaNi_{4.9}Al_{0.1}$ (LANA10) material, which is why it is designated as such in the most recent report. It was seen to be a slightly La-poor, which was a typical manufacturing specification used during that early time period. It was also seen to be slightly Ni-rich, i.e. Al-poor. This is likely due to the large difference in melting point of Al and Ni and La, which allows Al loss to occur during the alloy formation process.

At or near the time of purchase, Dr. J. R. Wermer proceeded to study the materials using all three isotopes on the LANA05 material but only H and D on the LANA10 material. The LANA05 material was further used in a single sample for tritium aging studies as well, and tritium aging times of ~4 years were tested. These results were apparently never published. In the older studies, the material was treated similarly to the reported methods used in the recent reports. Manifolds used for both T and H/D studies were constructed of SS. All data recording was done manually in laboratory notebooks or record books, and then entered into spreadsheets for computation of isotherms. These spreadsheets and/or isotherms were typically printed out and inserted into the notebooks, and it is these sheets that have provided the data for this analysis. The spreadsheets themselves are apparently lost. The hardcopy data have been re-entered into Excel spreadsheets to construct the Figures presented in this report. The data show variation similar to that discussed in the most recent report[1]. However, this variation does not significantly affect the determined plateau pressures used in constructing van't Hoff plots due to the flatness of the plateaux.

3.0 Results and Discussion

Figure 1 presents Wermer's van't Hoff data for the LANA05 material. The equation parameters are shown in Table 1 (A and b). This data serves as the basis for estimating the T_2 van't Hoff plot for the LANA10 material. The Wermer H and D van't Hoff plots and Shanahan H van't Hoff plot for the LANA10 material are shown in Figure 2. The Shanahan and Wermer H data are in substantial agreement. The disagreement between capacities and plateau pressures falls within the general range of experimental error anticipated in the case of H/M capacity from the results detailed in the most recent report, and in the case of the plateau pressures, based upon standard variation between Type K thermocouples combined with the use of different experimental apparatus.

Manufacturing specifications on Type K thermocouples are typically +/- 2 °C. The Wermer isotherm was acquired at nominally 31.5 °C, and the Shanahan one at nominally 30.3 °C. Plateau pressures taken directly from the isotherms are 1386 Torr for the Wermer data at 31.5C (but note that the point seems slightly elevated) and 1166 Torr at 30.3 °C for the Shanahan data. The van't Hoff predictions from Wermer's equation gives a predicted plateau pressure of 1367 torr at 31.5 °C. The predicted Shanahan value at 30.3 °C is 1206 Torr, only 40 Torr higher than measured (out of 1200). The Shanahan equation gives 1266 Torr for the same temperature (31.5 °C), an ~100 Torr difference between the two predicted values, but the predicted Shanahan value at 33.5 °C is 1374 Torr. In other words, the temperature uncertainty from the thermocouple coupled with the experimental setup covers the apparent difference between the two researchers results. This '100 Torr out of 1200' represents less than a 1% error, which is probably better than could be expected if the experiments were repeated multiple more times. In other words, the precision is unlikely to be better that roughly +/-5% overall.

The T_2 van't Hoff curve for the LANA10 material was estimated by comparing the changes between the H, D, and T van't Hoff curves for the LANA05 material with the change noted between the H and D values for the LANA10 material. Table 1 shows the data used to do this. First, the van't Hoff parameters are listed for the LANA05 and LANA10 materials and the % change from H to D and from D to T are noted in each. Second, it is noted that the H to D change in LANA10 seems smaller than in LANA05. Therefore, an initial estimate was made by simply multiplying the H LANA10 parameters by 5, which is shown in the table as "T2est". That equation was then added to the H and D van't Hoff plot of Figure 2. The initial estimate seemed slightly off, so the numbers were arbitrarily adjusted to those shown in Table 2 and the plot corrected on the chart. The values used to make the van't Hoff plot are also shown in Table 2.

One additional possible complication is that the tritium used in at least some of these studies was analyzed by the TF mass spectroscopy lab as containing only 95-99% T. The typical major component of the balance was D, with a small amount of H present. This can lead to slight shifts in the plateau pressure as well, and thus in the derived van't Hoff parameters. This effect has been noted in van't Hoff plots of H, D, T, and a 93.4%T mixture in Pd-X in Section 5 (esp. Figure 5.1) of Lässer[3].

It should be obvious that there is no theoretical basis for this estimation procedure. Likewise, there is insufficient data to accurately estimate the errors. However, given the strong desire for an initial guess for the T_2 plateau pressure for the LANA10 material and given the lack of data, this seems the best one can do at the moment. It is absolutely certain that *real* T_2 data should be acquired on LANA10 for accuracy considerations.

The T_2 data for the LANA05 material were not fully worked up in the notebooks, so the plateau pressures had to be estimated for 0 and 30 °C. The data in Table 3 is that used to make the T_2 van't Hoff plot. The fit quality was quite good, with the R^2 value being 0.998, based only on 4 data points however.

During this study, a figure was found showing the effects of 10 months of tritium aging on the LANA05 material. This figure is reproduced below as Figure 4. The tritium aging was carried out by loading the sample to a given overpressure of tritium, closing the sample cell, and allowing the sample to statically age for the given time. This allows the ^{3}He decay product to grow in within the solid, which is what leads to the changes in the isotherms. Details of this effort were not investigated, but it should be noted that tritium aging will eventually invalidate this entire methodology due to plateau pressure shifts and isotherm shape changes.

4.0 Conclusions

A crude estimate has been made for the van't Hoff tritium equation for the LANA10 material. That equation to calculate T plateau pressure is:

$$\log10(P) = 6.25-1830/T \text{ (P in atm and T in K)}$$

Typical tritium aging effects were found. These include plateau pressure depression and the growth of a 'heel' of tritium that requires higher temperature to remove.

5.0 Recommendations, Path Forward or Future Work

The results and conclusions reported herein should allow the Tritium Facilities to determine the SAS Compressor Bed 1 tritium plateau pressures for a given temperature within an error of perhaps +/-5%. However, more data is required to validate the proposed equation. This data can however be obtained at leisure at this point, if the proposed van't Hoff equation is found acceptable to the TF. In fact, it should be noted the plateau pressure data could be extracted during normal operations fortuitously or by simply pausing a desorption at or near the midpoint long enough to reach equilibrium. That process is recommended to validate the estimate given in this report.

6.0 References

1. "Characterization of the β-phase region of the SAS Compressor Bed 1 Material (LANA10)" Kirk L. Shanahan, June, 2020, SRNL-STI-2019-00157
2. "Materials Characterization for the Unloading Line B Project", Kirk L. Shanahan, March 24, 2011, SRNL-STI-2011-00750.
3. Tritium and Helium-3 in Metals, R. Lässer, Springer-Verlag, Berlin, 1989

Table 1. Initial T equation parameters

Van't Hoff data

		y=A*10e-b(1/T)		y is P in atm T in K	
		A	b	%Diff in A	%Diff in b
LANA05	H2	833110	1745.3		
	D2	2589200	1881.9	210.7873	7.826734659
	T2	16631063	2137.8	542.3244	13.59795951
LANA10	H2	433820	1643.1		
	D2	944380	1746.5	117.6894	6.292982776
	T2est.	2169100	1840.272		

Initial T2 est P = 2169100*10^(-1840/T)

Table 2. Estimated T plateau pressures for LANA10 used for Figure 2.

T2 est P = 1778279*10^(-1830/T)

log10(P)= 6.25 + (-1830/T)

1/T	T	P(atm)	logP	lnP
0.003661	0	0.355128	-0.44962	-1.03528
0.003193	40	2.547741	0.406155	0.935207
0.003002	60	5.714508	0.756979	1.743008

Table 3. LANA05 T Data used to construct van't Hoff line

LANA05 virgin T2

1/T	T	Pplat	ln(p,atm)	log10
0.003661	0	181	-1.43482	-0.62314
0.003299	30	1200	0.456758	0.198368
0.003193	40	1950	0.942266	0.409221
0.003002	60	4550	1.789564	0.777198

Figure 1. Van't Hoff Plots for H, D, and T desorption isotherms on LANA05 lot 1164

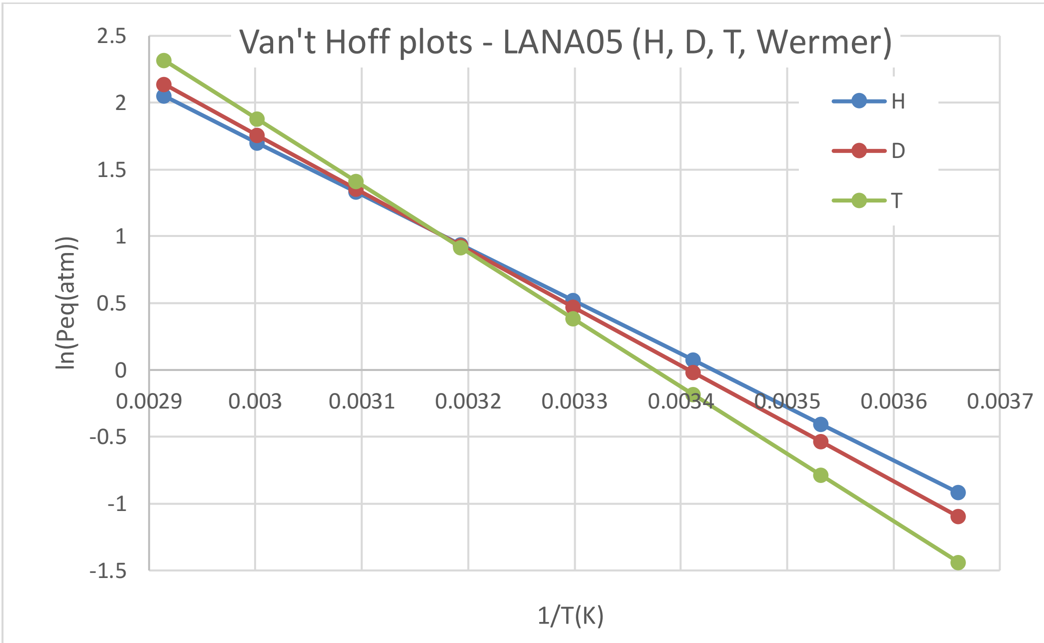

Figure 2. H and D van't Hoff plots for LANA10 lot 1500 comparing Shanahan and Wermer results, with estimated T van't Hoff plot

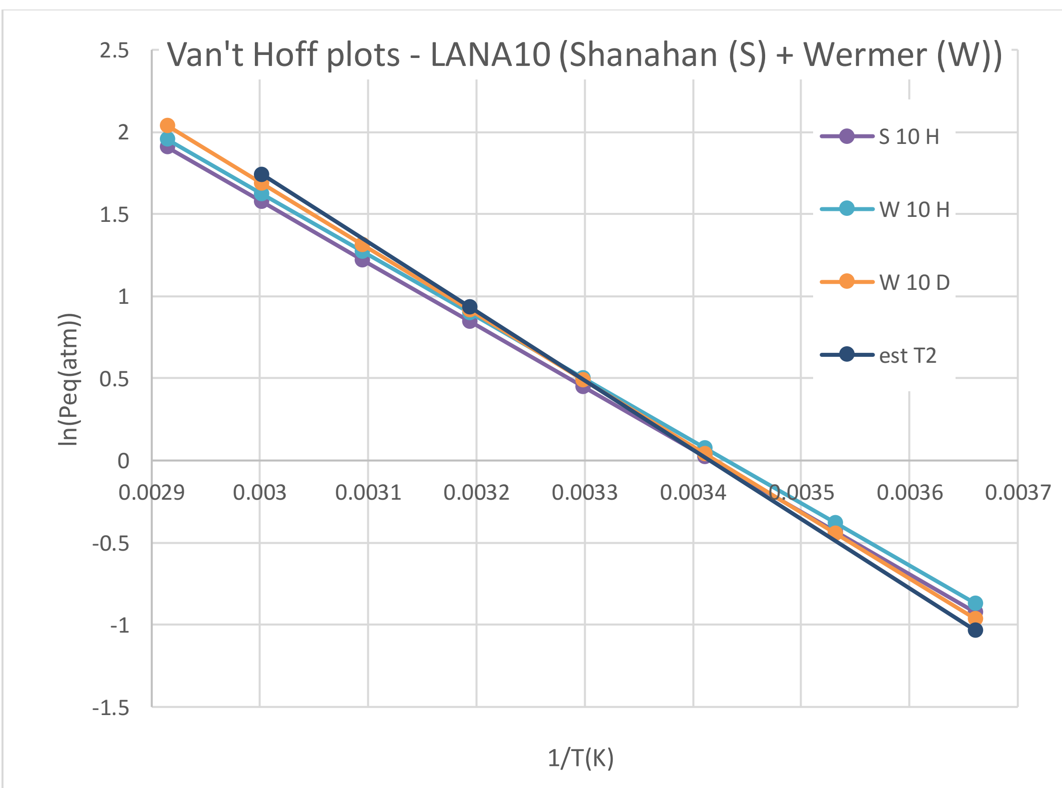

Figure 3. Comparison between Shanahan and Wermer H isotherms at ~31 °C.

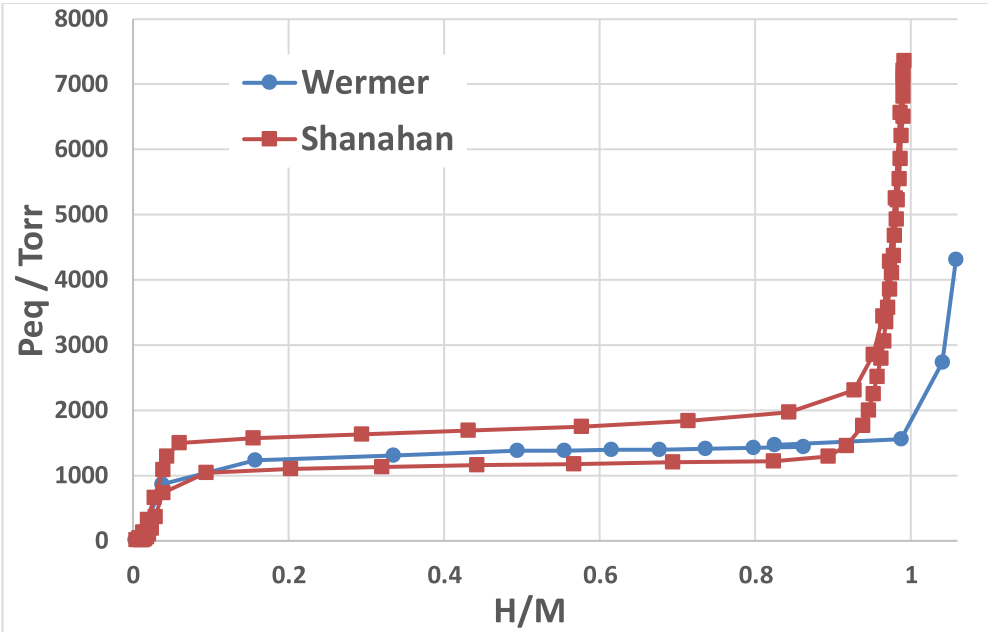

Figure 4. Wermer's Figure showing T aging effects on LANA05