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COMMENT ON "TRITIUM ABSORPTION-DESORPTION CHARACTERISTICS OF $LaNi_{4.25}Al_{0.75}$"

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ABSTRACT

The thermodynamic data for $LaNi_{4.25}Al_{0.75}$ tritide, reported by Wang et al. (W.-d. Wang et al., J. Alloys Compd. (2006) doi:10.1016/j.jallcom.206.09.122), are in variance with our published data. The plateau pressures for the P-C-T isotherms at all temperatures are significantly lower than published data. As a result, the derived thermodynamic parameters, $\Delta H°$ and $\Delta S°$, are questionable. Using the thermodynamic parameters derived from the data reported by Wang et al. will result in under estimating the expected pressures, and therefore not provide the desired performance for storing and processing tritium.

Wang et al. report tritium sorption data for $LaNi_{4.25}Al_{0.75}$ (LANA0.75) as part of a program to develop metal hydride technology for storing and processing tritium [1]. The authors state little work has been published on the basic tritium absorption-desorption characteristics, and therefore they are providing that data now. Some of the data they present are absorption-desorption Pressure-Composition-Temperature (P-C-T) isotherms, the derived standard thermodynamic parameters $\Delta H°$ and $\Delta S°$, the temperature dependent rate of tritium gas absorption and desorption for their particular LANA0.75 composition, and the trapping of ^3He upon desorption of tritium gas after seven days of tritium decay ageing.

The reported P-C-T isotherms [1] are in variance with our published data [2-4]. The authors provide a few of our references where tritium desorption isotherm data have been published for LANA0.75; these references, and more, for example, show 80°C tritium desorption P-C-T isotherms that are not aged, i.e. little time passed to allow tritium to decay to ^3He and alter the "virgin" plots after tritium absorption [4,5]. See the figure. These referenced data show 80°C tritium desorption plateau pressures for LANA0.75 of about 65-70 kPa at the midpoint of the

plateau, whereas Wang et al. show the same 80°C desorption plateau pressure of about 15 kPa. We assume the remaining isotherm pressures by Wang et al. also are low compared to the referenced data, and as such, the derived thermodynamic parameters based on these plateau pressures are questionable.

For example, our data for LANA0.75 tritide decomposition plateau pressures are very well described by the van't Hoff equation

$$RT \ln \frac{P}{P_o} = -\Delta H^o + T\Delta S^o \qquad (1)$$

with R = 8.314 J/K-mol, ΔH^o = 46.19 kJ/mole T_2 and ΔS^o = 127.2 J/K-mole T_2 [5,6]. This form of the van't Hoff equation (1) depicts the endothermic nature of a metal hydride desorption ($\beta \rightarrow \alpha$). The entropy change for the desorption process corresponds to the change from dissolved solid hydrogen to molecular hydrogen gas and is, therefore, $\Delta S_d \approx S^\circ$ = 130 J/K-mol H_2 for all metal-hydrogen systems, especially for LANA0.75 [7]. The difference between the standard gaseous entropy for hydrogen and the experimental entropies for metal hydrides lies almost exclusively in the entropy of interstitial atoms in the condensed state [6]. As a check on our data collection techniques, the exothermic absorption data we have for LANA0.75 for protium (H_2) are ΔH° = -44.06 kJ/mol H_2 and ΔS° = -117 J/mol-K; literature data are ΔH° = -44.35 kJ/mol and ΔS° = -118 J/mol-K [8]. The thermodynamic parameters derived from the data of Wang et al. are reported as ΔH° = -35.6 ±0.5 kJ/mole H_2 and ΔS° = -84.2 ±1.5 J/mole-K H_2 [1]. For this endothermic desorption process, the sign convention of positive enthalpy and entropy values should be followed. Using our thermodynamic parameters, the calculated tritium desorption plateau pressures for LANA0.75 are shown in the table along with the observed values of Wang et al.

Tritium desorption plateau pressures for LANA0.75

Temperature (°C)	Calculated (kPa)*	Wang et al.[1] (kPa)**
24	3.39	~1.4
50	15.26	~4.5
80	65.76	~15
110	225.38	~35

* Using Eq.(1)
**Approximate values, read from plot.

All of the decay ^{3}He remains in the solid for several years of tritium storage on LANA0.75 [4]. One of the effects of ^{3}He ingrowth is to lower the plateau pressure. This change in plateau pressure can be observed after only a few months of tritium storage [5]. For example, the 80°C desorption plateau pressure of LANA0.75 dropped from about 69 kPa after 20 days of tritium storage, to about 40 kPa after an additional 140 days, a 42% decrease in pressure. This aged isotherm exhibited a heel of deep trapped tritium at low solid composition, and a decreased capacity as measured by the length and slope of the plateau. For the lower plateau pressure data reported by Wang et al. to be the result of ^{3}He ingrowth, we estimate the sample would have to be approximately one year old before the isotherm was measured for a pressure decrease of about 77%. At that age, a much larger heel of deep trapped tritium at low solid composition would be observed, along with a noticeable increased slope to the plateau. We find none of these effects in the reported isotherms.

It is generally difficult to prepare an exact alloy of lanthanum, nickel and aluminum, and variations in the relative constituents can affect the plateau pressure. The aluminum content of the LANA0.75 primary phase controls the hydrogen absorption and desorption pressures [2,8]. The amount of aluminum (x) can be determined from the unit cell volume V(Å^3) by the relation

$$V = 3.28x + 86.78 \qquad (2)$$

Further, the relationship between hydrogen (protium) desorption pressure, hexagonal cell volume (aluminum content) and temperature may be described by a modified van't Hoff equation

$$\ln P(atm) = \frac{(43406 - 543V)}{T(K)} + 13.5 \qquad (3)$$

Using eqs. (2) and (3) as an exercise [9], the calculated aluminum content for the reported pressure at 80°C by Wang et al. for their material is approximately 0.97, i.e. the composition of their material should be about $LaNi_{4.1}Al_{0.9}$. Using our data in the table at 80°C, the same calculation returns a value for the aluminum content of about 0.68, better agreement with the value of 0.75. A variable composition of aluminum is entirely possible during the preparation of the LANA0.75 alloy, and could be the cause of the lower plateau pressures for Wang et al., although composition data are not reported.

The design for the Tritium Facility at the Savannah River Site is based in part on using LANA0.75 as a storage material for hydrogen isotopes [10]. The successful operation of this facility relies heavily on the thermodynamic properties of this aluminum substituted intermetallic AB_5 material. The large absorption capacity of 5 [T]/[La] at room temperature and *around* 1kPa overpressure as described by Wang et al. [1] will not be met as the room temperature plateau pressure is approximately 3.4 kPa. (Around 1 kPa could be interpreted to include 3.4 kPa.) Using the thermodynamic parameters derived from the data reported by Wang et al. will result in under estimating the expected pressures, and therefore not provide the desired performance for storing and processing tritium. We feel a comprehensive analysis of the alloy composition is in order.

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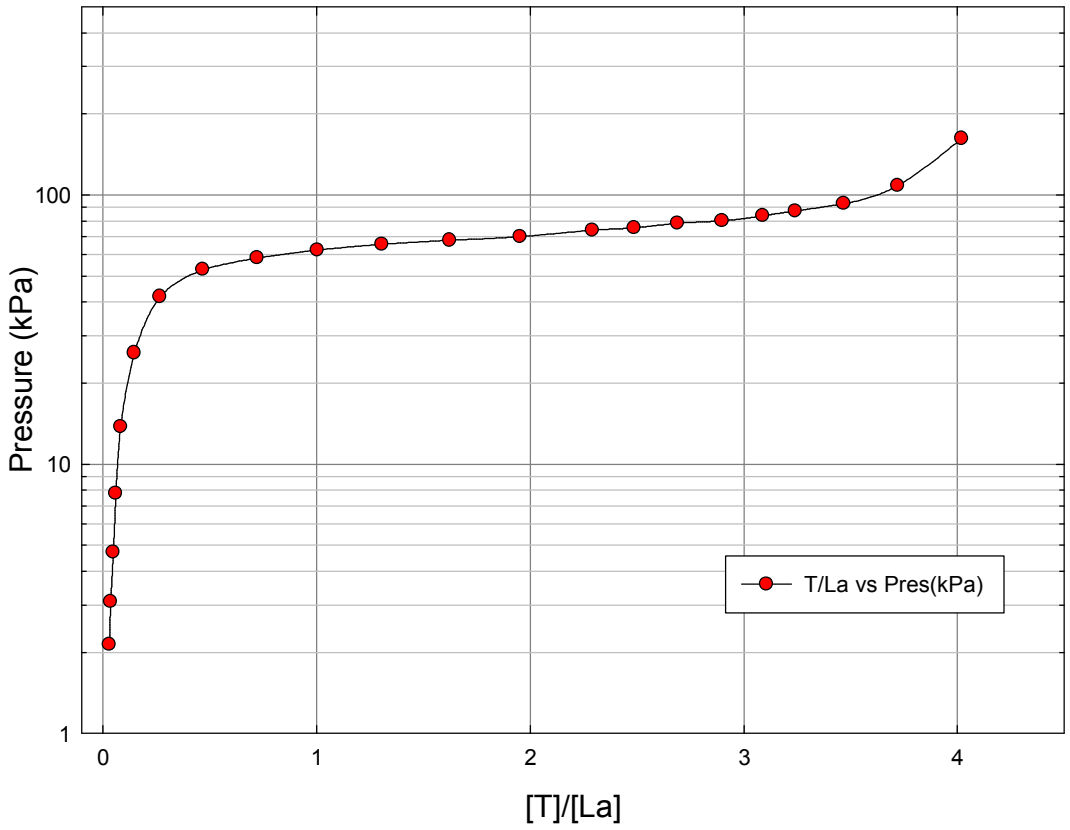

Fig. 80°C tritium desorption P-C-T isotherm for LANA0.7 [3] Data converted from [T]/[LANA] to [T]/[La].