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THE EXTRACTION OF TRITIUM FROM HELIUM STREAMS USING $La_{5.25}Ni$

by

D. H. W. Carstens

ABSTRACT

The rate of removal of tritium from helium-4 streams using molten $La_{5.25}$ near 600°C has been studied. At high concentrations (2-20% T_2) the gettering rate is rapid but drops as the concentration goes below about 100 ppm. Based on preliminary experiments using counting methods, these alloys are capable of gettering tritium to levels below 1 ppm.

I. INTRODUCTION

Liquid-metal binary alloys containing hydride-forming metals as the principal component have been proposed as tritium getters in controlled thermonuclear reactor (CTR) applications. The alloys appear to be applicable to reactor concepts using either solid, helium-cooled, or liquid-lithium blankets, although because of solubility and compatibility problems, their use with lithium blankets may be prohibited.

Measurements of the equilibrium deuterium absorption by alloys of cerium[1] and lanthanum[2] have been reported. These experiments indicated that the absorption capacities and equilibrium pressures of the alloys are, within about an order of magnitude, the same as those of the pure lanthanide metal. Absorption rates were rapid, at least at low concentrations of the deuteride in the liquid alloy. Thus, they seemed ideal for gettering applications in CTRs.

In this report experiments on the removal of tritium from helium-4 streams using liquid $La_{5.25}Ni$ are summarized. The circulation apparatus uses a mass spectrometer for concentration measurements that is capable of accurately measuring tritium in helium down to the 10- to 100-ppm range. The alloy at 600°C rapidly absorbs tritium to below this level and preliminary experiments using counting techniques indicated the gettering continued to below 0.1 ppm.

II. EXPERIMENTAL DETAILS

A. Materials

The simple alloy was prepared by arc melting weighed amounts of 99.9% lanthanum and reagent grade nickel, corresponding to a eutectic composition ($La_{5.25}Ni$) with a reported melting point of 495°C.[3] The stock tritium gas used had a composition, based on mass spectrometric analyses, of 96.7% T, 2.2% D, and 1.1% H at the start of the experiment, and 96.1% T, 3.0% D, and 0.9% H at the end, two months later. The differences reflect the accuracy of the analyses although the gas had lost some of the tritium because of aging.

B. Apparatus

The circulation apparatus is shown in Fig. 1. Most of its internal parts exposed to tritium were constructed of 300-series stainless steel. The five bellows-sealed valves used Teflon seats and gaskets, and the externally heated furnace was sealed with a copper gasket. The internal surfaces of the furnace were gold-coated to minimize tritium absorption. The molten sample was contained in either a tungsten (run 1) or stainless steel (run 2) crucible. The tube passing gas through the melt inside the furnace was, in both cases, made of stainless steel. Although one would expect reaction of either crucible material with the melt, over the short periods involved in these experiments (less than 30 h at the elevated temperature), there was only a slight attack of the walls.

Pressure near the mass spectrometer leak was measured with a Technical Hardware, Inc., digital 1000-torr pressure transducer standardized against a calibrated Wallace and Tiernan gauge. Primary parts of the apparatus were the furnace, a standard volume used to increase the capacity of the system (volume 320 cm^3), a uranium furnace containing 40 grams of depleted uranium for gas storage (40 cm^3), and the interconnecting manifold (73 cm^3). The gas was circulated with a Metal Bellows MB-41 pump, the flow rate was estimated from its specification sheets, and the pressure differential was read on the two compound gauges shown in the figure. In all experiments, circulation was counterclockwise.

C. Tritium Measurements

The concentration of tritium in the circulating gas was monitored continuously during the experiments using a mass spectrometer. A viscous leak was used consisting of a 50-cm length of stainless steel hypodermic tubing (inner diameter 0.4 mm) crimped off at the exit end until a satisfactory signal was obtained for helium at the operating pressure. The leak passed the gas at reduced pressures through a 1/4-in.-o.d. stainless steel tube (about 7 m long) into the ionization chamber of the detector, a CEC model 21-201 mass spectrometer equipped with new solid-state electronics. Tests indicated the leak-spectrometer combination reacted to a step change in pressure with a signal half-life of 19 s.

The stability of the mass spectrometer can be judged by the following: over the two-month period of the experiments, the helium-4 sensitivity factor (defined as the mass-4 signal divided by the pressure in the manifold) varied over the range 0.94×10^{-12} to 1.34×10^{-12} amp/torr. Generally, over periods of a few days, the variation in this value was less than 1%, and over a given experimental run, even less.

The concentration of tritium in the helium was calculated from the mass-4 (I_4) and mass-6 (I_6) ion currents, using several assumptions. It was assumed that I_4 arose totally from the helium-4, neglecting all hydrogen contributions (HT, D_2) that were small. Further, it was assumed in calculating the relative sensitivities that the tritium mix was pure T_2.

As above, the two sensitivity factors are defined by $f_4 = I_4/P_4$ and $f_6 = I_6/P_6$, where P_4 and P_6 are the helium-4 and tritium pressures in the circulation manifold. The ratio of these two factors $R = f_6/f_4$ was redetermined periodically during the experiments and was found equal to 4.09 ± 0.04. Since $P_4 + P_6 = P$, the total pressure in the manifold as measured on the digital gauge, from the above definitions it readily follows that $P_6 = CP/(1 + C)$, where $C = I_6/RI_4$.

This method of measuring the tritium assumes that the flow of each gas through the capillary to the spectrometer is directly proportional to its concentration in the sampled gas. Since in all the cases the pressures were kept fairly constant during a run, it was hoped that the flowing helium would sweep the tritium through the leak without any fractionating effects. Strictly speaking, in a viscous leak, if the viscosities of the two gases differ significantly, the minor component can drastically affect the flow rates and the apparent sensitivities. Thus, experiments were performed in order to determine the linearity and response of the leak. It was found that I_4 was directly proportional to P_4 for pure helium-4 gas over the range 1-1000 torr to within the readability of the transducer (± 1 torr). Similar results were found for pure tritium over the 1- to 1000-torr region. Finally, using the above calculational method, the equilibrium pressure of tritium over the UT_3 stored in the uranium bed was measured at several temperatures. The results of one such run are shown in Figure 2 in the form of a ℓn P versus 1/T plot. Here the circles are for increasing pressures and the squares for decreasing. The deviation between the two sets of data can be attributed to lack of pressure equilibrium; for some points the gradual change in temperature was halted to allow equilibration and these points tend to approach a common linear curve. In the figure the solid line is a least squares fit using all data points except the one at lowest pressure, which obviously deviates. The dashed line is from literature data.[4] The agreement is satisfactory, and moreover, the linearity of the experimental points down to at least 10^{-2} torr indicates the leak is behaving as hoped. This experiment was repeated several times and in all cases linear plots were obtained.

In a few absorption runs the tritium was measured using a counting technique. For these the leak was replaced with a 20-cm^3 ionization chamber (Overhoff and Associates) and the concentration was read from the associated electronics. The factory calibration was assumed.

D. General Techniques

All operations were carried out, and the apparatus was contained, in an inert atmosphere drybox equipped with a tritium removal system which maintained the tritium level in the box at about 1 ppm.

The procedure for the two main runs was essentially the same. A quantity of the alloy was broken up, weighed, and placed in the furnace, which was then sealed. After the furnace was connected to the circulation manifold, the entire system was filled to roughly 600 torr with helium gas. The furnace was then heated, and simultaneously, the uranium bed was brought up to the desired temperature. With the sample furnace valved off from the system, tritium was added to the circulating gas until the required pressure had been achieved, usually about 10 torr. After the signal became constant the bed was valved off and the valves to the furnace opened and the drop in tritium pressure was then monitored with the spectrometer. Every third or fourth addition was for more highly concentrated mixes (20%), which were carefully prepared and measured with the pressure transducer. These mixes were used to redetermine the relative sensitivities (R), as well as to check out the kinetics of absorption of large amounts of tritium.

All runs were performed with the total flow of the gas through the bellows pump of 120-140 cm^3/s (0.25-0.3 ft^3/s) with roughly equal amounts through the furnace and through the volume.

III. RESULTS

The experiments reported here consisted primarily of two runs, in both of which several additions of tritium were made to the $La_{5.25}Ni$ near 600°C and the absorptions were monitored with the mass spectrometer as discussed in the last section. Final tritium-to-lanthanum ratios in both cases were between 0.1 and 0.3. These two runs will be discussed in more detail below. In addition, extraction experiments using the uranium metal in the bed at ambient temperatures were made as a basis of comparison.

Limited experiments were also done using low concentrations and counting techniques. For these, box atmosphere gas (1 ppm tritium in helium-4) was circulated over the alloy at 600°C. Over periods of about one h the tritium was gettered to a third or less of this value. Additions of larger amounts of tritium (1%) were rapidly absorbed but the tritium was only gettered down to the 10- to 100-ppm range. These experiments suggested that at low levels, apparent gettering rates are determined by adsorption on, and release from, the internal surfaces of the apparatus.

Run 1 For this experiment 9.99 g of the alloy were placed in the apparatus, melted, and outgassed. On initial heating of the solidified sample with pressure on the inlet, gas began flowing at a temperature of about 550°C, indicating this is the approximate melting point of the alloy (probably high because of thermal lag in the furnace). Eight tritium additions were then made, all at 600°C: three low-concentration additions (10 torr tritium), followed by a high (100 torr tritium), two low, another high, and finally, one more low. The results are plotted in Figure 3, which shows on a log scale the decrease in pressure of tritium with time due to its absorption. In the figure, and elsewhere, n refers to the tritium-to-lanthanum ratio in the final product of each addition. The experimental results are further detailed in Table I which tabulates n, the temperature of addition, the pressure half-life over the approximately linear region of the curve in the middle stages of each addition, and an estimation of the final equilibrium pressure judged from the curve. Several general results can be deduced.

- At low concentrations and for low-level additions, the alloy is capable of gettering to the ppm range.
- For low concentrations the half-life of absorption is on the order of 20 s, but this increases as the concentration of tritium in the melt increases. The variations in this value are probably due to variations in the flow rate through the melt.

TABLE I

SUMMARY OF RESULTS

Run	Addition	n = T/L	T(^oC)	Half-life (s)	Final P (torr)
$\mathrm{La_{5.25}Ni}$ first	1	0.003	600	20	10^{-3}
	2	0.007		20	10^{-3}
	3	0.009		15	10^{-3}
	4	0.060		30	10^{-2}
	5	0.062		20	10^{-2}
	6	0.065		20	10^{-3}
	7	0.0132		60	10^{-2}
	8	0.0136		50	5×10^{-2}
$\mathrm{La_{5.25}Ni}$ second	1	0.003	600	20	4×10^{3}
	2	0.006	550	20	2×10^{-3}
	3	0.009	650	20	10^{2}
	4	0.100	600	70	8×10^{2}
	5	0.105	600	15	6×10^{2}
	6	0.109	650	20	0.3
	7	0.112	550	20	10^{-2}
	8	0.25	600	45	0.1
Uranium	1	0.55	84	25	10^{-2}
	2	0.55	45	30	10^{-2}

- For high-level additions the absorption rate decreases by a factor of about 2.
- After large additions, it takes a while for the alloy to recover, and approaches to equilibrium are slow.

Following the additions, the equilibrium pressure versus temperature was determined. These data in the form of a log P versus 1/T curve are given in Figure 4 and, as expected, a linear curve is obtained.

After the experiments, the crucible was broken up and the sample examined. On the surface of the solidified mass a dark coating was seen, presumably the tritide. The sample also had broken into small globules that stuck to the crucible, indicating that the gas had not been bubbling through the melt but rather was passing over it.

Run 2. This experiment was similar except only 6.01 g of the sample were used while adding similar amounts of tritium as before. In addition, the low-level additions were made at different temperatures to check for a temperature dependence in the absorption rate. The results of this run were essentially the same as for the previous, as can be seen in Table I. There was no discernible temperature effect in the rate; however, the increased equilibrium pressure at higher temperatures was evident. Again, P-vs-T data were taken for the final product. In this run, the data were taken twice, the second time following an annealing stage at 700°C. As can be seen in Figure 4, this step resulted in a decreased pressure, indicating the sample was not equilibrated fully for the first measurements.

In Fig. 4, results are also given for a blank run that was made using the empty stainless steel crucibles. As can be seen, this material absorbs T_2 at these temperatures, however, its equilibrium pressure is above that of $La_{5.25}Ni$. Thus, below 800°C the alloy should getter T_2 from stainless steel.

In Table II, the results obtained from fitting the data to the equation $\ell n\, P = A/T + B$ using a least squares calculation are summarized. For run 2, the results of both measurements and a combination using both sets of data are given. From the value of A, one can calculate an apparent value of the heat of formation

TABLE II

VARIATION OF PRESSURE WITH TEMPERATURE

Run	n = T/L	$A \times 10^{-3}$	B	$-\Delta H$ (kcal/mole T_2)
1	0.14	20.5 ± 2.6	19.8 ± 2.9	39.6 ± 5.2
2 (1st)	0.25	26.6 ± 2.0	26.7 ± 2.1	52.7 ± 4.0
(2nd)		24.8 ± 2.6	24.5 + 2.7	49.1 ± 5.2
(comb.)		25.6 ± 1.5	25.5 ± 1.6	50.7 ± 3.0

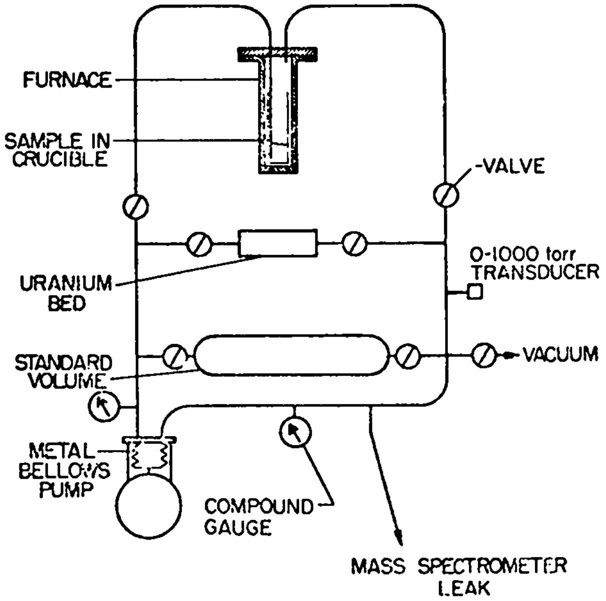

Fig. 1. Circulation apparatus.

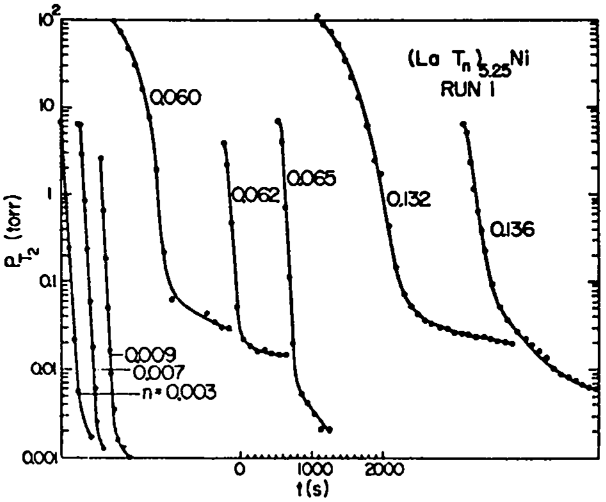

Fig. 3. Pressure drop with time of T_2 in helium circulated over $La_{5.25}Ni$ (run 1).

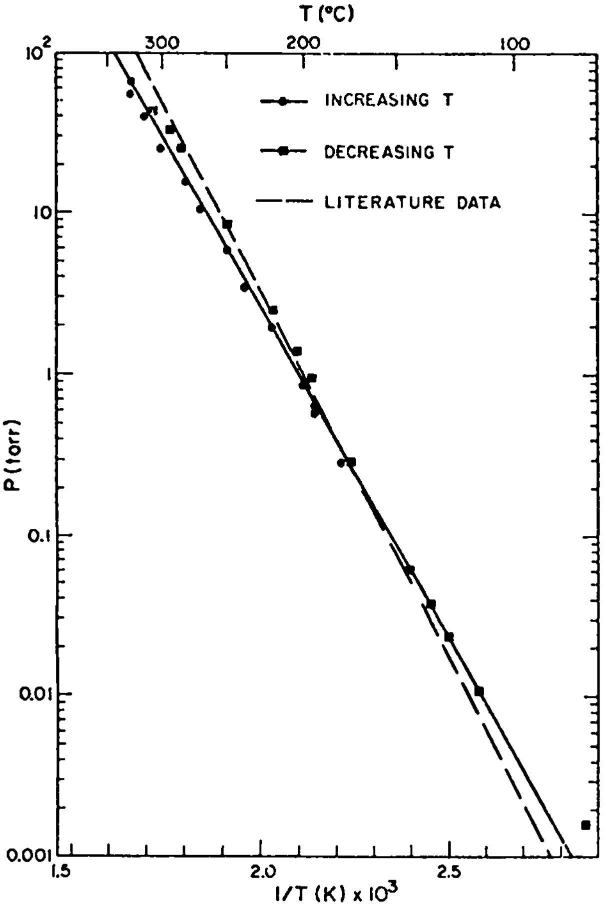

Fig. 2. Variation of T_2 pressure over UT_3 as measured with the mass spectrometer.

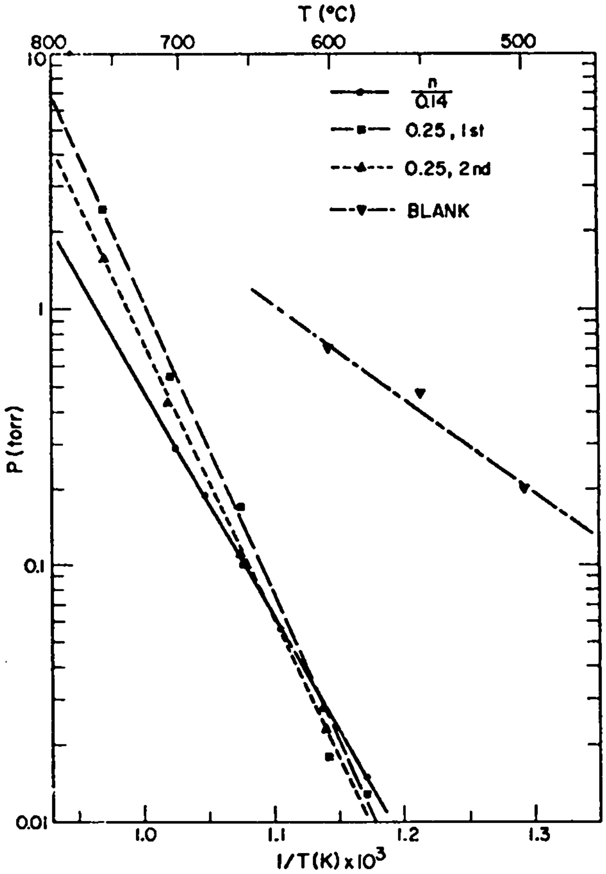

Fig. 4. Variation of equilibrium pressure of T_2 over $La_{5.25}Ni$.

of the tritide in the alloy, ΔH, and this is also tabulated in Table II. The variation between the first and second runs can be attributed to the differences in n. From similar experiments using D_2 one would expect a value of ∿ 50 kcal/mole T_2 for ΔH.

Uranium Runs. Two absorption runs were made using the uranium bed at temperatures near ambient. The results, summarized in Table I, indicate that the tritium gas is removed at about the same rate for the liquid alloy as for the uranium.

CONCLUSIONS

These experiments indicate that liquid $La_{5.25}Ni$ at temperatures near $600^{o}C$ rapidly, and essentially quantitatively, getters tritium from helium streams to levels on the order of 10 ppm, and over periods of about 1/2 h, to levels approaching 0.1 ppm. With efficient mixing within the liquid, equilibration rates should improve. Thus, this alloy, or others similar, should prove excellent as getters in CTR reactors. Two major questions remain to be examined: what conditions are needed to reverse the cycle (drive off the tritium), and what are the effects of impurities? Since impurity solids would tend to settle out of the melt, it is expected that gases in the helium stream should have a limited effect on the absorption efficiency.

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