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RADIATION EFFECTS *and* TRITIUM TECHNOLOGY *for* FUSION REACTORS

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THE URANIUM-TRITIUM SYSTEM - THE STORAGE OF TRITIUM

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ABSTRACT

The thermodynamics of the uranium-tritium system were determined over the pressure range of 2×10^{-4} to 20 atm from experimental composition-pressure-temperature data. Both enthalpy and entropy were shown to vary slightly with composition by analysis of van't Hoff plots for the U-D system and the U-T system. The evolution of helium-3 borne in the lattice of a fully tritiated sample of uranium was studied over a period of several months, and the relative proportion of helium-3 and tritium in the evolved gas from an aged UT_3 sample was determined at several temperatures. The desorption and absorption characteristics of a typical uranium-tritium storage bed have been studied and observed for several years.

Mound Laboratory has had an intimate involvement with the science and technology of preparing, handling, and determining the fundamental properties of metal hydrides, deuterides, and tritides for a number of years. Of the tritides we have determined the thermodynamic properties of Pd-T, Pd-Ag-T, V-T, and U-T. One of the more useful of these materials is uranium, because of its ability to rapidly retrieve, store, and dispense tritium gas. Uranium as uranium tritide is commonly used at Mound Laboratory in tritium-handling gas racks where it performs the functions mentioned - those of storage and purification of a tritium-containing gas stream. Figure 1 is a diagram of a tritium-handling gas rack intended for studies of metal hydrides over a pressure range of about 10^8 atm, from 10^{-5} to 10^3 atm. A U-bed, a vessel containing uranium tritide, is an essential part of such a

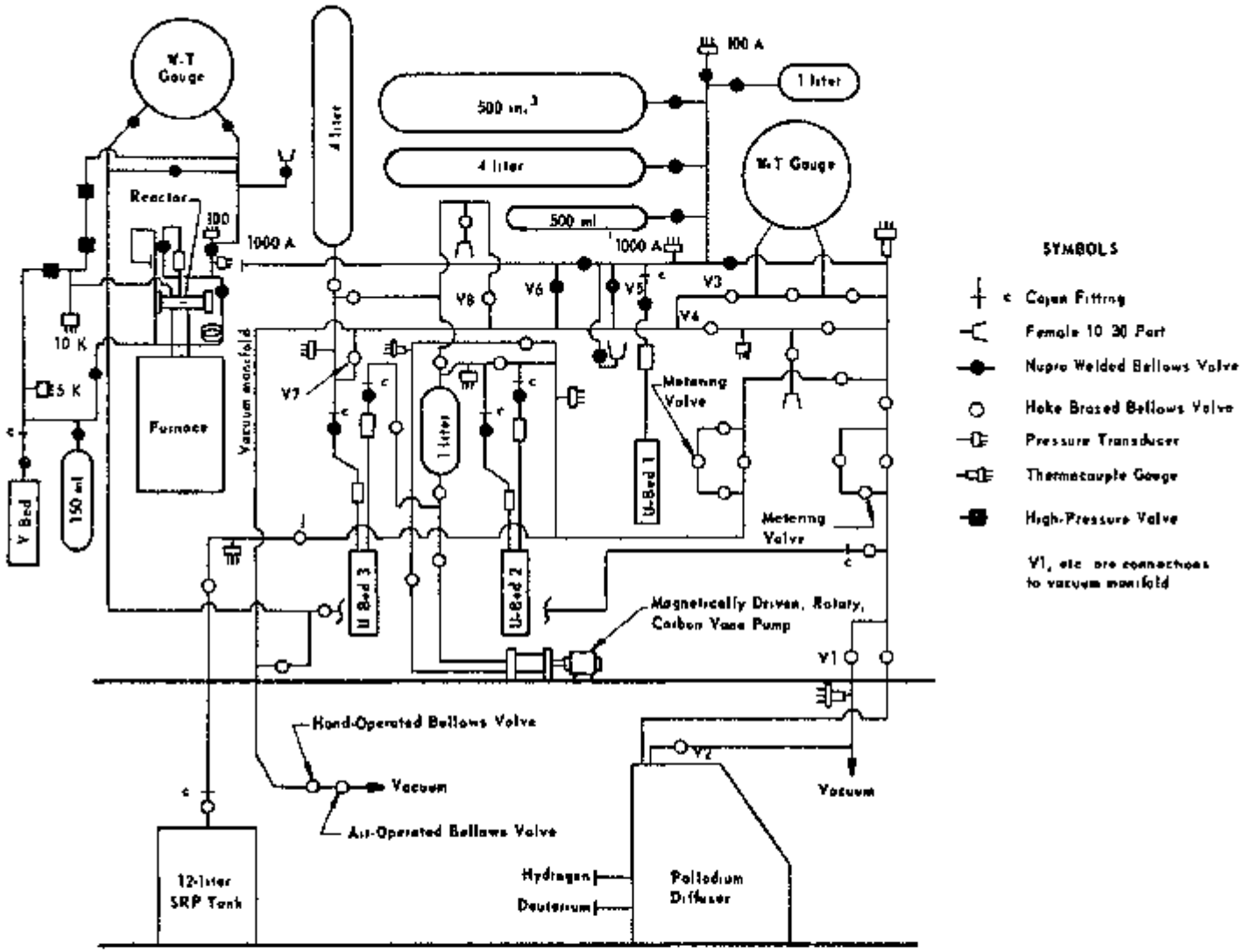

Fig. 1. Gas Rack Schematic.

gas rack. In this particular system, a palladium diffuser is used for purification of hydrogen and deuterium, and tritium is purified by circulation through a loop containing the U-bed.

Figure 2 is a photograph of this rack. It is located in a stainless steel fume hood 6 ft wide which has an air flow in excess of 200 linear ft/min with one door open. Type 347 stainless steel is the material of construction in the U-bed and in the doubly contained high pressure vessel in the vertical tube furnace. This material has performed satisfactorily at temperatures up to 700°C and at lower temperatures up to 1000 atm of tritium. Nupro stainless steel welded bellows valves and Hoke silver-soldered bronze bellow valves are used throughout and have given no trouble. HIP packed valves are used in the high pressure portion of the rack and do not leak if the valve stem is not moved while under high pressure. The opposite is also true. A HIP microcontrol valve permits withdrawing gas from the system at 13,000 psi and raising the pressure on the other side of the valve to 100 μm (as an example) following which the valve can be closed leak tight at the seat. This operation is repeatable many times but gas release is not reliable at low pressures; that is, at perhaps 2000 psi and under. A new rack built today would of course be doubly enclosed. Heating the exposed U-bed shown, which has a capacity of about 60 liters, to cycle the contained tritium of about 1 mole would release about 50 Ci.

This figure is cited to indicate the losses that would occur without double containment by simple diffusion alone. Even at ambient temperature, diffusion proceeds rapidly enough so that a storage tank once used to contain tritium will forever continue to contaminate cold gases contained within, even after numerous purges. Such a tank can easily add 1 ppm tritium to contained hydrogen or ~2.5 μCi/ml of

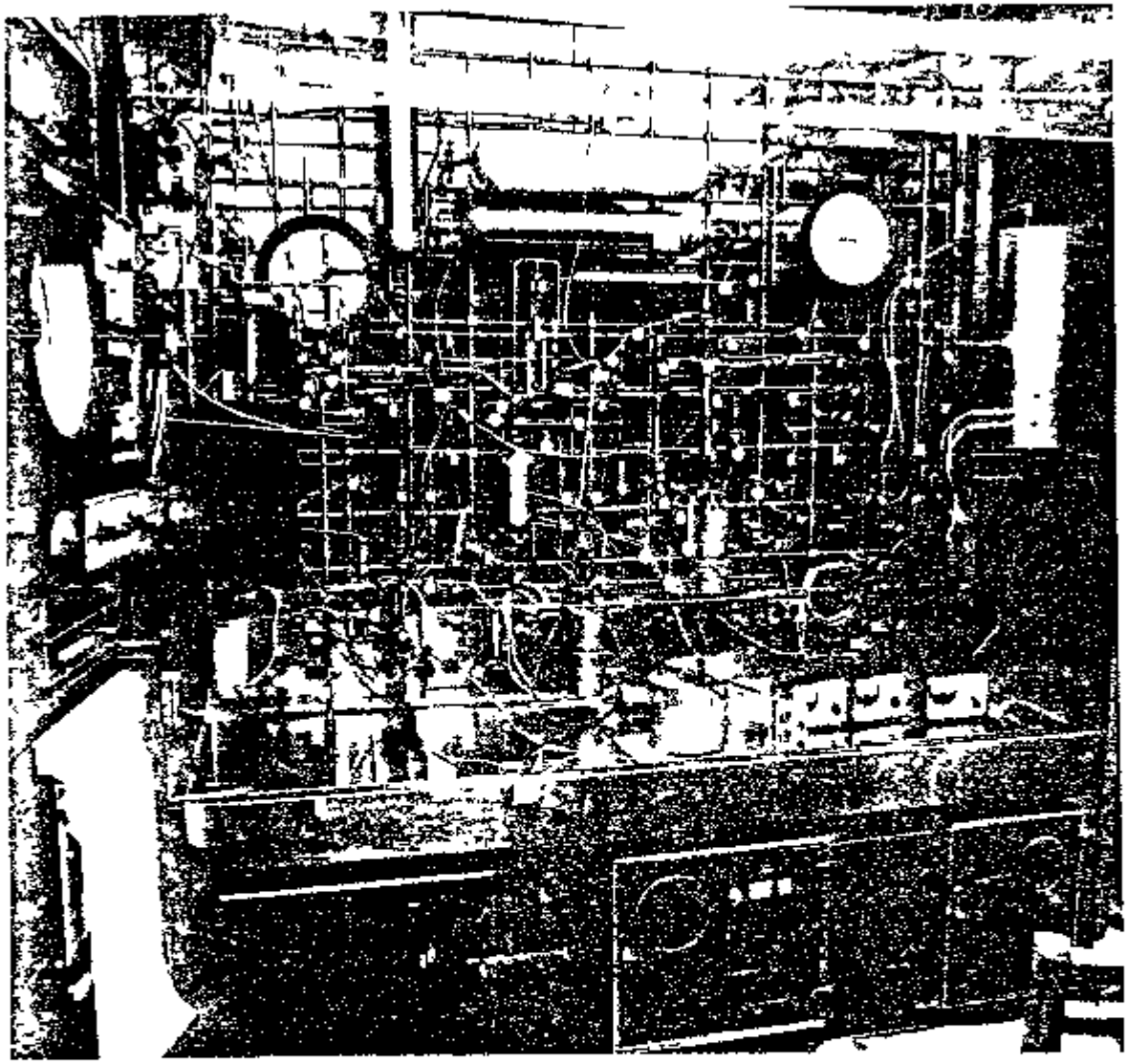

Fig. 2. Tritium Gas Handling Rack and Instrumentation.

hydrogen at STP. It should be remembered that 40 hr/wk of exposure to 1800 $\mu Ci/m^3$ of tritium (gas) or 5 $\mu Ci/m^3$ of HTO is equivalent to an adsorbed dose of 5 rem/yr.

The problem is the presence of helium-3 decay product in the tritium. A static system for separation of helium-3 from tritium will fail or, in other words, be of low efficiency in its ability to separate the isotopes because of "blanketing" of the gas-solid boundary by helium-3. Whether the boundary is palladium or uranium is relatively insignificant when the relative thermodynamic properties of the two materials are taken into consideration. The rate of generation of helium-3 in tritium is such that, after 10 days, 0.3% of the gas mixture is helium-3, yet this seemingly insignificant amount results in almost unsurmountable problems in static purification systems. Therefore, a dynamic purification system is imperative. Such a system should include, in addition to the palladium or uranium membrane, a storage vessel to permit a substantial volume of material to be handled and a rotary vane blower. A valveless pump such as a blower has the ability to operate at pressures down to any level of vacuum desired, whereas a valved pump will cease pumping when the system pressure drops below that required to open the valves. In the operation of the U-bed, introduction of impure tritium is periodically halted to allow the U-bed to absorb all the tritium in the loop; then the helium-3 is pumped off to the stack after passing through one or more scavenger U-beds to absorb any residual tritium. The cycle is then repeated.

Helium-3 buildup in the lattice of uranium tritide also contributes to the problem. Pure tritium is obtained from a U-bed by repeatedly cycling the system in such a manner as to desorb a substantial fraction of the tritium and helium-3 into a large volume, allowing the U-bed to cool, then reabsorbing the tritium, leaving the helium in the gas phase

to be pumped off. It is helpful in such a procedure to discard the first small aliquot of helium-rich gas.* Helium is desorbed from a U-bed at lower temperatures than tritium since it tends to accumulate in bubbles in the lattice, in contrast to tritium which occupies definite lattice sites. A second method by which essentially pure tritium can be obtained is to record the maximum temperature to which the U-bed is raised during the purification cycles; and then during the final desorption cycle of pure gas, the U-bed is heated to a temperature several degrees below the previous maximum. While I realize that tritium fuel for CTR machines can tolerate some helium contaminant, the foregoing is to be taken as advice.

Investigation of the properties of uranium tritide at Mound Laboratory has revealed some of the characteristics of helium release from a uranium tritide lattice. As mentioned, helium exists primarily as bubbles in the lattice, a topic to be fully described in the following talk by R. C. Bowman and A. Attalla of Mound Laboratory. Heating a uranium tritide lattice does not remove all the trapped helium-3. Furthermore, undisturbed uranium tritide slowly evolves helium-3 at a rate far less than the generation rate. Figure 3 is a plot of the helium release from uranium tritide with time. These data were obtained at Mound Laboratory by R. C. Bowman and C. J. Wiedenheft. This material was new uranium tritide which did not have a previous history of exposure to tritium and/or high temperature for any substantial length of time. It has a surface area of approximately 0.4 m^2/g. A similar experiment was conducted on uranium used in connection with studies of the thermodynamics

*As an example, during the 5th cycle (purification) helium-3 = 5.8% in initial 0.019 liter; 0.05% in following 0.75 liter (out of 20 liters total desorbed gas).

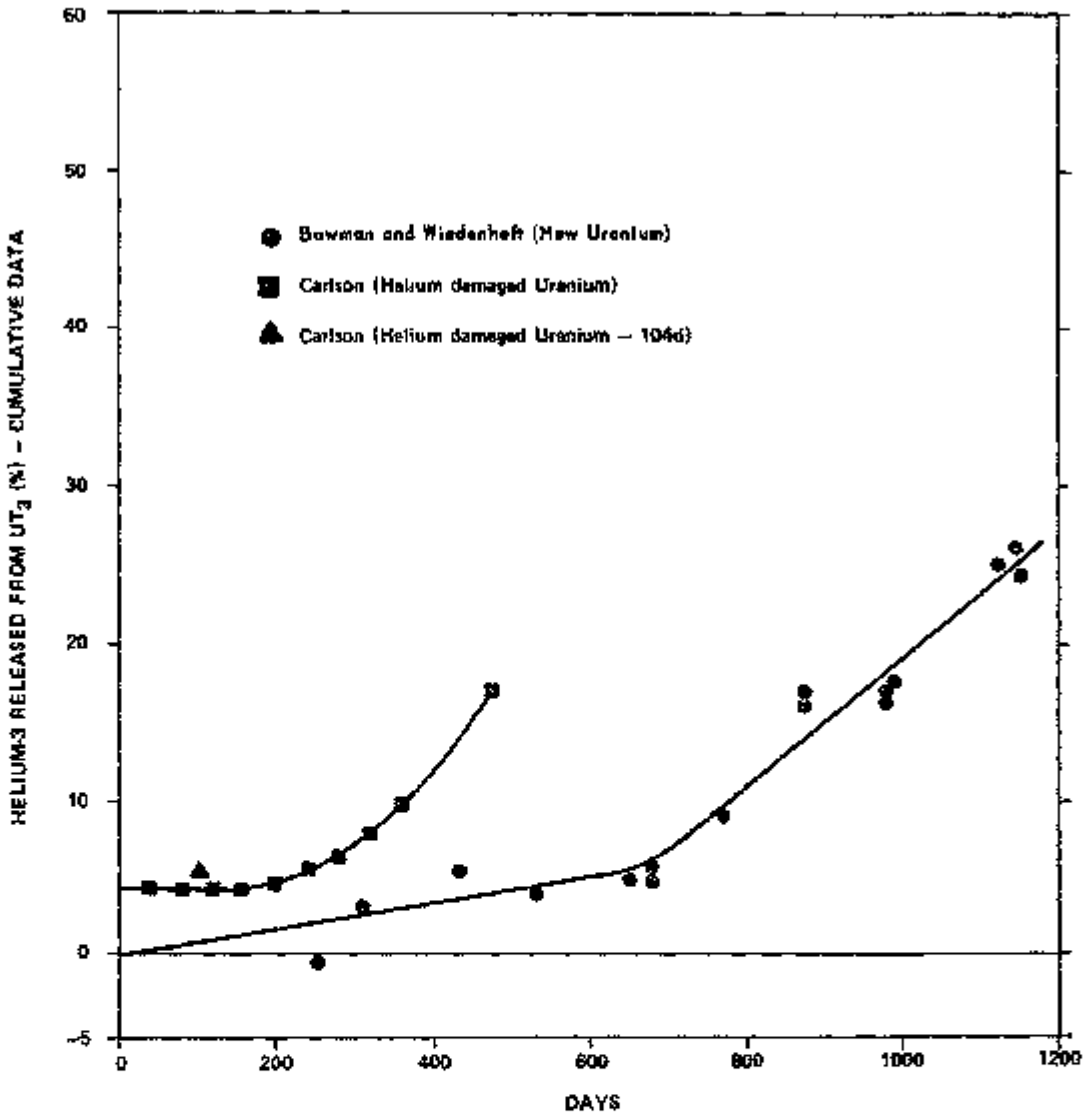

Fig. 3. Helium-3 Release Data for New and Old Samples of UT_3; Material Stored at Ambient Temperatures.

of the uranium tritide system (estimated to have a surface area of 1.5-2.0 m^2/g). At the beginning of this experiment, the high purity sample of uranium* I used had experienced a total of approximately 52 hr of exposure to tritium at temperatures of 450-600°C, the first half of the exposure being at a T/U ratio of 0.1 or less; the second half of the exposure to tritium being at a T/U ratio of 2.85 or greater. It can be postulated that deposition of helium-3 into a uranium lattice at high temperature would have created more damage than such deposition at room temperature. Of course, it can also be postulated that relaxation or healing processes also proceed faster at elevated temperature. It will be observed that release proceeds more rapidly for the first 1.3 yr with pre-aged uranium tritide than with new uranium tritide. Of course, the pre-aged uranium was not only damaged but still retained some fraction of the helium-3 previously trapped in the lattice before the experiment commenced, even though the sample had been heated to 700°C and stripped of all tritium, followed by thorough purging with deuterium and a second heating to 700°C to remove the deuterium, and followed finally by loading of tritium to a composition of $UT_{2.84}$. This material was allowed to stand for 104 days at room temperature; the evolved helium-3 overpressure was then measured and the gas sample analyzed by mass spectrometry. It was pure helium-3 and represented 5.4% of all the helium-3 born in the lattice. This helium-3 overgas was pumped off and the data in Figure 3 were subsequently obtained which agrees well with the 5.4% data point. It can be concluded that a damaged uranium lattice cannot be completely annealed at temperatures below 700°C and that the pre-induced lattice defects substantially increase the rate of helium release from uranium tritide.

*Analysis (ppm) Fe, 20; Si, 25; Mn, 5; Mg, 10; Ni, <10; Al, 25; Cu, <6; Cr, <8.

One other observation which may be of interest is that absorption of tritium dynamically on a U-bed proceeds smoothly and initially with great velocity generating substantial heat. Obviously the absorption of tritium eventually becomes self-limiting because of the exothermic nature of the reaction. Absorption ceases when an equilibrium temperature is reached, that is, equilibrium with reference to the composition-pressure-temperature plot of the uranium-tritium system. This temperature is about 400°C under normal conditions of about 1 atm tritium pressure. Emergency cooling is not really necessary because of this, as a runaway reaction is not possible; however, evolved heat must be removed to promote continued absorption. The observation I am referring to here is that after the composition of the U-bed has reached about T/U = 1.5, the absorption rate seemingly slows down. In other words, it is more difficult to absorb tritium on a half-filled U-bed than on an empty U-bed. This is contrary to the C-P-T plot which indicates a plateau or two-phase region of great width, from about $UT_{0.01}$ to $UT_{2.90}$, which implies no change in equilibrium pressure over that range. I believe this problem is related to the diffusion coefficient of tritium in the grain of uranium-uranium tritide in that after the grain of uranium is partly saturated, diffusion into the depth of the grain becomes the controlling factor in preventing rapid absorption of tritium into the uranium lattice.

Thus, a doubly contained U-bed, which has provisions for both circulation of gas through the bed and sufficient cooling capability to remove the heat of reaction and which is operated with some consideration of the relative properties of helium-3 and tritium in the lattice, has been found at Mound Laboratory to be one of the more useful devices for handling and storing tritium.

The thermodynamic properties of the uranium-tritium system were investigated over a pressure range of 10^5 atm from 119-572°C. The apparatus and material used were identical to those which were later used for the helium-3 release experiments, and exposure of the uranium metal to helium-3 damage at high temperature recurred during this experiment. Initially slices of high-purity uranium metal were deuterided and degassed until the massive metal was reduced to a fine powder. After all the deuterium had been removed by evacuating the system at 700°C at pressures in the micrometer region, the system was purged once with a small amount of tritium which was removed by the same method used to remove the deuterium.

A predetermined amount of tritium was now added to the uranium powder doubly contained in the high pressure reactor, and composition-pressure-temperature (CPT) points were obtained (Figure 4) by cycling the temperature up and then down stepwise, then recording the pressure and the temperature after they remained at equilibrium for 20-30 min. Equilibrium as here defined implies temperature and pressure changes no greater than ±0.5°C and ±0.2% of observed pressure for the period mentioned. All values for pressure are for desorption. Van't Hoff plots of 1000/T°K as a function of log pressure were then constructed at compositions of $UT_{2.90}$, $UT_{0.04}$, and by extrapolation $UT_{0.00}$. It will be noticed that the isotherms are not flat but are at lower pressures and are closer together at the high composition end of the plot. When van't Hoff plots of 1000/T°K as a function of log P are constructed (Figure 5), it will be noticed that the lines representing the three different compositions while straight are not quite parallel. No amount of redrawing sufficed to render the lines parallel. The conclusion is that ΔH and ΔS vary with composition for the uranium-tritium system.

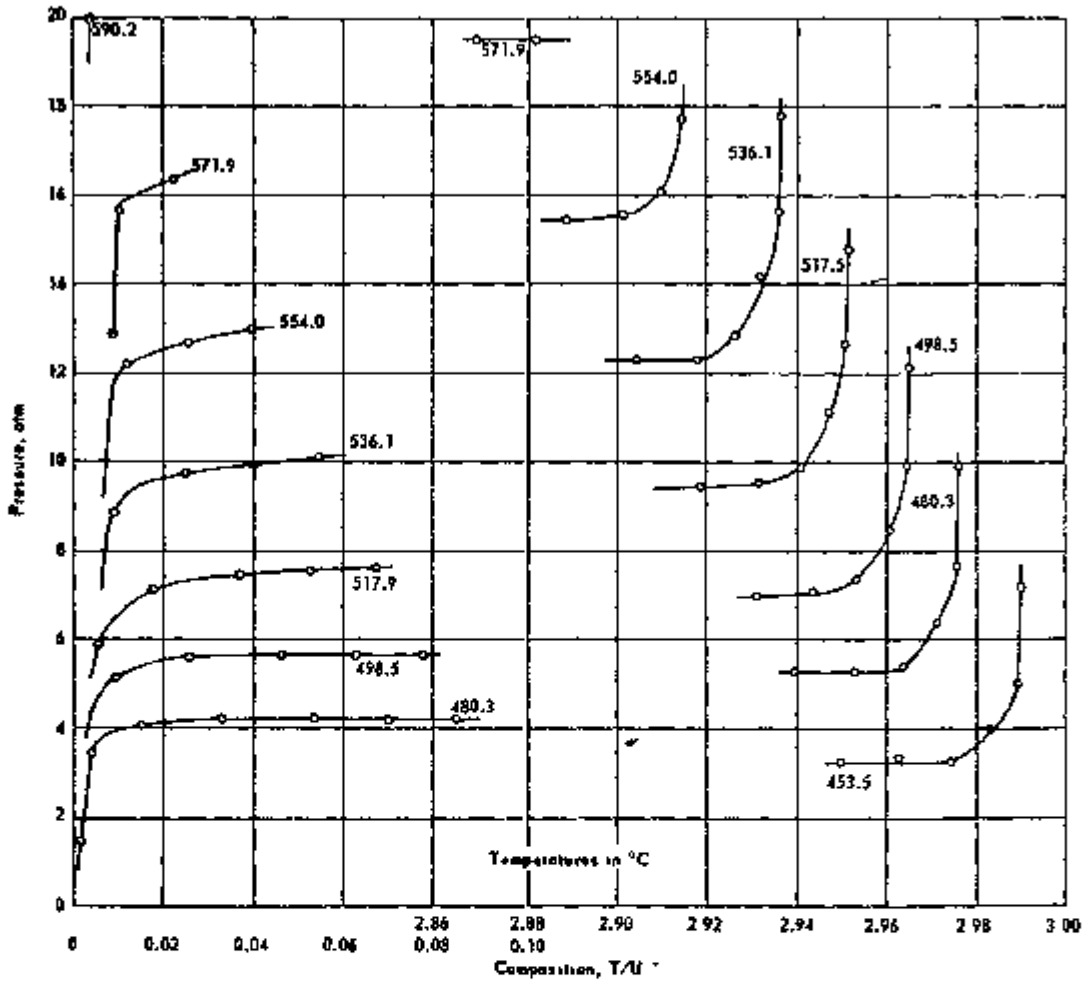

Fig. 4. Composition-Pressure-Temperature Plot of the Uranium-Uranium Tritide System.

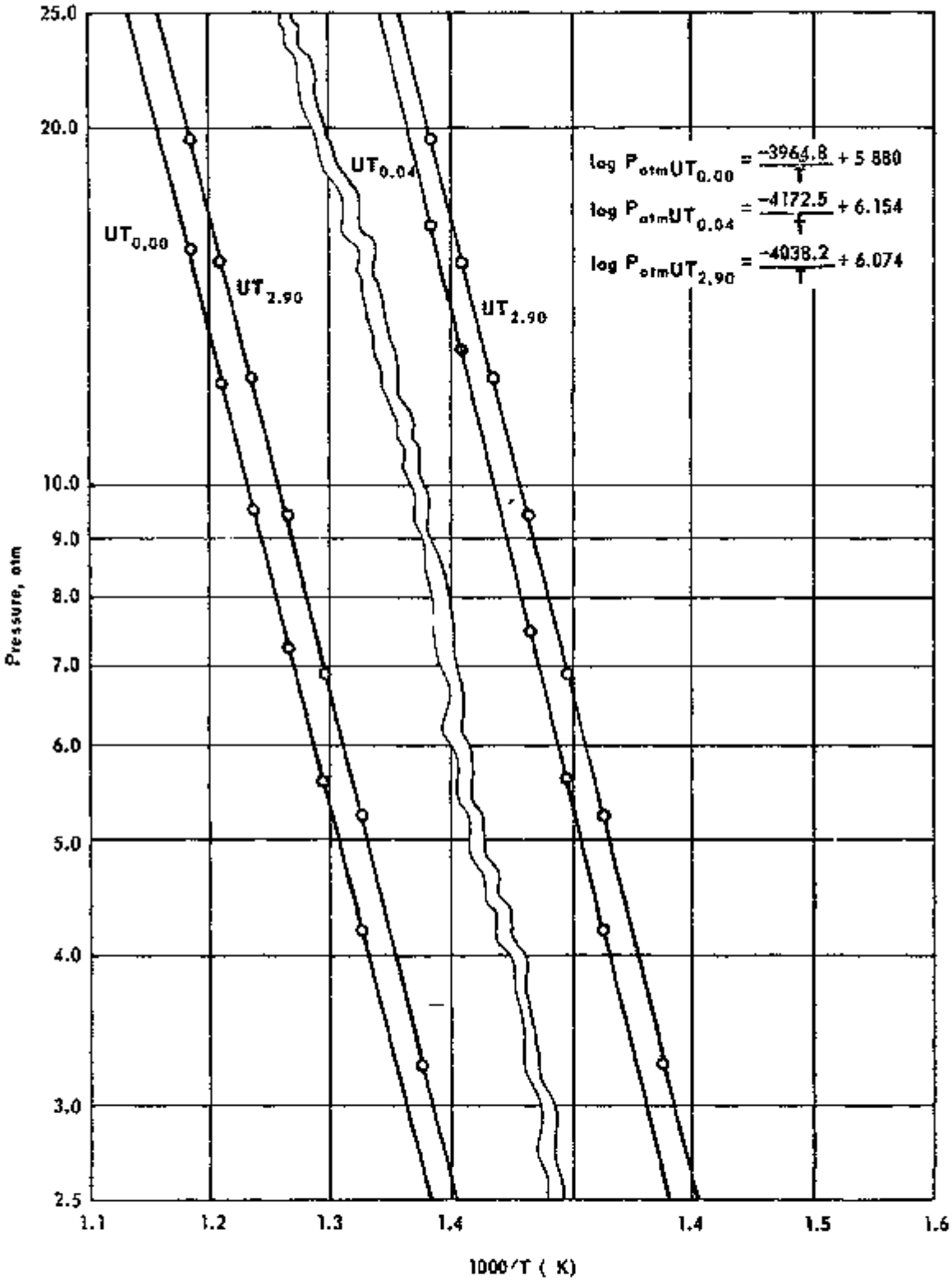

Fig. 5. Comparison of van't Hoff plots for Uranium-Uranium Tritide System.

To test this conclusion, an experiment was performed on the uranium after all the tritium was removed, whereby the system was deuterated to form UD_3 (Figure 6), and van't Hoff data were gained directly by lowering the composition stepwise to one of several values, which were then calculated. Next all valves were closed and the system was cycled up and down twice obtaining seven temperature-pressure equilibrium points during each cycle. When these data had been obtained, the composition was lowered to the next value and the cycles were repeated. All data were corrected for hot and cold volume and for small changes in composition caused by transfer of gas from solid to gaseous phase. In addition, the outer chamber of the doubly enclosed reactor was filled with argon, and this gas was periodically analyzed by mass spectrometry. Any deuterium buildup was noted and appropriate corrections were made. Van't Hoff plots constructed directly from these data were fitted to the equation $\log P\ atm = (-A/T°K) + B$, and ΔH and ΔS values were calculated from these constants and plotted as shown. In most cases the second set of data from each temperature cycle at any composition was slightly lower in value than the first set of data and these values were chosen to avoid any problems that might have been related to the uranium deuteride "remembering" a previous composition by not having relaxed completely to the new D/U ratio. It will be observed that ΔH and ΔS are at their highest when the D/U ratio is relatively low and when there is a high degree of disorder in the uranium lattice coupled with a plethora of sites capable of accepting a deuterium atom. Conversely, values of ΔH and ΔS are lowest when the lattice is almost completely converted to β-phase uranium deuteride at which point the amount of disorder created by the introduction of a new deuterium atom would be lowest, and the competition for bonding sites (the ΔH value) would be at the highest level. It will be observed therefore that ΔH and ΔS in both uranium tritide and uranium deuteride are

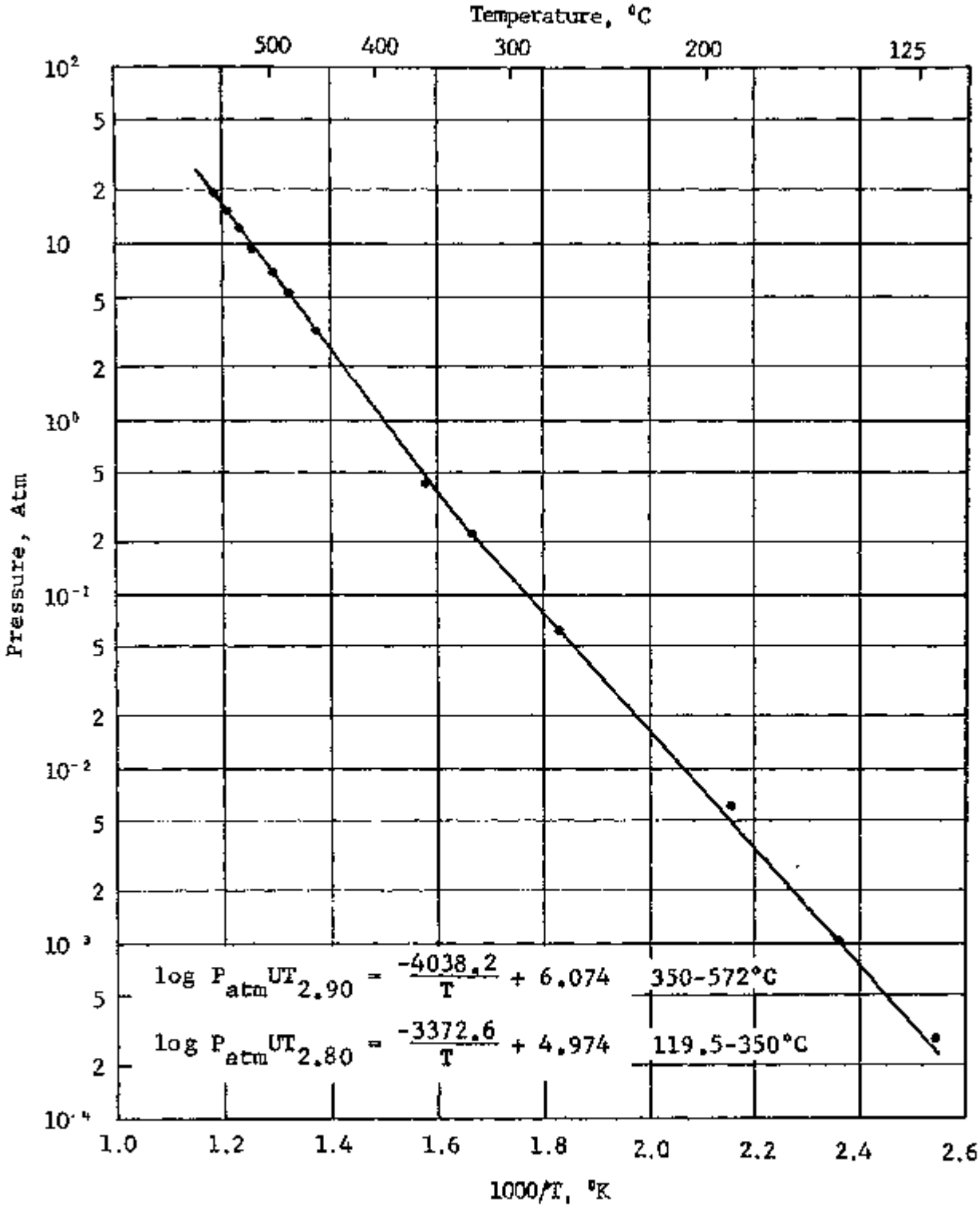

Fig. 6. Thermodynamic Properties as a Function of Composition for the Uranium-Deuterium System.

composition dependent and show similar shifts. I propose that it is erroneous to speak of the "two-phase plateau region" having horizontal parallel isotherms in this and other metal hydride systems. I suggest that minor factors not ordinarily considered in the phase rule may play a significant role in such systems and that the composition of the metal hydride under discussion should always be specified when thermodynamic data are mentioned.

Finally, this system was charged with tritium to form $UT_{2.80}$ and pressure-temperature data were obtained at low values of both in order to extend the van't Hoff plot (Figure 7) of the uranium-tritium system to lower temperatures than heretofore. Equilibrium data were obtained at several points and plotted. The lowest pressure measured, 0.215 mm (2.83×10^{-4} atm), was a difficult one to make because the rate of pressure increase due to helium evolution at this temperature was 0.55 mm/hr, and the time required for the system to come to equilibrium was on the order of 1.0-1.5 hr. It is gratifying that the last point fell near the line drawn through the other points. The slight difference in slope between the two sets of data is not understood at this time. A comparison of the thermodynamic data obtained from the study of these systems (U-D and U-T) with that of other workers is shown in Table 1. The most recent values seem to agree fairly well.

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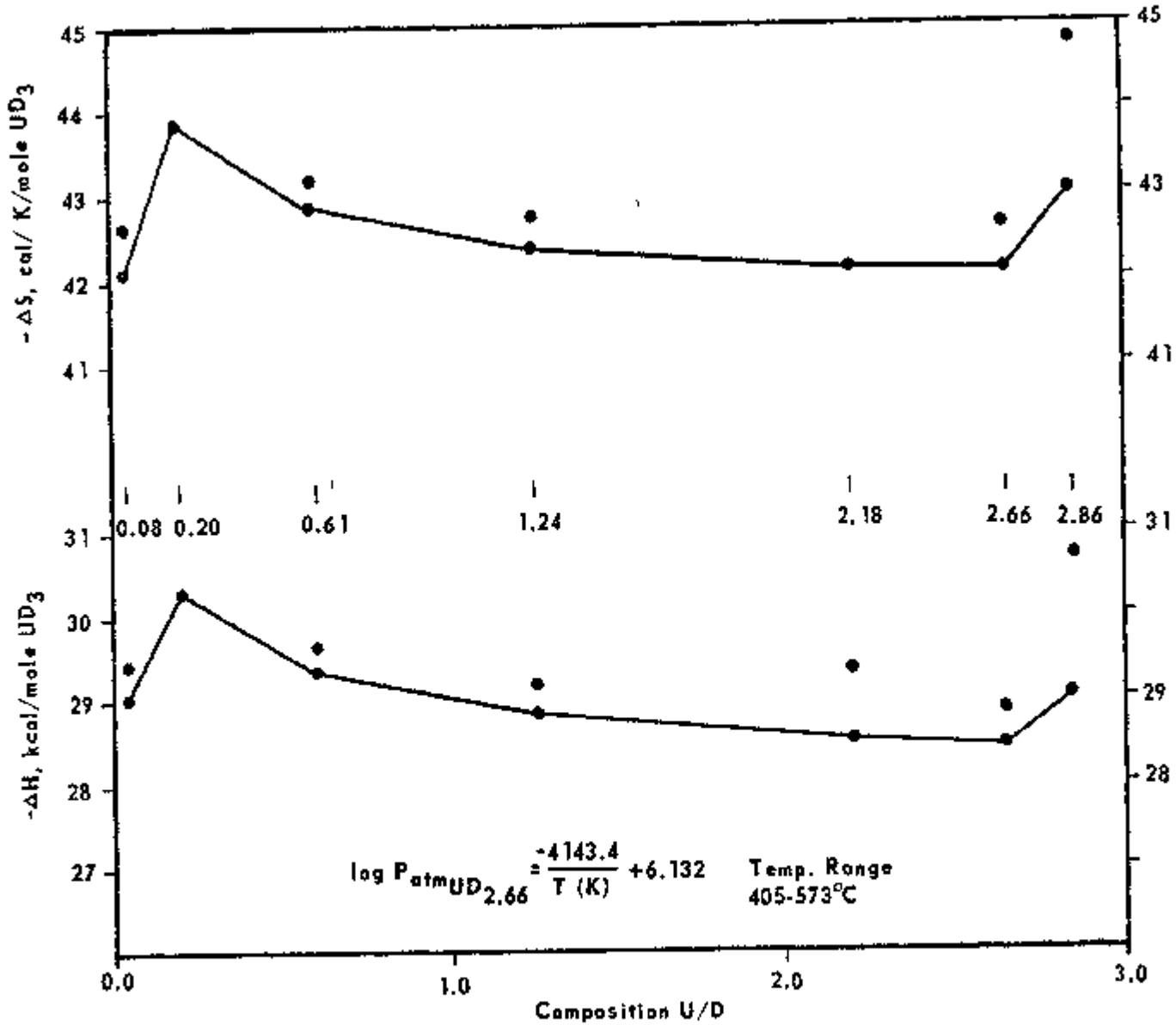

Fig. 7. Van't Hoff Plot for the Uranium-Uranium Tritide System.

Table I. Thermodynamic Properties of Uranium Hydrides

	ΔH_S (kcal/mole)	ΔS_S (cal/°K/mole)
UH_3[a,b,c]	-30.5[f]	-43.4
UH_3[d]	-28.96	-41.43
UD_3[b,c]	-30.8[g]	-44.8
$UD_{2.66}$[e]	-28.4	-42.09
UT_3[a]	-30.75	
$UT_{0.00}$[e]	-27.2	-40.4
$UT_{0.04}$[e]	-28.6	-42.2
$UT_{2.90}$[e]	-27.7	-41.7

[a] Reference 1

[b] Reference 2

[c] Reference 3

[d] Reference 4

[e] Present work by R. S. Carlson

[f] Average of data in References 1, 2, 3

[g] Average of data in References 2 and 3