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THERMODYNAMIC PROPERTIES OF PLUTONIUM HEXAFLUORIDE

A Preliminary Report

by

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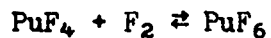
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ABSTRACT

Data obtained in a study of the equilibrium



have been used to determine ΔF , ΔH , and ΔS for the reaction. It was found that ΔH for the reaction is positive, i.e., a higher temperature favors the formation of PuF_6 .

The data reported are preliminary and are contingent upon the establishment of a proof that the method employed to measure the equilibrium does in fact measure the equilibrium.

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A preliminary study of the equilibrium, $\text{PuF}_4 + \text{F}_2 \rightleftharpoons \text{PuF}_6$, at several temperatures has yielded data from which preliminary values for ΔH , ΔF and ΔS of reaction have been calculated. Although more work is required for a complete understanding of the equilibrium process and to improve the accuracy and extend the temperature range of the data, the unusual finding that PuF_6 has a positive heat of reaction (i.e., it is more stable at high temperature than at low), at least over a moderate temperature range, makes it desirable to report the preliminary results at this time.

The finding of a positive heat of reaction for PuF_6 is not original in the present work, but the result was not on a very sound basis previous to the present work. First Brown and Hill¹, later Davidson, Katz and Orlemann² and again later Newton, Fisher, Vaslow and Tevebaugh³ invoked the possibility of a positive heat of formation for PuF_6 to explain perplexing results of attempts to measure the vapor pressure of PuF_6 . Indeed, the latter group of authors concluded this was the case, but since at the time of their investigations PuF_6 had not yet been isolated and identified, high reliability could not be attached to their data.

In the present work the equilibrium $\text{PuF}_4 + \text{F}_2 \rightleftharpoons \text{PuF}_6$ was studied at several temperatures in both the forward and reverse directions by analyzing the gas phase of the equilibrium mixture for both PuF_6 and F_2 . From these equilibrium data, ΔH , ΔF , and ΔS for the reaction have been calculated.

Apparatus and Experimental Procedure.

The reaction chamber for establishing the equilibrium is shown in Figure 1. It consisted of a welded nickel can (2 in. o.d. x 2 in. long) with a special,

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high-temperature, nickel valve at one end. The reaction chamber was connected through the valve by nickel and copper tubing to a manifold to which PuF_6 or F_2 could be supplied and from which samples could be withdrawn for analysis. To study the decomposition of PuF_6 a sample of PuF_6 was distilled into the reaction chamber and the valve closed. The reaction chamber was heated to the temperature at which an experimental point was desired and kept at that temperature for a sufficient time to permit the reacting materials to approach equilibrium. At the end of that time the nickel valve was opened and the volatile contents of the reactor were pumped out through the manifold into the analysis apparatus. It was assumed that these gases represented the equilibrium concentrations of PuF_6 and F_2 . In the analysis apparatus PuF_6 was frozen out in a liquid nitrogen cold trap and later washed out of the cold trap with nitric acid and determined by alpha counting. The F_2 passed through the cold trap into a tube filled with NaBr at 150° where F_2 was converted to Br_2 . The Br_2 was frozen out in a liquid nitrogen cold trap and later allowed to react with a solution of KI to produce a solution of I_2 in KI . This final solution was titrated with 0.1 N thiosulfate to determine I_2 . The molar amount of F_2 emerging from the reaction chamber was then equal to the molar amount of I_2 found in the titration.

At a given temperature, the ratio $\frac{[\text{PuF}_6]}{[\text{F}_2]}$ thus determined was taken as the equilibrium constant K for the reaction, $\text{PuF}_4 + \text{F}_2 \rightleftharpoons \text{PuF}_6$. After several determination of equilibrium constants using PuF_6 as the starting material, enough PuF_4 had been deposited in the reaction chamber so that it was only necessary to add F_2 to permit approach to equilibrium in the forward direction. After addition of F_2 the procedure in these runs was the same as described above.

Results.

The equilibrium constant, K , for the reaction $\text{PuF}_4 + \text{F}_2 \rightleftharpoons \text{PuF}_6$, at each temperature, T , can then be written $K = \frac{[\text{PuF}_6]}{[\text{F}_2]}$. By plotting $\ln K$ against $1/T$ the heat of reaction, ΔH , has been calculated (see Figure 2) from the slope of the line obtained in the plot. The free energy of reaction, ΔF , was obtained by applying the relation $\Delta F = -RT \ln K$, where R is the gas constant. The entropy of reaction, ΔS , was obtained from the relation $\Delta F = \Delta H - T\Delta S$. The equilibrium data and calculated quantities are summarized in Table I.

Table I

Thermodynamic Values for the Reaction $\text{PuF}_4 + \text{F}_2 \rightleftharpoons \text{PuF}_6$

Temperature °C.	$K = \frac{[\text{PuF}_6]}{[\text{F}_2]}$	ΔF Kcal	ΔH Kcal	ΔS e.u.
167	.0001	+8.05		
200	.00025	+7.8		
300	.0021	+7.0		
400	.0055	+6.97		
500	.011	+6.99		
600	.017	+7.03		
167 to 308			+11.5	+7.8
308 to 600			+ 6.77	-0.3

All the quoted values are subject to revision pending proof that the method used to measure the equilibrium does in fact measure the equilibrium. Since plutonium fluorides intermediate in composition between PuF_4 and PuF_6 and of comparatively low stability may exist in the equilibrium mixture, some doubt may be justly raised concerning the accuracy and applicability of the measured equilibrium values. It is thought, however, that such intermediate fluorides, even if shown to exist, would have little or no effect on the measured equilibrium values.

Thus far, the only reasonably reliable equilibrium data were obtained at elevated temperature with PuF_6 present only in the gas phase. The ΔH values derived from these data show an increase from +6.7 to +11.5 kcal/mole with decreasing temperature. The data are preliminary; however, the change appears to take place all at one temperature (more data would be necessary to prove this) rather than gradually over a range of temperatures. This would suggest that the change results from a phase change in the reacting material. One can speculate that at temperatures lower than those for which reasonably reliable equilibrium values have been obtained, additional phase changes may occur and possibly cause the ΔH value to become negative with the consequence of increasing stability for PuF_6 at still lower temperatures. It would be expected⁵ that liquid phase PuF_6 (heat of vaporization = 7.4 kcal) and especially solid phase PuF_6 (heat of sublimation = 12.1 kcal) would provide additional stability for PuF_6 at low temperatures. It is doubtful that such effects even if of appreciable magnitude at very low temperatures could prevent the self-alpha radiodecomposition of PuF_6 unless a catalyst could be found that would allow recombination by a path not requiring as high an activation energy as would be necessary for the direct synthesis. A three month observation of the decomposition of solid PuF_6 in equilibrium with its own vapor at room temperature showed no trend away from the decomposition rate of roughly 1% per day which can well be attributed to self-alpha radiodecomposition^{4,5}.

Bibliography:

1. Report CN-696
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3. Report CN-1783, Aug. 1944
4. A. E. Florin, Report LAMS-1118, Oct. 1950
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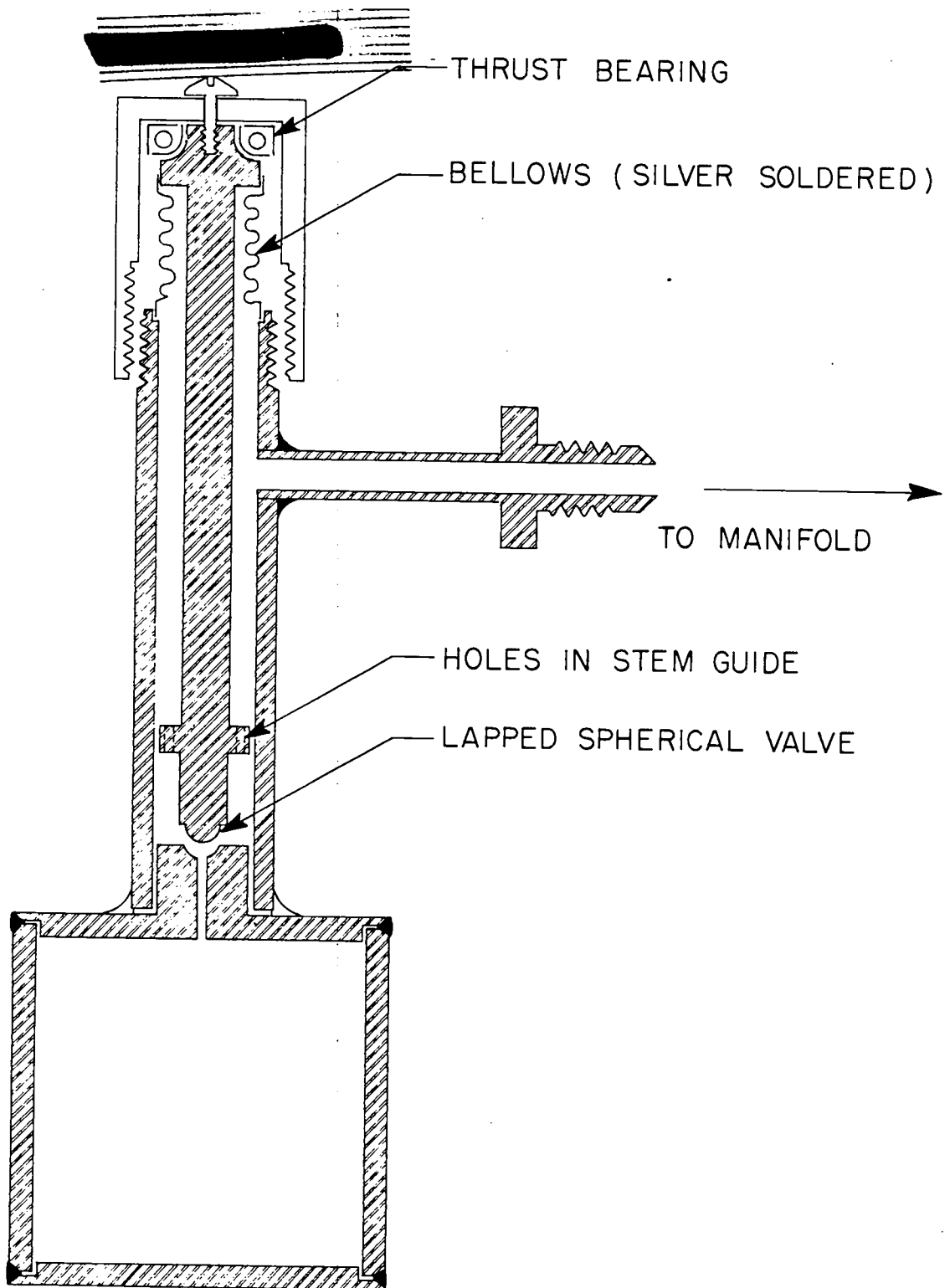


FIG. 1

EQUILIBRIUM CHAMBER MADE OF NICKEL

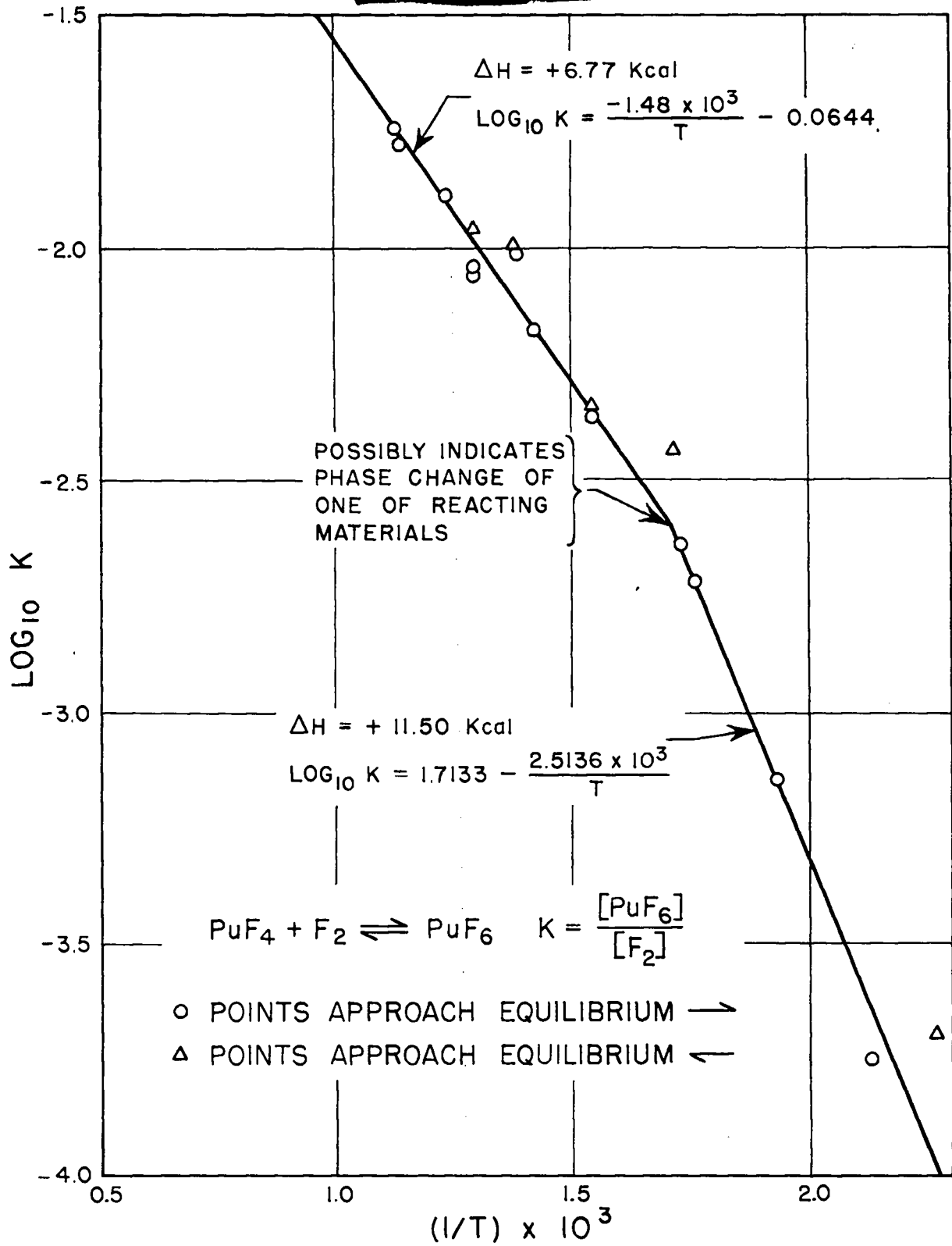


FIG.2
 EQUILIBRIUM DATA FOR PuF₆

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