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THE THERMODYNAMICS OF THE
REDUCTION OF URANIUM COMPOUNDS
TO URANIUM METAL

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July 21, 1952

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ABSTRACT

The thermodynamic study presented in this report was undertaken to guide the evaluation of new processes for the conversions of uranium compounds to uranium metal. The objective has been to show which processes might well justify experimental effort and which processes can be discarded from further consideration on the ground of thermodynamic impracticability. In this work, it has been necessary to evaluate critically the available experimental thermodynamic information so that the degree of reliance in the conclusions reached may be established. Also, because of the nonexistence of certain experimental values, estimations have been necessary. In all cases, these are so identified.

The study shows that:

1. No thermodynamically practical gaseous reductant has been found for reducing any uranium oxide, fluoride, chloride, or bromide to the metal.
2. The reduction of UCl_4 by Al to yield metal and a gaseous co-product was found not to be thermodynamically impractical. No statement of its feasibility can be made, however, in the absence of data on UCl_3 .
3. The reduction of all uranium halides to metal is thermodynamically possible with alkali metals such as sodium and potassium, with alkaline earths such as magnesium and calcium, and probably with the other members of these groups.
4. The reduction of uranium dioxide to metal by the alkali metals is not thermodynamically practical.
5. The reduction of uranium dioxide to metal proceeds, according to thermodynamics, with Ca, Mg, and probably the other alkaline earth metals, also.
6. The only uranium compound which has sufficient thermodynamic decomposition partial pressure to be of interest is UI_4 . Since thermodynamics indicate that this compound would be difficult to prepare from the oxide or other halides, it is unworthy of further consideration.

INTRODUCTION

This study of the thermodynamics of reactions of uranium compounds leading to the formation of uranium metal is a contribution from the Battelle Memorial Institute to the Long Range Survey of feed-material production which is being conducted for the New York Operations Office of the U. S. Atomic Energy Commission by the Catalytic Construction Company.

The objective of the over-all effort is to develop new processes for the production of feed materials, particularly uranium slugs. The attainment of this objective makes necessary the consideration of new chemical conversion routes from purified uranium compounds to metal.

The first step in this over-all program consists of the examination of the thermodynamic feasibility of various reactions which may be suggested. The thermodynamic feasibility of any reaction can be evaluated by consideration of the difference in free energy (a common thermodynamic function) between products and the reactants. A negative value for this difference indicates measurable driving force for formation of an amount of the product. The larger the negative value, the larger the amounts of the products in the reacting system at equilibrium will be. On the other hand, a positive value for the free-energy difference indicates the lack of a driving force to make the reaction occur, and the magnitude of the value gives the amount of work needed to make the reaction proceed. An electrolytic cell for metal recovery, i. e., sodium or aluminum, is an example of a reaction which has a positive free-energy difference for the reduction. The electrical power supplied to the cell provides the work required to make the reaction proceed.

Needless to say, for a desirable solution of the present problem, a reaction having a negative free-energy difference would be desirable. But one which was not spontaneous but could be adapted to something like an efficient electrolytic cell process would be acceptable. In addition, many of the processes which are found to be favorable thermodynamically will eventually be discarded on a practical basis because of difficulties in separating products and slags, etc.

In order for a complete thermodynamic analysis to be made of a given reaction, certain experimental results must be available. For example, specific heats (as a function of the temperature), heats of formation, and absolute entropies of each reactant and product component would make up a complete set of data needed to perform a complete thermodynamic analysis. Alternative sets are possible and in some cases sets of data with one or two minor parts missing can still be utilized by making use of certain empirical approximation methods available in the literature.

Of considerable value in checking the calculations where approximations are used are many of the reduction experiments which have been tried. A great many times even a crude trial will give sufficient information to verify qualitatively the results of a thermodynamic analysis. Also, conversely, calculated thermodynamic results when available, often serve to provide insight into the results of an actual experiment whose results are not clearly evident.

Work progressed by collecting all pertinent information from the literature, organizing it, and critically evaluating it to determine the most reliable values which could be used in the thermodynamic calculations. The calculational procedure followed the method as outlined in Lewis and Randall, Rossini, and many other standard thermodynamics texts. From necessity, in most cases, the free-energy change for a postulated reaction had as a basis the reactant and product components in their standard states, i.e., pure at one atmosphere pressure. In all cases where possible, however, the discussion following the tabulated values considers the probable error involved in using this assumption and discusses the influence on the conclusions reached.

The experimental data reported from the many literature sources at times were significantly controversial. In such cases, it was necessary where possible to select the most probable value by a critical evaluation of the various experimental methods used, and to some extent upon the reputation of the experimenter.

Probably the most reliable method for obtaining basic thermodynamic data is by use of some type of a calorimeter. Spectroscopic information is also quite reliable. Less reliable methods, unless performed with extreme care, are e.m.f., and equilibrium measurements. At times, the desired basic information can be obtained by measuring heats of solution of the various chemical components in a common solvent.

It is generally conceded by most thermodynamicists that experimental values obtained by careful calorimetric or spectroscopic methods are to be preferred over values obtained by other methods in case of disagreement. Comparable values obtained by different methods usually can be considered satisfactory.

One obvious short-coming in the literature is that many investigators fail to report the probable accuracy of their results and others overestimate the accuracy of experimental work. An independent analysis of the data reported shows that the precision inaccuracies should have been reported as about 5 times the value actually given. This is the case, also, with a majority of the thermodynamic literature.

For many of the uranium compounds herein considered, only the results from one group of investigators and one set of experiments are available. Usually, too, these experiments were made by methods of lower accuracy than calorimetric or spectroscopic ones. Consequently, it seems that a considerable amount of checking by independent investigators using different methods is in order.

At the request of the Catalytic Construction Company, attention has been confined to the reduction of uranium oxides and halides, and the report has been organized on the basis of types of reduction processes, as follows:

1. Gaseous reductants yielding gaseous by-products,
2. Nongaseous reductants yielding gaseous by-products,
3. Nongaseous reductants yielding nongaseous by-products, and
4. Thermal decompositions.

Results wherever possible have been tabulated and basic data, accuracy evaluation, sample calculations, etc., are found in the appendices. Complete references are given for all sources of information and these are listed in the bibliography. An attempt has been made to have all information available either in the appendices or bibliography so that any results presented herein may be reproduced if so desired. It is believed that this has been accomplished.

PROCEDURE

In accordance with the objectives of this study, as outlined in the introduction, the following procedure was used. Basic data with regards to the free energies of formation as a function of the temperature were collected from the literature. For most compounds, the desired information of sufficient accuracy was available directly, but for other compounds considerable effort was expended in deriving the desired information. See Appendix C for an example of this type of analysis. At times, considerable doubt of the reported level of accuracy arose. In such cases, the original reports of the experimental work were examined and a critical evaluation and selection was made. A later discussion will consider this point in detail.

With all the free energy of formation information available, it became a simple matter to add or subtract equations by the common technique and obtain an equation representing the desired reduction mechanism.

RESULTS

Results of the reduction mechanisms for uranium oxides and halides studied are given in Tables 1, 2, and 3 (a through d). Table 1 lists the standard free-energy values for reductions by gaseous reductants yielding gaseous by-products, Table 2 lists those for nongaseous reductants yielding gaseous by-products, and Tables 3a through 3d list the values for nongaseous reductants yielding nongaseous by-products. Free energy of formation values on which these are based are tabulated in Appendix B. Sample calculations are shown in Appendix A.

The thermal decomposition of uranium bromide and uranium iodide has also been investigated and the results of this investigation are shown in Figure 1 for uranium bromide and in Figure 2 for uranium iodide. Complete discussion of the results and their reliability is given in the following sections.

Accuracy of Basic Data

The accuracy of the basic data on which the values given in Tables 1 through 3d are based has been considered to be of prime importance in this study. Appendix B lists all of these basic data and gives the references from which they were obtained.

Common practice is to report values and their limits of accuracy which will give a 50-50 chance of the actual value being within the reported limits. Although it is believed that a 99 per cent chance would be more significant, the limits as reported here have better than a 50-50 chance of containing the actual value. The limits would be approximately three times as large if it were desired to increase the probability of the limits containing the actual value to 99 per cent.

The accuracy of the free energy of formation values for the uranium compounds reported herein is probably ± 2 kcal. while it is probably less than ± 1 kcal. for the other compounds reported. These data were taken from existing literature with two notable exceptions.

First, verification of the values on uranium dioxide using the newest, most reliable data led to the work shown in Appendix C. The values for this compound are now believed to be considerably more reliable than any previously reported. The value for the ΔH_f of UO_2 used in this report was taken from the classified literature⁽²⁵⁾ and has been published in the overt literature⁽³⁷⁾ by the same authors since these calculations were made. The

TABLE 1. GASEOUS REDUCTANTS FOR URANIUM OXIDES AND HALIDES WITH GASEOUS BY-PRODUCTS

Reaction	Ref.	ΔF° , kilocalories				Footnotes	
		298°K.	500°K.	1000°K.	1500°K.		
1. $\text{UO}_2(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{U}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$	(2,24)	+137.7	+135.1	+131.1	(+127.4)		
2. $\text{UO}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{U}(\text{s}) + 3\text{H}_2\text{O}(\text{g})$	(1,2,24)	+112.1	+108.0	+100.6	—		
3. $\text{UO}_3 + \text{H}_2(\text{g}) \rightarrow \text{UO}_2 + \text{H}_2\text{O}(\text{g})$	(1,2)	—25.5	—27.2	—30.4	—		
4. $\text{UO}_2(\text{s}) + 2\text{CO}(\text{g}) \rightarrow \text{U}(\text{s}) + 2\text{CO}_2(\text{g})$	(2,24)	+124.0	+125.4	+129.8	(+133.3)	(1)	
5. $\text{UO}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow \text{U}(\text{s}) + 3\text{CO}_2(\text{g})$	(1,2,24)	+91.7	+93.4	+98.8	—	(1)	
6. $\text{UO}_3 + \text{CO}(\text{g}) \rightarrow \text{UO}_2 + \text{CO}_2(\text{g})$	(1,2)	—32.4	—32.0	—31.1	—		
7. $\text{UO}_2(\text{s}) + \text{N}_2\text{H}_4(\text{g}) \rightarrow \text{U}(\text{s}) + \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	(2,13,24)	+99.8	+89.0	+55.1	(+23.9)	(2)	
8. $\text{UO}_3(\text{s}) + 3/2\text{N}_2\text{H}_4(\text{g}) \rightarrow \text{U}(\text{s}) + 3/2\text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$	(1,2,13,24)	+55.3	+35.2	—13.4	—	(2)	
9. $\text{UO}_3 + 1/2\text{N}_2\text{H}_4(\text{g}) \rightarrow \text{UO}_2(\text{s}) + 1/2\text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$	(1,2,13)	—44.5	—51.4	—68.4	—		
10. $\text{UO}_2(\text{s}) + 2\text{F}_2(\text{g}) \rightarrow \text{UF}_4 + \text{O}_2(\text{g})$	(5,24)	—174.3	—166.7	—151.8	(—141.0)		
11. $\text{UO}_2(\text{s}) + 3\text{F}_2(\text{g}) \rightarrow \text{UF}_6(\text{g}) + \text{O}_2(\text{g})$	(5,24)	—238.0	—231.9	—217.0	—		
12. $\text{UO}_2(\text{s}) + 4\text{HF} \rightarrow \text{UF}_4 + 2\text{H}_2\text{O}(\text{g})$	(2,5,7,24)	—25.8	—11.4	+18.9	(+44.0)		
13. $\text{UO}_2(\text{s}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{UCl}_4 + \text{O}_2(\text{g})$	(5,24)	+17.1	+24.1	+39.1	—		
14. $\text{UO}_2(\text{s}) + 4\text{HCl}(\text{g}) \rightarrow \text{UCl}_4 + 2\text{H}_2\text{O}(\text{g})$	(2,5,6,24)	—1.1	+12.3	+43.4	—		
15. $\text{UO}_2(\text{s}) + 2\text{CCl}_4 \rightarrow \text{UCl}_4 + 2\text{COCl}_2(\text{g})$	(5,6,15,24)	—48.5	—53.5	—62.8	—		
16. $\text{UO}_2(\text{s}) + 2\text{Br}_2(\text{g}) \rightarrow \text{UBr}_4 + \text{O}_2(\text{g})$	(5,24)	+56.8	+64.1	+76.9	—		
17. $\text{UO}_2(\text{s}) + 4\text{HBr}(\text{g}) \rightarrow \text{UBr}_4 + 2\text{H}_2\text{O}(\text{g})$	(2,5,14,24)	0.0	+13.7	+42.8	—		
18. $\text{UO}_2(\text{s}) + 2\text{C}(\text{s}) + 2\text{I}_2(\text{g}) \rightarrow \text{UI}_4 + 2\text{CO}(\text{g})$	(2,5)	+46.1	+43.3	+37.0	(+12.1)		
19. $\text{UF}_4 + 2\text{H}_2(\text{g}) \rightarrow \text{U}(\text{s}) + 4\text{HF}$	(5,7)	+163.4	+146.5	+112.2	(+83.4)		
20. $\text{UF}_4 + 1/2\text{H}_2(\text{g}) \rightarrow \text{UF}_3 + \text{HF}$	(5,7)	+17.4	306.2°K. $\text{HF}(1) \rightarrow \text{HF}(\text{g})$	+13.5	+10.3	1233°K. $\text{UF}_4(\text{s}) \rightarrow \text{UF}_4(1)$	+9.6
21. $\text{UF}_3 + 3/2\text{H}_2(\text{g}) \rightarrow \text{U}(\text{s}) + 3\text{HF}$	(5,7)	+146.1	306.2°K. $\text{HF}(1) \rightarrow \text{HF}(\text{g})$	+133.0	+101.9		+73.8
22. $\text{UF}_4 + \text{CO}(\text{g}) \rightarrow \text{U}(\text{s}) + \text{CF}_4 + 1/2\text{O}_2$	(2,5,7)	+301.9		+300.8	+297.2		+298.2 (3)

TABLE 1. (Continued)

Reaction	Ref	ΔF° , kilocalories				Foot- notes
		298°K.	500°K.	1000°K.	1500°K.	
23. $\text{UF}_4 + \text{N}_2\text{H}_4(\text{g}) \rightarrow \text{U}(\text{s}) + \text{N}_2(\text{g}) + 4\text{HF}$	(5,7,13)	+125.5	+98.0	+36.2	-20.1	(4)
24. $\text{UF}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{UF}_4 + 2\text{HF}$	(5,7)	-65.2	306.2°K. $\text{HF}(\text{l}) \rightarrow \text{HF}(\text{g})$ -64.8	-66.2	-	
25. $\text{UF}_6(\text{g}) + 3/2\text{H}_2(\text{g}) \rightarrow \text{UF}_3 + 3\text{HF}$	(5,7)	-47.8	-51.3	-55.9	-	1700°K. $\text{UF}_3(\text{s}) \rightarrow \text{UF}_3(\text{l})$
26. $\text{UF}_6(\text{g}) \rightarrow \text{U}(\text{s}) + 6\text{HF}$	(5,7)	+98.3	+81.8	+46.0	-	
27. $\text{UF}_6(\text{g}) + 3/2\text{CO}(\text{g}) \rightarrow \text{U}(\text{s}) + 3/2\text{CF}_4 + 3/4\text{O}_2(\text{g})$	(2,5,7)	+306.0	+313.2	+323.5	-	(3)
28. $\text{UF}_6(\text{g}) + 3/2\text{N}_2\text{H}_4(\text{g}) \rightarrow \text{U}(\text{s}) + 3/2\text{N}_2(\text{g}) + 6\text{HF}$	(5,7,13)	+41.4	+9.0	-68.0	-	(4)
29. $\text{UCl}_4 + 1/2\text{H}_2(\text{g}) \rightarrow \text{UCl}_3 + \text{HCl}$	(5,6)	+9.7	+5.8	863°K. $\text{UCl}_4(\text{s}) \rightarrow \text{UCl}_4(\text{l})$ -1.9	1115°K. $\text{UCl}_3(\text{s}) \rightarrow \text{UCl}_3(\text{l})$ -	
30. $\text{UCl}_4 + 2\text{H}_2(\text{g}) \rightarrow \text{U}(\text{s}) + 4\text{HCl}$	(5,14)	+138.7	+122.7	+87.5	1065°K. $\text{UCl}_4(\text{l}) \rightarrow \text{UCl}_4(\text{g})$ -	
31. $\text{UCl}_4 + 2\text{CO}(\text{g}) \rightarrow \text{U}(\text{s}) + 2\text{COCl}_2(\text{g})$	(2,5,15)	+164.2	+158.3	+146.8	-	(5)
32. $\text{UCl}_4 + \text{N}_2\text{H}_4(\text{g}) \rightarrow \text{U}(\text{s}) + \text{N}_2(\text{g}) + 4\text{HCl}(\text{g})$	(5,6,13)	+100.9	+74.4	+11.7	-	
33. $\text{UCl}_4 + 5\text{N}_2\text{H}_4(\text{g}) \rightarrow \text{U}(\text{s}) + \text{N}_2(\text{g}) + 4\text{N}_2\text{H}_4 \cdot \text{HCl}(\text{s})$	(5,13,26)	+9.6	400°K. +20.4	-	-	
34. $\text{UCl}_4 + 5\text{N}_2\text{H}_4(\text{g}) \rightarrow \text{UN} + 1/2\text{N}_2(\text{g}) + 4\text{N}_2\text{H}_4 \cdot \text{HCl}(\text{s})$	(5,13,26)	-65.4	-54.6	-	-	
35. $\text{UBr}_4 + 2\text{H}_2(\text{g}) \rightarrow \text{U}(\text{s}) + 4\text{HBr}(\text{g})$	(5,14)	+137.7	+121.5	792°K. $\text{UBr}_4(\text{s}) \rightarrow \text{UBr}_4(\text{l})$ +88.3	-	
36. $\text{UBr}_4 + \text{N}_2\text{H}_4(\text{g}) \rightarrow \text{U}(\text{s}) + \text{N}_2(\text{g}) + 4\text{HBr}$	(5,13,14)	+99.8	+73.0	+12.3	-	(6)

(1) The reaction as written neglects the formation of uranium carbide which is a probable product.

(2) There is a probability of the formation of the uranium nitride and at low temperatures of the hydrazine hydrate which will thereby require more hydrazine to complete the reaction as written.

(3) A possible product is also COF_2 . No thermodynamic information is available, however, which will permit its consideration.

(4) Uranium nitride and hydrazine hydrofluoride salt formation have been disregarded. Uranian compounds and hydrazine are known to form complexes⁽³⁹⁾.

(5) Formation of uranium carbide and the possibility of the products being $\text{U}(\text{s}) + \text{CCl}_4 + \text{CO}_2$ have been disregarded.

(6) Uranium nitride and hydrazine hydrobromide salt formation have been disregarded.

TABLE 2. NONGASEOUS REDUCTANTS FOR URANIUM OXIDES AND HALIDES YIELDING GASEOUS BY-PRODUCTS

Reaction	Ref.	ΔF° , kilocalories				Foot- notes
		298°K.	500°K.	1000°K.	1500°K.	
37. $\text{UO}_2(\text{s}) + \text{C}(\text{s}) \rightarrow \text{U}(\text{s}) + \text{CO}_2(\text{g})$	(2,24)	+152.7	+145.5	+128.5	(+111.3)	(1)
38. $\text{UO}_2(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{U}(\text{s}) + 2\text{CO}(\text{g})$	(2,24)	+181.3	+165.5	+155.4	(+104.5)	(1)
39. $\text{UO}_2(\text{s}) + 2\text{CaH}_2(\text{s}) \rightarrow \text{U}(\text{s}) + \text{CaO}(\text{s}) + 2\text{H}_2$	(2,3,24,28)	+28.0	+16.8	-11.2	—	(2)
40. $\text{UO}_3 + 3/2\text{C}(\text{s}) \rightarrow \text{U}(\text{s}) + 3/2\text{CO}_2(\text{g})$	(1,2,24)	+134.6	+123.5	+96.8	—	(1)
41. $\text{UO}_3 + 3\text{C}(\text{s}) \rightarrow \text{U}(\text{s}) + 3\text{CO}(\text{g})$	(1,2,24)	+177.6	+153.5	+94.9	—	(1)
42. $\text{UF}_4 + \text{C}(\text{s}) \rightarrow \text{U}(\text{s}) + \text{CF}_4(\text{g})$	(5,7)	145°K. $\text{CF}_4(\text{l}) \rightarrow \text{CF}_4(\text{g})$ +269.1	+263.6	+249.3	1233°K. $\text{UF}_4(\text{s}) \rightarrow \text{UF}_4(\text{l})$ +239.9	(1)
43. $\text{UF}_4 + 2\text{CaH}_2(\text{s}) \rightarrow \text{U}(\text{s}) + 2\text{CaF}_2(\text{s}) + 2\text{H}_2$	(5,7,14,28)	-63.2	-78.0	-106.0	—	(3)
44. $\text{UF}_4 + \text{Si}(\text{s}) \rightarrow \text{U}(\text{s}) + \text{SiF}_4(\text{g})$	(5,7)	208°K. $\text{SiF}_4(\text{l}) \rightarrow \text{SiF}_4(\text{g})$ +61.9	+53.6	+39.3	+27.0	
45. $\text{UCl}_4 + \text{C}(\text{s}) \rightarrow \text{U}(\text{s}) + \text{CCl}_4$	(5,6)	+213.4	349.9°K. $\text{CCl}_4(\text{l}) \rightarrow \text{CCl}_4(\text{g})$ +207.3	863°K. $\text{UCl}_4(\text{s}) \rightarrow \text{UCl}_4(\text{l})$ +192.4	1065°K. $\text{UCl}_4(\text{l}) \rightarrow \text{UCl}_4(\text{g})$ —	(1)
46. $\text{UCl}_4 + 2\text{CaH}_2(\text{s}) \rightarrow \text{U}(\text{s}) + 2\text{CaCl}_2(\text{s}) + 2\text{H}_2$	(5,6,14,28)	-60.3	-74.3	-108.0	—	(4)
47. $\text{UCl}_4(\text{l}) + 4/3\text{Al} \rightarrow \text{U}(\text{s}) + 2/3\text{Al}_2\text{Cl}_6(\text{g})$	(1)	—	453°K. $\text{Al}_2\text{Cl}_6(\text{s}) \rightarrow \text{Al}_2\text{Cl}_6(\text{g})$ —	863°K. +26.0	—	(5,6)
48. $\text{UCl}_4(\text{l}) + 4/3\text{Al}(\text{l}) \rightarrow \text{U}(\text{s}) + 4/3\text{AlCl}_3(\text{g})$	(5)	—	455°K. $\text{AlCl}_3(\text{l}) \rightarrow \text{AlCl}_3(\text{g})$ —	933°K. $\text{Al}_2\text{Cl}_6 \rightarrow \text{AlCl}_3$ +22.5	—	(5,6)
49. $\text{UCl}_4 + 2\text{Fe} \rightarrow \text{U}(\text{s}) + 2\text{FeCl}_2$	(1,5,16,)	—	—	863°K. +77.8	+70.9	+69.0
50. $\text{UCl}_4 + \text{Si} \rightarrow \text{U}(\text{s}) + \text{SiCl}_4$	(5,6)	+92.9	330.2°K. $\text{SiCl}_4(\text{l}) \rightarrow \text{SiCl}_4(\text{g})$ +85.8	+70.2	—	

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TABLE 2. (Continued)

Reaction	Ref.	ΔF° , kilocalories				Foot-
		298° K.		500° K.	1000° K.	notes
51. $\text{UBr}_4 + \text{C(s)} \rightarrow \text{U(s)} + \text{CBr}_4(\text{g})$	(5,11)	+198.1		+189.8	792°K. $\text{UBr}_4(\text{s}) \rightarrow \text{UBr}_4(\text{l})$	— (1)
52. $\text{UBr}_4 + \text{Si} \rightarrow \text{U(s)} + \text{SiBr}_4$	(5,11)	+96.2	426°K. $\text{SiBr}_4(\text{l}) \rightarrow \text{SiBr}_4(\text{g})$	+91.0	—	—
53. $\text{UBr}_4 + 4/3\text{Al} \rightarrow \text{U(s)} + 4/3\text{AlBr}_3$	(5,11)	+24.4	370°K. $\text{AlBr}_3(\text{s}) \rightarrow \text{AlBr}_3(\text{l})$	+30.1	536°K. $2\text{AlBr}_3(\text{l}) \rightarrow \text{Al}_2\text{Br}_6(\text{g})$	+36.9 — (5)
					932° K. $\text{Al(s)} \rightarrow \text{Al(l)}$	
54. $\text{UBr}_4 + 2\text{Ca} \rightarrow \text{U(s)} + 2\text{CaBr}_2$	(5,11)	-126.5		-125.9	-121.7	1038°K. $\text{CaBr}_2(\text{s}) \rightarrow \text{CaBr}_2(\text{l})$
						1082°K. $\text{CaBr}_2(\text{l}) \rightarrow \text{CaBr}_2(\text{g})$
						1125°K. $\text{Ca(s)} \rightarrow \text{Ca(l)}$

- (1) Neglects the possible formation of uranium carbide.
- (2) Calcium oxide forms a compound with UO_2 which would complicate this analysis (see reference); uranium hydride is also a possible product.
- (3) Possible combination of CaF_2 with UF_4 is neglected; uranium hydride formation should be possible.
- (4) Hydride formation possible; possible combination of CaCl_2 with UCl_4 is neglected.
- (5) Because of insufficient information, no allowance could be made for the aluminum-uranium alloy; intermetallic compound formation could increase the driving force of the reaction considerably.
- (6) See Appendix D for detailed information.

TABLE 3a. NONGASEOUS REDUCTANTS FOR URANIUM DIOXIDE YIELDING NONGASEOUS BY-PRODUCTS

Reaction	Ref.	ΔF° , kilocalories				Footnotes
		298°K.	500°K.	1000°K.	1500°K.	
55. $\text{UO}_2(\text{s}) + 4\text{Na} \rightarrow \text{U}(\text{s}) + 2\text{Na}_2\text{O}(\text{s})$	(3,24)	+68.0	371°K. $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{l})$ +73.1	+86.7	1153°K. $\text{Na}(\text{l}) \rightarrow \text{Na}(\text{g})$ (+133.7)	
56. $\text{UO}_2(\text{s}) + 4\text{K} \rightarrow \text{U}(\text{s}) + 2\text{K}_2\text{O}(\text{s})$	(10,24)	+93.5	335.5°K. $\text{K}(\text{s}) \rightarrow \text{K}(\text{l})$ —	—	1058°K. $\text{K}(\text{l}) \rightarrow \text{K}(\text{g})$ —	
57. $\text{UO}_2(\text{s}) + 2\text{Mg} \rightarrow \text{U}(\text{s}) + 2\text{MgO}(\text{s})$	(3,24)	-29.9	923°K. $\text{Mg}(\text{s}) \rightarrow \text{Mg}(\text{l})$ -26.9	-19.1	1380°K. $\text{Mg}(\text{l}) \rightarrow \text{Mg}(\text{g})$ -5.5	
58. $\text{UO}_2(\text{s}) + 2\text{Ca} \rightarrow \text{U}(\text{s}) + 2\text{CaO}(\text{s})$	(3,24)	-41.6	-38.7	-31.2	1124°K. $\text{Ca}(\text{s}) \rightarrow \text{Ca}(\text{l})$ -24.2	(1)
59. $\text{UO}_2(\text{s}) + 2\text{CaH}_2 \rightarrow \text{U}(\text{s}) + 2\text{CaO}(\text{s}) + 2\text{H}_2$	(2,3,24,28)	+28.0	+16.8	-11.2	1087°K. $\text{CaH}_2(\text{s}) \rightarrow \text{CaH}_2(\text{l})$ —	(2)
60. $\text{UO}_2(\text{s}) + 4/3\text{Al} \rightarrow \text{U}(\text{s}) + 2/3\text{Al}_2\text{O}_3(\text{s})$	(17,24)	-4.3	932°K. $\text{Al}(\text{s}) \rightarrow \text{Al}(\text{l})$ -1.3	+6.9	(+15.8)	(3)
61. $\text{UO}_2(\text{s}) + 2\text{Fe}(\text{s}) \rightarrow \text{U}(\text{s}) + 2\text{FeO}(\text{s})$	(3,24)	+129.7	+129.2	+127.8	1693°K. (+126.1) $\text{FeO}(\text{s}) \rightarrow \text{FeO}(\text{l})$	
62. $\text{UO}_2(\text{s}) + \text{Si}(\text{s}) \rightarrow \text{U}(\text{s}) + \text{SiO}_2(\text{s})$	(18,24)	+58.5	+60.0	+64.3	(+67.5)	
63. $\text{UO}_2(\text{s}) + 2\text{Ca}(\beta) + 2\text{SiO}_2 \rightarrow \text{U}(\text{s}) + 2\text{CaSiO}_3(\text{s})$	(8,27,26)			-80.6	1124°K. $\text{Ca}(\beta) \rightarrow \text{Ca}(\text{l})$ -95.5	(4)

(1) Calcium oxide and UO_2 combine chemically. (See Ref. 35.)

(2) See Note 1; also CaH_2 decomposes at 948°K.

(3) Effect of the uranium-aluminum alloy formation cannot be evaluated; intermetallic compound formation could increase the driving force of the reduction reaction considerably.

(4) The reduction of SiO_2 to Si by Ca is a possible, complicating side reaction.

TABLE 3b. NONGASEOUS REDUCTANTS FOR URANIUM TETRAFLUORIDE YIELDING NONGASEOUS BY-PRODUCTS

Reaction	Ref.	ΔF° , kilocalories				Footnotes
		298°K.	500°K.	1000°K.	1500°K.	
64. $\text{UF}_4 + 4\text{Na} \rightarrow \text{U(s)} + 4\text{NaF}$	(5,7)	-95.8	371°K. $\text{Na(s)} \rightarrow \text{Na(l)}$ -86.5	-71.0	1153°K. $\text{Na(l)} \rightarrow \text{Na(g)}$ -35.0 1265°K. $\text{NaF(s)} \rightarrow \text{NaF(l)}$	
65. $\text{UF}_4 + 4\text{K} \rightarrow \text{U(s)} + 4\text{KF}$	(5,7)	-87.3	335.5°K. $\text{K(s)} \rightarrow \text{K(l)}$ -84.9	-67.9	1058°K. $\text{K(l)} \rightarrow \text{K(g)}$ -24.4 1133°K. $\text{KF(s)} \rightarrow \text{KF(l)}$	
66. $\text{UF}_4 + 2\text{Mg} \rightarrow \text{U(s)} + 2\text{MgF}_2\text{(s)}$	(5,7)	-82.4	-79.1	923°K. $\text{Mg(s)} \rightarrow \text{Mg(l)}$ -69.0	1233°K. $\text{UF}_4\text{(s)} \rightarrow \text{UF}_4\text{(l)}$ -51.0	1536°K. $\text{MgF}_2\text{(s)} \rightarrow \text{MgF}_2\text{(l)}$
67. $\text{UF}_4 + 2\text{Ca} \rightarrow \text{U(s)} + 2\text{CaF}_2\text{(s)}$	(5,7)	-132.8	-133.5	-126.4	1124°K. $\text{Ca(s)} \rightarrow \text{Ca(l)}$ -114.6	1691°K. $\text{CaF}_2\text{(s)} \rightarrow \text{CaF}_2\text{(l)}$
68. $\text{UF}_4 + \text{CaH}_2\text{(s)} \rightarrow \text{U(s)} + 2\text{HF} + \text{CaF}_2$	(5,7,14,28)	+49.7	306.2°K. $\text{HF(l)} \rightarrow \text{HF(g)}$ +34.2	+3.3	1087°K. $\text{CaH}_2\text{(s)} \rightarrow \text{CaH}_2\text{(l)}$ —	
69. $\text{UF}_4 + 4/3\text{Al} \rightarrow \text{U(s)} + 4/3\text{AlF}_3$	(5,7)	+29.8	+30.7	932°K. $\text{Al(s)} \rightarrow \text{Al(l)}$ +34.0	1313°K. $\text{AlF}_3\text{(s)} \rightarrow \text{AlF}_3\text{(l)}$ +44.0	(1)
70. $\text{UF}_4 + 2\text{Fe} \rightarrow \text{U(s)} + 2\text{FeF}_2$	(5,7)	+106.0	+105.5	+109.0	1273°K. $\text{FeF}_2\text{(s)} \rightarrow \text{FeF}_2\text{(l)}$ +110.0	

(1) Effect of the uranium-aluminum alloy formation has been neglected because of insufficient quantitative information. Despite the seeming unfavorableness of the thermodynamic results, qualitative experimental work at Battelle has shown that a uranium-aluminum alloy at least up to 30% uranium can be obtained from reduction of UF_4 by aluminum in the presence of cryolite.

TABLE 3c. NONGASEOUS REDUCTANTS FOR URANIUM TETRACHLORIDE YIELDING NONGASEOUS BY-PRODUCTS

Reaction	Ref.	ΔF° , kilocalories				Foot- notes	
		298°K.	300°K.	1000°K.	1500°K.		
71. $\text{UCl}_4 + 4\text{Na} \rightarrow \text{U(s)} + 4\text{NaCl}$	(5,6)	-137.8	371°K. $\text{Na(s)} \rightarrow \text{Na(l)}$ -133.8	863°K. $\text{UCl}_4\text{(s)} \rightarrow \text{UCl}_4\text{(l)}$ -121.3	1073°K. $\text{NaCl(s)} \rightarrow \text{NaCl(l)}$ — 1153°K. $\text{Na(l)} \rightarrow \text{Na(g)}$ 1049°K.	—	
72. $\text{UCl}_4 + 4\text{K} \rightarrow \text{U(s)} + 4\text{KCl}$	(5,10)	-161.1	335.5°K. $\text{K(s)} \rightarrow \text{K(l)}$ -155.9	—	-139.5	$\text{KCl(s)} \rightarrow \text{KCl(l)}$ — 1058°K. $\text{K(l)} \rightarrow \text{K(g)}$ 1065°K. $\text{UCl}_4\text{(l)} \rightarrow \text{UCl}_4\text{(g)}$	
73. $\text{UCl}_4 + 2\text{Mg} \rightarrow \text{U(s)} + 2\text{MgCl}_2$	(5,6)	-53.1	-50.9	923°K. $\text{Mg(s)} \rightarrow \text{Mg(l)}$ -45.9 987°K. $\text{MgCl}_2\text{(s)} \rightarrow \text{MgCl}_2\text{(g)}$	—	1685°K. $\text{MgCl}_2\text{(l)} \rightarrow \text{MgCl}_2\text{(g)}$	
74. $\text{UCl}_4 + 2\text{Ca} \rightarrow \text{U(s)} + 2\text{CaCl}_2$	(5,6)	-129.9	-129.7	—	-127.9	1055°K. $\text{CaCl}_2\text{(s)} \rightarrow \text{CaCl}_2\text{(l)}$ — 1124°K. $\text{Ca(s)} \rightarrow \text{Ca(l)}$	
75. $\text{UCl}_4 + \text{CaH}_2\text{(s)} \rightarrow \text{U(s)} + 2\text{HCl(g)} + \text{CaCl}_2$	(5,6,14,28)	+39.2	+24.2	—	-10.2	1045°K. $\text{CaCl}_2\text{(s)} \rightarrow \text{CaCl}_2\text{(l)}$ — 1087°K. $\text{CaH}_2\text{(s)} \rightarrow \text{CaH}_2\text{(l)}$ 1124°K. $\text{Ca(s)} \rightarrow \text{Ca(l)}$	
76. $\text{UCl}_4\text{(l)} + 4/3\text{Al(s)} \rightarrow \text{U(s)} + 2/3\text{Al}_2\text{Cl}_6\text{(g)}$	(1)	—	—	863°K. +26.0	—	—	(1)
77. $\text{UCl}_4\text{(l)} + 4/3\text{Al(l)} \rightarrow \text{U(s)} + 4/3\text{AlCl}_3\text{(g)}$	(5)	—	—	—	+22.5	—	(1)

(1) Existence of the uranium-aluminum alloy has been neglected because of insufficient quantitative information. See also Appendix D for detailed information.

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TABLE 3d. NONGASEOUS REDUCTANTS FOR URANIUM TETRABROMIDE YIELDING NONGASEOUS BY-PRODUCTS

Reaction	Ref.	ΔF° , kilocalories				Foot- notes
		298° K.	500° K.	1000° K.	1500° K.	
78. $\text{UBr}_4 + 4\text{Na} \rightarrow \text{U(s)} + 4\text{NaBr}$	(5,11)	-145.6	371°K. $\text{Na(s)} \rightarrow \text{Na(l)}$ -142.0	792°K. $\text{UBr}_4\text{(s)} \rightarrow \text{UBr}_4\text{(l)}$ -126.9	1028°K. $\text{NaBr(s)} \rightarrow \text{NaBr(l)}$ — 1153°K. $\text{Na(l)} \rightarrow \text{Na(g)}$	
79. $\text{UBr}_4 + 4\text{K} \rightarrow \text{U(s)} + 4\text{KBr}$	(5,11)	-174.6	335.5°K. $\text{K(s)} \rightarrow \text{K(l)}$ -170.4	-154.5	1003°K. $\text{KBr(s)} \rightarrow \text{KBr(l)}$ — 1058°K. $\text{K(l)} \rightarrow \text{K(g)}$	14
80. $\text{UBr}_4 + 2\text{Mg} \rightarrow \text{U(s)} + 2\text{MgBr}_2$	(5,11)	-50.6	-50.5	923°K. $\text{Mg(s)} \rightarrow \text{Mg(l)}$ -47.3 983°K. $\text{MgBr}_2\text{(s)} \rightarrow \text{MgBr}_2\text{(l)}$	—	
81. $\text{UBr}_4 + 2\text{Fe} \rightarrow \text{U(s)} + 2\text{FeBr}_2$	(5,11)	+75.2	+74.2	+71.7	—	

FIGURE 1. THERMAL DECOMPOSITION OF URANIUM TETRABROMIDE

FIGURE 2. THERMAL DECOMPOSITION OF URANIUM TETRAIODIDE

difference in the ΔH_f value given in the overt and classified literature is within the experimental error of measurement. Second, so many inconsistencies existed in the literature with regards to aluminum chloride formation that the analysis discussed in detail in Appendix D was performed. Values in this report are based upon this work.

In general, it may be said that none of the conclusions reached in this report will be affected by the minor inaccuracies existing in the basic data. However, any possibilities of such effects are considered in detail in the following sections where the individual reactions are discussed.

Gaseous Reductants Yielding Gaseous By-Products

Without exception, none of the gaseous reducing agents considered show a favorable thermodynamic driving force for the formation of uranium metal. In some cases, the higher oxidation states can be reduced to lower oxidation states, i. e., Reaction 3, UO_3 reduction to UO_2 by means of hydrogen, but in no case can metal recovery be considered favorable.

The values in Table 1 are all valid to within approximately ± 3 kcal., and the magnitude of this probable error is not sufficient to affect the conclusion of unfavorableness of these reductions.

Only one statement has been found in all the literature investigated which is contradictory to the above conclusions. Dawson, Ingram, and Bircumshaw⁽³⁴⁾ state: "A . . . calculation for the reaction $UF_4 + 2H_2 = U + 4HF$ proves that . . . at $25^\circ(C.)$ the equilibrium lies well to the left-hand side, but this is reversed in the region of $1000^\circ(C.)$." It has been impossible to verify this statement and it is believed that it is without foundation in fact. However, if the authors quoted have verified this statement by quantitative experiment, it would mean that the present thermodynamic analysis is in error.

As will be seen from the footnotes of Table 1, the formation of other probable products other than the desired ones are neglected. In most cases, this is because of a lack of interest in the alternative product and the thermodynamic unfavorableness of the reaction to proceed as shown. In other cases, principally Reactions 22, 23, 28, 29, 31, and 36, there is insufficient thermodynamic information on which to consider the formation of the alternative products. It is quite likely that these alternative reactions would be thermodynamically favorable.

Nongaseous Reactant Yielding Gaseous By-Products

All reactions were chosen for inclusion in Table 2 which had any by-products gaseous below a temperature of 1500°K. Of interest are Reactions 43, 46, and 54. Reactions 43 and 46 represent the reduction of UF_4 and UCl_4 , respectively, with calcium hydride. Hydrogen is the gaseous by-product. They may not, however, offer any advantages over the calcium reduction of these compounds as reported in Reactions 67 and 74 in the preceding tables, which appear equally favorable thermodynamically and have been used in practice.

The only other favorable reaction of this classification is the reduction of UBr_4 with calcium metal. The by-product, $CaBr_2$ is gaseous above a temperature of 1082°K. This might be a significant proposed method if a simple method existed for the preparation of UBr_4 from the oxides or the higher halides. All methods available need several steps involving intermediate compounds such as UN or UC_2 .

Nongaseous Reductants Yielding Nongaseous By-Products

Uranium Oxides

Calcium and magnesium metal are both good thermodynamic possibilities for the reduction of uranium oxides to the metal as shown by Reactions 57 and 58 in Table 3a. Only one complicating factor exists. Calcium oxide, the by-product of the reaction, and UO_2 have been found to combine chemically⁽³⁵⁾. This may explain in part the unsatisfactory yields which have been obtained in experiments using this reducing agent.

Uranium Fluoride

Sodium, potassium, calcium, and magnesium are found to be thermodynamically satisfactory reducing agents for UF_4 as shown by Reactions 64, 65, 66, and 67 in Table 3b. As far as can be determined by studying the thermodynamics, no significant advantage is seen for any of these four reducing agents. It remains for experimental work to be done to evaluate properly the kinetics and other factors of these reactions.

Experimental evidence at Battelle⁽³⁸⁾ has shown that a uranium-aluminum alloy up to 30 per cent uranium can be obtained by reduction of uranium tetrafluoride with metallic aluminum. This is not indicated by the thermodynamic results of Reaction 69. A complicating factor in the analysis of the experimental results was that the reduction took place in the presence

of cryolite ($3\text{NaF} \cdot \text{AlF}_3$). This seeming disagreement might be explained by the difference in products between the postulated thermodynamic reaction and the experimental one. Experimental work at Battelle⁽⁴⁰⁾ on the uranium-aluminum alloy system showed intermetallic compound formation. Such compound formation could make the reduction reaction more favorable thermodynamically than the reaction postulated in this report.

Uranium Chloride

In the case of uranium chloride, similar reducing agents should be effective as evidenced by the thermodynamic results shown in Table 3c. The alkali metals and the alkaline earths are again effective reducing agents.

Because of the great interest in aluminum metal as a reducing agent, a thorough analysis has been performed on the thermodynamic information in the literature. Appendix D of this report gives a complete discussion of the situation and the conclusion is reached that the thermodynamics are not favorable. Despite this, in view of the discrepancy in the case of the fluoride, it is believed that sufficient doubt still exists so that a small experimental program to test the process qualitatively would be desirable.

Uranium Bromide and Iodide

Although uranium bromide can probably be easily reduced as shown by the thermodynamic results in Table 3d, the multistage process necessary for its production, i. e., through UN or UC_2 , probably makes it unworthy of further consideration. The same conclusions reached on the UCl_4 reduction by aluminum can be applied to the aluminum bromide reduction. In the case of the iodide, knowledge of any chemical method for its preparation from the oxides or the higher halides is lacking so that any reduction process would be purely of academic interest.

Thermal Decompositions

The only thermal decompositions that appear to be at all worthy of consideration are those of UBr_4 and UI_4 . Because of no known method of preparation of UI_4 from the oxides or the higher halides, this decomposition becomes one of academic interest only. The pertinent factors for these decompositions are shown in Figure 1 for the UBr_4 and in Figure 2 for the UI_4 . The processes are similar so that only the one for the UBr_4 will be described.

Two possible decompositions of UBr_4 are possible, i.e.,

It is desired to suppress Reaction (2) in favor of Reaction (1). With reference to Figure 1, the recommended process is as follows. UBr_4 is vaporized at 800°K . and the partial pressure of bromine in the system is maintained at 10^{-8} by a separate connecting Br_2 vaporizer. This effectively suppresses Reaction (2) and if the UBr_4 vapors are passed over a hot filament at 1900°K ., the equilibrium partial pressure of Br_2 is 10^{-7} atm. and consequently Reaction (1) will proceed. Molten uranium will be deposited on the filament. However, the low pressures and the high filament temperatures required seem to preclude the use of this process.

Although the pressures and temperatures are more favorable, i.e., 10^{-5} atm. and 1300°K ., for the UI_4 , the previously mentioned difficulty in its preparation probably precludes its consideration.

CONCLUSIONS

The alkali metals and the alkaline earths are probably the best reducing agents for the majority of the compounds considered with aluminum as an interesting possibility. The conditions for the thermal decompositions are probably too severe for a workable process to be developed. Although the statement made by Dawson, et al.⁽³⁴⁾, with regards to UF_4 reduction by hydrogen is considered to be impossible, it would seem desirable to consult them to see if any experimental evidence for the validity of their statement exists.

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APPENDIX A

SAMPLE CALCULATIONS

Calculation of the Standard Free Energy of Formation of a Reaction

The calculation of the standard free-energy change for the following reaction at 1000°K., will give a typical example of the computational method used in this report:

The standard free energy of formation of each compound was calculated at a particular temperature. For example, the free-energies of formation of $\text{UO}_2(\text{s})$, $\text{CaH}_2(\text{s})$, and $\text{CaO}(\text{s})$ were calculated at 1000°K., by substituting 1000° for "T" in the appropriate ΔF equation of Table B-1.

Equation 17, for $\text{UO}_2(\text{s})$ gave,

and at 1000°K.,

$$\begin{aligned}\Delta F_{1000}^\circ &= -258,893 - 3.823 \times 1000 \log 1000 - 0.31 \times 10^{-3} \times 10^6 \\ &\quad + \frac{177900}{1000} + 47,340\end{aligned}$$

$$\Delta F_{1000}^\circ = -223,154 \text{ calories}$$

For $\text{CaH}_2(\text{s})$, Equation 38, Table B-1, gives

$$\Delta F_{1000}^\circ = -44,800 + 2.303 \times 1000 \log 1000 + 27,900$$

$$\Delta F_{1000}^\circ = -9,991 \text{ calories}$$

For CaO(s) , Equation 2, Table B-1, gives,

$$\Delta F_{1000}^{\circ} = -152,771 + 2.12 \times 1000 \log 1000 - 1.62 \times 10^{-3} \times 10^{+6} \\ + \frac{0.54 \times 10^5}{1000} + 85.67 \times (1000)^{1/2} + 18,100$$

$$\Delta F_{1000}^{\circ} = -127,172 \text{ calories}$$

Collecting ΔF_{1000}° values, there is obtained,

	$\Delta F_{1000^{\circ}\text{K.}}^{\circ}$, calories
$\text{U(s)} + \text{O}_2(\text{g}) \longrightarrow \text{UO}_2(\text{s});$	-223,154
$\text{Ca}(\beta) + \text{H}_2(\text{g}) \longrightarrow \text{CaH}_2(\text{s});$	-9,991
$\text{Ca}(\beta) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CaO(s)};$	-127,172

The standard free-energy change for the required reaction was calculated as follows:

By cancelling and adding,

This value was rounded off to -11,210 calories and reported as -11.2 kcal., in Reaction 59, Table 3a.

Estimation of the Standard Entropy Change of a Reaction

The entropy change of a reaction was calculated whenever possible from the difference in absolute entropies of the reactants and products. When the absolute entropy of a compound taking part in a chemical reaction was unknown, the entropy change of the reaction was calculated according to Meissner's⁽³¹⁾ Rule.

An example of the calculation is given for $\text{N}_2\text{H}_4 \cdot \text{HCl}$ whose entropy is unknown.

$$\Delta S_{298}^\circ = 30\Delta_1 + \frac{80}{3}\Delta_2 + \frac{100}{3}\Delta_3 - \frac{20}{3}\Delta_4 - 4\Delta_5 + 20L + 10P_1 + 5P_2$$

where*,

- Δ_1 = moles of gaseous products minus moles of gaseous reactants (not counting H_2 , CO_2 , SO_2 , CO , NO , HCN , C_2H_2 , C_2H_4 , HCHO).
- Δ_2 = with reference only to gaseous H_2 , CO_2 , SO_2 , CS_2 , moles of products minus moles of reactants.
- Δ_3 = with reference only to gaseous C_2H_2 , C_2H_4 , HCHO , CO , NO , HCN , moles of products minus moles of reactants.
- Δ_4 = excluding boron, carbon, silicon, hydrogen and halides, number of atoms in solid and/or liquid products minus number of atoms in solid and/or liquid reactants.
- Δ_5 = with reference only to boron, carbon, silicon, and halides, number of atoms in liquid and/or solid products minus the number of atoms in liquid and/or solid reactants. (Note that no entropy contribution is made by hydrogen atoms in a liquid or solid compound.)
- L = moles of liquid products minus moles of liquid reactants.
- P_1 = with reference only to organic compounds, moles of solid products minus moles of solid reactants.

* The following definitions were taken from Reference 31.

P_2 = with reference only to inorganic compounds containing silver, thallium, monovalent copper, divalent iron, divalent chromium, or divalent manganese, moles of solid products minus moles of solid reactants. (P_2 is zero for all other solid inorganic compounds.)

With $N_2H_4 \cdot HCl$, the values become,

$$\Delta_1 = -1 \frac{1}{2} \qquad \Delta_5 = 1$$

$$\Delta_2 = -2 \frac{1}{2} \qquad L = 0$$

$$\Delta_3 = 0 \qquad P_1 = 0$$

$$\Delta_4 = 2 \qquad P_2 = 0$$

and, therefore,

$$S_{298}^\circ = -45 - \frac{200}{3} - \frac{40}{3} - 4 = -129.$$

By use of this ΔS_{298}° value, and known ΔH_f° and ΔC_p values, the free energy of the compound was calculated as a function of temperature, according to the method used in Appendix C. The calculation of the free energy of formation of $UO_2(s)$ in this appendix serves as an example of this type of calculation.

TABLE B-1. FREE ENERGIES OF FORMATION, TEMPERATURE FUNCTIONS

Reaction	Temp. Range, °K.	ΔF° Expression (calories)	Reference
1. $\text{Ca}(\alpha) + 1/2\text{O}_2 \rightarrow \text{CaO}(\text{s})$	298 – 673	$-152,879 - 0.14 T \log T - 0.66(10^{-3})T^2 + 0.54(10^5)T^{-1} + 85.67 T^{1/2} + 23.85 T$	3 (p. 18)
2. $\text{Ca}(\beta) + 1/2\text{O}_2 \rightarrow \text{CaO}$	673 – 873*	$-152,771 + 2.12 T \log T - 1.62(10^{-3})T^2 + 0.54(10^5)T^{-1} + 85.67 T^{1/2} + 18.10 T$	3 (p. 19)
3. $\text{Ca}(\text{l}) + 1/2\text{O}_2 \rightarrow \text{CaO}$	1124 and above	$-154,341 + 5.41 T \log T - 2.37(10^{-3})T^2 + 0.54(10^5)T^{-1} + 85.67 T^{1/2} + 10.29 T$	3 (p. 20)
4. $\text{Fe}(\alpha) + 1/2\text{O}_2 \rightarrow \text{FeO}(\text{s})$	298 – 1033	$-65,031 - 7.00 T \log T + 2.45(10^{-3})T^2 + 85.66 T^{1/2} + 33.21 T$	3 (p. 33)
5. $\text{Fe}(\alpha) + 1/2\text{O}_2 \rightarrow \text{FeO}(\text{s})$	1183 – 1642	$-68,592 - 11.88 T \log T + 1.588(10^{-3})T^2 + 85.66 T^{1/2} + 52.26 T$	3 (p. 35)
6. $2\text{Na}(\text{s}) + 1/2\text{O}_2 \rightarrow \text{Na}_2\text{O}(\text{s})$	298 – 371	$-94,736 - 46.15 T \log T + 6.32(10^{-3})T^2 - 1173.2 T^{1/2} + 197.89 T$	3 (p. 66)
7. $2\text{Na}(\text{l}) + 1/2\text{O}_2 \rightarrow \text{Na}_2\text{O}(\text{s})$	371 – 1150	$-93,143 - 34.68 T \log T + 0.78(10^{-3})T^2 - 1173.2 T^{1/2} + 165.26 T$	3 (p. 66)
8. $2\text{Na}(\text{g}) + 1/2\text{O}_2 \rightarrow \text{Na}_2\text{O}(\text{s})$	1150 ———	$-158,665 - 46.34 T \log T + 0.96(10^{-3})T^2 - 1173 T^{1/2} + 257.7 T$	3 (p. 67)
9. $\text{Mg}(\text{s}) + 1/2\text{O}_2 \rightarrow \text{MgO}$	300 – 923	$-146,378 - 0.07 T \log T - 0.026(10^{-3})T^2 - 0.704(10^5)T^{-1} + 85.68 T^{1/2} + 22.67 T$	3 (p. 47)
10. $\text{Mg}(\text{l}) + 1/2\text{O}_2 \rightarrow \text{MgO}$	923 – 1380	$-158,474 + 2.69 T \log T - 0.51(10^{-3})T^2 + 1.044(10^5)T^{-1} + 85.68 T^{1/2} + 26.98 T$	3 (p. 49)
11. $\text{Mg}(\text{g}) + 1/2\text{O}_2 \rightarrow \text{MgO}(\text{s})$	1380 ———	$-122,604 + 8.29 T \log T - 0.51(10^{-3})T^2 + 1.044(10^5)T^{-1} + 85.68 T^{1/2} + 16.60 T$	3 (p. 49)
12. $\text{Si}(\text{c}) + \text{O}_2 \rightarrow \text{SiO}_2(\text{glass})$	298 – 1200 (1500)	$-201,880 - 0.99 T \log T - 1.06(10^{-3})T^2 + 0.98(10^5)T^{-1} + 46.92 T$	18 (p. 58)
13. $2\text{Al}(\text{c}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{c})$	298 – 932	$-404,059 - 19.824 T \log T + 4.017(10^{-3})T^2 - 2.308(10^{-7})T^3 + 4.235(10^5)T^{-1} + 134.638 T$	17
14. $2\text{Al}(\text{l}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{c})$	932 – 2320	$-409,399 - 16.186 T \log T + 2.047(10^{-3})T^2 - 2.308(10^{-7})T^3 + 4.235(10^5)T^{-1} + 131.4 T$	17
15. $2\text{K}(\text{s}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{K}_2\text{O}(\text{s})$	298 – 3355	$-86,600 - 4.6 T \log T + 44.6 T$	10 (p. 307)
16. $\text{U}(\alpha) + \text{O}_2 \rightarrow \text{UO}_2$	298 – 941	$-261,364 - 20.47 T \log T + 3.91(10^{-3})T^2 + 2.179(10^5)T^{-1} + 95.46 T$	24
17. $\text{U}(\beta) + \text{O}_2 \rightarrow \text{UO}_2$	941 – 1047	$-258,893 - 3.82 T \log T - 0.31(10^{-3})T^2 + 1.779(10^5)T^{-1} + 47.34 T$	24
18. $\text{U}(\gamma) + \text{O}_2 \rightarrow \text{UO}_2$	1047 – 1300	$-261,378 - 6.77 T \log T - 0.31(10^{-3})T^2 + 1.779(10^5)T^{-1} + 58.62 T$	24
19. $\text{U}(\alpha) + 3/2\text{O}_2 \rightarrow \text{UO}_3$	298 – 941	$-295,194 - 17.32 T \log T + 3.509(10^{-3})T^2 + 1.019(10^5)T^{-1} + 104.78 T$	1 ⁽²⁹⁹⁾ , 24
20. $\text{U}(\beta) + 3/2\text{O}_2 \rightarrow \text{UO}_3$	941 – 1047	$-292,723 - 0.67 T \log T - 0.711(10^{-3})T^2 + 0.619(10^5)T^{-1} + 56.66 T$	1 ⁽²⁹⁹⁾ , 24
21. $\text{U}(\gamma) + 3/2\text{O}_2 \rightarrow \text{UO}_3$	1047 – 1300	$-295,208 - 3.62 T \log T - 0.711(10^{-3})T^2 + 0.619(10^5)T^{-1} + 67.94 T$	1 ⁽²⁹⁹⁾ , 24

TABLE B-1. (Continued)

Reaction	Temp. Range, °K.	ΔF° Expression (calories)	Reference
22. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	298 - 2273	$-43,690 + 3.46 T \log T - 0.155(10^{-3}) T^2 - 14.75 T$	6 (p. 870)
23. $2\text{Na}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl}(\text{s})$	298 - 371	$-197,510 - 7.55 T \log T + 1.44(10^{-3}) T^2 + 64.18 T$	6 (p. 871)
24. $2\text{Na}(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl}(\text{s})$	371 - 1073	$-197,660 + 3.91 T \log T - 3.92(10^{-3}) T^2 + 37.13 T$	6
25. $2\text{Na}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl}(\text{l})$	1187 - 1738	$-241,060 - 29.47 T \log T + 170.39 T$	6
26. $\text{Ca}(\alpha) + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$	298 - 673	$-191,510 - 7.18 T \log T + 0.26(10^{-3}) T^2 + 56.77 T$	6 (p. 870)
27. $\text{Ca}(\beta) + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$	673 - 1055	$-191,400 - 4.77 T \log T - 0.79(10^{-3}) T^2 + 50.48 T$	6
28. $\text{Ca}(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{l})$	1124 - 1760	$-192,580 - 19.16 T \log T + 94.14 T$	6
29. $1/2\text{Si}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 1/2\text{SiCl}_4(\text{l})$	298 - 330.2	$-78,420 - 14.81 T \log T + 70.00 T$	6 (p. 871)
30. $1/2\text{Si}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 1/2\text{SiCl}_4(\text{g})$	330.2-1683	$-72,550 + 0.3455 T \log T + 0.435(10^{-3}) T^2 - 0.2525(10^5) T^{-1} + 14.13 T$	6
31. $\text{Mg}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}_2(\text{s})$	298 - 923	$-154,590 - 9.07 T \log T + 0.07(10^{-3}) T^2 + 0.30(10^5) T^{-1} + 66.34 T$	6 (p. 871)
32. $\text{Mg}(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}_2(\text{l})$	987 - 1380	$-148,380 - 13.59 T \log T + 73.85 T$	6
33. $\text{Mg}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}_2(\text{l})$	1380 - 1691	$-184,140 - 19.00 T \log T + 116.74 T$	6
34. $1/2\text{C}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 1/2\text{CCl}_4(\text{l})$	298 - 349.9	$-18,560 - 14.6 T \log T + 70.81 T$	6 (p. 870)
35. $1/2\text{C}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 1/2\text{CCl}_4(\text{g})$	349.9-1373	$-12,870 - 2.6 T \log T + 0.935(10^{-3}) T^2 - 0.2925(10^5) T^{-1} + 23.93 T$	6
36. $\text{K}(\text{l}) + 1/2\text{Cl}_2 \rightarrow \text{KCl}(\text{s})$	298 - 1043	$-104,900 + 24.0 T$	10 (p. 307)
37. $\text{K}(\text{l}) + 1/2\text{Cl}_2 \rightarrow \text{KCl}(\text{l})$	1043 - 1680	$-116,600 + 35.2 T$	10
38. $\text{Ca}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{CaH}_2(\text{s})$	298 - 1000**	$-44,800 + 2.3 T \log T + 27.9 T$	28
39. $\text{Fe}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{FeCl}_2(\text{g})$	298 - 950	$-82,770 - 6.98 T \log T + 50.84 T$	16
40. $\text{Fe}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{FeCl}_2(\text{l})$	950 - 1300	$-68,450 + 15.22 T$	16
41. $\text{Fe}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{FeCl}_2(\text{g})$	1300 - 1808	$-25,250 + 23.0 T \log T - 89.65 T$	16

* The upper limit is due to the limit in the range of the Cp equation for $\text{Ca}(\beta)$, but this can probably be extrapolated to the melting point of 1124°K . without much error (Reference 3, p. 18).

** CaH_2 begins to decompose at 948°K .

Note: $\log x$ = common logarithm to base 10

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TABLE B-2. FREE ENERGY FUNCTIONS

Reaction	Ref.	$\frac{\Delta F^\circ - \Delta H^\circ_{298}}{T}$ Calories/mole-°K.				ΔH_{298} Kilocalories
		298°K.	500°K.	1000°K.	1500°K.	
1. $\text{U} + 3/2 \text{F}_2 \rightarrow \text{UF}_3$	(5)	59	58	58	57	-357 ± 4
2. $\text{U} + 2\text{F}_2 \rightarrow \text{UF}_4$	(5)	73	73	68	64	-443 ± 3
3. $\text{U} + 3\text{F}_2 \rightarrow \text{UF}_6(\text{g})$	(5)	67.2	66.5	64.8	—	-505
4. $\text{U} + 3/2 \text{Cl}_2 \rightarrow \text{UCl}_3$	(5)	54.01	53.51	51.65	49	-213.5 ± 1.5
5. $\text{U} + 2\text{Cl}_2 \rightarrow \text{UCl}_4$	(5)	71.2	70.7	67	—	-251.1 ± 0.5
6. $\text{Al} + 3/2 \text{Br}_2 \rightarrow \text{AlBr}_3$	(11)	46	36	—	—	-138 ± 2
7. $\text{Ca} + \text{Br}_2 \rightarrow \text{CaBr}_2$	(11)	37.6	37.3	35.5	33	-169.5 ± 1
8. $\text{Fe} + \text{Br}_2 \rightarrow \text{FeBr}_2$	(11)	33	33	30	26	-67.3 ± 0.2
9. $\text{K} + 1/2 \text{Br}_2 \rightarrow \text{KBr}$	(11)	21.9	22.3	22.5	20.3	-97.7 ± 0.2
10. $\text{Mg} + \text{Br}_2 \rightarrow \text{MgBr}_2$	(11)	36.4	36.1	34.4	30.0	-131.2 ± 0.5
11. $\text{Na} + 1/2 \text{Br}_2 \rightarrow \text{NaBr}$	(11)	21.4	21.7	22.0	19.5	-90.3 ± 0.4
12. $\text{Si} + 2\text{Br}_2 \rightarrow \text{SiBr}_4$	(11)	48	47	—	—	-108.2 ± 1
13. $\text{U} + 2\text{Br}_2 \rightarrow \text{UBr}_4$	(5)	71	71	65	—	-211.3 ± 0.5

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TABLE B-3. STANDARD FREE-ENERGY VALUES

Reaction	Ref.	ΔF° , kilocalories				Foot- notes
		298° K.	500° K.	1000° K.	1500° K.	
1. $2\text{Al} + 3/2\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3$	17	-376.8	-361.7	-324.3	-285.3	
2. $\text{Ca} + 1/2\text{O}_2(\text{g}) \rightarrow \text{CaO}$	3	-144.3	-139.3	-127.2	-115.1	
3. $\text{C}(\text{s}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$	2	-32.8	-37.2	-47.9	-58.4	
4. $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	2	-94.3	-94.4	-94.6	-94.7	
5. $\text{Fe} + 1/2\text{O}_2(\text{g}) \rightarrow \text{FeO}$	3	-58.6	-55.3	-47.7	-39.9	
6. $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	2	-54.6	-52.4	-46.0	-39.3	
7. $2\text{K}(\text{s}) + 1/2\text{O}_2 \rightarrow \text{K}_2\text{O}$	10	-76.7	-	-	-	
8. $\text{Mg} + 1/2\text{O}_2(\text{g}) \rightarrow \text{MgO}$	3	-138.4	-133.4	-121.1	-105.8	
9. $2\text{Na} + 1/2\text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{O}$	3	-89.5	-83.4	-68.3	-36.1	
10. $\text{Si}(\text{s}) + \text{O}_2 \rightarrow \text{SiO}_2$	18	-188.4	-179.8	-158.9	-138.5	
11. $\text{U}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{UO}_2(\text{s})$	24	-246.9	-239.9	-223.2	(-206.0)	
12. $\text{U}(\text{s}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{UO}_3$	1,24	-276.0	-265.1	-265.1	-	
13. $2/3\text{Al} + \text{F}_2(\text{g}) \rightarrow 2/3\text{AlF}_3$	7	-195.7	-187.9	-170.5	-151.5	(1)
14. $\text{Ca} + \text{F}_2(\text{g}) \rightarrow \text{CaF}_2$	7	-277.0	-270.0	-250.7	-230.8	(1)
15. $1/2\text{C}(\text{s}) + \text{F}_2(\text{g}) \rightarrow 1/2\text{CF}_4$	7	-76.1	-71.4	-62.9	-53.6	(1)
16. $\text{Fe} + \text{F}_2(\text{g}) \rightarrow \text{FeF}_2$	7	-157.6	-150.5	-133.0	-118.5	
17. $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{HF}$	7	-128.9	-130.0	-131.4	-131.8	(1)
18. $1/2\text{H}_2(\text{g}) + 1/2\text{F}_2(\text{g}) \rightarrow \text{HF}$	14	-64.7	-65.0	-65.6	-65.9	(2)
19. $2\text{K} + \text{F}_2(\text{g}) \rightarrow 2\text{KF}$	7	-254.3	-245.7	-221.4	-185.7	(1)
20. $\text{Mg} + \text{F}_2(\text{g}) \rightarrow \text{MgF}_2$	7	-251.4	-242.8	-222.0	-199.0	(1)
21. $2\text{Na} + \text{F}_2(\text{g}) \rightarrow 2\text{NaF}$	7	-258.5	-247.2	-222.9	-191.0	(1)
22. $1/2\text{Si} + \text{F}_2(\text{g}) \rightarrow 1/2\text{SiF}_4$	7	-179.6	-176.4	-167.9	-160.0	(1)
23. $\text{U} + 3/2\text{F}_2 \rightarrow \text{UF}_3$	5	-339.4	-328.0	-299.0	-271.5	
24. $\text{U}(\text{s}) + 2\text{F}_2 \rightarrow \text{UF}_4$	5	-421.2	-406.5	-375.0	-347.0	

TABLE B-3. (Continued)

Reaction	Ref.	ΔF° , kilocalories				Foot- notes
		298° K.	500° K.	1000° K.	1500° K.	
25. $\text{U} + 3\text{F}_2 \rightarrow \text{UF}_6(\text{g})$	5	-485.0	-471.8	-440.2	-	
26. $4/3\text{Al} + 2\text{Cl}_2(\text{g}) \rightarrow 2/3\text{Al}_2\text{Cl}_6(\text{g})$		-	(863°K.) -165.0	-	-	(5)
27. $4/3\text{Al}(\text{e}) + 2\text{Cl}_2(\text{g}) \rightarrow 4/3\text{AlCl}_3(\text{g})$	-	-	-	-161.6	-	
28. $\text{Ca} + \text{Cl}_2 \rightarrow \text{CaCl}_2$	6	-179.9	-172.7	-156.0	-142.7	
29. $1/2\text{C}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 1/2\text{CCl}_4$	6	-8.2	-4.2	+4.2	-	
30. $\text{C} + 1/2\text{O}_2 + \text{Cl}_2 \rightarrow \text{COCl}_2$	15	-49.3	-47.3	-42.6	-	
31. $\text{Fe} + \text{Cl}_2 \rightarrow \text{FeCl}_2$	16	-72.8	-66.8	-53.2	-50.2	
32. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	6	-45.6	-46.4	-48.2	-49.7	
33. $1/2\text{H}_2(\text{g}) + 1/2\text{Cl}_2(\text{g}) \rightarrow \text{HCl}$	14	-22.8	-23.3	-24.2	-24.2	(2)
34. $\text{K} + 1/2\text{Cl}_2 \rightarrow \text{KCl}$	10	-97.7	-92.9	-80.9	-63.8	
35. $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$	6	-141.5	-133.3	-115.0	-100.0	(3)
36. $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$	6	-183.8	-174.8	-152.7	-125.9	
37. $1/2\text{Si} + \text{Cl}_2(\text{g}) \rightarrow 1/2\text{SiCl}_4$	6	-68.5	-65.0	-57.0	-48.7	
38. $\text{U}(\text{s}) + 3/2\text{Cl}_2(\text{g}) \rightarrow \text{UCl}_3$	5	-197.4	-186.7	-161.9	-140.0	
39. $\text{U}(\text{s}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{UCl}_4$	5	-229.9	-215.8	-184.1	-	
40. $\text{U}(\text{s}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{UCl}_4(\text{l})$	1	-	(863°K.) -191.0	-	-	
41. $\text{Al} + 3/2\text{Br}_2 \rightarrow \text{AlBr}_3$	11	-124.3	-120.0	-	-	
42. $\text{Ca} + \text{Br}_2 \rightarrow \text{CaBr}_2$	11	-158.3	-150.9	-134.0	-120.0	
43. $\text{C} + 2\text{Br}_2 \rightarrow \text{CBr}_4(\text{g})$	11	+8.0	+14.0	-	-	
44. $\text{Fe} + \text{Br}_2 \rightarrow \text{FeBr}_2$	11	-57.5	-50.8	-37.3	-28.3	
45. $1/2\text{H}_2 + 1/2\text{Br}_2 \rightarrow \text{HBr}$	14	-13.1	-13.6	-14.5	-15.3	(2)
46. $\text{K} + 1/2\text{Br}_2 \rightarrow \text{KBr}$	11	-91.2	-86.6	-75.2	-67.3	
47. $\text{Mg} + \text{Br}_2 \rightarrow \text{MgBr}_2$	11	-120.4	-113.2	-96.8	-86.2	
48. $\text{Na} + 1/2\text{Br}_2 \rightarrow \text{NaBr}$	11	-83.9	-79.5	-68.3	-61.1	
49. $\text{Si} + 2\text{Br}_2 \rightarrow \text{SiBr}_4$	11	-93.9	-84.7	-	-	
50. $\text{U}(\text{s}) + 2\text{Br}_2 \rightarrow \text{UBr}_4$	5	-190.1	-175.8	-146.3	-	
51. $\text{Ca}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{CaH}_2(\text{s})$	28	-34.8	-27.7	-10.0	-	(4)
52. $\text{N}_2 + 2\text{H}_2 \rightarrow \text{N}_2\text{H}_4$	13	37.9	48.5	76.0	103.6	

(1) Values read from graph in Reference 7.

(2) Calculated from equilibrium constant values in Reference 14.

(3) Values read from graph in Reference 6.

(4) CaH_2 begins to decompose at 948°K.

(5) See Appendix D for detailed information.

APPENDIX C

THERMODYNAMICS OF URANIUM DIOXIDE FORMATION

For the reaction:

the following data were obtained from Moore and Kelley⁽²³⁾.

$$\text{U}(\alpha): C_p = 3.15 + 8.44 (10^{-3})T + 0.80 (10^5)T^{-2} \quad (298^\circ - 941^\circ\text{K.}; 0.2\%)$$

$$\text{U}(\beta): C_p = 10.38 \quad (941^\circ - 1047^\circ\text{K.}; 0.2\%)$$

$$\text{U}(\gamma): C_p = 9.10 \quad (1047^\circ - 1300^\circ\text{K.}; 0.1\%)$$

$$\text{UO}_2: C_p = 19.20 + 1.62 (10^{-3})T - 3.957 (10^5)T^{-2}$$

Heats of transition of U are:

$$\Delta H_{941^\circ\text{K.}} = 680 \text{ cal./g.atm.}$$

$$\Delta H_{1047^\circ\text{K.}} = 1165 \text{ cal./g.atm.}$$

The C_p of oxygen was taken from Kelley⁽²⁷⁾

$$\text{O}_2(\text{g}): C_p = 7.16 + 1.00 (10^{-3})T - 0.40 (10^5)T^{-2} \quad (298^\circ - 3000^\circ\text{K.})$$

$$C_p = C_p \text{UO}_2(\text{s}) - C_p \text{U}(\alpha) - C_p \text{O}_2(\text{g})$$

$$C_p = 8.89 - 7.82 (10^{-3})T - 4.357 (10^5)T^{-2}$$

$$\Delta H = \int_0^T \Delta C_p dT$$

$$\Delta H = \int_0^T (8.89 - 7.82 (10^{-3})T - 4.357 (10^5)T^{-2}) dT$$

$$\Delta H = \Delta H_o + 8.89T - 3.91 (10^{-3})T^2 + 4.357 (10^5)T^{-1}$$

Substituting the value of the heat of formation of UO_2 ^(25,37), i.e., $\Delta H_{298} = -259.6$ kcal./mole, and $T = 298^\circ K$. in the above equation, the value of ΔH_o is found. The source of this value has been discussed on page 12 of this report. Putting this value back into the original equation, we have an expression of ΔH in terms of T for the range $298^\circ - 941^\circ K$.

$$\Delta H = -261,364 + 8.89T - 3.91 (10^{-3})T^2 + 4.357 (10^5)T^{-1}$$

Combining the value for ΔH_{298} with $\Delta S_{298} = -42.5$ (1) in the expression:

$\Delta F_{298}^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ$, the value -246,935 calories for ΔF_{298}° is obtained.

From thermodynamic fundamentals it is known that,

$$\frac{d \left(\frac{\Delta F^\circ}{T} \right)}{dT} = \frac{-\Delta H}{T^2}$$

By inserting the above equation for ΔH in this expression, the following relationship is gained:

$$d \left(\frac{\Delta F^\circ}{T} \right) = (+261,364T^{-2} - 8.89T^{-1} + 3.91 (10^{-3}) - 4.357 (10^5)T^{-3})dT$$

Integrating and multiplying by T gives:

$$\Delta F^\circ = -261,364 - 8.89T \ln T + 3.91 (10^{-3})T^2 + 2.179 (10^5)T^{-1} + IT$$

Using the previously calculated value of ΔF_{298}° and the corresponding temperature, the value of I can be obtained which when inserted in the above expression gives a function of ΔF° in terms of T for the range $298^\circ - 941^\circ K$.

$$\Delta F^\circ = -261,364 - 8.89T \ln T + 3.91 (10^{-3})T^2 + 2.179 (10^5)T^{-1} + 95.46T$$

By substituting $T = 941^\circ K$. into the ΔH° expression, the value $\Delta H_{941} = -255,998$ calories is obtained. Combining this with the heat of transition of U at $941^\circ K$. gives the ΔH value for:

To obtain ΔH° and ΔF° expressions for $\text{U}(\beta) + \text{O}_2 \longrightarrow \text{UO}_2$, steps similar to those previously explained are followed

Thus:

$$\Delta C_p = 1.66 + 0.62 (10^{-3})T - 3.557 (10^5)T^{-2}$$

The ΔH_{941}° value found above is used to find the value of ΔH°

$$\Delta H^\circ = -258,893 + 1.66T + 0.31 (10^{-3})T^2 + 3.557 (10^5)T^{-1} \quad (941^\circ - 1047^\circ\text{K.})$$

$$\Delta F^\circ = -258,893 - 1.66T \ln T - 0.31 (10^{-3})T^2 + 1.779 (10^5)T^{-1} + 47.34T \quad (941^\circ - 1047^\circ\text{K.})$$

Also:

The work for $\text{U}(\gamma) + \text{O}_2(\text{g}) \longrightarrow \text{UO}_2(\text{s})$ follows the same pattern and gives:

$$\Delta C_p = 2.94 + 0.62 (10^{-3})T - 3.557 (10^5)T^{-2}$$

$$\Delta H^\circ = -261,378 + 2.94T + 0.31 (10^{-3})T^2 + 3.557 (10^5)T^{-1} \quad (1047^\circ - 1300^\circ\text{K.})$$

$$\Delta F^\circ = -261,378 - 2.94T \ln T - 0.31 (10^{-3})T^2 + 1.779 (10^5)T^{-1} + 58.62T \quad (1047^\circ - 1300^\circ\text{K.})$$

Summary of the Results

$$\Delta F^\circ = -261,364 - 8.89T \ln T + 3.91 (10^{-3})T^2 + 2.179 (10^5)T^{-1} + 95.46T$$

$T, ^\circ\text{K.}$	$\Delta F^\circ, \text{ calories}$
298	-246,935
500	-239,850
941	-225,131

$$\Delta F^\circ = -258,893 - 1.66T \ln T - 0.31 (10^{-3})T^2 + 1.779 (10^5)T^{-1} + 47.34T$$

$T, ^\circ\text{K.}$	$\Delta F^\circ, \text{ calories}$
1000	-223,154
1047	-221,586

$$\Delta F^\circ = -261,378 - 2.94T \ln T - 0.31 (10^{-3})T^2 + 1.779 (10^5)T^{-1} + 58.62T$$

$T, ^\circ\text{K}$	$\Delta F^\circ, \text{ calories}$
1300	-212,968

APPENDIX D

THERMODYNAMICS OF THE REDUCTION OF UCl₄ BY ALUMINUM METAL

The standard free-energy change for the reduction of UCl₄ by aluminum showed a favorable driving force using the thermodynamic data for aluminum chloride compiled by Villa⁽¹⁶⁾ and Kellogg⁽⁶⁾. The reaction appeared promising as shown in Table D-4, despite the known alloy formation of uranium and aluminum. Because these results for the reaction made it an important one, and because the direction of the free-energy change with temperature was opposite using Villa's⁽¹⁶⁾ and Kellogg's⁽⁶⁾ data, the thermodynamic data for aluminum chloride were appraised as shown in Tables D-1, D-2, D-3, and D-4.

Villa's equations, 1, 3, and 4, Reference 16, page S10, could be verified as shown in Tables D-1 and D-2. However, a discrepancy between the derivation of this report and Villa's for the significant Equation 2 was shown to exist. This discrepancy amounted to 10,900 calories at 863°K., for $1/3\text{Al}_2\text{Cl}_6(\text{g})$, and made the difference between a favorable and unfavorable reaction. Villa's equations were based on fundamental data by Gross⁽³²⁾, et al. Gross estimated the entropy of AlCl₃(g) at 298°K., by assuming vibrational frequencies and moments of inertia for this molecule. By substituting these values in the Sackur-Tetrode equation, he calculated S_{298}° and Cp as a function of temperature for AlCl₃(g).

Kellogg⁽⁶⁾ derived the equations of the free energy of formation of AlCl₃ by starting with calorimetric data for its heat of formation, and by calculating an entropy value from the Eastman-Latimer Rule. Villa⁽¹⁶⁾ discussed the reasons why this rule does not apply to AlCl₃.

Treadwell and Terebesi⁽²⁹⁾ calculated the free energy of formation of Al₂Cl₆(g) from electromotive-force measurements of a reversible cell. From their measurements and the sublimation equation for AlCl₃(s) given by Kelley⁽²⁷⁾, the entropy value of AlCl₃(s) at 298°K., was calculated. This is the only entropy value for AlCl₃(s) that has an experimental basis. The entropy value 22.8 e.u., agrees within four units with that of Villa, 26.25 e.u. Villa⁽¹⁶⁾ arrived at this value indirectly from Gross'⁽³²⁾ entropy estimation of gaseous AlCl₃. These entropy values are unexpectedly close to that estimated by Meissner's⁽³¹⁾ Rule, 24.5 e.u., which is not considered to be too accurate for highly halogenated compounds. Treadwell and Terebesi⁽²⁹⁾ in their free-energy equation for the formation of

$\text{Al}_2\text{Cl}_6(\text{g})$ assume that ΔC_p for the formation reaction is zero. Foster, Russell and Cochran⁽³⁰⁾ used the results of Treadwell and Terebesi in a recent paper almost without change in form.

As a result of the differences in values for the free energy of formation of Al_2Cl_6 , it was decided in this report to derive a set of new equations. These equations were derived on the basis of the heat of formation of solid AlCl_3 given in Selected Values⁽²⁶⁾, the entropy value of $\text{AlCl}_3(\text{s})$ calculated from Treadwell and Terebesi, and the sublimation equation of Kelley⁽²⁷⁾. The C_p values were taken for $\text{Al}(\text{s})$, $\text{Al}(\text{l})$, $\text{AlCl}_3(\text{s})$ and $\text{Cl}_2(\text{g})$ from Kelley's⁽²⁷⁾ compilation of experimental data and from his estimate of C_p for $\text{Al}_2\text{Cl}_6(\text{g})$. The value for C_p for $\text{AlCl}_3(\text{g})$ was taken from Gross⁽³²⁾. The average ΔC_p for the reaction over the range 300 to 800°K., is close to zero, justifying this assumption in the equations of Treadwell and Terebesi. The dissociation of $\text{Al}_2\text{Cl}_6(\text{g}) = 2\text{AlCl}_3(\text{g})$ was obtained from Smits and Meijering⁽³³⁾. The derived equations are shown in Table D-1. The standard free-energy change for the reaction:

$\text{UCl}_4(\text{s}) + 4/3 \text{Al}(\text{l}) \rightarrow \text{U}(\text{s}) + 2/3 \text{Al}_2\text{Cl}_6(\text{g})$ was +26,000 calories at 863°K. This value corresponds to a vapor pressure of 0.3 mm. Hg of $\text{Al}_2\text{Cl}_6(\text{g})$ over the reaction at chemical equilibrium. The entropy value for $\text{AlCl}_3(\text{g})$ at 298.16°K. calculated from these equations is 72.24 e.u., which compares with 74.63 e.u. estimated by Gross⁽³²⁾. From these results, it would be concluded that the reduction of UCl_4 by aluminum is not a favorable reaction. This conclusion is contrary to that predicted initially by use of the equations of Villa⁽¹⁶⁾ and Kellogg⁽⁶⁾.

TABLE D-1. EQUATIONS FOR THE STANDARD FREE ENERGY OF FORMATION OF ALUMINUM TRICHLORIDE

Source of Data	$\begin{array}{c} 2/3\text{Al}(s) + \text{Cl}_2(g) \rightarrow \\ 1/3\text{Al}_2\text{Cl}_6(g) \\ \Delta F^\circ_{298-453^\circ\text{K. (calories)}} \end{array}$	$\begin{array}{c} 2/3\text{Al}(s) + \text{Cl}_2(g) \rightarrow \\ 1/3\text{Al}_2\text{Cl}_6(g) \\ \Delta F^\circ_{453-933^\circ\text{K. (calories)}} \end{array}$	$\begin{array}{c} 2/3\text{Al}(s) + \text{Cl}_2(g) \rightarrow \\ 2/3\text{AlCl}_3(g) \\ \Delta F^\circ_{453-933^\circ\text{K. (calories)}} \end{array}$	$\begin{array}{c} 2/3\text{Al}(l) + \text{Cl}_2(g) \rightarrow \\ 2/3\text{AlCl}_3(g) \\ \Delta F^\circ_{933-1800^\circ\text{K. (calories)}} \end{array}$
Villa's ⁽¹⁶⁾ equations	$-115,000 - 21.75T \log T + 106.4T$	$-101,480 + 1.65T \log T + 1.41T$	$-92,100 + 1.65T \log T + 3.17T$	$-93,600 + 1.65T \log T + 4.7T$
Equations derived in this report using the basic data of Villa ⁽¹⁶⁾ (Villa-Battelle equations)	$-112,065 + 3.042T \log T + 0.54 \times 10^{-5}T^{-1} - 8.23 \times 10^{-3}T^2 + 37.18T$	$-102,365 - 2.713T \log T + 0.54 \times 10^{-5}T^{-1} + 1.1 \times 10^{-3}T^2 + 26.84T$	$-92,998 - 2.713T \log T + 0.54 \times 10^{-5}T^{-1} + 1.1 \times 10^{-3}T^2 + 15.94T$	$-94,265 + 0.67T \log T + 0.54 \times 10^{-5}T^{-1} + 0.03 \times 10^{-3}T^2 + 8.26T$
Equations derived in this report using a calorimetric heat of formation for $\text{AlCl}_3(s)$ from Selected Values ⁽²⁶⁾ , and a derived entropy for $\text{AlCl}_3(s)$ from Treadwell and Terebesi ⁽²⁹⁾ (Battelle equations)	$-110,332 + 7.554T \log T - 8.317 \times 10^{-3}T^2 - 0.34 \times 10^{-5}T^{-1} + 25.23T$	$-100,632 + 1.80T \log T + 1.02 \times 10^{-3}T^2 - 0.34 \times 10^{-5}T^{-1} + 14.89T$	$-91,266 + 1.80T \log T + 1.02 \times 10^{-3}T^2 - 0.34 \times 10^{-5}T^{-1} + 3.99T$	$-92,556 + 4.96T \log T + 0.027 \times 10^{-3}T^2 - 0.34 \times 10^{-5}T^{-1} - 3.09T$

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TABLE D-2. CALCULATED VALUES FOR THE STANDARD FREE ENERGY
OF FORMATION OF ALUMINUM TRICHLORIDE

Reaction	ΔF° , calories			
	Temp. °K.	Villa's* Equations	Villa-Battelle* Equations	Battelle's* Equations
$2/3\text{Al(c)} + \text{Cl}_2\text{(g)} \rightarrow 1/3\text{Al}_2\text{Cl}_6\text{(s)}$	298.16	-99,320	-97,822	-98,092
$2/3\text{Al(c)} + \text{Cl}_2\text{(g)} \rightarrow 1/3\text{Al}_2\text{Cl}_6\text{(g)}$	863	-96,082	-85,194	-82,500
$2/3\text{Al(c)} + \text{Cl}_2\text{(g)} \rightarrow 2/3\text{AlCl}_3\text{(g)}$	863	-85,183	-85,234	-82,541
$2/3\text{Al(l)} + \text{Cl}_2\text{(g)} \rightarrow 2/3\text{AlCl}_3\text{(g)}$	1000	-83,950	-83,911	-80,773

* See Table D-1 for these equations.

TABLE D-3. THERMODYNAMIC VALUES AT 298 AND 863°K., FOR ALUMINUM TRICHLORIDE

Source of Data	Standard Free Energy of Formation $\Delta F_{863^\circ\text{K.}}$, calories		Derived Thermodynamic Values at 298°K. for Al_2Cl_3 (Solid)			Calculated Entropy of Solid AlCl_3 at 298°K.
	Al_2Cl_6 Gas	$2/3\text{Al}_2\text{Cl}_6$ Gas	ΔH_{298}	ΔF°_{298}	ΔS_{298}	S°_{298}
H. Villa ⁽¹⁶⁾	-288,246	-192,164	-336,557	-297,988	-129.43	26.25
Equations derived in this report using Villa's basic data	-255,585	-170,390	-334,095	-297,858	-121.53	26.00
Equations derived in this report using a calorimetric heat of formation for $\text{AlCl}_3(\text{s})$ from Selected Values ⁽²⁶⁾ , and a derived entropy for $\text{AlCl}_3(\text{s})$ from Treadwell and Terebesi ⁽²⁹⁾	-247,500	-165,000	-332,400	-294,274	-127.87	22.80
Treadwell and Terebesi ⁽²⁹⁾	-253,505	-168,986	-336,955	-298,842	-127.83	22.80
Foster, et al. ⁽³⁰⁾	-251,658	-167,777	-334,048	-295,958	-127.75	22.86
Kellogg, H. H. ⁽⁶⁾	-277,080	-184,720	-330,679	-304,546	-87.69	42.90
Entropy calculated by Latimer-Eastman rule ⁽¹⁹⁾						40.50
Entropy calculated from Meissner's* rule ⁽³¹⁾						24.50

* This rule does not hold for highly halogenated compounds.

**TABLE D-4. STANDARD FREE-ENERGY CHANGE OF THE
REDUCTION OF UCl_4 BY ALUMINUM**

Source of Data	$\text{UCl}_4(\text{l}) + 4/3\text{Al}(\text{s}) \rightarrow \text{U}(\text{s}) + 2/3\text{Al}_2\text{Cl}_6(\text{g}) \Delta F^\circ_{863^\circ\text{K.}}$ calories	$\text{UCl}_4(\text{l}) + 4/3\text{Al}(\text{l}) \rightarrow \text{U}(\text{s}) + 4/3\text{AlCl}_3(\text{g}) \Delta F^\circ_{1000^\circ\text{K.}}$ calories
Villa ⁽¹⁶⁾	-1,160	+16,200
Villa-Battelle* equation	+20,618	+16,278
Battelle* equation	+26,000	+22,540
Kellogg, H. H. ⁽⁶⁾	+6,290	-160
Foster, et al. ⁽³⁰⁾	+24,070	+22,720
Treadwell and Terebesi ⁽²⁹⁾	+21,960	+20,830

* See Table D-1 for these equations.