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CHEMICAL TECHNOLOGY DIVISION

Unit Operations Section

DIRECT REDUCTION OF URANIUM HEXAFLUORIDE TO URANIUM
METAL BY SODIUM (DRUHM PROCESS)

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ABSTRACT

The chemical feasibility of the direct, continuous reduction of UF_6 to uranium with sodium was shown in several tests. Up to 93.5% of the uranium content of UF_6 continuously reduced by sodium in a reaction vessel was recovered as massive uranium metal of acceptable purity. A remaining problem is development of compatible materials of construction.

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1.0 INTRODUCTION

This report describes the Druhm process for direct reduction of uranium hexafluoride to metal, especially the design and testing of major reactor components and evaluation of materials of construction. Much of the product and tails from the gaseous diffusion process as well as the product from the volatility fuel processing scheme, which is UF_6 , will ultimately be reduced to uranium metal.¹ At present a two-step process involving a batch operation for this reduction has proved adequate.^{2,3} The Druhm program was initiated to establish the chemical and engineering feasibility of a one-step continuous reduction of UF_6 to uranium metal by use of sodium metal. The chemical feasibility of the process was established in a number of experimental tests.

The author acknowledges the large amount of experimental work done by W. G. Sisson in this program. Chemical, spectrographic, and x-ray analyses were made by the groups of G. R. Wilson, W. R. Laing, and R. L. Sherman and C. Feldman of the Oak Ridge National Laboratory Analytical Chemistry Division.

2.0 FLOWSHEET

A possible Druhm process flowsheet will provide for both the primary reduction step and for a slag processing step for reclaiming uranium carried over in the NaF slag (Fig. 2.1). The slag processing step may not be necessary if low levels of uranium carryover are maintained.

Fig. 2.1. Druhm Process Reduction and Salvage Flowsheets.

2.1 Reduction Step

In the reduction step, liquid or gaseous sodium and UF_6 vapor are continuously metered into a reactor where they react according to the equation

The resulting NaF slag and uranium metal are maintained as liquid in the bottom of the reaction vessel and continuously separated by difference in specific gravity, after which they may be removed from the reactor as separate liquid streams. The NaF stream may contain some uranium metal dispersion or incompletely reduced uranium compound.

2.2 Slag Processing

If it is necessary to further process the NaF slag, this can be accomplished by dissolution of the NaF with H₂O and filtration of the mixture to remove the remaining solid uranium-bearing material. It is anticipated that the uranium-bearing solids will not be appreciably water soluble.

3.0 THERMODYNAMIC CONSIDERATIONS

Standard free energy of reaction data (Table 3.1) indicate that any of the common alkali or alkaline earth metals are favorable for the reduction of UF₆ to uranium metal. Calcium would be the most favorable reducing agent, and has been found effective but difficult to handle in bomb reductions.⁴ Sodium would be more economical and easier to handle from an engineering standpoint because of its low melting and boiling points, low slag (NaF) melting point, and high slag solubility in water. Sodium was therefore used in this initial work.

Table 3.1. Standard Free Energy of Reaction for the Reduction of UF₆ to U at 1200°C by Various Reducing Agents^a

Reducing Agent	Reaction	ΔF° at 1200°C, kcal/g mole UF ₆
Calcium	UF ₆ + 3Ca = U + 3CaF ₂	-288
Lithium	UF ₆ + 6Li = U + 6LiF	-264
Magnesium	UF ₆ + 3Mg = U + 3MgF ₂	-198
Potassium	UF ₆ + 6K = U + 6KF	-150
Sodium	UF ₆ + 6Na = U + 6NaF	-174

^a Data from reference 5.

3.1 Free Energy and Heat of Reaction

Thermodynamic calculations indicated that, over the temperature range of interest, the complete reaction

is favorable and that there is a significant heat of reaction. The standard free energy of reaction, ΔF° , varies from -276 to -96 kcal/g mole of UF_6 over the temperature range 500-2000°K; the standard heat of reaction, ΔH° , varies from -313 to -82 kcal/g mole of UF_6 over the same temperature range (Table 3.2).

Formation of intermediate fluorides, particularly of UF_4 , the most stable, is also possible at higher temperatures (Fig. 3.1). The ΔF° for the reaction

is always a large negative number, but that of

becomes positive at about 1875°K. Obviously, if the amount of sodium available for the reaction is less than stoichiometric, there will also be intermediate fluoride formation by any temperature.

Table 3.2. Standard Change in Free Energy and Standard Heat of Reaction for the Reaction $UF_6 + 6Na = U + 6NaF^a$

Temp, °K	ΔF° , kcal/g mole UF_6	ΔH° , kcal/g mole UF_6
500	-276	-313
750	-252	--
1000	-234	-302
1250	-210	--
1500	-168	-368
1750	-138	--
2000	- 96	- 82

^a Data from reference 5.

3.2 Equilibrium Compositions

The equilibrium composition of the UF_6 -Na reaction was calculated with the assumption that uranium would be present only as UF_4 , UF_3 , and U. Since most of the thermodynamic data at the higher temperatures are extrapolated from much lower temperatures, the results of the equilibrium calculations show only qualitative results. These calculations (Sect. 8.1) show that for the temperature range tested (1132-1400°C) the equilibrium UF_4 and UF_3 contents were always small (< 1.2%), although they do increase with increasing temperature (Table 3.3). At the proposed operating temperature, 1200°C, the equilibrium contents of UF_4 and UF_3 were 0.001 and 0.026%, respectively. These calculations indicate that the intermediate fluoride formation should not prevent essentially complete reduction of the UF_6 at

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Fig. 3.1. Standard change in free energy for uranium reduction reactions with sodium. ΔF values from reference 5.

temperatures of interest. In the experimental program, no intermediate fluoride was identified under conditions of excess sodium and good reactant mixing although both UF_4 and NaF-UF_3 complex were identified in trace amounts by x-ray analysis when there was deficiency of sodium.

Table 3.3. Uranium Compound Equilibrium Composition
for the Reaction $\text{UF}_6 + 6\text{Na} = \text{U} + 6\text{NaF}$, Assuming
Excess Sodium Used^a

Temp, °C	Equilibrium Composition, mole %		
	U	UF_3	UF_4
1132	> 99.99	< 0.001	< 0.001
1150	> 99.99	0.001	< 0.001
1200	99.97	0.026	0.001
1250	99.93	0.061	0.009
1300	99.62	0.293	0.082
1350	98.39	0.987	0.725
1400	98.03	1.132	0.842

^a Thermodynamic data from reference 5.

3.3 Theoretical Reaction Temperature

The maximum theoretical reaction temperature for UF_6 reduction with a stoichiometric amount of sodium was calculated to be 1977°K, the boiling point of NaF, when the reactants were initially at 373°K. This value, obtained from thermodynamic values compiled by Glassner,⁵ indicates that the heat of reaction will probably be sufficient to maintain the reaction zone temperature at 1200°C.

4.0 REACTOR DEVELOPMENT

A semicontinuous reactor, for continuous reaction of UF_6 with sodium with batch collection of the products, was developed. This reactor was capable of operation above 1200°C with UF_6 rates up to 120 g/min for periods of time up to 60 min.

4.1 Description of Assembled Reactor

The semicontinuous reduction reactor which was used in the latter phase of the experimental program was composed of a 6-in. Inconel shell with top flange surrounding an insulated and graphite-lined reaction zone (Fig. 4.1). Holes through the top of insulating fire brick, MgO lid, and graphite lid were entrance ports to the reaction zone for a thermowell, the two reactant nozzles, and an off-gas line (Fig. 4.2). The top flange of the reaction vessel allowed entry of the reactant nozzles, three thermo-

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Fig. 4.1. Schematic of assembled Druhm reactor.

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Fig. 4.2. Druhm reactor top flange with insulating firebrick and MgO cap in place.

wells, an inert gas purge line, and an off-gas line with 1/2-in. valve.

4.2 Reactant Entrance Nozzles

Since the system operates with excess sodium, there was a continuous sodium phase in the reactor in contact with the outlet of the UF_6 entrance nozzle. The UF_6 -Na reaction appears to be very rapid, and significant reaction occurred at or near the tip of the UF_6 nozzle. This tended to cause excessive temperature at the nozzle tip, which necessitated heat removal at that point to prevent melting and/or corrosion of the nozzle.

Several different nozzle designs were tested (Fig. 4.3). The first type, a 1/4-in. cylindrical tube, proved to be inoperable regardless of UF_6 flow rate because of corrosion and/or melting when made of copper, Inconel, tungsten, graphite, Lavite, or magnesia.

The second type tested was a nested Inconel nozzle in which concentric tubes were used to introduce UF_6 in the center tube, an inert gas in the middle annulus, and liquid sodium in the outer. Inert gas was used to buffer the nozzle tip at the UF_6 exit in an attempt to decrease corrosion and temperature. Nozzles of this type were used without significant deterioration if relatively large inert gas flows were used (when the velocity of the inert gas was equal to or greater than that of UF_6). However, the use of large amounts of inert gas made it difficult to maintain adequate reaction zone temperatures and tended to cause carryover of fine solids in the off-gas stream.

A third type of nozzle tested was a massive piece of Inconel (1.5 in. dia) which had an exit hole for UF_6 in the center and liquid sodium exit in small holes surrounding the UF_6 exit. This nozzle proved fairly successful in heat removal from the nozzle tip by the metal itself with additional cooling by the liquid sodium as it entered the reaction zone.

The most successful UF_6 nozzle tested was one internally cooled. A 1/8-in. Inconel tube was surrounded by an Inconel jacket, which allowed a cooling gas to circulate around the tube, thus removing heat from the hot portion. This nozzle was operated for periods up to 44 min and at reaction zone temperatures greater than 1200°C without significant damage. Both N_2 and He were used as the coolant gases at flow rates up to 2.0 slpm and at initial temperatures from -50 to +30°C.

A 1/4-in.-o.d. stainless steel tube was used for the sodium inlet nozzle with no significant deterioration.

4.3 Reaction Zone Containment

A completely satisfactory method of reaction zone containment was not developed; however, a usable system was developed and possible revisions were indicated by experimental results.⁷ The philosophy used was to completely contain the reaction zone and reaction products while isolating them both physically and thermally from the reaction vessel proper. This isolation was necessary because of the high temperature and corrosive

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Fig. 4.3. Types of UF_6 nozzles tested in Druhm program.

nature of the reaction zone environment and its incompatibility with the Inconel reactor.

Graphite tended to withstand the temperature and corrosive action of the reaction zone better than did magnesium or alumina. However, graphite did tend to crack when severe thermal cycling occurred, especially when sodium was present. The biggest problem with the graphite reaction zone liner was that the NaF slag wetted the graphite and escaped the liner because of its porosity. Graphite contained the uranium metal which was formed and thus a separation of slag and metal was sometimes achieved.

There is some evidence that a ceramic coating on low-porosity graphite may prevent escape of the NaF slag without reducing the good thermal and corrosion resistance properties of the graphite. These types were not tested in the Druhm program.

In order to completely isolate the reaction zone, a 1/4- to 1/2-in.-thick graphite crucible with graphite lid was surrounded by a 1/2-in.-thick MgO crucible and lid, and these were placed in the Inconel reaction vessel. Two inches of MgO fire brick was placed on top of the MgO lid to further insulate the top of the reaction vessel and allow a simple gasket arrangement for the reactor top.

4.4 Auxiliary Equipment

The auxiliary equipment needed for the experimental facility (Fig. 4.4) consisted of (1) a sodium melting and metering section with provisions for vaporization prior to its entry to the reactor, (2) a UF_6 vaporizing and metering section, (3) an induction heater for initially heating the reactor to operating temperature, and (4) a reactor off-gas system capable of trapping sodium or UF_6 that escaped the reactor.

The sodium meter was an electromagnetic flow meter⁶ (Fig. 4.5) with control valve, and the sodium boiler was simply a coil of tubing heated by a tube furnace.

UF_6 was metered by an instrumented orifice meter with constant pressure control (Fig. 4.6). Reactor off-gas was treated by a cold trap for liquid sodium removal (packed column operating at 150°C) followed by an *n*-butyl alcohol wash to remove sodium vapor, and finally calcium sulfate traps for UF_6 removal. All process lines were heated to above 100°C throughout the system.

4.5 Experimental Procedures

For continuous reactor operation the reaction and product collection zones must be at temperatures above the melting point of uranium metal (1132°C) to expedite the separation of the NaF slag and uranium metal by difference in specific gravity. However, the system should be operated at as low a temperature as possible to decrease the undesirable effects of high-temperature operation such as corrosion and UF_4 formation. A temperature of 1200°C was chosen as the goal for operation of the reactor system.

Fig. 4.4. Druhm experimental facility for study of the continuous reaction of UF_6 with sodium.

Fig. 4.5. Sodium metering section of Druhm experimental facility.

Fig. 4.6. UF_6 metering system of Druhm experimental facility.

The reaction of UF_6 with various reactor components would be prohibitive if contact should be allowed at 1200°C . Therefore a sodium-rich atmosphere was maintained in the reaction zone at all times. An off-gas system to remove the excess sodium from the reaction zone therefore is required, which necessitates operation at atmospheric pressure for convenience.

In all experimental tests, the reaction zone was preheated to above the melting point of uranium metal ($> 1132^\circ\text{C}$). Sodium was then introduced to the reaction zone at a constant rate while helium was introduced through the UF_6 entrance nozzle to prevent plugging. Shortly after the initial sodium introduction, UF_6 was introduced at a constant rate that was less than the stoichiometric amount. The helium introduction rate to the UF_6 nozzle was gradually decreased until pure UF_6 was being introduced. The induction heating unit was turned off and the UF_6 and sodium rates were then adjusted to give the proper reaction zone temperature from their heat of reaction. The run was allowed to progress until approximately $1/3$ of the reaction zone was filled with reaction products or until there was an equipment malfunction.

In some of the later runs, the UF_6 nozzle was internally cooled with helium or nitrogen to prevent overheating, and a helium purge to the top of the reactor was used to prevent release of reactants and products to the reactor proper from the reaction zone.

5.0 EXPERIMENTAL RESULTS

Forty-eight tests were made in the semicontinuous reactor, using various entrance nozzle and reaction zone containment designs.

5.1 Chemical Feasibility of Reduction

Although the tests were made mainly to test the design of the various reactor components, the results also gave further indications of the chemical feasibility of the reaction $\text{UF}_6 + 6\text{Na} \rightarrow \text{U} + 6\text{NaF}$. Fourteen of the tests resulted in significant uranium metal production and consolidation (Table 5.1). All these runs were terminated because of failure, especially, of the UF_6 nozzle in earlier runs and of the reaction zone liner and plugging of the off-gas line in later runs.

Although no test was entirely satisfactory, some conclusions could be drawn about the effect of operating variables on the reduction. In general, temperatures above the melting point of uranium were necessary for good metal consolidation and recovery. Sodium excess greater than 100%, but not exceeding 200%, appeared necessary for complete reduction, and relatively low UF_6 feed rates ($< 40 \text{ g/min}$) were necessary to ensure good reactant mixing. These figures would be applicable only for the reactor geometry used in these tests.

Up to 93.5% of the uranium introduced was recovered as consolidated uranium metal (any mass of metal with a dimension greater than $1/4 \text{ in.}$) in a run which was terminated because of off-gas line plugging. In this run.

Table 5.1 Experimental Results of Semicontinuous Druhm Runs
Which Resulted in Significant Massive Metal Recovery
(> 10% of total uranium)

U Intro- duced as UF ₆ , g	Length of Run, min	Sodium Excess, %	Max Temp Inside Reactor, °C	U Recovered as Consoli- dated Metal, % of total
3750	41	2	1098	10.7
155	4	400	1200	16.7
426	20	49	1000	19.7
980	15	47	1147	27.9
1818	29	46	1153	29.7
1128	44	75	1084	41.7
743	31.5	220	1175	52.2
224	10	82	1121	56.8
364	22	78	1155	64.0
396	24.5	18	1275	67.2
1240	30	112	1250	69.7
361	17	100	1180	82.3
486	17	100	1165	88.3
156	16	180	1225	93.5

the entrance nozzles were not corroded, although there was some slag build-up. Both the graphite and MgO reaction zone liners were removed intact in this run and there was a uranium metal button in the bottom of the graphite liner (Fig. 5.1). The uranium material balance for this run was 98.3% (Table 5.2).

Table 5.2. Uranium Material Balance for Run in Which 93.5% of the
Uranium was Recovered as Massive Metal

Description of Material	Weight of Uranium, g	% of total U Introduced
Large metal button	122.0	78.4
Metal on liner walls	18.0	11.6
Metal on tip of nozzle	<u>5.4</u>	<u>3.5</u>
Total uranium as metal	145.4	93.5
Total uranium in other parts of reactor system	<u>7.4</u>	<u>4.8</u>
Total uranium recovered	<u>152.8</u>	<u>98.3</u>

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Fig. 5.1. Intact crucible and liner after run in which 93.5% of the uranium was recovered as massive metal.

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Fig. 5.2. Uranium metal button from one of better Druhm reduction tests.

In many runs there was evidence of considerable amounts of uranium metal present as unconsolidated powder. This lack of consolidation was probably due to low temperatures or a short run time. Since it was not possible to separate the fine uranium metal powder from the slag and liner walls without changing its chemical form, in many tests a low uranium metal production figure is indicated although appreciable amounts of metal were actually produced.

Under proper operating conditions a minimum of 93.5% of the uranium introduced as UF_6 should be recovered as consolidated uranium metal. This yield of uranium metal is approximately that routinely achieved in the conventional magnesium reduction of UF_4 , i.e., $UF_4 + 2Mg \rightarrow U + 2MgF_2$. This yield figure is probably conservative, and further development efforts will probably lead to a more operable reactor system and an increase in the metal yield.

5.2 Uranium Metal Purity

The uranium metal recovered from the better runs was consolidated in a metal button found in the bottom of the graphite liner. These buttons were comparable in appearance to the metal buttons from small UF_4 -calcium bomb reductions (Fig. 5.2).

Although the UF_6 feed was not analyzed, complete chemical and spectrographic analyses were made on some of the metal buttons (Table 5.3). This metal was up to 99.9% uranium, with the major contaminants, nickel and carbon, probably coming from the Inconel UF_6 nozzle and the graphite liner.

Table 5.3. Analysis of Reduced Metal Product

Element	present	Element	present
U	99.9 ^a %	Cu	8 ppm
C	0.036 ^a %	Ga	< 0.5 ppm
Ni	0.019 ^a %	Ge	< 0.5 ppm
Fe	0.014 ^a %	Mg	41 ppm
Ag	< 0.2 ppm	Mn	1.3 ppm
Al	30 ppm		
B	< 0.5 ppm	Mo	< 1 ppm
Be	0.6 ppm	Pt	< 5 ppm
Ca	4 ppm	Ti	13 ppm
Cd	< 10 ppm	V	< 1 ppm
Cr	< 5 ppm	Zr	< 1 ppm

^a Chemical determination; others determined spectrographically.

5.3 Slag Recycle Feasibility

In order to test the feasibility of the proposed slag recycle scheme for recovering uranium-bearing material in the slag (Fig. 2.1), the amount of water-soluble uranium in the products of several runs was determined. The amount of uranium soluble in two hot water rinses of all reactor components was found to be less than 0.5% of the total uranium present in all products analyzed:

<u>Uranium Material Balances, %</u>		
<u>Water-Soluble</u>	<u>As Massive Metal</u>	<u>In Other Solids</u>
0.40	19.7	79.9
0.03	41.7	58.3
0.30	82.3	17.4

If slag processing is necessary, water dissolution of the slag with recovery of the uranium bearing material as a solid appears to be feasible.

6.0 EVALUATION AND APPLICATION OF DRUHM PROCESS

The chemical feasibility of the Druhm process was confirmed to an extent which may make it competitive for the large-scale reduction of UF_6 to uranium metal. The engineering feasibility of such a process has not been fully established, and additional engineering development would be necessary before complete economic evaluation of the process would be possible.

A completely continuous reduction system would be desirable (Fig. 6.1). Such a system would include provisions for metering UF_6 vapor and liquid sodium into a lined reaction vessel. The reactor would be at a temperature high enough to ensure that all products were liquid so that the metal could be readily separated from the slag and there could be provisions for continuous removal of the products. An off-gas system would allow trapping and recycle of excess sodium.

It appears that such a system if operable, would offer several advantages over present methods, particularly where the UF_6 was highly enriched in U-235 content and criticality considerations were important. In such a system small batch reductions are expensive, and use of the continuous reduction system with removal of uranium metal as a liquid may also by-pass the metal casting operation. It appears that the reactor size used in the Druhm development program could be operated critically safe with high U-235 enrichment by a combination of mass flow rate control and geometry control.⁸

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Fig. 6.1. Proposed continuous Druhm process.

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8.0 APPENDIX

8.1 Equilibrium Composition of UF₆-Na Mixture

It was assumed that the reaction $\text{UF}_6 + \text{Na} \rightarrow \text{U} + 6\text{NaF}$ could be represented by the following stepwise reactions:

It was further assumed that the first reaction goes to completion. Thus the equilibrium composition of the reaction mixture of interest can be represented by

and the components at equilibrium will be UF₄, Na, UF₃, NaF, and U metal.

The temperature range of interest is from the melting point of uranium (~1405°K) to the boiling point of UF₄ (~1690°K).⁵ This will encompass the proposed operating temperature of 1473°K. Since available thermodynamic data are extrapolated to this temperature range, the results will be qualitative only. The physical state of each component will be:

<u>Component</u>	<u>Physical state</u> ⁵
UF ₄	liquid
Na	gas

UF ₃	solid
NaF	liquid
U	liquid

With a basis of 100 moles of UF₆ and 600N moles of Na, where $N > 1$ and represents sodium excess, the following nomenclature will be used for initial and equilibrium amounts of each component, the equilibrium amount being determined by simple material balance considerations:

Compound	Initial Amount, moles	Equilibrium Amount, moles
UF ₄	100	A
Na	600N-200	B = 600N - 600 + 4A + 3C
UF ₃	0	C
NaF	200	D = 600 - 4A - 3C
U	0	E = 100 - A - C
Total moles	600N + 100	600N + 100

For a total pressure of 1 atm, the thermodynamic equilibrium constant, K, for each reaction can be represented by

$$K_I = \frac{a_C a_D}{a_A} \frac{1}{\gamma_B N_B}$$

$$K_{II} = \frac{a_E a_D^3}{a_C} \frac{1}{\gamma_B^3 N_B^3}$$

where a_A , a_C , a_D , a_E = activities of UF₄, UF₃, NaF, and U

γ_B = fugacity coefficient of Na

N_B = mole fraction of Na in gaseous phase

The UF₄, UF₃, and NaF will probably form one liquid phase and uranium will form another. Assuming that the UF₄-UF₃-NaF phase forms an ideal solution, the activities are represented by⁹

$$a_A = M_A \quad a_C = M_C \quad a_D = M_D \quad a_E = 1$$

where M_A , M_C , M_D = mole fraction of UF₄, UF₃, and NaF in the UF₄ - UF₃ - NaF solution.

With the above values for the activities and assuming that Na is the only gas phase component ($N_B = 1$), the equilibrium constants can be expressed by

$$K_I = \frac{M_C M_D}{M_A}$$

$$K_{II} = \frac{M_D^3}{M_C}$$

Using the values of each component at equilibrium gives

$$M_A = \frac{A}{600 - 3A - 2C}$$

$$M_C = \frac{C}{600 - 3A - 2C}$$

$$M_D = \frac{600 - 4A - 3C}{600 - 3A - 2C}$$

which may be substituted in the equilibrium constant equations:

$$K_I = \frac{C(600 - 4A - 3C)}{A(600 - 3A - 2C)}$$

$$K_{II} = \frac{(600 - 4A - 3C)^3}{C(600 - 4A - 3C)^2}$$

Assuming that $(4A + 3C) \ll 600$ and $(3A + 2C) \ll 600$, these equations reduce to

$$K_I = C/A \text{ and } K_{II} = 600/C$$

from which

$$A = C/K_I = \text{mole \% UF}_4$$

$$C = 600/K_{II} = \text{mole \% UF}_3$$

These two equations were used to obtain equilibrium values of UF_3 and UF_4 at 1 atm and various temperatures in the temperature range 1132 - 1400°C (Table 3.3).

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