Catalytic activity of uranium compounds for hydrodesulfurization reactions
by Roger D Jensen

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

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Upanium compounds did not act as promoters for a cobalt-molybdate catalyst. Uranium oxysulfide was shown to have some activity when supported on low surface area supports. Uranium oxide and sulfides were shown to have activity on higher surface area,supports with uranium oxide showing the highest activity. The activity of uranium oxide catalyst was shown to increase with an increase in uranium concentration.

In general, all sulfur conversions with uranium catalysts were significantly lower than with cobalt-molybdate catalyst.

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TABLE OF CONTENTS

ABSTRACT

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Uranium compounds did not act as promotors for a cobalt-molybdate catalyst. Uranium oxysulfide was shown to have some activity when supported on low surface area supports. Uranium oxide and sulfides were shown to have activity on higher surface area supports with uranium oxide showing the highest activity. The activity of uranium oxide catalyst was shown to increase with an increase in uranium concentration.

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INTRODUCTION

Large stockpiles of uranium depleted in U_{235} have accumulated as a byproduct of national defense and nuclear energy development. The U. S. Atomic Energy Commission is interested in developing uses for this material and is sponsoring research in several possible areas of use. The research from which this thesis is taken was part of a project to examine uranium compounds as hydrodesulfurization and hydrodenitrogenation catalysts. The project was conceived at the suggestion of USAEC personnel at Oak Ridge, Tennessee, and performed at the Chemical Engineering Department, Montana State College.

There is increasing interest in hydrodesulfurization and hydrodenitrogenation reactions in the petroleum industry and development of a good catalyst would open the way to a large potential use of depleted uranium. Uranium and uranium compounds have been shown to have catalytic effects for many different reactions. Some of the more promising uses reported have been for polymerization of olefins (4), dehydrogenation of propane (11), alkylation (15), and catalytic cracking of petroleum fractions (12). Recent literature surveys on uses of depleted uranium list many other catalytic applications (2,3).

This thesis is a report on and discussion of the catalytic activity of various uranium compounds in the hydrodesulfurization of a Kuwait diesel oil fraction containing 1.83 - 1.84 weight percent sulfur.

Uranium compounds were investigated as promoters on a cobalt-molybdate catalyst and as catalysts supported on alumina, silica, silica-alumina, magnesia, and magnesia-alumina catalyst supports.

PROCEDURE AND APPARATUS

The initial treatment of each catalyst was essentially the same and for that reason will be discussed here. All of the cobalt-molybdate catalyst and catalyst supports used were in pelleted form. On the basis of information in the literature regarding catalyst preparation techniques (5) it was decided to deposit uranium on the pellets as a water soluble salt. Uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ was chosen since it is water soluble to a high degree, easily obtained, and readily converted to an insoluble oxide. Immersion of the pellets in a uranyl nitrate solution was the impregnation method used. The weight percent water adsorbed by the catalyst or support was determined by immersing the pellets in water and superficially drying them by gentle rolling on absorbent paper prior to weighing. After determining water adsorption data, the following procedure was used to calculate the concentration of uranyl nitrate required in the immersion solutions.

Example: 10% uranium desired in finished catalyst
water adsorbed by support = 45.7g/100g
11.1g U/100g support = 10% U
atomic weight uranium = 238
mol weight $UO_2(NO_3)_2 \cdot 6H_2O$ = 502

$$\frac{(502)}{(238)}\ 11.1 = 23.4\text{g } UO_2(NO_3)_2 \cdot 6H_2O/100\text{g support}$$

$$\frac{23.4}{45.7} = \frac{x}{100}$$

$$x = 51.3\text{g } UO_2(NO_3)_2 \cdot 6H_2O/100\text{g water}$$

A uranyl nitrate solution of the concentration prescribed by the above calculation was prepared, the pellets immersed, superficially dried, and then air dried at 110-120°C for 5 hours. A check on this method, by determining the weight increase of the support after treatment, showed that the expected amount of uranyl nitrate was added.

Treatment of the various catalysts differed substantially from this point on and will be discussed separately under Results. A schematic diagram of the apparatus used for further treating is shown on Figure 1, page 30. This apparatus consisted of a Vycor tube heated by an electric furnace. The atmosphere in the tube could be varied from pure air, nitrogen, methane, or hydrogen sulfide, to any mixture of these, through an arrangement of valves. In some of the treatments, CH_4 was saturated with CCl_4 vapor by passage through a sintered glass disk and then through a column of liquid CCl_4.

The catalysts were tested for hydrodesulfurization activity in a fixed-bed flow reactor as shown on Figure 2, page 31. Kuwait diesel oil was chosen as the feedstock because information was desired on a typical commercial product.

The fixed-bed reactor consisted of a vertical section of 3/4 in. ID stainless steel pipe 30 in. long. The outside of the pipe was wound with five nichrome heating coils and covered with magnesia insulation. Power was supplied to the heating coils through variable autotransformers (Variac).

Temperature in the reactor was measured by four iron-constantan thermocouples placed within a 3/16-in. stainless steel thermowell which extended down the center of the reactor. The reactor was packed with inert alundum balls at each end and the catalyst under study in the central portion.

Liquid feed was supplied to the top of the reactor by a Hills-McCanna pump. Hydrogen was passed through a DeOxo unit, dried, metered through a rotameter, and mixed with the liquid feed stream at the reactor top. Commercial bottled hydrogen was used and no attempt was made to recover or reuse it.

The reaction products leaving the bottom of the reactor were condensed under pressure, depressurized through a Grove back-pressure regulator, cooled in a secondary condenser, and the liquid and gaseous portions separated.

Samples of liquid product were briefly stripped with commercial bottled nitrogen to remove any dissolved H_2S and then analyzed for sulfur content with a combustion tube sulfur determination apparatus.

No attempt was made to identify any of the sulfur compounds in either the feed or product and the performance of each catalyst was based on the weight percent sulfur removed.

RESULTS

A total of 36 runs are reported in this thesis which include 8 control runs and 28 different catalyst treatments. The resultant catalysts may be divided into three groups as shown below:

1. Uranium promoted cobalt-molybdate (10 runs)
2. Low surface area uranium oxides and oxysulfides (16 runs)
3. Higher surface area uranium sulfides and oxides (10 runs)

The treatment and hydrodesulfurization results will be presented by groups in the order listed above.

<u>Group I</u>. Uranium-promoted Cobalt-molybdate

The purpose of this part of the investigation was to determine if uranium compounds in small concentrations had any beneficial effect upon commercial cobalt-molybdate catalyst. The catalyst used was Peter Spence Comox catalyst, (calcined 1/8" stearate tablets, CoO, 2.5%; MoO_3, 14%; supported on activated alumina). This laboratory has had considerable experience with this catalyst and it was known to be a good desulfurization catalyst. A total of ten runs are included in this group and are designated C-1 to C-10.

The catalyst treatment and average percent conversion of sulfur for these ten runs are given in Table I, page 25. The initial catalyst treatment of impregnation and drying, as discussed under Procedure and Apparatus, pages 6-8, was used in runs C-2, -3, -5, -6, -7, -9, and -10, and the concentration of uranium varied from 0.25-2.0 weight percent. Runs C-1, -4, and -8 were control runs in which no uranium was used.

The H_2/H_2S treatment used in runs C-4 through C-10 consisted of passing a commercially prepared mixture of 95% H_2, 5% H_2S over the catalyst in the reactor at 200 psig, 288°C for 24 hours. This treatment had proved to be beneficial to cobalt-molybdate catalyst in previous work done at this laboratory. These runs were made at the following conditions:

Feed stock:	Kuwait diesel oil (1.835% sulfur)
Catalyst charge:	65 ml
Space velocity:	5.0 ml feed per ml catalyst per hr
Reactor pressure:	200 psig
Reactor temperature:	371°C (700°F)
Hydrogen flow rate:	1000 SCF H_2 per bbl feed

Runs C-1 through C-7 were of 12 hours duration and runs C-8 through C-10 were of 24 hours duration. The first 4 hours of each run was considered to be lineout time and was not included in the conversion data. The catalysts for runs C-5 and C-7 differ only in that C-7 catalyst was impregnated four times with very dilute solution and dried 5 hours at 110-120°C after each impregnation. However, the final uranium concentration (0.5%) was the same in both catalysts. This was done to determine if the decrease in activity of the uranium promoted catalysts could be attributed to a mechanical blocking of the catalyst pores. This possibility is discussed by Folkins and Miller (5).

The catalyst for run C-10 was calcined in air at 450°C for one hour after the initial impregnation and drying, but prior to the H_2/H_2S treatment, in an attempt to produce a more active form of uranium. The conversions listed in Table I are average conversions over the entire run, after lineout time. Samples were taken every hour during runs C-1 through C-4, every second hour during runs C-5 through C-7, and every fourth hour during runs C-8, -9, and -10. Representative plots of conversion versus time for both 12 hr and 24 hr runs are shown on Figures 3 and 4, pages 32-33.

An examination of the conversion values indicates that for any given series of catalyst treatments the conversion decreases as the percent uranium increases.

(Example: C-4, 0% uranium, 63.2% conversion; C-5, 0.5% uranium, 59.8% conversion; C-6, 2.0% uranium, 59.0% conversion.)

The uranium compounds present on the catalyst do not appear to be extremely poisonous to the catalytic activity since low percentages of uranium had very little effect. The poisoning is probably caused by mechanical blocking of the catalyst pores by formation of large crystals around the pore openings. Immersion in more dilute solutions may tend to reduce the size crystal formed, as evidenced by the following results:

C-5, 0.5% uranium, 1 immersion, 59.8% conversion;

C-7, 0.5% uranium, 4 immersions, 63.3% conversion.

Calcining at 450°C (C-10) appears to decrease the activity significantly, probably by sintering the cobalt-molybdate catalyst slightly.

Group II. Low Surface Area Uranium Oxides and Oxysulfides.

The sixteen runs reported in this group (L-1 through L-16) were made to evaluate uranium compounds when deposited on various inert catalyst supports. Four catalyst supports were obtained from the Norton Company. These include silica-alumina, silica, magnesia-alumina, and magnesia supports. Their chemical analyses and physical properties as given by the manufacturer are in Table II, p. 26. In general, these were high service temperature materials with low surface area ranging from less than 1 to 6-8 m^2/g. The high temperature characteristic was desirable so that the catalyst could be treated with H_2S at high enough temperature to form uranium oxysulfide.

Each of these four catalyst supports were first tested without uranium or treatment. Three tests on each were run with 10% uranium. The treatments after impregnating with uranyl nitrate (as outlined in Procedure and Apparatus, p. 6) was either drying in air at 110°C, drying at 110°C and calcining in an electric oven for 100 minutes at 1000°C, or drying at 110°C and passing 100% H_2S over the catalyst at 1050°C. (Schematic flow diagram shown on Figure 1, p. 30 .).

A thermodynamic study shows that the heating of uranyl nitrate to 1000°C in the presence of air would result in a mixture of UO_3, U_3O_8, U_4O_9, and UO_2 with the equilibrium between these oxides favoring the formation of U_3O_8. (See Appendix, page 24.)

The treatment of uranyl nitrate with H_2S at 1050°C (the limiting temperature of existing equipment) is a relatively low temperature for the formation of uranium oxysulfide (UOS) according to Picon and Flahaut (14). They predict that at these temperatures UO_2 will be formed prior to formation of UOS, as illustrated in the following stepwise reaction:

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_3 \longrightarrow U_3O_8 \text{ (olive)}$$

$$UO_3 \xrightarrow[1050°C]{H_2S} UO_2 \text{ (brown - black)}$$

$$UO_2 \xrightarrow[1050-1350°C]{H_2S} UOS \text{ (black)}$$

In this work it was noted that catalysts of different colors were formed depending on whether they were cooled in air or H_2S. When cooled in air the catalyst was of a dark blue-green or black nature and was indistinguishable from catalyst formed by the calcining of uranyl nitrate in air at 1000°C (see above), while when cooled in H_2S, the catalyst was about half light brown and half black. Possibly the catalyst cooled in air ended up as a mixture of U_3O_8 and UO_2 and the catalyst cooled in H_2S ended up as a mixture of UO_2 and UOS. It was never determined analytically which compounds were present but in any event the latter treatment (H_2S cooled) was used in all four runs.

The treatment of each catalyst and percent conversion for each run is given in Table III, p. 27. The reactor conditions for these runs were identical to those for runs C-1 through C-10 except that the space velocity was lowered to 2.0 ml feed per ml catalyst per hr. All the runs were 24 hours long except L-7, which was terminated after 14 hours because of mechanical difficulty. The conversions in Table III are based on samples taken during the eighteenth hour of operation except for L-7 which was based on the twelfth hour.

All conversion values are very low and from Table III it is difficult to see if the treatments had any effect on the conversion. The same results are presented in Table IV, p. 28, in such a manner as to be easier to compare the various treatments.

The most significant improvement in conversion appears to be with the high temperature H_2S treatment (UOS) of uranyl nitrate supported on alumina-silica (LA-623) and alumina-magnesia (LMA-703). Both of these carriers are of considerably higher surface area than the other two and therefore could be expected to better show any trends.

An alternate conclusion which might be drawn from Table IV is that the combination of alumina and uranium might be the reason for any increased activity since alumina was a major constituent in the catalysts which showed improvement, while being absent in those which showed no improvement.

Group III. Higher Surface Area Uranium Sulfides and Oxides.

The ten runs in this section are composed of one control run (H-1), six sulfide runs (H-2 through H-7), and three oxide runs (H-8, -9, and -10). The support used in these runs was available in the laboratory but its origin is unknown and therefore the manufacturer's specifications were unavailable. Chemical analysis (emmission spectrometry) by the Chemistry Department, Montana State College, shows it to be 99+% alumina with traces of barium, cadmium, copper, iron, magnesium, sodium, and potassium compounds. Physical properties determined in our laboratory are as follows:

Bulk density:	0.85g/cc
Water adsorption:	37.2%
Max. service temp:	>700°C

The surface area of this support was not experimentally determined but was known to be higher than those obtained from Norton. This was evidenced by a noticeable amount of heat being evolved when this support was wetted while no heat was evolved by any of the Norton supports.

The sulfide and oxide runs are reported and discussed separately in this section with the same control run (H-1) being used as a comparison with both types. The conditions under which these runs were made are as follows:

Feed Stock: Kuwait diesel oil (1.835% sulfur)
Catalyst charge: 80 ml
Space velocity: 0.75 ml feed per ml catalyst per hr
Reactor pressure: 200 psig
Reactor temp: 371°C (700°F)
Hydrogen flow rate: 5000 SCF H_2 per bbl feed

All runs were 8 hours long except H-10, which was extended to 16 hours. All comparisons were made on the basis of average conversion during the seventh and eighth hours.

Part A. Uranium Sulfides

Uranium sulfides were examined because one of the possible mechanisms for cobalt-molybdate catalyst in hydrodesulfurization, postulated from previous work done in this laboratory, is as follows (1):

$$CoO + H_2S \longrightarrow CoS + H_2O$$

$$C_4H_4S + 2CoS \longrightarrow Co_2S_3 + C_4H_4$$

$$Co_2S_3 + C_4H_4 \xrightarrow{H_2} CoS + H_2S + C_4H_{10}$$

While this may not be the actual mechanism, it represents a mechanism in which the sulfur from the hydrocarbon fraction combines first with the active catalyst (i.e., CoO, MoO_3) which is in turn reduced by hydrogen. Investigation of uranium sulfides from this point of view was further justified on the basis of work done by Picon and Flahaut (14) who noted a change in uranium sulfide composition in the presence of H_2S at the temperature range of our reactor operation (370-380°C).

Six separate uranium sulfide catalysts (10% uranium) were prepared and tested (H-2 through H-7). The initial treatment of impregnation and drying was the same as outlined in Procedure and Apparatus, p. 6 .

Uranium sulfide can be formed in various ways. The method chosen in this study was (1) conversion of uranyl nitrate to an oxide by heating, (2) conversion of the oxide to the chloride, and (3) conversion of the chloride to the sulfide as shown below:

$$UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow{\Delta} UO_3 \text{ or } UO_2$$

$$UO_3 \text{ or } UO_2 \xrightarrow{CCl_4} UCl_4$$

$$UCl_4 \xrightarrow{H_2S} US_2$$

This treatment was done in the apparatus shown on Figure 1, p. 30.

The first treatment tried was passing pure CCl_4 vapor over the uranyl nitrate (or thermal decomposition product) at 400°C in an attempt to form UCl_4. This method was suggested by Katz and Seaborg (9) but proved unsuccessful as the reaction tube plugged within minutes. The next approach tried was to pass CH_4 saturated with CCl_4 vapor over the catalyst at 400°C. This treatment proved successful and was continued for 5 hours because at the CH_4 rate used, this length of time was necessary to insure an excess of CCl_4 being contacted with the uranyl nitrate. Methane was used as a carrier gas for two reasons, (1) availability at low pressure and (2) evidence by Katz and Seaborg (9) that under these conditions, CH_4 or H_2 produces a reactive form of UO_2.

$$UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow[400°C]{CH_4} UO_2$$

$$UO_2 \xrightarrow[400°C]{CCl_4} UCl_4$$

The resultant product from the above step was next treated <u>in situ</u> by a stream of H_2S, the temperature being raised from 400°C to 500°C in about 2 hours. The temperature was raised in this manner in an attempt to form a stable crystalline form of US_2 as indicated by Picon and Flahaut (14). This catalyst was then used in run H-2.

Variations of this treatment used were (1) doubling the time of CH_4 + CCl_4 treatment (10 hrs, H-3); (2) treating with CH_4 and CCl_4 using nitrogen as carrier gas, separately, (5 hrs each, H-4); (3) raising the CH_4 + CCl_4 treatment temperature from 400°C to 500°C (H-5, -6, and -7); (4) doubling the H_2S treatment time (4 hrs, H-6), and (5) raising the H_2S treatment temperature to 500-600°C, (H-7).

Examination of these treatments and results (Table V, p. 29) shows no significant increase in activity with any catalyst over the first treatment used (H-2). A significant decrease in H-3 and a slight decrease in H-4 are apparent, however. The decrease in H-3 may be explained by mechanical blocking of catalyst pores caused by a carbon laydown from the decomposition of CCl_4

$$CCl_4 \xrightarrow{\Delta} C + 2Cl_2 .$$

as evidenced by a black layer on the outside of the catalyst pellets.

In general, all sulfide treatments increased sulfur conversion over the support alone, with four of the six treatments increasing it 3-4 times. No significant differences were noted in these four runs.

Part B. Uranium Oxide of Varying Concentration

The effect of varying uranium concentration from 0-15% was studied by runs H-1, -8, -9, and -10. These catalysts were prepared by impregnation and drying as before, and subsequent calcining at 450-500°C for one hour. The calcining temperature was chosen arbitrarily, the main consideration being to keep it below the sintering point of the support.

As can be seen on Figure 6, p. 35, activity of this series does increase with uranium concentration, seeming to approach a value of about 20% conversion asymptotically.

Run H-10 (15% uranium) was extended to 16 hr to determine if activity decreased with time. As can be seen from Figure 5, p. 34, activity decreased sharply after about 12 hr on stream. This decrease in activity does not figure in the conversions plotted on Figure 6, however; these conversions were calculated from samples taken during the seventh and eighth hours of operation.

SUMMARY AND RECOMMENDATIONS

The hydrodesulfurization activity of the catalysts studied was determined by attempting to remove sulfur from a Kuwait diesel oil fraction containing 1.835% sulfur. The reaction was carried out at 700°F and 200 psig in a fixed-bed, continuous flow, catalytic reactor.

The addition of small amounts of uranium compounds to cobalt-molybdate catalyst as a promoter decreased its activity. The percent conversion experienced for sulfur removal with uranium on low surface area carriers was quite low, with uranium oxysulfide somewhat better than uranium oxides.

Sulfur removal with higher surface area catalysts (uranium sulfides and oxide) was considerably higher than with the low surface area supports, but this was accomplished with more severe operating conditions. Assuming a first order reaction (8) a comparison was made between conversion at these conditions and at the conditions used with the low surface area supports. The following relationship was used:

$$\ln(1-x_1) = \frac{(SV)_2}{(SV)_1} \ln(1-x_2)$$

where:

x_1 = sulfur conversion at (1) operating conditions

x_2 = sulfur conversion at (2) operating conditions

$(SV)_1$ = space velocity at (1) operating conditions

$(SV)_2$ = space velocity at (2) operating conditions

According to this comparison, the maximum observed conversion of 20.8% would be equivalent to about 8.5% conversion at the less severe conditions.

This is significantly higher than the maximum conversion with low surface area supports (3.75%). This was a definite improvement over low surface area supports and may be explained by the surface area difference.

Activity was definitely shown with both higher surface area oxides and sulfides, with the oxide being somewhat higher. Activity was shown to increase with an increase in uranium oxide concentration in the area investigated (0-15% uranium).

In general, all uranium compounds showed less activity than the commercial catalyst used, cobalt-molybdate.

It is recommended that any further work done in this area of research should begin with a study of hydrodesulfurization activity as a function of catalyst surface area. Once a correlation has been established, a further study of high surface area oxides, sulfides, and oxysulfides may be warranted. Before this can be done, however, high temperature, high surface area supports must be made available because of the high temperatures required to form uranium oxysulfide.

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APPENDIX

TABLE I. PROMOTION OF COBALT-MOLYBDATE CATALYST WITH URANIUM

Run No.	% Uranium	Catalyst Preparation	% Sulfur Conversion
C-1	0.0	Dry 110°C, 5 hr	51.2
C-2	0.5	Impregnate; Dry 110°C, 5 hr	47.3
C-3	2.0	Impregnate; Dry 110°C, 5 hr	36.2
C-4	0.0	Dry 110°C, 5 hr; H_2/H_2S at 288°C, 24 hr	63.2
C-5	0.5	Impregnate; Dry 110°C, 5 hr; H_2/H_2S at 288°C, 24 hr	59.8
C-6	2.0	Impregnate; Dry 110°C, 5 hr; H_2/H_2S at 288°C, 24 hr	59.0
C-7	0.5	Impregnate 4 times with very dilute solution and Dry 110°C, 5 hr after each; H_2/H_2S at 288°C, 24 hr	63.3
C-8	0.0	Dry 110°C, 5 hr; H_2/H_2S at 288°C, 24 hr	67.5
C-9	0.25	Impregnate; Dry 110°C, 5 hr; H_2/H_2S at 288°C, 24 hr	62.6
C-10	2.0	Impregnate; Dry 110°C, 5 hr; Heat 450°C in air, 1 hr; H_2/H_2S at 288°C, 24 hr	52.8

TABLE II. PROPERTIES OF CATALYST SUPPORTS

Chemical Analysis	Catalyst Designation			
	LA-623	LMA-703	LM-705	LS-438
Al_2O_3	77.0%	70.50%	0.13%	4.5%
SiO_2	21.2	0.01	2.69	94.0
FeO_3	0.2	0.08	0.05	0.5
TiO_2	0.5	0.01	--	0.3
Na_2O, K_2O	0.7	0.12	0.01	0.3
MgO	0.2	29.30	96.99	0.1
CaO	0.2	0.05	0.13	0.3
Physical Properties				
Porosity, %	60-65	50-54	43-45	30-35
Water Absorption, %	51-56	35-37	22-24	18-23
*Water Absorption, %	45.7	27.0	18.5	14.8
Bulk Density, g/cc	1.1-1.2	1.4-1.5	1.92	1.5-1.7
App. Sp. Gravity, g/cc	3.0-3.2	3.0-3.2	3.49	2.3-2.4
Packing Density, lb/ft^3	46	55-60	75	56-58
Surface Area, M^2/g	6- 8	3	less than 1	less than 1
Max. Service Temp., °C	1000	1400	1200	1200

*We determined this water absorption data experimentally and used it as the basis for calculating the concentration of the uranyl nitrate solutions.

TABLE III. URANIUM CATALYST ON LOW SURFACE AREA SUPPORTS

Run No.	Support	% U	Catalyst Preparation	% Conversion
L-1	LA-623	0	None	2.07
L-2	LMA-703	0	None	1.80
L-3	LS-438	0	None	1.31
L-4	LM-705	0	None	3.00
L-5	LA-623	10	Impregnate; Dry 110°C, 5 hr	2.45
L-6	LMA-703	10	Impregnate; Dry 110°C, 5 hr	1.58
L-7	LS-438	10	Impregnate; Dry 110°C, 5 hr	1.52
L-8	LM-705	10	Impregnate; Dry 110°C, 5 hr	1.96
L-9	LA-623	10	Impregnate; Dry 110°C, 5 hr; Heat in air at 1000°C, 100 min	1.80
L-10	LMA-703	10	Impregnate; Dry 110°C, 5 hr; Heat in air at 1000°C, 100 min	1.03
L-11	LS-438	10	Impregnate; Dry 110°C, 5 hr; Heat in air at 1000°C, 100 min	1.90
L-12	LM-705	10	Impregnate; Dry 110°C, 5 hr; Heat in air at 1000°C, 100 min	1.03
L-13	LA-623	10	Impregnate; Dry 110°C, 5 hr; Heat in H_2S at 1050°C, 1 hr	3.75
L-14	LMA-703	10	Impregnate; Dry 110°C, 5 hr; Heat in H_2S at 1050°C, 1 hr	2.45
L-15	LS-438	10	Impregnate; Dry 110°C, 5 hr; Heat in H_2S at 1050°C, 1 hr	1.25
L-16	LM-705	10	Impregnate; Dry 110°C, 5 hr; Heat in H_2S at 1050°C, 1 hr	2.45

TABLE IV. PERCENT CONVERSION FOR VARIOUS TREATMENTS ON LOW SURFACE AREA CATALYST SUPPORTS

Catalyst Support	Preparations			
	None	Impregnate Dry	Impregnate Dry Heat in H_2S	Impregnate Dry Heat in Air
LA-623	2.07	2.45	3.75	1.80
LMA-703	1.80	1.58	2.45	1.03
LM-705	3.00	1.96	2.45	1.03
LS-438	1.31	1.52	1.25	1.90

TABLE V. HIGHER SURFACE AREA URANIUM SULFIDES

Run No.	% U	Catalyst Preparation	% Conversion
H-1	0	None	3.8
H-2	10	CCl_4 + CH_4, simultaneously, 400°C, 5 hr; H_2S 400-500°C, 2 hr	13.3
H-3	10	CCl_4 + CH_4, simultaneously, 400°C, 10 hr; H_2S 400-500°C, 2 hr	7.5
H-4	10	CH_4, 400°C, 5 hr; CCl_4 (nitrogen carrier gas), 400°C, 5 hr; H_2S 400-500°C, 2 hr	12.1
H-5	10	CCl_4 + CH_4, simultaneously, 500°C, 5 hr; H_2S 400-500°C, 2 hr	13.1
H-6	10	CCl_4 + CH_4, simultaneously, 500°C, 5 hr; H_2S 400-500°C, 4 hr	13.3
H-7	10	CCl_4 + CH_4, simultaneously, 500°C, 5 hr; H_2S 500-600°C, 2 hr	13.7

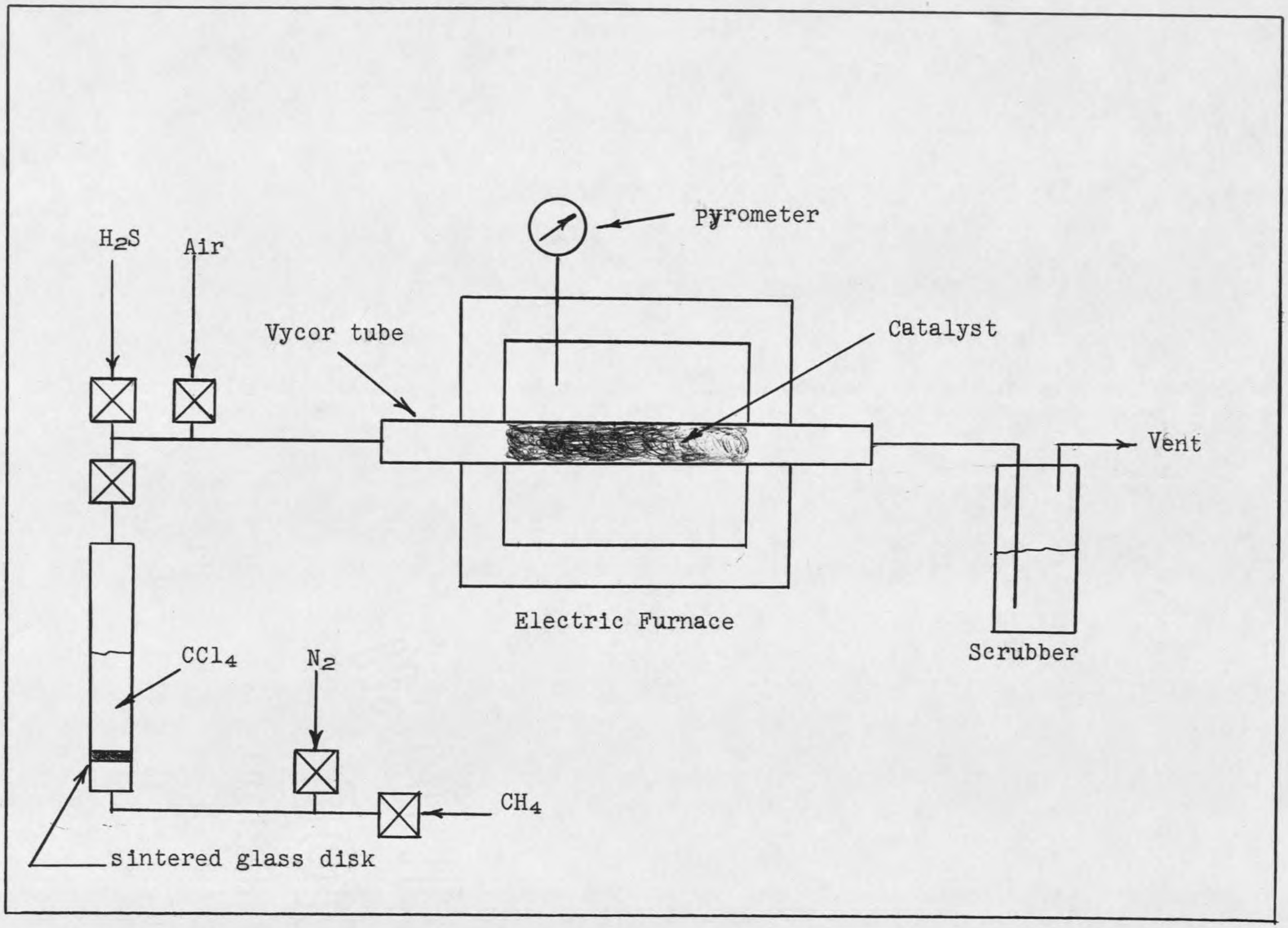


Figure 1. Schematic Diagram of Catalyst Preparation Apparatus.

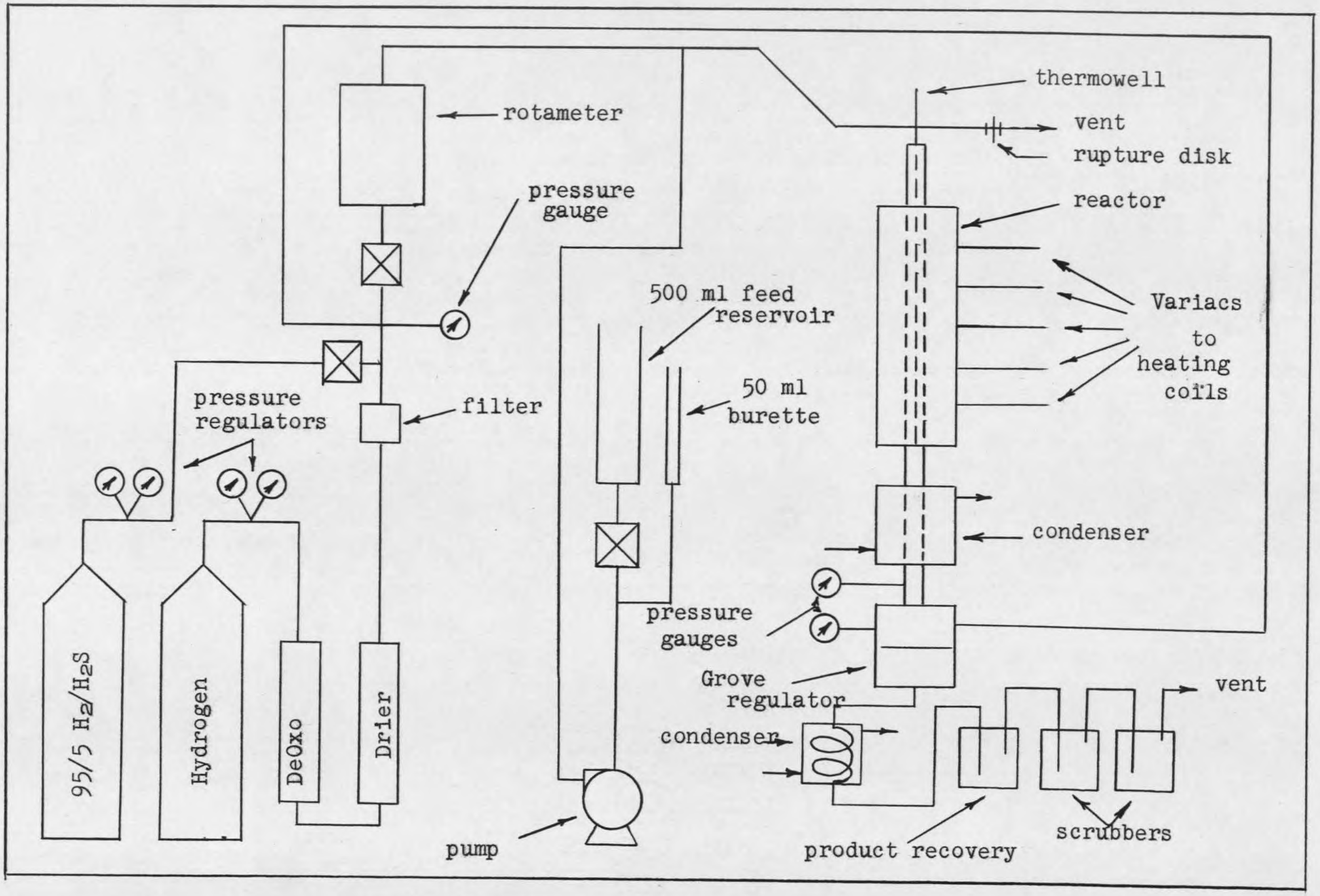


Figure 2. Schematic Flow Diagram of Catalyst Evaluation Unit.

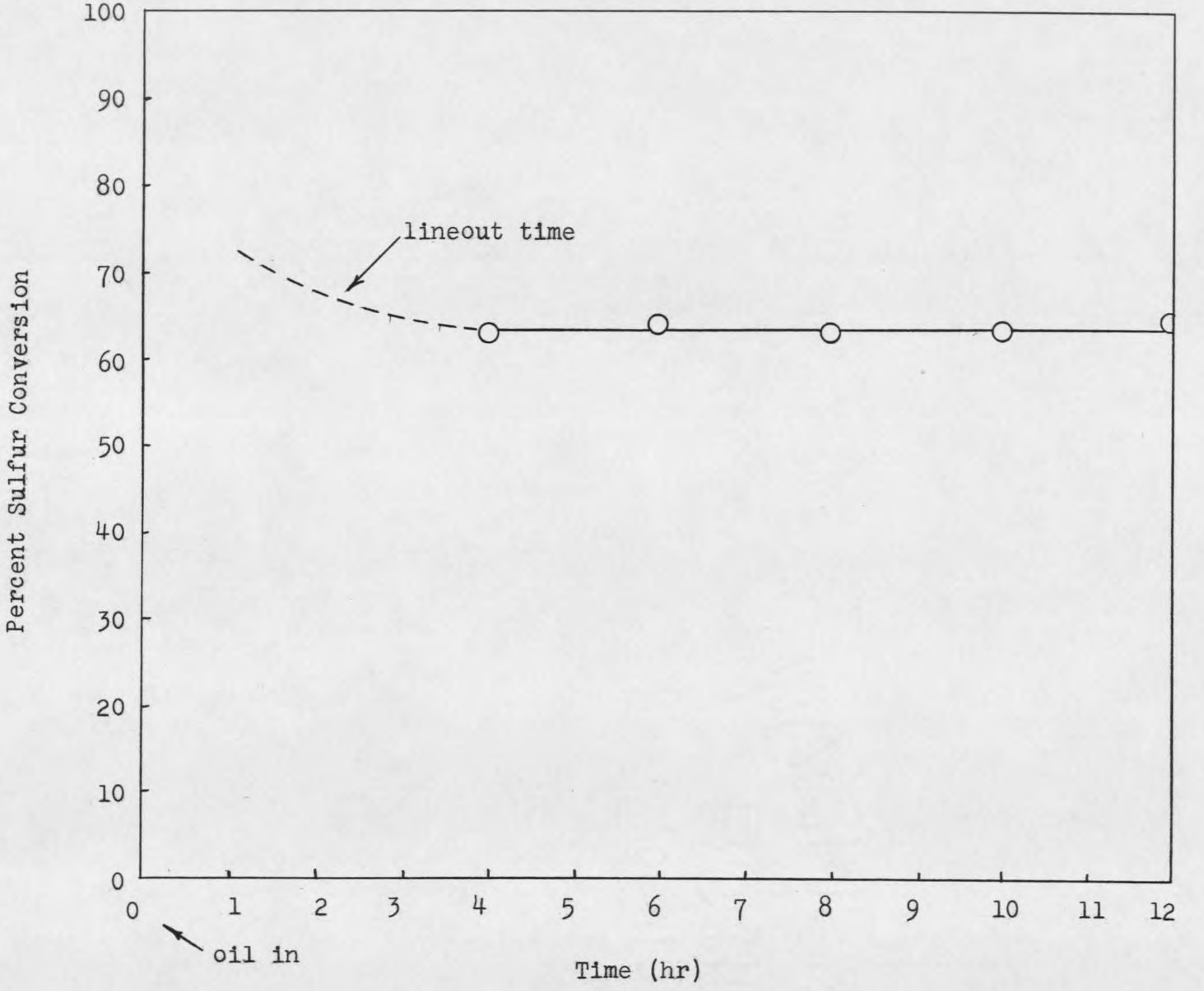


Figure 3. Plot of Sulfur Conversion vs. Time for Run C-7.

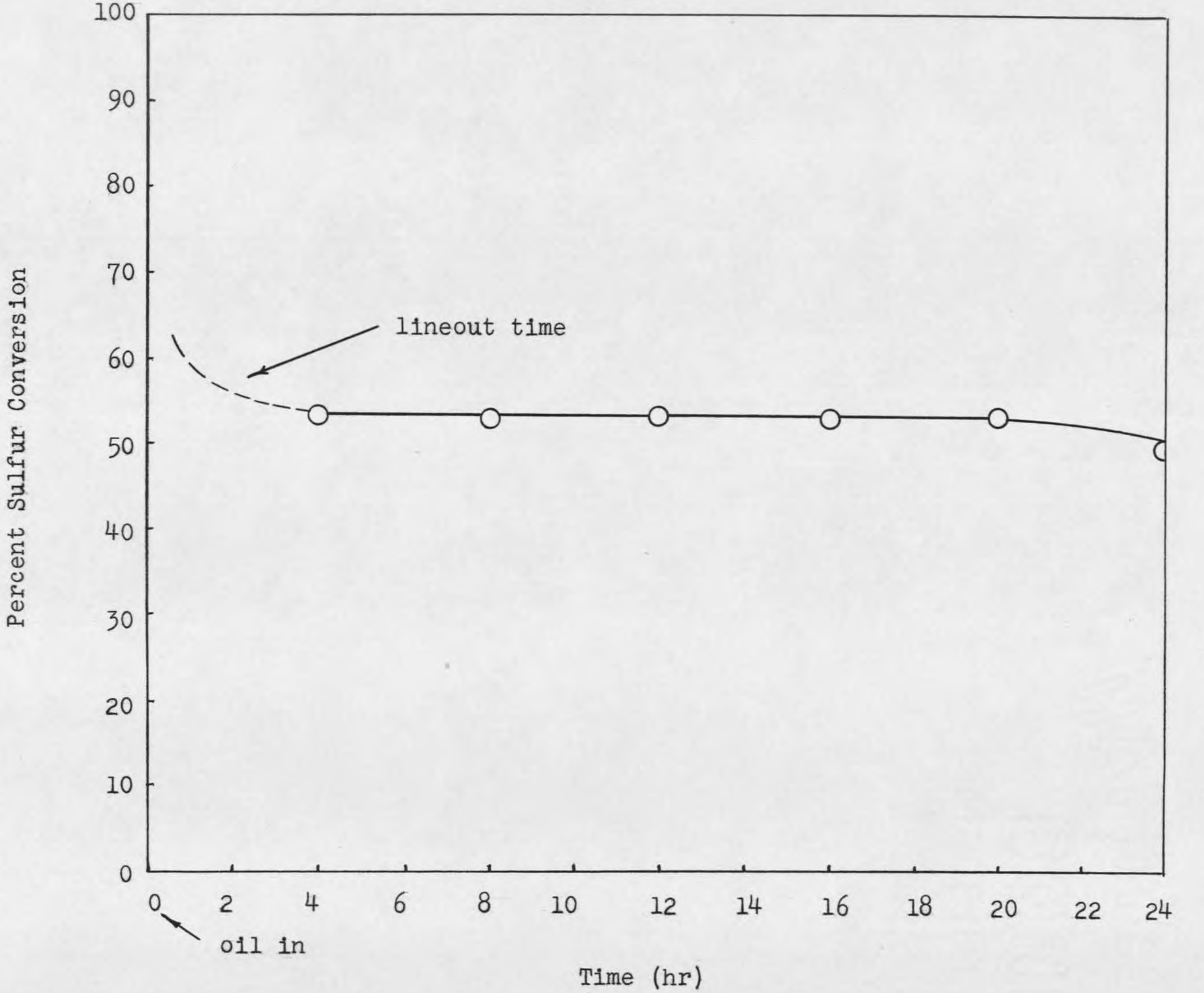


Figure 4. Plot of Sulfur Conversion vs. Time for Run C-10.

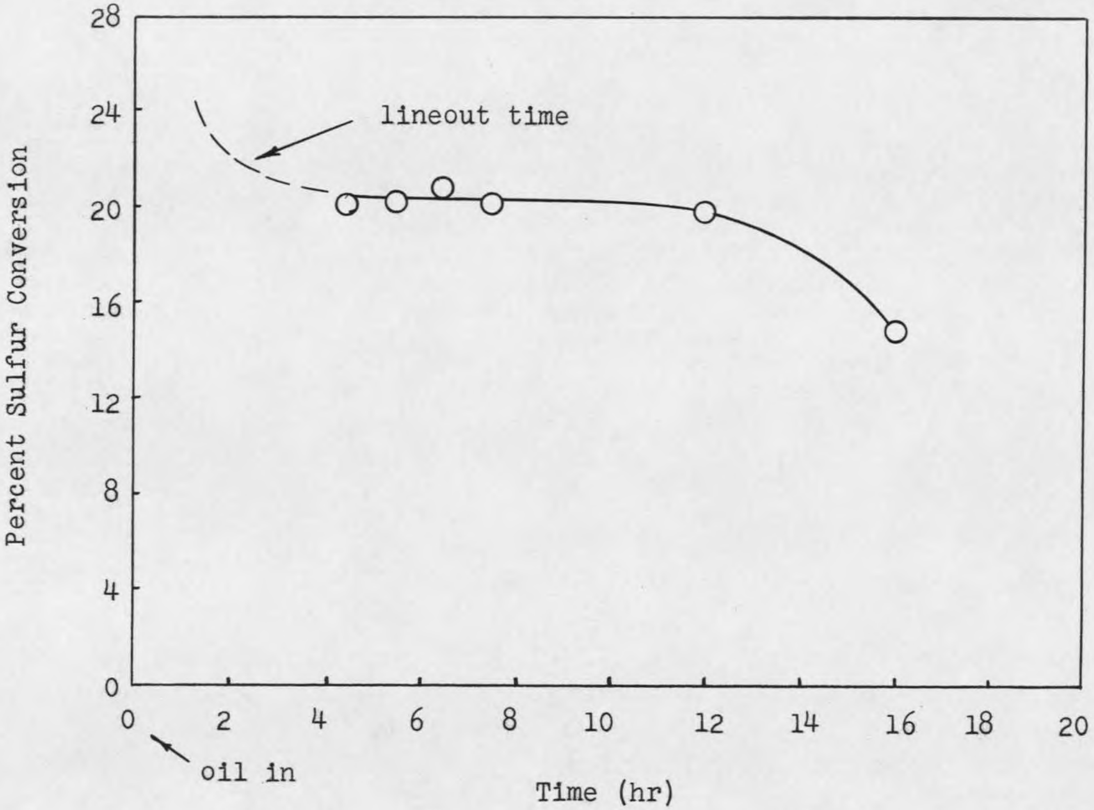
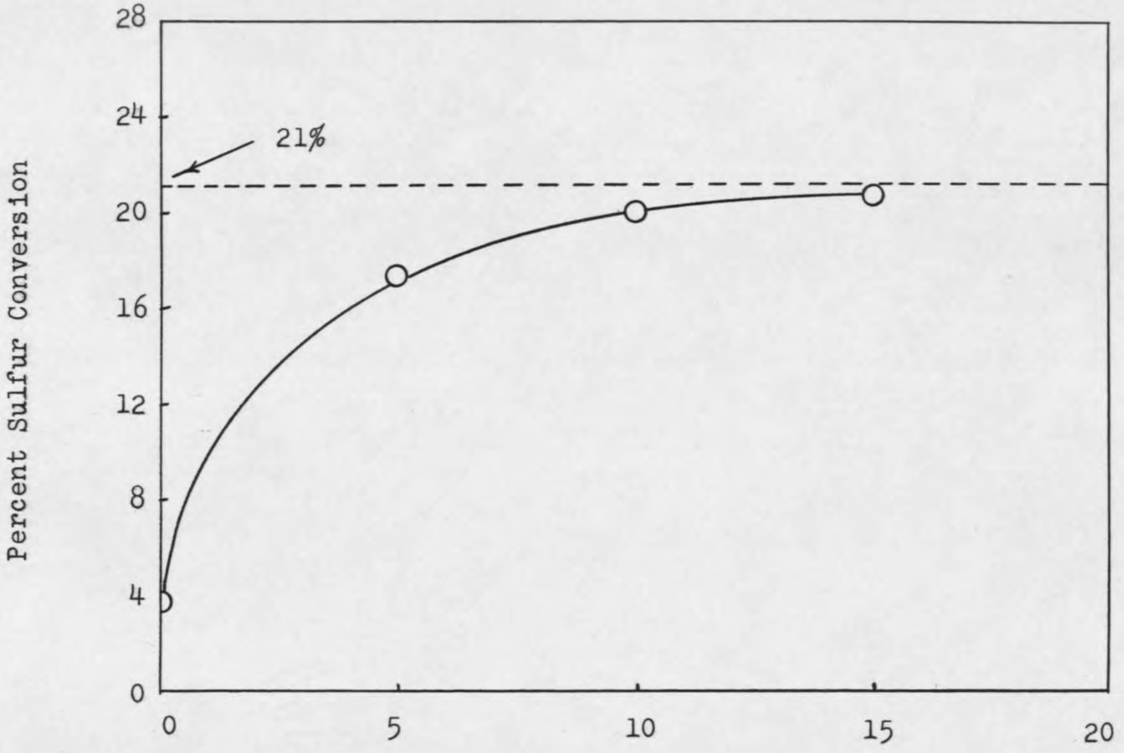


Figure 5. Plot of Sulfur Conversion vs. Time for Run H-10.



Weight Percent Uranium

Figure 6. Plot of Sulfur Conversion vs. Uranium Concentration for Higher Surface Area Uranium Oxide.

THERMODYNAMIC STUDY

of

HEATING URANYL NITRATE

from

298 to 1300°K

by

ROGER D. JENSEN

ABSTRACT

This thermodynamic study of heating uranyl nitrate shows the following:

1. At 120°C (393°K) the most probable product is $UO_2(NO_3)_2 \cdot 2H_2O$.

2. At 1000°K and 1300°K the most probable product is U_3O_8.

INTRODUCTION

This investigation was made to determine which uranium compound exists at each of several temperatures after the heating of uranyl nitrate. This problem arose during the preparation of catalysts in which inert supports were impregnated with uranyl nitrate solution, subsequently dried and heated.

Step 1. The first step in the investigation was to determine the feasibility of producing every known compound containing uranium and/or oxygen, nitrogen and water of hydration, from uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$) at 120°C (393°K). This temperature (393°K) was chosen because it is the temperature to which each batch of catalyst was initially heated.

Step 2. The second step in the investigation was to determine what compounds are formed upon heating the resultant compound from Step 1, from 393 to 1000°K. After determining which compounds could be formed at 1000°K or above, the equilibrium of these compounds was studied. This was done at 1000°K, which was chosen arbitrarily, and 1300°K which was the maximum temperature attained in the actual catalyst treatment.

RESULTS

Values used in the calculations are shown in Table AI, p. 42 and Table AII, p. 64. Values which could not be obtained in the literature were estimated. The entropy of $UO_4 \cdot 2H_2O$ was estimated by plotting entropy of the various oxides per uranium atom versus ratio of atoms of oxygen to atoms of uranium (Figure A1, p. 43) and then using the value from this plot ($UO_4 = 27.8$) as the initial point on a plot of the entropy of hydrated oxides versus moles of water of hydration (Figure A3, p. 44). The values for entropy of $UO_3 \cdot H_2O$ and $UO_3 \cdot 2H_2O$ were obtained in a similar manner from Figure A3.

The heat content (ΔH) of U_4O_9 was estimated by plotting ΔH for the other oxides and interpolating (Figure A2, p. 43).

The heat capacity (C_p) of U_3O_8 and U_4O_9 as a function of temperature was estimated by plotting C_p for UO_2 and UO_3, drawing in parallel curves for U_3O_8 and U_4O_9 (per uranium atom), and then fitting polynomials to the resulting curves (Figure A8, p. 66).

Free energies and temperatures of neutral equilibrium were calculated for equations 1-12. (See pages 45-50). Results of these calculations are shown in Figures A4 and A5. (Note: Equation 12 does not appear on these figures because the free energy and temperature of neutral equilibrium were so high as to put it off the scale.)

On the basis of results from this first step, equations 1-4 were investigated at 393°K. The equilibrium of hydrated nitrates was studied at 393°K (equations 13-15) and these results appear on page 54, Figure A6.

The study of heating $UO_2(NO_3)_2 \cdot 2H_2O$ from 393°K to 800°K (equations 16-22) is shown on pages 55-58. As a result of this study, the heating of $UO_3 \cdot 2H_2O$ from 800-1000°K was studied (equations 23-31). Results of this study appear on Figure A7, p. 63.

Heat capacity data on the oxides of uranium was used to study their equilibrium at 1000°K and 1300°K as precisely as possible (equation A-F, p. 71). Results of this study are shown on Figures A9 and A10, p. 72.

Investigation of the Heating of Uranyl Nitrate

$UO_2(NO_3)_2\cdot 6H_2O(s) + \text{heat}$

(1) $\longrightarrow UO_2(NO_3)_2\cdot 3H_2O(s) + 3H_2O(g)$

(2) $\longrightarrow UO_2(NO_3)_2\cdot 2H_2O(s) + 4H_2O(g)$

(3) $\longrightarrow UO_2(NO_3)_2\cdot H_2O(s) + 5H_2O(g)$

(4) $\longrightarrow UO_2(NO_3)_2(s) + 6H_2O(g)$

(5) $\longrightarrow UO_4\cdot 2H_2O(s) + 4H_2O(g) + 2NO_2(g)$

(6) $\longrightarrow UO_3\cdot 2H_2O(s) + 4H_2O(g) + 2NO_2(g) + 1/2\ O_2(g)$

(7) $\longrightarrow UO_3\cdot H_2O(s) + 5H_2O(g) + 2NO_2(g) + 1/2\ -_2(g)$

(8) $\longrightarrow UO_3(s) + 6H_2O(g) + 2NO_2(g) + 1/2\ O_2(g)$

(9) $\longrightarrow 1/3\ U_3O_8(s) + 6H_2O(g) + 2NO_2(g) + 2/3\ O_2(g)$

(10) $\longrightarrow 1/4\ U_4O_9(s) + 6H_2O(g) + 2NO_2(g) + 7/8\ O_2(g)$

(11) $\longrightarrow UO_2(s) + 6H_2O(g) + 2NO_2(g) + O_2(g)$

(12) $\longrightarrow UN(s) + 6H_2O(g) + NO_2(g) + 3O_2(g)$

TABLE A.1. Thermodynamic Values

Compound	S_{298} E.U./mole		ΔH_{298} kcal/mole	
$UO_2(NO_3)_2 \cdot 6H_2O(s)$	120.85 ± 0.6	(a)	-764.3	(a)
$UO_2(NO_3)_2 \cdot 3H_2O(s)$	(94)	(a)	-552.2	(a)
$UO_2(NO_3)_2 \cdot 2H_2O(s)$	(85)	(a)	-480.0	(a)
$UO_2(NO_3)_2 \cdot H_2O(s)$	(76)	(a)	-404.8	(a)
$UO_2(NO_3)_2(s)$	(66)	(a)	-329.2	(a)
$UO_4 \cdot 2H_2O(s)$	(43.8)	(*)	-436.0	(a)
$UO_3 \cdot 2H_2O(s)$	(40)	(*)	-446.4	(a)
$UO_3 \cdot H_2O(s)$	(34.4)	(*)	-375.4	(a)
UO_3 (s)	23.57	(a)	-291.6±3	(a)
U_3O_8 (s)	(66)	(d)	-853.5±1.6	(a)
U_4O_9 (s)	80.29±1	(a)	(-1081)	(*)
UO_2 (s)	18.6	(b)	-259.2±0.6	(b)
UN (s)	(18)	(a)	(-80)	(a)
H_2O (g)	45.11	(c)	-57.7979	(b)
NO_2 (g)	57.57	(c)	7.96	(b)
O_2 (g)	49.003	(c)	0.00	

Note 1: All the values in parentheses are estimates.
Note 2: See Literature Cited, page 23, for references below.
Note 3: (*) Estimated on following pages.

a) Katz, Joseph J., The Chemistry of the Actinide Elements. 1957.

b) Perry, John H. The Chemical Engineers' Handbook, 3rd Ed. 1950.

c) Handbook of Chemistry and Physics, 36th Ed. 1954-5.

d) Handbook of Chemistry and Physics, 40th Ed. 1959-60.

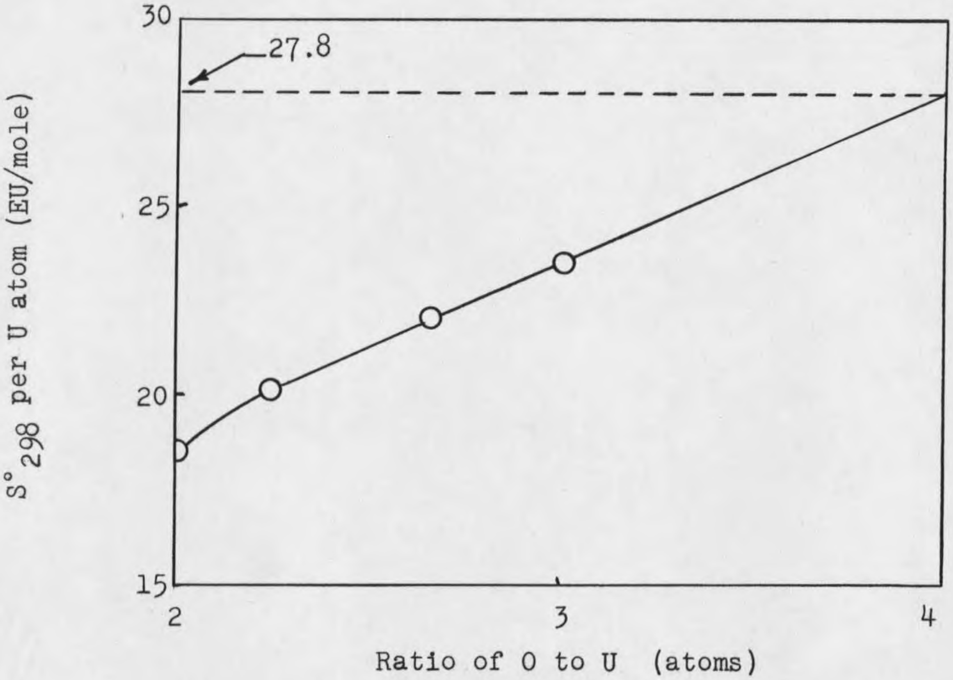


Figure A1. Entropy of Uranium Oxides.

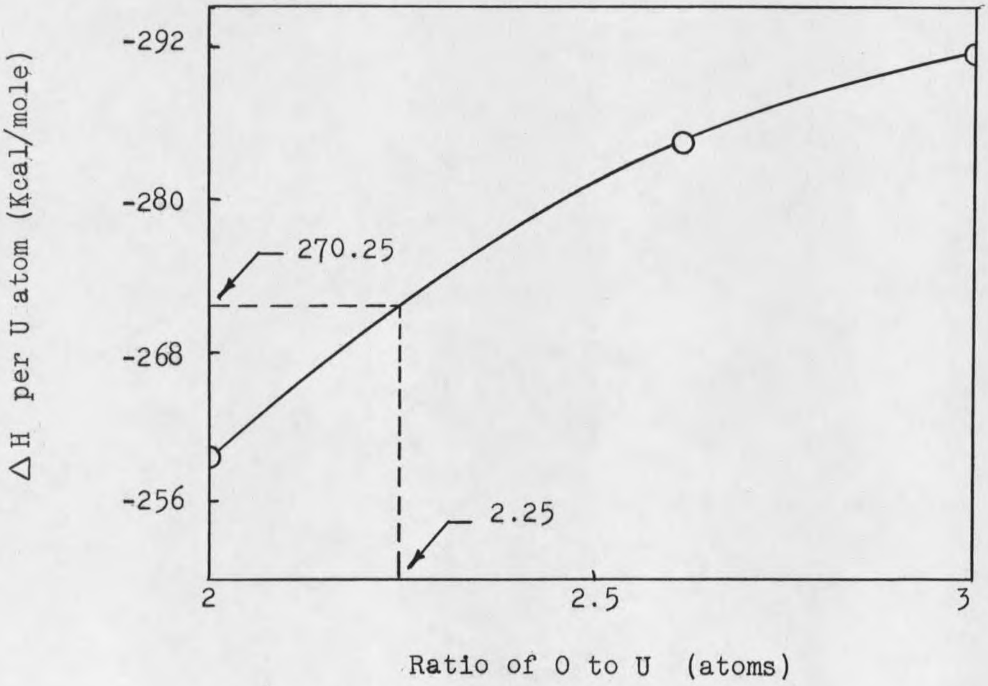
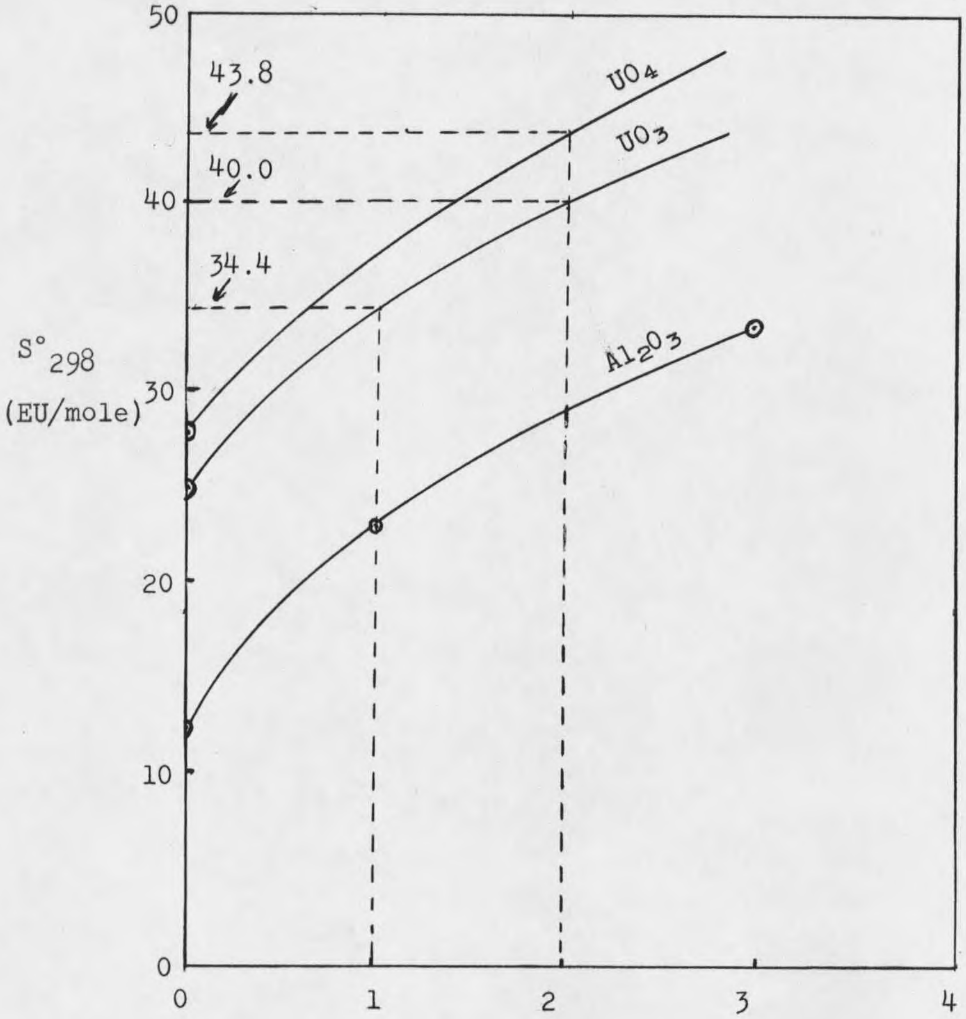


Figure A2. Heat Content of Uranium Oxides.



Moles of Water of Hydration

Figure A3. Entropy of Hydrated Oxides.

Equation 1.

$$UO_2(NO_3)_2\cdot 6H_2O(s) \longrightarrow UO_2(NO_3)_2\cdot 3H_2O(s) + 3H_2O(g)$$

ΔH_{298}	-764.3	-552.2	3(-57.8)
S_{298}	120.85	94	3(45.1)

ΔH_{298} = 38,700 cal/mole $\qquad T_{NE} = \frac{38700}{108.5} = 356°K$

ΔS_{298} = 108.5 E.U./mole

ΔF_{298} = 38700 - 298(108.5) = 6300 cal/mole

Equation 2.

$$UO_2(NO_3)_2\cdot 6H_2O \longrightarrow UO_2(NO_3)_2\cdot 2H_2O + 4H_2O$$

ΔH_{298}	-764.3	-480.0	4(-57.8)
S_{298}	120.85	85	4(45.1)

ΔH_{298} = 53,100 cal/mole $\qquad T_{NE} = \frac{53100}{144.6} = 364°K$

ΔS_{298} = 144.6 EU/mole

ΔF_{298} = 53100 - 298(144.6) = 9700 cal/mole

Equation 3.

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_2(NO_3)_2 \cdot H_2O + 5H_2O$$

ΔH_{298}	-764.3	-404.8	5(-57.8)
S_{298}	120.85	76	5(45.1)

$\Delta H_{298} = 70{,}500$ cal/mole $\qquad T_{NE} = \dfrac{70500}{180.7} = 390°K$

$\Delta S_{298} = 180.7$ EU/mole

$\Delta F_{298} = 70500 - 298(180.7) = 16700$ cal/mole

Equation 4.

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_2(NO_3)_2 + 6H_2O$$

ΔH_{298}	-764.3	-329.2	6(-57.8)
S_{298}	120.85	66	6(45.1)

$\Delta H_{298} = 88{,}300$ cal/mole $\qquad T_{NE} = \dfrac{88300}{215.8} = 409°K$

$\Delta S_{298} = 215.8$ EU/mole

$\Delta F_{298} = 88300 - 298(215.8) = 24100$ cal/mole

Equation 5.

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_4 \cdot 2H_2O + 4H_2O + 2NO_2$$

	$UO_2(NO_3)_2 \cdot 6H_2O$	$UO_4 \cdot 2H_2O$	$4H_2O$	$2NO_2$
ΔH_{298}	-764.3	-436	4(-57.8)	2(7.96)
S_{298}	120.85	43.8	4(45.1)	2(57.5)

$\Delta H_{298} = 113{,}000$ cal/mole $\qquad T_{NE} = \dfrac{113{,}000}{218.4} = 516°K$

$\Delta S_{298} = 218.4$ EU/mole

$\Delta F_{298} = 113{,}000 - 298(218.4) = 47{,}800$

Equation 6.

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_3 \cdot 2H_2O + 4H_2O + 2NO_2 + 1/2\ O_2$$

	$UO_2(NO_3)_2 \cdot 6H_2O$	$UO_3 \cdot 2H_2O$	$4H_2O$	$2NO_2$	$1/2\ O_2$
ΔH_{298}	-764.3	-446.4	4(-57.8)	2(7.96)	0
S_{298}	120.85	40.0	4(45.1)	2(57.5)	1/2(49.0)

$\Delta H_{298} = 102{,}600$ cal/mole $\qquad T_{NE} = \dfrac{102{,}600}{239.1} = 429°K$

$\Delta S_{298} = 239.1$ EU/mole

$\Delta F_{298} = 102{,}600 - 298(239.1) = 31{,}400$ cal/mole

Equation 7.

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_3 \cdot H_2O + 5H_2O + 2NO_2 + 1/2\ O_2$$

	$UO_2(NO_3)_2 \cdot 6H_2O$	$UO_3 \cdot H_2O$	$5H_2O$	$2NO_2$	$1/2\ O_2$
ΔH_{298}	-764.3	-375.4	5(-57.8)	2(7.96)	0
S_{298}	120.85	34.4	5(45.1)	2(57.5)	1/2(49.0)

ΔH_{298} = 115,800 cal/mole $T_{NE} = \frac{115,800}{278.6} = 514°K$

ΔS_{298} = 278.6 EU/mole

ΔF_{298} = 32,700 cal/mole

Equation 8.

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_3 + 6H_2O + 2NO_2 + 1/2\ O_2$$

	$UO_2(NO_3)_2 \cdot 6H_2O$	UO_3	$6H_2O$	$2NO_2$	$1/2\ O_2$
ΔH_{298}	-764.3	-291.6	6(-57.8)	2(7.96)	0
S_{298}	120.85	23.57	6(45.1)	2(57.5)	1/2(49.0)

ΔH_{298} = 141,800 cal/mole $T_{NE} = \frac{141,800}{312.9} = 453°K$

ΔS_{298} = 312.9 EU/mole

ΔF_{298} = 141,800 - 298(312.9) = 48,600 cal/mole

Equation 9.

$$UO_2(NO_3)_2\cdot 6H_2O \longrightarrow 1/3U_3O_8 + 6H_2O + 2NO_2 + 2/3\ O_2$$

	$UO_2(NO_3)_2\cdot 6H_2O$	$1/3U_3O_8$	$6H_2O$	$2NO_2$	$2/3\ O_2$
ΔH_{298}	-764.3	1/3(-853.5)	6(-57.8)	2(7.96)	0
S_{298}	120.85	1/3(66)	6(45.1)	2(57.5)	2/3(49.0)

$\Delta H_{298} = 148{,}900$ cal/mole $\qquad T_{NE} = \frac{148{,}900}{319.5} = 466°K$

$\Delta S_{298} = 319.5$ EU/mole

$\Delta F_{298} = 148{,}900 - 298(319.5) = 53{,}700$ cal/mole

Equation 10.

$$UO_2(NO_3)_2\cdot 6H_2O \longrightarrow 1/4\ U_4O_9 + 6H_2O + 2NO_2 + 7/8\ O_2$$

	$UO_2(NO_3)_2\cdot 6H_2O$	$1/4\ U_4O_9$	$6H_2O$	$2NO_2$	$7/8\ O_2$
ΔH_{298}	-764.3	1/4(-1081)	6(-57.8)	2(7.96)	0
S_{298}	120.85	1/4(80.29)	6(45.1)	2(57.5)	7/8(49.0)

$\Delta H_{298} = 163{,}400$ cal/mole $\qquad T_{NE} = \frac{163{,}400}{327.8} = 499°K$

$\Delta S_{298} = 327.8$ EU/mole

$\Delta F_{298} = 163{,}400 - 298(327.8) = 65{,}900$ cal/mole

Equation 11.

	$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow$	UO_2 +	$6H_2O$ +	$2NO_2$ +	O_2
ΔH_{298}	-764.3	-259.2	6(-57.8)	2(7.96)	0
S_{298}	120.85	18.6	6(45.1)	2(57.5)	49.0

$\Delta H_{298} = 174{,}200$ cal/mole $\qquad T_{NE} = \dfrac{174{,}200}{332.4} = 523°K$

$\Delta S_{298} = 332.4$ EU/mole

$\Delta F_{298} = 174{,}200 - 298(332.4) = 75{,}000$ cal/mole

Equation 12.

	$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow$	UN +	$6H_2O$ +	NO_2 +	$3O_2$
ΔH_{298}	-764.3	-80	6(-57.8)	7.96	0
S_{298}	120.85	18	6(45.1)	57.5	3(49.0)

$\Delta H_{298} = 345{,}500$ cal/mole $\qquad T_{NE} = \dfrac{345{,}500}{312.3} = 1105°K$

$\Delta S_{298} = 312.3$ EU/mole

$\Delta F_{298} = 345{,}500 - 298(312.3) = 252{,}300$ cal/mole

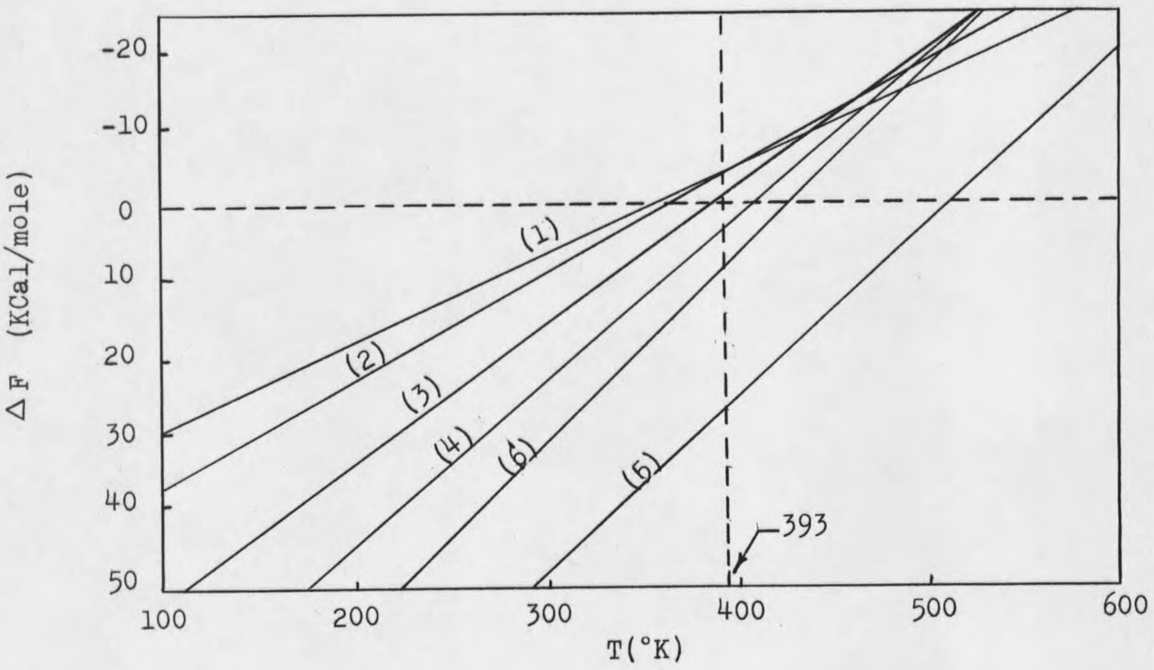


Figure A4. Free Energy vs. Temperature for Reactions 1-6.

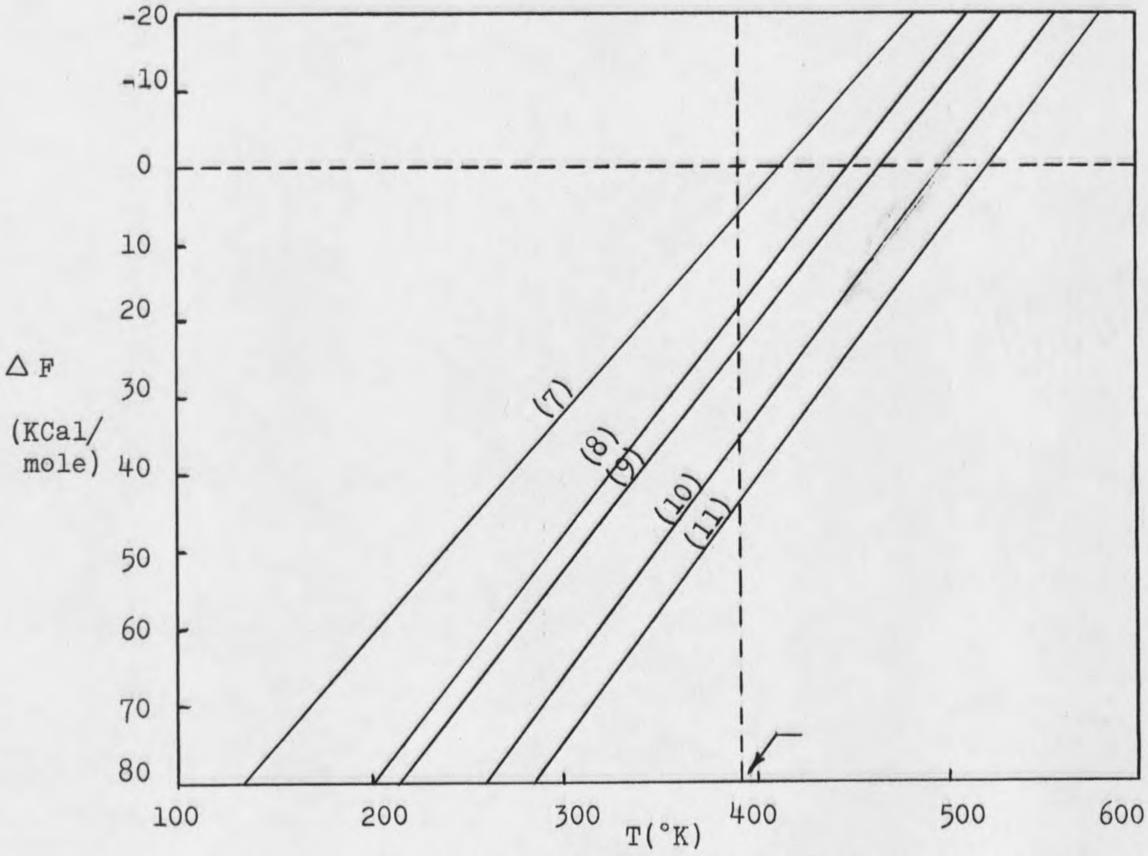


Figure A5. Free Energy vs. Temperature for Reactions 7-11.

Investigation at 393°K

Equation 1 at 393°K

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_2(NO_3)_2 \cdot 3H_2O \quad + \quad 3H_2O$$

$$\Delta F_{393} \cong 38{,}700 - 393(108.5) = -3900 \text{ cal/mole}$$

Equation 2 at 393°K

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_2(NO_3)_2 \cdot 2H_2O \quad + \quad 4H_2O$$

$$\Delta F_{393} \cong 53{,}100 - 393(144.6) = -3700 \text{ cal/mole}$$

Equation 3 at 393°K

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_2(NO_3)_2 \cdot H_2O \quad + \quad 5H_2O$$

$$\Delta F_{393} \cong 70{,}500 - 393(180.7) = -500 \text{ cal/mole}$$

Equation 4 at 393°K

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_2(NO_3)_2 \quad + \quad 6H_2O$$

$$\Delta F_{393} \cong 88{,}300 - 393(215.8) = 3500 \text{ cal/mole}$$

Equilibrium of Hydrated Nitrates at 393°K

Equation 13

$$UO_2(NO_3)_2 \cdot 3H_2O \longrightarrow UO_2(NO_3)_2 \cdot 2H_2O \quad + \quad H_2O$$

ΔH_{298}	-552.2	-480.0	-57.8
S_{298}	94	85	45.1

$$\Delta H_{298} = 14{,}400 \text{ cal/mole}$$

$$\Delta S_{298} = 36.1 \text{ EU/mole}$$

$$\Delta F_{393} \cong 14{,}400 - 393(36.1) = 200 \text{ cal/mole}$$

Equation 14.

$$UO_2(NO_3)_2\cdot 2H_2O \longrightarrow UO_2(NO_3)_2\cdot H_2O \quad + \quad H_2O$$

ΔH_{298}	-480.0	-404.8	-57.8
S_{298}	85	76	45.1

$\Delta H_{298} = 17,400$ cal/mole

$\Delta S_{298} = 36.1$ EU/mole

$\Delta F_{393} \cong 17,400 - 393(36.1) = 3200$ cal/mole

Equation 15

$$UO_2(NO_3)_2\cdot 3H_2O \longrightarrow UO_2(NO_3)_2\cdot H_2O \quad + \quad 2H_2O$$

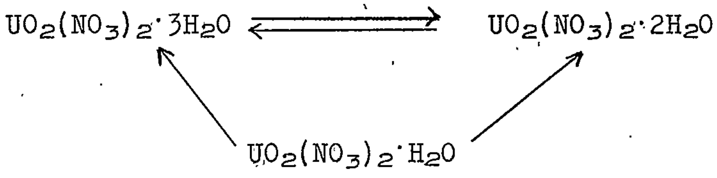
ΔH_{298}	-552.2	-404.8	2(-57.8)
S_{298}	94	76	2(45.1)

$\Delta H_{298} = 31,800$ cal/mole

$\Delta S_{298} = 72.2$ EU/mole

$\Delta F_{393} \cong 31,800 - 393(72.2) = 3400$ cal/mole

Figure A6. Results at 393°K



Investigation of Heating $UO_2(NO_3)_2 \cdot 2H_2O$ (393-800°K)

Equation 16

	$UO_2(NO_3)_2 \cdot 2H_2O \longrightarrow$	$UO_4 \cdot 2H_2O$	+ $2NO_2$
ΔH_{298}	-480.0	-436	2(7.96)
S_{298}	85	43.8	2(57.5)

$$\Delta H_{298} = 59{,}900 \text{ cal/mole}$$

$$\Delta S_{298} = 73.7 \text{ EU/mole}$$

$$\Delta F_{800} \cong 59{,}900 - 800(37.7) = 900 \text{ cal/mole}$$

Equation 17

	$UO_2(NO_3)_2 \cdot 2H_2O \longrightarrow$	$UO_3 \cdot 2H_2O$	+ $2NO_2$	+ $1/2\ O_2$
ΔH_{298}	-480.0	-446.4	2(7.96)	0
S_{298}	85	40.0	2(57.5)	1/2(49.0)

$$\Delta H_{298} = 49{,}500 \text{ cal/mole}$$

$$\Delta S_{298} = 94.4 \text{ EU/mole}$$

$$\Delta F_{800} \cong 49{,}500 - 800(94.4) = -26{,}000 \text{ cal/mole}$$

Equation 18

	$UO_2(NO_3)_2\cdot 2H_2O \longrightarrow$	$UO_3\cdot H_2O$ +	H_2O +	$2NO_2$ +	$1/2\ O_2$
ΔH_{298}	-480.0	-375.4	-57.8	2(7.96)	0
S_{298}	85	34.4	45.1	2(57.5)	1/2(49.0)

$\Delta H_{298} = 62,700$ cal/mole

$\Delta S_{298} = 133.9$ EU/mole

$\Delta F_{800} \cong 62,700 - 800(133.9) = -44,300$ cal/mole

Equation 19

	$UO_2(NO_3)_2\cdot 2H_2O \longrightarrow$	UO_3 +	$2H_2O$ +	$2NO_2$ +	$1/2\ O_2$
ΔH_{298}	-480.0	-291.6	(2)(-57.8)	2(7.96)	0
S_{298}	85	23.6	2(45.1)	2(57.5)	1/2(49.0)

$\Delta H_{298} = 88,700$ cal/mole

$\Delta S_{298} = 168.2$ EU/mole

$\Delta F_{800} \cong 88,700 - 800(168.2) = -45,800$ cal/mole

Equation 20.

$$UO_2(NO_3)_2 \cdot 2H_2O \longrightarrow 1/3\ U_3O_8 + 2H_2O + 2NO_2 + 2/3\ O_2$$

	$UO_2(NO_3)_2 \cdot 2H_2O$	$1/3\ U_3O_8$	$2H_2O$	$2NO_2$	$2/3\ O_2$
ΔH_{298}	-480.0	1/3(-853.5)	2(-57.8)	2(7.96)	0
S_{298}	85	1/3(66)	2(45.1)	2(57.5)	2/3(49.0)

ΔH_{298} = 79,900 cal/mole

ΔS_{298} = 174.8 EU/mole

$\Delta F_{800} \cong$ 79,900 - 800(174.8) = -60,000 cal/mole

Equation 21

$$UO_2(NO_3)_2 \cdot 2H_2O \longrightarrow 1/4\ U_4O_9 + 2H_2O + 2NO_2 + 7/8\ O_2$$

	$UO_2(NO_3)_2 \cdot 2H_2O$	$1/4\ U_4O_9$	$2H_2O$	$2NO_2$	$7/8\ O_2$
ΔH_{298}	-480.0	1/4(1081)	2(-57.8)	2(7.96)	0
S_{298}	85	1/4(80.3)	2(45.1)	2(57.5)	7/8(49.0)

ΔH_{298} = 110,300 cal/mole

ΔS_{298} = 183.1 EU/mole

$\Delta F_{800} \cong$ 110,300 - 800(183.1) = -36,200 cal/mole

Equation 22

$$UO_2(NO_3)_2 \cdot 2H_2O \longrightarrow UO_2 + 2H_2O + 2NO_2 + O_2$$

	$UO_2(NO_3)_2 \cdot 2H_2O$	UO_2	$2H_2O$	$2NO_2$	O_2
ΔH_{298}	-480.0	-259.2	2(-57.8)	2(7.96)	0
S_{298}	85	18.6	2(45.1)	2(57.5)	49.0

ΔH_{298} = 121,100 cal/mole

ΔS_{298} = 187.7 EU/mole

$\Delta F_{800} \cong$ 121,100 - 800(187.7) = -28,900 cal/mole

Investigation of Heating Hydrated Uranium-Trioxide (800-1000°K)

Equation 23

$$UO_3 \cdot 2H_2O \longrightarrow UO_3 \cdot H_2O + H_2O$$

	$UO_3 \cdot 2H_2O$	$UO_3 \cdot H_2O$	H_2O
ΔH_{298}	-446.4	-375.4	-57.8
S_{298}	40.0	34.4	45.1

ΔH_{298} = 31,200 cal/mole

ΔS_{298} = 39.5 EU/mole

$\Delta F_{1000} \cong$ 31,200 - 1000(39.5) = -8300 cal/mole

Equation 24

	$UO_3\cdot 2H_2O$	$\longrightarrow$	UO_3	+	$2H_2O$
ΔH_{298}	-446.4		-291.6		2(-57.8)
S_{298}	40.0		23.6		2(45.1)

$$\Delta H_{298} = 39,200 \text{ cal/mole}$$

$$\Delta S_{298} = 73.8 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 39,200 - 1000(73.8) = -34,600 \text{ cal/mole}$$

Equation 25

	$UO_3\cdot 2H_2O$	$\longrightarrow$	$1/3\ U_3O_8$	+	$2H_2O$	+	$1/6\ O_2$
ΔH_{298}	-446.4		1/3(853.5)		2(-57.8)		0
S_{298}	40.0		1/3(66)		2(45.1)		1/6(49.0)

$$\Delta H_{298} = 46,300 \text{ cal/mole}$$

$$\Delta S_{298} = 80.4 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 46,300 - 1000(80.4) = -34,100 \text{ cal/mole}$$

Equation 26

$$UO_3 \cdot 2H_2O \longrightarrow 1/4\ U_4O_9 \quad + \quad 2H_2O \quad + \quad 3/8\ O_2$$

ΔH_{298}	-446.4	1/4(-1081)	2(-57.8)	0
S_{298}	40.0	1/4(80.3)	2(45.1)	3/8(49.0)

$$\Delta H_{298} = 60{,}800 \text{ cal/mole}$$

$$\Delta S_{298} = 88.7 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 60{,}800 - 1000(88.7) = -24{,}900 \text{ cal/mole}$$

Equation 27

$$UO_3 \cdot 2H_2O \longrightarrow UO_2 \quad + \quad 2H_2O \quad + \quad 1/2\ O_2$$

ΔH_{298}	-446.4	-259.2	2(-57.8)	0
S_{298}	40.0	18.6	2(45.1)	1/2(49.0)

$$\Delta H_{298} = 71{,}800 \text{ cal/mole}$$

$$\Delta S_{298} = 93.3 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 71{,}800 - 1000(93.3) = -21{,}500 \text{ cal/mole}$$

Equation 28

$$UO_3 \cdot H_2O \longrightarrow UO_3 + H_2O$$

	$UO_3 \cdot H_2O$	UO_3	H_2O
ΔH_{298}	-375.4	-291.6	-57.8
S_{298}	34.4	23.6	45.1

$$\Delta H_{298} = 26,000 \text{ cal/mole}$$

$$\Delta S_{298} = 34.3 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 26,000 - 1000(34.3) = -8,300 \text{ cal/mole}$$

Equation 29

$$UO_3 \cdot H_2O \longrightarrow 1/3\ U_3O_8 + H_2O + 1/6\ O_2$$

	$UO_3 \cdot H_2O$	$1/3\ U_3O_8$	H_2O	$1/6\ O_2$
ΔH_{298}	-375.4	1/3(-853.5)	-57.8	0
S_{298}	34.4	1/3(66)	45.1	1/6(49.0)

$$\Delta H_{298} = 33,100 \text{ cal/mole}$$

$$\Delta S_{298} = 40.9 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 33,100 - 1000(40.9) = -7,800 \text{ cal/mole}$$

Equation 30

$$\begin{array}{lccccccc}
 & UO_3 \cdot H_2O & \longrightarrow & 1/4\ U_4O_9 & + & H_2O & + & 3/8\ O_2 \\
\Delta H_{298} & -375.4 & & 1/4(1081) & & -57.8 & & 0 \\
S_{298} & 34.4 & & 1/4(80.3) & & 45.1 & & 3/8(49.0)
\end{array}$$

$$\Delta H_{298} = 47{,}300 \text{ cal/mole}$$

$$\Delta S_{298} = 49.2 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 47{,}300 - 1000(49.2) = -1900 \text{ cal/mole}$$

Equation 31

$$\begin{array}{lccccccc}
 & UO_3 \cdot H_2O & \longrightarrow & UO_2 & + & H_2O & + & 1/2\ O_2 \\
\Delta H_{298} & -375.4 & & -259.2 & & -57.8 & & 0 \\
S_{298} & 34.4 & & 18.6 & & 45.1 & & 1/2(49.0)
\end{array}$$

$$\Delta H_{298} = 58{,}400 \text{ cal/mole}$$

$$\Delta S_{298} = 53.8 \text{ EU/mole}$$

$$\Delta F_{1000} \cong 58{,}400 - 1000(53.8) = 4{,}600 \text{ cal/mole}$$

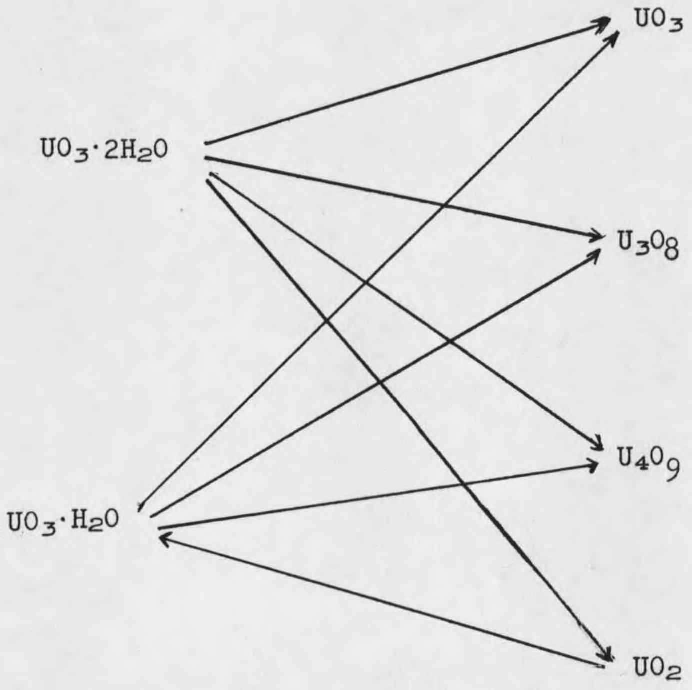


Figure A7. Results (1000°K)

Equilibrium of Uranium Oxides (1000-1300°K)

A. $UO_3 \longrightarrow 1/3\ U_3O_8 + 1/6\ O_2$

B. $UO_3 \longrightarrow 1/4\ U_4O_9 + 3/8\ O_2$

C. $UO_3 \longrightarrow UO_2 + 1/2\ O_2$

D. $1/3\ U_3O_8 \longrightarrow 1/4\ U_4O_9 + 5/24\ O_2$

E. $1/3\ U_3O_8 \longrightarrow UO_2 + 1/3\ O_2$

F. $1/4\ U_4O_9 \longrightarrow UO_2 + 1/8\ O_2$

Table AII. Thermodynamic Values

Compound	ΔH_{1000} Kcal/mole	ΔH_{1300} Kcal/mole	S_{1000} EU/mole	S_{1300} EU/mole
UO_3	-275.6 (1)	-269.2 (2)	50.6 (1)	56.6 (2)
U_3O_8	-804.7 (2)	-782.1 (2)	148.6 (2)	167.9 (2)
U_4O_9	-1022.3 (2)	-995.2 (2)	179.5 (2)	203.6 (2)
UO_2	-245.9 (1)	-239.7 (1)	41.0 (1)	46.4 (1)
O_2	5.4 (1)	7.8 (1)	58.2 (1)	60.4 (1)

(1) Kelley, K.K., Bureau of Mines Bulletin 584, 1960.

(2) Calculated from Heat Capacity Equations below.

$C_p(UO_3) = 22.09 + 2.54 \times 10^{-3}T - 2.97 \times 10^5T^{-2}$ (1)

$C_p(U_3O_8) = 3(22.34 + 2.65 \times 10^{-3}T - 2.92 \times 10^5T^{-2})$ (3)

$C_p(U_4O_9) = 4(20.40 + 2.35 \times 10^{-3}T - 3.14 \times 10^5T^{-2})$ (3)

(1) Kelley, K. K.

(3) Estimated on following pages

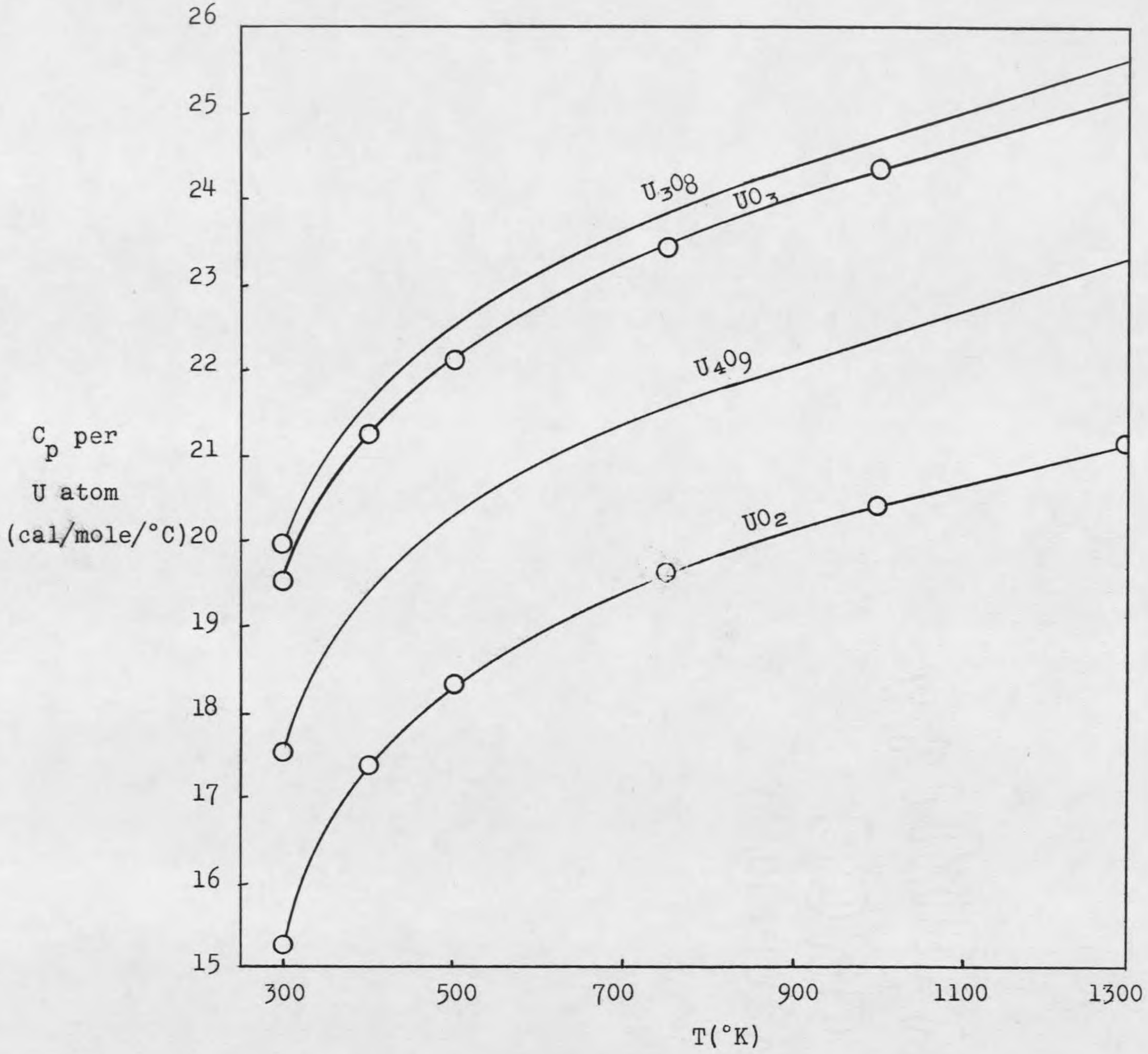


Figure A8. Heat Capacity of Uranium Oxides as a Function of Temperature.

UO_3

$$\triangle H_{1300} = \triangle H_{298} + \int_{298}^{1300} C_p dT$$

$$= -291.6 + \int_{298}^{1300} (22.09 + 2.54 \times 10^{-3}T - \frac{2.97 \times 10^5}{T^2})dT$$

$$= -269.2 \text{ kcal/mole}$$

$$S_{1300} = S_{298} + \int_{298}^{1300} C_p \frac{dT}{T}$$

$$= 23.57 + \int_{298}^{1300} (\frac{22.09}{T} + 2.54 \times 10^{-3} - \frac{2.97 \times 10^5}{T^3})dT$$

$$= 56.5 \text{ EU/mole}$$

U_3O_8

$$\triangle H_{1000} = \triangle H_{298} + \int_{298}^{1000} (67.02 + 7.95 \times 10^{-3}T - \frac{7.86 \times 10^5}{T^2})dT$$

$$= -853.5 + 48.4 = -804.7 \text{ kcal/mole}$$

$$\triangle H_{1300} = -853.5 + \int_{298}^{1300} (67.02 + 7.95 \times 10^{-3}T - \frac{7.86 \times 10^5}{T^2})dT$$

$$= -782.1 \text{ kcal/mole}$$

$$S_{1000} = S_{298} + \int_{298}^{1000} (57.02 + 7.95 \times 10^{-3}T - \frac{7.86 \times 10^5}{T^2})\frac{dT}{T}$$

$$= 66 + 82.6 = 148.6 \text{ EU/mole}$$

$$S_{1300} = 66 + \int_{298}^{1300} (67.02 + 7.95 \times 10^{-3}T - \frac{7.86 \times 10^5}{T^2})\frac{dT}{T}$$

$$= 66 + 101.9 = 167.9 \text{ EU/mole}$$

$\underline{U_4O_9}$

$$\Delta H_{1000} = -1081 + \int_{298}^{1000} (81.60 + 9.40 \times 10^{-3}T - \frac{12.56 \times 10^5}{T^2})dT$$

$$= -1022.3 \text{ kcal/mole}$$

$$\Delta H_{1300} = -1081 + \int_{298}^{1300} (81.60 + 9.40 \times 10^{-3}T - \frac{12.56 \times 10^5}{T^2})dT$$

$$= -995.2 \text{ kcal/mole}$$

$$S_{1000} = 80.29 + \int_{298}^{1000} (81.60 + 9.40 \times 10^{-3}T - \frac{12.56 \times 10^5}{T^2})\frac{dT}{T}$$

$$= 179.5 \text{ EU/mole}$$

$$S_{1300} = 80.29 + \int_{298}^{1300} (81.60 + 9.40 \times 10^{-3}T - \frac{12.56 \times 10^5}{T^2})\frac{dT}{T}$$

$$= 203.6 \text{ EU/mole}$$

Equation A (1000°K)	$UO_3 \longrightarrow$	$1/3\ U_3O_8$	$+\ 1/6\ O_2$
ΔH_{1000}	-275.6	-268.2	0.9
S_{1000}	50.6	49.5	9.7

$\Delta H_{1000} = 8300$ cal/mole

$\Delta S_{1000} = 8.6$ EU/mole

$\Delta F_{1000} = -300$ cal/mole

Equation A (1300°K)

ΔH_{1000}	-269.2	-260.7	1.3
S_{1300}	56.5	56.0	10.1

ΔH_{1300} = 9800 cal/mole

ΔS_{1300} = 9.6 EU/mole

ΔF_{1300} = -2700 cal/mole

Equation B (1000°K)

$UO_3 \longrightarrow 1/4\ U_4O_9 + 3/8\ O_2$

ΔH_{1000}	-275.6	-255.6	2.0
S_{1000}	50.6	44.9	21.8

ΔH_{1000} = 22,000 cal/mole

ΔS_{1000} = 16.1 EU/mole

ΔF_{1000} = 5900 cal/mole

Equation B (1300°K)

ΔH_{1300}	-269.2	-248.8	2.9
S_{1300}	56.5	50.9	22.6

ΔH_{1300} = 23,300 cal/mole

ΔS_{1300} = 17.0 EU/mole

ΔF_{1300} = 1200 cal/mole

Equation C (1000°K) $UO_3 \longrightarrow UO_2 + 1/2\ O_2$

ΔH_{1000}	-275.6	-245.9	2.7
S_{1000}	50.6	41.0	29.1

ΔH_{1000} = 32,400 cal/mole

ΔS_{1000} = 19.5 EU/mole

ΔF_{1000} = 12,900 cal/mole

Equation C (1300°K)

ΔH_{1300}	-269.2	-239.7	3.9
S_{1300}	56.5	46.4	30.2

ΔH_{1300} = 33,400 cal/mole

ΔS_{1300} = 20.1 EU/mole

ΔF_{1300} = 7200 cal/mole

Equation D (1000°K) $1/3\ U_3O_8 \longrightarrow 1/4\ U_4O_9 + 5/24\ O_2$

ΔH_{1000}	-268.2	-255.6	1.1
S_{1000}	49.5	44.9	12.1

ΔH_{1000} = 13,700 cal/mole

ΔS_{1000} = 7.5 EU/mole

ΔF_{1000} = 6200 cal/mole

Equation D (1300°K)

ΔH_{1300}	-260.7	-248.8	1.6
S_{1300}	56.0	50.9	12.6

ΔH_{1300} = 13,500 cal/mole

ΔS_{1300} = 7.5 EU/mole

ΔF_{1300} = 3700 cal/mole

Equation E (1000°K)	$1/3\ U_3O_8 \longrightarrow$	UO_2	$+\ 1/3\ O_2$
ΔH_{1000}	-268.2	-245.9	1.6
S_{1000}	49.5	41.0	19.4

ΔH_{1000} = 23,900 cal/mole

ΔS_{1000} = 10.9 EU/mole

ΔF_{1000} = 13,000 cal/mole

Equation E (1300°K)

ΔH_{1000}	-260.7	-239.7	2.6
S_{1000}	56.0	46.4	20.1

ΔH_{1000} = 23,600 cal/mole

ΔS_{1000} = 10.4 EU/mole

ΔF_{1000} = 10,100 cal/mole

Equation F (1000°K)	$1/4\ U_4O_9 \longrightarrow$	UO_2	$+\ 1/8\ O_2$
ΔH_{1000}	-255.6	-245.9	0.7
S_{1000}	44.9	41.0	7.3

ΔH_{1000} = 10,400 cal/mole

ΔS_{1000} = 3.4 EU/mole

ΔF_{1000} = 7000 cal/mole

Equation F (1300°K)

ΔH_{1300}	-248.8	-239.7	1.0
S_{1300}	50.9	46.4	7.6

ΔH_{1000} = 10,100 cal/mole

ΔS_{1000} = 3.1 EU/mole

ΔF_{1000} = 6100 cal/mole

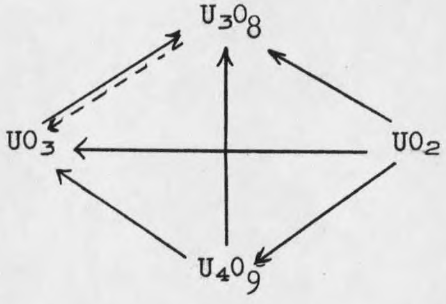


Figure A9. Equilibrium Between Oxides at 1000°K.

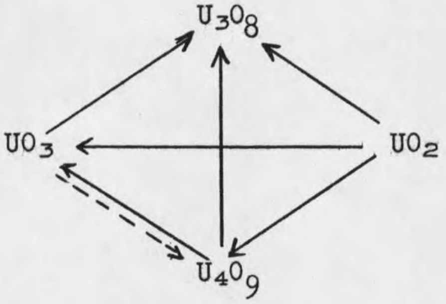


Figure A10. Equilibrium Between Oxides at 1300°K.

CONCLUSIONS

When uranyl nitrate is heated to 120°C (393°K), the only decomposition that occurs is dehydration. The formula change at this point is probably from $UO_2(NO_3)_2 \cdot 6H_2O$ to $UO_2(NO_3)_2 \cdot 2H_2O$.

Heating $UO_2(NO_3)_2 \cdot 2H_2O$ from 393-1000°K results in loss of the water of hydration, NO_2 gas and oxygen leaving only an oxide of uranium. Investigation of the equilibrium of uranium oxides at 1000°K and 1300°K shows the compound most likely to be predominate is U_3O_8.