

EQUILIBRIUM PRECIPITATION OF PROTACTINIUM OXIDE FROM
MOLTEN $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4-\text{PaF}_5$ MIXTURES*

O. K. Tallent and L. M. Ferris

MASTER

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The purpose of this work has been to develop a precipitation process for separating protactinium from an MSBR-type fuel salt without otherwise appreciable changing the salt. It was decided, based on previous studies, that a process in which the protactinium would be precipitated as Pa_2O_5 by passing mixed $\text{H}_2\text{O}-\text{HF}$ gas through the salt should be feasible. Some of the things that we wanted to find out about are:

1. What concentrations of H_2O and HF are required to affect the protactinium precipitation?
2. Does the ratio of water to HF effect the precipitation?
3. What is the effect of temperature?
4. What conditions result in uranium precipitation – what is something we do not want.
5. Is there a serious corrosion problem? I would like to answer this question now.

There does not appear to be a serious corrosion problem at the HF concentrations at which we are working. Mainly, we have used nickel and monel as a material of construction.

A diagram of the equipment we have used for this work is shown on the FIRST SLIDE.

S1

This equipment is located in a glove box in Building 3019. The salt is contained in a nickel liner in what we call a reaction vessel. The salt is maintained at a temperature of 600–650°C. An aqueous solution of hydrofluoric acid is added accurately at a controlled rate continuously from this syringe using a sage syringe pump. So far, we have used two HF concentrations,

14.6 and 27.5 M. The HF solution goes from the syringe into a vaporizer which is maintained at 150°C. The vaporizer is constructed out of monel and there is a gold foil cup in the bottom. Argon gas as a diluent is mixed with the HF and H₂O vapor in the vaporizer and the mixed gases are then passed through the salt melt. This diagram does not show it but the dip tube actually goes down into the salt. The gases then come off and go through scrubber traps.

The experimental procedure for this work has been to load 100-200 g of LiF-BeF₂-ThF₄-UF₄ (71-16-12-~0.8 mole %) salt in the reaction vessel including enough ²³¹Pa to give ~ 100 ppm and enough ²³³Pa tracer to give about 30,000 γ cts/g. The salt is melted and hydrofluorinated to assure that everything is in solution and that there are no residual oxides in the system. A mixed HF-H₂O-Ar gas is then passed through the salt to precipitate some of the Pa(V). Filtered samples of the salt are taken about once a day and the uranium and protactinium concentrations in the samples are determined by α pulse height analyses. The ²³³Pa is also determined by γ scan analyses. We have been able to correlate the two methods very well. The beauty of the γ scan method is that we can get quick answers – usually less than an hour.

The precipitation reaction can be considered in terms of the equilibrium shown on the NEXT SLIDE (SLIDE 2). The PaF₅ shown here is dissolved in the LiF-BeF₂-ThF₂-UF₄ salt. S2
 The H₂O and HF shown are passed through the salt as mixed gases and the Pa₂O₅ is formed as a crystalline solid. The equilibrium quotient can be expressed as is shown here – where P_{HF} is the partial pressure of the HF and the P_{H₂O} is the partial pressure of the water. The N_{PaF₅} represents the mole fraction of PaF₅ dissolved in the salt. If we let the P_{H₂O}/P_{HF} ratio equal A, then the expression for Q₁ can be simplified to the equation shown here.

if we solve the equation for N_{PaF} and write the resulting equation in logarithmic form, we get an equation showing that a plot of $\log N_{\text{PaF}_5}$ versus $\log (P_{\text{HF}}/A)$ should give a straight line with a slope of 2.5. I would like for you to notice that everything on this slide is based on theoretical considerations. At this point, before we start to look at the actual data, we don't know for sure that this is the reaction which occurs or that the protactinium which precipitates is Pa_2O_5 . If when we plot our data (Pa versus P_{HF}/A) we get a straight line with a slope of 2.5, it will be a strong indication that it is this reaction and that it is Pa_2O_5 , because there does not appear to be any other reaction involving these substances that would give a line with such a slope. Also, notice that if we get a value for Q_1 and if we know a value for the Pa concentration we want to get to, then we can calculate the P_{HF}/A concentration we have to use.

NEXT SLIDE (SLIDE 3) please. This slide shows our actual data. Here we have plotted Pa concentration on the ordinate and HF partial pressure over the water to HF ratio, A_r , on the abscissa. We have plots for both 600°C and 650°C. The lines have been drawn to have a slope of 2.5 and as you can see, the lines represent the data very well. The evidence we have strongly indicates that these are equilibrium data points. The circles represent our first experiment and to obtain these points we went up and down the line several times. The squares represent a second experiment made several months later. There was equipment trouble in between and a new batch of salt was used with new ^{231}Pa and ^{233}Pa — and the flow rates of HF, H_2O , and A_r were different — yet in effect we were able to repeat our first experiment since the data points fall on the same isotherm. The $\text{H}_2\text{O}/\text{HF}$ ratio used for the 600°C work was 3 and for the 650°C work was ~ 1.1. Notice that increasing the temperature from 600°C to 650°C with other conditions constant, that is with the ratio of P_{HF}/A constant, the PaF_5 concentration in the salt decreases.

These data – these lines – with the 2.5 slope – we take to mean that the reaction which was shown on the previous slide is the reaction which is occurring and that the Pa precipitate is Pa_2O_5 . We can take any point on one of these lines and calculate a Q_1 from the Pa concentration and the P_{HF}/A value.

NEXT SLIDE (SLIDE 4) please. Here we have on a semi-log plot the two quotients plotted as a function of the reciprocal of the absolute temperature. I've already pointed out some of the reasons why the values for this quotient are important. Here you can see another use which we may be able to make of them after we get enough data to really define this line. It is obvious that from a plot like this we should be able to calculate the heat of reaction and also the entropy change for the reaction – if certain assumptions are made. For the time being, I think it is enough to say that the curve looks about like you would expect – that is it is similar to a lot of other such curves that can be seen in the literature.

S4

I haven't said anything about how uranium acts in the system. Could I go back to the PREVIOUS SLIDE (SLIDE 3) please. The uranium concentration for the circular points was ~ 2.8 mg/g salt. The concentration for the data points in the squares was ~ 2.0 mg U/g salt. We have some data points with ~ 9.2 mg U/g salt that are not on this slide. These points are all up above ~ 40 ppm of Pa. We have a number of samples and data points down around the area of the lower part of the curves. These data points we have not included in this slide because the uranium is starting to precipitate in this area. In fact two of the points at the low end of this curve may be somewhat questionable. We do have uranium analyses for nearly all the samples shown on this slide.

NEXT SLIDE (SLIDE 5) please. Here again we have on the abscissa the P_{HF}/A that you have seen before and here again on the ordinate the Pa concentration. The line is

S5

not straight because we are using rectangular instead of log-log coordinates. This line was drawn from the line on the log-log plot where we had the data points. Moving to the upper part of the slide, we have the uranium concentration in mg U/g salt plotted on the ordinate. There are three plots – one each for 9.2, 2.8, and 2.0 mg U/g salt. The horizontal sections of the curves represent conditions where uranium is not precipitating but where protactinium is precipitating. The dashed lines represent conditions where uranium is precipitating. It is the break points that are of most interest, or rather it is the Pa and uranium concentrations or mole fractions at these points. Before we leave this slide, I want to point out that the data show that you can, with the right conditions, selectively precipitate Pa without precipitating uranium from the salt. Also, note that these break points are not well defined – that they could well be further over to the left so that the corresponding protactinium concentrations would be lower. Remember the three break points at 600°C.

NEXT SLIDE (SLIDE 6) please. These three N_{PaF} values and these three N_{UF_4} values represent the three 600°C break points shown on the previous slide. The mole fractions at 650°C were determined using the same method as was used for the 600°C points. With this information we have almost enough information to calculate a quotient for the equation shown at the top of the slide.

S6

$$Q_3 = \frac{N_{PaF_5} N_{UO_2}^{1.25}}{N_{UF_4}^{1.25}}$$

The N_{UO_2} values are available in the literature. The next slide (SLIDE 7) compares our values for Q_2 with values obtained by Ross, Bamberger, and Baes. Our values are consistently higher than theirs, but remember that our break points were not well defined

S7

and that the probable error was toward a lower N_{PaF_5} which would result in our Q_3 being lower. It should also be noted that Ross et al., used a different experimental method where the oxide was added as ThO_2 instead of as water vapor. These data indicate that the separation of uranium and Pa is better at 600°C than at 650°C and the implication is that the separation would be better still at 550°C .

NEXT SLIDE (SLIDE 8) please. I stated before that corrosion in this work does not appear to be a serious problem, but at the start of the work we did not know that this was true. We planned some experiments where we included H_2 in our mixed gas flow to help keep the metals, for example, the nickel containers in the reduced metal state. What I would like to shown on this slide is that if you react PaF_5 with H_2 you get $\text{PaF}_4 \cdot \text{Pa}^{4+}$ valent oxide, that is PaO_2 , is much more soluble than Pa_2O_5 .

NEXT SLIDE (SLIDE 9) please. The information on this slide comes as an added bonus from our hydrogen work. This is a log-log plot with the Pa concentration again plotted vs P_{HF}/A . The lines at 600° and at 650° were taken from our earlier data without hydrogen, of course. The four points were obtained with the partial pressures of hydrogen present which are indicated. The net effect is to increase the solubility of the Pa at a given P_{HF}/A . You can think of this occurring in the following manner. The H_2 reduces some of the Pa^{5+} that is in solution to Pa^{4+} so that there is not enough Pa^{5+} in solution to satisfy the equilibrium conditions at the given P_{HF}/A ratio so that more Pa^{5+} dissolves from the Pa_2O_5 precipitate. We do not put much dependence in these numbers at this time because there are other substances present such as nickel oxide which the hydrogen can reduce. The numbers do, however, demonstrate to some extent the effect of hydrogen on the Pa.

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S9

LIGHTS PLEASE. In conclusion, I believe we have at least partially answered the questions we set out to answer. We have shown that the precipitation reaction is the one we expected it to be namely

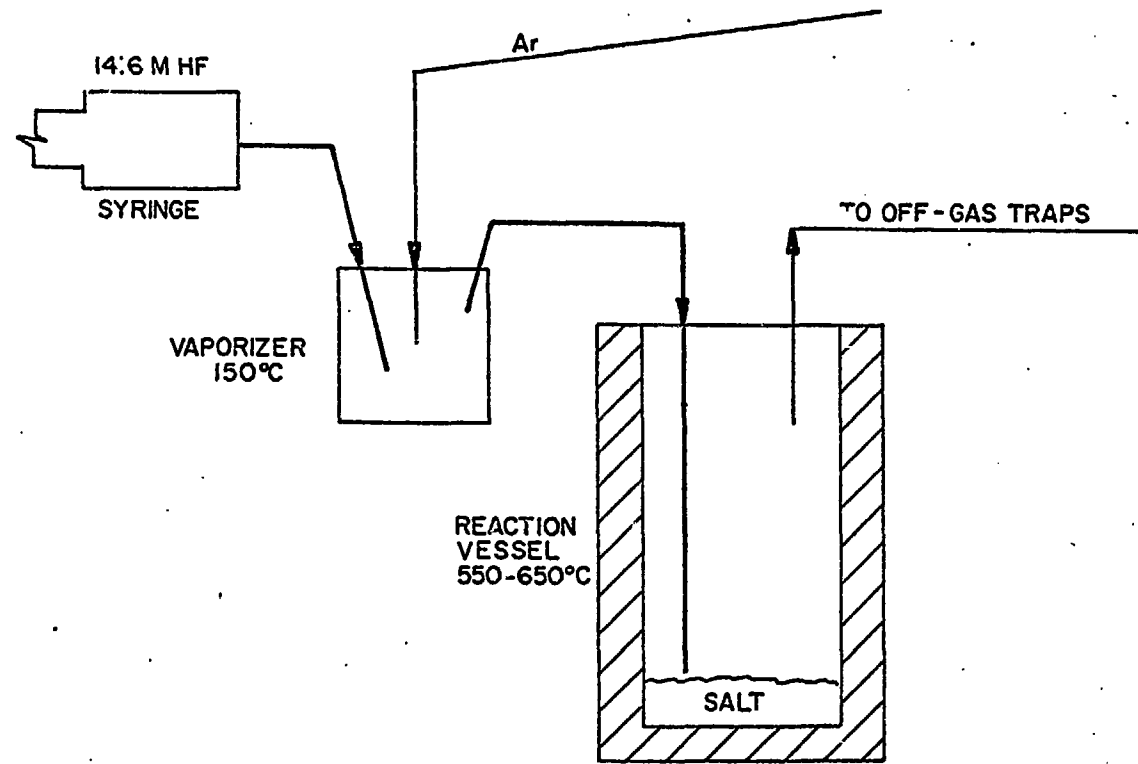


and that the Pa_2O_5 precipitates as a pure substance. We have evaluated Q_1 and thereby defined the HF and H_2O concentrations needed for the precipitation. We have defined only approximately conditions where uranium starts to precipitate; however, our data strongly indicate that it will be impossible to precipitate a large fraction of the protactinium without precipitating some UO_2 . Our work indicates that it is possible to remove protactinium from MSBR fuel salt by precipitation using HF and H_2O gas, but that there will be some restraints on the process and some limits as to what it can do.

Are there any questions?

Slide #1

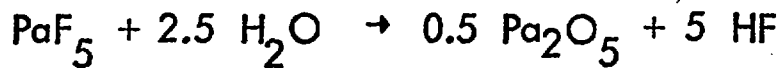
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PROTACTINIUM PRECIPITATION EXPERIMENT

Slide 2

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$$Q_1 = \frac{\rho_{\text{HF}}^5}{\rho_{\text{H}_2\text{O}}^{2.5} N_{\text{PaF}_5}}$$

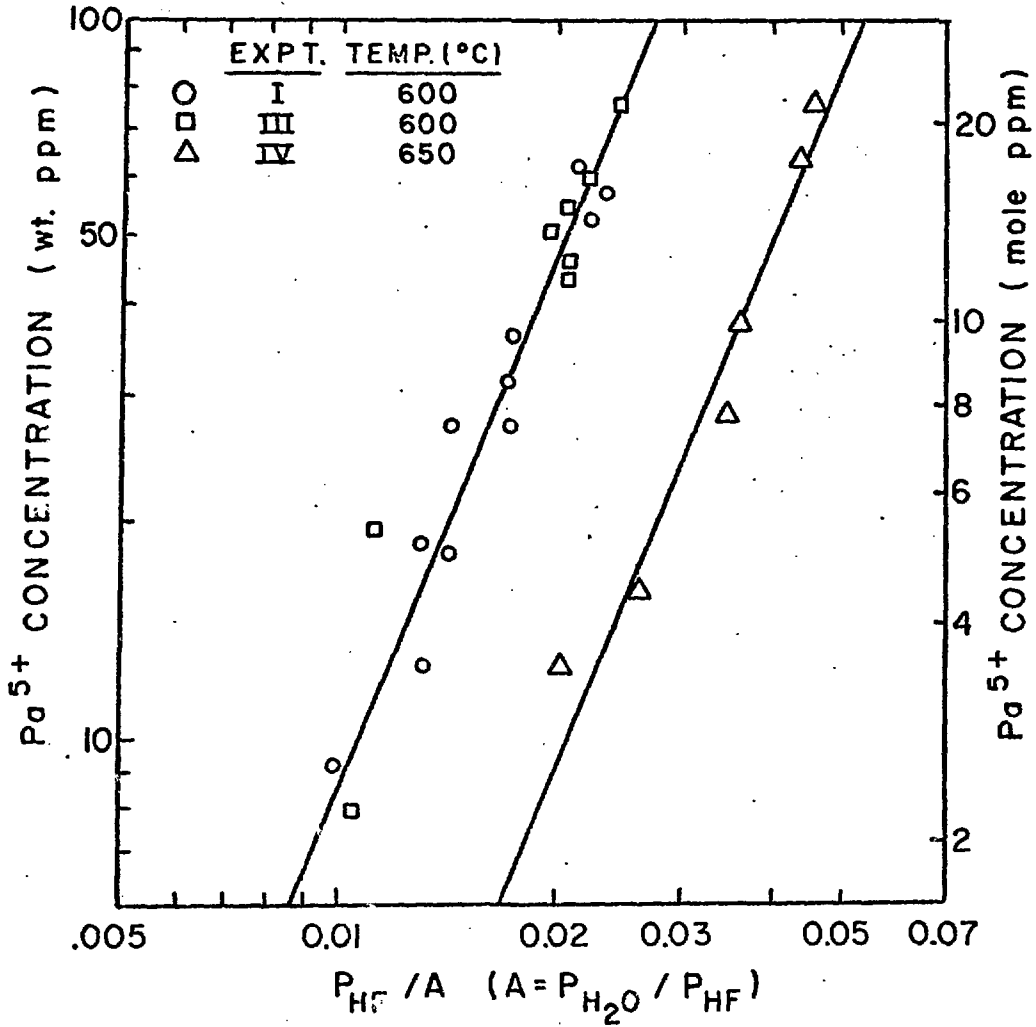
$$\text{LET } \frac{\rho_{\text{H}_2\text{O}}}{\rho_{\text{HF}}} = A$$

$$Q_1 = \left(\frac{\rho_{\text{HF}}}{A} \right)^{2.5} \frac{1}{N_{\text{PaF}_5}}$$

$$N_{\text{PaF}_5} = \left(\frac{\rho_{\text{HF}}}{A} \right)^{2.5} \frac{1}{Q_1}$$

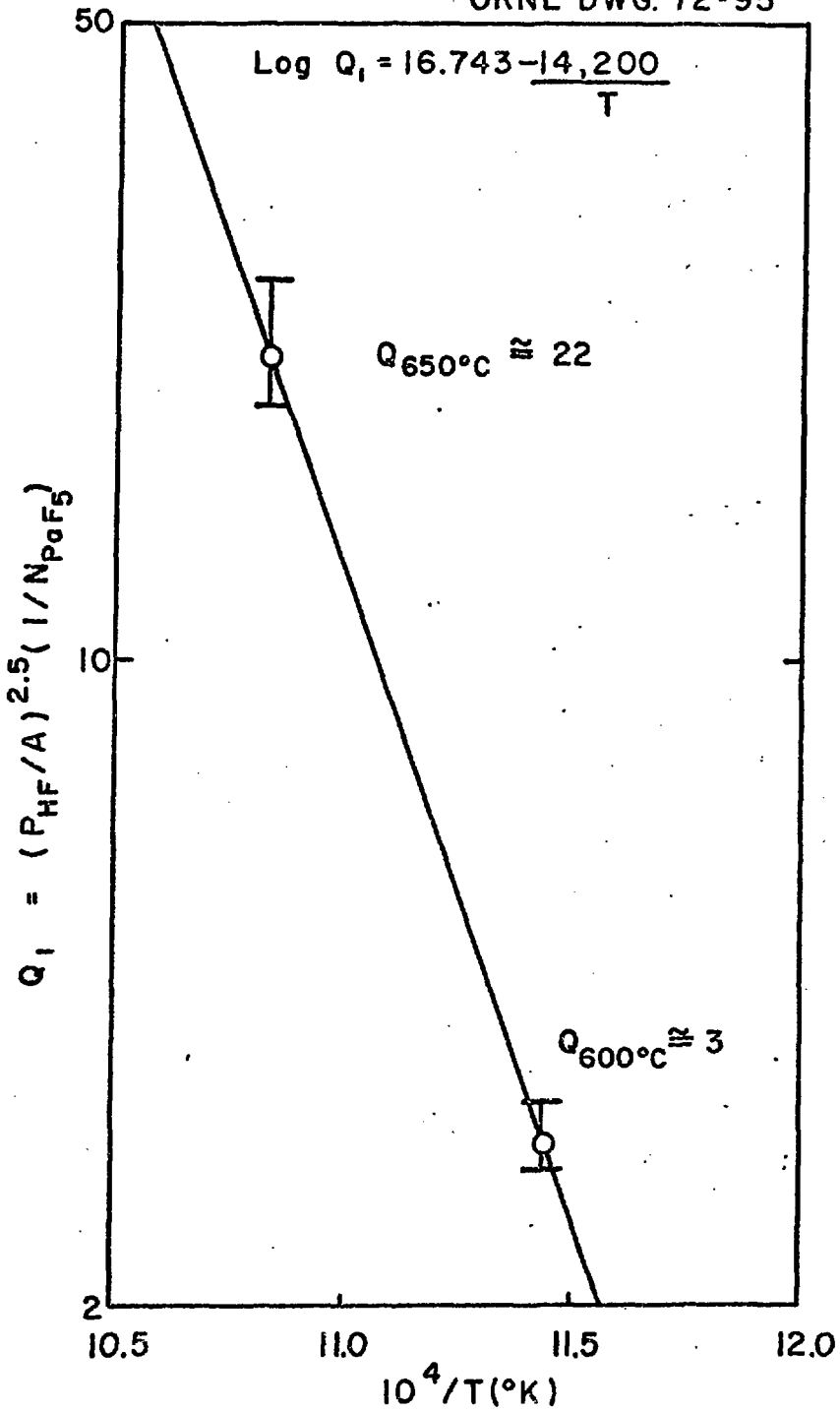
$$\text{Log } N_{\text{PaF}_5} = 2.5 \text{ Log } \left(\frac{\rho_{\text{HF}}}{A} \right) - \text{Log } Q_1$$

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Slide 4

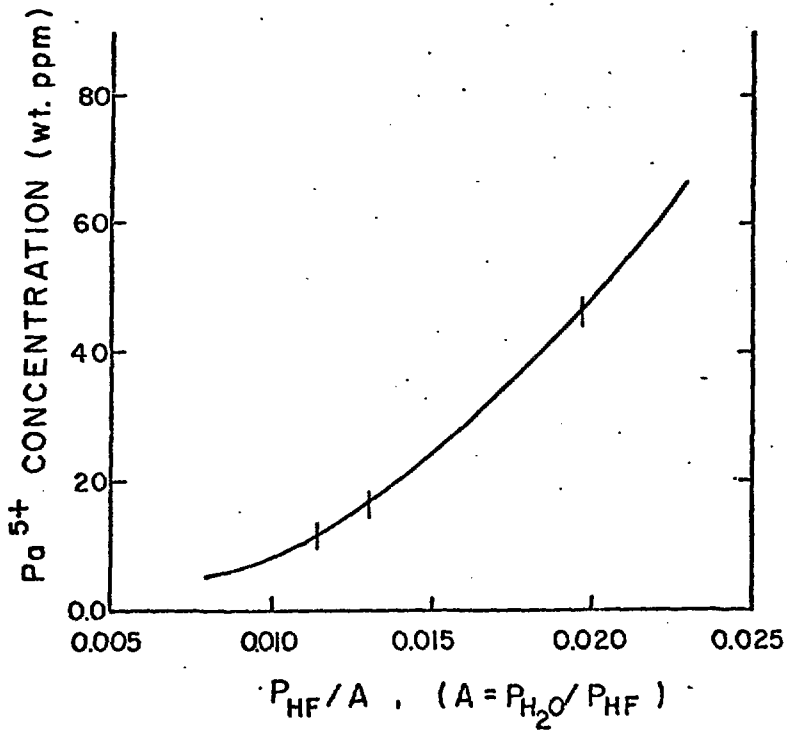
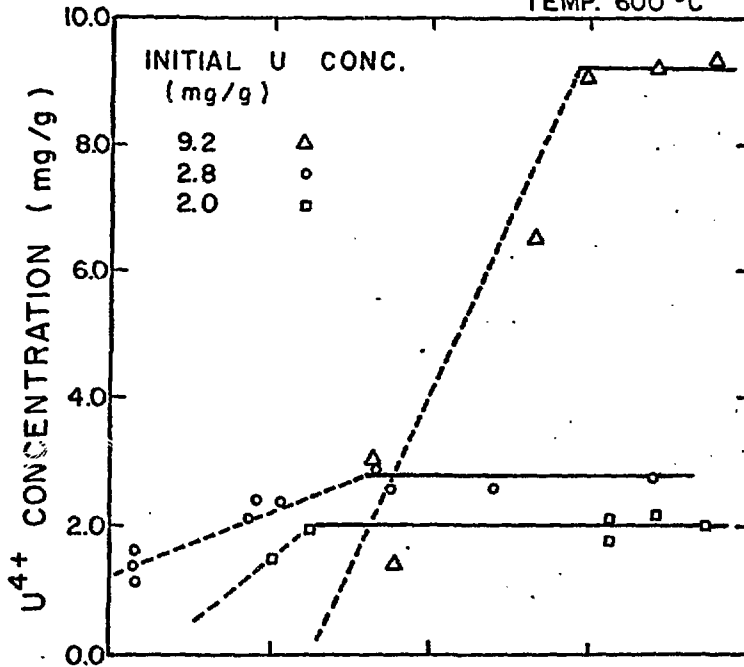
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Slide 5

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TEMP. 600 °C



Slide # 6

Table 5.4. Estimated Equilibrium Quotients for the Reaction
 $1/2 \text{Pa}_2\text{O}_5(\text{s}) + 5/4 \text{UF}_4(\text{d}) = \text{PaF}_5(\text{d}) + 5/4 \text{UO}_2(\text{ss})$

Temp. (°C)	$10^6 N_{\text{PaF}_5}$	$10^4 N_{\text{UF}_4}$	N_{UO_2}	Q_2
600	12.3	24.7	0.95	0.0212 ± 0.004
600	4.4	7.5	0.85	0.0280 ± 0.005
600	2.4	5.4	0.79	0.0216 ± 0.004
650	4.3	5.4	0.68	0.0328 ± 0.006

Slide #7

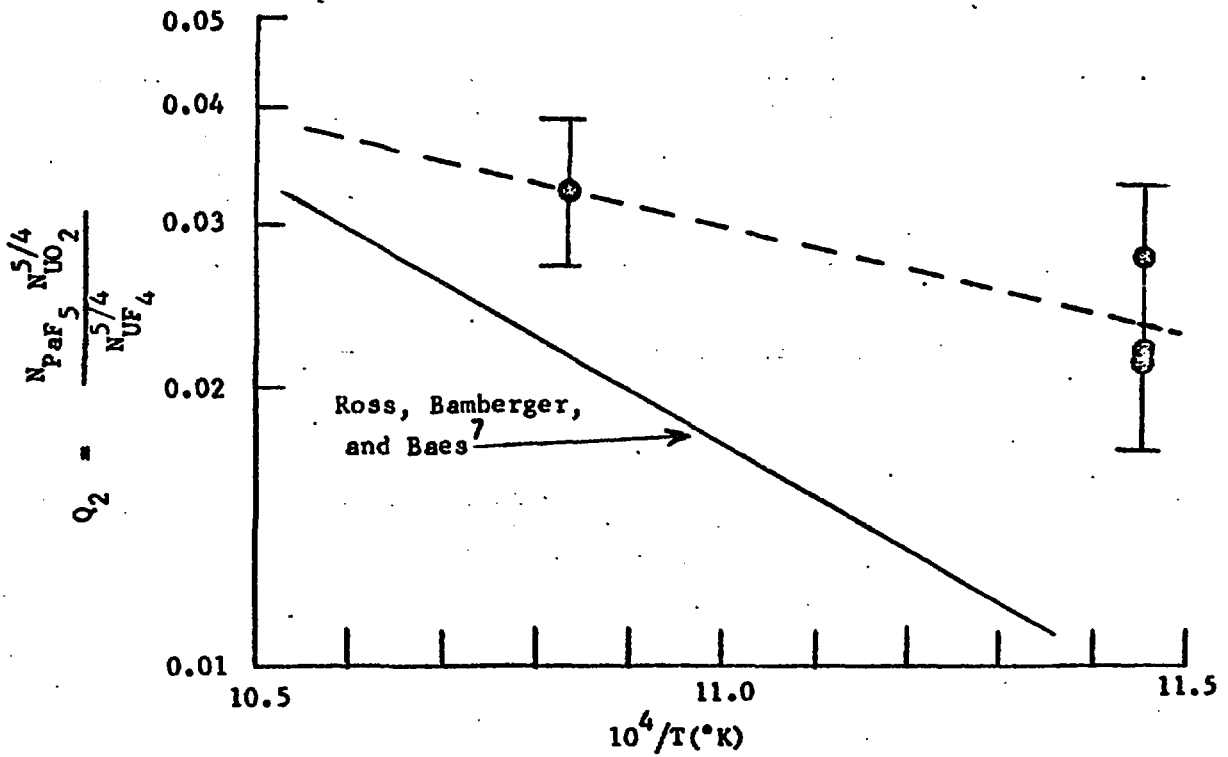
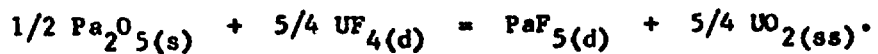


Fig. 5.3. Estimated Equilibrium Quotients for the Reaction



Slide 8

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EQUATION I

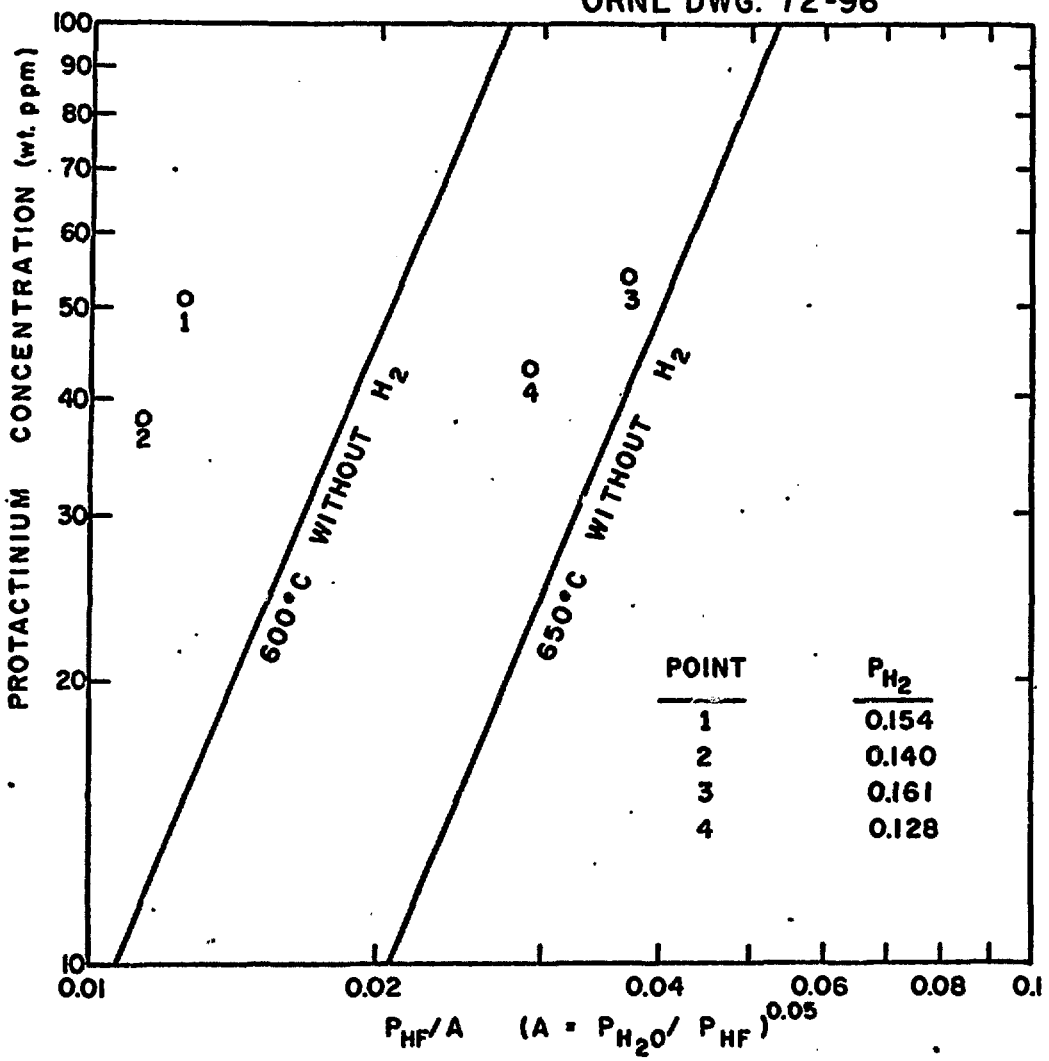


EQUATION II



Slidy 9

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APPARENT FORMATION OF PaF_4 BY SPARGING
 $LiF-BeF_2-ThF_4-UF_4-PaF_5$ MELTS WITH $HF-H_2O-H_2-Ar$
MIXTURES