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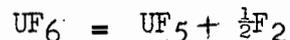
STABILITY OF UF₆ IN A PILE

D. E. Hull

One question which is of great importance to a conclusion on the feasibility of a pile employing 23 or 25 in the form of UF₆ is whether the chemical decomposition of the UF₆ under the ionizing influence of the pile radiations will be so serious as to prevent its use.⁽¹⁾

A few experiments to determine the extent of the decomposition of UF₆ by ionizing radiations were carried out by Jenks and Livingston at Chicago.⁽²⁾ Unfortunately, they were required to discontinue these experiments just when they showed promise of yielding quantitative data. Nevertheless, enough measurements were made that it is possible to estimate the extent of decomposition of the compound in a pile within an order of magnitude.

An analysis of their data taken on UF₆ under bombardment by electrons from the Notre Dame Van de Graaff accelerator shows that the decomposition of the liquid according to the equation



is reversible and that a steady state pressure of F₂ is developed. The back reaction is probably first order, in accordance with the fact that UF₅ is a solid with low solubility in liquid UF₆. Hence, it may be supposed that the decomposition of UF₆ by radiation can be largely repressed by the addition before irradiation of F₂ at a pressure equal to that which would be formed at the steady state.

Using the value for the limiting pressure found by Jenks and Livingston in the bombardment of UF₆ at 118° C. with 1.4 MEV electrons, and making the assumptions that the back reaction will not be accelerated by ionization, but is a thermal reaction which will proceed wherever UF₅ is found, and that the 200 MEV of energy released in fission will be equally effective with electrons in promoting the decomposition of UF₆, one can calculate that the steady state pressure of fluorine formed in a 30,000 kw. heterogeneous pile employing liquid UF₆ at 118° C. would be a few hundred atmospheres. If either of the assumptions is in error, it is very likely in the direction of overestimating the pressure. Also, both the theory and the experiments agree that the pressure will have a

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steep negative temperature dependence, and it is estimated that at 230°C . (the critical temperature of UF_6), this factor will cut the pressure to a few tens of atmospheres. Furthermore, the back reaction is probably limited by the small solubility of fluorine in liquid hex, so by going over to a gaseous fuel, one would gain this factor as well as that due to the reduced density of the UF_6 , leading to an estimated steady state pressure of the order of a tenth of an atmosphere. It can also be shown that in a homogeneous pile employing an inert solvent as moderator for the dissolved UF_6 , the decomposition of the UF_6 would be expected to be quite negligible. (This case involves the doubtful assumption that an inert solvent can be found.)

Since fluorine pressures of a few atmospheres at these temperatures fall well within the range of present technology, the conclusion is drawn that on the basis of present knowledge there is no reason to exclude from consideration a gaseous UF_6 pile with a heterogenous structure, or a homogeneous liquid pile, because of instability under radiation. The status of a liquid UF_6 pile is more questionable, but several factors which cannot be evaluated from present experimental data may well turn out to be of such a magnitude as to bring this design also within the limits of feasibility. Further experiments would be very desirable.

A theoretical analysis of the problem and the details of the calculations of the foregoing results from the experimental data are set out in the remainder of this report.

Experimentally, UF_6 is found to decompose to UF_5 and F_2 under the influence of radiation. UF_5 settles out of the liquid or vapor UF_6 as a gray solid. F_2 is released from the liquid UF_6 as a gas which builds up the pressure in an enclosed system.

Making certain reasonable assumptions, one can derive the law governing the kinetics of this reaction:

Assuming that the solubility of UF_5 in UF_6 is very small, the UF_5 may be regarded as a solid with a constant activity.

It is assumed that the F_2 has a finite but small solubility in UF_6 and that the UF_5 is kept well stirred so that the speed of the back reaction by the F_2 and UF_5 is not limited by the speed of mechanical mixing.

- I = Number ion-pairs formed per cc/sec. in UF_6
- E_1 = Number UF_6 molecules decomposed per ion-pair formed
- P = Partial pressure F_2 in gas phase
- L = Volume of liquid UF_6 exposed to radiation
- R = 82 cc-atmos/mole/degree
- n = Number molecules F_2 in system (practically all in gas phase)
- N = 6×10^{23} molecules/mole
- T = Temperature in degrees absolute
- V = Volume of gaseous phase

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- a = distribution coefficient (F_2 in liquid UF_6)/(F_2 in gas)
at temperature T
k = first order reaction rate constant in sec^{-1} at temperature T
 L^+ = volume of UF_6 in which back reaction occurs
 E_2 = chance that a molecule of F_2 will react with one ion-pair
formed per cc. to reform UF_6 .

Looking at the equation for the decomposition and reformation of UF_6 , we may write for the forward reaction

$$\left(\frac{dn}{dT}\right)_f = \frac{IE_1L}{2}$$

The differential equation for the reverse reaction will have a term due to the thermal reaction

$$kna \frac{L^+}{V}$$

and a term due to the reaction initiated by ionization,

$$IE_2na \frac{L}{V}$$

Thus

$$\left(\frac{dn}{dT}\right)_r = (kL^+ + IE_2L) \frac{a}{V} n$$

Setting

$$K = (kL^+ + IE_2L) \frac{a}{V} \quad (1)$$

we have for the net reaction

$$\frac{dn}{dT} = \frac{IE_1L}{2} - Kn$$

From the gas laws,

$$P = \frac{nRT}{NV} \quad (2)$$

therefore,

$$\frac{dP}{dT} = \frac{RT}{2NV} IE_1L - KP \quad (3)$$

This integrates in the most general case to

$$P = P_0 \left[1 - \left(1 - \frac{P_0}{P_\infty}\right) e^{-kT} \right] \quad (4)$$

where P_0 = the initial pressure of F_2

$$\text{and } P_\infty = \frac{RT}{2Na} \cdot \frac{IE_1L}{kL^+ + IE_2L} = \text{the steady state pressure of } F_2 \quad (5)$$

Applying these equations to the experimental data of Jenks and Livingston permits a check of the assumption that the back reaction is first order; and also an evaluation of the relative importance of the thermal and radiation-activated reactions.

Four experiments were done at a temperature of approximately $80^\circ C$. where

the rate of the back reaction was slow enough that the approach to steady state could be followed by measuring the pressure as a function of time. These data are presented in Figure 1, where $P_{\infty} - P$ is plotted on a logarithmic scale against time. According to equation (4),

$$\log (P_{\infty} - P) = \log (P_{\infty} - P_0) - kT \quad (6)$$

and this plot should give a straight line with a negative slope k .

While it is apparent that considerable variation occurred in the experiments, and no certain conclusions can be drawn from the curves, yet the trend suggests a first order law. The curves were taken under varying intensities of radiation and it is of interest to see whether any correlation exists between the rate constant k and the ionization intensity I , as suggested by equation (1)

$$k = a \frac{L'}{V} k + aE_2 \frac{L'}{V} I$$

According to this, a plot of k vs I should be a straight line with intercept proportional to the thermal reaction rate and slope proportional to the ionization reaction efficiency. Such a plot is shown in Figure 2, using electron current as proportional to I for the abscissa. Again no conclusions can be drawn.

Although little information is afforded by the analysis of the kinetics of the experiments of Jenks and Livingston, the measurements of the steady state pressures in a variety of experiments offers another angle of attack. The data in a series of experiments at different electron currents and at two different temperatures are given in Table I.

Table I

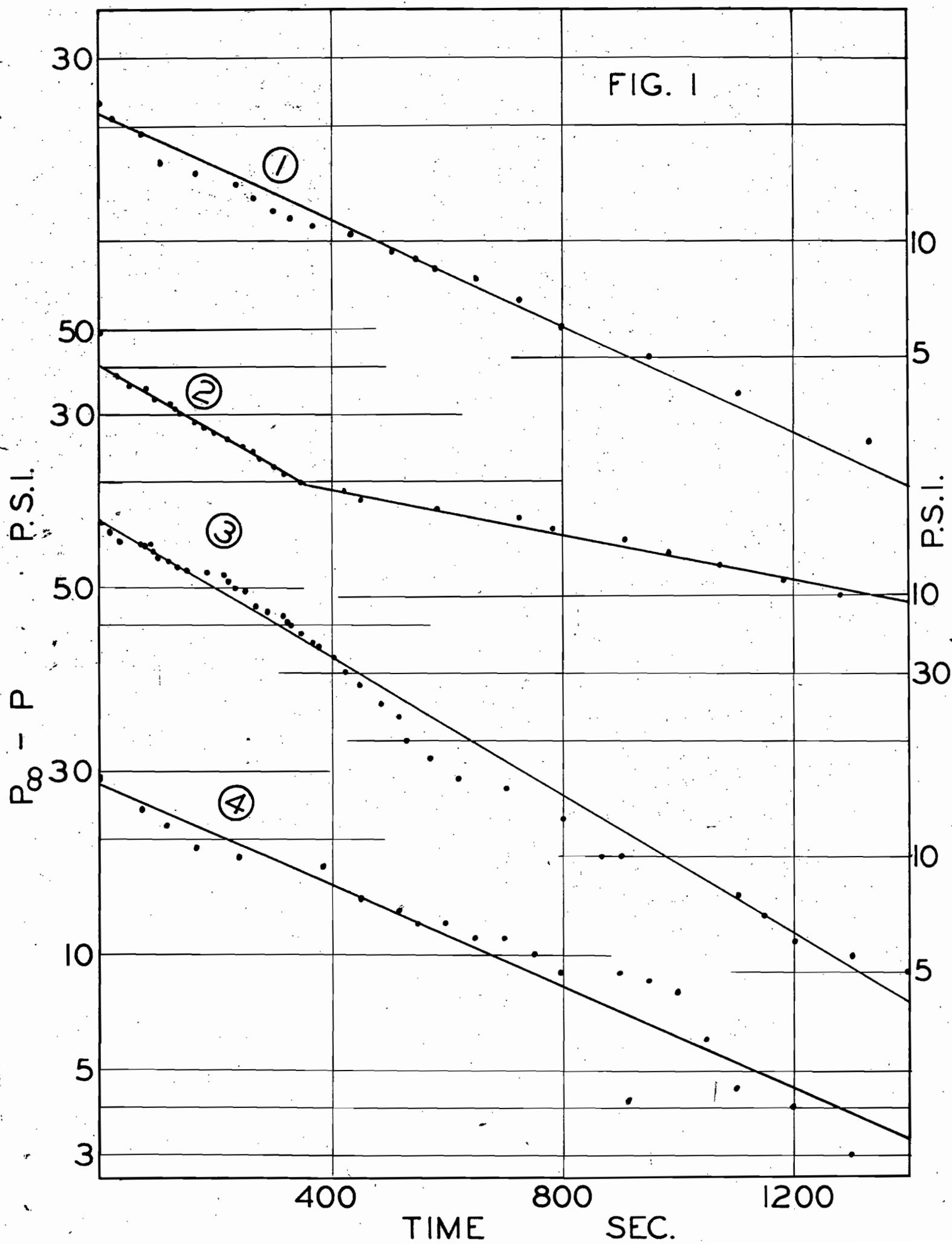
| Experiment No. | Temperature | Ion Current | P | $1/P_{\infty}$ | $1/\text{current}$ |
|----------------|-------------|-------------|--------|-------------------------|--------------------------|
| 1 | 80°C. | 10 A | 24 psi | 0.62 atm. ⁻¹ | 0.100 μA^{-1} |
| 2 | 80 | 30 | 48 | 0.31 | 0.033 |
| 3 | 80 | 35 | 74 | 0.20 | 0.029 |
| 4 | 80 | 30 | 78 | 0.19 | 0.033 |
| 5 | 80 | 35 | 99 | 0.15 | 0.029 |
| 6 | 118 | 35 | 20 | 0.75 | 0.029 |
| 7 | 118 | 50 | 34 | 0.44 | 0.020 |
| 8 | 118 | 60 | 39 | 0.39 | 0.017 |

All the values of the pressure are corrected for the vapor pressure of UF_6 at the temperature shown. There is an uncertain error in this correction introduced by the rise in temperature of the UF_6 under bombardment. This would make the values of p_{∞} smaller, the more so at the higher ion currents.

Now the inverse of equation (5) is

$$\frac{1}{P_{\infty}} = \frac{2Na}{RET_1} + E_2 \frac{L'}{L} \frac{k}{I}$$

FIG. 1



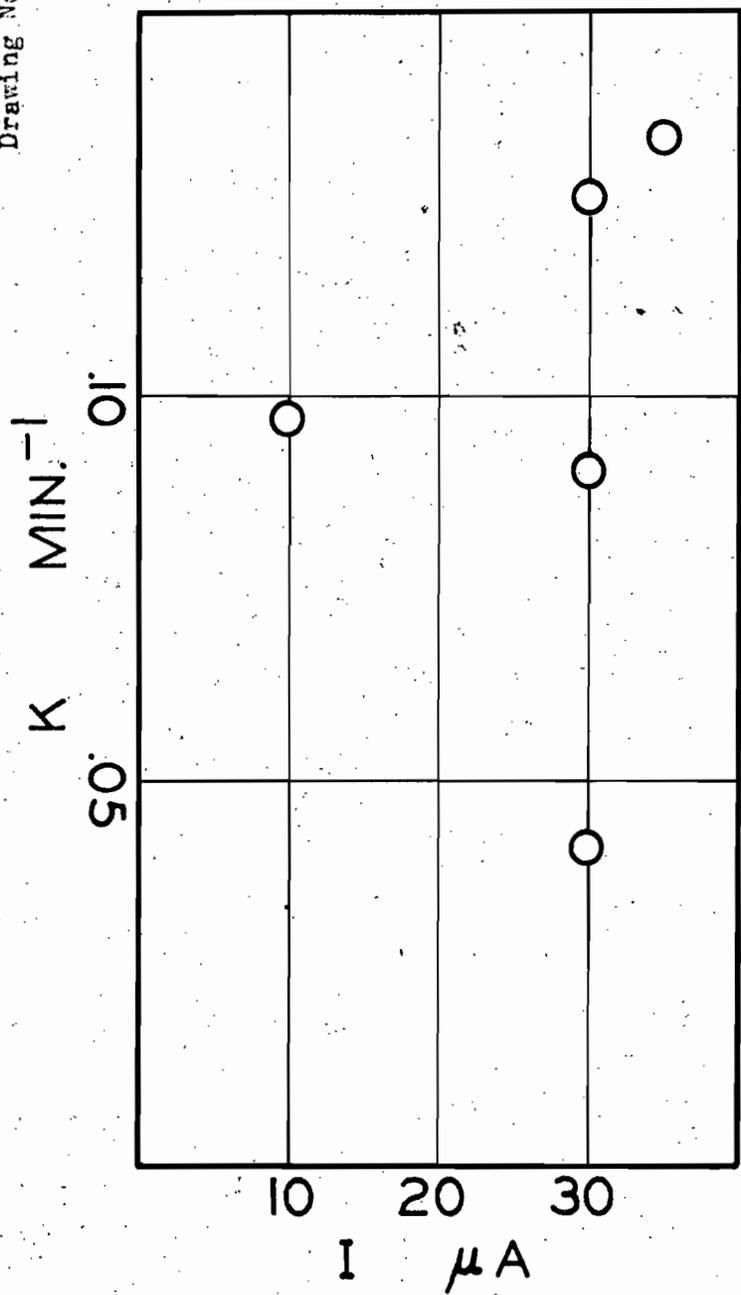


FIG. 2

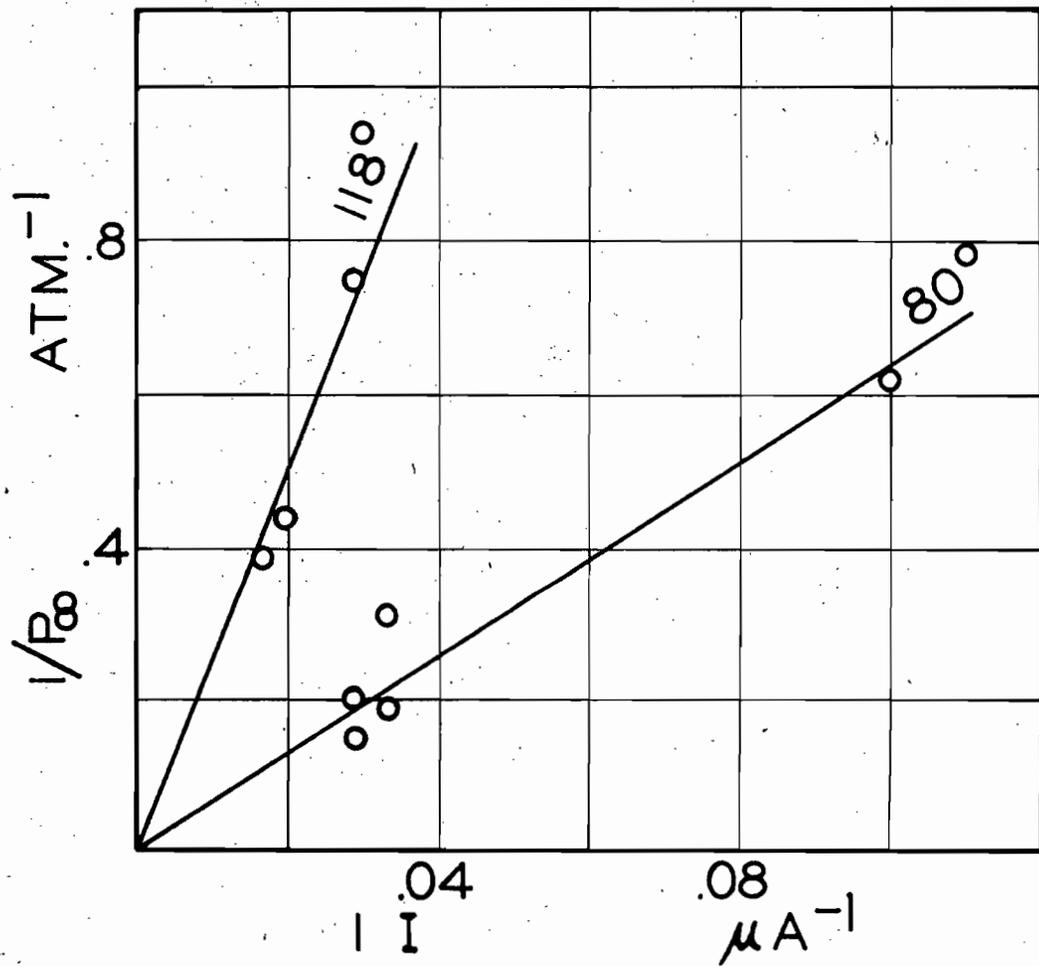


FIG. 3

From this it is seen that a plot of $1/p$ vs $1/I$ should give a straight line with intercept proportional to E_1 and slope proportional to k . Since k is a function of temperature, the series at different temperatures will give lines of different slopes.

The plot of these data in Figure 3 is in good agreement with these predictions of the theory. Two definite conclusions can be drawn from this graph:

1. The radiation-activated back reaction is of small importance compared to the thermal reaction in these experiments. (However, it is not possible to rule out a finite value of E_2 giving an intercept as high as 0.1 on the $1/p$ axis. Measurements at higher intensities of ionization would be needed to disclose the possible existence of a back reaction induced by ionization. Note that the neglected correction for excess vapor pressure of UF_6 would tend to raise the points at the low end of the curve and perhaps give a positive intercept.
2. The thermal reaction rate for reformation of UF_6 increases markedly with temperature. The slope of the plot is greater by a factor of 4 at 118° than at 80° . Since this slope is proportional to k/T (assuming the distribution coefficient a is constant; see equation 8), this corresponds to a ratio in the rate constants of $4 \times 391/353 = 4.5$. This shows definitely that raising the temperature of the UF_6 under bombardment will reduce the steady state pressure of F_2 .

From the data of Jenks and Livingston it is possible to make a rough quantitative estimate of the pressure of F_2 resulting from the decomposition of UF_6 in a pile. From equation (5), omitting the term for radiation back reaction, one can write for the ratio of pressure in a pile and in the Van de Graaff electron beam:

$$\frac{P_p}{P_e} = \frac{T_2 (ka)_1}{T_1 (ka)_2} \cdot \frac{I_p}{I_e} \frac{L_p}{L_e} \frac{L'_e}{L'_p} \frac{E_p}{E_e} \quad (9)$$

The factors T , k , and a are all temperature dependent in the same way in the pile as in the electron beam. At the same temperature then, the equation reduces to

$$\frac{P_p}{P_e} = \frac{I_p}{I_e} \frac{L_p}{L_e} \frac{L'_e}{L'_p} \frac{E_p}{E_e} \quad (10)$$

In the lack of any experimental information about the relative values of E_p and E_e , we take them as equal. If there is a difference, it would be expected that E_p is less than E_e , because of the greater intensity of ionization along the fission fragment track than along the electron track. Now we can calculate the quantity $I_p L_p$ for a 30,000 kw. pile employing liquid UF_6 as fuel in tubes surrounded by moderator, taking e as the energy in eV required to form one ion-pair in UF_6 .

$$I_p L_p = \frac{30 \times 10^6 \text{ watts} \times 3 \times 10^{10} \text{ fissions/watt sec.} \times 200 \times 10^6 \text{ eV/fissions}}{e \text{ eV/ion pairs}}$$

$$= 18 \times 10^{25}/e$$

Similarly, the intensity of ionization in the electron beam experiments can be calculated, with use of the data from experiment 8.

$$I_e L_e = \frac{60 \times 10^{-6} \text{ amperes} \times 1.4 \times 10^6 \text{ eV/electron}}{1.6 \times 10^{-19} \text{ ampere-sec./electron} \times E_I \text{ eV/ion-pair}}$$

$$= 5 \times 10^{20}/e \text{ ion pairs/sec.}$$

The volume of UF_6 in which the back reaction occurs in the electron beam experiments is difficult to estimate. The volume exposed to radiation is the area of the beam about 1 cm^2 times the range of the electrons in UF_6 , which can be calculated to be about 0.12 cm. Thus out of a total volume of UF_6 of about 50 cc., only about 0.12 cc. was exposed to the radiation. Convection currents set up by the heating of the irradiated portion caused some mixing, but since no provision was made for mechanical stirring, this process must have been quite inefficient. The value of L' to be used can only be guessed at. It certainly lies between 0.12 cc. and 50 cc., and probably much closer to the smaller figure. Let us take 1 cc. for the calculation.

The total volume of the liquid UF_6 in the pile will be effective in both the decomposition and the reformation of UF_6 , since the source of the ionization lies within the UF_6 itself. From some calculations of critical masses to be reported later, this volume may be taken as 2500 cc. Putting in these figures, we find

$$P_p = 2.5 \times \frac{18 \times 10^{25}}{5 \times 10^{20}} \times \frac{1}{2500} = 360 \text{ atm.}$$

A steady state pressure of 300 atmospheres is not unthinkable, but there are several ways in which this figure can be reduced by large factors. These are:

1. The temperature may be increased, speeding up the thermal back reaction, and reducing the steady state pressure in equation (9) as shown by the measurements of Jenks and Livingston. In order to calculate the pressure to be expected at a higher temperature, it is necessary to extrapolate the thermal rate constant. Assuming that $\log k$ is a linear function of $1/T$, the ratio of K at the critical temperature 230° , to that at the highest temperature studied, 118° , can be computed as follows:

$$\frac{\log (k_3/k_2)}{1/T_2 - 1/T_3} = \frac{\log (k_2/k_1)}{1/T_1 - 1/T_2}$$

$$\frac{\log (k_3/k_2)}{.00257 - .00199} = \frac{\log 4.5}{.00286 - .00257}$$

$$\frac{k_3}{k_2} = 20$$

At the critical temperature the steady state pressure will be smaller than at 118° by a factor of $20 \times 391/503 = 15$.

2. A gaseous UF_6 pile may be considered instead of a liquid. This will help in two ways. First, the volume of the hex will be considerably greater. At a pressure of 35 atmospheres, the same quantity of UF_6 as considered above will have a volume of 27,000 cc. Thus another factor of 10 is gained in equation (9).
3. Going from the liquid to the gaseous phase also helps by permitting homogeneous mixing of the fluorine, thus raising the factor a , representing the solubility of fluorine in hex from a small fraction up to unity. This works in the same direction as an increase in k , as can be seen from equation (9). To estimate the magnitude of this factor, we need to know the solubility of F_2 in liquid UF_6 . Unfortunately there do not appear to be any experimental data on this point. However, a rough estimate can be made, on the assumption that F_2 will give an ideal solution in UF_6 by a method outlined by Hildebrand. (3) This consists of determining a fictitious vapor pressure P^* of F_2 at the temperature under consideration by extrapolating the vapor pressure curve above the critical temperature and then substituting this value in the equation for an ideal solution

$$N_1 = P/P^* \quad (11)$$

where N_1 is the mol fraction of the gas at a partial pressure of P . Or since the solubility is very slight we can write for N_1 the mol ratio of F_2 to UF_6

$$\frac{n_1}{n_2} = \frac{P}{P^*} \quad (12)$$

To get the distribution coefficient a from this note that

$$a = \frac{n_1/L}{n/V} = \frac{n_2}{L} \frac{P}{P^*} \frac{n}{V}$$

n_2/L , the number of molecules of UF_6 per cc., is simply the density divided by the molecular weight P/M . Making this substitution along with $P = NRT/V$,

$$a = \frac{P}{M} \frac{RT}{P^*} \quad (14)$$

to get P^* , the following measured values of the vapor pressure of F_2 were extrapolated in a straight line on a plot of \log vs

Vapor Pressure of F₂

| | <u>T</u> | <u>P</u> | |
|----------------------|----------|----------|--------------------|
| Critical temperature | -157° | | 10.9 atm. measured |
| | -129° | 55 | measured |
| | 80° | 5000 | extrapolated |
| | 118° | 7000 | extrapolated |
| | 230° | 13000 | extrapolated |

Substituting other appropriate values we find for 118°

$$a = \frac{3.3}{352} \times \frac{82 \times 391}{7000} = .043$$

Now, putting these factors into equation (9) we calculate for a gaseous pile at 230°

$$P_p = 2.5 \times \frac{18 \times 10^{25}}{5 \times 10^{20}} \times \frac{1}{27,000} \times \frac{503}{391} \times \frac{1}{20} \times \frac{.043}{1} = 0.1 \text{ atmos.}$$

A pressure of only 0.1 atmosphere of fluorine at 230° is well within the present technological experience in the handling of fluorine. Actually, the pressure may turn out to be considerably less than this, as is apparent in the assumptions made, but even in the worst possible case, the pressure would not be expected to go above a few atmospheres.

It may be of interest to note the effect of mixing the UF₆ with some inert solvent in a homogeneous pile. For example, a solution of one part of UF₆ in 1000 parts of fluorocarbon oil gives a fuel mixture which would have a critical volume of about 5 m³. In such a mixture, the hex would absorb only a fraction of the total ionization equal to its weight fraction times its relative stopping power for fission fragments. The weight fraction in this ratio (with UF₆ = 3.45; CF₂ = 1.8) is 0.002. The mass stopping power can be calculated from data given by Segre and Wiegand (4) to be approximately 0.53. Thus the UF₆ will absorb about 0.001 of the total ionization. Putting this factor, together with other figures, into equation (9), we get for the pressure of fluorine developed by decomposition of UF₆ under these circumstances

$$P_p = 2.5 \times \frac{18 \times 10^{25}}{5 \times 10^{20}} \times \frac{1}{5 \times 10^6} \times 0.001 = 0.002 \text{ atmos.}$$

Thus the decomposition under these conditions would be quite negligible. Presumably the decomposition of the fluorocarbon under radiation would itself produce fluorine, but there is no experimental information on this point.

In conclusion, it may be stated on the basis of the foregoing analysis of the problem that the use of UF₆ in piles is certainly not ruled out by its decomposition under radiation, so far as present knowledge indicates. The measurement of the pressures developed over a sample of UF₆ in the neutron flux of a pile is a very desirable experiment, since it will eliminate at once the two chief sources of uncertainty entering into the present calculation, namely, the volume of UF₆ effective in promoting the back reaction, and the relative efficiency of fission fragments and electrons in decomposing

UF₆. Also, the possible use of fluorocarbons in a homogeneous pile should not be ruled out until some experimental evidence is at hand to support the view generally held that their decomposition in the pile will be serious.

I wish to acknowledge my debt to Messrs. Jenks and Livingston, who have kindly made available to me their original data and details of the experiments, and to Mr. A. O. Allen, for his stimulating discussion of several points in this paper.

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