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KINETICS OF THE THERMAL DECOMPOSITION OF URANYL FLUORIDE

I. PRELIMINARY RESULTS

L. M. Ferris
E. F. Gabbard

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Chemical Development Section B

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1.0 ABSTRACT

The thermal decomposition of uranyl fluoride was studied by a thermogravimetric technique between 750 and 880°C. The decomposition reaction at atmospheric pressure is $3\ UO_2F_2 \longrightarrow 2/3\ U_3O_8 + UF_6 + 1/3\ O_2$. In dry helium the rate of reaction was first order with respect to the mass of UO_2F_2, with indications that it also was dependent on the gas flow rate. The rate constants, determined with a constant flow rate of dry helium, may be expressed as $\log k\ (min^{-1}) = 11.57 - 15700/T$. In preliminary experiments with dry air and oxygen the rate decreased with increasing oxygen partial pressure; however, data were insufficient for a quantitative relation to be derived. UO_2F_2 sublimed, as a parallel first-order process, at temperatures above 825°C.

2.0 INTRODUCTION

This investigation was started to provide information on the high-temperature chemistry of UO_2F_2, which is basic to the development of the Fluorox process.[1] The present Fluorox process is based on the reaction $2\ UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$, which is rapid[2] at temperatures above 750°C. The original engineering studies[1,3] with moving-bed and fluidized-bed reactors were confined to the temperature range 700-800°C, where UO_2F_2 decomposes only very slowly.[4] However, because of certain limitations of moving-bed and fluidized-bed reactors, a $CO-O_2$ flame reactor,[5] which can produce temperatures of 1000-1500°C, is also being used in the most recent engineering studies. The chemistry of the process is essentially unknown at these temperatures, but earlier chemical studies[4,6,7] indicated that rapid decomposition of UO_2F_2 to uranium oxides may be expected. The method of decomposition must be known before appropriate recycle schemes can be devised. Design of a suitable flame reactor will be facilitated if the rates of decomposition are also known. This study, when completed, is intended to

yield the stoichiometry of the main decomposition reaction, the relative effects of any pertinent side reactions, and the rate of decomposition and the factors influencing it. This paper constitutes only a progress report, and many of the conclusions are highly tentative.

The authors wish to acknowledge J. F. Land for his assistance in performing many of the experiments. They are also indebted to the Analytical Chemistry Division of ORNL for the chemical and x-ray analyses, particularly the groups of G. R. Wilson, W. R. Laing, and R. L. Sherman.

3.0 STOICHIOMETRY OF THE UO_2F_2 DECOMPOSITION REACTION

Thermodynamic considerations, x-ray analyses of residues, weight losses, and chemical analyses showed conclusively that UO_2F_2 decomposes at temperatures below 900°C according to the reaction

$$3\ UO_2F_2 \longrightarrow 2/3\ U_3O_8 + UF_6 + 1/3\ O_2$$

3.1 Thermodynamics

Estimated standard free energy changes (Table 3.1) for the various reactions proposed to account for the solid decomposition products[4,6,8-10] show that, of the following, reaction 3 is the most favorable at temperatures below 1000°C if the system is kept free of moisture:

$$UO_2F_2 \longrightarrow UO_2 + F_2 \qquad (1)$$

$$2\ UO_2F_2 \longrightarrow UO_2 + UF_4 + O_2 \qquad (2)$$

$$3\ UO_2F_2 \longrightarrow 2/3\ U_3O_8 + UF_6 + 1/3\ O_2 \qquad (3)$$

$$4\ UO_2F_2 \longrightarrow UF_4 + U_3O_8 + 2\ F_2 \qquad (4)$$

$$3\ UO_2F_2 \longrightarrow 2\ UO_2 + UF_6 + O_2 \qquad (5)$$

$$UO_2F_2 + H_2O \longrightarrow 1/3\ U_3O_8 + 2\ HF + 1/6\ O_2 \qquad (6)$$

$$U_3O_8 \longrightarrow 3\ UO_2 + O_2 \qquad (7)$$

However, as is the case of the other reactions proposed, the ΔF^o is positive. Consequently UO_2F_2 would be expected to be highly stable with respect to any decomposition product. In order to achieve measurable decomposition of UO_2F_2 it appears necessary to drive the reaction by continuously removing one or more decomposition products. The rate of decomposition under these conditions is expected to be low. Similarly, the ΔF^o for reaction 7 shows that U_3O_8 should be relatively stable at temperatures below 1000°C.

3.2 Identification of Decomposition Products by X-ray Analysis

The x-ray analyses indicated that the thermodynamic estimates were valid and that reaction 3 is the decomposition reaction at temperatures below 900°C (Table 3.2). In most of the residue samples examined, undecomposed UO_2F_2 remained. Some of the samples were slowly scanned to bring out faint lines in the x-ray diffraction patterns due to minor constituents, but UO_2 was found only in the residue from a run made at a temperature above 900°C. There was no evidence of UF_4 in any of the residues. Flakes of NiO, picked up while the sample was being removed from the reaction chamber, were found in some cases.

3.3 Chemical Analysis and Weight Loss Data

The weight loss due to essentially complete decomposition and the percentage of U(IV) in the residue (Table 3.3) show reaction 3 to be the chief decomposition reaction, in agreement with x-ray data. Although the experimental weight losses were, in general, greater than expected for reaction 3, this is accounted for by sublimation of UO_2F_2

Table 3.1. Estimated Standard Free Energy Changes for Various Decomposition Reactions[4]

Reaction	ΔF^o, kcal/mole			
	400°C	600°C	800°C	1000°C
(1) $UO_2F_2 \longrightarrow UO_2 + F_2$	+100	+93	+86	+80
(2) $2\ UO_2F_2 \longrightarrow UO_2 + UF_4 + O_2$	+46	+37	+27	+19
(3) $3\ UO_2F_2 \longrightarrow 2/3\ U_3O_8 + UF_6 + 1/3\ O_2$	+42	+31	+20	+10
(4) $4\ UO_2F_2 \longrightarrow UF_4 + U_3O_8 + 2\ F_2$	+188	+173	+156	+142
(5) $3\ UO_2F_2 \longrightarrow 2\ UO_2 + UF_6 + O_2$	+76	+59	+39	+22
(6) $UO_2F_2 + H_2O \longrightarrow 1/3\ U_3O_8 + 2\ HF + 1/6\ O_2$	-2	-9	-17	-28
(7) $U_3O_8 \longrightarrow 3\ UO_2 + O_2$	+51	+42	+28	+18

Table 3.2. X-ray Analyses of Reaction Residues

Run No.	Temperature, °C	Solids in Residue	Remarks
6	825	$U_3O_8 + UO_2F_2$	
1,13	840	$U_3O_8 + UO_2F_2$	Residues scanned slowly but no UO_2 detected
18,19	880	U_3O_8 + NiO	Residues scanned slowly but no UO_2 detected; NiO resulted from flaking of reaction vessel
10	900	U_3O_8	
4	>900	$U_3O_8 + UO_2$	

Table 3.3. Comparison of Calculated Weight Losses and Chemical Analyses for Reactions 1-6 with Those Determined Experimentally

Run No.	Reaction	Amount, %			
		Weight Loss	U in Residue	U(IV) in Residue	F in Residue
Calculated for Complete Decomposition					
	None	---	77.28	---	12.33
	1	12.34	88.15	88.15	---
	2	5.19	81.51	81.51	13.01
	3	39.25	84.80	28.27	---
	4	6.17	82.38	41.19	6.57
	5	41.56	88.15	88.15	---
	6	8.87	84.80	28.27	---
Determined Experimentally[a]					
19	880°C	41.6	83.6	38.7	0.10
18	880°C	44.8	70.7[b]	31.6	0.14
10	900°C	46.2	85.3	34.6	0.16
4	>900°C	46.6	79.4	43.5	1.7
3	>900°C	50.0	82.1	38.4	2.0

[a] In each case the decomposition was essentially complete.

[b] Obviously too low.

(see Sec. 3.5). It is obvious from the weight loss data that reactions 1, 2, and 4 are not involved in the decomposition.

The percent conversion of all runs, as calculated from weight losses and chemical analyses, is given in Table 3.4. Separate columns are given for the weight losses determined by the thermobalance and those determined with the conventional analytical balance because in most cases the residue was allowed to cool overnight. Any further decomposition of UO_2F_2 on pickup of moisture was detected by the latter weighing. Percentage conversions calculated from the uranium, U(IV), and fluoride determinations in many cases showed a wide scatter. However, agreement among the calculated percentages was fair in runs 1, 3, 5, 6, 7, 8, 10, 14, 19, 20, and 21. Conversions determined by weight loss are considered the most accurate because, at best, only one chemical analysis could be made on each residue.

3.4 Formation of UF_6

At relatively high temperatures, i.e., above 850°C, where the rate of decomposition was fairly rapid, white fumes, undoubtedly UF_6, escaped from the top of the reactor. One run at 900°C was made in a 1-in.-dia tube furnace connected to a U-tube immersed in liquid nitrogen with helium sweep gas at a flow rate of 300 ml/min at 25°C. After about 4 hr, the white condensate in the U-tube was examined. It sublimed at about 60°C, as would be expected of UF_6.[11] No quantitative information was obtained on the condensate, but further experiments along this line are planned.

Serious consideration will probably not be given to the decomposition of UO_2F_2 as a primary method for producing UF_6 because of the extremely slow rate below 850°C, even in an inert gas. More important, the presence of oxygen in the sweep gas seriously retards the decomposition (Table 3.5). In effect, the decomposition is driven by

Table 3.4. Decomposition of UO_2F_2 According to the Reaction

$$3\ UO_2F_2 \longrightarrow UF_6 + 2/3\ U_3O_8 + 1/3\ O_2$$

Run No.	Temp., °C	Conversion, %							Material Balances, %		
		Based on Weight Loss			Based on Chemical Analyses						
		Thermo-balance	Analytical Balance	Average	U	F	U(IV)	Average	U and F	U(IV) and F	Average
8	750	3.1	---	3.1	2.4	6.2	2.3	3.6	99.9	96.4	98.1
7	775	9.7	11.1	10.4	12.4	4.8	9.9	9.1	105.5	105.2	105.3
15	800	19.5	19.8	19.7	39.5	21.6	27.8	29.6	93.4	103.3	98.3
20	825	29.5	22.7	26.1	28.2	25.5	33.9	29.2	97.9	104.4	101.2
6	825	36.8	39.2	38.0	42.2	29.9	25.0	32.4	99.0	99.8	99.4
13	840	8.7	14.3	11.5	5.1	63.7	92.5	53.8	98.3	97.9	98.1
12	840	7.5	8.1	7.8	---	46.2	63.8	36.7	100.5	95.6	98.1
11	840	1.6	4.2	2.9	10.8	16.4	21.4	16.2	99.5	100.9	100.2
9	840	10.9	8.9	9.9	9.3	32.2	40.8	27.4	97.7	95.9	96.9
2	840	107.3	---	107.3	145.9	82.6	60.0	96.1	83.6	93.1	88.3
1	840	71.1	71.0	71.0	93.8	62.5	61.4	72.5	91.5	103.8	97.6
14	840	28.7	26.8	27.8	30.5	28.9	31.9	30.4	98.5	100.9	99.7
22	850	73.9	64.4	69.1	81.8	64.4	101.4	82.5	92.9	130.1	111.5
21	850	102.2	89.2	95.7	99.5	85.8	---	92.7	95.6	---	95.6
17	860	80.4	83.6	82.0	91.4	75.8	68.5	78.6	97.5	97.9	97.7
16	860	36.7	37.3	37.0	50.9	45.7	60.1	52.2	94.3	106.4	100.3
19	880	105.6	106.3	105.9	110.7	99.5	131.4	113.9	98.7	137.7	118.2
18	880	113.4	78.2	95.8	109.9	99.2	127.5	112.2	83.4	112.9	98.2
10	900	---	111.2	111.2	113.3	99.3	113.6	108.4	100.5	123.8	112.1
5	>900	106.5	---	106.5	109.5	92.4	110.2	104.0	100.6	128.0	114.3
4	>900	108.8	99.5	104.1	112.0	91.6	154.4	119.3	91.2	107.6	129.4
3	>900	113.7	115.8	114.7	109.3	90.3	133.7	111.1	98.3	152.0	125.1

removing the gaseous products with an inert sweep gas. For this type of process the difference between the oxygen partial pressures at the solid-gas interface and in the gas phase should constitute a part, if not all, of the driving force. Further work on the effect of oxygen pressure on the decomposition rate is planned. Also, the rate of reaction could depend on the flow rate of the sweep gas. A decrease in rate with decreasing helium flow rate was actually observed. More work in this area is also planned.

In addition to the proposed experiments with the system at atmospheric pressure, a brief study of the decomposition under vacuum is contemplated. It may be possible to reduce the temperature required for rapid decomposition by 100-200°C if a high vacuum is used. Uranium hexafluoride could then be obtained from UO_2F_2 at more reasonable temperatures.

Table 3.5. Effect of Oxygen on the Rate of Decomposition of UO_2F_2

Initial weight of sample: 2 g
Gas flow rate: 300 ml/min at 25°C

Gas	Weight Loss, mg, after 3 hr at 840°C
Helium	320
	320
Air	43
	25
Oxygen	23
	20

3.5 Sublimation of UO_2F_2

Weight losses in excess of those expected from the decomposition alone could be attributed only to sublimation of UO_2F_2. A parallel reaction yielding UO_2 would produce the same effect, but UO_2 could not be detected in decomposition residues below 900°C. However, UO_2 will be a solid product if the decomposition is carried out at a temperature above 900°C. A study of the rate of decomposition of U_3O_8 to UO_2 at very high temperatures is planned. Rate data from such a study would allow prediction of the relative amounts of UO_2 and U_3O_8 in the solid product of a UF_4-O_2 reaction, the reaction in which UO_2F_2 is formed as a by-product in the Fluorox process. This information would be valuable for preparing flowsheets and devising appropriate recycle schemes for the solid residues.

3.6 High-temperature Reaction of UF_4 with O_2

If the oxidation of UF_4 should be carried out at a high temperature to increase the decomposition of the UO_2F_2 by-product, and thus increase the UF_6 yield, the reaction would be expected to yield U_3O_8 or a mixture of UO_2 and U_3O_8 (Table 3.2). The expected over-all stoichiometry for such a reaction at various temperatures is:

$$2\ UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2 \qquad (600\text{-}800^\circ C)$$

$$3\ UO_2F_2 \longrightarrow 2/3\ U_3O_8 + UF_6 + 1/3\ O_2 \qquad (800\text{-}950^\circ C)$$

$$3\ UF_4 + 4/3\ O_2 \longrightarrow 1/3\ U_3O_8 + 2\ UF_6 \qquad (800\text{-}950^\circ C)$$

$$U_3O_8 \longrightarrow 3\ UO_2 + O_2 \qquad (950\text{-}1500^\circ C)$$

$$3\ UF_4 + O_2 \longrightarrow UO_2 + 2UF_6 \qquad (950\text{-}1500^\circ C)$$

4.0 RATES OF DECOMPOSITION

The general equation

$$\log \left[\frac{(k + k_v)\ (w_s - w_s^o)}{(fk + k_v)\qquad w^o} + 1 \right] = \frac{-(k + k_v)t}{2.303}$$

was derived (see Appendix), assuming that UO_2F_2 decomposes by a first-order process and sublimes as a parallel first-order process. The symbols are defined as follows:

k = rate constant for the decomposition of UO_2F_2
k_v = rate constant for the sublimation of UO_2F_2
f = stoichiometry factor
w_s = sum of the weights of UO_2F_2 and U_3O_8 at any time t
w^o = weight of UO_2F_2 at t = 0

The above equation reduces to

$$\log \left[\frac{(w_s - w_s^o)}{fw^o} + 1 \right] = \frac{-kt}{2.303}$$

for the special case where k_v is zero, i.e., where the rate of sublimation is undetectable. For this case it is obvious that a plot of

$$\log \left[\frac{(w_s - w_s^o)}{fw^o} + 1 \right]$$

versus time should result in a straight line with k evaluable from the slope. A special technique (Appendix) was developed for the evaluation of k and k_v from weight-loss data obtained at temperatures where both decomposition and sublimation occurred. Figure 4.1 contains several examples of the expected first-order behavior at temperatures below 825°C where no sublimation occurred, and shows the type of plot which results if sublimation is ignored at temperatures above 825°C. Figure 4.2 contains representative plots obtained when the decomposition reaction and sublimation are considered as parallel first-order processes.

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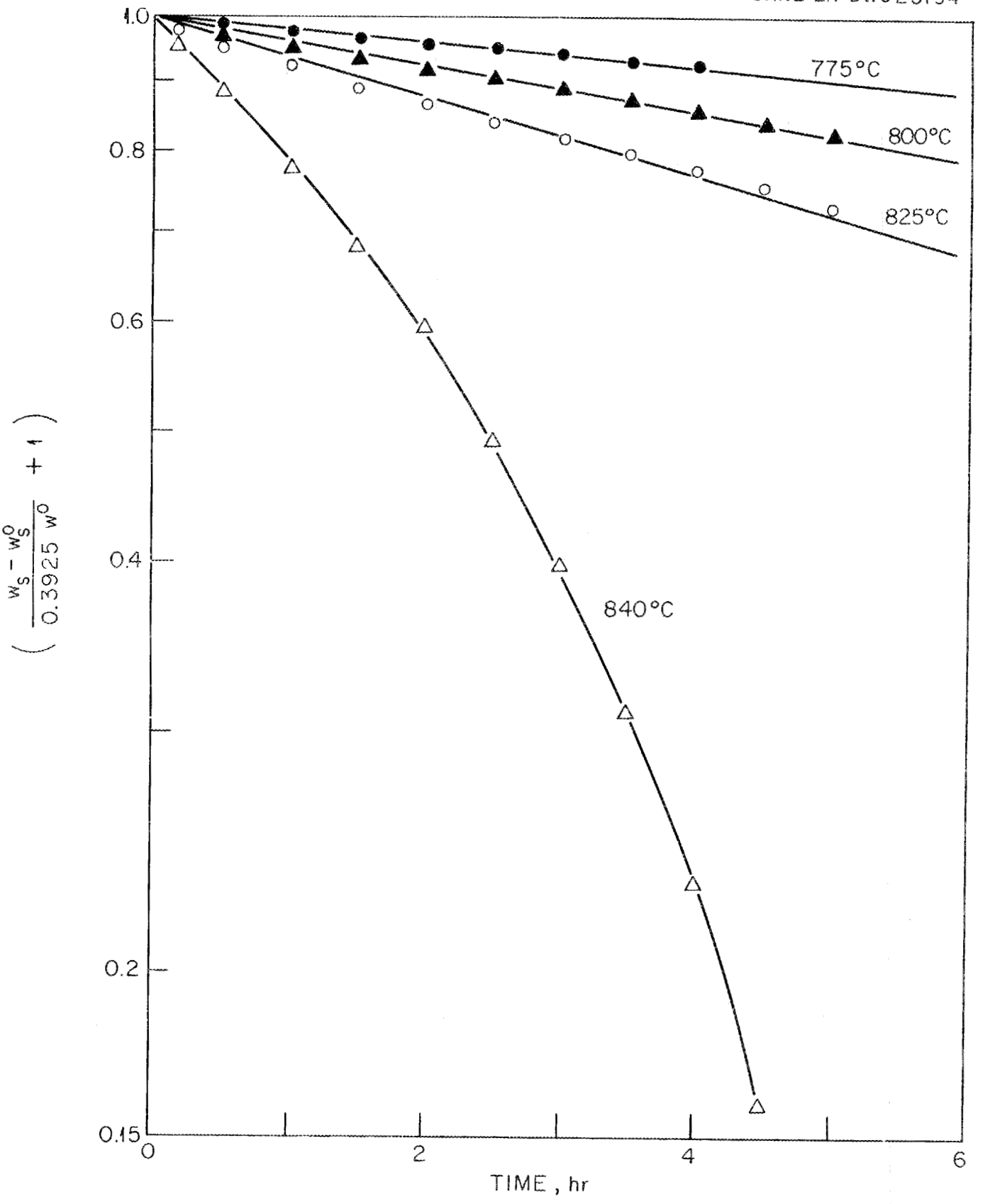

Fig. 4.1. Decomposition of UO_2F_2, Showing First-order Dependence below 825°C.

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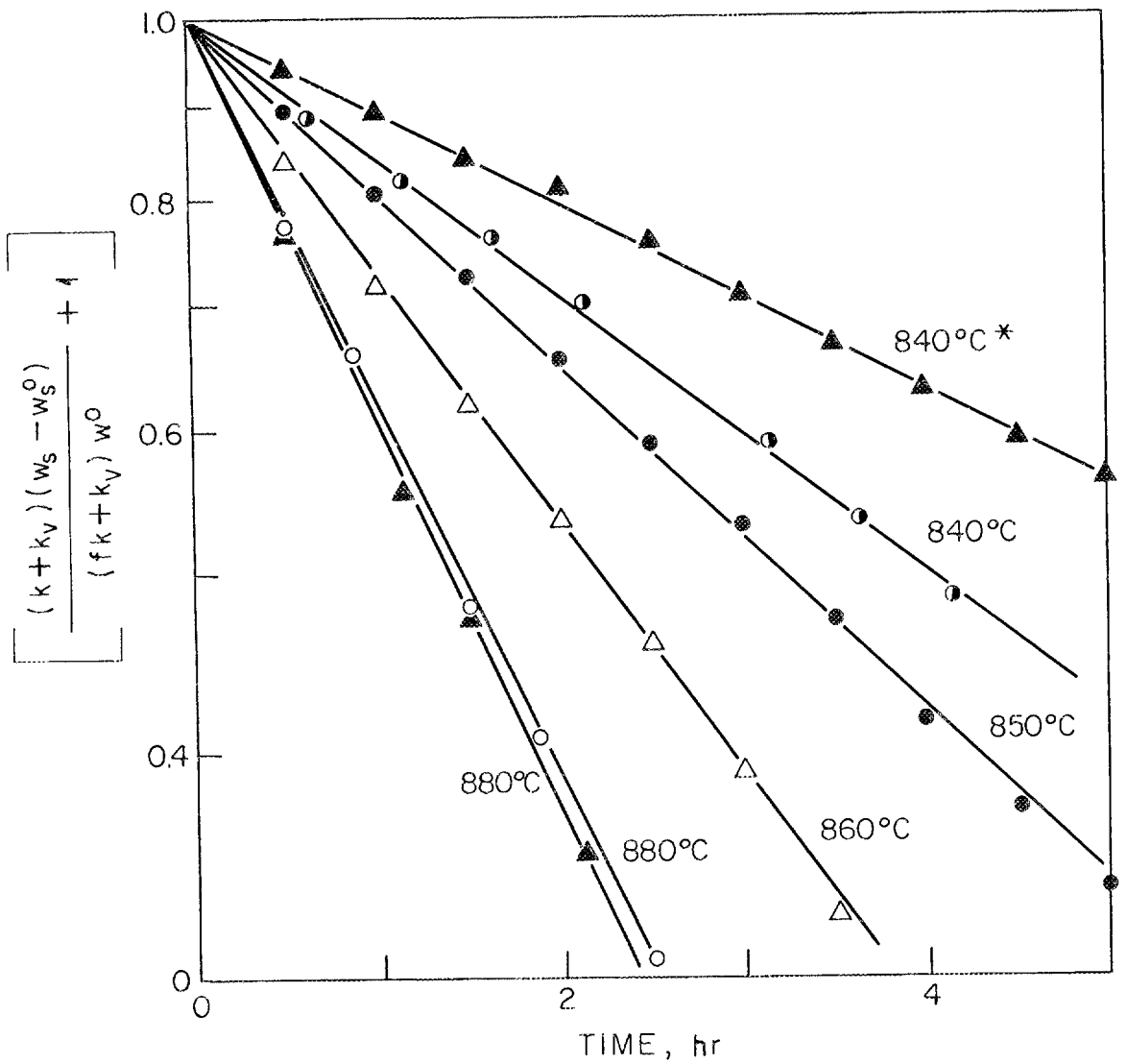

* Curve plotted from same weight-loss data as 840°C curve in Fig. 4.1

Fig. 4.2 Representative Plots When Decomposition And Sublimation of UO_2F_2 Are Considered as Parallel First-order Processes at Temperatures above 825°C.

Table 4.1 Rate Constants[a] for the Decomposition and Sublimation of UO_2F_2

Run No.	Temp.,[b] °C	$10^4/T$, $^oK^{-1}$	10^4k, min^{-1}	$t_{1/2}$, hr	10^4k_v, min^{-1}	$k_v/(k + k_v)$
8	750	9.78	1.4	82	---	0.0
7	775	9.54	3.6	32	---	0.0
15	800	9.32	6.9	17	---	0.0
1	800	9.32	4.1	28	---	0.0
2	800	9.32	4.7	25	---	0.0
6	825	9.11	18	6.3	0.1	0.005
20	825	9.11	22	5.3	---	0.0
1	840	8.98	20	5.7	9.3	0.32
14	840	8.98	24	4.8	---	0.0
21	850	8.90	32	3.6	11	0.26
22	850	8.90	30	3.8	5.1	0.14
16	860	8.83	43	2.7	7	0.14
17	860	8.83	51	2.2	6.3	0.11
18	880	8.67	56	2.1	27	0.33
19	880	8.67	56.5	2.0	26	0.31

[a] Rates measured in dry helium flowing at 300 ml/min at 25°C.[2]

[b] The precision claimed for the temperature measurements is ± 5°C.

Rate constants and half-times for the reaction $3\ UO_2F_2 \longrightarrow UF_6 + 2/3\ U_3O_8 + 1/3\ O_2$, obtained by the methods described in the Appendix, are given in Table 4.1. A least-squares plot of log k versus 1/T is found in Fig. 4.3. The equation for this line is

$$\log k\ (\mathrm{min}^{-1}) = 11.57 - 15700/T$$

from which an activation energy of 72 kcal/mole may be calculated.

A plot of log k_v versus 1/T is found in Fig. 4.4. Because of the wide scatter of points, the line in Fig. 4.4 was arbitrarily chosen. A heat of sublimation of 136 kcal/mole was estimated by assuming that the slope of the plot of log k_v versus 1/T was equal to the heat of sublimation. This value cannot be accepted with any confidence because of the questionable validity of the assumption and the wide scatter in points. In fact, the heat of sublimation calculated from the line in Fig. 4.4 appears to be high by a factor of 2 or 3 compared to that of other solids which are stable at relatively high temperatures.[12] The column $k_v/(k + k_v)$ in Table 4.1 gives the fraction of UO_2F_2 sublimed at each temperature.

5.0 EXPERIMENTAL DETAILS

5.1 Apparatus

The rate of decomposition of UO_2F_2 was measured with a semi-automatic recording thermobalance which provided a continuous plot of sample weight versus time. The details of this thermobalance and its auxiliary equipment have been reported elsewhere.[2]

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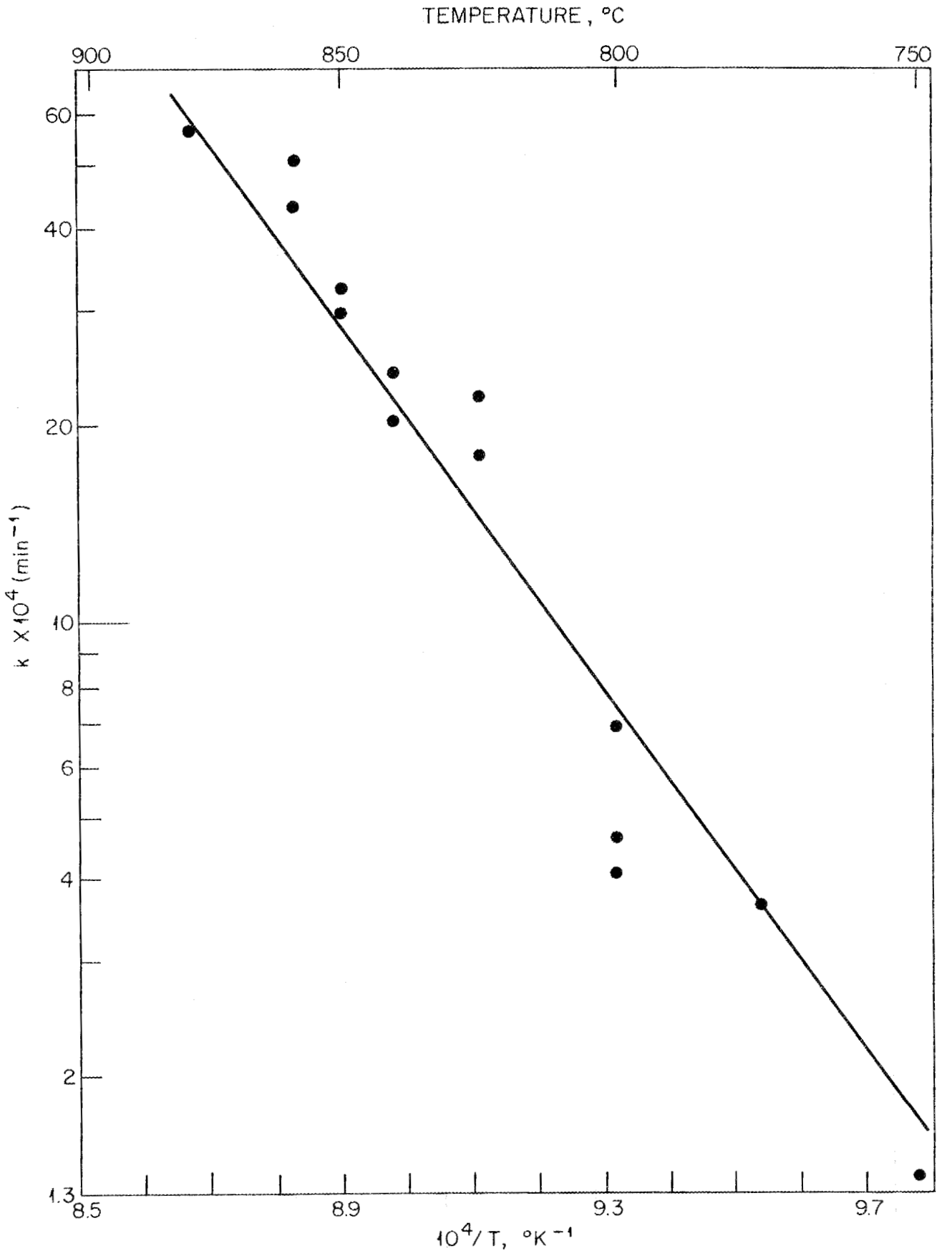

Fig. 4.3. Rate Constants for the Reaction $3UO_2F_2 \longrightarrow 2/3\ U_3O_8 + UF_6 + 1/3\ O_2$.

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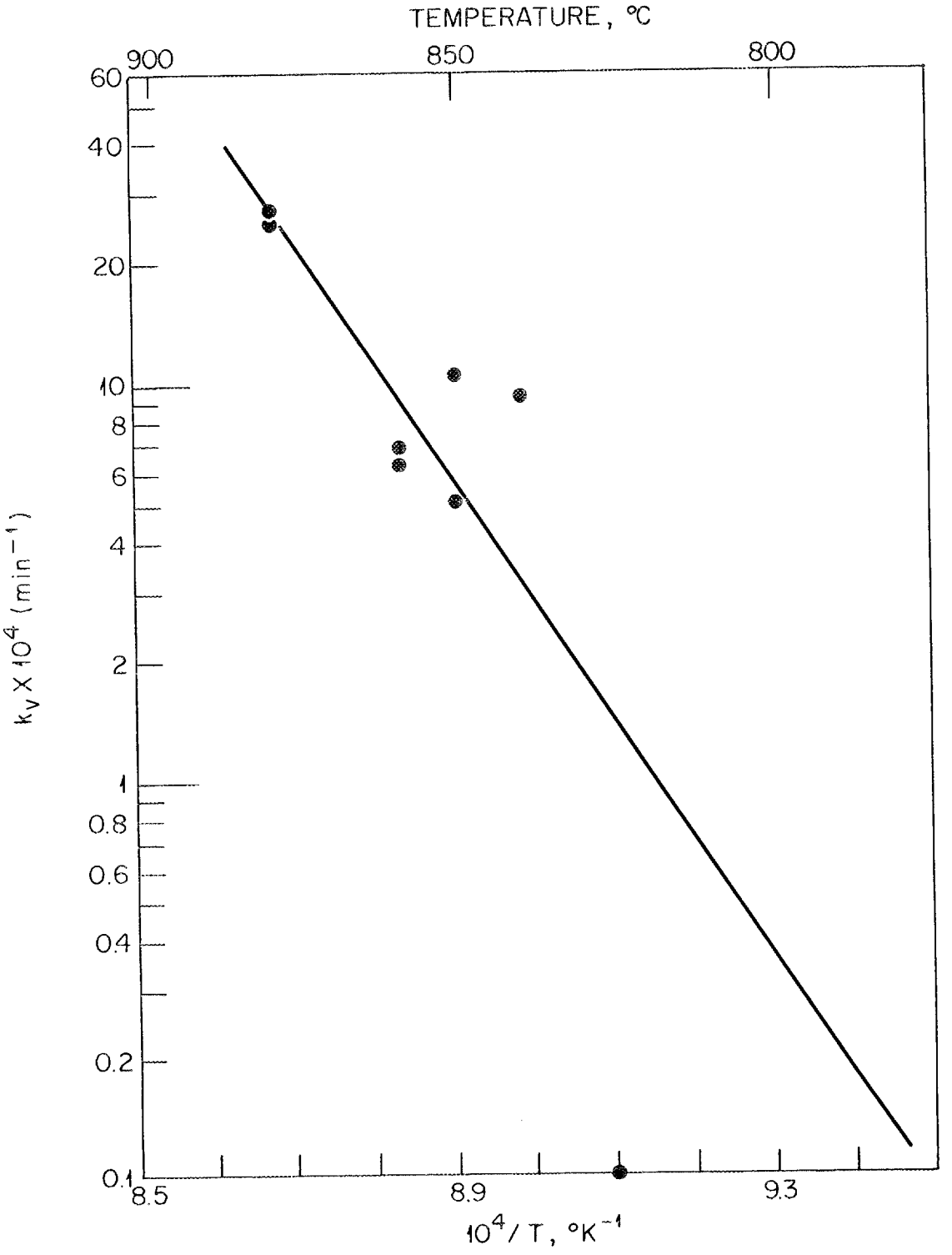

Fig. 4.4. Rate Constants for the Sublimation of UO_2F_2.

5.2 Materials

The uranyl fluoride used in this study was prepared by an ion exchange method. This material was extremely hygroscopic and initially contained 4.5 wt % H_2O (Table 5.1, analyses 1-3). However, the UO_2F_2 could be completely dehydrated at 100-200°C without pyrohydrolysis. Although the storage bottle was kept tightly stoppered, the water content increased to 6.2 wt % over a period of nine months (Table 5.1, analyses 4-6). This did not affect the ease of dehydration, however. The oxide content ($<0.5\%$) of the UO_2F_2 was low enough to be ignored. Therefore, essentially pure UO_2F_2 resulted from dehydration.

The high purity ($>99\%$) helium used in most of the experiments was carefully dried by passage through a charcoal bed, held at -196°C with liquid nitrogen, and two Drierite bulbs.

5.3 Procedure

At the start of each experiment approximately 2 g of the hydrated UO_2F_2 was weighed quickly into a small platinum basket,[2] using an ordinary analytical balance. This sample was then transferred rapidly to the thermobalance reaction chamber where it was heated in a stream of dry helium to about 230°C. Weight was lost rapidly during the heating. At 230°C no further weight loss occurred so the sample was considered completely dehydrated. Agreement between the weight loss due to dehydration and that expected from the water analysis was excellent. After dehydration the sample was assumed to be pure UO_2F_2 so that any further weight losses which occurred while heating to 750°C or higher were attributed to the slow decomposition of UO_2F_2 according to the reaction $3\ UO_2F_2 \longrightarrow 2/3\ U_3O_8 + UF_6 + 1/3\ O_2$. This allowed calculation of the weight of UO_2F_2 at any point on the weight-time plot. The point at which the temperature indicator

reached the predetermined temperature setting was carefully recorded on the weight-time plot and corresponded to "zero time" for the rate measurement.

Table 5.1 Chemical Analyses of UO_2F_2

Analysis No.	Analysis, wt %					Material Balance[a], %	
	U	U(IV)	F	H_2O	AOI[b]	Based on U(VI)	Based on F
1[c]	73.64	0.12	11.38	4.5	0.12	99.77	96.93
2[c]	73.54	0.16	11.07	4.5	---	99.64	94.46
3[c]	73.54	0.24	11.24	4.5	---	99.62	95.93
4[d]	72.50	0.36	11.38	6.21	0.059	99.97	98.91
5[d]	72.38	0.36	11.41	6.27	<0.05	99.87	99.22
6[d]	72.14	0.37	11.43	6.31	<0.05	99.60	99.43

[a] In calculation of the material balances the U(IV) was assumed to be entirely present as UO_2 and all fluoride was therefore taken as UO_2F_2.

[b] Ammonium oxalate insolubles (UO_2, U_3O_8).

[c] Analyses performed December, 1956.

[d] Analyses performed August, 1957.

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7.0 Appendix. EVALUATION OF RATE CONSTANTS

The rate at which a sample of initially pure UO_2F_2 will lose weight when the following parallel reactions occur

$$3\ UO_2F_{2(s)} \longrightarrow 2/3\ U_3O_{8(s)} + UF_{6(g)} + 1/3\ O_{2(g)} \tag{1}$$

$$UO_2F_{2(s)} \longrightarrow UO_2F_{2(g)} \tag{2}$$

is given by

$$\frac{-dw_s}{dt} = \left[\begin{matrix}\text{Rate of}\\ \text{Decomposition}\end{matrix} + \begin{matrix}\text{Rate of}\\ \text{Sublimation}\end{matrix}\right] \tag{3}$$

where w_s is the sum of the weights of UO_2F_2 and U_3O_8 at any time, t. The decomposition by reaction 1 of any amount of UO_2F_2, w_c, is related to the corresponding sample weight loss, L, by

$$L = fw_c \tag{4}$$

where f is a stoichiometry factor, 0.3925. But,

$$L = w_s^o - w_s \tag{5}$$

$$w_c = w^o - w \tag{6}$$

where w is the weight of UO_2F_2, and the superscript zeros refer to the weights when t = 0. Therefore, since w_s^o and w^o are constants at any one temperature,

$$\frac{dL}{dt} = f\frac{dw_c}{dt} = \frac{-dw_s}{dt} = -f\frac{dw}{dt} \tag{7}$$

It should be noted that Eq. 7 describes the total rate of weight loss of the sample only if decomposition is the only process occurring. Loss in weight attributable to sublimation may be expressed as

$$\frac{-dw_s}{dt} = \frac{-dw}{dt} \tag{8}$$

If it is assumed that decomposition and sublimation occur as

parallel first-order processes,

$$\frac{-dw_s}{dt} = fkw + k_v w \tag{9}$$

where k is the rate constant for reaction 1 and k_v is the rate constant for reaction 2. Equation 9 is obviously a special case of Eq. 3, where fkw and $k_v w$ correspond to the rates of decomposition and sublimation, respectively. Since $w = w^o \exp\left[-(k + k_v)t\right]$, equation 9 may also be expressed as

$$\frac{-dw_s}{dt} = (fk + k_v)\, w^o \exp\left[-(k + k_v)t\right] \tag{10}$$

For convenience, define

$$X = fk + k_v \tag{11}$$

$$Y = k + k_v \tag{12}$$

Then, integration of Eq. 10 with the boundary conditions that $w_s = w_s^o$ at $t = 0$ yields

$$w_s - w_s^o = \frac{Xw^o}{Y}\left[\exp(-Yt) - 1\right] \tag{13}$$

Rearranging Eq. 13 and converting to common logarithms gives

$$\log\left[\frac{Y\,(w_s - w_s^o)}{Xw^o} + 1\right] = \frac{-Yt}{2.303} \tag{14}$$

Equation 14 contains the two desired quantities, X and Y, in terms of experimentally measurable quantities, but cannot be used directly. However, inspection of Eq. 10 shows that the quantity X may be evaluated from the initial slope of a plot of sample weight versus time; i.e., at $t = 0$, Eq. 10 reduces to

$$\frac{-dw_s}{dt} = Xw^o \tag{15}$$

Once X is known it is possible to evaluate Y from Eq. 14 by successive approximations. Arbitrary values for Y are used in the calculation of $\log\left[\frac{Y\,(w_s - w_s^o)}{Xw^o} + 1\right]$. This logarithmic quantity is then plotted

versus time. If the value chosen for Y is not the correct one, a curved plot will result. Successive approximations are continued until the plot becomes linear (Fig. 4.2). Then, as required by Eq. 14, the value of Y used in the calculation of the logarithmic term will be equal to that calculated from the slope of the line. The rate constants k and k_v can then be obtained by solving Eq. 11 and Eq. 12 simultaneously.

For the special case where no sublimation occurs, Eq. 14 reduces to

$$\log \left[\frac{w_s - w_s^o}{fw^o} + 1 \right] = \frac{-kt}{2.303} \qquad (16)$$

A plot of the logarithmic term versus time should be linear (Fig. 4.1) with k evaluable from the slope.