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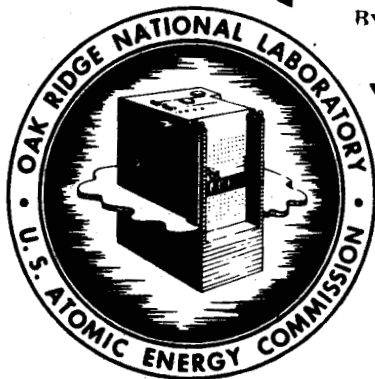
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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

LABORATORY DEVELOPMENT OF THE FLUOROX PROCESS:
II. THERMOGRAVIMETRIC STUDY OF THE CHEMICAL KINETICS
FOR THE REACTION OF UF_4 WITH DRY OXYGEN

L. M. Ferris
E. G. Carter

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1.0 ABSTRACT

Reaction rate constants for the reaction $2\text{UF}_4 + \text{O}_2 \longrightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$ are being determined by a thermogravimetric method. A semiautomatic recording thermobalance was constructed to continuously record the weight loss when UF_4 is oxidized. Operation of the thermobalance, treatment of data, and tentative rate constants are presented for the temperature range 600-800°C.

2.0 INTRODUCTION

In existing processes for making UF_6 from UF_4 , elemental fluorine is used. Since the discovery¹ in 1945 that UF_6 is a product of the reaction of UF_4 with dry oxygen, the possibility of a production scheme based on this reaction has been considered. Work on the Fluorox process,² in which moving-bed reactors have been used to date, points out the potential savings³ to be made by using O_2 instead of F_2 . (The use of other types of reactors such as fluid-bed- and flame-reactors is also being considered.) In designing large-scale equipment it is necessary to have a thorough knowledge of the nature of the reaction, i.e., the stoichiometry, side reactions, and chemical kinetics. Information on the stoichiometry and side reactions has been presented elsewhere.^{1,4,5} The present study was initiated to provide kinetic data required for equipment design.

The reaction $2\text{UF}_4 + \text{O}_2 \longrightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$ lends itself to a thermogravimetric approach in that approximately 50% of the weight of the sample is lost if the reaction goes to completion. For this reason a thermobalance was constructed⁶ which continuously records the weight change of a reacting sample. Interpretation of the weight loss vs. time curves should provide the kinetic data desired.

This report covers the calibration and operation of the

thermobalance and the status of the kinetic studies. The interpretations and conclusions are necessarily preliminary and tentative but should indicate the approximate dependence of the rate of the reaction on temperature. Summation of the data available at this time will aid in planning future work, and will possibly stimulate suggestions and constructive criticism from those interested in the Fluorox program.

3.0 EXPERIMENTAL WORK

3.1 Description and Operation of the Thermobalance

The essential components of the automatic recording thermobalance and auxiliary equipment (Fig. 1) are the oxygen supply (A); the helium supply (B); drierite bulbs (C); a fuming sulfuric acid bubbler trap (D); a trichloroethylene—dry ice cold trap (E); a rotameter (F) for measuring reactant (oxygen) gas flow; the reaction vessel (G); a high-temperature furnace (H); a pelleted-NaF trap (I); a 30-amp variac (J); a Pyr-o-Vane proportional temperature controller (K); a temperature recorder (L); an instantaneous weight change recorder (M); a modified analytical balance (N); and a rotameter (O) for measuring buffer (helium) gas flow. The oxygen and helium gases were thoroughly dried by passage through a fuming sulfuric acid bubbler, a trichloroethylene—dry ice cold trap, and two drierite bulbs. The gas flow rates were measured at room temperature by rotameters that had been calibrated against a precision wet test meter. The measured gas flow rates can be converted to linear velocities at the desired temperature by appropriate calculation if the cross-sectional area of the reaction vessel is known.

The thermobalance itself was made by modifying an analytical chainomatic balance. The UF_4 samples were contained in small platinum baskets (31 mm dia, 5 mm high) suspended from the left-hand balance

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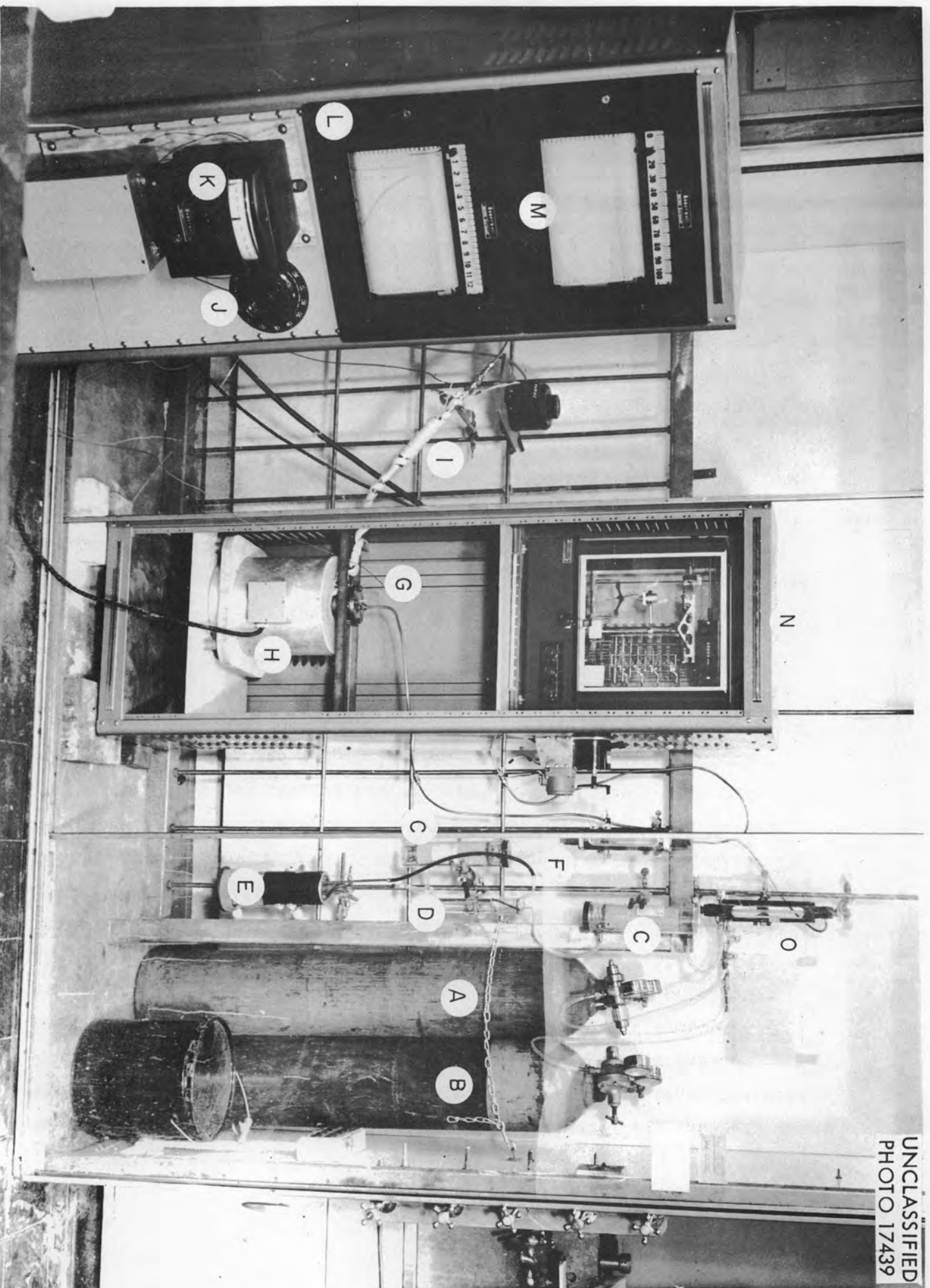


Fig. 1. Semiautomatic Recording Thermobalance and Auxiliary Apparatus.

pan into the reaction chamber by a 36-gage platinum wire. Changes in sample weight were detected by displacement of the core of a Schaevitz differential transformer, which is located between the left-hand balance pan and the beam. Electrical impulses produced by core displacement* are instantaneously picked up by a Helipot and transmitted to a servo-motor. The servo-motor changes the position of the 100-mg chain so that weight equal to the sample weight change is either added or subtracted from the right-hand side of the balance. For relatively slow weight changes the balance is kept at equilibrium, and the weight of the sample is known at any time. In other words, instantaneous weight changes are measured. For continuous recording of these weight changes the milligrams per revolution of the servo-motor drive shaft was determined. It was found that 10 revolutions of the shaft were required to completely traverse the 100-mg chain and that this relation was linear over a range of at least 100 mg.

The weight of the chain limits continuous recording to weight changes of 100 mg or less, and the period of the beam limits the speed of the drive motor. If the speed of the motor exceeds the period of the beam, only harmonic oscillations are recorded. Weight changes of greater than 100 mg can be recorded by a method described below.

The high-temperature furnace is resistance-wound, and has a maximum temperature of over 1100°C. The temperature is controlled to within 10°C by a platinum vs. platinum-10% rhodium thermocouple connected to a Pyr-o-Vane proportional controller.

The reaction vessel (Fig. 2) is made of nickel. The reactant gas is passed through a preheating section consisting of ~20 in. of 1/8-in. nickel tubing spiraled around the reaction vessel. An off-gas line inserted between the flanges is connected to the pelleted-NaF trap. The gaskets are monel rings. A 1/4-in. Swagelok fitting welded to the upper flange permits admittance of a slow stream of inert buffer

*A detailed explanation of the electronics involved is found in reference 6.

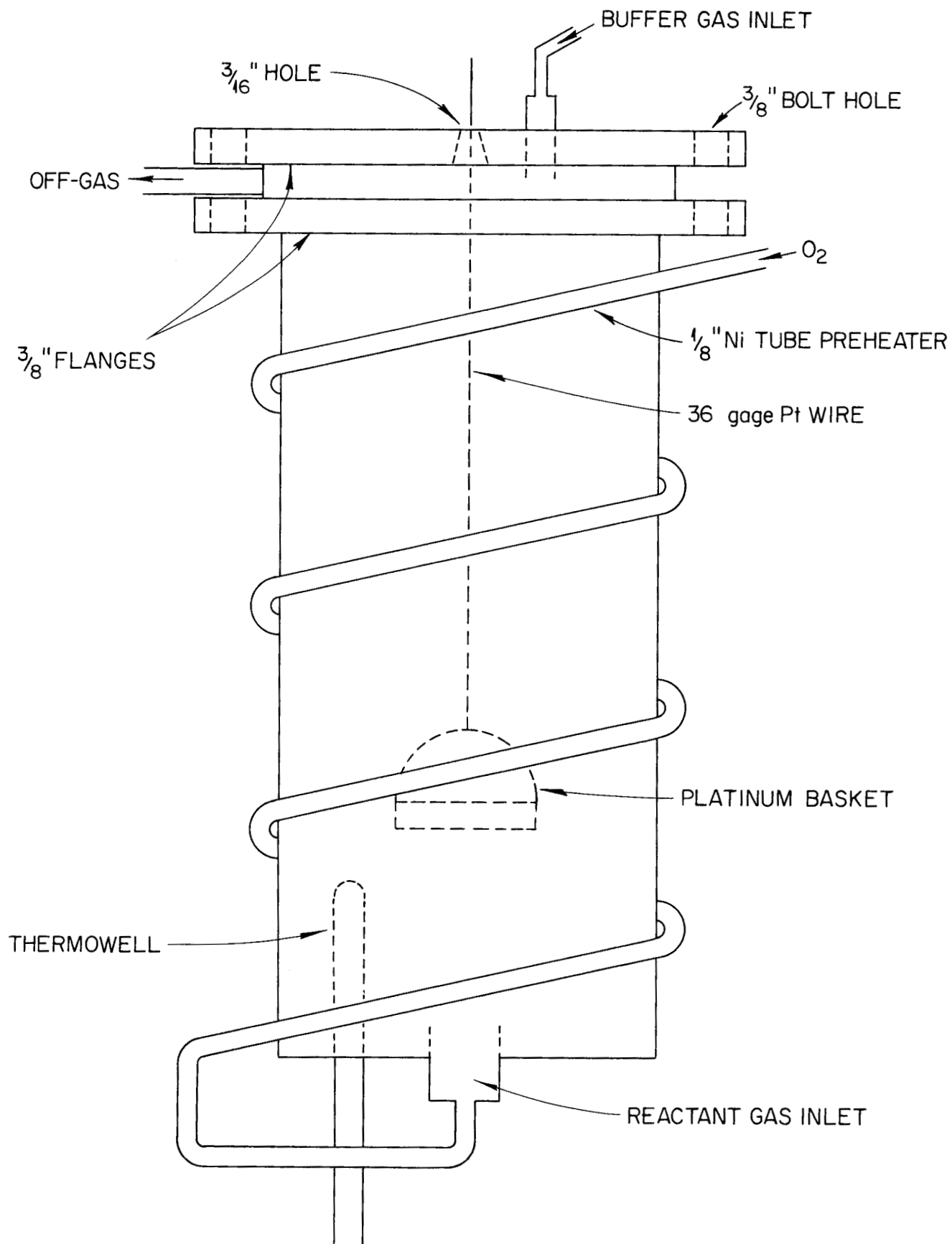


Fig. 2. Nickel Reaction Vessel Used in UF_4 Oxidation Studies.

gas, which prevents pluggings of the 3/16-in. hole through which the platinum wire is hung.

Usually it is necessary to calibrate a thermobalance for buoyancy and other effects manifested in a flowing gas system (see Appendix A). For the kinetic studies, however, it was sufficient to follow the weight change in the sample since the individual experiments were done at constant temperature and gas flow rate, and hence the buoyant effect was also constant.

For convenience, it may be well to consider the stepwise procedure used in performing an oxidation experiment with the thermobalance. The UF_4 sample is loaded into a weighed platinum basket. The basket containing the sample is suspended in the reaction chamber by the platinum wire. The upper flange of the reaction vessel is bolted securely after it is assured that the platinum wire hangs freely and does not contact the sides of the 3/16-in. hole. At this point dry helium is admitted to the vessel at a rate equivalent to the rate of oxygen to be used. A slow stream of helium is also admitted at the top of the reactor to act as a protective seal for the wire outlet. The entire system is then brought to the desired temperature, and any weight changes that occur during this period are continuously recorded. At the desired temperature, the helium is replaced by dry oxygen and the weight change produced during the oxidation is then continuously recorded. The system is cooled in helium after the oxidation is complete. The total weight loss is checked by weighing on a separate balance.

In the case of a total weight change of greater than 100 mg the following technique (Fig. 3) is used: The first 100 mg lost is continuously recorded, after which time the servo-motor necessarily stops. However, manual addition or subtraction of 100-mg weights from the balance pans causes abrupt changes in the equilibrium of the balance. Hence the servo-motor is activated and the position of the chain is brought to a point where equilibrium is re-established, and subsequent

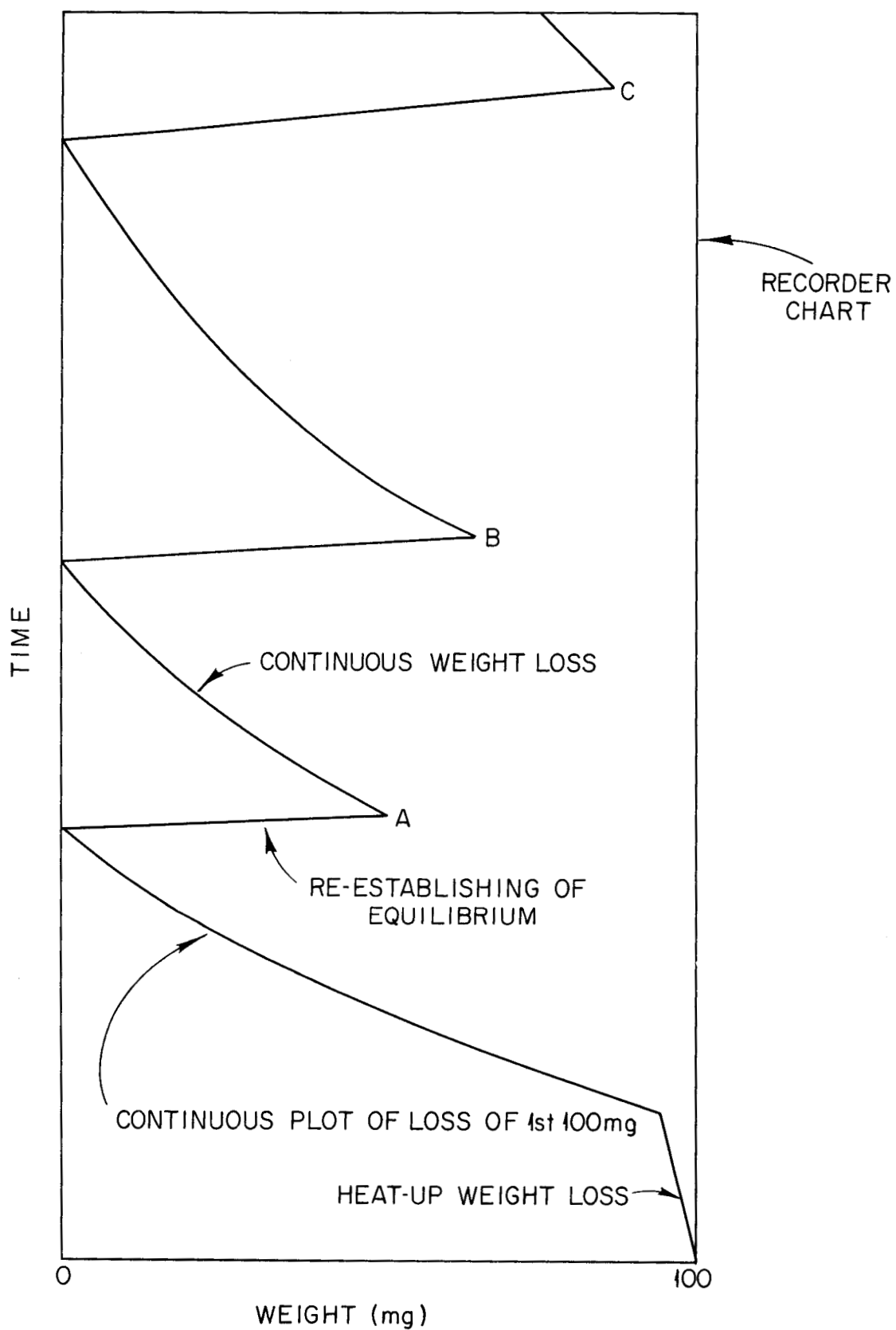


Fig. 3. Record of Weight Changes Greater than 100 mg.

weight losses are continuously recorded until the remainder of the 100-mg chain is used up. This technique may be repeated indefinitely to permit handling of relatively large samples.

For relatively fast reactions a similar technique may be used. Weights are added manually and points are obtained wherever equilibrium is reached momentarily (A,B, and C in Fig. 3). The curves obtained between points, however, do not represent instantaneous sample weight loss, but are linear and represent the maximum rate of weight change produced by the servo-motor.

3.2 Chemical Reagents

Commercially available oxygen and helium gases were used, and no further purification other than drying was performed. The oxygen content of the helium was less than 10 ppm. UF_4 of $\sim 99\%$ purity, based on the U(IV) determination, was obtained by water-leaching the UO_2F_2 from $\sim 97\%$ UF_4 containing 3% UO_2F_2 (Table 1). According to the analyses there should be $\sim 1\%$ UO_2F_2 remaining in the sample.

Table 1. Analyses of UF_4 Samples

Sample	Amount (wt %)				
	Total U	U(IV)	F	AOT ^a	H ₂ O
1	76.22	---	23.4	---	0.27
2	76.39	---	23.5	---	0.16
3	75.23	75.14	23.9	0.05	---
4	75.77	74.97	23.9	0.08	---
5	---	74.97	---	0.19	---
6	---	74.65	---	---	---
7	75.32	74.04	23.8	---	---
8	75.43	74.58	23.9	---	---
9	75.59	75.44	23.9	---	---
10	75.84	75.51	23.8	---	---

^aAmmonium oxalate insolubles (UO_2 ; U_3O_8).

4.0 DATA AND OBSERVATIONS

4.1 Vaporization of UF_4

Considerable weight losses were observed while heating UF_4 to temperature in a helium atmosphere prior to oxidation. The rate of weight loss in the temperature range $725\text{--}800^\circ\text{C}$ was quite high. Studies were therefore made of this effect with varying sample size, gas flow rate, and temperature. Samples of 0.35, 1.0, and 4.5 g were used. These were chosen because a 1-g sample made a layer one particle thick in the bottom of the platinum basket. The smaller sample was thinly scattered over the bottom of the basket, and the larger sample made several layers of UF_4 .

After each run a thin coating of U_3O_8 was found on the upper layer of UF_4 . In the case of 1- and 0.3-g samples all UF_4 particles had this black coating. With 4.5-g samples the lower layers of UF_4 were still their original green. The reason for this phenomenon has not been definitely established. Possibly it is due to desorption of moisture from the walls of the nickel reactor and subsequent pyrohydrolysis of UF_4 . Another possibility is the thermal decomposition of UO_2F_2 in the sample.

The observed weight losses at any given temperature and helium flow rate are almost linear with time (Fig. 4), suggesting that the loss in weight is caused by vaporization of the UF_4 . Also, the measured weight losses agree in magnitude with those expected from the reported⁷ vapor pressures of UF_4 . The rates of weight loss at the lower temperatures ($<725^\circ\text{C}$) are almost independent of sample size (Fig. 5). However, at temperatures above 725°C the sample size made a significant difference (Fig. 6). In fact, difficulties were encountered in duplicating results with samples of the same size.

Only slight changes in the amount of UF_4 vaporized were produced by changing the helium flow rate (Fig. 7).

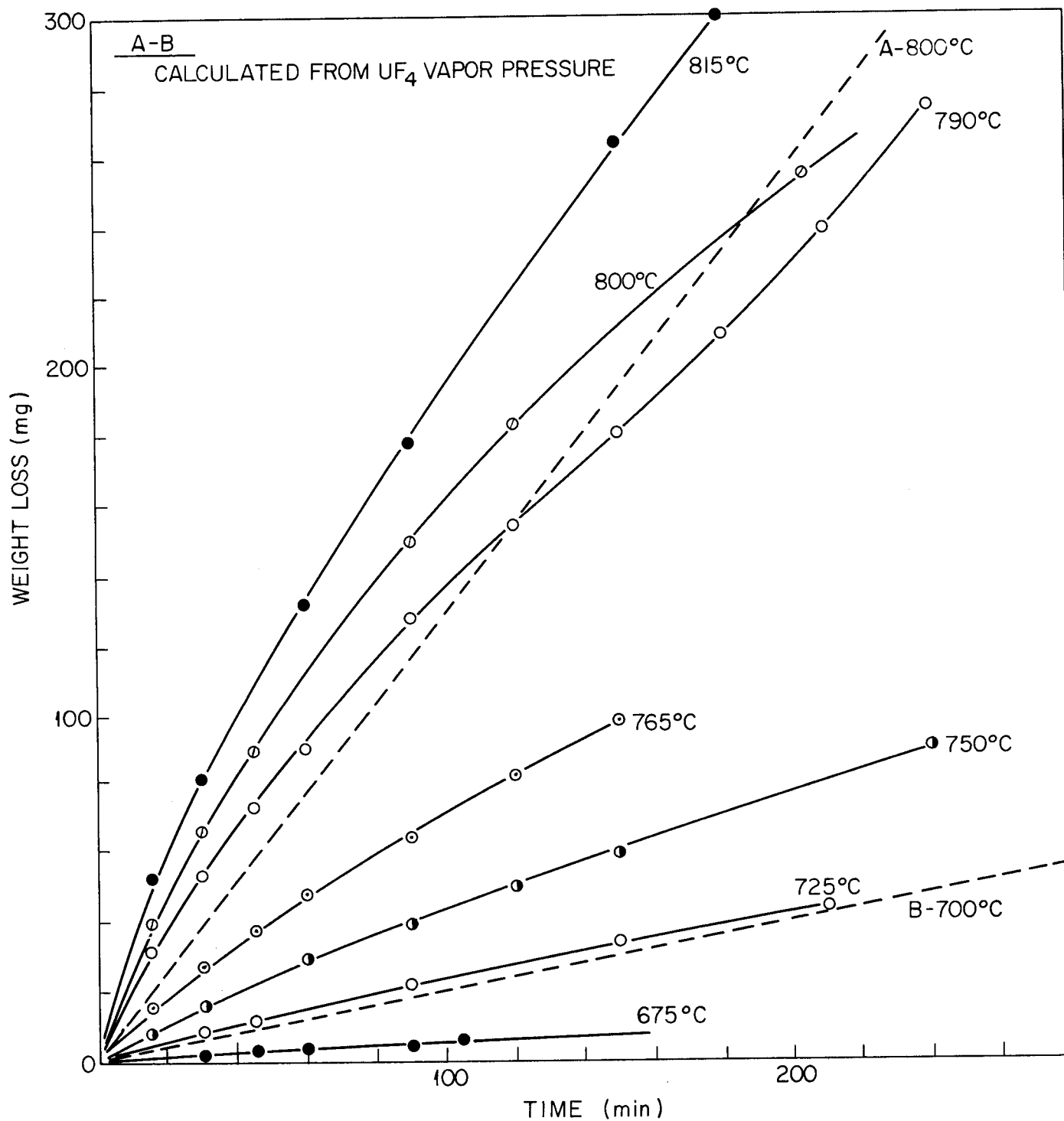


Fig. 4. Effect of Temperature on Vaporization of 1-g UF_4 Samples.
Helium flow rate, 300 ml/min.

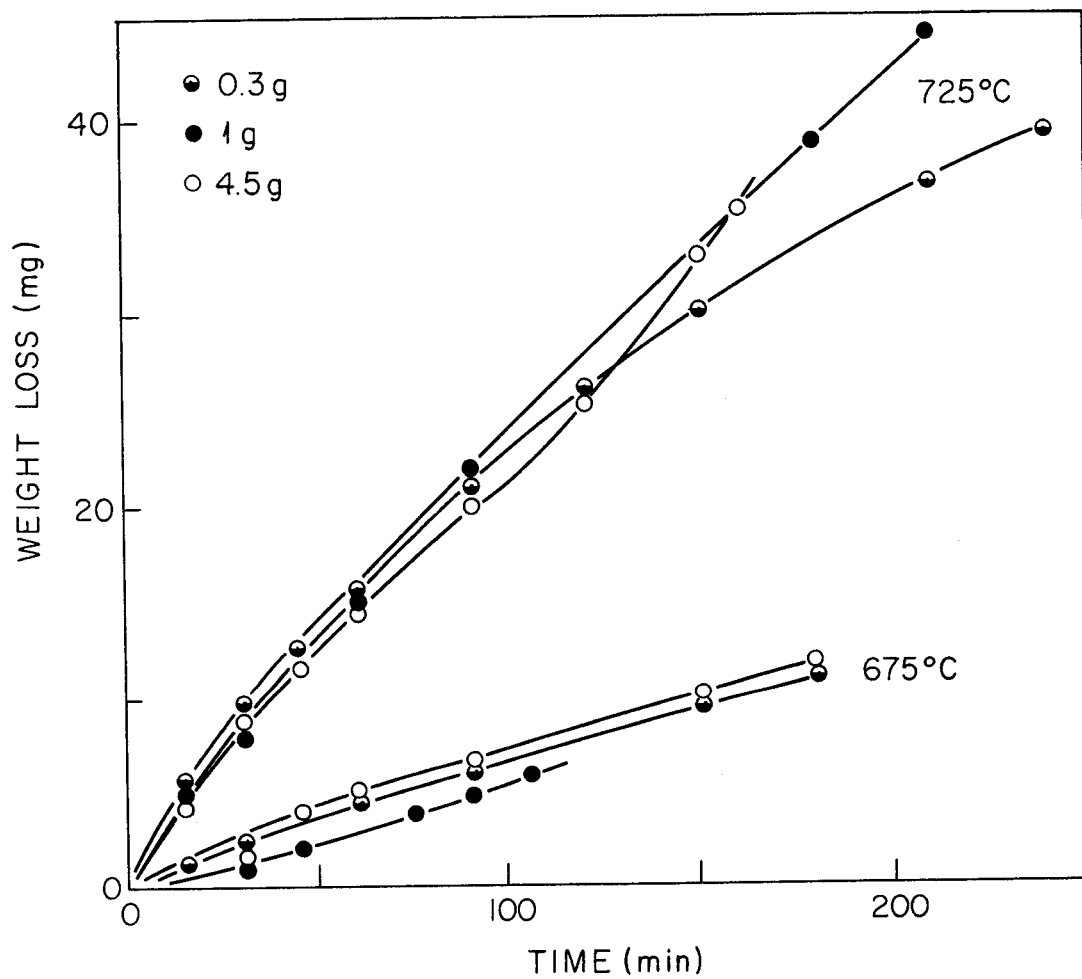


Fig. 5. Effect of Sample Size and Temperature on Vaporization of UF_4 at Moderate Temperatures. Helium flow rate, 300 ml/min.

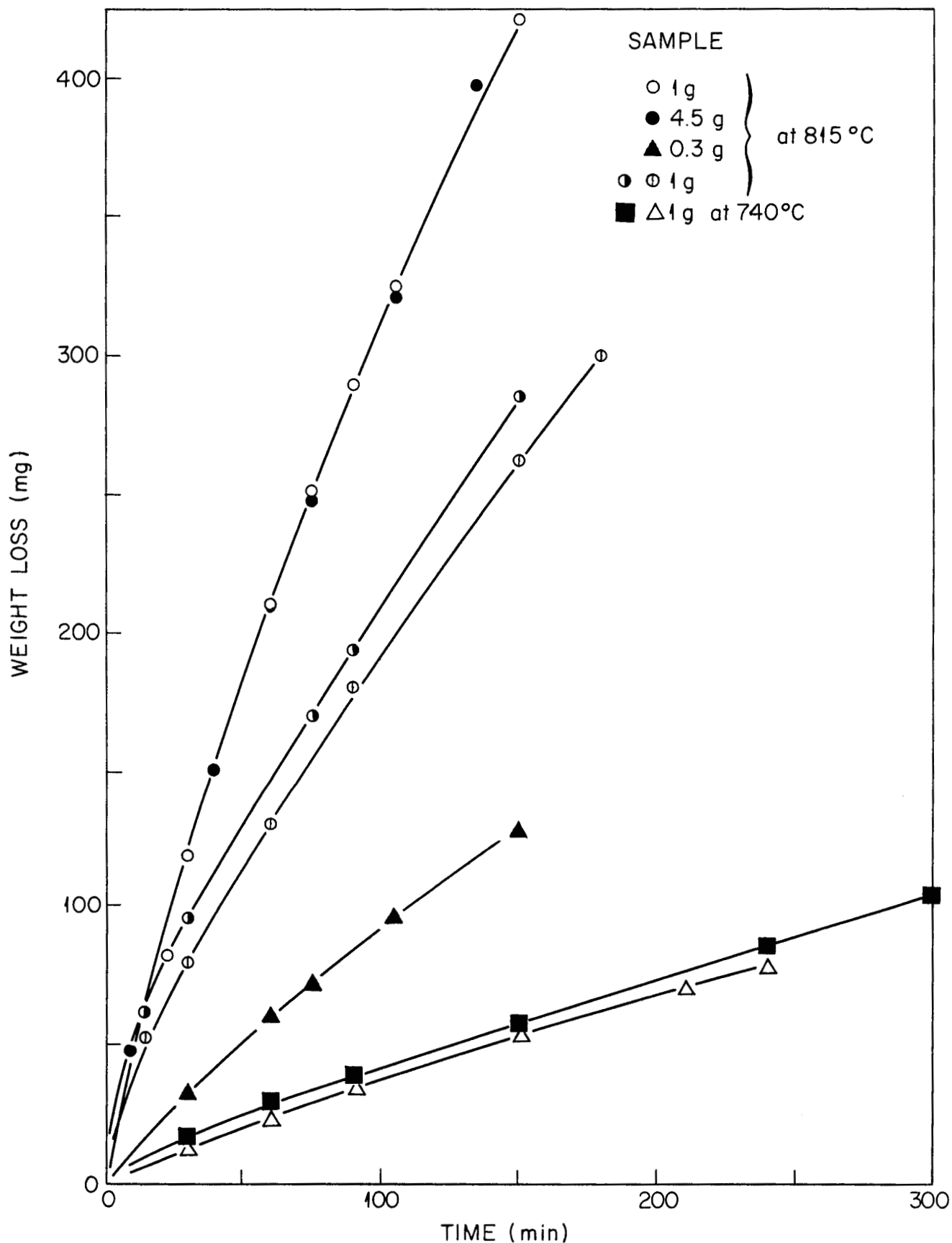


Fig. 6. Effect of Sample Size and Temperature on Vaporization of UF_4 at Higher Temperatures. Helium flow rate, 300 ml/min.

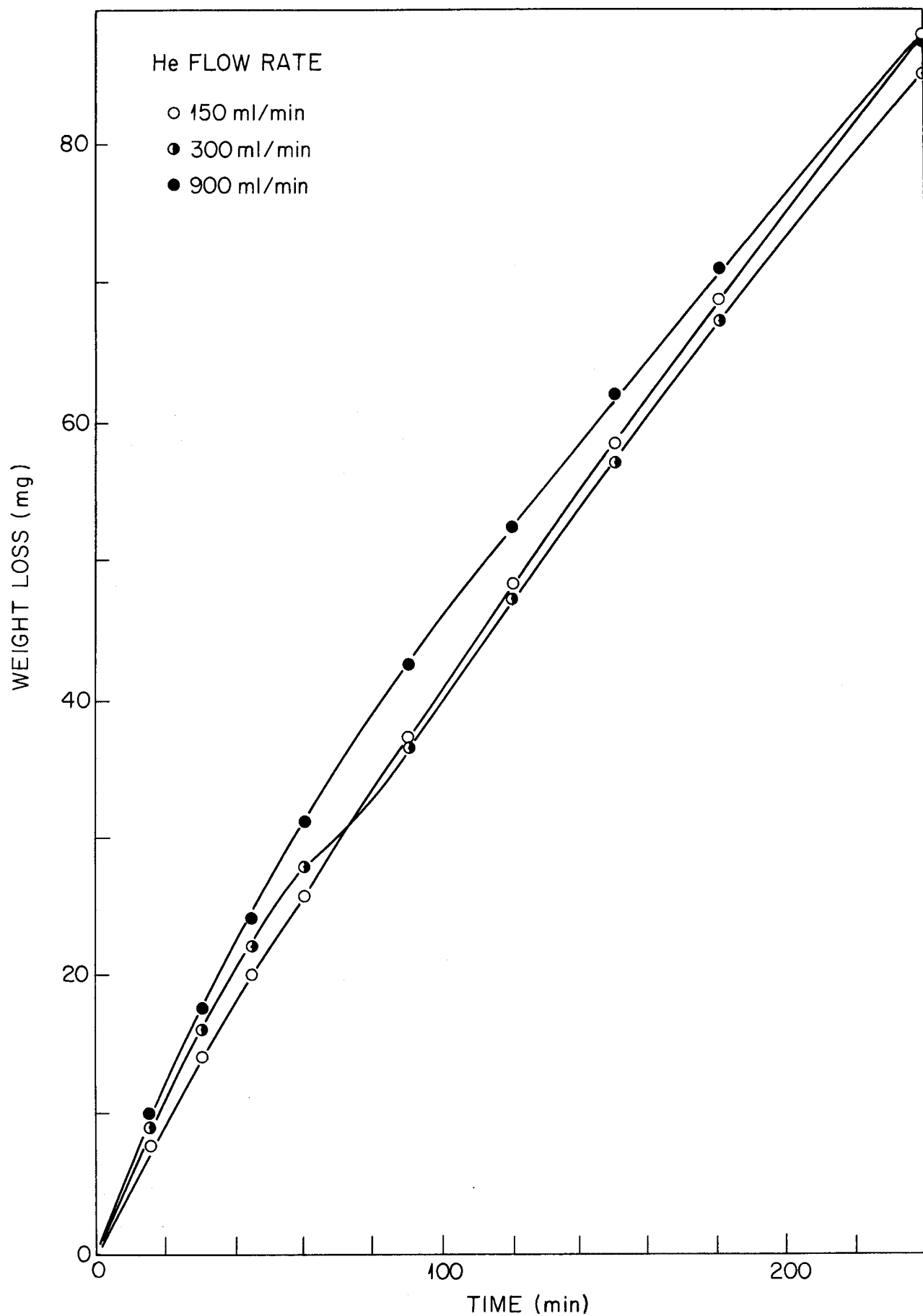


Fig. 7. Effect of Helium Flow Rate on the Vaporization of 1-g UF_4 Samples at 740°C.

4.2 Reaction of UF_4 with Dry Oxygen

Only a few oxidation data are available at this time. These data were obtained by oxidizing 1-g UF_4 samples with dry oxygen flowing at a rate of 300 ml/min as measured at room temperature.

It was immediately noticed that the total sample weight loss was greater than would be expected by the oxidation reaction alone. In fact, it appeared that the vaporization of UF_4 was occurring independently as the oxidation reaction proceeded. Therefore, to obtain reaction rate constants for the oxidation reaction, one must treat the oxidation and vaporization as two parallel reactions. If the UF_4 vaporization is considered to be independent of the oxidation, the rate linear with time, and the vapor pressure of UO_2F_2 exceedingly low at the temperatures used, the following general rate equation should describe the consumption of UF_4 , provided the oxidation reaction is pseudo-first order:

$$\frac{-dw}{dt} = k'w + \phi$$

where w = mass of UF_4 , mg

t = time, min

k' = specific reaction rate constant for the oxidation reaction, min^{-1}

ϕ = rate of vaporization of UF_4 , mg/min

The specific surface area of UF_4 is considered constant at all temperatures. Integration of the above equation and conversion to common logarithms gives

$$\log (k'w + \phi) = \frac{-k't}{2.303} + C_1$$

where C_1 is a constant of integration. It will be observed immediately that the desired quantity, k' , appears on each side of the equation, and no simple explicit solution for k' is apparent. However, k' may be evaluated by the method of successive approximations if w and ϕ are known. In this method a value of k' is selected arbitrarily, subsequently calculated values of $\log (k'w + \phi)$ are plotted versus t , and a new value for k' is calculated from the slope of that curve. The method

is repeated until the value of k' obtained from the slope is the same as that chosen for calculating $\log (k'w + \phi)$.

For convenience and clarity, the following sample calculation is presented: The top curve in Fig. 8 is the continuous weight change when an ~ 1 -g sample of UF_4 is reacted with dry O_2 (300 ml/min) at 765°C . The bottom curve shows the rate of weight loss when UF_4 is vaporized at this temperature and flow rate. For any interval of time, then, the loss in sample weight due solely to oxidation may be obtained by subtraction of the curves. The amount of UF_4 consumed by oxidation may then be calculated, assuming the stoichiometric relation $2\text{UF}_4 + \text{O}_2 \longrightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$. Hence, at any time the amount of UF_4 consumed is the sum of the loss by vaporization and the amount oxidized. For example, consider 45 min for the case illustrated by Fig. 8. From the vaporization-only curve it is found that 30 mg of UF_4 vaporized during this time interval. Subtraction of this curve from the vaporization-oxidation curve shows that the sample lost 343 mg as the UF_4 was oxidized. Because the amount of UF_4 vaporized is small compared to the total consumption, a plot of $\log w$ vs. t should yield a fair approximation for k' . The top curve in Fig. 9, plotted from data in Table 2, shows such a plot for the case in point. A value of $\sim 30 \times 10^{-3} \text{ min}^{-1}$ is obtained for k' from the slope of this curve. Using this value for k' , values of $(k'w + \phi)$ are calculated (see Table 3) and are plotted on semilog paper vs. t . The k' obtained from the slope of this first approximation curve is $27.7 \times 10^{-3} \text{ min}^{-1}$. By repeating the calculations, a singular value of $28 \times 10^{-3} \text{ min}^{-1}$ for k' is found from the slope of the second approximation, using this value for k' .

Similar treatment of the data at other temperatures results in the rate constants listed in Table 4. Figure 10 is an Arrhenius plot of these data with the maximum deviation which could be caused by an error of 5°C indicated by the size of each point. The heat of activation calculated from the slope of the line shown is $\sim 38 \text{ kcal/mole}$. This value falls within the range of 30-40 kcal/mole found in batch experiments.⁵

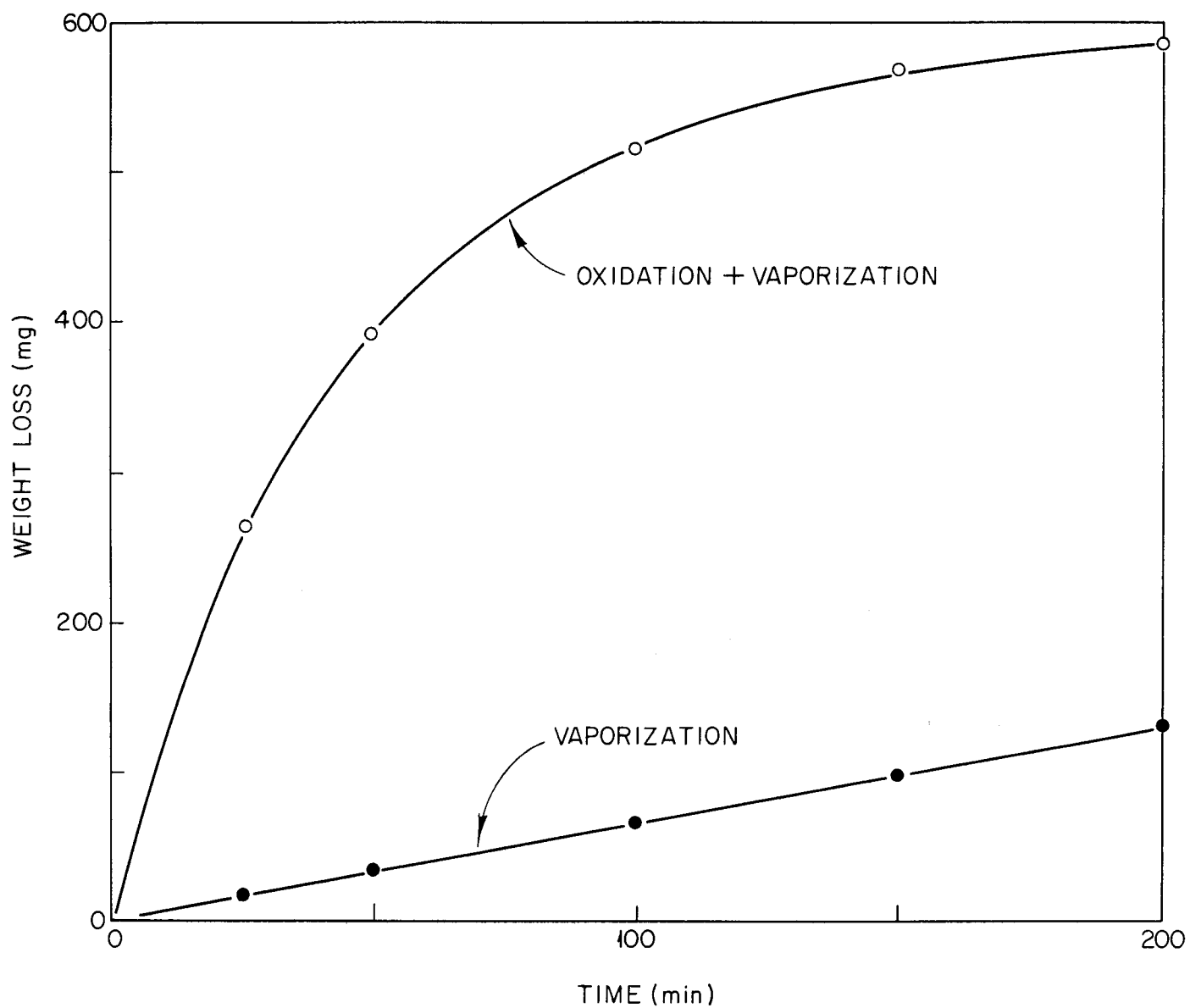


Fig. 8. Oxidation and Vaporization of a 1-g UF_4 Sample at 765°C.

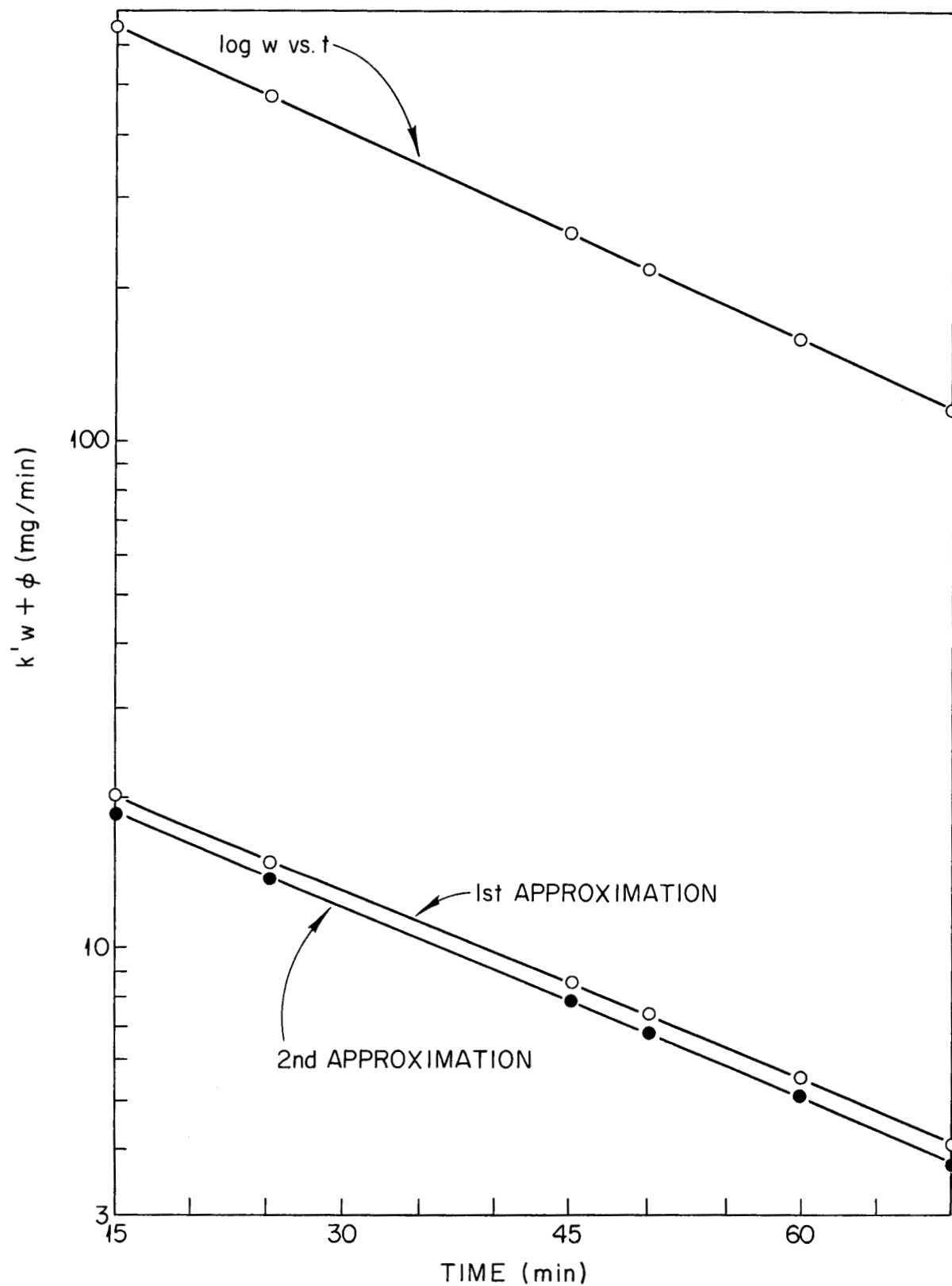


Fig. 9. Evaluation of k' by Successive Approximations.

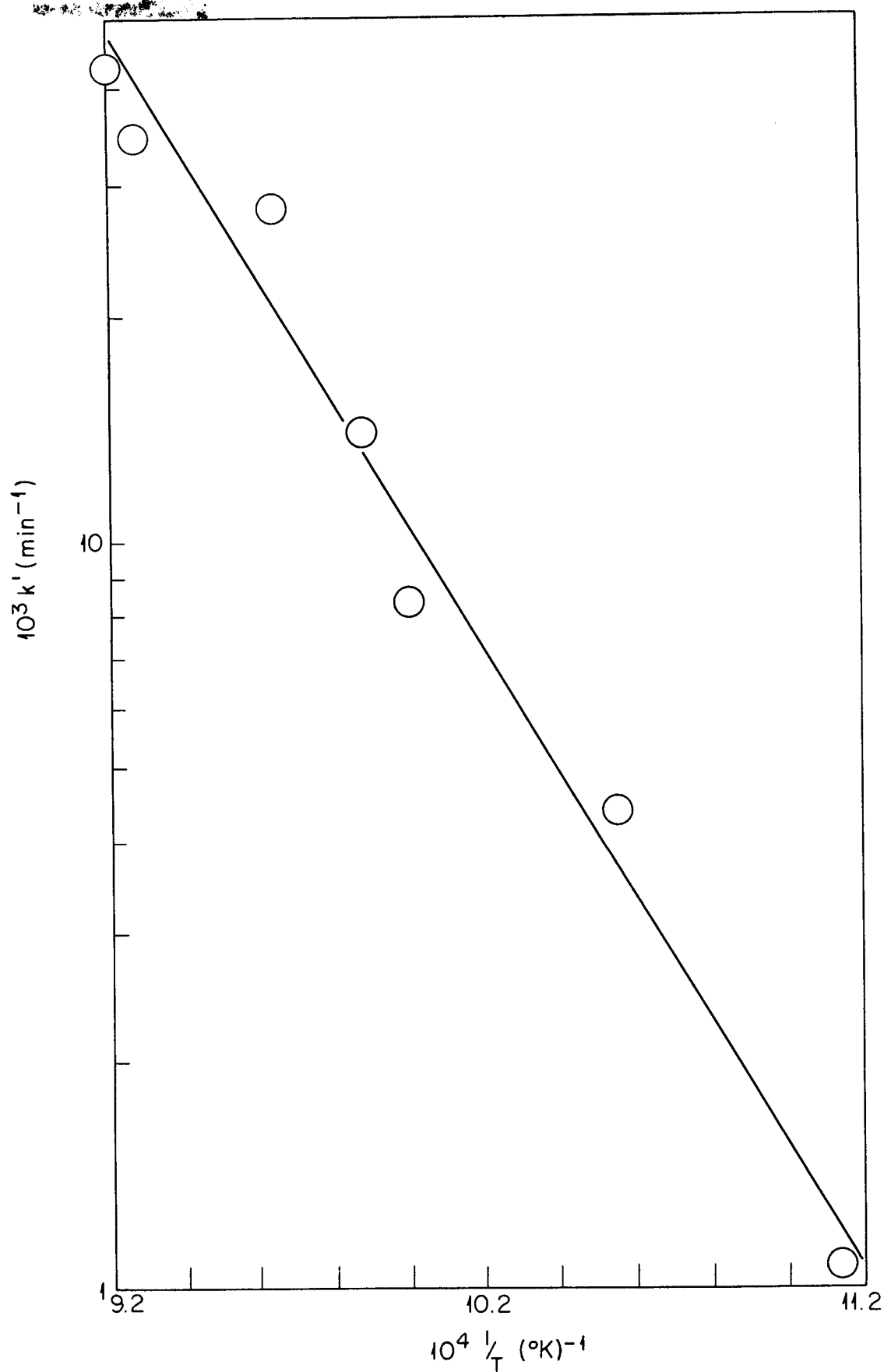


Fig. 10. Specific Reaction Rate Constants for the Reaction $2\text{UF}_4 + \text{O}_2 \longrightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$.

Table 2. Time Variation for The Consumption of UF_4 by Simultaneous Vaporization and Oxidation at $765^\circ C$

Time, t (min)	Wt. Loss by Vaporization (mg)	Sample Wt. Loss by Oxidation (mg)	UF_4 Wt. Loss by Oxidation (mg)	Wt. of UF_4 Remaining, w (mg)
0	0	0	0	993
15	10	170	347	646
25	17	248	506	470
45	30	343	700	263
50	34	359	733	226
60	40	389	794	159
70	47	410	836	110
100	67	449	917	9

Slope of vaporization curve, $\phi = 0.67 \text{ mg/min}$
Slope of plot of $\log w$ vs. t (Fig. 9) = -0.0133 min^{-1}
 $k'_1 = (2.303)(0.0133) = 30.6 \times 10^{-3} \text{ min}^{-1}$

Table 3. Evaluation of k' by Successive Approximations

Time (min)	$k'w$ (mg/min)	$k'w + \phi$ (mg/min)	$\phi = 0.67 \text{ mg/min}$ (Table 2)
First approximation: use $k' = 30 \times 10^{-3} \text{ min}^{-1}$			
15	19.38	20.05	Slope of first approximation curve (Fig. 9) = -0.0120 min^{-1} $k'_1 = (2.303)(0.0120) = 27.7 \times 10^{-3} \text{ min}^{-1}$
25	14.10	14.77	
45	7.89	8.56	
50	6.78	7.45	
60	4.77	5.44	
70	3.30	3.97	
Second approximation: use $k' = 28 \times 10^{-3} \text{ min}^{-1}$			
15	18.10	18.77	Slope of second approximation curve (Fig. 9) = -0.0121 min^{-1} $k'_2 = (0.0121)(2.303) = 28 \times 10^{-3} \text{ min}^{-1}$
25	13.18	13.85	
45	7.36	8.03	
50	6.33	7.00	
60	4.45	5.12	
70	3.08	3.75	

Table 4. Specific Reaction Rate Constants for the Reaction
 $2\text{UF}_4 + \text{O}_2 \longrightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$ at Various Temperatures

t (°C)	T (°K)	$\frac{1}{T} \times 10^4 (\text{°K})^{-1}$	$10^3 k' (\text{min}^{-1})$
625	898	11.14	1.07
675	948	10.56	4.4
725	998	10.00	8.3
740	1013	9.88	14
765	1038	9.65	28
805	1078	9.28	35
815	1088	9.20	43

$$\text{Slope} = \frac{\log 0.0488 - \log 0.00107}{(9.2 - 11.2) 10^{-4}} = \frac{-1.312 + 2.971}{-2 \times 10^{-4}} = \frac{-1.659 \times 10^4}{2}$$

$$\text{Slope} = -8.3 \times 10^3 \text{ deg}$$

$$\Delta H^\ddagger = (4.575)(8.3 \times 10^3) \text{ cal/mole} = 38 \text{ kcal/mole}$$

5.0 DISCUSSION OF RESULTS

Discussion will be limited to remarks on how the most profitable data can be obtained by the thermobalance method since the data presented in this report are insufficient for drawing exact conclusions. As was shown, the curves showing weight loss are complicated by vaporization of the UF_4 at high temperatures, and reproducible vaporization data are difficult to obtain above 750°C . It is desirable, then, to obtain most of the data at relatively low temperatures (600 – 750°C) where the UF_4 vaporization is almost insignificant. Not only could reproducible vaporization data be obtained at these temperatures, but the assumption of independent vaporization during an oxidation would be more nearly true. At least, the error introduced by this assumption would be reduced. Also, the vaporization curves at these temperatures can be considered strictly linear without

introducing a large error. The low-temperature data could be extrapolated to obtain rate constants at the higher temperatures.

By way of comparison it might be worthwhile to mention that the heat of activation obtained by the thermobalance method agrees quite well with that obtained in batch experiments. It must be pointed out, however, that the rate constants obtained in this study do not include a correction for surface area changes. Many more data will be required before definite conclusions can be drawn.

Continuation of the present work is necessary. It appears essential to have accurate rate data for one type of UF_4 and one O_2 flow rate. Once such data are analyzed, the effect of other variables such as O_2 flow rate and pressure, UF_4 surface area, and sample size may be elucidated. Preliminary correlation between batch and thermobalance data indicates that the effect of these other variables may be predictable from complete information on a carefully controlled system, and that batch data, which are obtained rapidly, may be sufficiently accurate for production control.

If accurate data in the temperature range 600-900°C can be obtained, it may be possible to extrapolate these results to temperatures that would be attained in a flame reactor, and hence provide rate data for virtually all the types of engineering facilities that might be proposed.

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7.0 Appendix. CALIBRATION OF THE THERMOBALANCE

Since all the individual kinetic experiments were to be carried out at constant temperature and gas flow rate, the buoyant effect produced by gas velocity and/or gas density changes would be constant and would not affect the results. However, it was of interest to determine some of these effects primarily to check the sensitivity and accuracy of the balance.

It was suspected that the following variables might contribute to error due to buoyancy: (1) the distance of the platinum basket from the gas inlet (see Fig. 2); (2) whether or not the off-gas tube is connected to the NaF trap; (3) the magnitude of the load suspended by the platinum wire; (4) the density of the gas being admitted to the system; (5) the furnace temperature; (6) the effect of admitting a slow stream of buffer gas at the top of the reaction vessel while oxygen at a much higher rate is being admitted at the bottom; and (7) the geometry of the system, i.e., the ratio of the diameter of the platinum basket to the diameter of the reaction vessel. The trend of effects of temperature, sample size, and off-gas connection is shown in Fig. 11. It is seen that connecting the off-gas line to the NaF trap causes a slight increase in the buoyant effect on a 30-g basket located ~ 3 in. from the gas inlet. Also, a lighter basket (14 g) is subjected to more pronounced buoyant effects than is the heavier basket. Increasing the weight of the basket to almost 20 g did not alter the buoyant effect on the 14-g basket. The buoyant effects produced by gas density changes at 715°C are seen to be of a much higher order of magnitude than at room temperature, as would be expected. Removing the basket to 6 in. from the gas inlet greatly reduced the buoyant effect. For example, at 25°C there was an apparent weight loss of only 1 mg in the weight of a 30-g platinum basket as the oxygen flow rate was increased from 75 to 1500 ml/min. The buoyant effects in this case were a factor of 3 lower than those for a basket of the same weight suspended only 3 in. from the gas

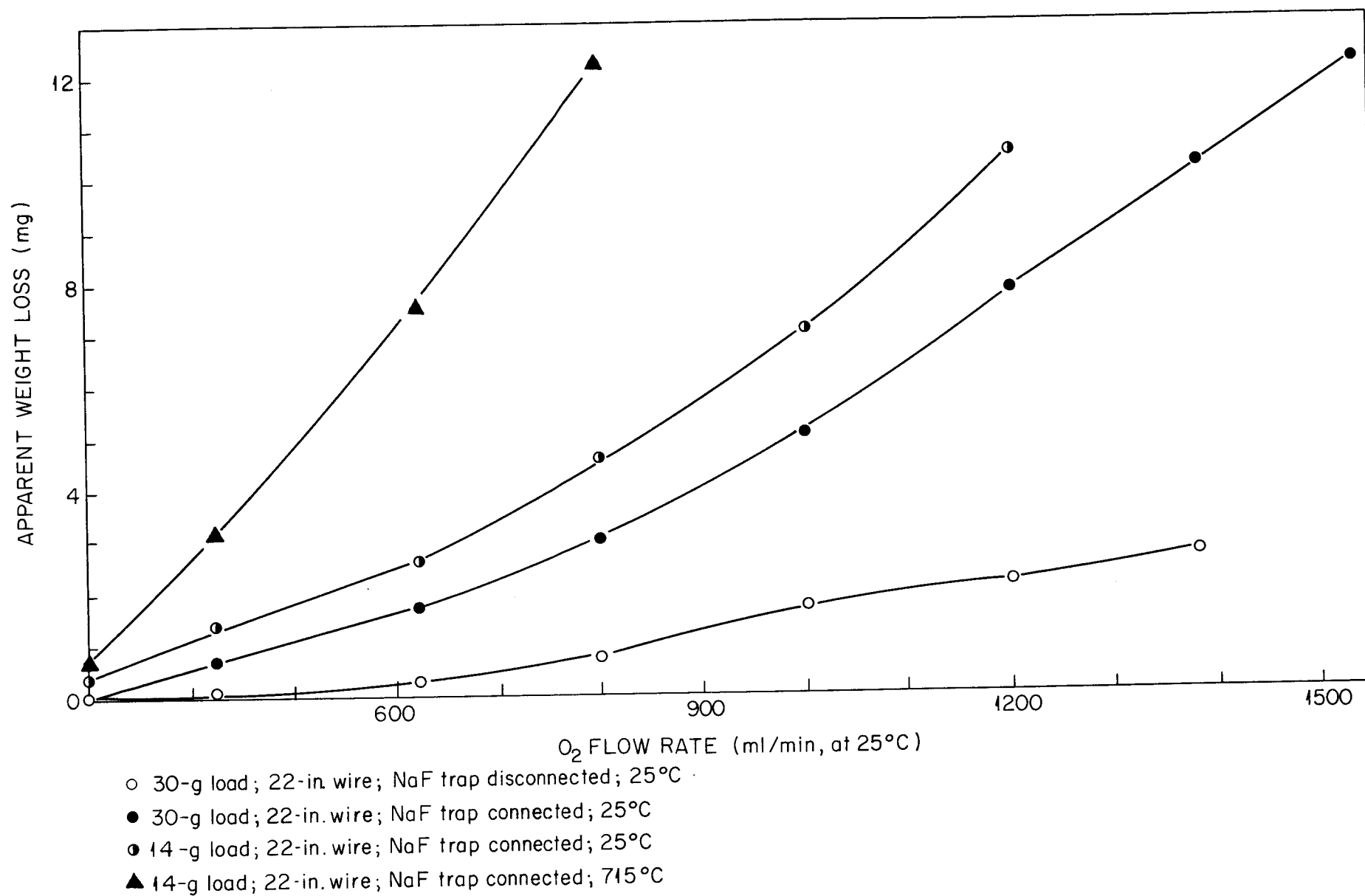
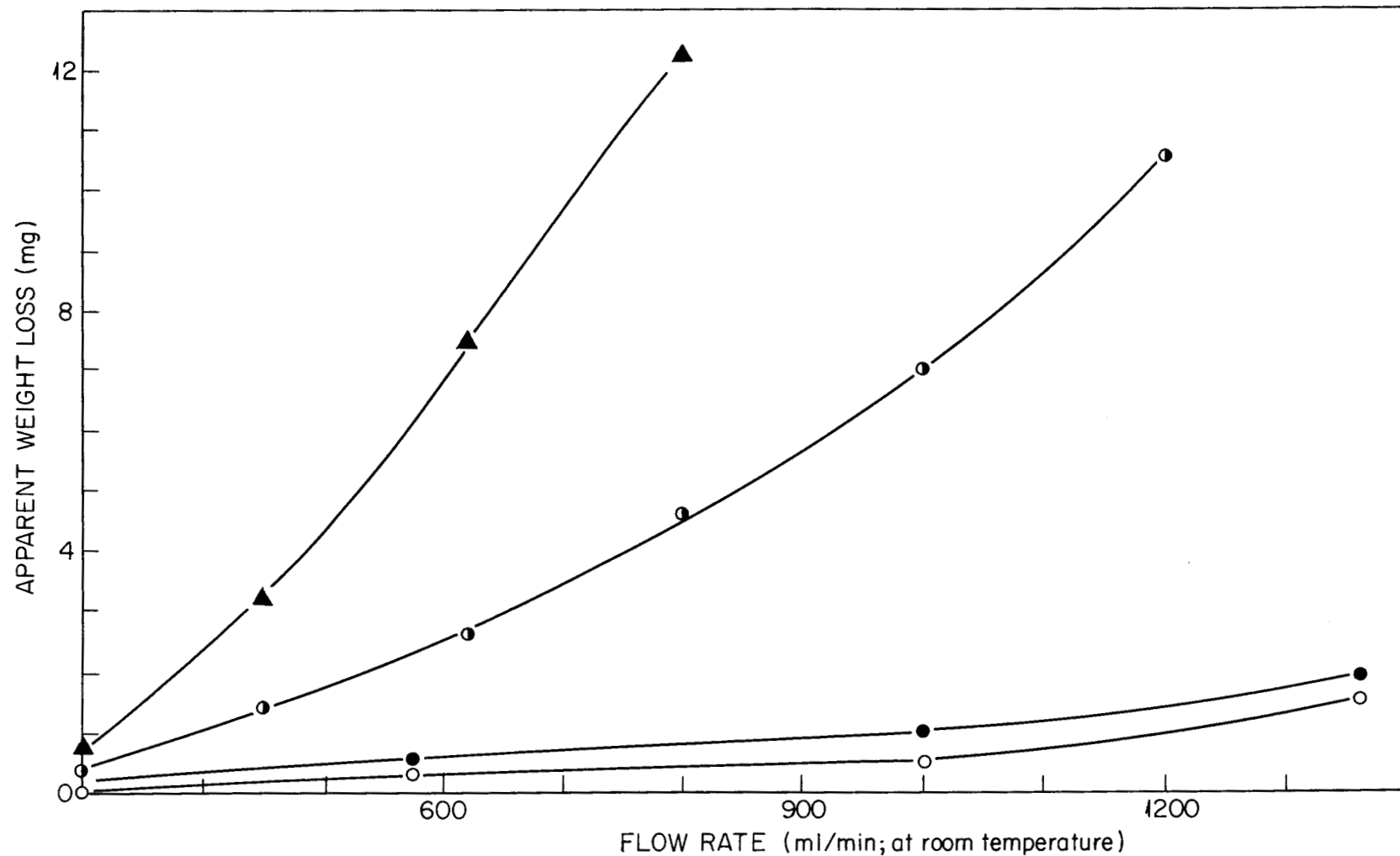


Fig. 11. Comparison of Buoyant Effects Produced by Temperature, Load, and Distance from Gas Inlet.

inlet. The admission of a buffer gas at the top of the reactor did not alter the buoyant effects. The buoyancy effects mentioned up to this point are only for oxygen; helium gives comparable results at the very low gas flow rates, but deviation became quite marked above ~300 ml/min (Fig. 12). As also shown in Fig. 12, temperature affects the helium buoyancy effects only very slightly. It must be mentioned that all the buoyant effects tabulated are for a 31-mm-dia platinum basket in a 44-mm-dia vessel; any change in this relation may change the buoyancy, especially if the basket diameter is increased, causing the basket to act more like a piston.

The reproducibility of weighings on the thermobalance was within 0.5 mg.



- 14-g load ; 22-in. wire ; NaF trap connected ; 25°C in He
- 14-g load ; 22-in. wire ; NaF trap connected ; 715°C in He
- ◐ 14-g load ; 22-in. wire ; NaF trap connected ; 25°C in O₂
- ▲ 14-g load ; 22-in. wire ; NaF trap connected ; 715°C in O₂

Fig. 12. Comparison of Buoyant Effects Produced by Helium and Oxygen.