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REPROCESSING OF URANIUM CARBIDE BY A NITRIDE – CARBIDE CYCLE

II. KINETICS OF NITRIDE CONVERSION TO CARBIDE

AEC Research and Development Report

ATOMICS INTERNATIONAL

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NAA-SR-9161
METALS, CERAMICS,
AND MATERIALS
31 PAGES

REPROCESSING OF URANIUM CARBIDE BY A NITRIDE – CARBIDE CYCLE II. KINETICS OF NITRIDE CONVERSION TO CARBIDE

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ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: OCT 15 1964

DISTRIBUTION

This report has been distributed according to the category "Metals, Ceramics, and Materials" as given in "Standard Distribution lists for Unclassified Scientific and Technical Reports" TID-4500 (24th Ed.), October 1, 1963. A total of 630 copies was printed.

ACKNOWLEDGMENT

The author would like to acknowledge helpful discussions with Dr. W. G. Smiley. The chemical analyses were conducted by members of the Analytical Chemistry Unit at Atomics International with x-ray diffraction examinations by W. W. Houk. The surface area measurements were carried out by R. G. Wilbourn.

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ABSTRACT

The reconversion of uranium nitride-carbon mixtures (obtained by reacting UC with nitrogen) to uranium carbide has been investigated as one step in a nitride-carbide cycle for UC fuel reprocessing. Reaction rates were determined by measuring the evolution of nitrogen from samples heated in vacuum in a thermogravimetric balance. The reaction of U_2N_3 + C occurs in two steps; by decomposition to UN, then by conversion to UC.

The kinetics of the decomposition of uranium sesquinitride, without carbon present, to uranium mononitride was studied for comparison with the U_2N_3 + C decomposition. Comparison of the results indicate the sesquinitride containing carbon decomposed at a much lower rate with a higher activation energy.

The activation energies for the reactions studied were (1) 90.6 ± 11.8 kcal/mol for the decomposition of U_2N_3 + C to UN + C by a linear rate law, (2) 64.4 ± 7.7 kcal/mol for the decomposition of U_2N_3 to UN based on a linear rate law, and (3) 31.3 ± 1.1 kcal/mol for conversion of UN + C to UC by a parabolic rate law.

I. INTRODUCTION

Uranium carbide is being investigated as a fuel for nuclear power reactors. One phase of this investigation consists of research on fuel reprocessing methods. Low decontamination methods for reprocessing uranium carbide are under study at Atomics International.

In the past, processes utilizing gas reactions with solid fuels have been studied. The oxidation-reduction (AIROX) of UO_2 fuel is one example.[1,2] Another process investigated consists of an oxidation carbothermic reduction cycle (CARBOX) for UC fuel.[3,4] An alternate method for reprocessing UC involving a nitride-carbide cycle is currently being studied.

In the nitride-carbide process, uranium carbide is reacted with nitrogen to form a mixture of uranium nitride and carbon followed by reconversion to uranium carbide by heating in vacuum. The kinetics of nitride formation was the subject of an earlier report.[5] This report presents the results of experiments on the kinetics of nitride decomposition and conversion to carbide. A subsequent report will include additional nitride-carbide experiments and fission product distribution studies.[6]

Although U_2N_3 loses nitrogen in vacuum at temperatures above 700 to 800°C, UN is reported to be stable in vacuum up to 1700°C and higher.[7] However, a reaction of UN with carbon resulted when UN + C mixtures were heated at 1800°C in argon.[8] No kinetic data were found in the literature on either uranium nitride decomposition or reconversion of uranium nitride-carbide mixtures to uranium carbide. The present study was undertaken to provide this information.

II. EXPERIMENTAL

A. EQUIPMENT

A schematic of the apparatus used for the majority of the experiments is shown in Figure 1. Only a brief description will be included here, since a detailed description of this apparatus appears in a previous report.[9]

The reaction was followed by measuring sample weight loss (weight of nitrogen evolved) continuously with an Ainsworth recording balance during heating in vacuum. The balance unit is enclosed in the vacuum system and is equipped with a magnetic damper. Weight readings are sensitive to a few tenths of a mg and the recorder has a full span of 100 mg with automatic weight changes of up to 4 gm.

Nitride-carbon samples were heated by a resistance furnace also enclosed in the vacuum system. Furnace temperature was controlled by a powerstat connected to the tantalum heating element. Temperature uniformity in the sample zone during an experiment was believed to be ±10°C. Sample temperature readings were made by means of a micro-optical pyrometer focused on the sample holder by sighting through the sight glass with a mirror. The temperature was corrected for the mirror and sight glass and was considered accurate to 2%.

The uranium nitride decomposition experiments were carried out in the apparatus shown in Figure 1 except that the furnace chamber was replaced with a quartz tube which provided the vacuum seal with the balance. Samples were heated by a resistance furnace which surrounded the quartz tube. A calibrated chromel-alumel thermocouple positioned inside the quartz tube on a horizontal plane with the sample was used to measure and control the temperature.

Several of the experiments on U_2N_3 + C samples were carried out in the gravimetric balance system described in NAA-SR-8388.[5] That apparatus is similar to the one described in this report with the exception that sample temperatures were read with a Pt-Pt-10%-Rh thermocouple. Use of a thermocouple in place of an optical pyrometer for temperature readings resulted in a more accurate determination of the initial decomposition temperature.

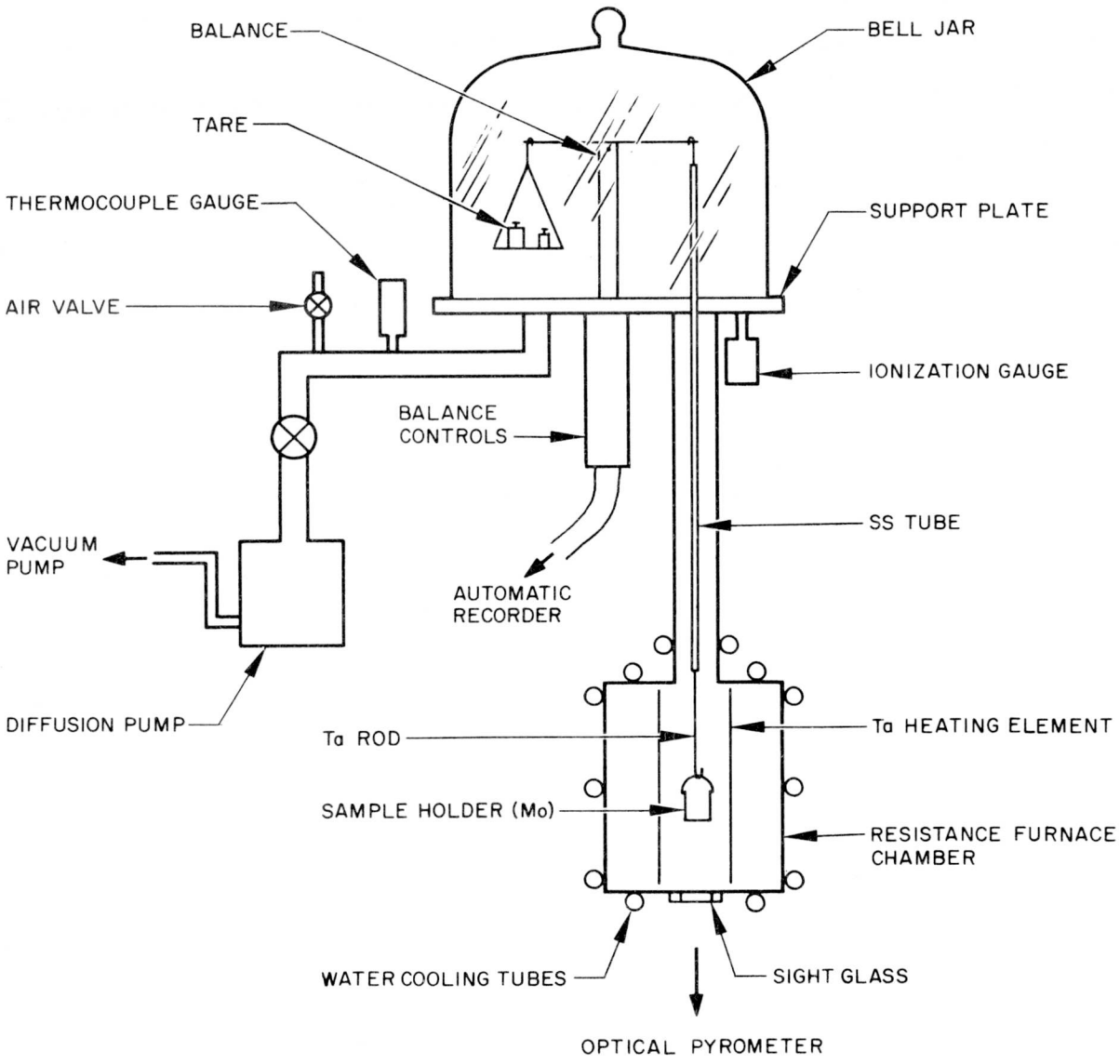

Figure 1. Schematic of Thermogravimetric Balance System

B. PROCEDURE

In a typical experiment, a weighed sample consisting of 2 to 3 gm was loaded in the tared sample holder (1-in. molybdenum crucible) and placed in the system. The balance was calibrated, the bell jar moved into place, and the system evacuated to less than 0.1μ. The balance recorder was started (recording sample weight as a function of time) and the furnace was brought to temperature. During heating, the vacuum in the system varied as a function of the rate of nitrogen evolution. In general, a pressure reading of up to 10μ was obtained during the initial stage of reaction, followed by a rapid decrease to less than 1μ during the remainder of the reaction.

At the completion of an experiment, the sample was cooled to room temperature in vacuum and finally weighed on an analytical balance as a check on the recording balance. The weight loss indicated by the recorder agreed within 1% of the analytical balance determination. The product was then transferred to an inert atmosphere glove box for sampling and storage. Random samples were taken for x-ray diffraction, surface area, nitrogen, and carbon analysis.

C. SAMPLE PREPARATION

The nitride-carbon samples used in this study were prepared by reaction of uranium carbide with nitrogen. The uranium carbide was cast fuel rods which were subjected to a hydrogen reduction treatment.[9] The fuel rods were broken into coarse granules in an inert atmosphere, then the granules were allowed to "age"[5] by exposure to laboratory air. The UC composition was 4.80 ± 0.03 wt % carbon and the major impurity was 0.10 to 0.15 wt % oxygen. The nitrogen used in the sample preparation was a prepurified grade of compressed gas having a listed minimum purity of 99.996%.

The higher nitride-carbon mixtures, nominally U_2N_3 + C, were prepared by reacting UC contained in a molybdenum crucible in 0.9 atm of nitrogen for 3 to 6 hr at a temperature of 800 to 900°C in a resistance furnace. The reaction reduced the sample to a dark grey powder. X-ray diffraction examinations indicated the major constituent was U_2N_3, identified as the $UN_{1.43}$ and $UN_{1.52}$ patterns. Traces of UO_2 were also identified in the samples.

The mononitride-carbon mixtures were made by reacting UC contained in a molybdenum crucible in 0.5 to 0.7 atm of nitrogen for 4 to 14 hr at a temperature

of 1300°C in a high-frequency induction furnace. Samples were heated in nitrogen* rapidly (1 to 2 min) to temperature and also cooled rapidly (40 sec to cool from 1300 to 700°C) at the completion of the reaction. This treatment was necessary to minimize formation of higher nitrides. In contrast to the U_2N_3 + C samples, the UN + C samples were not pulverized to any extent; however, the product had a dull grayish color in place of the original UC luster. The product, as determined by x-ray diffraction, was UN and graphite with traces of UO_2.

The uranium nitride was prepared by reacting wafers from a normal uranium rod, cleaned in aqua regia, in 0.6 atm of nitrogen for 4 to 7 hr at a temperature of 700 to 800°C in the thermogravimetric balance system. The product, a grey colored powder, was determined by x-ray diffraction to be U_2N_3 with some UN_2.

The composition of samples was determined from the weight gain during reaction and from analyses of nitrogen by the Kjeldahl method and carbon by combustion. Carbon analysis of both nitride-carbon compounds indicated no loss of carbon occurred in sample preparation. Prepared samples were stored in either vacuum or in a dry inert atmosphere prior to reconversion to prevent oxidation of the nitride.[5]

The surface area of samples was measured with the BET adsorption apparatus described in NAA-SR-5319.[10]

*Heating the UC in vacuum to 1400 to 1500°C before introducing nitrogen rendered the UC nearly "inactive" towards nitrogen.

III. RESULTS AND DISCUSSION

The two nitride-carbon mixtures used in this investigation involved the sesquinitride, U_2N_3 + C, and the mononitride, UN + C. The original intention was to study reconversion using only the sesquinitride-carbon. But, rate values for the reaction below the UN composition could not be correlated between experiments because of a decrease in sample surface area during the reaction. Therefore, samples of mononitride-carbon were prepared and their surface area measured so a study of the temperature effect on reconversion below the UN + C composition could be carried out. The decomposition of U_2N_3 (no carbon) was studied primarily to provide a comparison with the U_2N_3 + C experiments. Results for each type of material are presented separately.

A. RECONVERSION OF THE SESQUINITRIDE-CARBON

The reaction of the sesquinitride-carbon was studied up to a temperature of 1300°C. Results of typical experiments are illustrated in Figure 2. The reaction temperature is indicated above the curve to which it corresponds and the vacuum reading in the system is listed below the curve. The theoretical compositions for U_2N_3 + C and UN + C are shown for reference.

The data have some characteristic features. No reaction occurred below a temperature of 730 ± 5°C. Nitride decomposition resulted as the temperature was increased; however, the reaction stopped when the temperature was held constant at 800 or 900°C (rate curve 0 in Figure 2). The lowest temperature for which a continuous reaction occurred was found to be 950°C. The reaction rate increased sharply with increased temperature. The reaction rate was initially linear until the composition of UN was reached, then the rate decreased asymptotically, approaching a different limit at each temperature.

X-ray diffraction examination of representative products from reconversion experiments on U_2N_3 + C can be summarized as follows:

1) UN was identified in all the samples
2) UC was identified in products from experiments at 1100°C and above
3) U_2N_3 with a possibility of UN_2 was identified in samples from experiments at 950 and 1000°C where products were only slightly reconverted.
4) Traces of UO_2 were found in most of the samples.

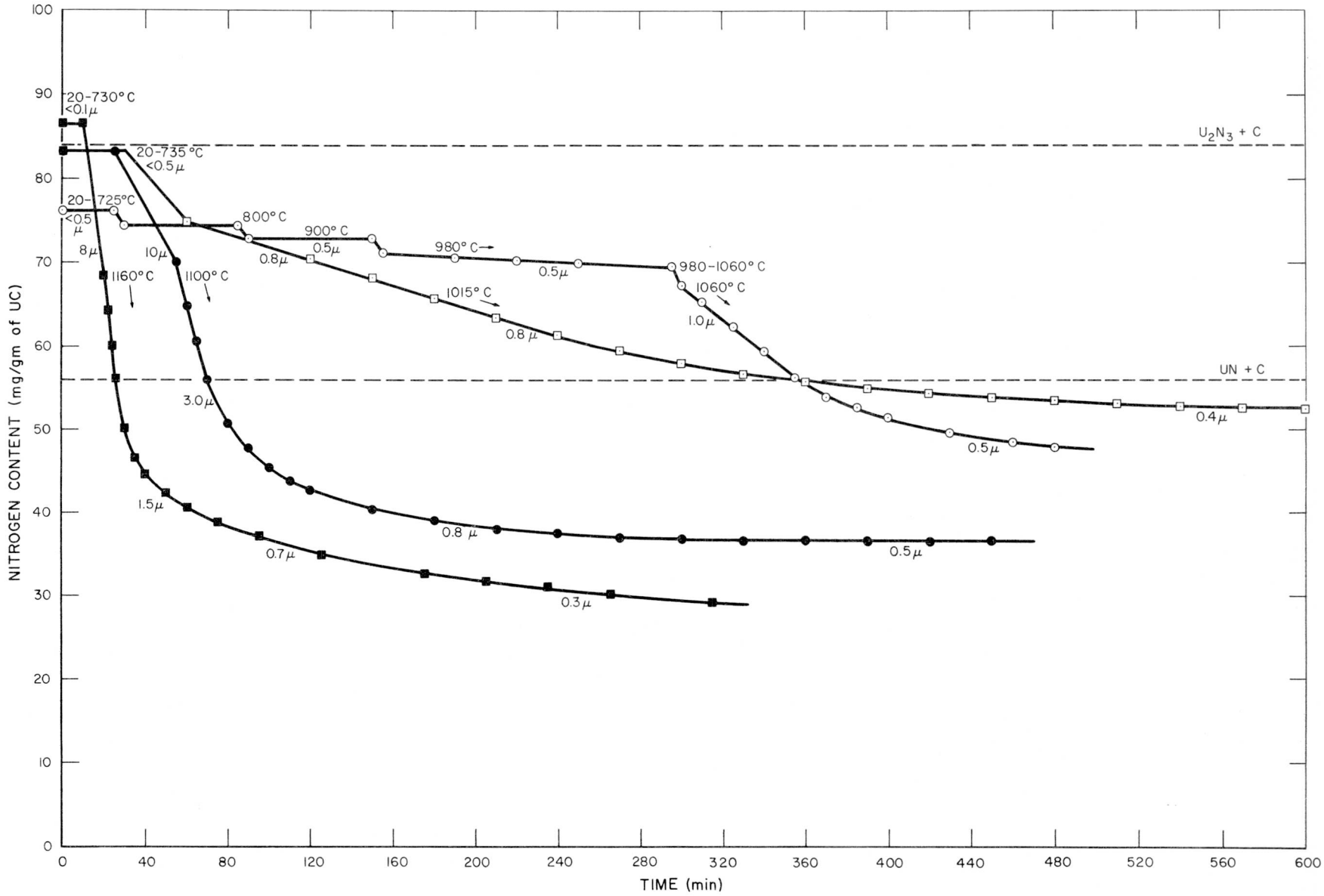

Figure 2. Typical Plots of Nitrogen Weight Loss From U_2N_3 + C Samples During Heating in Vacuum

The nitrogen content of the products was calculated from the initial nitrogen content and the weight loss during reconversion. Chemical analyses of several products for nitrogen were in agreement with the calculated values. Carbon analyses of several of the products indicated no loss of carbon from the samples occurred in these experiments.

As a further attempt to identify the reaction product, a sample was decomposed to a nitrogen content of 5.30 wt % ($UN_{1.0}$ + C) and then examined by x-ray diffraction. The product was UN containing trace amounts of UN_2. The amount of free carbon (determined by HCl-H_2O_2 leaching)[8] was essentially the same as the total carbon content, indicating carbon was not a reactant.

Based on interpretation of the plots in Figure 2 and the reaction product analyses, the reaction of U_2N_3 + C to form UC appears to occur in a two-step manner which can be represented as follows:

$$\text{Step 1} \quad U_2N_3 + 2C \longrightarrow 2UN + 2C + 1/2\ N_2 \uparrow$$

(Thermal decomposition)

$$\text{Step 2} \quad 2UN + 2C \longrightarrow 2UC + N_2 \uparrow$$

(Reconversion)

Complete reconversion to UC was not achieved in any of the experiments; however, the maximum temperature was only 1300°C. The reaction would not be expected to go to completion except at higher temperature in view of the reported stability of UN.[7]

The rate of nitride reconversion may be expressed by an equation of the form:

$$w = kt^n \qquad \ldots(1)$$

where

w = sample weight loss in mg/m^2

k = rate constant

t = time in minutes

n = a constant depending on the rate law followed.

Values for w, based on the initial sample surface area, were calculated for each experiment. Typical plots of w as a function of time are shown in Figure 3. Utilizing Equation 1, where n = 1 for a linear rate law, values for k were determined from the slope of the linear part of the w vs t plots. Table I lists results of the U_2N_3 + C reconversion experiments.

One observation derived from Table I by comparing initial and final surface areas is that a decrease in sample surface area occurs during reaction. There are several possible explanations for this decrease in sample surface area. Particle sintering could result from heating at high temperature. Also, the evolution of nitrogen would reduce the size of sample particles since UN has a higher density than U_2N_3.[7] The values for k obtained for the linear reconversion rate were assumed to be unaffected by the change in sample surface area. Although this assumption is open to criticism, no other satisfactory solution was found.

Figure 4 is a plot of ln k (natural log of the linear rate constant) vs the reciprocal of the absolute temperature. The straight line was determined by a least squares treatment of the data. After calculating the standard (root-mean-square) error in ln k, the corresponding error in k was found to be a factor of 1.13. From the Arrhenius expression

$$\ln k = -\frac{\Delta E^*}{RT} + \ln A \qquad \ldots(2)$$

and using the slope of the straight line, 90.6 ± 11.8 kcal/mol was calculated for ΔE^* (the activation energy). An average value of 32.0 for ln A (A = frequency factor) was also calculated using experimental values in Expression 2. The rate equation for the decomposition of U_2N_3 + C to UN + C can be written as:

$$\ln k = 32.0 - \frac{45{,}600}{T}$$

with a standard error of 0.123 in ln k [k is in $(mg/m^2)/min$].

Some typical curves showing rates (w vs t) for reconversion following the linear rate period are shown in Figure 3, particularly for experiments at

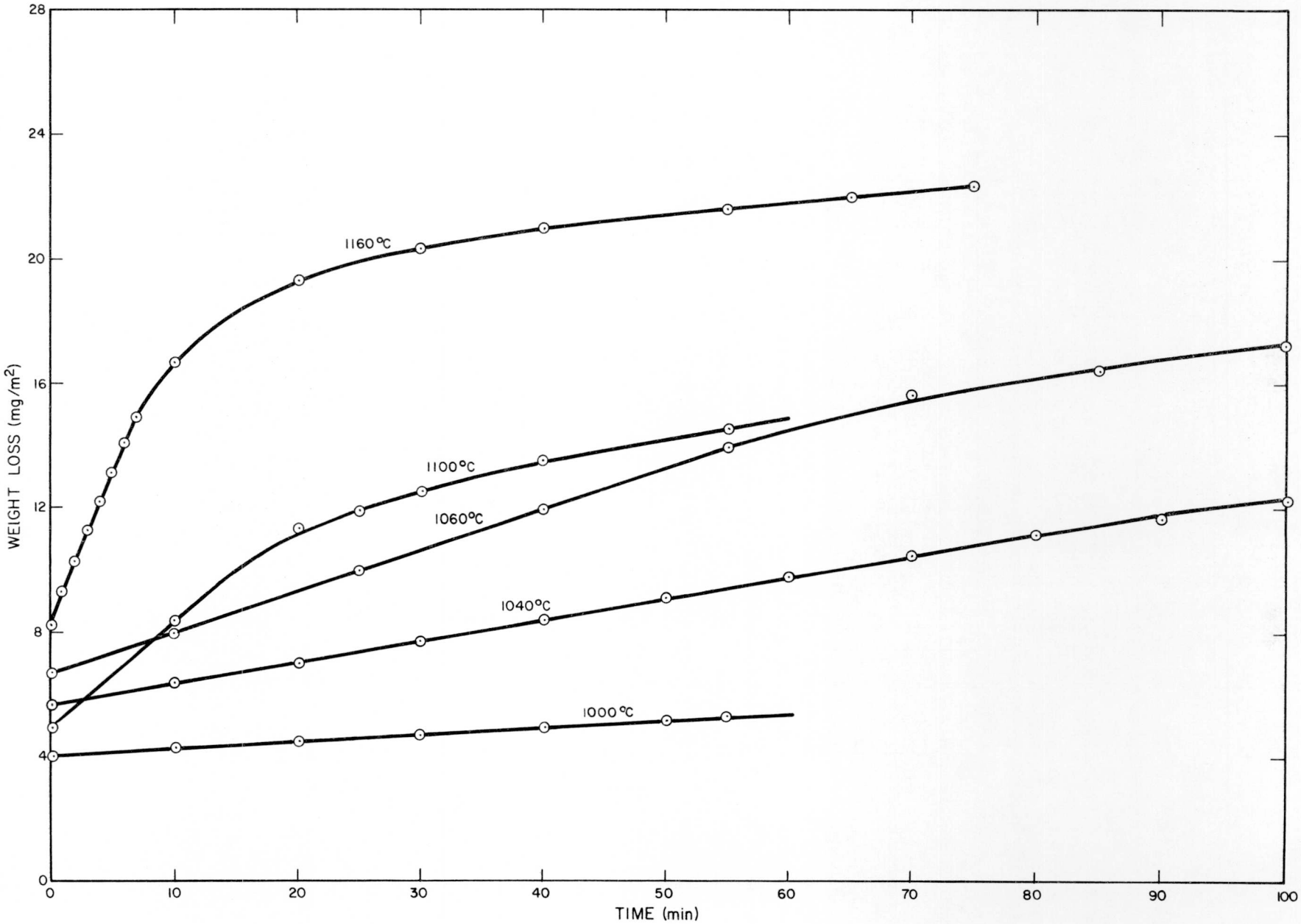

Figure 3. Typical Rate Plots for U_2N_3 + C Reconversion

TABLE I

REACTION DATA FOR U_2N_3 + C EXPERIMENTS

Experiment No.	Nitrogen Content (wt %)		Surface Area (m^2/gm)		Reconversion			Linear Rate Constant, k x 10^{-2} (mg/m^2)/min	ln k
					Time (min)	Temperature			
	Initial	Final	Initial	Final		°C	1000/T(°K)		
I	7.7	5.1	2.0 ± 0.1	-	540	1015	0.776	3.62	-3.32
II	8.0	3.3	2.0 ± 0.1	0.79 ± 0.04	330	1130	0.713	60.6	-0.50
III	8.0	- 1.6	2.0 ± 0.1 -	-	185 155	1040 1300	0.761 -	6.89 -	-2.68 -
IV	8.0	2.8	2.0 ± 0.1	-	295	1160	0.698	96.8	-0.03
VI	7.7	3.6	2.5 ± 0.1	1.0 ± 0.04	395	1100	0.728	33.3	-1.10
VII	8.0	6.7	2.5 ± 0.1	0.95 ± 0.04	55	1000	0.785	2.32	-3.76
VIII	7.3	6.8	1.2 ± 0.1	-	240	950	0.818	0.433	-5.45
IX	7.1	- 4.6	1.4 ± 0.1 -	- 0.71 ± 0.04	140 180	980 1060	0.798 0.750	1.01 13.2	-4.60 -2.30

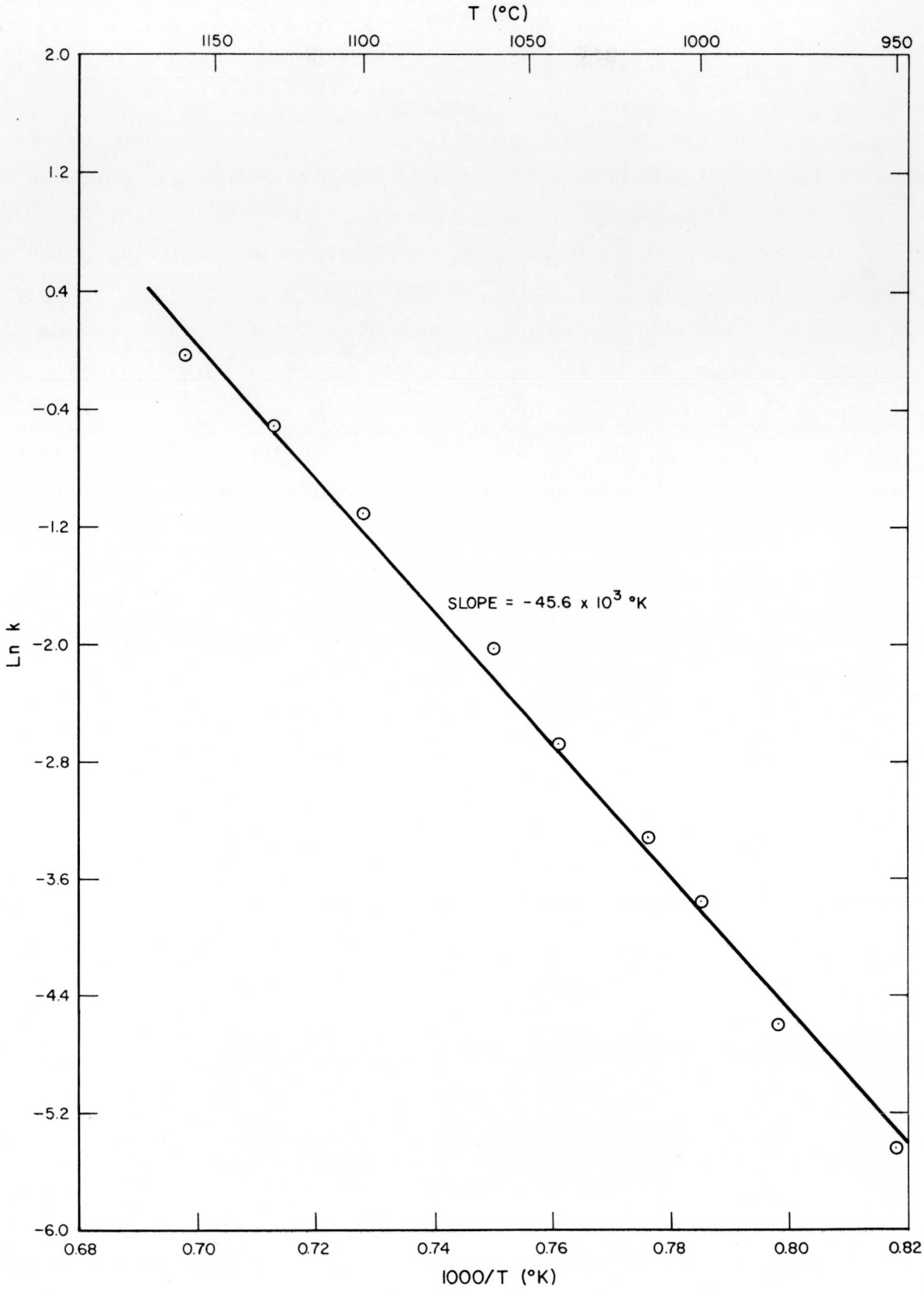

Figure 4. Variation of Linear Rate Constant With Temperature for Decomposition of U_2N_3 + C to UN + C

1160, 1100, and 1060°C. Using Equation 1, the reconversion data appeared in general to fit a parabolic rate expression (n = 1/2); however, k values determined from w vs $t^{1/2}$ plots showed no correlation between experiments. Use of the original surface area for calculating values of w during the nonlinear rate step was believed to contribute to the random results. Although numerous trial and error solutions were tried, no satisfactory method of predicting the sample surface area at the end of the linear rate step (i.e., at the beginning of the nonlinear rate step) was found. However, this problem was circumvented by preparation and subsequent reaction of UN + C samples. Another possible solution would have been to determine the sample surface area by BET analysis at the end of the linear rate prior to continuing the reaction.

In experiment No. V, the sample was heated rapidly to 1200°C, resulting in powder being blown from the holder by rapid evolution of nitrogen. In view of this effect, heating these powders stepwise to high temperature is recommended.

B. DECOMPOSITION OF THE SESQUINITRIDE

The results of decomposition in vacuum of uranium nitride, principally U_2N_3 (no carbon), are illustrated in Figure 5. The dashed lines indicate increases in temperature and for simplicity are drawn straight. This nitride began decomposing at a temperature of 650 ± 10°C. At 700 and 800°C the nitride decomposed with a nonlinear rate; but at 880°C and above, decomposition was initially linear followed by a continuously decreasing rate. Complete conversion to UN required only 2 to 3 hr at 1000°C. Essentially no decomposition below UN occurred even at 1100°C in a vacuum of 0.03 μ.

The product from Experiment No. B was determined by x-ray diffraction to be UN with no evidence of higher nitrides or uranium metal. Chemical analyses for nitrogen indicate the nitrogen content was about 10% lower than the value expected based on the initial content and the weight loss during decomposition. These results may be explained as either an error in nitrogen determination or nitride oxidation or hydrolysis in air prior to the analysis.

Based on the initial sample surface area, values for w, weight loss per unit area, were calculated for each experiment. Although no simple mathematical relationship was found for the entire decomposition using Equation 1, the data did follow a linear rate law initially over the N/U ratio range of 1.5 (U_2N_3) to about 1.3. Values of k for these linear rates were determined and are listed in Table II along with relevant data.

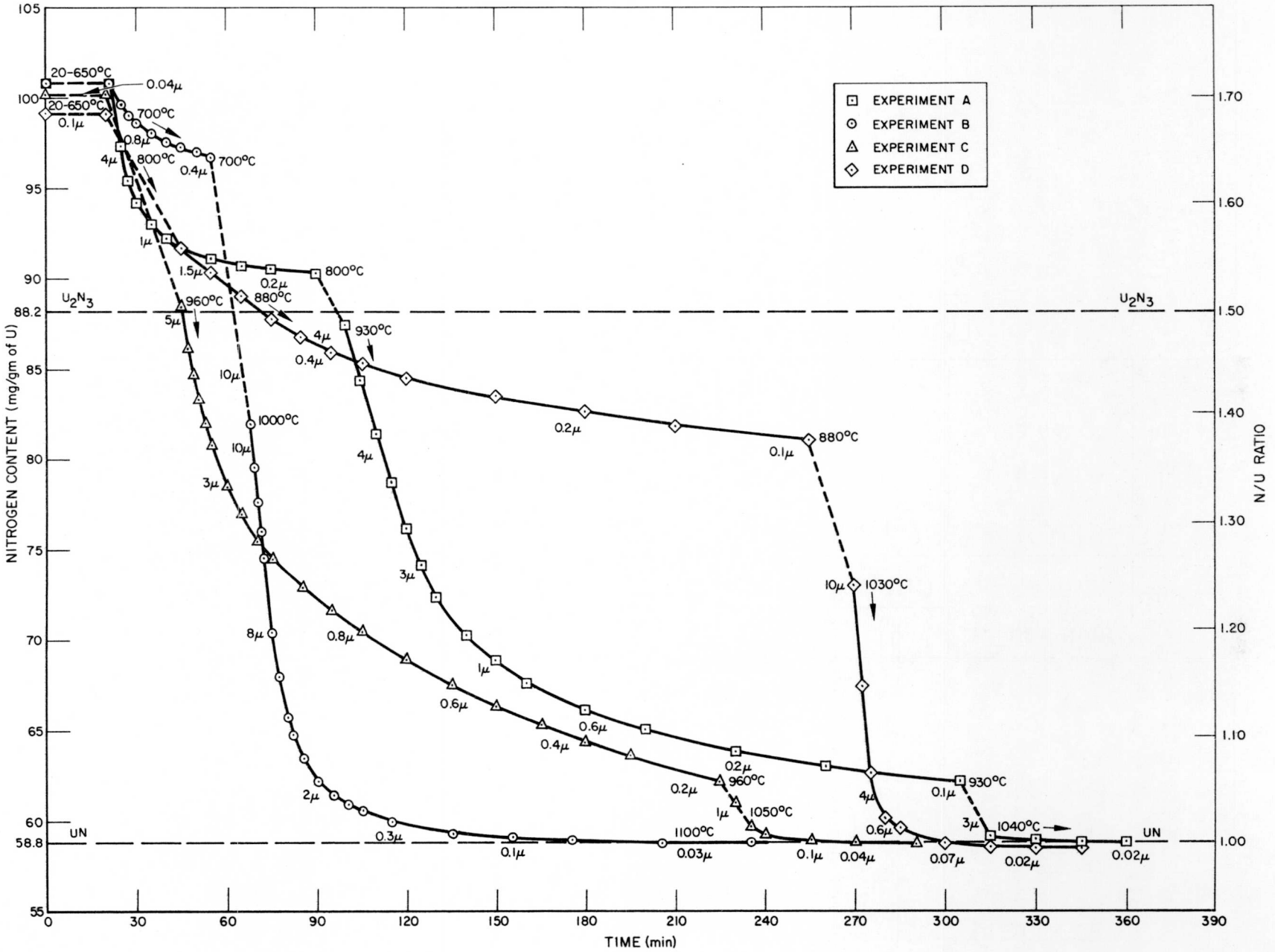

Figure 5. Nitrogen Weight Loss From Uranium Nitride Samples During Heating in Vacuum

TABLE II

REACTION DATA FOR U_2N_3 EXPERIMENTS

Experiment No.	Initial Nitrogen Content (wt %)	Surface Area (m^2/ gm)		Temperature		Linear Rate Constant, k (mg/m^2)/min	ln k
		Initial	Final	°C	1000/T(°K)		
A	9.16	0.27 ± 0.01	---	930	0.831	1.89	0.63
B	9.16	0.27 ± 0.01	0.035 ± 0.002	1000	0.786	6.35	1.85
C	9.11	0.27 ± 0.01	---	960	0.811	2.64	0.97
D	9.02	0.27 ± 0.01	---	880	0.867	0.46	-0.77

The reason for an observed decrease in decomposition rate after the brief linear period was not known. Some deviation may be associated with a decrease in sample surface area during decomposition, as shown in Table II. However, the possibility that the decomposition follows a different rate law after the linear rate can not be ruled out and, in general, the rate appeared characteristic of a diffusion controlled process.

The variation of ln k (linear rate constant) with temperature is plotted in Figure 6 and the solid line represents a least squares treatment of the points. By calculating the standard (root-mean-square) error in ln k, the corresponding error of 1.12 in k was determined. From Equation 2 and using the slope of the least squares line, 64.6 ± 7.7 kcal/mol was calculated for ΔE^*, the activation energy. This value is in reasonable agreement with the reported[11] value of -58.3 ± 1.0 kcal/mol N_2 determined for the heat of the reaction ($4\ UN + N_2 \longrightarrow 2U_2N_3$) over the temperature range from 800 to 1000°C.

Comparison of the linear rate constant, k, at 1000°C for the decomposition of U_2N_3 (6.35 mg/m^2/min) and of U_2N_3 + C (2.32×10^{-2} mg/m^2/min) shows that the presence of carbon impeded the decomposition. Some contribution to the difference in rates could be caused by the U_2N_3 + C sample having a larger surface area. However, the portion of the U_2N_3 + C surface area attributable to the carbon (carbon was evidently not a reactant) was unknown so that any exact comparison of the rates would be complex. Also, the activation energy values for the two types of material differ and it is possible different reactions are involved.

One hypothesis for the lower rates in the case of the U_2N_3 + C material can be given as follows: The nitrogen on the surface of discrete particles should be removed first in the reaction. This converted layer on the surface then acts as a barrier for diffusion of nitrogen from the inside of the particle. The linear rate of nitrogen removal which occurred could result from nitrogen diffusing faster within the particle than through the barrier.

C. RECONVERSION OF THE MONONITRIDE-CARBON

Reconversion of the mononitride (UN + C) was studied from room temperature to 1645°C. Values for the nitrogen content were plotted as a function of time for each experiment. Typical results are illustrated in Figure 7 (see also Table III). The reaction temperature is indicated above each curve and the pressure in the system below the curve.

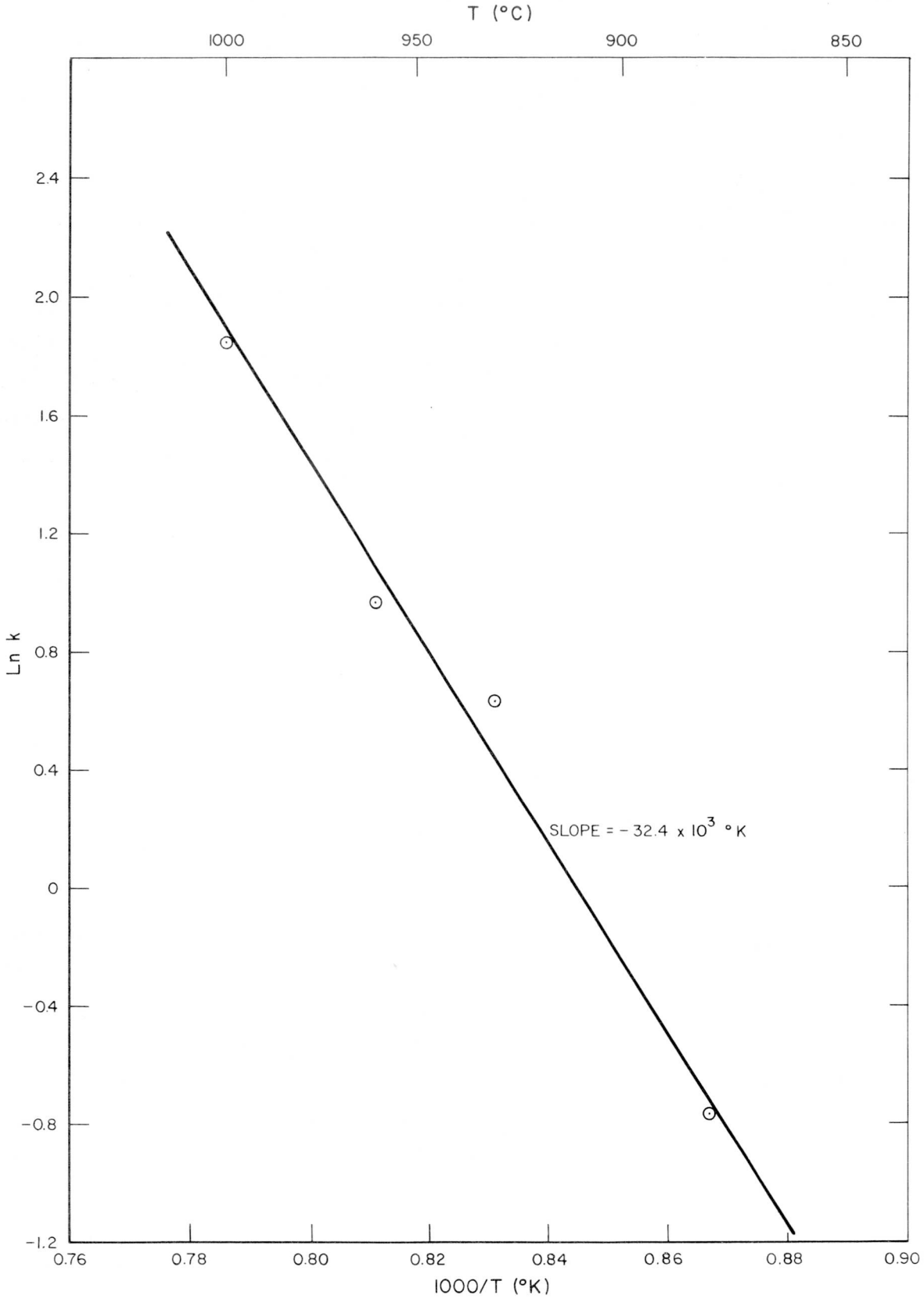

Figure 6. Variation of Linear Rate Constant With Temperature for the Decomposition of U_2N_3

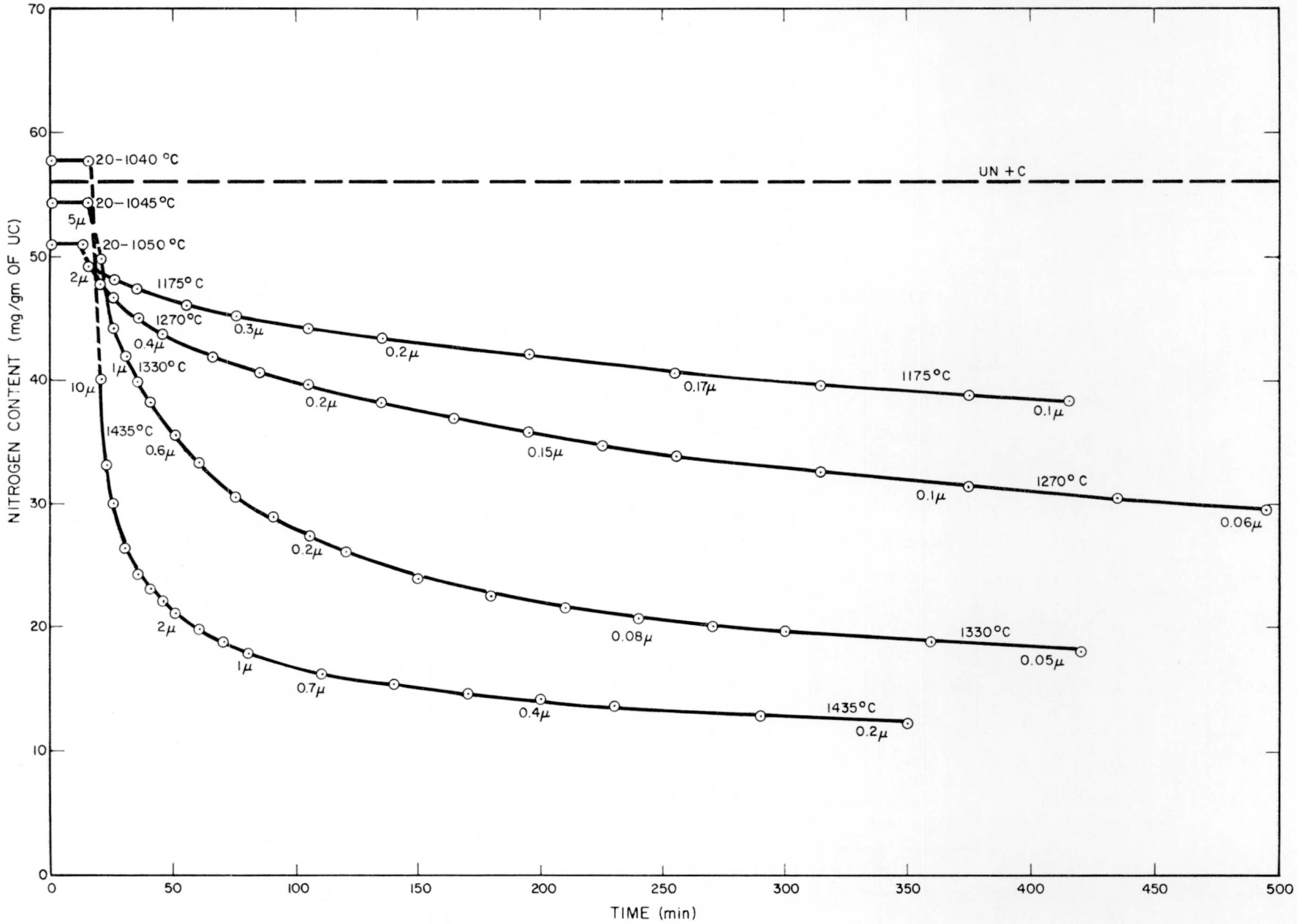

Figure 7. Typical Rate Plots of UN + C Reconversion

TABLE III

REACTION DATA FOR UN + C EXPERIMENTS

Experiment No.	Surface Area (m^2/g)		Product* Nitrogen Content (wt %)	Reconversion			Parabolic Rate Constant, k $(mg/m^2)/(min)^{1/2}$	ln k
	Initial	Product		Time (min)	Temperature °C	Temperature 1000/T (°K)		
1	0.22 ± 0.01	-	3.40	365	1205	0.677	3.62	1.29
		0.13 ± 0.01	0.90	118	1505	0.562	19.16	2.95
2	0.22 ± 0.01	0.14 ± 0.01	1.45	580	1410	0.594	13.36	2.59
3	0.22 ± 0.01	0.062 ± 0.005	0.70	270	1645	0.521	40.0	3.69
4	0.22 ± 0.01	0.083 ± 0.005	1.04	720	1470	0.574	16.6	2.82
5	0.22 ± 0.01	-	2.85	480	1270	0.648	5.30	1.67
6	0.22 ± 0.01	-	0.83	450	1565	0.544	29.8	3.39
7	0.22 ± 0.01	0.22 ± 0.01	3.68	400	1175	0.691	2.66	0.98
8	0.30 ± 0.01	0.20 ± 0.01	1.79	400	1330	0.624	8.24	2.11
9	0.30 ± 0.01	-	2.71	330	1235	0.663	4.55	1.51
10	0.30 ± 0.01	-	2.16	330	1295	0.638	6.51	1.87
11	0.30 ± 0.01	-	1.23	330	1435	0.585	15.0	2.70
IX†	-	0.71 ± 0.04	4.6	125	1060	0.750	1.13	0.12

*Initial Nitrogen Content of samples varied from 4.85 to 5.46 wt %
(theoretical composition for UN + C is N = 5.30 wt %, C = 4.54 wt %)
†Original sample was U_2N_3 + C (see Experiment IX, Table I)

A number of observations can be made which characterize the UN + C reaction. Nitrogen evolution began at a temperature of 1040 ± 20°C. At each temperature, the rate decreased continuously with time, and a smooth rate curve resulted. The higher the reaction temperature, the more complete was the reconversion. Final reaction rates for experiments at temperatures above 1400°C were very low. For example, the rate of the last hour at 1565°C was less than 0.08 mg/gm of UC (0.35 mg/m^2)/hr. The reaction did not go to completion in any of the experiments, even for long heating times (580 and 720 min).

Examination of representative products from the UN + C reconversion experiments were made by x-ray diffraction. The results are listed as follows:

1) UC was identified as the major constituent in all the samples examined.
2) UN was identified in products containing over 2.0 wt % nitrogen.
3) No nitride pattern was identified in products containing less than 1.8 wt % nitrogen, although this amount of nitrogen in a UN-UC mixture corresponds to over 30% UN.
4) No uranium oxide was identified in the products.

The nitrogen content of representative product samples was determined by chemical analysis and the results agreed to 1.5% of the nitrogen content calculated using the initial sample content and the weight loss (corrected for CO loss) in reconversion. Carbon analyses of products indicate a loss of carbon from samples occurred during reconversion. The average carbon loss for all the samples analyzed was 0.2 wt % with a loss of 0.3 wt % resulting in one experiment. UO_2 was not identified in the products although present in samples prior to reconversion. Calculations based on the amount of carbon and oxygen removed during reaction indicate they were removed as CO. This is in agreement with other results reporting a reduction in carbon content from UC containing oxide when sintered at 1870°C.[12]

These results indicate that the reconversion of UN + C can be represented as:

$$UN + C \longrightarrow UC + 1/2\ N_2 \uparrow \quad ,$$

which is the expression for the second step in the U_2N_3 + C reconversion. The reaction was not complete even for samples heated for a long time at high temperature and the actual product was a uranium nitride-carbide solid solution. A more realistic representation of the reconversion would be

$$UN + C \longrightarrow U(N_{1-x}, C_x) + \frac{x}{2}N_2\uparrow + C_{1-x} \quad ,$$

where x is the mol fraction of nitrogen removed from the sample. Work at Battelle[8] has also shown detailed evidence of U(C, N) solid solutions.

Based on Equation 1, the data were found to most nearly fit a parabolic rate expression ($w = kt^{1/2}$) characteristic of a diffusion controlled reaction. Typical plots of weight loss per unit area (initial surface area) vs the square root of time are shown in Figure 8. Table III lists data for the UN + C reconversion experiments.

One important observation from the data of Table III is that sample surface area decreases during the reaction. This same effect was noted in the other experiments. Therefore, values of w based on the initial surface area would be incorrect near the end of the reaction. However, values of w for the initial reaction appear valid, particularly in view of the results of Experiment No. 7. In this experiment at 1175°C, no change in sample surface area occurred during reaction and only minor deviation occurred from the straight line (see Figure 8) representing a parabolic rate.

Values for the parabolic rate constant, k, were determined from the slopes of the linear portion of the w vs $t^{1/2}$ plots. Deviation below the straight line is attributed to the decrease in surface area of the samples during the experiment. The variation of ln k (parabolic rate constant) with temperature is illustrated in Figure 9. The solid line represents a least squares treatment of all the points. After calculation of the standard (root-mean-square) error of 0.035 in ln k, the corresponding error in k was found to be 1.036. Using Equation 2 and the slope of the least squares line, an activation energy of 31.3 ± 1.1 kcal/mol was calculated. The average value for ln A (A = frequency factor) was calculated to be 11.9.

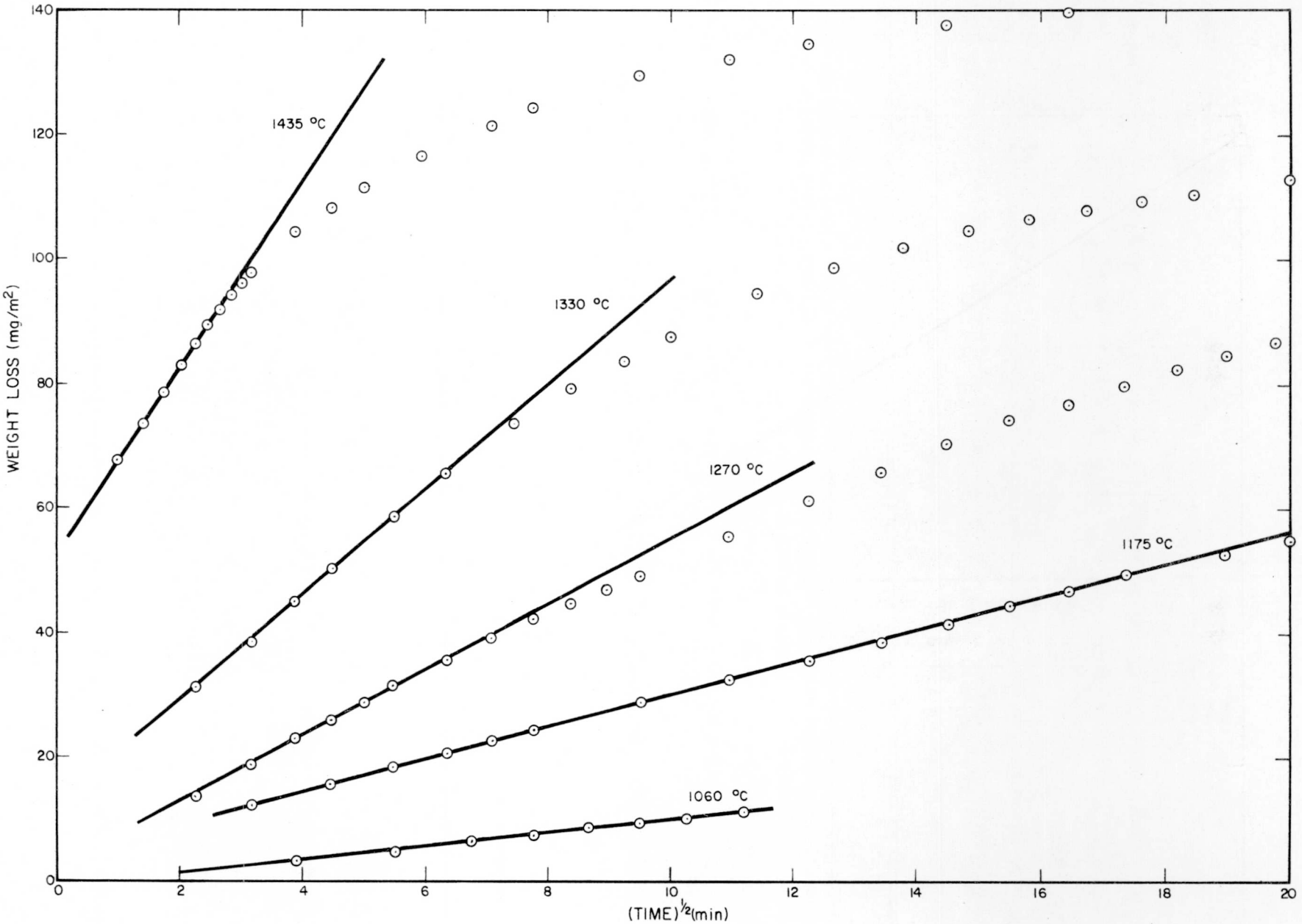

Figure 8. Typical Parabolic Rate Plots of UN + C Reconversion to UC

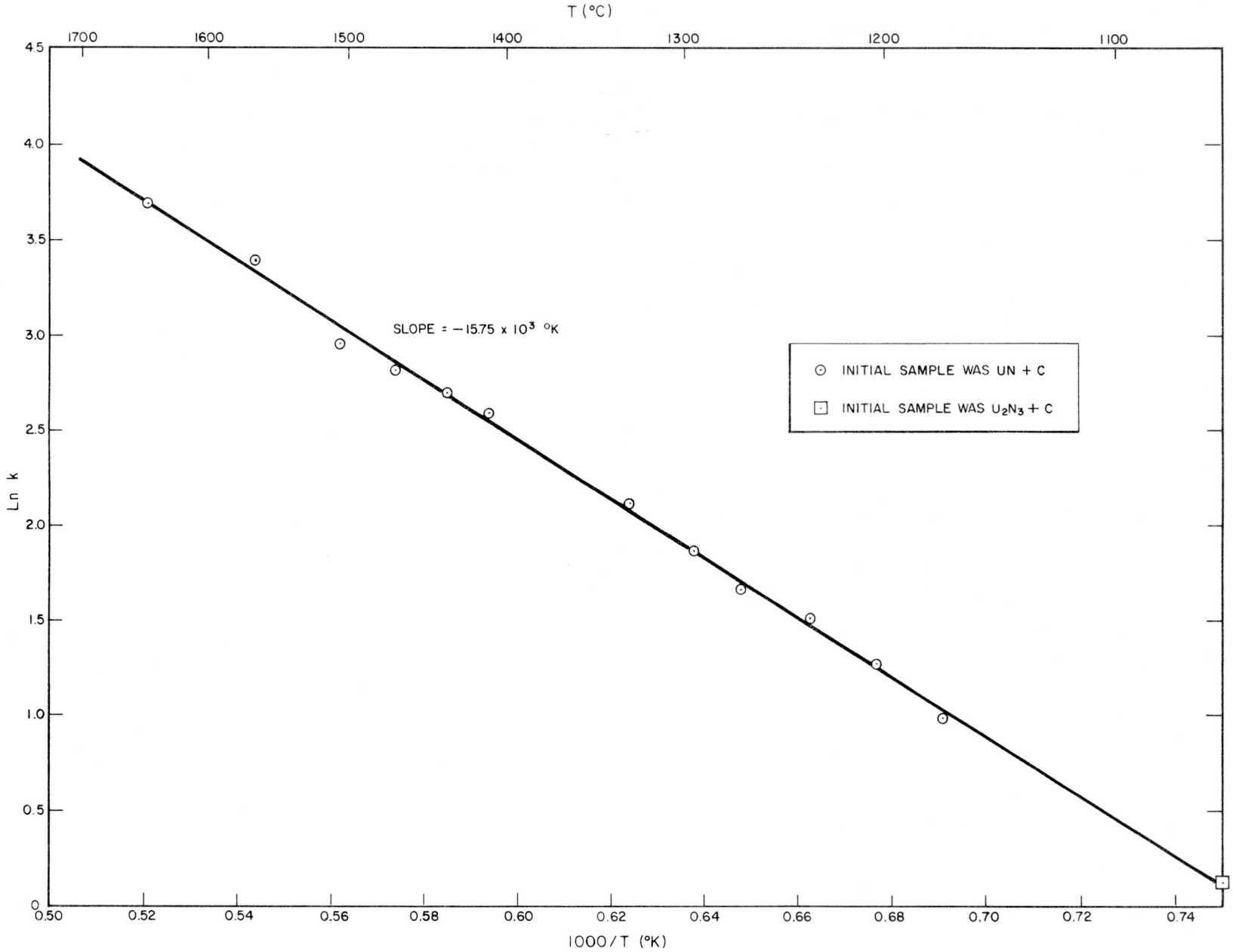

Figure 9. Variation of Parabolic Rate Constant With Temperature for Reconversion of UN + C to UC

The reaction of UN + C can be expressed by the following equation:

$$\ln k = 11.9 - \frac{15,750}{T} \quad ,$$

where units of k are $(mg/m^2)/min^{1/2}$.

A correlation between experiments on U_2N_3 + C and UN + C was obtained using Experiment No. IX of Table I and II. In this experiment, run at 1060°C, decomposition below UN was continued only briefly. Values of weight loss per final sample surface area were calculated for reconversion below the UN + C composition. These values are plotted against the square root of time in Figure 8 and a parabolic rate constant determined for this plot. The rate constant determined from this experiment is included in the Arrehenius plot of Figure 9. Excellent agreement with the least squares line was obtained, indicating the similarity in behavior of the UN + C obtained by direct preparation and from U_2N_3 + C decomposition. Although this correlation is based on only one experiment, the kinetics of the second step of the U_2N_3 + C reaction is believed to be identical to UN + C reconversion.

The method of preparing the UN + C sample should be clarified in view of some results obtained by Austin and Gerds.[8] They reported that U_2N_3 + graphite was the product when UC specimens were heated in a nitrogen atmosphere at 1300 and 1550°C and cooled slowly in nitrogen. In our work, the nitride produced at 1300°C was cooled rapidly to limit U_2N_3 formation known to occur at 800 to 900°C.

A comparison of initial sample surface areas from Table I and Table III indicates the U_2N_3 + C samples have a surface area a factor of 5 to 10 larger than the UN + C samples. The significance of this fact becomes evident when comparing the rate data from the two tables. For example, heating in vacuum at 1160°C for 295 min reduced the content of U_2N_3 + C sample to 2.8 wt % nitrogen (Experiment IV, Table I); whereas, heating a UN + C sample at 1175°C for 400 min only reduced the nitrogen content to 3.68 wt % (Experiment 7, Table III). Thus, samples having larger surface area per gram resulted in more rapid and more complete reconversion at comparable temperatures. It is obvious from these results that preparation of the higher nitride would facilitate the reconversion step in a nitride-carbide processing cycle for UC fuel.

IV. SUMMARY AND CONCLUSIONS

The conversion of uranium nitride-carbon mixtures to uranium carbide by heating in vacuum occurs by a two-step reaction:

$$U_2N_3 + 2C \longrightarrow 2UN + 2C + 1/2\ N_2 \uparrow$$

$$2UN + 2C \longrightarrow 2UC + N_2 \uparrow$$

The first reaction follows a linear rate law and has an activation energy of 90.6 ± 11.8 kcal/mol. The second reaction follows a parabolic rate with an activation energy of 31.3 ± 1.1 kcal/mol.

The activation energy for the decomposition of U_2N_3 (no carbon) to UN was 64.4 ± 7.7 kcal/mol based on an initial linear rate over the temperature range of 880 to 1000°C. This value for the activation energy is in agreement with the value for the heat of reaction. Comparison of the data for the decomposition of U_2N_3 + C and of U_2N_3 indicates that the existence of carbon in the nitride markedly lowered the decomposition rate and increased the activation energy.

Although these nitride-carbon experiments resulted in formation of uranium nitride-carbide mixtures, complete conversion to UC by heating to slightly higher temperatures would seem feasible. Also, in view of the high temperatures essential in the reconversion, fission product decontamination of spent reactor fuel would be expected.

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