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Kinetics of Thermal Decomposition of Copper (II) Sulfate and Copper (II) Oxysulfate

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KINETICS OF THERMAL DECOMPOSITION OF COPPER (II) SULFATE AND COPPER (II) OXYSULFATE

by

I. D. Shah¹ and S. E. Khalafalla²

ABSTRACT

Thermal decomposition of copper (II) sulfate (CuSO_4) and copper (II) oxysulfate ($\text{CuO}\cdot\text{CuSO}_4$) are important steps in the overall oxidative roasting of covellite (CuS) and chalcocite (Cu_2S). Nonisothermal thermogravimetric techniques were used to investigate the decomposition reactions in flowing N_2 and air. Thermal decomposition of CuSO_4 and $\text{CuO}\cdot\text{CuSO}_4$ followed "linear" kinetics with an apparent activation energy of 55 ± 2 and 66 ± 3 kcal per mole decomposed, respectively. These apparent activation energies comply with those previously reported when isothermal kinetic techniques were used. The addition of oxygen decreased the rate of decomposition, while small amounts of iron which were admixed with $\text{CuO}\cdot\text{CuSO}_4$ did not have a significant effect. Neither oxygen nor iron had any appreciable effect on the apparent activation energy of the decomposition reaction.

INTRODUCTION

Roasting reactions are important in copper extraction metallurgy. A basic understanding of the process may lead to the replacement or improvement of the existing process. There appears to be a lack of sufficient information on the systematic investigation of the kinetics and mechanism of oxidation of copper sulfides, perhaps owing to the complexity of the process.

Copper (II) sulfate and copper (II) oxysulfate are formed during the roasting of copper sulfides. Kellogg (7)³ made an excellent review of the sulfation equilibria. Alcock, Sudo, and Zabor (1) and Ingraham (5) studied the thermodynamics of copper (II) sulfate and copper (II) oxysulfate. Ingraham and Marier (6) investigated the isothermal kinetics of the thermal decomposition of CuSO_4 and $\text{CuO}\cdot\text{CuSO}_4$. They reported that the reactant-product interface within the pellet was well defined. By normalizing the decrease in the interfacial area with the weight fraction of the pellet decomposed, they found that the interface migrated into the pellet at a uniform rate at

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³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

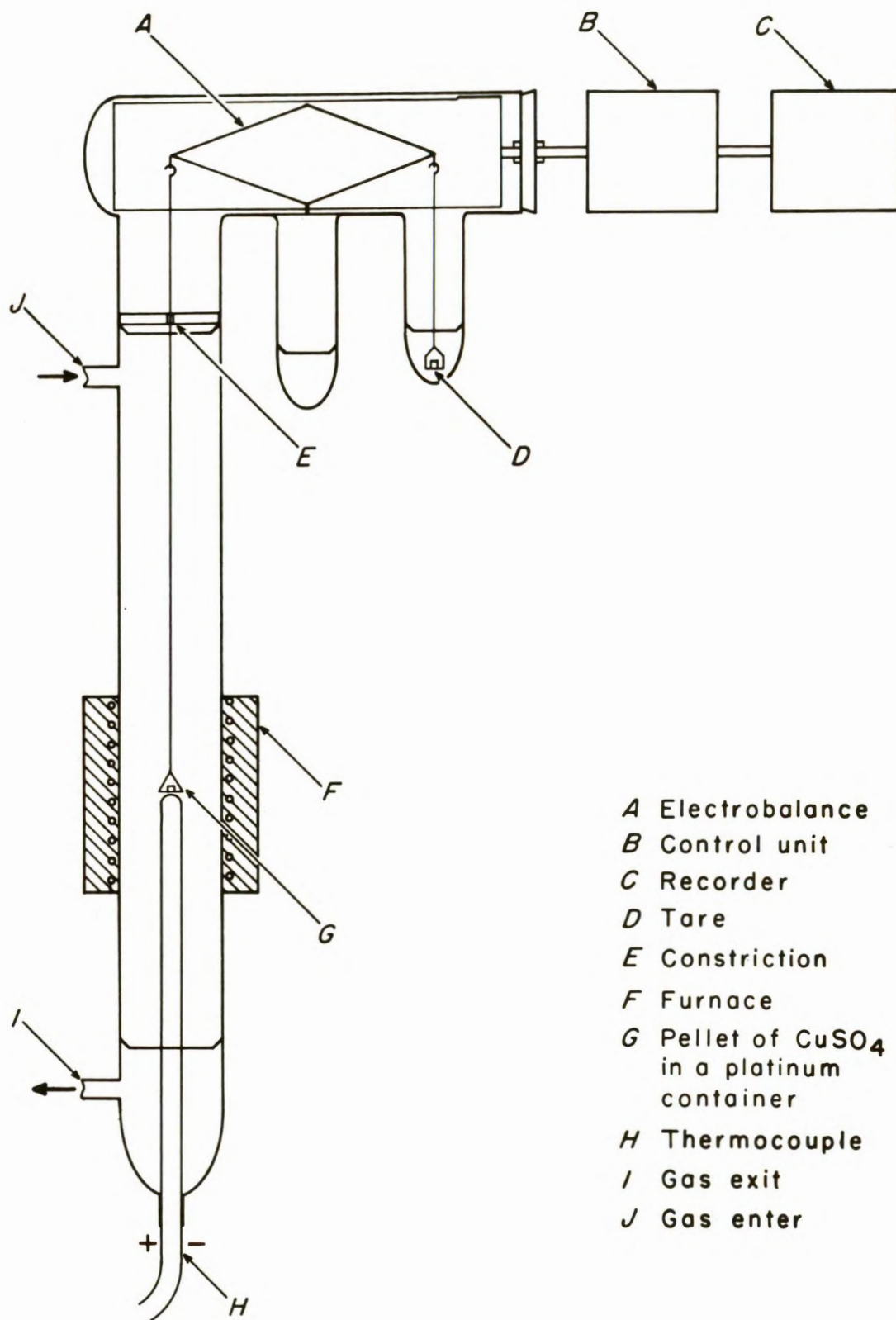


FIGURE 1. - Schematic Drawing of the Thermal Gravimetric Analysis Equipment.

constant temperature and gas flow rate. They also observed an increase in the decomposition rate of CuSO_4 and $\text{CuO}\cdot\text{CuSO}_4$ as the rate of flowing nitrogen was increased. However, the rate of nitrogen flow did not have any effect on the apparent activation energy of the process.

Thermal decomposition of CuSO_4 and $\text{CuO}\cdot\text{CuSO}_4$ constitute two terminal reactions in the roasting process. The object of this Bureau of Mines paper is to report on the kinetics of these decomposition reactions. Individual decomposition reactions are studied in N_2 and air by thermogravimetry where a linearly programmed heating rate was utilized. The effect, when small amounts of iron were externally added, was also studied.

EXPERIMENTAL METHOD AND APPARATUS

A differential thermal analysis (DTA) apparatus with stainless steel sample-holders fitted with platinum-platinum, 10 percent rhodium thermocouples was used in this work. Differential thermocouple junctions were centrally located in the sample cells. A platinum-platinum, 10 percent rhodium thermocouple, placed in the center of the sample block, was connected to a programmer and temperature recorder and controller to program the linear heating rates and to record and control the block temperature. The programmer gave a good linear heating rate, the maximum deviation being 2 percent over any 100°C interval.

The thermogravimetric analysis equipment used is shown in figure 1. It consisted mainly of the Cahn⁴ RG automatic electrobalance assembled so that the DTA recording and control unit could be utilized along with the TGA unit. A platinum-platinum, 10 percent rhodium thermocouple made from 0.010-in-diameter reference grade wire was enclosed in a 0.12-in-OD quartz protection tube and placed under the platinum holder. This thermocouple was used for programming as well as for recording and controlling the temperature of a sample. The Vycor reaction tube of 19 mm ID, with gas inlet near the top, enclosed the sample holder which, in turn, was connected to the weighing mechanism by a platinum wire. A ground glass joint with gas outlet was connected to the bottom of the tube to facilitate insertion of the thermocouple. A resistance furnace was used throughout this study.

Material

The chemical analysis of reagent grade anhydrous CuSO_4 is given in table 1. Copper (II) oxysulfate was prepared by heating copper (II) sulfate in air for 36 hr (with frequent rabbling) at 650°C . X-ray diffraction patterns of the product revealed a very small peak of CuSO_4 . High purity nitrogen and filtered air were passed through drying towers containing Drierite before entering the reaction chamber.

⁴Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 1. - Chemical analysis of anhydrous copper (II) sulfate

Analysis	Percent
CuSO ₄	99.8
Insoluble matter.....	0.006
Chloride.....	.0006
Substances not precipitated by H ₂ S (as SO ₄).....	.03
Iron (Fe).....	.003
<u>Ammonium sulfide metals, other than iron.....</u>	<u>.004</u>

Kinetic Method

Various methods have been utilized recently for the estimation of overall kinetic parameters from thermogravimetric traces. Freeman and Carroll's (3) method has been widely applied to estimate the energy of activation and the order of reaction from a single experimental thermogravimetric curve. If various transformations take place within a narrow temperature range, an overlapping of the reaction rate curve may be obtained. In such a case, using Freeman and Carroll's method, kinetic parameters for individual reactions would not be able to be determined.

In our study, Chatterjee's (2) simple and versatile method was employed. Chatterjee has applied this method successfully on the thermal decomposition kinetics of calcium oxalate monohydrate (CaC₂O₄·H₂O). Results compare favorably with the data reported in literature. It requires that two determinations be made with different sample weights under similar reaction conditions. The heterogeneous kinetic reaction can be represented by the following general equation for the rate, R:

$$R = - \frac{dw}{dt} = kw^n, \quad (1)$$

where k = reaction rate coefficient,

w = active weight of the reacting material,

t = time elapsed from the start of the experiment,

and n = pseudo order of reaction.

Mechanisms derived for a heterogeneous reaction from the pseudo order of reaction are of little intrinsic significance and, at best, represent a gross approximation. If k is expressed in terms of an Arrhenius equation, then

$$k = Ae^{-Q/RT}, \quad (2)$$

where A = preexponential term,

Q = apparent activation energy,

T = absolute temperature,

and R = molar gas constant.

Substituting equation 2 into equation 1,

$$R = Aw^n e^{-Q/RT} \quad (3)$$

or
$$n \log w - \log R = \frac{Q}{2.303RT} - \log A . \quad (4)$$

For thermograms obtained for two different initial weights of the starting substance under similar experimental conditions, equation 4 gives

$$n \log w_a - \log R_a = \frac{Q}{2.303RT} - C \quad (5)$$

and
$$n \log w_b - \log R_b = \frac{Q}{2.303RT} - C . \quad (6)$$

The pseudo order of the reaction, n , then can be determined from the equation

$$n = \frac{\log R_a - \log R_b}{\log w_a - \log w_b} . \quad (7)$$

Usually a series of n values are determined at various temperatures to determine whether n remains constant in the temperature range studied for a particular reaction. The value of Q can be determined by plotting ($n \log w - \log R$) versus $1/T$. The slope of the plot will give the value of $\frac{Q}{2.303R}$, and the intercept will equal the constant C .

EXPERIMENTAL PROCEDURE

Cylindrical pellets of 80 percent true bulk density, 0.56 cm diameter, and different height were made from CuSO_4 and $\text{CuO} \cdot \text{CuSO}_4$ powder under high compressive pressures. The height of the pellets varied from 0.14 cm to 0.56 cm. The TGA apparatus gave a continuous record of change in weight as a function of temperature. The pellet was heated at a constant rate of 6°C/min from room temperature to about 850°C in gas flowing at 190 cu cm/min. The recorded thermogram, representing the change in weight as a function of temperature, was utilized to calculate the kinetic parameters.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 represents an exploratory DTA trace that was run on CuSO_4 powder heated (12°C/min) in air flowing at 150 cu cm/min. The endotherms ϵ and ζ in

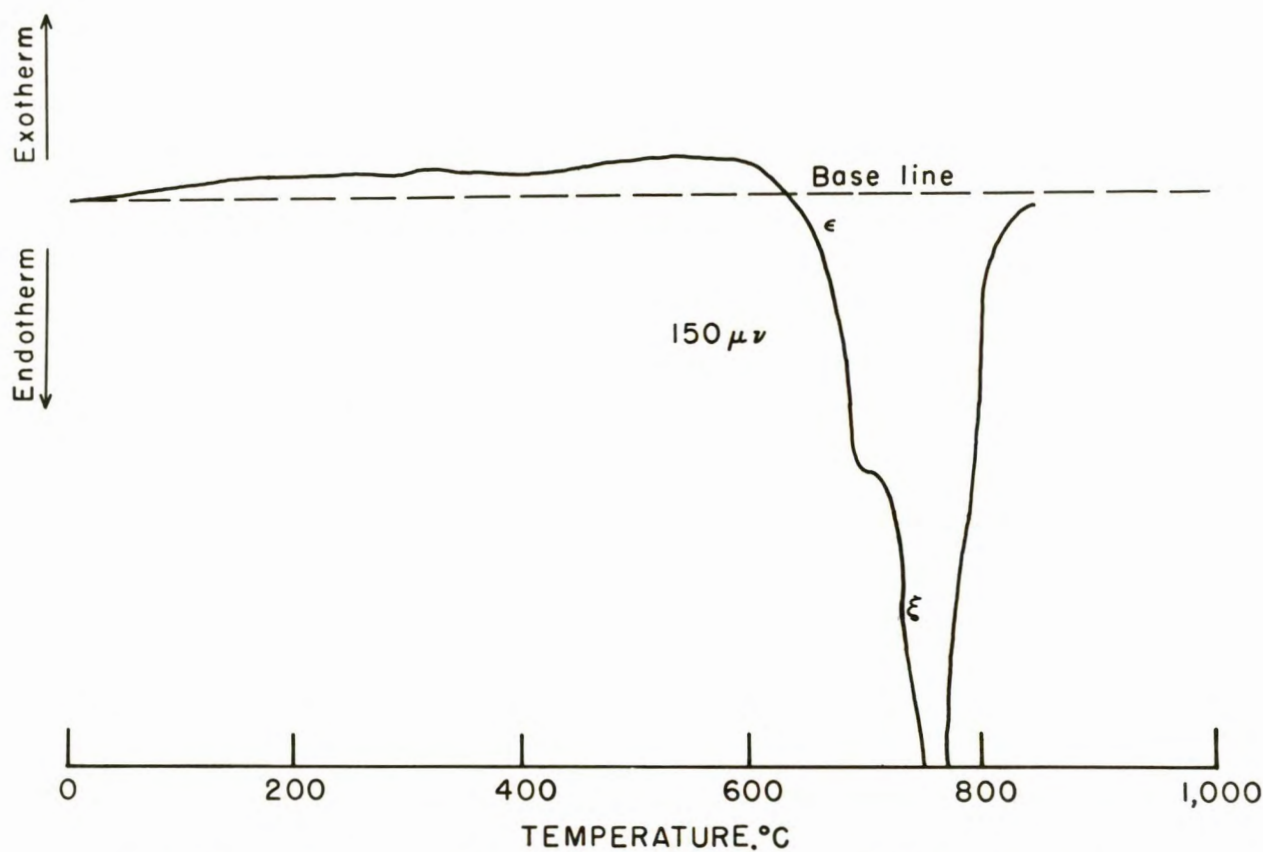
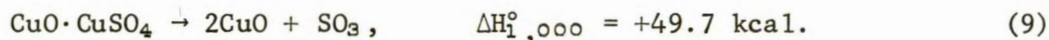
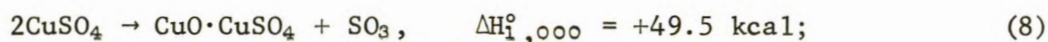


FIGURE 2. - Differential Thermal Analysis of Anhydrous CuSO_4 in Air Flowing at 150 cu cm/min.

figure 2 indicate that at approximately 600°C , CuSO_4 decomposes to $\text{CuO}\cdot\text{CuSO}_4$, and at about 700°C , $\text{CuO}\cdot\text{CuSO}_4$ decomposes to CuO as follows (7):



Similarly, when heated in the TGA equipment at $6^\circ\text{C}/\text{min}$ from room temperature in air flowing at 190 cu cm/min, CuSO_4 pellets began to decompose at about 600°C . According to equation 8, each 80 mg loss in weight due to SO_3 is associated with the formation of 240 mg of solid product copper oxysulfate. The active weight of copper sulfate, w , was therefore calculated from the instantaneous sample weight, w_t , by subtracting four times the weight loss from the initial weight of the sample. Thermograms a and b in figure 3 represent the variation in active weight of copper (II) sulfate with time, for pellets of different weights subjected to thermal decomposition in flowing air. Rate of heating was constant up to 700°C ; beyond that, slight variations in the heating rate were noticed. Instantaneous decomposition rate, R , as defined by equation 1, was determined by graphical differentiation of the thermograms in figure 3. Gravimetric data needed for determining Q and the kinetic parameter n are contained in table 2.

TABLE 2. - Thermogravimetric data for calculating the kinetic parameters for the thermal decomposition of CuSO_4 in air

Time, min	Temp, ° C	Sample number	Instantaneous weight, w_t , mg	Active weight, w , mg	$R = -\frac{dw}{dt}$, mg min ⁻¹	Log w	Log R	Reaction order, n	$1,000/T$, ° K ⁻¹	Log $w - \log R$
0	560	a	325	325	-	2.512	-	-	1.201	{ -
		b	136	136	-	2.133	-			
15	630	a	321	309	4.4	2.490	0.644	0.93	1.107	{ 1.846
		b	135	132	2.0	2.121	.301			
20	650	a	314	281	8.0	2.449	.903	1.00	1.083	{ 1.546
		b	132	120	3.4	2.079	.531			
25	675	a	301	229	13.0	2.360	1.114	1.05	1.055	{ 1.246
		b	126	96	5.2	1.982	.716			
30	700	a	281	149	17.6	2.173	1.245	1.14	1.028	{ 0.928
		b	119	68	7.2	1.832	.857			
32.5	710	a	269	101	22.8	2.004	1.358	-	1.017	{ .646
		b	114	48	8.8	1.681	.944			

Reaction order, n , was calculated from equation 7 at temperatures of 630°, 650°, 675°, and 700° C, and was found to be 1.03 ± 0.12 . Microscopic examination of the polished cross-section of the pellet showed a well-defined reactant-product interface. By normalizing the decrease in interfacial area with the weight fraction of the pellet decomposed, Ingraham and Marier (6) showed that the interface advanced into the pellet at a uniform rate at constant temperature. Present data support this finding.

A plot of $(n \log w - \log R)$ versus the reciprocal absolute temperature is shown in figure 4. From the slope of this curve (equation 4), the apparent activation energy, Q , is estimated to be 55 ± 2 kcal. Ingraham and Marier (6) reported an apparent activation energy of 57 ± 7 kcal for the thermal decomposition of CuSO_4 carried out isothermally in flowing nitrogen. Also, they have shown conclusively that an increase in the flow rate of N_2 progressively increased the thermal decomposition rate, but did not have an appreciable effect on the activation energy. The rate of CuSO_4 thermal decomposition in flowing air (190 cu cm/min) and at a constant heating rate (6° C/min) can be described by the equation

$$n \log w - \log R = \frac{12,000}{T} - 11.5, \quad (10)$$

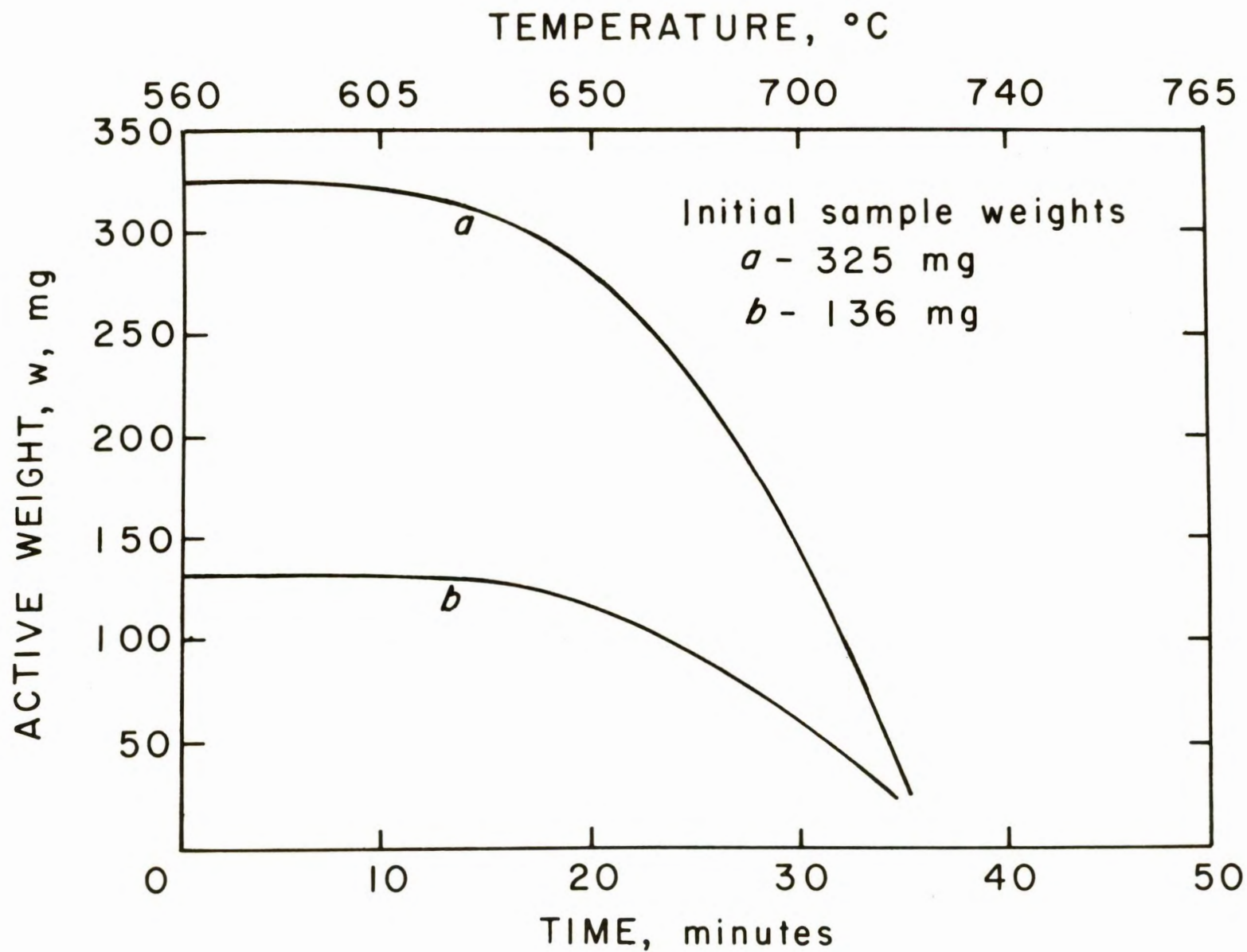


FIGURE 3. - Variation of Active Weight of Copper Sulfate With Both Time and Temperature.

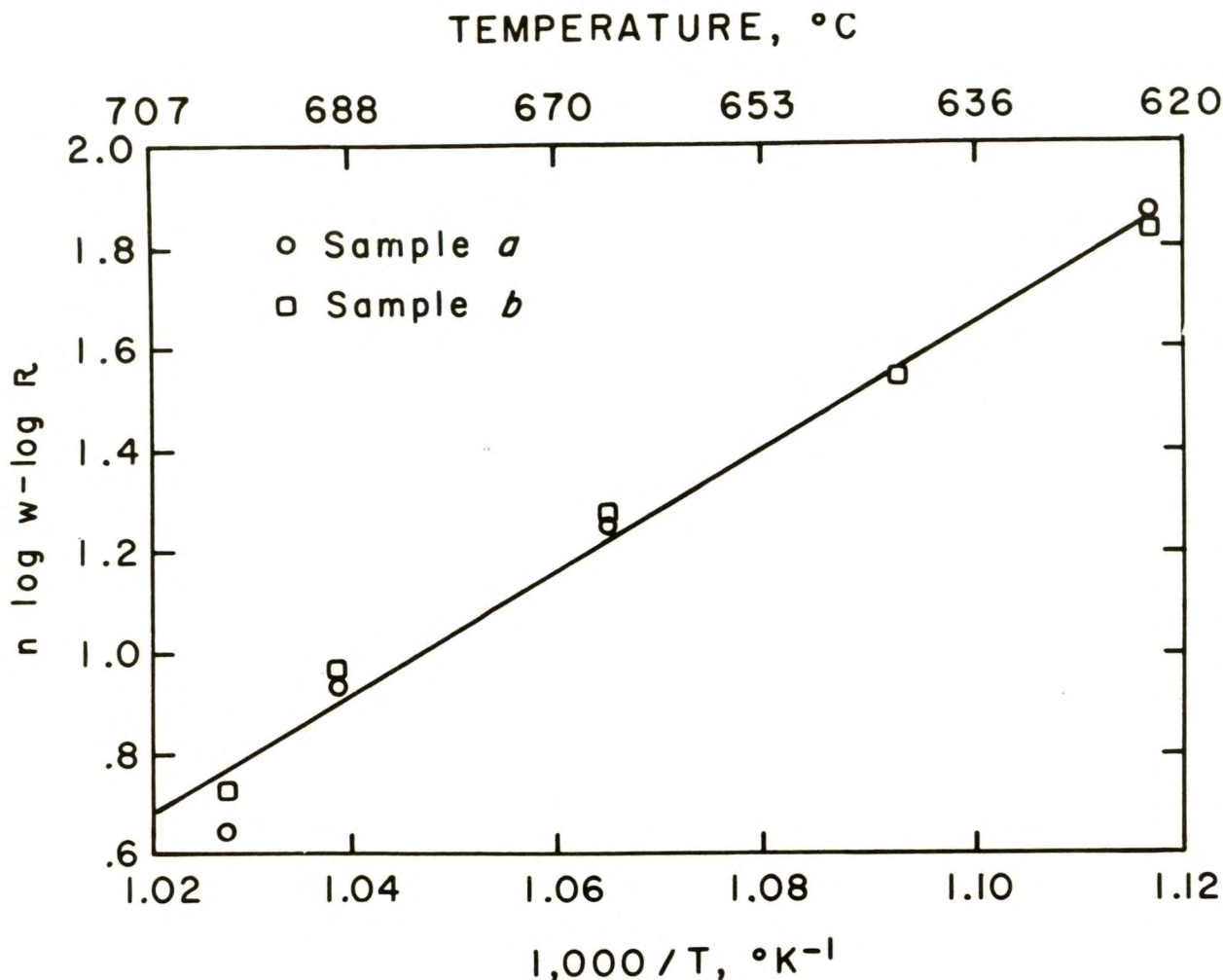


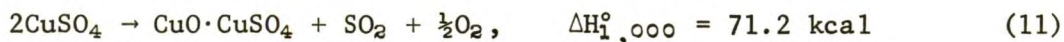
FIGURE 4. - Temperature Dependence of the Quantity ($n \log w - \log R$) for the Thermal Decomposition of CuSO_4 in Air.

where $n = 1$, the order of reaction,

w = active weight of the reactant,

and $R = -\frac{dw}{dt}$, the thermal decomposition rate.

The thermal decomposition of CuSO_4 (equation 8) is an endothermic reaction associated with the absorption of 49.5 kcal per mole of SO_3 formed. From this datum and newly determined activation energy, one can calculate a small activation energy of 6 ± 3 kcal for the complete sulfatization of copper oxysulfate. A further conclusion from the data is that the decomposition of CuSO_4 involves an initial formation of SO_3 which will later decompose to SO_2 and O_2 . Any mechanism based on reactions such as



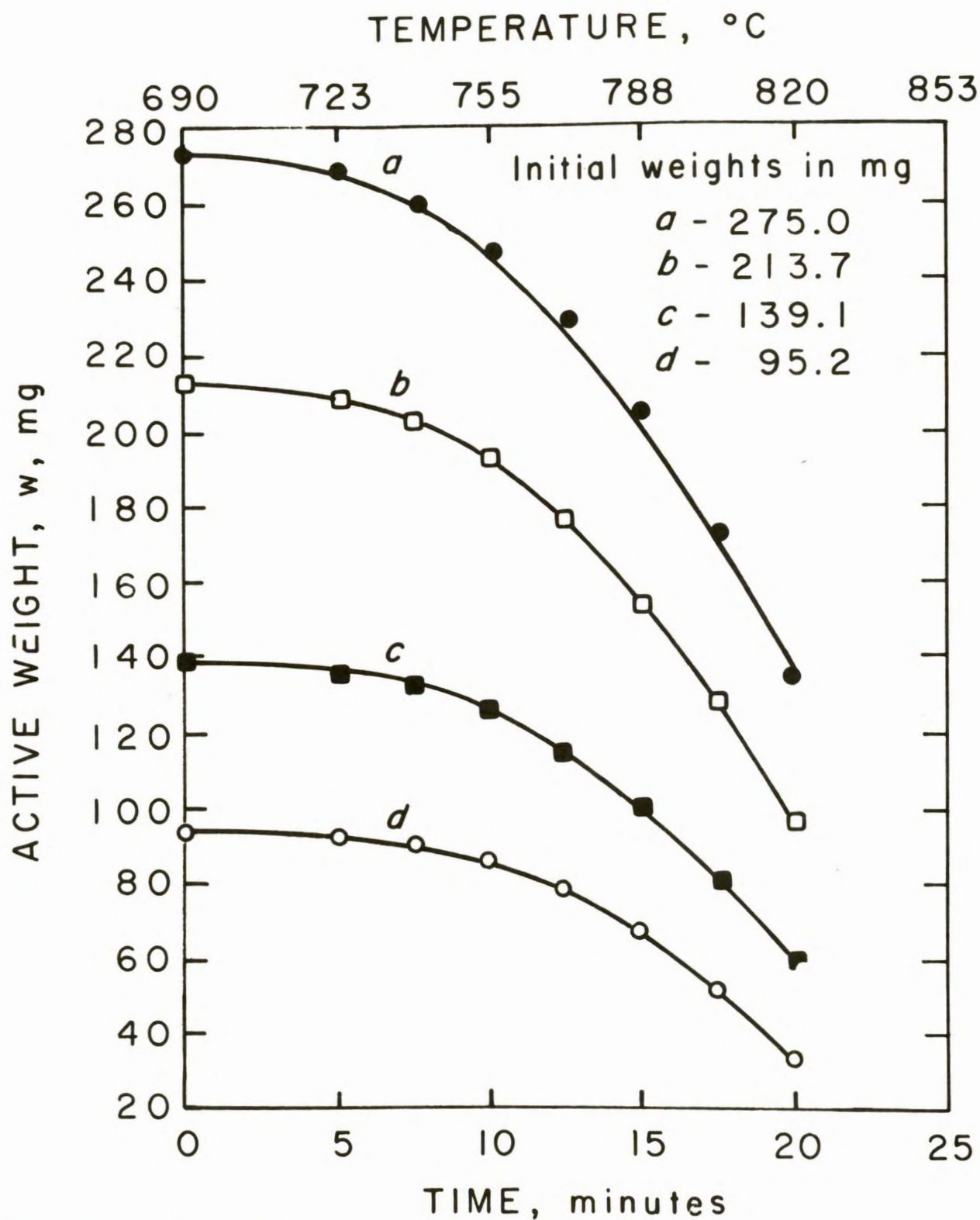


FIGURE 5. - Variation of Active Weight of Copper (II) Oxysulfate With Time and Temperature.

should be untenable since the height of the reaction potential energy barrier requires that $Q \geq \Delta H^\circ$ for an endothermic reaction.

Similar experiments were conducted to study the decomposition kinetics of copper (II) oxysulfate. Cylindrical pellets were heated at 6.5°C/min in air flowing at 190 cu cm/min . $\text{CuO} \cdot \text{CuSO}_4$ begins to decompose at about 690°C , yielding CuO and SO_3 as products (equation 9). Stoichiometrically, each 240 mg of copper (II) oxysulfate decomposes to yield 160 mg of solid CuO and 80 mg of gaseous SO_3 . The active weight, w , of $\text{CuO} \cdot \text{CuSO}_4$ was calculated from the instantaneous sample weight, w_t , by subtracting three times the sample weight loss from the initial weight of the sample. In the present work, final weight losses indicated on the thermograms were in agreement with theoretical values with an error of less than 1 percent.

Figure 5 shows the variation of active weight, w , of $\text{CuO} \cdot \text{CuSO}_4$ versus both time and temperature for the samples investigated. A Gerber derivimeter was used to obtain the slope, R , of these curves at selected points. The average pseudo order of reaction for the entire temperature range was determined to be 0.95 ± 0.20 . There was no calculation made on the last point of the thermograms in view of the uncertainties in their slopes. The polished section of the partially decomposed $\text{CuO} \cdot \text{CuSO}_4$ pellet revealed a concentric $\text{CuO} \cdot \text{CuSO}_4$ zone uniformly surrounded by a layer of CuO . For $\text{CuO} \cdot \text{CuSO}_4$ it has been shown (9) that the fractional thickness of the reaction product, f , was linear with respect to time. This linearity implies a uniform rate of interface advancement at constant temperature. From data in table 3, a plot of $(n \log w - \log R)$ versus reciprocal absolute temperature was constructed as shown in figure 6. Apparent activation energy, Q , is calculated to be $66 \pm 2 \text{ kcal}$. Thermal decomposition of $\text{CuO} \cdot \text{CuSO}_4$ in air could therefore be represented as

$$(n \log w - \log R) = \frac{14,400}{T} - 12.4 . \quad (12)$$

These results are in agreement with those of Ingraham and Marier (6), who reported an activation energy of $67 \pm 8 \text{ kcal}$ for the thermal decomposition of $\text{CuO} \cdot \text{CuSO}_4$ in flowing nitrogen. Since the heat of the $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition is 49.7 kcal , and the activation energy, Q , is determined to be $66 \pm 2 \text{ kcal}$, one can estimate a value of about 15 kcal for the sulfatization activation energy of CuO .

Similarly, the kinetics of $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition in flowing N_2 were determined and the data tabulated as shown in table 4. Thermal decomposition of $\text{CuO} \cdot \text{CuSO}_4$, heated at 6.5°C/min in N_2 flowing at 190 cu cm/min as shown in figure 7, could be described by a least squares regression line as

$$n \log w - \log R = \frac{13,400}{T} - 11.86 . \quad (13)$$

For comparison, the $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition in air is included in figure 7. These results clearly indicate that an increase of O_2 content in the flowing gas decreased the rate of thermal decomposition, but activation energy remained practically constant.

TABLE 3. - Thermogravimetric data for calculating the kinetic parameters for the thermal decomposition of CuO·CuSO₄ in air

Time, min	Temp, ° C	Sample number	Instantaneous weight, w _t , mg	Active weight, w, mg	$R = -\frac{dw}{dt}$, mg min ⁻¹	Log w	Log R	Average reaction order, n	1,000/T, ° K ⁻¹	Log w - log R
0	690	a	139.1	139.1	-	-	-	-	-	-
		b	95.2	95.2	-	-	-			-
		c	275.0	275.0	-	-	-			-
		d	213.7	213.7	-	-	-			-
5	723	a	138.2	136.4	1.13	2.135	0.053	1.03	1.004	2.082
		b	94.6	93.4	0.75	1.970	.125			2.095
		c	273.0	269.0	2.25	2.430	.352			2.078
		d	212.1	208.9	1.80	2.320	.255			2.065
7.5	739	a	136.9	132.5	1.94	2.122	.288	1.10	0.988	1.834
		b	93.9	91.3	1.30	1.961	.114			1.847
		c	270.2	260.6	4.10	2.416	.613			1.803
		d	210.1	202.9	3.10	2.307	.491			1.816
10	755	a	134.7	125.9	3.15	2.100	.498	0.97	.973	1.602
		b	92.4	86.8	2.15	1.939	.332			1.607
		c	266.2	248.6	6.00	2.396	.778			1.618
		d	206.7	192.7	4.85	2.285	.686			1.599
12.5	771	a	131.4	116.0	4.65	2.065	.667	.85	.956	1.398
		b	90.2	80.2	3.30	1.904	.518			1.386
		c	260.0	230.0	8.15	2.362	.911			1.451
		d	201.7	177.7	6.60	2.250	.820			1.430
15	788	a	126.7	101.9	6.95	1.995	.842	.79	.943	1.153
		b	86.4	68.8	4.90	1.838	.690			1.148
		c	252.4	207.2	11.50	2.303	1.067			1.236
		d	194.1	154.9	9.0	2.190	.954			1.236
17.5	804	a	120.0	81.8	8.4	1.912	.924	-	.929	0.988
		b	81.2	53.2	7.8	1.726	.892			.834
		c	241.4	174.2	15.5	2.241	1.190			1.050
		d	185.3	128.5	12.0	2.109	1.079			1.030

TABLE 4. - Thermogravimetric data for calculating the kinetic parameters for the thermal decomposition of $\text{CuO} \cdot \text{CuSO}_4$ in N_2

Time, min	Temp, °C	Sample number	Instantaneous weight, w_t , mg	Active weight, w , mg	$R = -\frac{dw}{dt}$, mg min^{-1}	Log w	Log R	$1,000/T$, K^{-1}	Log $w - \log R$
0	690	a	98.4	98.4	-	1.993	-	1.038	-
		b	227.3	227.3	-	2.357	-		-
		c	243.0	243.0	-	2.386	-		-
		d	153.6	153.6	-	2.186	-		-
5	720	a	97.0	94.2	1.9	1.974	0.279	1.007	1.695
		b	223.1	209.7	4.30	2.322	.634		1.688
		c	239.0	231.0	4.30	2.364	.634		1.730
		d	150.4	144.0	3.10	2.158	.491		1.667
7.5	735	a	95.0	88.2	3.1	1.945	.491	0.992	1.455
		b	218.3	195.3	6.7	2.291	.826		1.465
		c	234.8	218.4	6.3	2.339	.799		1.540
		d	146.9	133.5	4.8	2.126	.681		1.445
10	750	a	91.8	78.6	4.4	1.895	.643	.977	1.252
		b	211.5	174.9	9.2	2.243	.964		1.279
		c	229.0	201.0	8.8	2.303	.945		1.358
		d	142.0	118.8	6.7	2.075	.826		1.249
12.5	765	a	87.5	65.7	6.0	1.818	.778	.963	1.040
		b	203.3	150.3	11.5	2.177	1.061		1.116
		c	220.6	174.8	11.4	2.243	1.057		1.186
		d	135.5	99.3	8.3	1.997	.919		1.078
15	780	a	81.7	48.3	7.4	1.684	.869	.949	0.815
		b	192.3	117.3	14.0	2.069	1.146		.923
		c	210.4	145.2	14.1	2.162	1.149		1.013
		d	127.9	76.5	10.1	1.884	1.004		.880

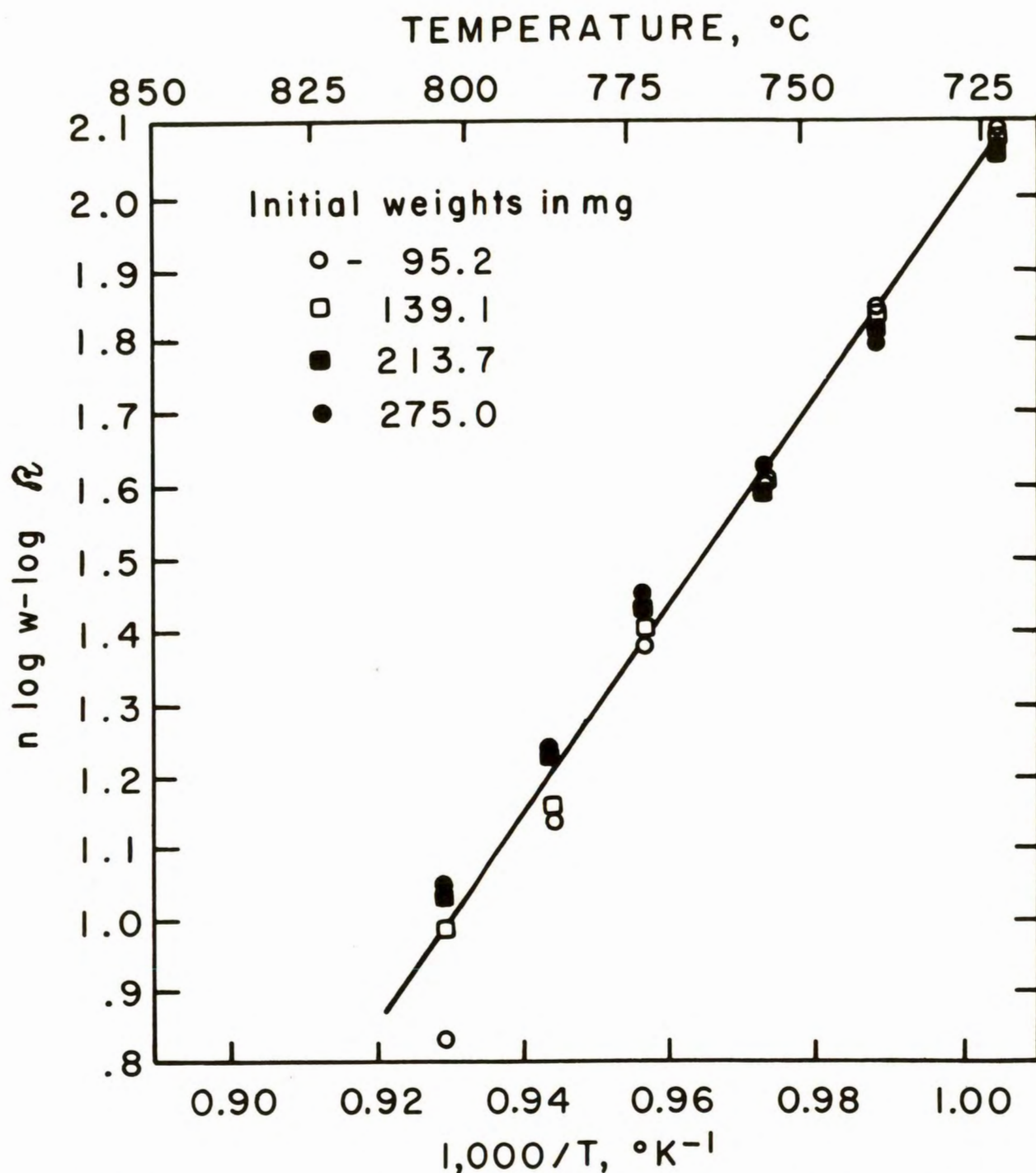


FIGURE 6. - Temperature Dependence of the Quantity ($n \log w - \log R$) for the Thermal Decomposition of Copper (II) Oxysulfate in Air.

It has been shown previously (8) that small amounts of externally added iron increase the rate and extent of sulfate formation during CuS roasting. The effect of iron on $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition was studied. It was

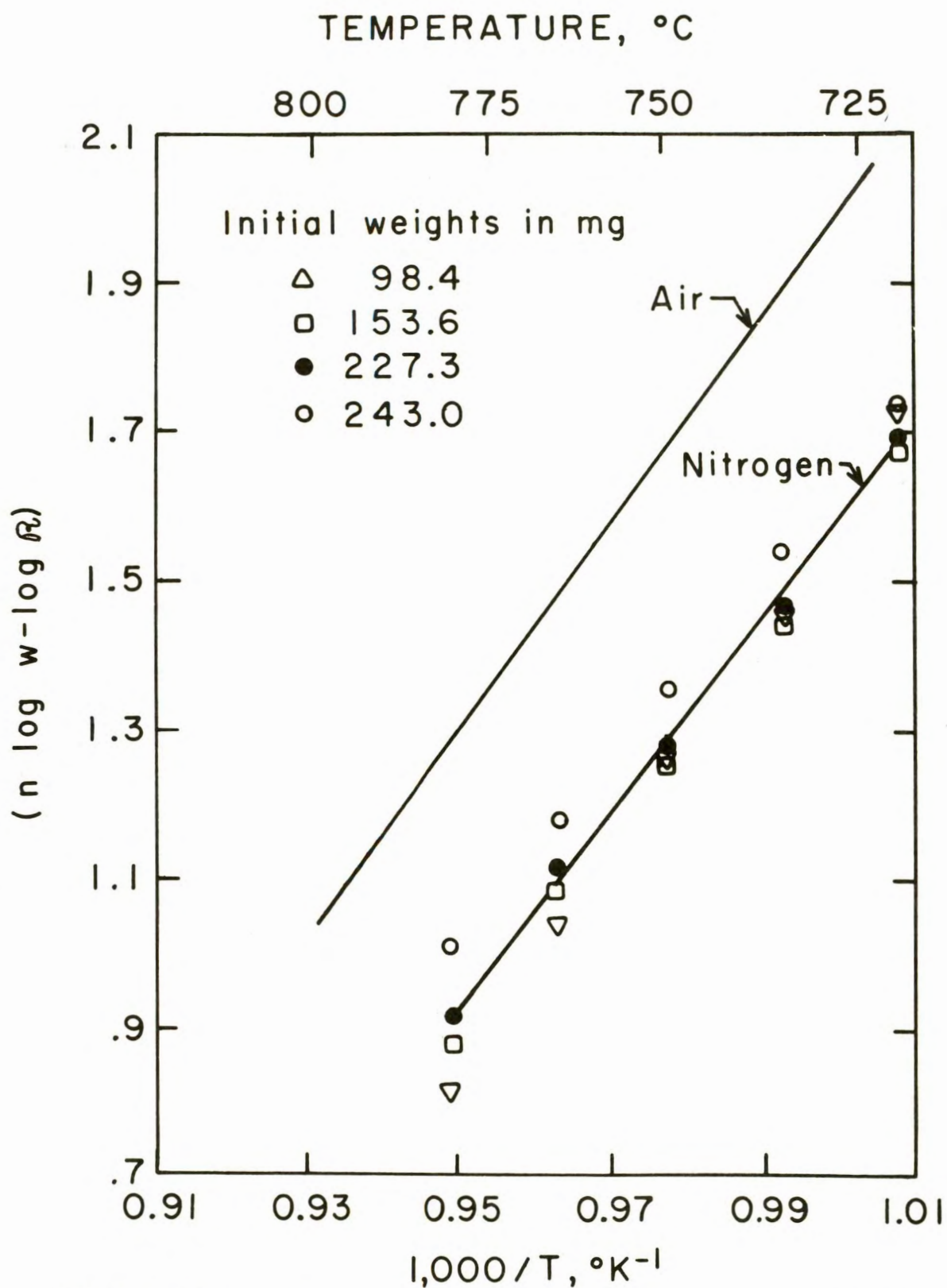


FIGURE 7. - Temperature Dependence of the Quantity $(n \log w - \log R)$ for the Thermal Decomposition of $\text{CuO} \cdot \text{CuSO}_4$ in N_2 .

found that the addition of 0.6 percent iron powder had no appreciable effect on the rate of $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition in air and nitrogen. Results for the thermal decomposition in air are tabulated in table 5. Figure 8 clearly indicates that externally added iron neither affects the rate nor the activation energy of $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition in air and nitrogen.

TABLE 5. - Thermogravimetric data for the thermal decomposition of $\text{CuO} \cdot \text{CuSO}_4$ in air in absence and presence of iron

Time, min	Temp, ° C	Instantaneous weight, w_t , mg	Active weight, w , mg	$R = -\frac{dw}{dt}$, mg, min ⁻¹	Log w	Log R	Log $w - \log R$	$1,000/T$, ° K ⁻¹
0	690	{ ¹ 139.1 153.4	139.1 153.4	- -	- -	- -	- -	-
5	723	{ 138.2 152.4	136.4 150.4	1.13 1.02	2.135 2.183	0.053 .009	2.082 2.174	1.004
7.5	739	{ 136.9 151.2	132.5 146.8	1.94 1.85	2.122 2.167	.288 .267	1.834 1.899	} 0.988
10	755	{ 134.7 149.0	125.9 140.2	3.15 3.05	2.100 2.147	.498 .484	1.602 1.622	} .973
12.5	771	{ 131.4 145.8	116.0 130.6	4.65 4.85	2.065 2.116	.667 .686	1.398 1.430	} .956
15.0	788	{ 126.7 141.9	101.9 118.9	6.95 6.47	1.995 2.075	.842 .811	1.153 1.264	} .943
17.5	804	120.0	81.8	8.4	1.912	.924	0.988	.929

¹Lower numbers in each row refer to samples containing iron.

In a recent publication, Hills (4) has shown that certain diagnostics of chemically controlled reactions, such as high activation energy and linear dependence of weight change per unit area with time, are also displayed in reactions controlled by heat and mass transport. He showed this to be particularly true for the thermal decomposition of CaCO_3 . The possibility of heat transfer as a controlling step in the thermal decomposition of CuSO_4 was therefore investigated. Figure 9 shows the temperature profiles in both N_2 and O_2 measured by a probe thermocouple placed near the pellet and a measuring thermocouple placed in the center of a reacting pellet at 643° C. It is apparent from these curves that the temperature of the pellet does not change appreciably during decomposition; heat transfer to the receding interface as a controlling step can be ignored.

The rate of thermal decomposition of copper-oxysulfate decreased as the partial pressure of O_2 in the flowing gas increased; the slowest rate was

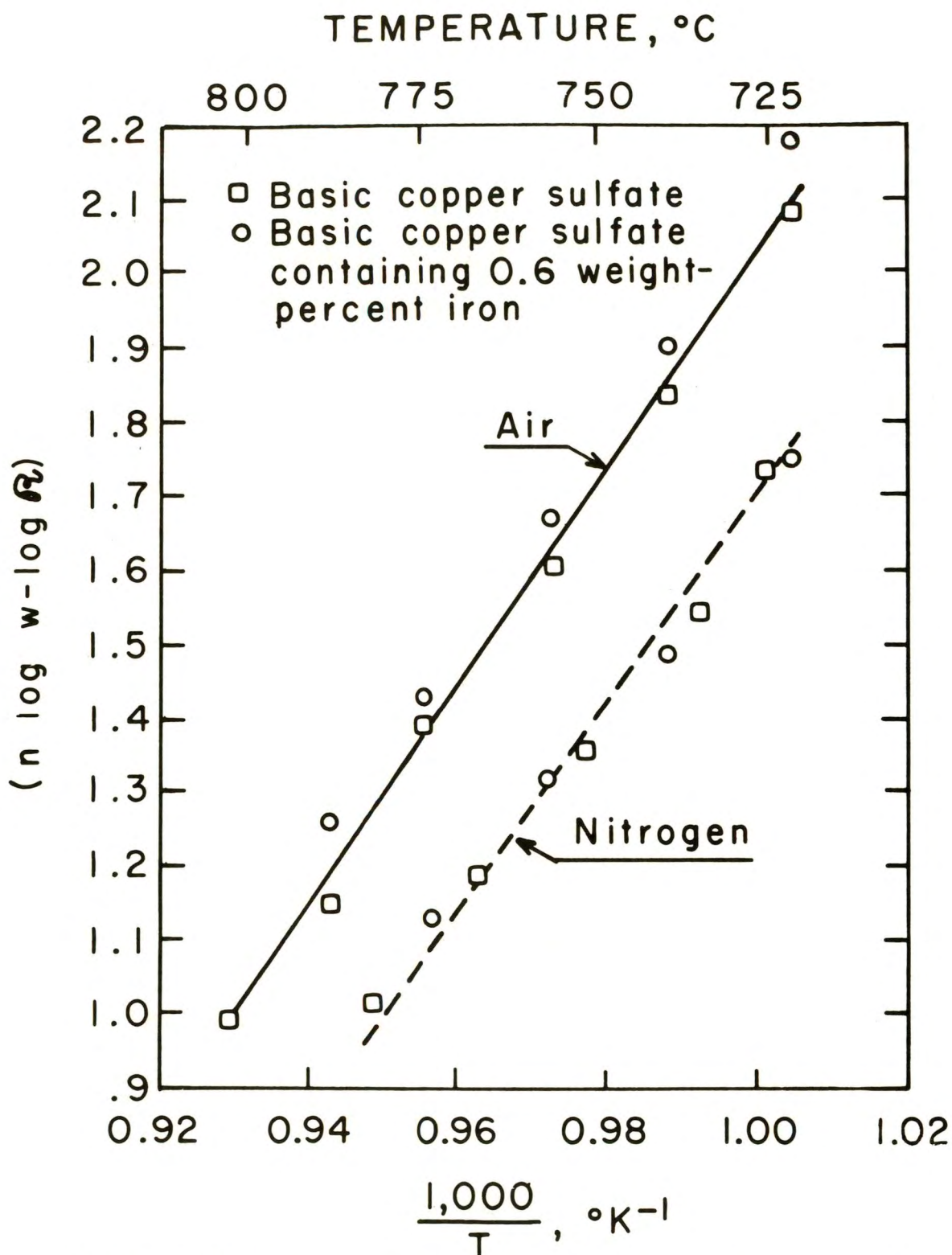


FIGURE 8. - Effect of Iron on the Kinetic Parameters for Thermal Decomposition of $CuO \cdot CuSO_4$ in Air and N_2 .

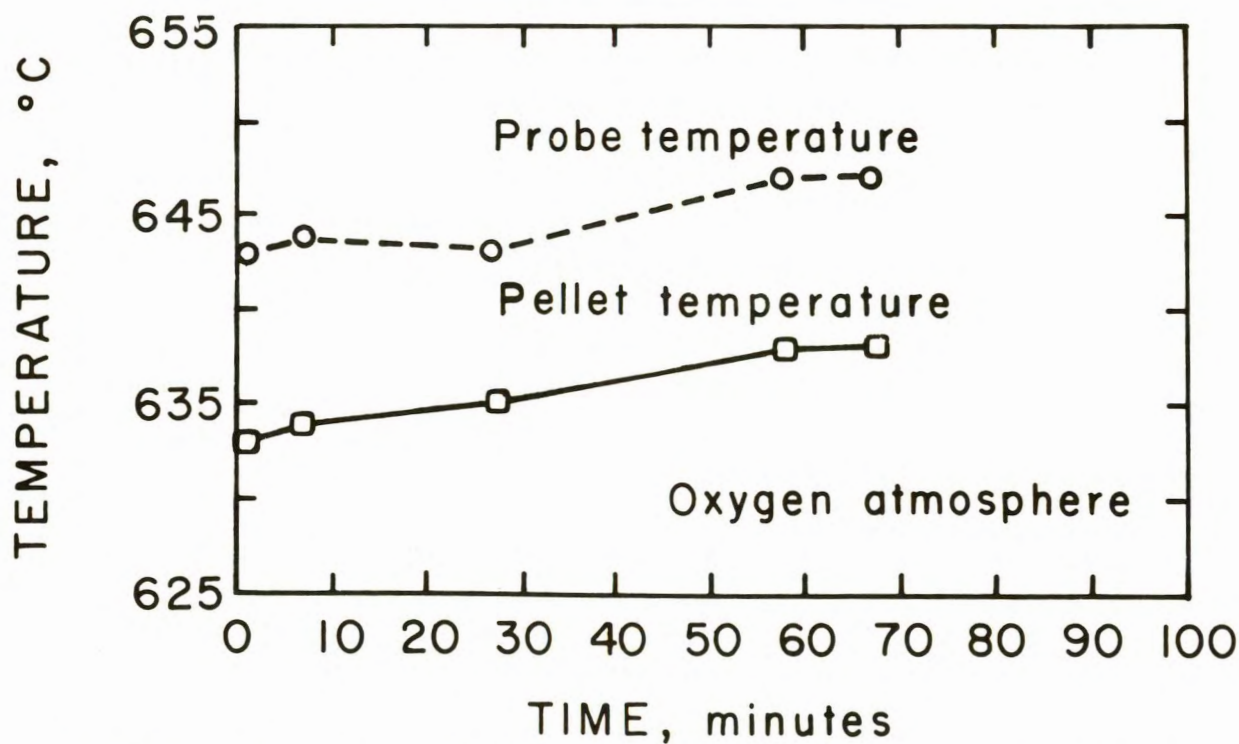
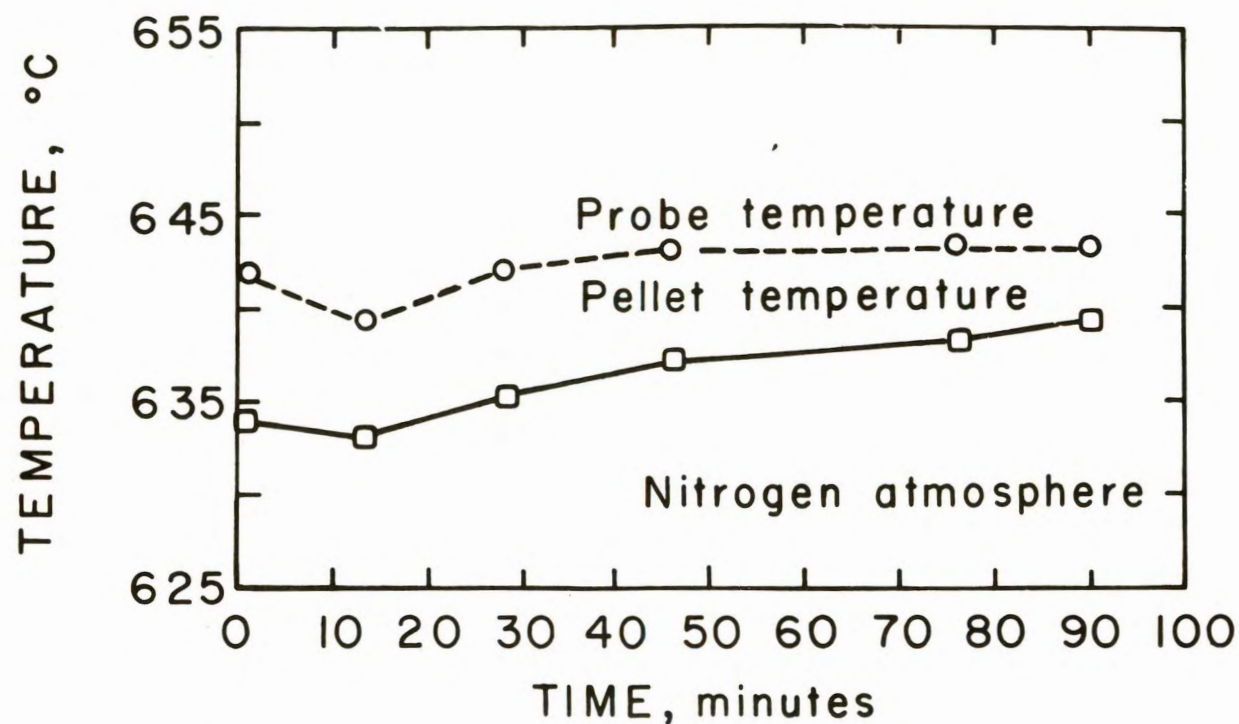


FIGURE 9. - Temperature of the Center of a Pellet and a Probe Temperature During the Thermal Decomposition of Copper (II) Sulfate at 643° C in N_2 and O_2 .

found in pure O_2 (fig. 10). This decrease could be due to the adsorption of oxygen which decreases the number of reactive sites on the reaction interface. This contention is in agreement with similar postulates of Ingraham and

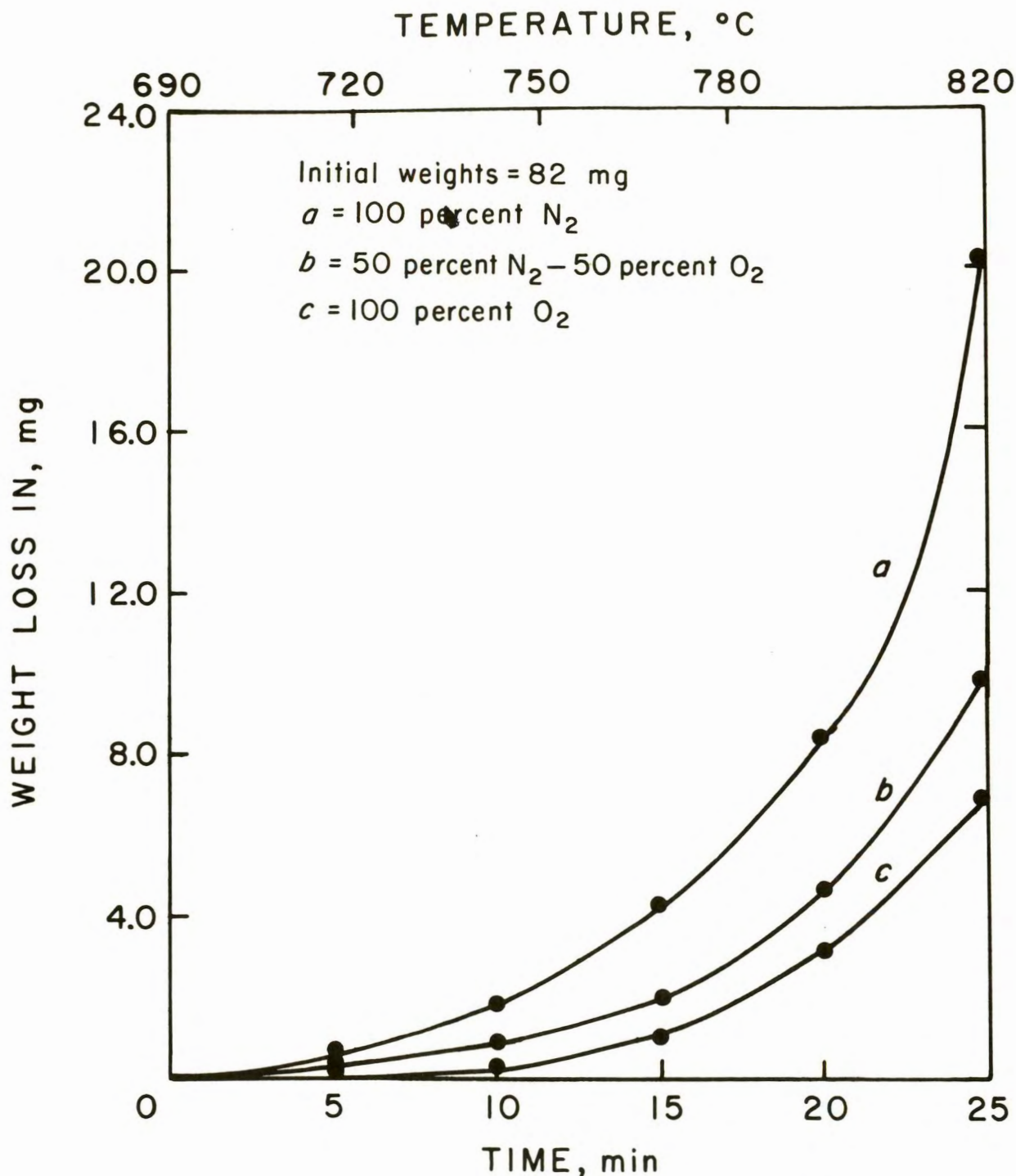


FIGURE 10. - Effect of Oxygen on the Thermal Decomposition of $CuO \cdot CuSO_4$.

Marier (6), who studied rates of the decomposition reaction in a flowing $\text{SO}_2\text{-O}_2$ gaseous mixture as a function of SO_3 partial pressure. Based on their experimental results, they postulated that the reaction rate may be controlled by SO_3 adsorption on the reaction interface. This coincides with the postulate that the presence of oxygen decreases the number of active sites on the reaction interface.

SUMMARY

Thermal decomposition of copper (II) sulfate in air followed "linear" kinetics with an apparent activation energy of 55 ± 2 kcal. Thermal decomposition of copper oxysulfate in both air and nitrogen followed "linear" kinetics with an apparent activation energy of 66 ± 3 kcal. An increase in oxygen content in the flowing gas progressively decreased the rate of $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition. Small quantities of iron powder, admixed with $\text{CuO} \cdot \text{CuSO}_4$, did not have an effect on the kinetics of $\text{CuO} \cdot \text{CuSO}_4$ thermal decomposition.

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