

STUDIES ON THERMAL DECOMPOSITION OF
AMMONIUM COPPER CHROMATE

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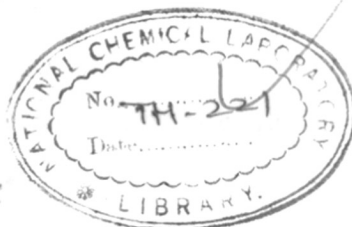
A Thesis Submitted to the
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PHYSICAL CHEMISTRY

by

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January 1978


[S. G. Pataskar]

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SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Copper chromite catalyst is an important commercial catalyst and has been extensively used for the industrial hydrogenation processes. It is known for its ability to hydrogenate functional groups in aliphatic and aromatic compounds selectively, without affecting the benzene nucleus. The thermal decomposition of ammonium copper chromate is one of the most important steps in the preparation of active copper chromite catalyst.

The present work was undertaken with the following objectives : [I] To study the DTA, TG and DGA of ammonium copper chromate and the phases of the solid products of thermal decomposition of ammonium copper chromate at different temperatures by X-ray diffraction and also by the chemical analysis of the solid products. [II] To establish the kinetics of thermal decomposition of ammonium copper chromate at the temperatures (275^o-350^oC) which are generally used for obtaining an active copper chromite catalyst for the vapour phase hydrogenation processes, viz. reduction of nitrobenzene and nitrotoluenes to the corresponding amines.

[I] THERMAL ANALYSIS OF AMMONIUM COPPER CHROMATE

The decomposition of ammonium copper chromate has been

studied by the TG, DGA and DTA in the temperature range 30° to 1000°C. The solid products of the decomposition in the various stages of decomposition were characterised by the chemical, X-ray and IR analysis. The results lead to the conclusion that the decomposition of ammonium copper chromate occurs in four stages as evidenced by the TG, DGA and DTA studies. The overall decomposition of ammonium copper chromate can be explained by the following reactions.

Decomposition at 250°-350°C

Major reaction:



Minor reaction:



Decomposition at 350°-500°C



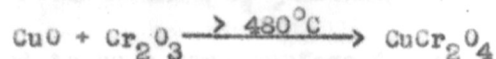
Decomposition at 780°-870°C



Decomposition at 960°-1000°C



Other Probable Side Reactions:



The decomposition of the γ -irradiated ammonium copper

chromate was also found to occur in the different stages as discussed above. However the γ -irradiation shifted the weight losses and the temperatures corresponding to the DGA or DTA peaks to the higher side. The increase in the decomposition (i.e. weight loss) may be due to the creation of an additional active centres for the nuclear growth. The shift of the DTA or DGA peak temperature to the higher side indicates the enhancement of the thermal stability of the ammonium copper chromate and also its solid product of decomposition because of γ -irradiation.

(II) KINETICS OF DECOMPOSITION OF AMMONIUM COPPER CHROMATE

The decomposition of ammonium copper chromate has been studied in the temperature range 275^o to 350^oC. The decomposition curves [fractional decomposition vs time] were of typical sigmoidal shape showing a rapid evolution of gases due to initial process of decomposition and a very short induction period followed by acceleratory and decay periods.

The initial process of decomposition could be expressed by the first order decomposition expression

$$\log (1-x) = C_1 - (k/2.3) t$$

and was found to be a true surface decomposition process as evidenced by the high activation energy [$E = 10.8 \text{ kcal gmol}^{-1}$].

In case of acceleratory and decay periods the decomposition data was fitted graphically to the contracting cube expression, the Avrami-Erofeev expression and the Prout-Tompkins expression.

Contracting cub expression: $1 - (1-x)^{1/3} = k(t + t_0)$

Avrami-Erofeev expression: $\left\{ \log [1/(1-x)] \right\}^{1/3} = (k'/2.3) (t + t'_0)$

Prout-Tompkins expression: $\log [x/(1-x)] = (k''/2.3) (t + t''_0)$

All these models were found to give a good graphical fit to the data. Further, the activation energy values for these models were nearly the same but the values of frequency factor were different.

The analysis of the residual sum of squares of these models showed that the Prout-Tompkins expression gives the best fit to the decomposition data. Further, the comparison between the variance of the three models [F-test] leads to the conclusion that the Prout-Tompkins rate expression fits the data more adequately than the other two models. Though the Avrami-Erofeev expression gives comparable fitting to the data at temperatures 275°, 300° and 350°C, it is less adequate at 325°C than the Prout-Tompkins expression. The average deviation of the estimated fractional decompositions from the observed ones have been found to be 2.7% for the Prout-Tompkins expression.

CHAPTER 1

INTRODUCTION

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INTRODUCTION

1.1 GENERAL

Copper chromite catalyst is an important commercial catalyst and has been extensively used for the industrial hydrogenation processes. It is known for its ability to hydrogenate functional groups in aliphatic and aromatic compounds selectively, without affecting the benzene nucleus. It is applied in both the liquid phase and the vapor phase hydrogenation processes. For example, it selectively hydrogenates the carbonyl group [1] in aldehydes, ketones and esters and converts them into the corresponding alcohols. Examples of gas phase reactions catalysed by copper chromite are the hydrogenation of nitrobenzene to aniline and of nitrotoluenes to toluidines. It is also used as an oxidation catalyst for the conversion of carbon monoxide in automobile exhaust. The thermal decomposition of ammonium copper chromate is one of the most important steps in the preparation of active copper chromite catalyst.

1.2 LITERATURE SURVEY : THERMAL DECOMPOSITION OF AMMONIUM

COPPER CHROMATE

The literature on the thermal decomposition of ammonium copper chromate is very scarce. Stroupe [2] studied the structure of CuCr_2O_4 and $\text{Cu}_2\text{Cr}_2\text{O}_4$ obtained from the thermal decomposition of ammonium copper chromate by x-ray analysis. The decomposition at relatively low temperature gave an equimolar mixture of CuO and CuCr_2O_4 , while at very high temperature $\text{Cu}_2\text{Cr}_2\text{O}_4$ was formed. Recently, Pashkova and co-workers [3] have collected kinetic data on the thermal decomposition of ammonium copper chromate in the temperature range 230° to 270°C . However the details on the kinetics and the rate models for the decomposition are not available. Goncharov and co-workers [4] have reported the application of thermal dilution method for the thermal analysis of ammonium copper chromate.

Shandilya and co-workers [5] have studied the crystal phases in the solid product of the decomposition of ammonium copper chromate prepared by the precipitation from a mixture of copper sulphate and potassium dichromate by aqueous ammonia with various molar ratios of CuO and ammonia and constant potassium dichromate concentration.

The precipitated phases observed were tetragonal $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$ - [i] at $\text{CuO} : \text{NH}_3 = 1 : 7$, major phase was $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$ and minor phase was CuSO_4 , $3 \text{Cu}(\text{OH})_2$; [ii] at $\text{CuO} : \text{NH}_3 = 1.12 : 25$, major phase was CuSO_4 , $3 \text{Cu}(\text{OH})_2$ and minor phase was $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$; [iii] at $\text{CuO} : \text{NH}_3 = 1 : 18$ with heating of a sample initially containing mostly $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$, the major phases observed were $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$ at $< 200^\circ\text{C}$; $\text{CuCrO}_4 + \text{CuO}$ at 300°C ; CuO , CuCr_2O_4 at 400°C ; $\text{CuO} + \text{orthorhombic CuCr}_2\text{O}_4$ ($a = 4.8$, $b = 3.895$, $c = 3.000 \text{ \AA}$) at 600 to 800°C ; and $\text{Cu}_2\text{Cr}_2\text{O}_4$ at 900° to 1000°C .

1.3 SCOPE OF THE PRESENT WORK

As seen from the existing information reviewed briefly on thermal decomposition of ammonium copper chromate, following conclusions may be drawn: [i] No study has been reported on the thermogravimetric analysis and differential thermal analysis of ammonium copper chromate. [ii] Little information regarding kinetic and rate models for thermal decomposition of ammonium copper chromate is available.

The present work was therefore undertaken with the following objectives:

- [a] To study the DTA, TG and DGA of ammonium copper chromate and the phases of the solid

products of thermal decomposition of ammonium copper chromate at different temperatures by x-ray diffraction and also by the chemical analysis of the solid products.

- [b] To establish the kinetics of thermal decomposition of ammonium copper chromate at the temperatures (275-350°C) which are generally used for obtaining an active copper chromite catalyst for the vapour phase hydrogenation processes, viz. reduction of nitrobenzene and nitrotoluenes to the corresponding amines.

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4. Goncharov, S. P.; Merzhanov, A. G.; Shteinberg, A. S. and Ledovskaya, N. A. (USSR) Tr. Gos. Inst. Prikl. Khim. 68 [1973], 60-6. [Russian] [CA, 82, 1975, 77578. (u)].
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CHAPTER 2

**THERMAL ANALYSIS OF AMMONIUM
COPPER CHROMATE**

CHAPTER 2THERMAL ANALYSIS OF AMMONIUM COPPER CHROMATE2.1 INTRODUCTION

Decomposition of ammonium copper chromate is one of the most important steps in the preparation of copper chromite catalyst. The physico-chemical and catalytic properties of this catalyst are affected by the temperature of the decomposition and also by the conditions or atmosphere used during the decomposition. Further, the preparation conditions of ammonium copper chromate [e.g. $\text{CuO} : \text{NH}_3$ ratio, way of precipitation, temperature, etc.] and the starting chemicals used for the preparation may also affect the products of decomposition. Very little information is available on the thermal decomposition of ammonium copper chromate to various gaseous and solid products in the temperature range 100° to 1000°C .

The present investigation consists of the study of thermal gravimetric analysis [TGA] and differential thermal analysis [DTA] of ammonium copper chromate and the solid products of the decomposition in the temperature range 300° to 1000°C by X-ray diffraction, IR spectroscopic,

and chemical analysis.

2.2 EXPERIMENTAL

2.2.1 Chemicals

Chemicals used for the preparation of ammonium copper chromate were as follows:

1. Cupric Nitrate trihydrate [B.D.H. L.R.]
2. Ammonium Dichromate [B.D.H. L.R.]
3. Liquor Ammonia 28% [C.P.]

Chemicals used for the chemical analysis were as follows:

1. Sodium Peroxide [A.R.B.D.H.]
2. Sodium Hydroxide Pellets [A.R.B.D.H.]
3. Ferrous Ammonium Sulphate [A.R.]
4. N-Phenyl Anthranilic Acid indicator
5. Phosphonic Acid [C.P.]
6. Hydrochloric Acid [A.R.]
7. Potassium Dichromate [A.R.B.D.H.]

2.2.2 Preparation of Ammonium Copper Chromate

Ammonium copper chromate was prepared by a method similar to that described by Adkins and Connor [1] [i.e. co-precipitating it from a solution containing cupric nitrate and ammonium dichromate with aqueous ammonia at room temperature and at pH 7-7.2]. Resulting precipitate was filtered under vacuum using buckner funnel, washed with

distilled water until it was free from nitrate ions. The filtered cake was dried in an air oven at 80° - 100°C for 24 hours. The dried mass was powdered to 200 mesh size and preserved in a dessicator.

Y-Irradiation of Ammonium Copper Chromate:

Y-Irradiated sample was prepared by irradiating the ammonium copper chromate by Y-rays using Gamma Cell-220 at the dose rate 22.65 Krcel/hr for 72 hrs.

2.2.3 DTA/TGA/DGA

The DTA/TGA/DGA thermograms of ammonium copper chromate were taken on an automatic unit MOM BUDAPEST DERIVATOGRAPH [Type 00-102 B] with following details:-

1. Sample size : 200 mg
2. Reference compound : α -Alumina
3. Sample pretreatment : Sample 200 mesh dried at 80°C for 24 hours
4. Sample holder : Platinum crucible resting on thermocouple lead
5. Temperature Range : 25° to 1100°C
6. Linear heating Rate : 10°C/min
7. Atmosphere : In air under suction

2.2.4 Isothermal Decomposition of Ammonium Copper Chromate

The isothermal decomposition of ammonium copper

chromate has been studied using the set-up shown in Fig. [2.1]. The total weight loss on decomposition was determined from the initial and final weight of the decomposition tube. The gas evolved during decomposition was measured by collecting it over water. The gas collected in the gas collector was measured by measuring accurately the water displaced by the gas. The amount of water formed during decomposition was measured by absorbing it in calcium chloride trap and knowing the initial and final weights of the trap. In order to check up an evolution of ammonia during the decomposition, the decomposition gases were bubbled through 0.1 N Hydrochloric acid and the change in the hydrochloric acid concentration was determined.

2.2.5 Preparation of Solid Samples for X-ray and Chemical Analysis

The solid samples were prepared by decomposing ammonium copper chromate for 24 hours at the required temperature [310°, 400°, 500°, 750° and 1000°C]. The temperatures for the decomposition were chosen by studying the DTA/TGA thermograms.

2.2.6 X-ray Analysis

X-ray diffraction patterns of the solid products of the decomposition were obtained using a Debye-Scherrer

- 1 DECOMPOSITION TUBE
- 2 FURNACE
- 3 Hg MANOMETER
- 4 $CaCl_2$ TRAP
- 5 GAS INLET TUBE
- 6 GAS COLLECTOR
- 7 WATER RESERVOIR
- 8 PRESSURE ADJUSTING DEVICE
- 9 GRADUATED BURETTE

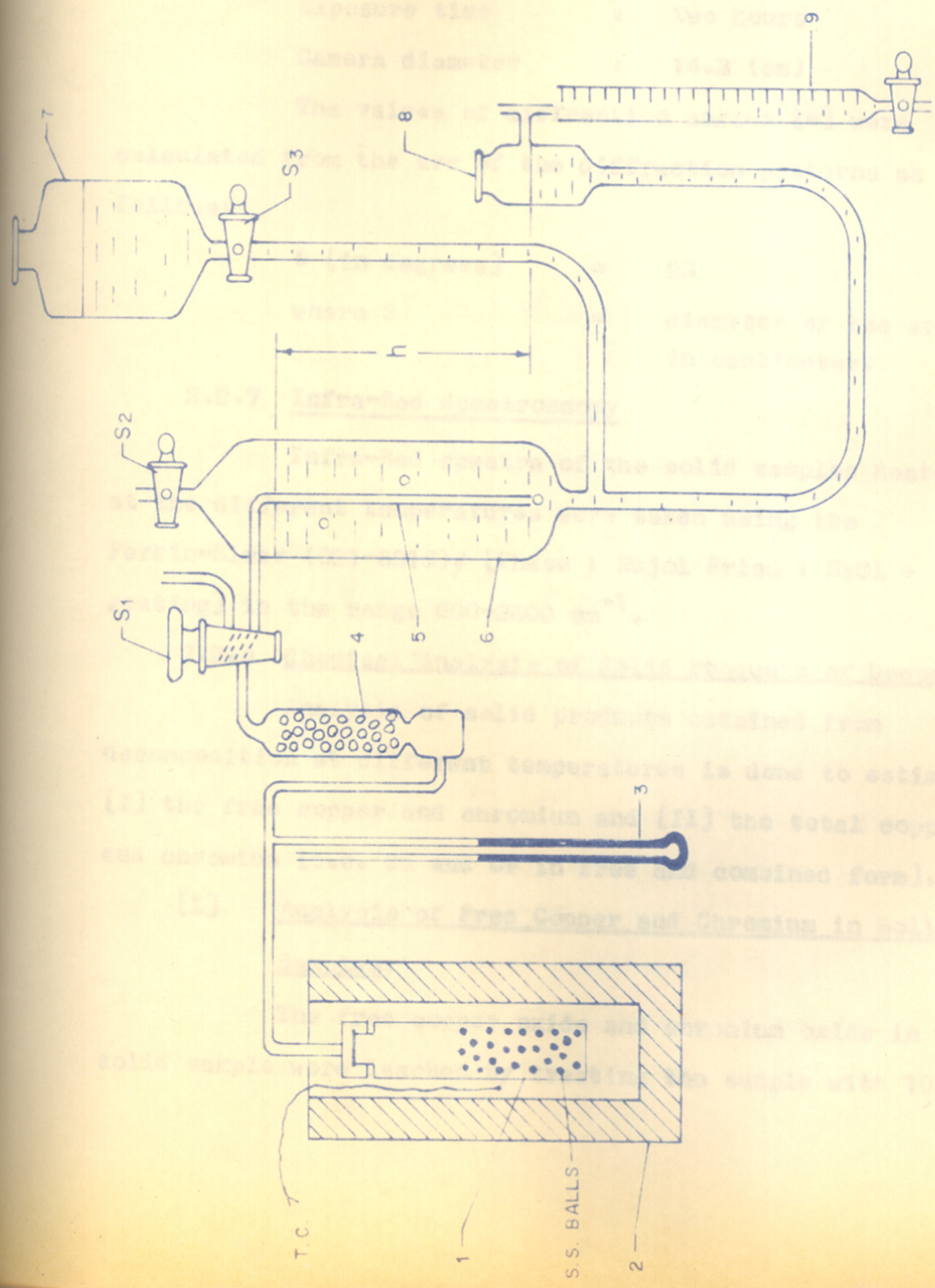


FIG. 2-1 EXPERIMENTAL SETUP FOR THE DECOMPOSITION

camera with the following details:

X-ray Radiation : $\lambda = 0.70926$ [Source-
Mo K α , filter Zirconium]
Exposure time : Two hours
Camera diameter : 14.3 (cm)

The values of diffraction angles $[\theta]$ were calculated from the arc of the diffraction patterns as follows:

θ [in degrees] = 2S
where S = diameter of the arc
in centimeter.

2.2.7 Infra-Red Spectroscopy

Infra-Red spectra of the solid samples heated at the different temperatures were taken using the Perkin-Elmer (021-6318) [Phase : Nujol Prism : NaCl + grating] in the range 600-3800 cm^{-1} .

2.2.8 Chemical Analysis of Solid Products of Decomposition

Analysis of solid products obtained from decomposition at different temperatures is done to estimate [I] the free copper and chromium and [II] the total copper and chromium [i.e. Cu and Cr in free and combined form].

[I] Analysis of Free Copper and Chromium in Solid

Samples:

The free copper oxide and chromium oxide in the solid sample were leached by treating the sample with 10% HCl

for 24 hours. The filtrate containing copper and chromium was further quantitatively analysed. The residue which contained copper and chromium in the combined form [i. e. copper chromite] was dried at 80°C in vacuum oven for 24 hours and weighed. Copper and chromium in the combined form as copper chromite were calculated as follows:

$$\text{wt\% of copper chromite} = \frac{\text{wt. of residue}}{\text{wt. of sample}} \times 100$$

[II] Analysis of Total Copper and Chromium in the Solid Samples

A known amount of the solid sample is fused with a mixture of sodium peroxide (Na_2O_2) and sodium hydroxide (NaOH) in a nickel crucible, initially heating on a low flame and finally upto a red hot. The fused mass after cooling was leached with distilled water and boiled to decompose the excess of peroxide. This gave a clear yellow solution which was further analysed for its copper and chromium contents.

Analysis of copper and chromium was performed by the procedures discussed in details elsewhere [2].

Analysis of Copper by Electrolytic Method

A known volume of solution [say 50 ml] was used for the electrolysis. About 1 ml con. H_2SO_4 and 2 ml con. HNO_3 were added to the solution and the electrolysis

was carried out using platinum screened electrode initially at a current of 1 amp. The current was then gradually increased to 4 amps. The electrolysis was carried out till no more copper remained in the solution. The platinum cathode was washed with distilled water and then with acetone and dried in vacuum oven, and weighed. The increase in the weight of the cathode gave the total amount of copper present in the solution.

% of copper in sample [free or combined] /

$$= \frac{Z \cdot Y}{V \cdot W} \times 100$$

where W = weight of sample (g)

Y = total volume of solution (ml)

Z = weight of copper deposited during electrolysis of copper contained in V (ml) of solution (g).

Analysis of Chromium by Ferrous Ammonium Sulphate Method

A known volume of solution [say 50 ml] was pipetted from the made up solution and a 50 ml of 0.1 N ferrous ammonium sulphate was added together with 200 ml of 2 N sulphuric acid and 0.5 ml of N-phenyl anthranilic acid as ^{an} indicator. The mixture was titrated with 0.1 N $K_2Cr_2O_7$ till green colour changes to violet red.

Similarly, a blank titration was carried out and, from the difference, the amount of chromium present in the solution was determined.

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In case of analysis of free chromium in the sample, the solution was boiled with H_2O_2 with 1 ml of 0.1 N $AgNO_3$ to convert Cr^{+3} to Cr^{+6} and then analysed for the chromium by the procedure described above.

Calculation :

1 ml of 1 N ferrous ammonium sulphate
 \equiv 1 ml of 1 N potassium dichromate solution
 \equiv 0.01734 g Cr/
 \equiv 0.02534 g Cr_2O_3

wt% Cr in the sample [free or combined] was calculated by using the relation:

$$wt\% Cr = 1.734 \frac{V \cdot D \cdot N}{W}$$

where N = Normality of $K_2Cr_2O_7$

V = Titer value (ml)

W = wt. of sample (g)

D = Multiplication factor (i.e. volume of total solution/volume of solution taken for analysis)

2.3 RESULTS AND DISCUSSION

2.3.1 Thermogravimetric and Differential Thermal Analysis

2.3.1.1 TGA, DGA and DTA of Ammonium Copper Chromate

The TG, DGA and DTA curves for the ammonium copper chromate have been shown in Figs. 2.2 and 2.3.

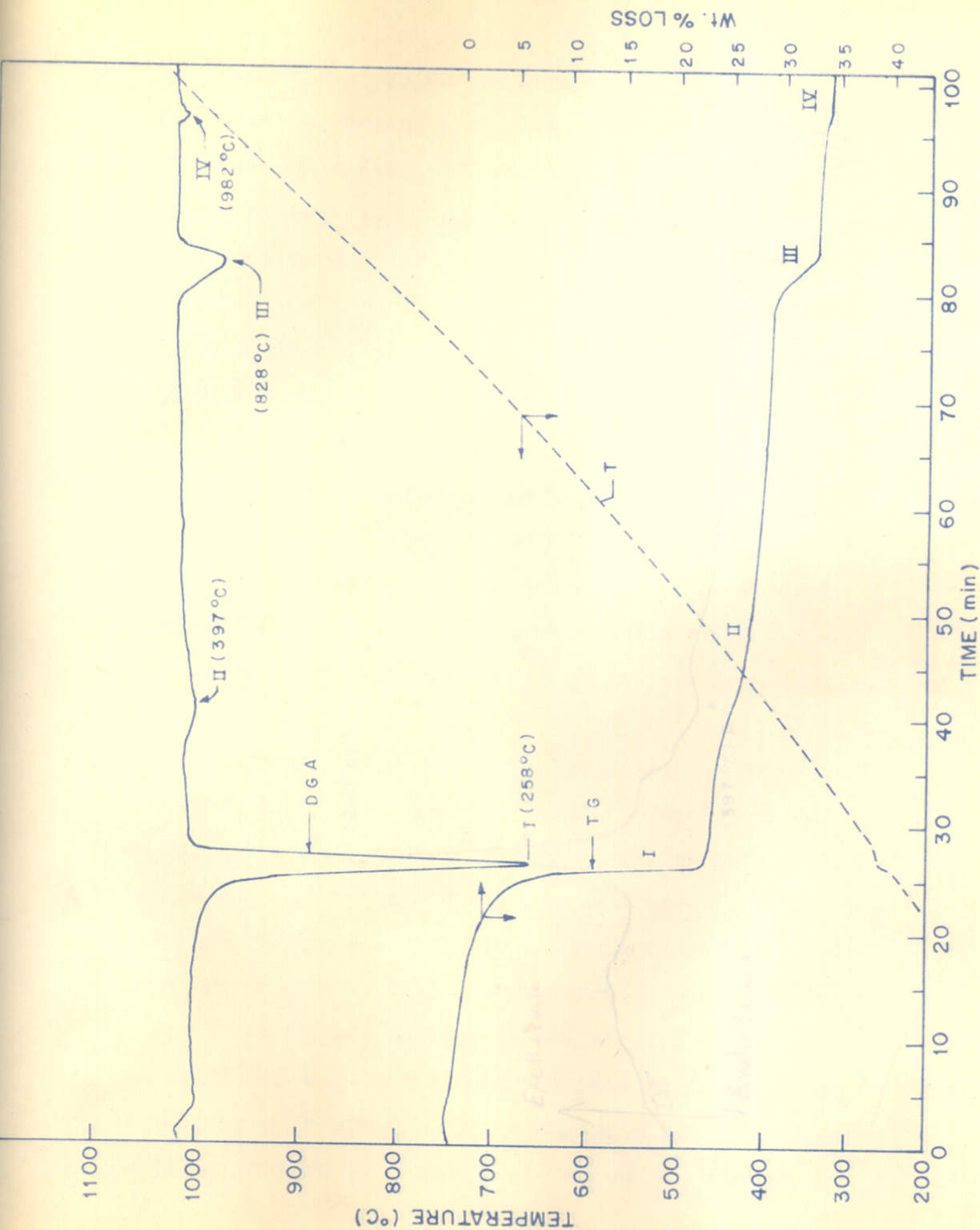


FIG. 2-2 THERMAL GRAVIMETRIC AND DIFFERENTIAL THERMAL GRAVIMETRIC CURVES FOR AMMONIUM COPPER CHROMATE

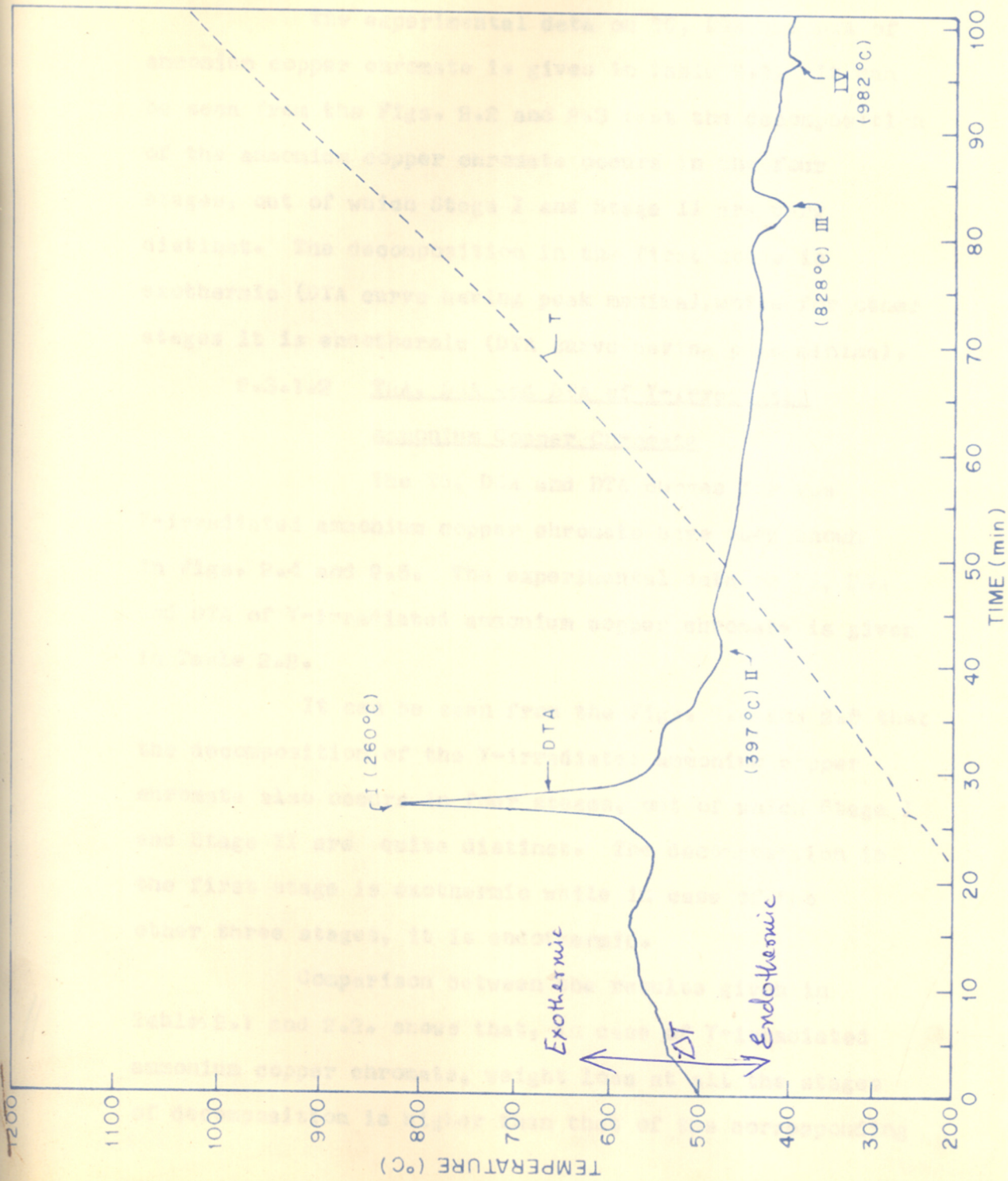


FIG 2-3 DIFFERENTIAL THERMAL ANALYSIS CURVE FOR AMMONIUM COPPER CHROMATE

The experimental data on TG, DGA and DTA of ammonium copper chromate is given in Table 2.1. It can be seen from the Figs. 2.2 and 2.3 that the decomposition of the ammonium copper chromate occurs in the four stages, out of which Stage I and Stage II are very distinct. The decomposition in the first stage is exothermic (DTA curve having peak maxima), while for other stages it is endothermic (DTA curve having peak minima).

2.3.1.2 TGA, DGA and DTA of Y-Irradiated Ammonium Copper Chromate

The TG, DGA and DTA curves for the Y-irradiated ammonium copper chromate have been shown in Figs. 2.4 and 2.5. The experimental data on TG, DGA and DTA of Y-irradiated ammonium copper chromate is given in Table 2.2.

It can be seen from the Figs. 2.4 and 2.5 that the decomposition of the Y-irradiated ammonium copper chromate also occurs in four stages, out of which Stage I and Stage II are quite distinct. The decomposition in the first stage is exothermic while in case of the other three stages, it is endothermic.

Comparison between the results given in Tables 2.1 and 2.2. shows that, in case of Y-irradiated ammonium copper chromate, weight loss at all the stages of decomposition is higher than that of the corresponding

TABLE 2.1

Experimental Results of TG, DGA and DTA of
Ammonium Copper Chromate

Stage No./ Peak No.	wt% loss	Temperature (°C)		Peak characteristic
		DGA Peak	DTA Peak	
I	24.0	258	260	exothermic
II	4.0	397	397	Endothermic
III	5.3	828	828	Endothermic
IV	0.7	982	982	Endothermic

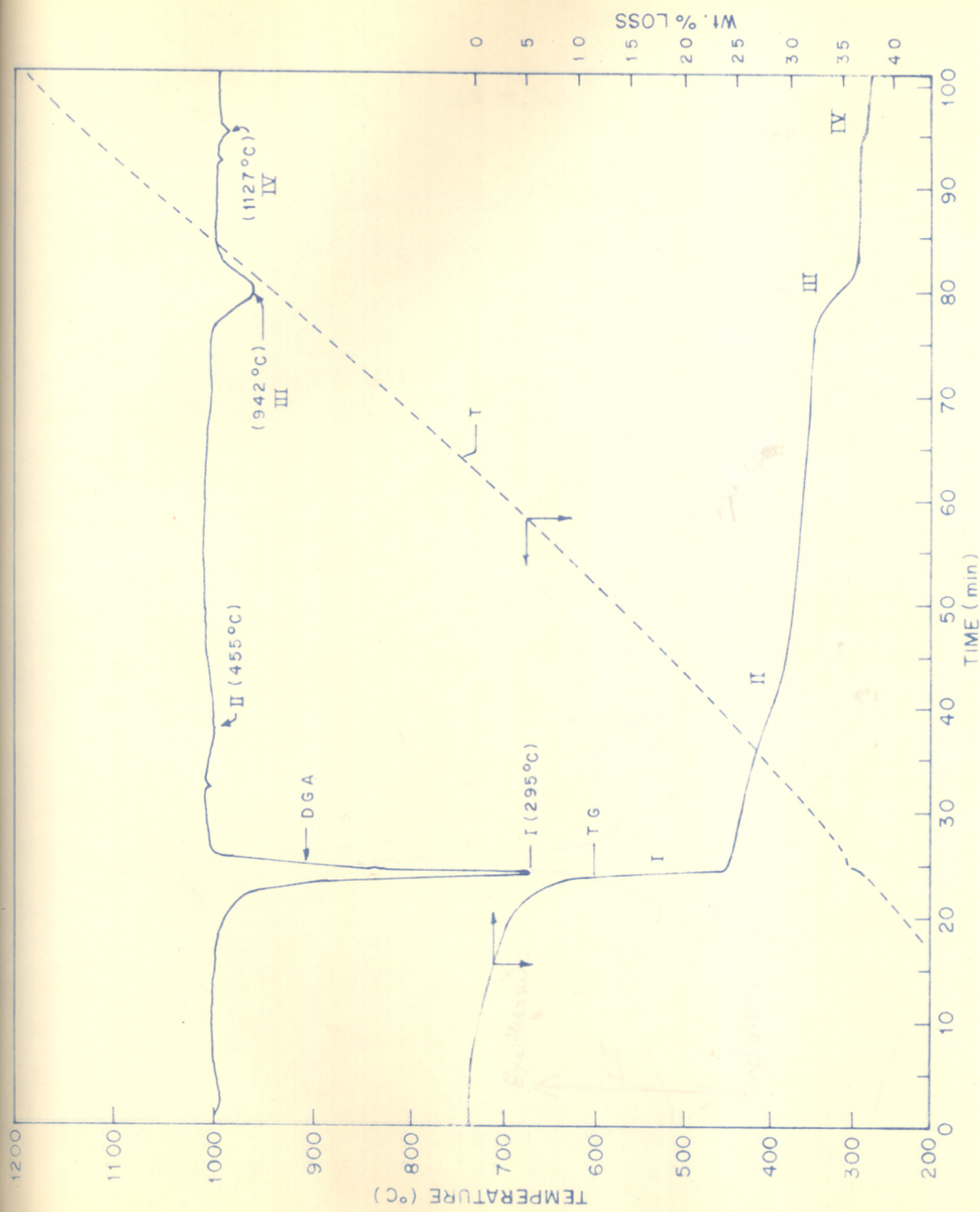


FIG. 2.4 THERMAL GRAVIMETRIC AND DIFFERENTIAL THERMAL GRAVIMETRIC CURVES FOR Y-IRRADIATED AMMONIUM COPPER CHROMATE

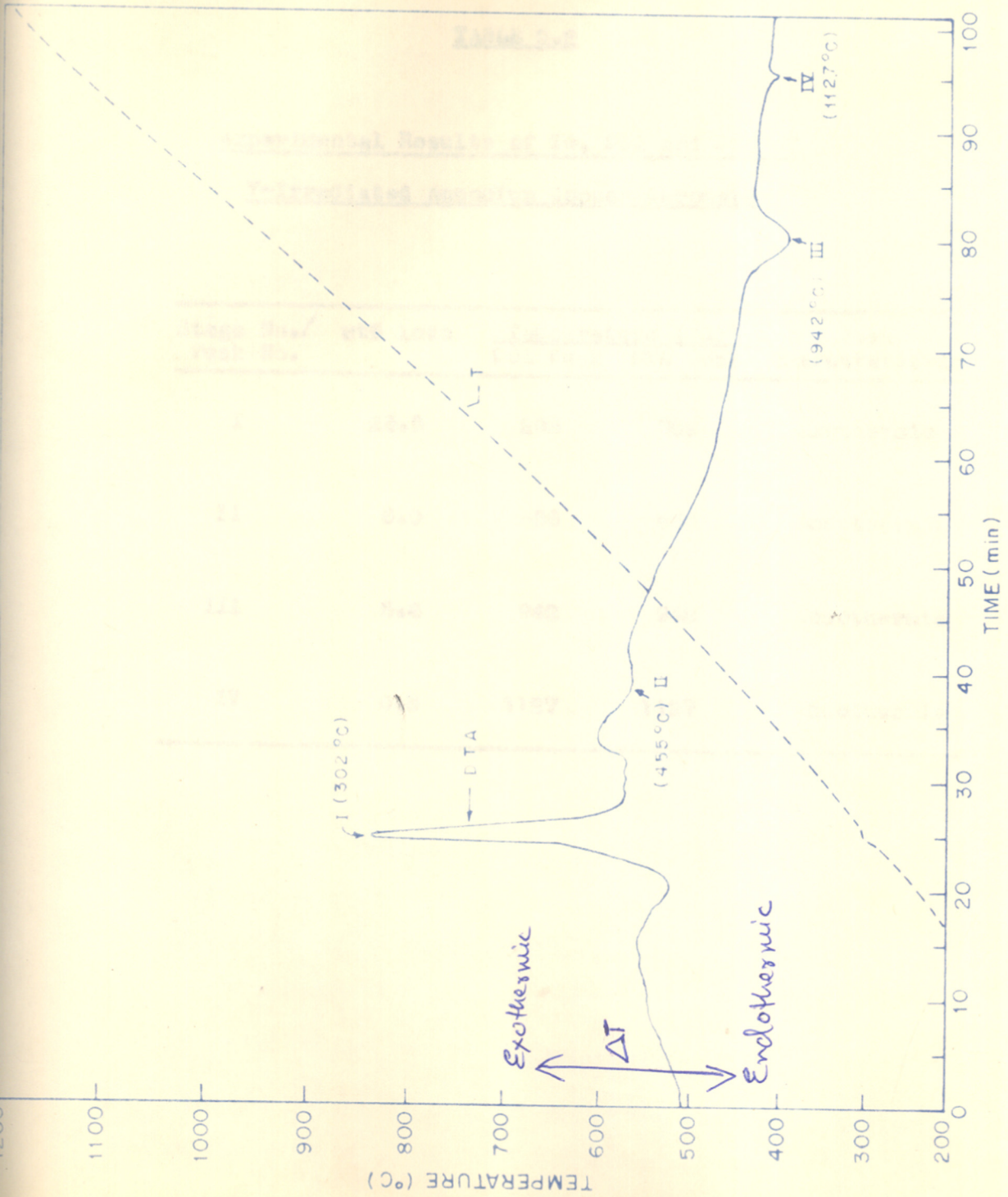
FIG 2.5 DIFFERENTIAL THERMAL ANALYSIS CURVE FOR γ -IRRADIATED AMMONIUM COPPER CHROMATE

TABLE 2.2

Experimental Results of TG, DGA and DTA of
Y-Irradiated Ammonium Copper Chromate

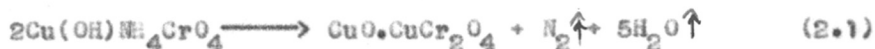
Stage No./ Peak No.	wt% loss	Temperature (°C)		Peak characteristic
		DGA Peak	DTA Peak	
I	25.5	295	302	Exothermic
II	6.0	455	455	Endothermic
III	5.4	942	942	Endothermic
IV	0.8	1127	1127	Endothermic

stage of the decomposition of ammonium copper chromate. It is also interesting to note that the temperature corresponding to the DTA or DGA peak has been found to shift to the higher temperature side for all the stages of decomposition because of the γ -irradiation of ammonium copper chromate. Thus the γ -irradiation increases the thermal stability of the ammonium copper chromate and also its solid products of decomposition.

2.3.2 Isothermal Decomposition of Ammonium Copper Chromate

The results of the decomposition at 350°C are presented in Table 2.3. The formation of ammonia was not detected in the gaseous products of the decomposition at this temperature. However, at 275° and 300°C, some traces of ammonia (Table 2.4) were detected.

The above results (Table 2.3) indicate that the decomposition at 275°-350°C occurs according to the reaction:



However the evolution of the traces of ammonia at 275° and 300°C indicates the formation of copper chromate in small amounts according to the reaction:



The decomposition according to the above reaction (2.2) was of the order 0.5% to 0.9% (Table 2.4).

TABLE 2.3

Experimental Results of Decomposition of
Ammonium Copper Chromate at 350°C.

S.No.	Observation	Experimental	Theoretical (According to squn. 2.1)
1	Total wt. loss on decomposition per gram of solid	0.263 g	0.275 g
2	Nitrogen evolved on decomposition per gram of solid	54.9 ml at N.T.P. or 0.068 g	52.3 ml at N.T.P.
3	Formation of water in decomposition per gram of solid	0.195 g	0.2098
4	Formation of ammonia in decomposition	Nil	Nil

TABLE 2.4

Experimental Results of Evolution of Ammonia in the
Decomposition of Ammonium Copper Chromate
at 275° to 400°C.

Decomposition Temperature (°C)	Amount of Ammonia Evolved (g mole/g)
275	0.00039 g/g of sample
300	0.00072 g/g of sample
350	Undetectable
400	Undetectable
Theoretical quantity of NH_3 evolved according to Eqn. [2.2]	: 0.0793 g (NH_3)/g

2.3.3 Chemical Analysis of Solid Products

The results of chemical analysis of the solid products of the decomposition at different temperatures are presented in Table 2.5.

The dependence of copper (as free copper and in combination with chromium) upon pretreatment temperature (or decomposition temperature) is shown in Fig. 2.6, while that for chromium (as free chromium and in combination with copper) is shown in Fig. 2.7.

It can be seen from Fig. 2.6 that the total copper content of the sample does not change due to an increase in temperature, the copper in the free form (as CuO) decreases slowly upto 750°C and there is a sharp decrease from 750° to 1000°C, while copper content of the residue (i.e. in the form of copper chromite) increases gradually from 400° to 750°C and then there is sharp increase above 750°C. These changes of copper content of the solid products of decomposition at different temperatures can be explained by the following phase transition reaction:



This is also supported by the results shown in Fig. 2.7. The chromium content of the residue (i.e. in the form of

TABLE 2.5

Experimental Results of Chemical Analysis of Solid Products of Decomposition at Different Temperatures

Sample pretreatment temp. (°C)	Sample wt. x(g)	Wt. of Residue after leaching y(g)	Wt % of Residue $\frac{x}{y} \times 100$	Wt % free Cu	Wt % Cu in residue	Wt % free Cr	Wt % Cr in residue	Wt % Cu total	Wt % Cr total	Cu/Cr (atomic ratio)	Solid phases (wt%)
310	1.0322	0.596	57.76	26.15	25.1	2.04	50.7	40.64	31.32	1.062	Cr ₂ O ₃ : 3.0 CuO : 32.7 CuCr ₂ O ₄ : 57.3
400	1.0216	0.729	71.39	22.30	24.1	2.00	44.8	39.54	32.0	1.011	Cr ₂ O ₃ : 3.0 CuO : 27.9 CuCr ₂ O ₄ : 71.4
500	1.600	1.1763	73.52	19.9	28.9	4.37	39.6	41.15	33.50	1.005	Cr ₂ O ₃ : 6.4 CuO : 24.9 CuCr ₂ O ₄ : 73.5
750	1.4958	1.1303	75.53	17.45	29.5	5.68	36.8	39.77	33.49	0.972	Cr ₂ O ₃ : 8.3 CuO : 21.8 CuCr ₂ O ₄ : 75.5
1000	2.0590	1.9739	95.83	1.277	40.5	3.40	31.4	40.13	33.50	0.981	Cr ₂ O ₃ : 5.0 CuO : 1.6 CuCr ₂ O ₄ : 95.3
Catalyst CuO.CuCr ₂ O ₄	3.11	2.32	74.42	20.43	27.4	-	44.92	40.84	33.44	1.000	
CuCr ₂ O ₄	-	-	-	-	27.4	-	44.9	-	-	0.5	
Cu ₂ Cr ₂ O ₄	-	-	-	-	43.1	-	35.3	-	-	1.0	

CHROMIUM UPON PRETREATMENT TEMPERATURE

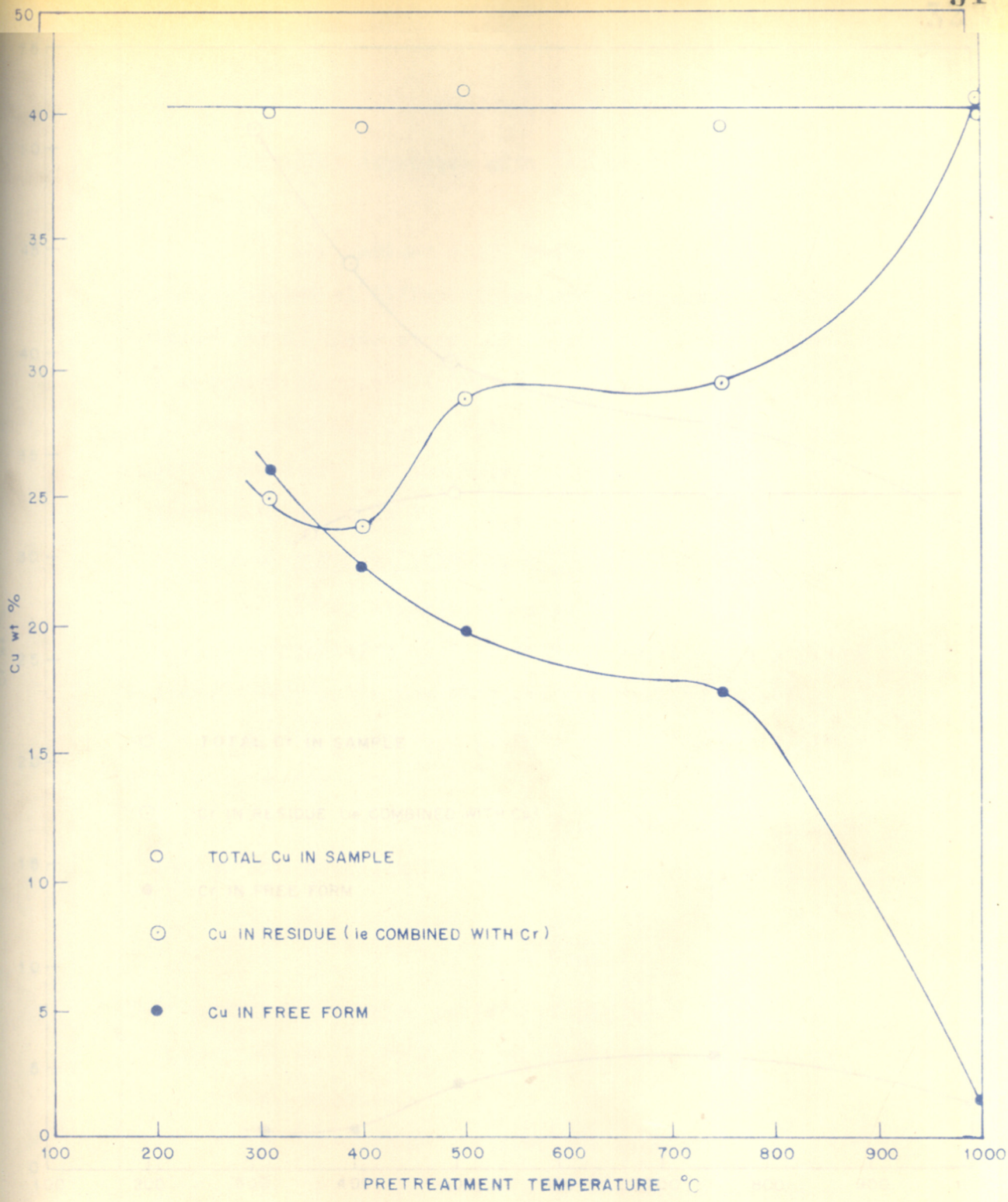


FIG. 2-6 DEPENDANCE OF COPPER AS FREE COPPER AND IN COMBINATION WITH CHROMIUM UPON PRETREATMENT TEMPERATURE

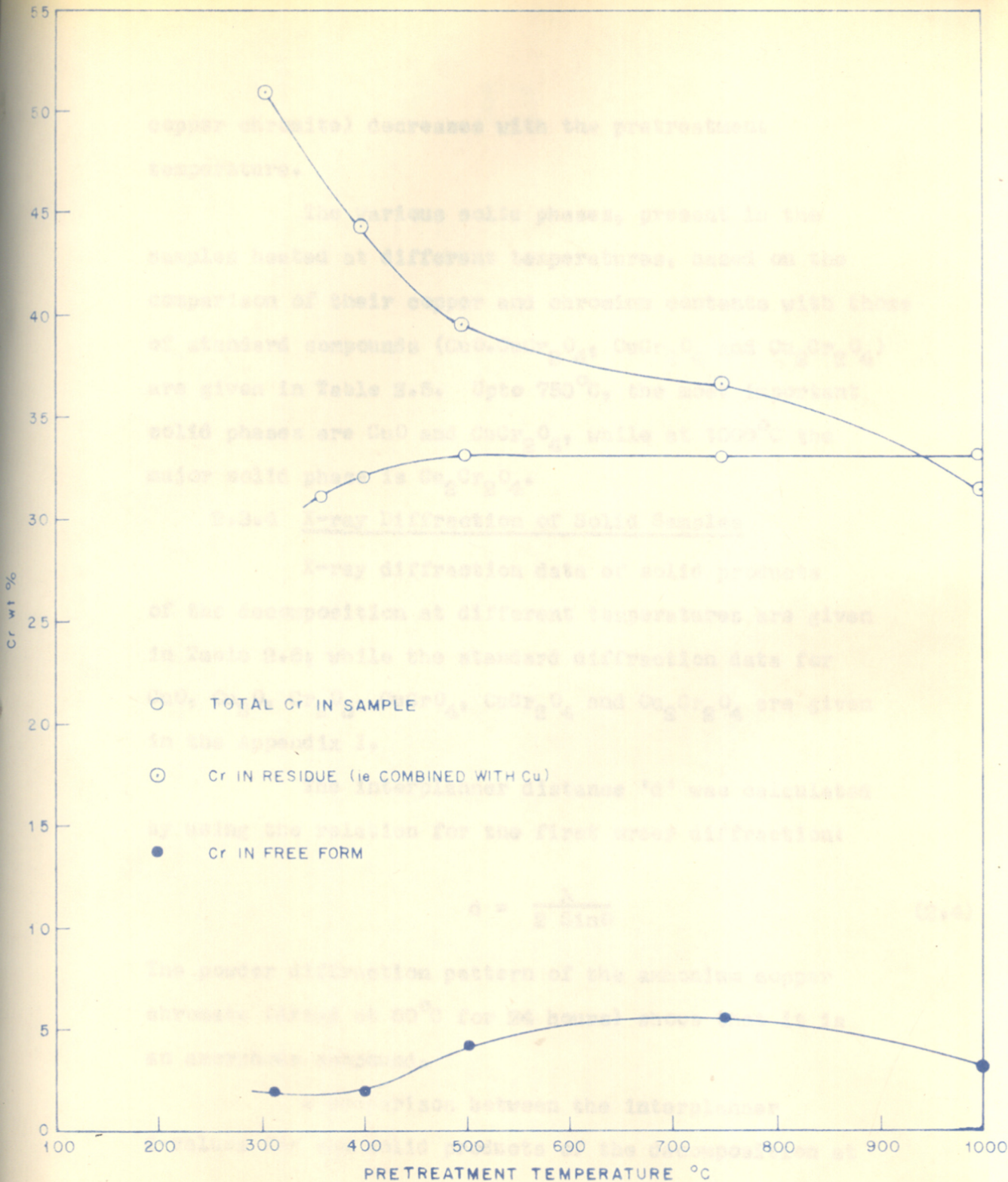


FIG. 2-7 DEPENDANCE OF CHROMIUM AS FREE CHROMIUM AND IN COMBINATION WITH COPPER UPON PRETREATMENT TEMPERATURE

copper chromite) decreases with the pretreatment temperature.

The various solid phases, present in the samples heated at different temperatures, based on the comparison of their copper and chromium contents with those of standard compounds ($\text{CuO} \cdot \text{CuCr}_2\text{O}_4$, CuCr_2O_4 and $\text{Cu}_2\text{Cr}_2\text{O}_4$) are given in Table 2.5. Upto 750°C , the most important solid phases are CuO and CuCr_2O_4 , while at 1000°C the major solid phase is $\text{Cu}_2\text{Cr}_2\text{O}_4$.

2.3.4 X-ray Diffraction of Solid Samples

X-ray diffraction data of solid products of the decomposition at different temperatures are given in Table 2.6; while the standard diffraction data for CuO , Cu_2O , Cr_2O_3 , CuCrO_4 , CuCr_2O_4 and $\text{Cu}_2\text{Cr}_2\text{O}_4$ are given in the Appendix I.

The interplaner distance 'd' was calculated by using the relation for the first order diffraction:

$$d = \frac{\lambda}{2 \sin \theta} \quad (2.4)$$

The powder diffraction pattern of the ammonium copper chromate (dried at 80°C for 24 hours) shows that it is an amorphous compound.

A comparison between the interplaner d-values for the solid products of the decomposition at

TABLE 2.6

X-Ray Diffraction Data for the Solid Products
of Decomposition at Different Temperatures

Temp (°C)	Arc dia. S (cm)	θ = 2θ (degrees)	d (Å°)	Standard 'd' values		Crystall- ine phases
				CuO	CuCr ₂ O ₄	
310	4.06	8.150	2.511 (w)	2.52 (100)	--	CuO
400	4.355	8.710	2.342 (v)	2.323 (96)	2.401 (60)	CuO
	4.005	8.010	2.545 (v)	2.523 (100)	2.556 (100)	and CuCr ₂ O ₄
	3.440	6.880	2.961 (v)	--	3.01 (15)	--
500	7.120	14.240	1.442 (vw)	1.505 (20)	1.442 (40)	CuO
	6.765	13.530	1.516 (vw)	--	1.505 (30)	--
	6.280	12.560	1.631 (vw)	--	--	and
	4.450	8.900	2.292 (v)	2.373 (96)	1.629 (40)	--
	3.970	7.940	2.567 (s)	--	2.556 (100)	--
	3.500	7.00	2.909 (vw)	--	2.874 (35)	--
750	8.110	16.220	1.269 (vw)	--	1.276 (15)	--
	7.145	14.290	1.436 (w)	--	1.442 (40)	CuO
	6.790	13.580	1.510 (w)	--	1.505 (30)	--
	6.250	12.500	1.638 (w)	--	1.629 (40)	and
	5.935	11.870	1.724 (vw)	--	1.706 (15)	--
	4.350	8.700	2.344 (s)	2.321 (96)	2.401 (60)	--
3.980	7.960	2.561 (vs)	--	2.556 (100)	--	
3.465	6.970	2.922 (vw)	--	2.874 (35)	--	

cont'd

TABLE 2.6 cont'd

Temp ($^{\circ}$ C)	Arc dia. S (cm)	$\theta = 25$ (degrees)	d (\AA)	Standard 'd' values			Crystall- ine phases
				CuO	CuCr ₂ O ₄	Cu ₂ Cr ₂ O ₄	
1000	10.10	20.20	1.027(vw)	--	--	1.030(20)	Cu ₂ Cr ₂ O ₄
	9.445	18.89	1.095(vw)	--	--	1.015(15)	
	8.655	17.310	1.192(vw)	--	--	1.172(5)	
	7.785	15.570	1.321(vw)	--	--	--	
	7.170	14.340	1.432(w)	--	--	--	
	6.895	13.790	1.487(w)	--	--	1.319(20)	
	6.200	12.100	1.651(ms)	--	--	1.426(30)	
	4.665	9.340	2.187(s)	--	--	1.488(35)	
	4.115	8.230	2.477(vs)	--	--	1.640(45)	
3.545	7.090	2.873(s)	--	--	2.470(100)		
						2.85(40)	

Note : Relative intensities are given in the brackets.

different temperatures and those of CuO , CuCr_2O_4 and $\text{Cu}_2\text{Cr}_2\text{O}_4$ is given in Table 2.6.

The results shows that at 310°C the solid product of the decomposition appears to be amorphous and the single line shown on the diffraction pattern may be due to CuO . The crystallization started at and above 400°C as evidenced by the more and more lines on the diffraction pattern. From the comparison of the observed d-values with the standard d-values of CuCr_2O_4 , $\text{Cu}_2\text{Cr}_2\text{O}_4$ and CuO , it can be concluded that upto 750°C the solid product of the decomposition contained CuO and CuCr_2O_4 , while at 1000°C it was $\text{Cu}_2\text{Cr}_2\text{O}_4$. Thus a transition from CuCr_2O_4 to $\text{Cu}_2\text{Cr}_2\text{O}_4$ occurred between the temperatures 750° and 1000°C .

2.3.5 Infra-Red Analysis of Solid Samples

The IR spectra of the ammonium copper chromate and the solid products of the decomposition at different temperatures are given in Figs. 2.8 and 2.9, respectively. The standard IR spectra of $\text{Cu}_2\text{Cr}_2\text{O}_4$ and CuCr_2O_4 are represented in Fig. 2.10. The spectral data for $\text{Cu}_2\text{Cr}_2\text{O}_4$, CuCr_2O_4 and the solid products of the decomposition at different temperatures are given in Table 2.7.

It can be seen from Fig. 2.9 that the spectra for the solid samples obtained at 310° , 400° , 500° and 750°C are almost similar, except a weak absorption

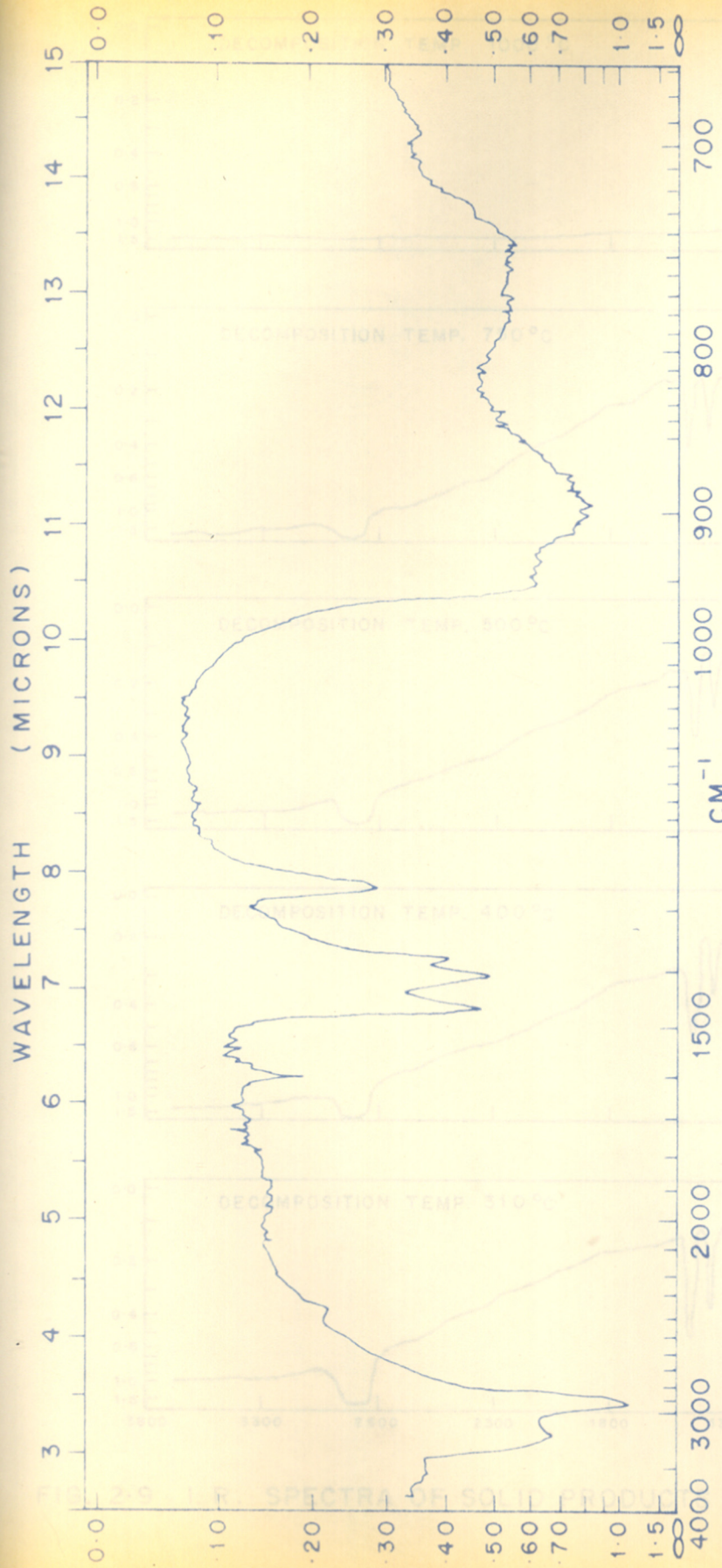


FIG. 2-8 I.R. SPECTRUM OF AMMONIUM COPPER CHROMATE

FIG. 2-9 I.R. SPECTRA OF SOLID RESIDUES OF DECOMPOSITION

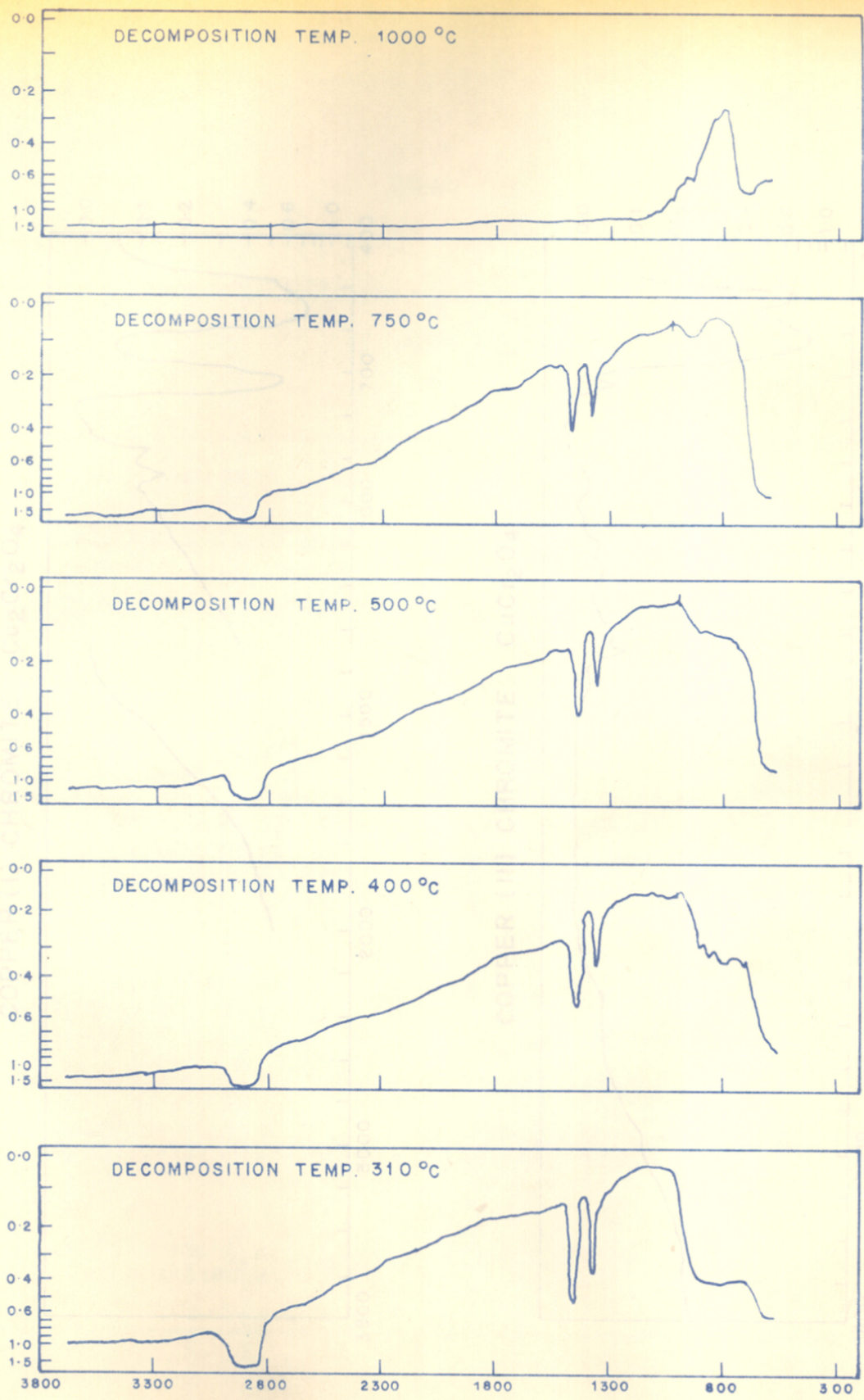
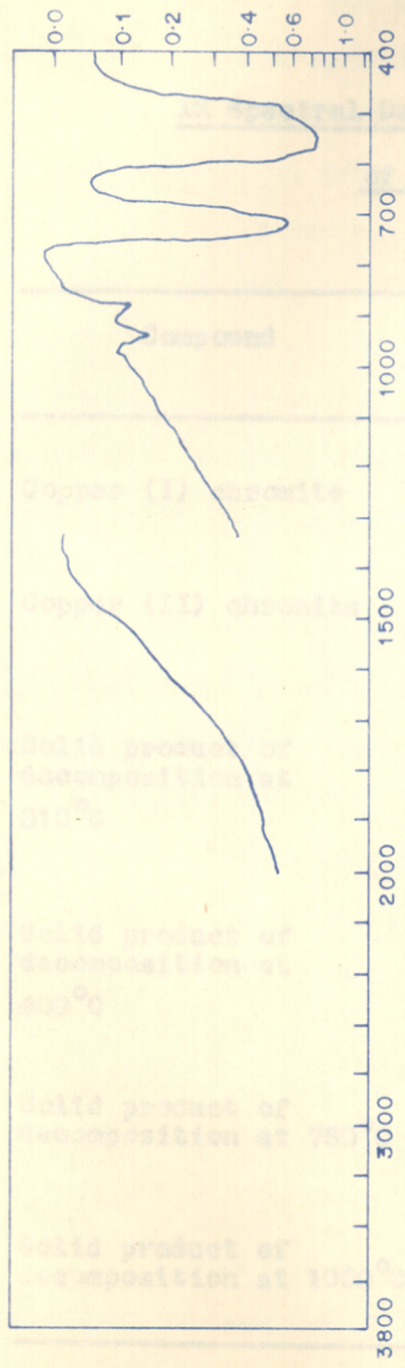


FIG. 2.9 I. R. SPECTRA OF SOLID PRODUCTS OF DECOMPOSITION

COPPER (I) CHROMITE $Cu_2Cr_2O_4$



COPPER (II) CHROMITE $CuCr_2O_4$

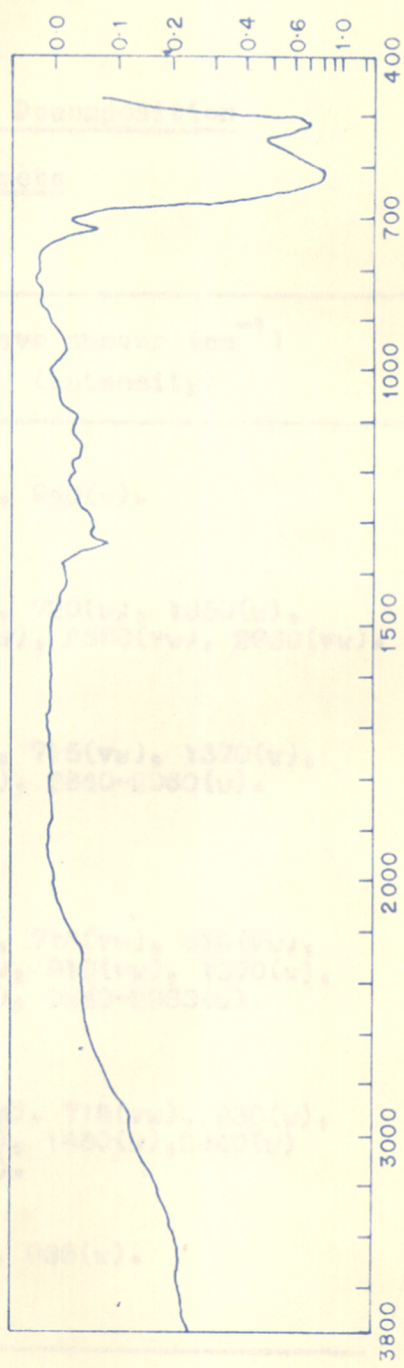


FIG. 2·10 THE STANDARD I.R. SPECTRA OF COPPER(I) CHROMITE AND COPPER(II) CHROMITE

RICHARD A. NYQUIST AND RONALD O. KOGEI
INFRA-RED SPECTRA OF INORGANIC COMPOUNDS, ACADEMIC PRESS, NEW YORK (1971)

TABLE 2.7

IR Spectral Data for the Decomposition
of Solid Products

Compound	Wave number (cm ⁻¹) (Intensity)
Copper (I) chromite	<u>715(s)</u> , 940(w).
Copper (II) chromite	<u>615(g)</u> , 720(w), 1350(w), 1400(vw), 2850(vw), 2930(vw).
Solid product of decomposition at 310°C	<u>600(s)</u> , 715(vw), 1370(w), 1450(w), 2840-2960(w).
Solid product of decomposition at 400°C	<u>600(s)</u> , 715(vw), 810(vw), 870(vw), 910(vw), 1370(w), 1450(w), 2840-2960(w).
Solid product of decomposition at 750°C	<u>600(g)</u> , 715(vw), 930(w), 1360(w), 1450(w), 2840(w) 2920(w).
Solid product of decomposition at 1000°C	<u>710(s)</u> , 935(w).

band at 930 cm^{-1} for the solid obtained at 750°C .

The spectrum of the solid obtained at 1000°C is quite different from the other spectra, thus showing a probable phase transition.

It can be seen from the spectral data (Table 2.7) and also from the comparison between the spectra of the solid samples (Fig. 2.9) and the standard spectra of $\text{Cu}_2\text{Cr}_2\text{O}_4$ and CuCr_2O_4 (Fig. 2.10) that the spectrum of the solid obtained at 1000°C is mostly due to $\text{Cu}_2\text{Cr}_2\text{O}_4$, because the strong and weak absorption bands at 710 cm^{-1} (strong) and 975 cm^{-1} (weak) correspond to the absorption bands of the copper (I) chromite at 715 cm^{-1} (strong) and 940 cm^{-1} (weak). The strong absorption band at around 600 cm^{-1} of the solid samples obtained at temperatures 310° to 750°C correspond to the strong absorption band at 615 cm^{-1} of CuCr_2O_4 . This comparison shows the presence of CuCr_2O_4 in the solid samples obtained in the temperature range 310° to 750°C .

Further the presence of a weak band at 935 cm^{-1} for the solid obtained at 750°C shows the existence of the traces of $\text{Cu}_2\text{Cr}_2\text{O}_4$.

It may be concluded from the above discussion that the transition of CuCr_2O_4 to $\text{Cu}_2\text{Cr}_2\text{O}_4$ occurs between the temperature 750°C and 1000°C .

2.3. 6 Reactions involved in Decomposition of Ammonium

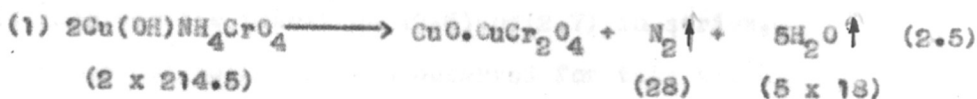
Copper Chromate

As evidenced by the TG, DGA and DTA studies (Figs. 2.2 and 2.3 and Table 2.1), the decomposition of ammonium copper chromate occurs in four distinct stages. Reactions involved in these stages of decomposition are explained below.

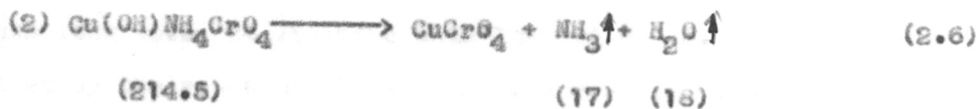
Stage I of the Decomposition:

Decomposition in this stage is exothermic and occurs at about 260°C (DGA peak at 258°C and DTA peak at 260°C) with the weight loss 24%.

The probable reactions explaining the decomposition are as follows:



$$\text{wt\% loss} = \frac{28 + (5 \times 18)}{(2 \times 214.5)} = 27.5$$

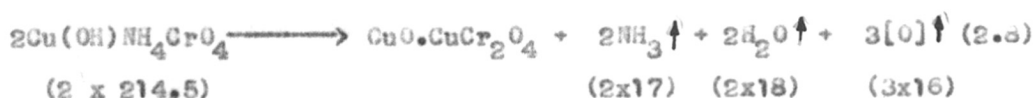


$$\text{wt\% loss} = \frac{(17) \times (18)}{(214.5)} = 16.3$$



$$\text{wt}\% \text{ loss} = \frac{(3 \times 16)}{(2 \times 179.5)} = 13.37$$

or by combining Equn. [2.6] and [2.7] we get



$$\text{wt}\% \text{ loss} = \frac{(2 \times 17) + (2 \times 18) + (3 \times 16)}{(2 \times 214.5)} = 27.5$$

Out of these two reactions (2.5 and 2.8), the reaction (2.8) may be discarded because of the following reasons.

- (1) It involves the reactions (2.6) and (2.7) in series, but only one DGA peak has been observed for this stage of decomposition, this shows the occurrence of only one reaction. If it is assumed that only the reaction (2.6) occurs at this stage of decomposition, the observed weight% loss (i.e. 24%) is more than that (i.e. 16.3%) required by the reaction (2.6).
- (2) The reaction (2.8) involves the formation of NH_3 to the extent that required by the reaction (2.6), which was not observed (Table 2.4). The evolution of traces of NH_3 accounts only for about 0.5 to 0.9% decomposition according to the reaction (2.6).

(3) The reaction (2.5) is the most probable reaction for the decomposition at this stage because the observed wt% loss (i.e. 24%) is very close to that (27.5%) required by the reaction (2.5) and also the results of the decomposition at 350°C (Table 2.3) gave a very close material balance for the products of the decomposition as required by the reaction (2.5). A somewhat lower wt% loss and the evolution of traces of NH₃ in the decomposition may be due to the occurrence of the reaction (2.6) to a small extent.

It may be concluded from the above discussion that the reactions involved in the initial decomposition of ammonium copper chromate (i.e. decomposition at the first stage) are as follow:

Major reaction



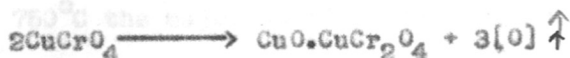
Minor reaction



Stage II of the Decomposition

The endothermic decomposition at this stage occurs at about 397°C (both the DGA and DTA peaks at 397°C), with the wt% loss 4.0%. It may be accounted for the decomposition of copper chromate formed in small quantities according to the reaction (2.6) in the first

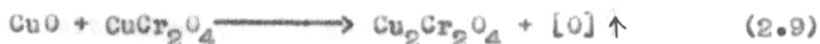
stage of decomposition of ammonium copper chromate. The decomposition of copper chromate proceeds [3] according to the reaction (2.7):



It is also interesting to note that the overall weight% loss at the second stage of decomposition of ammonium copper chromate is 28%, which is very close to the value 27.5% as expected for the complete decomposition of ammonium copper chromate to $\text{CuO} \cdot \text{CuCr}_2\text{O}_4$ according to the reactions (2.5) and (2.8). This fact is also an additional proof for the mechanism suggested above for the decomposition of ammonium copper chromate in the first and second stages of decomposition. The chemical analysis, X-ray diffraction and IR spectroscopic studies of the solid products of the decomposition at 400° and 500°C have also indicated that the major solid phases present in the products are CuO and CuCr_2O_4 .

Stage III of the Decomposition

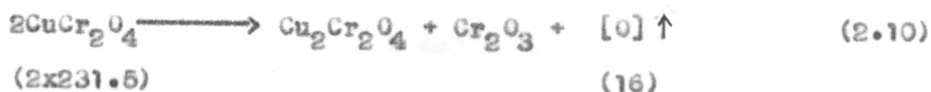
The decomposition in the third stage is also endothermic and occurs at about 828°C (DTA and DGA peaks at 828°C) with weight loss 5.3%. The decomposition at this stage is mostly due to the phase transition of $\text{CuO} \cdot \text{CuCr}_2\text{O}_4$ to $\text{Cu}_2\text{Cr}_2\text{O}_4$.



This is confirmed by the chemical, X-ray and IR analysis of the solid products of the decomposition at 750° and 1000°C. At 750°C the major solid phases present in the decomposition of solid products are CuO and CuCr₂O₄, while at 1000°C the Cu₂Cr₂O₄ is the only important solid phase.

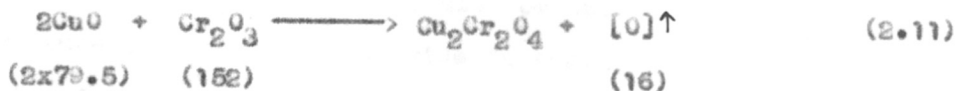
Stage IV of the Decomposition

The decomposition at this stage is also endothermic and occurs at about 982°C (DTA and DGA peaks at 982°C) with weight loss 0.7%. A small weight loss at this stage of decomposition may be due to either the decomposition of unconverted CuCr₂O₄ according to the reaction:



$$\text{wt\% loss} = \frac{16}{463} = 3.46$$

or by the reaction between the free CuO and Cr₂O₃ as



$$\text{wt\% loss} = \frac{16}{(2 \times 79.5) + (152)} = 5.1$$

Since the chemical analysis of the solid products

of the decomposition at 1000°C shows the presence of free CuO and Cr₂O₃, the reaction (2.11) is the most probable reaction accounting for the small weight loss at this stage of decomposition.

Reactions of free CuO and Cr₂O₃:

Since free copper and chromium oxides are observed (Table 2.5) in the products of the decomposition, the following reactions may be taking place during the course of heating.



Keely and Mathes [4] studied the reactions between CuO and Cr₂O₃ in the temperature range 260° to 1200°C and found that CuCr₂O₄ was formed at 480°C, while Cu₂Cr₂O₄ was appeared at 870°C.

Decomposition of CuCr₂O₄:

The decomposition of CuCr₂O₄ to Cu₂Cr₂O₄ according to reaction (2.10) may also be accounted for the presence of free chromium oxide in the solid products of the decomposition at higher temperatures.

2.4 SUMMARY AND CONCLUSIONS

The decomposition of ammonium copper chromate has been studied by the TG, DGA and DTA in the temperature range 300°C to 1000°C. The solid products of the decomposition in the various stages of decomposition were characterised by the chemical, X-ray and IR analysis. The results lead to the conclusion that the decomposition of ammonium copper chromate occurs in four stages as evidenced by the TG, DGA and DTA studies. The overall decomposition of ammonium copper chromate can be explained by the following reactions.

Decomposition at stage I (at 250°-350°C)

Major reaction:



Minor reaction:



Decomposition at stage II (at 350°-500°C)

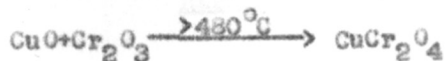


Decomposition at stage III (at 780°-870°C)



Decomposition at stage IV (at 960°-1000°C)



Other Probable Side Reactions:

The decomposition of the Y-irradiated ammonium copper chromate was also found to occur in the four distinct stages as discussed above. However the Y-irradiation shifted the weight losses and the temperatures corresponding to the DGA or DTA peaks to the higher side. The increase in the decomposition (i.e. weight loss) may be due to the creation of an additional active centres for the nuclear growth. The shift of the DTA or DGA peak temperature to the higher side indicates the enhancement of the thermal stability of the ammonium copper chromate and also its solid product of decomposition because of Y-irradiation.

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CHAPTER 3

KINETICS OF DECOMPOSITION OF
AMMONIUM COPPER CHROMATE

CHAPTER 3KINETICS OF DECOMPOSITION OF AMMONIUM COPPER CHROMATE3.1 GENERAL - DECOMPOSITION OF SOLID

Solid material on heating can either decompose or sinter. If decomposition occurs, sintering generally delays until after the production of new material. Mechanism of decomposition depends upon the past history of the material and also upon the experimental condition.

A particularly important condition which affects the mode of decomposition is the particle size. Decomposition reaction commences at the formation of nucleus on the surface which increases in size as the decomposition proceeds.

3.1.1 General Form of Decomposition Curve

In general, decomposition reaction can be represented as



In the general case, the decomposition curve [x vs t] has the following features, illustrated in Fig. 3.1. The curve shows the following distinct parts :

- A - Initial rapid evolution of gas [0.5-5% decomposition]
- B - Induction period
- C - Acceleratory period

D - Decay period
 E - Retention

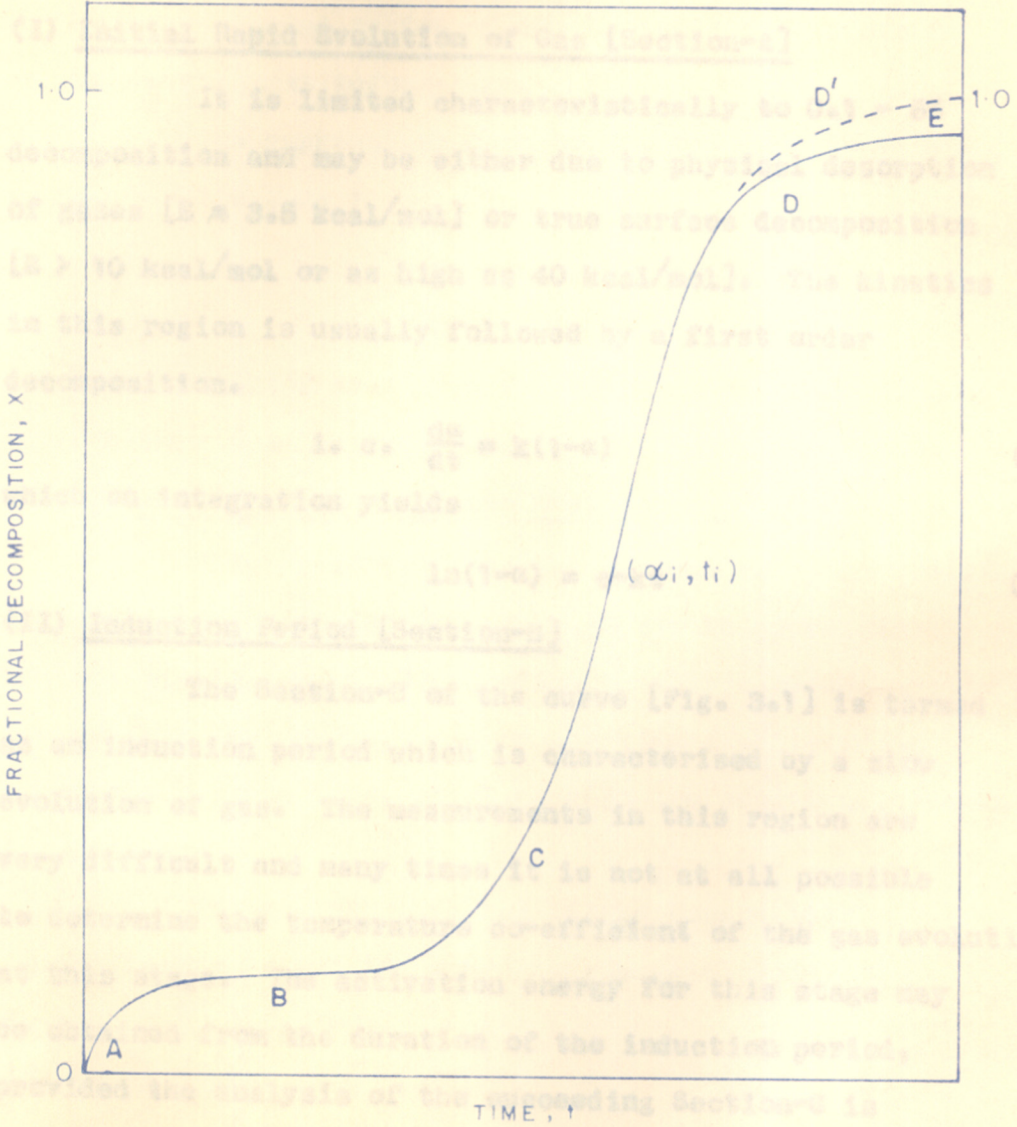


FIG. 3-1 A TYPICAL DECOMPOSITION CURVE

- A INITIAL RAPID EVOLUTION OF GAS
(0.5 - 5% DECOMPOSITION)
- B INDUCTION PERIOD
- C ACCELERATORY PERIOD
- D DECAY PERIOD
- E RETENTION

D - Decay period

E - Retention

(I) Initial Rapid Evolution of Gas [Section-A]

It is limited characteristically to 0.1 - 5% decomposition and may be either due to physical desorption of gases [$E \approx 3.5$ kcal/mol] or true surface decomposition [$E > 10$ kcal/mol or as high as 40 kcal/mol]. The kinetics in this region is usually followed by a first order decomposition.

$$\text{i. e. } \frac{d\alpha}{dt} = k(1-\alpha) \quad (3.1)$$

which on integration yields

$$\ln(1-\alpha) = c-kt \quad (3.2)$$

(II) Induction Period [Section-B]

The Section-B of the curve [Fig. 3.1] is termed as an induction period which is characterised by a slow evolution of gas. The measurements in this region are very difficult and many times it is not at all possible to determine the temperature co-efficient of the gas evolution at this stage. The activation energy for this stage may be obtained from the duration of the induction period, provided the analysis of the succeeding Section-C is carried out successfully.

(III) Acceleratory Period [Section-C]

The induction period is invariably succeeded by an acceleratory period, which normally extends upto fractional

decomposition (α_1) between 0.1 and 0.5, though α_1 values above this range have been observed. It is the most extensively studied region of the decomposition curve as it yields the most information.

The expressions used to fit the data in this region has the form :

$$\alpha = (\text{Exp } k t) \quad (3.3a)$$

$$\alpha = f(k t^n) \quad (3.3b)$$

and exceptionally, nearly perfect fits have been obtained with these simple expressions.

(IV) Transition Region Between Sections C and D

This region defines the maximum rate and contains the inflexion point (α_1, t_1). In case simple expressions are not applicable, it is possible to determine the activation energy from the maximum rate or the time (t_1) taken to reach the maximum rate, provided only one activated process is involved.

The maximum rate has little theoretical significance unless it occurs at a special value of α , e.g. 0.5, 0.67 or 1.

(V) Decay Period

It is less valuable as it depends markedly on the details of the particle size distribution. Provided the particle size effects are eliminated, the data in this region can be fitted to a power function representing a contracting envelope of same kind or a first order expression.

(VI) Retention

The deviation 'E' shown in Fig. 3.1 is termed as the retention, which is believed to arise mostly from a combination of particle size effects and the reduction of chemical reactivity by poisoning or sintering or the chemisorption of product gas on the solid product.

The initial process and the retention are the least studied features of the decomposition curve.

3.1.2 Kinetic Rate Models for Decomposition of Solid

3.1.2.1 Development of Rate Expression by Avrami

According to Avrami [1] there exists a certain number of germ nuclei capable of developing into observable growth nuclei at the commencement of the transformation. As the transformation proceeds, the number of germ nuclei no longer available for activation is determined by a combination of two effects. The first effect is the normal activation of germ nuclei, and the second effect is the incorporation of germ nuclei by actively growing growth nuclei which thus renders the germ nuclei inoperative.

Based on the above consideration, he has developed a most general expression:

$$\ln\left(\frac{1}{1-\alpha}\right) = 6 k^n \cdot \text{No.} \left[\exp(-kt) - 1 + kt - \frac{(kt)^2}{2!} + \frac{(kt)^3}{3!} \right] \quad (3.4)$$

for the case of random nucleation of the three dimensional product nuclei. Various useful limiting cases can be obtained from the [Equn. (3.4)] which are as follows :

Case (I) : When t is large (i.e. t >> 1)

$$\ln\left(\frac{1}{1-\alpha}\right) = k^n \cdot \text{No.} \cdot t^3 \quad (3.5a)$$

or

$$\alpha = 1 - \exp(-k^n \cdot \text{No.} \cdot t^3) \quad (3.5b)$$

This form is applicable to decay period.

Case (II) : When $\alpha < 1$

$$\alpha = 6 k^n \cdot \text{No.} \cdot \left[\exp(-kt) - 1 + kt - \frac{(kt)^2}{2!} + \frac{(kt)^3}{3!} \right] \quad (3.6)$$

Case (III) : When No. is large and k is small

$$\alpha = 6 k^n \cdot \text{No.} \cdot \frac{(kt)^4}{4!} \quad (3.7)$$

Though these expressions of Avrami are of great theoretical value, they are limited in practice in the form of the nucleation law. Avrami's approach to the problems of nucleation and growth was directed invariably towards metallurgical problems and terminology must be recast before application to solid decomposition.

3.1.2.2 Erofeev Equation

Erofeev [2] developed an expression,

$$\alpha = 1 - \exp(-kt^n) \quad (3.8)$$

based on the nucleation law derived by Bagdassarian [3].

The equation (3.8) can be rearranged as

$$\left[\ln\left(\frac{1}{1-\alpha}\right) \right]^{1/n} = k' t, \text{ where } k' = k^{(1/n)} \quad (3.9)$$

3.1.2.3 Mampel's Equation

Mampel [4] considered nucleation and growth in

systems consisting of microcrystals in the form of spheres. His approach was limited to random nucleation, so it is not surprising that the final formulae are somewhat similar to those of Avrami, but the method is instructive and enables one to estimate the probable effects of particle size as the decomposition kinetics.

Mampel divided each spherical particle into concentric shells. He then treated the problems of overlapping and ingestion by considering the various ways in which a surface corresponding to the external area of the outermost shell could be covered by discs of confetti. Having established a solution to this problems, he integrated over all shells to obtain the fractional decomposition $\alpha(t)$.

Mampel's treatment to decomposition is considered to be the most exact one. According to him the following simplified expressions should fit the decomposition data in different regions.

(I) Induction stage:

$$\alpha = k t^4 \quad (3.10)$$

(II) Intermediate stage:

$$1 - (1-\alpha)^{1/3} = kt \quad (3.11)$$

$$(1-\alpha)^{1/3} = 1 - kt \quad (3.12)$$

which is known as contracting cube formula.

(III) In the final period:

$$\ln(1-\alpha) = C - kt \quad (3.13)$$

3.1.2.4 Prout-Tompkins Equation

The Prout-Tompkins [5] equation in the differential form is given as

$$\frac{d\alpha}{dt} = k \alpha (1-\alpha) \quad (3.14)$$

which on integration yields

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = C + kt \quad (3.15)$$

The Equn. (3.15) is very similar to Ostwald's equation for autocatalysis of the second type.

This expression describes the kinetics of a reaction progressing via linear branching chains which can be terminated on reacting any part of the phase.

3.1.2.5 First order Decomposition Equation [Decay period]

For the equation

$$\ln(1-\alpha) = C - kt \quad (3.16)$$

to be applicable to decay period, one of two situations must be created, first by chance the particle size distribution of completely nucleated particle is exponential or second as a result of separation of the reactant matrix during the acceleratory period, one can obtain a large number of precisely equivalent particles which do not contain active growth nuclei. The first order equation was applied to some early work and is still occasionally used, but it is seldom of real value [6].

The analysis of decay period is an integral part of the use of the Mampel, Avrami and Eroshfeev equations.

Kinetic Expressions for the different stages of Decomposition

Kinetic expressions used for fitting the decomposition of solid data fall into four general types

$$\alpha = k t^n + K \quad (3.17a)$$

$$(1-\alpha) = k(t + K)^n \quad (3.17b)$$

$$\alpha = k + K e^{-nt} \quad (3.17c)$$

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = kt + K \quad (3.17d)$$

Initial Process [A]

$$\ln(1-\alpha) = C - kt \quad (3.18a)$$

or

$$\log(1-\alpha) = C - \frac{k}{2.3} (t) \quad (3.18b)$$

Induction period [B]

$$\alpha = k t^n + K \quad (3.19a)$$

or

$$\alpha = k(t-t_0)^n \quad (3.19b)$$

or

$$\alpha^{1/n} = k't - k't_0 \quad (3.19c)$$

i.e. $\alpha^{1/n} = k't - C$ (3.19d)

Decay period [D]

$$\ln(1-\alpha) = C - kt \quad (3.20)$$

Acceleratory period [C and D]

(1) Mampel's Contracting Cube Expression

$$1 - (1-\alpha)^{1/3} = kt + C \quad (3.21a)$$

or

$$(1-\alpha)^{1/3} = 1 - kt - C = -k(t-t_0) \quad (3.21b)$$

(2) Erofeev Expression

$$\alpha = 1 - \exp(-kt^n) \quad (3.22a)$$

or

$$\left[\ln\left(\frac{1}{1-\alpha}\right) \right]^{1/n} = k(t+t_0) \quad (3.22b)$$

(3) Avrami-Erofeev Expression

$$\left[\ln\left(\frac{1}{1-\alpha}\right) \right]^{1/3} = k(t+t_0) \quad (3.23)$$

(4) Prout-Tomkins Expression

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = kt + C \quad (3.24a)$$

or

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = k(t+t_0) \quad (3.24b)$$

3.1.3 Present Investigation

The decomposition of ammonium copper chromate to an active copper chromite catalyst is one of the most important steps in the catalyst preparation. However very little is known about the kinetics of this reaction. Recently Russian workers [7, 8] have reported some kinetic data on the decomposition in the temperature range 230° to 270°C but there is no information available on the kinetic rate model.

The present investigation has been therefore undertaken to study the decomposition kinetics of ammonium copper chromate under the conditions which are actually used for obtaining the active copper chromite catalyst for the

hydrogenation of nitrobenzene to aniline. The decomposition data has been collected in the temperature range 270° to 350°C by qualitatively measuring the volume of nitrogen gas evolved as a function of time during decomposition.

3.2 EXPERIMENTAL

3.2.1 Ammonium Copper Chromate

The preparation of ammonium copper chromate has already been discussed in the Section 2.2.2. The ammonium copper chromate samples for the decomposition experiments were prepared by heating the ammonium copper chromate [particle size : 200 to 250 mesh] in an air oven at 80°C for four hours and kept in a dessicator for further use.

3.2.2 Experimental Set-Up

Experimental set up for collecting kinetic data on the decomposition is shown in Fig. 3.2. It consisted of a tubular furnace with temperature controller, an all glass decomposition reactor, a mercury manometer for measuring the pressure of decomposition gases, a fused calcium chloride trap for removing water vapors and a gas collecting and measuring unit.

The decomposition reactor was provided with a sample tube [as shown in Fig. 3.2] attached to it by B14 socket joint, ^{and} a thermocouple well for measuring the temperature of the decomposition bulb. The volume of the decomposition bulb was about 5 ml and it was packed with $1/8"$ dia S.S. balls. The bent of the sample tube and the

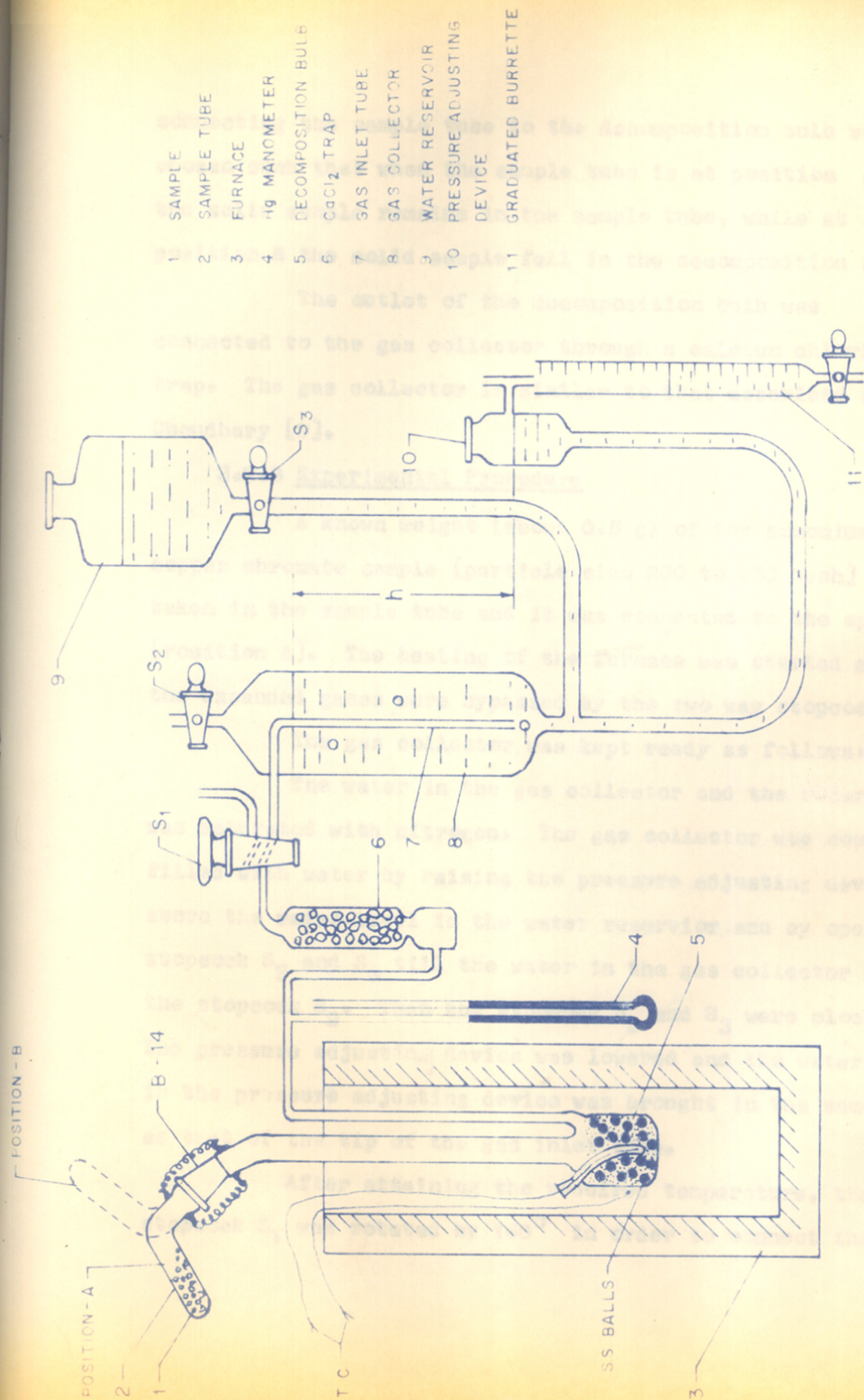


FIG. 3.2 EXPERIMENTAL SET-UP FOR THE DECOMPOSITION

connecting the sample tube to the decomposition bulb was chosen such that when the sample tube is at position A, the solid sample remains in the sample tube, while at position B the solid sample falls in the decomposition bulb.

The outlet of the decomposition bulb was connected to the gas collector through a calcium chloride trap. The gas collector is similar to that described by Choudhary [9].

3.2.3 Experimental Procedure

A known weight (about 0.5 g) of the ammonium copper chromate sample (particle size 200 to 250 mesh) was taken in the sample tube and it was connected to the system [Position A]. The heating of the furnace was started and the expanded gases were bypassed by the two way stopcock (S_1).

The gas collector was kept ready as follows:

The water in the gas collector and the reservoir was saturated with nitrogen. The gas collector was completely filled with water by raising the pressure adjusting device above the water level in the water reservoir and by opening stopcock S_2 and S_3 till the water in the gas collector reached the stopcock S_2 . Then the stopcock S_2 and S_3 were closed. The pressure adjusting device was lowered and the water level in the pressure adjusting device was brought in the same level as that of the tip of the gas inlet tube.

After attaining the required temperature, the stopcock S_1 was rotated by 180° in order to connect the

decomposition apparatus to the gas collector. The water level in the gas inlet tube was adjusted very close to the tip of the tube by lowering or raising the pressure adjusting device. The bubbled gas, if any, in the gas collector was removed by following the procedure discussed earlier. Thus the system was made ready for the decomposition experiment.

The sample was dropped in the decomposition bulb by turning the sample tube by 180° [i.e. Position B] and the water displaced by the incoming decomposition gas was collected and measured quantitatively [volumetrically] as a function of time using graduated burette.

The pressure of the gas collected in the gas collector was obtained by the equation:

$$P = p' - \left(\frac{h}{13.6}\right) - p'' \quad (3.25)$$

where

P = pressure of the gas collected [mm Hg]

p' = atmospheric pressure [mm Hg]

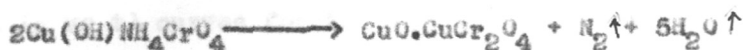
h = height between the water levels as shown in Fig. 3.2 [mm]

p'' = vapour pressure of water [mm Hg]

In the absence of S.S. balls, the temperature rise due to the exothermic reaction of the decomposition was found to be about 10°C but when the S.S. balls were used the temperature rise was hardly 2°C . This is because of the high heat capacity of the steel balls which take care of the heat evolved during decomposition.

3.3 RESULTS AND DISCUSSION

As discussed earlier [in Chapter 2] the decomposition of ammonium copper chromate in the temperature range 275° to 350°C covered in the present study occurs as follows:



However, small traces of ammonia were detected in the decomposition gases at 275° and 300°C showing the formation of copper chromate. But since the amount of ammonia formed was negligibly small [Table 2.4], the kinetic analysis is based only on the above reaction scheme.

3.3.1 Calculation of Fractional Decomposition Data

The decomposition data was calculated from the total volume [at NTP] of gas evolved as a function of time by using the relation:

$$x = \frac{\text{[ml of gas evolved (at NTP) per g sample in the decomposition]}}{\text{[ml of gas evolved (at NTP) per g sample in the complete decomposition]}}$$

The volume of gas evolved [ml at NTP] per gram of the sample was calculated from the experimental data as follows:

$$V = \frac{273 \cdot v \cdot P}{760 \cdot W \cdot T_g} \quad (3.26)$$

where,

V = volume of gas [at NTP] evolved per g of sample in the decomposition at time t [ml]

v = volume of gas collected at time t [ml]

P = pressure of the gas collected at time t [mm Hg]
[obtained by Equn. (3.25)]

W = weight of sample [g]

T_g = temperature of gas collected [°K]

3.3.2 Analysis of Kinetic Data

Experimental conversion data of the isothermal decomposition of ammonium copper chromate at 275°, 300°, 325° and 350°C are presented in Table 3.1. The fractional conversion (x vs t) curves for the decomposition at the different temperatures are presented in Fig. 3.3.

It can be seen from the Fig. 3.3 that the x vs t curves have a typical sigmoidal shape showing an appreciable initial decomposition followed by a short induction period and usual acceleratory and decay periods.

3.3.2.1 Initial Process of Decomposition

The kinetics of an initial process of decomposition is generally expressed by a first order decomposition expression,

$$\frac{dx}{dt} = k_1(1-x)$$

which on integration yields

$$\begin{aligned} \log(1-x) &= C_1 - \frac{k_1 t}{2.3} \\ &= \frac{-k_1}{2.3} (t-t_0) \end{aligned} \quad (3.27)$$

$$\text{where } \frac{k_1}{2.3} t_0 = C_1$$

where

- x = fractional decomposition
- k₁ = rate constant for the initial process of decomposition [sec⁻¹]
- C₁ = constant

TABLE 3.1

Experimental Conversion Data of the Isothermal
Decomposition of Ammonium Copper Chromate

Time (sec)	N_2 evolved [ml ² (at N.T.P)/g]	Fractional decomposition
1	2	3

Temperature : 275°C

10	1.79	0.03
15	4.98	0.09
20	5.78	0.11
40	7.38	0.13
50	10.57	0.19
60	11.37	0.21
70	12.56	0.23
80	13.36	0.24
100	14.56	0.27
140	14.95	0.27
160	15.75	0.29
180	16.94	0.31
210	18.145	0.33
245	18.94	0.35
275	19.34	0.35
290	20.13	0.37
305	20.54	0.37
365	22.14	0.40

Temperature : 300°C

5	2.08	0.04
10	4.16	0.08
25	7.07	0.13
30	8.32	0.15
35	9.15	0.17
60	10.81	0.20
75	12.47	0.23
90	14.55	0.26
100	16.63	0.30

Table 3.1 cont'd

1	2	3
<u>Temperature : 300°C</u>		
120	18.71	0.34
140	22.87	0.42
150	24.95	0.45
160	27.03	0.49
180	31.18	0.57
205	34.51	0.63
225	37.42	0.68
240	38.67	0.70
<u>Temperature : 325°C</u>		
10	3.73	0.07
20	10.10	0.18
25	11.22	0.20
30	13.09	0.24
40	13.84	0.25
50	18.70	0.34
60	22.44	0.41
75	29.22	0.54
90	33.66	0.61
95	37.40	0.68
100	39.26	0.72
110	41.14	0.75
115	43.02	0.78
120	44.88	0.82
130	46.75	0.85
140	48.62	0.89
150	49.75	0.91
175	52.00	0.95
200	53.48	0.97
210	54.23	0.98
<u>Temperature : 350°C</u>		
5	10.67	0.19
10	13.20	0.24
15	14.62	0.27
25	28.52	0.52
30	35.64	0.65
35	42.78	0.78
40	48.13	0.88
45	48.48	0.88
60	54.30	0.98
70	54.90	0.99

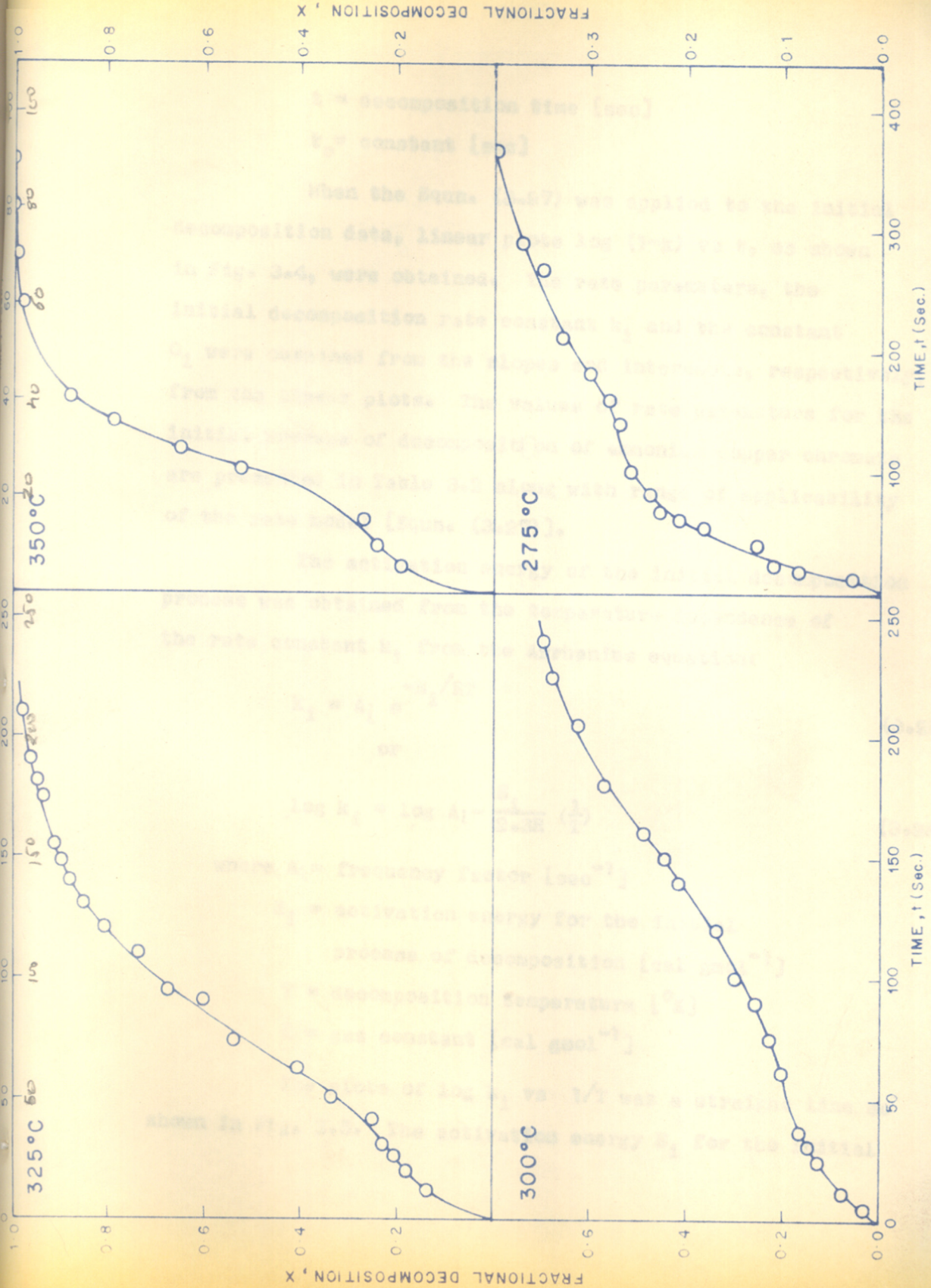


FIG. 3-3 FRACTIONAL DECOMPOSITION VS. TIME CURVES FOR ISOTHERMAL DECOMPOSITION OF AMMONIUM COPPER CHROMATE

t = decomposition time [sec]

t_0 = constant [sec]

When the Equn. (3.27) was applied to the initial decomposition data, linear plots $\log(1-x)$ vs t , as shown in Fig. 3.4, were obtained. The rate parameters, the initial decomposition rate constant k_1 and the constant C_1 were obtained from the slopes and intercepts, respectively, from the linear plots. The values of rate parameters for the initial process of decomposition of ammonium copper chromate are presented in Table 3.2 along with range of applicability of the rate model [Equn. (3.27)].

The activation energy of the initial decomposition process was obtained from the temperature dependence of the rate constant k_1 from the Arrhenius equation:

$$k_1 = A_1 e^{-E_1/RT} \quad (3.28a)$$

or

$$\log k_1 = \log A_1 - \frac{E_1}{2.3R} \left(\frac{1}{T}\right) \quad (3.28b)$$

where A_1 = frequency factor [sec^{-1}]

E_1 = activation energy for the initial process of decomposition [cal gmol^{-1}]

T = decomposition temperature [$^{\circ}\text{K}$]

R = gas constant [cal gmol^{-1}]

The plots of $\log k_1$ vs $1/T$ was a straight line as shown in Fig. 3.5. The activation energy E_1 for the initial

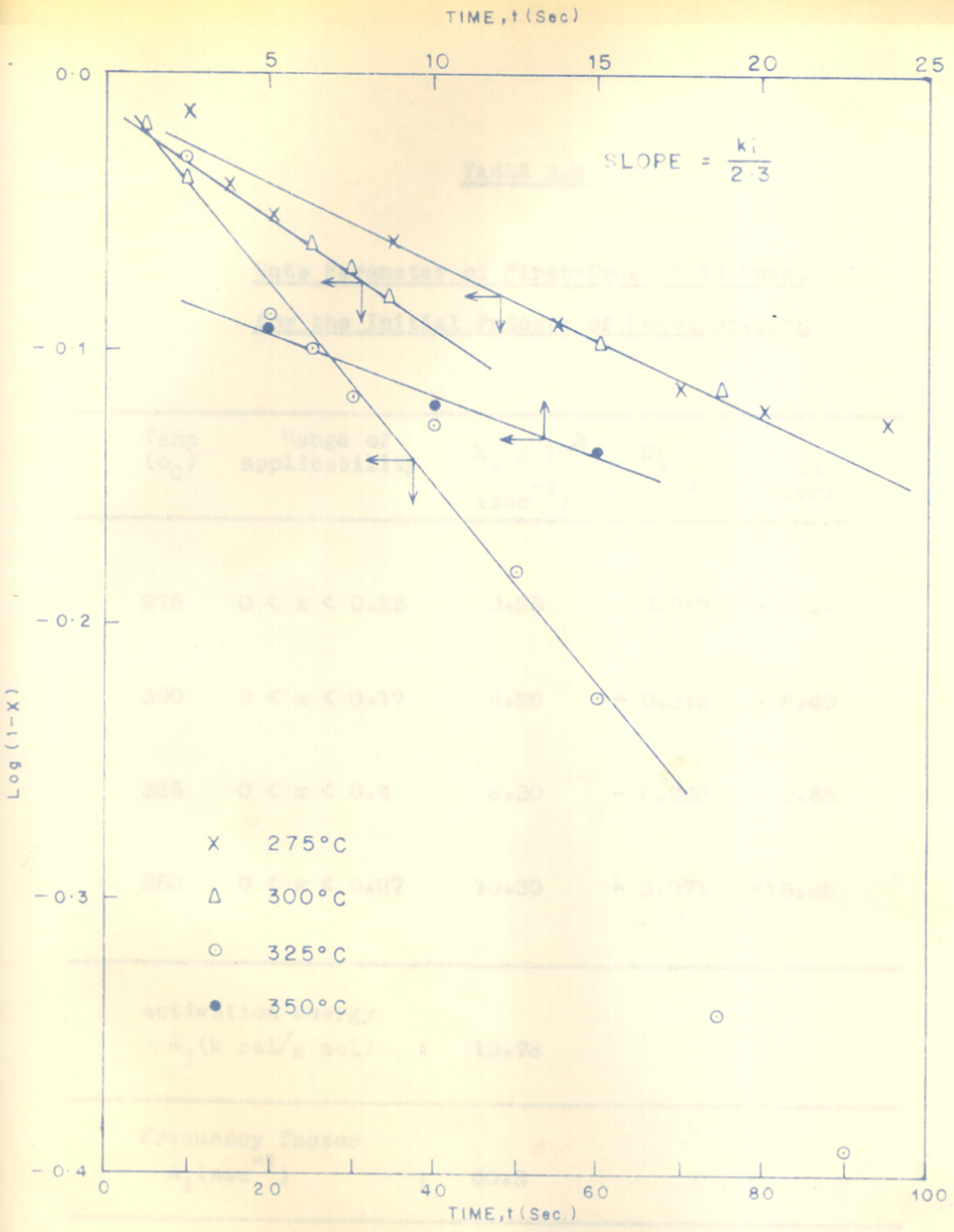


FIG. 3-4 FIRST ORDER PLOTS [Log(1-X) VS. t] FOR THE INITIAL DECOMPOSITION.

TABLE 3.2

Rate Parameter of First-Order Rate Model
for the Initial Process of Decomposition

Temp (°C)	Range of applicability	$k_1 \times 10^3$ (sec ⁻¹)	C_i	t_{01} (sec)
275	0 < x < 0.25	3.25	- 0.012	- 8.49
300	0 < x < 0.17	4.26	- 0.012	- 6.49
325	0 < x < 0.4	8.30	- 0.002	- 0.55
350	0 < x < 0.27	10.30	- 0.071	-15.85
<hr/>				
Activation Energy				
E_1 (k cal/g mol) : 10.78				
<hr/>				
Frequency factor				
A_1 (sec ⁻¹) : 60.3				
<hr/>				

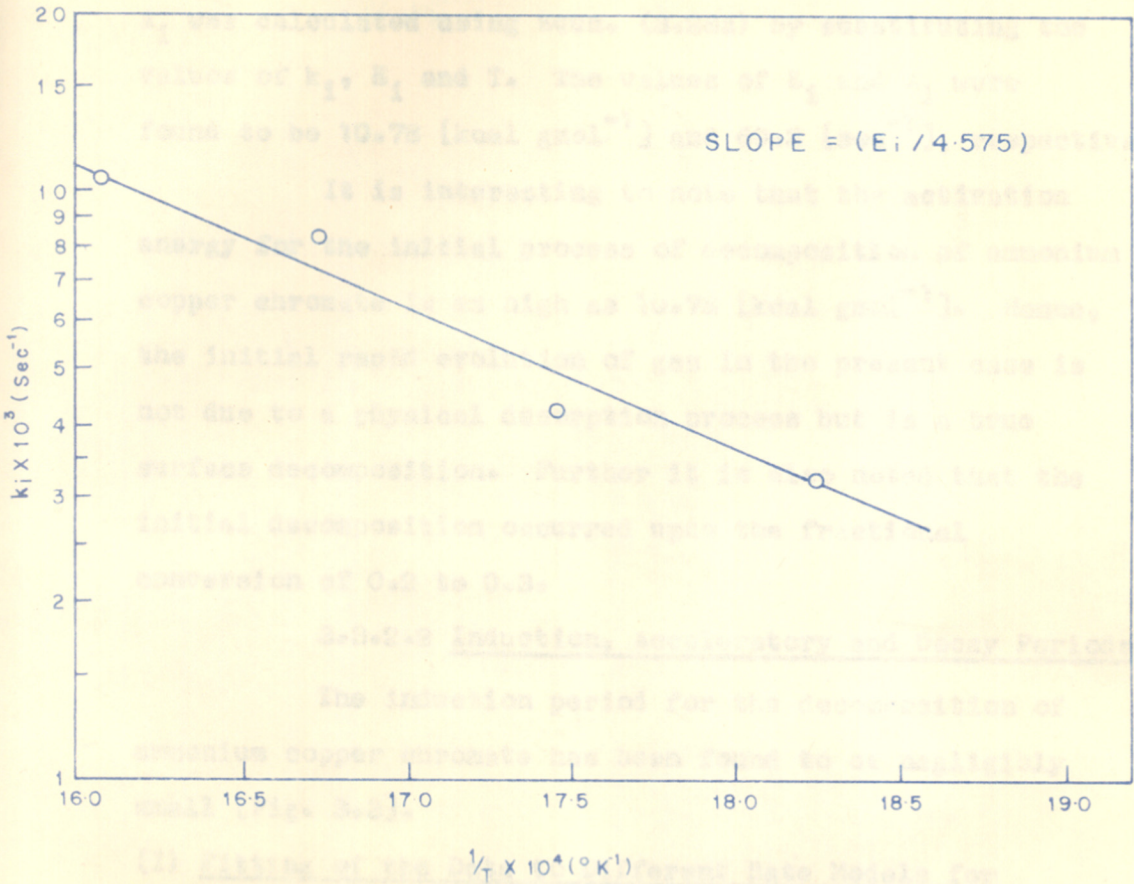


FIG. 3.5 ARRHENIUS PLOT FOR THE INITIAL DECOMPOSITION

and decay periods.

People's Constructive Case Representation

$$1 - (1-x)^{1/3} = k(t - t_0)$$

$$(1-x)^{1/3} = c - kt$$

$$\text{where } c = 1 - kt_0$$

decomposition process was obtained from the slope of the linear Arrhenius plot [Fig. 3.5]. The frequency factor A_1 was calculated using Equn. (3.28a) by substituting the values of k_1 , E_1 and T . The values of E_1 and A_1 were found to be 10.78 [kcal gmol⁻¹] and 60.3 [sec⁻¹], respectively.

It is interesting to note that the activation energy for the initial process of decomposition of ammonium copper chromate is as high as 10.78 [kcal gmol⁻¹]. Hence, the initial rapid evolution of gas in the present case is not due to a physical desorption process but is a true surface decomposition. Further it is also noted that the initial decomposition occurred upto the fractional conversion of 0.2 to 0.3.

3.3.2.2 Induction, Acceleratory and Decay Periods

The induction period for the decomposition of ammonium copper chromate has been found to be negligibly small [Fig. 3.3].

(I) Fitting of the Data to Different Rate Models for Acceleratory and Decay Periods

The following kinetic rate models have been employed for fitting the decomposition data in the region of acceleratory and decay periods.

Mampel's Contracting Cube Expression:

$$1-(1-x)^{1/3} = k(t + t_0) \quad (3.29a)$$

or

$$(1-x)^{1/3} = C - kt \quad (3.29b)$$

$$\text{where } C = 1-kt_0$$

Avrami-Erofeev Expression

$$\begin{aligned} [\log \left(\frac{1}{1-x} \right)]^{1/3} &= \frac{k'}{2.3} (t + t'_0) \\ &= \frac{k'}{2.3} t + C' \end{aligned} \quad (3.30)$$

$$\text{where } C' = \frac{k'}{2.3} t'_0$$

Prout-Tomkins Expression

$$\frac{dx}{dt} = k'' x(1-x) \quad (3.31a)$$

or in the integrated form

$$\begin{aligned} \log \left(\frac{x}{1-x} \right) &= \frac{k''}{2.3} (t + t''_0) \\ &= \frac{k''}{2.3} t + C'' \end{aligned} \quad (3.31b)$$

where

$$C'' = \frac{k''}{2.3} t''_0$$

The contracting cube plots $[(1-x)^{1/3}]$ vs t for the decomposition were found to be linear as shown in Fig. 3.6, thus showing a good fit of data to the Equn. [3.29].

The plots $\left\{ \log \left[\frac{1}{1-x} \right] \right\}^{1/3}$ vs t are shown in Fig. 3.7. These plots were also linear according to Equn. [3.30], thus showing a good fit of the data to the Avrami-Erofeev expression.

The Prout-Tomkins Expression [Equn. 3.31] has also been found to give a good fit to the data as evidenced by the linear plots of $\log [x/(1-x)]$ vs t as shown in Fig. 3.8.

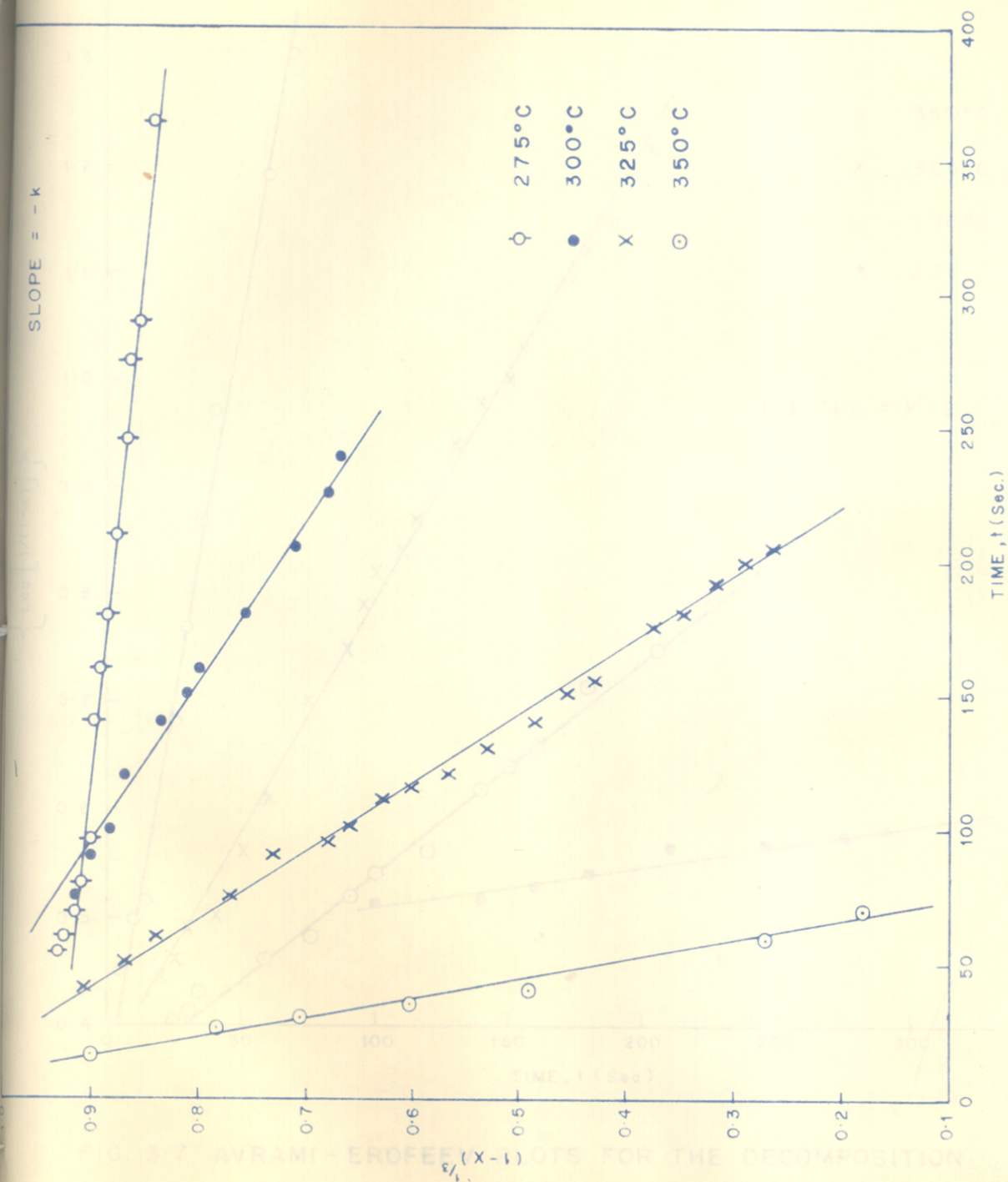


FIG. 3.6 CONTRACTING CUBE PLOTS FOR THE DECOMPOSITION

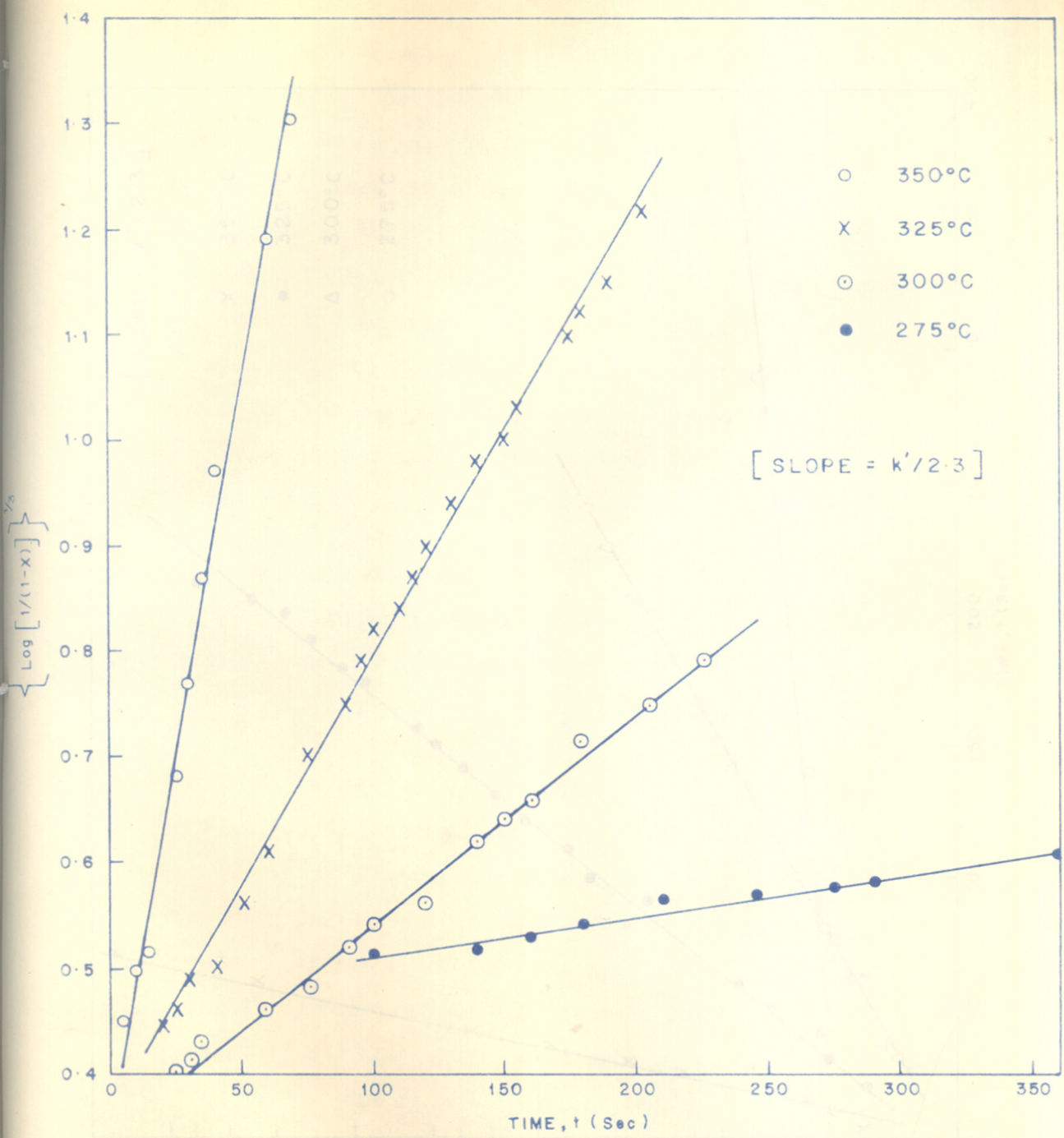


FIG. 3-7 AVRAMI - EROFEEV PLOTS FOR THE DECOMPOSITION

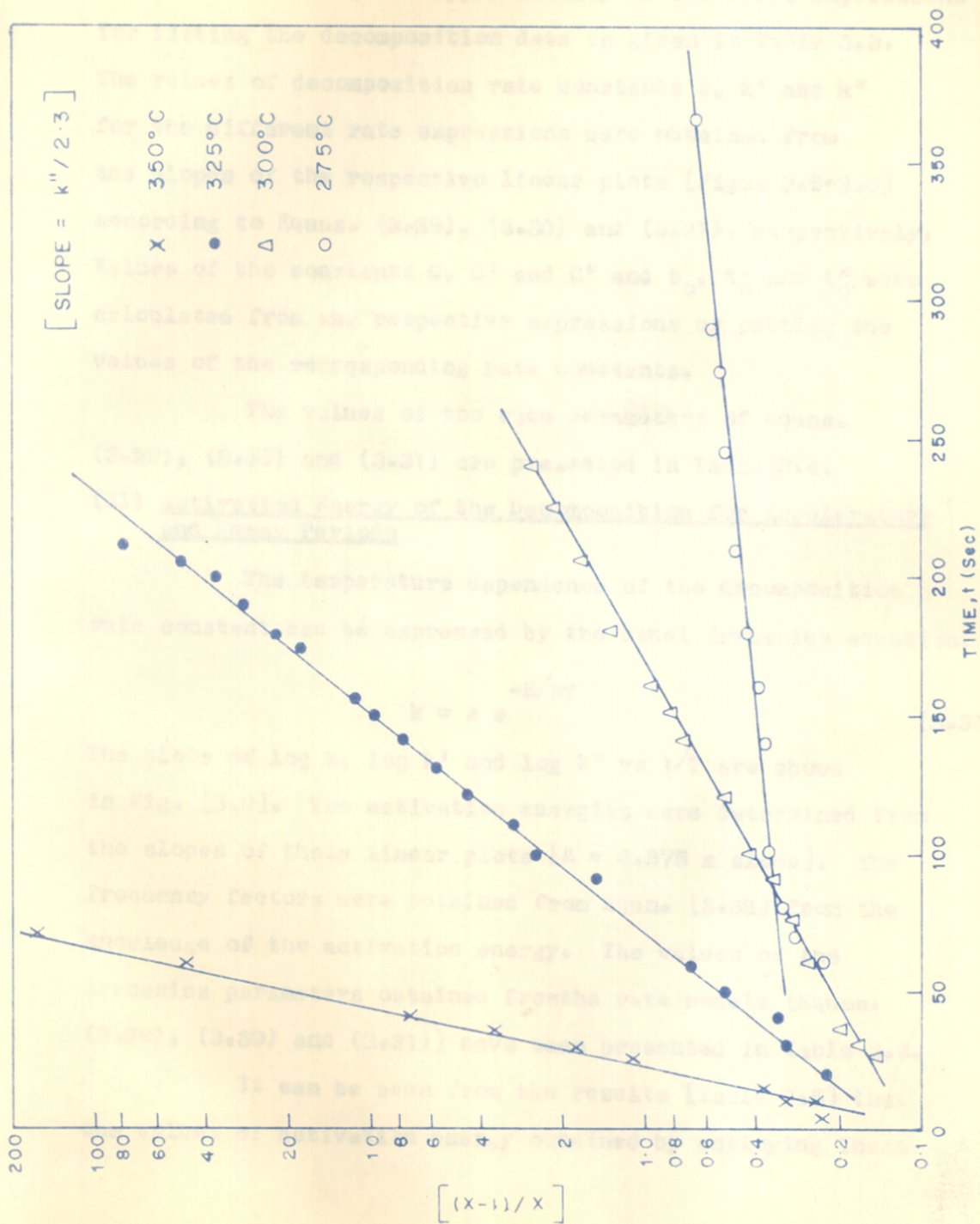


FIG. 3.8 PROUT-TOMPkins PLOTS FOR THE DECOMPOSITION

The range of applicability of the above expressions for fitting the decomposition data is given in Table 3.3. The values of decomposition rate constants k , k' and k'' for the different rate expressions were obtained from the slopes of the respective linear plots [Figs. 3.6-3.8] according to Equns. (3.29), (3.30) and (3.31), respectively. Values of the constants C , C' and C'' and t_0 , t_0' and t_0'' were calculated from the respective expressions by putting the values of the corresponding rate constants.

The values of the rate parameters of Equns. (3.29), (3.30) and (3.31) are presented in Table 3.4.

(II) Activation Energy of the Decomposition for Acceleratory and Decay Periods

The temperature dependence of the decomposition rate constant can be expressed by the usual Arrhenius equation,

$$k = A e^{-E/RT} \quad (3.32)$$

The plots of $\log k$, $\log k'$ and $\log k''$ vs $1/T$ are shown in Fig. [3.9]. The activation energies were determined from the slopes of these linear plots [$E = 4.575 \times \text{slope}$]. The frequency factors were obtained from Equn. [3.32] from the knowledge of the activation energy. The values of the Arrhenius parameters obtained from the rate models [Equns. (3.29), (3.30) and (3.31)] have been presented in Table 3.5.

It can be seen from the results [Table 3.5] that the values of activation energy obtained by employing these

TABLE 3.3

Range of Applicability of Different Rate Models for
the Decomposition (Acceleratory and Decay Periods)

Temp ($^{\circ}\text{C}$)	Contracting Cube expression [Eqn. (3.29)]	Avrami-Erofeev expression [Eqn. (3.30)]	Prout-Tompkins expression [Eqn. (3.31)]
275	$x \geq 0.19$	$x \geq 0.24$	$x \geq 0.23$
300	$x \geq 0.20$	$x \geq 0.13$	$x \geq 0.13$
325	$x \geq 0.21$	$x \geq 0.18$	$x \geq 0.18$
350	$x \geq 0.24$	$x \geq 0.19$	$x \geq 0.19$

TABLE 3.4

Rate Parameters of Different Rate Models for the Decomposition
(Acceleratory and Decay Periods)

Temp °C	Contracting cube expression [Equn. (3.29)]			Avrami-Erofeev expression [Equn. (3.30)]			Prout-Tompkins expression [Equn. (3.31)]		
	$k \times 10^3$ (sec ⁻¹)	C	t_0 (sec)	$k' \times 10^3$ (sec ⁻¹)	C'	t'_0 (sec)	$k'' \times 10^3$ (sec ⁻¹)	C''	t''_0 (sec)
275	0.274	0.94	226.5	0.877	0.472	1237.0	2.42	-0.568	-526.0
300	1.666	1.06	-36.0	4.459	0.350	180.6	13.11	-0.959	-163.0
325	3.926	1.06	-13.7	9.646	0.375	89.5	28.87	-0.893	-71.1
350	13.095	1.10	-7.6	32.920	0.350	24.4	106.85	-1.071	-17.5

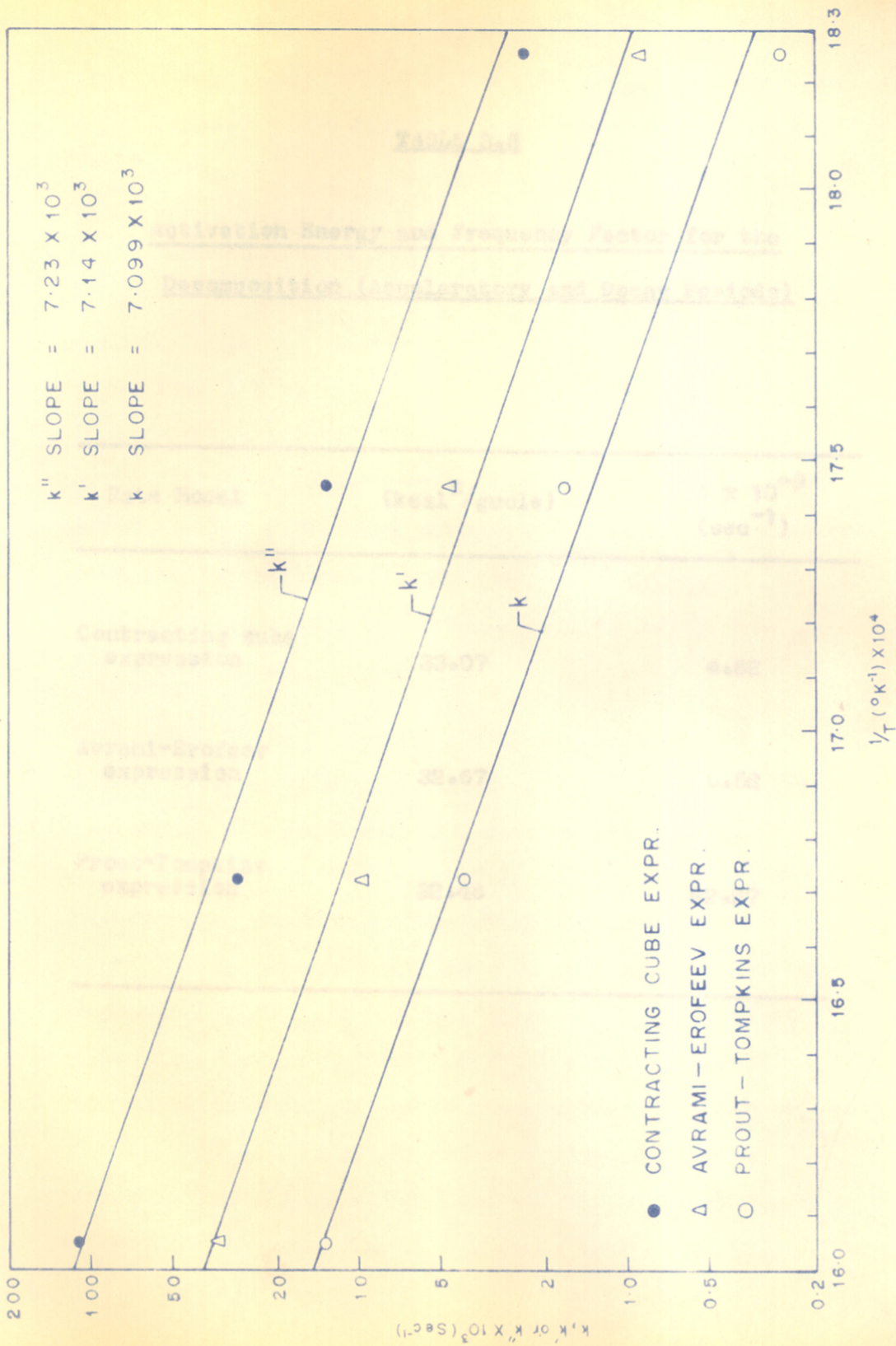


FIG. 3.9 ARRHENIUS PLOTS FOR THE DECOMPOSITION

(ACCELERATORY & DECAY PERIOD)

TABLE 3.5

Activation Energy and Frequency Factor for the
Decomposition (Acceleratory and Decay Periods)

Rate Model	(kcal ^E /gmole)	A x 10 ⁻⁹ (sec ⁻¹)
Contracting cube expression	33.07	4.62
Avrami-Erofeev expression	32.67	8.52
Prout-Tompkins expression	32.48	22.27

three rate models are nearly the same [$E_{(av.)} = 32.7 \text{ kcal gmol}^{-1}$], however the values of the frequency factors are different.

(III) Comparison between the Rate Models for their Relative Adequacy of Fit

It can be seen from the Figs. [3.6], [3.7] and [3.8] that all the rate models [Eqns. (3.29), (3.30) and (3.31)] give a good fit to the decomposition data for the acceleratory and decay periods.

[A] Residual Sum of Squares : A residual of the model is defined as the difference between the experimental and the predicted [or estimated] values of the fractional decomposition. Hence the residual sum of square [R.S.S.] can be written as

$$\text{R.S.S.} = [x_{(\text{experimental})} - x_{(\text{estimated})}]^2 \quad (3.33)$$

It is a measure of the inability of the model to describe exactly the kinetic data. The model which has the minimum residual sum of squares is considered to be the most probable model among the rival models.

The experimental and the predicted fractional conversions for the three rate models are presented in Table 3.6. The predicted fractional conversion were calculated by using an electronic programmable calculator [MOSCAL 1080 PS]. The programmes for computing the predicted fractional conversions and the residual sum of squares for the rate models are given in Appendix II.

TABLE 3.6

Comparison Between Experimental and Calculated
Fractional Decomposition for the Express-
ions (3.29), (3.30) and (3.31)

Time (sec)	x (Expt.)	x (calculated)		
		[Eqn. (3.29)]	[Eqn. (3.30)]	[Eqn. (3.31)]
1	2	3	4	5
<u>Temperature : 275°C</u>				
80	0.24	0.226	0.253	0.254
100	0.27	0.240	0.263	0.263
140	0.27	0.267	0.284	0.282
160	0.29	0.280	0.294	0.292
180	0.31	0.293	0.305	0.302
210	0.33	0.313	0.321	0.318
245	0.35	0.335	0.340	0.336
275	0.35	0.353	0.356	0.353
290	0.37	0.363	0.365	0.361
305	0.37	0.372	0.373	0.370
365	0.40	0.407	0.408	0.404
<u>Temperature : 300°C</u>				
60	0.20	0.115	0.208	0.193
75	0.23	0.162	0.244	0.228
90	0.26	0.246	0.282	0.264
100	0.30	0.287	0.309	0.290
120	0.34	0.363	0.366	0.347
140	0.42	0.435	0.424	0.408
150	0.45	0.468	0.454	0.440
160	0.49	0.500	0.454	0.473
180	0.57	0.561	0.544	0.538
205	0.63	0.629	0.617	0.618
225	0.68	0.678	0.673	0.678
240	0.70	0.712	0.712	0.719

Table 3.6 cont'd

1	2	3	4	5
<u>Temperature : 325^oC</u>				
25	0.20	0.11	0.224	0.2088
30	0.24	0.164	0.251	0.2336
40	0.25	0.264	0.308	0.2890
50	0.34	0.356	0.368	0.352
60	0.41	0.439	0.432	0.420
75	0.54	0.551	0.529	0.528
90	0.61	0.647	0.625	0.633
95	0.68	0.676	0.654	0.666
100	0.72	0.702	0.684	0.697
110	0.75	0.752	0.739	0.754
115	0.78	0.775	0.765	0.780
120	0.82	0.796	0.789	0.804
130	0.85	0.834	0.833	0.845
140	0.89	0.867	0.871	0.879
150	0.91	0.895	0.902	0.907
175	0.95	0.948	0.956	0.952
200	0.97	0.979	0.984	0.976
210	0.99	0.987	0.989	0.982
<u>Temperature : 350^oC</u>				
10	0.24	0.09	0.241	0.198
15	0.270	0.262	0.339	0.297
25	0.520	0.539	0.557	0.552
30	0.650	0.646	0.663	0.677
35	0.780	0.736	0.758	0.782
40	0.880	0.810	0.836	0.859
45	0.880	0.866	0.896	0.912
60	0.980	0.969	0.983	0.981
70	0.990	0.994	0.997	0.993

The values of the residual sums of square for the rate models are given in Table 3.7. It can be seen from the results that the Prout-Tomkins expression [Eqn. (3.31)] has the lowest residual sum of squares for all the temperatures of decomposition studied. Based on this fact, it can be concluded that the Prout-Tompkins rate expression fits the decomposition data more adequately than the other two models and hence can be considered as the best rate expression for the decomposition of ammonium copper chromate for acceleratory and decay periods. But more firm decision on the statistical basis can only be obtained by comparing their variances of residuals.

[B] Variance Analysis of the Rate Models : The F test [involving the comparison of two variances] can be used for comparison between two models in respect of their adequacy of fit for a particular set of data.

For such purpose F is expressed as

$$F = \frac{\text{Variance of model 1 [i.e. } \sigma_1^2 \text{]}}{\text{Variance of model 2 [i.e. } \sigma_2^2 \text{]}} \quad (3.34)$$

The variance of $[\sigma^2]$ or residual mean of squares [R.M.S.S.] is defined as

$$\sigma^2 = \frac{\{x_{(\text{experimental})} - x_{(\text{predicted})}\}^2}{n-1} \quad (3.35)$$

where n = number of data points. If the calculated value of F is significant [i.e. F-calculated > F-table], then the model 1 fits the data less adequately than that of model 2

TABLE 3.7

Analysis of Variance of Equns. (3.29), (3.30) and (3.31)

Temp (°C.)	Deg- ree of free- dom	Residual sum of squares $\times 10^4$		Residual mean sum of squares		F (calculated)	F Table at 95% confi- dence				
		Equn. (3.29)	Equn. (3.31)	Equn. (3.29) $\sigma_1^2 \times 10^4$	Equn. (3.30) $\sigma_2^2 \times 10^4$			Equn. (3.31) $\sigma_3^2 \times 10^4$			
275	10	18.0	7.9	8.9	1.80	0.79	0.89	2.28	2.02	0.89	2.97
300	11	113	16.0	22.2	10.60	2.36	2.01	4.49	5.27	1.17	2.82
325	18	188.0	97.5	38.4	10.44	5.42	2.13	1.93	4.90	2.54	2.22
350	8	303.0	91.3	57.1	37.90	11.40	7.14	3.32	5.31	1.60	3.44

Equn. (3.29) : Contracting cube expression; Equn. (3.30) : Avrami-Erofeev expression;

Equn. (3.31) : Prout-Tompkin expression.

at the confidence level corresponding to that of the table value of F . Further if the calculated value of F is one [i.e. when $\delta_1^2 = \delta_2^2$], then both the models fit the data adequately to the same extent. If the value F is very much less than one, then the value of F should be calculated as

$$F = \frac{\delta_2^2}{\delta_1^2} \quad (3.36)$$

Now if F calculated $>$ F -table then model 2 fits the data less adequately than that of model 1; if F calculated $<$ F -table, then F is not significant and hence both of the models fit the data adequately to the same extent.

The variance analysis of the rate models [Eqns. (3.29), (3.30) and (3.31)] has been presented in Table 3.7. The variance, δ_3^2 , of the Prout-Tompkins expression is the lowest among the variances of the rate models.

Comparison Between Contracting Cube Expression and Avrami-Erofeev Expression :

At 275° , 325° and 350°C

$$F \text{ [calculated]} < F \text{ [table]}$$

i.e. F is not significant and hence both the models fit the data adequately to the same extent.

At 300°C

$$F \text{ [calculated]} > F \text{ [table]}$$

i.e. F is significant and hence Avrami-Erofeev rate expression [Eqn. (3.30)] fits the data more adequately than the contracting cube expression [Eqn. (3.29)].

Comparison Between Contracting Cube Expression and

Prout-Tompkins Expression :

At 275°C

$$F \text{ [calculated]} < F \text{ [table]}$$

i.e. F is not significant and hence both the models fit the data adequately at 275°C to the same extent.

At 300°, 325° and 350°C

$$F \text{ [calculated]} > F \text{ [table]}$$

i.e. F is significant and hence the Prout-Tompkins expression fits the data more adequately than the contracting cube expression.

Comparison Between Avrami-Erofeev Expression and Prout

Tompkins Expression :

At 275°, 300° and 350°C

$$F \text{ [calculated]} < F \text{ [table]}$$

i.e. F is not significant and hence both the models fit the data adequately to the same extent at these temperatures.

At 325°C

$$F \text{ [calculated]} > F \text{ [table]}$$

i.e. F is significant and hence the Prout-Tompkins expression fits the data more adequately than the Avrami-Erofeev expression.

(IV) Final choice of the Rate Model for the Decomposition

The comparison between the R.S.S. and variance of

the three models leads to the conclusion that the Prout-Tompkins rate expression fits the data more adequately than the other two models. Though the Avrami-Erofeev expression gives comparable fitting to the data at temperatures 275°, 300° and 350°C, it is less adequate at 325°C than the Prout-Tompkins expression.

A graphical comparison between the experimental and predicted values of fractional decomposition from the Prout-Tompkin expression is presented in Fig. 3.10. It can be seen from the Fig. 3.10 that there is only a slight deviation of the predicted fractional decompositions from the experimental ones. The average deviation of the predicted conversions from the experimental ones are 2.55% at 325°C, 2.54% at 300°C, 2.47% at 325°C and 4.94% at 350°C.

3.4 SUMMARY AND CONCLUSIONS

The decomposition of ammonium copper chromate has been studied in the temperature range 275° to 350°C. The decomposition curves [fractional decomposition vs time] were of typical sigmoidal shape showing a rapid evolution of gases due to initial process of decomposition and a very short induction period followed by acceleratory and decay periods.

The initial process of decomposition could be expressed by the first order decomposition expression and was found to be a true surface decomposition process as

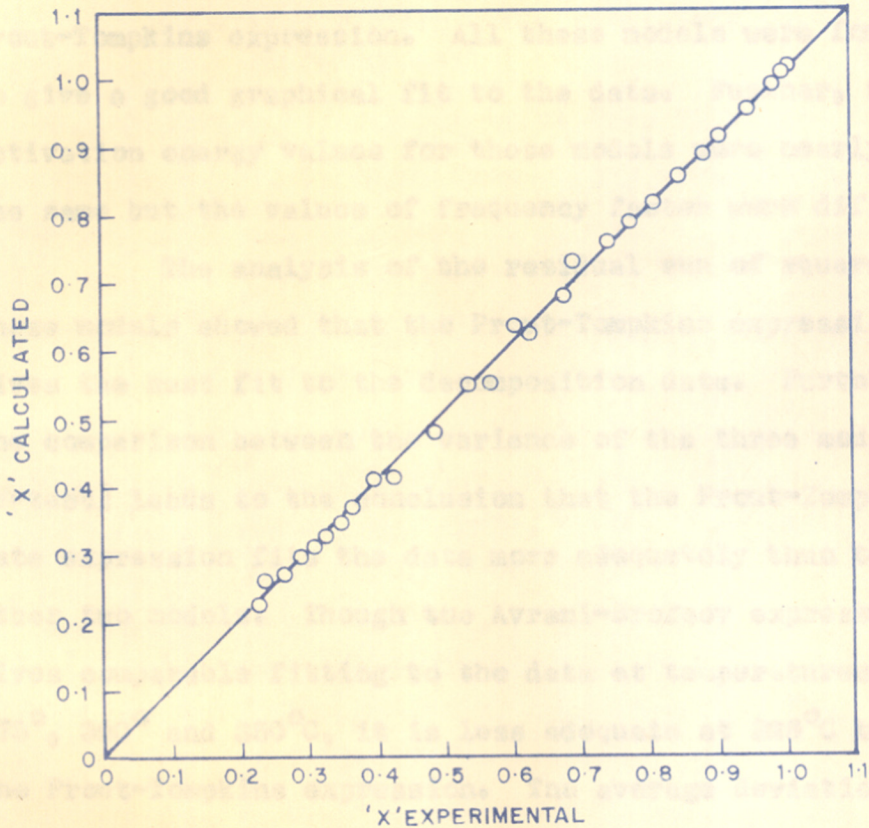


FIG. 3.10 COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL FRACTIONAL DECOMPOSITION FOR PROUT-TOMPKINS RATE MODEL

evidenced by the high activation energy [$E = 10.8 \text{ kcal gmol}^{-1}$].

In case of acceleratory and decay periods, the decomposition data was fitted graphically to the contracting cube expression, the Avrami-Erofeev expression and the Prout-Tompkins expression. All these models were found to give a good graphical fit to the data. Further, the activation energy values for these models were nearly the same but the values of frequency factor were different.

The analysis of the residual sum of squares of these models showed that the Prout-Tompkins expression gives the best fit to the decomposition data. Further, the comparison between the variance of the three models [F-test] leads to the conclusion that the Prout-Tompkins rate expression fits the data more adequately than the other two models. Though the Avrami-Erofeev expression gives comparable fitting to the data at temperatures 275° , 300° and 350°C , it is less adequate at 325°C than the Prout-Tompkins expression. The average deviation of the estimated fractional decompositions from the observed ones have been found to be 2.7% for the Prout-Tompkins expression.

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APPENDIX-1

Standard 'd' values (A) for Cr_2O_3 , CuO , Cu_2O ,

CuCrO_4 , CuCr_2O_4 and $\text{Cu}_2\text{Cr}_2\text{O}_4$

Cr_2O_3	CuO	Cu_2O	CuCrO_4	CuCr_2O_4	$\text{Cu}_2\text{Cr}_2\text{O}_4$
1.67(100)	<u>2.52(100)</u>	<u>2.47(100)</u>	<u>4.20(100)</u>	4.87(15)	5.69(< 5)
	<u>2.32(96)</u>	2.14(37)	<u>2.57(100)</u>	3.02(15)	<u>2.85(40)</u>
2.67(70)	2.53(49)	1.51(27)	<u>2.14(62)</u>	<u>2.874(35)</u>	2.57(20)
1.47(70)		1.28(17)	6.1(5)	<u>2.656(100)</u>	<u>2.47(100)</u>
3.63(50)		1.23(4)		<u>2.401(60)</u>	<u>2.210(40)</u>
				1.960(10)	1.911(5)
				1.70(15)	1.640(45)
				<u>1.629(40)</u>	<u>1.483(35)</u>
				<u>1.505(30)</u>	1.439(5)
				<u>1.442(40)</u>	1.426(30)
				1.293(5)	1.319(20)
				<u>1.276(15)</u>	1.275(15)
				1.195(5)	1.234(10)
				1.106(5)	1.172(< 5)
					1.105(45)
					<u>1.030(20)</u>
					0.288(5)
Card No.	Card No.	Card No.	Card No.	Card No.	Card No.
3-1124	S = 0661	S = 0667	1-0257	S = 0657	S = 0668

Values given in the brackets are the relative intensities.

APPENDIX-II

Programme for Calculating Predicted Fractional Conversions and Residual Sum of Squares for Various Rate Models

(I) Contracting Cube Model [Eqn. (3.29)]

$$1-(1-x)^{1/3} = k(t + t_0)$$

or

$$(1-x)^{1/3} = C-kt$$

$$\text{where } C = 1-kt_0$$

$$x = (C-kt)^3$$

$$= (kt-C)^3$$

	M	0	1	2	3	4	
		k	C	t	x		$(x_1-x)^2$
0		C		25		1	
1		CM		26]	
2		4		27		SQ	
3		MC		28			
4		5		29		x	
5		H/R (feed k)		30		3	
6		SM		31		=	
7		0		32		-	
8		C		33		+	
9		H/R (feed C)		34		1	
10		SM		35		=	
11		1		36		H/R (feed x_1)	
12		C		37		+	
13		H/R (feed t)		38		H/R (feed x)	
14		SM		39		=	
15		2		40		SQ	
16		C		41		M +	
17		[42		4 =	
18		RM		43		GOTO	
19		0		44		1	
20		x		45		2	
21		RM		46		JUMP	
22		2		47		RM4 =	$(x_1-x)^2$
23		-					
24		RM					

(II) Avrami-Brofesov Model [Equn. (3.30)]

$$\left[\log \left(\frac{1}{1-x} \right) \right]^{1/3} = \frac{k'}{2.3} (t + t_0')$$

$$= \frac{k}{2.3} (t) + C'$$

where $C' = \frac{kt_0'}{2.3}$

$$x_2 = 1 - \exp \left[-2.3 \left(\frac{k't}{2.3} + C' \right)^3 \right]$$

M	0	1	2	4	5
	k'	C'	t	$\sum (x_2 - x)^2$	2.3

0	C	25	1
1	CM	26	=
2	4	27	x
3	H/R (feed k)	28	3
4	SM	29	x
5	0	30	RM
6	C	31	5
7	H/R (feed C')	32	=
8	SM	33	Exp
9	1	34	1/x
10	C	35	-
11	H/R (feed t)	36	1
12	SM	37	=
13	2	38	H/R (Resd-x ₂)
14	C	39	+
15	RM	40	H/R (feed x)
16	0	41	=
17	x	42	Sq
18	RM	43	M+
19	2	44	4
20	-	45	GOTO
21	RM	46	1
22	5	47	0
23	+	48	JUMP
24	RM		

(III) Prout-Tompkins Model [Equn. (3.31)]

$$\frac{dx}{dt} = k'' x(1-x)$$

or

$$\log \left(\frac{x}{1-x} \right) = \frac{k''}{2.3} (t + t_0'') = \frac{k''}{2.3} t + C''$$

$$\text{where } C'' = \frac{k''}{2.3} t_0''$$

$$\ln \left(\frac{x}{1-x} \right) = k'' t + 2.3 C''$$

$$\frac{1}{x} - 1 = \exp [-k'' t - 2.3 C'']$$

$$x_3 = 1/[1 + \exp (-k'' t - 2.3 C'')]$$

M	0	1	2	3	4
	k''	C''	t	$2.3 C''$	$\sum (x_3 - x)^2$

0	C	25	x
1	CM	26	RM
2	4	27	2
3	H/R (feed k'')	28	+
4	SM	29	RM
5	0	30	3
6	C	31	= x
7	H/R (feed C'')	32	e ^x
8	SM	33	1/x
9	1	34	+
10	C	35	1
11	H/R (feed 2.3)	36	=
12	x	37	1/x
13	RM	38	H/R (Read x ₃)
14	1	39	-
15	=	40	H/R (feed x)
16	SM	41	=
17	3	42	SQ
18	C	43	M+
19	H/R (feed t)	44	4
20	SM	45	GOTO
21	2	46	1
22	C	47	8
23	RM	48	JUMP
24	0		
