CHAPTER II

CHAPTER-II

PREPARATION AND THERMOGRAVIMETRIC ANALYSIS OF MIXED NICKEL-CADMIUM OXALATES

The thermal analysis technique of thermogravimetry (TG) is one on which the change in sample mass is recorded as a function of temperature, preferably linear. The resulting mass change versus temperature curve (Thermogram) provides information concerning the thermal stability and composition of the initial sample, the thermal stability and composition of any intermediate compounds that may be formed and the composition of the residue.

The thermal stability is defined as a general term[63] indicating the stability of a substance to maintain its properties as nearly unchanged as possible on heating. The thermobalance is a useful technique for studying the ability of a substance to maintain its mass under a variety of conditions. The first thermobalance was developed in 1915 by Honda.[64] Guichard,[65] and Duval[66] used the thermobalance to create an interest in thermogravimetry in the late 1940s and early 1950s. He applied this technique for a wide range of materials, mainly in air, but in a few cases in an inert atmosphere or in a vacuum. He reports the decomposition with a somewhat restricted air supply, at a heating rate of 8-10°/min of oxalates of sixteen metals. Robin[67] reported that thermal decomposition in air of oxalates of certain bivalent metals, gave in certain circumstances first the metal, and that this was oxidised almost immediately to the oxide.

This chapter deals with the reaction of the type:

$$\text{Solid (A)} \longrightarrow \text{Solid (B)} + \text{Gas (C)}$$

and the effect of cadmium oxalate on the thermal behaviour of nickel oxalate.

Preparation of Mixed Nickel-Cadmium Oxalates

Mixed oxalates of nickel and cadmium were prepared by co-precipitation method. All chemicals were of Analar Reagent grade quality. Nickel nitrate and cadmium nitrate solutions of 1 M were prepared and mixed in the required proportions. The mixed solutions thus prepared were added dropwise to 1 M solution of oxalic acid. A series of mixed Ni-Cd oxalates were thus prepared. The proportion of the solutions taken and the compositions of the precipitated oxalates obtained are given in Table-II.

The oxalic acid solution was taken in a 500 ml beaker to which were added drop by drop the mixed solution of nickel nitrate and cadmium nitrate. The solutions were stirred vigorously during mixing and for further half an hour to complete the reaction. The precipitates obtained were filtered on a ground sintered glass funnel, washed free of oxalic acid and nitrate ions with distilled water and dried at 100°C. The cadmium and

TABLE-II

COMPONENTS AND COMPOSITIONS OF MIXED NICKEL-CADMIUM OXALATES

Nickel Nitrate solution (1 M) ml	Cadmium Nitrate solution (1 M) ml	Oxalic acid solution (1 M) ml	Composition of the precipitate in atomic percentage of the metals	
			Ni	Cd
100.00	00.00	200	100.00	00.00
90.00	10.00	200	87.84	12.16
80.00	20.00	200	76.13	23.18
70.00	30.00	200	67.94	32.06
60.00	40.00	200	58.60	42.35
50.00	50.00	200	47.68	52.32
40.00	60.00	200	39.15	60.85
30.00	70.00	200	29.95	70.05
20.00	80.00	200	19.30	80.70
00.00	100.00	200	00.00	100.00

nickel contents in the final samples were determined by conventional chemical analysis methods. The composition showed some deviation from the proportions of the two salt solutions taken. This may be due to incomplete formation of the precipitated product. This is evident from the fact that filtrate contained some dissolved cadmium and nickel as indicated by its colour.

Thermogravimetric Study of Nickel-Cadmium Oxalates

Thermogravimetry probably has a large number of variables because of the dynamic nature of the temperature change of the sample. And the nature, precision and accuracy of the experimental results are affected by the large number of factors. Basically, the factors that can influence the thermogram of a sample fall into the following two categories, viz.,

1. Instrumental factors, and
2. Sample characteristics.

The former includes:

1. Furnace heating rate
2. Recording or chart speed
3. Furnace atmosphere
4. Geometry of sample holder
5. Sensitivity of recording and mechanism
6. Composition of sample

Sample characteristics are:

1. Amounts of sample
2. Particle size
3. Solubility of evolved gases in sample
4. Heat of reaction
5. Sample packing
6. Nature of the sample
7. Thermal conductivity.

Due care was taken to these factors to obtain reproducible and comparable conditions for the study of the series of samples prepared by us.

Thermogravimetric Apparatus

The thermogravimetric apparatus is 'Derivatograph, MOM Hungarian Optical Works, Budapest.' It consists of the following parts:

Data Specifications

1. Balance: Air-damped analytical balance equipped with an automatic weight loading device.
   - i) Basic sensitivity: 20 mg/0-100 divisions ± 0.2 mg.
   - ii) Measuring range: 0-10 grams.
   - iii) Sensitivity variability: 50, 100, 200, 500, 1,000, 2,000 mg/100 divisions.

iv) Actual weights: 10, 10, 20, 50, 50, 100, 100, 200, 500, 1,000, 2,000, 5,000 mg.

v) Measuring accuracy

for 20 mg fundamental sensitivity ± 1 per cent

for 50-100 mg fundamental sensitivity ± 0.5 per cent

for 200-2,000 mg fundamental sensitivity ± 0.2 per cent

vii) Sprint level: Circular level 17 mm dia. constant 6'.

2. Dilation

i) Measuring range: maximum ± 1.3 mm

ii) Readout accuracy: ± 0.02 mm

iii) Test specimen size: 16 x 10 mm, length variable between 15-40 mm

iv) Compressing force: approx. 5,000 kg.

v) Temperature range: Maxi. upto 1050°C.

3. Galvanometers: Three type Kipp and Zonen, String and mirror galvanometers:

i) Sensitivity: 1.10^{-10} A/mm/m

ii) Internal resistance: 350-400 Ohms.

iii) Swing duration: 10-11 sec.

iv) Sensitivity reduction:

(1) DTA: 1/1, 1/1.5, 1/2, 1/3, 1/5, 1/10, 1/15, 1/20, 1/30, 1/50, 1/100, 1/200.

(2) DTG: 1/1, 1/1.5, 1/2, 1/3, 1/5, 1/10, 1/15, 1/20, 1/30, 1/50, 1/100, 1/200.

(3) T: 125°C, 250, 500, 1,000, 1,500°C

v) Measurement: With a Pt-PtRh thermocouple

Upto 1050°C of 0.35 mm dia.

Upto 1500°C of 0.5 mm dia.

4. Annealing furnace: Designed in a double layout, provided with an automatic lifting mechanism.

i) Maximum temp. : 1050°C.

ii) Maximum heating voltage: 220 V.

iii) Furnace internal dimensions: 70 dia. x 120 mm.

5. Temperature Regulator: Built-in-temp. regulator.

i) Temp. range: 0-160°C.

ii) Measurement: With a Pt-Pt-Rh thermocouple.

6. Recorder: Operating with photographic recording

i) Speeds: 6, 25, 50, 100, 200, 400, minutes/300°C

ii) Recording paper size: 430 x 230 mm ± 0.5 mm

iii) Recording paper: Forte Dokubrom.

The derivatograph has been designed for the simultaneous measurement of weight change/TG/, weight change rate/DTG/, enthalpy variation/DTA/ and temp. change/T/ of the test samples, meanwhile the temperature of the furnace is rising with a nearby uniform rate.

RESULTS

THERMOGRAVIMETRIC RESULTS

The results were plotted as per cent mass loss versus temperature (Figs. 1-A, 1-B, 1-C).

The first part of the thermogram corresponds to the dehydration step representing loss of water of crystallization. The second part represents decomposition.

DEHYDRATION STEP

The first part of Figs. 1-A, 1-B, 1-C corresponds to the dehydration step. With increasing percentage of cadmium, onset dehydration temperature decreases (Fig. 3-A).

For 12.16 per cent Cd the onset dehydration temperature is decreased, it again increases for 23.82 per cent Cd. But it decreases as the cadmium component in the sample goes on increasing and reaches to 42.33 per cent Cd. It is unchanged for 60.85 per cent Cd. Further as the cadmium component increases onset dehydration temperature decreases.

Generally, the dehydration step and its range become smaller as the percentage of Cd increases and it disappears for pure Cd oxalate, indicating that Cd oxalate does not contain the water of crystallization.

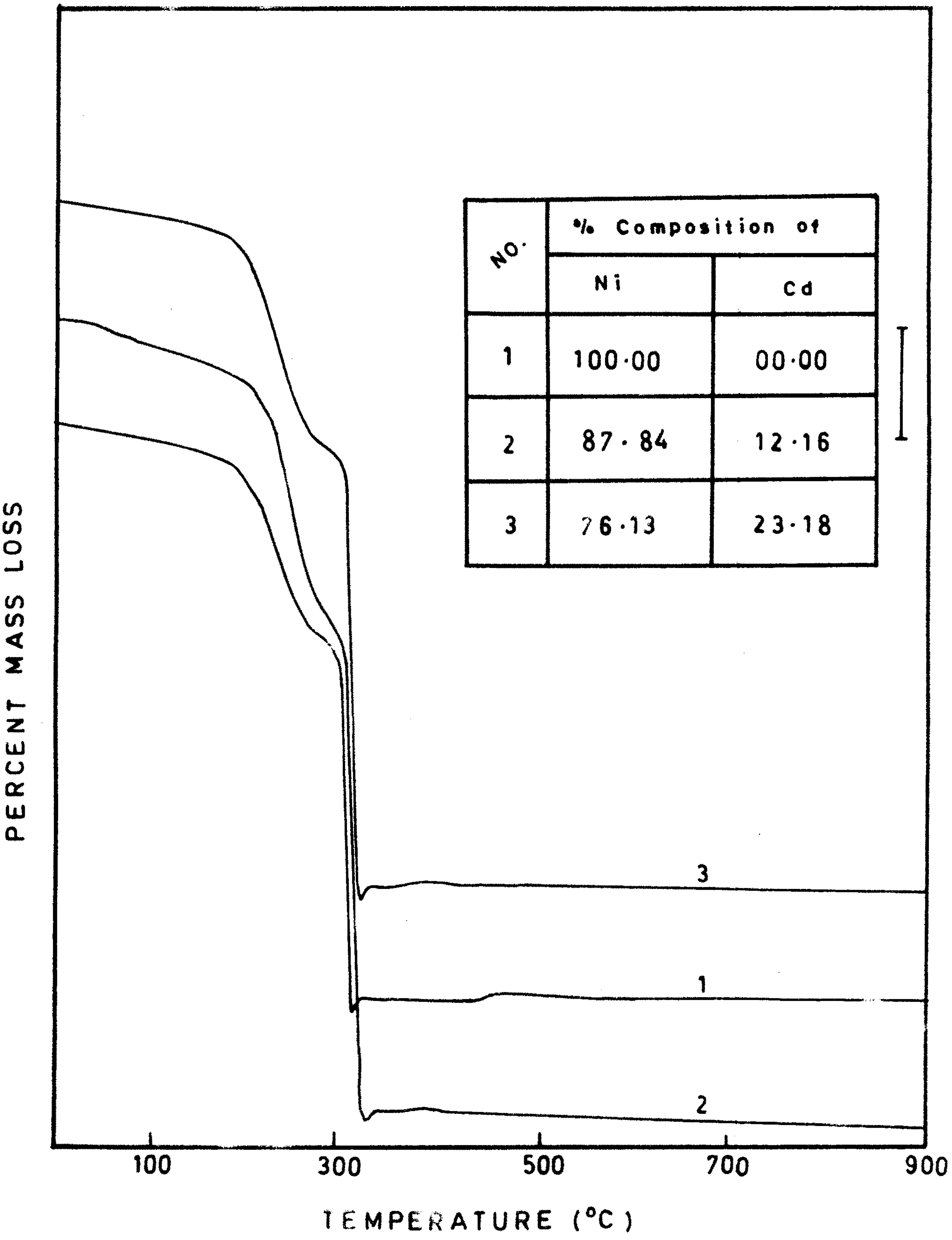
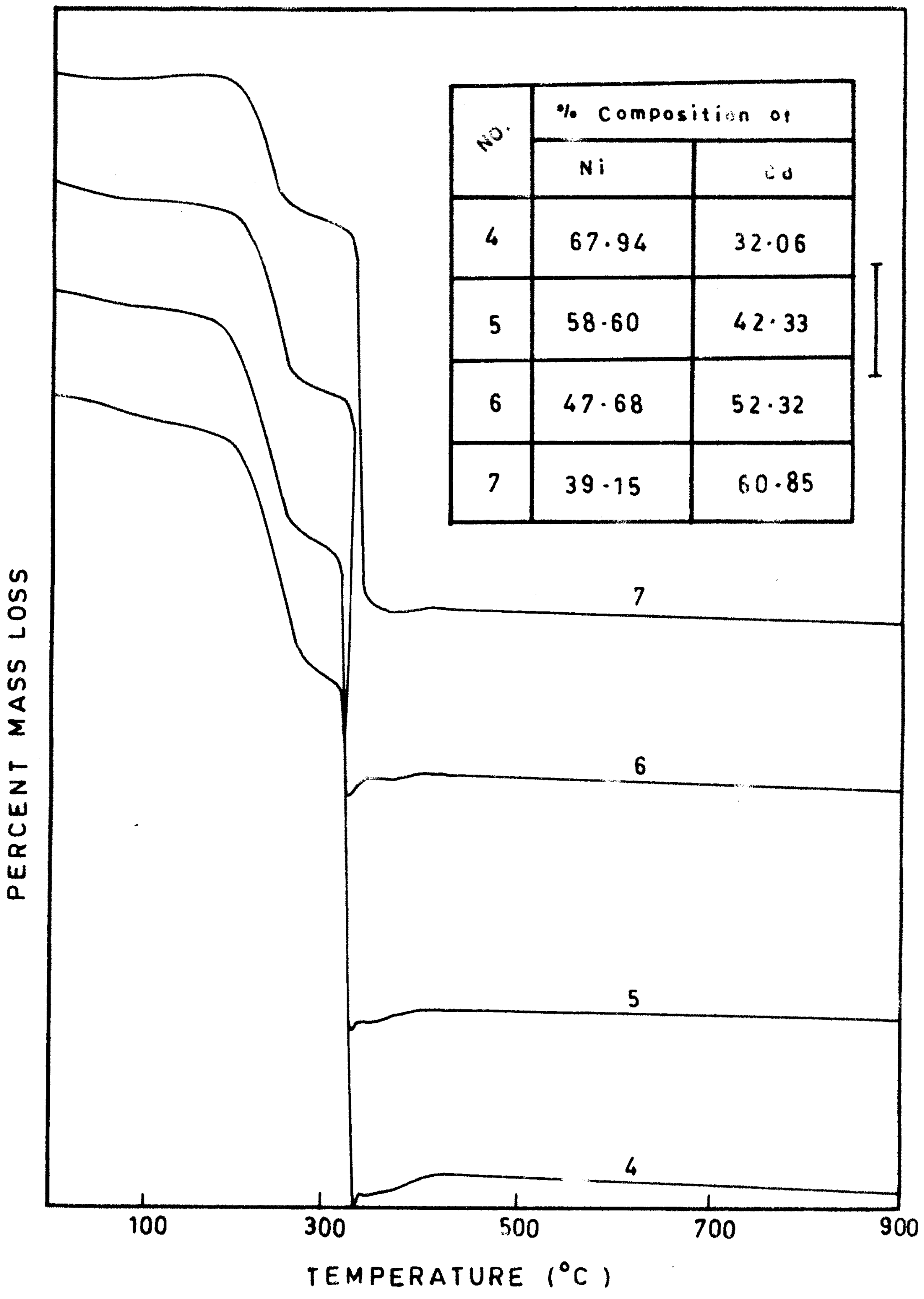
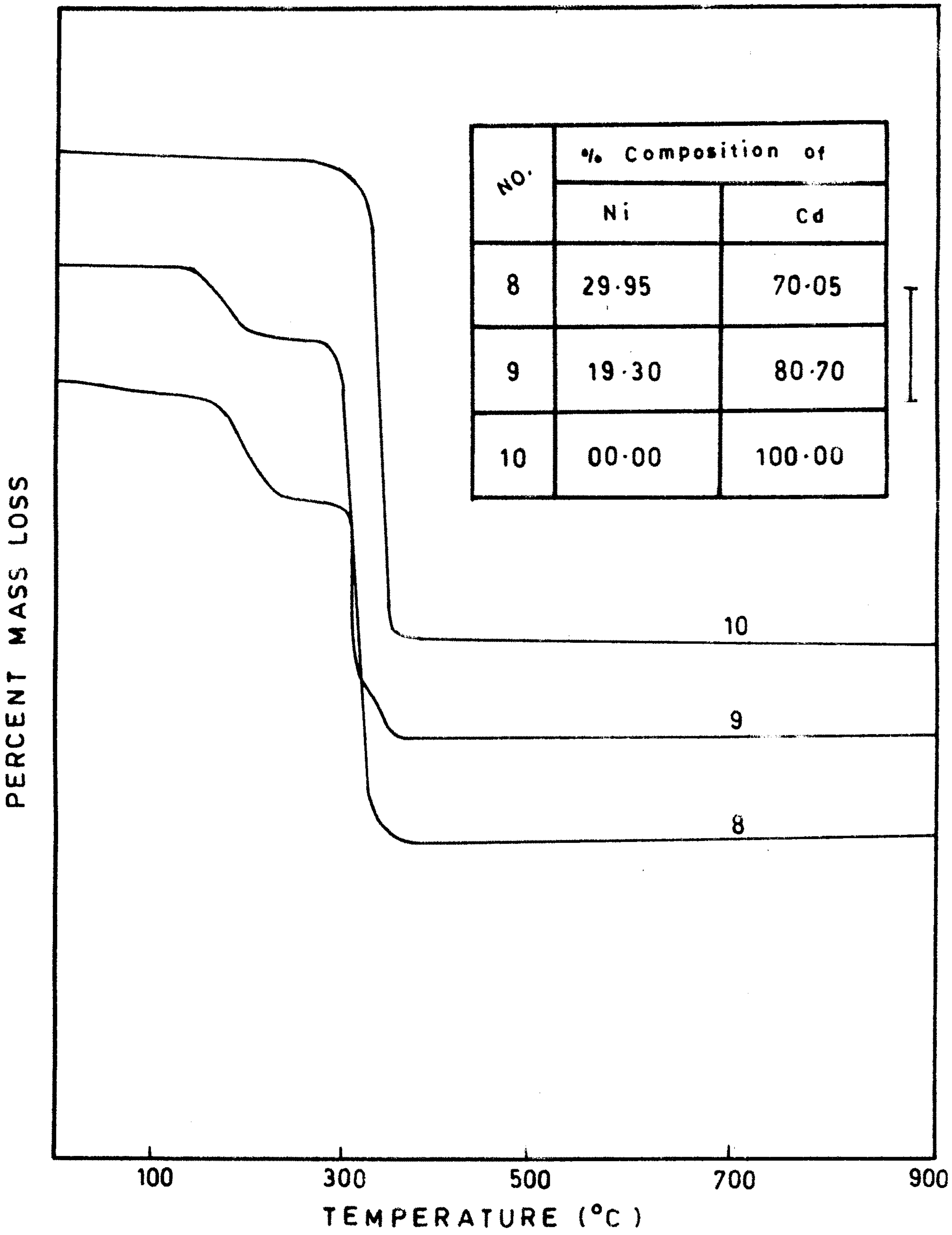


FIG-1-A : PERCENT MASS LOSS V/S TEMPERATURE CURVE .



NO.	% Composition of	
	Ni	Cd
4	67·94	32·06
5	58·60	42·33
6	47·68	52·32
7	39·15	60·85

FIG.1-B : PERCENT MASS LOSS V/S TEMPERATURE CURVE .



NO.	% Composition of	
	Ni	Cd
8	29·95	70·05
9	19·30	80·70
10	00·00	100·00

FIG. 1-C : PERCENT MASS LOSS V/S TEMPERATURE CURVE.

DECOMPOSITION STEP

The second part of the Figs. 1-A, 1-B, 1-C corresponds to the decomposition of anhydrous oxalate. No linearity is observed regarding the onset decomposition temperature (Fig. 3-B). For 12.16, 23.82, 32.06 and 42.33 per cent Cd onset decomposition temperature is unchanged. It is decreased for 52.32 per cent Cd and remains unchanged for 60.85 per cent Cd. It again increased for 70.05 per cent Cd and then decreased.

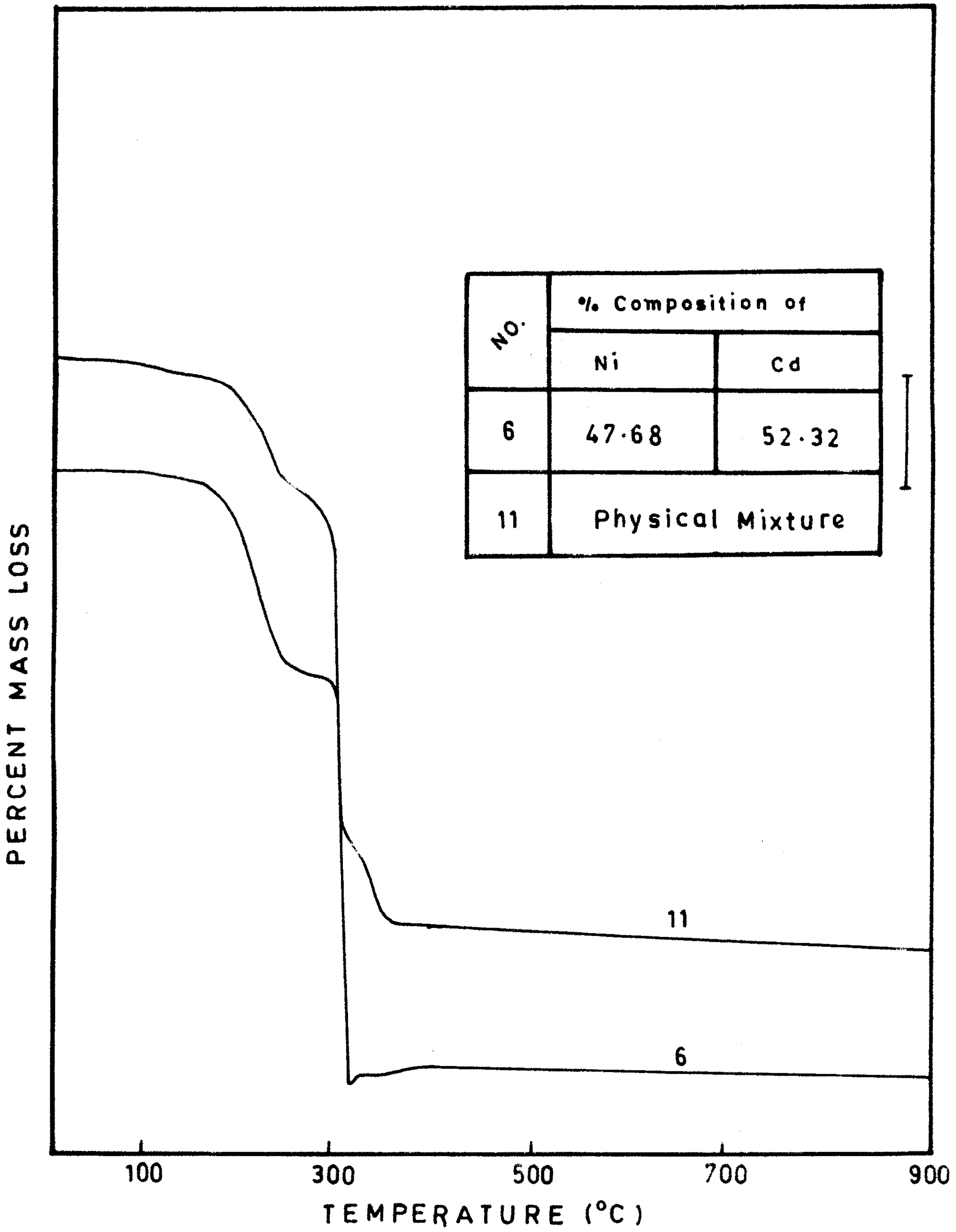
The ranges for dehydration and that for decomposition are recorded in Table-III.

Details of the mass losses incurred during dehydration and decomposition are given in Table-IV.

In case of physical mixture two steps for decomposition are observed whereas for all the co-precipitated samples only one step for decomposition has been observed indicating that mixed oxalates are not physical mixtures (Fig.2).

CALCULATION OF RATE PARAMETERS

Freeman and Caroll[68] as well as Coats and Redfern[69] have shown that the kinetic parameters of any decomposition process could be calculated from the characteristics of the thermogram. It was found that Freeman and Caroll relationship is not very suitable in the present case. However, the relationship by



NO.	% Composition of	
	Ni	Cd
6	47·68	52·32
11	Physical Mixture	

FIG. 2 — PERCENT MASS LOSS V/S TEMPERATURE CURVE.

TABLE-III

THE RANGE OF DEHYDRATION TEMPERATURE AND DECOMPOSITION TEMPERATURE OF Ni-Cd OXALATES

Composition per cent of Cd	Dehydration Temperature		Dehydration Range	Decomposition Temperature °C		Decomposition Range
	onset °C	Termi. °C		onset °C	Termi. °C	
00.00	180	255	75	300	340	50
12.16	175	260	85	300	340	40
23.82	190	265	75	300	360	60
32.06	180	260	80	300	360	60
42.33	170	250	80	300	355	55
52.32	175	240	65	280	355	75
60.85	175	230	55	280	360	80
70.05	160	220	60	290	345	55
80.70	140	200	60	280	355	75
100.00	-	-	-	280	390	110

TABLE-IV

LOSS (%) OF MIXED OXALATES

Composition per cent of cadmium	Loss (%) on dehydration		Loss (%) on decomposition	
	Found (from graph)	Calculated	Found (from graph)	Calculated (assuming) oxide as end product
00.00	19.00	19.70	46.00	48.15
12.16	16.57	17.20	43.00	47.63
23.81	14.96	15.00	45.29	47.13
32.06	12.83	13.38	45.02	46.79
42.33	10.54	11.36	44.30	46.36
52.32	8.00	9.39	40.00	45.92
60.85	7.00	7.71	43.07	45.57
70.05	5.20	5.90	44.89	45.18
80.70	3.00	3.80	45.00	44.73
100.00	-	-	45.10	43.15

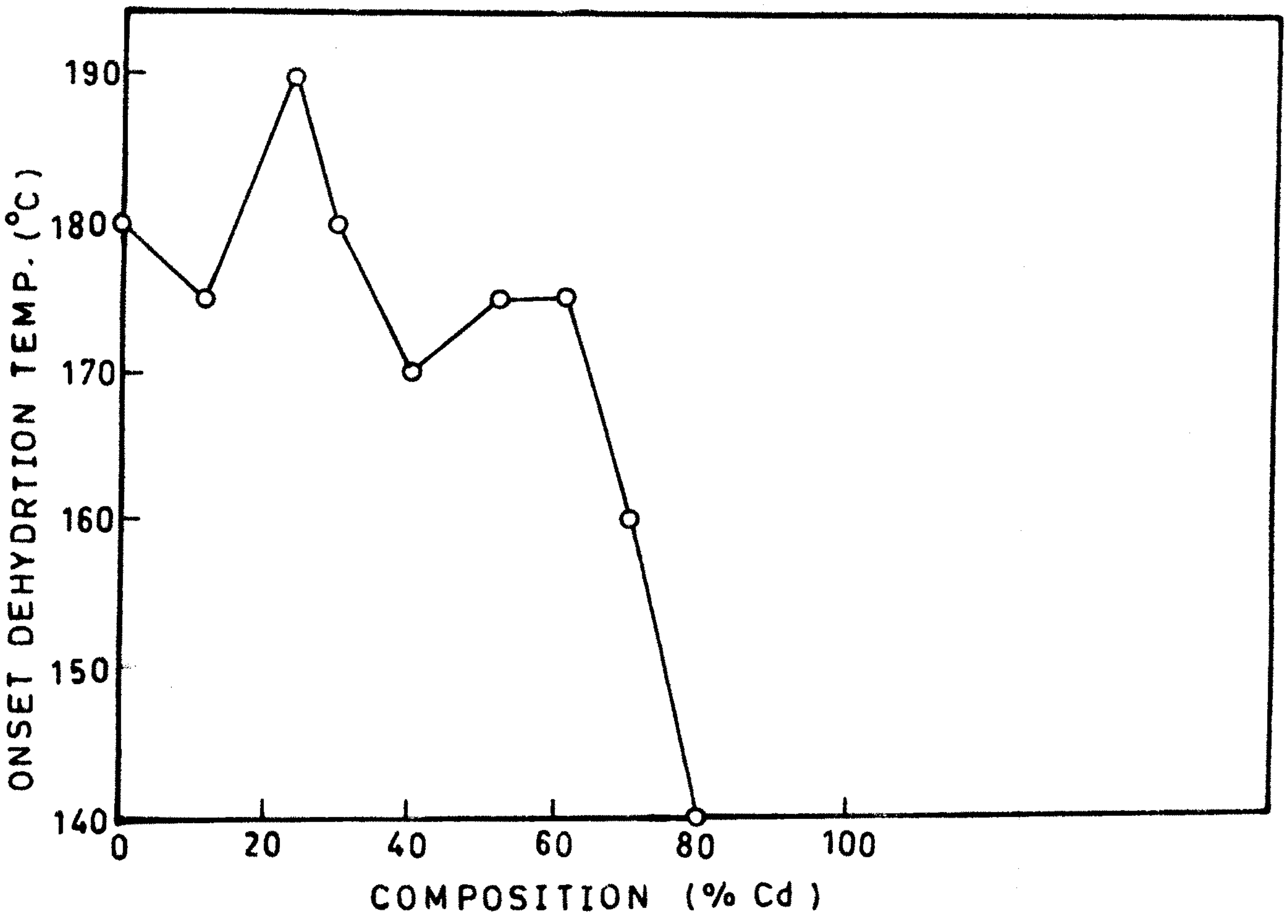


FIG. 3-A – ONSET DEHYDRATION TEMP. V/S COMPOSITION.

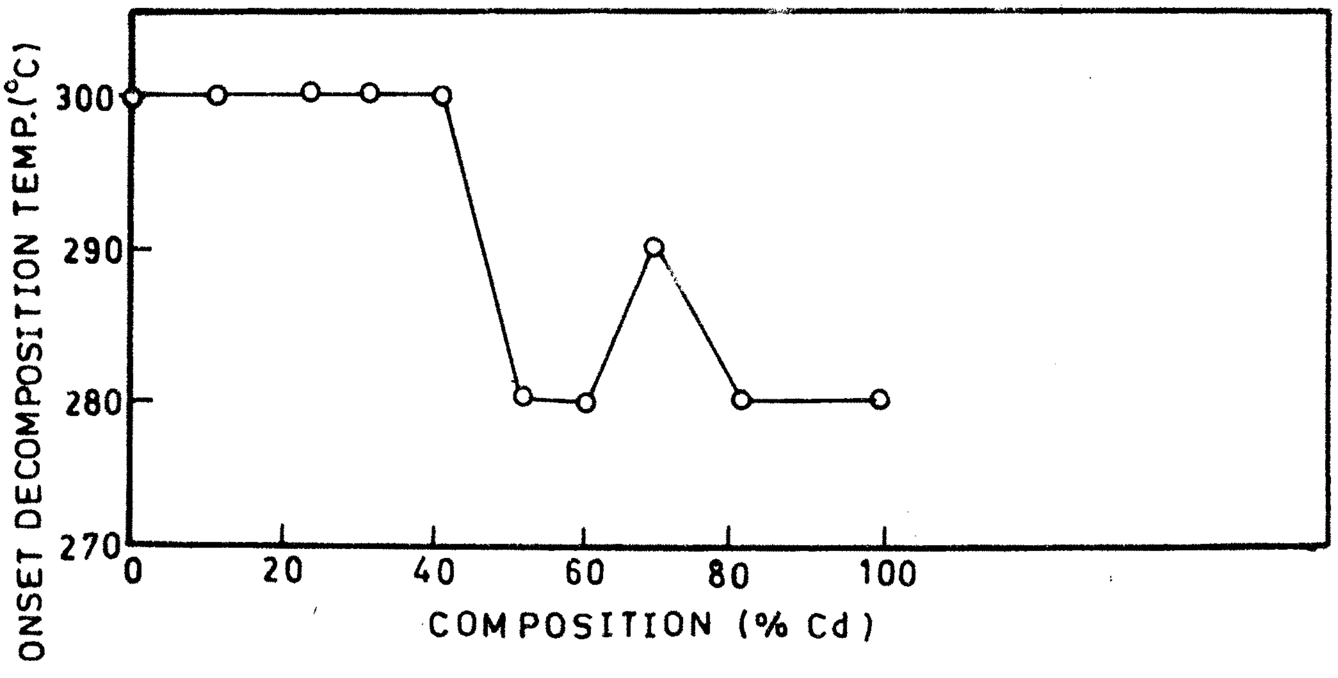


FIG. 3-B – ONSET DECOMPOSITION TEMP. V/S COMPOSITION.

Coats and Redfern was found to be quite satisfactory to the thermograms of the mixed Ni-Cd oxalates.

They have shown that

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$$

$$= \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3\ RT}$$

For all values of n except n = 1 in which case

$$\log_{10}\left[\frac{-\log_e(1-\alpha)}{T^2}\right]$$

$$= \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{-E}{2.3\ RT}$$

where n = order of reaction,

α = fraction of decomposition,

T = temperature in degrees Kelvin,

A = frequency factor,

R = gas constant,

a = heating rate in degrees/min

E = energy of activation.

Thus the plot of either

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \text{ Against } 1/T$$

or when n = 1

$$\log_{10}\left[\frac{\log_e (1 - \alpha)}{T^2}\right] \text{ against } 1/T$$

should result in a straight line of slope $-E/2.3R$ for the correct values of n, since it could be shown that for most values of E and for the temperature range over which reactions generally occur the expression,

$$\log_{10}(AR/aE)\left[1 - (2RT/E)\right]$$

is sensibly constant.

The values of activation energy for dehydration and decomposition processes, calculated with the help of above method are given in Table-V. It is seen that activation energy does not bear a linear relationship with the composition of the mixed oxalates.

DISCUSSION

Dollimore and co-workers[70] results on the decomposition of $NiC_2O_4.2H_2O$ in air medium show that dehydration to the anhydrous salt took place upto 270°C and above 300°C the decomposition was very rapid. They have not reported the temperature ranges for dehydration and decomposition steps.

In our studies, we have observed that the dehydration range for $NiC_2O_4.2H_2O$ is from 180°C to 255°C. In case of

TABLE-V

ACTIVATION ENERGY OF CO-PRECIPITATED Ni-Cd OXALATES HAVING DIFFERENT COMPOSITIONS

Percentage of composition of Cd	Dehydration K.cal/mole	Decomposition K.cal/mole
00.00	10.12	18.40
12.16	13.71	20.99
23.82	13.20	18.03
32.06	11.96	10.12
42.33	10.67	9.75
52.32	4.78	4.78
60.85	10.12	8.79
70.05	6.53	11.04
80.70	6.90	7.08
100.00	-	19.78

Order of reaction for dehydration = 0.66

Order of reaction for decomposition = 0.50

decomposition of anhydrous salt, we have observed the range from 300°C to 340°C.

In view of the above observation, it may be suggested that the decomposition of nickel oxalate follows one of the two mechanisms as mentioned below.

The first one being due to Kadlec and Danes.[11]

The first step proposed in this mechanism is the formation of small amount of nickel oxide as

$$Ni\ (COO)_2 = NiO + CO + CO_2$$

The secondary steps are

$$NiO + CO = Ni + CO_2$$

$$Ni\ (COO)_2 = Ni + 2CO_2$$

The small amount of metallic nickel formed from NiO acts as a catalyst in the decomposition of nickel oxalate and hastens the decomposition.

Second mechanism is suggested by Jacobs and Kureisky.[71] According to them, initial declaratory reaction is attributed to the decomposition of the surface layer, followed by an induction period and the main acceleratory reaction (second step in decomposition) which results from the two dimentional growth of the nuclei.

The solid end product in both the mechanisms is metallic nickel. But from the per cent mass loss Table-IV it is clear that the end product is NiO. This means that the Ni metal formed during decomposition in air in the initial stage oxidises to oxide. This is supported by the second exothermic peaks in DTA studies.

From the above discussion it is clear that the decomposition of nickel oxalate follows the mechanisms suggested by Jacobs and Kureisky.

In case of cadmium oxalate, we have observed one step for decomposition from 280°C to 390°C.

The observation of a single decomposition step in the thermograms of the co-precipitated oxalates, in air may be taken as indication of a homogeneous phase. In view of this observation it may be expected that mixed crystals of nickel oxalate and cadmium oxalate or a compound of the type $Ni[Cd(COO)_4]$, similar to $Ni[Cu(CO_3)_2]$[33] may have been formed.

The activation energy for dehydration lies between 4.78 K.cal/mole to 14.71 K.cal/mole. Also for decomposition it lies between 4.78 K.cal/mole to 20.99 K.cal/mole.

It is seen that activation energy does not bear a linear relationship with the composition of the mixed exalates. This may be due to the fact that the accuracy in the determination of activation energies is of the same order as errors involved in the above equation due to approximations.