# CHAPTER III

# CHAPTER-III

# DIFFERENTIAL THERMAL ANALYSIS OF MIXED NICKEL-CADMIUM OXALATES

Differential Thermal Analysis (DTA) is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert material, is recorded as a function of the sample temperature, as the sample is heated or cooled at a uniform rate. Temperature changes in the sample are due to exothermic or endothermic enthalpic transitions of reactions such as those caused by phase changes (fusion), crystalline structure inversion, dehydration, decomposition, dissociation, reduction and some decomposition reactions produce endothermic effects, whereas crystallization, oxidation and some decomposition reactions produce exothermic effects.

A sample of the material being investigated is heated up side by side with a sample of thermally inert material in a suitable dual special holder, and the difference in temperature between them is noted as they are heated. When no such change occurs in the specimen, there is no difference in the temperature of the two samples, but as soon as any transition begins, the specimen becomes hotter or cooler than the reference material and a peak develops on the curve for difference in temperature ($\Delta T$) against time ($t$) or temperature ($T$).

The number, shape and position of the various endothermic and exothermic peaks with respect to the furnace temperature may be used as a means for the quantitative identification of the substance under investigation. Also, since the area under the peak is proportional to the heat changes involved, the technique is useful for the semi-quantitative determination of the heat of reaction or transformation.

The peak temperature, the general shape of the curve and also the magnitude of the peaks and peak area depend on the various (a) instrumental and (b) sample parameters.

The instrumental factors include (1) furnace atmosphere, (2) furnace size and shape, (3) sample holder material, (4) sample holder geometry, (5) wire and bead size of thermocouple junction, (6) heating rate, (7) speed and response of recording instrument, (8) thermocouple location in sample, etc. The sample characteristics consist of (i) partical size, (ii) thermal conductivity, (iii) heat capacity, (iv) packing density, (v) swelling or shrinkage of sample, (vi) amount of sample, (vii) effect of diluent (viii) degree of crystallinity, etc.

## APPLICATION OF DTA TO THE STUDY OF CATALYSIS

In recent years, the technique of DTA has been employed as a tool to provide supporting evidence on the structure of catalysts of technical importance.

In characterization of some nickel-silica catalysts Voothurjsen and Franzen[72] used this technique as an adjunct to the well established X-ray diffraction method. Mukherjee, Chatterjee and Roy[73] have studied the differential thermal analysis of fused iron catalyst (for $NH_3$ synthesis) and the difference in DTA behaviour was attributed to the method of preparation and annealing process of the catalyst samples. Bhattacharya et al.,[74] have applied the DTA technique to characterize solid catalyst systems such as $Al_2O_3$-ZnO, $Al_2O_3$ - $ZrO_2$, $Al_2O_3$ - MgO, $ZrO_2$ - $Fe_2O_3$, $Cr_2O_3$ - ZnO, $Cr_2O_3$ - $Al_2O_3$. They have correlated the results of DTA with reference area and with catalytic conversion of ethanol or butadiene.

Swamy[75] used this technique to study the nature of unsupported and supported iron-oxide catalysts. Comparison of the DTA curves of unsupported and supported ferric oxide samples shows that the introduction of Kieselguhr as support results in suppression of peaks obtained at 540°C which can possibly be ascribed to the relatively small amounts of $Fe_2O_3$ in the samples. The introduction of support facilitates the easy removal adsorbed water as seen by the shifting of the endothermic peak from 184°C to around 110°C, but does not help the crystallization of amorphous $Fe_2O_3$ (because the dispersion of the oxide on the surface of the support) which is indicated by the shift of the endothermic peak from 356°C to a higher temperature (400-430°C). The absence of a second endothermic peak in the DTA curves of a second $Fe_2O_3$ Kieselguhr samples is indicative of the absence of iron-silicate in them. Hagihra and Echigoya[76] studied the DTA of silica supported and unsupported cobalt carbonates which were prepared by impregnation as well as co-precipitation method. They found that except for Co-$SiO_2$ catalyst produced by co-precipitation, the DTA curves exhibited by the various supported cobalt oxide catalysts were almost identical with that of basic cobalt carbonate. For Co-$SiO_2$ catalyst endothermic peak was clearly observed between 500° and 700° above the dehydration temperature. This may be attributed to the decomposition of hydrosilicate (orthotype) into cobalt oxide, silica and water.

Surface heterogeneity nature of catalysts were studied by G.G. Shehibrya <u>et al</u>.[77] Thermal analysis technique was used for studying the nature of inhomogeneity on catalysts and sorbents surface were examined. Theoretical equation for determining the nature of the inhomogeneities, the surface coverage, the heat of desorption and the corresponding activation energy at the highest adsorbing parts of surface were derived.

R. Swaminathan and M. Ravindram[78] used DTA technique to study the effect of doping on the activity of catalysts. Doping of ZnO with $Al_2O_3$ increases its activity for the dehydration of $CH_3CH_2OH$. While addition of $Li_2O$ decreases its activity. The results were discussed in terms of the variation in electrical conductivity caused by doping. Binary catalysts $MoO_3$-$Bi_2O_3$ of different compositions were studied by means of DTA and electrical conductivity method of A. Popescu <u>et al</u>.[79] The real activity of these catalysts during oxidation of MeOH via $H_2CO$ was found. The crystallization of the compounds $Bi_2O_3$-$3MoO_3$ and $Bi_2O_3$-$MoO_3$ at 300 and 380°C respectively, was pointed out. The electrical conductivity and the real activity of these catalysts were discussed with respect to their structure and chemical compositions.

Arora, B.R. et al.,[80] applied DTA technique for the study of FeO and $Fe_2O_3$-CrO catalysts. DTA showed that $Fe_2O_3$ corresponded to removal of loosely bound $H_2O$. The presence of CrO shifts the first peak to 165° and the 2nd peak to 460°. In $Fe_2O_3$-CrO catalyst and endothermic peak also occurs at 700°. Grinding of $Fe_2O_3$ and $Fe_2O_3$-CrO results in appearance of an exothermic peak 700° and splitting of the earlier endothermic peaks.

## DTA INSTRUMENT

The DTA instrument is 'Derivatograph, MOM Hungarion Optical Works, Budapest', which is described in the previous chapter.

## EXPERIMENTAL AND RESULTS

Preparation and composition of Nickel oxalate and cadmium oxalate and their co-precipitated mixtures have been described earlier.

It was observed that nickel oxalate gives one endothermic peak for dehydration at 235°C and other two exothermic peaks for decomposition at temperatures 325°C and 365°C (Fig. 4-A), whereas

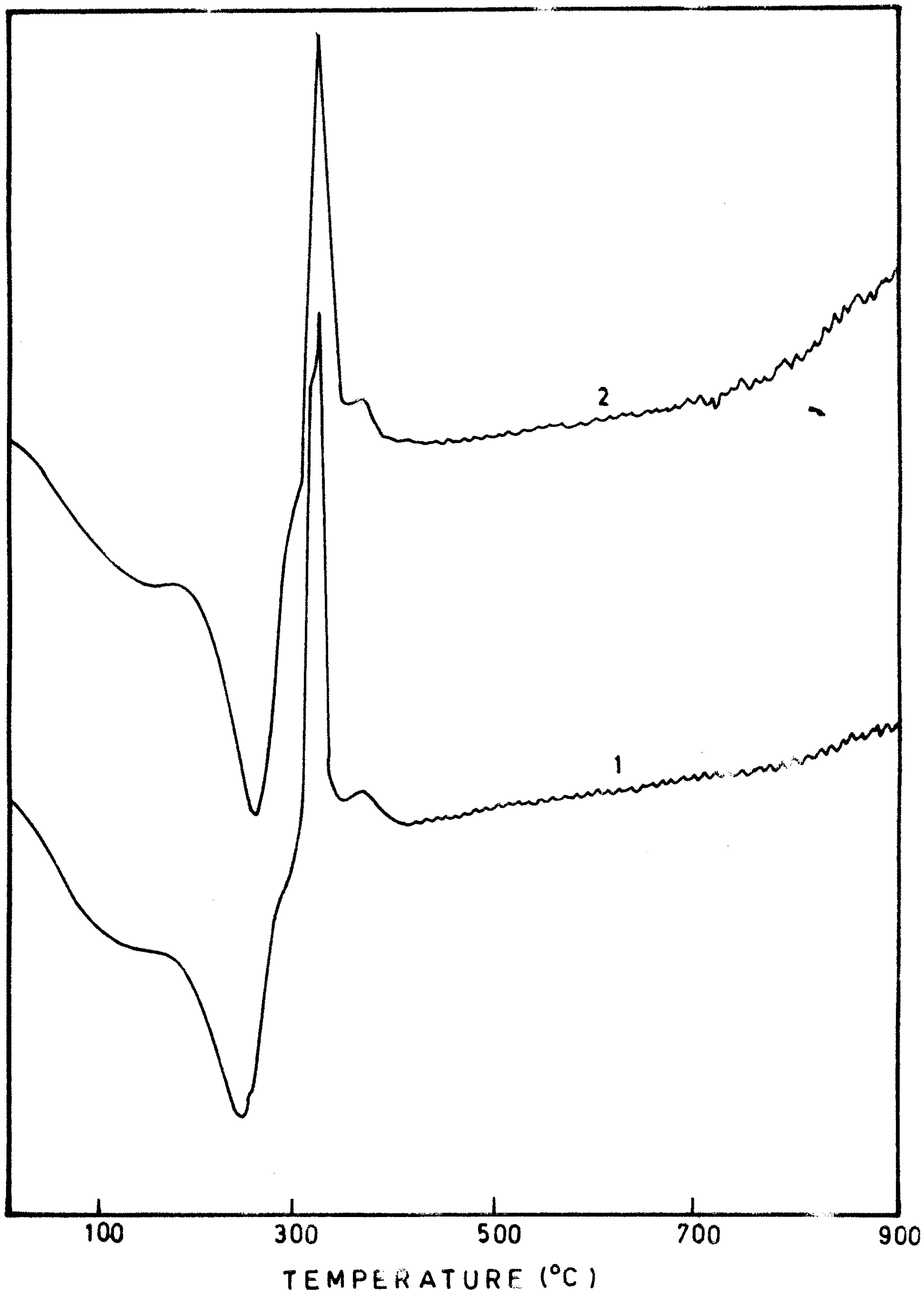

FIG. 4-A — DTA OF (1) 100 % Ni OXALATE AND

(2) 12·16 % Cd OXALATE.

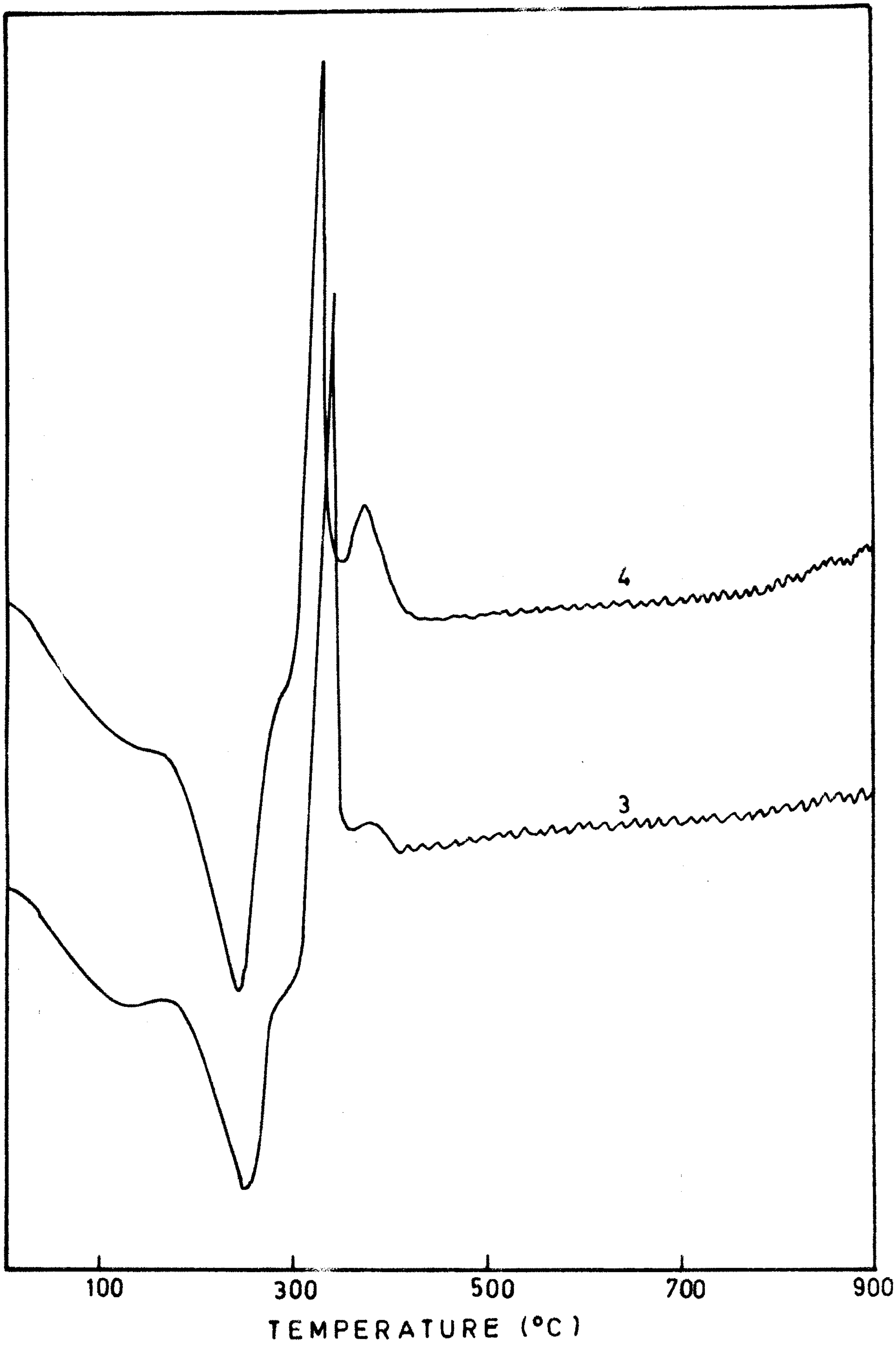

FIG.4-B - DTA OF (3) 23·82 % Cd OXALATE AND

(4) 32·06 % Cd OXALATE.

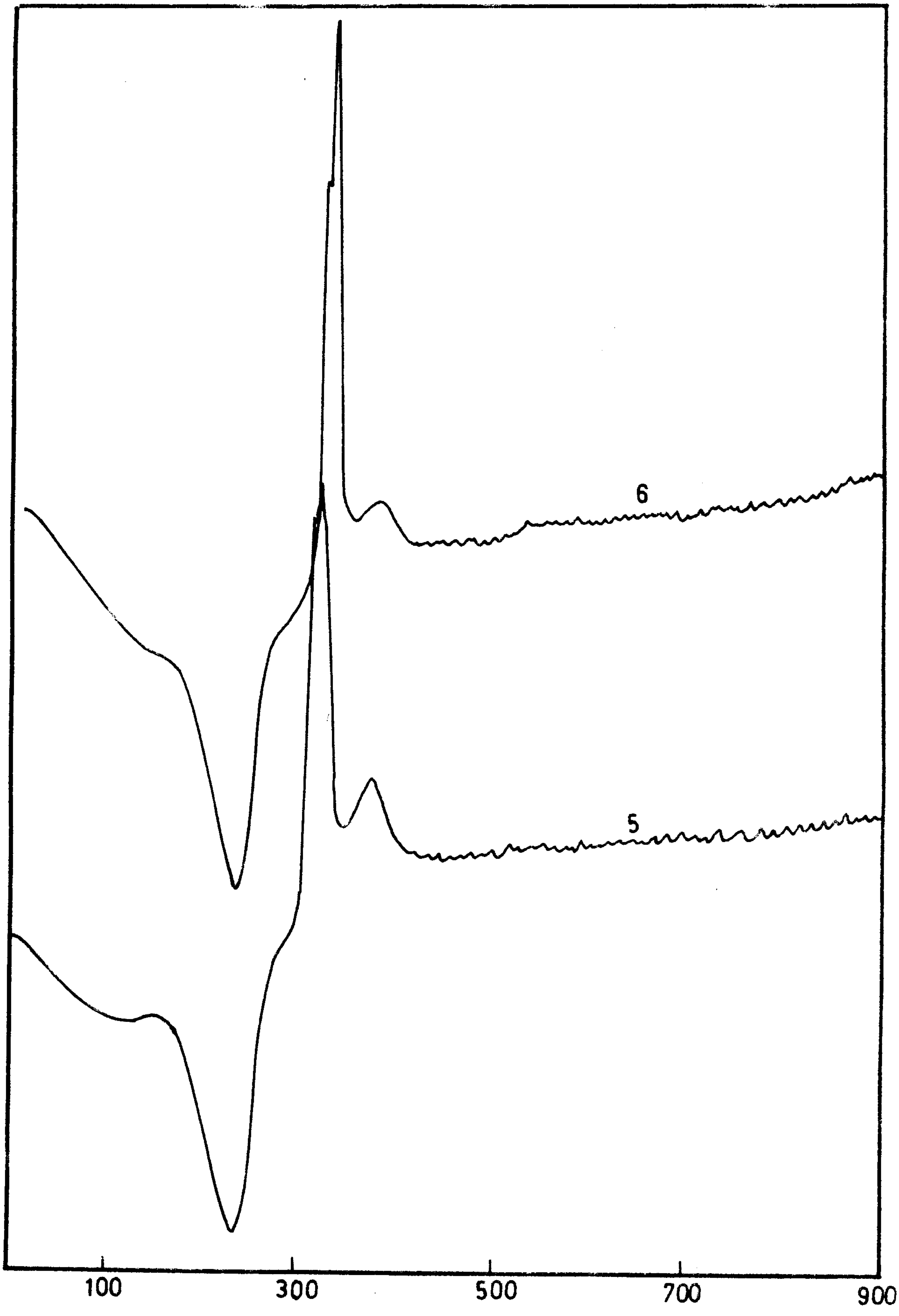

FIG.4-C – DTA OF (5) 42·33 % Cd OXALATE AN
(6) 52·32 % Cd OXALATE.

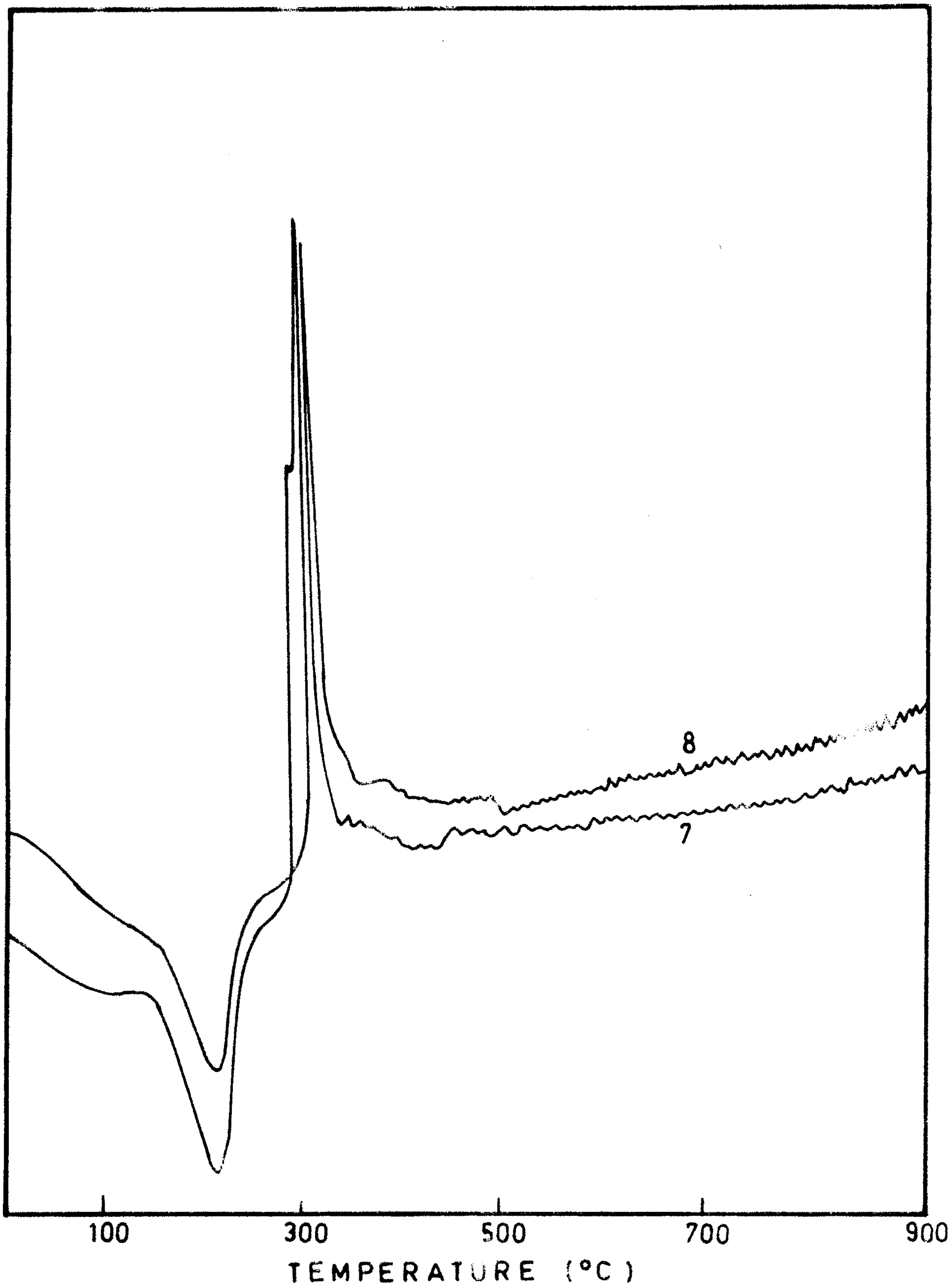

FIG. 4-D — DTA OF (7) 60·85 % Cd OXALATE AND
(8) 70·05 % Cd OXALATE.

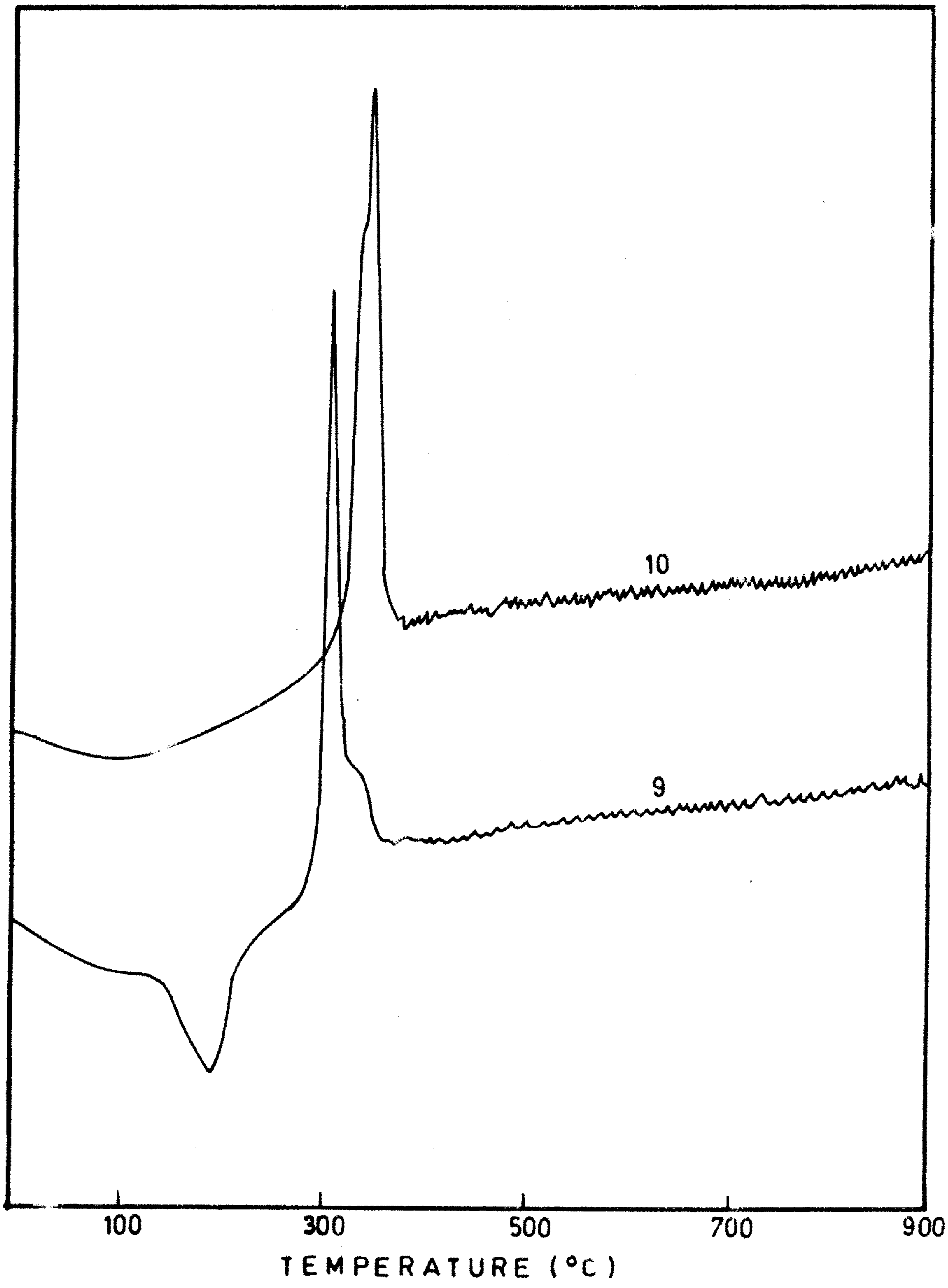

FIG. 4-E - DTA OF (9) 80.70 % Cd OXALATE AND

(10) 100 % Cd OXALATE.

TABLE-VI

## THE RANGE OF DEHYDRATION TEMPERATURE AND DECOMPOSITION TEMPERATURE OF NICKEL-CADMIUM OXALATES

| Composition percentage Cd | Dehydration Range | | | Decomposition Range for 1st peak | | | Decomposition Range for 2nd peak | | | Total decomposition Range | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Onset Temperature °C | Termin Temp. °C | Range | Onset Temp. °C | Termin Temp. °C | Range | Onset Temp °C | Termin. Temp °C | Range | Onset Temp °C | Termin Temp °C | Range |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| 00.00 | 155 | 285 | 130 | 295 | 340 | 45 | 340 | 395 | 55 | 295 | 395 | 100 |
| 12.16 | 180 | 295 | 115 | 300 | 360 | 60 | 360 | 400 | 60 | 300 | 400 | 100 |
| 23.82 | 180 | 280 | [illegible] | 310 | 360 | 50 | 360 | 405 | 45 | 310 | 405 | 95 |
| 32.06 | 165 | 290 | 125 | 305 | 355 | 50 | 355 | 420 | 65 | 305 | 420 | 115 |
| 42.33 | 160 | 280 | 120 | 300 | 355 | 55 | 355 | 420 | 65 | 300 | 420 | 120 |
| 52.32 | 170 | 270 | 100 | 300 | 360 | 60 | 360 | 405 | 45 | 300 | 405 | 105 |
| 60.95 | 160 | 260 | 100 | 300 | 360 | 60 | - | - | - | 300 | 360 | 60 |

cont'd.

## TABLE-VI
contd.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 70.05 | 160 | 255 | 95 | 295 | 365 | 70 | - | - | - | 295 | 365 | 70 |
| 80.70 | 140 | 205 | 65 | 280 | 360 | 80 | - | - | - | 280 | 360 | 80 |
| 100.00 | - | - | - | 310 | 400 | 90 | - | - | - | 310 | 400 | 90 |

## TABLE-VII

### DIFFERENTIAL THERMAL ANALYSIS OF Ni-Cd OXALATE SYSTEM (ENDOTHERMIC DEHYDRATION CURVES)

| Composition % of Cd | Weight of sample gms. | Peak Temp. $T_{max}$ °C | Area under curve per gm $Cm^2$ | Heat of Dehydration ΔH K.cal/mole | (ΔH $NiC_2O_4.2H_2O$ + ΔH Cd $C_2O_4$) = ΔH observed |
|---|---|---|---|---|---|
| 00.00 | 0.179 | 235 | 24.14 | 160.901 | - |
| 12.16 | 0.237 | 240 | 17.30 | 110.721 | +30.614 |
| 23.82 | 0.213 | 235 | 17.84 | 114.184 | +08.390 |
| 32.06 | 0.266 | 230 | 17.39 | 110.683 | -01.367 |
| 42.33 | 0.232 | 215 | 15.08 | 96.557 | -03.766 |
| 52.32 | 0.201 | 220 | 18.41 | 117.819 | -41.102 |
| 60.85 | 0.205 | 215 | 10.24 | 65.566 | -02.573 |
| 70.05 | 0.201 | 200 | 16.92 | 108.264 | -60.074 |
| 80.70 | 0.207 | 180 | 6.52 | 41.744 | -10.690 |
| 100.00 | 0.230 | - | - | - | - |

## TABLE-VIII

## DIFFERENTIAL THERMAL ANALYSIS OF Ni-Cd OXALATE SYSTEM (EXOTHERMIC DECOMPOSITION CURVES)

| Composition % of Cd | Weight of sample gms | Peak Temperature $T_{max}$ °C |  | Area under curve $Cm^2$/gm | Heat of Decomposition ΔH K.cal/mole | ($\Delta H\ NiC_2O_4.2H_2O + \Delta H\ CdC_2O_4$) - ΔH observed |
|---|---|---|---|---|---|---|
|  |  | Ist peak | 2nd peak |  |  |  |
| 00.00 | 0.179 | 325 | 365 | 25.42 | 162.693 | - |
| 12.16 | 0.237 | 340 | 375 | 13.92 | 89.119 | 66.310 |
| 23.82 | 0.213 | 340 | - | 15.02 | 96.154 | 52.311 |
| 32.06 | 0.266 | 345 | 380 | 16.73 | 107.073 | 36.471 |
| 42.33 | 0.232 | 340 | 385 | 18.97 | 121.384 | 16.387 |
| 52.32 | 0.201 | 340 | 380 | 10.95 | 70.053 | 61.538 |
| 60.85 | 0.205 | 335 | - | 15.61 | 99.903 | 26.443 |
| 70.05 | 0.201 | 335 | - | 10.45 | 66.865 | 53.937 |
| 80.70 | 0.207 | 330 | - | 10.46 | 98.944 | 15.547 |
| 100.00 | 0.230 | 375 | - | 16.09 | 102.964 | - |

cadmium oxalate does not show a peak for dehydration confirming that it did not contain water of crystallization and this is consistent with TG results. It also shows one exothermic peak for decomposition at temperature $375^{\circ}$C (Fig. 4-E).

The range of decomposition for cadmium oxalate is from $310^{\circ}$ to $400^{\circ}$C and for nickel oxalate from $295^{\circ}$C to $340^{\circ}$C. The dehydration range for nickel oxalate is from $155^{\circ}$C to $285^{\circ}$C. The corresponding dehydration step in the TG for nickel oxalate is $180^{\circ}$C to $255^{\circ}$C and for decomposition $300^{\circ}$C to $340^{\circ}$C. The decomposition of cadmium oxalate takes place in the temperature range $280^{\circ}$C and $390^{\circ}$C in TG.

In case of co-precipitated nickel-cadmium oxalates, it was observed that there is one endothermic peak for dehydration, one exothermic peak for decomposition. Second exothermic peak is also observed for pure nickel oxalate and co-precipitated oxalates having 12.16, 32.06, 42.33 and 52.32 per cent Cd. The results are given in Figs. 4-A, 4-B, 4-C, 4-D, 4-E.

For dehydration it was observed that peak temperature ($T_{-max}$) of these oxalates, at beginning upto 12.16 per cent Cd and then decreases slowly upto 42.33 per cent Cd. It then increases for 52.32 per cent Cd. And after that decreases slowly upto 80.70 per cent Cd (Fig. 6-A).

In case of first peak for decomposition at the beginning $T_{-max}$ increases sharply upto 12.16 per cent Cd, remains

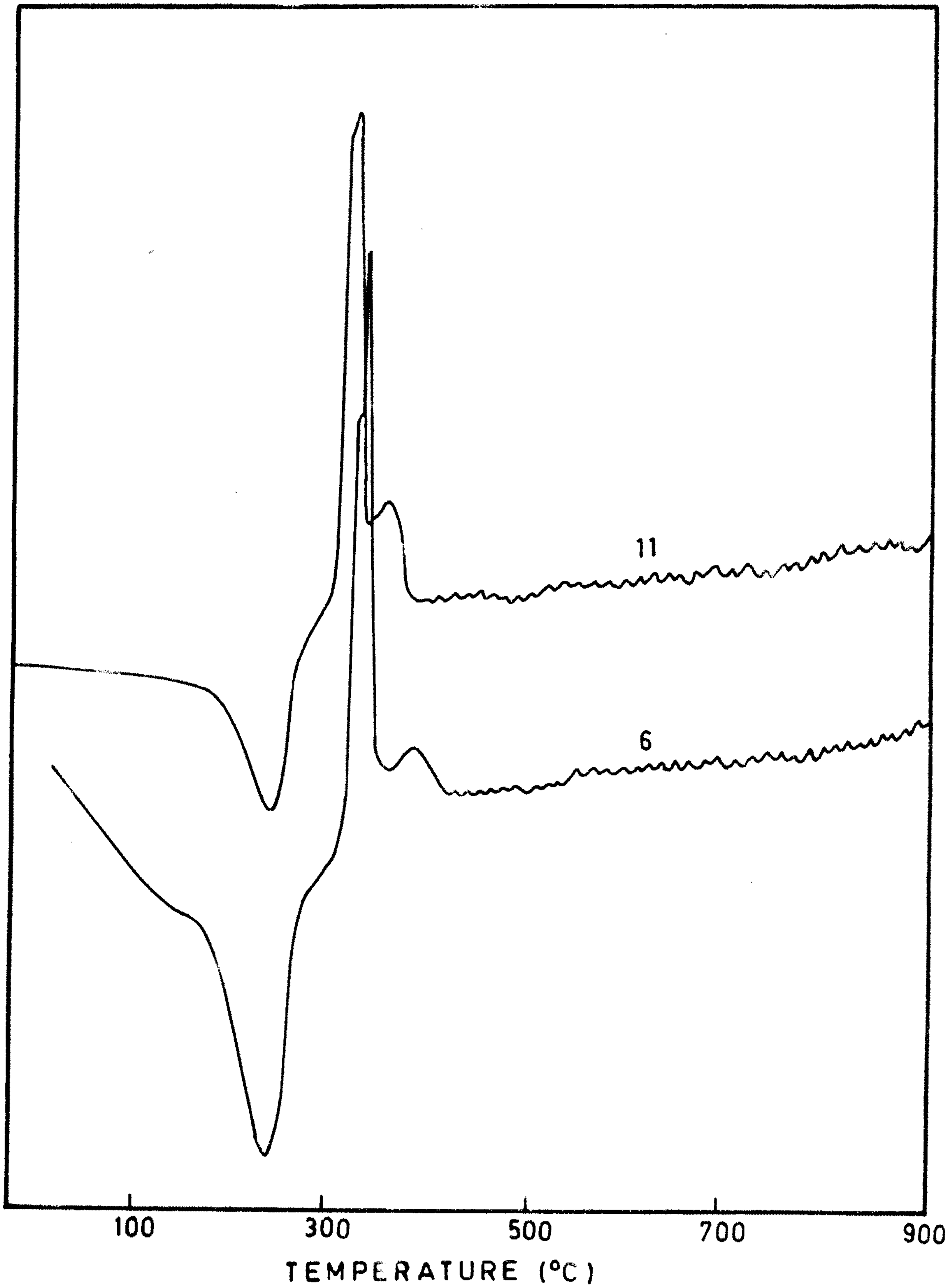

FIG. 5 — DTA OF (6) 52·32 % Cd OXALATE AND (11) PHYSICAL MIXTURE.

constant for 23.82 per cent Cd. Then increases for 32.06 per cent Cd. Again decreased for 42.33 per cent Cd, remains constant for 52.32 per cent Cd. Then decreased and remains constant for 60.85 per cent and 70.05 per cent Cd. Then decreased for 80.07 per cent Cd. And sharply increases for 100 per cent Cd (Fig. 6-B).

In case of second peak for decomposition $T_{max}$ increases upto 12.16 per cent Cd. It is absent for 23.82 per cent Cd. And for 32.06, 42.33 and 50.32 per cent Cd it remains almost constant. For the remaining compositions (60.85, 70.05, 80.07 per cent Cd and pure Cd) second peak for decomposition is absent (Fig. 6-C).

The DTA of physically mixed (50:50) nickel-cadmium oxalate was carried out. It was observed that there is one peak for dehydration and two distinct exothermic peaks for decomposition step, first exothermic peak corresponding to nickel oxalate decomposition and cadmium oxalate decomposition, and second with only cadmium oxalate decomposition. The DTA of this physically mixed oxalate and co-precipitated mixed (52.32 per cent Cd) oxalate have been shown in Fig. 5.

The heat of decomposition for Ni-Cd oxalates is calculated using the equation

$$\Delta H = \gamma \int_{T_1}^{T_3} \theta . dt$$

where $\int_{T_1}^{T_2} \theta . dT$ is area under the curve and $\gamma$ instrument

FIG.6-A : PEAK TEMPERATURE V/S COMPOSITION FOR DEHYDRATION OF Ni-Cd OXALATES.

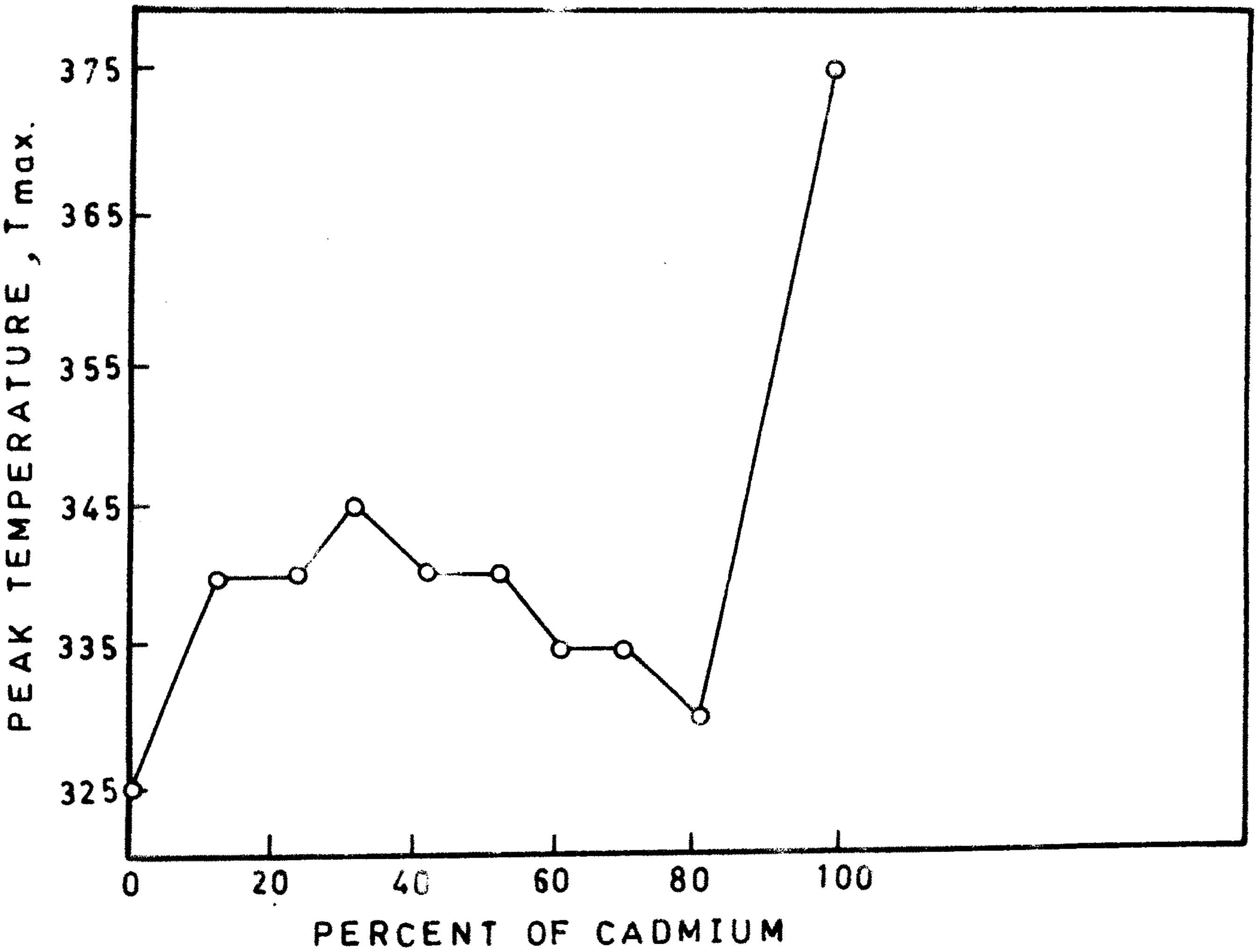

FIG.6-B – PEAK TEMPERATURE V/S COMPOSITION FOR DECOMPOSITION (I$^{st}$ STEP) OF Ni-Cd OXALATES .

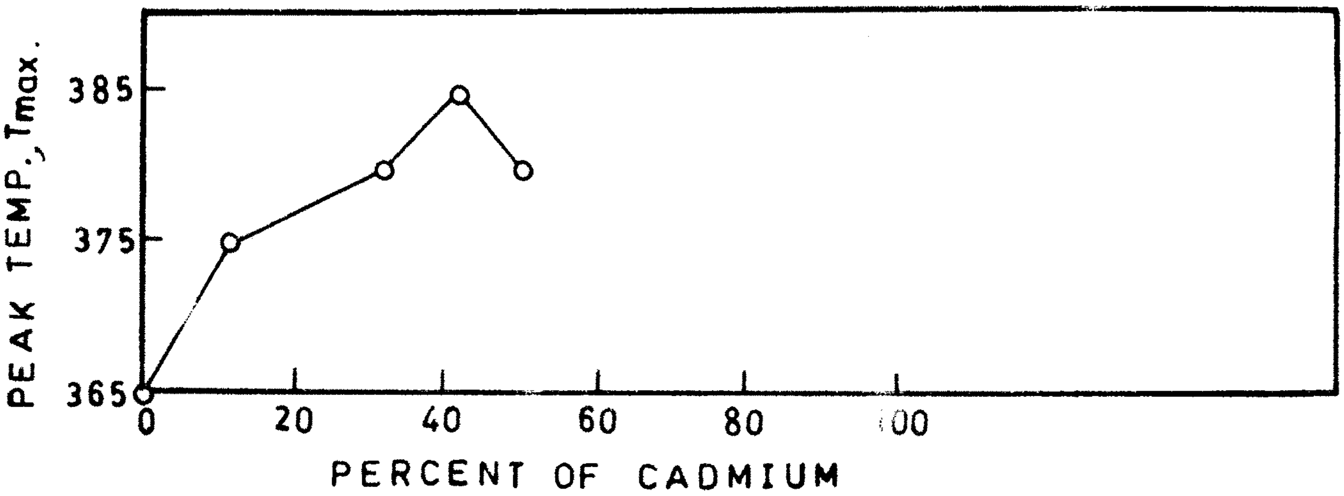

FIG.6-C – PEAK TEMPERATURE V/S COMPOSITION FOR DECOMPOSITION (II$^{nd}$ STEP) OF Ni-Cd OXALATES .

constant, is evaluated experimentally using silver nitrate as standard material.

The peak temperature ($T_{max}$), area under the curve and heat of dehydration and decomposition (ΔH) are summarized in Tables VI, VII and VIII.

The dehydration peak temperature versus composition of cadmium is shown in Fig. 6-A, whereas the decomposition peak temperatures (corresponding to 1st and 2nd peaks) versus composition of cadmium are shown in Figs. 6-B and 6-C.

The results of heat of dehydration and heat of decomposition are plotted against per cent composition of cadmium and is shown in Fig. 6. Similarly, the results of ($\Delta H\ NiC_2O_4 \cdot 2H_2O + \Delta H\ CdC_2O_4$)-ΔH observed are plotted against per cent composition of cadmium and is shown in Fig. 8.

## DISCUSSION

Single peak in the DTA curves for decomposition supports the homogeneous phase in the co-precipitated nickel-cadmium oxalates. But as can be seen from Figs. 6-A, 6-B, 6-C, 7 and 8 the peak temperatures as well as heat of reaction ΔH, does not have any linear relationship with the composition; the formation of a compound with definite composition is not indicated. This view is supported by the thermogravimetric analysis of these compounds and interplaner spacings (d-values) given in Chapter-IV.

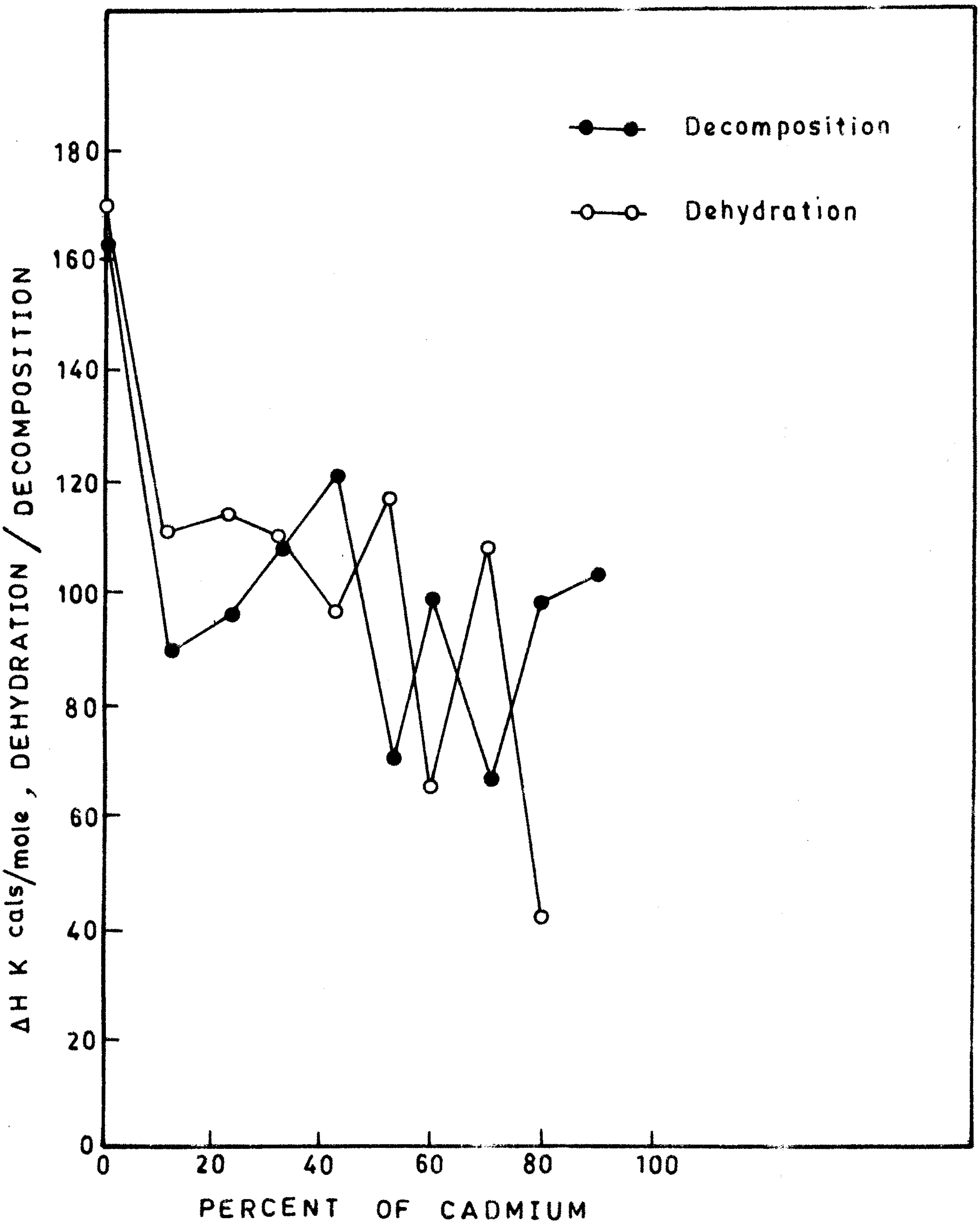

FIG. 7 – ΔH DEHYDRATION/ DECOMPOSITION V/S PERCENT COMPOSITION OF CADMIUM.

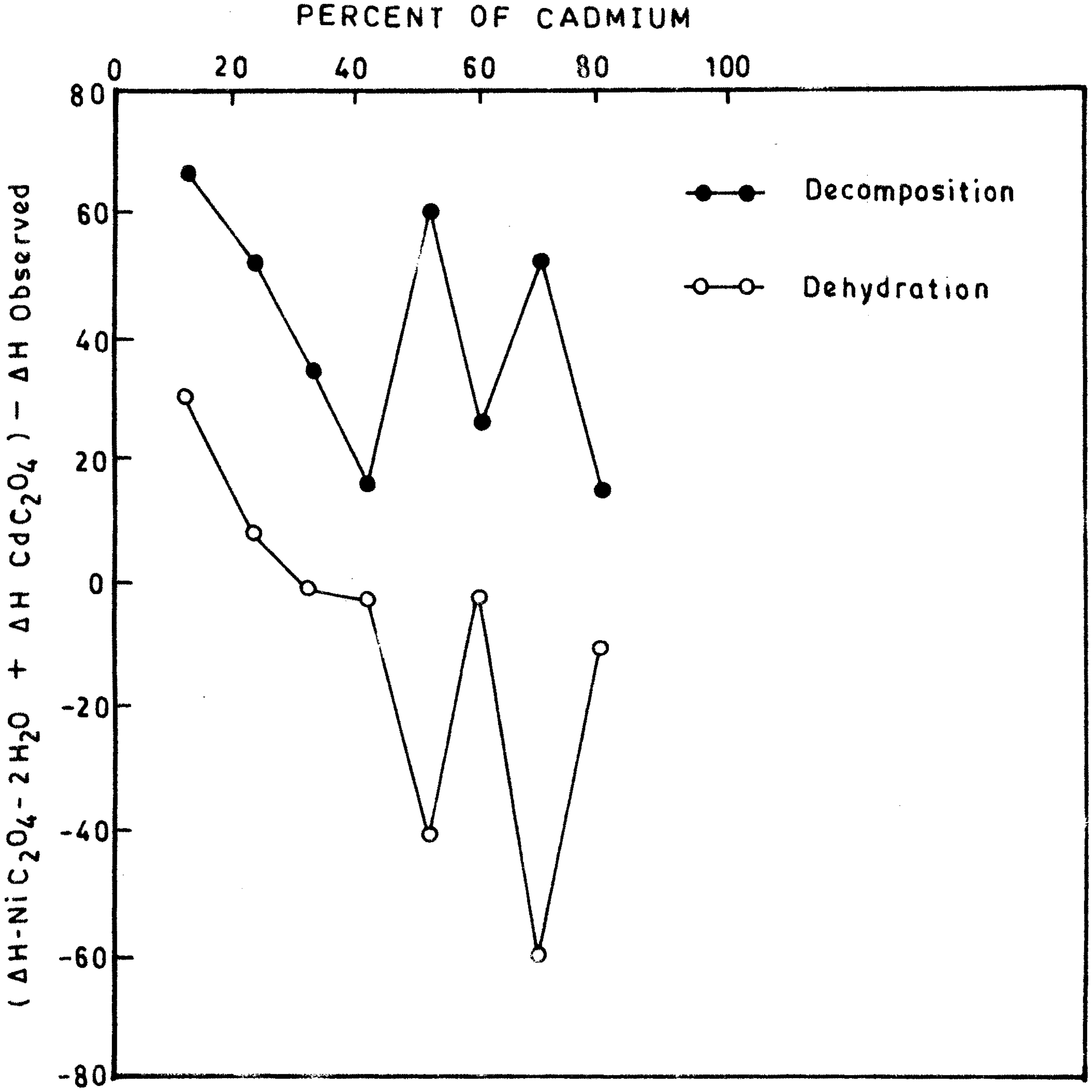

FIG. 8 – ( $\Delta H\text{-}NiC_2O_4\text{-}2H_2O$ + $\Delta H\text{-}CdC_2O_4$ ) – ΔH Observed V/S PERCENT COMPOSITION OF CADMIUM.

Ya.A. Ugai[81] has given the ranges for exothermic peaks of nickel oxalate dihydrate as 275°-295°C for first peak and 400°-405°C for second peak. In our results corresponding ranges for decomposition of these two peaks are 295°-340°C and 340°-395°C respectively. The difference can be attributed to DTA apparatus and experimental conditions.

We have observed a exothermic peak for $CdC_2O_4$ decomposition. The range is 310°-400°C.

In case of nickel oxalate dihydrate we have observed an endothermic peak for dehydration ranging from 155°-285°C. But in case of cadmium oxalate we have not observed any peak for dehydration, indicating that it did not contain water of crystallization and this is supported by TGA results.

In case of dehydration peaks for nickel-cadmium oxalates (Fig.8) generally the heat of reaction ΔH decreases. Initially it decreased as the percentage of Cd increases upto 12.16 per cent Cd. Then, it alternatively increased and decreased. The value of ΔH for mixed oxalates is below the sum of individual components in the case of dehydration.

In case of decomposition step pure nickel oxalate shows maximum value of ΔH. Initially ΔH decreased rapidly upto 12.16 per cent Cd. Then it slowly increased upto 42.33 per cent Cd. Then it rapidly decreased for 52.32 per cent Cd. Again it increased for 60.85 per cent Cd and decreased for 70.05 per cent Cd. Then it increased. The value of ΔH for mixed oxalates is below the sum of individual components in the case of decomposition peaks. This indicates that co-precipitated nickel-cadmium oxalates are not physical mixtures but there is a close association of the two components suggesting a homogeneous phase (or mixed crystals).