THermal Decomposition Studies in Air of Nickel Formates and of Its Coprecipitated Mixtures with Copper and Cobalt Formates: Simultaneous Differential Thermal Analysis and Thermogravimetric Analysis

In the technique of differential thermal analysis (D.T.A.), the heat effects, associated with physical and chemical changes of a system are measured as it is being heated at a uniform rate. These thermal effects can either be exothermic or endothermic and may be caused by phase transitions such as magnetic transitions, crystalline structure inversions and chemical decomposition.

A sample under investigation is heated at a uniform rate along with a thermally inert material as reference and the difference in temperature between the two is noted. If no phase changes occur in the specimen in the range of temperature studied, there is no difference in the temperature of the two samples. If any of the above mentioned transitions take place accompanied by absorption or evolution of heat, an anomalous change of temperature of the material in relation to the reference may be observed as maxima or minima in the differential temperature curve.
The number, shape, and position of various endothermic and exothermic peaks with respect to the ambient temperatures may be used as a means for the formation or identification of a substance. The area under the peak is proportional to the heat changes involved and therefore this technique can be used for the semi-quantitative or quantitative determination of the heat of reaction or transformations.

The peak temperature, the general shape of the differential thermal analysis curve and the area under the peak depend on the various instrumental and sample parameters as mentioned in the earlier chapter.

The technique of the D.T.A. has been utilized in many areas of investigations such as order-disorder transformations, radiation damage, geological studies, kinetics of solid state reactions and to a great extent also in catalysis. We review here briefly some of the important applications in catalysis.

Kodama used differential thermocouple to indicate the exothermic reaction associated with the catalytic activity of Ni, Co and Fe in the reduction of CO by H₂. Ghosh et al. found that the maximum catalytic activity and the adsorption capacity of Zn (OH)₂ correspond to the temperature at which dehydration appears to be complete. Albareda et al. studied the role of cations in bentonite clays and their catalytic
properties for the vapour phase oxidation of ethyl alcohol. Bhattacharyya et al.\textsuperscript{11} showed that the solid catalysts such as Cr$_2$O$_3$ and Fe$_2$O$_3$ had maximum surface areas at a temperature corresponding to termination of an exothermic peak, in agreement with X-ray studies which showed a gradual crystallization of the various phases. The effect of water vapour on the irreversible transformation and the catalytic activity of mixed silica-alumina gels were investigated by Trambouze et al.\textsuperscript{12} with the help of the D.T.A. data.

Irie et al.\textsuperscript{13} investigated the dehydration characteristics of catalysts, composed of ZnO-CrO$_3$ for synthesis of methanol. Chang et al.\textsuperscript{14} in a study of Co catalyst of the Fisher-Tropsch type used the D.T.A. technique and showed that an interaction between CoCo$_3$ and Kieselguhr produced various amounts of a Co-Si complex.

Swamy\textsuperscript{16} compared the D.T.A. curves of unsupported and supported ferric oxide samples and showed that the introduction of Kieselguhr as support results in the suppression of peaks obtained at 540°C and 810°C which can possibly be ascribed to relatively small amounts of Fe$_2$O$_3$ in the samples. The introduction of support facilitates the easy removal of adsorbed water as seen by the shifting of the endothermic peak from 184°C to around 110°C, but does not help the crystallisation of amorphous Fe$_2$O$_3$ (because of 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°C-430°C). The absence of a second endothermic peak in the D.T.A. curve of Fe$_2$O$_3$ - Kieselguhr samples is an indication of the absence of iron hydrosilicates in them.

Hagihara and Echigoya$^{16}$ studied the D.T.A. of silica supported and unsupported cobalt carbonates which were prepared by an impregnation as well as coprecipitation method. They found that except for Co-SiO$_2$ catalyst produced by the coprecipitation, the D.T.A. curves exhibited by the various supported cobalt oxide catalysts were almost identical with that of basic cobalt carbonate. For Co-SiO$_2$ catalysts prepared by coprecipitation, however, only one broad endothermic peak was clearly observed between 500°C and 700°C above the dehydration temperature. This was attributed to the decomposition of hydrosilicate (ortho type) into cobalt oxide, silica and water.

Locke and Rase$^{17}$ made use of D.T.A. to determine the optimum conditions for the use of nickel hydrogenation catalyst. To characterise some of nickel-silica catalysts, Voorthuijsen and Franzen$^{18}$ used this technique as an adjunct to the well established X-ray diffraction method. Mukherjee et al.$^{19}$ have studied the differential thermal analysis of fused iron catalyst (for ammonia synthesis) and the difference in the D.T.A. behaviour was attributed to the method of preparation and annealing process of the catalyst samples.
This brief review of some of the important investigations in catalysis using the D.T.A. technique indicates that a great deal of valuable information such as the nature and temperature of decomposition, crystallinity and structure changes, phase distributions and the effect of preparative conditions of materials used as catalysts can be obtained. These are all useful in determining the suitability or characterising the property of a catalyst especially when it is prepared by direct thermal treatment of a compound.

Thus the two methods of investigation, viz., D.T.A. and T.G.A., have found wide applications in various areas of investigation during the past three decades. A combination of these two techniques in any particular investigation can give much more information than can be obtained by only one at a time e.g. the information on the composition of the intermediate or the final product can be obtained by T.G.A. and not by D.T.A., while any phase change involving heat changes would be detected only by D.T.A. If the data of the two techniques are obtained in a single run, then correlation of the results obtained under the same known and comparable conditions is greatly facilitated. However, in many cases, it may be difficult to correlate the information obtained from these two techniques if one or some of the unknown parameters are changed even if the instrumental and sample characteristics are not varied. For example, in a thermal
decomposition reaction strongly dependent upon the nature of external atmosphere, e.g., presence of water vapour, it may not always be possible to reproduce the same experimental conditions. Notz and Jaffe\textsuperscript{20} have given a method of correlating the decomposition temperatures obtained from T.G.A. and D.T.A. analyses. It is, therefore, desirable that during a thermal decomposition reaction the thermal effects and mass changes at a temperature interval are followed by simultaneous measurement of mass and temperature on the same specimen and environment.

Papailhau\textsuperscript{21} was probably one of the earliest to construct an equipment for recording D.T.A. and T.G.A. data simultaneously. During the last five years, a number of workers have made use of simultaneous recording of the D.T.A. and T.G.A. data during a thermal decomposition reaction.

Many types of commercial D.T.A. cum T.G.A. apparatus are now available.

In our present investigation we have made use of a 'Derivatograph' described by Paulik \textit{et al.}\textsuperscript{22} and marketed by M/s. Metripex Budapest, Hungary, the description of which is given in brief in the next section.
DESCRIPTION OF THE APPARATUS

The Derivatograph is shown schematically in Fig. 18. It consists of the following principal parts:

i) balance with automatic mass loading device, (ii) galvanometers, (iii) sample holder crucibles, (iv) electric furnace, (v) program control unit, (vi) voltage regulator, (vii) temperature regulator and (viii) recorder.

The temperature of the weighed sample (taken in a platinum crucible) is increased at a uniform rate in an electric resistance furnace (A). The crucible is placed on the beam of an analytical balance (B). Any change in the mass of the sample causes a deflection of the balance, and a light signal coming from a slit (S₁) fixed on the pointer of the balance draws a thermogravimetric curve on a light sensitive paper placed on a rotating cylinder.

By using a magnet (M) suspended from the balance beam and a coil surrounding the magnet, the apparatus simultaneously measures the rate of mass change, since a current proportional to the velocity of the moving magnet is induced in the coil. Thus the light signal coming from a galvanometer (G₁) connected to the poles of the coil registers the derivative curve (D.T.G.) of the basic thermogravimetric curve.
The crucible for holding the sample has been designed so as to permit the introduction of the thermocouple junction (inserted in the double bore of the porcelain tube) inside the sample i.e. on the indented part of the crucible. This thermo-element is coupled opposite to another one reaching into the centre of another crucible filled up with inert material. The light signal of a galvanometer \( G_3 \) connected to the poles of the thermocouples will register differential thermal analysis curve.

A third galvanometer \( G_2 \) inserted between the poles of the thermocouple reaching inside the sample records the temperature of the sample. Hence the T.G., D.T.G. and D.T.A. curves of a single sample are recorded at the same time on a single photo-sensitive paper.

Our main object is to study the effect of addition of copper formate, and of cobalt formate on the reduction temperature of nickel formate. This will help in obtaining salt compositions with lower reduction temperatures so as to enable us eventually to prepare suitable hydrogenation catalysts by wet reduction in oil.

STUDIES ON THE THERMAL DECOMPOSITION BEHAVIOUR OF NICKEL, COBALT AND COPPER FORMATES AND OF THEIR BINARY MIXTURES IN AIR

The method of preparation and compositions of the nickel, cobalt and copper formates and of their coprecipitated
mixtures have been described earlier (Chapter 2). The rate of heating used on the 'Derivatograph' was 5°C/minute. About 200 mg. of samples were used in a current of air atmosphere. α-Alumina was used as a reference material.

Experiments with calcium oxalate monohydrate were carried out to check the accuracy and reproducibility of measurements under comparable experimental conditions. The D.T.A., T.G.A., and D.T.G. curves in the 25°C - 450°C region are shown in Fig. 19 A, B and C.

In the D.T.A. curve the endothermic peak at 20°C is due to the loss of water of hydration and the exothermic peak at 65°C is due to oxidation/disproportionation of anhydrous calcium oxalate to calcium carbonate. The corresponding dehydration and decomposition steps in the T.G. curve occur at a mass loss of 12 per cent in the 150-230°C interval and a mass loss of 31.5 % in the 400-470°C temperature interval respectively.

The maxima of the two peaks observed in D.T.G. curve at 200°C and 460°C correspond to the temperature at which the rate of dehydration and decomposition to calcium carbonate are maximum.

The temperature ranges for the dehydration as well as the decomposition steps in the D.T.A. (150-230°C, 400-475°C)
and T.G.A. (150-230°C, 400-470°C) were found to be reproducible within ± 5°C and are in general agreement with the literature values.

Although several studies of the decomposition of 3d-transition metal formates, in vacuum and in inert atmosphere have been reported, few studies have been made in air. Zapletal et al. studied the thermal decomposition of Mn(II), Fe(II), Zn(II), Co(II), Ni(II), Cu(II) and Mg(II) formates using the D.T.A. and T.G.A. techniques. They found that the nickel and magnesium formates decompose immediately after dehydration, whereas in others the anhydrous salts show a finite thermal stability range. Duval has reported that nickel formate dihydrate when heated at the rate of 2.5°C/minute loses water of crystallization upto 240°C-250°C and the anhydrous salt is stable upto 270-275°C.

Kornienko studied the kinetics of decomposition of the formates of bivalent Mn, Fe, Cu, Ni, and Co. They showed that absolute temperatures of equal decomposition time are inversely proportional to the total ionization potentials of cations and that the decomposition products contained metal oxides.

Kohlschutter studied the thermal decomposition of copper formate in vacuum. The compound was decomposed in two
ways to give (i) H₂, CO₂ and Cu and/or (ii) CuCO₃, CO and H₂. Schuffenecker et al.²⁸ found from a p.g.a. analysis of copper formate in vacuum that the decomposition is auto-catalytic.

Korosy²⁹ reported that copper formate decomposes at about 200°C with the evolution of a volatile compound which immediately decomposes forming a red smoke of elementary copper. However, the formates of Ni, Fe, Co, Zn and Cd decomposed without mirror formation. The existence of copper carbonyl was also postulated by several authors.²⁵,³⁰,³¹

Duval²⁵ showed that copper formate tetrahydrate heated at the rate of 2.5°C/min. loses water continuously upto 120°C and the anhydrous salt is stable from 120°C-205°C. This salt then decomposes beyond 205°C, yielding water and carbon monoxide viz.,

\[ \text{Cu(HCOO)₂} \rightarrow \text{H}_2\text{O} + \text{2CO} + \text{CuO} \]

They reported that the CuO was formed at 240°C.

Erofeev³² showed that the thermal decomposition of cobalt formate at 218°C takes place according to following equation:

\[ \text{Co(HCOO)₂} \rightarrow \text{Co} + \text{H}_2 + 2\text{CO}_2 \]

Duval²⁵ found that when cobalt formate is heated at the 2.5°C/min. rate it progressively becomes anhydrous
between 152°-209°C. It was observed that the mass level corresponding to the anhydrous formate is not perfectly horizontal. The decomposition sets indefinitely around 260°C and becomes rapid in the vicinity of 300°C. It was observed that Co₃O₄ is not obtained at once as the furnace atmosphere is reducing in character. A slow oxidation is observed between 372°-400°C.

Dollimore and Tonge studied the thermal decomposition of the anhydrous formates of manganese and zinc as well as their dihydrates by means of T.G., D.T.A., and gas evolution analysis. They attributed the different behaviour of zinc formate to the facility with which zinc oxide catalyses reactions between carbon monoxide and hydrogen to form formaldehyde. It was observed that the thermal decomposition mechanism for zinc formate is primarily the same as outlined for manganous formate.

The studies on thermal decomposition of various formates thus provide useful information which can be used in preparing and correlating the activity of a catalyst especially when it is prepared by direct thermal treatment of a compound. Our work is concerned with the preparation of a series of hydrogenation catalysts by direct thermal treatment of the formates of Ni, Co, and Cu and of their mixtures formed by coprecipitation, in hydrogen atmosphere. However, a study of the thermal behaviour in air of the above compounds by T.G.A.,
D.T.A. and D.T.G. techniques has been made. Since no such systematic studies have been reported so far in the literature the results may be useful in understanding the pyrolytic behaviour of the compounds and in characterising the properties of products obtained through thermal decompositions.

THERMAL DECOMPOSITION STUDIES OF NICKEL FORMATE DIHYDRATE IN AIR

The D.T.A., T.G.A. and D.T.G. curves for nickel formate dihydrate are shown in the Fig.20 A, B and C.

It will be observed from the T.G. curve that nickel formate dihydrate is stable up to 145°C, indicated by the horizontal portion in the temperature range 25-145°C after which the dehydration starts and the rate of dehydration becomes maximum at 182°C corresponding to the peak in the D.T.G. curve. The dehydration is complete when approximately 19 per cent mass loss has occurred at 192°C. The decomposition of the anhydrous formate starts almost immediately as shown by the absence of any horizontal portion but during the temperature range 195°C-245°C the rate of decomposition is slow. Soon after the temperature of 245°C is reached, the rate of decomposition rises sharply and reaches a maximum at 250°C corresponding to the second peak in the D.T.G. curve. A maximum mass loss of 67 per cent occurs at 260°C which
Fig. 20. Densitograph record of Nickel Sulfate Hydrate in air.

A - 6.9. C - D. Temperature recorded.
indicates that the reaction product in the decomposition of nickel formate even in this air ambient at a temperature of 260°C is metallic nickel which later undergoes slow oxidation to NiO. The oxidation of metallic nickel to NiO is complete at 400°C as shown by the horizontal portion in the T.G. curve. There is a reasonable agreement between the final mass loss of 60 per cent compared to calculated value of 59.55 per cent assuming the final product to be NiO.

In the D.T.A. curve, the first endothermic peak at 185°C is due to dehydration and is followed by a small exothermic peak at 250°C which soon gives way to another endothermic peak at 255°C due to the decomposition of the formate to the metallic nickel. The exothermic peak at 250°C may be due to the oxidation or disproportionation of CO and other organic products formed during the decomposition of nickel formate.

A small exothermic peak at 278°C is due to the immediate oxidation of the active surface of the finely divided metallic nickel to NiO. A broad exothermic peak in the region 300°C-400°C with a $T_{\text{max}}$ at 366°C may be attributed to the slow oxidation of metallic nickel to NiO in agreement with the thermogravimetric data.

The T.G. and D.T.A. data show that nickel formate dihydrate first undergoes dehydration and then decomposition.
to metallic nickel but the two steps are not clearly resolved since there is no distinct step corresponding to the presence of anhydrous formate.

**THERMAL DECOMPOSITION STUDIES OF COBALT FORMATE DIHYDRATE**

The curves for D.T.A., T.G.A. and D.T.G. of cobalt formate are shown in Fig. 21 A, B and C. It can be seen from the T.G. curve that it is stable in the range 25°-124°C. However, the sample loses adsorbed water around 55° C indicated by a small deviation from the horizontal slope showing the range in which the dihydrate is stable. It starts losing water of hydration at about 124°C and the dehydration is complete at 169°C, corresponding to the loss in mass of 19 per cent. Theoretical value for the loss of 2H₂O is 19.5%.

The peak in the D.T.G. curve at 165°C corresponds to the temperature at which the rate of dehydration is maximum. The completion of this step is not indicated by any horizontal stage in the T.G. curve. The dehydration step is soon followed by decomposition, but in the range 169°C-212°C the process is slow. It then increases suddenly and reaches a maximum at 250°C. The two peaks at 245°C and 250°C in the D.T.G. curve indicate that the decomposition of anhydrous formate takes place in two steps, viz. a slow reaction followed by a faster one.
The mass loss of 59.0 per cent at 252°C is in good agreement with the calculated value of 59.5 per cent, if the reaction product is CoO. CoO thus formed slowly oxidizes to Co$_3$O$_4$. The completion of the reaction is shown by the horizontal portion in the T.G. curve beyond 380°C. The final loss of 56.0 per cent is well comparable to calculated loss of 56.5 per cent for the end product Co$_3$O$_4$.

In the D.T.A. curve the small endothermic peak at 55°C is due to the loss of capillary adsorbed water, and the two well defined endothermic peaks, one at 165°C, the other at 252°C, are due to dehydration and decomposition respectively. The small exothermic peak at 248°C can be attributed to the oxidation of CO produced in the decomposition reaction (2) discussed in the next section. The other exothermic peaks with $T_{\text{max}}$ 297°C and broad peak centered at about 340°C may be attributed to the initial fast rate and the subsequent slow rate of oxidation of CoO to Co$_3$O$_4$ in agreement with the nature of T.G. curve.

**THERMAL DECOMPOSITION STUDIES OF COPPER FORMATE DIHYDRATE IN AIR**

The D.T.A., T.G.A. and D.T.G. curves are shown in the Fig.22 A, B and C. The T.G. curve shows two distinct steps, the first step is due to dehydration and the second one
Fig 2. Derivatograph record of copper formate dihydrate in air
to decomposition. It is stable up to \( \approx 70^\circ C \) indicated by the horizontal portion in the temperature range \( 27^\circ -72^\circ C \). Soon after \( 72^\circ C \), it starts losing water of hydration and one molecule of water is lost before \( 92^\circ C \). The horizontal portion in the range \( 92^\circ -165^\circ C \) corresponds to the presence of the stable cupric formate monohydrate. The further dehydration of \( \text{Cu} (\text{HCOO})_2 \cdot \text{H}_2 \text{O} \) and decomposition begins at \( 167^\circ C \) and the sharp peak observed in D.T.G. curve at \( 200^\circ C \) indicates the temperatures at which the rate of decomposition is maximum. There is no step corresponding to the formation of anhydrous formate.

From the mass loss curve it can be seen that the final loss at \( 228^\circ C \) is 59.5 per cent. This is a little lower than the calculated value of 62.3 per cent for cuprous oxide \( (\text{Cu}_2\text{O}) \) formation and is higher than the calculated value of 58 per cent for cupric oxide \( (\text{CuO}) \) formation indicating that the final product obtained at \( 228^\circ C \) is a mixture of \( \text{Cu}_2\text{O} \) and \( \text{Cu}_2\text{O} \) (approximately in the proportion \( 70 \text{ Cu}_2\text{O} : 30 \text{ CuO} \)). As further heating is carried in air, \( \text{Cu}_2\text{O} \) in the \( (\text{Cu} + \text{Cu}_2\text{O}) \) mixture is oxidised to cupric oxide as shown by increase in mass observed in the T.G. curve 22-B.

In general, formates of divalent metals decompose according to either of the following reactions:

\[ \text{Cu}_2\text{O} \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \]
\[ \text{Cu}_2\text{O} \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \]
with small quantities of organic products such as CH₃OH, formaldehyde and formic acid. Since the major components of the decomposition products are CO, CO₂ and H₂, the atmosphere surrounding the primary product Cu₃O, is of a slightly reducing nature, leading to the formation of cuprous oxide. This may be the reason for the presence of a mixture of Cu₂O and CuO in the decomposition product of cupric formate dihydrate.

In the D.T.A. curve the endothermic peak at 90°C is due to the loss of one molecule of water of hydration. This is followed by an exothermic peak with T_max 228°C. The latter is due to a secondary reaction (see below) which masks the endothermic peak due to decomposition of the anhydrous cupric formate.

Carbon monoxide, one of the products of the decomposition, is thermodynamically unstable under the prevailing conditions. It disproportionates according to the following equation, in the absence of oxygen,

\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \]  \hspace{1cm} (3)

commonly called Boudonard Reaction, or oxidises to carbon
dioxide in the presence of air according to equation

\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \]  

(4)

The presence of the transition metal may in fact catalyse these reactions.

As both reactions (3) and (4) are exothermic, the heats produced in these secondary reactions as well as in the combustion of organic byproducts would be large enough to mask the endothermic effect accompanying the thermal decomposition. This would explain the presence of a large exothermic peak in the D.T.A. curve after the formation of cupric formate monohydrate. It also shows that the decomposition of cupric formate takes place predominantly by reaction (1) shown above while that of nickel formate takes place predominantly by reaction (2), in which the proportion of CO produced in smaller and give rise to only a small exothermic effect at 250°C (see Fig.20 A).

THERMAL DECOMPOSITION STUDIES OF MIXED FORMATES

a) Nickel : Copper Formates in air

The D.T.A., T.G.A. and D.T.G. curves for a physically mixed (50:50) nickel-copper formates sample are shown in Fig.23. The T.G. and D.T.A. curves show that the two component formates of nickel and copper maintain their
Fig. 23. Densitograph record of a physical mixture (50:50) of nickel copper. Formula in our A.O.A. G.R.C. and D. temperature results.
individuality. It is stable to dehydration up to $72^\circ C$ and later it starts losing one molecule of water of hydration from cupric formate leading to a residue of composition $\text{Cu(HCOO)}_2 \cdot \text{H}_2 \text{O}$ and $\text{Ni(HCOO)}_2 \cdot 2\text{H}_2 \text{O}$, which is stable in the region $90^\circ-174^\circ C$. Thereafter, it loses 3 molecules of water of hydration, one from the cupric formate monohydrate and two from the nickel formate dihydrate simultaneously. The dehydration step is completed at around $205^\circ C$ corresponding to a mass loss of 19.5 per cent (theoretical value 19.25 per cent), after which the decomposition of the two formates starts and is complete within 3 minutes. The slow change of the T.G. curve beyond the portion corresponding to the maximum mass loss of 62.5 per cent, can be interpreted as being due to the slow oxidation in air of the reaction (metallic) products. (See the individual formate T.G. curves). The endothermic peaks with $T_{\text{max}}$ at $90^\circ C$ and $T_{\text{max}} = 200^\circ C$ in D.T.A. curve are due to loss of one molecule of water of hydration from $\text{Cu(HCOO)}_2 \cdot 2\text{H}_2 \text{O}$ and three molecules of water of hydration from $\text{Cu(HCOO)}_2 \cdot \text{H}_2 \text{O}$, $\text{Ni(HCOO)}_2 \cdot 2\text{H}_2 \text{O}$. The double humped broad exothermic peak in the temperature range $300^\circ-425^\circ C$ is due to slow and independent oxidation of the two reaction products viz., metallic nickel and cuprous oxide.

The corresponding D.T.A., T.G.A., and D.T.G. curves for various compositions of co-precipitated Ni-Cu formates are shown in Figs. 24-27.
Fig. 24. Derivatograph record of nickel-copper fomade (300°C) in air.

Fig 25. Derivatograph record of Nickel-Copper Formate (15.25) in air:
Figure 1: Dervatograph record of Nickel-Copper formate (95:5) in air.

In contrast to the behaviour of the 50:50 physical mixture, the co-precipitated sample of the same composition behaves thermally as a single homogeneous compound. There is only one dehydration step in the T.G. curve and only one endothermic peak in the D.T.A. curve corresponding to the loss of all water of hydration from both nickel and cupric formate dihydrates.

The D.T.A. curve also shows one single broad exothermic peak at $(T_{\text{max}} = 305^\circ C)$ corresponding to the slow oxidation in air of the intermediate reaction products, whereas in the physical mixture there are two partially resolved oxothermic peaks at $T_{\text{max}} = 352^\circ C$ and $T_{\text{max}} = 405^\circ C$.

The decomposition of the anhydrous formates in the physical mixture as well as the co-precipitated sample is accompanied by a net exothermic effect due to the heat evolved in the oxidation of CO produced in the decomposition of the formates as pointed earlier (pages 74 and 75).

It can be seen from the mass loss curves of the co-precipitated mixed formates that the maximum mass loss is 65.0 per cent which is in agreement with the calculated value of 65.25 per cent assuming the primary decomposition product to be a mixture of metallic nickel and cuprous oxide. The mass loss at the final stage is 59.0 per cent in reasonable agreement with calculated loss of 58.82 per cent, if we assume
that the intermediate products viz., metallic nickel and cuprous oxide are oxidised to NiO and CuO. The thermal behaviour of other co-precipitated compositions is very similar as shown by their T.G. and D.T.A. curves. The T.G. curves show that in the 50:50 co-precipitated formate the decomposition starts after the dehydration is complete but for the other composition viz., 75:25, 90:10 and 95:5, it starts much earlier than the completion of the dehydration.

The D.T.G. curve of the physical mixture shows two maxima corresponding to two stages in dehydration in the T.G. curve, although the second peak is closely followed by the decomposition step, whereas the D.T.G. curves of the co-precipitated formates show a single step for dehydration. These results are recorded in Table 9.

In the light of the observations made above, it is concluded that the thermal decomposition of a physical mixture takes place with the component formates decomposing independently, whereas the co-precipitated formates do so like that of a single phase. These results provide evidence of the formation, by co-precipitation, of a homogeneous phase. These are also in agreement with the evidence obtained from the reduction studies described in the earlier Chapter 3.
<table>
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<th>D.T.G.</th>
<th>D.T.A.</th>
<th>Decomposition</th>
<th>D.T.G.</th>
<th>D.T.A.</th>
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<td>-</td>
<td>86</td>
<td>90</td>
<td>174</td>
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</table>
b) **Nickel : Cobalt Formates in Air**

The typical D.T.A., T.G.A. and D.T.G. curves of various compositions are shown in Figs. 28-31.

The curves of a physically mixed (50:50) nickel-cobalt formate are shown in Fig. 32.

These show that the two formates in a physical mixture behave independently. It starts losing (capillary adsorbed) water at 52°C and is stable to dehydration up to 135°C. The dehydration step is complete at 193°C showing a mass loss of 19.5 per cent in agreement with the calculated value of 19.5 per cent. Immediately, after this, the decomposition starts. In the region 193°C-230°C the rate of decomposition is slow, after which the rate suddenly increases and the reaction is complete within 6 minutes. The shape of the T.G. curve beyond the portion indicates the maximum mass loss of 63.5 per cent which can be accounted as due to the slow oxidation in air of the primary reaction products (mixture of Ni and Co).

As pointed out earlier, the maxima of the dehydration step of Ni(HCOO)₂·2H₂O and Co(HCOO)₂·2H₂O occur at the temperatures 185°C and 165°C respectively (see Figs. 20 and 21). It can be seen from the D.T.A. curve of the physical mixture that the endothermic peak in the temperature range 138°C-235°C is composed of two partially resolved peaks with \( T_{\text{max}} \) at
Fig 31. Derivatograph record of Nickel-Cobalt Formate (95:5) in air
Fig. 32. Derivatograph record of a physical mixture (50:50) of Nickel-Cobalt formate in air.

$170^\circ$ and $186^\circ$C indicating that the dehydration of the two formates is taking place at two different temperatures. The two partially resolved peaks observed in the D.T.G. curve (Fig. 32 C) indicate the temperatures at which the individual formate dehydration rates are maximum.

The decomposition of the anhydrous formates in the physical mixture is accompanied by a net endothermic peak in the $235^\circ$-$280^\circ$C with $T_{\text{max}}$ at $250^\circ$C. It can be seen from the D.T.G. curve that the two maxima at $235^\circ$C and $246^\circ$C indicate the two-stage decomposition steps. This confirms that the decomposition of the component formates proceeds independently. The D.T.A. curve also shows one broad exothermic peak at $T_{\text{max}}$ ($360^\circ$C) corresponding to the slow oxidation of the reaction products.

It will be observed that the nature of the T.G. curves are same for various compositions. These samples are stable upto temperatures of about $135^\circ-145^\circ$C before the dehydration step takes place. The first step of the curve represents the loss of water of hydration followed by a sharp mass loss step due to decomposition. A comparison of the T.G. curves of nickel-cobalt formates with those of nickel-copper formates indicates that the decomposition step in the former system does not follow the dehydration step immediately as found in the latter system, although there is no horizontal portion due to stable anhydrous formate.
The D.T.A. curves of co-precipitated formates show only one symmetrical endothermic peak due to dehydration, which corresponds to the step observed in the T.G. curves and another endothermic peak due to decomposition which corresponds to the sharp decomposition step in T.G. curves. These results are summarized in Table 10.

The shapes of the dehydration as well as the decomposition steps shown in D.T.A. and T.G. curves of the co-precipitated Ni-Co formate system provide evidence of the formation of a homogeneous phase.

**COMPARISON OF THE T.G. AND D.T.A. CURVES OF THE THREE FORMATES**

On the basis of the results described above, the following general observations and comparisons can be made. The regions of stability of the hydrated formates in respect of loss of water of crystallisation and thermal decompositions in air are assembled in Table 11.

The data noted under 'T.G.A. Unit' are those obtained (Chapter 3) in our improvised T.G.A. unit and those under 'Derivatograph' are obtained in a simultaneous record of T.G.A., D.T.G. and D.T.A. results in a single run as described before. In the former case the rate of heating was 2°C/min. However, the results in the respective stages are well comparable.
TABLE 10

Dehydration and decomposition temperature ranges and peak temperatures (D.T.A. and D.T.G.) of coprecipitated Ni-Co formates

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Co</td>
<td>On set</td>
<td>Final</td>
<td>Mean</td>
<td>On set</td>
<td>Final</td>
<td>Mean</td>
</tr>
<tr>
<td>50  50</td>
<td>135</td>
<td>185</td>
<td>150</td>
<td>175</td>
<td>180</td>
<td>230</td>
</tr>
<tr>
<td>75  25</td>
<td>140</td>
<td>184</td>
<td>162</td>
<td>172</td>
<td>178</td>
<td>235</td>
</tr>
<tr>
<td>90  10</td>
<td>142</td>
<td>182</td>
<td>162</td>
<td>168</td>
<td>175</td>
<td>236</td>
</tr>
<tr>
<td>95  5</td>
<td>145</td>
<td>192</td>
<td>169</td>
<td>185</td>
<td>189</td>
<td>238</td>
</tr>
<tr>
<td>Physical mixture (1:1)</td>
<td>135</td>
<td>193</td>
<td>164</td>
<td>165</td>
<td>182</td>
<td>230</td>
</tr>
</tbody>
</table>
### TABLE 11

Dehydration and decomposition temperatures (ranges and peaks) of Ni, Co and Cu formates in air (from T.G.A. and Derivatograph)

<table>
<thead>
<tr>
<th>Compound</th>
<th>T.G.A. unit</th>
<th>Dehydration</th>
<th>D.T.G.</th>
<th>D.T.A.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range °C</td>
<td>Peak °C</td>
<td>Range °C</td>
<td>Peak °C</td>
<td>D.T.G. peak °C</td>
</tr>
<tr>
<td>Ni(HCOO)₂.2H₂O</td>
<td>140-182</td>
<td>161</td>
<td>145-192</td>
<td>169</td>
<td>182</td>
</tr>
<tr>
<td>Co(HCOO)₂.2H₂O</td>
<td>120-170</td>
<td>145</td>
<td>124-169</td>
<td>147</td>
<td>165</td>
</tr>
<tr>
<td>Cu(HCOO)₂.2H₂O</td>
<td>75-98</td>
<td>87</td>
<td>72-92</td>
<td>82</td>
<td>86</td>
</tr>
</tbody>
</table>

#### Decomposition

<table>
<thead>
<tr>
<th>Compound</th>
<th>Range °C</th>
<th>Peak °C</th>
<th>Temperature °C</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(HCOO)₂.2H₂O</td>
<td>250-261</td>
<td>256</td>
<td>246-260</td>
<td>253 Decomposition</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300-400</td>
<td>350 Disproportionation</td>
</tr>
<tr>
<td>Co(HCOO)₂.2H₂O</td>
<td>220-255</td>
<td>238</td>
<td>212-252</td>
<td>232 Surface oxidation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300-380</td>
<td>340 Bulk oxidation</td>
</tr>
<tr>
<td>Cu(HCOO)₂.2H₂O</td>
<td>170-233</td>
<td>202</td>
<td>167-228</td>
<td>197 Decomposition</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>310-380</td>
<td>340 Conversion of Cu₂O → Cu.</td>
</tr>
</tbody>
</table>

*Conversion of Cu₂O → Cu.*
It is interesting to note that the Derivatograph recorded a number of additional information particularly in its D.T.A. records.

(a) Nickel formate dihydrate and cobalt formate dihydrate lose both molecules of water of hydration around 140°-182° and 120°-170°, respectively, whereas cupric formate loses one molecule of water of hydration in the first stage at about 150°-98° and the loss of the second water of hydration and the decomposition takes place simultaneously in the second stage at about 170°-233°C.

(b) The thermal decomposition of nickel formate takes place mainly in the following manner

\[ \text{Ni(HCOO)}_2 \rightarrow \text{Ni} + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \]
\[ \rightarrow \text{Ni} + \text{2CO}_2 + \text{H}_2 \]

and the thermal decomposition of cobalt formate proceeds mainly by the following reaction

\[ \text{Co(HCOO)}_2 \rightarrow \text{CoO} + \text{CO} + \text{CO}_2 + \text{H}_2. \]

The end products formed immediately after the decomposition of nickel formate is metallic nickel and finally NiO. For cobalt formate it is CoO in the intermediate stage and finally Co3O4.

The thermal decomposition of copper formate proceeds predominantly by the reactions

\[ \text{Cu(HCOO)}_2 \rightarrow \text{Cu}_2\text{O} + 2\text{CO} + \text{H}_2\text{O} \]
\[ \rightarrow \text{CuO} + \text{CO} + \text{CO}_2 + \text{H}_2 \]

forming a mixture of Cu2O and CuO and finally CuO.
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