CHAPTER I

CHAPTER-I

INTRODUCTION

Several methods of 'thermal analysis' are applied to various subjects of interest. The term 'Thermal Methods of Analysis' is defined by Wendlandt[1] as 'The techniques in which some physical parameters of the system are measured as a function of temperature'. A group of analytical techniques developed to continuously monitor physical or chemical changes of a sample which occur as the temperature is varied.

The various thermal techniques, the physico-chemical parameters measured, and the instruments employed in their measurements are summarized in Table below (I). Modern commercial instruments, many incorporating microprocessors, are available for TG, DTA and DSC type of thermoanalyses.

Any type of physiochemical process which involves a change in sample mass may be observed by TG with the aid of thermobalance. TG can be applied to surface layer in a similar way as for the bulk material. Mass losses are observed for dehydration, decomposition, desorption, vaporization, sublimation, pyrolysis and chemical reactions of the sample with the atmosphere in the oven.

DTA method involves the monitoring of the temperature difference between a sample and inert reference material as they are simultaneously heated, or cooled, at a predetermined rate.

Table-I

Name of the Technique	Physical parameter measured as a function of temperature	Name of the instrument employed
Thermogravimetric analysis	Change in mass	Thermobalance
Differential thermogravimetric analysis	First derivative of change in mass	Thermobalance or differential thermobalance
Differential thermal analysis	Temperature difference between sample and reference material	DTA apparatus
Derivative differential thermal analysis	First derivative of temperature difference	DTA apparatus
Differential scanning colorimetry analysis	Heat change supplied to sample	Differential colorimetry.
Gas evolution analysis; linear pyrolysis	Gas thermal conductivity	Thermal conductivity cell
Pyrolysis	Pyrolysis fragments	Gas chromatography; mass spectrometers, infrared spectrophotometer and others.

contd.

Table-I

contd.

Name of the Technique	Physical parameter measured as a function of temperature	Name of the instrument employed
Thermoluminescence; oxyluminiscence	Light emission	Photomultiplier tube in Thermoluminescence apparatus.
Dilatometry	Change in volume	Dilatometer
Electrical conductivity	Change in electrical resistance	Resistance bridge
High temperature X-ray diffraction	Change in d-spacing	X-ray diffractometer
Thermometric titrimetry	Temperature change Vs. time or volume of titrant	Thermometric titrameter
Thermal analysis	Temperature Vs time or heat content	Colorimeter, thermal analysis apparatus
Dynamic reflectance spectroscopy	Reflectance of sample	Spectroreflectometer

Thermocouples and thermistors are the most common temperature sensors used for this purpose.

In DSC a sample and a reference are individually heated by separately controlled resistance heaters, at a pred~~ominant~~etermined rate while they are kept constant.

Other methods are thermomechanical analysis (can be used to evaluate the physical stability of structural or electronic components), thermoluminescence (often used for authenticating ancient objects), emanution thermal analysis and evolved gas analysis (used to determine gaseous products, often from destructive oxidation), and thermomagnetic analysis (can be used to determine Curie point of metals).

It is observed that there is a large interval between the development of a technique and its application in case of TGA and DTA e.g., the first thermobalance was developed by Honda[2], in the year 1915, yet it was not until 1947 that Duval[3] called attention to its application to the field of inorganic gravimetric analysis. A similar situation is noted with DTA which was originally conceived by Le-Chatelier[4] in 1887 and further modified by Austan[5] in 1899. For many years DTA was an invaluable technique for the identification of minerals, clays, etc., but was virtually ignored by chemists. In recent years, however, DTA has been successfully applied, either by itself or in conjection with other thermal techniques, to the elucidation of problems of chemical interest.

In many cases the use of only a single thermal technique may provide insufficient information to characterize a chemical reaction or system. There is a chance of getting complementary or supplementary information, by the use of other thermal methods of analysis.

It may be stated that a single thermal property[1] is not sufficient to characterize a chemical reaction or system, but that as many thermal methods as possible be employed.

In this thesis we have reported the results of our investigations on the thermal behaviour and structural properties of co-precipitated Nickel-Cadmium oxalates which are supplemented by X-ray diffraction.

REVIEW OF THE LITERATURE

The work described in this thesis constitutes 'change in mass' which takes place when Nickel-Cadmium mixed oxalates are heated in air medium. The reactions involve a single stage decomposition of type,

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

for anhydrous salt, whereas for hydrates oxalate decomposition involves several intermediate stages.[6]

Kadlec and Danes[7] have reported mechanism of thermal decomposition for oxalates of Ni, Co, Fe, Mn, Zn, Pb and Mg. The change of the chemical components of products was followed during the decomposition. In all cases the kinetic curves were S shaped. The activation energies were determined respectively as 32.6, 44.0, 40.0, 40.0, 37.9, 37.7, 36.0 and 45.0 K·cal/mole. They observed that in the decomposition of Ni, Co, Fe, and Pb oxalates a mixture of metal and oxide is formed. The relative amount of oxide decreases and that of metal increases during decomposition.

In the Ni oxalates decomposition, following reactions were reported:

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

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

$$NiO + CO = Ni + CO_2$$

In case of Mg and Zn oxalates only oxide is formed. In the Co and Fe oxalate decomposition the oxide is primarily formed which is subsequently reduced to metal by CO from the decomposed gases.

Rao and Gandhe[8] studied thermal decomposition of oxalates of formula $M_2C_2O_4$ (M = Mn, Zn, Pb, Co) which was resulted in the production of CO and CO_2. Gas chromatographic analysis of the gas products indicated that the oxalates were decomposed to MCO_3 + CO and MCO_3 further decomposed to MO + CO_2. They also studied thermal decomposition of oxalates of formula $M'C_2O_4$ (M' = Fe, Ni, Cu) which was resulted in the production of M' and CO_2 only.

Fabbri and Baraldi[9] studied thermal decomposition of metal oxalates: $K_2C_2O_4$, H_2O; $Ag_2C_2O_4$; MC_2O_4 (M = Cd, Cu, Pb, Sn); MC_2O_4: H_2O (M = Ba, Ca) and MC_2O_4: $2H_2O$ (M = Co, Fe, Mg, Mn, Ni, Zn) in air and vacuum. They used emission, IR spectroscopy. In air K, Ba, Ca oxalates were decomposed to carbonates at 7 470°, 7 380° and 7 370° respectively; and Ag oxalate in air and in vacuum decomposed to metallic Ag. In vacuum K, Ba and Ca oxalates decomposed to respectively carbonates. But Cd, Cu, Pb, Sn, Co, Fe, Mg, Mn, Ni and Zn oxalates in air decomposed to respective metal oxides and in vacuum to oxide or oxide plus metal.

Catalytic effect of thermal decomposition of the mixed Co-Ni oxalates was studied by Kadlec and Rosmusova[10]. In the thermal decomposition of Ni(II) oxalates and of the Co(II) oxalate. The metal oxides are formed at the beginning in both cases. With proceeding decomposition, the portion of free metals in the product increases, so that the product of the complete decomposition of the Ni oxalate contains 95 mole per cent of the metallic Ni in addition to the NiO and in case of Co oxalate the product contains 43-51 mole per cent of metallic Co.

It was observed that in Ni oxalate decomposition with comparable rate at temperature, which is 60° lower than Co oxalate. The course of thermal decomposition is strongly affected by even small Ni contents in the mixed Co-Ni oxalates; the rate constant increases, the activation energy decreases and the composition of the decomposition product is significantly changed.

Kadlec and Danes[11] have also studied the kinetics of decomposition and the composition of products from the thermal decomposition of anhydrous mixed Ni-Mg and Co-Mg oxalates under reduced pressure. They observed that an increasing content of Mg in mixed oxalates, the molar ratio of Ni and Co, to the sum of Ni and Co in the products of complete decomposition, first increases and later decreases. This fact was attributed to the increased extent of the reduction of oxides to the respective metals, caused by a higher content of CO in the gaseous products formed from Mg oxalates, as well as by the formation of isomorphous mixed Ni-Mg and Co-Mg oxides which were found to be difficult to reduce.

The decomposition of Ni-Mg oxalates did not proceed uniformly as a consequence of the chemical composition of the individual mixed oxalates. Decomposition of such inhomogeneous sample, proceeded in such a way that the portions richer in Ni oxalates decompose first and gradually the portions with decreasing content were decomposed (in the range of 0-30 % of Mg oxalates), the mechanism of direct catalytic decomposition of Ni oxalate to metallic Ni, gradually changes to the decomposition to oxide with subsequent reduction with CO. The mechanism of decomposition of mixed Co-Mg oxalates was described as follows.

The products of the decomposition were oxides from which Co oxide as far as it was present in reducible form, was reduced to metal by CO present in an increased amount, in the gaseous products. The activation energy of the decomposition was 44 K.cal/mole and was nearly high as for pure Mg oxalate.

With heavy metal oxalates, stages include the formation of an anhydrous oxalates and transient conversion into metal[12] which in the presence of air would be re-oxidised immediately. An intermediate carbonate stage would not be expected to be stable.[13]

Thermal decomposition of various oxalates of the general formula, $MC_2O_4.2H_2O$ (M = Zn, Mn, Fe, Co, Ni) and $Cr_2(C_2O_4).6H_2O$, $Fe_2(C_2O_4)_3.5H_2O$ and $CuC_2O_4.1/2\ H_2O$ were studied by Dollimore and Nicholson.[14] Their main subject was to study surface area changes (measured by volumetric adsorption) which occur when heavy metal oxalates are heated at various temperature.

As the surface area of a solid depends on its previous history, oxides prepared by decomposing oxalates would differ in their surface properties, from similar oxides prepared by thermal decomposition of other oxalates. They also studied theories outlined by Gregg,[6] for the production of greater number of product particles from a given number of reactant particles, can be extended to the more complicated decomposition processes taking place on the thermal treatment of oxalates in air.

Two competing processes contribute to surface area changes at given temperature (1) those increasing surface area, such as strains resulting from the difference between the specific volumes of reactants and solid product, which are opposed by sintering processes, which tend to reduce surface area. (2) As the decomposition temperature is raised, the second process which proceeds mainly by diffusion mechanism,[15] becomes faster and more important. In general the lower the temperature of decomposition, the greater will be the increase of surface area expected, as sintering will be slow. However, if the reaction is relatively slow, it is possible for the strains set up to be dissipated and hence there is no increase in surface area. All the oxalates gave a surface area peak at or immediately before the position, where the decomposition to the oxide was complete.

Macklen[16] studied the thermal decomposition of Mn, Co and Ni oxalates dihydrates by TGA and DTA in air and nitrogen atmosphere. In nitrogen atmosphere the decomposition of the oxalates first yields metal oxide, MO, which in case of Co and Ni is reduced to metal by nacent CO. Correlation between decomposition temperatures and cation electronegativities were obtained. In air, decomposition is initiated at lower temperature than in nitrogen by the oxidation of the cation from the divalent to trivalent state and correlation between ease of oxidation and temperature of reduction was found.

Thermal decomposition of MC_2O_4 (M = Co, Mn, Ni) in vacuum and in air was studied by Bakcsy and Hegedus[17] with the use of a vacuum microbalance and in air with the use of derivatograph also. In vacuum, in the 1st step the Co and Mn oxalates were decomposed into oxides but the Ni oxalate into metallic Ni, depending on the magnitude of the crystal field stabilization energy. In secondary reactions Co and Mn oxides will partly be reduced by the evolved CO to the metal and a minute part of the metallic Ni can be oxidized depending on the partial pressures of the O_2, CO_2, H_2O components of the residual gas. In air the first step of thermal decomposition is the $M^{2+} \text{\_\_\_} M^{3+}$ oxidation of the central cation, this is also obtained from the linear relation between the temperature of the maximum decomposition rate and the ionization energy. Some inconsistencies found in the literature were elucidated. Deviations appearing in inert and oxidative atmosphere with lower and higher partial pressure of O_2, showed that the thermal stability of the solid complexes is influenced by the surrounding atmosphere similar to the stability of dissolved complexes in a solvent.

Kornienko and Dubrovskya[18] studied thermal decomposition of Iron group metal oxalates, at 351 - 420 °C, by a dynamic method based on the determination of the amount of CO and CO_2 liberated during the reaction. The experimental data described by equation

$$\alpha = 1 - e^{-kt^n}$$

α = fraction of solid decomposed at time 't'.k and n are constants.

The average energy of activation (E) for decomposition of $FeC_2O_4.2H_2O$, $NiC_2O\ .2H_2O$ and $CoC_2O_4.2H_2O$ was calculated as 43.2, 40.5 and 41.2 K. cal/mole respectively.[19] Rate of decomposition depends upon the polarising power of cations and difference in free energy change.

The thermal decomposition of oxalates of the formula $MC_2O_4.nH_2O$ (M = Fe, Ni, Cu, Zn) and their mixtures in the $KClO_3$ were investigated by gas flow DTA, X-ray diffraction, IR spectral analysis and gas analysis by Ishii and co-workers.[20] In flowing N_2 (60 ml/min) and static air the oxalate decomposed to show an endothermic DTA peak arising from the dehydration of water of crystallization and another endothermic peak was seen arising from the reactions.

$$FeC_2O_4 = FeO + CO_2 + CO$$

$$NiC_2O_4 = Ni + 2CO_2$$

$$CuC_2O_4 = Cu + 2CO_2$$

$$ZnC_2O_4 = ZnO + CO_2 + CO$$

Gas analysis revealed that a small amount of CO and/or CO_2 was evolved near the end of dehydration process by partial decomposition of oxalates. In flowing O_2 (60 ml/min) all DTA curves of oxalates except for the Zn salt show an explosive exothermic peak immediately after the dehydration peak.

All above oxalates contained $KClO_3$ (10-15 mole %) which show a sharp exothermic peak (P_m) in flowing N_2 over a temperature range of 330-360°. Since pure $KClO_3$ does not show any DTA peak in this temperature range, P_m was due to the thermal interactions of oxalates and $KClO_3$.FeO obtained by rapid cooling after the decomposition of FeC_2O_4 in flowing N_2 is ignitable in air, but not when it was cooled slowly over 4-5 hours.

The thermal dehydration and decomposition of the oxalates of mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) were investigated by DTA, TG, DSC, EGA, XRD analysis and reflectance and IR spectra by Nagase and co-workers.[21] In general, the temperature at which the oxalates were dehydrated increased with $^1/r$ where r denotes the radius of metal ion. The heats of dehydration ($\Delta H_{H_2O}\cancel{K}$) of the alkaline earth metal oxalates increased with $^1/r$ but those of transition metal ~~d/e~~ oxalates decreased as $^1/r$ increased. By considering the decomposition products, the reactions of anhydrous oxalates were classified into 3 groups and the relations between the decomposition temperatures and $\frac{1}{r}$ were discussed for each group.

The thermal decomposition of $CdC_2O_4.3H_2O$ was studied by Kornienko et al.,[22] at 350-390°C under isothermal condition at atmospheric pressure by analysing both solid and gaseous products of decomposition. They reported thermodynamics of the decomposition of Ag, Cd, Mn, Cu, Fe, Co and Ni oxalates and discussed metal - O - bond energies. As oxalate C - C bond was the initial stage in decomposition of metal oxalates, with exception of $Ag_2C_2O_4$, where Ag-O and C-C bond energies are comparable.

Louise[23] studied thermal decomposition of pure Ni oxalate and decomposition on a support and characterization of the solids from this reaction. Specific surface area S = 6.5 - 107 cm^2/g for $Nic_2O_4.\overset{\epsilon}{\cancel{2}}H_2O$ ($\epsilon = 0.8$ %) were obtained by dehydration of $Nic_2O_4.\underset{2.}{\epsilon}H_2O$ at 130° under static vacuum, under 2 - 30 Torr. water vapour and in air, the largest S was obtained in after nearly 8 hours and the smallest S was obtained for dehydration of previously rehydrated sample. Decomposition of solid started after 96 per cent dehydration. At nearly 250°, decomposition occured as

$$NiC_2O_4 + \epsilon\, H_2O \longrightarrow NiC_2O_4 + \epsilon\, H_2O \text{ (gas)}$$

$$NiC_2O_4 \longrightarrow Ni + 2CO_2$$

with secondary reactions

$$Ni + H_2O\text{ (g)} \rightleftharpoons NiO + H_2$$

and

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

decomposition was faster under H_2 than under dynamic vacuum, and increased with increasing S.

From decomposition at 245°, under dynamic vacuum, the total S (st) of the sample went through a maximum of fraction $\alpha = 0.15$ of total decomposition and the S of Ni (S_{Ni}) went through a maximum at $\alpha = 0.5$; under H_2, St was maximum at $\alpha = 0.1$ and S_{Ni} increased linearly with α. Application of Erofeev's equation (1946) showed that instantaneous nucleation growth of cylindrical nuclei. A SiO_2, 86%, Al_2O_3 14 % support affected NiC_2O_4. $2H_2O$ decomposition only at low Ni concentration, the low S_{Ni} values ($\leq$ 4 m^2/g catalyst) increased linearly with the Ni concentration on the support. The catalytic activity (γ) of supported Ni for hydrogenation of benzene at 90° for $\frac{1}{2}$ hour of catalysis, increased linearly with S_{Ni}, after 3 hours, γ decreased irreversibly by nearly 80%.

Dehydration of $MC_2O_4.2H_2O$ (M = Ni, Mn, Co, Fe, Mg) $CaC_2O_4.H_2O$, $Fe_2(C_2O_4)_3.5H_2O$ (I) and $Th(C_2O_4)_2.6H_2O$ (II) was studied by the derivatography method under non-isothermal conditions by Shkarin and co-workers.[24] Weight change, differential weight change and differential temperature change were recorded as a function of time. The order of reaction, activation energy and frequency factor were determined for each experiment, both under air and nitrogen. All reactions were endothermic regardless of gas phase composition. The reaction orders are nearly 1, activation energies 20-23 K.cal/mole and frequency factors 2.6 x 10^0 to 1 x 10^{10} min^{-1}. The dehydration reactions of I and II follow different patterns. I is simultaneously converted to FeC_2O_4 while II is dehydrated to two stages. The measured values were compared with those for isothermal conditions given by other authors and good agreement was found.

Broadbent and co-workers[25] have reported thermal decomposition of oxalates of cobalt and effect of prior dehydration conditions on subsequent decomposition of cobalt oxalate. Co-oxalate dehydrated at 150°, is porous and subsequent isothermal decomposition in a vacuum to cobalt, differs considerably from the isothermal decomposition of the anhydrous oxalate prepared at higher temperature. The characteristic feature of porous anhydrous Co oxalate is the retention of a constant rate of reaction upon the last 10% of the decomposition. A possible explanation of this is offered in terms of reaction interface advancing simultaneously from the interior and exterior surfaces.

Thermoanalytical study of $ZnC_2O_4.2H_2O$ by Giovinoli[26] showed that the activation energy of ZnC_2O_4 above 340° is 40.4 ± 2.6 K.cal/mole. Dehydration of $ZnC_2O_4.2H_2O$, produces a considerable inner surface of ZnC_2O_4, not accessible to gas adsorption. This surface is considered to be covered by adsorbed water, which would explain the remarkable amount of water retained during dehydration.

Lagier and Pezerat[27] reported phases obtained on preparation of transition metal oxalates, $MC_2O_4.2H_2O$ (M = Ni, Zn, Fe and Mn), prepared by reaction of metal salts with either alkali metal oxalates or oxalic acid. The prepared oxalates exhibited two sets of reflections by X-ray analysis first set corresponding to an otthorhombic A phase, other a mixture of A and B phases. They also observed that after prolonged boiling with $(NH_4)_2C_2O_4$, A phase transforms to B phase.

The low temperature (250-400°C) decomposition of mixtures of Fe and Ni oxalates makes possible accurately controlled production of fine powder of Fe-Ni alloys, either in α or γ crystal structure type of pure metals or in diphase mixtures $(\alpha + \gamma)$ of intermediate compounds. Dormix and co-workers[28] prepared mixed oxalates and studied their decomposition in hydrogen atmosphere together with DTA, TGA and automatic gas chromatography. They have reported that the reactions of the oxalates with hydrogen are strongly exothermic, chiefly because of conversion of CO formed to CH_4.

Thermal studies were performed on mixtures of Fe, Cd, Ni and Fe, Cd, Mn oxalates by Peshev and Tsyrnorehki.[29] In all runs the Fe_2O_3 content was held at 50 per cent while CdO content was varied from 5-45 per cent with NiO or MnO comprising remainder.

In the first series, ~~th~~rough~~s~~ at 230° and 385° were found to correspond to the dehydration of Cd and Ni oxalates respectively. A peak at 420-55° was attributed to oxidation of metallic Cd. Above 505°, Fe and Ni are oxidised. The second series has similar thermogram except that Mn oxalate dehydration through at 410°. Above 675° γ-Fe_2O_3 underwent transition to α-Fe_2O_3.

Schoroeder[30] studied decomposition of mixed oxalates of Ni and Fe. He studied kinetics of low temperature spinel formation of nickel ferrite. The conditions were examined under which a maximum formation of nickel ferrite is obtained, upto 600°, in the decomposition in air, of mechanically mixed and simultaneously prepared Ni-Fe oxalates; using the methods of TG, DTA and magnetic analysis. The decomposition and oxidation kinetics of Fe and Ni oxalates used to starting material were studied. The phases existing after decomposition were found to be in the state corresponding to the temperature at which they have actually been formed. The amounts of exothermic heat generated during oxidation play an important role.

Thermal decomposition of mixed Zn and bivalent oxalates have been reported by Sviridov and Pavlova.[31] $ZnC_2O_4.2\ FeC_2O_4.6\ H_2O$, in the presence of air at nearly 250° gives $ZnFe_2O_4$. Mechanical mixtures as descrete substance and decomposition is only slightly slower than the decomposition of zinc oxalate. With slowly rising the temperature the components of mechanical mixtures decompose independently.

Kucerra and Nikolajenko[32] have studied the products of decomposition of mixed Zn-Ni oxalates in vacuum. The chemical compositions and the structure of products were studied. At 300-320°, ZnO, metallic Ni and Ni-Zn alloy are formed.on heating the products in vacuum at 450-1100°, metallic Ni is alloyed with Zn and sample contains two alloys in addition to ZnO: α-Ni-Zn with 15 ± 1 atomic %. Zn with lattice parameter of a 3.552°A and a hitherto alloy with ~ 50 atomic % Zn. The latter alloy has like the α-alloy, a face centered cubic lattice with a 3.631 °A. Additional very weak lines were observed for this alloy, the indices of which can be assigned with double lattice constants; so that the possibility of a super structure is indicated.

Biswas and co-workers[33] have reported, thermal reduction of co-precipitated basic Ni-Cu carbonates in hydrogen medium shows a single sharp step in the mass loss vs. temperature curves. The reduction temperature decreases with composition from 210° for $NiCO_3$ to 140° for $CuCO_3$. These studies and X-ray analysis of the mixed oxides and of metals (obtained by reduction in H_2 atmosphere) indicate the formation of interpreterating gel structures during co-precipitation, these have been described as metastable solid solution in dry state.

Dollimore and Griffiths[34] carried out differential thermal analysis of some metal oxalates, in controlled atmosphere of oxygen and nitrogen. Accordingly, Ni and Cu oxalates show exothermic peak in oxygen, because the oxidation of initial solid products is strongly exothermic and superimposes itself on the much weaker decomposition endotherm.

The catalytic effect of Ni oxalate(I) on the thermal decomposition Ca oxalate(II) was studied by TGA both under H_2 and N_2 atmospheres and in vacuuo, by Runaecker and Toursel.[35] The decomposition of pure-I occurs in two and that of pure-II in three separate steps. In the decomposition of a mixed precipitates of I and II, I decomposes together with II during second decomposition step of II. This indicates the formation of mixed crystals of I and II an unexpected result in view of the great difference of their decomposition temperatures and mechanisms and the ionic redii of Ca and Ni.

The same behaviour was found for the mixed precipitates of II with Co and Fe oxalates. The Ba and Sr oxalates however do not form mixed crystals with I, the precipitates are only the mixtures and the metallic Ni formed by decomposition of I is responsible for the catalytic effect. The advantage of TGA is the fact that a very limited mixed crystals formation can be detected, its limitation being that the decomposition temperatures of the pure components have to differ quite appreciably.

Thermal decomposition of solid solutions of Ni and Mg oxalates was studied by Guslev and co-workers.[36] At the initial stage of the thermal decomposition of Ni-Mg oxalate solid solutions, the reaction is localized in the centres of the impurity cation oxalate occlusion. This occurs independently of thermal stability of the occluded oxalate in its individual state. The decomposition is partially due to the polarization effect of the occluded cation and predominantly due to the distortion of the $C_2O_4^{-2}$ symmetry by the occluded cation. The mechanism of decomposition was studied by the electron microscopy of the solid products and by the mass spectra of the gaseous products of the decomposition.

Thermal decomposition characteristics of some Ni compounds of catalytic importance were studied by Banerjee and co-workers.[37] $Ni(C_2O_4).2H_2O$ lost lattice H_2O at 210° in a single step. It decomposed in air at 310° forming finely divided Ni particles which then oxidised to give NiO as the end product. Formation of Ni particles in N_2 atmosphere was confirmed by kinetic measurements. The observed magnetic moments at 25° for Ni ions in the compounds studied by them confirmed the proposed formula of the precipitates.

The mechanism of the decomposition reaction of $Fe_{1-x}Ni_xC_2O_4.2H_2O$(I) ($x = 0 - 1.0$), forming powdered Fe-Ni alloys at 300-380° by heating at 200°/hr in a H_2 current was studied by DTA[38]. For $x < 0.10$ and $x > 0.15$, the bcc α-phase, and the α + fcc γ phases were produced; respectively. DTA of I at

280-380° gives 2 peaks for $x < 0.25$ and 1 peak for $x > 0.25$. The peaks correspond to the evolution of CO, CH_4, CO_2, C_2H_6 and H_2O and to the formation of Fe_3C(or Fe_5C_2) during the decomposition of I and the rapid hydrogenolysis of the carbide forming CH_4. The mechanism is confirmed by decomposition reduction of I ($x = 0.1$) at 330° and I ($x = 0.3$) at 340° in a H_2 current.

Thermal decomposition of Co oxalate dihydrate studied by Khundkar and co-workers[39] in air and in vacuum, the study includes TG under a dynamic N_2 atmosphere which leads to the formation of CoC_2O_4 by thermal dehydration in N_2 and air. The end products of decomposition in N_2 and vacuum are metallic Co and that in air CoO. Possible dehydration and decomposition mechanisms of $CoC_2O_4.2H_2O$ are suggested.

Thermolysis of cobalt oxalate dihydrate studied by Parinet and co-workers,[40] reveal that $CoC_2O_4;2H_2O$ dehydrates in vacuum at 125° in air or Ar at 152°. Decomposition begins at 300° in vacuum at 305° in Ar, and at 210° in air. Under continuous pumping CoC_2O_4 decomposed endothermically (ΔH = 29.6 K.cal/mole) to CoO, CO and CO_2. If the reaction products are allowed to accumulate some CoO is reduced to Co by CO. In air all the Co and CoO are oxidised to Co_3O_4 to make the decomposition exothermic (ΔH = - 52.2 K.cal/mole).

Thermal decomposition of Co oxalate was studied by Taskinen and co-workers.[41] The kinetics and mechanism of the reaction were also studied, including the morphological effects and particle size. TG was used as an experimental method. The thermal decomposition mechanism of CoC_2O_4 is determined by the prior history of the powders. One type of powder had small amounts of α-phase and the other was a well developed α - β mixtures.

The influence of the environment on the thermal decomposition of oxysalts was studied by Dollimore, D.[42] He reported that the environment can influence the thermal decomposition of an oxysalt by causing a change in the course of chemical decomposition or by causing an alteration in the physical nature of the solid product or solid intermediates. The environment can also affect the equilibrium condition of the course of the kinetics. The use of special techniques such as TG, DTA or DSC to study the decomposition means that a special environment is imposed on the oxysalt and this affects the thermal decomposition process.

Further he reported that the influence of the environment in changing the course of a chemical reaction can be illustrated by reference to the decomposition of ZnC_2O_4 and NiC_2O_4. The decompositions are endothermic in inert atmosphere but exothermic in air or O_2. Although the product of decomposition of ZnC_2O_4 is ZnO, the change in character of the decomposition from endothermic to exothermic is due to the catalytic oxidation of CO to CO_2 in the presence of O_2. The similar change in the character of NiC_2O_4 decomposition is however due to Ni formation in an inert atmosphere, and NiO in air or O_2. The alteration in the physical nature of the solid products is illustrated by surface area measurements on solid residue from the decomposition of carbonates or oxalates.

Mechanism of thermal decomposition of Ba, Sr and Mg oxalates was studied by Derouane and co-workers.[43] They used combination of techniques, including thermal analysis, mass spectrometry of the effluent gases and ESR of the adsorbed residues. TG data and mass spectrometry data indicate that Ba, and Sr oxalates decomposed in the same manner while the decomposition of Mg oxalate followed a different reaction path. Two different and adsorbed paramagnetic CO species are identified by ESR as well as, in the case of MgC_2O_4, CO_2^{-2} adsorbed species. It is concluded that MgC_2O_4 decomposed in straight forward manner into CO, CO_2 and MgO. While for the Ba and Sr oxalates dissutation of CO can occur, leading to coking of the solid surface which then shows acidic properties.

Thermal decomposition of oxalic acid salts was studied by Honma and co-workers.[44] They reported that anhydrous MgC_2O_4(I) and MnC_2O_4(II) thermally decomposed at high temperature and proceeded by two step reactions, i.e., carbonates(III) are formed as intermediates and then the end products. At normal pressure, the decomposition temperatures for I, II and III are so close that the decomposition seems to proceed a single step reaction. The thermal decomposition of ZnC_2O_4 was also studied.

Brown and co-workers[45] studied thermochemical investigation of the decomposition of Mn(II) oxalate dihydrate. They used DSC technique for this purpose. They reported that the enthalpy of dehydration, ie 65 ± 3 KJ/mol water. The value calculated from the literature standard enthalpies is 31 KJ/mole water; the discrepancy is due to the uncertainty in the value of (ΔH^o). The enthalpy of the exothermic creation in O_2 is 300 KJ/mol water. This does not agree with the estimated value assuming Mn_2O_3 to be final product. The decomposition is in 3 stages. The respective enthalpy values are calculated.

Nissen, D.A.[46] studied the thermal decomposition of plutonium(IV) oxalate hexahydrate, $Pu(C_2O_4)_2.6H_2O$, in both Ar and O_2 using a combination of TG and Ir spectroscopy. Decomposition in an inert Ar atmosphere involves reduction of the cation to the trivalent state and its subsequent reoxidation to form PuO_2. In an oxidizing atmosphere; with unrestricted access of O, reduction of the cation does not take place and decomposition of PuO_2 is through the oxycarbonate. The reduction of Pu (IV) appears to take place by a CO-catalyzed mechanism and the presence of C in the PuO_2 decomposition product is attributed to the disproportionation of CO.

Thermal decomposition of praseodymium oxalate have been reported by Saito, Yasutoshi, Sasaki and Seihiro.[47] $Pr_2(C_2O_4)_3 \cdot 10\,H_2O$ was studied in atmospheres of He + O_2, He and CO_2 by a multiple technique of simultaneous TG and DTA coupled with evolved gas analysis. The decomposition occurs as

$$Pr_2(C_2O_4)_3 \cdot 10\,H_2O \longrightarrow Pr_2(C_2O_4)_3 \longrightarrow Pr_2O(CO_3)_2 \longrightarrow Pr_2O_2CO_3 \longrightarrow Pr\cdot\text{Oxide}$$

In the atmosphere of (4:1) He + O_2 mixture $Pr_2(C_2O_4)_3 \cdot 10H_2O$ yields Pr_7O_{12} and Pr_2O_3 in He and in CO_2 as end products.

In CO_2 atmosphere the decomposition of anhydrous oxalate took place at higher temperature than in any other atmospheres due to the stabilization of intermediate carbonates. In He and CO_2 atmosphere all the DTA peaks were endothermic, whereas exothermic peaks were also detected in He + O_2 due to oxidation of CO and deposited carbon and the disproportionation of CO. In inert atmosphere finely divided carbon particles were markedly deposited, and then reacted with CO_2 which was evolved during the decomposition of $Pr_2O_2CO_3$.

Instead of the disproportionation of CO, the direct formation of C and CO_2 from $Pr_2O(CO_3)_2$ is proposed as a possible mechanism for the deposition of C particles.

Dollimore <u>et al.</u>,[48] studied the thermal decomposition of manganese(II) oxalates in a Nitrogen medium. They reported comparative studies of the kinetics of the isothermal and non-isothermal dehydration and decomposition of $Mn(C_2O_4).2H_2O$ in an atmosphere of N_2. There is agreement between the values of energy of activation for the isothermal and the nonisothermal dehydration at high heating rates. At low heating rate, value of activation energy is comparable with the enthalpy of dehydration. The energy of activation of isothermal decomposition is 143 KJ/mole whereas 242 KJ/mole for nonisothermal decomposition. This difference is attributed to the condition of anhydrous salt used in both cases.

Ageev Yu and co-workers[49] studied thermal decomposition kinetics of $Y_2(C_2O_4)_3$ in CO and CO_3 atmospheres by chromatographic and TG analysis. The reaction proceeds in two stages. In the first stage CO_2 slows the reaction and increases the duration of the decomposition. The activation energies for the two stages are 18.2 and -33.3 KJ/mole respectively.

Shkarin, A.V. and co-workers[50] studied the kinetics of thermal decomposition of vanadyl oxalate dihydrate under non isothermal conditions. The decomposition of vanadyl oxalate dihydrate in vacuum starts by dehydration at 40 - 250°. The activation energy is 25.2 KJ/mole and preexponential factor 10^{-26} min^{-1}. The decomposition in vacuum or inert gases gives V_2O_4 as the end product.

Kropanev A. Yu and co-workers[51] studied the thermal decomposition of Samarium and cobalt oxalates. They established the conditions for the precipitation of $Sm_2(C_2O_4)_3.10.3H_2O.Co_3O_4$ is formed during the thermolysis of oxalate of Co at 220-300°.

Wu. Jingxue[52] studied the chemical reaction for $SrC_2O_4.nH_2O, Eu_2(CO_3)_3.nH_2O$ and $CaC_2O_4.nH_2O$ by thermogravimetrically and by X-ray diffraction. The activation energy for the dehydration of $CaC_2O_4.nH_2O$ is 21.34 K.cal/mole and the order of reaction 1. The dehydration of $SrC_2O_4.nH_2O$ occurs at 200-250° and the activation energy is 22.05 K.cal/mole. Dehydrated oxalate decomposes to carbonate and oxide, respectively, at 500-550° and 950-1150°.

Reddy,V.B. and Mehrotra, P.N.[53] studied the thermal decomposition of $PbZrO(C_2O_4)_2.6H_2O$(I) by TG, DTG and DTA, chemical analysis and IR methods. The decomposition proceeds through four steps. The dehydration of lead zirconyl oxalate hexahydrate occurs in two steps at $\angle$ 260°, the third step involves the decomposition of oxalate at 260-416° to give an intermediate carbonate and the last step is the decomposition of carbonate to a mixed oxide. $PbZrO_3$, at 415-575°. The end product was characterized by IR and X-ray diffraction studies.

Thermal decomposition of zinc zirconyl oxalate pentahydrate was studied by Reddy, V.B. and co-workers[54] using TG, DTA and DTG techniques and chemical analysis. The first dehydration step of pentahydrate was occurred at 303-474°K. This was followed by decomposition of $ZnSrO(C_2O_4)_2$ at 473-613°K to give $ZnSrO_4.(C_2O_4)CO_3$ as an intermediate residue. The third state is decomposition of this compound at 613-833°K to give $ZnSrO_3$. The mechanism was confirmed by IR and X-ray analysis.

Alloun, Azeddine; Nair, C.G.R.[55] studied the thermal decomposition of nickel(II) oxalate dihydrate in nitrogen atmosphere. They found two clean cut and non-overlapping stages as

1) dehydration:

$$NiC_2O_4.2H_2O \longrightarrow NiC_2O_4 + 2H_2O$$

and 2) decomposition:

$$NiC_2O_4 \longrightarrow NiO + CO + CO_2$$

The temperatures of initiation, completion and maximum rate of decomposition are recorded. Kinetic parameters as E_a and log A were computed by the Coats-Redfern method. The E_a ranges from 15-20 K.cal/mole for dehydration and from 50-70 K.cal/mole for decomposition. The log A varies from 5 to 8 for dehydration and from 18 to 25 for decomposition.

Fatemi, N.S., Dollimore, D., and Heal, G.R.[56] studied the thermal decomposition of $CdC_2O_4.3H_2O$. Under various conditions, DTA, TG and other complementary techniques are employed to identify the decomposition steps and the nature of the obtained residues when the sample is decomposed in air or in N. Certain usual aspects of the CdC_2O_4 decomposition are noticed. These are due to high reactivity of the metallic product, which is capable of being oxidized by CO_2 gas and the vaporization of product Cd at elevated temperatures. The full Ni adsorption isotherms on the various heat treated samples, are also reported and provides additional information concerning the relevant textural changes which occur in the decomposition process.

IR, X-ray diffraction and thermal studies of cadmium zirconyl oxalate pentahydrate was carried out by Reddy, V.B., Mehrotra, P.N.[57]. The thermal decomposition product of $CdZrO(C_2O_4)_2.5H_2O$ is orthorhombic $CdZrO_3$ with a 8.673, b 14.700, and c 8.842 A^o. Dehydration of cadmium zirconyl oxalate pentahydrate was occurred at 20-190^o and $CdZrO(C_2O_4)_2$ decomposed to the $CdZrO_3$ at 190-550^o.

Gangadevi, T., Rao, M. Subba, Kutty, T.R., Narayanan[58] studied the thermal decomposition of barium zirconyl oxalate. They standardized the conditions for the preparation of stoichiometric $BaZrO(C_2O_4)_2.7H_2O$. The thermal decomposition of barium zirconyl oxalate was investigated by TG, DTG and DTA techniques and chem. and gas analysis. The decomposition proceeds through four steps and is not affected much by the surrounding gas atmosphere. Both dehydration and oxalate decomposition take place in two steps. The formation of a transient intermediate containing both oxalate and carbonate groups is inferred. The decomposition of oxalate groups results in a carbonate of composition $Ba_2Zr_2O_5Co_3$, which decomposes between 600 and 800° and yields $BaZrO_3$.

Reddy, V.B. and Mehrotra, P.N.[59] studied the thermal decomposition of calcium zerconyl oxalate. They prepared $CaZrO(C_2O_4)_2.5H\ O$ by treating aq. oxalic acid with aq. Zr oxychloride and $CaCl_2$ and characterized by chemical analysis, IR spectroscopy, X-ray crystallography and thermal analysis. Calcium zirconyl oxalate pentahydrate dehydrated in two steps at 30-100 and 100-260° and decomposed at 650-850° to give $CaZrO_3$. The activation and thermodynamic enthalpies of dehydration and oxalate decomposition were calculated to be 19.50 and 41.14 K.cal/mole, respectively.

The thermal decomposition of Ni-Pb oxalates was studied by Chavan, A.M. and Shelke, R.G.[60] using techniques such as TGA, DTA and the oxalates were examined by X-ray diffraction method. They have reported that the single peak in the DTA curves both for dehydration and decomposition supports the presence of homogeneous phase in the co-precipitated Ni-Pb oxalates. No linearity was observed for the relationship between the heat of reaction (ΔH) and percentage composition of lead for decomposition step. The value of ΔH for mixed oxalates is below the sum of individual components in the case of decomposition peaks with the exception of co-precipitated oxalates containing 10.02 per cent and 23.65 per cent lead. This indicates that the co-precipitated Ni-Pb oxalates are not physical mixtures but there is a close association of the two components suggesting a homogeneous phase (or mixed crystals).

The thermal decomposition of Ni-Cu oxalates was studied by Chavan, A.M. and Phatak, S.E.[61] They have reported that single peak in the DTA curves both for dehydration and decomposition supported the presence of homogeneous phase in the co-precipitated Ni-Cu oxalates. No linearity was observed for the relation between the heat of reaction (ΔH) and percentage composition of Cu for decomposition step. The values of ΔH for mixed oxalates were below the sum of individual components in the case of decomposition peaks, with the exception of co-precipitated Ni-Cu oxalates were not physical mixture but there was a close association of the two components suggesting homogeneous phase (or mixed catalysts).

The thermal behaviour of Cu-Zn oxalates was studied by Chavan, A.M. and Dalvi, B.D.[62] using techniques such as TG and DTA. The mixed oxalates and their decomposed products in air and nitrogen were also examined by X-ray diffraction, magnetic susceptibility and electrical conductivity.

The details of the preparative conditions and the effect of atmosphere on the thermal decomposition of nickel-cadmium oxalates of various compositions (ranging from 10 per cent Ni to 90 per cent Ni, that is, with 90 per cent Cd to 10 per cent Cd) are given in Chapter-II. The DTA of these compounds has been done and the data obtained is presented in Chapter-III, which provides additional information about their behaviour as a supplement to the results of thermogravimetric analysis. The X-ray diffraction data of the above mentioned oxalates and the oxides prepared from those oxalates is presented in Chapter-IV.

The results have been compared with those reported for individual (nickel and cadmium) oxalates and mixed oxalates of divalent metals studied by various methods.

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