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Evaluation of thermo dynamical parameters of synthesized triheteropolymolybdate containing Zn^{2+} and Cu^{2+} cations

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ABSTRACT

The triheteropolyoxomolybdate containing Zn^{2+} and Cu^{2+} cations was synthesised in the dilute acid medium adjusting pH of the solution 4.5 at reflux temperature. The thermal stability analysis of the product was performed and it was observed that the complex involve one step decomposition according to TGA graph producing about 9.01% weight loss which was also duly supported by DTA graph indicating one large exothermic peak maxima a 334.06^0 C. The thermo dynamical parameters evaluation of thermal decomposition reaction of complex suggests the transaction at high temperature indicating the phase transition with a change in entropy of the system. This type of phase transition at high temperature is attributed as discontinuous change accompanied by the release of heat energy. The product recovered was light bluish-green in appearance. The magnetic moment value at room temperature indicate the six co-ordinate distorted octahedral around Cu (II) environmental in the weak field. The IR spectrum of the isolated product indicates the presence of NH_4^+, Mo=O, Mo-O-Mo, Hydrogen bonded H_2O group, Zn-O and Cu-O. On the basis of analytical, I.R. spectral, thermal stability and thermo dynamical parameters determination the composition of the product is assigned as $(NH_4)_2[ZnCuMo_5O_{18}]_2.14H_2O$.

KEYWORDS

Triheteropolymolybdate (THPM) preparation;
I.R.Studies;
Thermal analysis and thermo dynamical parameter evaluation.

INTRODUCTION

The thermo dynamical parameters studies of any condensed matter is related to the phase transition of that product since the driving parameter is temperature which usually suggest the phase transition of the matter involves a change of entropy of the system. In this research paper we have given the emphasis on the evaluation of thermodynamic parameters such as activation energy evaluation, the entropy change as well as free energy change determination for the temperature involving exothermic heat changes (heat energy released) as per the DTA graph of the product. The TGA graph is also taken into consideration for the loss of weight by the product. The earlier reports also established the fact that the thermo dynamical stabilities of the compound depend on the value of thermo dynamical state function as if change in entropy is maximum at particular temperature in the case of formation or decomposition may attain the stable equilibrium state. However if the other state function like enthalpy change and free energy change of the same system have minimum values then

only stable equilibrium state[1,2] may be achieved. The purpose of synthesis of triheteropolymolybdate containing two hetero cations Zn^{2+} and Cu^{2+} is to increase the surface area of the isopolymolybdate anion and also to increase micro porosity[3,4] of surface area which ultimately increase the thermal stability[5] of the prepared oxometalate cluster. The weak acidic medium for the preparation of triheteroplymolybdate complex is necessary since the alkaline medium as well as strong acidic medium produce decomposition of poly anions[6]. The thermal studies of synthesized product is also must as the product contain large number of water molecules as water of hydration which may occupy either position between the interstices or at peripheral region of the solid state product[7]. The important techniques for thermal studies of oxometalate complexes may be applied such as TGA, DTA etc[8]. The thermo dynamical parameters determination of the prepared product is based on Freemann Caroll method.

EXPERIMENTAL

The synthesis of oxometalate cluster is carried out in the weak acidic medium having pH value 4.5 with constituent compounds taken in the ratio 1:1:6:: zinc carbonate :copper carbonate : ammonium- molybdate. The elemental analysis and their estimation was performed according to the methods prescribed in the Voggel text book[9]. On the basis of elemental analysis and estimation results, the molecular composition of the synthesized product assigned as $(NH_4)_2[ZnCuMo_5O_{18}]2.14H_2O$ The product was named on the basis of IUPAC rule for nomenclature of heteropolyoxometalates[10] as Diammonium 5-molybdo-1-zincatocupratehydrate. It had been noticed that the ratios of the constituents taken for the purpose of synthesis is not retrained completely[11]. The pH of the solution 4.5 is also considered on the basis of pH studies of the constituent materials which indicate a constant pleatue at mentioned pH suggesting the interaction between the layer of isopolymolybdate anion and the two hetero cations Zn^{2+} and Cu^{2+} considered for the synthesis of triheteropolymolybdate complex compound[12].

RESULT AND DISCUSSION

I.R. spectral result

The I.R. spectrum of triheteropolymolybdate product with Zn^{2+} and Cu^{2+} hetero cations exhibit very strong band around 3155.54 to 2825 cm^{-1} may be attributed to strong hydrogen bounded H_2O and NH_4^+ cations. The prominent δ (NH_2) and β (NH_2) of NH_4^+ cation are appeared at 1649 and 1402 cm^{-1} respectively. The broad and weak bands of 954 cm^{-1} and 935 cm^{-1} are to NH_4^+ rocking band. The prominent and strong band observed at 810 cm^{-1} is assigned to Mo=O. The band at 738 cm^{-1} and 682 cm^{-1} are assigned to Mo-O-Mo. The medium I.R. band observed at 584.43 cm^{-1} and 532.35 cm^{-1} are attributed to γ (Cu-O) vibration. The band at 462.92 cm^{-1} is assigned to γ (Zn-O) vibration.

Thermal studies

The TGA and DTA curves of triheteropolymolybdate containing Zn^{2+} and Cu^{2+} hetero cations exhibit single step elimination and decomposition of the product. The measure weight loss of the product is accompanied by phase transfer as indicated in the DTA graph suggesting exothermic peak maxima at 334.06° temperature having area 5379.841 μvxsecond and peak height -27.882μv.

The following thermal decomposition reaction may be suggested on the basis of TGA Curve of the triheteromolybdate product.

$$(NH_4)_2[ZnCuMo_5O_{18}]2.14H_2O$$

50^0 C to 400^0 C
The weight loss
is 9.01%

$-3.14\ H_2O$
$-2NH_3$

The DTA curve for the sample indicate exothermic nature with peak maxima at 334.06^0 C having peak area 5379.84 μv x second with peak height -27.882

$$[ZnCuMo_5O_{17}]$$

$$\equiv ZnO \cdot CuO \cdot 5MoO_3$$

The residue product after 400^0C heating up to 600^0C involve no further weight loss. The composition of the residue product after 400^0C to 600^0C temperature may be attributed as $[ZnO \cdot CuO \cdot 5MoO_3]$ The small exothermic peak maxima is also observed at 545.71^0 C which may be attributed to minor phase

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transfer of the residue product to settle for the long higher temperature range.

Order of the decomposition reaction of the synthesised product

As per analysis of the TGA graph of the synthesized triheteropolymolybdate product's decomposition reaction, the following chart had been prepared:

TABLE 1

$\frac{\log dw/dt}{\log w_r}$	$\frac{\Delta 1/T}{\log w_r}$	$\frac{\log dw/dt}{\log w_r}$	$\frac{\Delta 1/T}{\log w_r}$
1.7117	6.934	1.5629	2.5997
1.7052	6.1818	1.5970	2.406
1.6322	5.4243	1.2783	2.1418
1.8008	3.3567	1.0234	1.752
1.6865	3.0924	0.8458	1.2533
1.7904	2.835	1.0665	1.1101

According to the chart of the Grap-4 had been drawn.

The graph of the decomposition reaction indicates the order of the reaction 1.1 which may be regarded as the first order decomposition reaction of the synthesised product.

The half decomposition temperature is 310°C (or 583k).

Thermo dynamical parameter determination

(a) Activation energy (Ea)

According to the Freeman Carroll method, the activation energy (Ea) of the decomposition reaction of synthesised product at 334.06° C exhibiting the exothermic peak maxima may be calculated on the basis of following expression:

$$\frac{\frac{-Ea}{2.303}\Delta(1/t)}{\Delta \log w_r} = -n + \frac{\Delta \log(dw/dt)}{\Delta \log w_r}$$

Or

$$\frac{\Delta \log(dw/dt)}{\Delta \log w_r} = (-Ea)/2.303R) - \frac{\Delta(1/T)}{\Delta \log w_r} + n$$

Where,

Ea = Activation energy of decomposition reaction
T = Temperature in Kelvin scale
R = Universal gas constant
n = order of reaction
$w_r = w_c - w$
w_c = weight loss at the completion of reaction at definite time
w = Total weight loss up to time t

For Temp 613k

$\Delta(1/T)x10^{-5} = 5.5$
T = 613k
R = 1.987 cal $deg^{-1}mol^{-1}$
n = 1.1 (from graph) as per freeman carroll method
$w = w_c - w$
$w = 1.8579x10^{-3}g$
$w = 1.8188x10^{-3}g$
$w_r = 0.0409x10^{-3}g$
$\log w_r = (-) 4.3882$

By putting the values in the final expression as per the Freeman Carroll method

Activation energy (Ea) = 0.9280x 4.184
= 3.882 J/mol

(b) Entropy change ΔS

$$\text{Intercept} = \frac{\log KR}{h\varphi Ea} + \frac{\Delta S}{2.303R}$$

Where,

K = Boltzmann constant = $1.3806x10^{-16}$ erg/deg/mole
= $5.6885x10^{-9}$ cal/mole
R = 1.987 cal/deg/mole
h = planks constant = $6.625x10^{-27}$ erg.sec

$$= \frac{6.625\times10^{-27}}{0.2427\times10^{-7}} = 27.279x10^{-20} \text{ cal}$$

Φ = 0.166
ΔS= change in entropy
Ea= Activation energy

By putting the value in equation, ΔS calculated as (-) 47.26x4.184 = 197.73 joule/mole

(c) Free energy changes (ΔG)

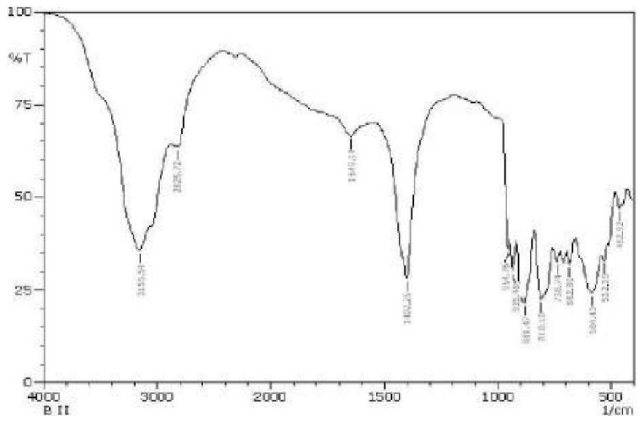
$(\Delta G) = \Delta H - T\Delta S$

Where,

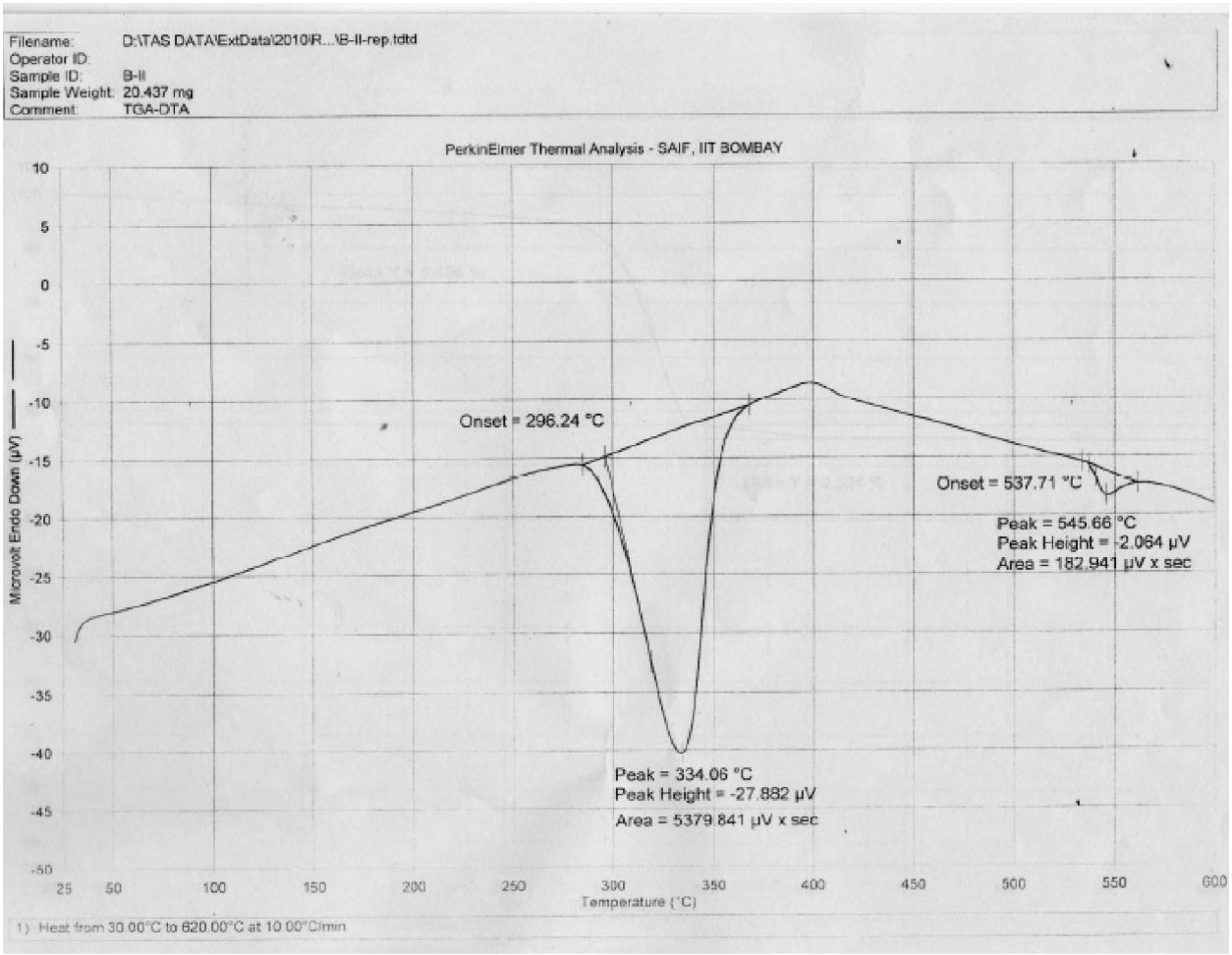
ΔH = Enthalpy change = Activation energy
T = Temp in Kelvin
ΔS = Entropy change
Hence (ΔG) = ΔH - TΔS
(ΔG) = 0.928 – 613x (-47.26)
Free energy changes (ΔG) = 28.695 k.cal/mole (120.05 KJ/mole)

CONCLUSION

The thermo gravimetric analysis of Diammonium 5-molybdo-1-zincatocupratehydrate based on weight change as a function of time and temperature which provide the basic information about the thermal stability of the synthesised product. The thermal decomposition of the triheteropolymolybdate complex starts from 50^0C temperature involving loss of water molecules present in different mode and complete at 400^0C temperature by further loosing ammonia molecule and water of constitution. The kinetic parameter evaluation by Freeman Carroll method suggest almost first order decomposition reaction; however, the isopoly molybdate complexes usually decompose completely at much lower temperature as compared to the complete dissociation temperature 400^0C of the synthesised triheteropoly molybdate complex ion containing Zn^{2+} and Cu^{2+} hetero cations. Thus the role of the association of two hetero cations with isopoly molybdate anion may be attributed as to increase the thermal stability of the prepared triheteropolymolybdate complex compound. The ionic nature of ammonium ion (NH_4^+) in the complex is established by fact that when aqueous solution of NaOH was allowed to react with the synthesised product on heating the ammonia gas was evolved.



Graph 1 : IR of polymolybdate



Graph 2 : DTA of polymolybdate

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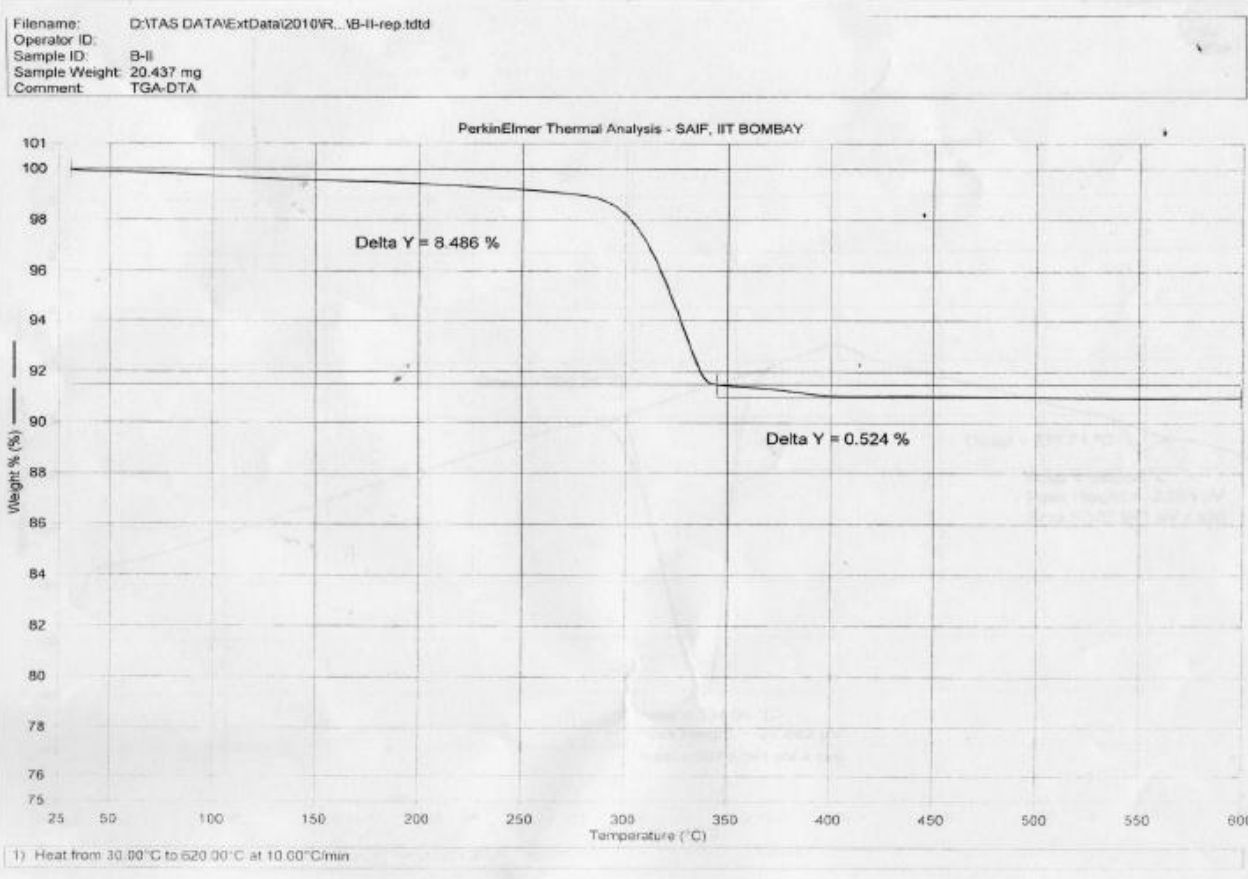
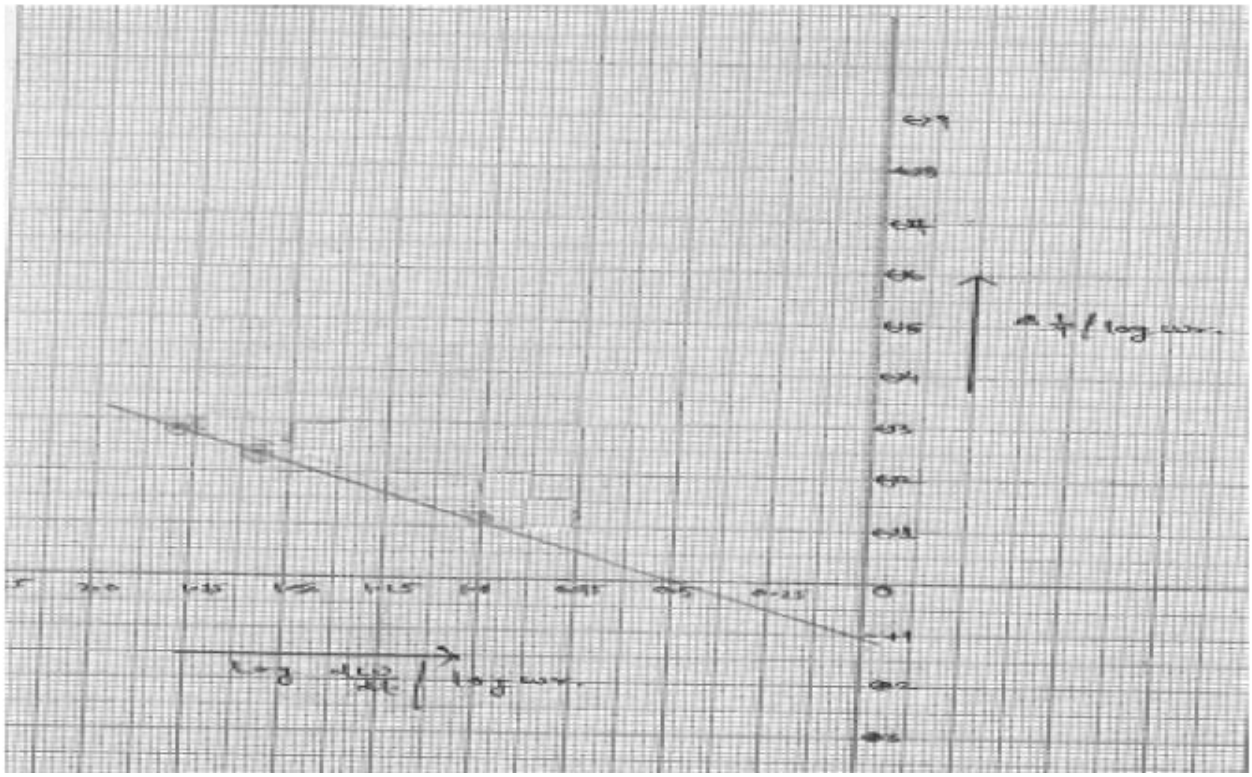


Graph 3 : TGA of polymolybdate



Graph 4 : Graph of the decomposition reaction

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