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## Kinetics and mechanism of thermal decomposition of binary mixture of barium oxalate and copper oxalate in the (1:2) mole ratio

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### ABSTRACT

The non- isothermal decomposition study of individual  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  by TGA technique shows three steps with  $\text{BaCO}_3$  and  $\text{BaO}$  as final product when heated to  $1000^\circ\text{C}$  with three dimensional diffusion ( $D_4$ ) and two dimensional phase boundary reaction ( $R_2\alpha$ ) mechanism. The energy of activation ( $E_a$ ) of non- isothermal method is 36.80 KJ/mole and isothermal method is 34.09 KJ/mole. The  $\text{CuC}_2\text{O}_4$  shows two step decomposition with  $\text{CuO}$  as end product when heated to  $320^\circ\text{C}$  by random nucleation (Avrami equation) mechanism. The  $E_a$  for non- isothermal and isothermal method is 140.46 KJ/mole and 172.40 KJ/mole respectively. The non- isothermal study of the binary mechanical mixture of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  in mole ratio (1:2) by TGA and EGA when heated up to  $1000^\circ\text{C}$  shows mixture of  $\text{BaO}$  and  $\text{CuO}$ . The  $\alpha$  Vs time plots of isothermal study of mixture shows two dimensional diffusion ( $D_2$ ) and three dimensional diffusion (Ginling Braunshtein equation) ( $D_4$ ) mechanism. The applicability of Ginling Braunshtein equation to the kinetic data is up to  $0.60 < \alpha < 0.99$ . The  $E_a$  of this binary mixture in mole ratio (1:2) by non- isothermal method 36.56 KJ/mole and isothermal method is 31.41 KJ/mole. The end products were characterized using X-ray diffraction technique. The kinetic parameters like energy of activation ( $E_a$ ), pre-exponential factor ( $A$ ) and Correlation factor ( $r$ ) were obtained from isothermal TGA and EGA.

**Keywords:**  $\text{CuC}_2\text{O}_4$ ,  $\text{BaC}_2\text{O}_4$ , TGA, EGA, Kinetics, Oxalates.

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## INTRODUCTION

Thermal decomposition study of metal oxalates is useful for preparation of mixed metal oxides possessing pores, lattice imperfections and therefore they acts as reactive solids [1]. The mixed metal oxides may result in the modification of their thermal behavior, geometry and electronic properties which lead to changes in their catalytic functions [2]. It is found that many workers studied thermal decomposition of mixed metal oxalates preparing them by different techniques [3]. The objective of this work is to investigate the mechanism by which metal oxalate shows thermal decomposition. So far, nobody found to have reported on the thermal behavior of mechanical mixtures of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  in (1:2) mole ratio. In last few years some workers have studied the binary mixtures of oxalates by thermal decomposition to find out the kinetics and mechanism [4-5], but we have chosen quite new method to study the binary mixture by mechanically mixing two oxalates by definite proportion as 1:1, 1:2, 2:1, 1:3 etc [6]. Generally, the kinetics of solid state thermal decomposition can be followed either by isothermal and non-isothermal methods [7]. The decomposition in oxalates may be with the heterolytic dissociation of C-C bond forming  $\text{CO}_2$  and  $\text{CO}_2^{2-}$ , if it involves the cleavage of the C-C bond then the products are CO and  $\text{CO}_2$ . In many cases the C-C bond cleavage is the rate determining step. If cleavage is heterolytic then it produces  $\text{CO}_2$  and  $\text{CO}_2^{2-}$  and if homolytic then it produces two  $\text{CO}_2^-$  anions [8-11]. Thermo-gram obtained from TGA; provide the information about the sample composition, thermal stability as well as the kinetic data relating the chemical changes occur on heating [12]. The kinetic parameters of non-isothermal method of TGA and EGA are close to those obtained for isothermal decomposition in the air atmosphere. EGA is known as one of thermal analysis method for measuring the amount of generated gases from a sample as a function of temperature [13]. The kinetic analysis data was performed by using computer for calculation of energy of activation and mechanism. The end product of thermal decomposition of oxalate mixture was characterized by using X-ray diffraction techniques [14].

## EXPERIMENTAL

### Material

Pure Barium (II) oxalate and Copper (II) oxalate were used of BDH A. R. quality.

### Apparatus:-

The EGA technique in which furnace is made up of indigenous material with quartz tube closed from one side with chromel-alumel as thermocouple. Pyrometer (Tempo Industrial corp., BPL-INDIA) with range  $0\text{ }^\circ\text{C}$  to  $1200\text{ }^\circ\text{C}$  ( $\pm 1\text{ }^\circ\text{C}$ ) and the temperature regulator (Argo transformers Co.Ltd., India) of 15 amp capacity is used. In the non-isothermal studies the temperature was raised up to  $1000\text{ }^\circ\text{C}$  at heating rates of  $\pm 4\text{ }^\circ\text{C}/\text{min}$ . TGA is set up by using thermobalance K-14 super (K.Roy and Co., India) of 100 g capacity with an accuracy of  $\pm 0.1\text{ mg}$ . The furnace used for TGA is prepared by using indigenous material. The DTA technique Detector DTG-60H where atmosphere is air with flow rate 50 ml/min.

X-ray powder diffraction analysis of the solid decomposition products was carried out using a Bruker AXS D8 Advance X-ray diffractometer. For the identification purpose, the relative intensities ( $I/I_0$ ) and the d-spacing ( $\text{\AA}$ ) were compared with standard diffraction patterns of the ASTM powder diffraction files [15].

**Data analysis:**

The activation parameters were then calculated by using the Coats-Redfern equation written in the form:

$$\log_{10}\{1-(1-\alpha)^{1-n}/T^2(1-n)\} = \log_{10}AR/aE[1-2RT/E] - E/2.303RT \quad (1)$$

Where  $\alpha$  = the fraction of the sample decomposed at time t

n = order of reaction

T = temperature ( $^{\circ}\text{K}$ )

A = pre-exponential factor

R = gas constant

E = activation energy

a = conversion factor to transfer from a time scale to a temperature scale,

i.e. a = dT / dt

In Coats-Redfern equation  $\log_{10}AR/aE [1-2RT / E]$  remains constant over temperature range of the decomposition, then plot

$\log_{10}\{1- (1-\alpha)^{1-n} / T^2 (1-n)\}$  against  $1 / T$

It results straight line and slope give the value of  $-E / 2.303 R$  [16].

For isothermal conditions, the rate expression can be written as

$$G(\alpha) = kt \quad (\text{integral form}) \quad (2)$$

$\alpha$  = the fraction of the sample decomposed at time 't'.

For a given isothermal run at  $T_i$ , the constant k ( $T_i$ ) can be calculated from the TGA and EGA Curve using the integral method. TGA and EGA experiments for isothermal analysis are performed at five isothermal temperatures. There is a certain k ( $T_i$ ) and certain f ( $\alpha$ ) or G ( $\alpha$ ) for each  $T_i$ . If f ( $\alpha$ ) or G ( $\alpha$ ) are all the same for each  $T_i$ , then

$$\ln [G(\alpha) / 1.921503T] = \ln (AE / BR) + 3.7720501 - 1.921503 \ln E - E / RT \quad (3)$$

Where

E = slope x R

And

$$A = \exp (\text{intercept} - 3.772051 + 1.9215031 \ln E) \times BR / E \quad (4)$$

Where E = activation energy, B = heating rate, A = frequency factor, and  $\alpha$  = fraction of the sample decomposed at time 't' [17].

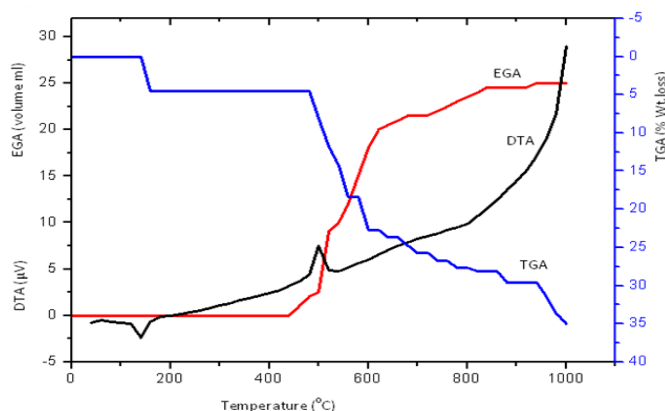
A computer program has been written for the calculation of kinetic data by using Coats-Redfern equation, in which data can be cycled for any value of n (order of reaction) until the best fit is obtained (by least mean squares) . The kinetic data are also analyzed by two dimensional diffusion equation and by three dimensional phase boundary reaction (Table 1). Plots for typical experiments are shown for non-isothermal TGA, EGA and DTA of  $BaC_2O_4 \cdot 0.6H_2O$ ,  $CuC_2O_4$ , and binary mechanical mixture of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  in mole ratio (1:2) in **Figure1**, **Figure2** and **Figure3**.

**Table1: Activation parameters of the non-isothermal and isothermal decomposition in air of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  by TGA and EGA method.**

Method of analysis	Ea (activation energy) in KJ/mole.	A,(frequency factor)	r, (correlation coefficient)	n, Order of reaction
Non-isothermal TGA.	36.80	$1.08 \times 10^2$	0.9999	1
Isothermal TGA by three dimensional diffusion (Jander equation) of Barium (II) oxalate	34.09	$1.54 \times 10^3$	0.9996	1
Isothermal TGA by two dimensional phase boundary reaction of Barium (II) oxalate	48.85	$3.87 \times 10^3$	0.9999	1
Non-isothermal EGA of Barium (II) oxalate	39.21	$2.98 \times 10^7$	0.9995	1.05
Isothermal EGA by three dimensional diffusion (Ginling Braunshtein equation) of Barium (II) oxalate	34.24	$1.49 \times 10^3$	0.9998	1.05
Isothermal EGA by random nucleation (Avrami equation) of Barium (II) oxalate	20.00	$2.36 \times 10^3$	0.999	1.05
Non-isothermal TGA of Copper (II) oxalate	140.46	$1.95 \times 10^6$	0.9948	1.35
Isothermal TGA by random nucleation (Avrami equation) of Copper (II) oxalate	172.40	$1.95 \times 10^6$	0.9999	1.35
Non-isothermal EGA of Copper (II) oxalate	158.82	$1.56 \times 10^3$	0.9994	0.35
Isothermal EGA by random nucleation (Erofeev equation) of Copper (II) oxalate	144.31	$3.51 \times 10^8$	0.9999	0.35

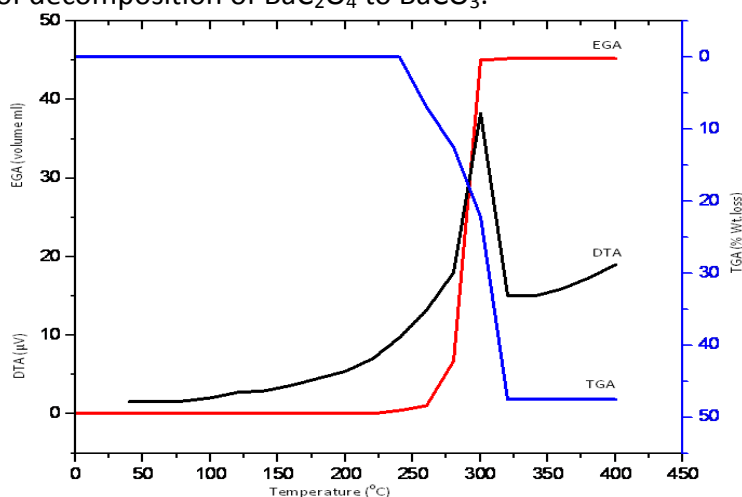
## RESULT AND DISCUSSION

### DTA-TG, EGA



**Fig1:** DTA-TGA-EGA curves of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  in air at heating rate of  $4^\circ\text{C min}^{-1}$ .

The TGA, EGA and DTA of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  are shown in **Figure 1**. The  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  is decomposed within three steps (Fig2). The first step is observed at  $160^\circ\text{C}$  to  $180^\circ\text{C}$  and is accompanied by 4.54% mass loss [18]. This is attributed to the 0.6 water molecule (calculated mass loss 4.57%). The second step shows decomposition to  $\text{BaCO}_3$  at  $450^\circ\text{C}$  to  $560^\circ\text{C}$  accompanied by 12.59% mass loss while calculated mass loss is 12.42% [19]. The third step shows decomposition of  $\text{BaCO}_3$  to 80%  $\text{BaO}$  in the temperature range  $600^\circ\text{C}$  to  $1000^\circ\text{C}$  [20] accompanied by 17.83% mass loss while calculated mass loss is 17.83%. The pure individual barium (II) oxalate shows complete decomposition at  $1385^\circ\text{C}$  [21] this is due to  $\text{CO}$  formed in the temperature range  $480^\circ\text{C} - 500^\circ\text{C}$  is again recombine to form  $\text{BaCO}_3$ , it may be due to small crystallite size of  $\text{BaCO}_3$  or due to formation of defects in the crystallite. EGA study shows the volume for decomposition of  $\text{BaC}_2\text{O}_4$  by calculation at N.T.P condition is 24.56 ml and observed volume at N.T.P is 25.00 ml, which results in decomposition of  $\text{BaC}_2\text{O}_4$  to  $\text{BaCO}_3$  up to  $1000^\circ\text{C}$ . The DTA shows 'Endo' peak at  $180^\circ\text{C}$  for water loss and sharp 'Exo' peak at  $500^\circ\text{C}$  indicating starting of decomposition of  $\text{BaC}_2\text{O}_4$  to  $\text{BaCO}_3$ .

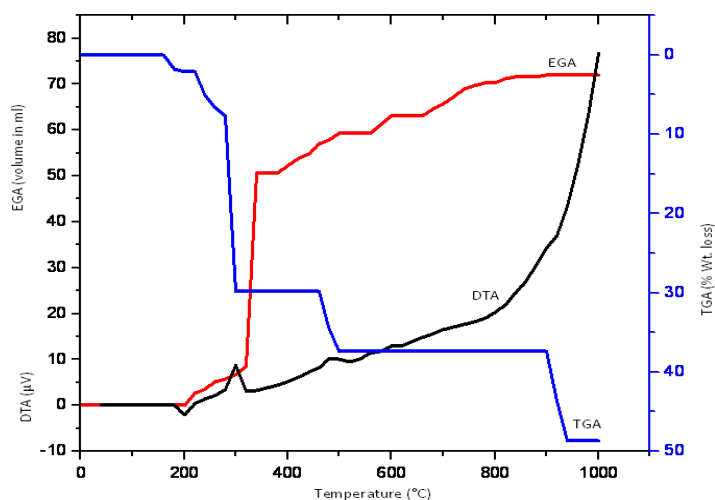


**Figure2: DTA-TGA-EGA curves of  $\text{Cu}_2\text{O}_4$  in air at heating rate of  $4\text{ }^\circ\text{C min}^{-1}$ .**

The TGA, EGA and DTA of  $\text{Cu}_2\text{O}_4$  are shown in **Figure 2**. The TGA shows single step decomposition in the temperature range  $260\text{ }^\circ\text{C}$  to  $320\text{ }^\circ\text{C}$  showing weight loss 47.50% against the calculated mass loss is 47.51% [22-23]. This mass loss corresponds to the complete conversion of  $\text{Cu}_2\text{O}_4$  to  $\text{CuO}$ . EGA shows the theoretical volume, for decomposition at N.T.P condition is 45.02 ml against the observed volume at N.T.P is 45.25 ml which results in decomposition of  $\text{Cu}_2\text{O}_4$  to  $\text{CuO}$  at  $320\text{ }^\circ\text{C}$ . The DTA shows sharp 'Exo' peak at  $300\text{ }^\circ\text{C}$  for decomposition of  $\text{Cu}_2\text{O}_4$ . The kinetic parameters evaluated by TGA using non-mechanistic equations are given in **Table 2**.

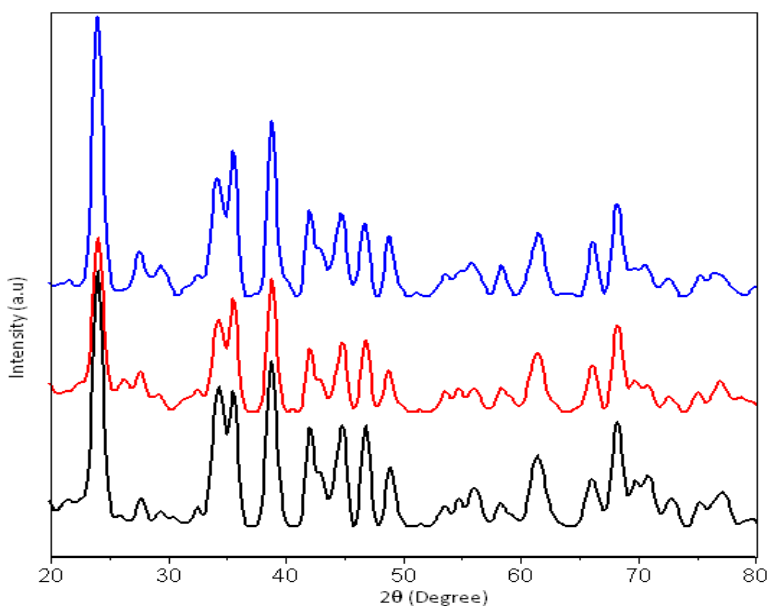
**Table2: Activation parameters of the isothermal and dynamic decomposition in air of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{Cu}_2\text{O}_4$  (1:2) mole ratio mixture by TGA and EGA method.**

Method of analysis	Ea (activation energy) in KJ/mole.	A, (frequency factor)	r, (correlation coefficient)	n, Order of reaction
Non-isothermal TGA	36.56	$4.071 \times 10^9$	0.9995	0.20
Isothermal TGA by two dimensional diffusion	28.29	$2.087 \times 10^3$	0.9993	0.20
Isothermal TGA by three dimensional diffusion (Ginling Braunshtein equation)	31.41	$1.305 \times 10^3$	0.9995	0.20
Non-isothermal EGA	23.72	$1.624 \times 10^9$	0.9983	0.20
Isothermal EGA by two dimensional diffusion	24.25	$1.927 \times 10^3$	0.9995	0.20
Isothermal EGA by three dimensional diffusion (Ginling Braunshtein equation)	28.26	$1.451 \times 10^3$	0.9999	0.20


**Fig 3: DTA-TGA-EGA curves of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{Cu}_2\text{O}_4$  in mole ratio (1:2) in air at heating rate of  $4\text{ }^\circ\text{C min}^{-1}$ .**

The TGA, EGA and DTA of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  in mole ratio (1:2) are shown in **Figure 3**. In the mixture of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  in mole ratio (1:2) shows four distinct steps for mass loss. The complete dehydration is observed in the temperature range  $180\text{ }^\circ\text{C}$  -  $200\text{ }^\circ\text{C}$  and is accompanied by 2.09% mass loss [24]. This is attributed to the 0.6 water molecules (calculated mass loss 2.04%). Anhydrous mixture is thermally unstable and shows distinct three consecutive mass loss steps. In the second step the decomposition of  $\text{CuC}_2\text{O}_4$  to  $\text{CuO}$  in the temperature range  $240\text{ }^\circ\text{C}$  to  $300\text{ }^\circ\text{C}$  is observed with mass loss 27.70% [25] and calculated mass loss is 27.81%. The third step is the decomposition of  $\text{BaC}_2\text{O}_4$  to  $\text{BaCO}_3$  in temperature range  $480\text{ }^\circ\text{C}$  to  $500\text{ }^\circ\text{C}$  [26] where observed mass loss is 7.55% and calculated mass loss is 7.49%. The X-ray study of end product of binary mixture of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  in mole ratio (1:2) taken at  $500\text{ }^\circ\text{C}$  support the formation of  $\text{BaCO}_3$  and  $\text{BaCu}_2\text{O}_3$ . This occurs at lower temperature than the decomposition of pure  $\text{BaC}_2\text{O}_4$ . The mixture shows 88% conversion of  $\text{BaCO}_3$  to  $\text{BaO}$  in temperature range  $900\text{ }^\circ\text{C}$  to  $920\text{ }^\circ\text{C}$  and is supported by X-ray taken at  $700\text{ }^\circ\text{C}$  and  $900\text{ }^\circ\text{C}$ . While pure  $\text{BaC}_2\text{O}_4$  shows the slow conversion of  $\text{BaCO}_3$  to  $\text{BaO}$  is reported in the temperature range  $600\text{ }^\circ\text{C}$  to  $1000\text{ }^\circ\text{C}$  [27], where 80%  $\text{BaO}$  formation takes place. Last step of mixture shows the 88% decomposition of  $\text{BaCO}_3$  to  $\text{BaO}$  in temperature range  $900\text{ }^\circ\text{C}$  to  $920\text{ }^\circ\text{C}$  where observed mass loss is 11.33% and calculated mass loss is 11.31% [28]. In pure  $\text{BaC}_2\text{O}_4$  the conversion of  $\text{BaCO}_3$  to  $\text{BaO}$  takes place at temperature greater than  $1000\text{ }^\circ\text{C}$  [29]. The decomposition of  $\text{BaCO}_3$  to  $\text{BaO}$  occurs at lower temperature where the  $\text{CuO}$  acts as catalyst. EGA study shows the volume for decomposition at N.T.P condition is 71.91 ml and observed volume at N.T.P is 72.00 ml, which results in decomposition of  $\text{BaC}_2\text{O}_4$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio mixture to  $\text{CuO}$  and  $\text{BaCO}_3$  at  $1000\text{ }^\circ\text{C}$  [30].

#### X-ray diffraction:-

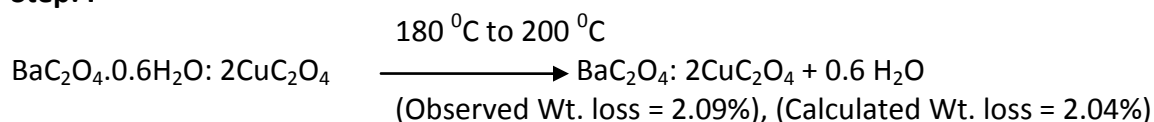


**Fig 4:** X-ray powder diffractograms of solid  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio mixture obtained at (a)  $500\text{ }^\circ\text{C}$ , (b)  $700\text{ }^\circ\text{C}$  and (c)  $900\text{ }^\circ\text{C}$ .

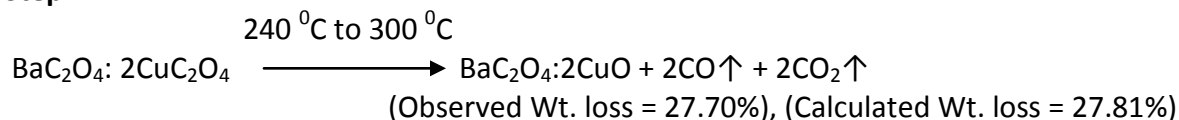
The XRD diffraction pattern of the initial mixture matched the standard data compiled in the JCPDS data. The sample of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  in mole ratio (1:2) is heated in an open air at  $500^\circ\text{C}$ ,  $700^\circ\text{C}$  and  $900^\circ\text{C}$  with a linear heating rate of  $4^\circ\text{C}/\text{min}$  and their XRD pattern is recorded in  $2\theta$  range of  $20\text{--}80^\circ$ . The XRD pattern of the sample at  $500^\circ\text{C}$  showed the formation of orthorhombic  $\text{BaCu}_2\text{O}_3$  (JCPDS no.391497) and orthorhombic  $\text{BaCO}_3$  (JCPDS no.410373) [31]. The XRD pattern of the sample at  $700^\circ\text{C}$  and  $900^\circ\text{C}$  showed the formation of orthorhombic  $\text{BaCu}_2\text{O}_3$  (JCPDS no.391497). The  $\text{BaCO}_3$  then further decomposed to  $\text{BaO}$  at  $1000^\circ\text{C}$ .

The decomposition reaction of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  in mole ratio (1:2) for TGA is shown below.

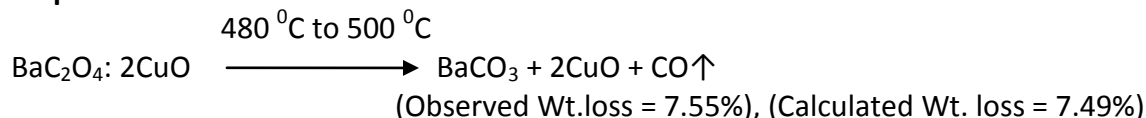
**Step I**



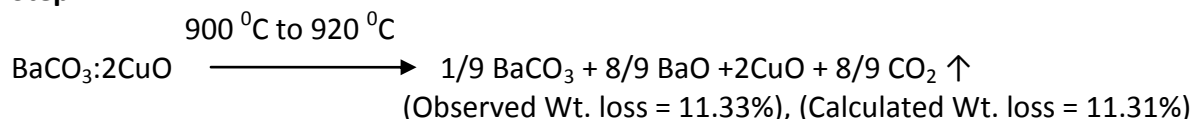
**Step II:**



**Step III:**



**Step IV:**



Seven different temperatures  $850^\circ\text{C}$ ,  $750^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $550^\circ\text{C}$ ,  $450^\circ\text{C}$ ,  $350^\circ\text{C}$  and  $250^\circ\text{C}$  were selected for conducting isothermal kinetic studies of TGA and  $750^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $550^\circ\text{C}$ ,  $450^\circ\text{C}$ ,  $350^\circ\text{C}$  for EGA techniques. TGA and EGA (**Figure.2 and 3**) shows the variation of degree of decomposition ( $\alpha$ ) of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio mixture to  $\text{CuO}$ ,  $\text{BaCO}_3$  and  $\text{BaO}$  with time at different isothermal conditions [32]. The data obtained from isothermal method using TGA and EGA techniques are plotted as degree of decomposition ( $\alpha$ ) as a function of time ( $t/t_{0.5}$ ) (**Figure.4 and 5**) [33]. These sigmoid shaped curves are characteristics of a mechanism by which the decomposition occurs at the interface between the product and un-decomposed reactant.



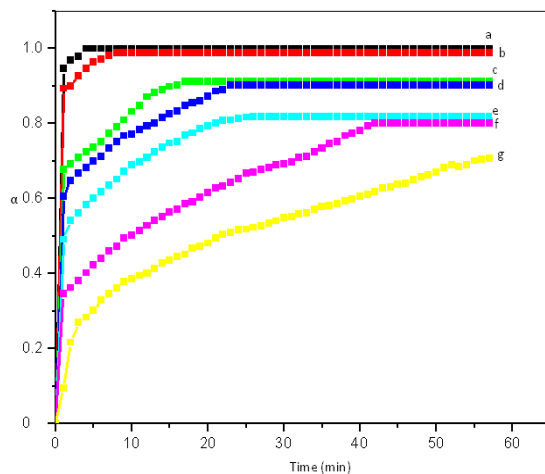


Fig 5: Isothermal decomposition curves (TGA) for  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio mixture at a) 850 °C, b) 750 °C, c) 650 °C, d) 550 °C, e) 450 °C, f) 350 °C and g) 250 °C.

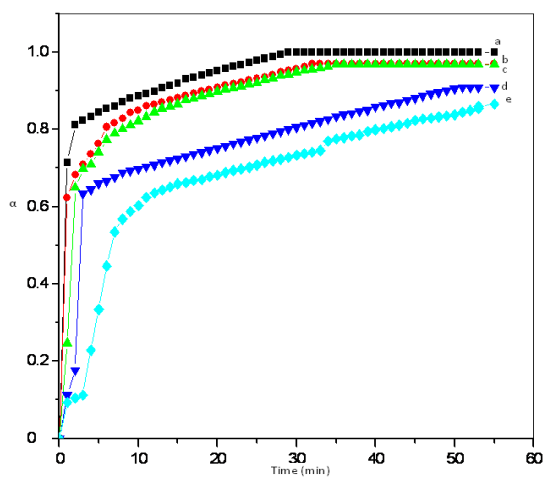


Fig 6: Isothermal decomposition curves (EGA) for  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio mixture at a) 750 °C, b) 650 °C c) 550 °C, d) 450 °C, and e) 350 °C.

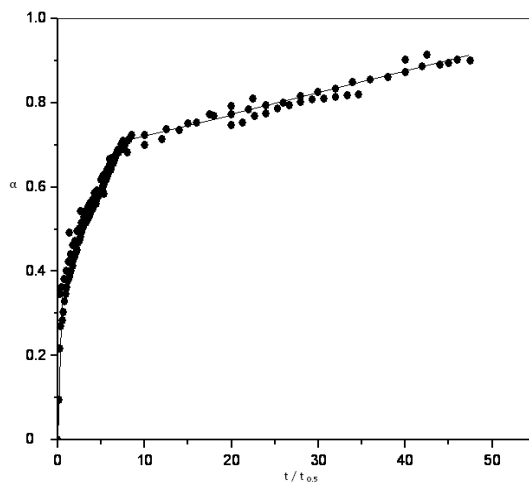


Fig 7:  $\alpha$  Vs.  $t / t_{0.5}$  plots of TGA for isothermal decomposition of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio.

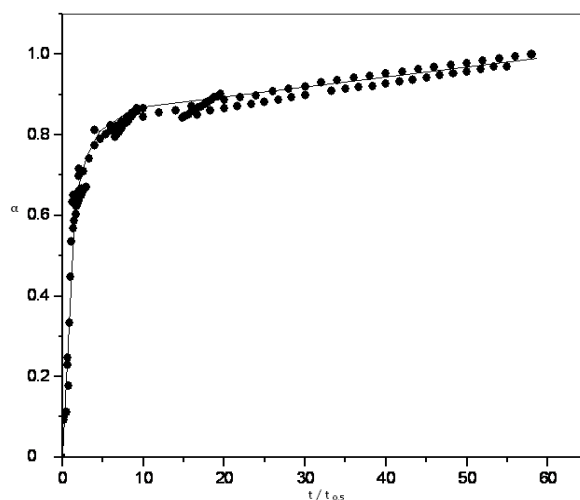


Fig 8:  $\alpha$  Vs.  $t / t_{0.5}$  plots of EGA for isothermal decomposition of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio.

The kinetic parameters evaluated by TGA using non-mechanistic equations are given in table2. The  $E_a$  of decomposition process using non-isothermal TGA and EGA method [34] is found to be 36.56 KJ/mole and 23.72 KJ/mole by plotting  $\ln k$  Vs.  $T^{-1} \cdot 10^3 / K^{-1}$  respectively (Fig.9 and 10) [35- 37]. The order (n) of decomposition reaction of binary mixture using TGA and EGA is 0.20 [38].

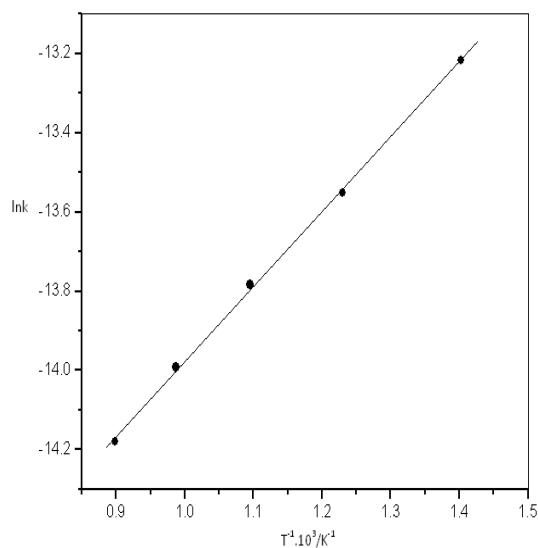


Fig 9: Arrhenius plot: of  $\ln k$  Vs.  $T^{-1} \cdot 10^3 / K^{-1}$  of dynamic TGA of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio.

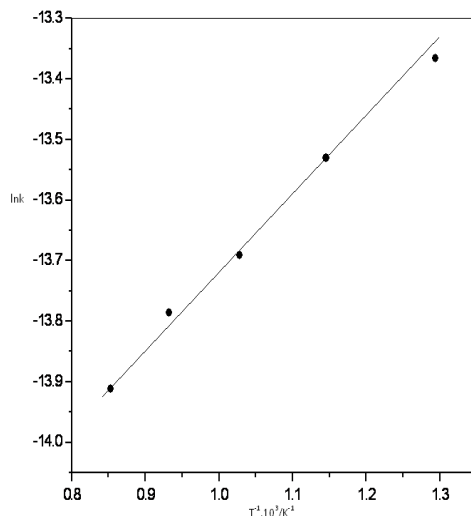


Fig 10: Arrhenius plot: of  $\ln k$  Vs.  $T^{-1} \cdot 10^3 / K^{-1}$  of dynamic EGA of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio.

Isothermal TGA method using two dimensional diffusion is 29.89 KJ/mole and three dimensional diffusion (Ginling Braunshtein equation) is 31.41 KJ/mole by plotting  $\log (1-\alpha) \ln (1-\alpha) + \alpha$  Vs  $T^{-1} \cdot 10^3 / K^{-1}$  and  $\log [1- 2\alpha / 3] - (1-\alpha)^{2/3}$  Vs.  $T^{-1} \cdot 10^3 / K^{-1}$  (fig.11 and 12) respectively. The EGA method using two dimensional diffusion is 24.54 KJ/mole and three dimensional diffusion (Ginling Braunshtein equation) is 28.26 KJ/mole by plotting  $\log (1-\alpha) \ln (1-\alpha) + \alpha$  Vs  $T^{-1} \cdot 10^3 / K^{-1}$  and  $\log [1- 2\alpha / 3] - (1-\alpha)^{2/3}$  Vs.  $T^{-1} \cdot 10^3 / K^{-1}$  (fig.13 and 14) respectively. In EGA technique the decomposition temperature is high due to closed system. The correlation coefficient (r) for TGA and EGA are in the range 0.9982 - 0.9999, indicating nearly perfect fits [39].

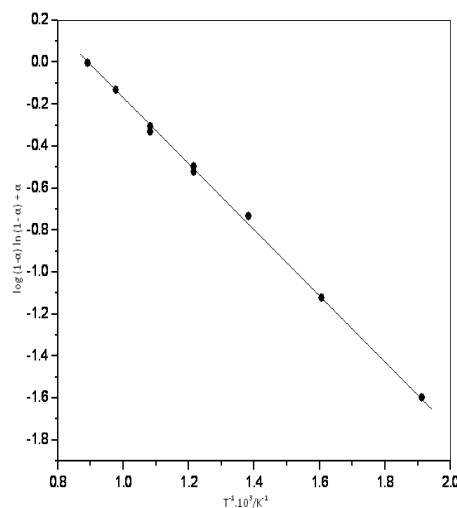


Fig 11: Arrhenius plot for TGA of  $\log (1-\alpha) \ln (1-\alpha) + \alpha$  Vs  $T^{-1} \cdot 10^3 / K^{-1}$  for decomposition of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio.

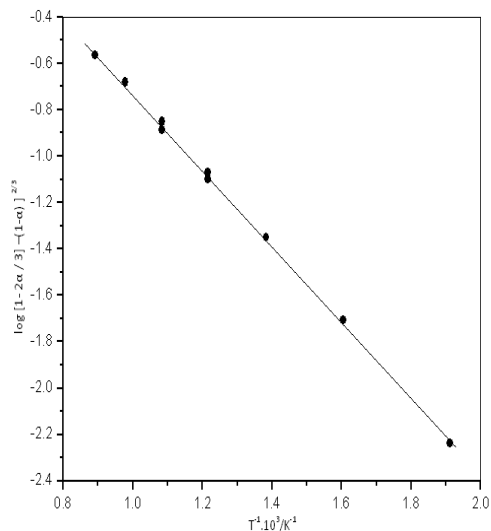


Fig 12: Arrhenius plot for TGA of  $\log [1 - 2\alpha / 3] - (1-\alpha)^{2/3}$  Vs  $T^{-1} \cdot 10^3 / K^{-1}$  for decomposition of  $BaC_2O_4 \cdot 0.6H_2O$  and  $Cu_2O_4$  (1:2) mole ratio.

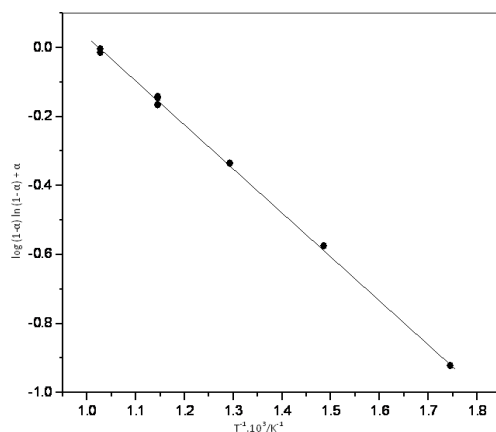
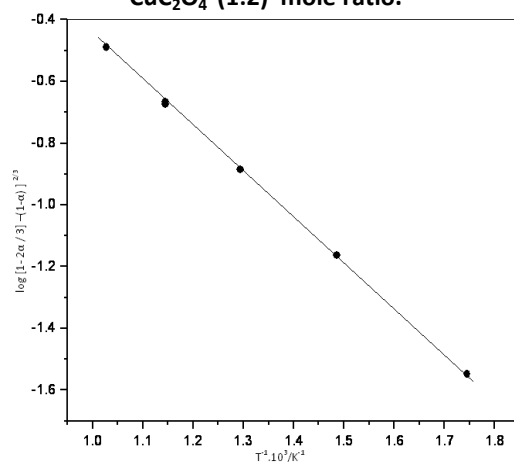
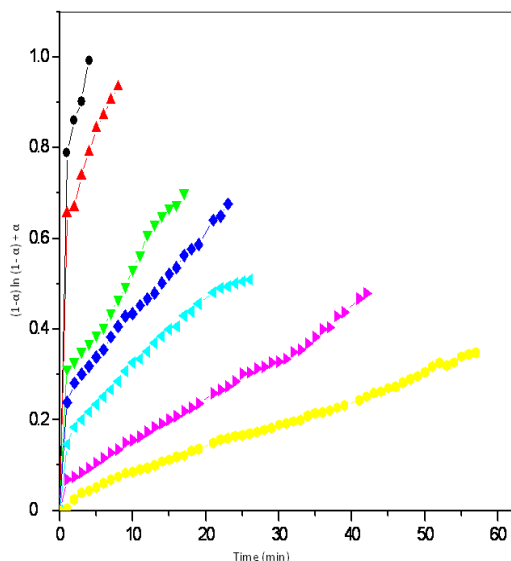


Fig 13: Arrhenius plot for EGA of  $\log (1-\alpha) \ln (1-\alpha) + \alpha$  Vs  $T^{-1} \cdot 10^3 / K^{-1}$  for decomposition of  $BaC_2O_4 \cdot 0.6H_2O$  and  $Cu_2O_4$  (1:2) mole ratio.

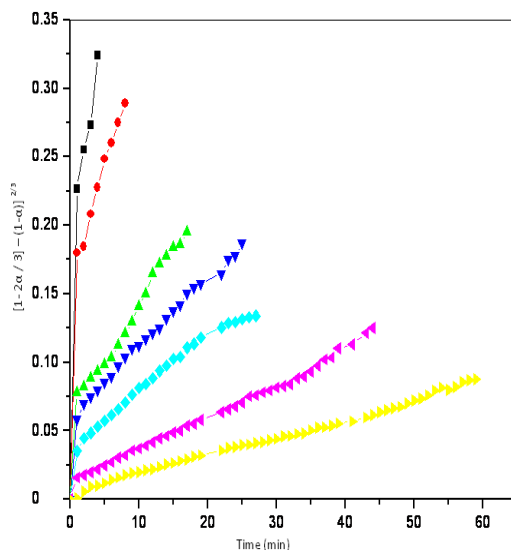


**Fig 14: Arrhenius plot for EGA of  $\log [1 - 2\alpha / 3] - (1-\alpha)^{2/3}$  Vs  $T^{-1} \cdot 10^3 / K^{-1}$  for decomposition of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio.**

The decomposition of binary mixture using TGA and EGA can be found out by plotting  $(1-\alpha) \ln (1-\alpha) + \alpha$  Vs. time (min) and  $[1 - 2\alpha / 3] - (1-\alpha)^{2/3}$  Vs. time (min) (Fig.15, 16, 17 and 18)) and obey two dimensional diffusion followed by three dimensional diffusion (Ginling Braunshtein equation) [40-42].



**Fig 15: (TGA) plot of  $(1-\alpha) \ln (1-\alpha) + \alpha$  Vs time (min) of decomposition of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio.**



**Fig 16: (TGA) plot of  $[1 - 2\alpha / 3] - (1-\alpha)^{2/3}$  Vs time (min) of decomposition of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio.**

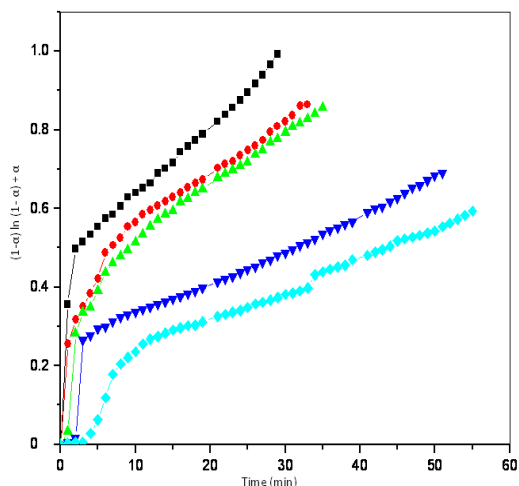


Fig 17: (EGA) plot of  $(1-\alpha) \ln (1-\alpha) + \alpha$  Vs time (min) of decomposition of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio.

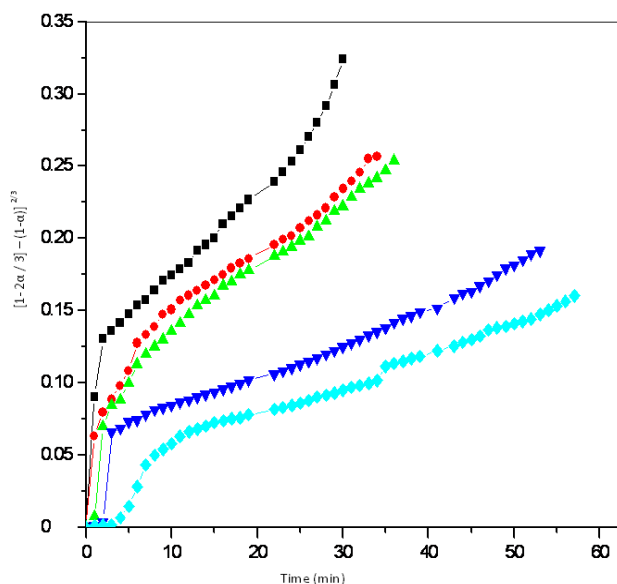


Fig 18: (EGA) plot of  $[1 - 2\alpha / 3] - (1-\alpha)^{2/3}$  Vs time (of decomposition of  $BaC_2O_4 \cdot 0.6H_2O$   $CuC_2O_4$  (1:2) mole ratio.

### CONCLUSION

TGA experiment of  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio mixture in air shows complete decomposition to  $BaO$  and  $Fe_2O_3$  at  $1000^\circ C$  through four well-defined steps while EGA technique shows decomposition to  $BaCO_3$  and  $2CuO$  at  $1000^\circ C$ . The non-isothermal TGA of  $BaC_2O_4 \cdot 0.6H_2O$  shows 80 % formation of  $BaO$  while in the  $BaC_2O_4 \cdot 0.6H_2O$  and  $CuC_2O_4$  (1:2) mole ratio mixture shows 88 % formation  $BaO$  this is due to the catalytic effect of  $CuO$ . Intermediates, decomposition products as well as the final products were characterized by X-ray diffraction techniques. The increase in the intensity of the diffraction lines by raising the calcination temperature from  $500^\circ C$  to  $900^\circ C$  is attributed to the grain growth of the

decomposition products. XRD experiments show the decomposition of  $\text{BaC}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4$  (1:2) mole ratio mixture to BaO and 2CuO.

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