

# Calculation of Kinetic and Thermodynamic Parameters of Gel-Grown Lead-Cobalt Mixed Levo-Tartrate Crystals by C-R Relation

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**ABSTRACT:** Metal tartrate compounds find various applications. Lead tartrate finds application as additive in gasoline to prevent knocking in motors and calcium tartrate is well known for its ferroelectric applications. In the present study, lead and cobalt mixed levo-tartrate crystals were grown using silica hydro-gel as growth medium. Dendrite crystals were obtained at the gel-liquid interface. The crystals were characterized by Thermo gravimetric analysis and kinetic as well as thermodynamic parameters were evaluated for the dehydration and carbonate stage by C-R relation.

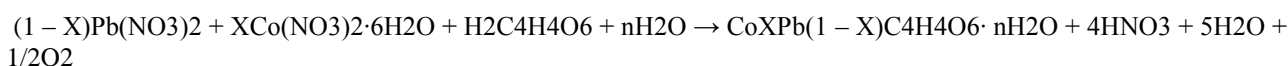
**KEYWORDS:** Lead-cobalt mixed levo-tartrate crystals, gel growth, thermo gravimetric analysis, kinetic parameters, thermodynamic parameters.

## I. INTRODUCTION

The metal tartrate compounds find various applications in different fields, for example, application of tartrate ions to treat prostate cancer [1], iron tartrate complex ions play important role as contrast blocks of renal tissues prior to their dehydration [2], iron tartrate is one of the prominent species in apple juice [3], calciphylactic responses of various ferrous tartrate compounds to prevent anemia in animals [4], the potential for iron(III) tartrate to act as a photo activator in light-induced oxidative degradation of white wine [5], ferroelectric, dielectric, optical and thermal properties of calcium tartrate [6], piezoelectric application of cadmium tartrate [7] and the addition of lead tartrate in gasoline to prevent knocking in motors [8]. The gel growth technique is found to be suitable to grow tartrate compound crystals and many authors have reported the growth of metal tartrate crystals [9-12], mixed metal tartrate crystals [13,14] and ternary metal tartrate crystals [15,16] in gel medium. In the present study, the present author has attempted to grow the crystals of lead-cobalt mixed levo-tartrate and characterized them by TGA and evaluated the kinetic as well as thermodynamic parameters for the dehydration and decomposition stage.

## II. MATERIALS AND METHOD

In the present study, the single diffusion method [12,15-17] was employed for the growth of lead-cobalt mixed levo-tartrate crystals. The silica hydro gel was used as a growth medium. To prepare the gel, a solution of sodium metasilicate of 1.05 specific gravity and 1 M solution of levo tartaric acid were mixed in such a manner that the pH of the mixture was set at 4.5. The gel solution was poured in to glass test tubes of 15 cm length and 2.5 cm diameter and allowed to set in the gel form. The supernatant solution containing the mixture of 1 M, 6 ml lead nitrate solution and 1 M, 4 ml cobalt nitrate hexahydrate solution was poured on the set gel carefully without damaging the gel. All the chemicals were of AR grade and obtained from Sigma Aldrich. The following reaction is expected to take place in the formation of lead-iron mixed levo-tartrate crystals.



The amount of  $\text{HNO}_3$  produced is very less in comparison to the nutrients being supplied to the growing crystals and hence no major limitation is imposed [5,14-17].

Photograph of the grown crystals is shown in the figure 1.

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Fig. 1. Growth of crystals inside the test tube

The growth of crystals was started approximately after 36 hrs after pouring the supernatant solution. The crystals were grown at the gel-liquid interface. The crystals were dendrite in nature, white, dense and long.

### III. CHARACTERIZATION TECHNIQUES

The grown crystals were characterized by TGA. The TGA was recorder on Perkin Elmer make instrument, model Pyris-1 DSC, Pyris-1 TGA, DTA-7. The data were recorded from room temperature to 700°C at a heating rate of 10°C min<sup>-1</sup> in atmosphere of air in standard Al<sub>2</sub>O<sub>3</sub> crucible.

### IV. RESULT AND DISCUSSION

The crystals were dendrite in nature. Mechanism of dendrite crystal growth was studied by Fujiwara and Nakajima [18]. Dendrite type growth morphology has been observed by several authors in the gel grown crystals, such as lead tartrate [19], cadmium tartrate [20], ammonium tartrate [21] and lanthanum tartrate [22]. There are reports available in literature on thermal studies of metal tartrate systems [13,15,16,17].

The TGA curve for lead-cobalt mixed levo-tartrate crystals is shown in figure 2.

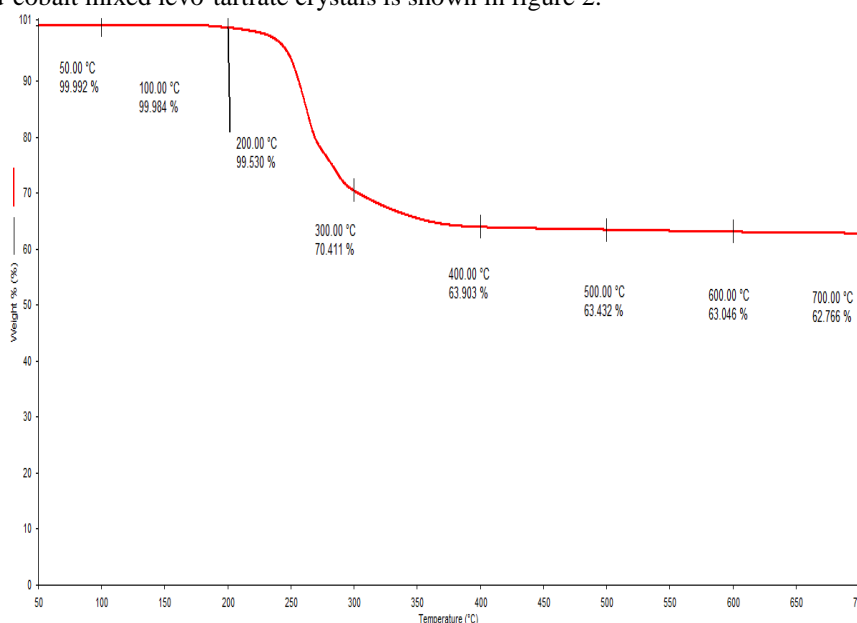


Fig 2. TG curve for lead-cobalt mixed levo-tartrate crystals

There are three stages of decomposition starting from room temperature of 500 °C. There is no decomposition of sample upto temperature 190 °C. The first stage of decomposition is observed in the temperature interval of 190 to 220 °C with the weight loss is about 1.06%. The second stage of decomposition is in the temperature interval of 220 to 280

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°C with the weight loss is about 24.77 %. The third stage of decomposition is observed in the temperature interval of 280 to 400 °C with the weight loss is about 36.94%. The number of water molecules associated with the crystals was calculated and found to be 0.2.

Many researchers have used thermo gravimetric data to calculate the kinetic parameters of solid state reaction including mass [23-26]. By using kinetic parameters such as order of reaction, frequency factor and energy of activation, the shape of curve is determined. With the help of Coats and Redfern [25] relation the kinetic parameters were calculated. In the present study, the kinetic and thermodynamic parameters have been calculated for dehydration as well as for decomposition of crystals.

Coats and Tedfern relation is given by

$$\log_{10} \left[ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \left\{ \log_{10} \left[ \frac{AR}{\alpha E} \right] \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \right\}$$

Here,  $\alpha = \frac{W_o - W}{W_o - W_f}$ ,  $W_o$  the initial weight,  $W$  the weight at time  $t$ ,  $W_f$  the final weight,  $n$  the order of reaction,  $A$  the frequency factor,  $E$  the activation energy of the reaction,  $R$  a gas constant and  $\alpha$  the heating rate in °C/min.

To determine the value of activation energy and order of reaction, a plot of  $\log_{10} \left[ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right]$  versus  $\frac{1}{T}$  is

drawn for different values of  $n$  and the best linear plot gives the correct value of  $n$ . This equation is valid for all values of  $n$  except  $n = 1$ .

Figure 3 is a plot of Coats and Redfern equation for the mixed crystals of lead-cobalt levo-tartrate. Plot 1 is for dehydration stage and plot 2 is for decomposition stage.

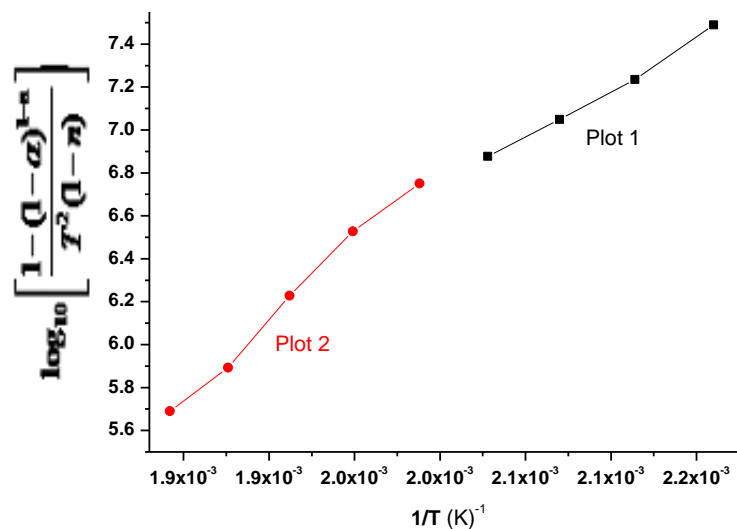


Fig 3. A plot of Coats and Redfern relation for lead-cobalt mixed levo-tartrate crystals

The values of order of reaction, activation energy and frequency factor for the dehydration as well as decomposition stage are listed in the table 1.

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Table 1. Kinetic parameters for lead-cobalt mixed levo-tartrate crystals

Stage	n	Activation energy (kJ mol <sup>-1</sup> )	Frequency factor
Dehydration	5	88.25	6.042 × 10 <sup>-20</sup>
Decomposition	0.25	144.58	2.806 × 10 <sup>-25</sup>

The thermodynamic parameters have been evaluated for the dehydration as well as decomposition stages by using the standard relations [27]. The standard enthalpy of activation  $\Delta^{\#}H^{\circ}$  was calculated by using the relation

$$\Delta^{\#}H^{\circ} = E - 2RT$$

The standard entropy of activation  $\Delta^{\#}S^{\circ}$  was calculated by using relation

$$\Delta^{\#}S^{\circ} = 2.303 \times R \times \log_{10} \left[ \frac{Ah}{kT} \right]$$

Here,  $k$  is the Boltzman constant,  $h$  the Planck constant,  $T$  the temperature and  $A$  is the frequency factor.

The standard Gibbs free energy of activation  $\Delta^{\#}G^{\circ}$  is estimated by using the relation

$$\Delta^{\#}G^{\circ} = \Delta^{\#}H^{\circ} - T \Delta^{\#}S^{\circ}$$

The values of standard enthalpy, standard entropy and standard Gibbs free energy for the dehydration as well as decomposition stage are listed in the table 3.

Table 3. Thermodynamic parameters for lead-cobalt mixed levo-tartrate crystals

Stage	Standard enthalpy $\Delta^{\#}H^{\circ}$ (kJ mol <sup>-1</sup> )	Standard entropy $\Delta^{\#}S^{\circ}$ (kJ mol <sup>-1</sup> )	Standard entropy $\Delta^{\#}G^{\circ}$ (kJ mol <sup>-1</sup> )
Dehydration	80.38	0.149	80.23
Decomposition	140.23	0.237	135.65

Positive values of the standard enthalpy and the standard entropy of activation suggest that the process is spontaneous at high temperatures and the positive values of standard Gibbs free energy suggest that the process is thermodynamically unstable [15].

## V. CONCLUSIONS

Lead-cobalt mixed levo-tartrate crystals were grown in silica gel by using the mixture of 1 M, 6 ml lead nitrate and 1 M, 4 ml cobalt nitrate hexahydrate solution as supernatant solution. From TG curves, it was found that the crystals were thermally unstable. Upon heating, they become anhydrous and decomposed into metal oxide through a single stage of carbonate. The kinetic parameters were evaluated for both the stages by using Coats and Redfern relation. The thermodynamic parameters were evaluated for both the stages by using the standard relations. The presence of water molecules was detected and calculated.

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