International Journal of Applied Research

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Calculation of kinetic and thermodynamic parameters of gel-grown lead iron 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 iron tartrate finds application as one of the prominent species in apple juice. In the present study, lead and iron 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 different stage of decomposition.

Keywords: Lead-iron mixed levo-tartrate crystals, gel growth, thermo gravimetric analysis, kinetic parameters, thermodynamic parameters.
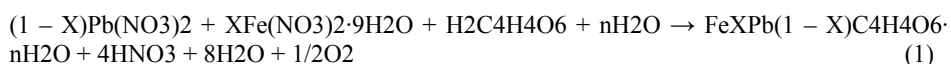
1. Introduction
The metal tartrate compounds find various applications in the different fields of science and technology, for example, ferroelectric applications of calcium tartrate [1], piezoelectric application of cadmium tartrate [2], addition of lead tartrate in gasoline to prevent knocking in motors [3] and application of carbonate solutions containing Co(II) tartrate complexes in an electrochemical procedure of anodic deposition of cobalt oxyhydroxide film on a glassy carbon substrate in an alkali medium [4]. The gel growth technique is found to be suitable to grow tartrate compound crystals, which is elaborately described by Henisch [5]. The growth of several tartrate compound crystals by the gel technique and their characterization were reported, for instance, cadmium tartrate [6-11], iron tartrate [12] and lead tartrate [13, 14]. In the present study, the present author has attempted to grow the crystals of lead-iron mixed levo-tartrate and characterized them by TGA and evaluated the kinetic as well as thermodynamic parameters for the dehydration and decomposition stage.

2. Experimental
In the present study, the single diffusion method [14-17] was employed for the growth of lead-iron 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, 8 ml lead nitrate solution and 1 M, 2 ml iron nitrate nonahydrate 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.

$$(1 - X)Pb(NO_3)_2 + XFe(NO_3)_2 \cdot 9H_2O + H_2C_4H_4O_6 + nH_2O \rightarrow Fe_XPb(1 - X)C_4H_4O_6 \cdot nH_2O + 4HNO_3 + 8H_2O + 1/2O_2 \tag{1}$$

The amount of 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].

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

Fig 1: Dendrite crystals of lead-iron mixed levo tartrate

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 700ºC at a heating rate of 10ºC min^{-1} in atmosphere of air.

3. Result and Discussion

There are reports available in literature on thermal studies on pure and mixed metal tartrate systems, for example, cadmium tartrate [18], mercuric iodate crystals [19], iron-manganese levo-tartrate tartrate compound [20], ternary iron-manganese-cobalt tartrate compound [15], ternary iron-manganese-nickel tartrate compound [16] and lead-cadmium mixed levo-tartrate crystals [17].

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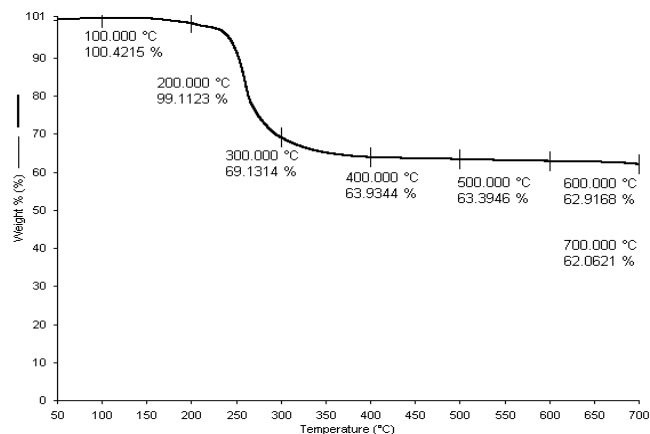

Fig 2: TG curve for lead-iron mixed levo-tartrate crystals

There are three stages of decomposition starting from room temperature of 45 ºC. There is no decomposition of sample upto temperature 160 ºC. The first stage of decomposition is observed in the temperature interval of 160 to 200 ºC with the weight loss is about 0.875%. The second stage of decomposition is in the temperature interval of 200 to 280 ºC with the weight loss is about 26.10 %. The third stage of decomposition is observed in the temperature interval of 280 to 400 ºC with the weight loss is about 36.60%. The number of water molecules associated with the crystals was calculated and found to be 0.17.

Many researchers have used thermo gravimetric data to calculate the kinetic parameters of solid state reaction including mass [21-25]. 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 [23] 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

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

Here, $\alpha = \dfrac{W_O - W}{W_O - W_f}$, 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 α the heating rate in ºC/min.

To determine the value of activation energy and order of reaction, a plot of $\log_{10}\left[\dfrac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ versus $\dfrac{1}{T}$ 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-iron levo-tartrate. Plot 1 is for dehydration stage and plot 2 is for decomposition stage.
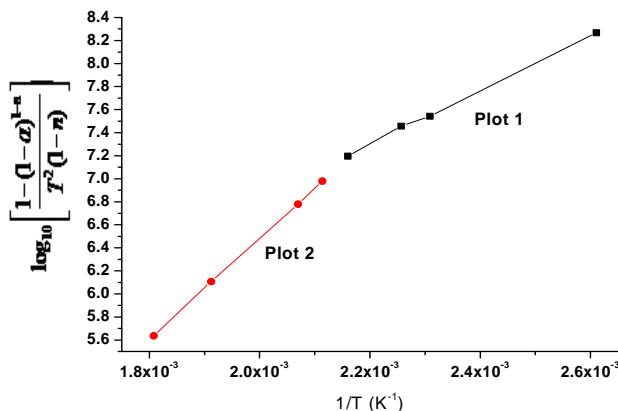

Fig 3: A plot of Coats and Redfern relation for lead-iron mixed levo-tartrate crystals

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.

Table 1: Kinetic parameters for lead-iron mixed levo-tartrate crystals

Stage	n	Activation energy (kJ mol^{-1})	Frequency factor
Dehydration	0	45.11	8.36×10^{16}
Decomposition	0	83.50	6.13×10^{19}

The thermodynamic parameters have been evaluated for the dehydration as well as decomposition stages by using the standard relations [26]. The standard enthalpy of activation $\Delta^{\#}H^o$ was calculated by using the relation 3.

$$\Delta^{\#}H^o = E - 2RT \quad (3)$$

The standard entropy of activation $\Delta^{\#}S^o$ was calculated by using relation 4.

$$\Delta^{\#}S^o = 2.303 \times R \times \log_{10}\left[\frac{A\,h}{k\,T}\right]$$

(4)

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

The standard Gibbs free energy of activation $\Delta^{\#}G^o$ is estimated by using the relation 5.

$$\Delta^{\#}G^o = \Delta^{\#}H^o - T\,\Delta^{\#}S^o \qquad (5)$$

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-iron mixed levo-tartrate crystals

Stage	Standard enthalpy $\Delta^{\#}H^o$ (kJ mol^{-1})	Standard entropy $\Delta^{\#}S^o$ (kJ mol^{-1})	Standard entropy $\Delta^{\#}G^o$ (kJ mol^{-1})
Dehydration	37.91	0.075	5.042
Decomposition	75.14	0.129	9.994

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].

4. Conclusion
Pure lead-iron mixed levo-tartrate crystals were grown in silica gel by using the mixture of 1 M, 8 ml lead nitrate and 1 M, 2 ml iron nitrate nonahydrate 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. 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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