

## THEORETICAL ESTIMATION OF ACTIVATION ENERGY OF DEHYDRATION OF $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$

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The activation energies for dehydration steps of hydrated crystal of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  grown at  $12.5^\circ\text{C}$  have been calculated using only DTG instead of both DTG and isothermal data. The method provides an easy means of estimating the activation energies of the dehydration steps.

**Key Words :** DTG of Crystals; Theoretical Estimation of Activation Energy; Dehydration Steps; Hydrated Solids

### INTRODUCTION

CRYSTALS of cobalt sulphate grown below  $40.6^\circ\text{C}$  are heptahydrate and those grown above this temperature are hexahydrate in nature. A heptahydrate crystal of  $\text{CoSO}_4$  loses one molecule of water quickly when exposed to dry air. It has been reported<sup>1</sup> that the heptahydrated  $\text{CoSO}_4$  is completely dehydrated at  $250^\circ\text{C}$  and of other form complete dehydration occurs between  $300$  and  $420^\circ\text{C}$ . Nandi *et al*<sup>2</sup> have studied dehydration of  $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  of freshly prepared crystals at  $12.5$ ,  $40$  and  $50^\circ\text{C}$ . An attempt is made to estimate the activation energy for all dehydration steps of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , crystal grown at  $12.5^\circ\text{C}$  from DTG curve alone and are reported in this paper. Adgaonkar *et al*.<sup>3</sup> have already reported similar work for  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and  $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$  crystals by this approach.

The DTG curve for the thermal dehydration of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  grown at  $12.5^\circ\text{C}$  is reproduced<sup>2</sup> in Fig. 1 here, for the purpose of theoretical calculations. The rate of heating of the crystal was  $5^\circ\text{C}/\text{min}$  in their case.

### THEORY

It is assumed that for slow rate of heating ( $5^\circ\text{C min}^{-1}$ ) and the peak value of temperature for all dehydration steps being sufficiently large, following equation for isothermal measurement should be appropriate

$$\frac{d\alpha}{dt} = kF(\alpha),$$

where  $\alpha$  is the fraction of reactant dehydrated at time  $t$  and  $k$  is the rate constant<sup>4</sup>

Integration of the equation gives—

$$\int \frac{d\alpha}{F(\alpha)} = kt = tZ e^{-E/RT},$$

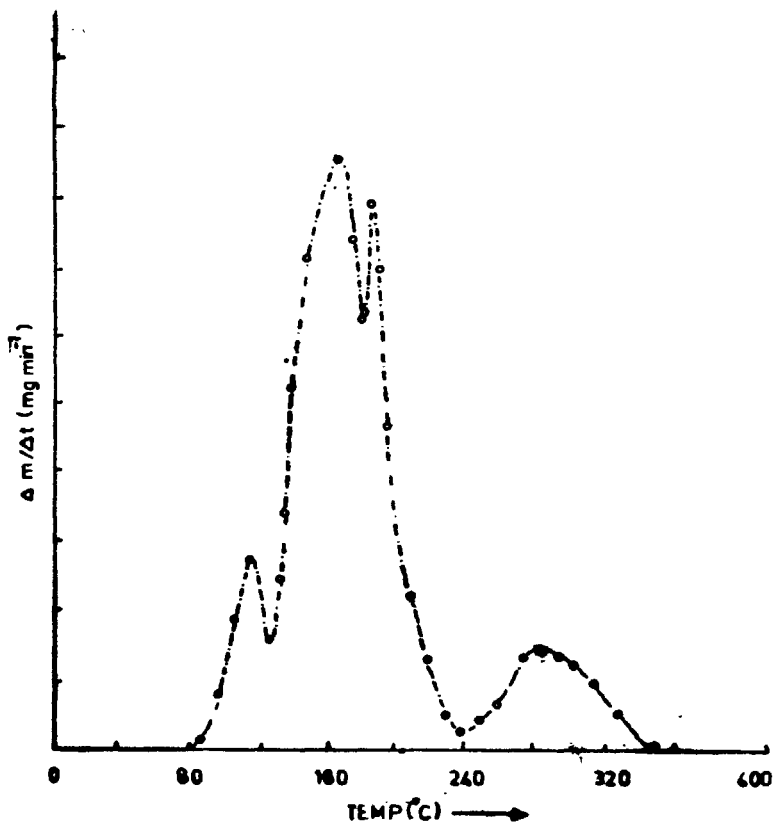


FIG 1 DTG curve for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  crystal grown at  $12.5^\circ\text{C}$ .

where  $Z$  is the collision number, the value of which is equivalent to frequency factor  $A$ .

Here we used the value of  $Z$  as

$$Z = 4\sigma^2 \left( \frac{\pi RT}{M} \right)^{1/2},$$

where  $\sigma$  is the diameter of the water molecule<sup>4</sup> and  $R$ ,  $T$  and  $M$  have their usual meanings.

The form of the function  $F(\alpha)$  is taken as

$$[-\ln(1 - \alpha)]^{0.4}$$

where  $\alpha = N_1/N_0$  and

$N_1$  — number of water molecules lost upon heating

and  $N_2$  — total number of water molecules present.

The choice of  $F(\alpha) = [-\ln(1 - \alpha)]^{0.4}$

was made by plotting  $F(\alpha) = [-\ln(1-\alpha)]^n$  vs time for  $n$  values ranging from 0.25 to 0.75.

Power  $n = 0.4$  gives fairly linear variation of  $F(\alpha)$  with time for all dyhydration steps and as such used for further calculations.<sup>5</sup> The curves are given in Fig. 2 (a, b, c & d). The change in the slope appears at the dehydration steps.

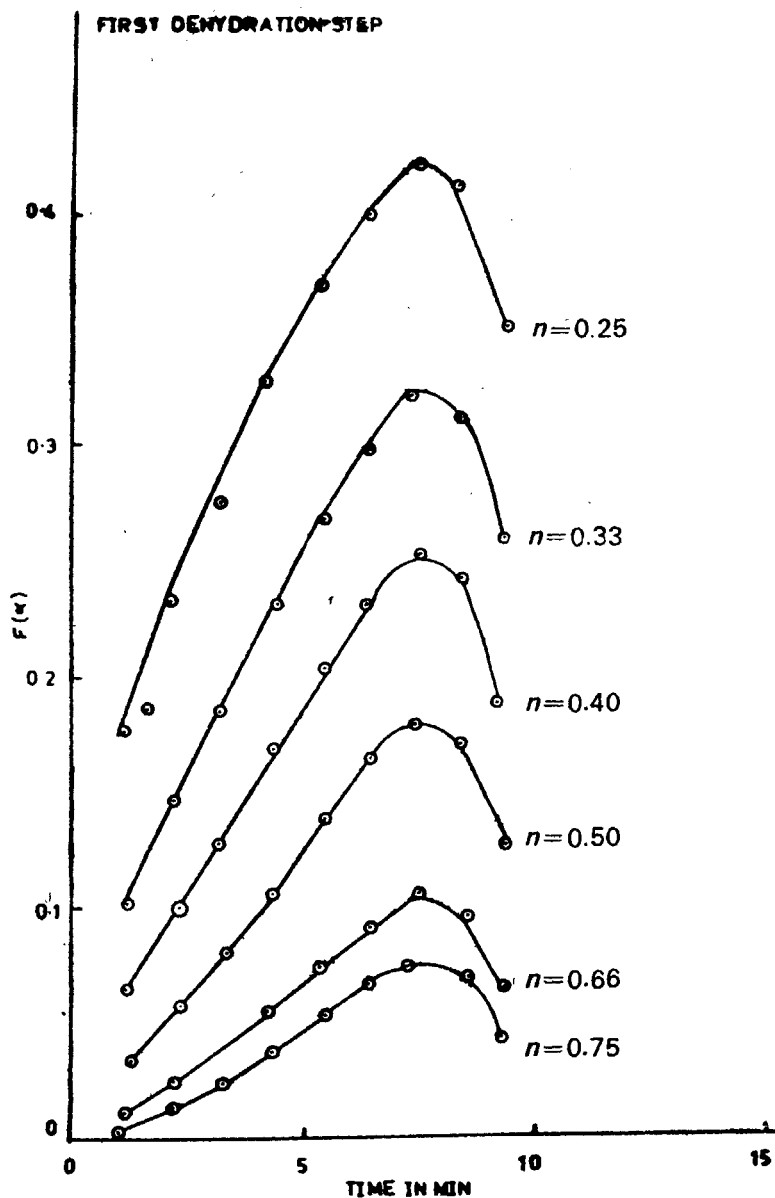


FIG 2a Function  $F(\alpha)$  variation with time.

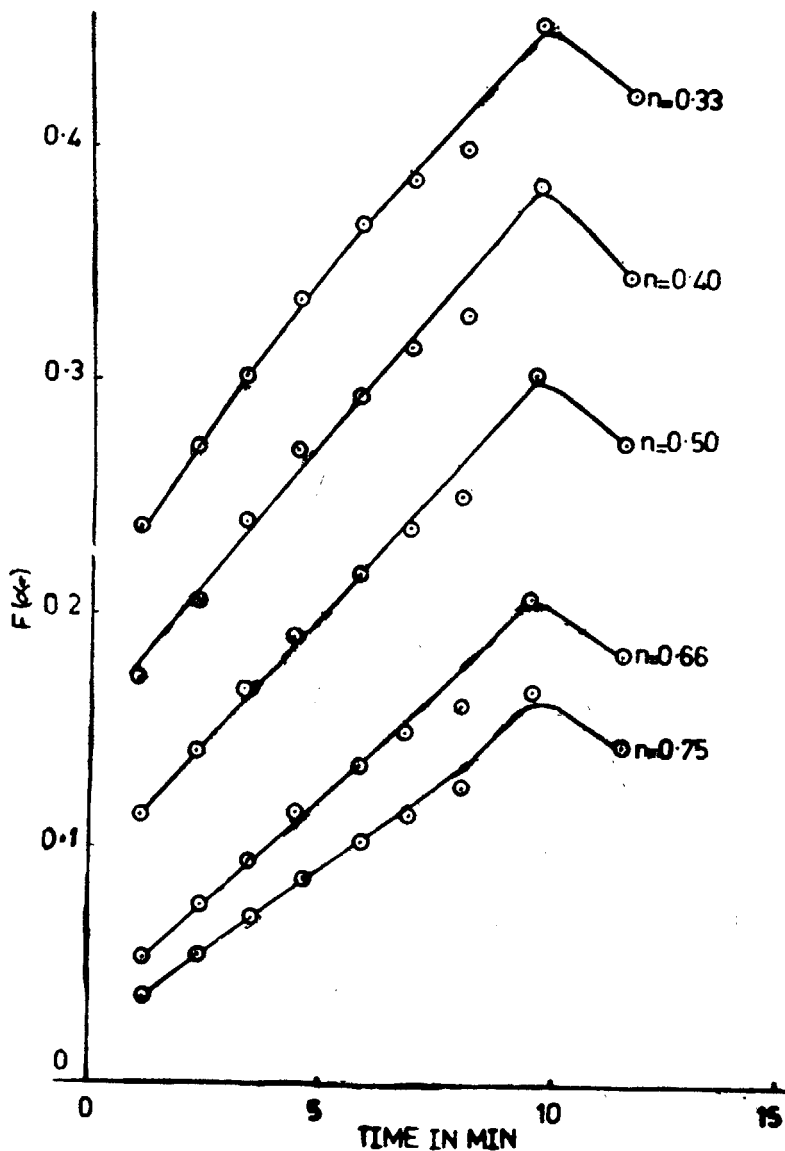


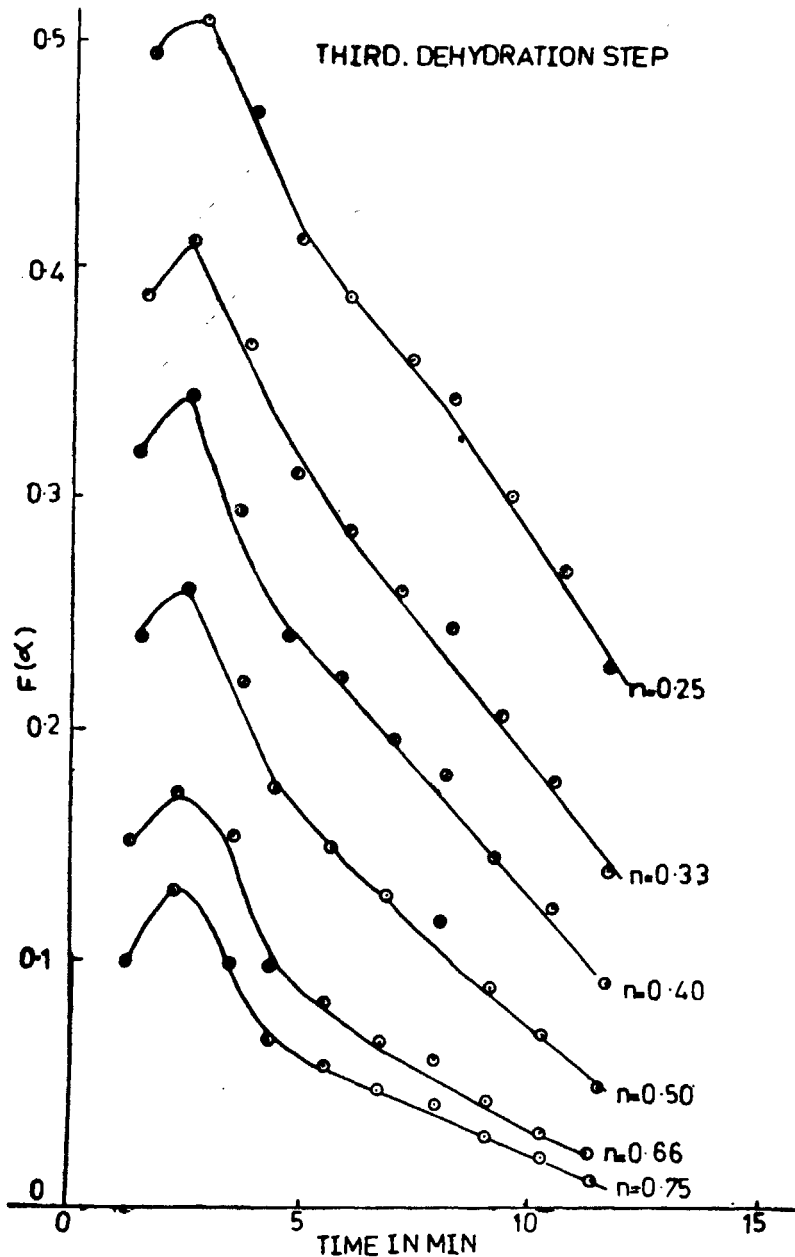
FIG 2b Function  $F(x)$  variation with time.

The value of  $t$  in the rate equation is taken equal to total time required for a particular dehydration step and is taken from DTG graph.

The activation energies thus calculated are given in Table I.

#### RESULTS AND DISCUSSION

It can be seen that the values of the activation energies calculated by this method are well in order. The activation energy for detachment of  $H_2O$  molecule from

FIG 2c Function  $F(\alpha)$  variation with time.

water is 9.7 kcal/mole at temperature 373 °K. In case of hydrated crystal of cobalt sulphate the  $\text{H}_2\text{O}$  molecules are attached to the crystal molecules in lattice. In hydrated cobaltous salts six water molecules often surround the metal ion<sup>6</sup> (as in case of  $\text{Ni}(\text{H}_2\text{O})_6\text{SO}_4 \cdot \text{H}_2\text{O}$  which is usually written as  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ).

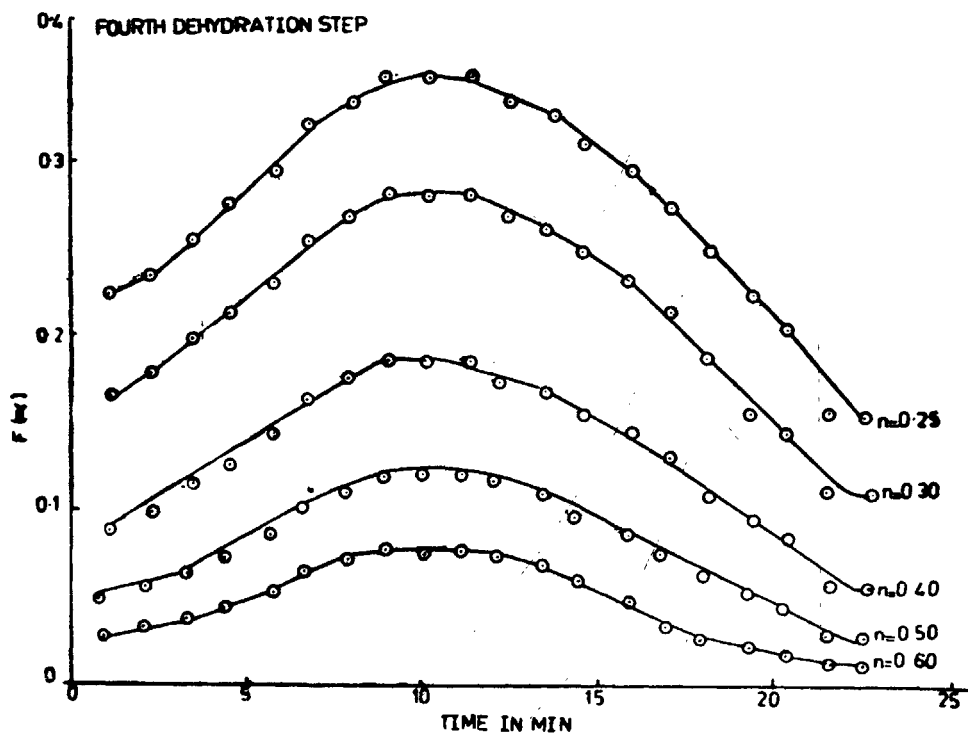
FIG 2d Function  $F(\alpha)$  variation with time.

TABLE I

Peak No.	$F(\alpha)$	Peak Temp. °K	Activation energy kcal/mole
1	0.2519	390.3	$12.344 \pm 0.1581$
2	0.3296	438.6	$13.899 \pm 0.1584$
3	0.3481	467.1	$14.818 \pm 0.1586$
4	0.1831	558.6	$16.147 \pm 0.1445$

\*Error shown in each activation energy value is maximum.

Thus in  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  crystal octahedrally coordinated  $\text{Co}^{II}$  is present giving rise to  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions.<sup>7,8</sup> At the first dehydration step water molecule attached to  $\text{SO}_4^{2-}$  is detached.

All the dehydration steps in the present case are above 373 °K and therefore, the activation energy for the dehydration step should always be greater than 9.7 kcal/mole. Our values are in agreement with this idea.

After the first dehydration step has occurred the rearrangement of the crystal molecules and the remaining  $\text{H}_2\text{O}$  molecules of crystallisation must take place and the strength of the bond must be higher else all water molecules of crystallisation

would have left at the same dehydration step I. Thus, it is evident that more activation energy should be required for the second dehydration step and should be greater for step three and higher for the last step i.e., fourth step. Our values are in agreement with this idea too.

Due to the proximity of dehydration step 2 and 3 there is a possibility of slight error in the assessment of  $t$  for step 3. However, the maximum error in the estimation of the activation energy is very small compared to the difference of activation energies between consecutive dehydration steps. This shows well-defined bonds.

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