

## THE POSSIBILITY OF RESOLVING OVERLAPPING DECOMPOSITION REACTIONS BY THE KINETIC PLOTS OF THERMOGRAVIMETRIC DATA \*

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### ABSTRACT

The dehydration reactions of some malatoquo complexes, namely,  $\text{MnMal} \cdot 3 \text{H}_2\text{O}$ ,  $\text{CoMal} \cdot 3 \text{H}_2\text{O}$ ,  $\text{NiMal} \cdot 3 \text{H}_2\text{O}$ , and  $\text{CuMal} \cdot \text{H}_2\text{O}$ , under non-isothermal conditions were studied kinetically using the integral methods of Coats and Redfern and Horowitz and Metzger. It has been concluded that multistep reactions may be investigated using kinetic plots and accurate isolation of the overlapping reactions could be obtained. The value for the order of reaction which gives the best linear relations may be the overall order of reaction in such multistep reactions. This is true only when more than one linear portion characterizes the kinetic plots at some other value of the order of reaction.

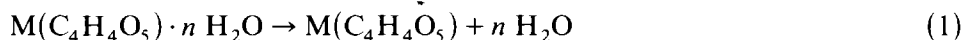
### INTRODUCTION

Several authors have reported on kinetic investigations of solid-state reactions carried out under non-isothermal conditions by applying mathematical expressions which have been derived in the last two decades. Such studies may help in studying the mechanisms of the thermal decomposition reactions [1], interpreting some reactions in terms of some basic mechanisms [2, 3] or evaluating the applicability of some expressions to solid-state reactions [4] or solution reactions [5]. It is also good practice to compare the kinetic results obtained from DTA curves [6] with those obtained from thermogravimetric data [7] for the same decomposition reactions. In some of the kinetic methods, several values have to be presumed for the order of reaction,  $n$ , and the value which offers the best linearity is considered as the true order of reaction. Computer systems, then, can be helpful in such methods [8]. The increment by which the order of reaction is changed can be minimized until the exact value is reached [9].

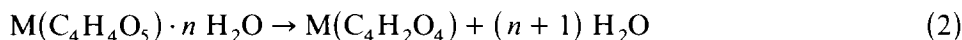
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In this paper, the integral methods of Coats and Redfern [10] and Horowitz and Metzger [11] are applied to the solid-state dehydration reactions of some malatoquo complexes of divalent transition metals, namely, triaquomalatomanganese, triaquomalatocobalt, triaquomalatonickel, and aquomalatocopper. The dehydration reactions studied are



where  $M = Mn$  or  $Co$  and



where  $M = Ni$  or  $Cu$ .

The differential method of Freeman and Carroll [12] is not used in this work because the DTG peaks related to these reactions are not symmetrical [13]. The asymmetric form of the DTG peaks has led to the conclusion that these reactions are two-step reactions [14].

## EXPERIMENTAL

The malatoquo complexes were prepared as described earlier [14]. The TG analyses were performed on an MOM derivatograph (Hungarian Optical Works). Samples weighing 100 mg were placed in platinum crucibles and heated at a rate of  $5^\circ C \text{ min}^{-1}$  under static (air) and dynamic nitrogen atmospheres.

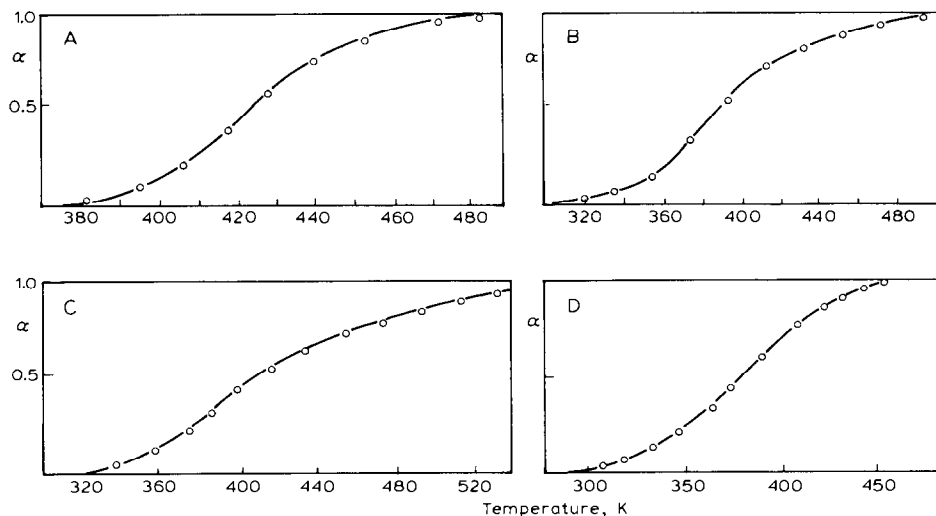


Fig. 1. The degree of conversion vs. absolute temperature for the dehydration of the malatoquo complexes of: A, Mn; B, Co; C, Ni; and D, Cu.

All the values of  $\alpha$ , the fraction of material decomposed, are the mean values of the three thermograms made. A typical spread of the experimental values are shown graphically in Fig. 1.

## RESULTS AND DISCUSSION

### *Estimation of activation energy and order of reaction*

The expressions employed in this study are, firstly, the Coats–Redfern: for the order of reaction,  $n$  equal to 1

$$\ln \left[ \frac{\ln(1-\alpha)}{T^2} \right] = \ln \frac{ZR}{E} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{R} \frac{1}{T} \quad (3)$$

and for  $n \neq 1$

$$\ln \left[ \frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \frac{ZR}{E} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{R} \frac{1}{T} \quad (4)$$

and, secondly, Horowitz–Metzger: for  $n = 1$

$$\ln \ln \left( \frac{1}{1-\alpha} \right) = \frac{E}{RT_s^2} \theta \quad (5)$$

and for  $n \neq 1$

$$\ln \frac{[1 - (1-\alpha)^{1-n}]}{1-n} = \frac{E}{RT_s^2} \theta \quad (6)$$

where  $\alpha$  is the fraction decomposed;  $T$  is the absolute temperature;  $Z$  is the frequency factor ( $\text{s}^{-1} \text{mole}^{-1}$ );  $R$  is the gas constant ( $8.3 \text{ J mole}^{-1} \text{ deg}^{-1}$ );  $\phi$  is the heating rate, ( $\text{deg. min}^{-1}$ );  $E$  is the activation energy;  $n$  is the order of reaction;  $T_s$  is a reference temperature when the rate of the decomposition is at a maximum; and  $\theta = T - T_s$ , where  $T$  is any temperature on the curve.

The values of  $n$  examined here are:  $1/3$ ,  $1/2$ ,  $2/3$ ,  $1$ ,  $3/2$  and  $2$ . The most linear plots are considered for the correct values of  $E$ , which are usually determined from the slope of the straight lines.

The dehydration of malatoaquocopper(II) follows first-order kinetic equations as indicated in Fig. 2. It is clear from Figs. 3–7, that for  $n = 1$ , the plots corresponding to the Mn, Co and Ni complexes are characterized by two linear parts with different slopes. However, almost unique straight lines are obtained for  $n = 2$ . Isothermal decomposition reactions are often described by two-step linear kinetic plots [15]. Kolta and Askar [16] have interpreted the two-stage kinetic plot of the isothermal decomposition of copper(II) sulphate as corresponding to a two-step reaction. Similar results were reported on the application of the Coats–Redfern method to the dehydration

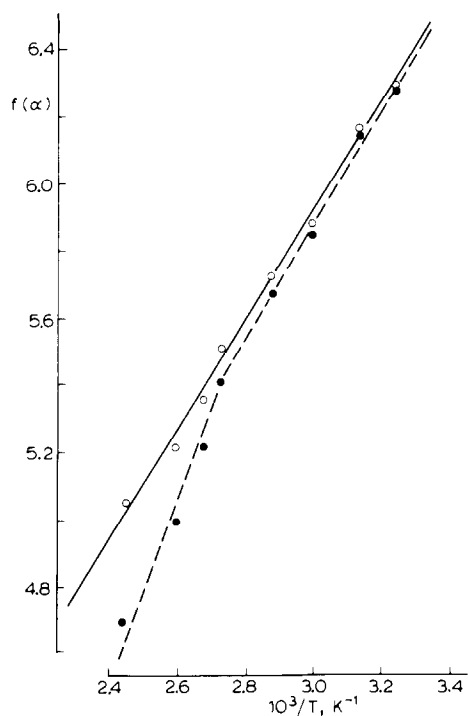


Fig. 2. Coats-Redfern kinetic plots for the dehydration of the copper complex.  $\circ$ ,  $n = 1$ ;  $\bullet$ ,  $n = 2$ .

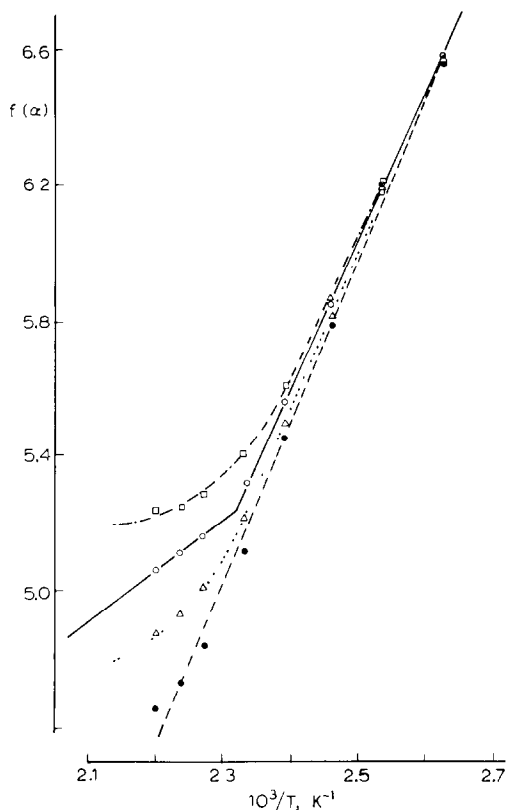


Fig. 3. Coats-Redfern kinetic plots for the dehydration of the manganese complex.  $\square$ ,  $n = 1/2$ ;  $\circ$ ,  $n = 1$ ;  $\triangle$ ,  $n = 3/2$ ;  $\bullet$ ,  $n = 2$ .

of some trisethylenediamine complexes by Zsako et al. [17]. They referred such observations to the decomposition of a surface layer of the crystal in the first kinetic stage and the hindered diffusion of water vapour, which makes the TG curves flatter. Hung [18] reported kinetic profiles for the decomposition of some crystalline amino acids, which follow the first order. For each compound, three distinguishable linear portions were observed in the plots, indicating three separate component reactions in the overall processes.

In the present case, the temperatures at which the slopes occur are 433, 399 and 410 K for Mn, Co and Ni complexes, respectively. According to Fig. 1, the values of  $\alpha$  corresponding to these temperatures are, respectively, 0.63, 0.62 and 0.51. The first two correspond to the loss of two water molecules from a total of three and the last value to the loss of two water molecules from a total of four in the case of the nickel complex, which dehydrates directly in the maleate [14]. As a result of this, the dehydration of the

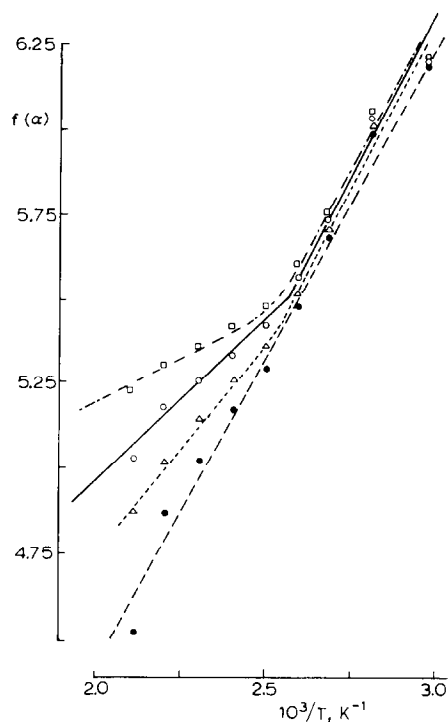
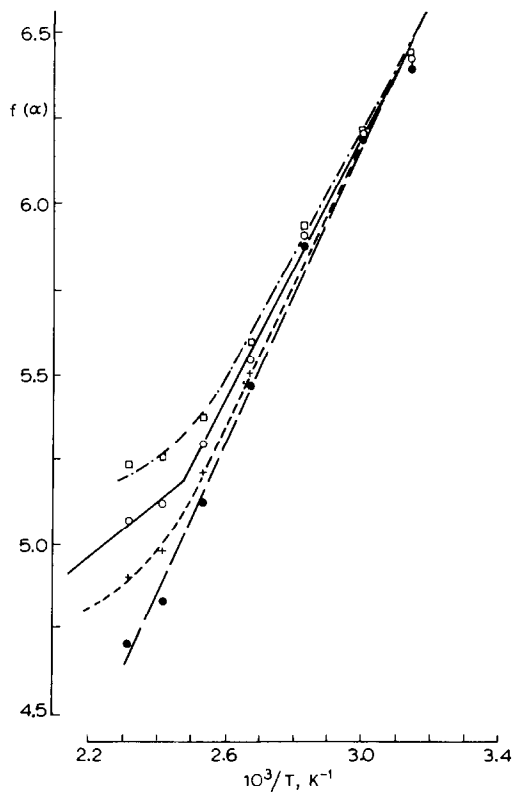


Fig. 4. Coats-Redfern kinetic plots for the dehydration of the cobalt complex.  $\square$ ,  $n = 1/2$ ;  $\circ$ ,  $n = 1$ ;  $\times$ ,  $n = 3/2$ ;  $\bullet$ ,  $n = 2$ .

Fig. 5. Coats-Redfern kinetic plots for the dehydration of the nickel complex.  $\square$ ,  $n = 1/2$ ;  $\circ$ ,  $n = 1$ ;  $\Delta$ ,  $n = 3/2$ ;  $\bullet$ ,  $n = 2$ .

TABLE 1

Activation energy values obtained for the dehydration reactions. Values in  $\text{kJ mole}^{-1}$ .

Complex	Coats-Redfern		Horowitz-Metzger	
	$n = 1^a$	$n = 2$	$n = 1^a$	$n = 2$
MnMal·3 H <sub>2</sub> O	104.3	105.4	105.0	106.8
CoMal·3 H <sub>2</sub> O	29.9	40.9	40.0	49.1
NiMal·3 H <sub>2</sub> O	39.2	42.7	46.9	46.1
CuMal·H <sub>2</sub> O	15.4	31.4	14.0	19.7
	41.4		45.3	
	18.2		20.4	
	31.8		16.9	

<sup>a</sup> The values for the two steps are indicated.

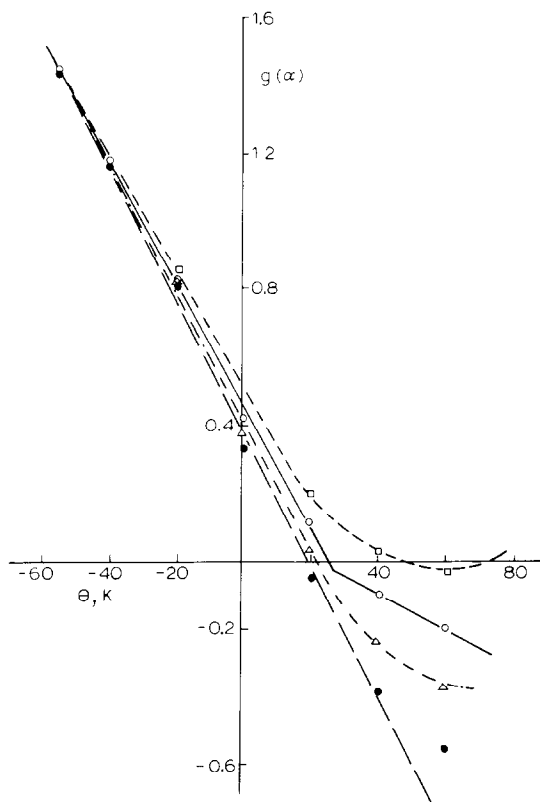


Fig. 6 Horowitz-Metzger kinetic plots for the dehydration of the cobalt complex.  $\square$ ,  $n = 1/2$ ;  $\circ$ ,  $n = 1$ ;  $\Delta$ ,  $n = 3/2$ ;  $\bullet$ ,  $n = 2$ .

malotriaquo complexes of Mn(II), Co(II) and Ni(II), are two step, first-order reactions with the formation of the monoquo complex as the intermediate product. The monoquo complexes suggest a tetrahedral structure similar to that given for the malatoaquocopper(II) complex [14]. The activation energy values of the first stage of the reactions are greater than that of the second stage. The values corresponding to  $n = 2$ , which is seen to give unique linear plots over the whole temperature range, may, therefore, correspond to the overall order of reaction. The activation energy values obtained by these methods are listed in Table 1.

Marcu and Segal [19] have recently reported a model for studying two consecutive reactions occurring during a decomposition by (non-isothermal) kinetics on the basis of calculated thermograms. In the present case and although the reactions are two-step, they do not follow this model. This is because the two reaction steps are defined by a certain temperature interval, i.e. there is no overlap over the temperature range involved.

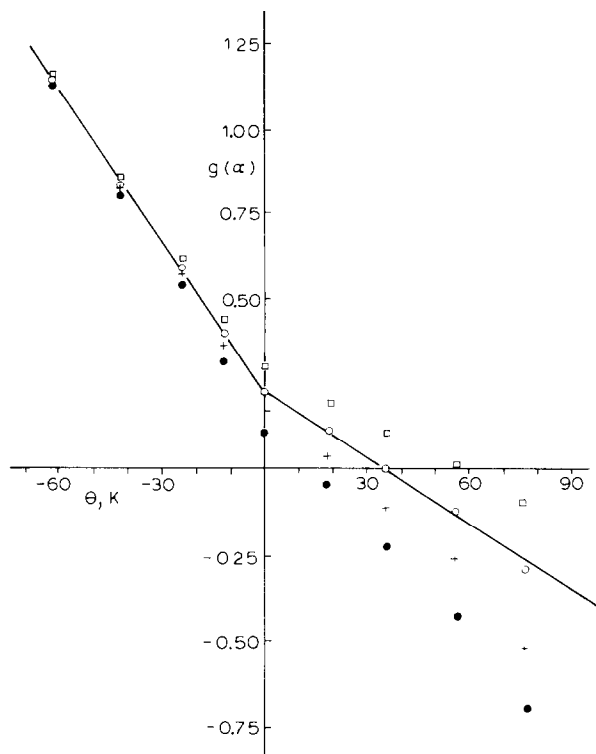


Fig. 7. Horowitz-Metzger kinetic plots for the dehydration of the nickel complex.  $\square$ ,  $n = 1/2$ ;  $\circ$ ,  $n = 1$ ;  $\times$ ,  $n = 3/2$ ;  $\bullet$ ,  $n = 2$ .

## CONCLUSION

Only weak evidence was obtained from the DTG curves to indicate that the dehydration of the malatoquo complexes of Mn, Co and Ni are two-step reactions [14]. Using the TG curves for the estimation of the kinetic parameters of these reactions, it has been shown that the kinetic plots can be utilized for resolving the two steps of the reactions. Consequently, the kinetic data characterizing each step can be estimated. The methods used in this study depend on trying different values for the order of reaction until the functions fit straight lines. There was greater possibility, therefore, of finding different relations between the points for the different values of  $n$ . The overall reactions were of second order with two steps proceeding as first-order reactions.

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