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KINETICS OF THERMAL DEHYDRATION AND DECOMPOSITION OF Fe(III) CHLORIDE HYDRATE ($FeCl_3 \cdot xH_2O$)

*S. B. Kanungo** *and S. K. Mishra*

Regional Research Laboratory, Bhubaneswar-751013, Orissa, India

Abstract

Fe(III) chloride hydrate ($FeCl_3 \cdot xH_2O$) undergoes simultaneous dehydration and dehydrochlorination from its molten phase in the temperature range 100–200°C. The kinetics of these two parallel thermal processes has been studied by both isothermal and non-isothermal methods. Whereas for the dehydration reaction at temperature below 125°C a second order rate model (F_2) fits well, a three-dimensional diffusion (D_3) model is found to fit better at temperature above 135°C. For the dehydrochlorination reaction an interface growth controlled model of 1/3 order (F 1/3) appears to be the most suitable over a wide range of reaction. Dynamic thermogravimetry reveals two major steps in the temperature range 50–250°C. The first step which corresponds to the loss of about 4 mols of H_2O, invariably follows second order kinetics (F_2). The second step which is predominantly a process of dehydrochlorination, generally fits mixed diffusion controlled models due to the overlapping with the dehydration process. There is an excellent agreement in results among the isothermal and non-isothermal methods of determining kinetic parameters.

Keywords: dehydration and decomposition, kinetics, Fe(III) chloride

Introduction

In the preceding paper [1] it has been shown that both dehydration and dehydrochlorination of Fe(III) chloride hydrate takes place simultaneously from its molten phase at temperature above 100°C. To study the kinetics of such a process it is necessary to determine the rates of these two parallel reactions separately. To our knowledge no work has been reported so far on the kinetics of this important thermal decomposition process and the aim of this paper was to study this aspect using both isothermal and non-isothermal methods.

Experimental

The experimental procedure including chemical analysis of the products of dehydration and dehydrochlorination at different temperatures has been described in

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* Author to whom all correspondence should be addressed.

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detail in the preceding paper [1]. In this context it may be added that though the isothermal method used by us was not as sophisticated as compared to the commercial TA equipments, our duplicate/triplicate measurements never gave an error more than 4%. Because of this, we were able to obtain rate curves at the interval of 10°C using even such a 'simple' experimental procedure. If we would have used isothermal TG, a substantial mass loss would have occurred before the attainment of constant temperature because of the rapid dehydration/decomposition reaction. As a result, kinetics of the entire initial state of the above reactions would have remained obscure to us. We came to this conclusion after a considerable initial trial to obtain reproducible isothermal TG curves using DT 40. Besides, no other suitable method is available to determine separately the rates of dehydration and dehydrochlorination without performing chemical analysis of the solid product obtained after batchwise calcination for different periods of time. Though it is not claimed that this problem of isothermal TG has been solved in the present method, we have only tried to minimise it. In the case of isothermal method fraction decomposed (α) was determined from the ratio of loss of H_2O or HCl or a combination of both at any instant of time t to the corresponding type of the total loss observed after 1 h of calcination at 200°C. In the case of nonisothermal method values were determined on the basis of mass loss at the first plateau region in the TG curves at temperature around 250°C.

Results and discussion

Isothermal dehydration and decomposition

The total mass loss behaviour due to isothermal heating of $FeCl_3 \cdot 8H_2O$ as a function of time and temperature is shown in Fig. 1. The deceleratory nature of the curves suggests either diffusion or growth of reaction interface controlled mechanism for such a phenomenon. After a careful examination of the computer data for various model equations used to describe solid-state reactions (Table 1), it has been found that in the temperature range 105–135°C, the total mass loss curves in Fig. 1 follow D_3 model best up to 40% of reaction as illustrated in Fig. 2. In this case the three dimensional diffusion does not necessarily refer to spherical symmetry, but takes place through a solid product layer of a certain thickness to enable the diffusion to occur in all directions giving a semblance to the spherical symmetry [2]. It may be mentioned here that D3 is a special case of D1 under the hypothetical assumption that spherical particle behaves a like a flat surface. Became of this the model follows only for a limited conversion in the initial strage. Unlike nickel and cobalt chloride hydrates melting of Fe(III) chloride hydrate takes place at temperature around 35–40°C and instead of forming spherical droplets or globules of molten salt, the entire mass becomes a free-flowing liquid. Surface encrustation of solid product tends to grow covering the liquid surface. Once such an encrustation is grown to sufficient thickness, diffusion through the moist surface becomes the slow process and therefore, rate-controlling. Consequently, beyond $\alpha = 0{,}41$ (corresponding to the loss of about 4 moles of H_2O) kinetics follows the parabolic rate law

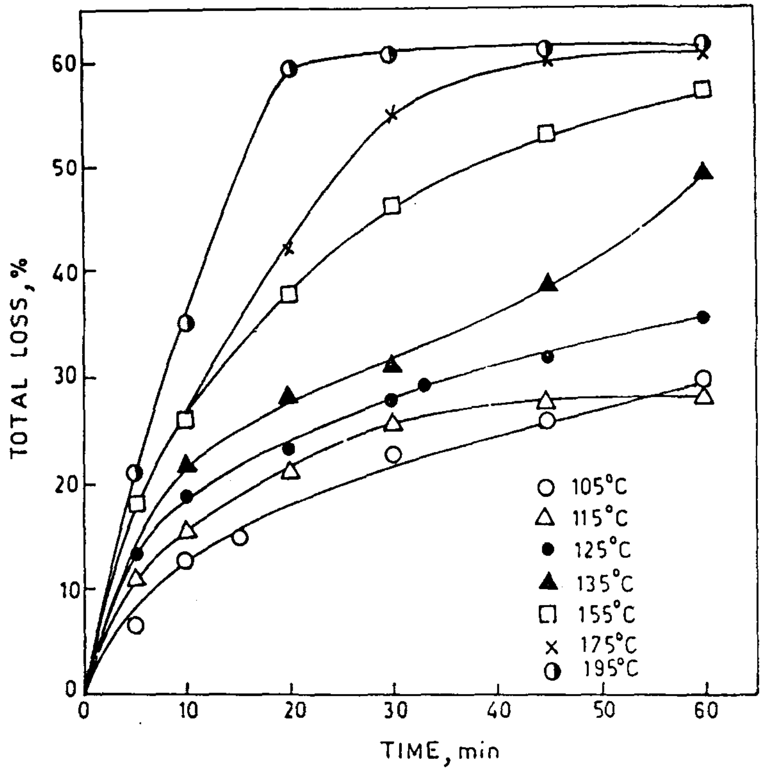

Fig. 1 Total mass loss as a function of time during the calcination of Fe(III) chloride hydrate at different temperatures

(D_1) from a constant surface area up to $\alpha=0.92$. Figure 3 demonstrates the linear plots of $(\alpha')^2$ *vs.* t', where, $\alpha'=\alpha-0.41$ and $t'=t-t_{0.41}$. Without such a correction simple plots of α^2 *vs.* t tend to form irregular cluster of points in the initial period of 10 minutes (figure not shown). Arrhenius plots for the two different kinetic mechanisms representing total mass losses from $FeCl_3{\cdot}8H_2O$ yield the apparent E values of 57.7 kJ mol^{-1} and 51.7 kJ mol^{-1} respectively (Table 2).

As described in the preceding paper [1] the amount of chlorine lost as HCl from $FeCl_3$ hydrate can be estimated from the chemical analysis of solid products formed at different periods of time and at different temperatures. Figure 4 demonstrates the loss of HCl as function of time in the temperature range 125–195°C. Though the occurrence of a short acceleratory region is suggestive of nucleation and growth type mechanism, best linear fits were, however, not necessarily observed for such a mechanism as revealed by computer analysis of the data. However, an interface growth-controlled model with 1/3 order ($F_{1/3}$) shows better fit of the data for the dehydrochlorination of $FeCl_3{\cdot}8H_2O$ (Fig. 5). Similar mechanism has also been observed for the decomposition of nickel chloride hydrate [3]. Though 1/3 order of reaction as such, has no physical significance in solid-state reaction, crystal growth

Table 1 Mechanistic model equations in integral form

Model code	Mechanistic model	Integrated form of equation $g(\alpha)$
D_1	1–D diffusion	α^2
D_2	2–D diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$
D_3	3–D diffusion (Jander's eqn.)	$[1-(1-\alpha)^{1/3}]^2$
D_4	Ginstling-Brounshtein eqn.	$(1-2/3\,\alpha)-(1-\alpha)^{2/3}$
AJ	Anti-Jander eqn.	$[(1+\alpha)^{1/3}-1]^2$
ZLT	Zhuravlev, Lesokhin & Tempel'mann eqn.	$[(1-\alpha)^{-1/3}-1]^2$
A_n	Avrami-Erofeev eqn. (n = 1.5, 2, 3, 4)	$[-\ln(1-\alpha)]^{1/n}$
R_2	Contracting geometry cylindrical symmetry	$1-(1-\alpha)^{1/2}$
R_3	Contracting geometry spherical symmetry	$1-(1-\alpha)^{1/3}$
P_n	Power law (n = 1, 2, 3, 4)	$\alpha^{1/n}$
$F_{1/3}$	One-third order of reaction	$1-(1-\alpha)^{2/3}$
F_1	First order eqn.	$-\ln(1-\alpha)$
F_2	Second order eqn.	$(1-\alpha)^{-1}-1$

may take place in such a preferred direction that the order becomes an intermediate between zero (flat plate) and 0.5 (cylindrical symmetry). Apparent E value derived from Arrhenius plots is 54.2 kJ mol^{-1} which is close to that found for the kinetics of total weight loss in the same temperature range (Table 1).

Subtracting the loss of HCl from the total mass loss at any instant of time one obtains the loss due to water only. Figure 6 shows the percent loss of H_2O only as a function of time and temperature. Unlike nickel and cobalt chloride hydrates [3] the nature of the curves is closely similar to those of total mass loss curves in Fig. 1. This strongly suggests the occurrence of parallel reactions of dehydration and dehydrochlorination in Fe(III) chloride hydrate. The deceleratory nature of the curves in Fig. 6 can be described by either a diffusion or a reaction order based model. While at temperature below 135°C F_2 is followed, D_3 is the predominantly rate-controlling mechanism from 140 to 195°C. As stated in the preceding paragraph that as the dehydration of molten $FeCl_3$ hydrate proceeds, an encrustation of product builds up over the surface of the liquid melt. Dehydration of hydrated salt is known to proceed by nucleation and growth mechanism [4, 5]. The second order mechanism considered here is a special case of nucleation and growth [6] at sufficiently large interval of time t to yield

$$\frac{1}{1-\alpha} = 1+\sigma N_g G t \tag{1}$$

where, σ is the shape factor, G is the linear growth rate of the new phase and N_g is the initial density of germ nuclei. The composite term $\sigma N_g G$ is considered as the formal rate constant k. As dehydration proceeds at a faster rate at higher tempera-

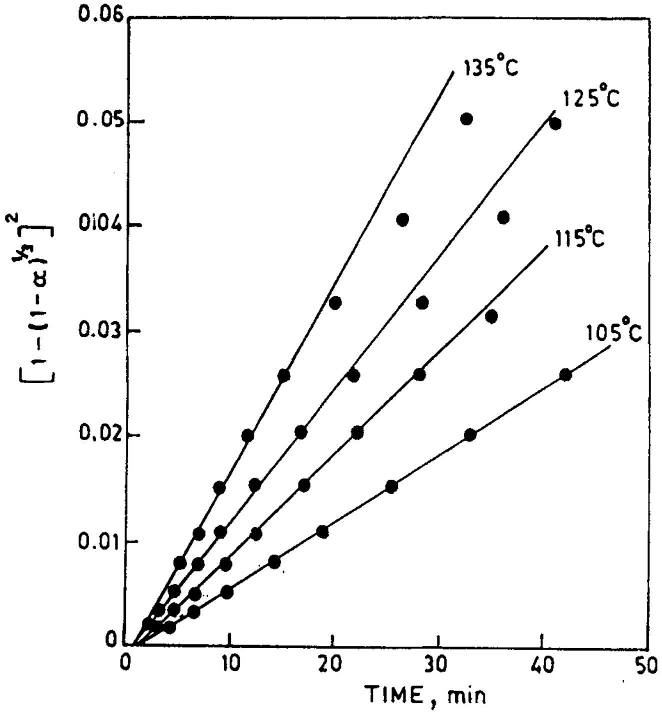

Fig. 2 Application of D_3 kinetic model to the initial state of total mass loss during the isothermal heating of Fe(III) chloride hydrate

ture (>130°C) diffusion through the upper product layer becomes rate controlling. Figure 6a shows that for the initial stage of dehydration F_2 mechanism follows up to 135°C and the *E* value is 57.4 kJ mol^{-1}. This value is closely comparable to the *E* values obtained either from total mass loss curves or from HCl loss curves (Table 2). Figure 7a also demonstrates that there is a break in the initial linear behavior around $\alpha=0.37$ at 125 and 135°C, indicating the onset of gradual transition from kinetic to diffusion regime. Figure 7b shows that although F_2 mechanism is still valid in the α range 0.37–0.80, the lower *E* value (36.9 kJ mol^{-1}) in the narrow temperature range 125–155°C indicates the increasing influence of the diffusion of H_2O vapour (D_3) through the solid product layer with an *E* value of 25.8 kJ mol^{-1}. However, the overall mechanism of dehydration and decomposition may be explained from the principle of parallel reactions as follows.

Let us consider for simplicity two homogeneous first order irreversible reactions* when a reactant A decomposes to two products B and C. If *a* be the moles of

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* This is justified, sience completely molten salt is considered as a solvent free homogeneous solution [15]

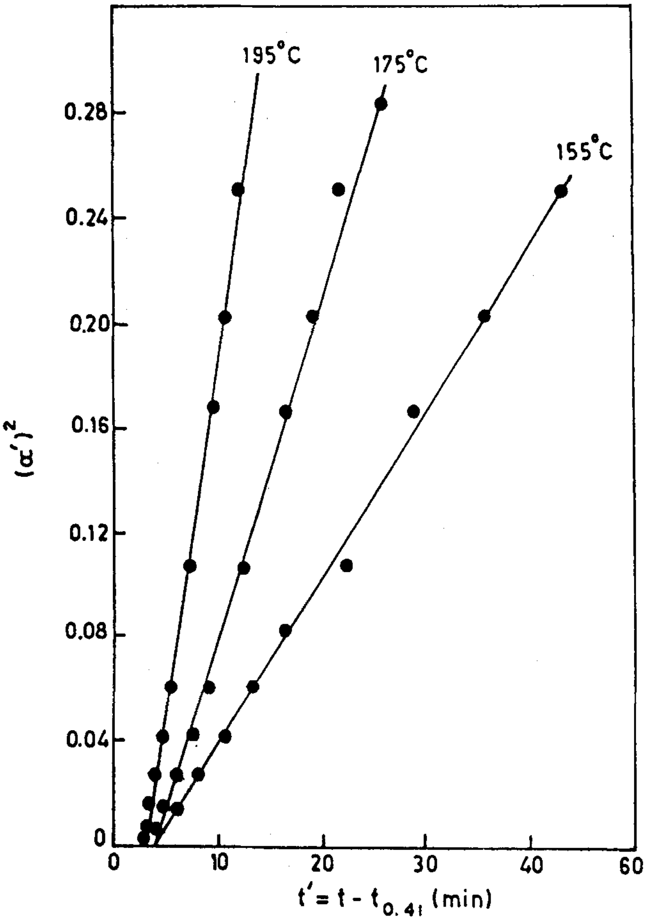

Fig. 3 Application of D_1 model to the final stage of total mass loss during isothermal heating of Fe(III) chloride hydrate. Non-zero intercepts on time – axis are due to the initial disturbance in the attainment of stable temperature in the sample

A at $t=0$ and x_1 and x_2 are the moles of B and C respectively at any instant t the rate expression may be written as

$$\frac{dx_1}{dt} = k_1(a-x) \quad (2)$$

$$\frac{dx_2}{dt} = k_2(a-x) \quad (3)$$

$$\frac{dx}{dt} = (k_1+k_2)\,(a-x) \quad (4)$$

where, $x=(x_1+x_2)$.

Table 3 Kinetic parameters obtained from isoconversion method of Ozawa, Flynn and Wall (OFW) and Kissinger's peak temperature method for the non-isothermal decomposition of Fe(III) chloride hydrate in two different equipments

Fraction decomposed	Netzsch, STA-409 ($FeCl_3{\cdot}8.5H_2O$)				Shimadzu DT-40 ($FeCl_3{\cdot}8.8H_2O$)			
	OFW method			Kissinger's method	OFW method			Kissinger's method
α	Moles of H_2O lost	E/ kJ mol^{-1}	Mean E/ kJ mol^{-1}	E/kJ mol^{-1}	Moles of H_2O lost	E/ kJ mol^{-1}	Mean E/ kJ mol^{-1}	E/kJ mol^{-1}
0.05	0.325	31.5			0.34	44.0		
0.10	0.650	29.6			0.68	48.8		
0.15	0.975	31.2			1.02	42.1		
0.20	1.300	34.4			1.36	45.9		
0.25	1.625	35.4			1.70	44.0		
0.30	1.950	37.3			2.04	47.9		
0.35	2.275	37.3			2.38	47.9		
0.40	2.600	38.2			2.72	48.4	45.9	
0.45	2.925	38.2	33.6	28.0	3.06	53.6		
0.50	3.250	40.2			3.40	53.6	53.6	56.5
0.55	3.575	40.2			3.78	70.8		
0.60	3.900	42.1	41.1		4.08	78.5		
0.65	4.225	44.9			4.42	88.1		
0.70	4.550	51.6			4.76	90.0		
0.75	4.875	52.6			5.10	86.2		
0.80	5.200	52.6			5.44	93.8	84.5	80.4
0.85	5.525	52.6						
0.90	5.850	57.4						
0.95	6.175	57.4	52.7	56.5				

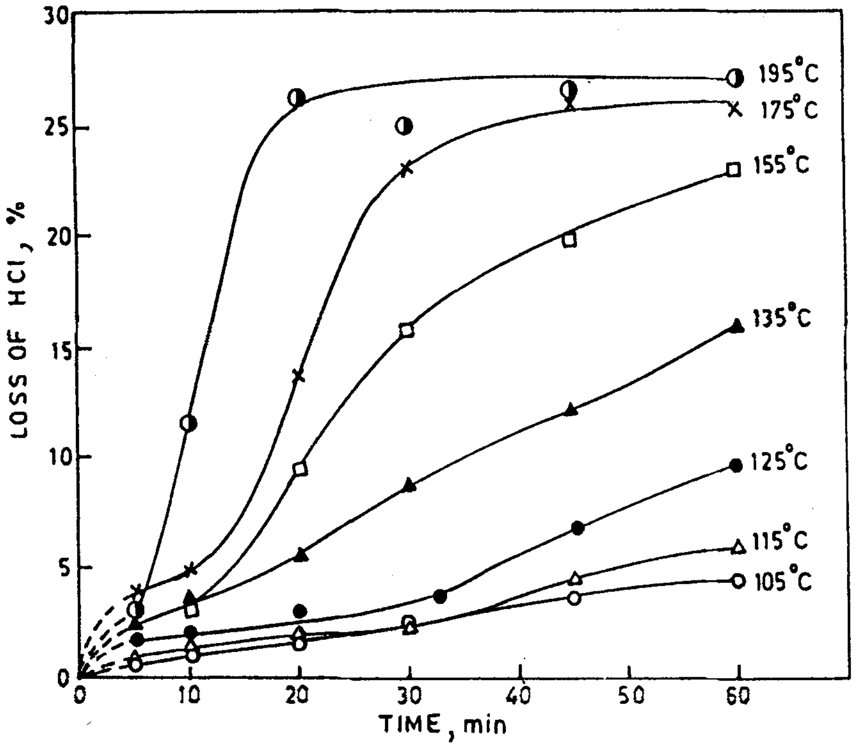

Fig. 4 Loss of HCl only as a function of time and temperature during isothermal heating of Fe(III) chloride hydrate

Integrating Eqs (2)–(4) it can be shown that

$$x_1 = (ak_1/k)[1-\exp(-kt)] \tag{5}$$

$$x_2 = (ak_2/k)[1-\exp(-kt)] \tag{6}$$

$$x = a[1-\exp(-kt)] \tag{7}$$

where, $k=(k_1+k_2)$.

Assuming that the rate constants follow Arrhenius equation, it can also be shown that

$$x_1/x_2 = k_1/k_2 = A_1/A_2[-\exp(E_1-E_2)/RT] \tag{8}$$

Equation (8) implies that the ratio of the products is constant i.e., independent of the initial concentration of the reactant. For parallel independent reaction the ratio of the products or the ultimate product yield is also independent of temperature i.e., $E_1=E_2$ [7]. Consequently, the E value for the overall reaction is same as that of individual reactions. Therefore, for such reaction

$$x_1/x_2 = k_1/k_2 = A_1/A_2 \tag{9}$$

However, at temperature above 130°C the rate of evaporation and consequent growth of the product phase is so rapid that diffusion (D_3) through the product phase becomes rate-controlling. As stated earlier, the E value for this mechanism is 25.8 kJ mol^{-1}, whereas for the dehydrochlorination reaction the E value is 57.7 kJ mol^{-1} up to 195°C. Since the temperature dependence of the latter reaction is higher, this step will be predominant at temperature higher than 130°C. In such a circumstance decomposition of Fe(III) chloride hydrate will proceed through parallel competitive reactions and condition in Eq (9) will be invalid. A comparison of the rate curves in Figs 4 and 6 clearly indicates that dehydrochlorination begins to take place only at 125°C and increases sharply up to 175°C, whereas the rate of loss of water does not show much increase beyond 155°C.

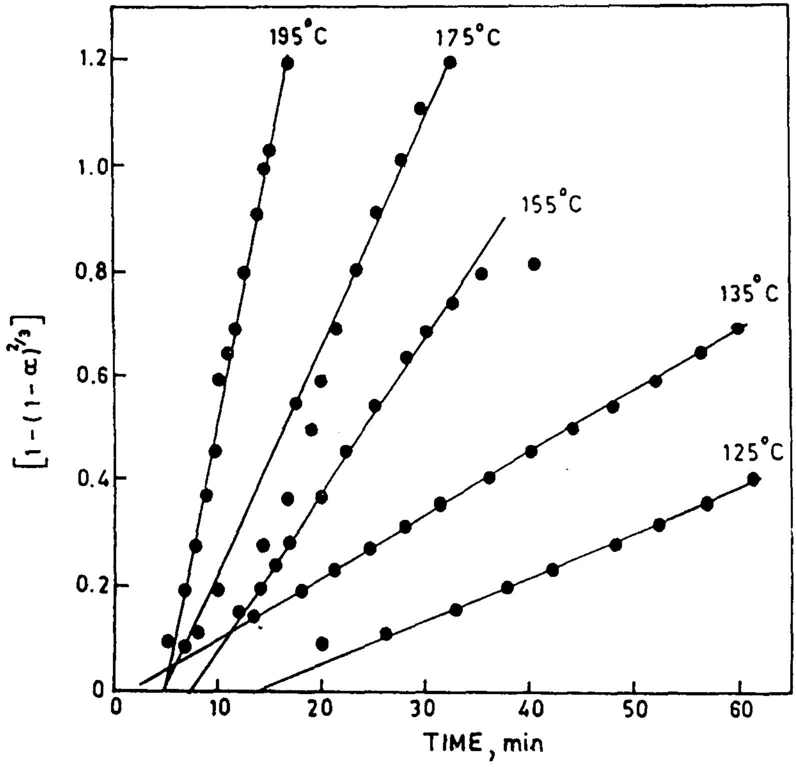

Fig. 5 Application of F1/3 kinetic model to the rate of HCl loss from Fe(III) chloride hydrate at different temperatures. Due to the complexity of the decomposition reaction before the attainment of steady temperature, the straight lines show intercepts on time axis

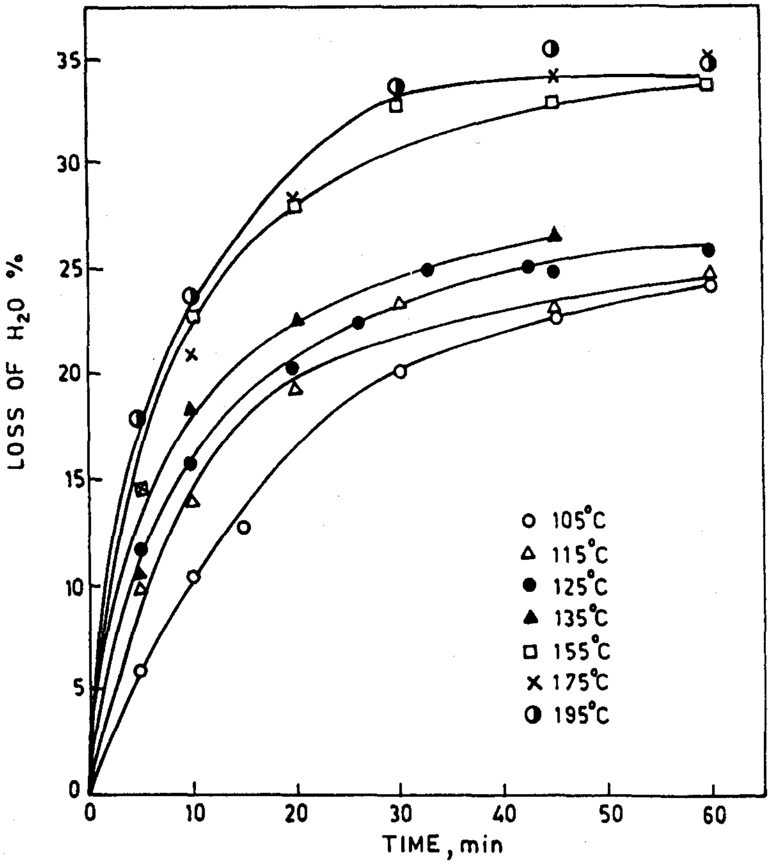

Fig. 6 Loss of H_2O only as a function of time and temperature during isothermal heating of Fe(III) chloride hydrate

Non-isothermal kinetics of dehydration and decomposition

Model independent method

The effect of heating rate on both DTA and TG traces provides opportunity to determine E values by the model independent method of Ozawa-Flynn-Wall (OFW) [8, 9]. According to this method plots of log(heating rate) *vs.* $1/T$ yield a series of straight lines for different values of α. If the E values calculated from the slopes of these lines do not show any significant variation (i.e., parallel lines) in the range of α studied then the reaction proceeds with the same mechanism. Table 3 gives the E values obtained by this method from the two TA equipments at different degrees of conversion. For STA-409 the E values increase from 30 kJ mol^{-1} at $\alpha=0.1$ to 57.5 kJ mol^{-1} at $\alpha=0.95$. This indicates that the mechanism of the overall mass loss changes with increase in α. However, a close examination of the data in Table 3

Table 2 Kinetic parameters for the isothermal dehydration and decomposition of $FeCl_3 \cdot 8H_2O$ and the corresponding thermodynamic functions for the formation of the activated complex

Mechanistic model	Temperature range/ °C	α-range	E/ kJ mol^{-1}	log$A$/ min^{-1}	r^2	$\Delta H^{\#}$/ kJ mol^{-1}	$-\Delta S^{\#}$/ J mol^{-1} K^{-1}	r^2
Loss of H_2O only								
F_2	105–135	0–0.40	57.2±2.0	6.57	0.9908	54.2±2.0	129.8	0.9896
F_1	125–155	0.37–0.76	36.9±7.1	3.21	0.9898	33.4±7.1	194.5	0.9808
D_3	105–175	0–0.65	25.8±0.1	1.00	0.9961	22.3±0.1	270.9	0.9949
Loss of HCl only								
$F_{1/3}$	125–195	0–0.95	54.2±0.6	5.04	0.9880	50.6±0.6	194.0	0.9863
Total (combined) mass loss								
D_3	105–135	0–0.41	51.7±1.5	3.88	0.9675	48.4±1.5	215.4	0.9629
D_1	155–195	0.41–0.92	57.7±1.5	4.84	0.9985	53.9±1.5	198.2	0.9983

suggests at least three sets of nearly close *E* values for the entire range of dehydration and decomposition. Thus, up to $\alpha=0.45$, corresponding to the loss of 2.92 moles of H_2O the average *E* value is 33.6 kJ mol^{-1}. In the range of $\alpha=0.50$–0.60 (loss of 4 moles of H_2O) the average *E* value is 41.1 kJ mol^{-1}. Finally, in the α range of 0.65–0.95 the average *E* value is 52.7 kJ mol^{-1}. These values are little lower than those found by isothermal method for combined loss, especially below $\alpha=0.6$. But the values are closer to those obtained for isothermal dehydration reaction.

However, the application of OFW method to the TG data derived from DT 40 equipment gives results which are somewhat different from the above. The *E* value up to the loss of about 2.72 moles of H_2O is reasonably constant (46 kJ mol^{-1}) but increases only by about 5 kJ for a further loss of about 0.7 mole of H_2O. These values are in good agreement with those obtained by the isothermal method. Further loss of about a mole of H_2O brings about sharp increase in the *E* value from 70.8 to 88.1 kJ mol^{-1} and remain essentially constant up to the loss of another mole of H_2O ($\alpha=0.80$) indicating that both dehydration and dehydrochlorination takes place in this region. Beyond $\alpha=0.80$ the overall mass loss data fails to follow OFW method and therefore no data is reported in Table 3. This difference in behavior between the two equipments is rather intriguing and may possibly be attributed to the difference in the design of the detectors.

From the shift in DTA peak temperature with increase in heating rate an attempt has been made to determine the *E* values by the Kissinger's method [10]. The DTA of Fe(III) chloride hydrate exhibits two major peaks, mainly due to dehydration and dehydrochlorination. However, in DT 40 an intermediate weak endothermic effect

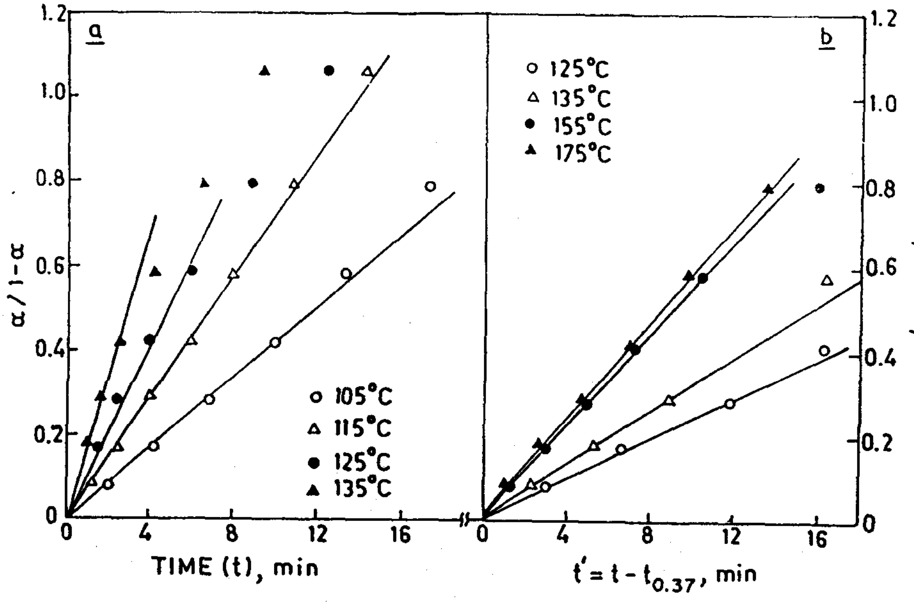

Fig. 7 Application of F_2 model, (a) to the initial stage ($\alpha=0$–0.37) and (b) to final stage ($\alpha=0.37$–0.80) of the H_2O loss

is also observed [1]. Figure 8 shows the plots of $\log(b/T_{m2})$ *vs.* $1/T_m$ for all these DTA peaks. It may be noted that the E values obtained by this method are in good agreement with those derived from OFW method (Table 3).

Model based methods

Since the non-isothermal mass loss data cannot distinguish between the two concurrent or parallel reactions it is rather difficult to derive meaningful kinetic parameters from such data. However, with the help of both DTA and DTG it has been possible to achieve some success to delineate predominantly dehydration regime from that of the combined effect of dehydration and decomposition. An attempt has therefore been made to determine the kinetic parameters from DTG curves using the four different methods namely, (i) Horowitz and Metzger [11], (ii) Coats and Redfern, [12], (iii) Maccallum and Tanner [13] and (iv) Zsakó and Zsakó [14]. All these four methods were examined for 21 kinetic model equations (Table 1); and one or two of these which exhibit highest correlation coefficients were selected as 'best fit' model. As the first two methods (HM and CR) were derived on the basis of order of reaction, application of the two methods to purely physical model of solid-state reaction is questionable. Therefore, in the case of diffusion-controlled reaction the results from these two methods have been omitted. All these computations were carried out in a PC-AT computer (IBM compatible) using suitable programs written in both BASIC and LOTUS 1-2-3.

Effect of heating rate

At low heating rate the two TA equipments yield different kinetic parameters by all the four methods for the same mechanistic model (F_2) for the first stage of dehydration. Thus, while STA-409 gives an average E value of 30 kJ mol^{-1} at 2°C min^{-1}, DT 40 gives an average E value of 61 kJ mol^{-1} by all the four methods at the heating rate of 4°C min^{-1}. This is possibly due to the difference in sensitivity of the two difference in sensitivity of the two different types of detector in the two equipments. At heating rate higher than 4°C min^{-1} the kinetic parameters obtained by all the four methods are closely similar and the results are summarized in Table 4.

Table 4 depicts not only the average values of E and $\log A$ but also the standard deviation (σ_0) which helps to compare the suitability of different methods for this particular reaction. It can be seen that using STA-409 HM method shows minimum deviation for the first step of dehydration, whereas both MT and ZZ methods show almost equally good result for the second step of dehydration and decomposition with D_1 as the 'best fit' mechanistic model followed by AJ model. All these data are in agreement with those obtained by isoconversion method of OFW.

With DT 40 equipment the first step of dehydration of $FeCl_3 \cdot 8.8H_2O$ also shows F_2 as the best fit model by all the four methods. However, CR method appears to give lowest standard deviation. Unlike STA-409 the TG curves obtained from DT 40 show a small intermediate step of dehydration corresponding to the loss of about 1.2 moles of H_2O for which F_2 model is also found to be valid. The standard

Table 4 Kinetic parameters for non-isothermal dehydration and decomposition of Fe(III) chloride hydrate as obtained by different methods using TG data at different rates of heating (5–20°C min^{-1})

	Netzsch, STA–409					
	1st stage of dehydration Temp. range: 60–70°C; α range: 0.025–0.420			2nd stage of decomposition Temp. range:140–270°C; α range: 0.46–0.99		
Method used	Kinetic model	Av. E/kJ mol^{-1}	Av. log$A$/s^{-1}	Kinetic model	Av. E/kJ mol^{-1}	Av. log$A$/s^{-1}
Horowitz	F2	51.60	4.22	–	–	–
& Metzger		(1.15)	(0.21)			
Coats &	F2	42.60	2.56	–	–	–
Redfern		(2.29)	(0.23)			
MacCallum	F2	40.90	2.52	D1	46.00	2.33
& Tanner		(2.43)	(0.23)		(3.00)	(0.31)
				AJ	37.70	0.31
					(2.55)	(0.30)
Zsakó &	F2	44.00	2.79	D1	47.00	2.37
Zsakó		(2.65)	(0.29)		(3.09)	(0.33)
				AJ	39.00	0.33
					(2.00)	(0.26)

Table 4 Continued

	Shimadzu, DT 40								
	1st stage of dehydration Temp. range: 60–115°C α range: 0.027–0.340			2nd stage of dehydration Temp. range: 115–180°C α range: 0.34–0.60			3rd stage of decomposition Temp. range: 175–230°C α range: 0.60–0.98		
Method used	Kinetic model	Av. *E*/ kJ mol^{-1}	Av. log*A*/ s–1	Kinetic model	Av. *E*/ kJ mol^{-1}	Av. log*A*/ s^{-1}	Kinetic model	Av. *E*/ kJ mol^{-1}	Av. log*A*/ s^{-1}
Horowitz & Metzger	F2	55.60 (1.52)	5.63 (0.22)	F2	30.60 (2.15)	1.19 (0.37)	–	–	–
Coats & Redfern	F2	49.10 (1.34)	3.96 (0.19)	F2	23.80 (2.67)	0.32 (0.40)	–	–	–
MacCallum & Tanner	F2	47.60 (1.35)	3.77 (0.18)	F2	22.40 (2.72)	0.41 (0.38)	D3	95.60 (9.24)	7.77 (1.12)
							D1	62.90	4.56
Zsakó & Zsakó	F2	50.50 (1.73)	4.15 (0.24)	F2	24.60 (2.97)	0.45 (0.48)	D3	97.30 (10.00)	8.01 (1.20)
							D1	67.00	5.02

Values within parentheses represent standard deviations for four heating rates

deviation data of the kinetic parameters obtained at different heating rates indicate the suitability of HM method with an average E value of 30 kJ mol^{-1}. The third step in TG which is predominantly a diffusion controlled process gives D3 as the best fit model. However, the E value for this step is higher (95.6 kJ mol^{-1}) than that obtained from the second step of STA-409. This value is however closer to those obtained from the isoconversion method of OFW in the α range of 0.7–0.8 and also from Kissinger's method [Table 3]. The high E value is possibly due to the narrow temperature range for this step in DT 40 compared to that of the second step in STA-409.

The effect of the variation of sample size on the kinetics of dehydration and decomposition of Fe(III) chloride hydrate has also been investigated using the thermograms derived from STA-409. It has been observed that increase in sample size from 15 mg to 53 mg has little effect on the kinetic parameters which are essentially similar as those observed in Table 4. Kinetic parameters for dehydration also

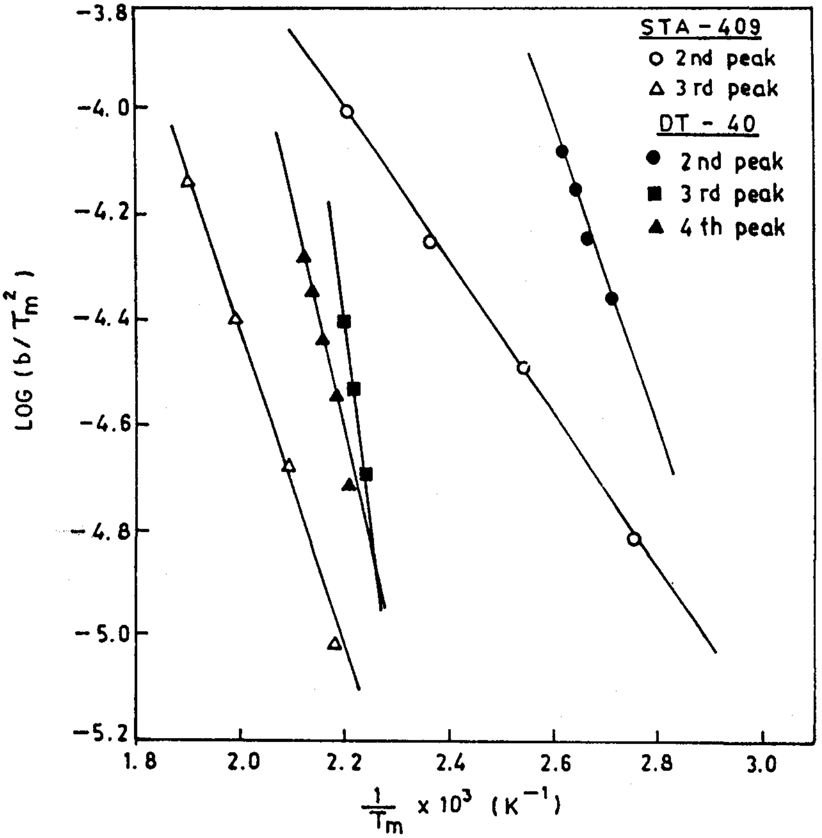

Fig. 8 Kissinger's plot for the different stages of dehydration and decomposition of Fe(III) chloride hydrate using DTA peak temperatures (T_m) at different heating rates (b, °C min^{-1})

do not show any significant variation even in flowing nitrogen (50 ml min^{-1}) environment.

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