Thermochimica Acta, 51 (1981) 175—189
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

COMBINED DIFFERENTIAL AND INTEGRAL METHOD FOR ANALYSIS OF NON-ISOTHERMAL KINETIC DATA

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(Received 12 May 1981)

ABSTRACT

The generally accepted integral and differential forms for analysis of non-isothermal kinetic data are

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp(-E/RT)\, dT$$

and

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT)\, f(\alpha)$$

Very often, these equations do not clearly and unambiguously indicate the reaction mechanism involved. The general trend to determine the mechanism on the basis of goodness of mathematical fit of data makes the task more formidable. Two other forms of integral and differential methods have been proposed to obviate this difficulty. These, in logarithmic forms, are

$$\ln g(\alpha) - \ln(T - T_0) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT}$$

and

$$\ln\left[\frac{\dfrac{d\alpha}{dT}}{f(\alpha)\left\{\dfrac{E(T-T_0)}{RT^2} + 1\right\}}\right] = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT}$$

The analysis, based on these two equations, requires a logical choice of the functions f(α) and g(α) by trying out in turn all the known forms available in literature. Amongst all the logical possibilities, the one with comparable E and A obtained for both the forms is suggestive of the possible reaction mechanism.

The equation (valid for linear rate of heating, β) is derived by replacing the time of reaction, t, by $(T - T_0)/\beta$. The differential form is solved by an iterative method to obtain consistent values of E and A.

Experimental data of thermal dehydroxylation of $Mg(OH)_2$, as published by Fong and Chen, are re-analyzed by these two methods. The results indicate that a diffusion-controlled mechanism is involved.

0040-6031/81/0000—0000/$02.75

INTRODUCTION

For analyses of kinetic problems, two different types of equations are used. One equates the rate of reaction with a function of α as

$$\frac{d\alpha}{dt} = k\, f(\alpha) \tag{1}$$

The other equates another function of α with reaction time (t) as

$$g(\alpha) = kt \tag{2}$$

Equations (1) and (2) are interrelated and, for isothermal cases, differentiation of eqn. (1) gives eqn. (2). The relationship between $f(\alpha)$ and $g(\alpha)$ is given by

$$f(\alpha) = \frac{1}{g'(\alpha)} \tag{3}$$

where

$$g'(\alpha) = \frac{d}{d\alpha}[g(\alpha)] \tag{3a}$$

The relationship between the kinetic constant (k) and temperature (T) of reaction is expressed by the well-known Arrhenius equation

$$k = A \exp(-E/RT) \tag{4}$$

It is believed that these relationships [eqns. (1)—(4)] are also valid for non-isothermal cases (at least, empirically). It may be argued that in this case, E and A will not have the same significance as they have for isothermal homogeneous reactions. To bypass this dilemma, it may be assumed that for non-isothermal heterogeneous reactions, E is the "derived activation energy" and A is the "derived frequency factor" (whatever may be their theoretical meanings).

For a constant heating rate (β), the relationship between temperature (T) and time (t) is

$$T = T_0 + \beta t \tag{5}$$

where T_0 = reaction onset temperature.

In order to obtain an overall relationship for non-isothermal kinetics, eqns. (1), (4) and (5) are combined to yield

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT)\, f(\alpha) \tag{6}$$

or

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp(-E/RT)\, dT \tag{7}$$

This, when integrated between proper limits, gives

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^{T} \exp(-E/RT)\, dT \tag{8}$$

TABLE 1

Different types of relationships for non-isothermal kinetics

Starting equations	Kinetic equations for non-isothermal reactions	
	Integral	Differential
(i) $\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\mathrm{f}(\alpha)$	$\mathrm{g}(\alpha) = \frac{A}{\beta}\int_0^T \exp(-E/RT)\,\mathrm{d}T$	$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp(-E/RT)\,\mathrm{f}(\alpha)$
(ii) $k = A\exp(-E/RT)$	Eqn. (10)	Eqn. (6)
(iii) $T = T_0 + \beta t$		
(i) $\mathrm{g}(\alpha) = kt$	$\mathrm{g}(\alpha) = \frac{A}{\beta}\exp(-E/RT)\,(T - T_0)$	$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp(-E/RT)\left[1 + \frac{E(T - T_0)}{RT^2}\right]\mathrm{f}(\alpha)$
(ii) $k = A\exp(-E/RT)$		
(iii) $T = T_0 + \beta t$	Eqn. (11)	Eqn. (14)

As the rate of reaction is very slow in the temperature range 0—T_0, the following approximation is assumed [1] to be valid

$$\int_{T_0}^{T} \exp(-E/RT)\,dT = \int_{0}^{T} \exp(-E/RT)\,dT \tag{9}$$

Hence, eqn. (8) assumes the form

$$g(\alpha) = \frac{A}{\beta}\int_{0}^{T} \exp(-E/RT)\,dT \tag{10}$$

When the values of α are known as a function of T, eqn. (10) is used to determine E and A. The exponential integral is evaluated with the help of various approximate solutions suggested [2—6] so far. When the reaction rate $d\alpha/dT$ is known as a function of T, eqn. (6) may be used to determine E and A.

Apart from eqns. (6) and (10), another set of relationships may be formulated if eqns. (2), (4) and (5) are combined to get

$$g(\alpha) = \frac{A}{\beta}\exp(-E/RT)\,(T - T_0) \tag{11}$$

On differentiation, eqn. (11) becomes

$$g'(\alpha)\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-E/RT) + \frac{A}{\beta}\exp(-E/RT)\frac{E}{RT^2}(T - T_0) \tag{12}$$

Or, on re-arrangement

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-E/RT)\left[1 + \frac{E(T-T_0)}{RT^2}\right]\frac{1}{g'(\alpha)} \tag{13}$$

Recalling eqn. (3), eqn. (13) may be rewritten as

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-E/RT)\left[1 + \frac{E(T-T_0)}{RT^2}\right]f(\alpha) \tag{14}$$

Equations (11) and (14) may also be taken as valid relationships for non-isothermal kinetics if the results obtained by analyzing non-isothermal data by these two methods can easily be explained logically. Thus, four different relationships, as tabulated in Table 1, are obtained for non-isothermal kinetics. To test their applicability some published data are re-analyzed by these methods.

ANALYSIS OF KINETIC DATA

Fong and Chen [7] have published some experimental data for the thermal dehydroxylation of $Mg(OH)_2$. Their data are reproduced in Table 2. For a single sample, they have taken duplicate data curves and denoted them as Traces 1 and 2 [cf. Fig. 2 of ref. 7]. A constant heating rate of $\beta = 0.0833$ K

TABLE 2

Data for the thermal dehydroxylation of $Mg(OH)_2$ [7]

Data point	Trace 1				Trace 2			
	Time (s)	T (K)	α	$(d\alpha/dT) \times 10^2$ (K^{-1})	Time (s)	T (K)	α	$(d\alpha/dT) \times 10^2$ (K^{-1})
1	0	618	0.0251	—	0	616	0.0229	—
2	48	622	0.0342	—	36	619	0.0275	—
3	84	625	0.0478	0.390	72	622	0.0344	0.336
4	120	628	0.0592	0.443	108	625	0.0528	0.427
5	168	632	0.0797	0.532	156	629	0.0619	0.527
6	204	635	0.0957	0.622	192	632	0.0780	0.603
7	240	638	0.1162	0.736	228	635	0.1055	0.690
8	276	641	0.1435	0.871	264	638	0.1284	0.793
9	324	645	0.1777	1.077	312	642	0.1583	0.958
10	360	648	0.2141	1.243	348	645	0.1950	1.103
11	408	652	0.2620	1.462	384	648	0.2202	1.261
12	432	654	0.2894	1.565	420	651	0.2661	1.426
13	468	657	0.3485	1.703	456	654	0.3165	1.590
14	504	660	0.4100	1.812	504	658	0.3762	1.787
15	552	664	0.4715	1.897	540	661	0.4289	1.902
16	588	667	0.5308	1.905	576	664	0.4977	1.972
17	624	670	0.5900	1.859	612	667	0.5528	1.982
18	672	674	0.6538	1.710	648	670	0.6147	1.914
19	708	677	0.7107	1.533	696	674	0.6789	1.668
20	744	680	0.7563	1.305	732	677	0.7294	1.342
21	792	684	0.7950	—	780	681	0.7706	—

s^{-1} was maintained throughout the experiment. Reaction onset temperature (T_0), which may be defined as a temperature at which α is negligibly small, is 618 K for Trace 1 (here $\alpha = 0.0251$) and 616 K for Trace 2 (here $\alpha = 0.0229$). Using the value of T_0, the time of reaction (i.e. t) may be calculated using

TABLE 3

Kinetic parameters obtained by various methods for the thermal dehydroxylation of $Mg(OH)_2$ as reported by Fong and Chen [7]

Compouting Method	Trace 1			Trace 2		
	E	A	n	E	A	n
Integral						
(i) Coats and Redfern [4]	231.45	0.37E + 16	1.5	235.91	0.91E + 16	1.5
(ii) Šatava [9]	232.39	0.38E + 16	1.5	236.90	0.95E + 16	1.5
Differential						
(i) Chen and Fong [8]	221.90	0.12E + 16	1.6	223.57	0.16E + 16	1.6

E = Derived activation energy (kJ $mole^{-1}$).
A = Derived frequency factor (s^{-1}).
n = Order of reaction.

TABLE 4

Kinetic functions (integral and differential forms) used for the present analysis

Function no.	Name of the function	Mechanism [a]	$g(\alpha)$	$f(\alpha)$
1	Parabolic law	Diffusion, 1D	α^2	$1/(2\alpha)$
2	Valensi (Barrer) eqn.	Diffusion, 2D	$\alpha + (1-\alpha)\ln(1-\alpha)$	$(-\ln(1-\alpha))^{-1}$
3	Ginstling–Brounshtein eqn.	Diffusion, 3D (cylindrical symmetry)	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	$\frac{3}{2}((1-\alpha)^{-1/3}-1)^{-1}$
4	Jander eqn.	Diffusion, 3D (spherical symmetry)	$[1-(1-\alpha)^{1/3}]^2$	$\frac{3}{2}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
5	Anti-Jander eqn.	Diffusion, 3D	$[(1+\alpha)^{1/3}-1]^2$	$\frac{3}{2}(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$
6	Zhuralev, Lesokin and Tempelman eqn.	Diffusion, 3D	$[\{1/(1-\alpha)\}^{1/3}-1]^2$	$\frac{3}{2}(1-\alpha)^{4/3}[\{1/(1-\alpha)^{1/3}-1\}]^{-1}$
7	Valensi–Carter eqn. [b]	Diffusion, 3D	$[(1+(Z-1)\alpha]^{2/3}+(Z-1)(1-\alpha)^{2/3}-Z)/(1-Z)$	$\frac{3}{2}(Z-1)^{-1}[\{1+(Z-1)\alpha\}^{-1/3}-(1-\alpha)^{-1/3}]$
8	Avrami-Erofeev eqn.	N and G ($n = 1$)	$-\ln(1-\alpha)$	$(1-\alpha)$
9	Avrami–Erofeev eqn.	N and G ($n = 1.5$)	$[-\ln(1-\alpha)]^{1/1.5}$	$\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$

10	Avrami—Erofeev eqn.	N and G ($n = 2$)	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[1-\ln(1-\alpha)]^{1/2}$
11	Avrami—Erofeev eqn.	N and G ($n = 3$)	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
12	Avrami—Erofeev eqn.	N and G ($n = 4$)	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
13		Contracting geometry (cylindrical symmetry)	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
14		Contracting geometry (spherical symmetry)	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
15	Mampel Power Law		α	1
16	Mampel Power Law		$\alpha^{1/2}$	$2\alpha^{1/2}$
17	Mampel Power Law		$\alpha^{1/3}$	$3\alpha^{2/3}$
18	Mampel Power Law		$\alpha^{1/4}$	$4\alpha^{3/4}$
19	Second order	Chemical reaction	$(1-\alpha)^{-1}-1$	$(1-\alpha)^{2}$
20	One and one-half order	Chemical reaction	$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$

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[a] N and G = nucleation and growth.

[b] Here Z = volume of product formed per unit volume of reactant consumed [21]. For the thermal dehydroxylation of $Mg(OH)_2$, $Z = 0.4535$.

the relationship [derived from eqn. (5)]

$$t = (T - T_0)/\beta \tag{5a}$$

Fong and Chen [7] used both differential and integral methods to analyze their data. For the differential method [eqn. (6)] they used a combined numerical method which was proposed by them [8]. To analyze the same data by the integral method [eqn. (10)], they employed the methods of Coats and Redfern [4] and Šatava [9]. They, after all these analyses, have concluded that the reaction obeys a kinetic law of the type

$$f(\alpha) = (1 - \alpha)^n \tag{15}$$

where n = order of reaction.

Different values of n, E and A, as reported by Fong and Chen [7], are given in Table 3. The results presented in Table 3 show that the values of E and A are comparable by the two methods of analysis — differential and integral forms; but the exponent n depicting the kinetic law is different. The reason for accepting $n = 1.6$ has not been stated by Fong and Chen [7], except that this value of n gives the best mathematical fit ($r = 0.999$) of the experimental data. In order to re-analyze these data by the new type of integral method as suggested here [eqn. (11)], it would be helpful to rewrite eqn. (11) in logarithmic form

$$\ln g(\alpha) - \ln(T - T_0) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \tag{16}$$

The data are fitted to eqn. (16) by linear least-squares method. Different published forms of g(α), as tabulated in Table 4, were used. The results obtained are given in Tables 5 and 6.

The new type of differential method [eqn. (14)] is non-linear in nature. This, in logarithmic form, becomes

$$\ln\left[\frac{\dfrac{d\alpha}{dT}}{f(\alpha)\left\{\dfrac{E(T - T_0)}{RT^2} + 1\right\}}\right] = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \tag{17}$$

Equation (17) may be solved by iterative method. Any arbitrary value may be assumed for E ($E > 0$) and, using this value, the value of the expression on the left-hand side may be calculated for each data point. This, when plotted against ($1/T$) by linear least-squares method, gives new values of E (from the slope) and A (from the intercept). This modified value of E is used as a starting value for the next iteration which yields another modified value of E. Thus, after a few iterations, consistent values of E and A will be obtained. Using all the forms of f(α), as tabulated in Table 4, these data were analyzed by eqn. (17) and the results are given in Tables 5 and 6.

The results clearly show that acceptable values of E and A are obtained only for the first seven functions (all of which denote a diffusion-controlled mechanism), leading to the conclusion that the thermal dehydroxylation process of $Mg(OH)_2$ is a diffusion-controlled process — a premise which is

TABLE 5

Results of analysis of the thermal dehydroxylation data of $Mg(OH)_2$ by integral [eqn. (16)] and differential [eqn. (17)] methods. Trace I

Mechanism [a]	Function No.	Integral method				Differential method			
		E (kJ mole^{-1})	A (s^{-1})	r	Variance	E (kJ mole^{-1})	A (s^{-1})	r	Variance
Diffusion	1	225.71	0.194E + 15	0.993	0.023594	209.10	0.885E + 13	0.956	0.102581
Diffusion	2	247.80	0.659E + 16	0.995	0.019807	242.43	0.235E + 16	0.979	0.064293
Diffusion	3	256.37	0.750E + 16	0.996	0.018252	255.33	0.590E + 16	0.985	0.050865
Diffusion	4	273.55	0.198E + 18	0.996	0.018626	280.51	0.674E + 18	0.992	0.030498
Diffusion	5	201.42	0.201E + 12	0.991	0.024043	191.05	0.319E + 11	0.944	0.113485
Diffusion	6	329.44	0.837E + 22	0.995	0.036930	357.29	0.129E + 25	0.999	0.007137
Diffusion	7	272.26	0.708E + 17	0.996	0.019246	277.60	0.975E + 17	0.990	0.036088
N and G	8	82.74	0.373E + 04	0.923	0.037093	124.78	0.701E + 07	0.990	0.007454
N and G	9	10.76	<1.0	0.256	0.045264	67.95	0.256E + 03	0.972	0.006847
N and G	10	–ve	<1.0	0.546	0.050037	–ve			
N and G	11	–ve	<1.0	0.829	0.055201	–ve			
N and G	12	–ve	<1.0	0.882	0.057990	–ve			
Cont. geom.	13	62.92	0.426E + 02	0.906	0.026970	91.73	0.270E + 04	0.943	0.026185
Cont. geom.	14	69.28	0.956E + 02	0.913	0.029783	102.55	0.363E + 05	0.967	0.018201
Power Law	15	45.32	0.297E + 01	0.868	0.021044	60.73	0.438E + 02	0.778	0.060622
Power Law	16	–ve	<1.0	0.789	0.037927	–ve			
Power Law	17	–ve	<1.0	0.889	0.046329	–ve			
Power Law	18	–ve	<1.0	0.912	0.050989	–ve			
Chemical reaction	19	129.22	0.259E + 08	0.931	0.079051	195.23	0.385E + 13	0.992	0.015843
Chemical reaction	20	104.82	0.125E + 06	0.930	0.053798	159.40	0.462E + 10	0.997	0.004160

[a] N and G = nucleation and growth.

TABLE 6

Results of analysis of the thermal dehydroxylation data of $Mg(OH)_2$ by integral [eqn. (16)] and differential [eqn. (17)] methods: trace 2

Mechanism [a]	Function No.	Integral method				Differential method			
		E (kJ mole^{-1})	A (s^{-1})	r	Variance	E (kJ mole^{-1})	A (s^{-1})	r	Variance
Diffusion	1	238.64	0.216*E* + 16	0.992	0.030665	226.34	0.215*E* + 15	0.968	0.089062
Diffusion	2	259.29	0.566*E* + 17	0.994	0.026921	257.10	0.361*E* + 17	0.984	0.055409
Diffusion	3	267.15	0.566*E* + 17	0.994	0.026355	268.83	0.738*E* + 17	0.988	0.043972
Diffusion	4	283.01	0.118*E* + 19	0.995	0.026502	291.77	0.564*E* + 19	0.994	0.026758
Diffusion	5	215.05	0.253*E* + 13	0.989	0.031934	208.75	0.837*E* + 12	0.958	0.100148
Diffusion	6	334.15	0.209*E* + 23	0.994	0.044026	361.60	0.309*E* + 25	0.998	0.009175
Diffusion	7	281.98	0.441*E* + 18	0.995	0.027545	289.56	0.928*E* + 18	0.998	0.031012
N and G	8	82.51	0.353*E* + 04	0.909	0.050211	126.28	0.956*E* + 07	0.992	0.006518
N and G	9	7.44	<1.0	0.166	0.061329	67.73	0.254*E* + 03	0.976	0.005952
N and G	10	—ve	<1.0	0.545	0.067800	—ve			
N and G	11	—ve	<1.0	0.811	0.074974	—ve			
N and G	12	—ve	<1.0	0.866	0.078702	—ve			
Cont. geom.	13	64.27	0.538*E* + 02	0.877	0.039291	96.22	0.167*E* + 05	0.961	0.019690
Cont. geom.	14	70.15	0.110*E* + 03	0.886	0.042363	106.08	0.712*E* + 05	0.977	0.013736
Power Law	15	47.97	0.474*E* + 01	0.832	0.032262	67.77	0.160*E* + 03	0.845	0.046984
Power Law	16	—ve	<1.0	0.752	0.054458	—ve			
Power Law	17	—ve	<1.0	0.868	0.065076	—ve			
Power Law	18	—ve	<1.0	0.895	0.070970	—ve			
Chemical reaction	19	124.70	0.112*E* + 08	0.918	0.091987	189.98	0.156*E* + 13	0.988	0.021500
Chemical reaction	20	102.62	0.826*E* + 05	0.912	0.067322	157.63	0.351*E* + 10	0.994	0.007239

[a] N and G = nucleation and growth.

TABLE 7

Results of analysis of the thermal dehydroxylation data of $Mg(OH)_2$ by the method of Coats and Redfern [eqn. (18)]: traces 1 and 2

Mechanism[a]	Function No.	Trace 1				Trace 2			
		E (kJ $mole^{-1}$)	A (s^{-1})	r	Variance	E (kJ $mole^{-1}$)	A (s^{-1})	r	Variance
Diffusion	1	350.12	0.416*E* + 26	0.988	0.092471	370.81	0.219*E* + 28	0.987	0.109099
Diffusion	2	372.37	0.155*E* + 28	0.992	0.068219	391.58	0.620*E* + 29	0.991	0.082829
Diffusion	3	380.92	0.179*E* + 28	0.993	0.059246	399.31	0.618*E* + 29	0.992	0.076132
Diffusion	4	398.03	0.489*E* + 29	0.995	0.044670	415.32	0.138*E* + 31	0.994	0.056549
Diffusion	5	325.96	0.413*E* + 23	0.984	0.103044	347.41	0.250*E* + 25	0.984	0.121512
Diffusion	6	454.05	0.214*E* + 34	0.999	0.007644	466.54	0.278*E* + 35	0.998	0.014714
Diffusion	7	396.87	0.178*E* + 29	0.995	0.045602	414.37	0.521*E* + 30	0.994	0.058112
N and G	8	207.04	0.122*E* + 15	0.997	0.006853	214.66	0.540*E* + 15	0.996	0.009022
N and G	9	134.48	0.196*E* + 09	0.997	0.002756	139.46	0.524*E* + 09	0.996	0.004374
N and G	10	98.14	0.231*E* + 06	0.997	0.001794	101.99	0.495*E* + 06	0.996	0.002427
N and G	11	61.80	0.261*E* + 03	0.997	0.000788	64.35	0.433*E* + 03	0.996	0.001302
N and G	12	43.67	0.915*E* + 01	0.996	0.000685	45.55	0.133*E* + 03	0.995	0.000858
Cont. geom.	13	187.32	0.129*E* + 13	0.993	0.014022	196.40	0.759*E* + 13	0.992	0.017442
Cont. geom.	14	193.68	0.299*E* + 13	0.995	0.010961	202.35	0.162*E* + 14	0.995	0.013604
Power Law	15	169.65	0.821*E* + 11	0.987	0.023467	180.00	0.609*E* + 12	0.987	0.027768
Power Law	16	79.54	0.575*E* + 04	0.985	0.005930	84.66	0.157*E* + 05	0.985	0.007232
Power Law	17	49.32	0.221*E* + 02	0.983	0.002802	52.88	0.444*E* + 02	0.983	0.003353
Power Law	18	34.26	0.161*E* + 01	0.980	0.001626	36.97	0.259*E* + 01	0.980	0.002014
Chemical reaction	19	253.51	0.101*E* + 19	0.999	0.003369	256.73	0.199*E* + 19	0.999	0.002585
Chemical reaction	20	229.14	0.449*E* + 16	0.999	0.002008	234.75	0.137*E* + 17	0.999	0.003044

[a] N and G = nucleation and growth.

contra-indicated by Fong and Chen [7]. From a physical point of view also, it appears probable that on decomposition (in the solid state) $Mg(OH)_2$ forms a solid layer of MgO covering the surface of $Mg(OH)_2$. So, for further reaction to occur, the product molecules of H_2O must diffuse out through the solid layer of MgO. With time (t) the thickness of the product layer (i.e. diffusion path) will increase. Under such circumstances the likelihood of a diffusion-controlled mechanism cannot be ruled out.

To pin-point the exact kinetic law, the results obtained should be examined more critically. It is obvious that for the proper functional forms of $g(\alpha)$ and $f(\alpha)$, the results obtained by integral method [eqn. (16)] should closely agree with those obtained by differential method [eqn. (17)]. This condition is satisfied when Function No. 3, i.e. Ginstling—Brounshtein's equation, is used. So, it may be concluded that the thermal dehydroxylation process of $Mg(OH)_2$ obeys Ginstling—Brounshtein's equation. It would, perhaps, not be irrelevant here to note that many other solid-state reactions which are diffusion-controlled follow Ginstling—Brounshtein's equation [10,11].

Other kinetic parameters for this thermal dehydroxylation process are

(i) $E \doteq 256$ kJ mole^{-1} and $A \doteq 7.5 \times 10^{15}$ s^{-1} (Trace 1)

(ii) $E \doteq 267$ kJ mole^{-1} and $A \doteq 6.0 \times 10^{16}$ s^{-1} (Trace 2)

For comparison, these data were also analyzed by the method of Coats and Redfern [4] which is based on eqn. (10). The form of the equation proposed by them is

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \tag{18}$$

All the forms of $g(\alpha)$, as tabulated in Table 4, were used to fit the data to eqn. (18). Fong and Chen [7] have also analyzed their data by the method of Coats and Redfern. As a check, we have independently analyzed these data by the method of Coats and Redfern and the results obtained by us, which agree with those reported by Fong and Chen [7], are given in Table 7. It is seen that the values of correlation coefficients (r) for most of the cases are greater than 0.990. So, it is rather difficult to pin-point the exact form of $g(\alpha)$ unequivocally. Fong and Chen [7], however, proposed Function No. 20, i.e. $f(\alpha) = (1 - \alpha)^{1.5}$, as the proper kinetic law. But the idea of ascertaining the kinetic law chiefly from the value of correlation coefficient has been objected to by Šesták [12]. Therefore, it is difficult to draw logically acceptable conclusions regarding reaction mechanistics from the results tabulated in Table 7. But, when the results obtained from eqns. (16) and (17) are examined, it is easily possible to identify the proper kinetic law and to rule out others. These two methods are therefore more sensitive than other methods so far as the logical discrimination is concerned.

DISCUSSION

Equation (14) has been derived earlier by various authors [13—15]. MacCallum and Tanner [13] pointed out that the rate $d\alpha/dt$ of a reaction under non-isothermal reaction should be written as

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T + \left(\frac{\partial \alpha}{\partial T}\right)_t \left(\frac{\partial T}{\partial t}\right)_\alpha \tag{19}$$

Thus

$$\frac{d\alpha}{dt} \neq \left(\frac{\partial \alpha}{\partial t}\right)_T$$

Unless

$$\left(\frac{\partial T}{\partial t}\right)_\alpha = 0$$

According to them, eqn. (6) should not be used for non-isothermal reactions and eqn. (19) should be used instead; various arguments have been given [16—18] against this proposal. It has been shown [17] that the term $(d\alpha/dT)_t$ has no physical meaning, because one cannot change temperature (T) keeping time (t) constant. Even if, for argument's sake, we assume that instantaneous change is possible, $\partial\alpha$ must be zero, because α cannot change instantaneously. But what is more important is that α is a path function and not a state function, so eqn. (19) is not valid thermodynamically.

Fevre et al. [14] have published a special review on the methods of analysis of non-isothermal kinetics. They have pointed out that the rate of reaction ($d\alpha/dt$) with non-isothermal kinetics depends upon a supplementary factor: the heating rate (β). They have stressed on the fact that the degree of conversion (α) of reaction is a function of three variables: T (temperature), t (time) and β (heating rate). Thus the total differential $d\alpha$ is, according to them

$$d\alpha = \left(\frac{\partial \alpha}{\partial t}\right)_{T,\beta} dt + \left(\frac{\partial \alpha}{\partial T}\right)_{t,\beta} dT + \left(\frac{\partial \alpha}{\partial \beta}\right)_{t,T} d\beta \tag{20}$$

Using eqn. (20) they have deduced relationships similar to eqn. (11) [cf. eqn. (10) of ref. 14] and eqn. (14) [cf. the equation given on p.432 of ref. 14]. They have used these relationships to analyze the TG data of the thermal dehydration of gypsum, calcium sulfate hemihydrate and calcium oxalate monohydrate, under non-isothermal conditions (with various heating rates). The results obtained with this method of analysis led them to believe that theoretical formulations of eqns. (11) and (14) are correct.

Later, Norwisz [15] also proposed a relationship similar to eqn. (14) which is based on eqn. (19). This was subjected to severe criticism [19]. The objections were raised chiefly from a mathematical point of view. But there is no doubt regarding the applicability of eqns. (11) and (14) for non-isothermal kinetics simply because the results obtained therefrom are logically acceptable. Still, the deductions of these two equations will not be free from mathematical discrepancies if eqn. (19) or (20) is used as a starting equation. However, the procedure followed by the present authors to arrive at eqns. (11) and (14) is free from any mathematical inconsistency.

A casual glance at eqn. (14) will lead one to conclude that insertion of an

F factor, where

$$F = 1 + \frac{E(T - T_0)}{RT^2} \tag{21}$$

will give higher values of $d\alpha/dT$ than those predicted by eqn. (6). The present authors, however, subscribe to the views expressed by Šesták [19] that the reactions really do not proceed faster under non-isothermal conditions, as was erroneously concluded by Norwisz [15].

Koch et al. [20] have analyzed kinetic data of some uni- and biomolecular reactions by using eqns. (6) and (14). They observed that the results obtained closely agree with isothermal experiments when eqn. (6) was used to analyze non-isothermal kinetic data. But, using the same data, the values of E and A become much less when analyzed using eqn. (14) than those obtained from isothermal analysis. This led them to conclude that eqn. (14) should not be applied to non-isothermal analyses.

As observed by Šesták [12], it is necessary to focus attention on "the reliability of the $g(\alpha)$ function, the correct establishment of which should be the real goal of chemical kinetics". Only after having logical forms of $g(\alpha)$ and $f(\alpha)$ should one determine the corresponding E and A values therefrom. We therefore believe that Koch et al. [20] would possibly have concluded differently had they tried to fit all the functional forms of $f(\alpha)$, as tabulated in Table 4, into eqn. (14); this would clearly indicate the most logically acceptable form of $f(\alpha)$. After establishing the proper form of $f(\alpha)$, the corresponding E and A values should be determined, otherwise one may arrive at a wrong conclusion. For example, if one analyzes the thermal dehydroxylation data of $Mg(OH)_2$ as shown here (Table 2), from eqn. (6) one obtains [7] a kinetic function of the form

$$f(\alpha) = (1 - \alpha)^{1.5} \tag{22}$$

with $E = 229.14$ kJ mole^{-1} (for Trace 1) and $E = 234.75$ kJ mole^{-1} (for Trace 2) [cf. Table 7]. But when the same data are re-analyzed by eqn. (14) using the same $f(\alpha)$ as shown in eqn. (22), it is observed that $E = 159.40$ kJ mole^{-1} (for Trace 1; cf. Table 5), and $E = 157.63$ kJ mole^{-1} (for Trace 2; cf. Table 6). The reason for this drastic decrease in the value of E is not due to the fault of eqn (14), it is due to the faulty assumption that the process obeys a kinetic law as shown in eqn. (22). If, on the other band, Ginstling—Brounshtein equation is used for $f(\alpha)$ (cf. Table 4) reasonable values of E will be obtained, e.g. $E = 255.33$ kJ mole^{-1} (for Trace 1; cf. Table 5), and $E = 268.83$ kJ mole^{-1} (for Trace 2, cf. Table 6). It thus becomes evident that if the data are analyzed by eqn. (14), all the forms of $f(\alpha)$ should be used so as to single out the most probable form of $f(\alpha)$, values of E and A are to be determined thereafter.

CONCLUSIONS

Differential [eqn. (14)] and integral [eqn. (11)] methods are proposed for the analysis of non-isothermal kinetics. Derivations of these two laws do not involve any mathematical or thermodynamical discrepancy.

When non-isothermal kinetic data are analyzed by these two methods, both the methods yield reasonably good results. The two methods are sensitive enough to enable discrimination of the proper mechanistic model of the reaction in an unambiguous way.

Various criticisms were raised against these methods when they were proposed earlier. Attempts have been made here to discuss some of those objections in a logical manner.

Both the methods [eqns. (16 and (17)] are suitable for computer programming for fast computations.

ACKNOWLEDGEMENT

The authors wish to thank Prof. H.S. Ray (I.I.T., Kharagpur) for his helpful comments and suggestions in writing this paper.

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