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Selection of the kinetic equations for isothermal conditions by means of statistical criteria

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Abstract

The analytical models for three different chemical reactions/processes in isothermal–isobaric conditions have been studied. The analysis of the degree of conversion versus time, temperature and initial parameter interdependences enables the kinetics to be approximated by means of many $g(\alpha)$ functions or even by the polynomial relationships which include the independent variables time, temperature, their interactions, etc. The evaluation and analysis of the isokinetic effect, if supplemented by some further information, provide the possibility of suggesting the most probable kinetic equation from many $g(\alpha)$ values used.

LIST OF SYMBOLS

a, b	coefficients
$a_0, a_1, a_2, a_{1,1}, a_{2,2}, a_{1,2}$	coefficients of polynomial approximation (22)
A	frequency constant in Arrhenius equation/min^{-1}
A, B, C, D	labels for chemical compounds
c	molar concentration/mol dm^{-3}
c_0	initial molar concentration/mol dm^{-3}
E	activation energy/J mol^{-1}
$f(\alpha)$	symbol of the function representing the process mechanism
F	F test
$g(\alpha)$	weight integral
k	reaction rate constant/min^{-1}
k_1, k_2	reaction rate constants of the different dimensions
n	reaction order
N	number of measurements
p	parameters derived by means of statistical procedures
r	chemical reaction rate/mol dm^{-3} min^{-1}
R	universal gas constant ($R = 8.314$ J mol^{-1} K^{-1})

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R^2	determination coefficient for functions of one and many variables/%
t	temperature/°C
T	temperature/K
V	volume/dm^3
x_1, x_2	dimensionless independent variables of (1) time and (2) temperature in the range $\in \langle -1, +1 \rangle$

Greek symbols

α	degree of conversion
α_0	initial degree of conversion
ε	porosity, $0 \leq \varepsilon \leq 1$
ν	stoichiometric coefficients
τ	time/min

Subscripts

A, B, C, D	refer to chemical compounds

TABLE 1

List of $f(\alpha)$ and $g(\alpha)$ functions

Mechanism	$f(\alpha)$	$g(\alpha) = \int_0^{\alpha} d\alpha/f(\alpha)$
F1	$1-\alpha$	$-\ln(1-\alpha)$
F2	$(1-\alpha)^2$	$\alpha(1-\alpha)^{-1}$
F3	$(1-\alpha)^3$	$\frac{\alpha(2-\alpha)(1-\alpha)^{-2}}{2}$
R1	$(1-\alpha)^0 \equiv 1$	α
R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
D1	α^{-1}	$\frac{\alpha^2}{2}$
D2	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
D3	$(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$\frac{3}{2}[1-(1-\alpha)^{1/3}]^2$
D4	$[(1-\alpha)^{-1/3}-1]^{-1}$	$\frac{3}{2}\left[1-\frac{2\alpha}{3}-(1-\alpha)^{2/3}\right]$
A1	$\alpha(1-\alpha)$	$\ln\frac{\alpha}{1-\alpha}$
A2 [a]	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3 [a]	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$

[a] The Kekam, JMA, or Avrami–Erofeev equation.

1. INTRODUCTION

The description of solid state reactions in terms of integrated functions $g(\alpha)$ derived from the function $f(\alpha)$ (see Table 1) can be disputed on the grounds that the statistical procedures may be inadequate. As a result, the process mechanism may not always be properly explained by the above mentioned functions. The isokinetic relationship between E and A

$$\ln A = a + bE \tag{1}$$

is often found for isothermal–isobaric and non-isothermal (dynamic) conditions for various systems [1–15].

TABLE 2

Theoretical kinetic models for homogenic reactions in isothermal conditions

Eqn. no.	Model/formula	Assumptions
(2)	$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$	T = constant; V = constant; pressure, not taken into account
(3)	$r_A = -\mathrm{d}c_A/\mathrm{d}\tau = k_1 c_A^{n_A} c_B^{n_B} - k_2 c_C^{n_C} c_D^{n_D}$	Reversible reaction $k_1, k_2 > 0$
(4)	$\mathrm{d}\alpha/\mathrm{d}\tau = k_1 (c_{0A})^{n_A+n_B-1}(1-\alpha)^{n_A}\left(\frac{c_{0B}}{c_{0A}} - \frac{\nu_B}{\nu_A}\alpha\right)^{n_B} - k_2 (c_{0A})^{n_C+n_D-1} \frac{\nu_C^{n_C}\nu_D^{n_D}}{\nu_A^{n_C+n_D}} \alpha^{n_C+n_D}$	
(5)	$\mathrm{d}\alpha/\mathrm{d}\tau = k(1-\alpha)^{n_A}\left(\frac{c_{0B}}{c_{0A}} - \frac{\nu_B}{\nu_A}\alpha\right)^{n_B}$	Irreversible reaction, $k_2 = 0$, $k = k_1(c_{0A})^{n_A+n_B-1}$
(6)	$\mathrm{d}\alpha/\mathrm{d}\tau = k(1-\alpha)^{n_A+n_B} = k(1-\alpha)^n$	When $c_{0B}/c_{0A} = \nu_B/\nu_A = 1$, $n_A + n_B = n$

2. THEORETICAL KINETIC MODELS

Usually kinetic models deal in concentration terms, but if α is defined as the extent of the reaction, then for the reversible reaction (2) (see Table 2), provided some further assumptions are made, the generalisation in terms of α can be written in the form of eqn. (6), as can also be compared from eqns. (2)–(5) in Table 2.

$$\mathrm{d}\alpha/\mathrm{d}\tau = k(1-\alpha)^n \tag{6}$$

or formulated in the general form

$$\mathrm{d}\alpha/\mathrm{d}\tau = kf(\alpha) \tag{7}$$

Then, writing limits $\tau = 0$, $\alpha = \alpha_0$ we finally obtain

$$\int_{\alpha_0}^{\alpha} \mathrm{d}\alpha/f(\alpha) = \int_0^{\alpha} \mathrm{d}\alpha/f(\alpha) - \int_0^{\alpha_0} \mathrm{d}\alpha/f(\alpha) = g(\alpha) - g(\alpha_0) = k\tau \tag{8}$$

The aim of our work is to analyse procedures of the selection of the $g(\alpha)$ function for isothermal experiments, which is sufficient to describe the kinetics of the chemical reactions. The examples were selected both from among kinetic models theoretically assumed and empirical equations obtained by fitting the measurements taken for the individual reaction proceeding in time (τ) at various isothermal levels (T). Thus the symbol $[\tau * T]$ is used in our paper to designate such isothermal conditions. Knowledge of the stoichiometric coefficients, the initial concentration and if possible the initial value of the degree of conversion (α_0) of the reaction determined under non-isothermal conditions is essential for use of eqn. (8). The most common forms of the $g(\alpha)$ functions analysed are shown in Table 1. Functions which can involve reversible reaction (4), i.e. those incorporating the extent of reaction having some defined powers, with the + sign on the right side of eqn. (7), have not been included in Table 1.

2.1. Example I

The progress of the irreversible, isothermal ($t = 174$°C) reaction of esterification in the liquid phase for the initial conditions $c_{0B}/c_{0A} = 1.4$, $\nu_B = \nu_A = 1$, provided that $n_A = n_B = 1$ and the degree of conversion changes as follows: α (τ/min), 0.05 (0), 0.23 (5), 0.56 (20), 0.71 (35), 0.82 (50), 0.86 (65), 0.91 (80), 0.93 (95), 0.95 (110), 0.96 (125), 0.97 (140), has been described on p. 132 of ref. 16. As is evident from Fig. 1 the kinetic model (5) (see also Table 2)

$$\mathrm{d}\alpha/\mathrm{d}\tau = k(1-\alpha)(1.4-\alpha)$$

in its integral form can be substituted by the Jander equation (Table 1, D3 model), which fulfils the conditions of thermal dissociation for spherical molecules in the diffusion range. It is hard to believe, however, that the progress of the homogenous and practically irreversible esterification is described by means of the above mentioned interpretation. Neglecting the effect of $g(\alpha_0) = 0.00043$ (i.e. $g(\alpha_0) \approx 0$), results in the conclusion that the D3 model is an approximation of the actual kinetic mechanism which can be used without the need to determine the initial condition and to specify chemical eqn. (2). It is worth noting that in this particular case so called dissipations or residues of the experimental data from the improperly selected models with reference to the zero line are distinctive and sharply shaped. The worst approximation is given by the A1 model.

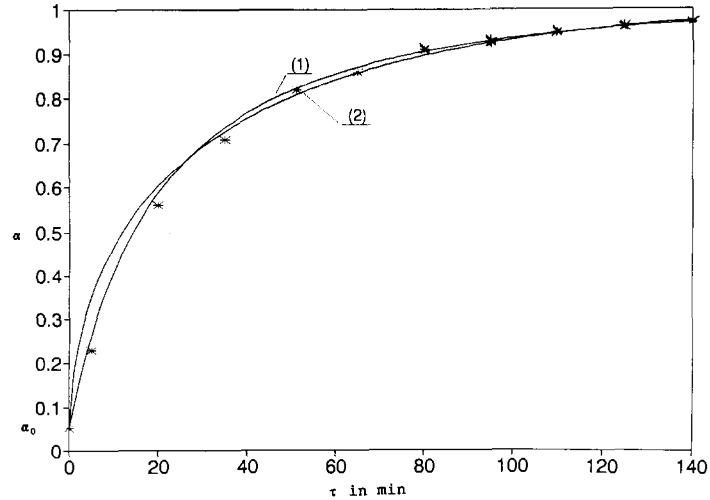

Fig. 1. The effect of time on conversion degree: comparison of experimental data (*) with those obtained according to the kinetic and D3 ($\alpha_0 = 0.05$) models (——). Curve 1, $(2.5 \ln(1.4-\alpha)/(1-\alpha)) - 0.8785 = 0.0410\tau$; $R^2 = 99.94\%$, $F = 15639.5$. Curve 2, $(3/2)(1-(1-\alpha)^{1/3})^2 - 0.00043 = 0.0053\tau$; $R^2 = 99.81\%$, $F = 5239.5$.

3. KINETIC MODELS DERIVED FROM MEASUREMENTS OF THE [$\tau * T$] TYPE AT POLYISOTHERMAL LEVELS

If we take measurements by changing time for constant temperature and next repeating the process at another isothermal level, then taking into account the Arrhenius rule, eqn. (8) can be shaped to the form

$$g(\alpha) - g(\alpha_0) = A e^{-E/RT} \tau \tag{9}$$

Two possible kinetic approximations result from eqn. (9)

$$\ln \frac{g(\alpha) - g(\alpha_0)}{\tau} = \ln A - \frac{E}{RT} \tag{10}$$

and

$$\ln[g(\alpha) - g(\alpha_0)] = \ln A - \frac{E}{RT} + p \ln \tau \tag{11}$$

Intuitively the statistical parameter p introduced in eqn. (11) should be close to unity, which underlines the time influence, but p can also take values of $0 < p < 2$.

The new forms of the $g(\alpha)$ functions can be generated if we assume the significance of p in the kinetic equation, for $p \neq 1$

$$[g(\alpha) - g(\alpha_0)]^{1/p} = k\tau \tag{12}$$

The parameter p, if one omits $g(\alpha_0)$ (assuming $g(\alpha_0) = 0$), is important when discussing the differentiation of the F1, A2 and A3 models (Table 1), which after transformations may reduce to one dependence. For $p = 2$ the D3 model converts to the R3 one. The discussion suggests trying to build new forms of the $g(\alpha)$ function by modification of the first order kinetic notation.

$$f(\alpha) = \frac{1-\alpha}{1+\alpha} \qquad g(\alpha) = -\alpha - 2\ln(1-\alpha) \tag{13}$$

Mechanism $(-\mathrm{R1} + 2\mathrm{F1})$

$$f(\alpha) = \frac{1-\alpha}{1+(1-\alpha)} = \frac{1-\alpha}{2-\alpha} \qquad g(\alpha) = \alpha - \ln(1-\alpha) \tag{14}$$

Mechanism $(\mathrm{R1} + \mathrm{F1})$

$$f(\alpha) = \frac{1-\alpha}{1+(1-\alpha)^{1/2}} \qquad g(\alpha) = 2[1-(1-\alpha)^{1/2}] - \ln(1-\alpha) \tag{15}$$

Mechanism $(\mathrm{R2} + \mathrm{F1})$

$$f(\alpha) = \frac{1-\alpha}{1+(1-\alpha)^{1/3}} \qquad g(\alpha) = 3[1-(1-\alpha)^{1/3}] - \ln(1-\alpha) \tag{16}$$

Mechanism $(\mathrm{R3} + \mathrm{F1})$

The functions (13) are used to describe the kinetics of the Boudouard reaction, $C + CO_2 \rightleftharpoons 2CO$ [17]. It can be easily seen that dependences (13) to (16) are not equivalent to the definition in eqn. (5).

The selection of the $g(\alpha)$ function is realised using the R^2 and F statistical tests and by assuming that $F > F_{\mathrm{critical}}$. In this particular case there is no need to revise the degree of freedom of the determination coefficient R^2. For the different ln A values eqns. (10) and (11) will have a common factor of $(-E/R)$.

3.1. *Example II*

The results of the thermal dissociation of $CaCO_3$ in a specially designed thermobalance at constant (0.533 kPa) CO_2 pressure, whilst changing the time from 30 to 75 min and the temperature from 750 to 850°C, and a maximal α value of 0.16, have been presented in ref. 18. Twenty measurements ($N = 20$) of the $[\tau * T]$ type have been taken. The calculations using eqns. (13)–(16) by means of the correlations (10) and (11) are performed for the functions shown in Table 1 (excluding the A1 model). The final result is

$\mathrm{F3} > \mathrm{F2} > (2\mathrm{F1} - \mathrm{R1})$

$(R^2/\% = 99.87 > 99.84 > 99.83)$

$F = 14037 > 11340 > 10871$

All the models formed are statistically significant at the 0.01 level. For the F3 model $E = 218.84\ \mathrm{kJ\ mol^{-1}}$ and $\ln A = 17.540$.

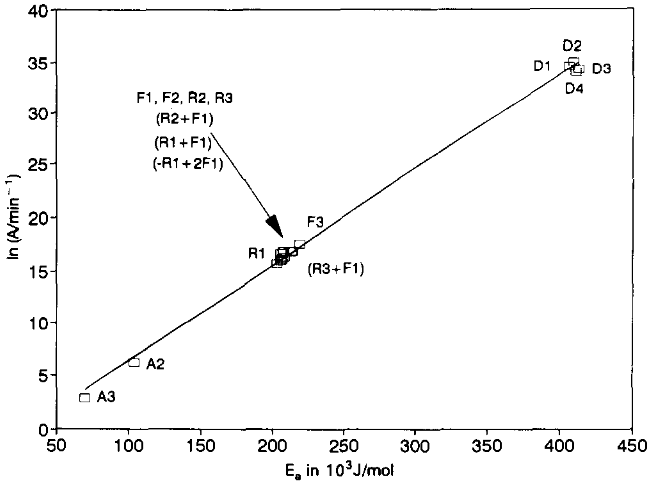

Fig. 2. Isokinetic effect of the thermal $CaCO_3$ dissociation reaction from the selection of sixteen forms of the $g(\alpha)$ function: $\ln A = -2.702 + 0.0912 \times 10^{-3}E$ ($R^2 = 99.75\%$; $F = 5598.9$).

For low values of the extent of reaction α we obtain

$$f(\alpha) = \frac{1-\alpha}{1+\alpha} \approx (1-\alpha)^2$$

This makes eqn. (13) close to the F2 mechanism. Comparison with refs. 12, 18–20 shows there are different possibilities for the description of this process; for example, with a model of the R or F type ($n = 0, 2/3, 1$) or with equations of the Kekam type, especially with the exponent of 1/2 [12]. On the basis of the temperature criterion [10, 16] one obtains an activation energy E of 203.1 kJ mol^{-1} which is consistent with the analysis of the isokinetic effect giving for these data $E = 210$–220 kJ mol^{-1} (Fig. 2). The resulting F3 model is difficult to interpret, but by referring to Maciejewski [12] one can try to explain it by the influences on its subsequent progress of the polymorphic conversions and sintering of calcium carbonate at the non-isothermal stage of the reaction.

4. THEORETICAL KINETIC MODELS BASED ON [$\tau * T$] MEASUREMENTS

4.1. Experimental

To continue the discussion, complex investigations of the following reaction in the liquid phase have been performed:

$$2NH_4Cl + Na_2CO_3 \rightleftharpoons (NH_4)_2CO_3 + 2NaCl \quad (17)$$

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O \quad (18)$$

This reaction is of major importance in the coke industry, where we find the necessity of conversion of non-volatile ammonia, occurring mainly as NH_4Cl, into volatile substances that can be eliminated from the waste water before its recirculation as coke quenching medium or its final purification. The investigations were performed in a tank reactor packed (for 7 examples amongst the 8 analysed) with rings or cylinders of the appropriate porosity and capacity 100 cm^3 (Table 3). The substrates of reaction (17) were used at a concentration of about 2.5 g dm^{-3}. The stoichiometric amount of Na_2CO_3 solution at approximately the desired temperature was added quickly to the reactor containing NH_4Cl solution preheated to the required temperature. Mixing was realised by passing of heated air. Time was measured starting from the complete addition of the second reagent. The pressure was fixed at 0.981 kPa (100 mm H_2O) using a water-suction pump. The reactor was of the periodic type. Thus after some time the reaction mixture was removed and the molar concentration of NH_4Cl was determined by means of an indirect method (by total ammonia). The following settings were applied to perform the analysis: time ranged from 5 to 20 min with 5 min steps; isothermal levels were changed from 50 to 90°C in 10 K steps. Seven series of measurements with the packed reactor and one with the unpacked one were performed using the full procedure, which gives for each series $4 \times 5 \times 2 = 40$ measurements, which makes $40 \times 8 = 320$ in total.

4.2. Discussion

Assuming that A is NH_4Cl, B is Na_2CO_3 and $\tau = 0$, $\alpha_0 = 0$, for the following measurements settings: $c_{0B}/c_{0A} = \nu_B/\nu_A = 1/2$, one can anticipate a reaction order of 2 as the most probable (before 3 or 1), according to eqn. (5).

The calculation cycle was performed for the linear formulae (10) and (11), taking the $g(\alpha)$ values shown in Table 1 (except for the A1 model). The following procedures were used: (a) for each series separately, i.e. $N = 40$ measurements; (b) taking the average from all the series to obtain one set of data $N = 40$ measurements; (c) accumulating the measurements for all the series to obtain one set of data of $N = 8 \times 40 = 320$ points.

Although $g(\alpha)$ functions were supplemented with the forms that take into account the inadequacy of the initial stages, i.e. unfitted stoichiometry, $c_{0B}/c_{0A} = 1$, $\nu_B = \nu_A = 1/2$, $n_A = 2$ or 1 and $n_B = 1$

$$f(\alpha) = (1-\alpha)^2(2-\alpha) \qquad g(\alpha) = \frac{1}{1-\alpha} - \ln\frac{2-\alpha}{1-\alpha} \tag{19}$$

$$f(\alpha) = (1-\alpha)(2-\alpha) \qquad g(\alpha) = \ln\frac{2-\alpha}{1-\alpha} \tag{20}$$

TABLE 3

Results of calculations identified as the most advantageous

Procedure according to Section 4.2	Dimensions of the bed elements/mm^2	Bed porosity ε	Mechanism	Activation energy E_a/kJ mol^{-1}	Frequency constant according to eqn. (10): $\alpha_0 = 0$, ln(A/min^{-1})	R^2/%	F test	N [a]
(a)	1.65 × 5.4	0.35	D3	79.60	21.890	95.42	791.4	40
(a)	50% 1.65 × 5.4 50% 2.3 × 6.1	0.39	F2	63.87	18.945	85.94	232.3	40
(a)	2.3 × 6.1	0.43	F2	67.29	20.372	84.44	206.1	40
(a)	3.0 × 10.06	0.46	F2	60.73	17.932	85.45	223.2	40
(a)	50% 3.0 × 10.06 50% 4.3 × 14.5	0.63	D3	67.53	17.773	94.86	701.6	40
(a)	4.3 × 14.5	0.80	D3	70.68	19.030	95.64	833.8	40
(a)	Fenski rings ($\varnothing = 3.6$ mm)	0.23	D3	70.78	18.738	92.17	447.1	40
(a)	Reactor without fulfilment	$\equiv 0$	D2	94.75	27.566	94.09	605.4	40
(b)	For middle concentrations, 1st–8th rows	–	D2	76.06	21.375	98.26	2151.2	40
(c)	For whole collection of data	–	F3/F2	70.75/57.63	22.004/17.098	81.23/ 79.80	1376.7/ 1256.2	320

[a] N is the number of measurements.

they appeared to be inadequate and were abandoned after the calculation cycle.

The best calculation results are shown in Table 3. The following conclusions for procedure (a) can be drawn from the details of the calculations (not shown):

(i) With a few exceptions for the A3 model, according to eqn. (10) all the analyses show the significance of the $g(\alpha)$ models.

(ii) Models A2 and A3 (according to eqn. (11)) appeared to be identical, giving one function $g(\alpha) = [-\ln(1-\alpha)]^{1-2}$, which means weakening of the time factor influence.

(iii) Equation (1) determines the differentiation of the Arrhenius equation parameters for eqns. (10) and (11) with determination of coefficient $R^2 = 98$–99.8%.

Let us omit discussion of the isokinetic effect proved for procedures (b) and (c) ($R^2 = 98.1$–98.7%) and analyse it for the data of the most advantageous calculation from Table 3.

As is apparent from Fig. 3 the relations fall along two straight lines of the one common equation

$$\ln A = 1.069 + 0.27 \times 10^{-3} E \qquad (R^2 = 85.74\%,\ F = 54.1) \tag{21}$$

To make it more convincing let us analyse the same data plotted as activation energy versus bed porosity (Fig. 4(a)). The lowest activation energy state can be ascribed to the bed porosity $\varepsilon = 0.46$, i.e. close to the

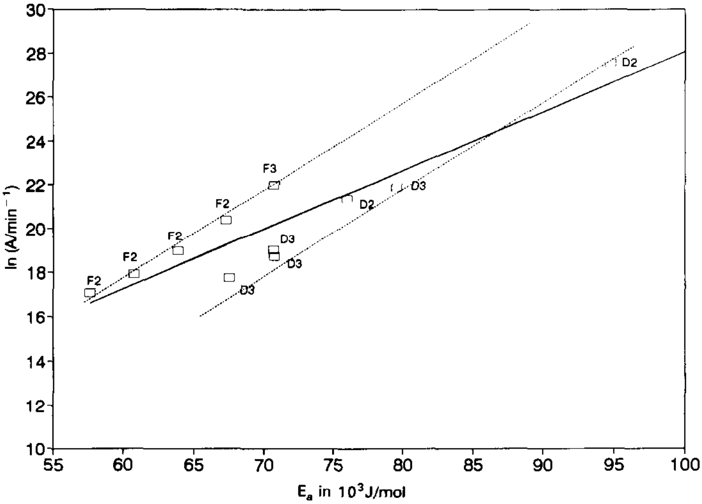

Fig. 3. Isokinetic effect for reactions (17) and (18) from their different settings, systematisation of the experimental data and the best selection of the $g(\alpha)$ function.

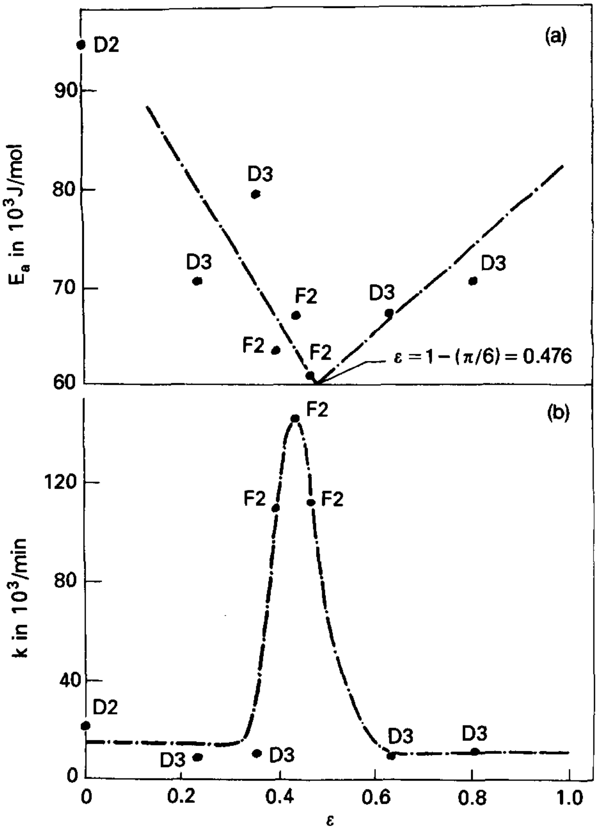

Fig. 4. Influence of bed porosity ε on (a) activation energy and (b) reaction rate constant at $t = 90°C$.

porosity of spheres in a rectangular prism ($\varepsilon = 1 - (\pi/6) = 0.476$). The second order kinetics as referred to the NH_4Cl conversion describes the process in this case. The isokinetic effect was found and the dependence of the reaction rate constant on the bed porosity at $t = 90°C$ according to the Arrhenius equation is shown in Fig. 4(b). If unified according to eqn. (7) the reaction rate constant can be separated into two levels differentiating the order and characterised by the common reciprocal time dimension. This example illustrates that description of the experimental results by the kinetic equation derived from the theoretical kinetic model requires some approximations, i.e. both F2 and D3(D2) models are correct.

5. INTERPRETATION OF [$\tau * T$] MEASUREMENTS BY MEANS OF THE POLYNOMIAL APPROXIMATION

The analysis of the kinetics of the chemical reaction resolves itself into determining the rate of the conversion process with time and temperature. The results of the measurements and analyses suggest that from the above mentioned parameters the influence of time seems to be dominated by the temperature effect. Finally it is worth finding the polynomial approximation correlating the experimental data to solve the problem definitely. Transforming the independent variables of time (x_1) and temperature (x_2) into the dimensionless interval of $\in \langle -1, +1 \rangle$ we obtain

$$\begin{aligned} &\alpha = a_0 + a_1 x_1 + a_2 x_2 + a_{1,1} x_1^2 + a_{2,2} x_2^2 + a_{1,2} x_1 x_2 \\ &x_1 \in \langle -1, +1 \rangle \qquad x_2 \in \langle -1, +1 \rangle \end{aligned} \tag{22}$$

One can precisely estimate the effect of each factor on the conversion process; then statistically insignificant factors can be eliminated by analysing the F test, and even an extrapolation to α_0 for the actual time of $\tau = 0$ can be performed. The mathematical formalism and procedures detailed in ref. 21 are omitted in this paper.

For the thermal dissociation of $CaCO_3$ (analysed in Example II) we obtain

$$\begin{aligned} &\alpha = 0.0447 + 0.0212 x_1 + 0.0508 x_2 + 0.021 x_2^2 + 0.0184 x_1 x_2 \\ &x_1 = \frac{2\tau - 105}{45} \qquad x_2 = \frac{2t - 1600}{100} \\ &(R^2 = 99.59\%, F = 904.9, N = 20) \end{aligned} \tag{23}$$

Estimating separately the effects of each factor for the degree of conversion the following order of importance can be observed: temperature (75.12%), time (14.54%), interaction of time and temperature (5.44%), squared temperature (4.49%), which makes a total of $R^2 = 99.59\%$. Thus the temperature effect distinctly dominates the time influence.

A similar analysis for reactions (17) and (18) (procedure (b)) gives the following final results:

$$\begin{aligned} &\alpha = 0.3220 + 0.1073 x_1 + 0.2362 x_2 + 0.0715 x_2^2 + 0.0404 x_1 x_2 \\ &x_1 = \frac{2\tau - 25}{15} \qquad x_2 = \frac{2T - 686}{40} \\ &(R^2 = 99.21\%, F = 1095.3, N = 40) \end{aligned} \tag{24}$$

Thus for the average data derived from procedure (b) the individual factor effects are as follows: temperature (77.65%), time (17.80%), squared temperature (2.49%) and interaction (1.26%), making a total of $R^2 = 99.21\%$.

Assuming $x_2 = 0$ (arithmetic mean for minimum and maximum temperatures), the linear effect of time on the degree of conversion becomes clear ($\alpha = 0.322 \pm 0.1073$, $x_2 = 0$). Further, the extrapolated $\alpha_0 = 0.042$ was used to perform the next correlations based on eqn. (9) and linearisation represented by eqns. (10) and (11) for procedure (b). The best results, as previously, were obtained for the diffusion models D2, D4, D3 and D1, but in this group the F2 mechanism also appears of significance in the form of the following equation:

$$\frac{\alpha}{1-\alpha} - 0.0438 = 13.656 \times 10^7 e^{-62586.8/RT} * \tau$$
$$(R^2 = 97.74\%, F = 1647.3) \tag{25}$$

It can be concluded by comparison with the analysis of the results from Section 4.2 that diffusion models labelled D are less sensitive to the initial extent of reaction ($\tau = 0$). Hence a distinct difference from the approach based on the theoretical model arises, which requires the introduction of the above mentioned parameter into the equation analysed. It can also be seen that the discussion of the kinetic model was enriched by using the polynomial approximation (24) resulting in the final eqn. (25) (see Fig. 5).

6. CONCLUSIONS

By analysing the conversion as a function of time, temperature and initial parameters in isothermal–isobaric conditions and assuming the irreversibility of the reaction as comes from the theoretical kinetic and empirical approaches, the following conclusions have been drawn.

The kinetic model, involving initial parameters (including stoichiometric coefficients) of the chemical reaction can be approximated by some $g(\alpha)$ functions, but the interpretation of the mechanism so concluded may be difficult. For the unknown kinetic model the selection of $g(\alpha)$ functions can be performed on the basis of statistical tests. The final result obtained would not, however, necessarily represent the actual reaction mechanism. In isothermal tests of the experimental system $[\tau * T]$, distinctive differentiation of the Arrhenius equation parameters can be anticipated, which results in the isokinetic effect. The effect can be explained by the predominant influence of the temperature factor compared to the time factor, as can be proved by the polynomial approximation (22).

It appears that results of kinetic studies cannot be described by an infinite group of $g(\alpha)$ functions. In this work some new forms of the function shown in eqns. (12)–(16) and (19), (20) have been proposed. These functions very often describe the process in a statistically adequate manner. The multiple possibilities of process/reaction paths are also emphasised by such an approach; those distinctly inconsistent with the actual process are then abandoned. Knowing the initial conversion α_0 is of major importance, in particular for selecting many of the $g(\alpha)$ functions for the equations closely related to the kinetic theoretical model (Fig. 5).

Some supporting parameters (for example, bed porosity), if used to interpret the isokinetic effect referring to the conditions of the chemical

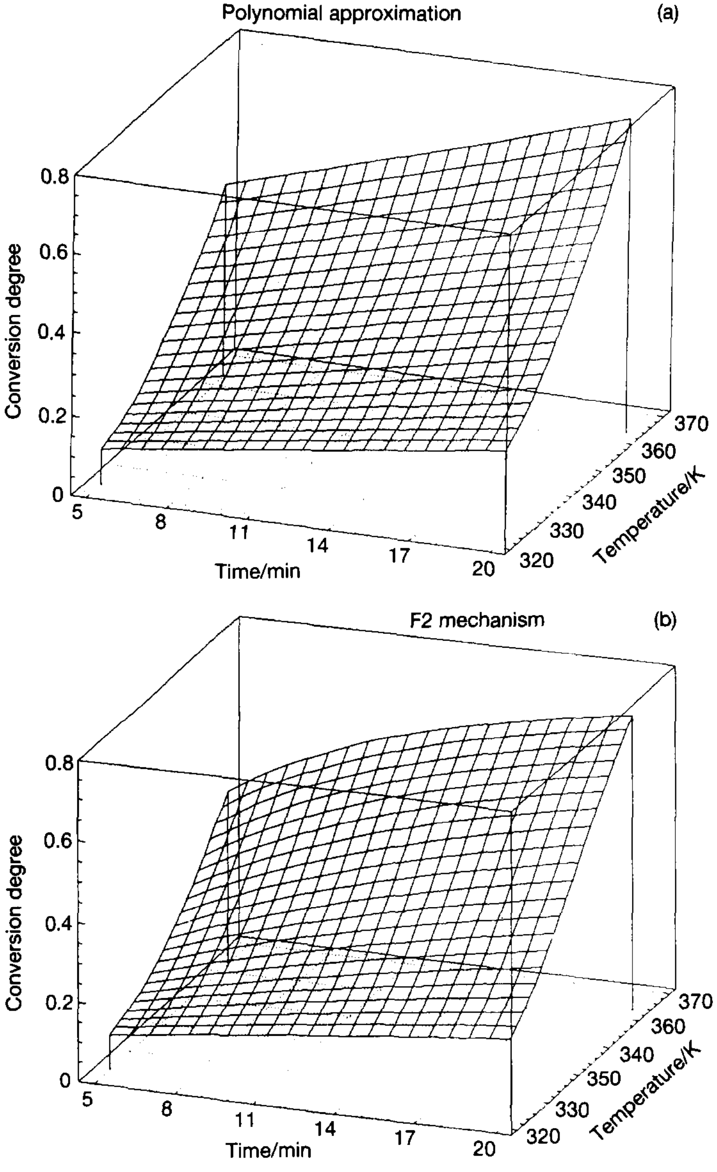

Fig. 5. Conversion degree of NH_4Cl as a function of time and temperature: (a) according to eqn. (24); (b) according to eqn. (25).

reactions performed, can give much information. It has been shown that the reaction rate constant determined for individual temperatures depends upon the above mentioned parameter (Fig. 4(b)). This fact can perhaps be explained by the different definitions of the kinetic constants, of reversed time dimension, by eqn. (3) and the general eqn. (7).

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