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A COMPUTER METHOD TO DETERMINE THE KINETIC LAW OF SOLID-STATE REACTIONS FROM DSC CURVES

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ABSTRACT

A computer program has been worked out to evaluate the activation energy, the Arrhenius pre-exponential factor and the mechanism of solid-state reactions from non-isothermal measurements. A univocal determination of the reaction mechanism is obtained by the simultaneous application of two selection criteria: (a) activation energy value by the Ozawa method; (b) degree of linearity in the Šatava method.

A modification of the Rogers and Smith method was then used to obtain empirically complete agreement between kinetic expression and experimental results when the kinetic law has to be improved to account for a whole experimental curve.

The accuracy of the computer method has been checked through a calibration of the program by means of 16 theoretical functions proposed by Šesták.

INTRODUCTION

The problem of deriving kinetic parameters from curves obtained under non-isothermal conditions has been faced by many authors and some of them transposed their method into computer programs: while a complete review can be found in ref. 1, a successive work by Škvára and Šesták[2] pointed out the difficulty to obtain a univocal determination of the kinetic parameters by such treatments.

Various laws can be reasonably proposed to describe the mechanism of reactions in solids. The problem lies in choosing the most suitable of them for each experimental case studied. The criteria of such a choice must be the most general and, at the same time, sufficiently restrictive to discriminate not arbitrarily among different sets of parameters.

Škvára and Šesták proposed 3 criteria for choice:

(a) the interval of linearity in the plot of the integral function $g(\alpha)$ vs. $1/T$, α being the transformed fraction of reagent at temperature T (Šatava method[3]);

(b) the minimum value of the standard deviation in the considered interval of α;

(c) the value of the pre-exponential factor of the Arrhenius law, Z, which must lie between 10^4 and 10^{24} sec^{-1}.

Such a procedure, however, does not enable one to distinguish among different nucleation mechanisms[2].

A preliminar evaluation of activation energy, E, by the Kissinger[4, 5] and Ozawa[5] methods has been recently suggested to overcome this difficulty[6, 7]. Both methods, in fact, when applied to recrystallization of copper, gave E and Z in good agreement with the isothermal data.

A prosecution of this work has been undertaken by transferring the method into a computer program to favour the choice among very similar mechanisms.

METHOD

Several analytical methods from the literature are applied to DSC peaks step by step, while rejecting the mechanisms unsuitable to account for the experimental thermograms or yielding erroneous parameters.

First of all, an analysis of the peak shifts as a function of the heating rate Φ is carried out. The T_m temperature of the maximum of the peaks and T_α temperature at constant α transformed fraction are employed to obtain respectively the plots by Kissinger ($\ln\Phi/T_m^2$ vs. $1/T_m$) and Ozawa ($\log \Phi$ vs. $1/T_\alpha$). The activation energy is then obtained from the slope of these straight lines, without making any hypothesis as to the mechanism acting in the process examined. These methods are quite general for reactions occurring through a single mechanism at T_m or α transformed fraction[5] and avoid the risk of achieving false kinetic parameters as occurs with methods based on more restrictive assumptions[8].

Then, single peak analysis by the Šatava method is undertaken and the energies obtained from different $g(\alpha)$ functions are compared with the values previously determined from Kissinger and Ozawa plots.

The $g(\alpha)$ function is defined as in ref. 3

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{ZE}{R\Phi}\,p(x) \qquad x = -\frac{E}{RT}$$

being, as in ref. 1,

$$f(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p$$

The agreement of the energy values from all the methods is the principal criterium of selection among various mechanisms which has been adopted to eliminate the uncertainties expressed by Škvára and Šesták[2]. Their discriminating criterium, degree of linearity in the Šatava plot, is then applied to make a choice among kinetic laws giving acceptable E values.

In practical cases[1, 6, 9], the plot of $\log g(\alpha)$ vs. $1/T$ for the best integral function may have a degree of linearity well below 90–100%. Such a theoretical $g(\alpha)$, therefore, does not account for the whole progress of the process investigated. In order to make up for this misfit an empirical $f(\alpha)$ function is taken into consideration, the n exponent

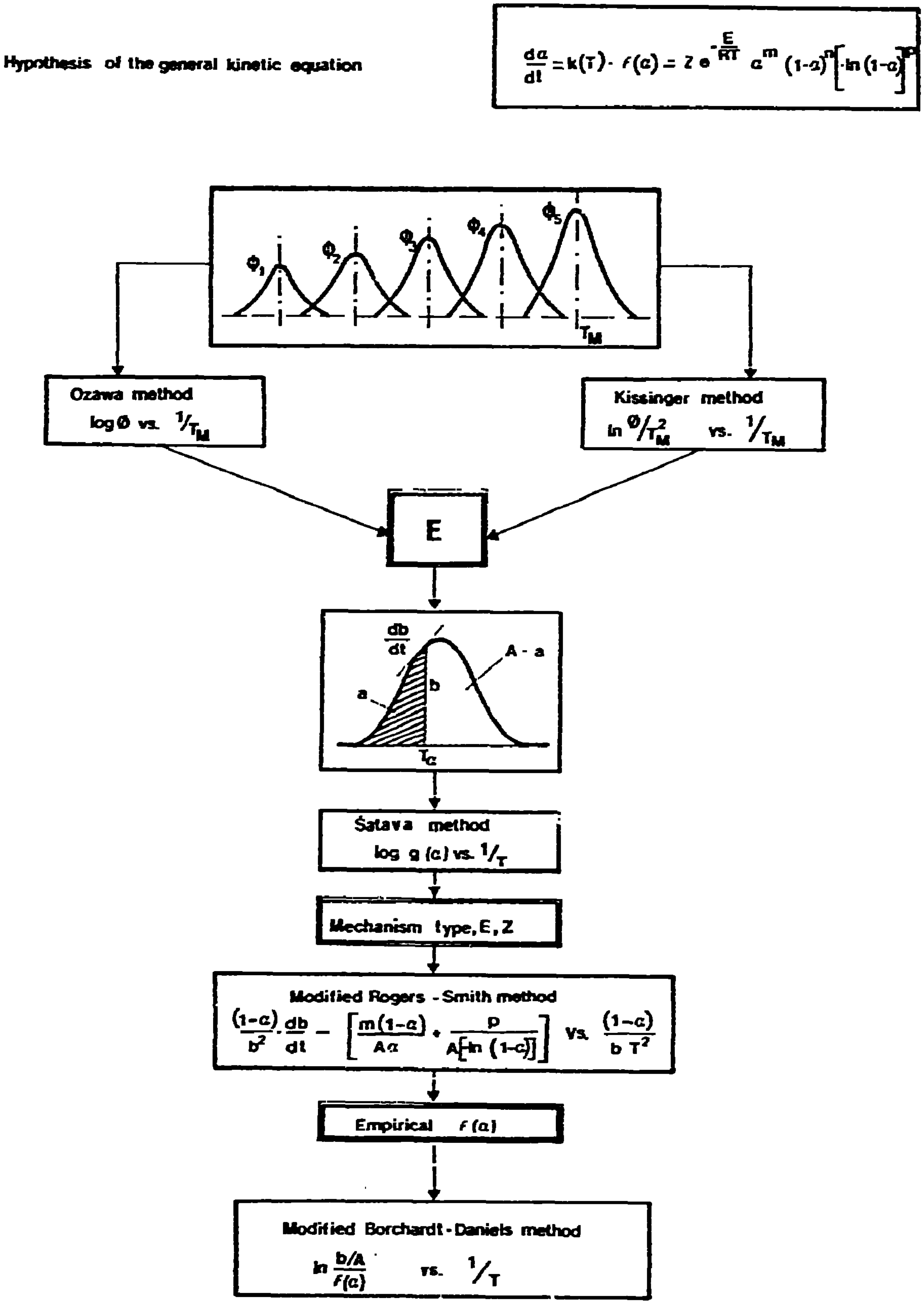

Fig. 1. Scheme to determine kinetic parameters and law followed in the computer program.

of which is drawn from the Rogers and Smith method modified by Lucci and Tamanini[6] through the expression:

$$\frac{db}{dt} = b^2 \left[\frac{m}{A\alpha} - \frac{n}{A(1-\alpha)} + \frac{p}{A(1-\alpha)[-\ln(1-\alpha)]} + \frac{\Phi E}{RT^2} \cdot \frac{1}{b} \right]$$

where b is the distance of the DSC curve from the baseline and A the total subtended area.

Following Šesták[1], m and p in the above formula are alternatively set to zero; the non-null exponent is given the value obtained by differentiating the known g(α); E and n are deduced from the slope and the intercept at the origin of the straight line in the plot of

$$\frac{(1-\alpha)}{b^2} \cdot \frac{db}{dt} = \left[\frac{m(1-\alpha)}{A\alpha} + \frac{p}{A[-\ln(1-\alpha)]} \right]$$

against $(1-\alpha)/b \cdot T^2$. Z is computed by starting from the condition $db/dt = 0$ at the maximum of the peak[6]. Agreement of E with the previously obtained values and a low standard deviation permit to accept the empirical kinetic law. Finally, as a test of validity of the new f(α), the approximated modified Borchardt–Daniels formula[6]

$$\ln \frac{b}{A \cdot f(\alpha)} = -\frac{E}{RT} + \ln Z$$

is applied to re-evaluate E and Z. Figure 1 represents the exposed method schematically.

PROGRAM

The program is written in FORTRAN IV language.

Input data are the following: the Φ heating rates and the T_α temperatures at which a maximum occurs for each corresponding peak, the number of peaks to be examined and, for each of them, the N number of experimental points, their h scanning interval, the initial temperature, the b deflections from the baseline.

A standard least-square technique is used to compute slopes and intercepts of all plots.

The α transformed fractions are computed from the beginning of the peak for every successive temperature step by using the Simpson integration method. The transformed fraction at the maximum of the peak is computed too, as a control of its constant value.

The Šatava method is applied to a set of 16 kinetic equations involving theoretical g(α) functions which represent reaction mechanisms in the solid state[6]. These are listed in Table 1 together with the corresponding f(α) function derived by Šesták[10].

The simple linear Doyle approximation[1, 6], sufficiently good in the range $20 < x < 60$, which covers a large number of experimental cases, is used for p(x) function.

The interval of linearity of the plot of log g(α) vs. $1/T$ expressed in per cent of the

TABLE 1

KINETIC FUNCTIONS

$g(\alpha)$	$f(\alpha)$	*Symbol*	*Type*
α^2	α^{-1}	D1	Diffusion
$(1 - \alpha)\ln(1 - \alpha) + \alpha$	$[-\ln(1 - \alpha)]^{-1}$	D2	
$[1 - (1 - \alpha)^{1/3}]^2$	$(1 - \alpha)^{1/3}[-\ln(1 - \alpha)]^{-1\,a}$	D3	
$(1 - 2/3\alpha) + (1 - \alpha)^{2/3}$	$[-\ln(1 - \alpha)]^{-1\,a}$	D4	
$1 - (1 - \alpha)^{1/2}$	$(1 - \alpha)^{1/2}$	B1	Phase boundary reaction
$1 - (1 - \alpha)^{1/3}$	$(1 - \alpha)^{2/3}$	B2	
$[-\ln(1 - \alpha)]$	$(1 - \alpha)$	N1	Nucleation
$[-\ln(1 - \alpha)]^{2/3}$	$(1 - \alpha)[-\ln(1 - \alpha)]^{1/3}$	N2	
$[-\ln(1 - \alpha)]^{1/2}$	$(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$	N3	
$[-\ln(1 - \alpha)]^{1/3}$	$(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$	N4	
$[-\ln(1 - \alpha)]^{1/4}$	$(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$	N5	
$\alpha^{1/4}$	$\alpha^{3/4}$	P1	Power law
$\alpha^{1/3}$	$\alpha^{2/3}$	P2	
$\alpha^{1/2}$	$\alpha^{1/2}$	P3	
α	1	P4	
$\alpha^{3/2}$	$\alpha^{-1/2}$	P5	

[a] According to Šesták [10].

considered range (namely $0.01 < \alpha < 0.99$), is determined by rejecting one by one in successive iterations the points which depart from the straight line by more than a certain value of accuracy, established in advance (usually, when examining experimental data, accuracy is set[2] to 10%).

The derivatives, db/dt, at temperature T, are evaluated by means of an approximated numerical formula, derived from definite difference interpolation formulae and similar to the one proposed by Šesták[1]:

$$\frac{db}{dt} = \frac{1}{h}\left[\frac{b_{+h} - b_{-h}}{2} + \frac{b_{+2h} - 2b_{+h} + 2b_{-h} - b_{-2h}}{12} + \right.$$

$$\left. + \frac{b_{+3h} - 4b_{+2h} + 5b_{+h} - 5b_{-h} + 4b_{-2h} - b_{-3h}}{240}\right]$$

where the subscripts refer to points at a $\pm\, n\, h$ distance from T.

Every part of the program prints out the values of the kinetic parameters and the standard deviation with respect to the least-square straight line. Supplementary prints give the transformed fractions and the derivatives.

CHECK OF THE PROGRAM—RESULTS AND DISCUSSION

The program has been tested by sets of theoretical data calculated according to the functions listed in Table 1 together with symbols for every function, which will be used in the following, and by setting arbitrary values for E and Z in the Arrhenius law. In this way, a calibration of the program has been obtained both to test the achievable accuracy in the parameter evaluation and to verify if a number of functions could yield results so close as to show the insufficiency of the proposed criteria of choice.

The temperatures corresponding to half the transformed fractions have been computed for six heating rates from 5.5 to 70°C min^{-1} to be used in the Kissinger and Ozawa plots. In single peak analysis, 25-30 points per curve had to be computed to achieve a good evaluation of the parameters. In fact, a high number of points, corresponding to a narrow scanning interval, enables one to obtain a better approximation of the transformed fractions and the derivatives owing to the use of numerical formulae. The beginning and the end of the peaks have been taken when α was not higher than 0.001 and not lower than 0.999, respectively.

The theoretical activation energy values and those computed according to Kissinger and Ozawa are reported in Table 2. As clearly appears, the Ozawa method permits a particularly good reproduction of the theoretical data, whereas the Kissinger method leads to slightly underestimated results for E. The same applies to Z which has been computed after choice of the mechanism. The knowledge of the activation energy from this treatment represents the starting point to carry on the mechanism analysis from the feature of the peaks.

Results found by the application of the Šatava method are reported in Table 3 for some of the functions used with particular reference to those cases in which the choice of the reaction mechanism could not be made on the basis of the Škvára–Šesták criteria. In previous treatments the greatest doubts arise when considering nucleation and power laws. In these cases, the theoretical data are fitted by more than one kinetic equation of the same family (leading to different slopes of the straight line)

TABLE 2

THEORETICAL PARAMETERS AND RESULTS FROM APPLICATION OF Kissinger AND Ozawa METHODS

Function tested	E_{th}	$\log Z_{th}$	E_O	$\log Z_O$	E_K	$\log Z_K$
D1 a	18	9	17.99	8.99	17.52	8.62
D1 b	40	10	39.91	9.97	39.19	9.69
B1	40	13	39.84	12.94	39.63	12.84
B2	40	10	39.87	9.96	39.19	9.70
N2 a	40	10	39.91	9.98	39.10	9.67
N2 b	33	13	32.98	13.00	32.74	12.87
N3	40	10	39.91	9.97	39.09	9.66
N4	40	10	39.99	10.00	39.15	9.68
N5	40	10	39.93	9.98	39.09	9.66
P3	40	10	39.97	9.99	39.14	9.68
P4	40	10	39.97	9.99	39.18	9.69
P5	40	10	39.93	9.98	39.19	9.69

TABLE 3

RESULTS FROM APPLICATION OF Šatava METHOD

Function tested	Functions from Šatava	E(kcal mol⁻¹)	log Z(sec⁻¹)	% linearity	Standard deviation
D1 a	D1	19.50	9.87	83	0.00001
—	D2	21.17	10.69	69	0.00010
—	D3	23.08	11.33	69	0.00059
—	D4	22.36	10.83	83	0.00069
—	P5	14.63	7.03	83	0.00001
D1 b	D1	41.00	10.29	82	0.00197
—	D2	42.15	10.42	67	0.02047
—	D3	42.95	10.07	54	0.03080
—	D4	42.58	9.92	67	0.02818
—	P5	30.75	7.27	82	0.00147
B1	B1	39.83	12.94	78	0.00014
—	N2	30.77	9.91	78	0.00026
—	P4	35.78	11.62	66	0.00052
B2	D4	84.06	23.28	98	0.02004
—	B1	41.54	10.64	67	0.01763
—	B2	42.04	10.64	98	0.01302
—	N1	43.52	11.63	49	0.00937
—	P4	40.92	10.72	41	0.02093
N2 a	N1	61.23	16.33	99	0.00696
—	N2	40.82	10.24	99	0.00460
—	N3	30.62	7.23	99	0.00345
—	N4	20.41	4.27	99	0.00230
—	N5	15.31	2.83	99	0.00172
N2 b	N1	48.90	20.60	99	0.00346
—	N2	33.27	13.12	99	0.00231
—	N3	24.95	9.41	99	0.00173
—	N4	16.63	5.75	99	0.00346
—	N5	12.47	3.96	99	0.00088
N3	N1	80.94	22.26	99	0.01499
—	N2	53.97	14.15	99	0.00999
—	N3	40.47	10.13	99	0.00750
	N4	26.98	6.17	99	0.00500
	N5	20.24	4.22	99	0.00191
	P3	38.43	9.49	44	0.00586
N4	N2	80.80	22.23	99	0.00190
	N3	60.60	16.15	99	0.00142
	N4	40.40	10.12	99	0.00095
	N5	30.30	7.14	99	0.00071
	P2	38.43	9.51	33	0.00455
N5	N3	80.67	22.16	99	0.00061
	N4	53.77	14.08	99	0.00041
	N5	40.34	10.08	99	0.00032
P3	P1	20.54	4.31	79	0.00148
	P2	27.39	6.29	79	0.00127
	P3	41.09	10.33	79	0.00294
	P4	82.21	22.66	79	0.00594
P4	D1	82.74	22.83	82	0.01091
	B1	43.25	10.74	68	0.01246
	B2	43.90	10.78	68	0.01794
	N1	43.75	11.22	37	0.00922
	P3	20.68	4.35	82	0.00273
	P4	41.37	10.41	82	0.00545
	P5	62.06	16.60	82	0.00818
P5	D1	54.95	14.44	83	0.00946
	D2	56.26	14.61	57	0.01924
	D4	57.16	14.28	69	0.03194
	B1	28.50	6.37	57	0.01351
	B2	28.87	6.32	57	0.01749
	P3	13.73	2.39	83	0.00236
	P4	27.47	6.31	83	0.00473
	P5	41.21	10.35	83	0.00709

within accuracy limits that can be fixed when experimental data are examined: no remarkable difference is found in the degree of linearity while the standard deviations and Z are equally acceptable.

Table 3 shows in fact that when N2, N3, N4 functions are tested all the nucleation laws (excepted N1 for N4) can be considered possible. Analogously P3 data are also fitted by P1, P2; P4 data by P3, P5 and P5 data by P3, P4.

Therefore, only previous knowledge of the activation energy allows the choice of the correct kinetic function in all these examples.

Sometimes, more functions than the expected one lead to energies near the real one: for instance D2, D3, D4 in the D1 case; P3 in the N3 case; B1, N2, N1 in the P4 case. The lower degree of linearity, however, helps in rejecting these functions. The deviations from the real values of E and Z used to build up the theoretical peaks may be attributed to the influence of the truncation of the peak tails on evaluation of the transformed fractions. In conclusion, it is always possible to select the foreseen mechanism univocally by applying both the conditions of E and the degree of linearity.

As already said, the modified Rogers and Smith method can furnish the n exponent of an empirical f(α) function able to account for phenomena which cannot be completely framed in one of the kinetic laws reported in Table 1. The present tests of the program are performed, on the contrary, on theoretically computed data, obviously giving an almost complete linearity for the proper function. In this case, the check of the Rogers and Smith method is expected to exactly reproduce the theoretical f(α) function: this is in fact verified and the results are reported in Table 4. Activation energies and pre-exponential factors reasonably agree with those previously calculated.

TABLE 4

RESULTS FROM APPLICATION OF Rogers Smith AND Borchardt-Daniels METHODS

Function tested	*Function type checked by Rogers–Smith method*	n_{RS}	E_{RS}	Z_{RS}	n_{RS}	E_{BD}	Z_{BD}
D1 a	D1	0	18.70	9.38	−0.04	18.62	8.98
D1 b	D1	0	40.90	10.13	0.07	40.64	9.98
B1	B1	1/2	40.02	13.38	0.55	43.76	14.76
	B2–N1–P4	2/3-1-0	40.02	13.38	0.55	43.76	14.76
B2	B2	2/3	40.51	10.77	0.74	39.82	10.40
	B1–N1–P4	1/2-1-0	40.51	10.77	0.74	39.82	10.40
N2 a	N2	1	40.27	10.38	1.06	39.15	9.89
N2 b	N2	1	34.15	13.81	1.11	32.76	13.08
N3	N3	1	42.29	11.07	1.09	39.42	10.09
	P3	0	42.41	11.11	0.87	39.56	10.13
N4	N4	1	42.67	11.69	1.12	38.53	10.01
	P2	0	42.82	11.74	0.83	38.72	10.06
P4	P4	0	40.60	11.79	0.02	40.14	10.01
P5	P5	0	40.43	10.34	0.02	40.79	10.04

Some scatter can be ascribed to the errors introduced by the numerical computation of the derivatives of the DSC curves. The effect of this approximation on the empirical f(α) are shown by the standard deviation of 0.08 of the n parameter which indicates the limits within which it can be determined.

An interesting aspect of the present treatment concerns the checking of functions which do not correspond with the theoretical one and give a lower degree of linearity in the Šatava plot. If such functions are passed to the successive step of the program to get a better empirical fitting by the modified Rogers and Smith method, this latter changes the E and n values deduced from the Šatava plot and makes them converge on the correct values. Table 4 shows some examples of this kind. Theoretical data obtained by means of the B1 function lead to $E = 35.78$ kcal mol^{-1} and 66% linearity in the Šatava plot for the P4 function (Table 3): the next calculation of E and n, being $m = p = 0$, gives $E = 40.02$ kcal mol^{-1} and the modified exponent $n = 0.55$. N1 and B2 functions, showing a worse linearity, converge to the same results, too. Similarly, the analysis of a peak built up according to B2, the integral form of which is 67% fitted by B1 with $E = 41.54$, 41% by P4 with $E = 40.92$ kcal mol^{-1} and 49% by N1 with $E = 43.52$ kcal mol^{-1}, leads in all cases to $E = 40.51$ kcal mol^{-1} and $n = 0.74$.

An analogous convergence may be observed in a very recent work by Chen and Fong[11], who simultaneously compute all the parameters by means of least squares. In fact by treating data relative to the dehydration of gypsum with the hypothesis of a $(1 - \alpha)^n$ mechanism, they found $E = 26.8$ kcal mol^{-1} and $n = 0.998$ and with a α^m. $(1 - \alpha)^n$ mechanism $E = 29.2$ kcal mol^{-1}, $n = 1.033$ and $m = 0.085$. These results should be considered equivalent. It is therefore questionable if it is possible to distinguish among mechanisms of the N or P type by this method, when experimental data, affected by usual errors, are run.

The aptitude of the Roger and Smith method to empirically increase the linearity of the Šatava plot results from the following examples. When theoretical input data of a $(1 - \alpha)$. $[-\ln(1 - \alpha)]^p$ N type function are run for a α^m P type law with $m = p$, the Šatava plot is fitted by 35–40% and E, Z values are almost the correct ones (see for instance N3-P3 and N4-P2 cases in Table 3). The following Rogers and Smith treatment (Table 4), while improving Arrhenius parameters, recognizes the necessity of introducing the $(1 - \alpha)^n$ function and finds n not far from 1 (0.87 and 0.83 for the mentioned cases).

The final step of the program (modified Borchardt and Daniels expression) controls the accuracy of the empirical formula obtained before. E_{BD} and Z_{BD} parameters reported in Table 4 are found in sufficient agreement with the preceding evaluation.

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