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A COMPARISON OF SOME INTEGRAL METHODS

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The integral methods proposed to compute the kinetic parameters of heterogeneous reactions under non-isothermal conditions are usually worked by the help of the least squares method and the obtained correlation coefficient is taken as a criterion to choose the best integral method.

An analysis of several experimental data by mean of three different integral methods was performed by us and the results pointed out that this criterion, by itself, is not enough to provide reliable information on the kinetic parameters.

It appears, thus, that the use of an integral method or another is a simple matter of researcher's choice.

Keywords: integral methods, kinetics

Introduction

Most of the integral methods used to compute the kinetic parameters of heterogeneous reactions under nonisothermal conditions may be written generally as [1]

$$\ln\int_0^\alpha \frac{dx}{f(1-x)} - s\ln T = -E/RT + \ln A/\beta + L \qquad (1)$$

where α, T, E, R, A and β have their usual meanings, L is an adjusting parameter and s=0, 1 or 2. For the different values of s and L some known integral methods are obtained, i.e.

$s=0$, $L=\ln E/R-5.33$ lead to Flynn and Wall's method [2]

$s=0$, $L=\ln \Delta T$ lead to Reich's method [3]

$s=2$, $L=\ln\frac{R}{E}(1-\frac{2RT}{E})$ lead to Coats and Redfern's method [4]

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$s = 2$, $L = \ln \dfrac{R}{E+2RT}$ lead to Gorbachev's method [5].

In order to compute the kinetic parameters, the set of experimental data (α, T) are used to plot

$$\left(\ln \int_0^{\alpha} \frac{\mathrm{d}x}{f(1-x)} - s \ln T\right) \; vs. \; 1/T \tag{2}$$

and for a proper choice of $f(1-\alpha)$ this plot leads to a straight line whose slope allows to compute the activation energy, E. The last kinetic parameter, A, the pre-exponential factor, may be obtained by subsequent computing from the intercept of the straight line.

For the sake of simplicity we consider [6]

$$f(1-\alpha) = (1-\alpha)^n \tag{3}$$

where n is the so-called reaction order.

To obtain the parameters of the straight line of the plot (2), the least squares method may be used and the correlation coefficient which results may be considered as a comparison index of the various integral methods. We shall consider, thus, that an integral method is more accurate than another if its correlation coefficient is closer to unity.

In the following we shall try to apply this method to evaluate the integral methods, when various reactions are investigated.

Table 1 Dehydration of calcium oxalate monohydrate. Conversion degrees and corresponding temperatures at various heating rates

α	Heating rate / deg·min^{-1}			
	2.3	7.4	14.8	10
0.1	426	446	450.5	430.5
0.2	440	461.5	467	441
0.3	449	471.5	478	450
0.4	455	479.5	486	456
0.5	460.5	485.5	493	461
0.6	465.5	491.5	499.5	467
0.7	471	496.5	505	471.5
0.8	475	501	509.5	475.5
0.9	479.5	507	514.5	481

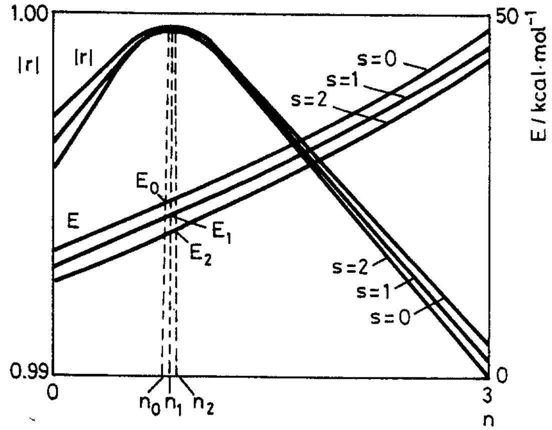

Fig. 1 Variation of the correlation coefficient, |r|, and activation energy, E, for different integral methods, when the reaction order, n, ranges from 0 to 3

The first reaction we have taken into account was the dehydration of calcium oxalate monohydrate, at various heating rates. The pairs (α,T) are given in Table 1 and the calculations were performed using a computer programme.

The data for heating rates of 2.3, 7.4 and 14.8 deg/min were taken from the literature [7] and those for the heating rate of 10 deg/min have been obtained by means of a Derivatograph Q 1500 D, Paulik-Paulik-Erdey type.

The plot of the absolute value of the correlation coefficient, r, computed using the programme, *vs.* the reaction order, n, for the three values of s (0, 1 and 2 respectively), as shown in Fig. 1, shows that there is one maximum value of n in the investigated range (from 0 to 3) and it is almost the same for all the three integral methods.

The maximum value of the correlation coefficient offers, as shown in Fig. 1, the values of the reaction, order, n, and activation energy, E, which are considered as the most accurate for the integral method used.

For all the data of Table 1 similar plots have been drawn and the values of the maximum correlation coefficient, r, and the corresponding values of n and E are given in Table 2.

The data in Table 2 suggest that the method $s=0$ is the most accurate one for the data of Table 1.

One may notice, also, that methods $s=1$ and $s=2$ cannot be discriminated from the accuracy standpoint.

By comparing the results of Table 2 with those from the literature [8], i.e. $n=0.71$ and $E=21.4$ kcal/mol, one finds that the closest results are those obtained for $s=1$, $\beta=10$ deg/min.

Table 2 Kinetic parameters and correlation coefficients computed by the help of various integral methods for the dehydration reaction of calcium oxalate monohydrate

Heating rate / deg·min^{-1}	Integral method	Corr. coeff. $\lvert r\rvert$	Reaction order n	E / kcal·mol^{-1}
2.3	$s = 0$	0.99982	0.48	19.5
	$s = 1$	0.99978	0.49	18.6
	$s = 2$	0.99979	0.48	17.7
7.4	$s = 0$	0.99993	0.44	18.5
	$s = 1$	0.99991	0.44	17.8
	$s = 2$	0.99992	0.45	16.9
14.8	$s = 0$	0.99988	0.33	17.4
	$s = 1$	0.99984	0.34	16.5
	$s = 2$	0.99983	0.34	15.6
10	$s = 0$	0.99927	0.77	22.7
	$s = 1$	0.99919	0.77	21.7
	$s = 2$	0.99913	0.78	20.9

Another set of (α,T) values, for a hypothetical reaction, was taken from the literature [9]. It was obtained by computer simulation with input data of E=30.0 kcal/mol, n,=1.00, $A/\beta = 10^6$ K^{-1}.

Table 3 contains the data corresponding to this simulation.

Table 3 Conversion degrees and temperatures corresponding to the simulated reaction

α	T / °K
0.1039	770
0.1723	790
0.2724	810
0.4067	830
0.5675	850
0.7323	870
0.8691	890
0.9540	910
0.9898	930

By using, again, the computer programme for s=0, 1 and 2 respectively, and the plotting the correlation coefficient r *vs.* n, the results given in Table 4 were obtained as those corresponding to the maximum correlation coefficient.

Table 4 Kinetic parameters and correlation coefficients computed by the help of various integral methods for the simulated decomposition reaction

Integral method	Correlation coeff., $\lvert r \rvert$	n	E / kcal·mol^{-1}
$s = 0$	0.9999973	0.99	33.0
$s = 1$	0.9999924	1.00	31.5
$s = 2$	0.9999972	1.01	30.0

The most accurate integral method, according to the criterion given above, is s=0, and the least accurate one is s=2, but the values obtained for E and n are the closest to those used for simulation when s=2 is used.

One may conclude, therefore, that the definition of the accuracy of an integral method based on the linearity of the plot (2) is questionable.

Moreover, this definition cannot be used to discriminate between methods s=1 and s=2 (Table 2) and it is very likely that for other experimental data even s=0 may be in the same position.

Thus, according to the results presented above, one cannot state that an integral method, as described by Eq. (1), is more accurate than another, and consequently that the elaboration of new integral methods should be discouraged. In fact the use of one method or another is a simple matter of the investigator's choice.

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Zusammenfassung — Integrationsmethoden zur Berechnung kinetischer Parameter von heterogenen Reaktionen unter nicht isothermen Bedingungen werden im allgemeinen nach der Methode der kleinsten Quadrate erarbeitet und der ermittelte Korrelationskoeffizient dient als ein Kriterium für die Auswahl der besten Integrationsmethode.

Mittels drei verschiedenen Integrationsmethoden wurde eine Analyse verschiedener experimenteller Daten durchgeführt. Die Ergebnisse zeigen, daß dieses Kriterium allein nicht ausreicht, um ausreichende Informationen über die kinetischen Parameter zu liefern.

Es scheint deshalb, daß die Verwendung der einen oder anderen Integrationsmethode einfach eine Wahl des Anwenders darstellt.