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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. COMPARISON OF INTEGRAL DISCRIMINATION METHODS

A. ROMERO SALVADOR

*Dpto. Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense,
28040 Madrid (Spain)*

E. GARCIA CALVO * and P. LETON GARCIA

*Ingeniería Química, Facultad de Ciencias, Universidad de Alcalá,
28871 Alcalá de Henares (Spain)*

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ABSTRACT

The Coats–Redfern and the Romero et al. integral discrimination methods are compared through kinetic analysis of thermogravimetric data. Both are used to determine the kinetic model an obtain kinetic parameters from $\alpha - T$ data generated from a wide range of kinetic parameters and nine different kinetic models.

The Romero et al. method allows determination of the kinetic model in all cases. The Coats–Redfern method does not allow discrimination between most of the models.

When the kinetic model is known, both methods calculate kinetic parameters with accuracy.

INTRODUCTION

The practical importance of thermal decomposition kinetics in solids has led to a very extensive effort to understand the mechanisms which control these reactions.

Thermogravimetric (TG) analysis is the experimental method most commonly used for determining the model which best describes the decomposition reaction.

Several techniques [1–6] are used to analyse weight loss vs. temperature data obtained using TG. The most common of these techniques is the one developed by Coats and Redfern [1].

In this paper, conversion vs. temperature data are generated using different models and kinetic parameters at different heating rates. These data are

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* Author to whom all correspondence should be addressed.

used to compare the Coats–Redfern technique with the one proposed by Romero et al. [6] so that the advantages of each can be established.

Coats–Redfern method

The mathematical description of solid weight loss during heating can be represented with an Arrhenius-type reaction equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\ \exp(-E/RT)\mathrm{f}(\alpha) \tag{1}$$

If the reaction is carried out at a constant heating rate β, defined as

$$T = T_0 + \beta t \tag{2}$$

we can use α and T to remove the time dependence in eqn. (1)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\ \exp(-E/RT)\mathrm{f}(\alpha) \tag{3}$$

and then integrate the equation

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \mathrm{g}(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} \exp(-E/RT)\ \mathrm{d}T \tag{4}$$

We can then apply the Coats–Redfern approximation, supposing $(1 - 2RT/E) = 1$, to obtain

$$\ln \frac{\mathrm{g}(\alpha)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \tag{5}$$

A linear regression of this expression is required to obtain kinetic parameters. The A and E values can be estimated from the values of the slope and the intercept.

Romero et al. method

By using several heating rates, it is possible to split the temperature and conversion influences in a two-part analysis. The first is at constant temperature and the second at constant conversion [6].

Points that correspond to the same temperature for a set of α–T experimental curves at different heating rates are used to study the conversion influence. Each of these points corresponds to a time t obtained from eqn. (2). The α–t data have to fulfil the condition

$$\mathrm{g}(\alpha) = K_{\mathrm{ni}}t \tag{6}$$

where

$$K_{\mathrm{ni}} = \frac{\int_{T_0}^{T} A\ \exp(-E/RT)\ \mathrm{d}T}{T - T_0} \tag{7}$$

Using the Coats–Redfern simplification to integrate eqn. (7), we obtain the relationship between the kinetic constant K and the slope of eqn. (6) K_{ni}

$$K = \frac{K_{ni}(T - T_0)E}{RT}\left(1 - \frac{2RT}{E}\right) \tag{8}$$

Assuming $(1 - 2RT/E) = 1$, K_{ni} values can be used to obtain A and E by taking into account the Arrhenius equation

$$\ln \frac{K}{E} = \ln \frac{A}{E} - \frac{E}{RT} \tag{9}$$

The temperature influence is obtained by analysis at constant conversion, i.e. using temperature values for a given conversion in a set of α–T experimental curves. From eqn. (5) we obtain

$$\ln \frac{\beta}{RT^2} = \ln \frac{A/E}{g(\alpha)} - \frac{E}{RT} \tag{10}$$

It is possible to obtain values for the kinetic parameters for any given constant α.

GENERATION OF α–T DATA

In order to compare the Coats–Redfern and the Romero et al. methods, sets of α–T data were generated at five different heating rates (0.5, 1, 2, 5 and 10 K min^{-1}). Simpson's rule ($\Delta T = 0.1$–0.25 K) was used to integrate the right side of eqn. (4) and to obtain the α–T data.

With $E = 30$ kcal mol^{-1} and $A = 10^6$ min^{-1}, nine sets of experimental α–T data were obtained, corresponding to each of the models in Table 1. From these data it was possible to determine the influence of the conversion on the method of discrimination.

In order to determine the influence of the kinetic parameters on the method of dicrimination, three sets of generated α–T data with different kinetic parameters were used with the R3 model. The initial kinetic parameters for each set were $E = 10$ kcal mol^{-1} and $A = 100$ min^{-1}; $E = 30$ kcal mol^{-1} and $A = 10^6$ min^{-1}; and $E = 70$ kcal mol^{-1} and $A = 10^7$ min^{-1}.

ANALYSIS OF THE α–T DATA

Analysis of the kinetic data by the Coats–Redfern method requires only one of the α–T curves from each set. In this paper the curves used were for $\beta = 1$ K min^{-1}, but curves for different heating rates yield similar results.

Applying the Romero et al. method requires the set of five α–T curves.

TABLE 1

Conversion functions of different models

Rate mechanism	Symbol	f(α)	g(α)
Nucleation and nuclei growth			
(a) Random nucleation	F1	$1-\alpha$	$-\ln(1-\alpha)$
(b) Two-dimensional nuclei growth	F2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$-[\ln(1-\alpha)]^{1/2}$
(c) Three-dimensional nuclei growth	F3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$-[\ln(1-\alpha)]^{1/3}$
Diffusion			
(a) One-dimensional transport	D1	α^{-1}	$\alpha^2/2$
(b) Two-dimensional transport (cylindrical geometry)	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
(c) Three-dimensional diffusion (spherical geometry)	D3	$[(1-\alpha)^{-1/3}-1]$	$\frac{3}{2}[1-2\alpha/3-(1-\alpha)^{3/2}]$
Phase boundary reaction			
(a) One-dimensional (zero order)	R1	Constant	α
(b) Two-dimensional (cylindrical geometry)	R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
(c) Three-dimensional (spherical geometry)	R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$

TABLE 2

Coats and Redfern method: discrimination between models

True model $E = 30$ kcal mol^{-1} $A = 10^6$ min^{-1}	Number of α–T points		Probed model F1	F2	F3	R1	R2	R3	D1	D2	D3
F1	270	A (min^{-1})	8.2 E5	16.1	0.33	3.4 E7	2.8 E3	6.9 E3	2.4 E8	2.2 E9	6.9 E9
		E (kcal mol^{-1})	29.8	13.3	7.8	19.2	22.9	24.8	41.5	45.6	47.7
		r	0.999	0.999	1.000	0.956	0.982	0.990	0.963	0.975	0.981
F2	125	A (min^{-1})	8.1 E14	7.9 E5	6.1 E2	2.6 E10	9.7 E11	3.8 E12	5.8 E23	3.7 E25	2.5 E26
		E (kcal mol^{-1})	62.7	29.8	18.8	47.3	53.7	56.3	97.8	105.1	108.6
		r	0.999	1.000	0.999	0.982	0.994	0.997	0.983	0.990	0.993
F3	100	A (min^{-1})	7.2 E21	2.8 E9	1.6 E5	2.6 E14	7.3 E16	9.1 E17	4.4 E31	2.2 E34	4.6 E35
		E (kcal mol^{-1})	88.2	42.5	27.3	62.0	71.7	76.1	127.3	137.9	143.3
		r	0.999	0.999	0.999	0.976	0.991	0.995	0.978	0.986	0.989
R1	155	A (min^{-1})	3.1 E7	1.2 E2	1.4	8.3 E5	2.2 E6	2.7 E6	7.8 E14	2.9 E15	4.4. E15
		E (kcal mol^{-1})	34.7	15.9	9.6	29.9	32.1	32.9	62.7	65.4	66.6
		r	0.992	0.992	0.991	1.000	0.998	0.997	0.999	0.999	0.999
R2	173	A (min^{-1})	2.8 E7	1.1 E2	1.37	1.9 E5	8.4 E5	1.3 E6	4.6 E13	2.8 E14	5.6 E14
		E (kcal mol^{-1})	33.6	15.3	9.3	27.0	29.9	31.0	57.0	60.4	61.8
		r	0.995	0.994	0.993	0.997	1.000	0.999	0.997	0.999	0.999
R3	180	A (min^{-1})	2.4 E7	1.0 E2	1.3	8.9 E4	4.8 E5	8.3 E5	1.0 E13	7.7 E13	1.7 E14
		E (kcal mol^{-1})	32.8	15.0	9.0	25.6	28.6	29.9	54.0	57.6	59.2
		r	0.997	0.997	0.996	0.993	0.999	1.000	0.994	0.998	0.999
D1	263	A (min^{-1})	1.8 E2	0.19	1.3 E − 2	19.4	27.2	26.5	8.5 E5	1.4 E6	1.6 E6
		E (kcal mol^{-1})	16.1	6.7	3.6	13.6	14.8	15.2	29.9	31.3	31.9
		r	0.991	0.988	0.983	1.000	0.998	0.996	1.000	0.999	0.999
D2	276	A (min^{-1})	1.9 E2	0.19	1.4 E − 2	13.5	22.2	23.3	4.3 E5	8.5 E5	1.0 E6
		E (kcal mol^{-1})	15.8	6.5	3.5	12.8	14.1	14.6	28.3	29.9	30.6
		r	0.993	0.991	0.986	0.999	0.999	0.998	0.999	1.000	0.999
D3	282	A (min^{-1})	2.0 E2	0.20	1.4 E − 2	11.6	20.6	22.4	3.2 E5	6.8 E5	8.7 E5
		E (kcal mol^{-1})	15.6	6.5	3.4	12.4	13.8	14.4	27.5	29.2	29.9
			0.994	0.993	0.991	0.997	0.999	0.999	0.998	0.999	1.000

TABLE 3

Coats and Redfern method: kinetic parameters calculated using the various models

Kinetic parameters	True values	Model								
		F1	F2	F3	R1	R2	R3	D1	D2	D3
A (min^{-1})	100	8.2 E2	0.52	3.2 E−2	29.1	62.8	74.4	1.2 E6	3.4 E6	4.6 E6
E (kcal mol^{-1})	10	10.8	4.5	2.4	8.4	9.5	9.9	18.6	19.8	20.4
r	(181) [a]	0.997	0.997	0.997	0.993	0.999	1.000	0.995	0.998	0.999
A (min^{-1})	10^6	2.4 E7	1.0 E2	1.3	8.9 E4	4.8 E5	8.3 E5	1.0 E13	7.7 E13	1.7 E14
E (kcal mol^{-1})	30	32.8	15.0	9.0	25.6	28.6	29.9	54.0	57.6	59.2
r	(180) [a]	0.997	0.997	0.996	0.993	0.999	1.000	0.994	0.998	0.999
A (min^{-1})	10^7	3.9 E8	3.3. E2	2.5	5.6 E5	4.2 E6	8.7 E6	6.5 E14	6.9 E15	1.9 E16
E (kcal mol^{-1})	60	66.2	30.5	18.6	51.0	57.2	59.9	107.1	114.3	117.6
r	(115) [a]	0.996	0.995	0.995	0.993	0.999	1.000	0.994	0.998	0.999

[a] Values in parentheses represent number of $\alpha - T$ points.

Coats–Redfern method

Table 2 shows the calculated kinetic parameters and the correlation coefficients obtained when each of the nine kinetic models is used to fit the α–T data generated from each of the nine kinetic models. The kinetic parameters obtained when the probed model is the best fitting one are very close to the initial values. In practice, however, the initial values and/or kinetic model are obviously unknown. The only way to discriminate between models is by the value of the correlation coefficient, but this is so high in all cases that choosing between models is impossible.

Table 3 shows the kinetic parameters obtained for each of the nine models used to fit the α–T data generated with the R3 model and three different combinations of kinetic parameters. Again, discrimination between the models is difficult.

Romero et al. method

From an analysis at constant temperature, α–T data corresponding to a given set were fitted using eqn. (6). Table 4 shows the results of fitting data generated with $E = 30$ kcal mol^{-1}, $A = 10^6$ min^{-1} and $g(\alpha) = 1 - (1 - \alpha)^{1/3}$. In all of these cases, discrimination between models is achieved by comparing the correlation coefficients. The kinetic parameters are obtained from the slopes generated with each model and using eqns. (8) and (9) (see Table 5).

It is clear that the kinetic parameters that are most like the initial ones are the parameters obtained when the R3 model is used. However the value of the correlation coefficient is insufficient for discrimination between the nine models. An analysis at constant conversion is necessary to obtain the kinetic parameters and compare these with those obtained in the analysis at constant temperature.

Table 6 shows the E and $A/g(\alpha)$ values obtained when eqn. (10) is applied to fit data generated at five different constant conversions. The correlation coefficient is 1.000 in all cases. The E values are very close to those obtained in the analysis at constant temperature with $g(\alpha)$ corresponding to the R3 model.

Table 7 shows the A values at any given constant α and considering the nine possible models. All the A values are around 10^6 and the influence of α is not pronounced. However, A decreases for the F, R1 and R2 models and increases for the D models with increasing α. The A values for R3 are similar to those obtained at constant temperature for any conversion level.

The R1 and R2 models also generate A values which are close to the initial values but very different from those obtained in analysis at constant temperature (see Table 5).

TABLE 4

Romero et al. method: analysis at constant temperature, fitting using eqn. (6)

T (K)		Model								
		F1	F2	F3	R1	R2	R3	D1	D2	D3
710	Slope	6.48 E−5	1.84 E−4	2.25 E−4	6.22 E−5	3.18 E−5	2.13 E−5	4.95 E−6	2.54 E−5	1.71 E−6
	Intercept	−2.16 E−5	6.93 E−2	0.175	3.82 E−4	9.18 E−5	3.87 E−5	−7.57 E−4	−3.91 E−4	−2.63 E−4
	Coefficient	1.000	0.984	0.970	1.000	1.000	1.000	0.973	0.972	0.972
740	Slope	1.66 E−4	2.88 E−4	3.00 E−4	1.49 E−4	7.85 E−5	5.33 E−5	2.98 E−5	1.59 E−5	1.09 E−5
	Intercept	−9.24 E−4	0.111	0.241	1.87 E−3	2.65 E−4	2.00 E−5	−4.70 E−3	−2.56 E−3	−1.76 E−3
	Coefficient	1.000	0.985	0.971	1.000	1.000	1.000	0.976	0.974	0.973
770	Slope	4.10 E−4	4.46 E−4	3.97 E−4	3.12 E−4	1.78 E−4	1.24 E−4	1.39 E−4	8.20 E−5	5.79 E−5
	Intercept	−6.33 E−3	0.171	0.323	1.04 E−2	1.49 E−3	3.12 E−5	−2.16 E−2	−1.34 E−2	−9.60 E−3
	Coefficient	1.000	0.987	0.973	0.999	1.000	1.000	0.981	0.977	0.975
800	Slope	1.04 E−3	7.07 E−4	5.40 E−4	5.33 E−4	3.65 E−4	2.73 E−4	4.43 E−4	3.19 E−4	2.45 E−4
	Intercept	−4.22 E−2	0.250	0.420	4.94 E−2	8.02 E−3	3.11 E−5	−5.83 E−2	−4.96 E−2	−4.02 E−2
	Coefficient	0.998	0.991	0.979	0.992	0.999	1.000	0.993	0.984	0.980
830	Slope	3.12 E−3	1.62 E−3	1.12 E−3	1.11 E−3	8.94 E−4	7.11 E−4	1.19 E−3	9.81 E−4	8.07 E−4
	Intercept	−0.127	0.319	0.507	0.113	2.07 E−2	2.08 E−5	−7.93 E−2	−9.04 E−2	−8.18 E−2
	Coefficient	0.996	0.997	0.991	0.986	0.999	1.000	0.999	0.994	0.990

TABLE 5

Kinetic parameters from analysis at constant temperature, using eqns. (8) and (9)

Model	E (kcal mol^{-1})	A (min^{-1})	r
F1	35.64	1.65 E8	0.9960
F2	19.04	1.62 E3	0.9874
F3	13.53	26.65	0.9707
R1	21.50	5.14 E3	0.9878
R2	27.43	2.09 E5	0.9991
R3	29.87	8.33 E5	1.0000
D1	43.75	9.80 E9	0.9850
D2	49.49	3.15 E11	0.9916
D3	52.29	1.57 E12	0.9943

TABLE 6

Romero et al. method: analysis at constant conversion

α	E (kcal mol^{-1})	$A/g(\alpha)$ (min^{-1})
0.1	29.87	0.24 E8
0.3	29.85	0.73 E7
0.5	29.86	0.40 E7
0.7	29.84	0.24 E7
0.9	29.84	0.15 E7

TABLE 7

Pre-exponential factor from an analysis at constant conversion

Model	$A\times10^{-6}$ (min^{-1})				
	$\alpha = 0.1$	$\alpha = 0.3$	$\alpha = 0.5$	$\alpha = 0.7$	$\alpha = 0.9$
F1	2.53	2.6	2.77	2.89	3.45
F2	7.79	4.36	3.33	2.63	2.28
F3	11.30	5.18	3.54	2.55	1.98
R1	2.40	2.20	2.00	1.68	1.35
R2	1.23	1.19	1.17	1.08	1.03
R3	0.83	0.82	0.82	0.79	0.80
D1	0.24	0.66	1.00	1.17	1.21
D2	0.12	0.37	0.61	0.81	1.00
D3	0.08	0.25	0.44	0.61	0.83

Comparing the E values in Table 6 with those in Table 5 is usually sufficient to indicate the true model. If this were not possible, comparing A values would allow discrimination between models. Table 8 shows kinetic parameters obtained from α–T data generated for nine different models

TABLE 8

Influence of the kinetic model on the calculated kinetic parameters (initial parameters: $E = 30$ kcal mol^{-1}, $A = 10^6$ min^{-1})

Model	E (kcal mol^{-1})		$A \times 10^{-6}$ (min^{-1})	
	Analysis with T constant	Analysis with α constant	Analysis with T constant	Analysis with α constant
F1	28.67	29.87	0.38	0.82
F2	27.04	29.84	0.14	0.81
F3	27.35	29.89	0.17	0.88
R1	29.58	29.87	0.69	0.82
R2	29.65	29.87	0.72	0.82
R3	29.70	29.89	0.75	0.84
D1	29.83	29.87	0.81	0.83
D2	29.84	29.88	0.82	0.83
D3	29.87	29.88	0.83	0.83

TABLE 9

Influence of the initial kinetic parameters on the calculated parameters (data generated with the R3 model)

E (kcal mol^{-1})			A (min^{-1})		
Initial	Calculated		Initial	Calculated	
	Analysis with T constant	Analysis with α constant		Analysis with T constant	Analysis with α constant
10	9.80	9.85	10^2	0.67×10^2	0.71×10^2
30	29.70	29.89	10^6	0.75×10^6	0.84×10^6
60	59.46	59.82	10^7	0.75×10^7	0.85×10^7

using $E = 30$ kcal mol^{-1} and $A = 10^6$ min^{-1}. In all cases, discrimination between models is easy and, as can be seen in Table 8, the kinetic parameters obtained are very close to the original ones.

Table 9 shows the kinetic parameters obtained from α–T data corresponding to the R3 model and three different combinations of initial parameters. Discrimination between models is easy, and the kinetic parameters obtained from both analyses at constant temperature and at constant conversion are very similar. The lower the E and/or A value, the greater the error with respect to the true value. However, the errors are not excessive in any case.

CONCLUSIONS

The Coats–Redfern method is useful for calculating kinetic parameters when the kinetic model is known, but that is not always the case.

The Romero et al. method allows discrimination between models in all cases, and the calculated kinetic parameters are very close to the true values.

LIST OF SYMBOLS

A = frequency factor (min^{-1})
E = activation energy (kcal mol^{-1})
$f(\alpha)$ = conversion influence on the rate of decomposition
$g(\alpha)$ = $\int d\alpha/f(\alpha)$
K = reaction rate constant (min^{-1})
R = gas constant (kcal mol^{-1} (K^{-1})
T = temperature (K)
t = time (min)

Greek letters

α = fractional conversion
β = heating rate (K min^{-1})

Subscripts

ni = observed from non-isothermal data
0 = initial

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