

## EVALUATION OF KINETIC CONSTANTS FOR THE SOLID STATE REACTIONS UNDER LINEAR TEMPERATURE INCREASE CONDITIONS

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### ABSTRACT

The theory of solid state reaction kinetics considers the dependence of reaction rates on temperature ( $T$ ) and progress of the reaction ( $\alpha$ ). The term describing the dependence of reaction rates on temperature is usually assumed to be an Arrhenius-type equation:  $k(T) = Z \exp(-E/RT)$ , or the equation predicted by transition state theory:  $k(T) = ZT^b \exp(-E/RT)$ . With these assumptions, the equation  $g(\alpha) = tk(T)$  has been derived, and this form has been satisfactorily applied for the description of solid state reaction kinetics under isothermal conditions. In this work equations similar to those applied in the case of isothermal conditions are proposed for describing the reaction kinetics under linear temperature increase conditions

$$g(\alpha) = \frac{T}{\phi} Z \exp(-E/RT) \quad \text{if } k(T) = Z \exp(-E/RT)$$

$$g(\alpha) = \frac{T}{\phi} Z T^b \exp(-E/RT) \quad \text{if } k(T) = Z T^b \exp(-E/RT)$$

An attempt has been made to apply the above equations, as well as the differential form from the first equation

$$d\alpha/dt = f(\alpha)Z(1 + E/RT) \exp(-E/RT)$$

to a non-isothermal thermogravimetric experiment. The evaluated kinetic constants are in good agreement with those estimated previously by applying widely used methods of calculation. Therefore, these equations may be considered as simpler and more adequate forms for the description of reaction kinetics under linear temperature increase conditions.

Two new statistical functions have been applied in this work which permit the evaluation of  $E$  and  $Z$  from any kinetic equation. These functions may be used instead of the linear interpolation method, because they allow one to distinguish more easily between possible forms of  $g(\alpha)$  or  $f(\alpha)$  functions. This approach is recommended especially if one intends to use differential kinetic equations.

### INTRODUCTION

Knowledge of reaction kinetics is important for pure scientific, as well as practical reasons. The primary objectives of kinetic considerations are: (i) to attempt to determine simple mathematical descriptions of the process, and (ii) to calculate kinetic parameters (or constants). Several physical models

have been proposed for the description of the kinetics of gaseous systems [1–5]. Some of these have been extended to the liquid state [5,6]. Solid state reaction kinetics is still tenuous and a general theory which could explain satisfactorily most of the interesting problems is yet to come [7–9]. In most work authors have attempted to adjust the accepted models for gaseous and liquid phase reaction kinetics to the solid state reaction kinetics. The general approach based on an Arrhenius-type equation has been adopted successfully in isothermal methods [8]. Additional problems appeared, however, when it was necessary to extend the same approach to non-isothermal conditions. These problems have arisen from both the imperfections of the accepted models for solid state reactions, and from difficulties in the discovery of appropriate equations describing the reaction kinetics. The dynamic methods of investigation are becoming increasingly popular, so it is understandable that the validity of applied mathematical apparatus is very important.

In this communication I would like to present some observations which occurred to me during the search for a more accurate method of calculating non-isothermal kinetics. Of course these are concerned with the basic derivative form proposed in the literature for the description of reaction kinetics under linear temperature increase conditions.

Within the past 10 years, the greatest attention has been given to proving (or disproving) the validity of the equation

$$d\alpha = \left( \frac{\partial \alpha}{\partial t} \right)_T dt + \left( \frac{\partial \alpha}{\partial T} \right)_t dT \quad (1)$$

which is a consequence of the assumption that the degree of conversion ( $\alpha$ ) is a function of temperature ( $T$ ) and reaction time ( $t$ ) in the case of experiments performed under non-isothermal conditions [9–42]. It is not my intention to extend the discussion concerned with the above problem; rather, I would like to mention some consequences which could arise if eqn. (1) is assumed to be valid. I decided to publish this note, because, in spite of general disapproval of eqn. (1), some aspects of this problem are still under consideration [38–42].

#### THE GENERAL KINETIC EQUATIONS

The rate of isothermal processes involving solids may be considered as a function of two parameters: temperature ( $T$ ), and degree of conversion ( $\alpha$ ). Bradley [43], starting from the assumption of Polanyi and Wigner [44], derived an equation which was satisfactorily applied for the description of various heterogeneous processes [17,45–47].

$$\frac{d\alpha}{dt} = f(\alpha) k(T) [1 - \exp(\Delta G/RT)] \quad (2)$$

where  $t$  is time, and  $\Delta G = RT(X/K)$  ( $K$  is the equilibrium constant and  $X$  is the product of activities of all components). For most processes  $\Delta G$ , which

represents Gibbs free energy difference, reaches high negative values [17,47]. This means that the given process takes place "very far" from equilibrium and this permits us to neglect the last term in eqn. (2).

$$\frac{d\alpha}{dt} = f(\alpha) k(T) \quad (3)$$

The form of function  $k(T)$  depends on the character of the heterogeneous reactions. For most chemical processes the assumption is made that solid state reactions are activated-type processes. In this case, the function  $k(T)$  may be expressed in the form of the Arrhenius equation [7-9]

$$k(T) = Z \exp(-E/RT) \quad (4)$$

where  $E$  is the apparent activation energy, and  $Z$  is the pre-exponential factor. The transition state theory, as well as other modern theories of reaction rate, predict the following general relationship [24,48-50]

$$k(T) = ZT^b \exp(-E/RT) \quad (5)$$

where  $b$  is constant.

The degree of conversion ( $\alpha$ ) is a function of all parameters which determine the kinetics of a given process [17]. Among the parameters influencing  $\alpha$ , only time and temperature have been distinguished in the description of the reaction kinetics. One may assume that other parameters remain constant during the course of the reaction. They describe the overall mechanism of a given process, i.e., the form of function  $f(\alpha)$  in eqn. (3).

There is much controversy as to whether the fraction reacted ( $\alpha$ ) can be considered as a function of both time and temperature, or only of time [9-42]. As was mentioned earlier in this work, we assume  $\alpha = f(t, T)$ . Therefore, the following expression may be written

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T + \left(\frac{\partial \alpha}{\partial T}\right)_t \frac{dT}{dt} \quad (6)$$

In isothermal experiments  $(\partial \alpha / \partial T)_t$  remains constant and  $dT/dt = 0$ , so the last term of eqn. (6) is equal to 0. Therefore, considering eqns. (3), (5) and (6) one may obtain

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} \equiv g(\alpha) = t Z T^b \exp(-E/RT) \quad (7)$$

where  $t$  results from the integral  $\int_0^t dt$ .

The functions describing the mechanism of the thermal processes,  $g(\alpha)$  and their differential forms  $f(\alpha)$ , have been discussed elsewhere by many authors [51-56]. In non-isothermal experiments, however, conditions under which the thermal process takes place differ from those for isothermal measurements. It is difficult to discuss generally problems concerned with non-isothermal reaction kinetics. Therefore, further considerations will be limited to the linear temperature increase conditions, wherein  $dT/dt = \phi$  (heating rate). For the first term of the right-hand side of eqn. (6) one can substitute the appropriate forms for isothermal conditions [eqns. (3), (4) or (5)]. This

leads to the following equation

$$g(\alpha) = \frac{Z}{\phi} \int_0^T T^b \exp(-E/RT) dT + \frac{1}{f(\alpha)} \int_0^T \left( \frac{\partial \alpha}{\partial T} \right)_t dT \quad (8)$$

The functional dependence of the degree of conversion on temperature generally is not known. Therefore, it is impossible to predict the values of  $(\partial \alpha / \partial T)_t$ . The above discussed problem can be resolved, however, if one assumes that the dependence of  $\alpha$  on  $T$  results from the kinetic relationships for isothermal conditions. After differentiation of eqn. (7) one may obtain

$$g'(\alpha) \left( \frac{\partial \alpha}{\partial T} \right)_t = tZ \left( \frac{\partial [T^b \exp(-E/RT)]}{\partial T} \right)_t \quad (9)$$

But  $g'(\alpha) = 1/f(\alpha)$ , and this fact results directly from eqn. (7) [33]. On the other hand,  $t$  may be expressed as

$$\int_0^t dt = 1/\phi \int_{T_0}^T dT \quad t = \frac{T - T_0}{\phi} \quad (10)$$

where  $T_0$  is the initial temperature.

Substitution of eqns. (9) and (10) into eqn. (8) leads to the form

$$g(\alpha) = \frac{Z}{\phi} \int_0^T T^b \exp(-E/RT) dT + \frac{Z}{\phi} \int_0^T (T - T_0) \left\{ \frac{\partial [T^b \exp(-E/RT)]}{\partial T} \right\}_t dT \quad (11)$$

Application of the integration procedure presented in Appendix A results in the final equations

$$g(\alpha) = \frac{Z}{\phi} T^b (T - T_0) \exp(-E/RT) \quad (12)$$

and in the case  $b = 0$

$$g(\alpha) = \frac{Z}{\phi} (T - T_0) \exp(-E/RT) \quad (13)$$

By differentiating eqn. (12) and taking into account that  $g'(\alpha) = 1/f(\alpha)$  and  $dT/dt = \Phi$ , one may obtain

$$d\alpha/dt = f(\alpha) Z T^b [1 + (b/T + E/RT^2)(T - T_0)] \exp(-E/RT) \quad (14)$$

or in the case  $b = 0$

$$d\alpha/dt = f(\alpha) Z [1 + E/RT^2 (T - T_0)] \exp(-E/RT) \quad (15)$$

Equation (15) is well known and has been considered by many authors in the description of reaction kinetics under non-isothermal conditions [17,18,24,27,28,38-42]. This equation has been found to be adequate if one considers the degree of conversion as being a function of time and temperature of the reacting system.

## METHODS OF EVALUATING KINETIC CONSTANTS

Equation (12) may be presented in the more convenient logarithmic form

$$\ln \frac{g(\alpha)}{T^b (T - T_0)} = \ln \frac{Z}{\phi} - \frac{E}{R} \frac{1}{T} \quad (16)$$

The above expression is suitable for applying linearization procedures. The linear interpolation method, based on the least squares assumption, permits calculation of  $E$  and  $Z$  [59]. Also, the correlation coefficient ( $r$ ) may be considered as an indicator permitting the choice of the most adequate function  $g(\alpha)$ . Unfortunately, in most cases  $r$  values do not differ enough to distinguish between possible reaction mechanisms [60–62]. It is necessary to look for other methods of calculation allowing one to choose more easily the most probable reaction mechanism. Most equations applied in reaction kinetics may be rearranged to forms in which all variables are placed on the left-hand side and at least some constants on the right-hand side. For example, rearranging eqns. (12) and (15) gives

$$\Delta \equiv \frac{g(\alpha)}{T^b (T - T_0) \exp(-E/RT)} = \frac{Z}{\phi} \quad (17)$$

$$\Delta^* \equiv \frac{d\alpha/dt}{f(\alpha)[1 + E/RT^2 (T - T_0)] \exp(-E/RT)} = Z \quad (18)$$

The right-hand side of both the above equations should be constant. This fact results from kinetic considerations, as well as experimental conditions. Therefore, also the left-hand sides of eqns. (17) and (18) should be constant for any experimental points ( $\alpha_i$ ,  $T_i$  and  $d\alpha_i/dt_i$ ) if the reaction mechanism [form of functions  $g(\alpha)$  or  $f(\alpha)$ ] and kinetic parameters  $E$ ,  $T_0$ , and  $b$  are chosen correctly. In reality, values  $\Delta_i$  ( $\Delta_i^*$ ) differ, so the functions

$$\nu = \frac{\frac{1}{N} \sum_{i=1}^N |\Delta_i - \bar{\Delta}|}{\bar{\Delta}} \quad (19)$$

$$\delta = \frac{\sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta_i - \bar{\Delta})^2}}{\bar{\Delta}} \quad (20)$$

where  $\bar{\Delta} = \frac{1}{N} \sum_{i=1}^N \Delta_i$ , and  $N$  = number of experimental points

may be used as statistical parameters in the search for an adequate reaction mechanism, as well as the values of kinetic constants [59]. It is convenient to establish criteria for applying the trial and error procedure.

(i) Functions  $\nu$  or  $\delta$  reach minimum for the best choice of  $E$ ,  $T_0$  and  $b$  for a given reaction mechanism. Therefore, for a given function  $g(\alpha)$  or  $f(\alpha)$  and at the assumed values of  $T_0$  and  $b$ , it is possible to vary  $E$  to reach the minimum of  $\nu$  or  $\delta$ .  $E$  corresponding to these minimum values can be considered as the best fit to the experimental data.

TABLE 1  
Kinetic constants for thermal dissociation of  $\text{Rb}_2\text{PbCl}_6$  (see ref. 54; Fig. 1, Table 4) calculated using eqn. (12) \*

Symbol of the mechanism [54]	Method of evaluation of kinetic constants											
	$T_0 = T_{\alpha=0.01}; b = 0$			$T_0 = 300 \text{ K}; b = 0$			$T_0 = 0 \text{ K}; b = 0$			$T_0 = 0 \text{ K}; b = 0.25$		
	L	M		L	M		L	M		L	M	
	E	E	E	E	E	E	E	E	E	E	E	
	Z	Z	Z	Z	Z	Z	Z	Z	Z	Z	Z	
	r	$\nu$	r	r	$\nu$	r	r	$\nu$	r	r	$\nu$	
R1	3.09 04	3.15 04	4.68 04	4.67 04	5.22 04	5.21 04	5.10 04	5.09 04	5.10 04	5.10 04	5.09 04	
	4.33-01	4.92-01	5.06 00	4.94 00	7.43 00	7.30 00	1.19 00	1.16 00	1.19 00	1.19 00	1.16 00	
	0.99784	1.4219-03	0.99980	7.5285-04	0.99983	7.4625-04	0.99982	7.5107-04	0.99982	0.99982	7.5107-04	
R2	3.83 04	3.80 04	5.43 04	5.36 04	5.96 04	5.90 04	5.85 04	5.79 04	5.85 04	5.85 04	5.79 04	
	1.20 00	1.12 00	1.40 01	1.22 01	2.06 01	1.80 01	3.30 00	2.92 00	3.30 00	3.30 00	2.92 00	
	0.99355	3.4824-03	0.99888	1.9433-03	0.99915	1.8417-03	0.99914	1.8264-03	0.99914	0.99914	1.8264-03	
R3	4.10 04	4.03 04	5.70 04	5.59 04	6.23 04	6.13 04	6.12 04	6.01 04	6.12 04	6.12 04	6.01 04	
	1.87 00	1.27 00	1.74 01	1.39 01	2.55 01	2.05 01	4.08 00	3.26 00	4.08 00	4.08 00	3.26 00	
	0.99152	4.3305-03	0.99802	2.7858-03	0.99846	2.6818-03	0.99842	2.6615-03	0.99842	0.99842	2.6615-03	
P1	1.67 04	1.73 04	3.26 04	3.25 04	3.80 04	3.79 04	3.68 04	3.67 04	3.68 04	3.68 04	3.67 04	
	2.76-02	3.15-02	3.23-01	3.16-01	4.74-01	4.67-01	7.59-02	7.42-02	7.59-02	7.59-02	7.42-02	
	0.99321	1.3953-03	0.99977	5.6682-04	0.99982	5.6263-04	0.99980	5.6860-04	0.99980	0.99980	5.6860-04	
P2	1.19 04	1.24 04	2.79 04	2.78 04	3.32 04	3.32 04	3.21 04	3.20 04	3.32 04	3.32 04	3.20 04	
	1.11-02	1.22-02	1.29-01	1.27-01	1.90-01	1.88-01	3.03-02	2.99-02	3.03-02	3.03-02	2.99-02	
	0.98715	1.3998-03	0.99975	5.0284-04	0.99981	5.0387-04	0.99979	5.0556-04	0.99979	0.99979	5.0556-04	
P3	2.47 03	2.86 03	1.84 04	1.83 04	2.38 04	2.37 04	2.26 04	2.25 04	2.38 04	2.38 04	2.25 04	
	1.77-03	1.92-03	2.06-02	2.02-02	3.03-02	2.99-02	4.84-03	4.75-03	3.03-02	3.03-02	4.75-03	
	0.79262	1.4296-03	0.99968	3.8113-04	0.99978	3.7997-04	0.99975	3.8637-04	0.99975	0.99975	3.8637-04	
E1		-8.04 04		-6.52 04		-5.98 04		-6.09 04			-6.09 04	
		-6.17-11		-6.21-10		-9.18-10		-1.49-10			-1.49-10	
		-1.0255-02		-1.1688-02		-1.1785-02		-1.1807-02			-1.1807-02	

B1	5.28 04	6.58 04	7.09 04	6.97 04
	-2.52 02	-1.50 03	-2.08 03	-3.29 02
	--1.0949-01	-1.0896-01	--1.0893-01	-1.0892-01
P4	-1.17 04	4.17 03	9.54 03	8.37 03
	1.13-04	1.32-03	1.93-03	3.09-04
	0.98747	0.99843	0.99960	0.99943
F1	4.68 04	6.27 04	6.61 04	6.49 04
	1.65 01	1.93 02	1.88 02	4.54 01
	0.98683	0.99560	4.5798-03	0.99638
A2	1.04 04	2.63 04	3.07 04	3.05 04
	1.09-02	1.27-01	1.52-01	2.99-02
	0.90977	0.99372	2.2255-03	0.99576
A3	-1.71 03	1.42 04	1.89 04	1.84 04
	9.49-04	9.04-04	1.41-02	2.60-03
	0.41403	3.0915-03	1.4532-03	0.99503
D1	8.78 04	1.04 05	1.09 05	1.08 05
	2.61 04	3.05 05	4.43 05	7.34 04
	0.99958	1.8685-03	1.5036-03	0.99985
D2	9.71 04	1.13 05	1.19 05	1.17 05
	1.13 05	1.32 06	2.20 06	3.09 05
	0.99873	3.6913-03	2.2585-03	0.99967
D3	1.08 05	1.24 05	1.28 05	1.28 05
	3.07 05	3.59 06	3.99 06	5.34 05
	0.99661	7.1776-03	5.6326-03	0.99851
D4	1.01 05	1.17 05	1.22 05	1.21 05
	5.76 04	6.72 05	9.83 05	1.58 05
	0.99812	4.8025-03	3.2319-03	0.99988

\* Calculations were performed on a TI 59 calculator. Values are presented in computer notation, e.g., -5.00-05 =  $-5.00 \times 10^{-5}$ .

E = Apparent activation energy ( $\text{J mole}^{-1}$ ); Z = constant ( $\text{s}^{-1} \text{K}^{-1}$ ).

L = Linearization procedure by least squares method ( $|r|$  = correlation coefficient).

M = Absolute mean deviation method; E and Z values were calculated using eqn. (17);  $\nu$  values were calculated using eqn. (19).

TABLE 1 (continued)

Symbol of the mechanism [54]	Method of evaluation of kinetic constants											
	$T_0 = 0 \text{ K}; b = 0.5$			$T_0 = 0 \text{ K}; b = 0.75$			$T_0 = 0 \text{ K}; b = 1$					
	L	M		L	M		L	M		L	M	
R1	E	4.98 04	4.98 04	E	4.87 04	4.86 04	E	4.75 04	4.74 04	E	4.74 04	4.74 04
	Z	1.90-01	1.88-01	Z	3.04-02	2.97-02	Z	4.86-03	4.74-03	Z	4.74-03	4.74-03
	r	0.99981	7.5676-04	r	0.99980	7.5847-04	r	0.99978	7.6097-04	r	0.99978	7.6097-04
R2	E	5.73 04	5.67 04	E	5.61 04	5.56 04	E	5.50 04	5.44 04	E	5.44 04	5.44 04
	Z	5.23-01	4.64-01	Z	8.43-02	7.54-02	Z	1.35-02	1.20-02	Z	1.20-02	1.20-02
	r	0.99912	1.8044-03	r	0.99910	1.7891-03	r	0.99908	1.7671-03	r	0.99908	1.7671-03
R3	E	6.00 04	5.90 04	E	5.88 04	5.78 04	E	5.77 04	5.66 04	E	5.66 04	5.66 04
	Z	6.52-01	5.29-01	Z	1.04-01	8.40-02	Z	1.67-02	1.33-02	Z	1.33-02	1.33-02
	r	0.99888	2.6456-03	r	0.99884	2.6237-03	r	0.99829	2.6060-03	r	0.99829	2.6060-03
P1	E	3.56 04	3.56 04	E	3.45 04	3.44 04	E	3.33 04	3.32 04	E	3.32 04	3.32 04
	Z	1.21-02	1.20-02	Z	1.94-03	1.91-03	Z	3.10-04	3.04-04	Z	3.04-04	3.04-04
	r	0.99978	5.7314-04	r	0.99976	5.7484-04	r	0.99974	5.7849-04	r	0.99974	5.7849-04
P2	E	3.09 04	3.08 04	E	2.97 04	2.97 04	E	2.86 04	2.85 04	E	2.85 04	2.85 04
	Z	4.85-03	4.75-03	Z	7.75-04	7.71-04	Z	1.24-04	1.22-04	Z	1.22-04	1.22-04
	r	0.99977	5.1113-04	r	0.99974	5.1607-04	r	0.99971	5.1777-04	r	0.99971	5.1777-04
P3	E	2.14 04	2.14 04	E	2.03 04	2.02 04	E	1.91 04	1.90 04	E	1.90 04	1.90 04
	Z	7.74-04	7.71-04	Z	1.24-04	1.22-04	Z	1.98-05	1.95-05	Z	1.95-05	1.95-05
	r	0.99971	3.8985-04	r	0.99966	3.9596-04	r	0.99960	4.0525-04	r	0.99960	4.0525-04
E1	E	-6.22 04	-6.22 04	E	-6.34 04	-6.34 04	E	-6.34 04	-6.45 04	E	-6.45 04	-6.45 04
	Z	-2.31-11	-2.31-11	Z	-3.68-12	-3.68-12	Z	-3.68-12	-5.97-13	Z	-5.97-13	-5.97-13
	r	-1.1819-02	-1.1819-02	r	-1.1840-02	-1.1840-02	r	-1.1840-02	-1.1858-02	r	-1.1858-02	-1.1858-02



B1		6.84 04	6.73 04	6.60 04
		-5.11 01	-8.30 00	-1.29 00
		-1.0892-01	-1.0891-01	-1.0890-01
P4	7.20 03	7.20 03	6.06 03	4.87 03
	4.94-05	4.94-05	7.94-06	1.26-06
	0.99915	2.2228-04	2.3379-04	0.99770
F1	6.57 04	6.37 04	6.26 04	6.34 04
	7.25 00	4.74 00	7.69-01	1.85-01
	0.99622	4.5405-03	4.5194-03	0.99600
A2	2.93 04	2.84 04	2.72 04	2.70 04
	4.78-03	3.91-03	6.21-04	1.22-04
	0.99549	2.1827-03	2.1642-03	0.99486
A3	1.72 04	1.66 04	1.55 04	1.49 04
	4.16-04	3.64-04	5.91-05	1.06-05
	0.99448	1.4096-03	1.3942-03	0.99300
D1	1.07 05	1.06 05	1.05 05	1.04 05
	1.14 04	9.84 03	1.63 03	2.93 02
	0.99984	1.5364-03	1.5243-03	0.99983
D2	1.16 05	1.17 05	1.15 05	1.14 05
	4.94 04	6.04 04	8.09 03	1.34 03
	0.99967	2.2710-03	2.2423-03	0.99966
D3	1.27 05	1.25 05	1.24 05	1.23 05
	1.35 05	8.85 04	1.47 04	3.45 03
	0.99850	5.4840-03	5.4725-03	0.99846
D4	1.20 05	1.19 05	1.18 05	1.17 05
	2.52 04	2.18 04	3.62 03	6.45 02
	0.99938	3.1681-03	3.1424-03	0.99936
				3.1280-03

(ii) In ideal circumstances  $\nu$  or  $\delta$  should be equal to 0 if  $g(\alpha)$  or  $f(\alpha)$  functions describe exactly the mechanism of the reaction. In reality, the random errors influencing experimental data, as well as imperfections of the assumed reaction model cause  $\nu$  or  $\delta$  to reach values other than 0. One may consider, however, that these functions  $g(\alpha)$  or  $f(\alpha)$  fit the experimental data better when  $\nu$  or  $\delta$  reach lower values.

The function  $\delta$  represents the ratio of the square root of the variance to the mean value. Similar parameters have been proposed for the same purposes by Zsako [63] and recently by Swaminathan et al. [55]. However, in our opinion, it is better to use the  $\delta$  function, which represents the standard deviation in relation to the mean value. This parameter is recommended for statistical considerations [59].

It is worth noting that the linear interpolation method and the  $\delta$  function are the same in nature, i.e. are based on the least squares assumption. On the other hand, the  $\nu$  function is based on the least absolute deviation assumption. Both  $\nu$  and  $\delta$  functions, together with the linear interpolation method, were applied to the thermogravimetric data presented previously [54], for the purpose of evaluating the kinetic parameters based on the approach proposed in this work. The results are listed in Tables 1 and 2.

TABLE 2

Kinetic constants for the thermal dissociation of  $\text{Rb}_2\text{PbCl}_6$  (see ref. 54: Fig. 1, Table 4) calculated using differential equations \*

Symbol of the mechanism [54]	Method of calculation					
	Apparent activation energy ( $\text{J mole}^{-1}$ )		Z constant ( $\text{s}^{-1}$ )		$\delta$ [eqn. (20)]	
	A	B	A	B	A	B
R1	5.26 04	4.83 04	6.96 00	3.39 01	4.1869-02	4.2678-02
R2	7.06 04	6.62 04	1.63 02	1.02 03	4.1727-02	4.0967-02
R3	7.68 04	7.24 04	4.14 02	2.81 03	6.6872-02	6.8044-02
P1	3.82 04	3.40 04	4.28-01	1.60 00	4.1402-02	4.2166-02
P2	3.34 04	2.93 04	1.69-01	5.71-01	4.1285-02	4.2022-02
P3	2.37 04	1.98 04	2.57-02	6.81-02	4.1122-02	4.1788-02
E1	-9.33 03	-8.66 03	-4.89-04	5.52-04	-1.0717-01	4.1468-02
B1	3.24 04	2.83 04	7.82-01	2.58 00	1.2993-01	1.2919-01
P4	8.62 03	5.57 03	1.46-03	2.17-03	4.1158-02	4.1556-02
F1	8.94 04	8.50 04	1.91 04	1.50 05	1.2554-01	1.2465-01
A2	5.25 04	4.82 04	9.21 00	4.49 01	9.3351-02	9.2558-02
A3	4.02 04	3.60 04	6.55-01	2.56 00	8.2950-02	8.2213-02
D1	1.10 05	1.05 05	4.70 05	3.95 06	4.5269-02	4.6105-02
D2	1.26 05	1.21 05	8.11 06	7.77 07	2.3288-02	2.1903-02
D3	1.57 05	1.52 05	1.75 09	2.08 10	1.6509-01	1.6422-01
D4	1.32 05	1.27 05	6.82 06	6.84 07	5.0715-02	4.9901-02

\* Calculations were performed on a TI 59 calculator. The values are presented in computer notation.

\*\* A, Based on eqn. (18);  $T_0 = 0$  K.

$$\text{B, Based on the eqn. } \Delta^{**} \equiv \frac{d\alpha/dt}{f(\alpha) \exp(-E/RT)} = Z$$

## DISCUSSION

Application of integral eqn. (15) to the experimental thermogravimetric data [54] leads to the kinetic constants and statistical parameters ( $|r|$  and  $\nu$ ) listed in Table 1, from which some general conclusions may be derived.

For all considered  $g(\alpha)$  functions, correlation coefficients reach the highest values in the case  $T_0 = 0$  K,  $b = 0$ . Values of  $E$  in the case  $T_0 = 0$  K,  $b = 1$  present simply Coats and Redfern's approach [54]. Therefore, one may notice that linearization procedures based on eqn. (15) give better fits to the experimental data than that based on the method of Coats and Redfern.

Values of the  $\nu$  function [eqns. (17) and (19)] do not show similar regularities. For most  $g(\alpha)$  functions,  $\nu$  reaches the highest values in the case  $T_0 = T_{\alpha=0.01}$ . Values of  $\nu$  change slightly if  $T_0$  is kept at 0 K, and  $b$  varies between 0 and 1. Applying both the linearization procedure based on eqn. (16) and a trial and error procedure based on eqn. (17), similar values of  $E$  and  $Z$  were obtained, despite the fact that both methods are based on different assumptions.

Changes of both statistical parameters show that an increase in  $|r|$  value corresponds to a decrease in  $\nu$  value. However, differences between  $\nu$  values are more distinct than those between appropriate correlation coefficients. Therefore, examination of  $\nu$  values makes it easier to distinguish between possible  $g(\alpha)$  functions.

The differences between the values of apparent activation energy resulting from application of eqn. (16) and other integral methods (ref. 54: Table 4) are higher for lower values of  $E$ . If  $E > 10^5$  (J mole<sup>-1</sup>) these differences become much lower in comparison with those resulting from experimental uncertainties (ref. 54: Table 5).

The values of  $Z$  obtained based on eqn. (16) differ significantly in comparison with those resulting from the application of other integral methods (ref. 54: Table 4). Generally, the application of eqn. (16) leads to lower values of  $Z$ . This is not an unexpected conclusion, however, if one compares the intercepts of eqn. (16) and, for example, Coats and Redfern's equation [54]. It is worth noting that significant differences between  $Z$  values have also been found when several integral methods have been applied to the same experimental data [31,54,64–66].

Comparison of the values of statistical parameters listed in Table 1 indicates that the best fit of integral eqns. (16) and (17) to the experimental data were obtained when the initial temperature ( $T_0$ ) was assumed to be 0 K. These regularities do not seem to be accidental.  $T_0$  has been introduced during the integration procedure resulting in eqn. (10). It represents the lower integration limit and corresponds to  $t = 0$ . In non-isothermal experiments the initial temperature has no significant meaning. Some authors consider  $T_0$  as the equilibrium temperature [18,20].  $T_0$  may be assumed to be room temperature, i.e. the temperature at the beginning of the experiment, but not necessarily at the onset of the reaction. Further,  $T_0$  may be considered as the temperature at the beginning of the thermal process, for example,  $T_0 = T_{\alpha=0.01}$ . Lastly, it is best to assume that  $T_0$  is 0 K. The above assumption

seems to be the logical extension of the analogous assumption which has been accepted for the temperature integral [e.g. in eqn. (8)]. In non-isothermal measurements it is not important at which moment one starts to count time for the experiment. However, the actual temperature of the sample is important; this describes the thermal behaviour of the material at a certain moment, and so also the kinetics. It is obvious that  $T_0$  should be reproducible for any experiment, and the reaction rate at  $T_0$  should be negligible. These requirements correspond best when  $T_0 = 0$  K. Therefore, taking into account the above considerations, the following integral forms may be proposed for the description of reaction kinetics under linear temperature increase conditions

$$g(\alpha) = \frac{T}{\phi} Z T^b \exp(-E/RT) \quad (21)$$

if  $k(T)$  is expressed by eqn. (5), or

$$g(\alpha) = \frac{T}{\phi} Z \exp(-E/RT) \quad (22)$$

if  $k(T)$  is expressed by the Arrhenius-type eqn. (4). It is worth noting that both the above forms can be obtained if one substitutes  $t = T/\phi$  in the integral equation derived for isothermal conditions [for example in eqn. (7)].

The differential forms which correspond to integral eqns. (21) and (22) are presented below [compare with eqns. (14) and (15)]

$$d\alpha/dt = f(\alpha) Z T^b (b + 1 + E/RT) \exp(-E/RT) \quad (23)$$

$$d\alpha/dt = f(\alpha) Z (1 + E/RT) \exp(-E/RT) \quad (24)$$

The values of the kinetic constants and  $\delta$  calculated based on the differential equations are presented in Table 2. It is interesting to compare the values listed in Table 2 with those resulting from the application of integral methods (Table 1) [54], as well as with those resulting from the application of Freeman and Carroll's approach [54]. A comparison of the apparent activation energy and  $Z$  calculated by method B with those estimated based on Freeman and Carroll's approach (ref. 54: Table 4), indicates significant differences between the values of the kinetic parameters. This is an unexpected result because both the above methods of calculation are based on the same differential equation. The values of the kinetic constants calculated by method B (Table 2) show better agreement with the corresponding values of  $E$  and  $Z$  evaluated by integral methods than with those obtained applying Freeman and Carroll's approach (ref. 54: Table 4). This may result from the fact that in Freeman and Carroll's method the relative differences between  $f(\alpha)$ ,  $1/T$ , and  $d\alpha/dt$  are taken into account; so, any random errors influencing reference point may cause significant changes in the relative differences. On the other hand, in the approach proposed in this work, one assumes all experimental points to have equal statistical weights.

No general regularities are found if one compares the values of the kinetic constants resulting from the application of integral eqn. (22) (Table 1) or differential eqn. (24) (Table 2: method A). For most functions describing

the reaction mechanism, values of  $E$  and  $Z$  are slightly higher if one uses differential eqn. (24). Despite the fact that values of  $E$  and  $Z$  result from the application of different forms of the kinetic equations and slightly different experimental data, the agreement between them is quite good.

Application of differential eqn. (24) (method A) leads to  $E$  values higher than those obtained by method B (Table 2). On the other hand,  $Z$  values show reversed regularities, i.e. are higher in the case of method B. The latter dependence results from the fact that  $Z(1 + E/RT)_{(\text{method A})} \simeq Z_{(\text{method B})}$ .

Taking into account that  $E$  has to have values higher than  $\Delta H_a^0$  [54] and examining the results in Tables 1 and 2, one may conclude that mechanism D2 gives the best fit to the experimental data (ref. 54: Fig. 1).

## CONCLUSIONS

The results presented in this work indicate that the general equations derived for the description of reaction kinetics under linear temperature increase conditions, using the assumption that  $\alpha = f(t, T)$ , fit as well to the experimental data as do the widely used and recommended calculation methods in the literature [7,9,54]. Furthermore, proposed integral eqns. (21) and (22) are accurate from the pure mathematical point of view, while those integral methods proposed in the literature are based on approximations of Euler-type integrals. Therefore, using the latter methods of calculation, one usually obtains different values for the kinetic constants (see, for example, refs. 31, 54, 64–66). Therefore, the equations proposed in this work may be considered as adequate forms for the description of reaction kinetics under linear temperature increase conditions. It is obvious that, before acceptance of this approach, further experimental confirmation is necessary.

The results presented here are not able to answer the questions as to whether the calculated kinetic constants resulting from the approach used in this work may be compared with those obtained for isothermal conditions, or whether the assumed  $k(T)$  functions are the best possible description of solid state reaction kinetics [7,35,67,68]. Reviewing published kinetic data, one raises the question as to whether or not comparison of kinetic parameters resulting from application of different experimental techniques is possible at all. It seems that the present knowledge of solid state reaction kinetics employs mathematical descriptions that are really only formal approaches for empirical convenience. The kinetic parameters, apparent activation energy and especially  $Z$ , should be considered rather as empirical constants without theoretical significance [7,69,70].

Some remarks may be made regarding the methods of application of differential or integral equations for the purpose of evaluating the kinetic constants. In most of the methods proposed in the literature, kinetic equations were transformed to forms which permitted the use of a linear interpolation procedure. The above approach is very useful but may lead to inadequate results, especially if one uses differential kinetic equations. In the case of differential equations the approach proposed here, which is based on a search for the minimum values of  $\nu$  or  $\delta$  functions, may be recommended over that of Freeman and Carroll [51].

## APPENDIX A

$$\left\{ \frac{\partial [T^b \exp(-E/RT)]}{\partial T} \right\}_T = bT^{b-1} \exp(-E/RT) + \frac{E}{R} T^{b-2} \exp(-E/RT) \quad (\text{A1})$$

For further consideration it is convenient to introduce the substitution  $x = E/RT$ . Taking the right-hand side of eqn. (A1) together with eqn. (11) one may obtain

$$g(\alpha) = (b+1) \frac{ZE}{R\phi} \left(\frac{E}{R}\right)^b \int_x^\infty x^{-(b+2)} e^{-x} dx + \frac{Z}{\phi} \left(\frac{E}{R}\right)^b \left(\frac{E}{R} - bT_0\right) \int_x^\infty x^{-(b+1)} e^{-x} dx - T_0 \frac{Z}{\phi} \left(\frac{E}{R}\right)^b \int_x^\infty x^{-b} e^{-x} dx \quad (\text{A2})$$

Integrals in eqn. (A2) are examples of Euler's integrals for which the following relationship exists [57,58]

$$\int_x^\infty x^a e^{-x} dx = a \int_x^\infty x^{a-1} e^{-x} dx + x^a e^{-x} \quad (\text{A3})$$

if  $\text{Re}(x) > 0$ .

Therefore eqn. (A2) may be transformed to the simpler form

$$g(\alpha) = (b+1) \frac{Z}{\phi} \left(\frac{E}{R}\right)^b \left[ \frac{E}{R} - \left(\frac{E}{R} - bT_0\right) - bT_0 \right] \int_x^\infty x^{-(b+2)} e^{-x} dx + \frac{Z}{\phi} \left(\frac{E}{R}\right)^b \left( \frac{E}{R} x^{-(b+1)} - T_0 x^{-b} \right) e^{-x} \quad (\text{A4})$$

It is easy to see that the term including the integral is equal to 0. Therefore, after transformation, the following equation is obtained

$$g(\alpha) = \frac{Z}{\phi} T^b (T - T_0) \exp(-E/RT) \quad (\text{A5})$$

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