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MECHANISM AND KINETICS FROM NON-ISOTHERMAL TG TRACES

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ABSTRACT

The TG trace corresponding to a heterogeneous process which proceeds with a constant increase of the temperature can be described by the equation

$$\log g(\alpha) - \log p(x) = B$$

where α is the fraction decomposed, function $g(\alpha)$ is given by the rate controlling process and function $p(x)$ depends on its activation energy. Both functions $\log g(\alpha)$ and $\log p(x)$ are approximately linear functions of $1/T$. The value of B is independent of the temperature. On plotting $\log g(\alpha)$ *vs.* $1/T_\alpha$ calculated from TG trace for different possible $g(\alpha)$ the most probable mechanism corresponding to the linear plot can be estimated. From the slope of this straight line the corresponding value of activation energy can be calculated.

INTRODUCTION

There are known many methods for the determination of the kinetic parameters from dynamic thermogravimetric measurements[1,2]. In the recent paper[3] a simple graphical method was recommended. The present paper tries to simplify the estimation of the reaction mechanism.

PRINCIPLE OF THE METHOD

On assuming that the non-isothermal experiment proceeds in an infinitesimal time interval isothermally, the rate of it may be described by the equation

$$\frac{d\alpha}{dt} = Z \cdot e^{-E/RT} \cdot f(\alpha) \tag{1}$$

where α is the fraction decomposed in the time t, $f(\alpha)$ depends on the mechanism of the process, E is the activation energy and Z is the preexponential factor. In the case of the constant temperature increase $dT/dt = q$ the integration of Eqn. (1) leads[1,4] to

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{E}{Rq} \cdot p(x) \tag{2}$$

The function p(x) is defined as[1–4]

$$p(x) = \frac{e^{-x}}{x} - \int_{+x}^{\infty} \frac{e^{-u}}{u} du = \frac{e^{-x}}{x} + Ei(-x) \qquad (3)$$

where $u = E/RT$, $x = E/RT_\alpha$ and T_α is the temperature at which the fraction α of the starting material has reacted.
From the logarithmic form of Eqn. (2)

$$\log g(\alpha) - \log p(x) = \log \frac{ZE}{Rq} \qquad (4)$$

it can be seen that its right hand side is independent of the temperature. Thus the difference of log g(α) and log p(x), both functions of the temperature, does not depend upon the temperature in the whole temperature interval in which the process proceeds. The function log p(x) is, to a first approximation, a linear function of $1/T_\alpha$ if x is sufficiently large[5] (see Fig. 1) and, therefore, log g(α) must also be a linear function of $1/T_\alpha$. For the correct mechanism log [g(α)] thus be linear function of $1/T_\alpha$. The values of log g(α) calculated for the various rate processes using TG trace and plotted *vs.* the corresponding $1/T_\alpha$ values should give a straight line only for the rate process [log g(α)] which can be designated as the most probable. The others, for which this plot is not linear, can be refused. The sensitivity of this procedure for the mechanism determination is, as in all non-isothermal methods, not too high. But it yet gives valuable and useful informations. The determination of the rate process is not completely unambiguous as it can be seen from the example in Fig. 2. The bottom curve represents the TG trace for a process which can be described by the kinetic equation

$$-\ln(1-\alpha) = kt \qquad (5)$$

This type of the equation is frequently employed in the literature[4]. The upper curves are the plots of log $g(\alpha)$ *vs.* $1/T_\alpha$ being calculated from the scanned TG trace employing various kinetic equations (see Table I). The symbols used are the same as in the paper of Sharp *et al.*[6] (for more detailed review of functions g(α) and f(α) see Ref. 7).

TABLE I

KINETIC EQUATIONS

Function	*Equation*	*Rate-controlling process*
D_1	$\alpha^2 = kt$	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D_3	$[1-(1-\alpha)^{\frac{1}{3}}]^2 = kt$	Three-dimensional diffusion, spherical symmetry; Jander equation
D_4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{\frac{2}{3}} = kt$	Three-dimensional diffusion, spherical symmetry; Ginstling–Brounshtein equation
F_1	$-\ln(1-\alpha) = kt$	Random nucleation, one nucleus on each particle
A_2	$\sqrt{-\ln(1-\alpha)} = kt$	Random nucleation; Avrami equation I
A_3	$\sqrt[3]{-\ln(1-\alpha)} = kt$	Random nucleation; Avrami equation II
R_2	$1-(1-\alpha)^{\frac{1}{2}} = kt$	Phase boundary reaction, cylindrical symmetry
R_3	$1-(1-\alpha)^{\frac{1}{3}} = kt$	Phase boundary reaction, spherical symmetry

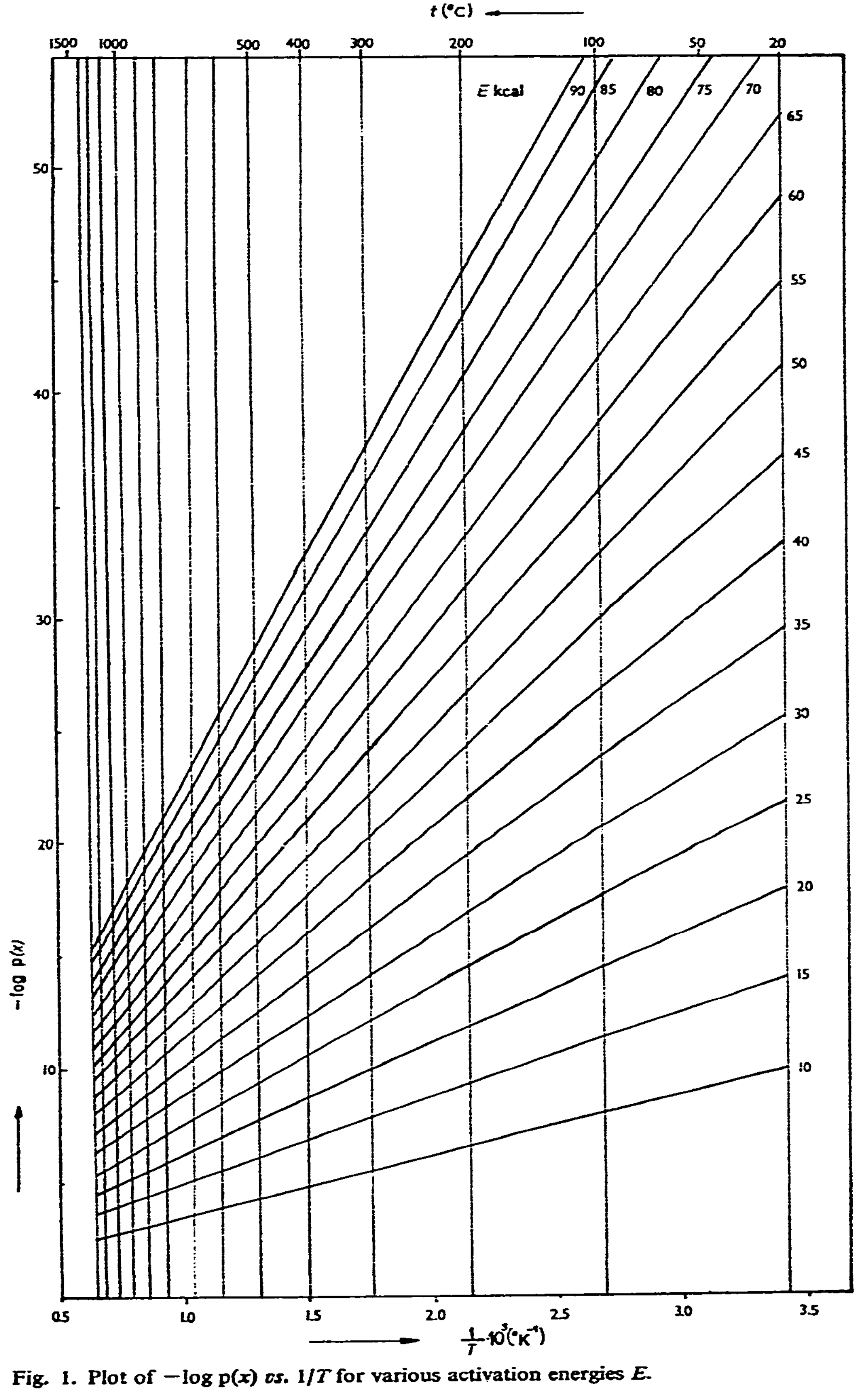

Fig. 1. Plot of $-\log p(x)$ *vs.* $1/T$ for various activation energies E.

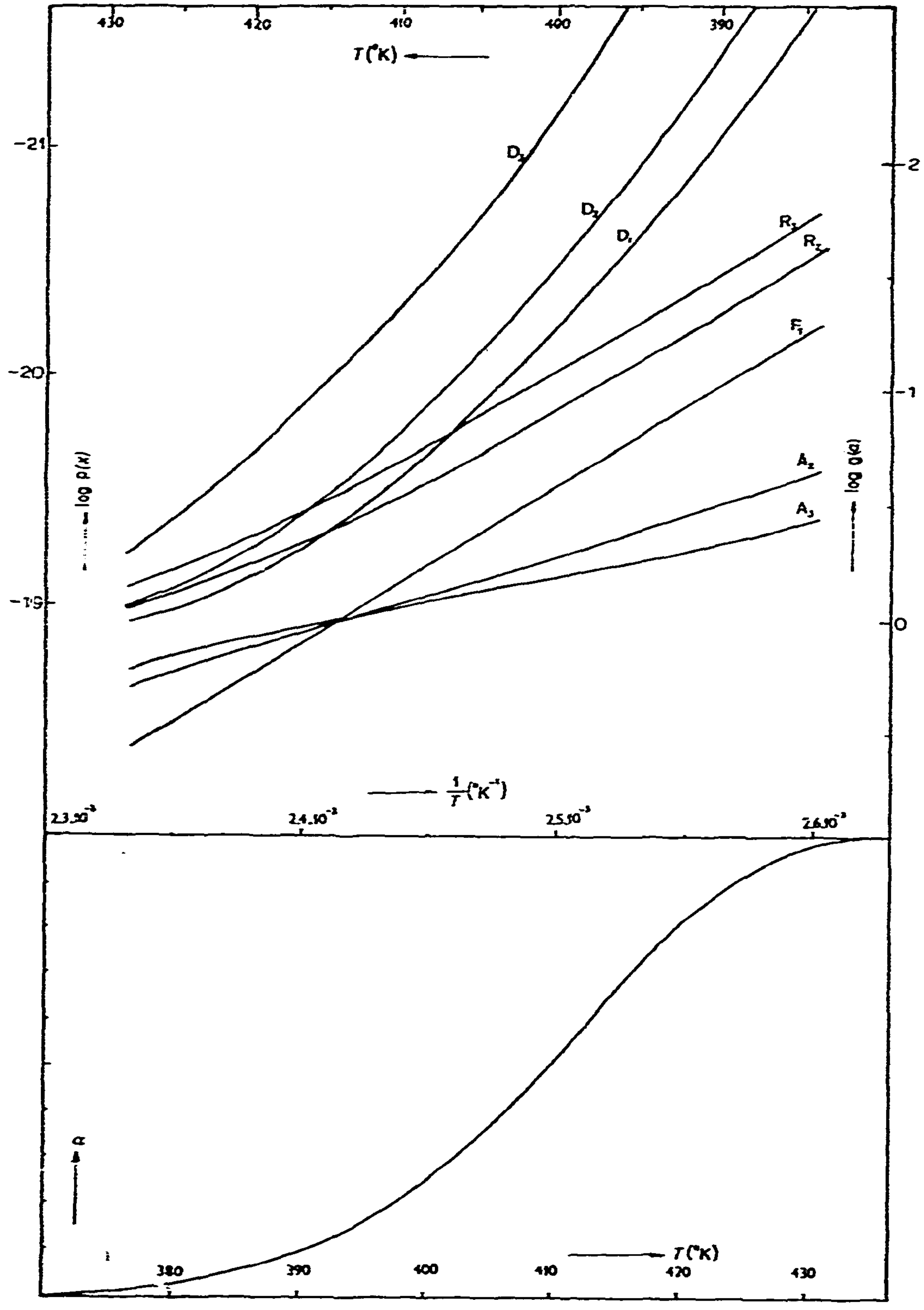

Fig. 2. Procedure for evaluating TG curve. Lower curve complies with kinetic equation F_1 (see Table I) $E = 30$ kcal·mol^{-1}, $Z = 10^{13}$s^{-1}·mol^{-1} and $q = 1$°C·min^{-1}. Upper curves are plots of log $g(\alpha)$ *vs.* $1/T_\alpha$ calculated from TG curve for various kinetic equations. The straight line for kinetic equation F_1 coincides with the plot of $-\log p(x)$ *vs.* $1/T$ for $E = 30$ kcal/mol.

Only the plot for Eqn. (5) (F_1) gives a straight line. The other equations can be refused. Deviations from the linearity are comparatively very small in the case of the Eqns. A_2 and A_3. The other informations about the process studied are evidently required for the correct decision concerning the choise of the true mechanism for the process investigated. The value of activation energy E can be determined by the trial and error method. Introducing the slope of log g(α) *vs.* $1/T_\alpha$ and the mean value of the temperature from the interval in which the process proceeds the following equation can be derived (see Appendix)

$$\mathrm{tg}\,\alpha = \frac{\mathrm{d}\log \mathrm{p}(x)}{\mathrm{d}\frac{1}{T}} = -\frac{E}{R}\left[\frac{1}{x(\mathrm{i}-x.\mathrm{e}^{x}.\ Ei(-x))}\right] \tag{6}$$

and the value of E can be calculated.

For large values of x the activation energy can be calculated approximately from the equation

$$E \cong -\mathrm{tg}\alpha + \sqrt{tg^2\alpha + 8\,\mathrm{tg}\alpha \cdot \overline{T}} \tag{7}$$

where tgα is the slope of the selected linear plot of log g(α) *vs.* $1/T_\alpha$ and $\overline{T}$ is the mean temperature. The value of E can be found easy by a comparison of the slope of the straight line of log g (α) *vs.* $1/T_\alpha$ with a set of the lines of log p(x) *vs.* $1/T$ (Fig. 1) constructed for the different values of E. The slope of both functions should be the same in the temperature interval in which the process proceeds.

APPENDIX

The function p(x) is defined by the equation

$$\mathrm{p}(x) = \frac{\mathrm{e}^{-x}}{x} + Ei(-x) \tag{A1}$$

where the exponential integral[6] is defined as

$$Ei(-x) = \frac{\mathrm{e}^{-x}}{x}\left(1 - \frac{1}{x} + \frac{2!}{x^2} - \frac{3!}{x^3} + \frac{4!}{x^4} - \ldots\right) \tag{A2}$$

$$\text{for } x = \frac{E}{RT} \tag{A3}$$

Than

$$\mathrm{p}(x) = \frac{\mathrm{e}^{-x}}{x}\left[\frac{1}{x} - \frac{2!}{x^2} + \frac{3!}{x^3} - \frac{4!}{x^4} + \ldots\right] \tag{A4}$$

and

$$\log \mathrm{p}(x) = -x + \log\left[\frac{1}{x^2} - \frac{2!}{x^3} + \frac{3!}{x^4} - \ldots\right] \tag{A5}$$

The differentiation of Eqn. (5) gives

$$\frac{\mathrm{d} \log \mathrm{p}(x)}{\mathrm{d}x} = -\frac{1}{1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \ldots} \tag{A6}$$

Rearranging Eqn. (6) and introducing Eqn. (2) it can be obtained

$$\frac{\mathrm{d} \log \mathrm{p}(x)}{\mathrm{d}x} = -\frac{1}{x\left[1 - x.\mathrm{e}^x\, Ei(-x)\right]} \tag{A7}$$

The slope of log p(x) *vs.* $1/T$ is then

$$\frac{\mathrm{d} \log \mathrm{p}(x)}{d\frac{1}{T}} = -\frac{E}{R}\left[\frac{1}{x\left[1 - x.\mathrm{e}^x\, Ei(-x)\right]}\right] \tag{A8}$$

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