# Reliability of Methods for Determination of Kinetic Parameters from Thermogravimetry and DSC Measurements

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## INTRODUCTION

Thermoanalytical measurements, thermogravimetry (TG), and differential scanning calorimetry (DSC) are relatively fast and exact methods which can be used for determination of kinetics of degradation and other reactions. Conversion of data from curves given by the instrument into kinetic parameters, energy of activation, reaction order, rate constant, and preexponential factor is based on the utilization of classical laws of kinetics. The rate of chemical reaction, $d\alpha/dt$, can be expressed as a function of the degree of conversion, $\alpha$, using general formulation:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{1}$$

where $k$ is rate constant and $f(\alpha)$ is some function of the degree of conversion.

In thermogravimetry, $\alpha$ can be expressed using initial ($Wo$), instantaneous ($W$) and final ($W\infty$) mass of the sample by:

$$\alpha = \frac{Wo - W}{Wo - W\infty}$$

Thus $\alpha$ changes with temperature or time from 0 to 1. In calorimetric measurements, $\alpha$ is the ratio of enthalpies up to a given degree of conversion ($H$) and total enthalpy of reaction ($H_T$) i.e., $\alpha = H/H_T$, which is equivalent to the ratio of areas under the DSC curve ($a/A$) corresponding to given conversions. It should be added that although TG and DSC measure different physical properties there is a full analogy between the derivative TG curve (DTG) and DSC curve where both represent the rates of change of measured properties $dw/dt$ or $dH/dt$ as a function of temperature or time. Both are obtained automatically on modern instruments. TG instruments also give a form of integral curve (i.e., the residue (mass) is given as a function of temperature or time), while DSC integral curves usually have to be constructed from differential curves.

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In Eq. (1), the parameter $k$ depends on temperature ($T$) according to the Arrhenius relationship

$$k = Ae^{-E/RT} \tag{2}$$

where $R$ is the gas constant, $A$ is pre-exponential (frequency) factor, and $E$ is energy of activation.

For simple reactions, $f(\alpha)$ usually has the form $f(\alpha) = (1 - \alpha)^n$ where $n$ is reaction order. Combining Eqs. (1) and (2) the following expression is obtained:

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT} \cdot (1 - \alpha)^n \tag{3}$$

Experiments in thermal analysis are carried out isothermally or at a constant rate of heating $B = dT/dt$. In the latter case, Eq. (3) can be written in the form:

$$\frac{d\alpha}{dT} = \frac{A}{B} \cdot (1 - \alpha)^n \cdot e^{-E/RT} \tag{4}$$

Determination of parameters $A$, $E$, and $n$ is based on the solution of Eqs. (3) and (4). A number of methods for the calculation of kinetic parameters have been developed. They can be divided into integral or differential methods depending whether integral or differential forms of Eqs. (1), (3), and (4) are used. Extensive review of methods for the treatment of TG and DSC results is given by Doyle,[1] Manche and Carroll,[2] and Flynn and Wall.[3]

Nishizaki et al. have compared the results of application of different methods for determination of kinetic parameters for the process of polystyrene degradation measured by TG.[4] However, this assessment of different methods was qualitative because the true values for the kinetic constants were not known. To remove this uncertainty, a synthetic TG curve was constructed in this paper, based on a given energy of activation, reaction order, and pre-exponential factor. Different methods were applied to the theoretical (synthetic curve) to back-calculate the values of $E$, $A$, and $n$, which were then compared with the given ones. Since, in development of these methods, various approximations are made, the error magnitude is expected to vary from method to method. The same list of methods was used as in the work of Nishizaki et al.[4]

Some methods allow calculation of all kinetic parameters while in others only some of them can be obtained. Also, some methods require assumption of reaction order, and the correctness of the results for other kinetic parameters depends on the accuracy of the assumption. The magnitude of the error when incorrect order was assumed was examined in some methods. If the method requires the knowledge of reaction order, which can be determined from the curve, to calculate energy of activation as in the Kissinger method, then the calculated value of $n$ was used. The error in this part will be reflected in the error of activation energy. Since some methods require curves at several heating rates, curves at $B_1 = 0.1$°C/s and 0.2°C/s were generated for each of five given reaction orders 0, 0.5, 1, 2, and 3.

## Generation of Synthetic Thermoanalytical Curves

To derive the equations of synthetic TG, DTG, or their DSC counterparts, one starts from expressions for the reaction rate (3) or (4). If a new variable $x = -E/RT$ is introduced into Eq. (4) after integration, an expression relating degree of conversion to temperature or variable $x$ is obtained:

$$(1 - \alpha) = [(n - 1)\phi + 1]^{1/(1-n)} \tag{5}$$

where $n \neq 1$

and

$$(1 - \alpha) = e^{-2\phi} \quad \text{for } n = 1 \tag{6}$$

where $\phi = \dfrac{A \cdot E}{B \cdot R} \cdot p(x)$

and $p(x)$ is an exponential function defined by Doyle[5] as:

$$p(x) = -\frac{e^x}{x} + \int_{-x}^{x} \frac{e^x}{x} dx \tag{7}$$

Since there is no exact analytical solution for $p(x)$, a number of approximate expressions and semiempirical formulas were developed. The Schlomlich series expansion chosen in this work displays high accuracy after only a few terms:[3]

$$p(y) = \frac{e^{-y}}{y(y+1)}\left(1 - \frac{1}{y+2} + \frac{2}{(y+2)(y+3)} + \frac{4}{(y+2)\cdot\cdot(y+4)} + \cdots\right) \tag{8}$$

where $y = -x$ for $y \geqslant 15$

To obtain TG and DTG curves, activation energy $E = 251, 16$ kJ/mol (60 kcal/mole), pre-exponential factor $A = 10^{15}\text{s}^{-1}$ and heating rates $B = 0.1$°C/s and 0.2°C/s were taken. Reaction order was varied from 0 to 3. Figures 1 and 2 display synthetic TG and DTG curves were obtained for $E = 251, 12$ kJ/mol, $A = 10^{15}\text{s}^{-1}$, $B = 0.1$°C/s and $n = 0, 0.5, 1, 2$, and 3.

## Survey of Methods for Kinetic Analysis Used in This Paper

Basic equations for three differential methods analyzed in this paper are given in Table I, while integral methods are given in Table II. The Kissinger method[6] allows calculation of activation energy from one point (maximum on DTG curve) at several heating rates:

$$\frac{d\left(\ln \dfrac{B}{T_m^2}\right)}{d\left(\dfrac{1}{T_m}\right)} = -\frac{E}{R} \tag{13}$$

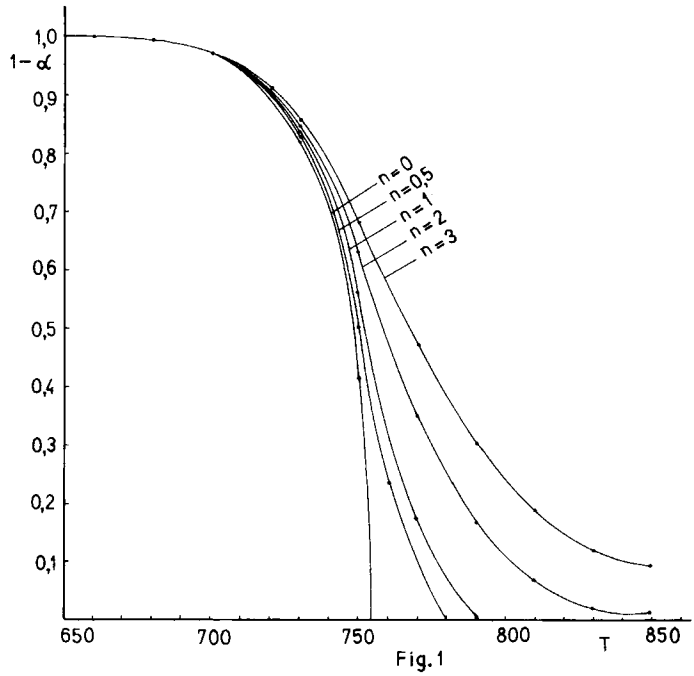


Fig. 1. Synthetic TG curve obtained at $E$ = 251, 12 kJ/mole, $A$ = $10^{15}/s^{-1}$, and $B$ = 0.1°C/s.

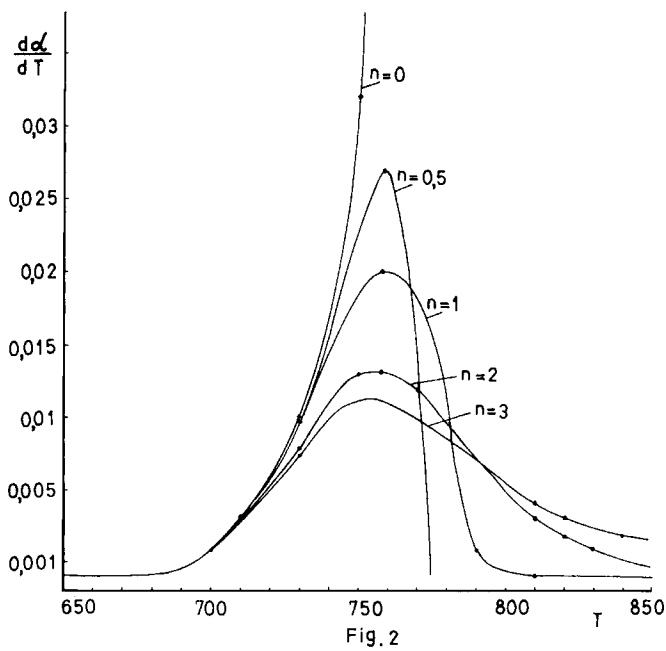


Fig. 2. DTG curves obtained at the same conditions as Fig. 1.

TABLE I
Differential Methods Used in This Work

| Method | Basic equations | Remark |
|---|---|---|
| Kissinger[6] | $n(1-\alpha)_m^{n-1} \approx (n-1)\cdot\frac{2RT_m}{E}$; | $T_m$ – temp. at the maximum rate (maximum on DTG or DSC curves) |
| | $n \neq 1$ ..... (9) | |
| | $\ln(1-\alpha)_m = \left(1 - \frac{2RT_m}{E}\right)$; | S-parameter of the peak asymmetry |
| | $n = 1$ ..... (10) | |
| | $n = 1.26\,S^{0.5}$ | |
| | $S = \frac{(d^2\alpha/dt^2)_1}{(d^2\alpha/dt^2)_2}$ | indices 1 and 2 correspond to inflexion points of the rate peak |
| Friedman[7] | $\ln B\left(\frac{d\alpha}{dT}\right) = \ln A + \ln f(\alpha) - \frac{E}{RT}$ | (11) |
| | $f(\alpha) = (1-\alpha)^n$ | |
| Freeman and Carroll[8] | $\frac{\Delta \log \frac{d\alpha}{dT}}{\Delta \log(1-\alpha)} = n - \frac{E}{2.3R}\cdot\frac{\Delta\left(\frac{1}{T}\right)}{\Delta \log(1-\alpha)}$ | values are taken in regular intervals of $(1/T)$ (12) |

TABLE II
List of Integral Methods Used

| Method | Basic equations | Remarks |
|---|---|---|
| van Krevelen et al.[9] | $\ln\left[\frac{(1-\alpha)^{1-n}}{1-n}\right] = \ln\left[\frac{A}{B}\left(\frac{0.368}{T_m}\right)^{E/RT_m} \cdot \frac{1}{\frac{E}{RT_m}+1}\right] + \left(\frac{E}{RT_m}+1\right)\cdot \ln T,$ for $n \neq 1$ .....(14) and for $n = 1$ $\ln\ln(1-\alpha) = \left(\frac{E}{RT_m}+1\right)\ln T$ .....(15) | $T_m$ is the temperature at the maximum rate of conversion (max. of DTG or DSC peak) |
| Coats and Redfern[10] | $\log\frac{\alpha}{T^2} = \log\frac{A\cdot R}{B\cdot E}\left(1-\frac{2RT}{E}\right) - \frac{E}{2.3R}\cdot\frac{1}{T}$ .....(16) | Valid for small $\alpha$ (Less than 0.1). $n = 0$ is assumed |
| Horowitz and Metzger[11] | $\ln\ln(1-\alpha) \approx \ln\frac{A\cdot E}{B\cdot R} - 5.33 - \frac{1.052}{T_s} + \frac{1.052E\cdot\theta}{R\cdot T_s^2}$ .....(17) for $n \neq 1$, $T_s$-temperature at maximum rate of conversion; $\theta = T - T_s$. | |

$\alpha_s = n^{1/(1-n)}$ is conversion at $T_s$

For $n = 1$, $\ln\ln(1 - \alpha) \approx \dfrac{E \cdot \theta}{R \cdot T^2}$ .....(18)

and $T_s$ is the temperature at which $1 - \alpha = \dfrac{1}{e} = 0.368$

Reich I[12]

$$\ln\ln(1 - \alpha) = -\frac{E}{RT} + \ln\left(\frac{A \cdot \Delta T}{B}\right)$$

for $n = 1$ .....(19)

or $\ln \alpha \approx \dfrac{E}{RT} + \ln\left(\dfrac{A \cdot \Delta T}{B}\right)$

for $n = 0$ .....(20)

$\alpha$ is taken in regular $\Delta T$ intervals

Reich II[13]

$$E = \frac{4.6 \log(B_2/B_1)(T_1/T_2)^2}{(1/T_1 - 1/T_2)} \quad .....(21)$$

At least two curves at different heating rates are necessary

Ozawa[14]

$$-\log B_1 - 0.457\frac{E}{RT_1} = \log B_2 - 0.457\frac{E}{RT_2} = .....(22)$$

$$E = \frac{R \log(B_2/B_1)}{0.457[(1/T_1) - (1/T_2)]} \quad .....(23)$$

It appears that activation energy is independent of reaction order. Reaction order is assessed from the shape factor of the DTG peak.

If, however, the reaction order is known as well as the degree of conversion at the maximum rate ($\alpha_m$), then the energy of activation can be calculated from Eqs. (9) or (10) as in this work from a single thermogram. Reaction order was calculated from the shape factor $S$, i.e., from the slopes of tangents at the inflection points of the rate peak.

According to the method of Friedman,[7] a plot of $\ln(B \cdot d\alpha/dT)$ vs. $1/T$ was made. The values of $T$ at constant $\alpha$ were taken from curves obtained at different heating rates. In our case, $\alpha$ was varied in steps of 0.2 from 0.1 to 0.9. Thus, a family of parallel straight lines was obtained whose slope is $E/R$ and has intersection with ordinate producing $\ln[A \cdot f(\alpha)]$. By plotting $\ln[A \cdot f(\alpha)]$ vs. $\ln(1 - \alpha)$, both pre-exponential factor and reaction order were obtained. Thus, two diagrams are required by this method.

The Freeman and Carroll method allows calculation of $E$ and from a single thermogram. The basic assumption is that $f(\alpha) = (1 - \alpha)^n$ and that the Arrhenius law is valid. These assumptions are necessary for the first method also.

In the method of van Krevelen requiring the assumption of reaction order $n = 1$, $E$ is determined from the slope of line obtained by plotting $\ln\ln(1 - \alpha)$ vs. $\ln T$. The Coats and Redfern method starts from the fact that at low conversions reaction order can be taken as zero in any case. Activation energy is calculated from the slope of the $\log \alpha/T^2$ vs. $1/T$ line. Horowitz and Metzger[11] introduced the characteristic temperature $T_s$ and the parameter $\theta = T - T_s$. It should be noted that $T_s$ has different meaning when $n \neq 1$ and when $n = 1$. Activation energy is obtained from the slope of the line obtained by plotting $\ln\ln(1 - \alpha)$ vs. $\theta$. Reaction order is calculated from the conversion at $T_s$.

A double logarithmic plot of $(1 - \alpha)$ vs. $1/T$ is used in the Reich I method[12] for the case of $n = 1$ or $\ln \alpha$ vs. $1/T$ for $n = 0$. The energy of activation is obtained from the slope of the resulting straight lines, using an assumed reaction order. Another method by Reich[13] requires use of two curves obtained at different heating rates. If $T_1$ and $T_2$ are the temperatures for the same degree of conversion and heating rates $B_1$ and $B_2$, then $E$ can be calculated from Eq. (21) (Table II).

Ozawa's method also requires several curves at different heating rates. The energy of activation is obtained from the slope of lines of $\log B$ vs. $1/T$ for specific conversions. By taking the temperature $T$ for more degrees of conversions, a family of parallel straight lines is obtained provided that $E$ does not change with the degree of conversion. Activation energy is obtained from the slope of the lines or Eq. (23).

To calculate kinetic parameters from the synthetic curves, various methods require characteristic input data which is given in Table III.

Calculations of $E$, $n$, and $A$ by applying differential and integral methods on curves from Figures 1 and 2 are summarized in Table IV. Parameters $n_t$, $n_a$, and $n_c$ are true reaction order (at which the curves are synthesized), assumed reaction order if the method required it and calculated reaction order (where the method allowed it). Figures 3–8 illustrate relationships obtained by application of various methods. As can be seen from Figures

TABLE III
Parameters from Synthetic Curves Necessary for Integral and Differential Methods

| | Heating rate | | | | |
|---|---|---|---|---|---|
| | $B$ = 0.1°C/s | | | | $B$ = 0.2°C/s |
| Reaction order | Temp. at max. rate of conversion ($T_m$, $T_s$, $T_1$[a]) | Conversion at max. rate of conversion Cs[a] | Temp. at which $1 - \alpha = \frac{1}{e}$ ($T_s$)[a] | Shape factor $S$ | Temperature at max. rate of conversion $T_2$ |
| 0.5 | 759.3 | 0.7369 | 755.5 | 0.1708 | 772.0 |
| 1 | 758.9 | 0.6144 | 759.8 | 0.5636 | 771.7 |
| 2 | 758.1 | 0.477 | 770.0 | 1.088 | 771.0 |
| 3 | 757.3 | 0.3965 | 781.5 | 1.4934 | 770.0 |

[a] Explained in the text.

3–8, straight lines were obtained and the coefficient of correlation of the regression lines was close to unity in all cases.

In the case of the method of van Krevelen, the effect of assumed order on true first order reaction was examined (Table IV). It is interesting to note that the method gives higher activation energies than the true values with the error increasing with the increase of assumed order. The value of $E$ was better when incorrect order (0.5) was assumed than the correct one ($n$ = 1). Generally, these results are contrary to the ones obtained by Nishizaki,[4] who found a very low value of activation energy when the method was applied to polystyrene. Inspection of the expression[9] in that paper led us to conclude that an incorrect formula was used. In general, the method gives the correct results.

The Coats and Redfern method produces about 2% lower activation energies and pre-exponential factors with the latter decreasing (error is increasing) with the increase of order. Pre-exponential factors are very sensitive to the method of handling the results and the values obtained can be considered very reasonable. The best values were obtained when the correct order $n$ = 0 was tested.

The method of Reich I is limited to two cases (i.e., $n$ = 0 and $n$ = 1). Calculated values of $E$ are greater than true ones by approximately 4–5%. The values of $A$ were also higher than true ones but of the same order. Higher values for $E$ and $A$ were obtained by Nishizaki et al. as well.

The methods of Horowitz and Metzger, Kissinger, and Freeman and Carroll allow direct calculation of reaction order. The first method gave somewhat higher values while Freeman and Carroll's and Kissinger's methods gave lower values for $n$ than the true ones. Considerable errors in activation energies by the method of Horowitz and Metzger could not be explained. A possible cause is an inappropriate numerical form of the formula (17). Values for $A$ were wrong as well. According to Nishizaki's work, this method produces higher values for $E$ and especially for $A$ than other methods.

The Reich II method produces very good values for activation energy with error of approximately ±0.5%. The same is true for Ozawa's and Friedman's methods. The errors are probably caused by numerical calculation. Nishizaki

TABLE IV
Kinetic Parameters Obtained from Synthetic Curves with $E$ = 251.16 kJ/Mole and $A = 10^{15}\ s^{-1}$

| Method | $n_t$ | $n_a$ | $n_c$ | $E$, kJ/mole | Error, % | $A$, $s^{-1}$ |
|---|---|---|---|---|---|---|
| van Krevelen | 1 | 0.5 | | 256.78 | 2.24 | |
| | 1 | 1 | | 261.7 | | |
| | 1 | 2 | | 272.5 | 8.49 | |
| | 1 | 3 | | 284.24 | 13.17 | |
| Coats and Redfern | 0 | 0 | | 248.35 | −1.12 | $6.4 \cdot 10^{14}$ |
| | 0.5 | 0 | | 246.79 | −1.74 | $4.7 \cdot 10^{14}$ |
| | 1 | 0 | | 246.79 | −1.74 | $4.7 \cdot 10^{14}$ |
| | 2 | 0 | | 245.85 | −2.11 | $3.9 \cdot 10^{14}$ |
| | 3 | 0 | | 244.91 | −2.48 | $3.3 \cdot 10^{14}$ |
| Horowitz and Metzger | 0.5 | | 0.545 | 307.61 | 22.2 | $1.2 \cdot 10^{6}$ |
| | 1 | | — | 288.54 | 14.68 | |
| | 2 | | 2.3 | 193.10 | −23.25 | $1.3 \cdot 10^{5}$ |
| | 3 | | 3.4 | 177.03 | −17.89 | $1 \cdot 10^{5}$ |
| Reich I | 0 | 0 | | 264.91 | 5.47 | $8.3 \cdot 10^{15}$ |
| | 1 | 1 | | 259.29 | 3.24 | $3.1 \cdot 10^{15}$ |
| Reich II | 0.5 | | | 254.74 | 1.42 | |
| | 1 | | | 252.41 | 0.5 | |
| | 2 | | | 249.85 | −0.52 | |
| | 3 | | | 253.37 | 0.88 | |
| Ozawa | 0.5 | | | 252.88 | 0.68 | |
| | 1 | | | 250.68 | −0.19 | |
| | 2 | | | 248.24 | −1.16 | |
| | 3 | | | 251.56 | 0.16 | |
| Kissinger | 0.1 | | 0.52 | 468.69 | 86.6 | |
| | 1 | | 0.95 | 268.35 | 6.8 | |
| | 2 | | 1.31 | 54.65 | −78.2 | |
| | 3 | | 1.54 | 39.45 | −84.29 | |
| Friedman | 0 | | −0.21 | 251.56 | −0.16 | $9.3 \cdot 10^{11}$ |
| | 0.5 | | 0.52 | 251.03 | −0.05 | $7.3 \cdot 10^{14}$ |
| | 1 | | 0.93 | 250.35 | −0.32 | $8.5 \cdot 10^{14}$ |
| | 2 | | 1.14 | 251.51 | 0.14 | $8.1 \cdot 10^{14}$ |
| Freeman and Carroll | 0 | | −0.14 | 248.7 | −0.98 | |
| | 0.5 | | 0.47 | 246.1 | −2.01 | |
| | 1 | | 0.7 | 247.1 | −1.6 | |
| | 2 | | 1.7 | 248.8 | −0.94 | |
| | 3 | | 2.7 | 249.41 | −0.7 | |

found $E$ values for polystyrene degradation of 50.0 kcal/mole, 50.5 kcal/mole and 48.3 kcal/mole by Reich, Ozawa, and Friedman's methods, respectively. The Freeman and Carroll method produced very small errors in $E$ which are the consequence of numerical calculations only. However, when this method was applied to polystyrene, an energy of activation of 69.0 kcal/mole was obtained, which is about 40% higher than $E$ obtained by Ozawa's, Reich's, and Friedman's methods.

Application of Kissinger's method to the synthetic curve gave two sets of results. When expressions (9) and (10) from Table I were used to calculate

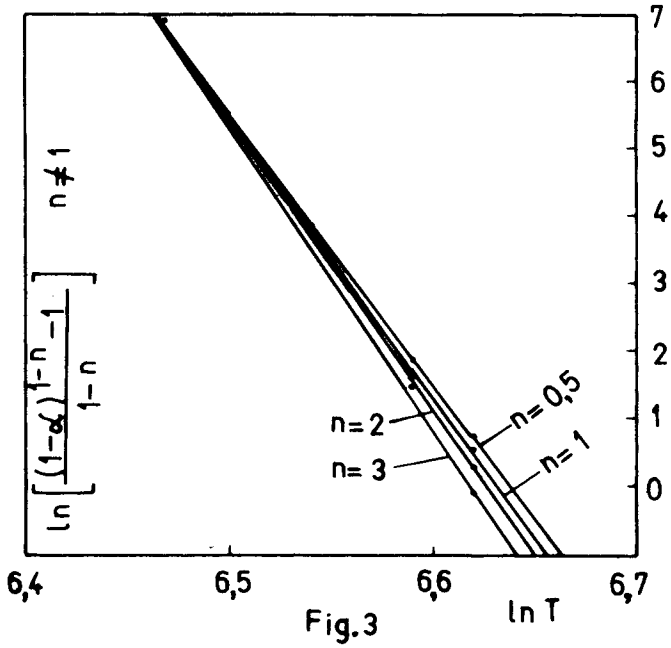


Fig. 3. Diagram illustrating application of the method of van Krevelen.

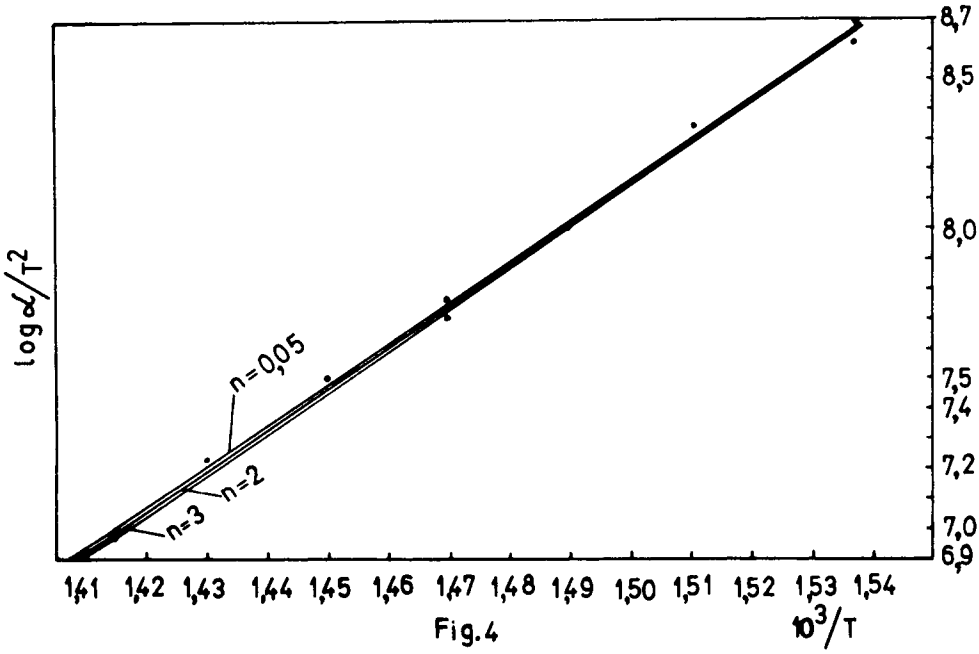


Fig. 4. Diagram obtained by application of the method of Coats and Redfern.

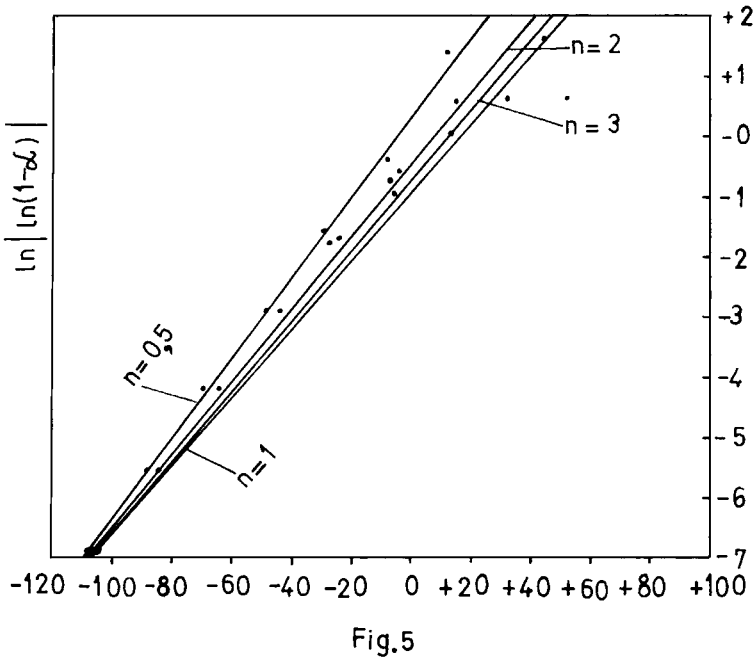


Fig. 5. Diagram illustrating the application of the method of Horowitz and Metzger.

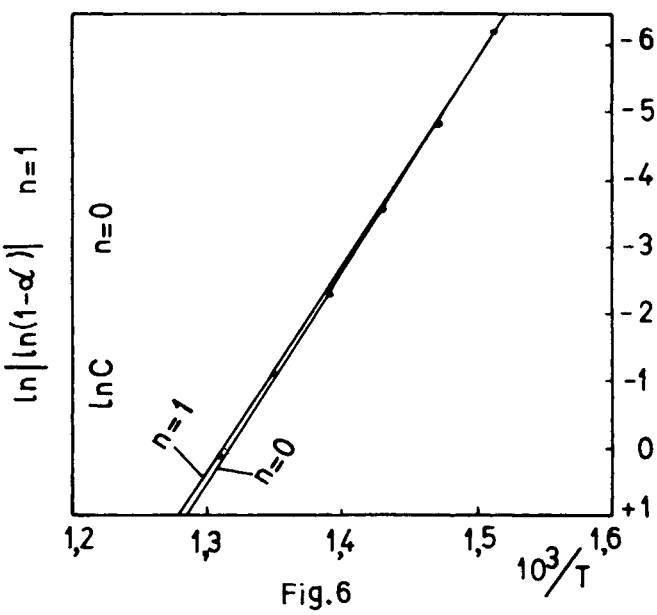


Fig. 6. Diagram showing the application of method I of Reich.

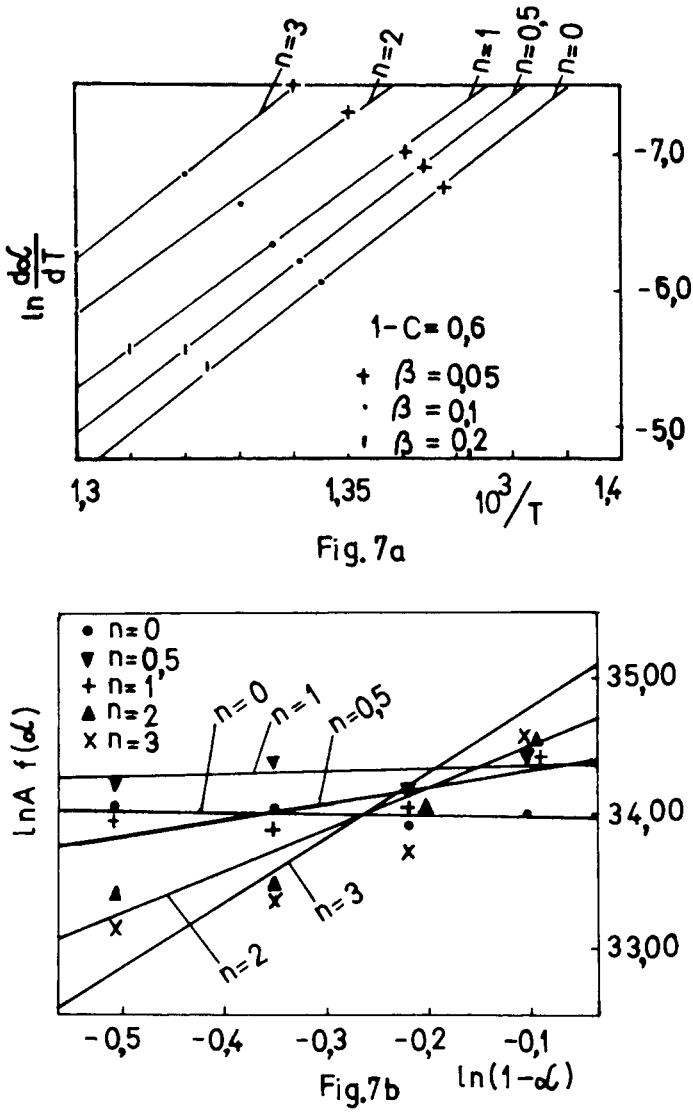


Fig. 7. Digram showing the application of the method of Friedman.

$E$ from a single curve, substituting values for $n$ calculated from the shape factor, resulted in considerable errors. Higher than true values were obtained for orders below $n = 1$ and lower for $n > 1$. If, however, expression (13) is applied which requires two TG curves at different heating rates, then very good values comparable to those of other methods were obtained:

| $n_t$ | $E$, kJ/mole | Error, % |
|---|---|---|
| 0 | 253.37 | 0.878 |
| 0.5 | 251.05 | −0.043 |
| 1 | 248.51 | −1.06 |
| 2 | 252.01 | 0.34 |

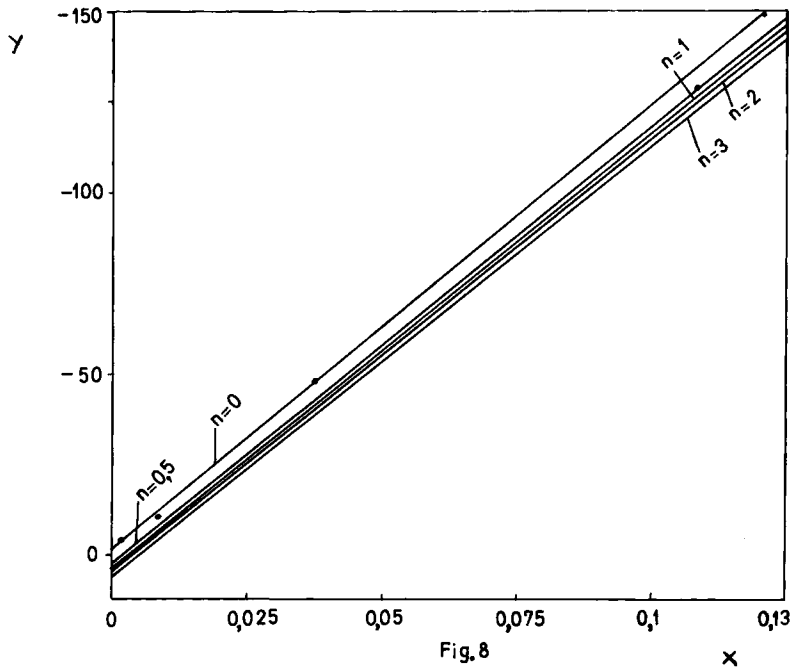


Fig. 8. Lines obtained by the application of the method of Freeman and Carroll.

Although it was not specified precisely, it seems that Nishizaki applied Kissinger's method on a single curve and obtained a high activation energy for polystyrene which was comparable to that obtained by Freeman and Carroll, Reich I (Reich and Levi), and Horowitz and Metzger.

In conclusion, all methods applied to an ideal curve produce correct results within limits of calculation error. However, if some of the assumptions, such as the form of the function $f(\alpha)$ are not valid, or if reaction is complex, the discrepancies among the methods will appear. It seems that methods based on several curves (at different heating rates) present a lower risk of creating errors than methods based on one curve or even a single-point measurement on a curve.

## CONCLUSIONS

Both integral and differential methods when applied to simple reaction kinetics produce correct values of the kinetic parameters. Methods requiring assumption of reaction order give results which depend on the accuracy of the guess. If the formulas are simplified, solutions of complex integrals of the results, as in the case of the method of van Krevelen, partly depend on approximations made. Only the method of Horowitz and Metzger gave great error.

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