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A method for kinetic analysis of thermoanalytical data of competitive reactions [1]

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Abstract

A method for kinetic analysis of thermoanalytical data of parallel competitive reactions is derived from non-isothermal kinetics of the process. By using simple relations among simultaneously measured rates of formation of products and overall conversion (or residual amount of reactant), a method to elucidate the mechanism and the kinetic parameters is proposed. This kinetic method can only be applied to data obtained by analytical types of thermal analysis, such as EGA and thermophotometry with FTIR.

The method was applied to numerically calculated thermoanalytical data and very good agreements were observed. The method is shown to be very useful and effective, and it is also discussed in relation to other methods utilizing iso-conversion relations and relations at a given temperature.

INTRODUCTION

In recent years analytical thermal analysis techniques, in which products are identified and measured, have been developed. These are thermophotometry (TP) by Fourier transformation infrared spectroscopy (FTIR), and evolved gas analysis (EGA) with a mass-spectrometer (MS) or various selective gas sensors, etc. Compared with thermogravimetry (TG) and differential scanning calorimetry (DSC), we can obtain much more detailed information by applying these analytical techniques, so that we can gain an insight into reaction mechanisms, even if the process is complicated.

To obtain this insight, a method for kinetic analysis should first be derived. For the first attempt, one of the present authors (TO) set out theoretical considerations on non-isothermal kinetics of parallel competitive reactions of the same mechanism. Some simple relations were derived [1] from which a method for kinetic analysis of thermoanalytical data of

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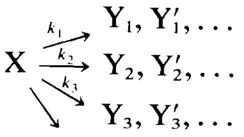
[1] Dedicated to Hans Georg Wiedemann.

these processes was derived. In this paper the method is applied to numerically calculated thermoanalytical data and its usefulness is demonstrated.

Some plots used in conventional methods for kinetic analysis of a single elementary process are also useful in kinetic analysis of the parallel competitive reactions. Therefore, the method proposed in this paper can be applied to both parallel competitive reactions and simple reactions of a single elementary process.

MODEL AND USEFUL THEORETICAL RELATIONS

The process dealt with in this paper is parallel competitive reactions [1]



The fundamental kinetic equations are

$$\frac{\mathrm{d}y_i}{\mathrm{d}t} = k_i g_i(x) \tag{1}$$

and

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = \sum_i k_i g_i(x) \tag{2}$$

where x, y_i, k_i, t and $g_i(x)$ are, respectively, the amount of residual reactant, the amount of products (Y_i, Y_i', etc.) corresponding to the extent of the ith reaction, the rate constant of the ith reaction, the time and a function of x expressing the reaction mechanism. The overall conversion is equal to $1 - (x/x_0)$, where x_0 is the initial value of x.

A simple relation can be obtained from eqn. (1) for the ratio among simultaneously observed rates of production, when $g_i(x)$ and $g_j(x)$ are identical

$$\frac{\mathrm{d}y_i/\mathrm{d}t}{\mathrm{d}y_j/\mathrm{d}t} = \frac{k_i}{k_j} \tag{3}$$

and assuming Arrhenius type temperature dependence of the rate constant

$$\frac{\mathrm{d}y_i/\mathrm{d}t}{\mathrm{d}y_j/\mathrm{d}t} = \frac{A_i}{A_j} \exp\left(\frac{\Delta E_j - \Delta E_i}{RT}\right) \tag{4}$$

where A, ΔE, R and T are the pre-exponential factor, the activation energy, the gas constant and the temperature, respectively. When $g_i(x)$ is not the same as $g_j(x)$

$$\frac{\mathrm{d}y_i/\mathrm{d}t}{\mathrm{d}y_j/\mathrm{d}t}=\frac{k_ig_i(x)}{k_jg_j(x)}=\frac{A_ig_i(x)}{A_jg_j(x)}\exp\left(\frac{\Delta E_j-\Delta E_i}{RT}\right) \tag{5}$$

At a given overall conversion, x, $g_i(x)/g_j(x)$ is a constant, irrespective of temperature mode.

By introducing reduced time θ for each reaction, we have [2]

$$\frac{\mathrm{d}y_i}{\mathrm{d}\theta_i}=A_ig_i(x) \tag{6}$$

and when $g_i(x)$ are identical

$$G(x)=\sum_i A_i\theta_i \tag{7}$$

where

$$G(x)=\int\frac{\mathrm{d}x}{g(x)} \tag{8}$$

Because the reduced time is inversely proportional to the heating rate at a given temperature [2], we have

$$\phi_1G(x)=\phi_2G(x)=\ldots \tag{9}$$

where ϕ is the heating rate.

METHOD FOR KINETIC ANALYSIS

Firstly, we should examine whether the observed process is in accordance with the model. In eqn. (3) it is shown that the ratio among concurrently observed rates of production $\mathrm{d}y_i/\mathrm{d}t$, is equal to the ratio among the rate constants when $g_i(x)=g_j(x)$. A plot of the logarithm of the ratio among $\mathrm{d}y_i/\mathrm{d}t$ against the reciprocal absolute temperature expresses the difference in temperature dependence of the rate constants. If it is Arrhenius type, we obtain a linear plot and the slope is equal to the difference between the activation energies

$$\log\frac{\mathrm{d}y_i/\mathrm{d}t}{\mathrm{d}y_j/\mathrm{d}t}=\log\frac{A_i}{A_j}-\frac{\Delta E_i-\Delta E_j}{RT} \tag{10}$$

When plots of the ratio are all on a horizontal line, the two products are formed by the same single elementary reaction. In such a case the conventional methods [2–11] can be applied. If the mechanisms of elementary reactions are different ($g_i(x) \neq g_j(x)$), we obtain multiple linear lines of the ratio among the concurrently measured production rates for different overall conversions (eqn. (5)). Thus, this case can be differentiated from the above case of the same reaction mechanism. If the plot of the ratio is not one of those described above, the observed process is not in accordance with the model.

The Friedman plot is also very useful for the model. Friedman proposed a method for kinetic analysis of nth order reactions in 1964 [5]. However, it was made clear in 1986 [6, 7] that this method has wide applicability and can be applied to various processes of a single elementary reaction. In this expanded Friedman method the logarithm of rate at a given conversion is plotted against the reciprocal absolute temperature, and the activation energy is estimated from the slope [5–7]. Similarly when we plot logarithm of $\mathrm{d}y_i/\mathrm{d}t$ at a given overall conversion, we obtain a linear plot and the activation energy can be estimated from the slope. From this plot we can also obtain the relation of the intercept versus the conversion, and this relation corresponds to the relation of $A_i g_i(x)$ versus x. After elucidating the form of $g_i(x)$, we can estimate the pre-exponential factor A_i. This further expanded Friedman plot can be applied to the model of different $g_i(x)$, and also to any mode of temperature change. Furthermore, when the temperature dependence is not Arrhenius type, we get curves at different overall conversions, and the curves can be superposed on each other by longitudinal shift.

Thus we obtain $g(x)$ and all sets of A_i and ΔE_i. Then if we ascertain the relation between $G(x)$ and $\sum_i A_i\theta_i$ and constancy of $\phi G(x)$ at a given overall conversion for the mechanism of the same $g(x)$, the validity of this kinetic analysis is proven.

Another method of examination is as follows. Because

$$\frac{\mathrm{d}y_i}{\mathrm{d}\theta_i} = \frac{\mathrm{d}y_i}{\mathrm{d}t}\exp\left(-\frac{\Delta E_i}{RT}\right) \tag{11}$$

for the Arrhenius type temperature dependence, the master curve (eqn. (6)) is obtained by plotting $\mathrm{d}y_i/\mathrm{d}\theta_i$ versus x using the estimated activation energy and eqn. (11), irrespective of the temperature change. Moreover, a relation similar to eqn. (11) is valid for any mode of temperature change, and can be used for examining the validity of the kinetic analysis [2].

CALCULATION OF THERMOANALYTICAL DATA

Thermoanalytical data for four cases were calculated numerically by a Runge–Kutta method. They are all parallel competitive reactions of two elementary processes as follows:

Case 1 $A_1 = 2 \times 10^{11}\,\mathrm{s}^{-1}$ $\Delta E_1 = 40\,\mathrm{kcal\,mol}^{-1}$
$A_2 = 1 \times 10^{19}\,\mathrm{s}^{-1}$ $\Delta E_2 = 60\,\mathrm{kcal\,mol}^{-1}$
$g_1(x) = g_2(x) = x$ (1st order reaction)
Case 2 $A_1 = 2 \times 10^{11}\,\mathrm{s}^{-1}$ $\Delta E_1 = 40\,\mathrm{kcal\,mol}^{-1}$
$A_2 = 1 \times 10^{19}\,\mathrm{s}^{-1}$ $\Delta E_2 = 60\,\mathrm{kcal\,mol}^{-1}$
$g_1(x) = g_2(x) = x^2$ (2nd order reaction)
Case 3 $A_1 = 4 \times 10^{2}\,\mathrm{s}^{-1}$ $\Delta E_1 = 30\,\mathrm{kcal\,mol}^{-1}$
$A_2 = 1.18 \times 10^{7}\,\mathrm{s}^{-1}$ $\Delta E_2 = 50\,\mathrm{kcal\,mol}^{-1}$
$g_1(x) = g_2(x) = x$ (1st order reaction)
Case 4 $A_1 = 2 \times 10^{11}\,s^{-1}$ $\Delta E_1 = 40\,\mathrm{kcal\,mol}^{-1}$
$A_2 = 1 \times 10^{19}\,\mathrm{s}^{-1}$ $\Delta E_2 = 60\,\mathrm{kcal\,mol}^{-1}$
$g_1(x) = x$ $g_2(x) = x^2$

RESULTS AND DISCUSSION

Calculated thermoanalytical curves of the fractional amount of the residual reactant (or one minus the conversion) for case 1 are shown in Fig.

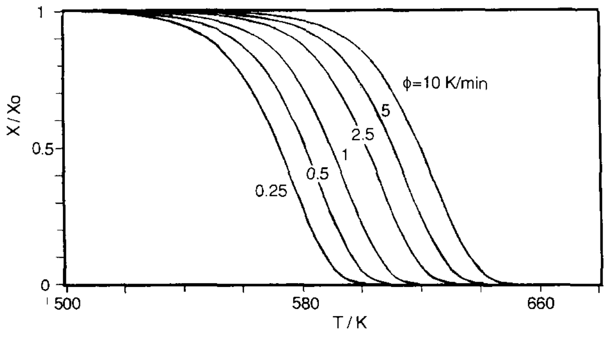


Fig. 1. Residual amount of reactant versus temperature for case 1.

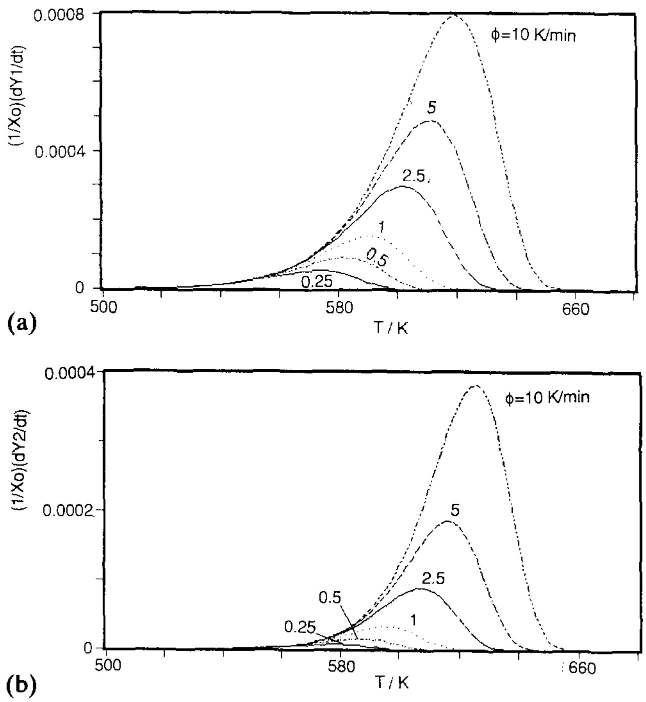


Fig. 2. Rate of production versus temperature for case 1: (a) first reaction; (b) second reaction.

1. Rates of formation for two products are also reproduced in Fig. 2. As is seen in Fig. 2, two elementary processes proceed in the same temperature range and the reactions are truly parallel and competitive, while the conversion of the reactant changes smoothly as if the reaction consisted of a single elementary reaction (Fig. 1). Figure 1 suggests the limitations of TG and the advantages of EGA with MS, TP by FTIR and so on.

The logarithm of the ratio of $\mathrm{d}y_1/\mathrm{d}t$ to $\mathrm{d}y_2/\mathrm{d}t$ obtained concurrently according to eqn. (10) is plotted against the reciprocal absolute temperature in Fig. 3. As is seen in Fig. 3, all plots are on the same linear line, irrespective of the heating rate and the overall conversion. This one-line plot shows that the observed process is a parallel competitive reaction of the same $g_i(x)$. From the slope and intercept of the above plot we can estimate the difference in the activation energies and the ratio between the pre-exponential factors. Table 1 shows the very good agreement with the theoretical parameters.

The logarithm of the rate is plotted against the reciprocal absolute temperature for a given overall conversion in Fig. 4. Linear plots are obtained for different overall conversions, and they are all parallel. From the slopes the activation energies are estimated and listed in Table 2. The agreements among the theoretical values and the estimated ones are also very good. From the intercepts we obtain relations between $A_i g_i(x)$ and x;

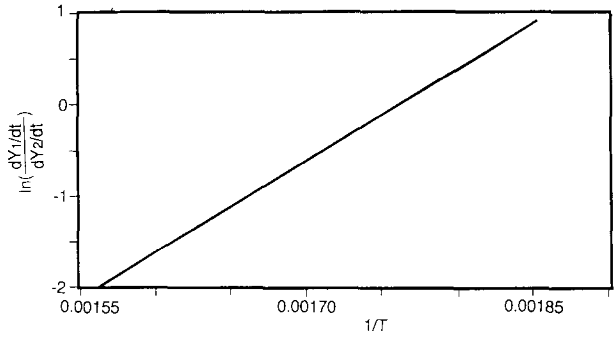


Fig. 3. Logarithm of ratio between rates of production versus reciprocal absolute temperature for case 1.

straight lines are obtained in accordance with the theoretical mechanism of the first order reaction. The pre-exponential factors estimated from the intercepts are tabulated in Table 2. The agreements are also very good.

Similarly the calculated thermoanalytical data of cases 2, 3 and 4 are analyzed. Typical results for case 4 are shown in Figs. 5–8 and the estimated parameters for the three cases are also tabulated in Tables 1 and 2. Similarly, good results are obtained for cases 2 and 3. In Fig. 7 multiple straight lines are obtained which is different from the other cases. These multiple lines are evidence for the different mechanism of the elementary reactions.

As is clearly visible in these figures and tables, linear plots can be obtained, and agreement between the theoretical kinetic parameters and the estimated ones is very good. It is clearly illustrated that thermoanalytical data of parallel competitive reactions can be kinetically analyzed by the present method. To examine the applied method furthermore, relations in eqns. (6) and (7) are also very useful.

TABLE 1

Comparison of estimated ratio of pre-exponential factor and difference in activation energies with theoretical values

Parameter[a]	Case 1	Case 2	Case 3	Case 4
Theoretical				
A_2/A_1	5.0×10^7	5.0×10^7	2.95×10^4	5.0×10^7
$\Delta E_2 - \Delta E_1$	20.00	20.00	20.00	20.00
Estimated				
A_2/A_1	5.004×10^7	4.979×10^7	2.94×10^4	–
$\Delta E_2 - \Delta E_1$	20.001	19.995	19.998	19.994[b]

[a] Pre-exponential factors in s^{-1} and activation energies in kcal mol^{-1} (1 cal = 4.186 J).
[b] The average obtained at different overall conversions.

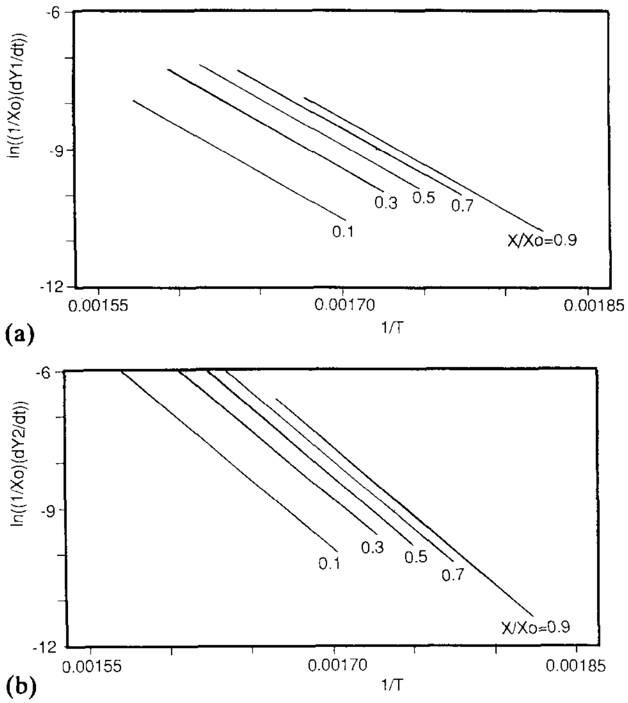


Fig. 4. Logarithm of rate of production versus reciprocal absolute temperature for case 1: (a) first reaction; (b) second reaction.

The present method is based on the useful and simple relations at a given overall conversion. Therefore, it can be considered to be one variety of iso-conversion method [7], namely, a further expanded Friedman method. In the other iso-conversion methods, i.e. Ozawa–Flynn–Wall method [2, 3, 8] and Kissinger–Akahira–Sunose method [3, 9, 11], simple relations of the reduced time at a given conversion are utilized [7]. However, in parallel competitive reactions, the overall conversion, the extent of elementary reaction and its maximum are all complicated functions of the reduced times, so that these relations cannot be applied to these processes.

In the present method, it is essential to use the relations at a given overall conversion, except eqns. (3), (4) and (5). If the overall converson cannot be measured, only these exceptional relations can be utilized. However, the overall conversion can not easily be measured in some cases. For example, the residual mass is not proportional to the overall conversion, if the non-volatile products obtained by different elementary reactions are not identical. Although IR absorption characteristic of the reactant can be used for this purpose, the precision of the measurement should be improved. However, if the stoichiometry of the reaction is elucidated, the overall conversion can be estimated.

TABLE 2

Comparison of estimated activation energy ΔE[a] and pre-exponential factor A[b] with theoretical values

	Case 1		Case 2		Case 3		Case 4	
	ΔE_1	ΔE_2	ΔE_1	ΔE_2	ΔE_1	ΔE_2	ΔE_1	ΔE_2
Theoretical	40	60	40	60	30	50	40	60
Estimated								
X/X_0								
0.9	39.995	59.998	39.994	59.985	29.998	49.994	39.998	59.974
0.7	39.998	59.997	39.998	59.993	29.999	49.990	39.998	59.997
0.5	40.005	60.002	40.014	60.013	30.001	49.998	40.002	60.005
0.3	40.010	60.010	39.998	59.993	30.017	50.020	40.019	60.028
0.1	40.030	60.038	40.009	60.019	30.019	50.028	40.050	60.019
Average	40.008	60.007	40.003	60.001	30.007	50.005	40.011	60.005
	Case 1		Case 2		Case 3		Case 4	
	A_1	A_2	A_1	A_2	A_1	A_2	A_1	A_2
Theoretical	2.0	1.0	2.0	1.0	4.0	1.18	2.0	1.0
Estimated	1.989	0.991	1.992	0.989	3.994	1.173	1.980	0.983

[a] Activation energies in kcal mol (1 cal = 4.186 J).

[b] Pre-exponential factors in s^{-1}; the number of the power is omitted.

Examples of parallel and competitive reactions have been postulated by Paloniemi et al. for some polymeric materials [12]. In these examples, three reactions proceed concurrently; they are thermal decomposition, thermo-oxidative degradation and hydrolytic reaction. These can be kinetically analyzed by thermal analysis, if highly sensitive analysis of the products can be applied to thermal analysis of the process and if the three reactions produce different products.

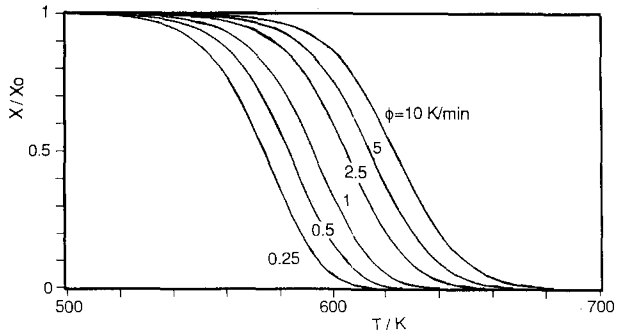


Fig. 5. Residual amount of reactant versus temperature for case 4.

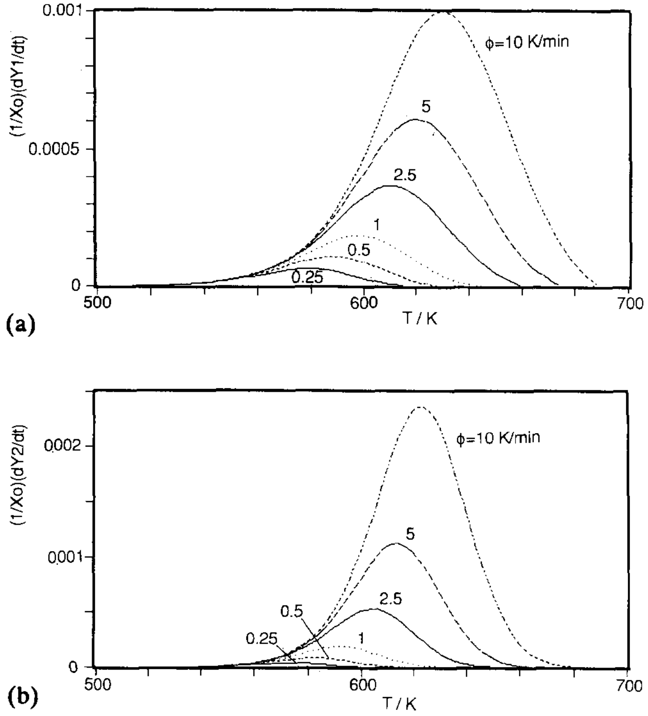


Fig. 6. Rate of production versus temperature for case 4: (a) first reaction; (b) second reaction.

CONCLUSIONS

The tables and figures presented here show that the method in this paper is valid and useful for kinetic analysis of parallel and competitive reactions, in which the reaction products are different. For this purpose, both the conversion and the rates of production are needed, and suitable equipment to observe both should be developed as powerful tools to analyze

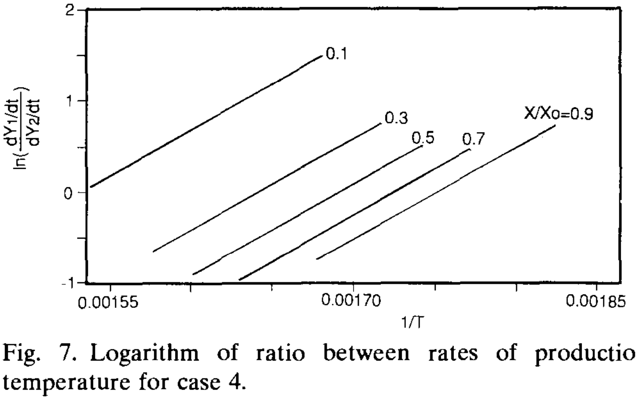


Fig. 7. Logarithm of ratio between rates of production versus reciprocal absolute temperature for case 4.

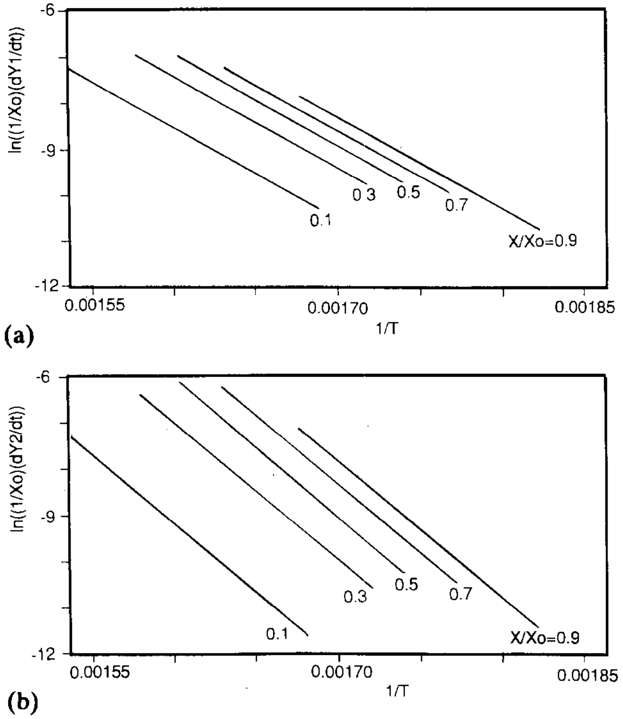


Fig. 8. Logarithm of rate of production versus reciprocal absolute temperature for case 4: (a) first reaction; (b) second reaction.

kinetically complicated processes in organic substances and polymeric materials.

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