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ESTIMATION OF NONISOTHERMAL KINETIC PARAMETERS FROM TG CURVE AT ANY TEMPERATURE AND SOME ASPECTS OF TG ANALYSIS RELATED TO INTERAISOKINETIC EFFECT

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ABSTRACT

A method has been suggested for the estimation of nonisothermal kinetic parameters from TG curve at any temperature. This would help to resolve reactions from a single thermogram. Some methods have been suggested to calculate nonisothermal kinetic parameters for some reactions. Intreraisokinetic or intrakinetic compensation effect technique is employed to resolve reactions. Calcium oxalate decomposition involves two consecutive reactions each of first order. Polycarbonate shows two simultaneous reaction of first order other second order while nickel and cobalt sulphate show single step fractional order reactions. HIPS and PS show single step first order reactions. HIPS and PS show single step fractional order.

Key Words: *TG Analysis, Isokinetic Effect, Consecutive Reaction, Simultaneous Reaction*

INTRODUCTION

Several methods have been suggested in the literature for determination of nonisothermal kinetic parameters from the thermogravimetric (TG) analysis data. The Ozawa (1965) method is used to reduce TG analysis data to reaction parameters. Viswanath and Gupta (1995 and 1997) suggested several methods for determination of non-isothermal kinetic parameters from TG curve data, assuming that the reaction follows a simple order. Doyle (1961) proposed a curve fitting method for a single thermogram by assuming an approximation, which reduces the speculative nature of the method for estimation non-isothermal kinetic parameters. Tsai *et al.*, (1994) for determination of activation energy and pre-exponential factor of a reaction, have extended Doyle's method considering the different heating rates. In the present communication, nonisothermal kinetic parameters have been determined at any temperature for single thermogravimetric analysis (TG) data. The activation energy-temperature curves for various reactions are presented for a single heating rate. Similar cures can also be obtained with other parameters.

MATERIALS AND METHODS

Thermogravimetry was carried out on a Perkin-Elmer TG Thermal system TDS2 in a flow of nitrogen gas in a alumna crucible at Regional Sophisticated Instrumentation Center, Nagpur University (presently known as Rastra Sant Tukadogi Maharaj Nagpur University), Nagpur. For carrying out the TG analysis the mass of the sample taken is about 10-15 mg. The compounds studied are (1) nickel sulphate at 5 K min⁻¹, (2) cobalt sulphate, (3) high impact polystyrene (4) polystyrene, (5) bisphenol A poly carbonate, and (6) calcium oxalate, at 10 K min⁻¹. The data for calcium oxalate is obtained from elsewhere (Schempt, 1966).

Method of calculating the parameters

The first derivative ($d\alpha/dT$) is calculated by the method suggested by Viswanath and Gupta (1997). This same method is extending for determination of second ($d^2\alpha/dT^2$) and third derivative ($d\alpha^3/dT^3$).

$$d\alpha/dT = (A/\beta)(1-\alpha)^n e^{-E_a/RT} \quad \dots\dots 1$$

Where α , n , E_a , A and β are fraction decomposed, order of reaction, activation energy, pre-exponential factor and rate of heating respectively. While fraction decomposed, α , defined by as

$$\alpha = (W_i - W_T)/(W_i - W_f) \quad \dots\dots 2$$

where W_i , W_f and W_T initial mass, residual mass and mass of the sample at any time T .

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Differentiating eq1 with respective temperature, T and simplifying the equation, the second derivative can be written as,

$$d^2\alpha/dT^2 = -n(1/(1-\alpha))(d\alpha/dT)^2 + E_a/RT^2(d\alpha/dT) \quad \dots\dots 3$$

Further differentiating eq 2 with respective temperature, T and simplifying the equation third derivative can be written as,

$$d^3\alpha/dT^3 = -n(2d\alpha^2/dT^2 + (d\alpha/dT)^2/(1-\alpha))((d\alpha/dT)/(1-\alpha)) + (E_a/R)(d\alpha^2/dT^2 - (2/T)(d\alpha/dT))(1/T^2) \quad \dots\dots 4$$

Solving eqs 2, 3 and 4, the values of n, E_a and A are obtained. The nonisothermal parameters E_a, n and A are considered as constants.

Activation-Temperature Plots

When activation energy is plotted against temperature, different types of curves are obtained. These curves are presented in Fig. 1a to 6a. Similar types of curves are also obtained when order of reaction or pre-exponential factor is plotted against temperature. In plotting these curves very high and negative activation energies are neglected. In plotting these curves 2K differences is taken for NiSO₄ and CoSO₄. For the rest of the compounds 1K differences is taken. The range of temperature at which the nonisothermal parameters remained constant is presented in Table 1.

Resolving the Curves

The activation energy and order of reaction plots are presented in the Fig. 1b to 6b, while ln(A) and order of reaction plots are presented in the Fig.1c to 6c. Each plot can be resolved into three parts. First and third parts give straight lines while middle portion, second part, gives a curve in all cases. The curved portion gives a second-degree polynomial equation. From the intersection of these two straight lines, the nonisothermal parameters are calculated. In Table 2 nonisothermal kinetic parameters for these compounds from these intersection points are presented.

The two equations for the activation energy and order of reaction plots can be written as

$$E_a = m_1 n + c_1 \quad \dots\dots 6$$

$$E_a = m_2 n + c_2 \quad \dots\dots 7$$

Where m₁ and m₂ are slopes of the lines while c₁ and c₂ are the intercepts of the lines. Similarly the two equations for the ln(A) and order of reaction plots can be written as

$$\ln(A) = x_1 n + y_1 \quad \dots\dots 8$$

$$\ln(A) = x_2 n + y_2 \quad \dots\dots 9$$

Where x₁ and x₂ are slopes of the lines while y₁ and y₂ are the intercepts of the lines. The middle portion gives second degree polynomial curve. As

$$E_a = a_1 n^2 + a_2 n + a_3 \quad \dots\dots 10$$

and

$$\ln(A) = b_1 n^2 + b_2 n + b_3 \quad \dots\dots 11$$

Where a₁, a₂, and a₃ and b₁, b₂ and b₃ are coefficients of respective polynomials.

The activation energy-temperature curves of NiSO₄ and CoSO₄ (Fig.1a and 2a) show that the parameters decrease first and remain constant over long range of temperature and again decrease. In the case of polystyrene (Fig.3a), the activation energy-temperature curve shows that continuous increase of parameters with temperature. In the case of calcium oxalate, the activation energy-temperature curve (Fig.4a) shows first increase in the parameters and then decrease and again increase. In the case of HIPS; the activation energy-temperature curve (Fig.5a) shows a similar trend as that shown by calcium oxalate. The activation energy-temperature plot of PC (Fig. 6a) shows the parameters decrease first then increase.

Isokinetic Effect or Compensation Effect

ln(A) verses activation energy plots show a linear relation as seen from fig.1d to 6d. Such linear relation can be expressed by logarithmic form of Arrhenius equation as

$$\ln(A) = E_a/RT_{iso} + \ln(k_{iso}) \quad \dots\dots 12$$

Where T_{iso} and k_{iso} are the isokinetic temperature and isokinetic reaction rate constant respectively. The Fig.1d to 6d are the plots of above relation. T_{iso} and k_{iso} are called isokinetic constants and the relationship

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is called isokinetic effect or compensation effect. Such a reaction rate compensation effect is normally associated with the variation of heterogeneous reaction rate in different solids (Cremer, 1996 and Fairbridge *et al.*, 1975). Numerous workers reported such compensation behavior and several theories predict such linear compensation behavior (Cremer, 1996; Fairbridge *et al.*, 1975; Feats and Harries, 1974; Adonyi and Körösi 1983; Azisis *et al.*, 1993; Lavergne *et al.*, 1993 and Galway, 1977). These theories suggest that the C.E. is due to entropy-enthalpy compensation, the tunneling effect, the simultaneous occurrence of reaction on the surface centers involving different activation energies, and the existence of interrelated kinetic behavior within a group of rate processes. The isokinetic temperature has been regarded either as the temperature at which relative rates within a group of reactions undergo inversion or the temperature at which the rate constant of all the reactions in the series have the same value.

In a plot of logarithm of the rate constant as function of reciprocal temperature for the same series of reactions display a point of concurrence and one isokinetic temperature and isokinetic rate constant. This type effect is termed as “true compensation effect” (Agarwal, 1986). This type of true compensation effect is related to bulk properties of metal oxides, such as different valence states. For example, this type effect is observed in the thermal oxidative degradation of polymers by different metal oxides having different valence states (Agarwal, 1988). But only linear correlation between $\ln(A)$ and E_a is observed for such series of reaction, such compensation effect is called “apparent compensation effect”. This may be related to the distribution of different kinds of active links in the polymer surface having different activation centers. It was further pointed out by Feates and Harris (1974) that when a reaction is changed from chemical-controlled to diffusion-controlled or visa versa, and active centers on the surface of the reactant may act as sites for simultaneous reactions with different activation energies, then the Arrhenius plots do not display a point of concurrence, even though the plots of $\ln(A)$ versus E_a show compensation behavior.

The above theories, even though applicable for a group of reaction, can also be applied to the present single component system. The E_a -n or $\ln(A)$ -n plots are divided into three parts. So there would be three $\ln(A)$ - E_a plots. Therefore there would be three isokinetic temperatures and three isokinetic rate constants. If the $\ln(k_{iso})$ are plotted against $1000/RT_{iso}$ a straight line is obtained. If this gives a perfect straight line, the reaction follows single step mechanism. NiSO_4 , CoSO_4 , HIPS and PS give this type of plots. Therefore they follow a single step mechanism.

Koga and Tanaka (1993) reported that the decomposition of NiSO_4 proceeds by surface and random nucleation growth near the reaction front as well as in the bulk. The decomposition of CoSO_4 is characterized by a contracting geometry and is effected by the distribution of the active surface.

In case of polymers, the thermal degradation of polymers occurs only after polymer melts. The polymers do not show a sharp melting point and melt over along range of temperature. The physical processes occurring in polymer degradation may be related to the distribution of different kinds of active links in polymer surface having different activation energies and diffusion of gaseous products. The chemical processes or different mechanisms occurring in polymer degradation process are random chain scission, depolymerization via chain end initiation, disproportionation or cyclization, free radical formation or macroradical formation etc. The first part is due to the physical process after onset of chemical reaction. The second part involves largely the chemical process and lesser extent involves creation or annihilation of active links and diffusion. The third is due to annihilation of active links and diffusion and lesser extent due to chemical reaction. Generally, in the polymer degradation process the end product is porous carbon mass.

In the case of PS, in the first part there is a sharp increase in the activation energy. In second part activation energy increase is steady. But in third part there is again a sharp increase in the activation energy. But HIPS shows a different trend, first activation energy increases then decreases and again increases sharply. Jellineck (1978) showed that thermal degradation of polymer via random chain scission by free radical formation is first order. But both PS and HIPS show first order reaction. PS degradation

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takes place at higher temperature and with higher activation energy. Cullis et al (1993) pointed, in their studies on carboxy terminated poly butadiene, higher activation energy is due to stabilization of polymer by cross linking and cyclization which would occur due to interaction of free macroradicals with the double bonds, due to the presence of butadiene.

In the case of calcium oxalate, the $\ln(k_{iso})-1000/RT_{iso}$ plot does not give a straight line. First and second $\ln(k_{iso})-1000/RT_{iso}$ points give one straight line while second and third $\ln(k_{iso})-1000/RT_{iso}$ points another straight line. This indicates that the calcium oxalate decomposition follows two-step mechanism. Mental and Anderson (1993) showed that in the decomposition of CaC_2O_4 there is an electron transition from oxalate to metal (Ca) through interstitial defects, and the reaction occurs at the interface separating the parent crystal and the product. Therefore, it may be concluded that calcium oxalate first decomposes into calcium carbonate and then the formed calcium carbonate decomposes into calcium oxide. It is a case of consecutive or successive reactions. First and second $\ln(k_{iso})-1000/RT_{iso}$ points give one straight line which corresponds to sum of the nonisothermal kinetic parameters of two reactions. Second and third $\ln(k_{iso})-1000/RT_{iso}$ points give another straight line which correspond to the second reaction. The difference between the parameters gives nonisothermal kinetic parameters of the first reaction.

But in case of PC, the activation energy decreases to minimum and increases. In PC there are two carbonate links, which are susceptible to decomposing even at low temperature by elimination of CO and CO_2 (Davis and Golden, 1965) which causes the decrease of activation energy, where as at higher temperature the degradation at isopropylidene site would be through the formation of tertiary free radical by removal of CH_3 . This free radical is eventually more stable. In such cases branching and cross linking is predominant. When branching and cross linking occurs volatile products like hydrogen or weak group are removed (Kamiya and Niki, 1978). This may be the case for further increase of activation energy after reaching the minimum. This is the case of simultaneous or parallel reaction. First and third $\ln(k_{iso})-1000/RT_{iso}$ points give one straight line which corresponds to sum of the nonisothermal kinetic parameters of two reactions. Second and third $\ln(k_{iso})-1000/RT_{iso}$ points give another straight line which correspond to the second reaction. The difference between the parameters gives nonisothermal kinetic parameters of the first reaction.

Plot of $\ln(k)$ versus $1000/RT_{iso}$ values give true activation energy and $\ln(A)$ values. These plots are shown in Fig.7. The slope of the line gives E_a and intercept gives $\ln(A)$ values. These values are presented in the Table III. If nearest whole number (in the case of polymers and covalent compounds) or fraction (in case of ionic solids) is assumed as order of reaction, more accurate values are obtained. These values are given in brackets of the Table III. Equations 6-11 are employed to calculate the E_a and $\ln(A)$ values.

On Set and End Set Temperatures

For onset temperature determination the relation ship between $\ln(1-\alpha)$ and temperature is employed which is given below,

$$T = p_1 \ln(1-\alpha) + T_o \quad \dots\dots 13$$

Where p_1 is slope and T_o is intercept, the on set temperature. Similarly the equation for end set temperature can be written as

$$T = p_2 \ln(\alpha) + T_e \quad \dots\dots 14$$

Where p_1 is slope and T_e is intercepting, the end set temperature. The plot of $\ln(1-\alpha)$ against temperature are given in Fig.8 and $\ln(\alpha)$ against temperature plots presented in Fig.9 for all compounds. In Table IV the on set and end set temperatures for all compounds are presented along with the isokinetic temperatures. These values of on set and end set temperatures tally almost with the observed values.

New Inflection Point Method for Determination Nonisothermal Parameters

Earlier Viswanath and Gupta (1995) suggested an inflection point method based on first derivative maximum, $(d\alpha/dT)_{max}$ where second derivative $(d^2\alpha/dT^2)$ becomes zero. In this method if second derivative maximum, $(d^2\alpha/dT^2)_{max}$ is considered third derivative, $(d^3\alpha/dT^3)$ becomes zero. Therefore eq 4 becomes zero and can be written as,

$$n\{(2(d\alpha^2/dT^2)_i + (d\alpha/dT)_i^2 / (1-\alpha_i)) / ((d\alpha/dT)_i / (1-\alpha_i)) / ((d\alpha^2/dT^2)_i - (2/T_i) (d\alpha/dT)_i) / (1/T_i^2)\} = E_a/R$$

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.....15

Where subscript i stand for the values at inflection point. If the expression in curl brackets is abbreviated as P the above eq 15, can be written as

$$nP = E_a/R \quad \text{.....16}$$

Taking the logarithmic form of eq 1 and substituting the nP for Ea/R in equation we can write the equation as,

$$\ln(d\alpha/dT) = n(\ln(1-\alpha) - P/T) + \ln(A/\beta) \quad \text{.....17}$$

The plot of $\ln(d\alpha/dT)$ against $(\ln(1-\alpha) - P/T)$ gives a straight line. From the slope of the line n and from intercept, $\ln(A)$ can be calculated. E_a can be calculated from the eq 15. Alternatively, substituting n for E_a/RP , the eq 15 can be written as,

$$\ln(d\alpha/dT) = (E_a/R)(\ln(1-\alpha) / P - 1/T) + \ln(A/\beta) \quad \text{..... 18}$$

The plot of $\ln(d\alpha/dT)$ against $(\ln(1-\alpha)/ P - 1/T)$ gives a straight line. From the slope of the line E_a and from intercept, A can be calculated and n can be calculated from the eq 16. This method may be called as absolute method from the second derivative maximum.

In another method, the differences of logarithmic form of eq1 at inflection point and at any point can be written as,

$$\ln(d\alpha/dT)_i - \ln(d\alpha/dT) = -(E_a/R)(1/T_i - 1/T) + n(\ln(1-\alpha_i) - \ln(1-\alpha)) \quad \dots 19$$

If the differences are abbreviated as Δ and final form of the equation is written as,

$$\Delta \ln(d\alpha/dT) / \Delta \ln(1-\alpha) = -(E_a/R) \Delta(1/T) / \Delta \ln(1-\alpha) + n \quad \text{.....20}$$

Plot of $\Delta \ln(d\alpha/dT) / \Delta \ln(1-\alpha)$ against $\Delta(1/T) / \Delta \ln(1-\alpha)$ gives a straight line with slope equal (E_a/R) and intercept equal to n. The pre-exponential factor, A may be calculated by substituting the E_a and n values in the logarithmic form of eq1 at inflection point. This method may be called as reference or difference method from the second derivative maximum. By substituting n value obtained from eq 16 or eq 19 in logarithmic form of eq.1 and plotting $\ln((d\alpha/dT)/(1-\alpha)^n)$ against $1/T$ gives a straight line. From this plot activation energy, E_a and the pre-exponential factor, A may be determined. This method may be called as standard method from the second derivative maximum. Since the temperature at which second derivative maximum observed falls on the flat portion of activation energy-temperature curve, these methods have some advantage over the earlier methods suggested by Viswanath and Gupta³. In Table V the non-isothermal kinetic parameters are presented for these compounds at different inflection points. When the order of the reaction is below one higher derivative gives good results while order of the reaction is above one first derivative gives good results.

RESULTS AND DISCUSSION

A solid state reaction studied by nonisothermal method (TG Analysis) may be divided into three parts. The first and third parts involve more of physical process and less of chemical process, while second part involves more of chemical process and less of physical process. The physical process involves nucleation and growth of active centers on the surface, diffusion of gas or gasses through porous solids or diffusion of species (electron or ions) through lattice, distribution of different kinds of active links in the polymer surface having different activation energies etc Arrhenius equation, activation energy as function of order of reaction can be written as

$$E_a = (RT \ln(1-\alpha))^n + (RT \ln(A/\beta) - RT \ln(d\alpha/dT)) \quad \text{..... 20}$$

This can be written as a linear equation for small temperature range as

$$E_a = m n + c \quad \text{..... 21}$$

Therefore any parameter can be written as linear function other parameter with in small range of temperature. Hence first and third parts equations are written as linear equations. Since the second part involves chemical process over long range of temperature, this equation may be written as second-degree polynomial equation in as

$$E_a = x_1 n^2 + x_2 n + x_3 \quad \text{..... 23}$$

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Where x_1 , x_2 , and x_3 are the coefficients of the polynomial. In all cases for the calculated data regression coefficient is considered as measure of accuracy. The regression coefficients in all case are always more than 0.99. So first and third parts are considered as physical process region while second part region is considered as chemical process region.

In the table I nonisothermal kinetic parameters of the compound along with range temperature are given. This indicates a constant process is occurring in that range of temperature. These parameters almost in call cases tally with parameters calculated by other methods. While in the table V nonisothermal parameters given for different inflection point methods. If the derivative maximum falls in the chemical process region then only it gives correct nonisothermal kinetic parameters. Therefore it is necessary to select exact chemical process region to proper paramerenters.

The isokinetic effect or compensation effect considered above is applied to present system of single compound. This type of isokinetic effect may be called intra isokinetic effect while that observed between group of compounds may termed as inter isokinetic effect. The plot of $\ln(k_{iso})$ against $1000/RT_{iso}$ does not give a straight line in case of calcium oxalate and PC. In case calcium oxalate the three iso kinetic points are in continues manner (secession). So the reaction are observed are consecutive reactions. In case of PC the two kinetic points are very near to each other (table IV) and the two lines originate from a single point. So theses reactions are considered to be simultaneous or parallel reactions. Since these reactions are very similar to the thermo chemical reactions the thermo chemical law of addition or subtraction applied to get the parameters of other reaction. In case of calcium oxalate reaction order is found to be above two while in case of PC reaction the order is found to be above three.

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Appendix: Tables and Figures

Table 1: The temperature range and nonisothermal kinetic parameters different compounds

Compound	Heating rate K min ⁻¹	Temperature Range (K)	Activation Energy kJ mol ⁻¹	Order of reaction	ln(A) s ⁻¹
NiSO ₄	5	1036-1054	270.1 ± 0.9	0.540 ± 0.077	24.03 ± 0.09
CoSO ₄	10	1066-1071	222.0 ± 0.3	0.401 ± 0.08	18.32 ± 0.4
CoSO ₄	10	1084-1103	230.9 ± 0.5	0.480 ± 0.003	19.34 ± 0.6
CaC ₂ O ₄	10	730-731	294.7 ± 0.3	1.121 ± 0.001	46.52 ± 0.5
HIPS	10	597-601	133.8 ± 0.3	1.390 ± 0.008	20.86 ± 0.07
HIPS	10	624-629	107.0 ± 0.3	0.977 ± 0.002	15.45 ± 0.14
PS	10	712-714	252.9 ± 2.4	0.959 ± 0.014	37.69 ± 0.41
PC	10	746-748	325.52 ± 0.8	1.874 ± 0.040	48.22 ± 0.14

Table 2: Nonisothermal kinetic parameters at by Intersection lines for different compounds

Compound	Activation Energy kJ mol ⁻¹	Order of reaction	ln(A) s ⁻¹	Remarks
NiSO ₄	274.6	0.470	24.54	Intersection of lines
CoSO ₄	228.2	0.436	19.02	Intersection of lines
PS	250.8	1.025	37.54	Intersection of lines
CaC ₂ O ₄	407.6	1.45	66.74	Intersection of lines
HIPS	125.7	1.09	19.00	Intersection of lines
PC	358	2.03	53.84	Intersection of lines

Table 3: Nonisothermal kinetic parameters from isokinetic effect method for different compounds

Compound	Order of reaction	Activation Energy kJ mol ⁻¹	ln(A) s ⁻¹	Remark
NiSO ₄	0.504	260.2	22.81	Single Reaction
	(0.50)	(260.5)	(22.81)	(Assumed Order)
CoSO ₄	0.422	223.4	18.4	Single Reaction
	(0.40)	(221.5)	(18.27)	(Assumed Order)
PS	1.03	268.7	40.75	Single Reaction
	(1.0)	(261.1)	39.10	(Assumed Order)
HIPS	1.02	111.3	16.2	Reaction Single
	(1.0)	(109.6)	(15.86)	(Assumed Order)
CaC ₂ O ₄	2.6	450.9	73.17	Consecutive Reaction
	(2.0)	(407.4)	(65.73)	(Assumed Order)
	1.4	156.7	26.66	First Reaction
	(1.0)	(128.6)	(21.83)	(Calculated Value)
	1.2	294.2	46.51	Second Reaction
PC	(1.0)	(278.8)	(43.9)	(Assumed Order)
	2.8	464.	70.97	Simultaneous Reaction
	(3.0)	(508.7)	(78.63)	(Assumed Order)
	0.76	106.9	17.43	First Reaction
	(1.0)	(15.8.1)	(26.1)	(Calculated Value)
	2.04	357.1	53.54	Second Reaction
	(2.0)	(350.6)	(52.43)	(Assumed Order)

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Table 4: The on set and end set temperatures and isokinetic temperatures of all compounds

Compound	Isokinetic Temperature $(T_{iso})_1$ (K)	Isokinetic Temperature $(T_{iso})_2$ (K)	Isokinetic Temperature $(T_{iso})_3$ (K)	Onset Temperature T_{ot} (K)	Onset Temperature T_{et} (K)
NiSO ₄	996	1036	1061	983	1099
CoSO ₄	1023	1060	1090	1000	1035
PS	688	695	708	679	740
HIPS	571	588	614	562	662
CaC ₂ O ₄	693	706	725	684	750
PC	725	733	735	721	785

Table 5: Non-isothermal kinetic parameters at different inflection points

Compound	Activation Energy kJ mol^{-1}	Order of reaction	$\ln(A)$ s^{-1}	Remarks
NiSO ₄	174.6	0.283	13.08	$(d\alpha/dT)_{\max}$
	269.8	0.549	23.99	$(d^2\alpha/dT^2)_{\max}$
CoSO ₄	172.3	0.318	12.83	$(d\alpha/dT)_{\max}$
	230.6	0.478	19.31	$(d^2\alpha/dT^2)_{\max}$
PS	253.9	0.977	37.88	$(d\alpha/dT)_{\max}$
CaC ₂ O ₄	305.8	1.03	48.51	$(d\alpha/dT)_{\max}$
	106.8	0.978	15.34	$(d\alpha/dT)_{\max}$
HIPS	133.3	1.375	20.6	$(d^2\alpha/dT^2)_{\max}$
PC	376.8	2.146	56.76	$(d\alpha/dT)_{\max}$

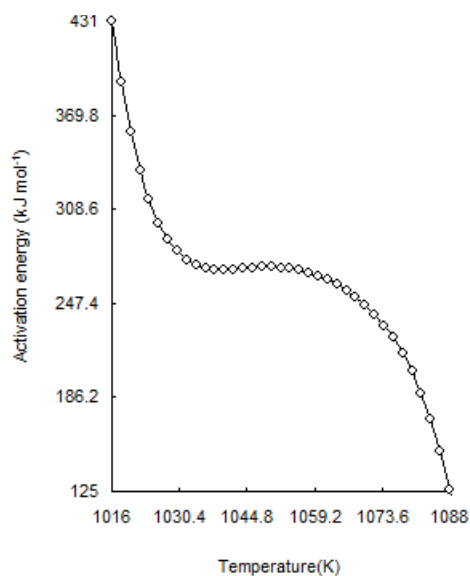


Figure 1a: Plot of activation energy versus temperature for the thermal decomposition of NiSO₄ at 5 K min⁻¹ heating rate

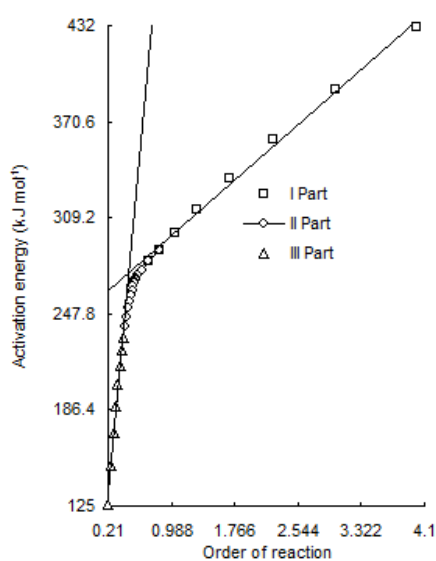


Figure 1b: Plot of activation energy versus order of reaction for thermal decomposition of NiSO₄

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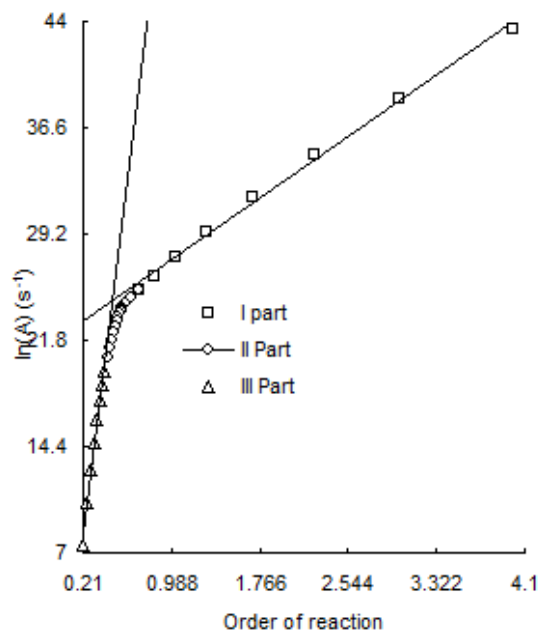


Figure 1c: Plot of $\ln(A)$ versus order of reaction for the thermal decomposition of NiSO_4

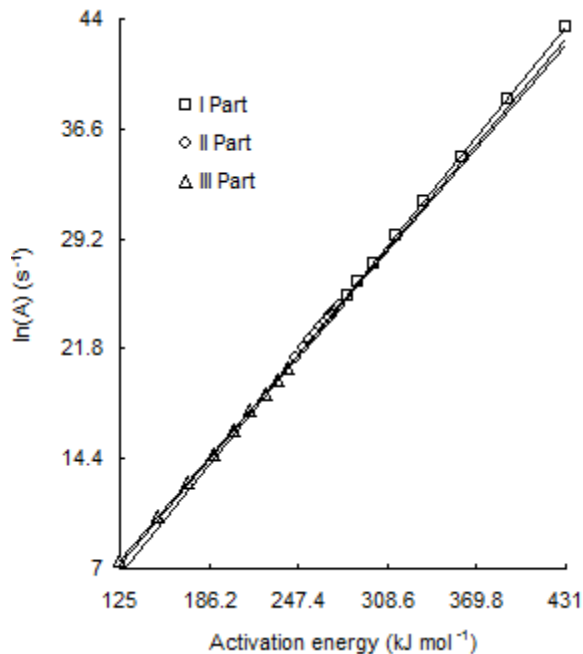


Figure 1d: Plot of $\ln(A)$ versus activation energy for the thermal decomposition of NiSO_4

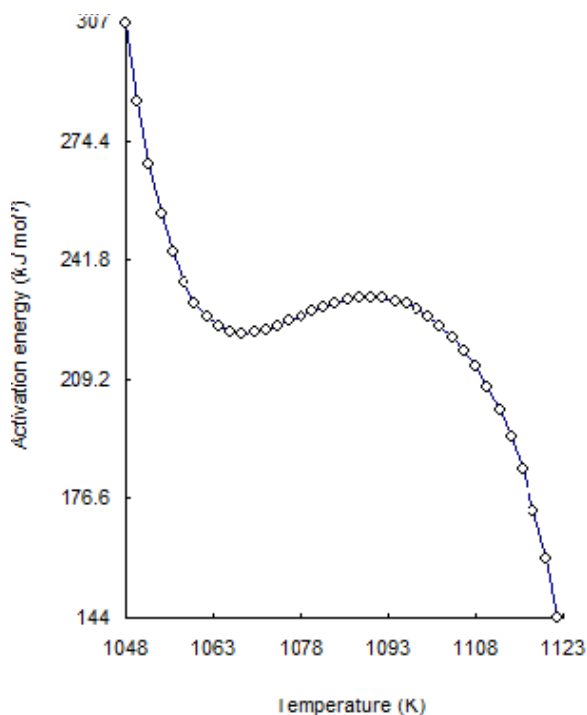


Figure 2a: Plot of activation energy versus temperature for the thermal decomposition of CO_2SO_4 at 10 K min^{-1} heating rate

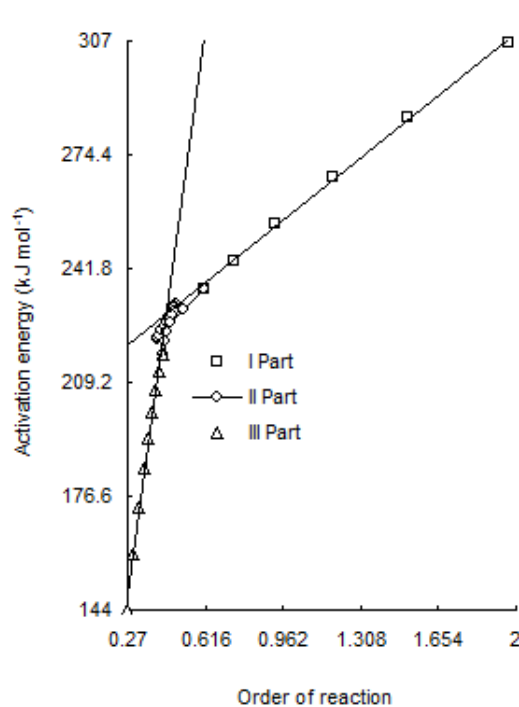


Figure 2b: Plot of activation energy versus order of reaction for the thermal decomposition of CO_2SO_4

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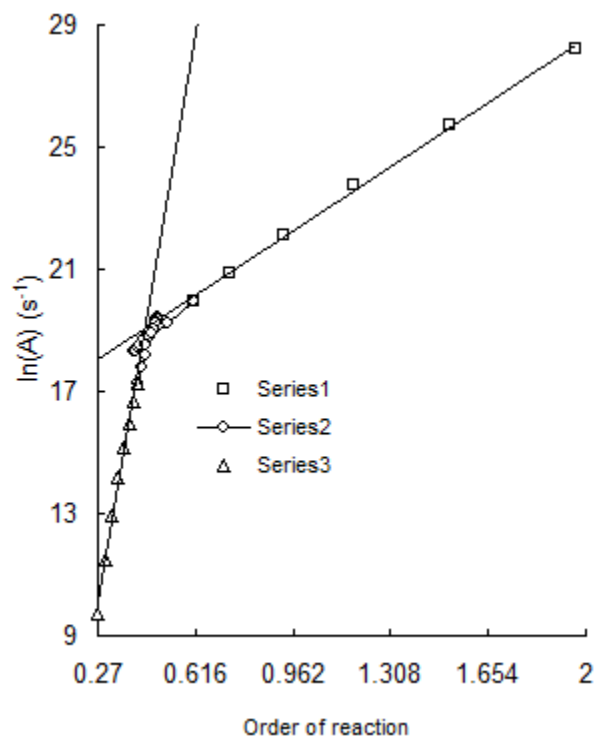


Figure 2c: Plot of $\ln(A)$ versus order of reaction for the thermal decomposition of C_0SO_4

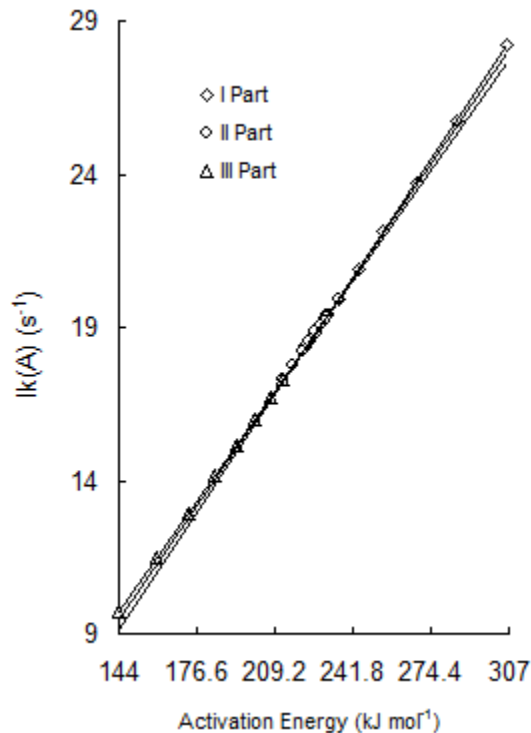


Figure 2d: Plot of $\ln(A)$ versus activation energy for the thermal decomposition of C_0SO_4

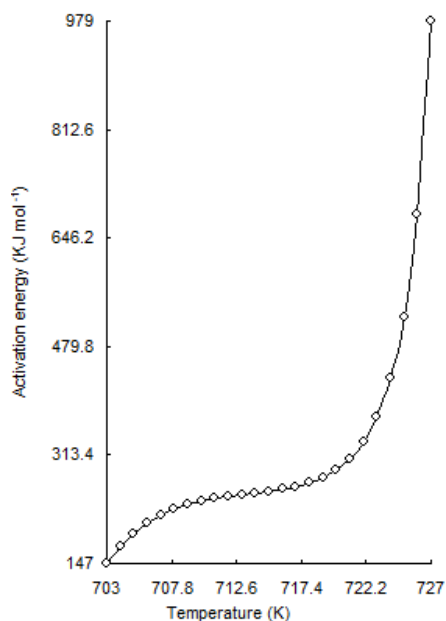


Figure 3a: Plot of activation energy versus temperature for the thermal degradation of PS 10 K min^{-1}

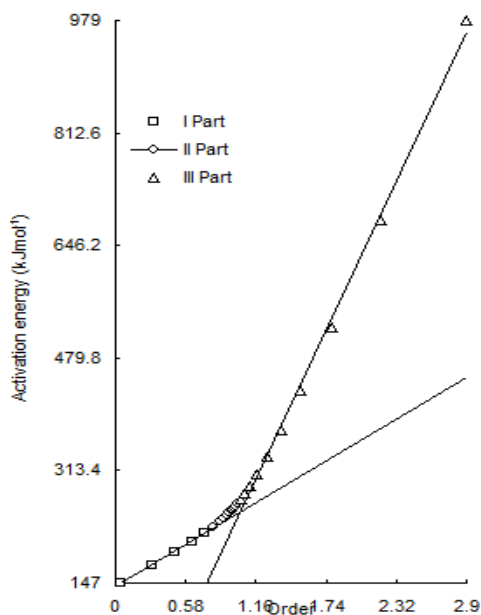


Figure 3b: Plot of activation energy versus order of reaction for the thermal degradation of PS

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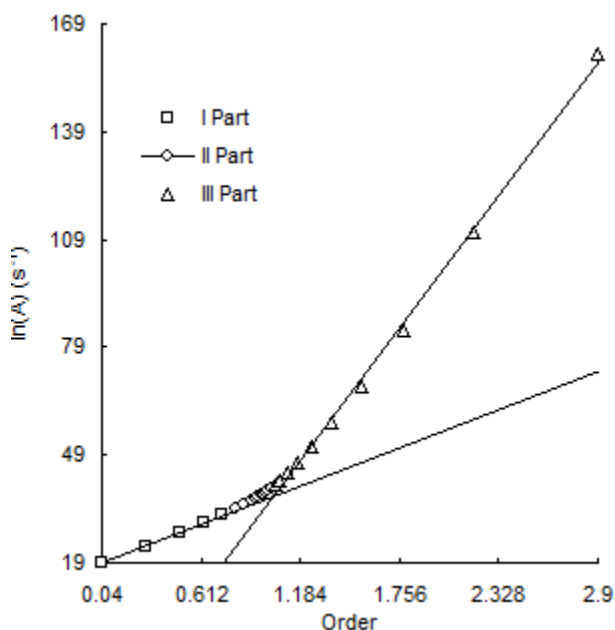


Figure 3c: Plot of $\ln(A)$ versus order for the thermal degradation of PS

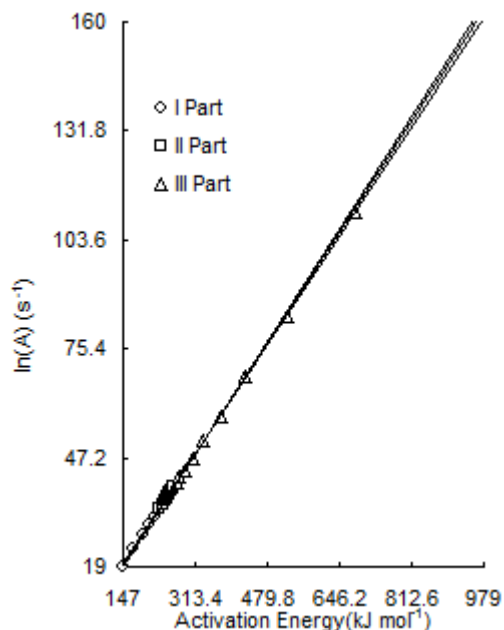


Figure 3d: Plot of $\ln(A)$ versus activation energy for the thermal degradation of PS

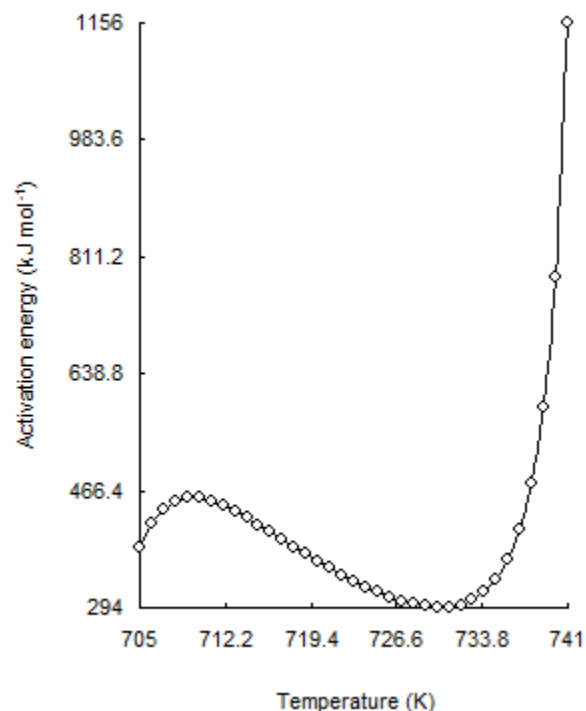


Figure 4a: Plot of activation energy versus temperature for the thermal decomposition of calcium oxalate at 10 K min^{-1} heating rate

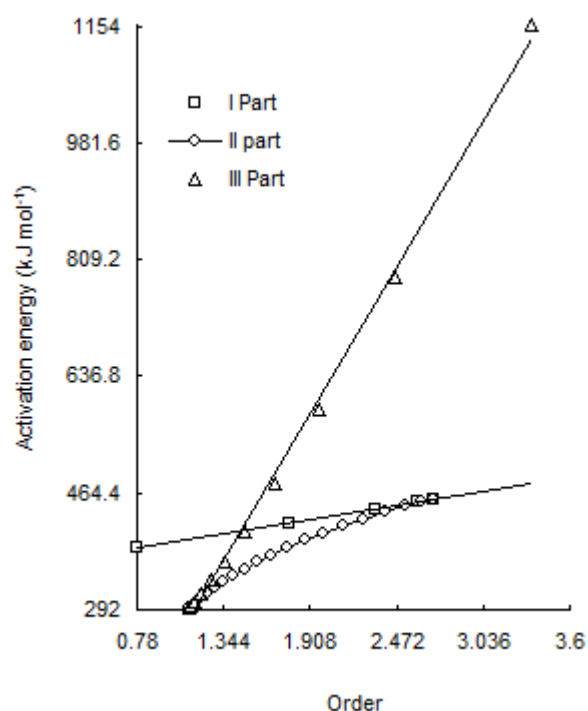


Figure 4b: Plot of activation energy versus order of reaction for the thermal decomposition of calcium oxalate

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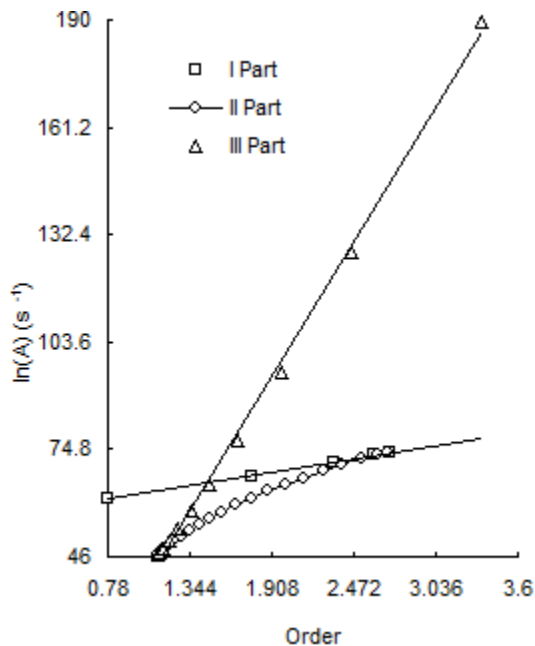


Figure 4c: Plot of $\ln(A)$ versus order of reaction for the thermal decomposition of calcium oxalate

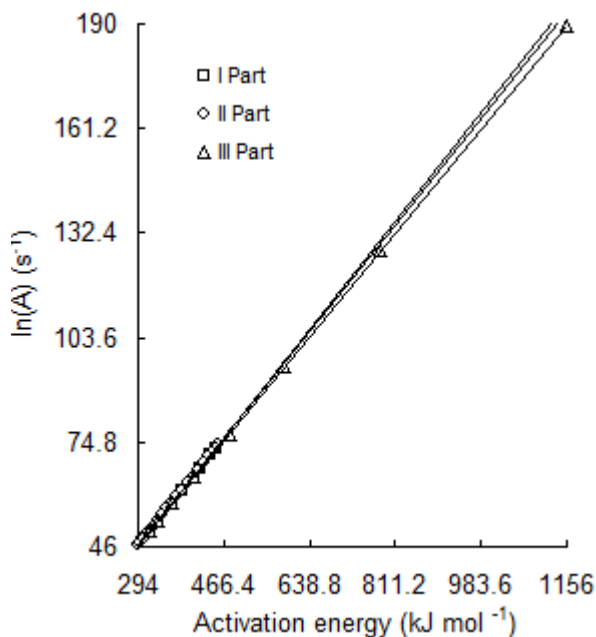


Figure 4d: Plot of $\ln(A)$ versus activation energy for the thermal decomposition of calcium oxalate

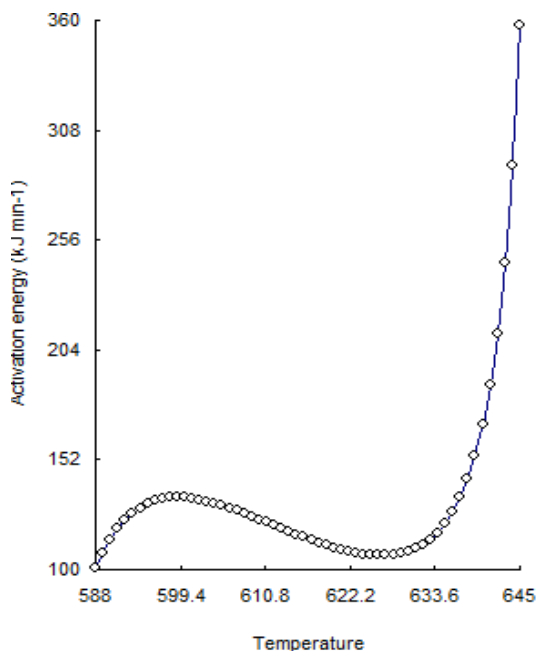


Figure 5a: Plot of activation energy versus temperature for the thermal degradation of HIPS at 10 K min^{-1} heating rate

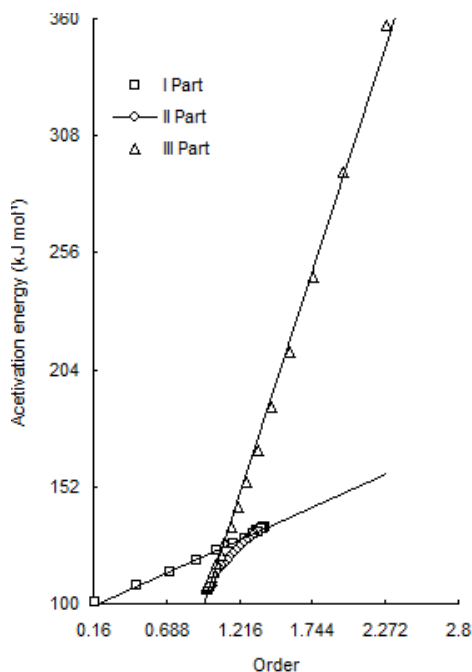


Figure 5b: Plot of activation energy versus order for the thermal degradation of HIPS

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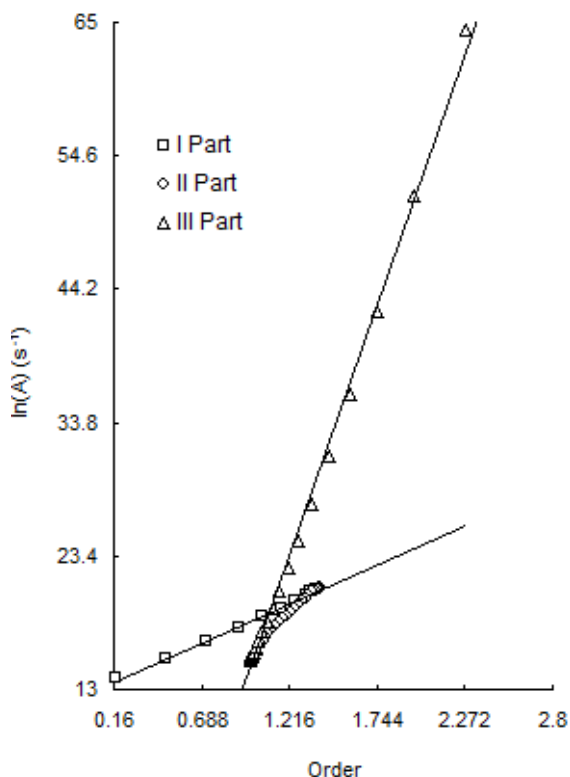


Figure 5c: Plot of order versus $\ln(A)$ for the thermal degradation of HIPS

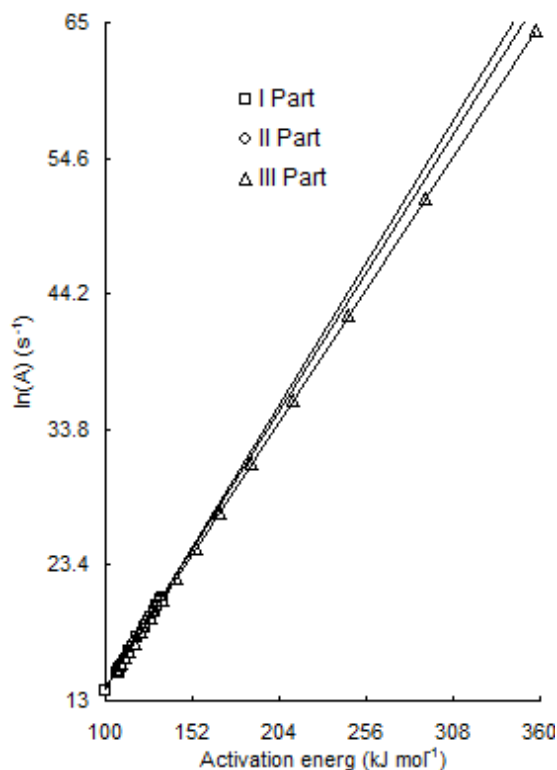


Figure 5d: Plot of $\ln(A)$ versus activation energy for the thermal degradation of HIPS

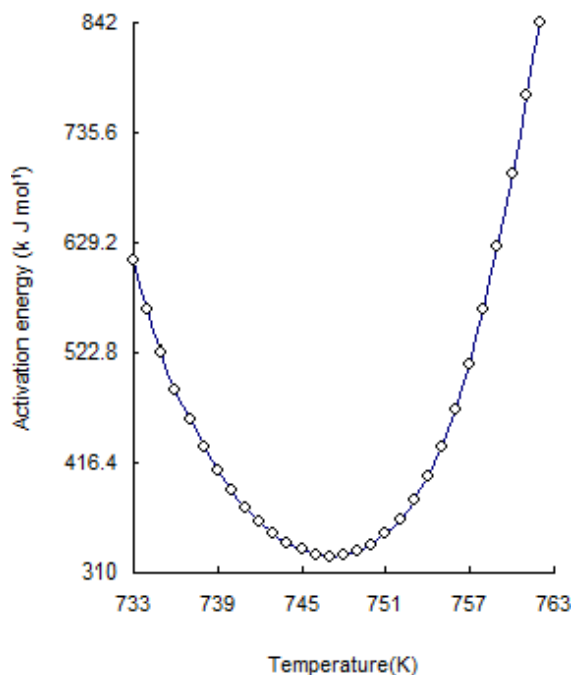


Figure 6a: Plot of activation energy versus temperature for the thermal degradation of PC at 10 K min⁻¹ heating rate.

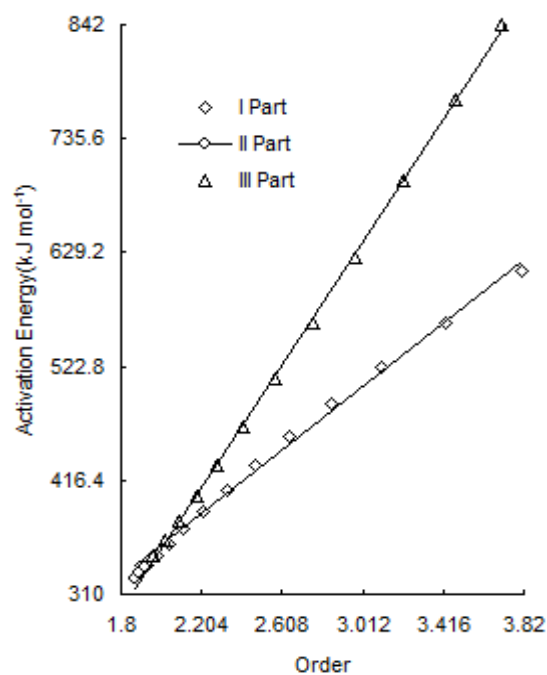


Figure 6b: Plot of activation energy versus order for the thermal degradation of PC

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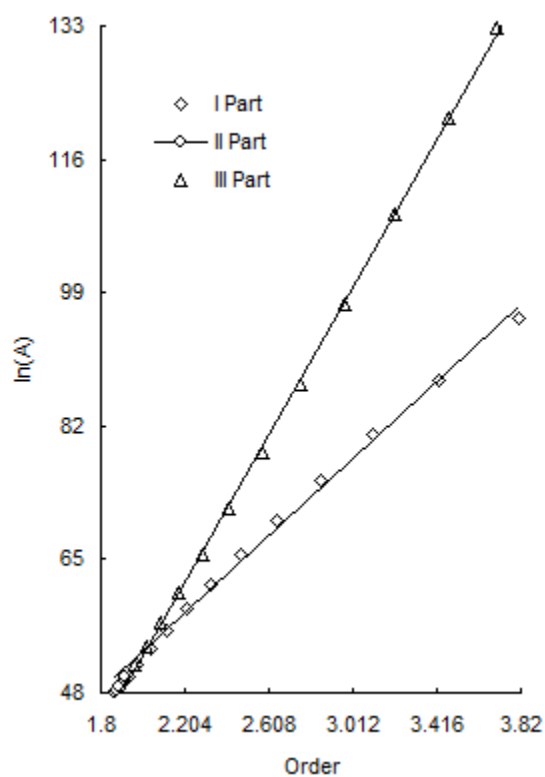


Figure 6c: Plot of $\ln(A)$ versus order for the thermal degradation of PC

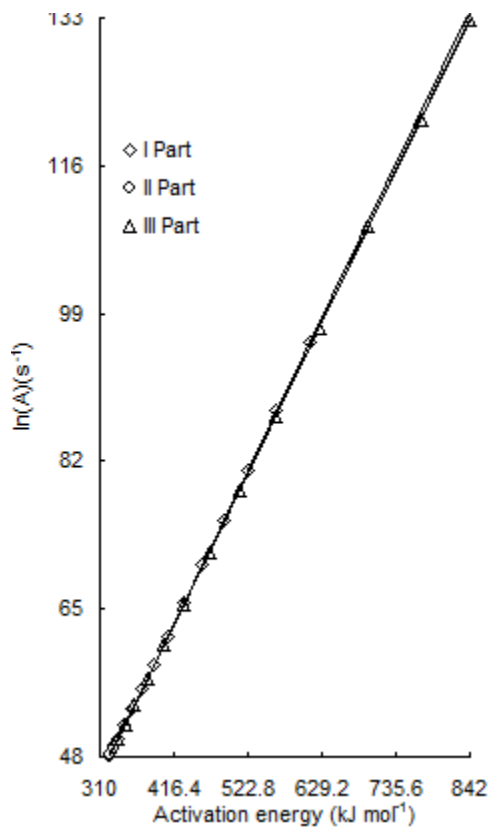


Figure 6d: $\ln(A)$ versus activation energy for thermal degradation of PC

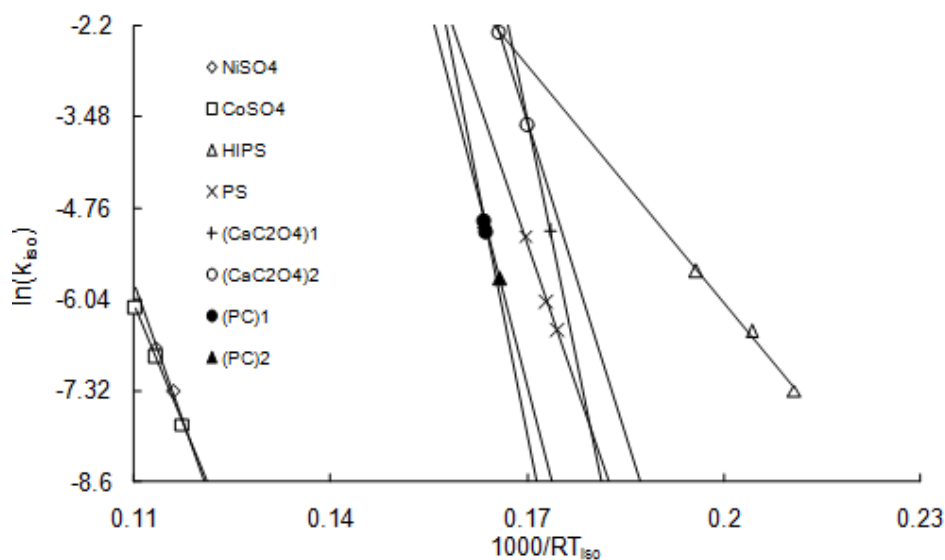


Figure 7: Plot of $\ln(k_{150})$ against $1000/RT_{150}$ for different compounds

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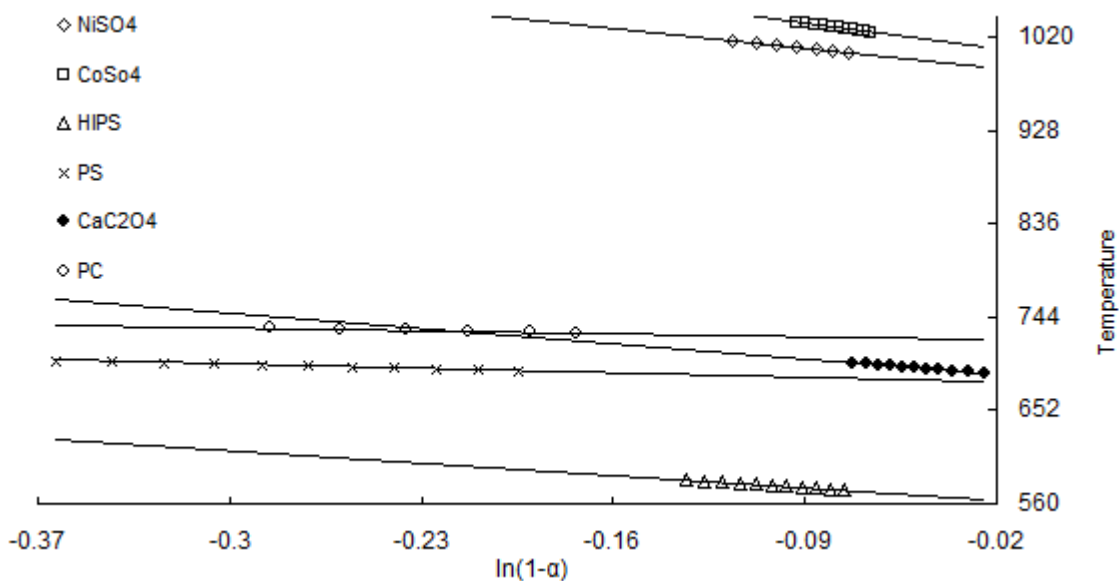


Figure 8: Plot of temperature against $\ln(1-\alpha)$ for the determination of temperature for the different compounds

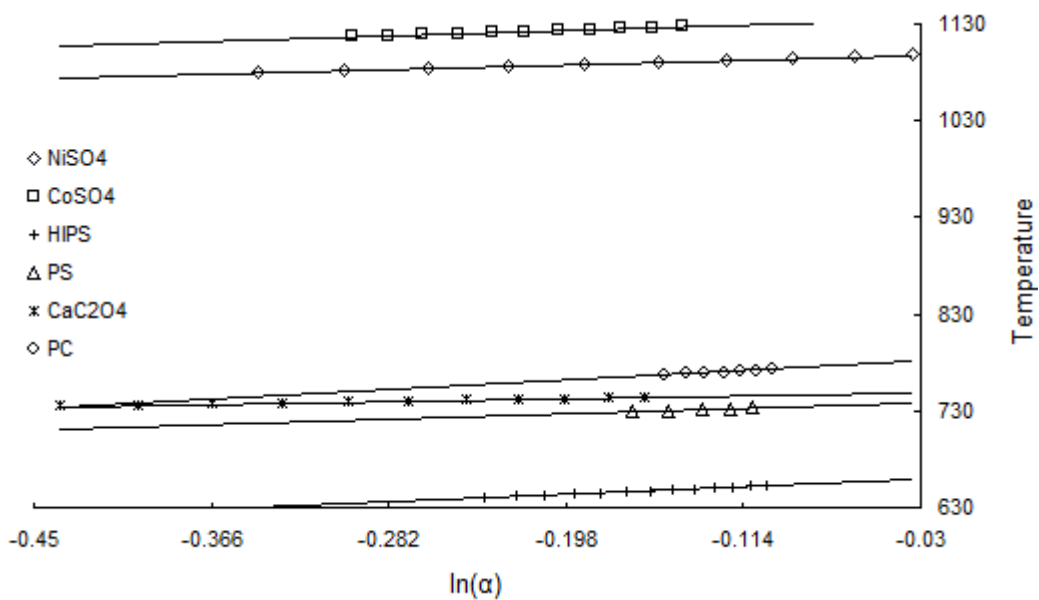


Figure 9: Plot of $\ln(\alpha)$ against temperature for the determination end set temperature for different compounds