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Thermal analysis methods used in solid state physics and chemistry to obtain kinetics and thermodynamics parameters of solid materials by TGA, DTA and DSC analyses

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This paper summarizes the utilization of theoretical methods to calculate kinetic parameters (reaction order n, activation energy E, and Arrhenius constant (K_o) and thermodynamic parameters entropy $\Delta S^{\#}$, enthalpy $\Delta H^{\#}$ and heat capacity (C_p) of the solid materials such as polymer, monomer, oligomer, metal complexes, alloys, composites, glasses and organic compounds. In order to determine these parameters, various methods have been developed in literature. In this paper, it is mainly also aimed how to be determined the kinetic and thermodynamics parameters and possible reaction mechanism in the any material studied.

Keywords: Thermal analysis, kinetic-thermodynamic parameters, TGA, DSC

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1. Introduction

The thermal analysis methods have been extensively studied in literature [1-5]. There are large varieties of theoretical models proposed to explain the thermal kinetics studies. The application of the thermal analysis techniques, such as differential thermal analysis (DTA), differential scanning caloritmetry (DSC) and thermogravimetry analysis (TGA), has been shown to be a simple and useful tool to obtain information nucleation and growth in solid materials.

Calorimetry is a universal method for the study of the physical and chemical transformations in a system, where heat changes occur [6]. DSC has a long and extensive application in the solid state physics, because it not only isolates the temperature-dependent behavior of a given chemical process but it also allows quantitative measurements of the heat associated with the process. DSC applications can be given as follows; (i) determine transition temperatures like T_m and T_g, (ii) determine the heat of fusion of any phase, (iii) studies of crystallization kinetics, (iv) determine heat capacity, C_p, etc.

In calorimetric measurements, two basic methods which are isothermal and non-isothermal conditions can be used. If material is bought quickly to a temperature above of glass transition, T_g, and the heat evolved during the thermal process is recorded as a function of temperature. This method is called as isothermal process. Whereas, in non-isothermal process, the material is heated at a fixed rate and the heat evolved is again recorded as function of temperature or time. The thermal analysis methods can be classified as differential and integral depending on heating rate. These methods of the kinetic integral analysis are used both to identify the mechanistic equation describing the decomposition, crystallization, reaction mechanism and to calculate the activation parameters. In this paper, it will be presented and discussed methods to evaluate non-isothermal kinetic and thermodynamic parameters from thermoanalytical curves.

2. Theoretical backgrounds

2.1. Friedman-Reich-Levi method (F-R-L)

The kinetics of heterogeneous condensed phase reactions occur in non-isothermal conditions is usually described by the equation [7],

$$\beta \frac{d\alpha}{dT} = Kf(\alpha) \qquad (1)$$

where α is the degree of conversion and reaction rate can be written as follows,

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} \qquad (2)$$

where the heating rate is defined as $\beta=dT/dt$. In Eq.(1), K is the defined as the reaction rate constant, which is usually assumed to be an Arrhenius temperature dependence,

$$K = K_o\, exp(-E/RT) \qquad (3)$$

where K_o is the Arrhenius constant. A combination of Eq.(1) and Eq.(3) leads to,

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = f(\alpha)K_o\, exp(-E/RT) \qquad (4)$$

where $f(\alpha)$ is function of conversion. In a logarithmic form,

$$ln(\beta\frac{d\alpha}{dT}) = ln\, K_o\, f(\alpha) - \frac{E}{RT} \qquad (5)$$

This is differential method. If $f(\alpha)$ in Eq.(4) is taken as $(1-\alpha)^n$, the equation becomes

$$\frac{d\alpha}{dt} = K_o\, exp(-E/RT)(1-\alpha)^n \qquad (6)$$

In this equation, for n=1, the following equation is obtained,

$$\frac{d\alpha}{dT} = \frac{K_o}{\beta} exp(-E/RT)(1-\alpha) \qquad (7)$$

The approximation integration of Eq. (7) will give,

$$ln\left[\frac{-ln(1-\alpha)(E+2RT)}{T^2}\right] = ln\frac{K_o R}{\beta E} - \frac{E}{RT} \qquad (8)$$

This equation can be solved with a multiple linear regression and K_o and E can be obtained from the intercept and slope of $[-ln(1-\alpha)(E+2RT)/T^2]$ versus $1/T$ without knowledge of reaction order. In the differential method, from Eq.(6), the differential kinetic model can be obtained,

$$ln\left[\frac{d\alpha}{dT}\frac{1}{(1-\alpha)^n}\right] = ln\frac{K_o}{\beta} - \frac{E}{RT} \qquad (9)$$

From experimental data, a plot of $ln[d\alpha/dT(1-\alpha)^n]$ *vs* $1/T$ is drawn and from the slope of this plot it is possible to deduce the value of activation energy, E

2.2. Kissenger method (K)

The classical Johnson-Mehl-Avrami (JMA) theoretical model [8], is defined as follows,

$$X = 1 - exp[-(Kt)^n] \qquad (10)$$

where X is the volume fraction, n is the Avrami parameter. K is the reaction rate constant, which is defined as by Eq.(3). In non-isothermal method, the sample is heated at a fixed rate and heat evolved is again recorded as a function of temperature. The relation between the sample temperature and the heating rate (β) is defined, $T=T_o+\beta t$, where T_o is the initial temperature. The kinetic parameters is obtained by taking the derivate of Eqs.(3) and.(10). The derivate of K and X is given by

$$\dot{K} = \frac{dK}{dT}\frac{dT}{dt} = \beta\frac{E}{RT^2}K_o\, exp\left(-\frac{E}{RT}\right) = \left(\frac{\beta E}{RT^2}\right)K \qquad \ldots.(11)$$

And

$$\dot{X} = n(Kt)^{n-1}[K + \dot{K}](1-X) \qquad (12)$$

$$\dot{X} = nK^n t^{n-1}[1 + \frac{\beta E}{RT^2}t](1-X) \qquad (13)$$

Kissinger argued [9] that $\beta E/RT^2 << 1$. Rearranging of Eq(13) yields

$$\dot{X} = [-ln(1-X)]^{n-1/n} nK(1-X) \qquad (14)$$

When the second derivate of Eq(13) is taken, $\ddot{X}$ becomes,

$$\ddot{X} = AnK(1-X)[\frac{\beta E}{RT^2} - AnK] = 0 \qquad (15)$$

Where, $A = [-ln(1-X)]^{(n-1)/n}$

Rearranging and taking logarithm of Eq(15) yields [9],

$$ln\left(\frac{\beta}{T_p^2}\right) = C - \frac{E}{RT_p} \qquad (16)$$

where $C=(ARnK_o/E)$, Tp is the peak temperature. The eq.(16) is used to obtain the activation energy using the linear relationship between $y=ln(\beta/T_p^2)$ and $x=1/T_p$. The intercept of the straight line can be used to calculate the pre-exponential factor. It is also suggests that the change of $ln(\beta/T^2)$ with a is negligibly small compared with the change of $ln\beta$, and therefore, the Kissinger equation can be simplified to [9],

$$ln(\beta) = -\frac{E}{RT_p} + constant \qquad (17)$$

2.3. Augis and Bennett method (A-B)

Austin and Bennett have developed a method using the Eq. (13),

$$\dot{X} = nK^n t^{(n-1)}[1+at](1-X) \quad (18)$$

where a=βE/RT^2 and in this equation, if *Kt=u* is taken, the equation becomes,

$$\dot{X} = n\dot{u}u^{(n-1)}(1-X) \quad (19)$$

where $\dot{u} = u[t^{-1} + a]$ and taking derivate of Eq(19),

$$\ddot{X} = [\ddot{u}u - (\dot{u})^2(nu^n - n + 1)]nu^{(n-2)}(1-X) = 0 \quad ...(20)$$

$$\ddot{u} = \dot{u}[t^{-1} + a] + u[-t^{-2} + \dot{a}] \quad (21)$$

Keeping in mind that $T=T_o+\beta t$, Eq(21) can be written as,

$$\ddot{u} = u[a^2 + 2aT_o / Tt] \quad (22)$$

when this equation is rearranged, the equation becomes,

$$nu^n - n + 1 = [at/(1+at^2)]^2 \quad (23)$$

Consequently,

$$u = (Kt)_p = K_o \exp(-E/RT_p)[(T_p - T_o)/\beta] \cong 1 \quad .....(24)$$

In a logarithmic form, the equation can be written as,

$$ln[\beta/(T_p - T_o)] = E/RT_p + \ln K_o \quad (25)$$

If $ln[\beta/(T_p-T_o)]$ is plotted as a function of *1/Tp*, the activation energy can be calculated from the slope of plot whose slope is E/R.

2.4. Horowitz-Metzger method (H-M)

The expression can be expressed by the following relationship [11],

For n=1

$$ln(-ln(1-\alpha)) = \frac{E}{RT_{ref}^2}T - T_{ref} \quad (26)$$

And for n≠1

$$ln\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right) = \frac{E}{RT_{ref}^2}T - T_{ref} \quad (27)$$

where *n* is the reaction order and *R* is the gas constant (8.315 J/mol.K).

2.5. Dharwadkary Karkhanavala method (D-K)

The expression is defined as [12], for n=1

$$ln[-ln(1-\alpha)] = \frac{E}{RT_i^2}\frac{100}{T_f - T_i}\theta + C \quad (28)$$

2.6. McCallum-Tanner method (M-T)

The method is defined as [13]

$$log(g(\alpha)) = log\frac{K_o E}{\beta R} - 0.483E^{0.435} - \frac{(0.448+0.217E)1000}{T} \quad ...(29)$$

where g(a)=-ln(1-a), for n=1.

2.7. Coats and Redfern method (C-F)

In this method, the kinetic equation of solid thermal decomposition is given as follows [14],

$$\frac{d\alpha}{dT} = \frac{K_o}{\beta}f(\alpha)exp(-\frac{E}{RT}) \quad (30)$$

where *f(α)* is the kinetic differential function and its integral form is given by,

$$g(\alpha)\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{K_o}{\beta}\int_0^T exp\left(-\frac{E}{RT}\right)dT \quad (31)$$

The equation can be solved using *f(a)* values listed in Table 1. In general form, this equation is written as,

$$ln\left(\frac{g(\alpha)}{T^2}\right) = ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (32)$$

where *g(a)* determines reaction mechanism (See Table 1).

2.8. Krevelen, Heerden and Huntjents method (K-H-H)

This method is described as [18]

$$ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right]=ln\left[\frac{K_o}{\beta}\left[\frac{0.368}{T_{ref}}\right]^{E/RT_{ref}}\right]\left[\frac{1}{E/RT_{ref}+1}\right]+\left[\frac{E}{RT_{ref}}+1\right]lnT \quad \ldots(33)$$

when n=1, the expression becomes,

$$ln[1-(1-\alpha)]=ln\left[\frac{K_o}{\beta}\left[\frac{0.368}{T_{ref}}\right]^{E/RT_{ref}}\right]\left[\frac{1}{E/RT_{ref}+1}\right]+\left[\frac{E}{RT_{ref}}+1\right]lnT \quad ...(34)$$

2.9. Mahusudanan-Krishan-Ninan method (M-K-N)

The equation of M-K-N is given as [19]

$$ln\frac{g(\alpha)}{T^{1.9215}}=ln\frac{K_oE}{\beta R}+3.7721-1.9215\,ln\,E-\frac{1.12039E}{T} \quad \ldots(35)$$

g(α)=-ln(1-α), for n=1

2.10. Achar differential method (A)

The equation is defined by Achar [20]

$$ln\left[\frac{d\alpha/dT}{g(\alpha)}\right]=-\frac{E}{RT}+ln\frac{K_o}{\beta} \quad (36)$$

3. Application of the models

3.1. Determination of glass transition activation energy

The relationship between glass transition temperature and heating rate can be given by,

$$T_g=A+B\ln\beta \quad (37)$$

where *A* and *B* are constants and β is the heating rate. This equation was suggested by Lasocka [21]. The thermal stability parameter is defined as [22] $K_{TS}=T_c-T_g/T_m-T_c$, where T_c is the crystallization temperature and T_m is the melting temperature. This parameter can be determined from DSC and DTA curves.

The Kissinger method can also used to calculate glass transition activation energy. The dependence of the glass transition temperature is given by the following relation,

$$ln\left(\frac{\beta}{T_g^2}\right)=-\frac{E}{RT_g}+constant \quad (38)$$

when a plot of $ln(\beta/T_g^2)$ *vs* $1/T$ is drawn, it is possible to calculate activation energy from the slope of this plot. The Kissinger equation can be simplified to calculate activation energy,

$$ln(\beta)=-\frac{E}{RT_g}+constant \quad (39)$$

On the other hand, a plot of $ln[-ln(1-\alpha)]$ versus $ln\beta$ for the sample studied at any fixed temperature gives a straight line and whose slope is, $-n=d[ln(-ln(1-\alpha))]/d[ln(\beta)]$. Eq. (10) can be rearranged in the form, $K=[ln(1-X)]^{1/n}/t$. Thus it is possible to use Eqs.(3) and (10) to calculate kinetic mechanism of the sample studied. Substituting a value n in the above equation, one calculates *K*. Then, According to Eq.(3), plotting *lnK* versus *1/T* give a straight line whose slope and intercept are respectively, *E/R* and lnK_o.

3.2. The crystallization activation energy

Coats-Redfern-Sestak suggested a method to determine the crystallization activation energy. Their model can be defined as [14,23]

$$ln[(ln(1-X)]/T^{2n}]=-n\ln\beta-nE_C/RT+constant \quad ...(40)$$

The activation energy can be determined from the linear relation between $[(-ln(1-X))/T^{2n}]$ with *1/T* at different heating rates. From the slope of this relation, the value of activation energy could be deduced.

The activation energy can be also calculated using single-scan technique through an improved signal DSC. For this model, the kinetic equation is given as,

$$n^{-1}\ln[-ln(1-X)]-2nT=ln(K_oR/nE\beta)-E/RT \quad \ldots(41)$$

if n is known, a plot of $n^{-1}ln[-ln(1-X)]-2lnT$ versus *1/T* yields a straight line whose slope is E/R. In this method, the volume fraction A(T) transformed after a given temperature T can be calculated from the thermograph using the equation, $X=A(T)/A$, where A is the total peak area and A(T) is the area under peak up to temperature T (see Fig.1). In Eq.(41), in case n is unknown, a plot of $n^{-1}ln[-ln(1-X)]$ versus *1/T* is carried out with n=1,2,3,4 to the select of n that gives the best linear relation.

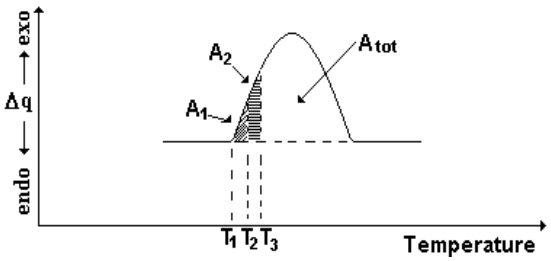


Fig. 1. A typical DSC curve

On the other hand, the crystallization mechanism may be correlated with the Avrami parameter n using the eq.(10)

$$n = (2.5/\Delta T)RT_p^2/E \qquad (42)$$

where ΔT is the width of the crystallization peak at half maximum.

According to Matsuia [24], the fraction crystallized, X, in the non-isothermal crystallization is given by

$$ln[-ln(1-X)] = -n\ln\beta - 1.052mE_c/RT + constant \qquad \ldots(43)$$

where n and m constant that depend on the nucleation and growth mechanism. A typical plot of *[-ln(1-X)] vs 1/T* gives a straight line and slope of the curve gives the activation energy. To determine value of n, the plot between *[-ln(1-X)]* and *lnβ* is drawn.

3.3. Determination of the kinetic and thermodynamics parameters from TGA

Thermodynamic parameters for decomposition such as such enthalpy $\Delta H^{\#}$ change, entropy change $\Delta S^{\#}$ and Gibbs free energy change $\Delta G^{\#}$ of the materials studied by TGA can be calculated using the following relations:

$$\Delta S^{\#} = ln(\frac{K_o h}{kT})R \qquad (44)$$

$$\Delta H^{\#} = E - RT \qquad (45)$$

$$\Delta G^{\#} = \Delta H - T\Delta S^{\#} \qquad (46)$$

where h is the Planck constant and T is the temperature involved in the calculations selected as the temperature at the end of the decomposition step, K_o is the Arrhenius constant. The entropy and activation energy were calculated using intercept and slope of the plot of $ln[g(\alpha)/T^2]$ vs. *1000/T* using,

$$intercept = ln(\frac{K_o R}{\beta E}) \qquad (47)$$

And

$$E = -slope x 8.315(kJ/mol) \qquad (48)$$

The g(α) functions are used to evaluate the kinetic parameters listed in Table 1. The goodness of fit is checked by calculating the correlation coefficient. The correlation coefficients for each function are calculated and the correlation coefficient having maximum value is chosen as the mechanism of reaction.

On the other hand, thermodynamics parameters (enthalpy, entropy and heat capacity) can be calculated from DSC curves using the following relations,

$$\Delta H = \frac{kA}{m} \qquad (49)$$

$$C_p = \frac{\Delta H}{\Delta T} \qquad (50)$$

and

$$\Delta S^{\#} = 2.303 C_p \log(T_2/T_1) \qquad (51)$$

where *k* is the calibration constant of the instrument and *A* is the area under peak studied, m is the mass of the sample. T_1 and T_2 are the peak temperatures studied.

4. Discussion

This study comprise the utilization of the thermal analysis methods to determine activation energy and reaction order and the possible mechanisms controlling the decomposition and crystallization processes of the various materials such as polymer, monomer, oligomer, metal complexes, alloys, composites, glasses and organic compounds subjected to DSC, DTA and TGA analyses. Determination of the possible reaction model mechanism has been carried out by means of the DSC, DTA and TGA measurements. For this purpose, DSC, DTA and TGA curves are recorded at different heating rates. The interpretation of thermal analysis methods is very important for obtain kinetic and thermodynamic parameters of the various materials. These parameters can be deduced using theoretical models methods described in this paper. These models enable the correct evaluation of such as the activation energy and reaction order. Several relationships between peak temperatures in thermal analysis experiments and heating rates have been described in this text, all aimed to extract the values of activation energy and other parameters.

This study proves that using TGA and DSC analyses the kinetic parameters and reaction mechanism for different process can be easily and rapidly obtained. TGA analyzer is used to obtain the kinetic parameters or reaction mechanism of the sample studied. When graphs are plotted for different mechanisms in described in this text, the best fits would be indicative of possible dominant reaction mechanism. It is evaluated that if reaction order n is unknown, the method used does not show a stable trend to obtain activation energy. Thus,

it is suggested that the variable rates method is more accurate than that with a single heating hate.

5. Conclusions

The thermal analysis methods described in this text proves how to be determined kinetic and thermodynamic for various solid materials in the Solid State Physics.

Table 1: The different reaction mechanism models [15-17]

No	f(α)	g(α)	Symb.	Mechanism
1	$(1-\alpha)$	$-\ln(1-\alpha)$	F1	Random nucleation with one nuclei on the individual particle
2	$(1-\alpha)^2$	$(1-\alpha)^{-1}$	F2	Random nucleation with two nuclei on the individual particle
3	$(1-\alpha)^3$	$(1-\alpha)^{-2}$	F3	Random nucleation with three nuclei on the individual particle
4	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$	Fn	Random nucleation with N-nuclei on the individual particle
5	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$-[-\ln(1-\alpha)]^{1/2}$	A2	Two-dimensional nucleation and growth
6	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	A3	Three-dimensional nucleation and growth
7	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	$[-\ln(1-\alpha)]^{(n-1)/n}$	An	N-dimensional nucleation and growth
8	$(0.5/\alpha)$	α^2	D1	One-dimensional diffusion
9	$[-\ln(1-\alpha)]^{-1}$	$\alpha + (1-\alpha)\ln(1-\alpha)$	D2	Two-dimensional diffusion
10	$1.5(1-\alpha)^{-2/3}[1-(1-\alpha)^{-1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$	D3	Three-dimensional diffusion
11	1	α	R1	Phase boundary controlled reaction (contracting line)
12	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$	R2	Phase boundary controlled reaction (contracting area)
13	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$	R3	Phase boundary controlled reaction (contracting volume)

References:

[1] C. W. Tang, Appl. Phys. Lett. 48 (1986) 183.
[2] H. Hoppe and N. S. Sariciftci, J. Mater. Res. 19, (2004) 1924.
[3] J. Rostalski and D. Meissner, Sol. Energy Mater. Sol. Cells 63, (2000) 37.
[4] D. Gebeyehu, B. Maennig, J. Drechsel, K. Leo, and M. Pfeiffer, Sol. Energy Mater. Sol. Cells 79, (2003) 81.

[5] D. Wöhrle et al., J. Mater. Chem. 5, (1995) 1819.
[6] P. Peumans, A. Yakimov, and S. R. Forrest, J. Appl. Phys. 93, (2003) 3693.
[7] P. Schilinsky, C. Waldauf, J. Hauch, and C. J. Brabec, Thin Solid Films 451, (2004) 105.
[8] D. Whorle, D. Meissner, Adv. Mater. 2_(1991) 129.
[9] J.B. Whitlock, P. Panayotatos, G.D. Sharma, G.R. Birds, Opt. Eng.32 (1993) 1921.
[10] S. Karg, M. Meier, W. Riess, J. Appl. Phys. 82 (1997) 1951.
[11] H. Bottcher, J. Prakt. Chem. 334 (1992) 14.
[12] J. Simon, J.J. Andre, Molecular Semiconductors, Springer-Verlag, Berlin, 1985.
[13] S. Gunster, S. Siebentritt, D. Meissner, Mol. Cryst. Liq. Cryst. 230 (1993) 351.
[14] K. Takahashi, S.I. Nakatani, T. Matsuda, H. Nambu, T. Kormura, K. Murata, Chem. Lett. 11 (1994) 2001.
[15] C. R., Newman, et al. Chem. Mater. 16, (2004) 4436,
[16] F. Yakuphanoglu, J. Phys. Chem. C. Article in press (2007).
[17] E.H. Rhoderick, R.H. Williams, Metal-Semiconductor Contacts, 2nd ed., 1988.
[18] S. Aydoğan, M. Sağlam, A. Türüt, Polymer 46 (2005) 10982.
[19] S.K. Cheung, N.W. Cheung, Appl. Phys. Lett. 49 (1986) 85.
[20] Ş. Karataş, A. Türüt, Nuclear Instruments and Methods in Physics Research A 566 (2006) 584.