

Kinetics of Solid State Decomposition Reactions

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Kinetics of decomposition of solids is usually studied widely by thermal route. On heating, the solids decompose in multiple steps at the temperature ranges of decomposition releasing the decomposition products in each step [1]. For example hydrated solids like copper sulphate decomposes first losing two water molecules and then another two water molecules and finally the last water molecules before the salt its decomposes to give rise to the oxide. Thus there are a variety of decomposition steps in the thermal decomposition of solids. Several decomposition studies have been reported in literature wherein estimation of activation energy is presented as a part of the work but no exclusive kinetic treatment of experimental data is reported. [2]. As far as thermal decomposition is concerned most of the studies are based on the method proposed by Kissinger. Conventionally the solid state decomposition is carried out either isothermally (at a constant temperature) or by imposing constant heating rate defined by β , with typical unit of deg/min. Table 1 lists typical values of the values of activation energy obtained for thermal decomposition of AB (ammonia Borane system with and without catalyst) and AB with catalysts as reported in literature. [3]. In most of the studies reported in literature, use of Kissinger method for the estimation of kinetic parameters is preferred. Normally, the low decomposition temperatures don't justify high values of activation energy. Also the use of Kissinger method may not be appropriate in case of solid state thermolysis as the reaction is heterogeneous while the Kissinger method is suitable for homogeneous reaction following first order kinetics. In this presentation some specific aspects of the kinetics of thermal decomposition of solids are presented and more detailed and comprehensive treatments will be given in subsequent presentations.

Table 1 The values of activation energy for the thermal decomposition of ammonia borane (AB) with various catalysts [Data reproduced from ref.[3]]

Material	E_a KJ/mol	Model/method	Ref
Neat AB	184	Calculated by integrating area under isothermal DSC curve	6
AB in SBA-15	67		
Neat AB	160	Kissinger plot for nonisothermal DSC	7
AB-16nmCC	150		
AB-7nmCC	120		
Neat AB	183	Arrhenius analysis	8
AB-LiH	75		
AB-MOF1	131	Kissinger Plot	4
AB-MOF2	160		
Neat AB	129	Kissinger Plot	5
AB + 2%Co	117.3		
AB+2%Ni	123.5		
Neat AB	181.7	Kissinger method	9
50%AB+MIL-101	91.4		
50%AB+Ni@MIL-01	69.6		

Solid state reactions are quite complex and different from the reactions in gas phase or liquid phase. Unlike gas phase or liquid phase reactions, solid state reactions are non-homogeneous, thus the homogeneous kinetics does not apply to these reactions. The kinetic behaviour of the heterogeneous rate processes are subject to a different set of controls from those operative in case of homogeneous reactions for e.g. the concept of concentration is not applicable to solid state reactions. Hence, the general method of using concentration or concentration raised to a power cannot be fitted in the kinetic expression for these processes. In general, the solid state reaction involves all or some of the following reaction steps: diffusion of reactant to the reactive surface, adsorption at the reactive surface, reaction on atomic scale on the reaction surface, nucleation of the product and growth and diffusion of the products away from the reactive interface [10-12].

Rate of the solid state reaction in general is described by the equation

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

Where, k is the rate constant, α is the fraction of reaction also called as extent of reaction and $f(\alpha)$ is the differential form of the reaction model. Extent of reaction is determined by

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (2)$$

Where m_i is the initial mass of the reactant, m_t is the mass at time t and m_f is the final mass at the end of reaction. The rate constant k largely depends on temperature and is the most important parameter as it is directly related to activation energy and pre-exponential factor by Arrhenius equation which is as follows.

$$k = A e^{\left(\frac{-E_a}{RT}\right)} \quad (3)$$

In the Arrhenius equation (equation 3) E_a is the activation energy, A is the pre-exponential factor, T is the absolute temperature and R is the gas constant. By rearranging the terms in equation 1 and integrating, following equation is obtained.

$$g(\alpha) = kt \quad (4)$$

Where, $g(\alpha)$ is the integral form of the kinetic model and t is the time. Table 2 lists various kinetic [12] models based on the physical phenomenon governing the solid state reaction and their differential and integral forms.

Based on the mechanistic assumptions, the kinetics models listed in table 2 can be broadly classified into four categories: The diffusion models, geometrical contraction (expansion models for the reverse reaction) models, the reaction order based models and nucleation models. Further, the nucleation models are either the power law models or Avrami-Erofeyev models [11]. Diffusion models are suitable to determine the rate of reaction involving the reactions between two solids. In diffusion models the diffusion of reactant or product is considered to be rate limiting, as such the reactions involving product forming reactions can be analyzed based on these models.

It is also observed that while doing kinetics analysis of solid state reactions usually the kinetic data is fitted into the order based models and fitting is obtained by varying the value of n . While doing so the data may fit in some equation but the physical significance of the fitted model

remains undefined. As the solid state reactions are non-homogeneous the method of forcefully fitting the kinetics data into the order based models may lead to erroneous results [13].

The geometric contraction models (dimensionality dependent) assume that the reaction occurs rapidly on the surface of the crystal. The reaction then advances inwards (outwards for growth process) and the rate of degradation is controlled by the resulting reaction interface progress toward the centre of the crystal. Depending on the crystal shape different models are derived and these are also listed in Table 2.

Nucleation models in general and Avrami-Erofeyev models in particular govern a large class of the solid state reactions namely crystallization, decomposition, hydration, desolvation and adsorption. Decomposition is of importance from this discussion viewpoint and therefore the nucleation models and in particular the Avrami-Erofeyev models are of extreme importance. A typical decomposition reaction has the following scheme:



Where, A is the solid reactant decomposing into a solid product B and a gaseous product C. In the solid structure, there is a fluctuation in the local energy due to the presence of defects, impurities, cracks. [10]. As the reaction activation energy is lowest at these imperfections they are the probable nucleation sites. Nucleation can be defined as the phenomenon of formation of the new product phase B in the reactant phase A. The nuclei formed start growing and finally the reactant A decomposes completely into product B and C. The growth process can be conceived as the reverse of this process.

Apart from the reaction based models, there are methods that facilitate estimation of the kinetics parameters without considering the reaction kinetics model. They are iso-conversion methods or model free methods. Use of iso-conversion kinetics for exploring the mechanisms of thermal processes is based on evaluating the dependence of the effective activation energy on conversion or temperature and using this dependence for making kinetic predictions.

Iso-conversion technique uses isothermal data for estimation of Arrhenius parameters. If the equation 3 and 4 are combined, following relationship is obtained.

$$g(\alpha) = A \exp\left(-\frac{E_a}{RT}\right) \cdot t \quad (5)$$

Taking logarithm and rearranging the terms following equation is obtained.

$$\ln(t) = \ln A - \ln g(\alpha) - (E_a/RT) \quad (6)$$

Since the value of $\ln(g(\alpha))$ is very small as compared to $\ln(A)$ it can be neglected and the value of E_a and A can be obtained from the plot of $-\ln(t)$ against $1/T$. The values of E_a and A so obtained will be corresponding to specific value of α and the time related to that α value [12].

In solid state decomposition reactions the rate of reaction using equation (1) and (2) can be written in the following form:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (7)$$

The Kissinger method is based on the study of the rate equation at maximum reaction rate. At the maximum reaction rate $d^2\alpha/dt^2$ is equal to zero and thus the following equation is obtained.

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{A}{RT_m^2}\right) + A f(\alpha_m) - E_a/RT_m = 0 \quad (8)$$

Where, T_m is the temperature, at which maximum reaction rate is observed and α_m is the fraction reacted at maximum reaction rate. Taking logarithm and rearranging the terms equation 8 reduces to following equation.

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{A}{RT_m^2}\right) + A f(\alpha_m) - E_a/RT_m \quad (9)$$

For the first order reaction $f(\alpha) = -1$ and the equation 9 becomes

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{A}{RT_m^2}\right) - \left(\frac{E_a}{RT_m}\right) \quad (10)$$

Equation 10 is known as Kissinger equation and is widely used with non-isothermal data particularly the thermo gravimetric data obtained at constant heating rate. Plot of $\ln(\beta/T_m^2)$ against $(1/T_m)$ can be used to estimate the activation [14] energy and the pre-exponential factor. It can be seen that the Kissinger method is similar to that of iso-conversion method with the difference being the use of constant heating rate in Kissinger method while isothermal data in case of iso-conversion method. Also it can be inferred that the activation energy obtained using the Kissinger equation is independent of the solid state reaction kinetics model. Only the pre-exponential factor will depend upon the model.

Now it is essential to make a few statements. Even though repeatedly the pre-exponential factor A has been referred to in this presentation no value has been given or discussed. For homogeneous reactions whose kinetic analysis is treated in terms of concentrations, its (A) value will be more or less equal to $[kT/h]$ where k and h are the Boltzmann and Planck's constants respectively and T is the value of temperature in absolute scale. Thus it is seen that the value will be in the range of 10^{12} - 10^{13} for homogeneous reactions. However in the case of heterogeneous reactions like the decomposition of solids, the value of A can vary widely and this situation arises due to specific nature of the sites on which the reaction is initiated and propagated. Equation 10 could be derived in a number of ways and alternate method of derivation has been presented in this website in another presentation. Equation 10 is also extensively used for treating Temperature Programmed Desorption (TPD) data which is a common technique to treat the heterogeneous surfaces. It is known that more detailed treatment may be useful and such an attempt will be made in a subsequent presentation in this site.

Table 2 Models for the solid state reactions (including decomposition) and the rate laws (A similar compilation has been made in various places including in this web site).

Description of the model	Differential form of the kinetic equation (f(α))	Integral form of the kinetic expression (g(α))
Nucleation and growth models		
Power law (P2)	$(2\alpha)^{1/2}$	$(\alpha)^{1/2}$
Power law(P3)	$(3\alpha)^{3/2}$	$(\alpha)^{2/3}$
Power law (P4)	$(4\alpha)^{3/4}$	$(\alpha)^{3/4}$
Avarami-Erofeyev (A2)	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avarami-Erofeyev (A3)	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avarami-Erofeyev (A4)	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$

Prout Tomkins(B1)	$A(1-\alpha)$	$[\ln(\alpha/1-\alpha)]$
	Geometrical contraction models	
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
Contraction volume (R3)	$3(1-\alpha)^{1/3}$	$[1-(1-\alpha)^{1/3}]$
	Diffusion models	
One dimensional diffusion (D1)	$1/2 \alpha$	$(\alpha)^2$
Two dimensional diffusion (D2)	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha) + \alpha]$
Three dimensional diffusion – Jander (D3)	$3(1-\alpha)^{2/3} + [1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Three dimensional diffusion – Ginstling Brounshtein (D4)	$[3/2(1-\alpha)^{-1/3} - 1]$	$[-(2\alpha/3) - (1-\alpha)^{2/3}]$
	Reaction order based models	
Zero order (F0/R1)	1	α
First order (F1)	$1-\alpha$	$[-\ln(1-\alpha)]$
Second order (F2)	$(1-\alpha)^2$	$[(1-\alpha)^{-1} - 1]$
Third order (F3)	$(1-\alpha)^3$	$[0.5(1-\alpha)^{-2} - 1]$

However, the following general statements may be appropriate.

1. The solid state decomposition kinetics is essentially dimensionality dependent because one is dealing with nucleation and its growth.
2. The pre-exponential factor has therefore understood in different language instead of the vibration frequency which results in the reaction in homogeneous systems.
3. The magnitude of the value of A and the variation usually found in these values have to be rationalized suitably.

In previous presentations in this web site some of these aspects have been already treated and in subsequent postings we shall be considering some of the aspects that have not yet been covered.

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