APPROPRIATENESS OF ARRHENIUS EQUATION FOR KINETIC ANALYSIS OF SOLID STATE REACTIONS

B. Viswanathan
National Centre for Catalysis Research
Indian Institute of Technology, Madras, Chennai 600 036

The kinetic parameters for solid state reactions (decomposition, phase change or compound formation) have been conventionally evaluated by treatment of isothermal or non-isothermal data of fraction reacted (α) as function of time in the case of isothermal studies and (α) as a function of temperature employing the conventional Arrhenius equation in the form, $k = A \exp(-E_a/RT)$. The applicability of Arrhenius equation for homogeneous molecular level reactions is well known and has been established beyond doubt since these systems obeys the Maxwell – Boltzmann distribution. However alternate functions like relating ln k with T or ln k with ln T in addition to ln k versus 1/T have also been proposed, but these relations have been considered as 'theoretically sterile' since the constants of these proposed equations do not lead to any deeper understanding of the steps of the chemical reaction [1]. Galwey and Brown [2] have raised this aspect in one of their innumerous publications in this area and provided a number of arguments justifying the use of Arrhenius equation to treat the kinetics of solid state reactions. The main argument provided by them concerns that solid state reactions are mostly promoted by interface sites and their energy levels. These energy states though normally obey for Fermi-Dirac statistics for electrons and Bose Einstein statistics for phonons, both these statistical functions can approximate to the conventional exponential function (Maxwell-Boltzmann distribution (MB)). Since obedience to Maxwell-Boltzmann statistics is the key for the application of Arrhenius equation, they justified the use of Arrhenius equation for treatment of solid state reaction kinetics implying the other two statistics can approximate to MB statistics.

The kinetics of solid state reactions is conventionally treated with a different model as compared to the reactions taking place in homogeneous solutions [3]. The reaction is considered to initiate and propagate at the interface of the solids and various types of kinetic expressions have been employed to represent the dimensionality and the progress of the reaction at the interface. These models are based on the consecutive steps of nucleus formation and its growth in one, two or three dimensions. A brief summary of the various kinetic expressions normally employed to treat the isothermal kinetics of solid state reactions is given in Table.1. These model kinetic expressions can be analyzed in terms of classifications like models based on nucleation, geometrical contraction or expansion, deceleratory or acceleratory or sigmoid type of kinetic curves, models based on diffusion and models based on reaction orders. Many of these models are unique to treatment of solid state reactions.

Similarly, non-isothermal data have also been analyzed based on various models. Typical expressions employed for treating kinetic data of non-isothermal measurements are assembled in Table 2. Most of these expressions given in Table 2 have been derived on some specific models as conceived by the respect authors. It is not clear, which of these expressions is more suitable to treat the non-isothermal data for an unknown system and in the absence of such a guideline, it has been customary to apply more than one of these expressions for the same set of experimental data on non-isothermal kinetics and then compare the values of derived parameters like activation energy E_a and the pre-exponential factor (A) of the Arrhenius equation. These values are analyzed for consistency or to interpret the mechanism of the solid state reaction. However this situation has led to many unclear situations, since the derived parameters of E_a and A from various models are not mostly consistent and hence the interpretation has to resort to some selection which could not be unbiased. Secondly, since not all the models are employed for treating a set of non-isothermal kinetic data, the selection and supposed applicability of a chosen model appears to be arbitrary. Whenever inconsistency is found in the values of the parameters of E_a and A, the analysis are most often silent or only looks at them as though the models are different, even then the suitability of one model over the other is not considered.

In order to substantiate our contention that the parameters of E_a and A have not been consistent, a chosen set of data collected from literature are given in Table 3. The data given in Table 3 should be taken as representative ones available in literature. No attempt has been made to collect the data extensively.

Galwey [27] has observed that the value of pre-exponential factors for nearly 50% (this estimate appears to be arbitrary) of solid state decompositions lie in the range of 10^8

– 10^{14} S^{-1}. In reality for most of the solid state reactions, the values of the pre-exponential factor vary widely and the spread is certainly too large and mostly differ from the standard value of 10^{13} S^{-1} based on Polyani-Wigner model. One can rise several questions based on the magnitude of the values of E_a and A reported in literature for the kinetics of solid state reactions. It is not our intention to list all these questions but only to indicate a few of them.

(i) What is the significance of values of A higher than 10^{13} S^{-1}?

(ii) What interpretation can be offered when the observed values of A is far less than $10^{13}S^{-1}$?

(iii) The values of activation energy do not usually lie in the range of 100-200 kJ/mol which is normal for bond breaking and bond forming steps being rate determining. If the values obtained were to be too low or too high, how are they to be rationalized?

Galwey and Brown [28, 29] have made a detailed analysis of the aspect of the applicability and justification of the use of Arrhenius type equation for the evaluation of two important kinetic parameters (activation energy and pre exponential factor).for solid state reactions. The reasons and arguments proposed by them can be summarized as follows:

(i) The mechanism of reaction in solid state may be different from that occurring in homogeneous systems, where movement and collision are envisaged as initiating steps of the reaction. In solids, the species are immobilized and hence this type of collisions may not be the initiator of the reaction.

(ii) The reactions (at least some of the reactions in solid state) may be due to bond activation through electronic energy or through phonon activation.

(iii) If softening and melting were to precede the solid state reaction, then one can visualize the reaction sequence as in homogeneous medium.

(iv) The variation of E with α the extent of reaction, (smooth or abrupt) denotes the nature of consecutive steps involved in solid state reactions.

(v) If the solid state reaction proceeds by the development and growth of a reaction interface, then the local strain, imperfections, the crystalline phases of the reactants and products all will contribute to the acceleration or deceleration of reaction rates as well as for the change of E_a with α. It is not yet clear how the various forms of the intervening phase, like a molten product, a defect crystalline phase or reorganizations in react (like removal of water) could provide a chemical environment where the conventional Polanyi-Wigner treatment will be as much applicable as in homogeneous phase.

(vi) In terms of energy transfer, the species in the interracial zone is more ordered in homogeneous liquid medium, but less ordered as compared to the fully crystalline phase. The in-between crystalline phases (interface region) may provide additional allowed energy levels in the forbidden regions of energy bands in the solid. The electronic energy levels though normally follow Fermi-Dirac statistics, can approximate to Maxwell-Boltzmann distribution under the temperature conditions employed for the solid state reaction. If this situation prevails then one can justify the use of Arrhenius equation for evaluating E_a and pre-exponential factor.

(vii) If on the other hand phonons are the mode of activation, then one can expect the Bose-Einstein statistics will approximate to Maxwell-Boltzmann distribution for the conditions prevailing under reaction conditions and hence the use of Arrhenius equation can still be justified.

Though the summary of the arguments given justify the use of Arrhenius type of relationship to evaluate the kinetic parameters (E_a and ln A) it has not provided any explanation for the variation of E_a and ln A. These variations are considered in terms of compensation between E_a and ln A, or by the variation of one (E_a or ln A) while the other remains constant.

The linear relationship between E_a and ln A is termed as compensation effect in the literature. The observance of this effect is usually identified by the inherent ‘heterogeneity’ of the surface and hence the changes in reactivity of these sites. However, a simple linear variation between E_a and ln A for sites of varying reactivity is not expected unless one has to invoke additional internal reorganizations which can give rise to smooth variation in both E_a and ln A.

It must be remarked that these solid state reactions were to involve an intermediate vapourization and condensation steps, then it is probable that one can still invoke Arrhenius type of equation for evaluating E_a and ln A. However not all solid state reactions do proceed by evaporation of reactant and condensation of the product.

It is appropriate to quote Flynn at this stage. He said “ the unfortunate fact is that, since in thermal analysis, properties of the system are measured as a function of (both) time and temperature, all thermo-analytical results are potentially kinetic data, and many people ill grounded on kinetics (like the present author) feel obliged to perform a kinetic analysis of them” [30]

Even if one were to admit inexperience in treating kinetic data from thermal analysis, the physical significance of the kinetic parameters derived from the analysis is not clear yet. Secondly, it is yet to resolved, why the same experimental data can be fitted to various models simultaneously? Do they reflect on the closeness of the models, or the inadequacy of the treatment of data based on the models chosen. The widely practiced method of extracting Arrhenius parameters from thermal analysis experiments involves ‘force fitting’ of experimental data to simple reaction order kinetic models [31]. The ‘force fit’ may not be suitable for the analysis of data of thermal analysis, outside the applicable range of variables and hence can be of limited utility for drawing mechanistic details of the reaction. It should be remarked that the concept of kinetic order of the reaction has to assume a new significance in the case of solid state reactions.

Even for simple decomposition reactions, the available models cannot appropriately take into account like sintering before decomposition, simultaneous existence of polymorphic transition.

It should be recognized that the models so far proposed, are oversimplified and envisages one nucleation site per particle. There can be multiple and different types of nucleation simultaneously and their growth may be a complex function which cannot be treated in terms of simple geometrical considerations.

The direct observation of the texture and morphology of the substances have to be coupled with the kinetic fit of the data for developing a model and draw meaningful deductions regarding nucleation and growth.

The values of the activation energy for solid state reactions can be rationalized only in some simple restricted conditions. For example for two systems if $g(\alpha)$ and A were to be equal then, the magnitude of E_a can be used to postulate on the reaction kinetics. However, even in these cases , if E_a were to vary with α , the fraction of the reaction, then it denotes changes in reactivity as a result of extent of reaction and the complex nature of the reaction.

There is overwhelming tendency to compare E_a values obtained for isothermal and non-isothermal experimental conditions. Even though time and temperature are mathematically related by the heating rate ($\beta = dT/dt$), it is not clear how the species of the system will respond to the bimodal variation. Whether the changes observed will be an arithmetic sum or product of the variations observed with each of these variables. It appears that it is neither of these two mathematical functions.

In conclusion, one can state that if carefully used and complemented with other techniques, the analysis of solid state kinetics can provide indications on the reaction mechanism and may yield information on reactivity which can be exploited for synthetic strategies.

Table 1 Some of the typical physico-geometric kinetic model functions for treating the conversion (α, fraction reacted) versus time data for solid state reactions.[3-5]

Designation of the model	f(α)	g (α)
Random nucleation	$1-\alpha$	$-\ln(1-\alpha)$
Generalized nth order	$(1-\alpha)^{n}$	$1/n\ [1-(1-\alpha)^{n-1}]$
Power law	$(2\alpha)^{1/2}$	$(\alpha)^{1/2}$
Power law	$(3\alpha)^{2/3}$	$(\alpha)^{2/3}$
Power law	$(4\alpha)^{3/4}$	$(\alpha)^{3/4}$
1D or 2D Avrami-Erofeyev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
2D or 3D Avrami-Erofeyev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
3D Avrami-Erofeyev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout Tomkins	$\alpha\ (1-\alpha)$	$\ln\ [\alpha/(1-\alpha)]$
Contracting area	$2(1-\alpha)^{1/2}$	$2\ [1-(1-\alpha)^{1/2}]$
Contraction volume	$3(1-\alpha)^{1/3}$	$[1-(1-\alpha)^{1/3}]$
Generalized model of Sestak	$(1-\alpha)^{n}\ \alpha^{m}$	-
One dimensional diffusion	$1/2\alpha$	$(\alpha)^{2}$
Two dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
Three dimensional diffusion Jander	$3(1-\alpha)^{2/3+[1-(}1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^{2}$
Three dimensional diffusion Ginstling-Brounshtein	$[3/2(1-\alpha)^{-1/3}-1]$	$1-(2\alpha/3) - (1-\alpha)^{2/3}$
Zero order	1	α
First order	$1-\alpha$	$-\ln\ (1-\alpha)$
Second order	$(1-\alpha)^{2}$	$(1-\alpha)^{-1} - 1$
Third order	$(1-\alpha)^{3}$	$0.5(1-\alpha)^{-2}-1$

Table 2 Typical models for the treatment of non-isothermal thermal data (only a selected models are given for others readers are referred to standard texts)[6-17]

Model	Relationship	Ref
Ozawa method	$(\log\ \beta) = (\log (AE/R) - 2.314 - 0.4567(E/RT) - (\log g(\alpha)$	6,7
Coats and Redfern	$\{(\log [1-(1-\alpha)^{1-n}/T^{2}(1-\alpha)]\} = (\log (AR/\beta E)(1-(2RT/E)) - (E/2.303RT)$ for n is not equal to 1	8,9
Coats and Redfern	$\{\log [-\log (1-\alpha)/T^{2}]\} = [\log (AR/\beta E)[1-(2RT/E) - (E/2.303RT)$ for n is equal to 1.	8,9
Freeman and Carrol	$[(\Delta \ln (d\alpha/dT) / \Delta \ln (1-\alpha)] = -E[\Delta(1/T) / R\Delta \ln (1-\alpha)] + n$	10
Friedman	$[\ln (\beta dx / dT)] = [\ln A + n \ln(1-\alpha) - (E/RT)$	11
Flynn - Wall	$[(\log\ \beta)] = [(\log (AE/R) - 2.314 - 0.4567(E/RT)]$	12

Table 3. Values of E_a and A deduced for some of the typical solid state reactions (include examples of decomposition, dehydration, solid state inorganic and organic reactions and phase changes)

Reaction	E_a (kJ/mol)	(A) (min^{-1}/sec^{-1})	Ref
Decomposition of poly carbonates			
Coats and Redfern	15.6	-	18
Freeman and Carrol	360.4	-	
Decomposition of Borax pentahydrate	92.	$2.35X10^{10}$	19
Dehydration	15.9	2.04	
Decomposition			
Formation of Nb_3Sn			20
Kissinger	312		
Flynn-wall	312		
Melting of ice	28.5 ± 3	10^9 (sec^{-1})	21
Decomposition of $Gd_2Mo_7O_{24}14.5$ H_2O	49.2		22
Horowitz- Metzer	30.6	$2.3 X10^2$	
Coats and Redfern	28.1	$1.9X 10^2$	
Piloyau-Novikova			
(β – γ) phase transition in sulanilamide	89 ± 8	$4.6 X 10^{9}$	23
Avramin-Erofeyev			
Cardow model	142 ± 14	$2.0 X10^{17}$	
Nucleatin	70 ± 4	$1.1X10^8$	
Growth			
Paddy husk	125.9	$3.7 X 10^9$	24
SiC from CNT and Si	96±30	-	25
Zinc Oxalate – isothermal method			26
Simple power law	250.5	$3.0X 10^{18}$	
Unimolecular law	258.3	$2.8 X 10^{21}$	

Dynamic method			
Coats and Redfern	257.5	$4.8X10^{20}$	
Zsako	215	$2.6X10^{17}$	
Nickel oxalate isothermal method			26
1. Prout –Tompkins	54.6	$3.7 X 10^{4}$	
2. Contracting Cube law	82.0	$6.9 X 10^{7}$	
3. Avrami-Erofeyev	66.2	$8.0 X 10^{4}$	
4. Unimolecular law	137.5	$1.8 X 10^{11}$	
Non-isothermal method			
Coats and Redfern	160.6	$1.1 X 10^{13}$	
Asako	140.8	$2 X 10^{12}$	
Thorium oxalate- Isothermal method			26
Exponential law	147.4	$6.8 X 10^{11}$	
Contracting cube law	226.1	$1.2 X 10^{17}$	
Non-isothermal data			
Coats and Redfern	209.9	$9.4 X 10^{16}$	
Zsako			
Contracting cube law	173.9	$3 X 10^{13}$	
Unimolecular law	173.9	$1 X 10^{14}$	

References:

[1] Laidler, K.J., J. Chem.Edn., 61, 494(1984).

[2] Galwey, A.K. and .Brown,M.E., Proc.R.Soc., London, A450, 501 (1995).

[3] A K Galwey and M E Brown, Kinetic background to Thermal Analysis and Calorimetry" in Hand book of thermal analysis and calorimetry, Vol.1, Principles and Practice, Ed. M E Brown, Elsevier, Amsterdam, 1998, pp 691.

[4] Jaana Kanervo, Kinetic analysis of temperature programmed reactions, Industrial Chemistry Publication series, Helsinki University of Technology, (2003).

[5] MalteBehrens,http://w3.rz-berlin.mpg.de/~jentoft/**behrens_solid_state_kinetics_** 161107.pdf

[6] Ozawa,T., Bull.Chem.Soc.Jpn., 38 1881 (1965).

[7] Oxawa, T., J Thermal Anal., 2, 301 (1970).

[8] Coats, A.W., and Redfern J.P., Nature, 201,68 (1964)

[9] Johnson D. W., and Gallagher, P.K., J.Phys.Chem., 76,1474 (1972).

[10] Freeman E.S., and B.Carrol, B., J.Phys.Chem., 62,394(1958).

[11] Friedman, J.Polym.Sci., C6,183 (1965).

[12] Flynn, J.H., in Schwenker, Jr., R.F., and Garn P.D., (Eds) Thermal Analysis Proceedings of ICTA2, Worcester 91968) Academic Press, 1969 pp.1111-1126.

[13] Zasko, J., Thermochimica Acta, 2, 145 (1970).

[14] Carr, N.J., and Galwey, A.K., Thermochim.Acta, 79,323 (1984).

[15] Sestak, J., Thermochim.Acta,83,391 (1985).

[16] Sestak, J., and Sestakova, Thermochim.Acta, 203, 1-526 (1992) { all articles in this issue}.

[17] Report of the ICTAC committee, in Thermochim.Acta, 256, 477 (1995).

[18]http://scholar.lib.vt.edu/theses/available/etd-05142001-092334/unrestricted/chapter3.pdf

[19] ÖMER Şahin, Bulutcu, A.N., Turk.J.Chem., 27, 197 (2003).

[20] Patankar, S.N., and Froes, F.H.,http://www.webs1.uidaho.edu/imap/new_page_2.htm

[21] Galwey A.K., Sheen, D.B., and Sherwood J.N., Thermochim. Acta, 375, 161 (2001)

[22] Hangloo, V., Bamzal,K.K., Kotru,P.N., and Koul, M.L., Bull Mat Sci., 27, 295 (2004).

[23] Sheridan, A.K., and Anwar, J., Chem.Materials 8, 1049 (1996).

[24] Jain, A.K., Sharma, S.K., and Daljit Singh, IEEE, 2274.

[25] Wang,Y., and Zerda, T.W., J.Phys Condens. Matter, 18, 2995 (2006)

[26] Palanisamy, T., Gopalakrishnan, J., Viswamathan, B., Srinivasan, V., Sastri, M.V.C., Thermochimica Acta, 2, 265, (1971).

[27] Galwey, A.K., Thermochim.Acta, 242, 259 (1994).

[28] A K Galwey and M E Brown, Kinetic background to Thermal Analysis and Calorimetry" in Handbook of thermal analysis and calorimety, Vol.1, Principles and Practice, Ed. M E Brown, Elsevier, Amsterdam, 1998, pp.691.

[29] Galwey, A.K., Brown, M. E., Application of the Arrhenius equation to solid. state kinetics: can this be justified? Thermochimica Acta, 2002. 386: p. 91-98.

[30] Maciejewski,M., J.Thermal.Anal., 33,1269 (1988).

[31] Vyazovkin, S and Wight, C.A., Annual Review of Physical Chemistry, 48, 125 (1997).