

Non-isothermal kinetics: some merits and limitations

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Abstract

An account of non-isothermal kinetics, with respect to origin, usefulness, limitations, successes and failures compared with isothermal kinetics as applied to solid state heterogeneous reactions, is presented and discussed. The so-called non-relevance of non-isothermal kinetics to such reactions is traced to the over-simplification of mathematical expressions and experimental factors rather than to the non-applicability of the Arrhenius equation itself to non-isothermal heterogeneous kinetics. The usefulness of the variation in A with variation in E as a function of experimental factors, as manifested in the kinetic compensation effect, is indicated to predict the effect of experimental parameters on kinetics.

INTRODUCTION

The concept of non-isothermal kinetics was first outlined as early as 1928 by Akahira [1]. Flynn and Wall [2,3] highlighted the potential applications of this technique which has since been the subject of both extensive and intensive investigations; moreover, there has been a recent rapid development in non-isothermal kinetics. Thus, Šesták et al. [4], as early as 1973, published an extensive review on the subject. Ever since, a large number of views have been expressed by various authors, both for and against the technique. Two international workshops, were held exclusively on this subject in Bratislava and Jerusalem during the 8th and 9th I.C.T.A. conferences. The papers presented at the Bratislava conference [5] appeared to express the general view that the non-isothermal technique was possibly passing through a critical stage or even a crisis. The papers presented at the Jerusalem conference [6–8], however, set aside the uncertainties of non-isothermal kinetics and established the technique on a firm path towards acceptance. The literature is now replete with articles [9–16] on this subject.

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

THE ARRHENIUS EQUATION

All controversies regarding the versatility or otherwise of non-isothermal kinetics stem from the applicability of this equation to solid state kinetics. Hence, let us examine this factor first.

Before the advent of modern thermal analysis techniques, the kinetics of chemical reactions were studied by isothermal methods. The sample under investigation is brought to a series of pre-determined temperatures, and the change in the weight of the sample (or any other suitable property of the material) is measured as a function of time. A relation is then obtained between the measured property and time, yielding a straight line relationship between the two quantities. From these straight lines, the rate constants are deduced. Arrhenius showed that the rate constant of a reaction varies with temperature and is given by

$$k = A \exp(-E/RT) \quad (1)$$

where k is the rate constant, A is known as the frequency factor, E is the activation energy for the reaction, R is the gas constant and T is the absolute temperature. The above expression was based on sound theoretical principles and was derived from the kinetic theory of gases. The equation applies where equilibrium exists between activated and non-activated molecules according to the Boltzmann distribution law. The chemical reaction should involve formation of an “activated” complex and its subsequent decomposition to the products. In solid phase decomposition reactions, destruction of the structure of the reactant solid takes place. Also, the collision of molecules, activation by collision, etc. which are applicable to gas phase and, to some extent, to liquid phase reactions, do not apply to solid phase reactions. Consequently, the concept of reaction order and activation energy as developed for gaseous reactions, are supposed to have no relevance to solid state reactions [17–20]. Moreover, E , as originally conceived for gaseous reactions, represents the energy barrier which the reactants must surpass to go to the products stage. The values A and E are used to provide information about the step identified as rate limiting [21]. Unfortunately, for solid state reactions these very values vary over a wide range as shown by Reading et al. [22]. This, coupled with the observation that the shape of TG curves depend on experimental conditions [23–25], questioned the very applicability of the Arrhenius equation to solid state reactions, whether the kinetic analysis is done by isothermal or non-isothermal techniques. Some authors [17,26], however, feel that the equation has limited applicability. Thus, it appears that E only reflects the influence of experimental parameters on kinetics. Modifications of the Arrhenius equation, therefore, were attempted [18,22,27–29] in order to obtain better kinetic values, but these modifications are thought to be of questionable validity [30].

Thus the non-applicability of the Arrhenius equation to solid state kinetics appears to be based on the influence on these kinetics of the mass and heat transfer, and the non-applicability of the Boltzmann law. However, it is well established that the Boltzmann distribution law forms the basis of the successful statistical theory of heat capacity in the solid state. Also, the Arrhenius equation is used to model the kinetics of sublimation [31]. On the basis of this evidence, Reading [6] has assumed the applicability of the Boltzmann distribution law to solid state kinetics. Further support for the application of the Arrhenius equation to solid state kinetics comes from Flynn [32], who has stated that “the Arrhenius equation is indeed quite successful in describing the temperature dependence of the rate for many thermal analysis systems.” According to him, the failure of the equation (and hence the failure of non-isothermal kinetics) is probably due to the complexity of the kinetics.

Now that we more or less accept at least the limited validity of the Arrhenius equation to solid state kinetics, we may now examine the cases that led to the failure of the equation for solid state kinetics.

FACTORS THAT AFFECT THE SOLID STATE KINETICS

Thermoanalytical curves are the raw or primary experimental material from which the understanding of a decomposition mechanism begins. Hence, they should be obtained with as much care as possible; otherwise the whole effort of understanding a process will go to waste. Because the kinetic parameters are derived from the thermoanalytical curves, the factors that affect the shape and hence the fraction reacted, α , also affect the kinetic parameters.

Mathematical limitations

The variation in the values of the Arrhenius parameters is, in the majority of opinions, due to mathematical approximations, not to the questionable basis of the mathematical theory itself [33]. For example, in deriving non-isothermal kinetic expressions from an isothermal basis, the rate constant is retained in many cases, although it is evident that the rate constant cannot have the same meaning in both cases. This fact was pointed out by De Bruijn et al. [34] (and analysed in detail by Šesták et al. [11]) by considering the Avrami–Erofeev equations. According to these authors, non-isothermal reactions in solid systems involving formation and growth of nuclei are often analysed using equations which are meant for isothermal analysis. In such cases, the values for E and A need not be the same for isothermal and non-isothermal methods. Keeping this in view, the authors solved fundamental equations for $d\alpha/dt$ of some simple and

frequently occurring types of transformation. Considering the two equations

$$[-\ln(1 - \alpha)]^{1/n} = kt = g(\alpha) \quad (2)$$

and

$$-\ln(1 - \alpha) = K * t^n = (g)^*(\alpha) \quad (3)$$

they found that eqn. (2) is applicable to non-isothermal kinetics and also to a unidimensional, constant number of nuclei model, while eqn. (3) is not applicable to non-isothermal kinetics. It is, therefore, evident that the isothermal kinetic expressions need not always apply to non-isothermal kinetics.

An error in E can also be due to the wrong choice of process model [35]. These authors have demonstrated that even a small error caused by choosing the contracting cylinder equation instead of the contracting sphere equation, leads to considerable errors in the activation energy. The validity of the kinetic models for solid state reactions is often questionable because they were derived from single-crystal decompositions. It should be borne in mind that even a good linear relationship obtained by plotting $\log g(\alpha)$ against $1/T$ is not sufficient proof of the validity of the model. Ray [36] has discussed this aspect at length in a recent publication. In fact, more than one model can be found to fit well for a particular set of data [37–39]. It has also been observed that the integrated form of a model equation ($g(\alpha)$) may not distinguish between reactions with formal orders of 1, 2/3 and 1/5, although the theoretical DTG curves constructed by using these values of n in model equations are distinctly different from one another [40].

Experimental factors

Change in heating rate may affect the shape of the thermal curve and, hence, the kinetic parameters A and E [13,41–44]. The morphology of the material can also affect the kinetics [44]. For a non-isotropic solid, rates of reaction in different directions of the crystal lattice may have different values and, hence, the overall weight loss may be misleading [45]. The reaction kinetics are also affected by diffusion phenomena [46]. The influence of grain size on the overall kinetics of surface-induced glass crystallization was observed by Mueller [47]. The kinetics are also affected by sample weight, particle size and its distribution, heating rate and the rate of flow of gas through or over the sample etc. [48]. The shape of the thermal curves can even be affected by the material of the sample cup used [49].

MATHEMATICAL BASIS FOR THERMAL ANALYSIS KINETICS

Statistical approach

There is a view that the variation in the Arrhenius parameters is at least partially due to mathematical approximations [11,33]. This is probably true because the experimental factors affecting the Arrhenius parameters are so numerous and interdependent that a simple mathematical theory is not possible. Therefore, it is inevitable that simplifications and approximations are made. If, however, a judicial selection of factors is made, the mathematical theory retains its usefulness, in many cases to a high degree of application.

As far as non-isothermal kinetics are concerned, we may set aside all those models that utilize order of reaction and concentration concepts, for the reasons mentioned above. This leaves us with the kinetic models based on reaction mechanism. Using the equation

$$g(\alpha) = \int_0^\alpha d(\alpha)/f(\alpha) = A/\beta \exp(-E/RT) \quad (4)$$

where B is a constant given by the relation $\beta = dT/dt$ and α denotes the degree of reaction at time t and temperature T , A and E are the kinetic parameters known, respectively, as the pre-exponential factor and activation energy, R is the gas constant and B is the heating rate which is always held constant.

The actual forms of $g(\alpha)$ and $f(\alpha)$ depend on the reaction mechanism chosen [11,51,52]. It is easily shown [53] that

$$\int \exp(-E/RT) dt = E/R \exp(-E/RT) \left[(RT/E)^2 - 2!(RT/E)^3 + 3!(RT/E)^4 \cdots \right] \quad (5)$$

The right-hand side of the above equation is an asymptotic expansion [54,55] where for most common values of T and E , the values of terms first diminish rapidly and then begin to increase with alternating sign. An approximate solution is obtained by considering only the first few terms [53–55]. One of the most popular approximations is by Coats and Redfern [56] who have shown that if $f(\alpha)$ has the form $(1 - \alpha)^n$, where $n \neq 1$, then $[1 - (1 - \alpha)]^n$ is approximately proportional to $\exp(-E/RT)$. Non-isothermal data have also been analysed using various other approaches [53,57–59]. An approximation has been solved by different authors in different ways. Doyle [60] suggested a trial and error curve-fitting method for the determination of E_a . Zsáko [61] simplified the method of Doyle by calculating the standard deviation instead of curve fitting. Using the equation

$$\log AE_a/RB = \log g(\alpha) - \log p(x) = \beta \quad (6)$$

The value of β depends upon the nature of the process (mechanism) studied and the heating rate, but it is independent of temperature. Zsáko [61] tabulated values of the integral function ($-\log p(x)$) corresponding to different temperatures (100–430°C) and activation energies (10–66 kcal mol⁻¹). For values of x greater than 50, the $-\log p(x)$ values were tabulated in this laboratory [62] using the approximate equation suggested by Zsáko [61]:

$$p(x) \approx (1/x^2 - 2/x^3) \quad (7)$$

The B values at various temperatures for a given mechanistic equation are calculated using $g(\alpha) = d\alpha/f(\alpha)$ and substituted in the equation

$$\delta = \sqrt{(\bar{B} - B_i)^2} / r \quad (8)$$

where δ is the minimum deviation, B_i is the individual B value, \bar{B} is the arithmetic mean of all B_i values and r is the number of B values used. From these δ values, the δ_{\min} value is noted. The process is repeated for various mechanistic equations and δ_{\min} values are tabulated. From these values, the $\min \delta_{\min}$ value is noted. The activation energy and the mechanistic equation corresponding to this lowest δ_{\min} value are taken to represent the correct activation energy and correct mechanistic equation.

While statistical methods are superior to graphical methods, they have one drawback: they may not detect a change in mechanism. To overcome this uncertainty, it was proposed [63,64] that an inspection may be made by first plotting $\log g(\alpha)$ versus $1/T$ for the entire range and then repeating the kinetic analysis over any regions of linearity which are apparent.

SOME SUCCESSES AND FAILURES OF NON-ISOTHERMAL KINETICS

So far, we have discussed thermal analysis kinetics as applied to solid state reactions and the factors that affect the kinetic parameters. Let us now examine the successes and failures of non-isothermal kinetics from the information available in the literature. Any success or failure of non-isothermal kinetics has an inevitable effect on isothermal kinetics because the latter forms the basis of the former.

It has been observed that isothermal kinetics may not distinguish between the heat of a reaction and the activation energy of the reaction. In other words, the ΔH and E values are the same. This had been observed by Ingraham and Marrier [65] and by Fishbeck and Snaidt [66] for endothermic reactions. The reason for the close correspondence of the two energies in the isothermal technique was attributed by Garner [67] to the reversibility of the reaction. However, Ingraham and Marrier [28] feel that the magnitude of the change in rate with change in temperature could be controlled by the magnitude of the heat of reaction, rather than by either

the activation energy of only the forward or reverse reaction. It is thus evident that non-isothermal methods, in the conditions of which a reversible reaction is not possible, should give an unambiguous activation energy. A case in point is the decomposition of calcium carbonate to CaO and CO₂. The isothermal activation energy for the decomposition is 40.6 kcal mol⁻¹ [68] and that established by a linearly programmed heating method is 48.4 kcal mol⁻¹ [28]. The same authors have established that the non-isothermal activation energy for the reverse reaction [28] is 7 ± 3 kcal mol⁻¹. The difference between the activation energies for forward and reverse reactions by the non-isothermal method is about 41 kcal, which agrees with the heat of reaction of 41.2 kcal mol⁻¹ [68]. This is a clear case of success for non-isothermal kinetics.

One very strong disadvantage of non-isothermal kinetics is that the scatter of the values of A and E is very high when compared with that of isothermal kinetics. Zsáko and Arz [69], for example, analysed 15 thermogravimetric curves for CaCO₃ decomposition that were reported in the literature and found that E varied between 26 and 377 kcal mol⁻¹ and A between 10² and 10⁶⁹. According to them, the variations do not arise because of the calculation techniques but are inherent in the process and are characteristic not only of the substance decomposed but also of the working conditions used. The scatter can also be due to the different expressions used by the different authors for the kinetic analysis. A correct kinetic expression eliminates scatter to a large extent.

The very nature of isothermal determinations dictates that the sample has to be “pre-heated” to the required temperature prior to the isothermal measurements being made. This leads to a considerable reaction under ‘non-isothermal’ conditions, which in the view of Draper [70] defeats the very purpose of isothermal studies.

When multiple reactions proceed concurrently in a system, the nature of the reactions may be revealed by varying the heating rate [71]. This is a definite advantage of non-isothermal kinetics because the majority of industrial reactions (especially metallurgical reactions) come under this category. Similar observations were also made by Collett and Rand [41] who observed that the apparent activation energy E_a increased with heating rate and attributed this to a change in the relative importance of different reactions.

Because of the above facts, only a limited number of kinetic expressions give the same results for both isothermal and non-isothermal experiments. This is the reason why sometimes there is agreement and sometimes disagreement between the two techniques [34,72].

Non-isothermal methods probably yield kinetic parameters more rapidly and give more data in comparison with the roundabout lengthy isothermal methods [73,74].

It is clear from the above discussion that the failure of non-isothermal

kinetics is not due to the technique itself but to the non-reproducibility of the experimental conditions, oversimplification of mathematical expressions and uncertainties inherent in the solid state reactions. By standardizing the experimental conditions and making judicial selection of models, one can get more accurate kinetic parameters from non-isothermal methods. One may, however, point out some aspects of these methods which put them at a slight disadvantage. Every reaction has a finite time in which it takes place. In isothermal analysis, this is accounted for because a run at a particular temperature lasts until the end of the reaction. In non-isothermal runs, this is not so; even with rates of heating considerably below $10^{\circ}\text{C min}^{-1}$, the reaction may proceed with variable rates owing to the rapidly increasing temperature and the consequent change in reaction rate. The linear programming may lead to mathematical approximations. However, Prakash and Ray [75] have shown that non-isothermal kinetic data can easily be analysed to obtain values of the kinetic parameters, even when the rate of heating is not constant. Taking as an example the reduction of iron ore with coal by the moving-bed technique, which is ideally suited for a non-constant heating rate, and assuming that the form of $f(\alpha)$ is established by isothermal experiments, they have shown that one can predict the course of reaction under fluctuating temperature conditions. Dixit and Ray [76] solved the mathematical complications that arise out of linear programming by introducing a reciprocal temperature-rise equation of the type

$$1/T = a - bt \quad (9)$$

where T is the absolute temperature, t is time, and a and b are constants. Use of this equation, according to them, leads directly to a simple and exact solution. A set of actual experimental data on the decomposition of CaCO_3 was analysed by the authors to substantiate the proposed approach.

GENERAL RECOMMENDATIONS

It is now appropriate to examine suitable proposals that make non-isothermal techniques more meaningful. As a general rule, as far as possible, one should try to use the smallest weight of the specimen that can be measured accurately and the lowest range of heating rates that time constraints allow [77]. Reading et al. [22] recommend the following to obtain meaningful values for E : (a) rejection of methods based on a single increasing temperature experiment; (b) keeping the partial pressure of the product gas (where applicable) in the sample environment as low as possible, especially for reversible reactions; (c) keeping the sample mass as low as possible to minimize self-cooling (self-heating?) effects.

To say what criteria should be used for deciding whether a measured E value is meaningful, the same authors recommend the following: (a) establish independence of sample size, i.e., establish a sample size below which

E is independent of sample size (mass); (b) establish independence of the experimental method; E must not depend on heating rate and gaseous (dynamic) atmosphere.

Similar views are expressed by Flynn [77]. It was also suggested that to achieve the above criteria, the “rate jump” method proposed by Reading et al. [22] and the CRTA method of Criado et al. [78] may be profitably used. However, to simulate real industrial conditions in the laboratory, the moving boat technique [50] may be used. An account of the fluctuating temperature approach [75] has already been given above.

Further points in favour of non-isothermal kinetics, according to the present authors, are the following:

(1) In practice, no reaction is strictly isothermal: owing to the exothermic and endothermic nature of chemical reactions, the temperature of the material under investigation varies from the surroundings.

(2) The material in isothermal runs develops a thermal history, i.e. the thermal properties of the substance at the beginning of a run at a particular temperature are not the same at subsequent temperatures in an isothermal run.

(3) It is often not possible to reproduce the same physical characteristics of the sample from run to run in isothermal experiments.

(4) Isothermal conditions are non-existent in actual practice.

(5) Reaction rates derived from isothermal experiments do not apply to real systems because such conditions do not exist.

All these points favour non-isothermal kinetics. It is now appropriate to quote from Reading's paper [6]: “Inadequate experimental methods and inappropriate methods of analysing experimental data will inevitably lead to a wide scatter of results and can lead to invalidation of a correct theoretical model and validation of a false one”. Draper [70] has even said that non-isothermal kinetic methods are the only valid measurements.

THE KINETIC COMPENSATION EFFECT

In traditional kinetic studies involving homogeneous reactions, the evaluation of the kinetic parameters (E and A) assumed importance because they were considered to be indicative of the reaction mechanism. However, in the case of heterogeneous reactions taking place in the solid state, both these parameters lose their relevance because the concepts of “order of reaction” and “concentration” are not applicable [79–81]. Rising temperature E and A values, which generally do not agree with isothermal values, have no well-defined meaning [15,27,82,83]. Thus E and A may be treated merely as derived parameters. It is also evident from the literature on the subject that the value of E depends heavily on various experimental factors such as sample size, particle size and its distribution, heating rate, presence of impurities in the sample, gaseous atmosphere in and around the sample

etc. Thus we may ask ourselves whether the experimentally determined Arrhenius parameters have any relevance to their practical application at all. The answer appears to be yes, because it has been observed [84–87] that for a set of related reactions or for a reaction under varying experimental conditions, there is a linear relationship between E and A . This relationship is generally known as the “kinetic compensation effect” (KCE or CE). It may be simply stated as follows: for any change in the experimental activation energy arising from experimental artifacts, a corresponding change in A also occurs, which can be expressed mathematically as [88,89]

$$\ln A = a + bE \quad (10)$$

where a and b are characteristic of the system. The observation of this relation has potential for predicting the effects of experimental factors on kinetic parameters. However, the full implication of this effect has not yet been realised.

CONCLUSION

The Arrhenius parameters, the activation energy E and the pre-exponential factor A , are subjective in nature when applied to heterogeneous solid state reactions. The isothermal kinetics that are popular and very useful in predicting reaction mechanisms in homogeneous gas-phase reactions, are of less significance for heterogeneous solid state reactions and even turn out to be cumbersome and indirect. Non-isothermal techniques appear to be of more relevance because they are less cumbersome and yield more useful data with less experimentation. Also, non-isothermal conditions are nearer to the real conditions existing in industrial practice. Although the absolute values of E and A cannot be evaluated by either isothermal or non-isothermal methods owing to their variation with experimental conditions, the linear relation between $\ln A$ and E (compensation effect) can be used to predict the effect of experimental parameters on kinetics. This gives hope for a better utilization of experimental E and A values in practical applications.

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