Special Review

THERMAL ANALYSIS KINETICS-PROBLEMS, PITFALLS AND HOW TO DEAL WITH THEM*

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The kinetics of the heterogeneous, condensed-phase systems studied in thermal analytical techniques are often complex and usually affected by many experimental factors such as specimen geometry, thermal history, gaseous environment, etc. These complications impose many problems in experimental design, data analysis, and especially in interpretation of results. This paper concerns itself with practical applications of thermal analysis kinetics. Ways of overcoming, or at least ameliorating, some of the above problems are suggested, and caveats concerning overly simple and "canned" techniques of analysis of kinetics data are given. The limitations of one's reasonable expectations for the theoretical significance and empirical application of derived kinetics parameters are discussed.

It is impossible to discuss kinetics without recourse to any equations, however this paper is not concerned with the derivations of all or even some of the many equations and methods for treating thermal analysis kinetics which overburden the journals, but rather I will attempt to present a review of what thermal analysis kinetics is, what theoretically or empirically useful results one might hope to obtain from an analysis of kinetics data and finally explain the reasons why one often can not obtain these useful results.

First we will review to which systems thermal analytical techniques may be applied.

Thermal analysis kinetics techniques

One may use thermogravimetric analysis, TG, and evolved gas analysis, EGA (combination mass spectrometry-gas chromatography is an example of the latter)

to look at degradation, decomposition, oxidation, evaporation, diffusion, sorption, etc., reactions—that is, any reaction in which weight is gained or lost. EGA methods have the advantage of measuring the kinetics for the change of each volatile species separately.

Differential scanning calorimetry (DSC) is even more versatile since most chemical and physical changes involve enthalpy changes. It is particularly useful in studying the kinetics of cure of resins and other reactions in liquids, such as biological reactions. DSC is widely used to study the kinetics of the reactions of polymers whose reactions take place very sluggishly, so much so that even the kinetics of physical transitions such as crystallization or glass transition may be investigated. However, in some cases, interpretation of DSC results is complicated by several changes occurring concurrently, e.g., loss of mass will cause the heat capacity or base line to change, while at the same time both endothermic and exothermic reactions may be taking place simultaneously.

Thermal mechanical analysis, TMA, which measures volume change or viscosity change is similar to DSC in its wide applicability, but mechanical property changes are not as directly or as often linearly related to the chemical and physical processes as enthalpy changes are.

The measurement of any property of a specimen undergoing a programmed temperature change is, by definition, thermal analysis. However, the above methods and dynamic mechanical analysis, DMA, the measurement of loss moduli or logarithmic decrement, are the main methods for which commercial equipment is available.

Problems in the collection of kinetics data

There are two classes of problems in the treatment of the kinetics of thermal analysis data. The first kind of problems deals with the collection of the data. The second type of problems involves the mathematical curve fitting of the kinetics data to rate equations.

Experimental problems

Experimental problems are the simplest to deal with so they will be discussed first. In a thermal analysis experiment, three variables are measured—time, temperature and some property of the system, for example, mass change in TG, enthalpy change in DSC, or dimension or viscosity change in TMA. Measurement of time has never been a problem. One can hope that the instrument is measuring its physical property properly. However, temperature measurement has always been and still is
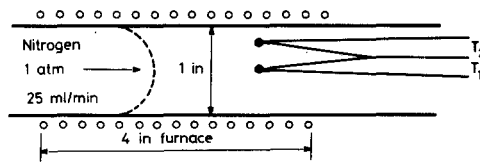
Fig. 1 Thermocouple placement in furnace tube

a serious problem. A recently published example [1], which was first presented at the NATAS Petersborough meeting in 1974, is shown in Figure 1.

Two thermocouples, one at the axis and the other 8 mm off center were placed in a 25.4 mm diameter glass tube heated by a 10 cm exterior furnace. At an axial temperature of 400° and a 25 ml/min flow of nitrogen through the tube, the two thermocouples registered a temperature difference of 40°! This is an extreme case, and the calculated Reynold's number for these conditions indicates that laminar flow is to be expected here. However, this difference points up the importance of exactly matching conditions for temperature calibration and temperature measurement. If the geometry of the system, the flow rate or the composition or pressure of the atmosphere differ between the calibration and the measurement, then large temperature measurement errors can be expected. (It is, of course, impossible to completely match atmospheres if autogeneous vapors are emitted by the specimen.) The best system is one in which the temperature sensor is in contact with the specimen. It was encouraging to see that the three commercial instruments exhibited at the 1986 NATAS Conference which measure TG and DSC simultaneously did actually have the temperature sensor in good contact with the specimen. Otherwise, the best compromise for TG is probably the Curie point standards or melting wires [2]. In any event, great care should be taken in exactly matching between calibration and experiment factors affecting temperature measurement such as positions of specimen and sensor and flow rate, composition and pressure of purge gases.

Material fluxes in a system whose kinetics are being measured are often sizable and for cases where they affect the rate terms for material diffusion should be included in the molecular modelling of kinetics even if this means including mathematically complex expressions based upon Fick's laws. However, thermal diffusion is seldom, if ever, included in a kinetics model. Actually thermal diffusion time constants are not that hard to measure. Figure 2 shows how this can be done for a DSC experiment by measuring the thermal resistance from the slope of a melting peak [3].

If, at constant heating rate, a material such as indium goes through a "sharp" endothermic or exothermic transition where the temperature over which the transition occurs is much smaller than the temperature change of the heating
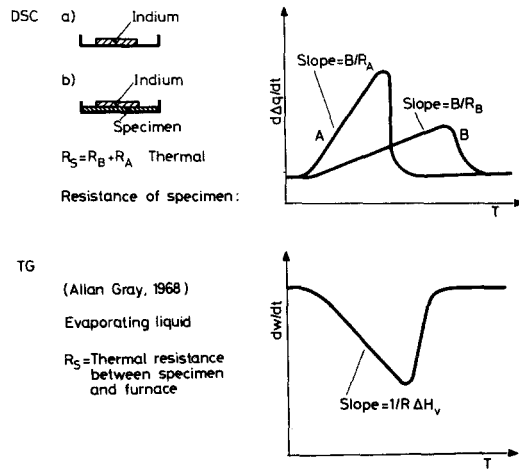
Fig. 2 Measurement of thermal resistances

calorimeter during the interval in which heat must flow to the indium to match the transition enthalpy, then, according to Newton's law, the heat flux will increase linearly as the temperature of the substance remains constant and the calorimeter temperature increases linearly. The steady slope of the leading edge of the transition peak will be equal to B/R where B is the heating rate and R is the thermal resistance between the the heater and the indium. If a sheet of the material of interest is placed between the indium specimen and the calorimeter cup, then the resistance to heat flow increases and the leading edge of the transition peak will have a slope B/R'. The thermal resistance of the material can be calculated from $R' - R$.

Gray [4] has shown how the thermal resistance can be determined for a TG system in a similar manner from the boiling peak of an evaporating liquid. For this case, the thermal resistance between the specimen and the furnace is inversely proportional to the leading slope of the boiling peak at constant heating rate.

In either case, the thermal resistance time constant is equal to the thermal resistance of the specimen multiplied by the heat capacity of the specimen and its container. If the thermal time constant for the material which you are investigating is the same order of magnitude as the time constant for the reaction of interest, then you are in trouble as you may be studying heat flow kinetics rather than reaction kinetics.

As a general rule as far as thermal and material gradients go, the best general advice is that one should try to get along with the smallest weight of specimen that can be measured accurately and use the slowest range of heating rates which time constraints will allow.

There are other mainly experimental "problems" in the treatment of kinetics

data. Some of these are specific to the method. For example, in TG, bumping and boiling in vacuum often cause vibrations that affect measurement. About all you can do in this case is to use milder conditions as suggested above. On the other hand, the release of volatile material at the beginning of a run which may obscure the initial kinetics of the reaction of interest can often be avoided by preheating the specimen in vacuum at a somewhat lower temperature for a while before beginning the run. Each of all the other thermal analysis techniques has its own specific problems, but these will not be discussed here.

Before we go on to the curve fitting part, there is one last thing to mention about measurement errors. Activation energy is the most important parameter in thermal analysis kinetics, especially if one wishes to make predictions such as time to failure and so on. Because of the exponential form of the Arrhenius equation, a relatively small error in activation energy may translate into a very large error in an extrapolated rate at another temperature [5]. For example, a one half kilocalorie per mole error in E will cause a 50% uncertainty at the 90% confidence level for an extrapolation of the rate from 400 to 25 degrees Celsius. On the other hand, if there is a systematic error in the temperature, it will have very little effect on the calculation of activation energy or extrapolations from it.

For the remainder of this paper, we will discuss problems in curve fitting and molecular modelling of thermal analysis data.

Problems in fitting kinetics data to rate equations

There are two fundamentally different reasons for which one may wish to investigate the kinetics of thermoanalytical reactions. One may be interested in the theoretical aspects of molecular modelling reactions and determining their mechanism. On the other hand one's interests may be more practical—the empirical use of thermal analysis kinetics parameters to apply these results to problems such as failure and service life prediction, oxidative stability, thermal breakdown, quality assurance and control, and optimization of conditions during industrial synthesis and fabrication. If the latter is the case, then much less rigorous and exhaustive studies are necessary. In mechanism studies, each procedural factor such as specimen weight, heating rate, purge gas conditions, etc., should be looked at systematically. In more practical applications, even methods which produce theoretically incorrect kinetic parameters may be sufficient if great care is taken not to allow any of the above procedural factors to change from experiment to experiment. These aspects will be discussed a little more later on.

Equation (1) is almost universally applied to the kinetics of these heterogeneous condensed phase systems. The rate of change dx/dt of the measured variable x is assumed to be equal to separable functions of the variable $f(x)$ and temperature $k(T)$.

$$dx/dt = f(x)k(T) \tag{1}$$

There is no real theoretical justification for the application of this linear differential equation for these systems, but we have to start somewhere. In fact, we know that often the kinetics is too complex to separate $f(x)$ and $k(T)$ like this, and in many cases other factors—physical, geometric, atmospheric and so on—affect the rate in ways that make kinetics modelling quite difficult if not impossible. However, this equation is a good place to start.

There is a tremenduous temptation to fit functions for parameters for $f(x)$ and $k(T)$ to a single experimental run in which x and T are both changing, such as at constant heating rate. This can be done successfully in only a very few cases. Often these are ones in which we know the simple kinetics beforehand. Many methods which try to do this often end up obtaining incorrect parameters for both the measured variable and the temperature functions as errors in the form of $f(x)$ will be compensated for by the parameters of $k(T)$. So a good general rule for kinetic analysis of thermal analysis data is:

To determine parameters for $f(x)$, fit data from an isothermal experiment!

If parameters are found for a $f(x)$ which seems to fit the data at one temperature well, then one can go on and obtain these parameters from experiments at various temperatures and from them determine the parameters for $k(T)$. $k(T)$ is almost always assumed to be described by the Arrhenius equation, equation (2)

$$k(T) = A \exp(-E/RT) \tag{2}$$

A is called the preexponential factor, E, the energy of activation, and R is the gas constant. The Arrhenius equation is indeed quite successful in describing the temperature dependence of the rate for many thermal analysis systems, however there are, of course, many other cases where the kinetics are too complex to obtain a single global activation energy.

Even if one can not obtain a good fit to an equation for $f(x)$ from isothermal experiments, it is often still possible to obtain the Arrhenius equation parameters by applying the second good general rule for thermal analysis kinetics:

To determine parameters for $k(T)$, compare data (from several experiments at differing temperatures) at the same degree of conversion, α

The reason for the "from several experiments" bit is because it is difficult to obtain values for the rate at different temperatures at the same degree of conversion from a single experiment. One way it can be done is by the temperature jump technique which was suggested about twenty years ago [6] but has never really become a popular method.

Lack of knowledge of the analytical form of $f(\alpha)$ can be gotten around quite easily. Combining the Arrhenius equation with our previous equation for the rate in terms of α, the fraction conversion, we obtain

$$d\alpha/dt = f(\alpha)A \exp(-E/RT) \tag{3}$$

and if we take the logarithms we obtain for a particular degree of conversion, α_i,

$$\ln(d\alpha/dt)_i = \ln A f(\alpha_i) - (E/R)(1/T_i) \tag{4}$$

$$(\alpha_i = \text{const.})$$

where $(d\alpha/dt)_i$ and T_i are the rate and temperature at which degree of conversion α_i was reached.

Therefore, if one plots logarithm of the rate against reciprocal temperature at a particular conversion for a number of experiments with differing temperature programs, then the slope will be E/R and the intercept will be $\ln Af(\alpha_i)$. This can be done for various degrees of conversion to see if E/R is constant with changes in both temperature and conversion. Thus we have a method for determining the activation energy which does not depend on a knowledge of the form of $f(\alpha)$. This method was first suggested by Henry Friedman in 1965 [7]. A short time later, Ozawa [8] and Flynn [9, 10] independently suggested doing the same sort of thing with constant heating rate experiments by plotting the logarithm of the heating rate against reciprocal absolute temperature to obtain equation (5). Again at constant conversion the slope of a plot of the logarithm of the heating rate B against the reciprocal of the temperature T_i to reach degree of conversion α_i is proportional to E/R.

$$E/R \cong 1.05(\Delta \ln B/\Delta T^{-1})$$

$$(\alpha_i = \text{const.}) \tag{5}$$

The nice thing about these methods is that $f(\alpha)$ which is always controversial and whose form is very difficult to pin down with any certainty can be ignored completely. The parameter E/R is the only one needed for many practical applications of thermal analysis kinetics for if E/R and the rate at one temperature
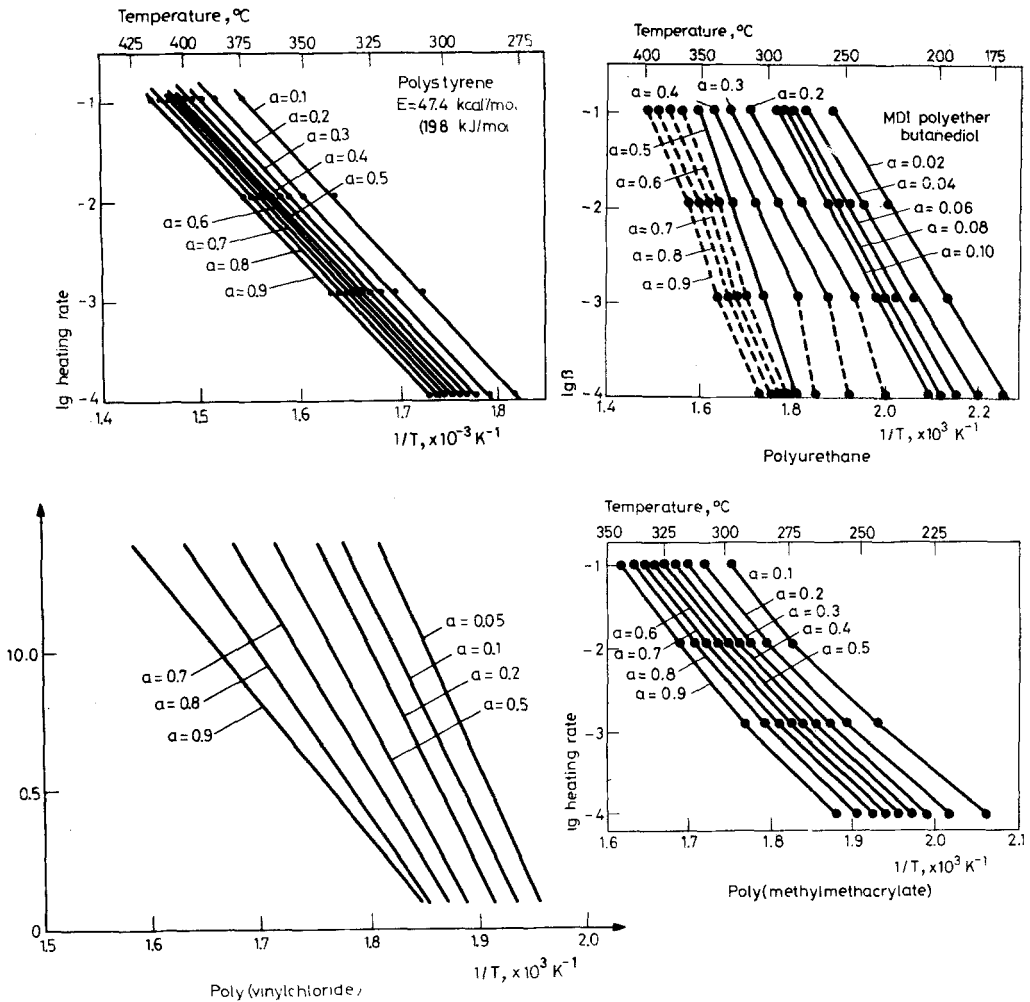
Fig. 3 Isoconversional plots for Polystyrene, Poly(vinylchloride), Polyurethane and Poly(methylmethacrylate)

T_1 is known, then the rate at any other higher or lower temperature T_2 can be predicted by

$$\ln(d\alpha/dt)_2 = \ln(d\alpha/dt)_1 + (E/R)(T_2 - T_1)/(T_1 T_2) . \qquad (6)$$

This is as good time as any to discuss problems in activation energy determination before we discuss problems in determining α and $f(\alpha)$. The problem isn't that great—either the temperature dependence follows the Arrhenius equation

or it doesn't. If one follows the precepts which I outlined previously and doesn't try to take short cuts by determining E/R and $f(\alpha)$ at the same time, then one should be able to test whether E/R is constant over the whole range of alpha and changing temperature. Some examples are shown in Figure 3.

Polystyrene is a case where all of the isoconversional lines in a plot of logarithm heating rate against the reciprocal absolute temperature at which degree of conversion $(\alpha)_i$ was reached are all parallel straight lines yielding the same activation energy. Another situation is seen for poly(vinyl chloride) where the early isoconversional lines are parallel, giving the same activation energy when HCl is splitting off, while the later isoconversionals give a lower activation energy for the polyene degradation. In the polyurethane example shown here, only for the first part of the reaction where the diisocyanate moiety is coming off do you get a constant slope and activation energy. In the final example, which is all too often the case, with poly(methylmethacrylate), all of the isoconversional slopes change with both temperature and degree of conversion. For this latter case, the simple kinetics equations which we assumed here are inadequate. However, with these differential and integral isoconversional methods, we are able to test our activation energy values and see whether they do stay constant over the range of temperature and conversion of our experiments.

Problems related to defining alpha and in determining $f(\alpha)$ are discussed in the remainder of this paper. Often in a thermal analysis experiment the reaction of interest will take place over only part of the range of the measured variable. For example, weight change experiments may be composed of several reactions or stages. For TG experiments at constant heating rate, the start and end of a reaction can be defined by two successive weight change plateaus. (Things are different for DSC experiments where the measured variable is proportional to the reaction rate, and reactions are defined by peaks so that the reaction variable must be obtained by integration of partial areas.) In any event, it is convenient to define a degree or fraction of conversion variable defined by

$$\alpha = (xi - x)/(xi - xf) \tag{7}$$

or

$$(1 - \alpha) = (x - xf)/(xi - xf) \tag{8}$$

where xi is the initial value of the reaction variable at an arbitrary zero time and xf is its final value at the completion of the reaction. It is often found convenient to use the reduced reaction variable α, particularly when only a part of the experimental data is being analyzed or several different experiments are being compared. Substitution of α for the reaction variable is not without some complicating factors. To take an example, fit of the conversion function is often attempted (and occasionally successfully) by assuming

$$f(x) = (x - xf)^n \tag{9}$$

so that for an isothermal reaction the rate is given by

$$dx/dt = k(x - xf)^n \tag{10}$$

where n is called, in analogy to homogeneous systems, the reaction order and k is the nth order rate constant. If we translate this equation into terms of α (degree of conversion) we obtain:

$$d(\alpha)/dt = k'(1 - \alpha)^n \tag{11}$$

so, therefore,

$$k' = k(xi - xf)^{(n-1)}. \tag{12}$$

This points up an often overlooked fact: that only in the case of a first order reaction are the rate constants of the dx/dt and the $d(\alpha)/dt$ equations equal. In all other cases k is a function of the reaction variable range which usually depends on specimen weight. As a result of the complex nature of these systems, either k, k', or neither may represent the true rate constant. It is good practice to:

Keep the initial specimen weight constant
when one intends to compare kinetic parameters from separate experiments.

This rule is especially true when these parameters are intended to be used for applied purposes. When a thorough investigation of the kinetics is being undertaken, then it is essential to determine the dependence of rate on not only the initial sample weight but also all the other procedural factors which may affect it such as surface to volume ratio, composition, pressure and flow rate of purge gas, heating rate, and so on. Testing the effect of sample dimensions is particularly important in TG experiments but can also affect DSC results where differing geometry will affect heat conduction or other experimental factors.

When only part of the experimental range of the measured variable is being used in calculating α, matching ranges of the variable should be used when values from several experiments are being compared. Even so, the range over which the reaction takes place may change when the thermal treatment is changed. For example, if poly(acrylonitrile) is heated slowly, then a ring closure reaction occurs and a large amount of carbonaceous residue is produced at higher temperatures. On the other hand, if it is heated rapidly enough, the temperature will quickly pass through the first stage and reach temperatures at which much more primary degradation reactions occur. This latter case results in chain scission so that more volatiles and less residue will result. Therefore it is impossible to define consistent ranges for α for
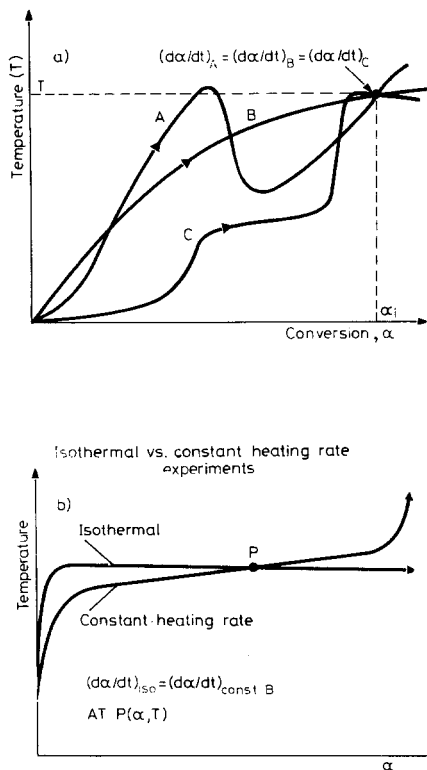
Fig. 4 a) Point of concurrence. b) Point of intersection for isothermal and constant heating rate experiments

the above reactions when experiments at differring heating rates are compared. Another example of changing α with temperature programming is the isothermal cure of resins. Since the cure reaction practically ceases when the glass transition temperature is reached and the glass transition temperature increases with increasing degree of cure, the reaction will stop when the glass transition temperature reaches the experimental temperature. Therefore, the higher the isothermal temperature, the greater the amount of cure reaction which will take place. Thus, for this system, the range over which α is measured will increase with increasing isothermal experimental temperature.

Fortunately there is a fool proof way for testing for thermal history dependence of reaction kinetics [11] although this simple test is but rarely intentionally performed. This method is illustrated in Figure 4a where reaction temperature is plotted against degree of conversion for three experiments with identical specimens, procedural factors and experimental variables other than temperature. (That is,

only the temperature programs were different.) Thus the three lines, A, B and C, represent the paths in temperature—conversion space of three experiments using identical specimens and procedural conditions but differing temperature programs. The three experiments are brought to the same temperature when at the same degree of conversion. If their rates at this point are equal, then there is no thermal history dependence at this point of concurrence. If their rates differ significantly at this point, then the reaction is path dependent and you are in trouble because kinetics parameters determined from the comparison of two or more experiments with differing temperature programs are probably in error. Figure 4b shows a simple way for producing a point of intersection from a constant heating rate and an isothermal experiment. In this case, one always has a point of intersection when the temperature of the constant heating rate experiment reaches the temperature of the isothermal experiment and the agreement of the rates can be observed at this point.

The methods for fitting the form of $f(x)$ to an analytical expression have been left to the end of this paper and for good reason. One must face it, it is practically impossible to devise satisfactory models for many cases. As a beginning, one may test to see if the kinetics follow a simple nth order reaction. Data from an isothermal experiment can be treated by the method of van't Hoff [12], as modified by Letort [13]. Thus, from the equation for an nth order reaction,

$$d\alpha/dt = k(1-\alpha)^n \tag{13}$$

upon taking logarithms, one obtains

$$\ln d\alpha/dt = \ln k + n \ln(1-\alpha). \tag{14}$$

Therefore one may plot $\ln d\alpha/dt$ against $\ln(1-\alpha)$ and obtain n from the slope and $\ln k$ from the intercept as in Figure 5a. The advantage of this method is that n and $\ln k$ are determined nonsubjectively whereas in integral techniques of kinetics analysis, a fit is forced to some nth order or other type equation. In these fits of integrated equations, significant inconsistencies may be ignored or assumed to be only minor and rationalized away.

Occassionly equation (13) will fit the data but, more often, it will not. Some other cases are given in Figure 5b. In Case A, the break in slope suggests that the reaction order n changes during the experiment. In case B, the curve has a constant slope only for part of the reaction. An example of this situation is a reaction system for which the kinetics eventually become diffusion-limited and follow negative first order kinetics. In case C, it appears the order remains the same, but the value of the rate constant changes during the reaction. In case D, which is unfortunately the most common, none of the reaction kinetics appear to follow nth order. In any
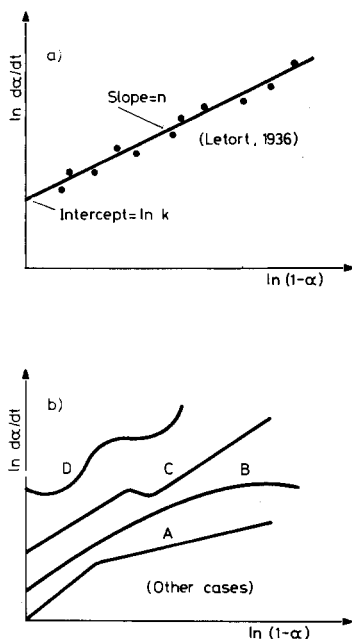
Fig. 5 a) Plot of ln dα/d*t* against ln (1 − α) for a *n*th order reaction. b) Plot of ln dα/d*t* against ln (1 − α) for four other cases

event, with this method, significant inconsistencies can not be ignored or rationalized away as often happens during integral curve fitting.

If the simple equation used in the Letort method is not sufficient, then more complex kinetic expressions must be tested. These may be selected for many reasons—1. from analogy to comparable systems, 2. from the chemistry and physics of the reaction, 3. from the energies of involved bonds, 4. from the geometry of the system, 5. from the overall shape of the experimental curves, and so on. Many large lists of specific equations to test—two or three dimensional diffusion, various Avrami type equations, contracting sphere or contracting cylinder geometry, Prout–Tomkins equation, autocatalytic (cure) reactions, free radical chain polymer degradations, etc., are found in journal articles and text books for both differential and integral forms and for both isothermal and constant heating rate cases. There are also, of course, computer programs for testing data to these equations. I prefer to fit the differential form of the rate equation as it is often simpler and can be done with less subjectivity. However, many other scientists prefer to test various integrated formulae individually.

The question, "How do know that you have the correct form for *f*(*x*)?" still has not been answered, and there is no simple answer. One has to test each proposed

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equation under many differing conditions and see how its parameters change with temperature, heating rate, and all of the other procedural variables which I have mentioned before.

Many of the suggestions presented in this review are summarized in the list of general rules given below.

Some general rules for the kinetics analysis of thermal data:

    I Match experimental conditions between calibration and experiment.
    II Use the smallest specimen which can be measured accurately.
    III Use the slowest heating rate (or lowest temperature) which time constraints allow.
    IV Vary each procedural factor (one by one) for theoretical studies.
    V Keep all procedural factors constant for practical applications of kinetics.
    VI Fit data from isothermal experiments to determine parameters for $f(\alpha)$.
    VII Fit data at the same degree of conversion to determine parameters for $k(T)$.
    VIII Keep initial specimen weights constant when comparing kinetic parameters from separate experiments.
    IX Test for thermal history dependence of the rate (at a point of concurrence).

(Note: Like all general "rules", the above list contains many oversimplifications. For example, rules II and III should be applied only in setting up empirical kinetics methods for characterization or quality control. In serious kinetics studies, wide ranges of heating rates, isothermal temperatures, specimen size, and other procedural variables should be investigated to more fully elucidate the kinetics behaviour of the system.)

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Zusammenfassung — Die Kinetik der mittels thermoanalytischer Techniken untersuchten heterogenen kondensierten Phasensysteme ist häufig komplex und gewöhnlich durch viele experimentelle Faktoren beeinflußt, wie Probengeometrie, thermische Vorgeschichte, Gasatmosphäre usw. Diese Komplikationen bringen viele Probleme hinsichtlich der Versuchausführung, der Datenanalyse und besonders der Interpretation der Ergebnisse mit sich. Die vorliegende Arbeit befaßt sich mit den praktischen Anwendungen der thermoanalytischen Kinetik. Wege zur Überwindung oder zumindest Vereinfachung der obigen Probleme werden vorgeschlagen und Einsprüche gegen übersimplifizierte Techniken erhoben. Die Grenzen verünftiger Erwartungen hinsichtlich der theoretischen Bedeutung und der empirischen Anwendung der abgeleiteten kinetischen Parameter werden diskutiert.

Резюме — Кинетика гетерогенных, фазо-конденсированных систем, изученная термоаналитическими методами, довольно сложная и обычно затрагивается многими экспериментальными факторами: геометрией образца, его термическим происхождением газовой атмосферой и дь. Эти осложнения вызывают много проблем при выборе экспериментальных условий, анализе данных и, особенно, при интерпретации результатов. Статья касается практического использования термоаналитической кинетики. Предложены пути преодоления или, по крайней мере, улучшения некоторых из вышеупомянутых проблем и приведены предостережения, касающиеся чрезмерно простых и «законсервированных» методов анализа кинетических данных. Обсуждены ограничения целесообразности методов для теоретического значения и эмпирического использования выведенных кинетических параметров.