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THE KINETIC STUDY OF ISOTHERMAL SOLID STATE DECOMPOSITIONS: A COMBINED NUMERICAL AND EXPERIMENTAL APPROACH

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ABSTRACT

This paper identifies and makes quantitative allowance for experimental errors in isothermal weight change data. For experiments which involve a purge gas to remove decomposition products, attention is directed to errors due to variations in the gas flow rate and the need to heat the sample initially to the temperature of study. For experiments carried out at reduced pressure, importance is also attached to the undesirable influence of draughting, buoyancy, pressure and convectional effects. An experimental procedure which minimises the errors due to some of these factors is discussed. The paper also examines how the non-linear least squares method employed to analyse the kinetic data may be extended to allow for error produced by the initial temperature change. This extended method is used to analyse weight change data which are consistent with a contracting-interface mechanism, and the results clearly demonstrate the improved accuracy of the kinetic parameter estimates.

INTRODUCTION

Many solid state decompositions can be described by a contracting-interface (CI) mechanism for which, under isothermal conditions, the fractional decomposition, α, has been expressed [1] as a function of time, t, by the equation ($n \neq 1$)

$$\alpha = 1 - [1 - kt(1-n)]^{1/(1-n)} \tag{1}$$

In this equation, the rate constant, k, and the so-called order of reaction, n, characterise the decomposition so that the determination of these parameters is clearly a prime objective of isothermal kinetic studies. The traditional approach adopted to determine k and n has been to select a value of n, rearrange eqn. (1) as

$$(1-\alpha)^{1-n} = 1 - k(1-n)t \tag{2}$$

and plot $(1\text{-}\alpha)^{1-n}$ as a function of t. The "correct" value of n is then taken as the value which gives the "best" straight line fit to the experimental data. The rate constant, k, is subsequently found from the slope of this line. Some of the subjectiveness of this approach is removed by replacing the plot by a *linear* least squares analysis, but the calculated values of k and n are not optimal values because they still depend upon the values of n selected for the analysis. Further, these selected values of n, e.g. 1/2 and 2/3, are normally chosen because they correspond [2,3] to "theoretically significant" mechanistic models of the decomposition process. Such models almost certainly represent [1,4—6] an oversimplified description of the actual mechanism.

Recent work [7,8] in this laboratory has involved an extensive study of computational methods which allow the optimal values of the kinetic parameters to be calculated without the need for making any prior assumptions as to the value of n. These methods accordingly provide a much more objective approach to the kinetic analysis. The results have demonstrated a preference for a *non-linear* least squares (NLLS) approach which uses eqn. (1) directly. The NLLS technique is highly accurate, computationally efficient and also provides estimates of the statistical errors in the kinetic parameters which are optimised.

Now, the dimensionless quantity α is not measured directly but is expressed, instead, in terms of an experimental quantity related to the amount of reactant removed or product formed. In the majority of cases, this quantity is the mass, m, of the solid material present at time, t, and α is then defined by

$$\alpha_t = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{3}$$

where the subscripts 0, t and ∞ correspond to the initial, instantaneous and final stages of reaction. In practice, of course, the balance transduces the mass to an equivalent voltage which is displayed typically as a chart reading, c, on a potentiometric recorder. Equation (3) is therefore more appropriately written as

$$\alpha_t = \frac{c_0 - c_t}{c_0 - c_\infty} \tag{4}$$

Combination of eqns. (1) and (4) leads to

$$c_t = c_\infty + (c_0 - c_\infty)[1 - kt(1 - n)]^{1/(1-n)} \tag{5}$$

which can be used to estimate k and n provided that the values c_0, c_t and c_∞ are known and are consistent, i.e. measured under the same experimental conditions. The consistency of these values of c is often assumed, but is actually much more difficult to establish [9,10]. Thus, in isothermal studies, reaction is usually initiated by a drastic change in the experimental conditions, e.g. a sudden decrease in the pressure or a rapid increase in the temperature. This procedure makes it highly likely that the value of c_0, measured accurately *before* reaction commences, is inconsistent with all subsequent values of c. In addition, unless the reaction rate is slow, a significant amount of reaction may occur before stable experimental conditions are re-established after initiation. It follows that an accurate and consistent value of c_0 is often difficult to measure directly, so that other methods must be considered if the power of the NLLS approach is to be exploited fully.

The present paper describes a combined experimental and numerical approach which attempts to overcome the problems outlined above. It discusses, firstly, under what circumstances the most serious errors can arise, and how the experiment may be designed to minimise them, so that the value of c_0 measured prior to reaction can be used as a reliable *initial estimate* of the consistent value. Following this experimental approach, the paper goes on to show how the NLLS method may be extended to refine this initial estimate and to determine the optimal value of c_0, k and n.

EXPERIMENTAL REDUCTION OF SYSTEMATIC ERROR IN CHART READINGS, *c*

In most commercial apparatus, gaseous decomposition products are swept out of the balance either by evacuation or by a unidirectional flow of purge gas past the sample container. In either case, the container is subjected to an upthrust or downthrust force, F, and if this varies significantly throughout the experiment then the chart readings, c, are bound to be inconsistent.

In experiments involving a purge gas at ambient pressure, it is normal practice to pre-set the gas flow rate prior to zeroing the balance. Accordingly,

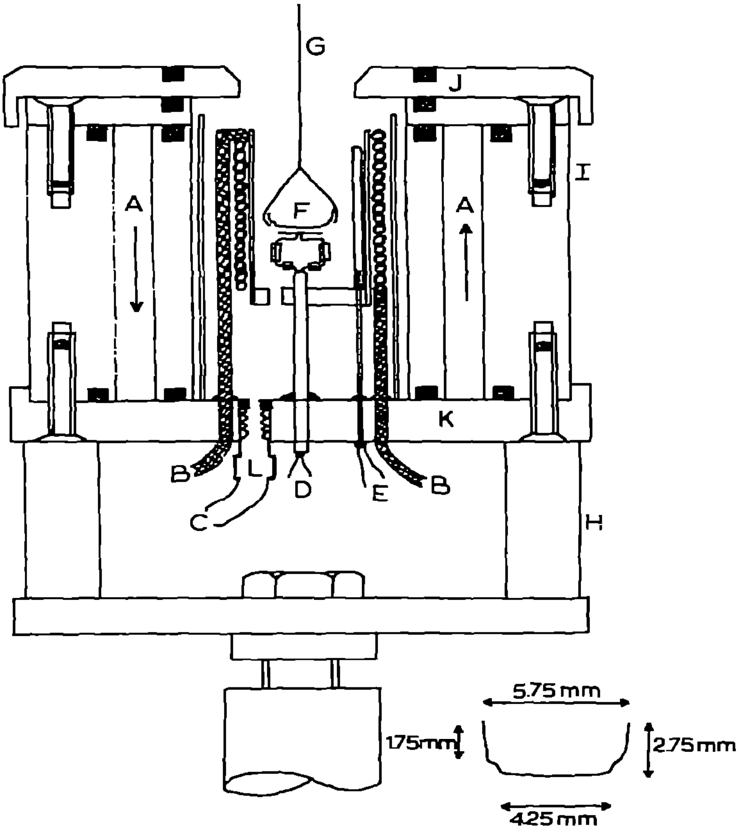

Fig. 1. Diagrammatic representation of the modified TG-750 micro-furnace assembly. A = Water channels; B = power supply to furnace; C = gas/vacuum outlet modification; D = sample thermocouple; E = control platinum resistor; F = sample container; G = hang-down from balance limb; H = furnace support; I = furnace casing; J = cover-plate/seal to balance assembly; K = base-plate; L = threaded brass stud. (Reproduced in part by kind permission of Stanton-Redcroft Ltd.)

provided that the partial pressure of product gases is always small by comparison with that of the purge gas, variations in F are anticipated to be minimal. This situation is clearly favoured by the use of small samples and low reaction rates.

In studies involving either ambient or reduced pressures, heating the sample to initiate reaction may cause buoyancy changes and also a variation in the convective flow of the sample atmosphere. Such disturbances are expected to make early chart readings, in particular c_0, inconsistent with later readings. In reduced-pressure studies, an additional problem is expected due to variations of pressure during pumping. Thus, as the pressure difference between the balance chamber and the main "vacuum" line decreases, the rate, f_r, of flow of effluent gases past the sample container will be reduced. As we have already indicated, this feature is expected to lead to a lower upthrust or downthrust force F causing a change in c which is unrelated to any mass loss.

The apparatus available in the authors' laboratory for weight change studies is a TG-750 thermobalance manufactured by Stanton Redcroft Ltd., London. As is common practice, evacuation of the balance is achieved via a single outlet, in this case above the sample container. In an attempt to minimise the experimental problems discussed above, we have modified this arrangement (Fig. 1) by incorporating an outlet in the base, K, of the

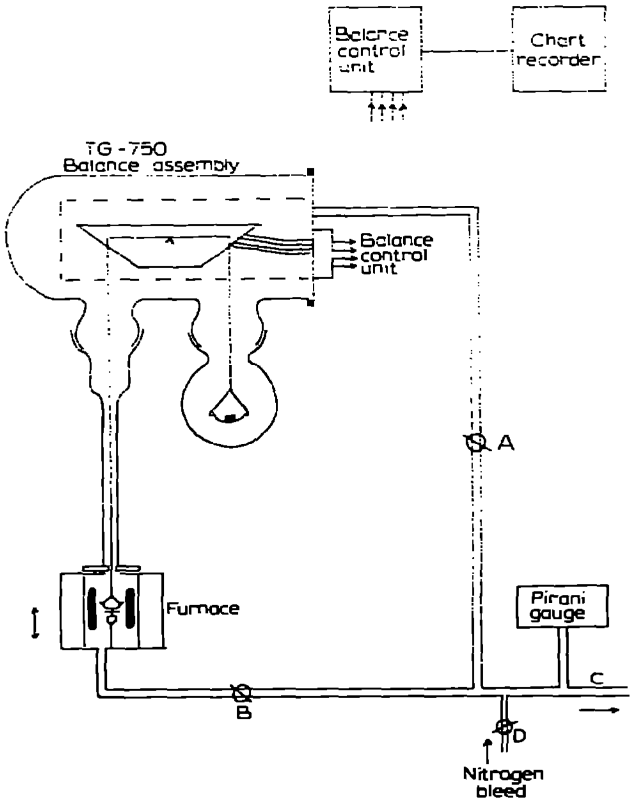

Fig. 2. Modified TG-750 apparatus for isothermal weight change experiments at reduced pressure.

furnace so that the system can be pumped from both above and below the sample container. The lower outlet comprises a 6 mm diameter copper tube, C, soldered into a brass stud, L, which is threaded to screw directly into the orifice in K provided by the manufacturers for purge- and product-gas removal. A small neoprene O-ring, liberally smeared with Apiezon T grease, located between the base plate and the end of the brass stud L provides a vacuum-tight seal. The end of the copper tube C needs to be set at a slightly oblique angle, prior to soldering, to enable a short length of polythene tube to be attached and taken to the main vacuum line. This section of flexible tube allows the furnace assembly to be moved up and down during sample loading. Vacuum-tight seals to this tubing are conveniently made by means of picein wax. Careful attention to all seals of the balance assembly permits the evacuation of the apparatus down to ca. 0.005 mm Hg if required.

In the above system, a unidirectional flow of effluent gas is not only avoided, but the pumping rate at each outlet can be controlled by means of the adjusting screws A and B (Fig. 2). Also, the gas pressure in the main vacuum line, C, can be held essentially constant by means of a controlled leak of a suitable (e.g. nitrogen) gas via the inlet D. This procedure minimises the pressure variations that change the forces acting upon the sample container and lead to inconsistent chart readings, c.

Systematic error introduced into c_0 as a result of convectional and other temperature-related effects can be minimised but not avoided using the present apparatus. Accordingly, we have attempted to solve this problem by refining the experimental value of c_0 by numerical optimisation. The detailed procedure is described below.

NUMERICAL REDUCTION OF SYSTEMATIC ERROR IN THE INITIAL CHART READING, c_0

An earlier paper [8] describes the use of the NLLS method to analyse (t, α) data and to obtain optimal values of k and n in eqn. (1). The treatment for (t, c) data is entirely analogous, but in addition, the method can be extended to optimise c_0 in eqn. (5). In this case the functional relationship previously written as

$$\alpha = \mathrm{f}(t, n, k)$$

becomes

$$c_t = \mathrm{f}(t, n, k, c_0)$$

and the estimate $s^{(q)}$ of the parameter s ($=k$, n or c_0) at the qth iterative step is improved by the expression

$$s^{(q)} = s^{(q-1)} + \Delta s^{(q-1)} \qquad q = 1, 2, 3, \ldots$$

The parameter corrections Δs are found by solving the three linear normal equations given by

$$\frac{\partial Q}{\partial \Delta k} = 2 \sum_{i=1}^{p} r_i \left(\frac{\partial f_i}{\partial k}\right) = 0 \tag{6}$$

$$\frac{\partial Q}{\partial \Delta n} = 2\sum_{i=1}^{p} r_i\left(\frac{\partial f_i}{\partial n}\right) = 0 \qquad (7)$$

$$\frac{\partial Q}{\partial \Delta c_0} = 2\sum_{i=1}^{p} r_i\left(\frac{\partial f_i}{\partial c_0}\right) = 0 \qquad (8)$$

where the summations extend over p sets of data and k, n and c_0 are the values at the current step, and

$$r_i = R_i + \left(\frac{\partial f_i}{\partial k}\right)\Delta k + \left(\frac{\partial f_i}{\partial n}\right)\Delta n + \left(\frac{\partial f_i}{\partial c_0}\right)\Delta c_0$$

Here

$$R_i = f(t_i, n, k, c_0) - c_i \qquad (9)$$

where c_i is the experimentally recorded chart reading and Q is the error sum of squares function given by

$$Q = \sum_{i=1}^{p} r_i^2 \qquad (10)$$

Near the minimum, $r_i \simeq R_i$ so that eqn. (10) written in terms of R_i provides a useful guide to the progress of the iterative search for the optimal parameter values. The derivatives $\partial f_i/\partial k$, $\partial f_i/\partial n$ and $\partial f_i/\partial c_0$ required in eqns. (6)—(8) are given by

$$\frac{\partial f_i}{\partial k} = -t_i(c_0 - c_\infty)\beta_i^n$$

$$\frac{\partial f_i}{\partial n} = \frac{\beta_i(c_0 - c_\infty)\{\ln \beta_i + kt_i\beta_i^{(n-1)}\}}{(1-n)}$$

$$\frac{\partial f_i}{\partial c_0} = \beta_i$$

where $\beta_i = \{1\text{-}kt_i(1\text{-}n)\}^{1/(1-n)}$. With this approach, the systematic error remaining in c_0 after experimental refinement can be estimated along with the kinetic parameters k and n.

To test the performance of the NLLS method when applied to optimising additionally upon c_0, simulated (t, c) data were generated from eqn. (5) using kinetic parameter values $k_{\text{sim}} = 0.01$ reciprocal time units and $n_{\text{sim}} = 0.2$—0.8 in combination with values $c_0 = 10.0$ and $c_\infty = 5.0$ chart units. These latter values of c correspond to a typical situation where the (t, c) trace extends over 50% of the chart width of 10 in. A total of 21 sets of test data were produced using time values $t = 0, 5, ..., 100$ time units. These values of t limit the simulated fractional decomposition, α, within the approximate range 0.0—0.9 ($n_{\text{sim}} = 0.2$) to 0.0—0.7 ($n_{\text{sim}} = 0.8$). Typical systematic error in c_0 was simulated by subsequently biasing the assigned value by +5% and using this modified value as the starting estimate, $c_0^{(0)}$, for determining the optimal value of c_0 (equal, of course, to the value 10.0 used in generating the simulated data). The initial estimate of $k = k^{(0)}$ was calculated from a linear least squares analysis using eqn. (2) with the value $n = n^{(0)} = 0.5$.

RESULTS AND DISCUSSION

Procedural factors influencing the consistency of chart readings, c

A. Experiments carried out using a purge gas at ambient pressure

(1) Flow rate effects. The magnitude of the forces F acting on the sample container was investigated by loading the thermobalance with a 5.0 mg calibration weight under static conditions. This load represents an inert sample for which no mass change occurs. The balance sensitivity was set for convenience at 10.0 mg full scale deflection (f.s.d.) *, and the apparatus was calibrated to produce an equivalent chart reading $c = 5.0$ chart units (=50% f.s.d.).

When the purge gas (nitrogen) is made to flow *down* past the sample container, c increases proportionately, as expected, with increasing flow rate (f_r). Thus, for $f_r = 100$ and 180 cm^3 min^{-1}, c assumes values of 5.19 and 5.37, respectively, corresponding in turn to an increased downthrust of ca. 4% and 8% of the original sample load. Correspondingly reduced values of c are observed when the purge gas is directed *up* past the sample container. These findings are in general agreement with the results of previous studies [11,12] involving a Chevenard thermobalance, but the magnitude of the changes in c is very much less in the present case. Calculations [13] show that for the TG-750 thermobalance the percentage error, E_c, introduced into a chart reading, c, can be estimated approximately from the expression

$$E_c \simeq \frac{\gamma \epsilon f_r}{cS} \tag{11}$$

where γ = ca. 2.0 is a calibration constant for the instrument under these conditions, ϵ is the fractional deviation in the flow rate (in cm^3 min^{-1}) from its pre-set value, f_r, and S is a sensitivity scale factor equal to the f.s.d. (in mg) of the balance. Thus, for a 10 mg f.s.d. balance sensitivity and for f_r = 200 (±10) cm^3 nitrogen min^{-1}, eqn. (11) predicts the maximum error in the full scale chart reading as

$$E_c \simeq 2.0 \times \frac{10}{200} \times 200 \times \frac{1}{10} \times \frac{1}{10}\%$$
$$= 0.2\%$$

At 50% f.s.d., E_c increases to 0.4%. In general, purge gas flow rate control of better than ±5% is not unreasonable, and hence for values of c close to f.s.d., errors in the chart readings due to flow rate changes may be assumed to be of only minor importance.

(2) Temperature-related effects. When the gas flow is in a downward direction and the flow rate is held constant, experiments show that increasing the

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* The TG-750 has a sensitivity range switch enabling sample masses of, for example, 2.5, 10.0, 25.0 and 100.0 mg to produce the 10 mV f.s.d. input for the chart-recorder.

temperature causes a small increase in the value of *c*. Such an increase has been attributed [14] to convection effects caused by the rising of hot gases along the furnace walls, although a buoyancy change due to the lower density of the sample atmosphere may also be involved. The increase in *c* is normally less than 0.2% f.s.d., for the 10 mg sensitivity range selected here, and so is clearly again of only minor importance.

B. Experiments carried out at reduced pressure

(1) Flow rate effects. Experiments involving an inert thermobalance load corresponding to $c = 5.0$ chart units at atmospheric pressure show the following features (Fig. 3) when the balance chamber is evacuated from only one side of the sample container.

(a) A rapid change (AB or FG) at the start of pumping due to the suddenly induced streaming of effluent gas past the sample. The magnitude and direction of the peak depends upon the size and relative position of the gas outlet involved.

(b) A subsequent partial return (BC or GH) to the original reading as the gas is withdrawn and hence as the flow rate decreases.

(c) A reduction in chart reading (CE or HJ) with decreasing pressure due to buoyancy changes which occur because of the different volumes of the sample and counterbalance assemblies [15].

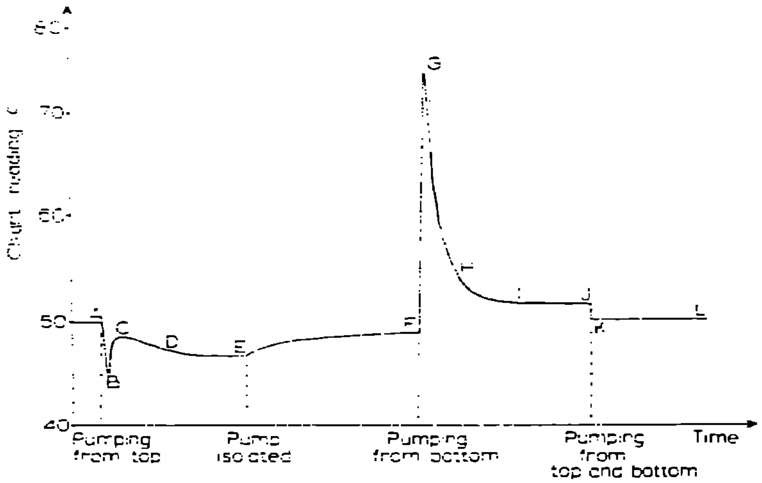

Fig. 3. The influence of pressure and draughting effects upon the recorded weight at ambient temperature. (TG-750 thermobalance electronically off-set to give chart reading = 5.0 mg at atmospheric pressure.)

Point	Pressure *p*(mm Hg)	*c*
A	Atmospheric	5.00
C	0.15	4.84
D	0.08	4.69
E	0.06	4.68
H	0.08	5.40
I	0.05	5.16

In contrast to results obtained from purge gas experiments, the above results show clearly that large errors (3—6% over the region CE) can be introduced into chart readings when evacuation is carried out from only one side of the sample container, and when there is no attempt to control the system pressure. On the other hand, when pumping is carried out from *both* sides of the sample container, using the modified apparatus described previously, *c* assumes its original value of 5.0 chart units (JK). In practice, some slight adjustment of the control screws A and B (Fig. 2) may be necessary to allow for the different sizes of the top and bottom outlets. Experiments with decomposing samples confirm that the controlled "leak" D ensures the maintenance of essentially constant pressure conditions throughout the course of reaction, i.e. problems due to pressure-dependent buoyancy changes are eliminated.

(2) Temperature-related effects. Decomposition experiments carried out using the modified system at a constant pressure of ca. 0.2 mm Hg show that the early chart readings are distorted considerably by a rapid increase in temperature. The extent of this distortion appears to depend upon several factors, e.g. the temperature of study, when decomposition first starts, etc., and is difficult to predict. Frequently, however, the early part of the (*t*, *c*) curve takes on the shape shown in Fig. 4. An initial increase in *c* (AB) is similar to that observed in purge gas studies, but is rapidly followed by a large decrease (BC). This decrease appears to arise from an increased upthrust caused by hot gas suddenly moving up past the sample container; the effect has been proved not to result from electrical interference associated with switching

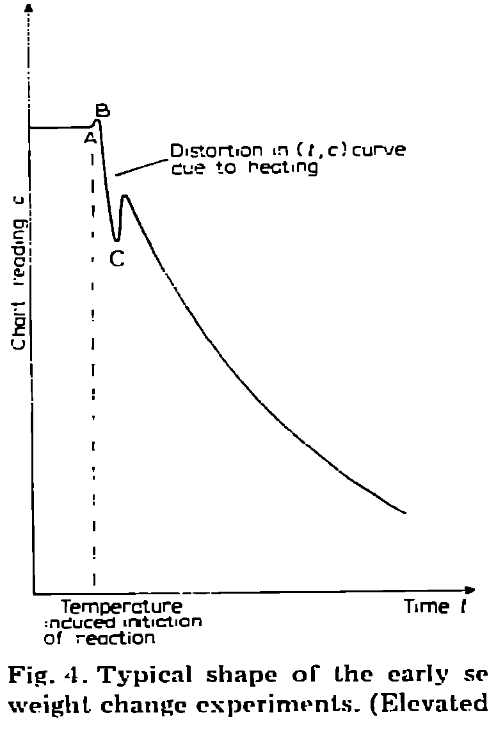

Fig. 4. Typical shape of the early section of the (*t*, *c*) curve obtained from isothermal weight change experiments. (Elevated temperature study.)

on the furnace. Unfortunately, the distortion in the (t, c) trace caused by this phenomenon cannot be avoided by experimental means. Accordingly, it must be accepted that a considerable discrepancy may exist between the value c_0 (measured at ambient temperature) and the consistent value of the chart reading at the elevated temperature, $c_0(T)$. Since the latter value is required in the data analysis, uncertainty in this parameter can have an important bearing upon the calculated kinetic results.

The influence of systematic error in $c_0(T)$ upon the calculated kinetic parameter values

Although the value $c_0(T)$ can be estimated with reasonable precision by an analytical or graphical procedure, e.g. back extrapolation, it is more convenient and reliable to optimise upon this parameter numerically as discussed in the introductory section of this paper. The effectiveness of the latter approach is demonstrated below.

Preliminary tests using simulated (t, c) data confirm that, in common with earlier findings [8] in which (t, α) data were employed, the "true" values of k and n in eqn. (5) may be estimated with high accuracy and precision by the NLLS method. In fact, as Table 1 shows, the simulated values of k and n are recovered to within better than 0.5% for all values of n_{sim} studied. These estimates of k and n are usually obtained within 3—4 iterative cycles.

Now the probable effect of systematic error in c_0 upon the calculated value of k can readily be predicted by rearranging eqn. (5) as

$$k = \frac{\{1-[(c_t-c_\infty)/(c_0-c_\infty)]^{1-n}\}}{t(1-\mathrm{n})} \tag{13}$$

and assuming that n remains constant (the effect of such error upon n is more difficult to ascertain in this way because of the complex nature of the rate expression). Hence, if c_0 has positive systematic error associated with it, then clearly the numerator within the brackets { } in eqn. (13) will be larger and therefore the values of k will be greater than its "true" (in this case

TABLE 1

The analysis of simulated (t, c) data, generated from eqn. (5), by the NLLS method; only k and n optimised $k_{\mathrm{sim}} = 0.01$ reciprocal time units; $n_{\mathrm{sim}} = 0.2$—0.8; c_0 unbiased.

n_{sim}	k	n	$Q(k, n)$ [a] × 10^{12}
0.2	0.0100 (0) [b]	0.200 (0)	5.46
0.4	0.0100 (0)	0.400 (0)	10.0
0.6	0.0100 (0)	0.600 (0)	12.7
0.8	0.0100 (0)	0.800 (0)	21.8

[a] $Q(k, n)$ is the error sum of squares given by eq. (10) written in terms of R_i.

[b] In this and subsequent tables, a number in parentheses indicates the standard deviation. Thus, in Table 2, 0.0130 (6) ≡ 0.0130 ± 0.0006. In Table 1 and Table 3, a value 0 indicates an exact determination within the limits of computer round-off error.

TABLE 2

The analysis of simulated (t, c) data, generated from eqn. (5), by the NLLS method, only k and n optimised $k_{\text{sim}} = 0.01$ reciprocal time units; $n_{\text{sim}} = 0.2$—0.8; c_0 biased by +5% of its original value, i.e. from 10.0 to 10.5 chart units.

n_{sim}	k	n	$Q(k, n) \times 10^2$
0.2	0.0130 (6)	0.551 (87)	7.10
0.4	0.0137 (8)	0.856 (111)	6.28
0.6	0.0144 (9)	1.15 (134)	5.74
0.8	0.0151 (10)	1.44 (156)	5.33

simulated) value. This prediction is borne out by the results presented in Table 2. Thus, when c_0 is biased by +5% of its actual value, and only k and n are optimised, it is seen that grossly distorted estimates of these latter parameters are obtained. This distortion is indicated by the high standard deviations in the parameter estimates (particularly in n) and the magnitude of the error sum of squares function, $Q(k, n)$.

In contrast to the above results, Table 3 shows that if k, n and $c_0(T)$ are simultaneously optimised, all three parameters are recovered with very high accuracy and precision. Again, comparison of the standard deviations in the parameter estimates and the value $Q(k, n, c_0)$ with the corresponding values shown in Table 2 confirms the very great improvement in the results obtained.

CONCLUSIONS

The results presented here have allowed us to identify the main sources of error, resulting from the procedures employed, in isothermal weight change studies. Experiments have shown that the most serious problems arise in reduced pressure studies. Controlled pumping from both above and below the sample container, rather than from only one direction as is common practice, has been found to alleviate many of these problems. In particular, using a controlled "leak" to maintain an essentially constant pressure avoids pressure-related buoyancy changes which lead to inconsistent chart readings.

TABLE 3

The analysis of simulated (t, c) data, generated from eqn. (5), by the NLLS method; k, n and c_0 optimised $k_{\text{sim}} = 0.01$ reciprocal time units; $n_{\text{sim}} = 0.2$—0.8; c_0 biased from 10.0 to 10.5 chart units.

n_{sim}	k	n	c_0	$Q(k, n, c_0) \times 10^{12}$
0.2	0.0100 (0)	0.200 (0)	10.00 (0)	<0.1
0.4	0.0100 (0)	0.400 (0)	10.00 (0)	10.9
0.6	0.0100 (0)	0.600 (0)	10.00 (0)	18.2
0.8	0.0100 (0)	0.800 (0)	10.00 (0)	21.8

It has not been possible to adopt an experimental procedure which avoids causing distortion in the initial chart readings when the sample is first heated to the temperature of study. This difficulty has been solved in the present case by modifying the non-linear least squares method used to analyse the data. The latter technique is recommended here as a very suitable means of analysing isothermal weight change data directly; it provides accurate and precise values of the kinetic parameters as well as their standard deviations.

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