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STEADY-STATE PARAMETER-JUMP METHODS AND RELAXATION METHODS IN THERMOGRAVIMETRY*

JOSEPH H. FLYNN AND BRIAN DICKENS
Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234 (U.S.A.)

ABSTRACT

We describe a technique for thermogravimetric analysis in which the magnitude of a rate-forcing variable such as temperature, pressure, gaseous flow-rate, gaseous composition, etc., is jumped by discrete steps. This method can be used to determine kinetic relationships between the rate of weight-loss and the jumped variable. The method avoids the disparate effects of separate experimental histories in methods in which two or more experiments are compared. The necessity for guessing the often complex rate vs. extent of reaction relationship in methods where the rate forcing variable is changed continuously in a single experiment is also avoided. The method is illustrated with examples from the oxidation of polystyrene.

Techniques involving multiple jumps and more complex programming are proposed. The fruitful investigation of weight-loss kinetics by the measurement of relaxation times during jumps or of phase lags while the rate forcing variables are oscillated is predicted for diffusion limited reactions and reactions with gaseous atmospheres.

INTRODUCTION

Weight-loss experiments measure processes which are heterogeneous by definition. The weight-loss step—matter leaving the force field of a condensed phase and entering the gaseous phase—involves simple vaporization, sublimation or desorption phenomena. However, the overall weight-loss kinetics are often complicated by chemical and physical processes which take place in the condensed phase. These complications stem from shifts in the coupled rate-limiting steps as the chemical stoichiometry and physical properties change during the course of the reaction. Also, gradients may develop from the flow of material and heat within the sample. These add to the overall complexity of the system. Many methods of kinetic analysis require the comparison of data from several separate experiments. In these cases, the correct interpretation of the data is obfuscated further by disparities in the physical and

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chemical states of the samples, either present initially or induced by the action of diverse values of the rate forcing variables. All of these factors render defining, modeling and analyzing weight-loss processes an elusive goal.

In this paper, we stress the inadequacies of conventional techniques of kinetic analysis in coping with these complexities. We describe new procedures which avoid many of the previous pitfalls. Finally, we suggest applications of relaxation techniques to these systems which may point up new facets of the kinetic processes.

LIMITATIONS OF CONVENTIONAL THERMOGRAVIMETRIC METHODS

The data from a typical thermogravimetric experiment at constant heating rate are not sufficient to allow the development of general kinetic equations for complicated weight-loss reactions. We will review briefly the treatment of the kinetics of weight-loss processes in order to illustrate the problems and limitations of such methods. As temperature is the variable programmed in dynamic thermogravimetric experiments, we will narrow our discussion to methods in which this single rate-forcing variable is changed in a continuous manner to simplify the presentation. However, much of the discussion is relevant to other variables such as pressure, flow-rate, gaseous composition, etc.

In a typical thermogravimetric experiment, the weight of sample, w, is monotonously decreasing and the temperature, T, is monotonously increasing with time, t. If all other variables are maintained at constant values, the rate of weight loss, $\dot{w}$, has been represented by (1)

$$\dot{w} = \mathrm{f}(w)\mathrm{k}(T)\mathrm{g}(w, T) \tag{1}$$

where $\mathrm{f}(w)$ and $\mathrm{k}(T)$ are separable functions of their respective variables and $\mathrm{g}(w, T)$ contains weight–temperature cross terms if any exist.

Equation (1) gives a false impression of generality and completeness. In the first place, it is often impossible to keep all other variables constant. This is particularly true for those variables which are functions of the physical properties and chemical composition of the sample. These, as well as the controllable variables such as pressure and composition of gaseous flow, even when held constant through an experiment, may affect the rate of weight-loss in ways which are dependent upon the previous history of the sample or the extent of reaction. Thus, in effect, all of these complex inter-relationships are lumped into the weight and temperature functions in eqn (1). As a result, the onus of kinetic analysis of thermogravimetric data is placed upon the selection of what often must be an extremely complicated and elusive analytical expression for $\mathrm{f}(w)$.

Much of the vast and repetitious literature on non-isothermal kinetic techniques contains many variations of methods for fitting experimental weight-loss, time and temperature data to analytical forms of the functions in eqns (2), (3), and (4).

$$\mathrm{f}(w) = [(w_t - w_\infty)/(w_0 - w_\infty)]^{n} \tag{2}$$

$$k(T) = A \exp(-E/RT) \tag{3}$$

$$g(w, T) = 1 \tag{4}$$

where w_t, w_∞, and w_0 are the weight at time, t, and the final and initial weights, respectively and n is the reaction order. A and E are the Arrhenius pre-exponential factor and activation energy, respectively, and R is the gas constant. The theoretical worth and practical value of kinetic parameters calculated from such methods depend on how well the kinetic models from which these forms were derived fit the actual physical system.

The assumption of eqn (2) that the weight fraction of sample remaining follows a simple reaction order, n, is applicable to only a few of the complex heterogeneous condensed phase systems of thermogravimetry. The application of these methods to systems for which, n, the order, is not constant has given a poor image to thermogravimetry as a means of kinetic analysis.

As both weight and temperature change simultaneously during thermogravimetry at constant heating rate, good models are needed for both $f(w)$ and $k(T)$. If the model for $f(w)$ is poor, then not only will its parameter be meaningless, but the parameters for $k(T)$ will be affected. For example, the kinetics of polymers degrading by random mechanisms are sometimes erroneously represented by eqn (2). As a result, E values from eqn (3) are much too large[2].

In general, eqn (2) is seldom useful in non-isothermal kinetic analysis. If the kinetic system has been shown to follow this simple equation, then the experiment is usually unnecessary. Otherwise, there are strong temptations to force fits of the data to such a favored kinetic model and the data are not sufficient to establish criteria to evaluate the validity of the assumption from these simple single-experiment methods[2].

The literature on the treatment of thermogravimetric data is becoming punctuated with an increasing number of well-conceived and prudent efforts to obtain realistic models for the weight-loss function, $f(w)$. Several examples of exceptionally good work are the kinetic models for random degradation of polymers[3] and for diffusion limited reactions[4] by Ozawa, and the systematic development of models for solid state reactions[5] and a formulation for cases in which w_∞ is a function of temperature, $[g(w, T) \neq 1]$, by Šesták[6] and others.

However, even in the application of these realistic models to appropriate thermogravimetric data, it is usually difficult to make judgments between nearly equivalent formulae for $(f(w)$. In the final analysis, many of these weight-loss functions are just too complicated to be definitively characterized by a single experimental method. It is necessary to examine their consistency over several experimental techniques.

On the other hand, eqn (3) (the Arrhenius equation) is often a successful model for the temperature dependence of the reaction rate. This exponential temperature relationship dominates in chemical and physical mechanisms. A "global" or overall activation energy may be calculated for even complex kinetic systems when the rate is proportional to a product of rate constants or to a sum of terms containing rate constants in which one term dominates.

However, if two or more reaction paths are in competition or several nearly equivalent rate constants in the same kinetic path are coupled, then the weight-loss temperature cross term of eqn (4) will not be unity and the parameters of eqn (3), E and A, will appear to change with fraction weight-loss and temperature as the dominance of one set of rate limiting reactions gives away to another.

The parameters of eqn (3), E and A, may be determined for systems which do not follow a constant order, n, by the comparison of rates at the same fraction of weight-loss from two or more experiments at different heating rates or different isothermal temperatures. A differential method comparing experiments at several heating rates was first developed by Friedman[7] and a similar integral method, by others[3,8,9].

These methods have the advantage over those based on a single experiment in that, by making comparisons at the same fraction weight-loss, they avoid the subjective and often misleading presumption that the isothermal kinetics follow a particular set of weight-loss functions such as eqn (2).

Also, these interexperimental comparison methods have the advantage that their assumed models may be tested for applicability by, for example, comparing activation energies for successive sets of fractional weight-loss[8]. A whole mosaic of relationships may be constructed if comparisons are made between constant heating rate and isothermal experiments[1]. Schneider[10–12] has used these techniques with considerable effectiveness in the investigation of polymer degradation mechanisms.

However, these methods in which two or more experiments at different rates of heating are compared suffer from the same problems inherent in isothermal or any other methods where data from separate experiments are compared. These comparisons may become distorted by cumulative differences developing as a result of their differing experimental histories. We will now examine the significance of these complications.

EFFECTS OF DISPARATE PHYSICAL AND CHEMICAL STATES UPON KINETIC ANALYSIS

The functional dependence of the rate of weight-loss upon a rate forcing variable is often determined by comparing two or more experiments in which only the variable of interest has been changed. This comparison will be deceptive if unperceived differences in the chemical or physical properties are present initially or if these differences develop as the reaction proceeds.

Initial differences between samples in physical properties such as surface areas, densities, particle size, porosities, degrees of mechanical strain, etc., are usually well recognized as sources of complication and taken into account when separate experiments are compared.

However, two solids may be physically identical initially, but differing experimental conditions may result in cumulative differences in their physical character at the same fraction weight-loss. These physical differences will complicate the interpretation of the weight-loss kinetics. Examples of this situation are found in reactions in which diffusion takes place through a non-reactive residual crust or a reacted (e.g., oxide) layer. Two distinct temperature treatments may result in quite different spatial distributions of reactive sites in the solid matrices and in different degrees of sintering or crack formation.

Thermal and material gradients are present in all weight-loss systems. If the substrate is a viscous fluid as is the case in many polymer degradations, large compositional gradients will develop. It is difficult to quantize these gradients and express their effect on the kinetics in a precise mathematical form. As a result, they are never explicitly included when model forms for f(w) and k(T) in eqn (1) are being formulated.

There is usually not a problem in achieving well-matched initial chemical compositions for separate samples. However, even in homogeneous chemical systems, if two or more consecutive or parallel reactions are in competition, the residual distribution of chemical species will depend upon the cumulative effects of the external variables upon the rates of each step in the reaction. For a case of two parallel reactions,

$$\begin{tikzcd}
 & \text{B}_1\text{ (condensed phase)} \arrow[r, "k_2"] & \text{X}_1\text{ (gas)} \\
\text{A (condensed phase)} \arrow[ur, "k_1"] \arrow[dr, "k_1'"'] & & \\
 & \text{B}_2\text{ (condensed phase)} \arrow[r, "k_2'"] & \text{X}_2\text{ (gas)}
\end{tikzcd}$$

where $k_i = A_i \exp(E_i/RT)$, if $E_1 \neq E_1'$, two isothermal experiments at different temperatures will not have the same relative concentrations of A and of intermediate species, B_1 and B_2, at the same fraction weight-loss. As the rates of weight-loss of the two separate experiments are measuring the volatilization of two different stoichiometric mixtures of chemical compounds, a "global" activation energy calculated from them will have obscure significance.

The distribution of size of fragments distilling from a sample are affected by the values of the reaction variables. If $E_2 \neq E_2'$ in the above example, then again the residual concentrations will not be equal at the same fraction of reaction for two different reaction temperatures.

The problems of dealing with complex stoichiometry are epitomized in investigations of polymer degradation kinetics. A typical radical disproportionation step postulated for polyethylene degradation,

$$R_n^{\cdot} + P_m \rightarrow P_n + P_{m-i} + R_i^{\cdot}$$

symbolizes more than 10^{20} reactions involving distinct chemical species for a sample whose initial molecular weight is 10^6. The only way by which a tractable kinetic model has been developed for these cases is to make the simplistic assumption that all reactions of homologous species have a single rate constant.

Reversible weight-loss reactions, such as $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$, pose additional problems in modeling their kinetics[6]. The final weight, w_∞, is a function of temperature so that $g(w, T)$ cross terms complicate the model.

These few examples illustrate some of the intractable problems typically encountered when one analyzes kinetic data from conventional thermogravimetric methods. Thus, they should point up the need for new techniques, bared of these complicating factors, in which the relationships between rate of weight-loss and rate forcing variables are determined at a discrete time for a single sample.

LIMITATIONS OF METHODS BASED ON INITIAL RATES

The rates at initial stages of weight-loss are often valuable in relating kinetics to mechanism. The specimen may be well characterized before the experiment is begun and changes which develop will be minimal early in the reaction.

There is a limiting factor in the determination of initial rates from isothermal experiments. There is always a "warm up" time during which the effect of the new magnitude of the rate forcing variable becomes equilibrated within the sample. This problem may be lessened by redesigning the apparatus so that the inertia of the system to the changing variable is reduced.

This "warm up" problem is less of a factor in the typical thermogravimetric experiment during which the temperature is raised at a continuous programmed rate from an initial non-forcing value. A method for determining initial activation energies from weight-loss experiments in which the temperature is increased linearly or parabolically with time has been published[13].

The relevancy of initial rates in kinetic analysis is often beclouded by complications which render these values atypical from the kinetics operative during the main course of the reaction.

These complications include both physical and chemical factors. The vaporization of absorbed gases and vapors, of solvents, and, in the case of polymers, of plasticizers and unreacted monomer, or the release of fine powders and particulate matter, will cause initial rates of weight-loss to be abnormally high.

Chemical effects from residual catalysts, antioxidants and stabilizers, and other impurities may bring about induction periods or periods of abnormally high rate of weight-loss. Relatively small numbers of labile linkages introduced during synthesis or storage of polymers also may affect their initial kinetics.

These complications often make extrapolation to initial conditions a meaningless exercise. Their disruptive effects may be lessened in many cases by treating the specimen for an extended period under conditions too mild to bring about the reaction of interest, but strenuous enough to bring the reactions responsible for initial irregularities to near completion. Specimens undergoing weight-loss may be quenched, recharacterized, and the kinetic investigation resumed, thus determining "initial" rates for the recharacterized specimen. However, the periodic repetition of such a procedure during the course of a reaction would be an extremely tedious exercise. Hence, the application of these methods has been limited to the early phases of reactions.

PARAMETER JUMP METHODS

The kinetic parameters for the relationship between the rate of weight-loss and a reaction forcing variable can be obtained unambiguously and independently of sample history only over a small time (or fractional weight-loss) interval in a single experiment during which the magnitude of only the variable of interest is changing.

There are at least two ways in which this may be accomplished. The magnitude of the rate forcing variable may be monotonously increased or decreased, or it may be varied periodically between several values. In the latter case, the change may be performed in a slow quasi-continuous manner or in discontinuous "jumps".

The typical thermogravimetric experiment at constant rate of temperature change is an example of a method in which the variable is changed continuously. In theory, the functional relationship between rate of weight-loss, fractional weight-loss and temperature might be deduced over a small interval. However, to do this, one would need almost unimaginably accurate measurement of the experimental variables. Attempts to approximate these methods over large ranges and the use of preconceived kinetic models for simplification have led to the abuses discussed in the previous sections. (A higher precision of measurement can be attained by stepping the temperature in a series of isothermal stages. This is a variation of the jump method which is described below.)

Two fundamentally distinct methods of kinetic analysis may be applied to data from a weight-loss experiment during which a rate-forcing variable was jumped back and forth between several values. Relaxation methods which measure the time constant for the perturbed weight-loss system to self adjust to a new value for the rate forcing variable are discussed in a subsequent section. Here, we develop a method in which the "steady state" or "quasi-stationary state" rates of weight loss before and after a jump in a rate forcing variable are extrapolated to a point in the region of the jump where their values may be used to determine kinetic parameters at that point.

This simple jump technique minimizes two problems which complicate conventional isothermal and non-isothermal methods of kinetic analysis. The first problem is that the cumulative effects from differing sample histories may invalidate the comparison of data from two separate experiments. The jump method reduces these effects to the two short periods of extrapolation before and after the jump. The second problem plagues methods during which the rate forcing variable is changed continuously. In order to obtain the functional relationship between the rate of weight loss and the changing variable, it is necessary in these methods to guess the correct model for the often complicated weight-loss vs. rate of weight-loss function, $f(w)$ in eqn (1). The problem is not necessarily solved by the jump method; however, it is avoided by obtaining rates corresponding to two values of the jumped variable at a single extent of reaction.

Any variable which perturbs the rate of weight-loss may be jumped. Possible reaction forcing variables include temperature, pressure, gaseous flow-rate, gaseous composition, radiant energy, physical properties of the sample, and electric, magnetic or gravitational field strength.

The technique is illustrated schematically for temperature jumps in Fig. 1, in which the rate of weight-loss, $\dot{w}$, is plotted as a function of time. The rate, at a constant temperature, T_1, is proceeding along a smooth curve until time, t_1, when the temperature is jumped to a new value, T_2. The rate of weight-loss at t_1 is $\dot{w}_{1,1}$. The rate of weight-loss adjusts to the new temperature, T_2, and as temporal lags dissipate, it follows a new steady-state rate curve. The curve may be extrapolated to time, t_1, to obtain a value for the rate, $\dot{w}_{1,2}$, for the new temperature, T_2. At time, t_2, the temperature is jumped from T_2 back to its original value, T_1. The rates of weight-loss before and after (by extrapolation) the jump, $\dot{w}_{2,2}$ and $\dot{w}_{2,1}$, respectively, are obtained as before. (Optimum values for the ratio of rates before and after a jump, $\dot{w}_{i,2}/\dot{w}_{i,1}$, can be obtained from both forward and backward extrapolations to a time, t_i, intermediate in the jump interval. Procedures for optimizing values obtained from temperature jumps will be described in a subsequent paper.)

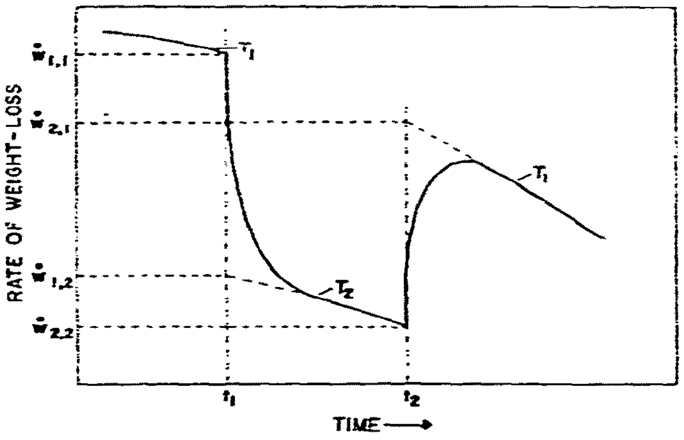


Fig. 1. Schematic temperature jump experiment. Rate of weight-loss vs. time, $T_1 \rightarrow T_2$ at t_1, $T_2 \rightarrow T_1$ at t_2.

The Arrhenius equation is the most successful model for the rate–temperature functional relationship. Thus, as all other variables are constant, we may calculate from eqn (5) an instantaneous activation energy, E_{t_i}, for each of m jumps ($T_1 \rightleftarrows T_2$) from

$$E_{t_i} = R\,[\ln(\dot{w}_{i,2}/\dot{w}_{i,1})](T_1^{-1} - T_2^{-1})^{-1} \quad (1 \leq i \leq m). \tag{5}$$

Any significant discontinuity or trend in E_{t_i} with respect to time will be assumed to reflect a change in the relationships between the steps which contribute to the weight-loss kinetics. A temperature-jump sequence of more than two temperatures, e.g., $T_1 \rightarrow T_2 \rightarrow T_3 \rightarrow T_1 \rightarrow T_2 \rightarrow T_3 \rightarrow \ldots$, will expose any change in E_{t_f} over the experimental temperature interval.

There is a period of transition during each jump while the system adjusts to the new value of the rate forcing variable. The time constant or lag time for reaching the new steady state value of the rate of weight-loss has three general components. The relative significance of each of these for a particular system will depend on the rate forcing variable of interest, the method of its measurement and the method by which it is jumped, as well as upon sample geometry and other factors.

The first component of the lag results from the time constants of the instrument, such as those associated with the electronics and the response of the sensor. The second is related to the resistance of the system to equilibration of the new value of the rate forcing variable. This resistance may be in the apparatus or in the sample, itself. For example, equilibration of temperature will be slow for materials of low thermal conductivity. When the composition of the gaseous flow is jumped, there may be problems from long sweep times and back diffusion of the gases.

The third time constant measures the response lag of the perturbed weight-loss kinetics in approaching a new steady or quasi-stationary state. Cases in which this latter relaxation process becomes dominant are discussed in the final section.

The quality of the data should be improved by developing apparatus and techniques which reduce the non-kinetic lag time. Further optimization involves adjustment of the size of the jump increments and periods. Larger jump increments allow the ratios of the weight-loss rates and changes in the rate forcing variables to be determined more precisely, but also increase the distance over which the rates must be extrapolated. Long periods between jumps improve the analytical fit of the extrapolation curve for the steady state kinetics, but reduce the number of jump points available for the statistical analysis of the data.

Optimization of these jump techniques will be discussed in greater detail in a later paper in which methods and programs are developed for the computation of kinetic parameters and for the statistical analyses of both the digitalized output from the apparatus and the computed parameters.

The jumps have been made between constant values of the rate forcing variables in the techniques discussed thus far and illustrated in Fig. 1. On the other hand, the rate of weight-loss may be jumped between values which are maintained constant by regulation of the rate forcing variable. The techniques and advantages of carrying out weight-loss experiments at constant rate of weight-loss rather than at constant temperature or constant heating rates have been summarized admirably by Rouquerol[14–16]. A weight-loss reaction from a solid matrix of constant dimensions or one for which the rate is surface limited may be investigated ideally by stepping back and forth between constant rates[16]. If isothermal rates are independent of the weight fraction remaining, i.e., zero order, then the temperature jumps will be between isothermals. For other cases, the temperature or some other rate forcing variable must be adjusted continuously to maintain the rate of weight-loss at a constant level.

Rouquerol[16] points out that such isokinetic programming keeps the thermal and material fluxes from within the sample constant in these cases, thus tending to stabilize the effects of thermal and gaseous diffusion. Also, if the experimental system is under evacuation, such programming keeps a constant autogeneous pressure in the environment of the sample. This is advantageous not only as the rates of weight-loss of many systems vary with respect to pressure, but also as the temperature calibration of many thermogravimetric instruments is a function of the pressure sensitive thermal resistance to flow of heat from the furnace to the sample.

On the other hand, weight-loss systems for which the rate is proportional to the sample mass (i.e., the bulk properties of the material) should most propitiously be jumped between successive constant values of $(1/w)$, $(\mathrm{d}w/\mathrm{d}t)$ or $\mathrm{dln}\, w/\mathrm{d}t$, so that the flux from the sample will be proportional to its dwindling mass. Here, if the isothermal rates are first order, the temperature jumps will be between isothermals. Keeping $\mathrm{dln}w/\mathrm{d}t$ constant for any other kinetic form would necessitate apparatus–computer interfacing of the analogue input to the furnace controller.

Jumps between relatively constant rates of weight-loss improve the final result of statistical analysis of the data. On the other hand, there are experimental problems in maintaining the rate of weight-loss at a prescribed value by continuously adjusting the sample temperature. Temperature is probably the most poorly measured experimental variable[17] and is often slow in its response to changes in the heat flux from a thermal source. We obtain better results by keeping the temperature constant during the interval between jumps. Any fall off of the rate as the reaction proceeds may be compensated for by jumping to higher temperatures. This permits the rates to be kept in a range where the precision of their values remains high.

The compromise described above is a good example of the practical considerations which enter into the optimization of these techniques. This may be done in a more quantitative manner with a system which is interfaced to a computer so that data may be monitored and analyzed and commands quickly fed back to a fully automated apparatus. Thence, more exotic techniques of programming may be developed such as cycling between several rates of heating or between time derivatives of other rate forcing variables.

The present discussion has particularly emphasized temperature jumps. The other rate forcing variables, e.g., pressure, gaseous composition, gaseous flow-rate, radiant energy and physical properties of the sample, may also be jumped during an experiment and their instantaneous functional relationships to rate of weight-loss established. Only by means of a complete array of such relationships plus adjunct stoichiometric analysis of reactants and products during the reaction will one be able to ferret out each region of multiparametric space which is dominated by a single kinetic mechanism.

SOME PRELIMINARY EXPERIMENTS USING THE PARAMETER JUMP TECHNIQUE

Experiments on the pyrolysis and oxidation of NBS-SRM 706 polystyrene in a modified Dupont 951 thermogravimetric analyzer are described in this section. The jumps were accomplished by manual manipulation of valves and instrument dials. These results are presented here for illustrative purposes rather than as examples of quantitative kinetic experiments. A companion publication[18] describes somewhat more sophisticated experiments for which the data were collected and statistically analyzed by computer methods. An automated and computer interfaced apparatus is in the process of assembly.

The easiest rate forcing variables to jump in a thermogravimetric flow system are pressure and rate of gaseous flow. The dependence of the rate of weight-loss on these variables can be particularly significant for cases in which diffusion of a product out from or a reactant into the condensed phase affects the kinetics. An integral weight-loss vs. time curve for polystyrene at 325 °C in nitrogen at a mass flow-rate of 1.2 Torr l sec^{-1} is shown in Fig. 2. The nitrogen pressure was jumped back and forth between 400 and 800 Torr at the points of the vertical lines. The average rate of weight-loss for the midpoint of each step from Fig. 2 is plotted against the fraction of weight-loss in Fig. 3. The points for the 400 Torr steps and the 800 Torr steps have been fitted respectively to smooth curves. The apparent large pressure dependence of rate in this region may be, in part, an artifact of the apparatus. The gaseous flow is laminar under these conditions and the calibration of the thermocouple may be altered by the jump in pressure, thus the sample temperatures may not be the same at the two flow-rates. Problems of temperature measurement and calibration in flow systems are discussed in another paper[17].

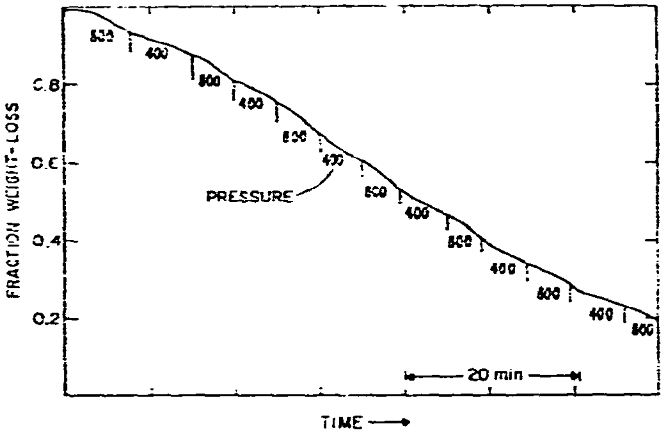


Fig. 2. Pressure jump experiment; weight-loss vs. time, 800 Torr ⇄ 400 Torr; 11.9 mg polystyrene, 325 °C, 1.2 Torr l sec^{-1}.

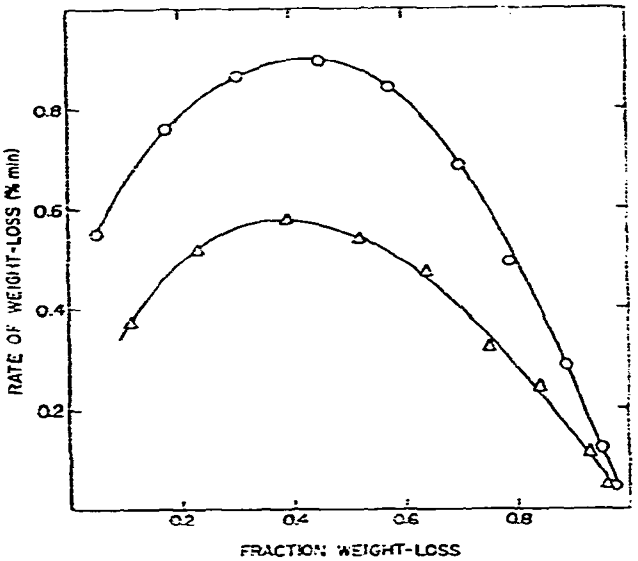


Fig. 3. Pressure jump experiment. Rate of weight-loss vs. fraction of weight-loss, same conditions as Fig. 2. ○ = 800 Torr; △ = 400 Torr.

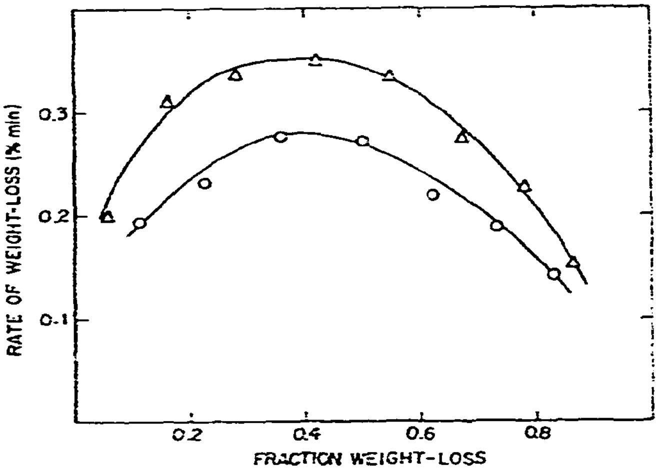


Fig. 4. Pressure jump experiment. Rate of weight-loss vs. fraction of weight-loss. ○ = 75μ ⇄ △ = 150μ. 12.0 mg polystyrene, 309°C, autogeneous pressure.

Jumping the pressure of a reacting gas such as oxygen may be used to establish the functional relationship between the rate of weight-loss and the partial pressure of the gas. However, the total gaseous pressure must be maintained at the same value before and after the jump.

Pressure manipulations are more limited in an evacuating static system. However, the pyrolysis of polystyrene at 309°C was investigated by jumping the autogeneous buildup of pressure from decomposition products between 75 and

150 μm through the adjustment of the leak to the vacuum pump. Again, the average rates of weight-loss at the midpoints of the jumps are plotted as a function of the fractional weight-loss in Fig. 4. There appears to be a substantial dependency of rate upon pressure in this range. Similar experiments in which the pressure of gaseous flows of nitrogen or oxygen were jumped in the 100 μm pressure range also yielded a rate decrease with increasing pressure.

Problems in design prevent evacuated thermogravimetric apparatuses from being molecular stills. Since volatile products must effuse from a confining vessel, the pressure about the sample will be a function of the rate of volatilization. The above demonstration of polystyrene's rate of weight-loss dependency upon autogeneous pressure in the low pressure range suggests that many thermogravimetric systems should be reinvestigated at a constant rate of weight-loss so that the pressure will also remain constant. Thence, complementary isothermal and isokinetic (isobaric) experiments may be correlated to determine functional relationships between the rate of weight-loss and both temperature and pressure—the two most fundamental rate forcing variables.

An example from a temperature jump experiment is shown in Fig. 5. The rate of weight-loss is plotted against fractional weight-loss for the oxidation of polystyrene

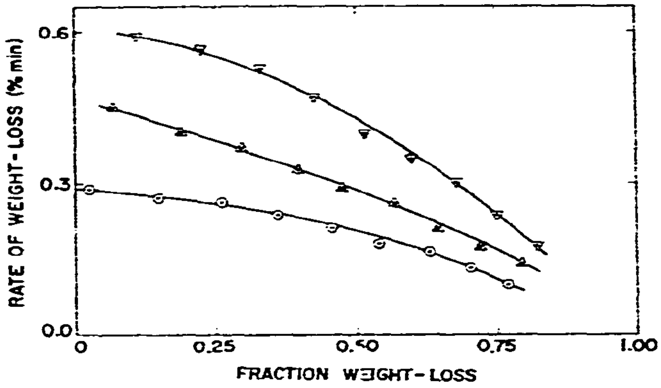
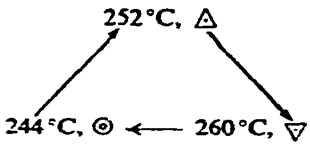


Fig. 5. Temperature jump experiment. Rate of weight-loss vs. fraction of weight loss, 12.0 mg polystyrene, 1.2 Torr l. sec^{-1}, oxygen at 100 Torr.



at 100 Torr oxygen pressure. The temperature was jumped according to the cycle, 244°C → 252°C → 260°C → 244°C → ..., and the average values of the rates of weight-loss during each constant temperature interval are plotted. This example is included to illustrate how a large amount of kinetic data may be obtained easily from a single experiment and is not a model for experimental design.

However, it was pointed out in the preceding section that the Arrhenius activation energy is the most useful single kinetic parameter for the diagnosis of changes in mechanism. Instantaneous activation energies from eqn (5) may be used to identify any such change over the entire range of weight-loss. Changes in activation energy as a function of temperature (and rate) may be monitored by the incorporation of three or more jump temperatures as in the example illustrated in Fig. 5. For example, calculated activation energies for each of the two temperature intervals in this case, do not differ significantly from an overall average value of 25 kcal mol^{-1}.

Similar multiple jumping techniques may be applied to other rate forcing variables to test the general appropriateness of a kinetic parameter in describing the relationship between the variable and the rate.

Eventually, jump methods in which several reaction forcing variables are changed simultaneously may be needed to expose the presence of positive or negative synergistic relationships (multiparameter cross terms) in the grand ensemble of functional relationships between the rate and all of the forcing variables.

RELAXATION OF RATE OF WEIGHT-LOSS JUMPS

The relaxation methods discussed in this section apply to weight-loss systems in which the reaction is proceeding at a steady state rate under a given set of values for the rate forcing variables. Following the sudden perturbation of a forcing variable, the relaxation of the rate of weight-loss is measured as it adjusts itself to new steady state conditions.

These relaxation techniques differ from those used for the investigation of the kinetics of fast gas phase or homogeneous solution reactions. In these latter techniques, an equilibrium system is perturbed by a sudden jump of a rate forcing variable such as temperature or pressure. Then the time constant is measured for the establishment of new equilibrium rather than steady state conditions as the rate approaches zero.

Relaxation phenomena may be studied either by measuring the time constant for a single jump directly, or by measuring the phase lag or amplitude change for a system which is oscillating between two limiting values of a forcing variable. This latter technique was first used in thermal analysis by Ångstrom[19] who determined the thermal conductivity of copper and iron rods by applying a fluctuating temperature to one end and measuring the temperature cycle at distances along the rods.

The experimental time constant for the re-establishment of steady state kinetics following a jump such as the temperature jumps in Fig. 1 was postulated to contain three components of which only one actually measures the kinetic response in approaching a new steady state. If the kinetic time constant is the same order of magnitude or larger than the time constants due to the instrument and the equilibration of the variable, then it can be determined by typical relaxation method techniques. Relaxation time constants should yield valuable information about the kinetics of intermediate steps within the condensed phase of these weight-loss systems.

Diffusional processes are often rate limiting for relaxation phenomena. These include either diffusion of chemical radicals and intermediates within a melt, or diffusion of material into or out of the condensed phase. It is possible that the hitherto intractable problem of measuring material or thermal gradients during weight-loss may be approached by relaxation methods.

As is the case with traditional relaxation techniques, rate of weight-loss methods during which the rate forcing variable is oscillated between two values are often more easily adaptable to specific systems. Diffusion coefficients of gases in polymers have been measured by a frequency response technique in which the changes in weight of the polymer were measured as the pressure of the permeating gas was varied sinusoidally at low frequencies[20].

Variables such as pressure and gaseous flow can be jumped quite rapidly, (in theory, at the speed of sound). However, such sudden changes may introduce noise into the weighing process. Low frequency oscillation of the composition of gaseous flow should become a fruitful method for investigation of reversible gas-condensed phase systems or weight-loss experiments involving reaction with gaseous oxygen, carbon dioxide, or water vapor.

If there is a transparent port opposite the sample in the apparatus, electromagnetic radiation—gamma rays, ultraviolet, visible, infrared, laser, etc.—may be jumped or oscillated at will during the weight-loss measurement.

The physical and geometrical properties of the sample are usually non-adjustable. However, occasionally, barriers may be built into the geometry of a sample which will produce a sudden change in a physical property. An example of this technique is a sample bucket with a discontinuous reduction in its radius so that the surface area of an evaporating liquid will change over a small weight-loss interval.

New experimental techniques and apparatus design will need to be developed to permit more rapid jumps and higher frequency oscillations. These will involve decreasing the size of samples and sensors, and changes in other characteristics of the apparatus which will reduce the inertia of the system toward the rate forcing variable of interest.

CONCLUSIONS

The physics and chemistry of the systems which are studied by thermogravimetric analysis are, on the whole, extremely complex. However, with the advances which are being achieved in automation and computer interfacing, we are obtaining the ability to exploit many imaginative techniques of applied kinetic analysis.

The jump techniques described in this paper offer a simple means for obtaining data which may be utilized to determine functional relationships between rate of reaction and the rate forcing variables. These relationships are for individual values from a single experiment in which only a single rate forcing variable has been perturbed. In other methods, time average values, either from different ranges of extent of reaction or from separate experiments, must be pieced together using models that are often discovered to be inappropriate. As a result, these traditional methods cannot separate out effects of synergistic character, i.e., functional cross terms of two or more rate forcing variables, or other gradual changes in the functional form of the rate equation.

There has also been great improvement in the programming and analyzing capabilities of instruments which measure the rates of evolution of gaseous products from a thermogravimetric system. Application of the new techniques of this paper to concurrent measurement of weight-loss and gas evolution analysis should contribute to the development of more sophisticated and realistic models to describe the kinetics of complex condensed phase reactions. However, a complete picture of the reaction stoichiometry is impossible in many cases, as continuous chemical analysis of the condensed phase remains an intractable problem.

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