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THERMAL ANALYSIS OF REACTIONS AND TRANSFORMATIONS IN THE SOLID STATE. II. THEORETICAL ANALYSIS OF DIFFERENT REACTION AND TRANSFORMATION SYSTEMS USING THERMOGRAVIMETRY*

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ABSTRACT

A new mathematical approach has been developed to follow the kinetics of reactions and transformations in the solid state using thermogravimetry. The technique requires a thermogravimetric trace containing both an integral and first derivative recorded at a single heating rate. The approach permits one to extract kinetic parameters from a wide range of systems as it can be readily adapted to most complications generally encountered, including the presence of inert material and changing atmosphere conditions. The approach can utilize one or more process models and in this way is able to account for the overlapping stages which can occur due to a change in the mechanism. The equations lend themselves well to graphical analysis, yielding linear plots from which kinetic parameters of desolvation, chemical degradation, and phase transformation of organic, inorganic, and polymeric compounds can be successfully extracted. The method provides a means to obtain kinetic parameters that must otherwise be obtained from more tedious, time consuming isothermal techniques.

INTRODUCTION

Our previous paper[1] showed that the non-isothermal TG methods currently used to study reactions and transformations in the solid state yielded significant variations in the calculated heats of activation due to the influence of procedural factors. For this reason, the kinetic parameters extracted have been referred to as "procedural" constants[2, 3]. Experimentally, it was found[1] that the extracted parameters showed very wide ranges of values as a function of the sample size and heating rate ratios.

The above showed that there was need for a method that would provide results which would be reproducible, independent of experimental parameters, and be accurate. The purpose of this manuscript is to present such an approach. Hopefully,

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this will permit others to investigate and to determine mechanisms which are involved in the solid state via non-isothermal thermogravimetric analysis with more confidence.

THEORETICAL CONSIDERATIONS

An analysis of the hypothetical character of the general equation used as a basis to derive all of these methods, as well as the assumptions inherent with each particular method, was made in order to determine all sources of the influence of procedural conditions on the kinetic parameters[1]. This analysis revealed the following implicit and explicit assumptions and suggested ways to overcome them.

(1) Equations were generally derived assuming that all solids decompose to another solid plus gas. This is not a unique system for solid reactions and transformations as other possibilities exist, such as solid decomposing completely to gas or interacting with the gas carrier in a complex way. Therefore, the equation should be individually derived for each and all possible processes which can be followed by dynamic thermogravimetry.

(2) The function of the mass change, $f(\alpha)$, is generally arbitrarily chosen to be $(1 - \alpha)^n$. The use of the fraction conversion, α, causes the calculated kinetic parameters to depend strongly on the specific experimental conditions used. It should be noted that reactions in the solid state are quite different from reactions in solution. As the sample is heated, molecules in the crystal lattice are often subjected to decomposition with very little interaction with other molecules. Therefore, the weight loss is a measure of many variables such as the surface area, volume, weight, and type of reaction or transformation, rather than the fraction conversion. This is apparent when α has to be differentiated with respect to temperature, as differentiation may scatter the data and maximize the error[4]. In addition, the fraction conversion changes on the temperature axis as a function of the experimental conditions[1]. This, in turn, affects the accuracy of the calculated $d\alpha/dT$. The value of n should not be an empirical constant but should depend solely on the reaction process itself. Therefore, in order to overcome the drawbacks of the arbitrary choice of $f(\alpha)$, one should take into consideration the analytical form of the reactants in the reaction in question from a classical sense. Since thermogravimetry monitors the weight change as a function of temperature and time, the analytical form of the reactants should be based on the mass balance of the reaction in question.

(3) The homogeneity factor, n, is frequently referred to as the reaction order in analogy with homogeneous kinetics. This factor has purely empirical significance and is by no means a universal constant for heterogeneous reactions[4].

(4) The furnace atmosphere generally was not taken into consideration. For many reactions, the results would change drastically with changes in furnace conditions, i.e. whether a dynamic or static atmosphere was used or whether an inert or reactive atmosphere was used. This can be overcome by standardizing the experimental conditions, especially those undergoing the TG runs under a dynamic inert atmosphere.

In addition, one should derive equations which account for systems with interacting gas conditions.

(5) The sample temperature was assumed to be the same throughout the specimen and to be equal to the furnace temperature. These assumptions can only be overcome by taking the thermal gradient into consideration. Under dynamic heating at a certain heating rate, the sample temperature is related to the furnace temperature by a uniform function because the existing thermal gradient generally has a uniform character. The sample's decomposition and/or phase transformation is a function of its real temperature. The mass loss, therefore, is a function of the sample temperature and is related to the recorded temperature by a thermal gradient function. If the analytical function of the mass loss of the reactants is taken into consideration using mass balance, and if the first derivative of the reactants' mass loss is obtained simultaneously under the same experimental conditions, the thermal gradient function should be cancelled if we divide the first derivative of the reactants' mass loss by the mass function of the reactants. That is to say, both the integral and its simultaneous first derivative should be used to calculate the kinetic parameters. This will cancel the influence of the experimental conditions on the extracted kinetic parameters. The above data analysis will also cancel the effect of a non-linear heating rate on the thermal gradient of the sample and, in turn, the kinetic parameters extracted.

(6) In the case of two TG curve methods, the assumption is made that the thermograms will show a parallel shift on the temperature axis with increasing heating rate or sample size. This assumption has been criticized by Zsako[3] and is said to be false, which agrees with our findings[1]. Since the shifts are not believed to be parallel, only one thermogram should be used for kinetic studies.

From the above analysis, it was decided to derive kinetic equations which are based on the specific physical and chemical models involved to follow reactions and transformations in the solid state. Since it was planned that the derived equations be applied to thermogravimetric studies, only the processes involving a weight loss or gain will be considered. These equations will be based on the following models.

Case I.

(a) liquid or solid $\xrightarrow{\Delta}$ gas

(b) liquid or solid $+ X_s \xrightarrow{\Delta}$ gas $+ X_s$

where X_s is an inert filler material.

Case II.

(a) (liquid or solid)$_1 \xrightarrow{\Delta}$ (liquid or solid)$_2$ + gas

(b) (liquid or solid)$_1 + X_s \xrightarrow{\Delta}$ (liquid or solid)$_2 + X_s$ + gas

Case III.

(a) (liquid or solid)$_1$ + gas $\xrightarrow{\Delta}$ (liquid or solid)$_2$

(b) (liquid or solid)$_1 + X_s$ + gas $\xrightarrow{\Delta}$ (liquid or solid)$_2 + X_s$

Case IV.

(a) (liquid or solid)$_1$ + gas $\xrightarrow{\Delta}$ (liquid or solid)$_2$ + gas$_2$
(b) (liquid or solid)$_1$ + X_s + gas$_1$ $\xrightarrow{\Delta}$ (liquid or solid)$_2$ + X_s + gas$_2$

Case V.

(a) (liquid or solid)$_1$ $\overset{\Delta}{\rightleftharpoons}$ solid$_2$ + gas$_1$
(b) (liquid or solid)$_1$ + X_s $\overset{\Delta}{\rightleftharpoons}$ solid$_2$ + gas$_1$ + X_s

Case VI.

(a) (liquid or solid)$_1$ + gas$_1$ $\overset{\Delta}{\rightleftharpoons}$ (solid or liquid)$_2$ + gas$_2$
(b) (liquid or solid)$_1$ + X_s + gas$_1$ $\overset{\Delta}{\rightleftharpoons}$ (solid or liquid)$_2$ + X_s + gas$_2$

It should be noted that any of the models I–IV can be reversible; however, only in cases II–IV would a study of the reverse reaction be feasible, and these are represented in case V (II and III) and case VI. In addition, system (b) for all cases I–VI is the same as system (a) with the exception that system (b) contains inert nonvolatile additives in addition to the reactant compound.

A number of examples of the above can be cited. Examples of case Ia are compounds which sublime or vaporize. An example of case IIa would be the desolvation (with no oxidation) of the organic solvate to the anhydrous crystalline form. An example of case IIIa would be a compound which interacts with a gas to form a solid with a higher molecular weight. Such processes cover reactions such as oxidation, gas adsorption, and hydrate formation. An example of case IVa would be more complex oxidation processes such as gas$_1$ being oxygen and gas$_2$ being a cleavage product or products. Case Va is the same as case IIa except that it involves equilibrium. Case VIa is the same as Case IVa except that it involves equilibrium.

MATHEMATICAL ANALYSIS OF PROCESSES WHICH LEND THEMSELVES TO STUDY BY TG

The equations which will be derived for the above cases will be based on classical kinetics and the analytical functions of the mass loss of the reactants of each reaction. The analytical functions of the mass loss of the reactants are based on mass balance.

The derivation of equations that will be used to study solid reactions and transformations will be derived assuming that the weight (W^T_{obs}) as a function of time and temperature (TGA) and the rate of mass change as a function of the time (dW^T_{obs}/dt) and temperature (dW^T_{obs}/dT) are experimentally available. Equations will be derived for both isothermal and non-isothermal conditions.

CASE Ia

liquid or solid $\xrightarrow{\Delta}$ gas
or
$A_s \xrightarrow{\Delta} B_g$
where A_s is the weight of the drug, organic compound, or intact polymer (the subscript

designates the state of the compound). It should be noted that if the solid melts during the run, it will affect the DTA observed but will not change the TGA or DTG.

In this case, the rate of mass loss can be written as

$$\frac{\mathrm{d}(A_s^t)}{\mathrm{d}t} = -k(A_s^t) \tag{1}$$

where k is the specific rate constant and A_s^t is the weight of the compound at time t.

Non-isothermal conditions. A more useful version of eqn. (1) can be obtained by introducing the heating rate, $\mathrm{d}T/\mathrm{d}t$, noted by the symbol a. The time derivative of the weight of the intact compound, eqn. (1), can be converted to a temperature derivative by dividing both sides of eqn. (1) by a since

$$\frac{\mathrm{d}(A_s^t)}{\mathrm{d}t}\,\frac{1}{a} = \frac{\mathrm{d}(A_s^t)}{\mathrm{d}T} \tag{2}$$

It should be noted that A_s^t in case I is also equal to the observed weight of the sample, W_{obs}^t, during the degradation process. Incorporating these changes into eqn. (1) yields the equation

$$-\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}T} = \frac{k}{a}(W_{\mathrm{obs}}^t) \tag{3}$$

The dependence of the specific rate constant on temperature must be considered. Therefore, using eqn. (3) and the Arrhenius equation $k = Z \exp[(-\Delta H^*)/RT]$[†], we may write

$$-\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}T} = \left[\frac{Z}{a}\right][\mathrm{e}^{-\Delta H^*/RT}](W_{\mathrm{obs}}^t) \tag{4}$$

Taking the logarithm of eqn. (4)

$$\log\left[\frac{[-\mathrm{d}(W_{\mathrm{obs}}^t)]/\mathrm{d}T}{(W_{\mathrm{obs}}^t)}\right] = \log\left[\frac{Z}{a}\right] - \frac{\Delta H^*}{2.303\,RT} \tag{5}$$

Despite the negative sign, it should be noted that the term $[-\mathrm{d}(W_{\mathrm{obs}}^t)]/\mathrm{d}T$ is positive as $\mathrm{d}(W_{\mathrm{obs}}^t)/\mathrm{d}T$ is negative since W_{obs}^t is decreasing during the study.

The above equation can be useful as a plot of the $\log[(-\mathrm{d}(W_{\mathrm{obs}}^t))/\mathrm{d}T]/(W_{\mathrm{obs}}^t)$ versus $1/T$ K will yield a linear function of slope equal to $-\Delta H^*/2.303\,R$ and an intercept of $\log[Z/a]$.

[†] It should be noted that much of the literature uses the internal energy ΔE^* rather than ΔH^*. This is not correct, however, for TGA studies as ΔE^* requires that the volume be constant. For a full discussion, see the discussion at the end of this paper.

Isothermal conditions. The integral form of eqn. (1) (using W^t_{obs} for A^t_s) is

$$\int_{W^0_{\text{obs}}}^{W^t_{\text{obs}}} \frac{d(W^t_{\text{obs}})}{(W^t_{\text{obs}})} = -\text{k} \int_0^t dt \tag{6}$$

Therefore,

$$\log (W^t_{\text{obs}}) = -\frac{kt}{2.303} + \log (W^0_{\text{obs}}) \tag{7}$$

where W^0_{obs} is the initial sample weight. According to eqn. (7), a plot of log (W^t_{obs}) versus time, t, will produce a straight line of slope $-k/2.303$.

CASE Ib

In this case, the sample contains inert nonvolatile material, X_s, and the reaction shown for case Ia must be written as.

$A_s + X_s \xrightarrow{\Delta} B_g + X_s$

Mass balance requires that

$$(W^t_{\text{obs}}) = A^t_s + X_s \tag{8}$$

Differentiating eqn. (8)

$$\frac{d(W^t_{\text{obs}})}{dt} = \frac{d(A^t_s)}{dt} + \frac{d(X_s)}{dt} \tag{9}$$

Since X_s is constant, $d(X_s)/dt$ is zero.

Non-isothermal conditions. From eqns. (1), (8) and (9), the rate expression for this case can be obtained. The resultant time derivative of the weight of the intact compound can then be converted to a temperature derivative using eqn. (2) to yield

$$\frac{d(W^t_{\text{obs}})}{dT} = \frac{k(A^t_s)}{a} = -\frac{k}{a}(W^t_{\text{obs}} - X_s) \tag{10}$$

The specific rate constant is temperature dependent. Therefore, using eqn. (10) and the Arrhenius expression gives

$$\frac{[-d(W^t_{\text{obs}})/dT]}{[(W^t_{\text{obs}}) - X_s]} = \left[\frac{Z}{a}\right] e^{-\Delta H^*/RT} \tag{11}$$

Taking the logarithm of eqn. (11) yields

$$\log \left[\frac{[-d(W^t_{\text{obs}})/dT]}{[(W^t_{\text{obs}}) - X_s]}\right] = -\frac{\Delta H^*}{2.303RT} + \log \left[\frac{Z}{a}\right] \tag{12}$$

A plot of log $[-d(W^t_{\text{obs}})/dT]/[(W^t_{\text{obs}}) - X_s]$ versus $1/T$ will give a straight line with a slope of $-\Delta H^*/2.303R$. In this non-isothermal equation, X_s is unknown, but its value can be obtained from a non-isothermal run where X_s is the amount not interacted at the end of the reaction, at infinite time.

Isothermal conditions. Equation (10) must be converted to the time derivative as $a = 0$ in an isothermal study.

$$\frac{\mathrm{d}(W^t_{\mathrm{obs}})}{(W^t_{\mathrm{obs}} - X_s)} = -k\,\mathrm{d}t \tag{13}$$

Therefore, the integration of eqn. (13) will yield

$$\log(W^t_{\mathrm{obs}} - X_s) = -\frac{kt}{2.303} + \log(W^0_{\mathrm{obs}} - X_s) \tag{14}$$

According to eqn. (14), a plot of $\log(W^t_{\mathrm{obs}} - X_s)$ versus time will produce a straight line of slope $(-k/2.303)$.

CASE IIa

(liquid or solid)$_1 \xrightarrow{\Delta}$ (liquid or solid)$_2$ + gas

$\mathrm{A_s \xrightarrow{\Delta} B_s + C_g}$

A_s is the weight of the intact compound, B_s is the product of the reaction in the solid or liquid state and C_g is the gaseous product which is carried out by the carrier gas.

Mass balance dictates that

$$A^0_s = A^t_s + (B_s + C_g)^t \tag{15}$$

where A^0_s is the initial amount of the compound and $(B_s + C_g)_t$ is equal to the amount of compound degraded at time t. The weight of compound degraded can be defined by

$$\text{amount degraded} = r(B^t_s) \tag{16}$$

where B^t_s is the amount of the solid or liquid product at time t, and r is the ratio of the molecular weight of A divided by the molecular weight of B. Since no inert material is present, A^0_{obs} equals W^0_{obs} and

$$W^0_{\mathrm{obs}} = A^t_s + r(B^t_s) \tag{17}$$

At any time t, the weight observed will be equal to the sum of both solid (or liquid) A^t_s and solid (or liquid) B^t_s. That is

$$W^t_{\mathrm{obs}} = A^t_s + B^t_s \tag{18}$$

Substituting A^t_s from eqn. (18) into eqn. (17) yields

$$W^0_{\mathrm{obs}} = (W^t_{\mathrm{obs}} - B^t_s) + r(B^t_s) \tag{19}$$

Rearrangement of eqn. (19) yields

$$B^t_s = \frac{W^0_{\mathrm{obs}} - W^t_{\mathrm{obs}}}{r - 1} \tag{20}$$

Differentiation of eqn. (20) yields

$$\frac{\mathrm{d}(B_s^t)}{\mathrm{d}t} = -\left(\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}t}\right)\left(\frac{1}{r-1}\right) \tag{21}$$

By taking the derivative of eqn. (17) and combining it with eqn. (21), the rate expression, eqn. (1), which characterizes the mass change for this model, can be written as

$$\frac{\mathrm{d}(A_s^t)}{\mathrm{d}t} = -r\left(\frac{\mathrm{d}\,B_s^t}{\mathrm{d}t}\right) = \left(\frac{r}{r-1}\right)\left(\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}t}\right) = -k(A_s^t) \tag{22}$$

Since differential thermogravimetry (DTG) takes into account the change in the weight observed and not the individual changes of A_s^t or B_s^t as a function of temperature, the rate expression $[\mathrm{d}(W_{\mathrm{obs}}^t)/\mathrm{d}T]$ must be used, not $[\mathrm{d}(A_s^t)/\mathrm{d}T]$ or $[\mathrm{d}(B_s^t)/\mathrm{d}T]$.

From eqns. (18) and (22),

$$\left(\frac{r}{r-1}\right)\left(\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}t}\right) = -k[(W_{\mathrm{obs}}^t) - B_s^t] \tag{23}$$

Substituting B_s^t from eqn. (20) into eqn. (23) yields

$$\left(\frac{r}{r-1}\right)\left(\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}t}\right) = -k\left[(W_{\mathrm{obs}}^t) - \left(\frac{(W_{\mathrm{obs}}^0) - (W_{\mathrm{obs}}^t)}{r-1}\right)\right] \tag{24}$$

Non-isothermal conditions. A more useful version of eqn. (24) can be obtained by introducing the heating rate, a, given by $(\mathrm{d}T/\mathrm{d}t)$ [see eqn. (2)] to convert the time derivative of the weight observed on the thermogram to a temperature (T K) derivative. As a result of these changes, eqn. (24) will transform to the following on rearrangement.

$$\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}T} = -\frac{k}{a}\left((W_{\mathrm{obs}}^t) - \frac{(W_{\mathrm{obs}}^0)}{r}\right) \tag{25}$$

Converting the specific rate constant to this temperature function by substituting the Arrhenius expression into eqn. (25) yields

$$-\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}T} = \left[\frac{Z}{a}\right]\left[\exp -\frac{\Delta H^*}{RT}\right]\left[(W_{\mathrm{obs}}^t) - \frac{(W_{\mathrm{obs}}^0)}{r}\right] \tag{26}$$

Taking the logarithm of both sides of eqn. (26) and rearranging it, yields

$$\log\left[\frac{-\,\mathrm{d}(W_{\mathrm{obs}}^t)/\mathrm{d}T}{(W_{\mathrm{obs}}^t) - (W_{\mathrm{obs}}^0)/r}\right] = \log\left[\frac{Z}{a}\right] - \frac{\Delta H^*}{2.303RT} \tag{27}$$

According to eqn. (27), a plot of the $\log\{[-\mathrm{d}(W_{\mathrm{obs}}^t)/\mathrm{d}T]/[(W_{\mathrm{obs}}^t) - (W_{\mathrm{obs}}^t)/r]\}$ versus $1/T$ K will yield a linear function with a slope of $-\Delta H^*/2.303R$ and an intercept of $\log(Z/a)$. All of this information can be obtained from a combined TGA and DTG record.

Isothermal conditions. The integral form of the time derivative version of eqn. (25) is

$$\int_{W^0_{obs}}^{W^t_{obs}} \frac{d(W^t_{obs})}{(W^t_{obs}) - (W^0_{obs})/r} = -k \int_0^t dt \tag{28}$$

Therefore

$$\log[(W^t_{obs}) - (W^0_{obs})/r] = -\frac{kt}{2.303} + \log\{[(W^0_{obs})/r](r-1)\} \tag{29}$$

A plot of $\log[(W^t_{obs}) - (W^0_{obs})/r]$ versus time should result in a straight line with a slope equal to $(-k/2.303)$.

CASE IIb

This case is the same as Case IIa except the sample contains inert nonvolatile material, X_s, and

$A_s + X_s \xrightarrow{\Delta} B_s + X_s + C_g$

Mass balance dictates that eqn. (15) converts to eqn. (30).

$$A^0_s + X_s = W^0_{obs} = A^t_s + X_s + (B_s + C_g)^t \tag{30}$$

and

$$(W^0_{obs}) = A^t_s + X_s + rB^t_s \tag{31}$$

Mass balance also dictates that

$$(W^t_{obs}) = A^t_s + X_s + B^t_s \tag{32}$$

Substituting A^t_s from eqn. (32) into eqn. (31)

$$(W^0_{obs}) = (W^t_{obs}) - X_s - B^t_s + X_s + rB^t_s = (W^t_{obs}) + B^t_s(r-1) \tag{33}$$

Solving eqn. (33) for B^t_s

$$B^t_s = \frac{(W^0_{obs}) - (W^t_{obs})}{r-1} \tag{34}$$

Differentiating eqn. (34) with respect to time will yield

$$\frac{d(B^t_s)}{dt} = -\left(\frac{d(W^t_{obs})}{dt}\right)\left(\frac{1}{r-1}\right) \tag{35}$$

Combination of eqns. (1) and (35) and the derivative of eqn. (31) can be used to describe the rate of mass change as follows.

$$\frac{d(A^t_s)}{dt} = -r\left(\frac{d(B^t_s)}{dt}\right) = \left(\frac{r}{r-1}\right)\left(\frac{d(W^t_{obs})}{dt}\right) = -k(A^t_s) \tag{36}$$

Substituting for A^t_s in eqn. (36) using eqn. (32) yields

$$\left(\frac{r}{r-1}\right)\left(\frac{\mathrm{d}(W^t_{obs})}{\mathrm{d}t}\right) = -k(W^t_{obs} - B^t_s - X_s) \tag{37}$$

Substituting for B^t_s from eqn. (34) into eqn. (37) and rearranging yields

$$\frac{\mathrm{d}(W^t_{obs})}{\mathrm{d}t} = -\frac{k}{r}\left[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})\right] \tag{38}$$

Non-isothermal conditions. Converting eqn. (38) to a temperature derivative [see eqn. (2)] and substituting the Arrhenius equation yields

$$-\frac{\mathrm{d}(W^t_{obs})}{\mathrm{d}T} = \left[\frac{Z}{ar}\right]\left[\exp - \frac{\Delta H^*}{RT}\right]\left[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})\right] \tag{39}$$

where a is the heating rate. Rearranging eqn. (39) and taking the logarithm yields

$$\log\left[\frac{-\mathrm{d}(W^t_{obs})/\mathrm{d}T}{r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})}\right] = -\left[\frac{\Delta H^*}{2.3RT}\right] + \log\left[\frac{Z}{ar}\right] \tag{40}$$

A plot of the left-hand side of eqn. (40) versus $1/T$ will yield a straight line with a slope of $-\Delta H^*/2.3R$ and an intercept of $\log(Z/ar)$.

Isothermal conditions. The integration of eqn. (38) will yield

$$\int_{W^0_{obs}}^{W^t_{obs}} \frac{r[\mathrm{d}(W^t_{obs})]}{[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})]} = -k\int_0^t \mathrm{d}t$$

Therefore

$$\log\left[r(W^t_{obs}) - (W^0_{obs}) - X_s(r-1)\right] = -\frac{kt}{2.303} + \log\left[(r-1)(W^0_{obs} - X_s)\right] \tag{41}$$

A plot of $\log[r(W^t_{obs}) - (W^0_{obs}) - X_s(r-1)]$ versus time will give a straight line with a slope of $-k/2.303$.

CASE IIIa

(liquid or solid)$_1$ + gas $\xrightarrow{\Delta}$ (liquid or solid)$_2$

$A_s + G_g \xrightarrow{\Delta} B_s$

In this case, the rate of mass loss can be written as

$$-\frac{\mathrm{d}(A^t_s)}{\mathrm{d}t} = k(G^t_g)(A^t_s) \tag{42}$$

where G^t_g is the amount of unreacted gas at time t. The reaction rate will be proportional to the pressure of the gas in the chamber. For convenience, however, the weight of the gas rather than its pressure will be used. This does not pose any problems as G^t_g for a chamber of a specified volume is given by

$$G^t_g = \left(\frac{M_g V}{RT}\right) P^t_g = BP^t_g \tag{43}$$

where M_g is the molecular weight of the reacting gas, V is the volume of the reaction chamber, P^t_g is the pressure of reacting gas in the chamber, G^t_g is the corresponding weight of the gas in the chamber and B is the proportionality constant between weights and pressures of gas.

Mass balance dictates that

$$W^t_{obs} = A^t_s + B^t_s = A^t_s + \frac{(A^0_s - A^t_s)}{r} \tag{44}$$

where $B^t_s = (A^0_s - A^t_s)/r$ and r is the ratio of the molecular weight of A divided by the molecular weight of B, or the ratio of A^0_s divided by B_s if the reaction goes to completion.

Since $(W^0_{obs}) = A^0_s$, eqn. (44) can be written as

$$A^t_s = \frac{(W^0_{obs}) - r(W^t_{obs})}{1 - r} \tag{45}$$

Differentiating eqn. (45) and substituting into eqn. (42)

$$-\frac{d(A^t_s)}{dt} = \left(\frac{r}{1 - r}\right)\left(\frac{d(W^t_{obs})}{dt}\right) = k(G^t_g)(A^t_s) \tag{46}$$

Substituting eqns. (43) and (45) into eqn. (46) and rearranging yields

$$+\frac{d(W^t_{obs})}{dt} = \frac{fkB}{r}(P^t_g)[(W^0_{obs}) - r(W^t_{obs})] \tag{47}$$

The constant f was included in eqn. (47) as the reaction rate is proportional to the effective pressure of the reacting gas at the solid surface which could be less than the measured pressure of the reacting gas in the bulk of the reaction chamber, and f is the proportionality constant between bulk and surface pressure of the gas.

There is an additional experimental condition that must be included in deriving the appropriate equation for case III as this system involves an environmental gas reacting with the solid. Obviously, the effective amount or concentration of gas as a function of time will differ for static or dynamic conditions. The derivation of an equation that would be applicable under all conditions of flow and reacting gas pressures would yield equations that would be very cumbersome and applicable only for the specific apparatus being used for the study. A more useful approach is to derive equations for specific conditions that can easily be experimentally attained and therefore would be generally applicable to all apparatus. In this way, one can ignore any thermal and/or concentration gradients of reacting and product gases. In the following sections, various flow and experimental conditions will be considered.

For constant gas flow. The simplest system that can be considered would be one in which a quasi-steady state gas pressure is maintained throughout the study. Obviously, the required steady state can be easily attained by the proper choice of experimental conditions such as heating rates, gas flow, sample size, etc. Under these conditions, the concentration of reacting gas at the solid surface is constant for the duration of the experiment and the observed kinetics would be pseudo-first order depending only on the activity of the solid.

For these conditions P_g^t in eqn. (47) becomes constant and is equal to the initial pressure of the gas, P_g^0.

Non-isothermal conditions. Converting the time derivative of the weight observed to a temperature derivative for the above conditions, eqn. (47) becomes

$$+\frac{\mathrm{d}(W_{\mathrm{obs}}^t)}{\mathrm{d}T} = \frac{BfP_g^0k}{ar}[(W_{\mathrm{obs}}^0) - r(W_{\mathrm{obs}}^t)] \tag{48}$$

Using the Arrhenius expression and eqn. (48), the following equation results after rearrangement.

$$+\frac{\mathrm{d}(W_{\mathrm{obs}}^t)/\mathrm{d}T}{[(W_{\mathrm{obs}}^0) - r(W_{\mathrm{obs}}^t)]} = \frac{Bf(P_g^0)Z}{ar}\left[\exp - \frac{\Delta H^*}{RT}\right] \tag{49}$$

Taking the logarithm of both sides of eqn. (49) yields

$$\log\left[\frac{+\,\mathrm{d}(W_{\mathrm{obs}}^t)/\mathrm{d}T}{[(W_{\mathrm{obs}}^0) - r(W_{\mathrm{obs}}^t)]}\right] = -\frac{\Delta H^*}{2.303RT} + \log\left[\frac{BZf(P_g^0)}{ar}\right] \tag{50}$$

According to eqn. (50), a plot of $\log\{[+\,\mathrm{d}(W_{\mathrm{obs}}^t)/\mathrm{d}T]/[(W_{\mathrm{obs}}^0) - r(W_{\mathrm{obs}}^t)]\}$ versus $1/T$ gives a straight line with a slope of $-\Delta H^*/2.303R$.

Isothermal conditions. The integral form of eqn. (47) for conditions of constant pressure is

$$\int_{W_{\mathrm{obs}}^0}^{W_{\mathrm{obs}}^t} - \frac{r\mathrm{d}(W_{\mathrm{obs}}^t)}{[(W_{\mathrm{obs}}^0) - r(W_{\mathrm{obs}}^t)]} = -Bf(P_g^0)k\int_0^t \mathrm{d}t$$

Therefore

$$\log[(W_{\mathrm{obs}}^0) - r(W_{\mathrm{obs}}^t)] = -\frac{Bf(P_g^0)kt}{2.303} + \log[(W_{\mathrm{obs}}^0)(1 - r)] \tag{51}$$

A plot of the left-hand side of the logarithmic term versus time will give a straight line with a slope equal to $Bf(P_g^0)k/2.303$ and an intercept equal to $\log[(W_{\mathrm{obs}}^0)(1 - r)]$. It should be reiterated that eqn. (51) will be valid only under conditions of quasi-steady state in which the ratio of the presence of reacting gas at the surface and in the bulk of the chamber does not change appreciably during the experiment. The effect of the above restriction can be minimized by using a sufficiently fast flow rate and high pressure of reacting gas, a large reacting chamber volume, and a small sample size.

For no gas flow. To be rigidly correct, one would need to assume a closed system so that gas flow could truly be considered zero. This can be done by sealing the reaction chamber outlet, loading the reaction chamber with the reacting gas and then closing the reaction chamber inlet. Often, however, the experiment can be designed to essentially simulate a closed system. Examples would be an environmental chamber that would greatly expand the volume of the reaction atmosphere or a system that is essentially reacting with air.

There are two possible gas conditions under no flow conditions. In the first situation, the amount of gas is in great excess so that its pressure is essentially not changing due to the amount reacting. In this case, the pressure of gas in the chamber remains constant and is equal to P_g^0 which means that eqns. (50) and (51) would be applicable. In the second situation, the pressure of gas is decreasing as a function of time and its decrease must be accounted for in the derived equations. In the second, situation, however, P_g^t is changing appreciably during the experiments and eqns. (50) and (51) are not applicable.

One can account for P_g^t changing during the experiment as obviously

$$P_g^t = P_g^0 - \Delta P_g^t \tag{52}$$

Mass balance dictates that ΔG_g^t, the decreases in weight of the gas at any time, is given by

$$\Delta G_g^t = (W_{obs}^t - W_{obs}^0) = B\Delta P_g^t \tag{53}$$

Equations (52) and (53) yield

$$P_g^t = P_g^0 - \frac{(W_{obs}^t - W_{obs}^0)}{B} \tag{54}$$

Non-isothermal conditions. Using both eqn. (47) and eqn. (54)

$$\frac{d(W_{obs}^t)}{dt} = \frac{fk}{r}[BP_g^0 + (W_{obs}^0) - (W_{obs}^t)][(W_{obs}^0) - r(W_{obs}^t)] \tag{55}$$

Substituting the Arrhenius equation into eqn. (55), converting to a temperature derivative and rearranging yields

$$\left[\frac{+\,d(W_{obs}^t)/dT}{[BP_g^0 + (W_{obs}^0) - (W_{obs}^t)][(W_{obs}^0) - r(W_{obs}^t)]}\right] = \frac{fZ}{ar}\left[\exp - \frac{\Delta H^*}{RT}\right] \tag{56}$$

Taking the logarithmic form for both sides of eqn. (56) will yield

$$\log\left[\frac{+\,d(W_{obs}^t)/dT}{[BP_g^0 + (W_{obs}^0) - (W_{obs}^t)][(W_{obs}^0) - r(W_{obs}^t)]}\right] =$$

$$-\left[\frac{\Delta H^*}{2.303RT}\right] + \log\left[\frac{Zf}{ar}\right] \tag{57}$$

According to eqn. (57), a plot of the left logarithmic terms versus $1/T$ K gives a straight line with a slope of $-\Delta H^*/2.303R$.

Isothermal conditions. Under this condition, the time derivative of eqn. (55) should be integrated as follows.

$$\int_{W_{obs}^{t=0}}^{W_{obs}^{t}} + \frac{d(W_{obs}^{t})}{[BP_g^0 + (W_{obs}^{t=0}) - (W_{obs}^{t})][(W_{obs}^{t=0}) - r(W_{obs}^{t})]} = \frac{fk}{r}\int_{0}^{t} dt \qquad (58)$$

Since the measurements were started after the compound had reached the equilibrated temperature, some of the compound W_{obs}^0 had degraded. The amount observed at the time of equilibrium temperature is referred to as the $W_{obs}^{t=0}$ which is different from the previous W_{obs}^0. Integration by the use of partial fractions will yield

$$\int_{W_{obs}^{t=0}}^{W_{obs}^{t}} + \frac{d(W_{obs}^{t})}{[BP_g^0 + (W_{obs}^{t=0}) - (W_{obs}^{t})][(W_{obs}^{t=0}) - r(W_{obs}^{t})]} =$$

$$\frac{1}{r\left[(W_{obs}^{t=0})\dfrac{(1-r)}{r} - BP_g^0\right]}\left[\int_{W_{obs}^{t=0}}^{W_{obs}^{t}} + \frac{d(W_{obs}^{t})}{[BP_g^0 + (W_{obs}^{t=0}) - (W_{obs}^{t})]} - \right.$$

$$\left.\int_{W_{obs}^{t=0}}^{W_{obs}^{t}} + \frac{d(W_{obs}^{t})}{[(W_{obs}^{t=0})/r - (W_{obs}^{t})]}\right] \qquad (59)$$

Equations (58) and (59) yield

$$\log\left[\frac{(W_{obs}^{t=0} - r(W_{obs}^{t})}{BP_g^0 + (W_{obs}^{t=0}) - (W_{obs}^{t})}\right] = \left[(W_{obs}^{t=0})\frac{1-r}{r} - BP_g^0\right]\frac{fkt}{2.303}$$

$$+ \log\left[\frac{(1-r)\,W_{obs}^{t=0}}{BP_g^0}\right] \qquad (60)$$

A plot of the left-hand side of the logarithmic term versus $1/T$ K will yield a straight line. The rate constant can then be extracted from the slope.

CASE IIIb

This case is the same as case IIIa except the sample contains inert material X_s, and

$$A_s + X_s + G_g \xrightarrow{\Delta} B_s + X_s$$

Mass balance dictates that

$$W^t_{obs} = A^t_s + X_s + B^t_s = A^t_s + X_s + \frac{(W^0_{obs} - A^t_s - X_s)}{r} \tag{61}$$

since

$$B^t_s = \frac{(W^0_{obs} - A^t_s - X_s)}{r}$$

Therefore

$$A^t_s = \frac{r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})}{(r-1)} \tag{62}$$

Substituting eqn. (62), the time derivative of eqn. (62) and eqn. (43) into eqn. (42)

$$-\frac{d(A^t_s)}{dt} = -\left(\frac{r}{r-1}\right)\left(\frac{d(W^t_{obs})}{dt}\right) = fkBP^t_g\left[\frac{r(W^t_{obs}) - X_s(r-1) - W^0_{obs}}{r-1}\right] \tag{63}$$

For constant gas flow. The introduction for Case IIIa is also applicable to this case.

Non-isothermal conditions. Converting the time derivative of the weight observed [from eqn. (63)] to a temperature derivative at constant gas flow, we get

$$-\frac{d(W^t_{obs})}{dT} = \frac{BkfP^0_g}{ra}[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})] \tag{64}$$

Using the Arrhenius equation, rearranging eqn. (64), and taking the logarithmic form for both sides of the resultant equation, will yield

$$\log\left[\frac{-d(W^t_{obs})/dT}{[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})]}\right] = -\frac{\Delta H^*}{2.303RT} + \log\left[\frac{ZfBP^0_g}{ar}\right] \tag{65}$$

According to eqn. (65), a plot of the left-hand side logarithmic term versus $1/T$ K gives a straight line with a slope of $-\Delta H^*/2.303R$.

Isothermal conditions. The integral form of eqn. (63) for constant gas pressure is

$$\int_{W^0_{obs}}^{W^t_{obs}} \frac{r d(W^t_{obs})}{[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})]} = \int_0^t (-fkBP^0_g)dt$$

Therefore

$$\log[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})] = -\frac{fkP^0_gB}{2.303}(t) + \log[(r-1)(W^0_{obs} - X_s)] \tag{66}$$

where $(fkBP^0_g)$ is a pseudo-first-order rate constant. A plot of $\log[r(W^t_{obs}) - X_s(r-1) - (W^0_{obs})]$ versus time should yield a straight line with a slope equal to $-fkBP^0_g/2.303$.

For no gas flow. The introduction given for Case IIIa is also applicable here. In this case, however, eqns. (65) and (66) are valid for conditions in which the amount of reacting gas is in great excess and therefore constant for the life of the experiment.

Non-isothermal conditions. Using a similar approach as shown in Case IIIa to derive eqn. (57), but using eqns. (63) and (54), the final equation was derived and is given by

$$\log\left[\frac{-\,\mathrm{d}(W^t_{\mathrm{obs}})/\mathrm{d}T}{BP^0_g + (W^0_{\mathrm{obs}}) - (W^t_{\mathrm{obs}})][r(W^t_{\mathrm{obs}}) - X_s(r-1) - (W^0_{\mathrm{obs}})]}\right] = -\frac{\Delta H^*}{2.303RT}$$

$$+ \log\left[\frac{Zf}{ar}\right] \qquad (67)$$

Equation 67 predicts that a plot of the left-hand side of the logarithmic form versus reciprocal absolute temperature will yield a straight line with a slope equal to $-\Delta H^*/2.303R$.

Isothermal conditions. The final equation is given by eqn. (68).

$$\log\left[\frac{W^0_{\mathrm{obs}} + (r-1)X_s - rW^t_{\mathrm{obs}}}{BP^0_g + W^0_{\mathrm{obs}} - W^t_{\mathrm{obs}}}\right] = -[rBP^0_g + (r-1)(W^0 - X_s)]\frac{fkt}{2.303r}$$

$$+ \log\left[\frac{(r-1)(X_s - W^0_{\mathrm{obs}})}{BP^0_g}\right] \qquad (68)$$

Equation (68) predicts that a plot of the left-hand side of the equation versus time will yield a straight line with a slope equal to $-[rBP^0_g + (r-1)(W^0 - X_s)]\,fk/2.303R$.

CASE IVa

(liquid or solid)$_1$ + gas$_1$ $\xrightarrow{\Delta}$ (liquid or solid)$_2$ + gas$_2$

or

(liquid or solid)$_1$ + gas$_1$ $\xrightarrow{\text{slow}}$ complex $\xrightarrow{\text{very fast}}$ (liquid or solid)$_2$ + gas$_2$

This case characterizes a complex oxidation process, in which gas$_1$, G_{g1}, is oxygen and gas$_2$, G_{g2}, is a cleavage product or products. This could be applied to the mechanism of the effect of oxygen on organic molecules. It should be noted that the observed weight in this case can increase or decrease with time depending on the molecular weights of gases 1 and 2.

For deriving the non-isothermal equation for this case, we assume in the latter equation that the complex is decomposing very quickly so that its amount is negligible.

Mass balance dictates that

$$W^t_{\mathrm{obs}} = A^t_s + B^t_s \qquad (69)$$

$$W^0_{obs} = W^t_{obs} + \Delta G^t_{g2} - \Delta G^t_{g1} \tag{70}$$

$$B^t_s = \frac{(W^0_{obs} - A^t_s)}{r} \tag{71}$$

where ΔG^t_{g2} is the amount of gas$_2$ formed up to time t, ΔG^t_{g1} the amount of gas$_1$ reacted with A up to time t, and r the ratio of the molecular weight A divided by molecular weight B.

From eqns. (69) and (71), we get

$$W^t_{obs} = A^t_s + \frac{(W^0_{obs} - A^t_s)}{r} \tag{72}$$

Therefore

$$A^t_s = \frac{W^0_{obs} - r(W^t_{obs})}{(1 - r)} \tag{73}$$

Equation (73) is identical to eqn. (45) in Case IIIa. Therefore, if gas$_1$ is used at a constant gas flow to help remove the gaseous product gas$_2$, eqn. (47) becomes

$$\frac{\mathrm{d}(W^t_{obs})}{\mathrm{d}t} = \frac{fkBP^0_{g1}}{r}(W^0_{obs} - r(W^t_{obs})) \tag{74}$$

where P^0_{g1} is the pressure of gas$_1$. Converting the time derivative of the weight observed to a temperature derivative yields

$$+\frac{\mathrm{d}(W^t_{obs})}{\mathrm{d}T} = \frac{fkBP^0_{g1}}{ar}[W^0_{obs} - r(W^t_{obs})] \tag{75}$$

For constant gas flow and non-isothermal conditions. Taking into consideration that the specific rate constant is temperature dependent

$$\frac{+\,\mathrm{d}(W^t_{obs})/\mathrm{d}T}{W^0_{obs} - r(W^t_{obs})} = \left(\frac{fBP^0_{g1}Z}{ar}\right)\left(\exp -\frac{\Delta H^*}{RT}\right) \tag{76}$$

Taking logarithms of both sides of eqn. (76) yields

$$\log\left[\frac{+\,\mathrm{d}(W^t_{obs})/\mathrm{d}T}{W^0_{obs} - r(W^t_{obs})}\right] = -\left(\frac{\Delta H^*}{2.303R}\right)\left(\frac{1}{T}\right) + \log\left(\frac{fBZP^0_{g1}}{ar}\right) \tag{77}$$

A plot of the logarithm term on the left-hand side of eqn. (77) versus $1/T$ K will yield a straight line from the slope of which ΔH^* can be obtained.

For constant gas flow and isothermal conditions. Equation (51) using P^0_{g1} for P^0_g can be used for Case IVa as well as Case IIIa. That is

$$\log[(W^0_{obs}) - rW^t_{obs}] = -\frac{BfP^0_{g1}kt}{2.303} + \log[(W^0_{obs})(1 - r)] \tag{78}$$

CASE IVb

(liquid or solid)$_1$ + gas$_1$ + X$_s$ → (liquid or solid)$_2$ + gas$_2$ + X$_s$
or
(liquid or solid)$_1$ + gas$_1$ + X$_s$ $\xrightarrow{\text{slow}}$ complex $\xrightarrow{\text{fast}}$ (liquid or solid)$_2$ + gas$_2$ + X$_s$

For this case, the mass balance is given as follows.

$$W^0_{\text{obs}} = A^0_s + X_s \tag{79}$$

$$W^t_{\text{obs}} = A^t_s + X_s + B^t_s \tag{80}$$

$$W^0_{\text{obs}} = W^t_{\text{obs}} + \Delta G^t_{g2} - \Delta G^t_{g1} \tag{81}$$

$$B^t_s = \frac{(W^0_{\text{obs}} - A^t_s - X_s)}{r} \tag{82}$$

Equations (80) and (82) yield

$$W^t_{\text{obs}} = A^t_s + X_s + \frac{(W^0_{\text{obs}} - A^t_s - X_s)}{r}$$

Therefore

$$A^t_s = \frac{r(W^t_{\text{obs}}) - X_s(r-1) - W^0_{\text{obs}}}{r-1} \tag{83}$$

If we use gas$_1$ at a constant gas flow to help to remove the gaseous product, gas$_2$, we will end up with eqn. (84) after converting the time derivative to $[\mathrm{d}(W^t_{\text{obs}})/\mathrm{d}T]$.

$$\frac{\mathrm{d}(W^t_{\text{obs}})}{\mathrm{d}T} = \left(-\frac{kfBP^0_{g1}}{ar}\right)[(W^t_{\text{obs}})\,r - X_s(r-1) - (W^0_{\text{obs}})] \tag{84}$$

For constant gas flow and non-isothermal conditions. Equation (84) and the Arrhenius equation will yield

$$\frac{\mathrm{d}(W^t_{\text{obs}})/\mathrm{d}T}{r(W^t_{\text{obs}}) - X_s(r-1) - (W^0_{\text{obs}})} = -\frac{fBP^0_{g1}Z}{ar}\left[\exp -\frac{\Delta H^*}{RT}\right] \tag{85}$$

Taking logarithms of both sides yields eqn. (86).

$$\log\left[\frac{-\,\mathrm{d}(W^t_{\text{obs}})/\mathrm{d}T}{r(W^t_{\text{obs}}) - X_s(r-1) - (W^0_{\text{obs}})}\right] = \log\left[\frac{fBP^0_{g1}Z}{ar}\right] - \frac{\Delta H^*}{2.303RT} \tag{86}$$

A plot of the left-hand expression of eqn. (86) versus $1/T$ K will yield a straight line with slope equal to $-\Delta H^*/2.303R$.

For constant gas flow and isothermal conditions. The integral form of eqn. (84) after conversion to a time derivative gives

$$\int_{W^0_{\text{obs}}}^{W^t_{\text{obs}}} \frac{r\mathrm{d}(W^t_{\text{obs}})}{r(W^t_{\text{obs}}) - X_s(r-1) - (W^0_{\text{obs}})} = \int_0^t fBP^0_{g1}k\,\mathrm{d}t \tag{87}$$

Therefore

$$\log\left[r(W^t_{\text{obs}}) - X_s(r-1) - (W^0_{\text{obs}})\right] = -\frac{fBP^0_{g1}kt}{2.303} + \log\left[(r-1)(W^0_{\text{obs}} - X_s)\right] \quad (88)$$

Therefore, a plot of the left-hand side versus time will yield a straight line with a slope equal to $-fBP^0_{g1}k/2.303$.

CASE V

(liquid or solid)$_1$ $\overset{\Delta}{\rightleftharpoons}$ (liquid or solid)$_2$ + gas

It is not recommended that the forward and backward reaction be studied simultaneously as this would unnecessarily complicate the system. It would be much simpler and more accurate to study the forward and backward reactions individually. This could be done by monitoring the furnace atmosphere. The forward reaction must be studied first under an inert atmosphere and the effluent gas analyzed and identified. The backward reaction can then be studied by using the identified gaseous product as the furnace atmosphere.

The kinetic analysis for this model under dynamic furnace atmosphere conditions can be studied using equations derived to suit Case IIa (for the forward reaction) and equations derived to suit Case IIIa (for the backward reaction). For the case of static furnace atmosphere, the equations which would monitor this system will be complicated and the experimental conditions difficult to control to yield meaningful results without an extensive investigation. Therefore, it is recommended that this system be studied under controlled furnace atmosphere which allows one to study the forward and the backward reaction separately.

CASE VI

(liquid or solid)$_1$ + gas$_1$ $\overset{\Delta}{\rightleftharpoons}$ (liquid or solid)$_2$ + gas$_2$

It is recommended that the forward and reverse reactions be individually studied as suggested and discussed under Case V.

The kinetic analysis for this model under controlled dynamic furnace atmosphere can be done using equations derived to suit Case IV [eqn. (72)] for both the forward and reverse reactions. For the study of the forward reaction, gas$_1$ at a known and constant pressure should be passed through the furnace. However, for the study of the backward reaction, gas$_2$ at a known and constant pressure should be passed through the furnace. The amount of gas can then be taken into consideration to use eqns. (77) and (78) to obtain the kinetic parameters. For reasons stated under Case V, it is not recommended that a static system be used to study this system.

EXPERIMENTAL REQUIREMENTS OF THIS APPROACH

The manner and type of data collected is an integral part of the proposed non-isothermal method and was developed throughout this study as part of the technique introduced.

The technique requires that both an integral (TG) and differential (DTG) curve as a function of time and temperature are available or calculable. For analysis, this technique only requires that the initial weights of gases in the reacting chamber be known and does not require that the weight of gaseous reactants and products be monitored as terms containing the gaseous change in weights have been converted to terms expressed in observed sample weights as a function of time, W^T_{obs}. In this way, the necessary data can be collected in one run using a single heating rate.

The experimental conditions, both sample-related and instrument-related, should be monitored and specified in any studies using this method. The furnace atmosphere for all thermogravimetric studies using this approach should be dynamic. The presence of a dynamic atmosphere can act either as a gas carrier in the case of an inert atmosphere to remove the gaseous product, prevent condensation and hinder reverse reactions so the gaseous product will not suppress the reaction, or to react with the sample. Examples of the latter are the cases of air or oxygen in oxidation processes and carbon dioxide in the case of studying the reverse reaction of calcium carbonate–calcium oxide equilibria. As previously noted, an inert atmosphere should be used in Cases I and II and the proper reacting gas should be chosen for Cases III–VI.

The sample holder should be a tall crucible which acts as a tare to prevent any spattering of the material during the process and the material of the crucible should be inert with respect to the sample studied and not act as a catalyst for the reaction taking place. The powder should be well ground prior to its use and mixed well when an interaction between two compounds is being studied.

RELATION BETWEEN ENTHALPY, ΔH^*, AND INTERNAL ENERGY, ΔE^*

For systems held at constant volume, i.e. allowing pressure to vary, studies as a function of the temperature yield changes in the internal energy. However, for a system at constant pressure, i.e. no restraint on the volume, studies as a function of the temperature yield changes in the enthalpy, not the internal energy, of the system during the process. If one assumes only PV work is done, the relationship between these thermodynamic parameters at constant pressure is given by $\Delta H^* = \Delta E^* + P\Delta V$. For systems in which the volume change is negligible, ΔH^* and ΔE^* can be considered to be equivalent.

The change in internal energy of the system during the process being studied, however, can be calculated from the change in enthalpy. For a system not involved in the production of gases, one can estimate the change in volume of the system during the process as the change in volume, ΔV, is given by $\Delta V = W(\rho_2 - \rho_1)/\rho_2\rho_1$ where ρ_2 is the density of the products and ρ_1 the density of the reactants. In most cases, this volume change would be insignificant.

PV work is the work a system must do in order to expand against the pressure of its atmosphere. For the production of a gas at 1 atm pressure, the volume change is approximately equal to 82.05 T ml/mole. The energy change for this work is approximately equal to RT cal. For example, a system composed of 1 mole of material which completely decomposes to a gas at 300°C will involve $P\Delta V$ work of almost 600 cal and a volume change of almost 25 l. Obviously, for solid–solid, liquid–liquid, and solid–liquid phase changes ΔH^* and ΔE^* are essentially equal.

EXPERIMENTAL APPLICATION OF THE MATHEMATICAL MODELS AND VERIFICATION OF THEIR VALIDITY

The application of models I and II under inert, dynamic, furnace atmosphere was done[5] on theophylline dehydration and phase transformation, methyl prednisolone Form II_b desolvation and chemical degradation and calcium oxalate dehydration[10] and chemical degradation[10]. The results show that the extracted kinetic parameters were consistent, reproducible, reliable, independent of the experimental conditions and in good agreement with values obtained from the more tedious, time consuming, isothermal approach. On the contrary, methods accepted in the literature yielded kinetic parameters for the above-mentioned compound using the same thermograms that depend on the experimental conditions[1].

The study of the applications was expanded to include not only organic and inorganic compounds, but also polymers. The application to the degradation of cross-linked polyethylene showed that the polymer decomposed in at least three overlapping stages, each with a characteristic activation energy[6]. In addition, the use of these mathematical models permitted the calculation[7] of enthalpies of sublimation and vaporization of a thermally stable (in the temperature range of vaporization or sublimation) compound from a single thermogram. The values obtained by this method were in excellent agreement with the values obtained from adiabatic calorimetry.

Finally, this approach was extended to thermal optical analysis[9] and thermal X-ray diffractometry[8]. These latter techniques contribute an additional dimension to the study of solid state processes which do not involve weight changes.

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