

CRITICAL THERMODYNAMIC ANALYSIS OF DIFFERENTIAL SCANNING CALORIMETRY FOR STUDYING CHEMICAL KINETICS

J. Zeng, L. T. Fan and J. R. Schlup***

Department of Chemical Engineering, Durland Hall, Kansas, State University, Manhattan
KS 66506 -5102, USA

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Abstract

A critical thermodynamic analysis of differential thermal calorimetry is reported herein to gain further insight into the phenomena leading to the reported differences between kinetic parameters extracted from isothermal DSC methods and those from dynamic DSC methods. The sources have been identified for the variations observed in the total heat of reaction as a function of the heating rate in dynamic DSC experiments. The analysis clearly indicates that these variations are, in fact, to be anticipated. The relationships necessary for extracting kinetic data from both isothermal and dynamic experiments are derived rigorously by resorting to classical thermodynamics.

Keywords: chemical kinetics, DSC, thermodynamic analysis

Introduction

The kinetics of chemical reactions involving condensed phases has often been determined through various techniques of differential scanning calorimetry (DSC), such as multiple isothermal DSC curves over a range of reaction temperatures, a single temperature scan, and multiple temperature scans at several heating rates (Prime, 1981). A basic assumption in studies of chemical kinetics via DSC is that the heat flow relative to the baseline is proportional to the reaction rate. In addition, both the temperature gradient within the sample and the temperature difference between the sample and reference cells are assumed to be small. Careful control of the sample size and shape as well as the operating conditions of the instrument is necessary to ensure that these assumptions are satisfied.

* Current Address: Thermal Designs, Inc., 5352 Prudence Street, Houston, Texas, 77045

** Author to whom all correspondence should be addressed.

Kinetic data can be obtained from either isothermal or dynamic DSC experiments. In an isothermal experiment, the sample is placed in the calorimeter cell at a temperature at which essentially no reaction takes place. Then, it is heated as rapidly as possible to the predetermined reaction temperature. Alternatively, the calorimeter can be preheated to the desired reaction temperature prior to placing the unreacted sample in the calorimeter cell. In both cases, the rate of heat generation at the reaction temperature is measured with respect to time. In an isothermal DSC experiment, the baseline is usually flat.

In a dynamic (temperature scan) DSC experiment, the sample is placed in the calorimeter cell at a temperature where the reaction rate is negligible. The rate of heat generation is monitored as the sample is heated at a constant rate. For temperature scan experiments, however, the heat capacity of the sample contributes to the heat flow (endothermic); a baseline correction is applied in the region of the exo- or endothermic peak produced by the reaction.

The value of DSC curve relative to its baseline, instead of the absolute value of heat flow itself, usually has been designated as dH/dt or dq/dt , which is the differential heat flux relative to its baseline [2]. If the reaction is the only thermal event, the conversion rate for the reaction is determined by

$$\frac{d\alpha}{dt} = \frac{(-dq/dt)}{-\Delta H_{rxn}}$$

and the degree of conversion at time t is given by

$$\alpha = \frac{(-\Delta H_t)}{(-\Delta H_{rxn})}$$

$(-\Delta H_t)$ is the partial peak area from the thermogram. Ideally, $(-\Delta H_{rxn})$ has been considered as the total heat liberated for complete conversion of the reactants. The total peak area, $(-\Delta H_{tot})$, from dynamic DSC data traditionally has been assumed to be equal to $(-\Delta H_{rxn})$; $(-\Delta H_t)$ is obtained from the same experimental data.

With an isothermal approach, several samples are cured isothermally for various lengths of time [1, 3]. The partially cured samples then are scanned in the DSC at a constant heating rate. The residual heat of reaction, $(-\Delta H_{t,resid})$, i.e., the heat evolved to obtain complete conversion of the partially reacted sample, is measured. The degree of conversion is calculated as

$$\alpha = \frac{(-\Delta H_{tot}) - (-\Delta H_{t,resid})}{(-\Delta H_{tot})}$$

The conversion rate, $d\alpha/dt$, can not be obtained directly from the curve; however, it can be obtained by taking the derivative of α with respect to t . A large number of samples are required to calculate accurate derivatives. This method loses

sensitivity as the residual exotherm diminishes. In addition, it becomes difficult to obtain accurate data when secondary phenomena, such as the glass transition of a partially reacted polymer system, immediately precede the small residual exotherm.

Kinetic parameters, e.g., the rate constants and reaction orders, can be extracted from two classes of methods, i.e., isothermal and dynamic DSC methods, on the basis of appropriate models for the reaction kinetics. The latter is more convenient experimentally than the former; moreover, differences between the kinetic parameters extracted from these two classes of methods can be appreciable. Much of the unreliability of dynamic kinetics has been attributed to factors such as the thermal lag of the instrument, inappropriate rate equations for the chemical kinetics, inaccurate experimental data, baseline effects, and volume changes during cure.

The argument has been made that the isothermal and dynamic rates are intrinsically different [4, 5]. In the case of epoxy cure reactions, Prime [6] proposed the following correction for dynamic DSC data by assuming the general expression for the isothermal rate to be

$$\left(\frac{\partial\alpha}{\partial t}\right) = f(\alpha)A \exp\left(-\frac{E}{RT}\right)$$

The dynamic rate, $d\alpha/dt$, has been correlated with the isothermal rate, $(\partial\alpha/\partial t)_T$, through the relationship

$$\frac{d\alpha}{dt} = Z\left(\frac{\partial\alpha}{\partial t}\right)_T \text{ and } Z = \left(1 + \frac{tE}{RT^2} \frac{dT}{dt}\right)$$

Although corrected dynamic DSC data have been found to be in close agreement with the isothermal results in some cases [7, 8], the theoretical validity of this approach has been questioned [9–12]. The topic has been discussed further in reviews by Prime [1] and by Barton [2].

It appears that a satisfactory interpretation is yet to be given for the discrepancies between kinetic data obtained from isothermal and dynamic DSC methods. A critical thermodynamic analysis of differential thermal calorimetry is described herein to gain further insight into the phenomena leading to the differences between the kinetic parameters extracted from isothermal DSC methods and those from dynamic DSC methods. The sources are identified for the variations observed in the total heat of reaction as a function of the heating rate in dynamic DSC experiments. The relationship necessary for extracting the kinetic data from DSC experiments are derived rigorously by resorting to classical thermodynamics.

Theoretical development

Various relationships are established among the reaction rate data, the degree of conversion, and the DSC curves. This is followed by an elaboration of the physical significances of such relationships in extracting the kinetic parameters from DSC curves.

Kinetic data and DSC curves

The theoretical development of the present work has been based upon consideration of a power compensating DSC apparatus [13–15]; nevertheless, the results should be equally applicable to other types of thermal analysis apparatus with appropriate modifications. Experimentally, the thermal masses of the sample and reference compartments are kept to a minimum to reduce the response time of the system. Careful control of the sample size and shape is necessary to enhance the rate of heat transfer and to decrease the thermal gradient within the sample. It is assumed that equilibrium is maintained in the system for a particular experiment.

In general, the stoichiometry of a chemical reaction can be expressed as

$$\sum \nu_i A_i = 0 \quad (1)$$

where A_i 's and ν_i 's represent the chemical species and stoichiometric coefficients, respectively; the latter are positive for products and negative for reactants. The change in the number of moles of species i , n_i , due to the chemical reaction is related to those of other species as

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \dots = \frac{dn_i}{\nu_i} = \dots \quad (2)$$

Moreover, n_i is related to its initial value, n_{oi} , and to the fractional extent of conversion, α , through

$$n_i = n_{oi} + \nu_i \left(\frac{n_o}{|\nu|} \right) \alpha \quad (3)$$

In this expression, $n_o/|\nu|$ stands for the smallest value of $n_{o,i}/|\nu_i|$, which would be specified by the limiting reactant. The degree of conversion, α , is defined as

$$\alpha = \left(\frac{|\nu|}{\nu} \right) \left(\frac{n - n_o}{n_o} \right)$$

For brevity, α is termed the conversion hereafter.

According to the first law of thermodynamics,

$$dH = dQ \quad (4)$$

for a process occurring at constant pressure. Thus, for both the sample and reference compartments of the apparatus, we have, respectively,

$$dH_s = dQ_s \quad (5)$$

$$dH_r = dQ_r \quad (6)$$

The above equation reduces to

$$n_r c_p^r dT_r = dQ_r \quad (7)$$

as the reference compartment contains the DSC cell only. Equation (5) gives rise to

$$\left(n_r c_p^r + \sum_1^i n_i c_p^i \right) dT_s + \left(\sum_1^i \nu_i h_i \right) \left(\frac{dn_i}{\nu_i} \right) = dQ_s \quad (8)$$

for the sample compartment, which includes the properties of both the sample and the DSC cell. The contribution of the DSC sample cell is identical to that of the reference cell in the reference compartment. By subtracting Eq. (7) from Eq. (8),

$$\left(\sum_1^i n_i c_p^i \right) dT_s + \left(\sum_1^i \nu_i h_i \right) \left(\frac{dn_i}{\nu_i} \right) + n_r c_p^r d(T_s - T_r) = (dQ_s - dQ_r) \quad (9)$$

If the response of the system is sufficiently rapid so that equilibrium states essentially are reached instantaneously, i.e., if $T_s = T_r = T$, then the above expression becomes

$$\left(\sum_1^i n_i c_p^i \right) \frac{dT}{dt} + \left(\sum_1^i \nu_i h_i \right) \left(\frac{dn_i}{\nu_i dt} \right) = \left(\frac{dQ_s}{dt} - \frac{dQ_r}{dt} \right) \quad (10)$$

or

$$\frac{1}{n_o} \left(\sum_1^i n_i c_p^i \right) \frac{dT}{dt} + \frac{1}{|\nu|} \left(\sum_1^i \nu_i h_i \right) \left(\frac{|\nu|}{n_o} \right) \frac{dn_i}{\nu_i dt} = \frac{1}{n_o} \frac{dQ}{dt} \quad (11)$$

where $dQ/dt = dQ_s/dt - dQ_r/dt$ is defined as the differential heat flow. From Eq. (2) and the definition of α , the rate of the reaction can be expressed as

$$\frac{d\alpha}{dt} = \left(\frac{|\nu|}{\nu}\right) \frac{dn}{n_o dt} = \left(\frac{|\nu|}{n_o}\right) \frac{dn_i}{\nu_i dt} \quad (12)$$

The enthalpy change of the reaction per mole of the limiting reactant is

$$\Delta H_{\text{rxn}} = \frac{1}{|\nu|} \left(\sum_1^i \nu_i h_i \right) \quad (13)$$

Hence, Eq. (11) can be rewritten as

$$\frac{1}{n_o} \left(\sum_1^i n_i c_p^i \right) \frac{dT}{dt} + \Delta H_{\text{rxn}} \frac{d\alpha}{dt} = \frac{1}{n_o} \left(\frac{dQ}{dt} \right) \quad (14)$$

An idealized thermogram plots the differential heat flow, dQ/dt , vs. temperature or time. If no reaction occurs in the sample, i.e., if $d\alpha/dt=0$, we have from Eq. (14)

$$\frac{1}{n_o} \left(\sum_1^i n_i c_p^i \right) \frac{dT}{dt} = \frac{1}{n_o} \left(\frac{dQ}{dt} \right) \quad (14a)$$

By comparing the two equations above, it can be readily discerned that a DSC curve of a sample undergoing chemical reaction comprises two parts: the sensible heat involved in heating the sample and the heat of reaction. For an idealized isothermal DSC experiment, the baseline of the curve will be a function of the changing composition of the sample as the reaction proceeds. The slope of the baseline will be negligible before the onset and after the completion of the reaction. For a dynamic DSC experiment, Eq. (14a), expressing the effect of sensible heat, constitutes the baseline of the curve. Indeed, a change in the slope of the baseline is anticipated during and even after completion of the reaction as a consequence of both the changing composition of the sample and the temperature dependence of the heat capacities of the components.

Upon rearranging Eq. (14),

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{\text{rxn}}} \left(\frac{1}{n_o} \right) \left[\frac{dQ}{dt} - \left(\sum_1^i n_i c_p^i \right) \frac{dT}{dt} \right] \quad (15)$$

The term

$$\frac{1}{n_o} \left[\frac{dQ}{dt} - \left(\sum_1^i n_i c_p^i \right) \frac{dT}{dt} \right]$$

in the above equation is the magnitude of DSC curve relative to its baseline, normalized per mole of the limiting reactant. If this term is defined as dq/dt [2], Eq. (15) becomes

$$\frac{d\alpha}{dt} = \frac{(-dq/dt)}{(-\Delta H_{rxn})} \quad (16)$$

Integrating this equation yields the following expression for the degree of conversion, α , at time t_1 .

$$\alpha = \int_{t_0}^{t_1} \frac{d\alpha}{dt} dt = \int_{t_0}^{t_1} \frac{(-dq/dt)}{(-\Delta H_{rxn})} dt \quad (17)$$

Although dq/dt and $(-\Delta H_{rxn})$ are normalized per mole of the limiting reactant, it is more convenient in practice to normalize them on the basis of the mass of all reactants present.

The temperature dependence of the heat of reaction, $(-\Delta H_{rxn})$, is of major concern here. The standard heat of reaction, $-\Delta H_{rxn}^0$, is the negative of the enthalpy change of reaction when the reactants in their standard states react isothermally and completely to form products in their standard states, ΔH_{rxn}^0 . For the purpose of calculating the enthalpy change for the reaction, ΔH_{rxn} , the standard states usually are defined as the states of pure substances under a pressure of 1 atm. Thus, the standard heat of reaction depends only on the temperature and is evaluated at the temperature at which the reaction proceeds. The reactants in DSC can usually be assumed to be in their standard states.

Interpretation of areas under DSC curves

Both dQ/dt and dq/dt are path variables. Their changes, therefore, depend not only on the time and temperature of the initial and final states, but also on the time-temperature path traveled by the system. Prior to the interpretation of areas under DSC curves, Eqs. (14 and 16) should be rearranged and integrated, respectively, as

$$\int_{(T_0,0)}^{(T_1,\alpha)} \left[\frac{1}{n_0} \left(\sum_i n_i c_p^i \right) dT + \Delta H_{rxn} d\alpha \right] = \int_{t_0}^{t_1} \frac{1}{n_0} \left(\frac{dQ}{dt} \right) dt \quad (18)$$

$$\int_0^{\alpha_1} (-\Delta H_{rxn}) d\alpha = \int_{t_0}^{t_1} \left(-\frac{dq}{dt} \right) dt \quad (19)$$

where both T and α are functions of time t . The right-hand sides of these two equations are, respectively, the partial peak area between the curves and instru-

mental baseline and that between the DSC curves and sample baseline. Note that the instrumental baseline does not reflect the heat capacity effects of the reactants and products in the sample cell; however, the sample baseline includes these effects.

Isothermal DSC measurements

For an isothermal DSC scan,

$$\frac{dq}{dt} = \frac{1}{n_o} \frac{dQ}{dt}$$

and $(-\Delta H_{\text{rxn}})$ is constant. If t_o and t_∞ are the times at the initiation and completion of the reaction, respectively, we obtain from Eq. (19)

$$(-\Delta H_{\text{rxn}}) \int_0^1 d\alpha = \int_{t_o}^{t_\infty} \left(-\frac{dq}{dt} \right) dt \quad (20)$$

$$(-\Delta H_{\text{rxn}}) = \int_{t_o}^{t_\infty} \left(-\frac{dq}{dt} \right) dt \quad (21)$$

which is the total peak area between the sample baseline and DSC curve. The isothermal reaction rate can be calculated by Eq. (16) on the basis of this heat of reaction, which, in turn, yields the degree of conversion, α , in conjunction with Eq. (17).

Dynamic DSC measurements

The dependence of ΔH_{rxn} on temperature can be expressed as (e.g., Kyle [16])

$$\Delta H_{\text{rxn}} = \Delta H_{\text{rxn},o} + \int_{T_o}^T \frac{1}{|v|} \sum v_i c_p^i dT$$

where c_p^i is a function of temperature. In the light of the above expression and Eq. (3), Eq. (18) can be rewritten as

$$\int_{(T_o, \alpha_o)}^{(T, \alpha)} \left[\frac{1}{n_o} \sum_1^i \left(n_{o,i} + v_i \frac{n_o}{|v|} \alpha \right) c_p^i dT + \left(\Delta H_{\text{rxn},o} + \int_{T_o}^T \frac{1}{|v|} \sum v_i c_p^i dT \right) d\alpha \right] = \int_{t_o}^{t_i} \frac{1}{n_o} \frac{dQ}{dt} dt \quad (22)$$

where both T and α are functions of time, t . By taking partial derivatives of the first term in the line integral on the left-hand side of this equation with respect to α ,

$$\frac{\partial}{\partial \alpha} \left(\frac{1}{n_o} \left(\sum_1^i \left(n_{o,i} + \nu_i \frac{n_o}{|\nu|} \alpha \right) c_p^i \right) \right) = \frac{1}{|\nu|} \sum \nu_i c_p^i \quad (23)$$

and the second term with respect to T ,

$$\frac{\partial}{\partial T} \left(\Delta H_{\text{rxn},o} + \int_{T_o}^T \frac{1}{|\nu|} \sum \nu_i c_p^i dT \right) = \frac{1}{|\nu|} \sum \nu_i c_p^i \quad (23a)$$

Obviously, the two partial derivatives above are identical, thereby indicating that the line integral on the left-hand side of Eq. (22) can be evaluated along any path of α vs. T . For an experiment where the reaction proceeds isothermally at T_o to a certain conversion α at which time the temperature is raised to T_1 without further reaction, Eq. (22) becomes

$$\Delta H_{\text{rxn},o\alpha_1} + \frac{1}{n_o} \int_{T_o}^{T_1} \left[\sum_1^i \left(n_{o,i} + \nu_i \frac{n_o}{|\nu|} \alpha_1 \right) c_p^i \right] dT = \int_{t_o}^{t_1} \frac{1}{n_o} \frac{dQ}{dt} dt \quad (24)$$

The left-hand side of this expression is the enthalpy difference of the reacting system between the state at $T=T_o$ and $\alpha=0$ and the state at $T=T_1$ and $\alpha=\alpha_1$. Note that T , α , and dQ/dt are all functions of time t ; moreover, these functions change with the temperature scanning rate, dT/dt . At time t_1 , therefore, the values of both sides of Eq. (24) are functions of the temperature scanning rate as well.

When $t_1 \rightarrow t_\infty$, Eq. (19) reduces to

$$\int_0^1 (-\Delta H_{\text{rxn}}) d\alpha = \int_{t_o}^{t_\infty} \left(-\frac{dq}{dt} \right) dt \quad (25)$$

In addition, the left-hand side of this equation can be expressed as

$$\int_0^1 (-\Delta H_{\text{rxn}}) d\alpha = \frac{\int_0^1 (-\Delta H_{\text{rxn}}) d\alpha}{\int_0^1 d\alpha} = (-\Delta H_{\text{avg}}) \quad (26)$$

Thus, Eq. (25) can be rewritten as

$$(-\Delta H_{\text{avg}}) = \int_{t_0}^{t_\infty} \left(-\frac{dq}{dt} \right) dt \quad (27)$$

Equation (26) signifies that $(-\Delta H_{\text{avg}})$ determined from a dynamic or nonisothermal DSC scan is the average value of $(-\Delta H_{\text{rxn}})$ weighted over the entire conversion range from $\alpha=0$ to $\alpha=1$. Furthermore, this average value depends on t_∞ according to Eq. (27); obviously, the faster the heating, the shorter the time to complete the reaction and vice versa.

Discussion

The derivation in the present work for recovering kinetic parameters from DSC data is compared with that in a landmark paper on the subject by Borchartd and Daniels [17]. The implication of the relations derived here is discussed in terms of the baseline profile of a DSC curve and the heat of reaction, which directly affect their applications to the determination of kinetic parameters of chemical reactions and phase-transition phenomena. A rationale is given for the variation of the total heat of reaction determined from dynamic DSC with the heating rate of the experiment.

Approach of Borchartd and Daniels

Major differences exist between the development in this work and that of Borchartd and Daniels [17]. First, unlike in the latter, the former takes into account the temperature dependence of the heat of reaction, $(-\Delta H_{\text{rxn}})$. Second, Borchartd and Daniels have derived the equations for DTA and DSC by visualizing that a reaction proceeds in a stirred dilute solution in the sample compartment and that a pure solvent is in the reference compartment. Moreover, they regarded the total heat capacity of the sample compartment and that of the reference compartment as identical because of the diluteness of the reactant solution. In contrast, the reference compartment in the present work is empty; in addition, an extra term is included for the heat capacities of the reactants and products in the sample compartment, which manifests itself in a baseline profile for the curve that may well change during the course of a DSC experiment (Eq. (14)).

Baseline of a DSC curve

To obtain $(-dq/dt)$ in Eqs (16 and 17), the baseline of a DSC curve needs to be determined first. As stated in the sub-section entitled Kinetic data and DSC

curves, the baseline profile is attributed to the sensible heat for heating the sample, which is affected by the sample's heat capacity and its temperature dependence. More often than not, however, the heat capacities and their variations with temperature are unknown; and, therefore, a straight line drawn between the assumed initial and final points of the event has conventionally been taken as the baseline.

The effects of baseline profile on the quantitative determination of enthalpy change have been discussed by Brennan *et al.* [18], Heuvel and Lind [19], and McNaughton and Mortimer [15].

Dependence of heat of reaction on temperature

Traditionally, the rate of reaction is determined from the expression

$$\frac{d\alpha}{dt} = \frac{(-dq/dt)}{-\Delta H_{\text{tot}}} \quad (28)$$

and the degree of conversion is given by

$$\alpha = \frac{(-\Delta H_t)}{(-\Delta H_{\text{tot}})} \quad (29)$$

where dq/dt is the differential heat flow relative to its baseline, $(-\Delta H_{\text{tot}})$ corresponds to the total heat released from the completely reacted sample as measured from the total peak area of a dynamic DSC curve, and $(-\Delta H_t)$ is equal to the heat released from the sample up to time t prior to the completion of the reaction as measured from the partial peak area of the curve [1]. As indicated in Eq. (27), $(-\Delta H_{\text{tot}})$ so obtained is, in fact, the conversion-weighted averaged of the heat of reaction, $(-\Delta H_{\text{avg}})$. The approach is equivalent to substituting $(-\Delta H_{\text{avg}})$ for $(-\Delta H_{\text{rxn}})$ in Eqs (16 and 17) while assuming that $(-\Delta H_{\text{rxn}})$ is independent of temperature. This may be one source of discrepancy between the results of isothermal and dynamic experiments; valid kinetic parameters can be recovered from dynamic DSC data only when the temperature dependence of $(-\Delta H_{\text{rxn}})$ is negligible.

Kinetics of phase transformation

Scanning DSC methods have been successfully applied to kinetic studies of crystallization, melting, condensation, and evaporation. Any of these phase-transition phenomena can be regarded as a simple reaction of the type, $A \rightarrow B$, ideally occurring at a specific temperature under constant pressure. The latent heat of a phase-transition phenomenon is defined at the temperature at which the phe-

nomenon takes place; it is not a function of temperature. Consequently, Eqs (16 and 17) are applicable only to dynamic DSC scan under these situations.

Areas under DSC curves

In a nonisothermal or dynamic DSC scan, the conversion, α , is related to the time elapsed during the scan, t , and the temperature of the reaction, T ; thus,

$$\alpha = g(T, t) \quad (30)$$

Since T is a unique function of t and vice versa for an individual DSC scan, the above expression can be rewritten as

$$\alpha = g_1[T(t), t] \quad (31)$$

Frequently, T varies linearly with t ; in this case, we have

$$T = \eta t + T_0 \quad (32)$$

where T_0 is the initial temperature, and η is the heating rate, typically a constant. Hence, for any given T_0 , combining Eqs (31 and 32) leads to

$$\alpha = g_2(\eta, t) \quad (33)$$

The heat of reaction, $(-\Delta H_{\text{rxn}})$, is solely a function of T , i.e.,

$$(-\Delta H_{\text{rxn}}) = f(T) \quad (34)$$

As a result, substituting $(-\Delta H_{\text{rxn}})$ in the left-hand side of Eq. (26) with the right-hand side of the above equation gives

$$\int_0^1 f(T) d\alpha = (-\Delta H_{\text{avg}}) \quad (35)$$

Substituting Eq. (33) into this expression, in turn, yields

$$(-\Delta H_{\text{avg}}) = \int_0^1 f(T) d[g_2(t, \eta)] \quad (36)$$

Since η is specified as a parameter for a given dynamic DSC scan, the above expression can be rearranged as

$$(-\Delta H_{\text{avg}}) = \int_{t_0}^{t_{\infty}} f(T) \frac{d[g_2(t, \eta)]}{dt} dt \quad (37)$$

Recall that $(-\Delta H_{\text{avg}})$ corresponds to the total heat released from the completely reacted sample as determined from the total area of a dynamic DSC curve. By relating T in Eq. (37) to t according to Eq. (32), we see that the average heat of reaction, $(-\Delta H_{\text{avg}})$, may depend on the heating rate, η , of a particular experiment.

Concluding remarks

The baseline profile of a DSC curve and temperature dependence of the heat of reaction have been identified as two major sources of error for measuring the reaction rate and conversion by dynamic DSC methods. The parameters for the rate equation obtained from dynamic DSC curves are considered intrinsically different from those extracted from isothermal DSC curves. The kinetic parameters of a phase transformation are more readily extracted than those of a chemical reaction from dynamic DSC. The dependence of the total heat generated by completing the chemical reaction as determined from the total area of a dynamic DSC curve on the scanning rate of an individual experiment has been elucidated in the light of the temperature dependence of the heat of reaction.

Notation

A_i	chemical species i
c_p^i	constant-pressure heat capacity for species i in the sample compartment
c_p^r	constant-pressure heat capacity for the reference cell
H	enthalpy
H_r	enthalpy for reference compartment
H_s	enthalpy for sample compartment (including sample and cell)
ΔH_{rxn}	enthalpy change of the reaction per mole of the limiting reactant
$-\Delta H_{\text{avg}}$	conversion-weighted average of $(-\Delta H_{\text{rxn}})$ over a temperature range
$-\Delta H_{\text{rxn}}^0$	standard heat of reaction
$-\Delta H_t$	partial peak area from a DSC curve
$-\Delta H_{\text{tot}}$	total or maximum, heat of cure from a dynamic scan
h_i	enthalpy for species i in the sample compartment
n_i	number of moles for species i in the sample compartment
n_r	number of moles for the reference compartment
n_{oi}	initial number of moles for species i in the sample compartment
$n_o/ n_l $	smallest value of $n_{oi}/ n_l $, i.e., the value for the limiting reactant
Q	heat flow
Q_r	heat flow for the reference compartment

Q_s	heat flow for the sample compartment
dQ/dt	$dQ_s/dt - dQ_r/dt$, the differential heat flow rate
dq/dt	value of DSC curve relative to its baseline, normalized per mole of the limiting reactant
T_r	temperature of the reference compartment
T_s	temperature of the sample compartment
t	time
t_0	time at the beginning of the reaction
t_∞	time at the completion of the reaction
Greek letters	
α	fractional extent of reaction defined according to the limiting reactant
η	heating rate
ν_i	stoichiometric coefficient of species i for a reaction

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