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Thermochimica Acta 279 (1996) 157–166

thermochimica  
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## Vaporization effects in evaluation of decomposition kinetic parameters by high-pressure DSC

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Received 26 June 1995; accepted 3 December 1995

### Abstract

Conventional analysis of High-Pressure DSC (HPDSC) data gives only approximate values for the onset temperature of decomposition and the decomposition kinetic parameters because the data are masked by vaporization effects. A model is proposed to calculate High-Pressure DSC heat flow data under conditions wherein both decomposition and vaporization occur simultaneously. The vaporization effects are modelled using a single mass transfer parameter. Experiments were carried out to show that the parameter, once evaluated from data at a slightly higher pressure, could be used to estimate vaporization effects at even higher pressures. A method is suggested for determining the true kinetic parameters of decomposition.

*Keywords:* High-pressure DSC; Mass energy balance; Kinetic parameters of decomposition

### List of symbols

$A_x$	interfacial mass transfer area/cm <sup>2</sup>
$A_f$	frequency factor/s <sup>-1</sup>
$C_p$	specific heat capacity/J g <sup>-1</sup> K <sup>-1</sup>
$E$	activation energy/J mol <sup>-1</sup>
$f$	fugacity/bars
$k_g$	mass transfer coefficient/cm sec <sup>-1</sup>
$k$	rate constant/s <sup>-1</sup>
$M$	molecular weight/g
$P$	pressure/bars

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$P^{\text{sat}}$	saturated pressure/bars
$T$	temperature/K
$T_d$	decomposition temperature/K
$V$	molar volume/cc mol <sup>-1</sup>
$v$	molecular volume/cc mol <sup>-1</sup>
$Z$	compressibility factor
$Z_v$	gas phase compressibility factor

### Greek symbols

$\alpha$	ratio of weight change
$\beta$	heating rate/°C s <sup>-1</sup>
$\delta$	film thickness/cm
$\lambda$	heat of vaporization/J mol <sup>-1</sup>
$\rho$	molar density/cc mol <sup>-1</sup>
$\omega$	acentric factor

## 1. Introduction

The decomposition characteristics of a solid sample may be evaluated by Differential Scanning Calorimetry (DSC). The DSC data (heat flow vs. temperature) may be analyzed, e.g. by the method of Daniel and Borchardt [1], to obtain the order and Arrhenius parameters of decomposition. In the case of volatile samples, the experiment is carried out under relatively high pressures to suppress vaporization and to ensure that the decomposition temperature ( $T_d$ ) is lower than the corresponding boiling point of the sample. The high-pressure DSC (HPDSC) data is then treated conventionally to obtain the kinetic parameters. However, the onset temperature and Arrhenius parameters thus derived are expected to be only approximate since vaporization is not eliminated but only suppressed. Thus the heat flow data are the net effect of two competing processes: heat liberation due to decomposition, and heat absorption due to sample vaporization. It is therefore desirable to develop a model to evaluate the true decomposition parameters while independently accounting for the vaporization losses.

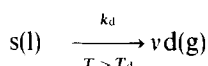
## 2. Modelling

### 2.1. Mass and energy balances

The HPDSC consists of a chamber (volume ~ 250 ml) with a bottom plate on which two aluminum cells (one empty as the reference cell and the other containing the sample of known weight) are placed. The chamber is initially purged and then pressurized by nitrogen to a desired value. The inlet flow valve is subsequently closed and the experimental is started. A more detailed explanation of the DSC can be found elsewhere [2].

The basic purpose of the DSC is to measure the heat flow as a function of temperature. This is achieved by measuring the difference in power required to maintain both the reference and the sample pans at a constant temperature. The present system of interest involves a liquid sample placed in the aluminum cell. The sample (initial weight  $W_{io}$ , volume  $V_{io}$ ) is initially maintained in a cell of total pressure  $P_o$  and temperature  $T_o$ , and is in equilibrium with its vapor (vapor volume  $V_g$ ). The sample is heated from  $T_o$  to  $T_f$  at a constant heating rate  $\beta^\circ\text{C min}^{-1}$  at a constant pressure. Since the cell has a small pin hole, the vapors and gases generated due to vaporization/decomposition will enter the bulk of the gas phase and finally escape through the pin hole. Since the volume of vapors/gases generated is negligible compared to that of the DSC cell, pressure may be assumed to be constant. As the sample is heated, the liquid level decreases with a corresponding increase in the vapor phase volume. The vapor composition also undergoes a change with time. The net heat liberated or consumed during the heating process may be obtained by solving the appropriate mass and heat balance equations along with the equilibrium relationships.

Assume one mole of sample (s) decomposes at a sufficiently high temperature ( $T_d$ ) according to first-order kinetics to form  $v$  moles of a gaseous product (d) as per the following stoichiometry



The overall mass balance for the gas phase gives

$$\begin{aligned} \text{rate of change of total} & \quad \text{rate of transfer of sample} & \quad \text{rate of generation of gaseous} \\ \text{no. of moles} & = \text{vapors from interface to} & + \text{product due to} \\ & \quad \text{the gas phase} & \quad \text{decompositon} \\ & & & - \text{rate at which the gas mixture is} \\ & & & \quad \text{leaving the cell} \end{aligned} \quad (1)$$

i.e.

$$\frac{d}{dt} [PV_g/ZRT] = A_\alpha [N_i + N_d] - \frac{d}{dt} [M_c] \quad (2)$$

or

$$\frac{dM_c}{dt} = A_\alpha [N_i + N_d] + \frac{P}{ZRT} \left[ \frac{V_g}{T} \beta + \frac{V_g}{Z} \frac{dZ}{dt} - \frac{dV_g}{dt} \right] \quad (3)$$

where  $A_\alpha$  is the interfacial area, (i.e. the cross sectional area of the cell),  $f_{li}$  and  $f_{gi}$  are the liquid and vapor phase fugacities of the sample respectively,  $Z$  is the gas phase compressibility factor,  $V_g$  is the gas phase volume,  $k_d$  is the decomposition rate constant, and  $\alpha$  is the fraction of the sample remaining and is defined as  $\alpha = W_i/W_{io}$ .

In Eqs. (2) and (3),  $N_i$  and  $N_d$  are the transfer rates of sample vapors and decomposition product, respectively, from the interface to the bulk. Employing the film model,  $N_i$  and  $N_d$  may be given by

$$\text{mass flux of sample across film} = \text{diffusive flux} + \text{convective flux}$$

i.e.

$$N_i = \frac{k_g}{RT} [f_{li} - f_{gi}] + x_i [N_i + N_d] \quad (4)$$

$$\begin{aligned} N_d &\sim x_d [N_i + N_d] = x_d [N_i + v k_d \alpha / A_\alpha] \\ &= x_d [N_i + v A_f \exp(-E/RT) (\alpha / A_\alpha)] \end{aligned} \quad (5)$$

where  $k_g$  is the gas phase mass transfer coefficient and the rate constant  $k_d$  obeys the Arrhenius law of temperature dependence, with  $A_f$  as the frequency factor and  $E$  the energy of activation. Further, in Eq. (5), diffusive flux is assumed to be negligible. Component mass balances for sample vapors and decomposed products may be similarly written as

$$\frac{P_i}{P} \frac{dM_c}{dt} = A_\alpha N_i + \frac{P_i}{ZRT} \left[ \frac{\beta V_g}{T} + \frac{V_g}{Z} \frac{dZ}{dt} - \frac{dV_g}{dt} + \frac{V_g}{P_i} \frac{dP_i}{dt} \right] \quad (6)$$

$$\frac{P_d}{P} \frac{dM_c}{dt} = \frac{P_d}{ZRT} \left[ \frac{\beta}{T} V_g + \frac{V_g}{Z} \frac{dZ}{dt} - \frac{dV_g}{dt} + v A_f \exp(-E/RT) \alpha + \frac{V_g}{P_d} \frac{dP_d}{dt} \right] \quad (7)$$

where  $P_i$  and  $P_d$  are the partial pressures of the sample vapors and decomposed product in the gas phase respectively.

Combining Eqs. (3), (6) and (7) gives

$$\frac{dP_i}{dt} = \left[ \frac{ZRT}{V_g} \right] \left[ \left( 1 - \frac{P_i}{P} \right) A_\alpha N_i - \left( \frac{P_i}{P} \right) v A_f \exp(-E/RT) \alpha \right] \quad (8)$$

$$\frac{dP_d}{dt} = \left[ \frac{ZRT}{V_g} \right] \left[ \left( \frac{P_d}{P} \right) A_\alpha N_i - \left( 1 - \frac{P_d}{P} \right) v A_f \exp(-E/RT) \alpha \right] \quad (9)$$

where the volume of the vapor space gap  $V_g$  is evaluated by

$$\frac{dV_g}{dt} = \left[ \frac{-1}{\rho_i} \right] \frac{dW_i}{dt} = [A_\alpha N_i + A_f \exp(-E/RT) \alpha] \frac{1}{\rho_i} \quad (10)$$

The energy balance for the system may be given as

$$\begin{array}{l} \text{rate of heat supply} \\ \text{to the sample cell} \end{array} = \begin{array}{l} \text{rate of change of} \\ \text{sensible heat in} \\ \text{the liquid sample} \end{array} + \begin{array}{l} \text{rate of heat utilized} \\ \text{for vaporization} \end{array} \quad (11)$$

i.e.

$$\frac{dQ}{dt} + \Delta H_d A_f \exp(-E/RT) \alpha = C_{pi} W_i \beta + \lambda A_\alpha N_i \quad (12)$$

where  $Q$  is the heat supplied to the sample by the DSC,  $\Delta H_d$  is the heat of decomposition,  $C_{pi}$  is the specific heat capacity of the sample, and  $\lambda$  is the latent heat of vaporization of the sample.

In Eqs. (8), (9), (10) and (12), the thermodynamic quantities  $f_{li}$ ,  $f_{gi}$ ,  $\rho_i$  and  $Z$  can be evaluated using an appropriate equation of state. Other quantities such as  $\Delta H_d$ ,  $C_{pi}$  and

$\lambda$  can be estimated using appropriate correlations. The gas phase mass transfer coefficient  $k_g$  may be obtained independently, and its evaluation, which is the main theme of this work, will be discussed in detail later. Hence, Eqs. (8), (9) and (12) are solved simultaneously with the initial conditions at  $t = 0$

$$W_i = W_{i0}, \quad V_g = V_{g0}, \quad T = T_o, \quad P_i = P_i^{\text{sat}}(T_o), \quad P_d = 0 \quad (13)$$

The heat flux profile ( $dQ/dt$  versus time) may be evaluated provided  $A_f$  and  $E$  are supplied. Alternatively, given the experimental heat flows,  $A_f$  and  $E$  can be calculated from the data by non-linear regression.

## 2.2. Evaluation of the mass transfer coefficient

If the transfer of vapors from the interface to the bulk of the gas phase occurs by diffusion alone, then the mass transfer coefficient may be given by

$$k_g = \frac{D}{\delta} \quad (14)$$

where  $\delta$  is the film thickness and  $D_i$  is the component diffusivity, which may be evaluated by an appropriate method. Using the Fuller equation [3] to describe  $D_i$

$$D_i = \frac{0.00143 T^{1.75}}{P [2M_1 M_2 / (M_1 + M_2)]^{1/2} [v_1^{1/3} + v_2^{1/3}]^2} \quad (15)$$

where  $M_1$  and  $M_2$  are the molecular weights of the sample and nitrogen respectively and  $v_1$  and  $v_2$  are their respective molecular volumes. The gas phase in principle comprises sample vapors, nitrogen and decomposition product, and thus forms a multicomponent mixture. In some situations (where component mobilities are widely different), the binary form of diffusion implied in the above equation may not be valid due to diffusion interactions [4]. However, it is expected that these interactions will be of second order in magnitude and were not considered here.

If  $D_i$  at any pressure and temperature is expressed as a product of a reference value  $D_{i0}$  (evaluated at  $T_o$  and  $P_o$ ) and a correction term  $\phi$ , (dependent on temperature and pressure) then Eq. (14) becomes

$$k_g = \frac{D_{i0}}{\delta} \left[ \left( \frac{P_o}{P} \right) \left( \frac{T}{T_o} \right)^{1.75} \right] \quad (16)$$

$$= k_{g0} \phi \quad (17)$$

It may be noted that transfer of vapor from the interface to the bulk may also take place due to phenomena such as natural convection (since the vapor that issues from the liquid phase is at a higher temperature than the gas phase). If such effects are relatively insensitive to temperature and pressure changes in the region of interest, the quantity  $k_{g0}$  may be considered as a constant parameter to be evaluated independently from the heat flux data obtained under conditions where decomposition is not important. For

such a situation, Eqs. (8) and (12) reduce to

$$\frac{dP_i}{dt} = \left[ \frac{ZRT}{V_g} \right] \left[ A_\alpha N_i \left( 1 - \frac{P_i}{P} \right) \right] \quad (18)$$

$$\frac{d}{dt} [Q] = C_{pi} W_i \beta + \lambda A_\alpha k_g [f_l - f_g] \quad (19)$$

As mentioned earlier, the objective of this paper is to suggest a way to account independently for heat effects due to vaporization. Thus, if  $k_{go}$  is determined from a set of DSC data obtained for a particular pressure and temperature range, the same value may then be used to evaluate vaporization effects at any other condition.

The model discussed cannot take into account effects such as bubble nucleation which becomes important as the boiling point is approached. The interface is then disturbed due to nucleation and the effective mass transfer area would be greater than the cross sectional area. It is difficult to determine the surface generation in these conditions and therefore the present set of equations are valid upto a temperature sufficiently below the boiling point. However this is not a serious handicap because experiments will be carried out at high pressures such that the decomposition temperature is well below the boiling point at the corresponding pressure.

### 3. Results and discussion

Pressure DSC experiments were conducted in a high-pressure differential scanning calorimeter (DSC Dupont Thermal Analysis System – 2000) with water (spectroscopic grade). Four sets of experiments at different pressures (1, 6.7, 10 and 50 atm) were conducted. In each set of experiments (at a particular pressure), three different heating rates (5, 10 and 20°C min<sup>-1</sup>) were selected. All experiments were carried out between the temperature limits of 27°C and the corresponding boiling point of the sample. Since water does not decompose, the gas phase was assumed to be a binary mixture of nitrogen and water vapor. Vapor and liquid phase fugacities were calculated using the Peng Robinson equation [3] of state

$$f_{gi} = [Z_v - 1] - \ln[Z_v - B] - \frac{A}{2\sqrt{2}B} \ln \left[ \frac{Z_v + (1 + \sqrt{2})B}{Z_v + (1 - \sqrt{2})B} \right] \quad (20)$$

$$f_{li} = f_{gi}(T, P_i^{\text{sat}}) \exp[V(P - P_i^{\text{sat}})/RT] \quad (21)$$

where  $Z_v$  is the compressibility factor of the gas mixture,  $V$  is the liquid molar volume of the sample,  $P_i^{\text{sat}}$  is the vapor pressure of the sample, and  $A$  and  $B$  are related to the equation of state (EOS) parameters of the component ( $a_i$  and  $b_i$ ) as per Eqs. (22)–(25)

$$A = \frac{aP}{(RT)^2} \quad (22)$$

$$B = \frac{bP}{RT} \quad (23)$$

$$a = y_1^2 a_1 + 2y_1 y_2 \sqrt{a_1 a_2} [1 - k_{12}] + y_2^2 a_2 \quad (24)$$

$$b = y_1 b_1 + y_2 b_2 \quad (25)$$

where  $y_i$  is the mole fraction of the  $i^{\text{th}}$  component in the gas phase and  $k_{12}$  the interaction parameter. As a first approximation,  $k_{12}$  was set to zero and this was not expected to result in significant change in the thermodynamic values [3]. The EOS parameters  $a_i$  and  $b_i$  are calculated in turn from the critical data by the following equations [3]

$$a_i = \frac{0.45724 [RT_c]^2}{P_{ci}} [1 + f_{wi} (1 - \sqrt{T_{ri}})]^2 \quad (26)$$

$$b_i = \frac{0.07780 RT_{ci}}{P_{ci}} \quad (27)$$

with

$$f_{wi} = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (28)$$

The heat of vaporization  $\lambda$  is estimated using the Pitzer acentric factor correlation [3]

$$\lambda = Rt_c [7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456}] \quad (29)$$

The vapor pressure of water was estimated using the following equation [3]

$$\ln \left[ \frac{P_i^{\text{sat}}}{P} \right] = \frac{c_1 x + c_2 x^{1.5} + c_3 x^3 + c_4 x^6}{(1 - x)} \quad (30)$$

where

$$x = 1 - T_r$$

Liquid molar volumes at different temperatures were estimated by the Hankinson Brobst Thomson method [3]

$$V = V_{ro} [1 - \omega V_{ri}] V_c \quad (31)$$

where

$$V_{ro} = 1 + c_5(1 - T_r)^{1/3} + c_6(1 - T_r)^{2/3} + c_7(1 - T_r) + c_8(1 - T_r)^{4/3} \quad (32)$$

and

$$V_{ri} = \frac{c_9 + c_{10} T_r + c_{11} T_r^2 + c_{12} T_r^3}{1 - T_r} \quad (33)$$

Values of the component critical properties are given in Table 1. The constants  $c_1 - c_{12}$  are obtained from the literature [3] and are given in Table 2. As mentioned earlier,  $k_{go}$  ( $= 3.1 \times 10^{-3} \text{ cm s}^{-1}$  at  $T_o = 30^\circ\text{C}$ ,  $P_o = 6.7 \text{ bar}$ ) was obtained by regressing the

Table 1  
Component properties

Property	Water	Nitrogen
Tc (K)	647.3	126.2
Pc (bar)	221.0	33.9
Vc (cc/mol)	57.1	89.8
$\omega$	0.344	0.039

Table 2  
Constants for Physical Property Evaluation of Water

Property	Constants used			
Vapour pressure	$c_1 = -7.7645$	$c_2 = 1.4583$	$c_3 = -2.7758$	$c_4 = -1.2330$
Liquid Molar	$c_5 = -1.5282$	$c_6 = 1.4391$	$c_7 = -0.8145$	$c_8 = 0.1905$
Volume	$c_9 = -0.2961$	$c_{10} = 0.3869$	$c_{11} = -0.0427$	$c_{12} = -0.0481$

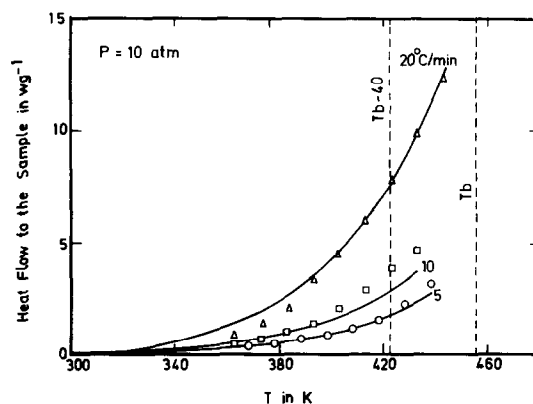


Fig. 1. Heat flow ( $\text{Wg}^{-1}$ ) to the sample vs. temperature (K) at a pressure of 6.7 atmospheres.

heat flow data obtained at 6.7 atm; the results are shown in Fig. 1. From the figure it may be seen that the model satisfactorily (avg. error = 4.5%) calculates heat flow data for all three heating rates up to  $130^\circ\text{C}$ , which is about  $40^\circ\text{C}$  below the corresponding boiling point of the water ( $170^\circ\text{C}$ ). However, above this value, the model underestimates (error = 15%) the heat flow values; the reasons for this were discussed earlier. The value of  $k_{\text{go}}$  obtained earlier ( $3.1 \times 10^{-3}$ ) was then used to predict heat flow profiles for the remaining set of experiments and the results are shown in Figs. 2 and 3. It may be observed from the figures that the model predictions are in good agreement (error < 10%) with the observed data in all cases upto  $T_b - 40$ .



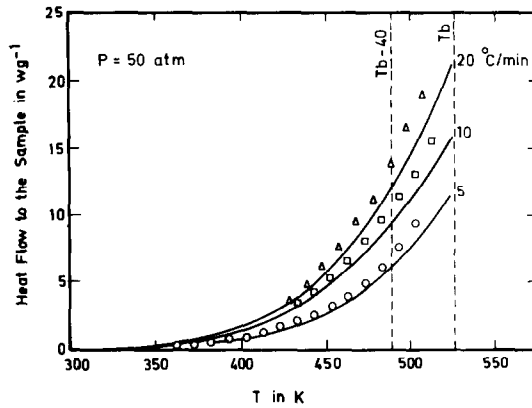


Fig. 2. Heat flow ( $\text{Wg}^{-1}$ ) to the sample vs. temperature (K) at a pressure of 10.0 atmospheres.

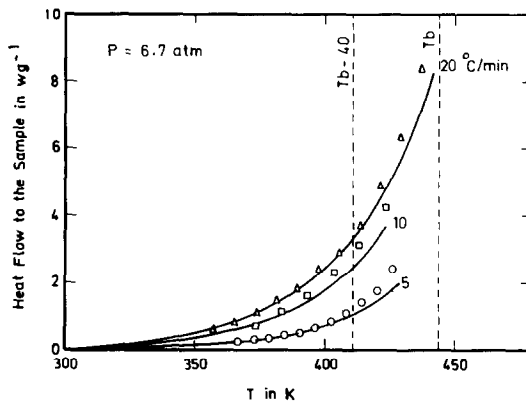


Fig. 3. Heat flow ( $\text{Wg}^{-1}$ ) to the sample vs. temperature (K) at a pressure of 50.0 atmospheres.

Thus, with a decomposable sample, it is possible to evaluate  $k_{go}$  independently from the data obtained at a relatively low pressure (under conditions where decomposition is unimportant), and to employ this value along with the model equations to obtain the decomposition parameters from data at high pressures. This work is presently in progress in our thermochemical laboratory.

#### 4. Conclusions

A model is proposed to calculate the HPDSC heat flow data while taking into account the heat liberation due to decomposition as well as the simultaneous heat absorption by vaporization. Furthermore, it is shown that a single mass transfer parameter explains vaporization effects over a wide pressure range.

### **Acknowledgements**

The authors thank Dr. K.V. Raghavan, Director CLRI, for his kind permission to publish this paper. The authors also thank Ms. S. Srilatha for technical assistance rendered in carrying out the HPDSC experiments.

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