

Problems arise with the left-hand side of this equation, i.e. the temperature integral

$$F(T) = A \int_{T_0}^T L(T) \exp(-E/RT) dT \quad (5)$$

due to the unknown form of $L(T)$.

The simplest case is to presume $L(T) = a_0$, which means a linear heating programme, but then $F(T)$ will be expressed by an asymptotic series [5] and the result will always be approximate [5,6]. This is one of the reasons for the search for non-linear programmes.

The second reason is that, during an experiment, some endothermic and/or exothermic effects of the studied reaction cause deviation from linearity of the $T(t)$ graph, and the mathematical model has to represent them. We discuss here two of the ways to obtain $F(T)$.

(a) Assuming temperature programmes of the general form [7]

$$L(T) = \frac{1}{T^2} \sum_i b_i T^i \quad (6)$$

The problem, in this form, was studied by Smutek for thermal desorption. From eqn. (6) he gets, by integration

$$\Delta t = b_1 \ln \frac{T}{T_0} + \sum_{i \neq 1}^z \frac{b_i}{i-1} \Delta T^{i-1} \quad (7)$$

where $\Delta t = t - t_0$ and $\Delta T^k = T^k - T_0^k$ and also obtains $F(T)$ for the general heating regime

$$F(T) = \frac{A}{T} \sum_i^z b_i T^i \left[E_{i(x)} - \left(\frac{T_0}{T} \right)^{i-1} E_{i(x_0)} \right] \quad (8)$$

where

$$E_{i(x)} = \int_1^{\infty} t^{-i} e^{-xt} dt \quad \text{and} \quad x = E/RT.$$

For positive integer values of i and large values of x , $E_{i(x)}$ becomes

$$E_{0(x)} = \frac{e^{-x}}{x}$$

which allows us to write the exact solution of $F(T)$ in the form

$$F(T) = A \frac{R}{E} \sum_i^z b_i T^{i-1} \exp(-E/RT) \quad (9)$$

(b) By generalization of a method earlier described by Marcu and Segal [2]

$$F(T) = A \sum_i^z a_i T^i \exp(-E/RT) \quad (10)$$

This method selects from the beginning the solutions which fulfil the

condition of solving exactly eqn. (5).

Noting

$$l(T) = \sum_i^z a_i T^i \quad (11)$$

$$F(T) = \int_{T_0}^T L(T) \exp(-E/RT) dT = Al(T) \exp(-E/RT)$$

which, by derivation and substituting eqn. (4) for $L(T)$ leads to

$$dt = \left(l' + \frac{E}{RT^2} l \right) dT \quad (12)$$

The integration of eqn. (12) using eqn. (11) give us the heating programmes as follows.

$$\Delta t = a_1 \left(\Delta T + \frac{E}{R} \ln \frac{T}{T_0} \right) + \sum_{i \neq 1}^z a_i \Delta T^{i-1} \left(\frac{E}{R} \cdot \frac{1}{i-1} + \Delta T \right) \quad (13)$$

Comparing eqn. (7) with eqn. (13), it is obvious that for small ΔT and $a_i(E/R) = b_i$ the two equations give the same solution.

With these results eqn. (1b) becomes

$$A \sum_i^z a_i T^i \exp(-E/RT) = \begin{cases} \frac{1 - (1 - \alpha)^{1-n}}{1 - n} & \text{for } n \neq 1 \\ -\ln(1 - \alpha) & \text{for } n = 1 \end{cases} \quad (1c)$$

which allows kinetic parameters to be determined.

Using equation (1c) for $z = 1$, the kinetic parameters of $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$ dehydration were determined. The results ($n = 0.95$; $E = 24.5 \text{ kcal mole}^{-1}$; $A = 10^6 \text{ sec}^{-1}$) are in good agreement with those found in the literature [1].

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Note

DIFFERENCES BETWEEN EQUILIBRIUM PHASE TRANSFORMATION ENERGIES AT LIQUID \rightleftharpoons SOLID TRANSITION TEMPERATURES IN SATURATED POROUS MATERIALS

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High resolution DSC curves [1] monitoring reversible liquid \rightleftharpoons solid phase transformations within saturated porous materials occur over temperature ranges, the magnitudes of which depend upon the pore size distribution (PSD) within a particular sample [1–3]. Recent developments in design and modification of commercially available heat flow scanning microcalorimeters permit accurate quantification of the energy liberated or absorbed when liquids or solids change phase within an accurately known temperature interval. Thus with suitable experimental design such DSC curves (which are considered to be envelopes corresponding to the summation of energy signals associated with phase transformations occurring over large temperature intervals) may be analyzed in differential elements [1,2].

The lowering of phase transformation temperatures of adsorbates becomes more pronounced as pore size becomes smaller, as predicted by capillary condensation theory [5,6]. Experiment has shown that lowering of equilibrium phase transformation temperature may be empirically related to pore size [2,7,8], and thus low temperature DSC curves may be used to determine wet PSD and the energy associated with phase transformations in pores of a particular size.

Everett and Haynes [9] have noted that during a cooling and heating cycle a graph of the amount of solid present against temperature could show a hysteresis loop similar to that obtained in a drainage/wetting cycle. There will be hysteresis between freezing and melting temperatures within porous materials if interfacial curvatures during freezing and fusion are different [8, 9].

Ultrasonic measurements in concrete of various compositions and degrees of saturation have shown ice content hysteresis during freezing and thawing [10]. Many other experimental data have also been published which show the presence of hysteresis between freezing and melting temperatures of water and ice in saturated porous materials (e.g. refs. 11 and 12). Providing suitable precautions are taken to avoid supercooling of water in pores [13], high resolution low temperature DSC may be used as a sensitive and power-

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ful tool to investigate freezing/melting temperature hysteresis. Recently, a theory has been developed for the influence of pore form on the equilibrium freezing and melting temperatures of water in porous materials [8]. This theory is supported by calorimetry which used the hysteresis between freezing and melting temperatures for water in two clays and never-dried polyacrylonitrile fibres. Theoretical curves (analogous to de Boer's [14] nitrogen isotherm shape groups) have been presented to permit pore form to be assessed in water saturated porous materials containing pores which are either cylindrical, wedge shaped, slot shaped or lying between parallel planes (or combinations of these forms) [8].

In this short note the author wishes to draw particular attention to a conclusion which does not appear to have been mentioned before in relation to experimental determination of phase transformation energy of liquids or solids within porous substances; namely, that when hysteresis exists between equilibrium freezing and melting temperatures of liquids or solids in saturated porous materials, the energy liberated when unit mass of liquid freezes in a saturated pore is not the same as the energy required to melt unit mass of solid in the same pore.

To illustrate the magnitude of the difference between phase transformation energies during freezing and melting we shall assume that water saturates a rigid porous region and that contraction of pore ice during melting results in melting of ice adjacent to the mouth of a pore (the ice expelled during freezing of the pore water) which then re-enters the pore space as liquid water. Support for this assumption may be found in X-ray diffraction data obtained from studying migration of interlamellar water during freezing and thawing wet bentonites [15], and in calorimetric data measuring porosity and PSD in water saturated kaolinites [4].

ANALYSIS

Let us consider a theoretical closed system involving only one pore filled with a mass, M , of water and surrounded by free water. Let the equivalent radius [16–18] of the pore be of such dimensions that equilibrium freezing of the pore water occurs at a temperature T_f (Kelvin), and let the energy associated with this phase transformation at T_f be L_f energy units. The forces associated with the volume change accompanying the water \rightarrow ice phase transformation are assumed to be dissipated by plastic flow of ice [9,19] as this seems to be a reasonable interpretation of experimental data [1–4,8,21].

Let T_f be the temperature at which water \rightleftharpoons ice phase transformations take place when hysteresis is absent, and let T_m be the temperature at which ice in the pore melts when temperature hysteresis between freezing and melting does exist. We shall assume that when no hysteresis exists between freezing and melting temperatures, the magnitude of the amount of energy evolved during equilibrium freezing of unit mass of water in the pore is the same as the magnitude of the heat absorbed to melt unit mass of ice in the same pore.

Let $C_w(T)$ and $C_i(T)$ refer to the specific heats at constant pressure of

water or ice in the pore, respectively. Because the process is reversible, the amount of heat exchanged when cooling from, say, 280 to 200 K, is equal to the magnitude of the amount of heat absorbed when the system is warmed from 200 to 280 K. For the case where no temperature hysteresis occurs, the amount of energy, $E_{200}^{280}(f)$, absorbed during warming unit mass of pore ice through its melting point to 280 K is

$$E_{200}^{280}(f) = \int_{200}^{T_f} C_i dT + L_f + \int_{T_f}^{280} C_w dT \quad (1)$$

and $E_{200}^{280}(f)$ is equal in magnitude to the amount of heat exchanged during cooling of the system from 280 to 200 K when $T_f = T_m$.

When hysteresis between freezing and melting temperatures occurs, the amount of heat absorbed during warming over the same temperature range is $E_{200}^{280}(m)$, and

$$E_{200}^{280}(m) = \int_{200}^{T_m} C_i dT + L_m + \int_{T_m}^{280} C_w dT \quad (2)$$

When $T_f \neq T_m$, the difference, $(|L_f| - |L_m|)$, between the magnitudes of the amount of heat liberated during equilibrium freezing and the amount of energy absorbed during equilibrium melting of unit mass of water or ice in the pore may be obtained from eqns. (1) and (2)

$$(|L_m| - |L_f|) = \int_{T_m}^{T_f} C_i dT + \int_{T_f}^{T_m} C_w dT = \int_{T_f}^{T_m} (C_w - C_i) dT \quad (3)$$

Experience in subjecting a wide variety of water saturated porous materials to freezing and thawing cycles shows that the equilibrium lowering of freezing temperature is apparently always larger than or equal to the equilibrium lowering of melting temperature, i.e. $T_f \leq T_m$. Making the reasonable assumption that the specific heat of pore water is greater than that of pore ice, ($C_w > C_i$), eqn. (3) shows that $|L_m| > |L_f|$ when $T_f < T_m$. In other words, more energy is absorbed when unit mass of ice melts at its melting point than the energy evolved when unit mass of water freezes (in the same pore) at its equilibrium freezing point when $T_f < T_m$.

Experiments with an illite [2] have shown that the lowest temperature for equilibrium freezing of pore water may be as low as 229.7 K, and theoretical considerations show that the ratio between the equilibrium freezing and melting temperatures of water or ice may be as large as 2 in certain pore forms [2]. Equation (3) shows that for small pores of a particular form [8], the difference in magnitude between L_m and L_f could be large enough to quantify using calorimetric investigations. If static calorimetry were used to measure L_f or L_m of the pore water or ice at the transformation temperatures, an approximate value of $(C_w - C_i)$ in eqn. (3) could be obtained. However, if scanning calorimetry were used to monitor the phase transformation energies, the area under the exothermic curve would be the same as the

area under the endothermic curve if a large temperature interval were chosen to define the baseline position, because the areas under the DSC curves are directly proportional (for a constant calibration function) to $\int M_s C_s dT$, where M_s is the mass and C_s is the specific heat of the entire sample. Therefore DSC curves may be used to determine phase transition temperatures [20], porosity, pore form and PSD within rigid [4], swollen [3], swelling [21], mineral [4,21] or organic [1–3] water saturated porous materials, as long as the baselines of the DSC curves are correctly constructed.

For the general case where we consider volume changes accompanying water \rightleftharpoons ice phase transformations within porous materials, an additional term may be added to the right-hand side of eqn. (3) to account for a mass, ΔM_i , of ice extruded from the pore to dissipate forces arising from the volume increase of water on freezing. If we assume that a mass of water ΔM_w migrates into the pore during melting of pore ice and that $\Delta M_i = \Delta M_w$ and that the work done during movement of ice out of the pore during freezing is equal to the work done by water moving into the pore during melting of pore ice, then the additional term to add to eqn. (3) is

$$\int_{T_f}^{T_m} \Delta M_w (C_i - C_{fi}) dT \quad (4)$$

where, M is the mass of pore water freezing and where C_{fi} is the specific heat of free ice. Writing $\Delta M_w \simeq 0.1 M$, and $C_i \simeq C_{fi}$, the contribution to eqn. (3) from eqn. (4) (with $M = 1$) would be almost negligible. A similar analysis applies mutatis mutandis when discussing the effect of temperature hysteresis on freezing and melting phase transformation energies for liquids which contract upon freezing (e.g. benzene).

SUMMARY

When hysteresis exists between the equilibrium temperature lowerings for freezing and melting of liquids or solids filling pores (in the absence of a vapour phase within the pores), the energy liberated during freezing of unit mass of pore liquid at its equilibrium freezing temperature is not the same as the magnitude of the energy required to melt unit mass of pore solid at its equilibrium melting temperature. The difference between the magnitudes of the two energy values (for a given ratio between the equilibrium temperature lowerings for freezing and melting) becomes more pronounced as the pore size diminishes.

Calorimetric data obtained after monitoring phase transformations of adsorbates within porous materials could differ, depending upon whether static or dynamic (DSC) calorimetric techniques were used to obtain the experimental data.

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