ENTHALPY AND PHASE RELATIONS AT MELTING IN HETEROGENEOUS SYSTEMS

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Received 7. 3. 1978

Equations for the calculation of enthalpy of eutectic and peritectic (incongruent) melting in multicomponent systems were derived on the basis of relations between enthalpy (and heat capacity) and phase (and chemical) composition of heterogeneous systems. In the derivation use was made of supplementary quantities related to the reference state represented by a heterogeneous mixture of molten pure components and to a model of regular melt behaviour. The relationship was further analysed between heat flux and the rate of melting during the heating up of a heterogeneous system; the model of sample with non-uniform temperature distribution has been suggested for the purpose of calculating the "equilibrium" curve of dynamic calorimetry from a known phase diagram.

INTRODUCTION

Dynamic calorimetry methods (including differential thermal analysis—DTA [1], [2], [3]) represent a valuable source of information on the behaviour of solids. Experimental results of these methods are usually the most readily available source of data on temperatures and enthalpies of melting and phase transformation processes. The rules for interpretation of experimental curves obtained by these methods have for the most part been derived from the laws of equilibrium (and kinetic) behaviour of one-component systems, which offer only limited application in the case of multicomponent systems. Study of these systems is of considerable significance for a number of manufacturing technologies, in particular in the fields of silicates and metallurgy.

The present study had the aim of analysing the results of the rules of equilibrium behaviour of multicomponent systems with respect to the character of enthalpic changes taking place during the heating up of a sample, and of deriving quantitative relationships which would allow the data on enthalpies of eutectic and incongruent melting to be utilized in calculations of phase diagrams [4] and of comparing the course of experimental curves obtained by dynamic calorimetry with the equilibrium behaviour of multicomponent heterogeneous systems.

ANALYSIS

Heterogeneous system and phase composition

A heterogeneous mixture containing as a whole n_i^i moles of individual components i is described by total chemical composition by means of total molar fractions X_i^i

$$X_{i}^{t} \equiv n_{i}^{t}/n_{t}; \qquad n_{t} \equiv \sum_{i=1}^{N} n_{i}^{t}; \qquad \sum_{i=1}^{N} X_{i}^{t} = 1,$$
 (1)

(where N is the number of components in the system).

The chemical composition of each of the phases forming the heterogeneous mixture is expressed by means of molar phase fractions X_{\cdot}^{φ}

$$X_i^{arphi} \equiv n_i^{arphi}/n_{arphi}; \qquad n_{arphi} \equiv \sum_{i=1}^N n_i^{arphi}; \qquad \sum_{i=1}^N X_i^{arphi} \equiv 1,$$
 (2)

where n_i^{φ} is the number of moles of component *i* contained in phase φ .

In addition to this the phase composition of a heterogeneous system may be conveniently described by means of *phase fractions* ξ_{φ}

$$\xi_{\varphi} \equiv n_{\varphi}/n_t; \qquad \sum_{\varphi=1}^P \xi_{\varphi} = 1,$$
 (3)

(where P is the number of phases in the system).

By combining the definition equations [1], [2], [3] one finds that the following system of equations holds for the given three types of fractions:

$$X_i^t = \sum_{\varphi=1}^P \xi_\varphi X_i^\varphi.$$
⁽⁴⁾

This represents the general lever rule from which it is possible to derive further relations, e.g. that from the two-phase region (phases α and β) of the N-component system by equation

$$\xi_{\alpha} = (X_i^t - X_i^{\beta}) / (X_i^{\alpha} - X_i^{\beta}), \tag{5}$$

$$X_j^{\beta} = [X_j^{\ell}(X_i^{\alpha} - X_i^{\beta}) - X_j^{\alpha}(X_i^{\ell} - X_i^{\beta})]/(X_i^{\alpha} - X_i^{\ell}).$$
(6)

In a heterogeneous closed system there may arise three types of equilibrium changes in relations to temperature. The continuous changes reflect the temperature dependence of components in the individual phases, the break changes arising as a result of at least one of the phases in the system beeing eliminated or created, and finally the step changes corresponding to the equilibrium situation where at least one of the phases of the original system is eliminated and simultaneously at least one new phase is formed. From the point of view of the Ehrenfest's classification of phase transformations in one-component systems the step changes (including for instance eutectic and incongruent melting) are related to the first order transitions whereas the break changes (e.g. attainment of the liquidus temperature) are similar to the second order transitions.

Enthalpy and thermal capacity of phases

Let molar enthalpy H_m^{φ} of phase φ be defined as a ratio of total enthalpy of this phase H_{φ} to the material amount of this phase n_{φ}

$$H_m^{\varphi} = H_{\varphi}/n_{\varphi}.$$
(7)

When calculating the enthalpy changes one need not necessarily know the absolute enthalpy values. When studying the melting processes it is convenient to operate with supplementary molar enthalpy^{*}) which is the difference between the actual state enthalpy and the reference state one, the latter being taken as a hypothetical heterogeneous mixture of molten pure components (i) at the given temperature.

The supplementary enthalpy value of any molten pure component at an arbitrary temperature (therefore even at temperatures lower than the melting one of the component) is equal to zero

$$H_{m,1}^{L}(T_{1}) = H_{m,1}^{L}(T_{2}) = H_{m,2}^{L}(T_{1}) = \dots = H_{m,N}^{L} = 0.$$
(8)

In view of the standard state chosen the supplementary molar enthalpy of a homogeneous melt is equal to its mixing enthalpy. If the melt constitution and the choice of the components [4] comply with the condition for application of the regular behaviour model, then the supplementary molar enthalpy of the melt H_m^L may be expressed as a function of its chemical composition (X_i^L) in the form

$$H_m^L(X_z^L) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N X_i^L X_j^L \mathcal{Q}_{ij}, \qquad (9)$$

where Ω_{ij} designates the quantities called interaction parameters.

Partial derivative of supplementary molar melt enthalpy with respect to temperature (supplementary molar heat capacity C_m^L) is equal to zero with respect to the standard state chosen when assuming that the Ω_{ij} interaction parameters are temperature-independent:

$$C_m^L \equiv (\partial H_m^L / \partial T)_{X_i^L} = 0.$$
⁽¹⁰⁾

In the determination of supplementary molar enthalpies of *solid phases* let us make use of the fact that enthalpy of congruent melting of a given phase ΔH_{φ}^{M} is the difference between the enthalpy of the melt the composition of which is identical with that of solid phase X_{φ}^{φ} and the required solid phase enthalpy H_{m}^{φ}

$$H_m^{\varphi} = H_m^L(X_i^{\varphi}) - \Delta H_{\varphi}^M. \tag{11}$$

The value of this quantity may also be obtained from the data on the enthalpy of combination ΔH_{φ}^{F} of the given phase from pure solid components and from the data of congruent melting enthalpies ΔH_{i}^{M} of these components:

$$H_m^{\varphi} = \Delta H_{\varphi}^F - \sum_{i=1}^N X_i^{\varphi} \cdot \Delta H_i^M.$$
(12)

Supplementary molar heat capacity of solid phases C_m^{φ} is found to be identical (with respect to [11] and [10]) with the negative value of the change in thermal capacity at congruent melting ΔC_m^M

$$C_{m}^{\varphi} = \frac{\partial H_{m}^{\varphi}}{\partial T} = -\frac{\mathrm{d} \Delta H_{\varphi}^{M}}{\mathrm{d}T} \equiv -\Delta C_{\varphi}^{M}.$$
(13)

This quantity may be used in a short Taylor's series for expressing the temperature dependence of congruent melting enthalpy

^{*)} The supplementary quantities have been introduced for instance in chemical thermodynamics of gaseous mixtures [5]. In view of the character of these quantities those introduced in the present study may be regarded as a certain extension of conception of homogeneous supplementary quantities applied to heterogeneous systems. The supplementary quantities should be distinguished from the excess ones for which an ideal homogeneous mixture is the reference state.

$$\Delta H^M_{\varphi}(T) = \Delta H^M_{\varphi}(T^M_{\varphi}) + (T - T^M_{\varphi}) \,\Delta C^M_{\varphi},\tag{14}$$

in which T_{a}^{M} designates the temperature of congruent melting.

The temperature dependence of the quantities in equation (12) may be expressed similarly. For the enthalpy of formation we may write

$$\Delta H^F_{\varphi}(T) = \Delta H^F_{\varphi}(T_0) + (T - T_0) \,\Delta C^F_{\varphi},\tag{15}$$

where ΔC_{σ}^{F} is the change in thermal capacity in the formation reaction

$${}_{i}^{L}\Delta C_{\varphi}^{F} = -\Delta C_{\varphi}^{M} + \sum X_{i}^{\varphi} \Delta C_{i}^{M},$$
⁽¹⁶⁾

(where ΔC_i^M are the changes in thermal capacities due to melting of pure components).

The supplementary molar capacity may be determined from molar heats C_p of the individual phases (insofar as they are available):

$$C_m^{\varphi} = C_p^{\varphi} - \sum X_i^{\varphi} C_{p,i}^L.$$
⁽¹⁷⁾

The data on molar enthalpies H_0 related to the usual standard state may likewise be used for expressing the supplementary enthalpies,

$$H^{\varphi}_{m}(T) = H^{\varphi}_{0}(T_{0}) - \sum X^{\varphi}_{0} H^{\varphi}_{0,i}(T_{0}) + \int_{T_{0}}^{T} C^{\varphi}_{m}(T) \, \mathrm{d}T.$$
(18)

APPLICATION

Enthalpy of a heterogeneous mixture

Supplementary molar enthalpy H_m^t of a heterogeneous system containing P phases is equal to the sum

$$H_m^t = \sum_{q=1}^{P} \xi_{\varphi} H_m^{\varphi}.$$
⁽¹⁹⁾

The course of temperature dependence of enthalpy of an equilibrium mixture can therefore be determined when temperature dependence of the phase fractions (phase diagram) and the enthalpy values of the individual phases are known. For example the enthalpy value of the system comprising a solid phase of constant composition (φ) and a melt (L) may be determined for an arbitrary temperature using the equation

$$H_{m}^{t}(T) = \frac{X_{i}^{t} - X_{i}^{L}(T)}{X_{i}^{\varphi} - X_{i}^{L}(T)} \left[H_{m}^{L}(X_{i}^{\varphi}) - \Delta H_{\varphi}^{M}\right] + \frac{X_{i}^{\varphi} - X_{i}^{L}}{X_{i}^{\varphi} - X_{i}^{L}(T)} H_{m}^{L}[X_{i}^{L}(T)], \quad (20)$$

into which the value on the liquidus curve corresponding to temperature T is substituted for X_{τ}^{L} .

Partial derivative of supplementary mixture enthalpy with respect to temperature is further on called supplementary molar heat capacity of mixture at constant phase composition and designated by the symbol C_m^t .

From equation (19) it follows that

$$C_m^t \equiv (\partial H_m^t / \partial T)_{\xi\varphi} = \sum_{\varphi} \xi_{\varphi} C_m^{\varphi}.$$
 (21)

Molar heat of C_n^t of such a mixture (at constant phase composition) can be determined

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by adding molar heats of pure component melts $(C_{p,i}^L)$ to the supplementary quantity or directly from molar heats of the individual phases (C_p^{\bullet})

$$C_{p}^{t} = C_{m}^{t} + \sum_{i} X_{i}^{t} C_{p,i}^{L} = \sum_{\varphi} \xi_{\varphi} C_{p}^{\varphi}.$$
 (22)

The slope of the temperature dependence of supplementary enthalpy for an equilibrium mixture containing $(P-1) \leq (N-1)$ of solid phases of fixed composition and a melt of variable composition can be determined from the total derivative

$$\frac{\mathrm{d}H_m^t}{\mathrm{d}T} = C_m^t + \sum_{i=1}^{P-1} \frac{\partial H_m^t}{\partial X_i^L} \frac{\mathrm{d}X_i^L}{\mathrm{d}T},\tag{23}$$

where for partial derivatives on the right-hand side one obtains

$$\frac{\partial H_m^t}{\partial X_t^L} = H_m^L \frac{\partial \xi_L}{\partial X_i^L} + \xi_L \left[\frac{\partial H_m^L}{\partial X_t^L} + \sum_{j=P}^{N-1} \frac{\partial H_m^L}{\partial X_j^L} \frac{d X^L}{d X_i^L} \right] + \sum_{\varphi \neq L} H_m^{\varphi} \frac{\partial \xi^{\varphi}}{\partial X_i^L}, \qquad (24)$$

where ξ_L is the melt phase fraction.

In the last equation derivative H_m^L is determined from the respective model (e.g. (9)), the derivative of phase fractions from the expressions for phase fractions (e.g. (5)), which are determined by solving the system (4) and in a similar way derivative dX_i^L/dX_i^L is determined [for instance by means of equation (6)]. For a mixture of solid phase φ of constant composition with melt (L) with regular behaviour one finds (in a binary system) that the equilibrium slope of temperature dependence of enthalpy, with respect to (9), (23) and (24) is given by the expression

$$\frac{\mathrm{d}H_{m}^{t}}{\mathrm{d}T} = -\frac{X_{2}^{t} - X_{2}^{L}}{X_{2}^{\varphi} - X_{2}^{L}} \Delta C_{\varphi}^{M} + \frac{X_{2}^{\varphi} - X_{2}^{t}}{(X_{2}^{\varphi} - X_{2}^{L})^{2}} \left[X_{2}^{\varphi} X_{2}^{L} \Omega \left(X_{2}^{L} + \frac{X_{2}^{\varphi}}{X_{2}^{L}} - 2 \right) + \Delta H_{\varphi}^{M} \right] \frac{\mathrm{d}X_{2}^{L}}{\mathrm{d}T}$$
(25)

At liquidus temperature ($T = T_L$, $X_L^L = X_L^t$) the slope of the enthalpy on temperature dependence undergoes a step change the quantity of which may be expressed by the following equation for the given system of phase φ and melt L:

$$\Delta \left(\frac{\mathrm{d}H_{m}^{t}}{\mathrm{d}T}\right) = \frac{X_{2}^{\varphi}X_{2}^{t}Q(X_{2}^{t}-2+X_{2}^{\varphi}/X_{2}^{L}) + \Delta H_{\varphi}^{M}}{X_{2}^{\varphi}-X_{2}^{t}} \cdot \left(\frac{\mathrm{d}X_{2}^{L}}{\mathrm{d}T}\right)_{T-T_{L}}$$
(26)

in which (dX_2^L/dT) is the reciprocal value of tangent line slope at point $X_2 = X_2^t$ of the liquidus curve (in phase diagram T vs. X_2).

Enthalpy at an invariant process

In a closed system $(X_i^t = \text{const.})$ containing (N + 1) phases of fixed composition $(X_i^{\varphi} = \text{const.})$ all the changes are only those in molar fractions. However, in view of (3) these changes are bound by the condition

$$\mathrm{d}\xi_{\psi} = -\sum_{\varphi \neq \psi} \mathrm{d}\xi_{\varphi}. \tag{27}$$

Moreover, as the phase fractions are bound to the molar fractions by a system of N equations (4), the shares of the increments

$$d\xi_{\varphi}/d\xi_{\psi} = \Delta\xi_{\varphi}/\Delta\xi_{\psi} \equiv -\bar{\xi}_{\varphi} = \text{const.}$$
(28)

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have a constant value in a closed system containing phases of fixed composition.

An infinitesimal change in molar enthalpy of such a system is then given by the expression

$$\mathrm{d}H_m^t = H_m^\psi \,\mathrm{d}\xi_\psi - \sum_{\varphi \neq \psi} H_m^\varphi \bar{\xi}_\varphi \,\mathrm{d}\xi_\psi \tag{29}$$

and for integral enthalpic change ΔH_m^t it holds that

$$\Delta H_m^t = (H_m^v - \sum_{\varphi \neq \psi} H_m^{\varphi} \bar{\xi}_{\varphi}) \, \Delta \xi_{\psi}. \tag{30}$$

On the basis of these considerations let us now derive equations for enthalpic changes due to step increment of melt in the system, that is eutectic or incongruent melting. In the course of such melting the system contains (N + 1) phases and it will be assumed that the composition of the phases involved is not subject to any change insofar as at least one of the initial set of phases has not ceased to exist.

Eutectic melting

Let us consider an equilibrium mixture of N solid phases of N-component system the total composition of which is identical with that of eutectic melt $X_i^t = X_i^E$. Phase fractions ξ_{φ}^* of this *eutectic mixture* can be determined from the system of equations (4)

$$X_i^F = \sum_{\varphi=1}^N \xi_{\varphi}^* X_i^{\varphi}.$$
(31)

After attaining eutectic temperature T_E all the original phases melt $(\Delta \xi_{\varphi} = -\xi_{\varphi}^*)$ producing a homogeneous melt $(\Delta \xi_L = 1)$.

$$\Delta \xi_{\varphi} = -\xi_{\varphi}^*; \qquad \Delta \xi_L = 1. \tag{32}$$

Using equation (28) we find that for a mixture of N phases contained in an eutectic mixture and a melt of eutectic composition it holds that

$$\bar{\xi}_{\varphi} = \xi_{\varphi}^*. \tag{33}$$

By substituting into the (30) the following equation is obtained for enthalpy of melting ΔH_*^F of eutectic mixture

$$\Delta H^F_* = H^L_m(X^F_i) - \sum \xi^*_{\varphi} H^{\varphi}_m. \tag{34}$$

The change in heat capacity corresponding to melting of eutectic mixture ΔC_*^F is determined from the derivative of enthalpic change ΔH_*^F with respect to temperature

$$\frac{\mathrm{d}\,\Delta H_*^F}{\mathrm{d}T} \equiv \Delta C_*^F = \sum_{\varphi=1}^N \xi_\varphi^* \,.\, \Delta C_\varphi^M. \tag{35}$$

The step change in phase composition at eutectic temperature T_E takes place in all systems containing the same system of phases as the eutectic mixture. Phase fractions ξ_{φ}^{0} of initial mixture of N solid phases are given by the system of equations

$$X_i^t = \sum_{\varphi} \xi_{\varphi}^0 X_i^{\varphi}.$$
(36)

After attaining temperature T_E there arises a mixture containing eutectic melt (having the composition X_i^E) in an amount corresponding to phase fraction ξ_L^E (which

simultaneously represents the increment of melt $\Delta \xi_L^E$ due to eutectic melting) and at least one solid phase (ω) disappears from the initial system in the course of melting. As regards the changes in phase fractions $\Delta \xi_{\varphi}^E$ of solid phases, equations (33) and (28) yield the relation

$$\xi^E_{\varphi} - \xi^0_{\varphi} \equiv \Delta \xi^E_{\varphi} = -\xi^*_{\varphi} \Delta \xi^E_L = -\xi^*_{\varphi} \xi^E_L. \tag{37}$$

The melt phase fraction $\xi_L^E \equiv \Delta \xi_L^E$ is determined from the balance of phase fractions

$$\xi_L^E = (1 - \sum_{\varphi \neq \omega} \xi_{\varphi}^*) / (1 - \sum_{\varphi \neq \omega} \xi_{\varphi}^0), \tag{38}$$

in which the sums do not include the phase fractions of phases ω which have disappeared during eutectic melting. By substituting into (30) and comparing with (34), (molar) enthalpy ΔH_t^E of eutectic melting of a general mixture is given as follows:

$$\Delta H_t^E = \xi_L^E \Delta H_*^E. \tag{39}$$



Fig. 1. Phase diagram and enthalpic quantities; H_m^L — enthalpy of melt, x — molar fractions of component B, ΔH_{φ}^F — formation enthalpies, T^M , ΔH^M — temperatures and enthalpies of congruent melting, T_E , ΔH_{\ast}^E — temperature and enthalpy of melting of cutectic mixture, T_P , H_{\ast}^P — temperature and enthalpy of incongruent melting.

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For enthalpy of melting of a *binary* eutectic mixture, on the basis of equation (34) $(x \equiv X_2)$ it follows

$$\Delta H_*^E = H_m^L(X_E) - \frac{X_E - X_{\psi}}{X_{\varphi} - X_{\psi}} H_m^{\varphi} - \frac{X_{\varphi} - X_E}{X_{\varphi} - X_{\psi}} H_m^{\varphi}.$$
(40)

Peritectic melting

Let us first consider an incongruent phase γ having the composition X_i^{γ} . On attaining peritectic temperature T_P the incongruent phase is completely decomposed $(\Delta \xi_{\gamma}^* = -1)$ producing a peritectic mixture containing peritectic melt (X_i^P) and (N-1) solid phases. Phase fractions ξ_{φ}^* of peritectic mixture are determined from the system of equations

$$X_{i}^{\gamma} = \xi_{L}^{*} X_{i}^{P} + \sum_{\varphi=1}^{N-1} \xi_{\varphi}^{*} X_{i}^{\varphi}.$$
(41)

For enthalpy of incongruent melting ΔH^P_{γ} of phase γ one finds

$$\Delta H_{\gamma}^{P} = \xi_{L}^{*} H_{m}^{L}(X_{i}^{P}) + \sum_{\varphi=1}^{N-1} \xi_{\varphi}^{*} H_{m}^{\varphi} - H_{m}^{\gamma}.$$
(42)

The change in heat capacity ΔC_{γ}^{P} due to incongruent melting is established from the derivative of the enthalpy change with respect to temperature

$$\frac{\mathrm{d}\,\Delta H^P_{\gamma}}{\mathrm{d}T} = \Delta C^P_{\gamma} = \Delta C^M_{\gamma} - \sum_{\varphi=1}^{N-1} \xi^*_{\varphi} \,\Delta C^M_{\varphi}. \tag{43}$$

The step change in phase composition takes place in all heterogeneous systems containing an incongruent phase γ . The initial mixture lacks at least one of the phases of the set comprising a peritectic mixture so that the total number of phases in the initial mixture is at the most N.

The phase fractions of the initial mixture are determined from the system of equations

$$X_{i}^{t} = \xi_{\gamma}^{0} X_{i}^{\gamma} + \sum_{\varphi=1}^{N-1} \xi_{\varphi}^{0} X_{i}^{\varphi}, \tag{44}$$

where X_i^P is substituted for the melt. The procedure employed for eutectic melting can be used for determining the enthalpy of peritectic melting ΔH_t^P

$$\Delta H_t^P = \xi_v^0 \cdot \Delta H_v^P. \tag{45}$$

Enthalpy of incongruent melting of *binary* phase γ can be described according to (42) $(x \equiv X_2)$

$$\Delta H^P_{\gamma} = \Delta H^M_{\gamma} - H^L_m(X_{\gamma}) + \frac{X_{\gamma} - X_{\varphi}}{X_P - X_{\psi}} H^L_m(X_P) + \frac{X_P - X_{\gamma}}{X_P - X_{\psi}} H^{\psi}_m.$$
(46)

Melting and heat flux in the course of heating

In dynamic calorimetry methods the rate of heat exchange between the sample and its environment is measured under conditions of continuous heating. Heat flux \dot{q} from the environment into the sample compensates the increase in sample enthalpy.

When considering a sample one mole in size there holds the equation

$$\hat{Q} (\equiv \dot{q}/n_t) = \mathrm{d}H_0^t/\mathrm{d}\tau, \tag{47}$$

where H_0^t is molar enthalpy of the sample related to standard state and τ is time.

The degree of conversion and the rate of melting

The increase in enthalpy can be divided with advantage to the stage involving an increase (change) in temperature and the state related to a change in phase composition; however, the latter can be characterized by a single parameter only, namely by the conversion degree α .

$$\dot{Q} = \left(\frac{\partial H_0^t}{\partial T}\right)_{\alpha} .. \dot{T} + \left(\frac{\partial H_0^t}{\partial \alpha}\right)_T \dot{\alpha} , \qquad (48)$$

where $\dot{T} = dT/d\tau$, $\dot{\alpha} = d\alpha/d\tau$.

Partial derivative of enthalpy with respect to temperature at constant phase composition is equal to molar heat of mixture C_p^t whereas the derivative of molar enthalpy (related to usual standard state) with respect to the degree of conversion is identical with the derivation of supplementary molar enthalpy. Using (22), equation (48) can be written in the form

$$\dot{Q} = \left(\sum_{i} X_{i}^{t} C_{p,i}^{L} + C_{m}^{L}\right) \dot{T} + \left(\partial H_{m}^{t} / \partial \alpha\right) \dot{\alpha}.$$

$$\tag{49}$$

We have so far not specified the conversion degree of α . When studying melting processes this transformation degree should be chosen advantageously so as to be equal to zero for the system free from melt ($\xi_L = 0$) and to attain unity value for the system containing the melt only ($\xi_L = 1$).

Supplementary enthalpy of the initial state ($\alpha = 0$) is then given by the equation

$$H^t_m(\alpha = 0) = \sum_{\varphi} \xi^0_{\varphi} H^{\varphi}_m, \tag{50}$$

where ξ_{φ}^{0} are phase fractions of solid phases before the onset of melting, and for the final stage (homogeneous melt) by the equation

$$H_m^t(\alpha = 1) = H_m^L(X_i^t).$$
 (51)

For general state of the system $(0 < \alpha < 1)$ the supplementary enthalpy is given by equation

$$H_m^t(0 < \alpha < 1) = \xi_L H_m^L(X_i^L) + \sum \xi_{\varphi} H_m^{\varphi}.$$
(52)

When choosing the conversion degree α it should be advantageous to require that the instantaneous enthalpy value be its linear function.*)

$$H_m^t(0 < \alpha < 1) = \alpha [H_m^t(\alpha = 1) - H_m^t(\alpha = 0)] + H_m^t(\alpha = 0).$$
(53)

Then partial derivative $(\partial H_m^t/\partial \alpha)^T$, further on called summary enthalpy of melting ΔH_{Σ}^M ,

$$(\partial H_m^t/\partial \alpha)_T \equiv \Delta H_{\Sigma}^M = H_m^t(\alpha = 1) - H_m^t(\alpha = 0)$$
(54)

^{*)} The problems of the conversion degree are also dealt with in ref. [6], [7].

is independent of conversion degree α , which in view of its being derived from enthalpic quantities will be called enthalpic advancement of melting (in contrast to actual advancement of melting which is given by the phase fraction ξ_L of melt) and will be designated α_H . The explicit expression for this quantity follows from equations (50)—(54)

$$\alpha_H = [\xi_L H_m^L(X_i^L) + \sum_{\varphi \neq L} (\xi_\varphi - \xi_\varphi^0) H_m^\varphi] / \Delta H_Z^M.$$
(55)

Let us express supplementary heat capacity of the mixture also as a linear function of this transformation degree

$$C_m^t(\alpha_H) = \sum_{\varphi} \xi_{\varphi} C_m^{\varphi} = \sum_{\varphi} \xi_{\varphi}^0 C_m^{\varphi} + \alpha_H \, \Delta C_{\Sigma}^M, \tag{56}$$

where

$$\Delta C_{\Sigma}^{M} \equiv C_{m}^{L} - \sum_{\varphi} \xi_{\varphi}^{0} C_{m}^{\varphi}.$$

$$C_{m}^{L} = 0,$$
((57)

If

then

$$C_m^t(\alpha_H) = (1 - \alpha_H) \sum_{\varphi} \xi_{\varphi}^0 C_m^{\varphi}.$$
(58)

By substituting (54) and (58) into equation (49) one obtains the relation between heat flux, the rate of heating and the enthalpic rate of melting $\dot{\alpha}_H$

$$Q = \left(\sum_{i} X_{i}^{t} C_{p,i}^{L} + (1 - \alpha_{H}) \sum_{\varphi} \xi_{\varphi}^{0} C_{m}^{\varphi}\right) \dot{T} + \Delta H_{\Sigma}^{M} \dot{\alpha}_{H}.$$
(59)

Experimental curves of dynamic calorimetry methods record the time course of heat flux $[\dot{q} = f(\tau)]$ and that of temperature $[T = f(\tau)]$. By integrating the difference between heat flux and the capacity term it is possible to determine summary enthalpy of melting,

$$\Delta H_{\Sigma}^{M} = \int_{\tau_{0}, \alpha_{H}=0}^{\tau_{f}\alpha_{H}\approx 1} (\dot{Q} - C_{p}^{t}\dot{T}) \,\mathrm{d}\tau$$
(60)

as well as the time course of enthalpic advacement of melting,

$$\alpha_H(\tau) = (1/\Delta H_{\Sigma}^M) \int_{\tau_0, \alpha_H=0}^{\tau} (\dot{Q} - C_p^t \dot{T}) \,\mathrm{d}\tau, \tag{61}$$

where the relationship of this quantity to the parameters of phase composition is given by the explicit expression (55).

Instantaneous enthalpic rate of melting $\dot{\alpha}_H$ can be determined from experimental curves of dynamic calorimetry as the difference

$$\dot{\alpha}_H = (\dot{Q} - C_p^t \dot{T}) / \Delta H_{\Sigma}^M. \tag{62}$$

This rate is of course a function of phase composition as well as one of temperature. If one desires to express it in a form suitable for description of invariant melting, it should be borne in mind that in the course of such melting the sample comprises (N + 1) phases. Phase composition of such a system is then determined by N independent parameters. In the case of systems where the melt is assumed to be a single phase of variable composition, phase fraction ξ_L of melt and (N - 1) molar fractions of melt X_i^L may be chosen as independent parameters of phase composition.

Enthalpic rate of melting is then found as a function of actual rate of melting ξ_L , of the rate of change in melt composition \overline{X}_i^L and of temperature \dot{T} ,

$$\dot{\alpha}_{H} = \frac{\partial \alpha_{H}}{\partial \xi_{L}} \dot{\xi}_{L} + \sum_{i=1}^{N-1} \frac{\partial \alpha_{H}}{\partial X_{i}^{L}} \dot{X}_{i}^{L} + \frac{\partial \alpha_{H}}{\partial T} \dot{T}, \qquad (63)$$

while the terms for the respective partial derivatives are determined from equation (55)

$$\frac{\partial \alpha_H}{\partial \xi_L} = [H^L_M(X^L_i) + \sum_{\varphi \neq L} H^{\varphi}_m(\partial \xi_{\varphi}/\partial \xi_L)] / \Delta H^M_{\mathcal{D}}, \qquad (64)$$

$$\frac{\partial \alpha_H}{\partial X_i^L} = [\xi_L(\partial H_m^L/\partial X_i^L) + \sum_{\varphi \neq L} H_m^{\varphi}(\partial \xi_{\varphi}/\partial X_i^L)] / \Delta H_{\Sigma}^M, \qquad (65)$$

$$\frac{\partial \alpha_H}{\partial T} = H_m^L(X_i^L) \sum_{\varphi} \left[\xi_{\varphi} - (1 - \xi_L) \, \xi_{\varphi}^0 \right] C_m^{\varphi} / (\Delta H_{\Sigma}^M)^2. \tag{66}$$

"Equilibrium" course of melting

The melting process is usually not an activated one [8], so that its time course is to a considerable degree given by the rate at which heat is supplied into the sample, by the rate of temperature increase, and by equilibrium dependence of phase composition on temperature. For this reason determination of an even approximate relation between the time course of heat flux and the sample temperature on the one hand and the equilibrium dependence of phase composition on the other is of considerable significance. For the purpose of deriving this relationship let us make use of the following consideration.

In a real experimental arrangement in dynamic calorimetry there exists a certain temperature distribution in the sample at each moment (with respect to spatial coordinates) so that in the course of heating the sample center exhibits a lower temperature than its surface. Let us assume that local phase composition corresponds to heterogeneous equilibrium for the respective local temperature ϑ . Enthalpy of the entire sample is then a sum of enthalpies of the individual volume elements of sample which may be expressed (in supplementary molar enthalpies) by equation

$$\mathscr{H}_{m}^{t}(T) = \int_{T_{\mathrm{MIN}}}^{T_{\mathrm{MAX}}} H_{m}^{t}(\vartheta) f(\vartheta) \, \mathrm{d}\vartheta / \int_{T_{\mathrm{MIN}}}^{T_{\mathrm{MAX}}} f(\vartheta) \, \mathrm{d}\vartheta, \tag{67}$$

where the integrating limits are the lowest $(T_{\rm MIN})$ and the highest $(T_{\rm MAX})$ local temperatures at the given moment and function $f(\vartheta)$ is a distribution function expressing the proportion of sample having an instant local temperature in the range from ϑ to $\vartheta + d\vartheta$. Derivation of this distributing function requires demanding solving of differential equations of heat flux for the given sample shape, necessarily using certain simplifying assumptions. For practical reasons let us accept such simplification which allows for simple solving of integrals in (67). This simplification is given by the assumption that the distributing function is specified by the conditions

$$f = 1 \quad \text{for } T_{\text{MIN}} \leq \vartheta \leq T_{\text{MAX}},$$

$$f = 0 \quad \text{for } \vartheta < T_{\text{MIN}} \text{ or } \vartheta > T_{\text{MAX}}.$$
 (68)

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When further assuming that T_{MAX} is identical with the sample temperature T measured and that the difference in temperature is designated by the symbol $\delta \equiv T_{\text{MAX}} - T_{\text{MIN}}$, equation (67) acquires the form

$$\mathscr{H}_{m}^{t}(T) = \frac{1}{\delta} \int_{T-\delta}^{T} H_{m}^{t}(\vartheta) \,\mathrm{d}\vartheta.$$
(69)

The increase in enthalpy of one mole of the temperature-non-uniform system specified in this way per unit of time is then given by the expression

$$\frac{\mathrm{d}H_0^t}{\mathrm{d}\tau} = \frac{\mathrm{d}H_0^t}{\mathrm{d}T} \cdot \dot{T} = \left[\sum_i X_i^t C_{o,i}^L + \mathrm{d}\mathscr{H}_m^t / \mathrm{d}T\right] \dot{T},\tag{70}$$

where the total derivative with respect to temperature is determined from (69),

$$d\mathscr{H}_m^t/dT = [H_m^t(T) - H_m^t(T - \delta)]/\delta$$
(71)

so that, using (47), the heat flux corresponding to equilibrium course of melting is described by equation

$$\dot{Q} = \{ \sum C_{p,i}^{L} X_{i}^{t} + [H_{m}^{t}(T) - H_{m}^{t}(T - \delta)] / \delta \} \dot{T}.$$
(72)

On the basis of equation (72), "equilibrium" dependence of heat flux on temperature was calculated for the course of melting of a hypothetical heterogeneous binary system $(X_2^{t} = 0.3, T_E = 700 \text{ K})$ with immiscible solid phases $(X_2^{\varphi} = 0, X_{\varphi}^{M} = 1)$, $\Delta H_{\varphi}^{M} = \Delta H_{\psi}^{M} = 20 \ 000 \text{ J/mole}, (T_{\varphi}^{M} = 1000 \text{ K})$ and ideal melt $(\Omega_{12} = 0)$, which is plotted in Fig. 2.



Fig. 2. Heat flux during heating of model heterogeneous system; Q — heat flux (full line), ξ_L — "equilibrium" advancement of melting (dashed line). Model binary system: $T_E = 700 \text{ K}; X_{\varphi}^{\varphi} = 0; X_{\varphi}^{\varphi} = 1; T_{\varphi}^{\varphi} = 1000 \text{ K}; \Delta H_{\varphi}^{M} = H_{\psi}^{M} = 20 \text{ kJ/mole};$ $\Omega_{12} = 0; \delta = 10 \text{ K}; X_{z}^{t} = 0.3; C_{\varphi}^{\Psi} = C_{\varphi}^{\Psi} = 0.$

DISCUSSION AND CONCLUSION

The analysis of relations between enthalpy and phase composition, which has been worked out in the present study, had the main aim of increasing the number of initial data for the calculation of phase diagram curves. The data on enthalpy and temperature of congruent melting required for the calculation of phase diagrams according to [4] are not available for phases which do not melt congruently or melt at excessively high temperatures. This represents a considerable restriction of the applicability ot more flexible models for the behaviour of melt and frequently makes calculation impossible. Experimentally available enthalpy values for eutectic and peritectic melting may advantageously supplement the set of input data for calculation, together with the data on summary enthalpies of melting, insofar as the relationships between these quantities and the other enthalpic data in the system are obvious. The choice of the reference state as well as that of the other assumptions has been conformed to the requirement of direct applicability of the equations derived for the purposes of numerical calculations based above all on quantities that can be obtained by the methods of dynamic calorimetry.

a) The main advantage of the chosen reference state (8) lies in that it allows to work out a complete set of mutually consistent thermodynamic data from temperatures and enthalpic changes measurable directly by DTA and DSC methods.

b) In view of the fact that the enthalpic data are measured in the same temperature range in which they are subsequently utilized in calculation, the chosen reference state permits a simple form of their temperature dependence to be chosen.

As the occurence of solid phases with a markedly variable composition is less frequent in ceramic systems, most of the relations have been derived for heterogeneous systems in which the melt is the sole phase of variable composition.

The concentration dependence of melt enthalpy is described by a regular model (9) based on the conception of pair interactions. Within the framework of the model, parameters Ω_{ij} of a general *N*-component system are identical with the interaction parameter of the respective binary system I - J. The model represents the simplest form of non-ideal concentration dependence which, owing to the low number of parameters, is advantageous for calculation of phase diagram curves from a small number of input data. In the case of phases and systems for which larger numbers of experimental data are available, it is possible to choose models allowing to describe more accurately the actual behaviour of the systems.

Determination of enthalpy of invariant melting, or possibly of further data useful for the determination of phase diagram curves is related to the problems of correct interpretation of experimental curves obtained by dynamic calorimetry methods (including DTA).

For this reason the final part of the present study is devoted to the relations between the conversion degree determined from experimental curves of dynamic calorimetry (enthalpic advancement α_H) and the phase composition parameters. For the course of melting in real arrangement of dynamic calorimetry use is made of a simplified model which allows "ideal equilibrium" curve of dynamic calorimetry to be calculated on the basis of data on enthalpies of the individual phases and from equilibrium curves of the phase diagram.

Extension of the calculation by "equilibrium" DTA curves, comparing the curves calculated in this way with experimental values and possible derivation of more realistic models of a sample with nonuniform temperature distribution should be the subject of further studies.

The relationships derived for melting processes are for the most part applicable also for processes involving phase transitions or other invariant changes (eutectoid and peritectoid decompositions) in solid phase and for processes taking place in systems solid phase — solution (solution = melt). However, they have been

	No.moles of <i>i</i> -th com- ponent	Molar fractions of <i>i</i> -th com- ponent	Phase fraction	Molar enthalpy	Molar heat	Supple- mentary molar enthalpy	Supple- mentary molar heat capacity
Phase φ	n_i^{φ}	X_i^{φ}	ξφ	H_0^{φ}	$C^{arphi}_{\ p}$	H^{φ}_{m}	C^{φ}_m
Homogeneous melt	n_i^L	X_i^L	ξL	H_0^L	C_p^L	H_m^L	C_m^{γ}
Melt of pure component			ξ_i^L	$H^L_{0,i}$	$C_{p,i}^L$	$H_{m,i}^L$	C ^L _{m, i}
Solid phase of pure component		5-3	ξs	H ⁵ _{0, i}	$C^{s}_{c,i}$	$H^{S}_{m/i}$	C ^S _{m, i}
Heterogeneous mixture of phases	n_i^t	Xţ	_	H_0^t	C_p^t	H_m^t	C_m^t

Variables characterizing individual phases and a heterogeneous system

Quantities characterizing the individual processes

	Temper- ature	Initial phase composition	Final phase composition	Com- position of final melt	Change in molar enthalpy	Change in molar heat
Congruent melting of phase	T^M_{arphi}	$\xi_{arphi} = 1$,	$\xi_L = 1$	$X_i^L = X_i^{\varphi}$	ΔH_{φ}^{M}	ΔC_{φ}^{M}
Phase formation from solid components	(T ₀)	$\{\xi_i^s = X_i^{\varphi}\}$	$\xi_{\varphi} = 1$	1. 	ΔH_{φ}^{F}	ΔC_{φ}^{F}
Melting of eutectic mixture	T_E	$\xi_L = 0$	$\xi_L = 1$	$\begin{array}{c} X_i^L = \\ = X_i^E = X_i^t \end{array}$	ΔH^{E}_{*}	ΔC^E_*
General eutectic melting	${T}_{E}$	$\xi_L = 0$	$0 < \xi_L \leq 1$	$X_t^L = X_t^E$	ΔH_t^E	ΔC_t^E
Incongruent melting of phase	T_P	$\xi_{\gamma} = 1$	$\xi_{\gamma} = 0$	$X_i^L = X_i^P$	ΔH_{γ}^{P}	ΔC_{γ}^{P}
Peritectic melting generally	T_P	$0 < \xi_{\gamma} \leq 1$	$\xi_{\partial} = 0$	$X_i^{\mathcal{L}} = X_i^{\mathcal{P}}$	ΔH_t^P	ΔC_t^P
Summary melting of system	$\langle T_E, T_L angle$	$\xi_L = 0$	$\xi_L = 1$	$X_i^L = X_i^t$	ΔH_{Σ}^{M}	ΔC_{Σ}^{M}

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derived for a closed system and thus do not allow, without respective adjustment, to describe processes including escape of gases from the system (evaporation, thermal decomposition — dissociation, sublimation) or interaction of gaseous atmosphere with the sample (oxidation, burning, condensation, reduction).

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List of Symbols

Quantities

- α conversion degree (α_H -enthalpic advancement)
- C_p molar heats
- C_m supplementary molar capacities
- H_0 molar enthalpy related to conventional standard state
- H_m suplementary molar enthalpy
- \mathscr{H}_m^t supplementary molar enthalpy of sample with non-uniform temperature distribution
- Δ differences (changes)
- N number of system components
- P number of system phases
- n material amount number of moles
- T temperature (T_L liquidus temperature)
- ϑ local temperature
- δ difference between maximum and minimum local temperature
- τ time
- X_i molar fractions
- ξ_{φ} phase fractions
- Ω interaction parameter

Indexes (exponents)

expressing relation of a quantity towards

- E eutectic melting
- F combining from pure solid components
- i, j individual system components (always index)
- φ individual phases of the system (also ψ , ω , α , β , γ)
- L melt
- M congruent (or summary) melting
- P peritectic (incongruent) melting (except for C_p quantities)

- t heterogeneous system as a whole
- * eutectic or peritectic mixture
- 0 initial phase composition of the system (except for quantities H_0)

Acknowledgement

The author expresses his thanks to his colleagues and former co-workers Ing. M. Nevřiva and Ing. E. Pollert from the Institute of Solid State Physics in Prague for their inspiring interest in the results of the present study, which has been decisive for the creation of this paper, and to my colleague Ing. J. Vinš from Institute of Inorganic Chemistry at Řež for valuable discussions and assistance in mathematical formulation of the model simulating the behaviour of sample with nonuniform temperature distribution. The author is further grateful to RNDr. M. Eliášová and Ing. I. Proks from Bratislava for their careful study of the manuscript and their valuable comments which have considerably contributed to improving the accuracy and consciseness of the present paper.

ENTALPIE A FÁZOVÉ POMĚRY PŘI TÁNÍ V HETEROGENNÍCH SOUSTAVÁCH

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Jsou odvozeny rovnice, které vyjadřují vztahy mezi celkovou entalpií uzavřené heterogenní N-složkové soustavy a fázovými poměry při jejím tání. Heterogenní směs je popsána souborem totálních molárních zlomků X_i^t , molárních zlomků fází X_i^{φ} a fázových zlomků ξ_{φ} . Doplňkové entalpické veličiny jsou vztaženy k referenčnímu stavu reprezentovanému hypotetickou heterogenní směsí tavenin čistých složek [rovnice (8)]. Pro molární entalpii homogenní taveniny H_m^L je použit model regulárního chování (9). Molární entalpie pevných fází H_m^{φ} souvisí s entalpií jejich kongruentního tání ΔH_{φ}^M a s entalpií jejich slučování (z čistých pevných složek) ΔH_{φ}^F . Jsou odvozeny rovnice pro teplotní závislost totální entalpie heterogenní soustavy H_m^t , pro entalpii tání eutektické směsi ΔH_{φ}^E a tání inkongruentního ΔH_{γ}^P (obr. 1). Je analyzován vztah mezi tepelným tokem měřeným při dynamické kalorimetrii a rychlostí procesu tání. Je navržen model teplotně ze známého fázového diagramu (výsledek pro ideální binární soustavu je uveden na obr. 2).

Odvozené rovnice jsou určeny pro výpočet fázových diagramů [1] z kalorimetrických dat a pro interpretaci experimentálních křivek získaných metodami dynamické kalorimetrie.

Obr. 1. Fázový diagram a entalpické veličiny;

 H_m^L — entalpie taveniny, x — molární zlomky složky B, ΔH^F — entalpie slučování z čistých složek, T^M , ΔH^M — teploty a entalpie kongruentního tání, T_E , ΔH_*^E — teplota a entalpie tání eutektické směsi, T_P , ΔH_*^F — teplota a entalpie inkongruentního tání.

Obr. 2. Tepelný tok při ohřevu modelové heterogenní soustavy;

 \hat{Q} — tepelný tok plná čára, ξ_L — "rovnovážná" pokročilost tání přerušovaná čára. Modelová binární soustava: $T_E = 700 \text{ K}; X_2^{\varphi} = 0; X_2^{\varphi} = 1; T_{\varphi}^M = 1000 \text{ K}; \Delta H_{\varphi}^M = \Delta H_{\psi}^M = 20 \text{ kJ/mol}; \Omega_{12} = 0; C_p^{\varphi} = C_p^{\psi} = 0; \delta = 10 \text{ K}; X_2^{t} = 0,3.$

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ЭНТАЛЬПИЯ И ФАЗОВЫЕ ОТНОШЕНИЯ ПРИ ПЛАВЛЕНИИ В ГЕТЕРОГЕННЫХ СИСТЕМАХ

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Выведены уравнения, связывающие общую энтальнию закрытой гетерогенной системы с фазовыми отношениями при ее плавлении. Гетерогенная смесь описана набором молярных долей смеси X_i^t , молярных долей фаз X_i^{φ} и фазовых долей ξ_{φ} . Допольнителные энтальпические величины относятся к основному состоянию, которым избрана гипотетическая гетерогенная смесь расплавленных чистых компонентов [уравнение(8)]. Для молярной энтальнии гомогенного расплава H_m^L используется модель регулярного поведения (9). Молярные энтальнии твердых фаз H_m^{φ} связаны с энтальниями их конгруентного плавления ΔH_{φ}^M и с энтальниями их образования (пз чистых твердых компонентов) ΔH_{φ}^F . Выведены уравнения для температурной зависимости общей энтальнии гетерогенной системы H_m^t , для энтальнии плавления эвтектической смеси ΔH_{ξ}^F и плавления инконгруэнтного ΔH_{γ}^P (Рис. 1). Рассматривается отношение между тепловым потоком, измераемым методом динамической калориметрии и скоростью ироцесса плавления. Предложена модель, которая позволяет расчет ,, равновесной" кривой динамиченой бинарной системы приведен на рис. 2).

Выведенные уравнения служат для расчетов диаграмм плавкости [1] из калориметрических данных и для обсуждения кривых эксперимента динамической калориметрии.

- Рис. 1. Фазовая диаграмма и энтальпические величины; H_m^L энтальпия расплава, x — молярные доли компонента B, ΔH^F — энтальпия образования из твердых компонентов, T^M , ΔH_{φ}^M — температуры и энтальпии конгруэнтного плавления, T^E , H_{\pm}^E — температура и энтальпия плавления эвтектической смеси, T^P , H_{\pm}^P температура и энтальпия инконгруэнтного плавления.
- Рис. 2. Тепловой поток при нагреве модельной гетерогенной системы; Q тепловой поток (полная кривая), ξ_L "равновесная" продвижность плавления (прерывистая кривая).
 - Модельная бинарная система: $T_E = 700 \ K; \ X_2^{\varphi} = 0; \ X_2^{\psi} = 1; \ T_{\varphi}^{M} = 1000 \ K;$ $\Delta H_{\varphi}^{M} = \Delta H_{\psi}^{M} = 20 \ \kappa \partial \kappa |$ моль; $\Omega_{12} = 0; \ C_{p}^{\varphi} = C_{2}^{\psi} = 0; \ \delta = 10 \ K; \ X_{2}^{t} = 0, 3.$