Thermochimica Acta, 101 (1986) 65–75
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HEAT CAPACITY OF HETEROGENEOUS SYSTEMS AND THERMAL ANALYSIS

V.K. FILIPPOV and G.G. CHERNIK

Department of Chemistry, Leningrad State University, Leningrad 199004 (U.S.S.R.)

(Received 25 September 1985)

ABSTRACT

Thermodynamic equations for the heat capacity of binary and multicomponent systems are given. Heat capacity changes on transition from homogeneous to heterogeneous states are shown to be directly connected with phase diagrams and thermodynamic properties of phases. Application of the relations obtained is considered. Experimental adiabatic calorimetry and DSC data are given for illustration.

INTRODUCTION

Heat capacity is a property of primary importance in chemical thermodynamics. However, specific heats of homogeneous systems are studied most often; much less attention has been given to the heat capacity of heterogeneous systems. Nevertheless theoretical investigations of this property lead to conclusions of great significance for thermal analysis.

Various binary and multicomponent systems containing substances of different classes: salts, metals, oxides, organic compounds, lyotropic and thermotropic liquid crystals, etc., are studied by means of thermal analysis methods [1,2]. For binary systems the results are most conveniently represented in the form of phase diagrams. Many problems connected with determination of phase boundaries are encountered in practice [2–4]. In this paper interpretation of DTA and DSC data for binary systems will be considered. Special attention will be given to the heat capacity jumps taking place when the number of phases present in the system is changed.

THEORY

Heat capacity of heterogeneous systems

According to the phase rule an n-component r-phase materially isolated system has two degrees of freedom if $r \leqslant n$. If the pressure is fixed, the

0040-6031/86/$03.50

system becomes monovariant. Its entropy is a sum of the entropies of the coexisting phases

$$S = \sum_{\alpha=1}^{r} m^{\alpha} s^{\alpha} \tag{1}$$

where S is the entropy per mole of heterogeneous system, s^{α} is the molar entropy of the α phase, and m^{α} is the molar fraction of the α phase, $\sum_{\alpha=1}^{r} m^{\alpha} = 1$.

The isobaric heat capacity of this system is then defined as

$$C_P(n;\, r) = T\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_P = T\left(\frac{\mathrm{d}}{\mathrm{d}T} \sum_{\alpha=1}^{r} m^{\alpha} s^{\alpha}\right)_P \tag{2}$$

As the temperature varies a redistribution of components among phases takes place in the materially isolated system which leads to changes in compositions, masses and molar entropies of phases. As a result, the heat capacity of a heterogeneous system is in general not equal to the sum of specific heats of the phases in equilibrium [5]:

$$\begin{aligned} C_P(n;\, r) &= T \sum_{\alpha=1}^{r} m^{\alpha}\left[\left(\frac{\mathrm{d}s^{\alpha}}{\mathrm{d}T}\right)_P + \sum_{i=1}^{n-1}\left(\frac{\partial s^{\alpha}}{\partial x_i^{\alpha}}\right)\left(\frac{\mathrm{d}x_i^{\alpha}}{\mathrm{d}T}\right)_P\right] + T \sum_{\alpha=1}^{r} s^{\alpha}\left(\frac{\mathrm{d}m^{\alpha}}{\mathrm{d}T}\right)_P \\ &= \sum_{\alpha=1}^{r} m^{\alpha} C_P^{\alpha} + T \sum_{\alpha=1}^{r} m^{\alpha} \nabla s^{\alpha}\left(\frac{\mathrm{d}\vec{x}_{\alpha}}{\mathrm{d}T}\right)_P + T \sum_{\alpha=1}^{r} s^{\alpha}\left(\frac{\mathrm{d}m^{\alpha}}{\mathrm{d}T}\right)_P \end{aligned} \tag{3}$$

where x_i^{α} is the molar concentration of component i of the α phase and C_P^{α} is the molar heat capacity of the α phase.

Thermodynamic equations linking compositional changes of phases with the temperature variation were previously derived [6]. These equations allowed a general relationship to be obtained for C_P of an n-component heterogeneous materially isolated system [5]:

$$C_P(n;\, r) = \sum_{\alpha=1}^{r} m^{\alpha} C_P^{\alpha} + T \sum_{\alpha=1}^{r} m^{\alpha} \left|\frac{\mathrm{d}\vec{x}_{\alpha}}{\mathrm{d}T}\right|_{\alpha}^{2} \tag{4}$$

where

$$\left|\frac{\mathrm{d}\vec{x}_{\alpha}}{\mathrm{d}T}\right|_{\alpha}^{2} = \frac{\mathrm{d}\vec{x}_{\alpha}}{\mathrm{d}T} G_{\alpha} \frac{\mathrm{d}\vec{x}_{\alpha}}{\mathrm{d}T} = \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} g_{ij}^{\alpha} \frac{\mathrm{d}x_i^{\alpha}}{\mathrm{d}T} \frac{\mathrm{d}x_j^{\alpha}}{\mathrm{d}T} > 0 \tag{5}$$

$\mathrm{d}\vec{x}_{\alpha}/\mathrm{d}T$ is a vector of the shift of the α phase composition with isobaric temperature variation and G_{α} is an operator corresponding to the matrix g_{ij}^{α}, formed by the second derivatives of the α phase molar Gibbs energy with respect to composition. According to ref. 7, the left-hand side of eqn. (5) can be interpreted as the square of the norm (length) of the $(\mathrm{d}\vec{x}_{\alpha}/\mathrm{d}T)_P$ vector in the α phase Gibbs potential metrics.

From eqns. (4) and (5) the following points can be made [8]:

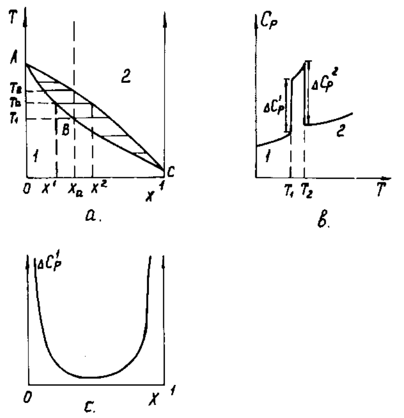

Fig. 1. Binary system with perfect miscibility in both phases 1 and 2: (a) phase diagram, (b) temperature dependence of the system's specific heat for $x = x_a$, (c) concentration dependence of the heat capacity jump at the transition from phase 1 to the heterogeneous state (ΔC_P^1 measured at the phase boundary ABC).

(1) Phase transformations leading to changes in phase compositions increase the heat capacity of a heterogeneous system so that it exceeds the sum of the specific heats of the individual phases, each phase of varying concentration making a positive contribution to this increase.

(2) It is only in the case of phase compositions that do not change with isobaric temperature variation, that the C_P value of a heterogeneous system equals the sum of the specific heats of the coexisting phases.

(3) On transition of the system from homogeneous to heterogeneous states, the heat capacity instantly increases

$$\Delta C_P^\alpha = C_P(m^\alpha \to 1) - C_P^\alpha = T\frac{\mathrm{d}\vec{x}_\alpha}{\mathrm{d}T} G_\alpha \frac{\mathrm{d}\vec{x}_\alpha}{\mathrm{d}T} > 0 \tag{6}$$

(4) If the number of phases is equal to the number of components, the compositional changes of phases do not depend upon the ratio of their masses, hence, the heat capacity of the system and ΔC_P are in this case linear functions of the system's overall composition.

In the particular case of a binary system, e.g. as shown in Fig. 1, at temperature T_a with overall molar composition x_a containing m^1 moles of phase 1 (molar composition, x^1; molar specific heat, C_P^1) and m^2 moles of phase 2 (concentration, x^2; specific heat, C_P^2) the specific heat is given by [5]

$$\begin{aligned} C_P(2;\,2) &= \sum_{\alpha=1}^{2} m^\alpha \left[C_P^\alpha + T g_{xx}^\alpha \left(\frac{\mathrm{d}x^\alpha}{\mathrm{d}T} \right)_P^2 \right] \\ &= \sum_{\alpha=1}^{2} m^\alpha \left[C_P^\alpha + \frac{T}{g_{xx}^\alpha} \left(\frac{\partial s^\alpha}{\partial x^\alpha} - \frac{s^2 - s^1}{x^2 - x^1} \right)^2 \right] \end{aligned} \tag{7}$$

Relationship (6) for the jump in heat capacity on transition from phase 1 to the two-phase region then reduces to

$$\Delta C_P^1 \equiv C_P(m^1 \rightarrow 1) - C_P^1 = T g_{xx}^1 \left(\frac{\mathrm{d}x^1}{\mathrm{d}T} \right)_P^2 > 0 \tag{8}$$

where g_{xx}^1, the second derivative of the Gibbs energy of phase 1 with respect to composition, is positive due to the phase stability requirement.

Heat capacity jumps

Heat capacity jumps at the boundary between homogeneous and heterogeneous states have been known [5,9,10], but an appropriate thermodynamic analysis is needed. Let us consider the concentration dependence of ΔC_P for binary systems of various types.

The phase diagram for completely soluble components is given in Fig. 1a. As can be seen from eqn. (8), the magnitude of the heat capacity jump, ΔC_P^1 (Fig. 1b), is greatly influenced by the value of the second derivative g_{xx}^1, which tends to infinity as $x \rightarrow 0$ and $x \rightarrow 1$; at the same time the derivative $(\mathrm{d}x^1/\mathrm{d}T)_P$ is finite over the entire concentration range (Fig. 1a). Consequently, $\Delta C_P \rightarrow \infty$ when $x \rightarrow 0$ and $x \rightarrow 1$ (Fig. 1c) in accordance with the requirement that the heat capacity of pure components is infinite at the transition points.

In Fig. 2a a phase diagram with maximum transition temperature is plotted. When $x \rightarrow 0$ or $x \rightarrow 1$ ΔC_P behaves as in the previous case. Also, when an extremum point is approached, the derivative $(\mathrm{d}x^1/\mathrm{d}T)_P$ tends to infinity; hence, ΔC_P tends to $+\infty$ (Fig. 2c), which is in agreement with the

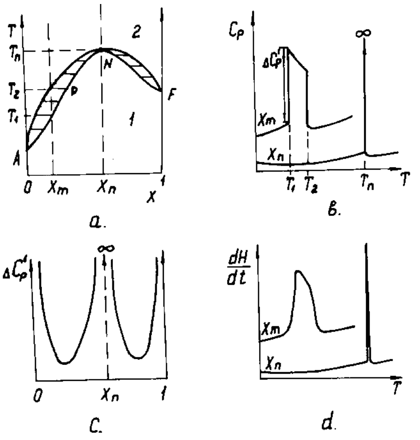

Fig. 2. Binary system with maximum phase transition temperature: (a) phase diagram, (b) temperature dependence of the system's specific heat for monovariant (x_m) and invariant (x_n) phase transitions, (c) concentration dependence of the heat capacity jump, ΔC_P^1 (measured at the phase boundary ADNF), (d) DSC curves for compositions x_m and x_n.

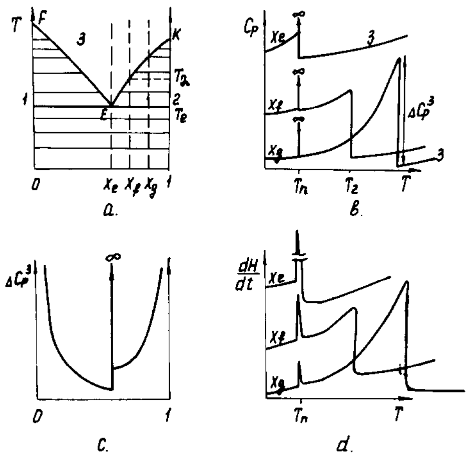

Fig. 3. Binary system with a simple eutectic: (a) phase diagram, (b) temperature dependence of the system's specific heat for compositions x_e, x_f and x_g, (c) concentration dependence of the heat capacity jump at the transition from phase 3 to the heterogeneous region (ΔC_P measured at the phase boundaries FEK), (d) DSC curves for compositions x_e, x_f and x_g.

fact that the extremum of the transition temperature is an invariant point.

For a binary system with a simple eutectic (Fig. 3a) the concentration dependence of ΔC_P^3 (Fig. 3c) is discontinuous at the eutectic point because of the intersection of two different liquidus curves. At the actual eutectic point a δ-function-like behaviour of C_P is observed.

Figure 4 gives the phase diagram for the system with a miscibility gap, and the system's heat capacity at $T = T'$. Regions I and II correspond to homogeneous states and region III represents the two-phase state. Whereas compositions of phases 1 and 2 change with temperature, a finite jump of C_P of the system occurs at the phase boundary. According to eqn. (7), the heat capacity is a linear function of x in the heterogeneous region. For the isotherm $T = T''$ the concentration dependence of C_P will be the same in spite of the fact that the mutual solubility of phases with $T = T'$ decreases and for $T = T''$ increases with increasing temperature. This is because the sign of ΔC_P is independent of the course of the phase composition change.

Equation (8) allows us to calculate the second derivative g_{xx}^1 at the

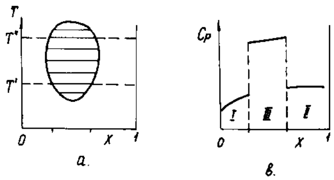

Fig. 4. Binary system with a miscibility gap: (a) phase diagram, (b) concentration dependence of the system's heat capacity for the isotherm $T = T'$.

boundary of phase 1 if the boundary $x^1(T)$ and the heat capacity jumps ΔC_P^1 are known. If g_{xx}^{α} is independently determined from activity measurements, one can verify the thermodynamic consistency of the data.

Compressibility and thermal expansion coefficients also undergo jump-like changes at the point of transition from homogeneous to heterogeneous states. Relationships for these thermodynamic properties were previously derived [11].

Application to thermal analysis

The thermodynamic equations obtained in the first section can readily be applied to thermal analysis. These equations are strictly valid only in the limiting case when the system is very close to equilibrium. However, as emphasized in ref. 2, thermodynamics give principal interpretation rules for the thermal analysis methods. Kinetic problems often encountered in practice are not discussed here, readers are referred to refs. 2–4, 12 and 13.

According to the phase rule there are two kinds of transitions in a materially isolated system at constant pressure. The first type is an invariant transition ($r = n + 1$) taking place at a single, precisely defined temperature until one phase disappears. Another type is a monovariant phase transition which occurs over a certain temperature interval. If $r \leqslant n$ the number of degrees of freedom is independent of r.

Interpretation of DTA data for binary systems

An invariant process is accompanied by a finite change in enthalpy, hence a plateau is formed in the T–t (temperature–time) curve. For monovariant transitions breaks in the T–t curve are observed.

Consider the eutectic-type binary system given in Fig. 5. Crystallization of pure components and the eutectic solution is represented by cooling curves with a single plateau. Other curves have a break (the beginning of a

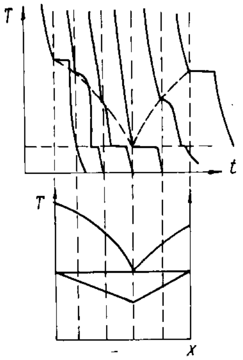

Fig. 5. Temperature–time curves for the binary system with a simple eutectic.

component's crystallization) and a plateau (crystallization of eutectic solution after one of the components partly evolves).

Usually, breaks in a *T–t* curve are considered to be due to evolution of the solid-phase crystallization heat. Strictly speaking this is true only for finite changes in enthalpy, i.e. for invariant processes. However, when the phase processes in a materially isolated system (which is usually the case in thermal analysis) do not change the number of degrees of freedom, the molar enthalpy of the system is continuous, i.e. infinitesimal changes in enthalpy correspond to infinitesimal variations of temperature. It is the rate of enthalpy change with temperature that varies for different states of the system (on different sides of the phase boundary). The rate of enthalpy change with temperature is actually the heat capacity of the system which, as has been shown, undergoes a finite increase (or decrease) when the phase state of the system changes.

It can be seen that the concentration dependence of ΔC_P shown in Fig. 3 is consistent with *T–t* or DTA curve changes as the composition is varied. Thus, when $x \to 0$ or $x \to 1$ the break in the *T–t* curve becomes sharper and the peak in the DTA curve increases in size. As the eutectic point is approached the break in the *T–t* curve becomes less sharp and the peak in DTA decreases. It is difficult to investigate the system in the vicinity of the eutectic point because the values of ΔC_P are small in this region. If the solution of the actual eutectic composition crystallizes ($\Delta C_P = \infty$), a plateau appears in the *T–t* curve along with a sharp peak in DTA.

Determination of phase boundaries from DSC curves

In differential scanning calorimetry heat flux is measured, so DSC curves reflect changes in the heat capacity of the system, although there is always some lag caused by temperature gradients or concentration fluctuations.

The difference between invariant and monovariant processes is often not appreciated in the interpretation of DSC data for binary systems (e.g. for some lipid–water lyotropic liquid crystalline systems). Sometimes a single transition temperature is determined for a clearly non-isothermal process. As a result, the phase diagrams obtained are schematic, and contain single boundaries between phases instead of the heterogeneous regions required by the phase rule.

The peak capacity of the system is infinite at the invariant point, whereas for monovariant processes heat capacity jumps, ΔC_P, attain finite values (Fig. 2b). Hence, the corresponding peaks in DSC differ in shape and width (Fig. 2d). However, it may be difficult to detect the type of process from a single DSC curve. One should compare DSC data for a number of compositions and evaluate the concentration dependence of the transition temperature.

An invariant process in a binary system is possible, besides transitions in pure components, either in the case of the transition temperature extremum or in the case of a three-phase equilibrium (eutectic, peritectic or incongruent melting). All the other phase processes in the system are monovariant.

The temperature dependence of C_P for the eutectic-type system (Fig. 3a) is given in Fig. 3b. At the eutectic temperature, T_e, sharp peaks are observed in the DSC curves for various compositions (Fig. 3d). Passage of the system from heterogeneous to homogeneous regions is characterized by a finite heat capacity jump (curves x_f and x_g) which can be clearly seen in the DSC curves.

Naturally, in the study of monovariant processes it is not sufficient to find the initial transition temperature T_1 alone, we must also estimate the temperature interval $\Delta T = T_2 - T_1$ (see Fig. 1). In the DSC method the shape and width of a peak depend upon the scanning rate and the transition enthalpy. There are different ways of taking thermal lag into account: either to determine the final transition temperature as the intersection of the baseline with the tangent to the right-hand side of the heating curve [14], or to determine peak onset and end temperatures for several scanning rates (< 0.5 K min^{-1}) and to extrapolate ΔT to zero scanning rate [15,16]. Knowing T_1 and ΔT for a number of concentrations one can plot boundaries of the heterogeneous region. Examples of DSC curves for phase diagrams of different kinds can be also found in refs. 2 and 3. Precise location of eutectic and peritectic points is based upon plotting transition enthalpies versus composition which gives two lines intersecting at the desired point [2,14,17].

In spite of being the most common method used for construction of phase diagrams thermal analysis has its own limitations. As can be seen from eqns. (4)–(6), the heat capacity of a heterogeneous system depends strongly upon the slope of phase boundaries, $x^{\alpha}(T)$. Consider a phase diagram of the type

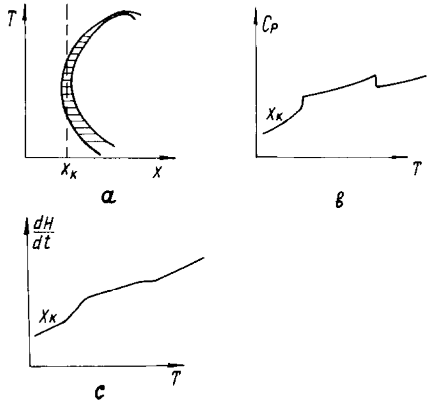

Fig. 6. Transition with nearly vertical phase boundaries: (a) fragment of the phase diagram, (b) temperature dependence of the system's specific heat for composition x_k, (c) DSC curve for $x = x_k$.

shown in Fig. 6a. It follows from eqn. (6) that in the case of nearly vertical phase boundaries the derivatives $(dx^{\alpha}/dT)_P$ and, hence, the heat capacity jumps are small (Fig. 6b). It would be extremely difficult to detect transitions of this kind using DSC data only. (This may be the reason why it was a problem to locate very steep phase boundaries by means of DSC in ref. 14.) The equations for ΔC_P explain the well-known fact that "the determination of a liquid miscibility gap or of a liquidus line with large slope is critical by thermal analysis, and other methods seem more appropriate" [18].

EXPERIMENTAL

Measurements were carried out with the help of a Setaram DSC-111 instrument. Samples were prepared by weight and sealed in steel cells. Twice-distilled water and chemically pure Na_2SO_4 were used. DSC traces were recorded from 294 to 325 K with heating rates of 1, 0.5, 0.25 and 0.1 K min^{-1}. For the specific heat measurements baselines with empty sample cells were first obtained.

RESULTS

Experimental data obtained by two different techniques are given here for illustration.

Figure 7 gives experimental results for the system KCl–water studied by means of adiabatic calorimetry [20]. The error in C_P is reported to be less than 0.1%. At temperatures below T_s crystals and solution are present in the system. At $T_s = 302.5 \pm 0.1$ K the system becomes homogeneous and an instant decrease in heat capacity takes place. The measured value of the heat capacity jump is $\Delta C_P = 0.3670 \pm 0.0015$ J g^{-1} K^{-1}. It is noted that the

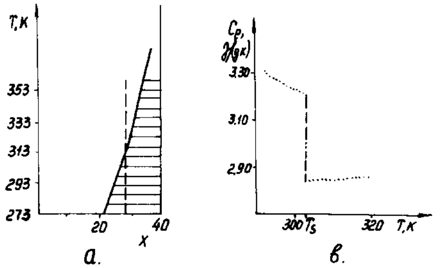

Fig. 7. KCl–water system: (a) fragment of the phase diagram [19], x = concentration of KCl, weight %, (b) temperature dependence of the system's specific heat from adiabatic calorimetry [20] for $x = 27.1\%$, temperature of saturation, $T_s = 302.5 \pm 0.1$ K.

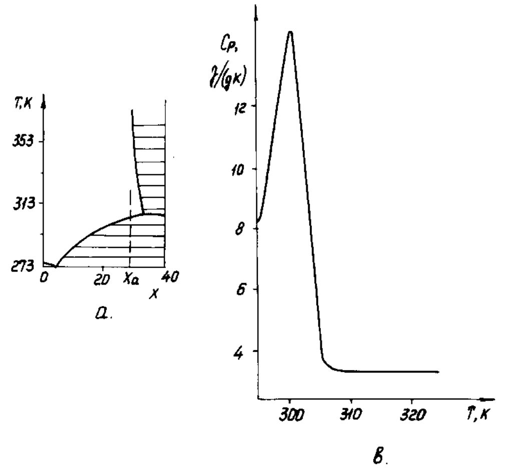

Fig. 8. Na_2SO_4-water system: (a) fragment of phase diagram [19], x = concentration of Na_2SO_4, weight %, (b) temperature dependence of the system's specific heat for composition x_a from differential scanning calorimetry (scanning rate 0.25 K min^{-1}).

process of dissolution of the crystals is very slow: it took several hours for the system to reach a state of thermodynamic equilibrium [20].

DSC is a less accurate but much faster experiment. A typical DSC curve for the system Na_2SO_4-water is given in Fig. 8. The right-hand edge of the DSC trace is not strictly vertical, but the tendency towards a finite decrease in C_p is clearly seen, and this is the case for all heating rates used. The magnitude of the heat capacity jump at the transition from heterogeneous to homogeneous states is > 10 J g^{-1} K^{-1}, which far exceeds the value of ΔC_p in the previous case. It can be explained by the fact that the phase boundary in the KCl-water system is very steep, while the slope of the solubility curve $(dT/dx)_p$ in the system Na_2SO_4-water is small (see eqn. 8).

CONCLUSIONS

Phase processes in binary and multicomponent systems cause changes in the system's heat capacity, which can be experimentally observed using thermal analysis methods. Values of heat capacity jumps taking place when the number of phase changes are directly connected with the phase diagrams and thermodynamic properties of the phases. Thermodynamic relations for C_p and ΔC_p can be useful in interpreting DTA and DSC data and in the construction of phase diagrams for various systems. Experimental investigation of heat capacity allows the consistency of data to be verified, and auxiliary information to be obtained on the thermodynamic characteristics of phases and phase processes.

ACKNOWLEDGEMENTS

The authors acknowledge the kind assistance of Dr. Jaroslav Šesták, Institute of Physics of the Czechoslovak Academy of Sciences, in communicating this article for publication in Thermochimica Acta.

REFERENCES

1 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, New York, 1974.
2 J. Šesták, Thermophysical Properties of Solids, Elsevier, Amsterdam, 1984.
3 J. Šesták, V. Šatava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
4 M. Nevřiva and J. Šesták, in Ž.D. Živkovič (Ed.), Thermal Analysis, Collection of Papers, Technical Faculty in Bor, Yugoslavia, 1984.
5 V.K. Filippov, Dokl. Akad. Nauk SSSR, 242 (1978) 376.
6 V.K. Filippov and M.M. Shultz, Dokl. Akad. Nauk SSSR, 235 (1977) 414.
7 V.K. Filippov, in Problems of Thermodynamics of Heterogeneous Systems and Theory of Interfaces, issue 2, University of Leningrad, Leningrad, 1973, p. 20 (in Russian).
8 V.K. Filippov, Vestn. Leningr. Univ., 22 (1980) 64.
9 I.R. Krichevsky and N.E. Hazanova, Zh. Fiz. Khim., 29 (1955) 1087.
10 A.L. Udovsky, A.M. Gaidukov and O.S. Ivanov, Phys. Lett., 72 (1979) 1.
11 V.K. Filippov, Dokl. Akad. Nauk SSSR, 254 (1980) 1778.
12 G. Vallebona, J. Therm. Anal., 16 (1979) 49.
13 A.A. Van Dooren and B.W. Müller, Thermochim. Acta, 49 (1981) 151.
14 C. Grabielle-Madelmont and R. Perron, J. Colloïd. Interface Sci., 95 (1983) 471.
15 R. Radomski, J. Cryst. Growth, 65 (1983) 509.
16 G.G. Chernik, V.K. Filippov, Vestn. Leningr. Univ., 18 (1985) 50.
17 G. Tammann, Lehrbuch der Heterogenen Gleichgewichte, Vieweg, Braunschweig, 1924.
18 M. Gaune-Escard and J.P. Bros, Thermochim. Acta, 31 (1979) 323.
19 A.N. Kirgintzev, L.N. Trushnikova and V.G. Lavrentjeva, Solubility of Inorganic Substances in Water, Khimia, Leningrad, 1972 (in Russian).
20 N.S. Zaugolnikova, G.I. Ovodov and A.L. Seifer, in Thermophysical Properties of Substances and Materials, issue 10, Publishing House of Standards, Moscow, 1976, p. 206 (in Russian).