

CLASSIFICATION OF PHYSICO-CHEMICAL TRANSFORMATIONS IN THERMAL ANALYSIS

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In the present classification the different types of physicochemical transformations are dealt with which may be useful in studying different substances by the methods of thermal analysis. Equations were derived for describing the correlation between the thermodynamic characteristics and the parameters of the differential thermal analytical (DTA) peaks for two classes of physicochemical transformations.

All experiments were conducted on DTA-4 instruments constructed in the Baikov Institute of Metallurgy, the USSR Academy of Sciences.

A large body of literature exists on the problems of using thermal analysis for the study of different types of physico-chemical transformations. There is no need to discuss the published papers since they have been amply reviewed in widely-known monographs [1–3].

According to the thermodynamic classification by Ehrenfest covering reversible processes, phase transitions of the 1st order are accompanied by an enthalpy jump and the tendency of the heat capacity to infinity; phase transitions of the 2nd order have no enthalpy jump, i.e. latent heat is neither liberated nor absorbed, but the heat capacity does undergo a jump.

Our classification is based on the same principle, but the scope of the transformations considered is much greater due to the inclusion of irreversible processes; thus, it covers all the possible types of physico-chemical transformations.

In spite of the differences in the mechanisms, all physico-chemical transformations can be divided into two large groups.

Transformations of the first group are characterized by the liberation or absorption of the latent heat of transformation. This group includes transformations of the 1st order, boiling, recrystallization, decomposition of solid solutions, and chemical reactions.

Transformations of the second group are characterized by an anomalous behaviour of the sample heat capacity in the stage where transformation takes place. The latent heat is neither liberated nor absorbed in this case. This group includes transformations of the 2nd order, ordering, magnetic transitions, and martensite transformations.

We have used such a division of transformations into two groups in order to derive mathematical relationships between the parameters measured in thermal analysis (temperature and temperature difference) and the thermodynamic functions which characterize given transformations.

Transformations of the first group

The following heat balance equation holds when no transformation takes place:

$$b_0 \cdot T_0 \cdot d\tau = M_0 \cdot C_0 \cdot dT_0 \quad (1)$$

where b_0 is the function of heat exchange responsible for heat transfer from the heater to the sample; ΔT_0 is the difference in temperature between the block and the sample at the moment τ ; M_0 is the mass of the sample; C_0 is the heat capacity of the sample; and T_0 is the temperature of the sample. When there is a transformation:

$$b_0(\Delta T_0 + \Delta T)d\tau = M_0 C_0 d(T_0 - \Delta T) + M_0 \Delta H_0 d\alpha \quad (2)$$

where ΔT is the deviation of the temperature of the sample from linear, caused by the transformation; α is the fraction of the reacted compound or of the newly-formed phase; and ΔH_0 is the specific latent heat of the transformation.

By solving Eqs (1) and (2) simultaneously, we obtain:

$$\frac{d\Delta T}{d\tau} = \frac{\Delta H_0}{C_0} \cdot \frac{d\alpha}{d\tau} - \frac{b_0}{M_0 C_0} \cdot \Delta T. \quad (3)$$

This linear homogeneous differential equation has a solution:

$$\Delta T = \frac{M_0 \cdot \Delta H_0}{b_0} \cdot \frac{d\alpha}{d\tau}. \quad (4)$$

Initially: $\tau = 0$, $\frac{d\alpha}{d\tau} = 0$, and $\Delta T = 0$.

Equation (4) is the main equation for transformations of the first group; it relates a thermal analysis parameter (ΔT) to physico-chemical parameters of the transformation $\left(\Delta H_0, \frac{d\alpha}{d\tau} \right)$.

The peak area under the curves $\Delta T(\tau)$ and $\Delta T(T)$ is, respectively:

$$\Delta S_\tau = \int_{\tau_1}^{\tau_2} \Delta T \cdot d\tau = \frac{M_0 \cdot \Delta H_0}{b_0} \quad (5)$$

$$\Delta S_T = \int_{T_1}^{T_2} \Delta T \cdot dT = \frac{M_0 \cdot \Delta H_0}{b_0} \cdot V \quad (6)$$

where V is the rate of sample heating.

The following is true for the peak amplitude:

$$\Delta T_{\max} = \frac{\Delta H_0 \cdot M_0}{b_0} \cdot \left(\frac{d\alpha}{d\tau} \right)_{\max} \quad (7)$$

Equations (4), (5), (6) and (7) coincide in form with similar equations given in [2], which have been derived for specific boundary conditions of heat exchange. Here we are considering a general case.

To describe chemical reactions and processes of decomposition of solid solutions, use is often made of the Arrhenius' equation in its simplest form:

$$\frac{d\alpha}{d\tau} = k \cdot e^{-k\tau}$$

where k is the rate constant.

For this case an equation is given in (2) in an approximate form ($E \gg RT$, where E is the activation energy):

$$\Delta T_{\max} = A \cdot V \quad (8)$$

where A is a constant.

The validity of this relationship can be confirmed (Fig. 1) by the experimental data obtained for the curve $\Delta T_{\max}(V)$ plotted for kaolinite in accordance with [4], and for the curve $\Delta T_{\max}(M_0)$ plotted for quartz in accordance with [5].

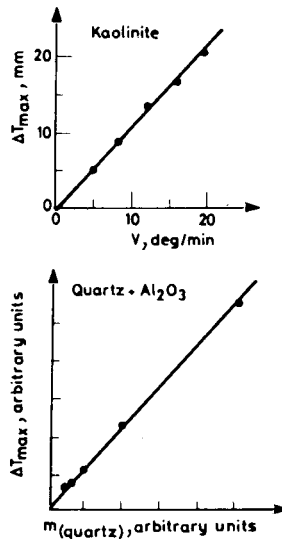


Fig. 1. Dependence of the DTA peak amplitude (ΔT_{\max}) on the heating rate (V) and the sample mass (m) for kaolinite and a mixture of quartz and aluminium oxide powders; the curve is plotted according to the data of Speil et al., and Grimshaw and Roberts

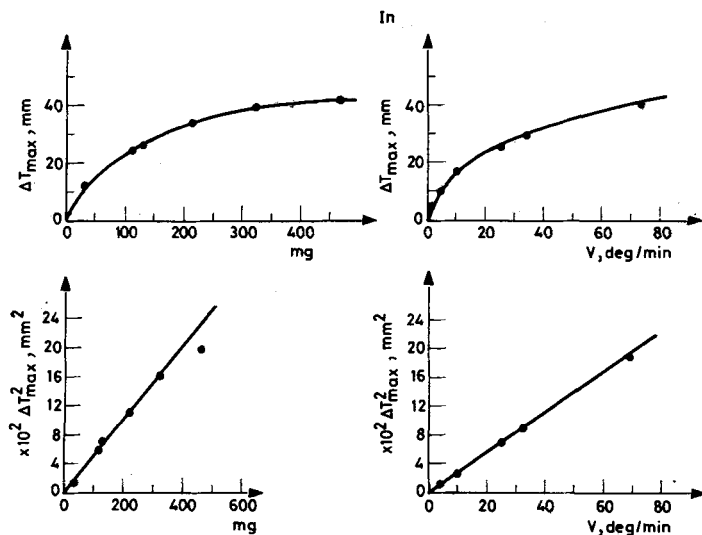


Fig. 2. Effect of heating rate (V) and sample mass (m) on the DTA peak amplitude (ΔT_{\max}) and square of the amplitude for the melting of indium

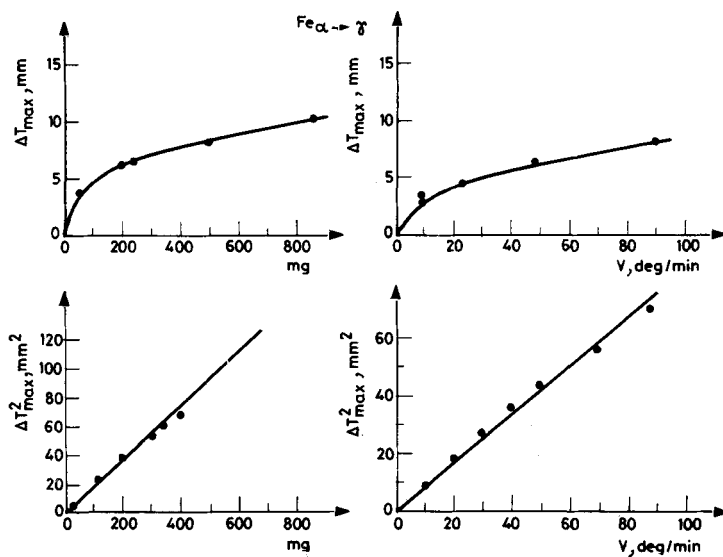


Fig. 3. Effect of heating rate (V) and sample mass (m) on the DTA peak amplitude (ΔT_{\max}) and the square amplitude (ΔT_{\max}^2) for the $\alpha \rightarrow \gamma$ transformation of iron

All the above is valid for transformations proceeding rather slowly. At high rates $\frac{d\alpha}{d\tau} \gg V$, and consequently $\frac{dT_0}{d\tau} = 0$ (Smitt problem) Eq. (8) will have another form.

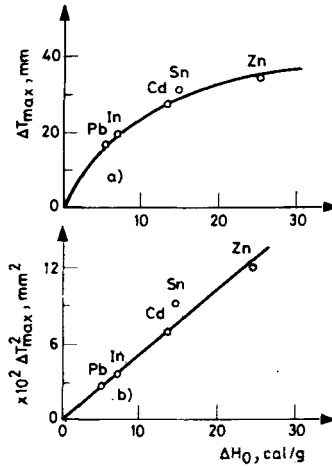


Fig. 4. DTA peak amplitude (ΔT_{\max}) and square amplitude (ΔT_{\max}^2) as functions of the latent specific heat of melting for some low-melting metals

After simple transformation, the area under the curve $T_0(\tau)$ extended in time can be written as:

$$\Delta\tau = \sqrt{\frac{2 \cdot \Delta H_0 \cdot M_0}{b_0 \cdot V}} \tag{9}$$

Then:

$$\Delta T_{\max} = \sqrt{\frac{2 \cdot \Delta H_0 \cdot M_0 \cdot V}{b_0}} \tag{10}$$

For the case of an infinite cylinder at $b_0 = 4\pi h$, where h is the cylinder height, we have:

$$\Delta T_{\max} = \sqrt{\frac{2\Delta H_0 \cdot M_0 \cdot V}{2\pi \cdot h \cdot \lambda}} \tag{11}$$

The validity of this equation can be shown by analysis of the relationships $\Delta T_{\max}(M_0)$, $\Delta T_{\max}(V)$, and $\Delta T_{\max}(\Delta H_0)$.

The first two relationships are confirmed by the data which we have obtained for the melting process of indium and for the $\alpha \rightarrow \gamma$ transformation in iron (Figs 2 and 3).

The relationship $\Delta T_{\max}(\Delta H_0)$ was supported by the measurements performed on some low-melting metals (Fig. 4).

The theoretical relationships are fulfilled very well in practice. This is seen in the plots $\Delta T_{\max}^2 f(V)$, $\Delta T_{\max}^2(M_0)$ and $\Delta T^2(\Delta H_0)$ given in the same Figures.

On account of an important circumstance we shall return to some of these relationships later.

In deriving the relationships obtained earlier by other authors, we paid attention to some peculiarities in the behaviour of ΔT_{\max} for slow and fast processes and confirmed them experimentally. However, in spite of the fact that the relationships we obtained in this section are known, we have shown that the approach we used in deriving the main equations of thermal analysis is really satisfactory. This is especially important in derivation of the equations of transformations of the second group.

Transformations of the second group

Without transformation, Eq. (1) is valid:

$$b_0 \cdot \Delta T_0 \cdot d\tau = M_0 \cdot C_0 dT_0. \quad (12)$$

When transformation does take place, we can write:

$$b_0 \cdot [\Delta T_0 + \Delta T] d\tau = M_0(\Delta C + C_0)d(T_0 - \Delta T) \quad (13)$$

where ΔC is the change in heat capacity in the transformation stage as compared with the usual run of the function $C_0(T)$.

Solving Eqs (9) and (10), we have:

$$\Delta T = \frac{M_0 \cdot \Delta C}{b_0} \cdot \frac{dT_0}{d\tau}. \quad (14)$$

This linear homogeneous differential equation, similarly to Eq. (3), has a solution:

$$\frac{d\Delta T}{d\tau} = \frac{b_0}{M_0 \cdot (C_0 + \Delta C)} \cdot \left(\Delta T \cdot \frac{\Delta C}{C_0} - \Delta T \right). \quad (15)$$

Initially:

$$\tau = 0, \Delta C = 0, \Delta T = 0.$$

This is the main relationship for transformations of the second group. By analogy with (5) and (6), for the area under the curves $\Delta T(\tau)$ and $\Delta T(T)$ we can write:

$$\Delta S_{\tau} = \int_{\tau_1}^{\tau_2} \Delta T \cdot d\tau = \frac{M_0}{b_0} \cdot \int_{T_1}^{T_2} \Delta C \cdot dT \quad (16)$$

$$\Delta S_T = \int_{T_1}^{T_2} \Delta T \cdot dT = \frac{M_0 \cdot V}{b_0} \cdot \int_{T_1}^{T_2} \Delta C \cdot dT. \quad (17)$$

For the amplitude of the DTA peak:

$$\Delta T_{\max} = \frac{M_0 \cdot V}{b_0} \cdot \Delta C_{\max} \quad (18)$$

It follows from Eq. (12) that the function ΔT is determined by ΔC . This was emphasized by Piloyan [2], who presented the experimental results for NaNO_3 [6].

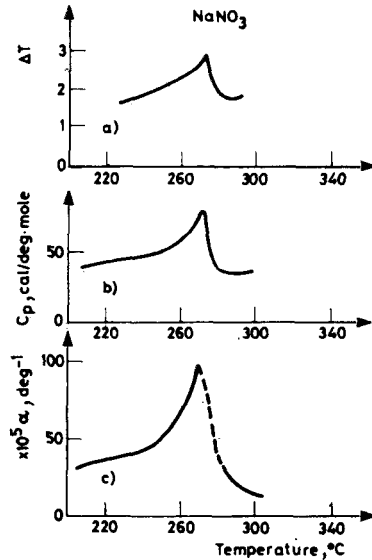


Fig. 5. DTA (a), heat capacities (b), and thermal expansion coefficients (c) as functions of temperature for NaNO_3 [6]

Figure 5 shows that the function $\Delta T(T_0)$ is very similar in form to the functions $C(T_0)$ and $\alpha'(T_0)$, where α' is the coefficient of thermal expansion. The same conclusion can be made on the basis of our experimental results, which include the relationships $\Delta T(T_0)$ and $C(T_0)$ for the ferromagnetic transitions in iron and nickel (Fig. 6), and the data for the process of melting of the bismuth-cadmium system (Fig. 7).

The validity of the equations derived is shown for the analysis of the parameters of the DTA peaks observed during the magnetic transformation in iron ($\alpha \rightarrow \beta$). Figure 8 illustrates the relationships $\Delta T_{\max}(V)$ and $S_T(V)$ for the ($\alpha \rightarrow \beta$) transformation in iron. It is seen that the experimental data are in a good agreement with theory.

In conclusion, we shall give an example of the practical application of the relationships obtained.

The thermogram of a typical alloy of the Si-Sn-As system (3 at. % - 77.6 at. % - 19.4 at. %) has two peaks in the melting region. A special experiment was

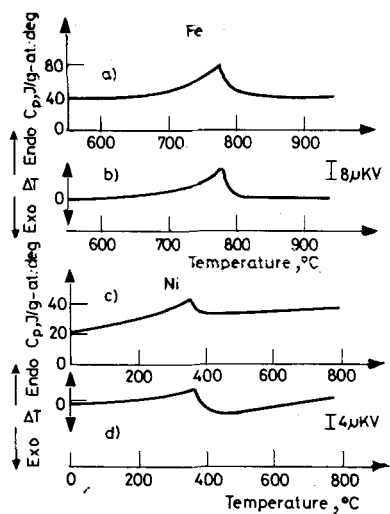


Fig. 6. Heat capacity (a, b) and DTA (c, d) as functions of temperature for iron and nickel

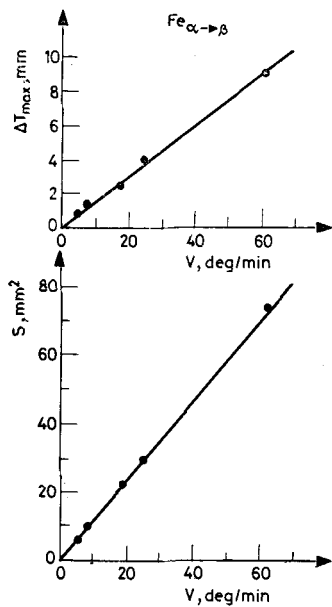


Fig. 7. Heat capacity (a, b) and DTA (c, d) as functions of temperature for alloys of the bismuth-cadmium system

performed to prove that one of the peaks corresponds to the first group transformation, and the other one to the second group transformation. We measured $\Delta T_{\max}(V)$ for these peaks. Figure 9 shows that curve 1 corresponds to the transformation of the first group, and curve 2 to the transformation of the second group.

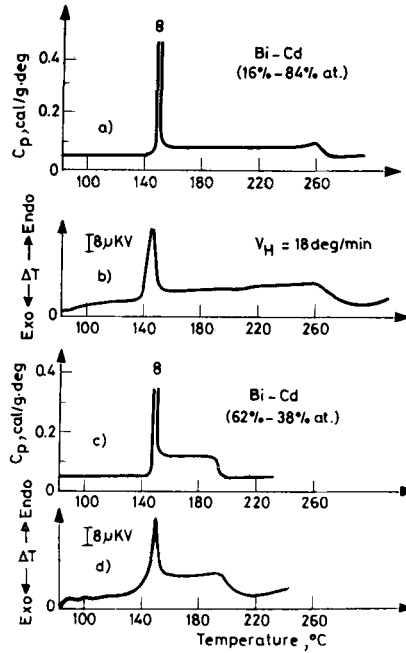


Fig. 8. Effect of heating rate on the DTA peak amplitude and its area for the $\alpha \rightarrow \beta$ transition in iron

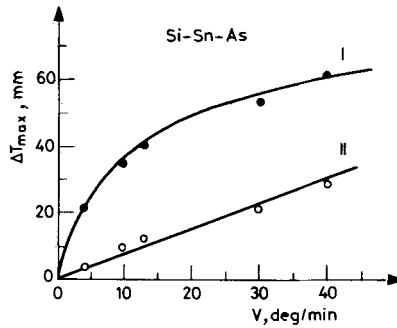


Fig. 9. Effect of the heating rate on the DTA peak amplitude for the alloy 3 at.% Si - 77 at.% Sn - 19.4 at.% As

The approach used by us can greatly decrease the number of samples for plotting the phase diagram, and help the investigator to understand the nature of the transformations recorded in DTA.

Conclusions

1. All physico-chemical transformations can be divided into two large groups. Transformations of the first group proceed with liberation (absorption) of latent heat and are described by the following equation:

$$\Delta T = \frac{M_0 \cdot \Delta H_0}{b_0} \cdot \frac{d\alpha}{d\tau}$$

Transformations of the second group proceed without liberation (absorption) of latent heat, but are characterized by an anomalous change in heat capacity in the transformation interval. They are described by the equation:

$$\Delta T = \frac{M_0 \cdot \Delta C}{b_0} \cdot \frac{dT_0}{d\tau}$$

This classification is convenient for studying physico-chemical transformations by the DTA method.

2. The amplitude of the DTA peak for transformations of the group is expressed in the general case as:

$$\Delta T_{\max} = \frac{\Delta H_0 \cdot M_0}{b_0} \cdot \left(\frac{d\alpha}{d\tau} \right)_{\max}$$

which for fast and slow processes takes the forms, $\Delta T_{\max} = \sqrt{\frac{2 \cdot \Delta H_0 \cdot M_0 \cdot V}{b_0}}$ and $\Delta T_{\max} = A \cdot V$, respectively.

For transformations of the second group, the DTA peak amplitude is described as:

$$\Delta T_{\max} = \frac{M_0 \cdot V}{b_0} \cdot \Delta C_{\max}$$

3. From the dependence of the DTA peak amplitude on the heating rate and the mass of the sample, it can be concluded to what group of transformations a given DTA peak belongs. This information can be useful for plotting phase diagrams.

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Резюме — Проведена классификация различных типов физико-химических превращений, которая может оказаться удобной при исследовании различных веществ методом термического анализа. Получены математические соотношения для двух классов физико-химических превращений, связывающие термодинамические характеристики превращения с параметрами пикор ДТА (дифференциального термического анализа). Теоретические положения статьи подтверждены экспериментальными результатами. Все эксперименты проводились на установке ДТА — 4, созданной в Институте Metallургии им. А. А. Байкова АН СССР.