© Mehtapress 2012
Cur.Chem.Res.

ISSN : 2278-0963

WWW.MEHTAPRESS.COM

Full Paper

Current
CHEMICAL RESEARCH

Received: 25/02/2010
Accepted: 18/03/2012

The thermographic method of determination of enthalpies, compositions and concentrations of phases in two-componential systems

B.G.Golovkin
Institute of Solid-State Chemistry, Ural Division, Russian Academy of Sciences,
Pervomaiskaya ul, 91. Yekaterinburg, 6200219, (RUSSIA)
E-mail: GBG1940@mail.ru

Abstract

The method of determination of enthalpies, chemical compositions and concentrations in two-componential equilibrium mixes without allocation of them is in the pure state offered according to curves DTA of reactions of synthesis only two samples of researched system.

Corresponding author's name and address
B.G.Golovkin
Institute of Solid-State Chemistry, Ural Division, Russian Academy of Sciences,
Pervomaiskaya ul, 91. Yekaterinburg, 6200219, (RUSSIA)

Search of new chemical compounds is connected to the phase analysis of products of the appropriate reactions in which the new phase can contain. Known quantitative methods of the phase analysis[1-5], as well as considered the present work a thermographic method demand the preliminary qualitative phase analysis of products of sintering of initial components of system in various ratio. It is necessary to fix the fact of existence of phases of unknown composition in samples and roughly to estimate an interval of concentration of components in which these phases are observed. However if for application of the mentioned above methods after a stage of the preliminary qualitative phase analysis it is necessary to prepare for equilibrium samples of the appropriate compositions that occupies long time (from several days about several months) the thermographic method of it does not demand.

As is known, in two-componential systems in balance can be no more than two phases. The offered method allows determining composition of these phases, not allocating them in the pure state. The thermal effect of reaction of interaction of initial components *A* and *B* is directly proportional to quantity of a formed phase at which formation it is allocated or absorbed warmth.

In samples *P* and *Q* there are reactions:

$$(1-p)A+pB=\alpha_p\frac{p}{x}(A_{1-x}B_x+\Delta H)+(1-\frac{p}{x})A \qquad (1)$$

$$(1-q)A+qB=\alpha_q\frac{1-q}{1-x}(A_{1-x}B_x+\Delta H)+\frac{q-x}{1-x}B \qquad (2)$$

Here ΔH – heat of formation of one asking phases X; a_p and a_q–a degree of completeness of course of reactions (1, 2) in conditions thermographic experiment. As the areas extremums S_p and S_q on curves DTA are proportional to thermal effects of reactions (1, 2) for their relation we have the equation:

$$\frac{S_p}{S_q}=\alpha_p\frac{p}{x}\Delta H:\alpha_q\frac{1-q}{1-x}\Delta H=\frac{p\alpha_p(1-x)}{x\alpha_q(1-q)} \qquad (3)$$

Having decided which, we shall receive:

$$x=\frac{p\alpha_q S_q}{p\alpha_q S_q+(1-q)\alpha_p S_p} \qquad (4)$$

However if curve DTA is removed up to rather high temperatures, sometimes down to temperature of formation of a liquid phase near to which speed of course of reactions sharply grows the degree of completeness of interaction appears close to unit:

$$\alpha_p\approx\alpha_q\approx 1 \qquad (5)$$

In the same cases when for any reasons shooting DTA at high temperatures appears impossible (presence of collateral reactions, phase transitions etc.), as in both samples *P* and Q the same reaction proceeds, its speeds in these samples will be relatives owing to what the approached equality should be carried out:

$$\alpha_p \approx \alpha_q \approx \alpha \tag{6}$$

At substitution α instead of α_p and α_q in the formula (4) factor α is reduced and resulting there is a formula:

$$x = \frac{pS_q}{pS_q + (1-q)S_p} \tag{7}$$

Quantities and concentration of a phase *X* it is calculated under formulas:

$$m_{xp} = \frac{p}{x} M_x \tag{8}$$

$$m_{xq} = \frac{1-q}{1-x} M_x \tag{9}$$

$$\mu_{xp} = \frac{pM_x}{x[(1-p)M_a + pM_b]} \tag{10}$$

$$\mu_{xq} = \frac{(1-q)M_x}{(1-x)[(1-q)M_a + qM_b} \tag{11}$$

Concentration of initial components we find on a difference:

$$\mu_{ap} = 1 - \mu_{xp} \tag{12}$$

$$\mu_{bq} = 1 - \mu_{xq} \tag{13}$$

With the account (7) heat of formation ΔH we shall find from the equation

$$\frac{p}{x} \Delta H = kS_p \tag{14}$$

where *k* – a constant of the device for the given conditions of shooting (it is determined by results of an estimation of the enthalpies in reactions with known heats of formation initial and end-products of reaction), equal:

$$\Delta H = \frac{kS_pS_q}{pS_q + (1-q)S_p} \tag{15}$$

EXAMPLE. In products of sintering $Ba_2V_2O_7$ with $Ba_4V_2O_9$[6] by the method of X-ray diffraction of the analysis was found out a phase which is distinct from initial phases. It is necessary to determine the quantitative contents of her, a chemical composition and enthalpy. For this purpose we prepare from $Ba_2V_2O_7$ and $Ba_4V_2O_9$ two stoichiometry for a mix P_0 from p = 0,25 composition $(Ba_2V_2O_7)_{0,75}$ $(Ba_4V_2O_9)_{0,25}$ and Q_0 from q = 0,75 composition $(Ba_2V_2O_7)_{0,25}$ $(Ba_4V_2O_9)_{0,75}$, carefully we fray, we remove them thermogram, we determine the areas экстремумов and we find in their equal S_p = 8,8 cm² and S_q = 9,1 cm². Under the formula (7) it is considered

$$x = \frac{0{,}25 \cdot 9{,}1}{0{,}25 \cdot 9{,}1 + 0{,}25 \cdot 8{,}8} \approx 0{,}51 \approx 0{,}5$$

Also we conclude, that the formed phase is $(Ba_3V_2O_7)$:

$$(Ba_2V_2O_7)_{0,49}\,(Ba_4V_2O_9)_{0,51} = Ba_{3,02}V_2O_8 \approx Ba_3V_2O_8.$$

Under formulas (19, 20) we calculate concentration of a phase *X* in samples *P* and *Q*:

$$\mu_{xp} = \frac{0{,}25 \cdot 641{,}904}{0{,}5(0{,}75 \cdot 488{,}564 + 0{,}25 \cdot 795{,}244} \approx 0{,}57$$

$$\mu_{xq} = \frac{0{,}25 \cdot 641{,}904}{0{,}5(0{,}25 \cdot 488{,}564 + 0{,}75 \cdot 795{,}244} \approx 0{,}54.$$

Considering, that for the given conditions of shooting a constant of the device on which carried out shooting by curve DTA,

k ≈ 6,0 kjoul / mole·mm².

We consider heat of formation $Ba_3V_2O_8$ from $Ba_2V_2O_7$ and $Ba_4V_2O_9$ for reaction:

$$Ba_2V_2O_7 + Ba_4V_2O_9 = 2Ba_3V_2O_8 + \Delta H \tag{16}$$

And that interval of temperatures at which there was a reaction of his synthesis, under the formula (15):

$$\Delta H = \frac{6 \cdot 8{,}8 \cdot 9{,}1}{0{,}25 \cdot 9{,}1 + 0{,}25 \cdot 8{,}8} = 107{,}4\,\text{kjoul / mole} \tag{17}$$

Enthalpies of formation standard conditions $\Delta_f H^0_{298K}$ $(Ba_2V_2O_7)$ and $\Delta_f H^0_{298K}$ $(Ba_4V_2O_9)$, designed on a method of cycle Born-Garber[7], are equal 3101,3 and 4500,2 kjoul / mole, accordingly. Enthalpy of formation $\Delta_f H^0_{298K}$ $(Ba_3V_2O_8)$, designed under Hess' law on the basis of the equation (16) in view of received in (17) values ΔH, it will be equal 3854,5 kjoul / mole. This size is close to the experimental value 3861,4 ± 12,2 kjoul / mole given in work[8].

Accuracy a thermographic method is determined by sensitivity of the device making shooting by curve DÒÀ, speed of shooting and accuracy of a way of measurement of the areas appropriate extremums. At an error of definition of the area of extremum on curve DTA ± 5 MM² accuracy of an estimation of structure of a phase can achieve 1-2 pier. %.

The described method is not applicable when in the field of temperatures at which reactions (1) proceed, takes place one or more phase transitions of initial components or products of these reactions, and also if the determined phase tests thermal disintegration. The method gives significant errors if initial components or formed phases have essential volatility.

REFERENCES

[1] B.G.Golovkin; Inorganic Materials, **45**, 1617-1618 (2009).

[2] B.G.Golovkin; Journal of Applied Spectroscopy, **75**, 416-418 (**2008**).

[3] Б.Г.Головкин; Заводская лаборатория. Диагностика материалов, **69**, 28-31 (**2003**).

[4] Б.Г.Головкин; Заводская лаборатория. Диагностика материалов, **69**, 20-24 (**2003**).

[5] Б.Г.Головкин; Заводская лаборатория. Диагностика материалов, **68**, 19-22 (**2002**).

[6] Б.Г.Головкин, Л.В.Кристаллов; Журнал неорганической химии, **35**, 253-255 (**1990**).

[7] Б.Г.Головкин; Журнал физической химии, **67**, 421-424 (**1993**).

[8] А.А.Фотиев, Б.В.Слободин, М.Я.Ходос; Ванадаты. Состав, синтез, структура, свойства, Изд. «Наука», Москва, (**1988**).