

# Thermodynamics of the enantiotropic phase transitions in condensed systems. I. One-component systems\*

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Thermodynamic analysis of the enantiotropic phase transitions of the 1st order in one-component systems is presented. The relations for the experimentally undeterminable temperature of fusion,  $T_{\alpha}^f$ , and for the enthalpy of the phase transition,  $\Delta H_{\alpha}^f$ , of the low-temperature  $\alpha$ -modification of the substance under investigation have been established.

In recent years, there has been a steadily increasing interest in substances which in the solid state may exist in various modifications, the transition from one modification to another one being characteristic of the phase transition of the 1st order. If this phase transition is accompanied by a sufficiently high value of the enthalpy of the phase transition, then these substances can be used as standards in the calibration of thermocouples [1].

The choice of these transition temperatures for the calibration has several advantages in comparison with the conventional method where the melting points of various metals and salts, respectively, are used as reference substances.

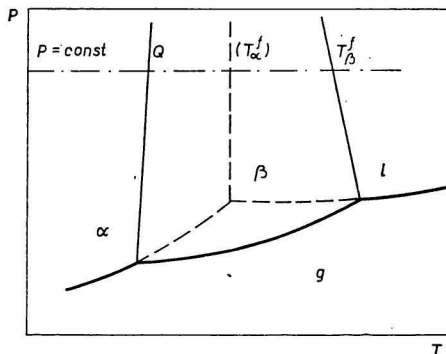
In spite of this increasing importance of the practical application of the temperatures of the polymorphous phase transitions, the thermodynamic aspects of these phenomena appear to be inadequately elaborated. This problem will be dealt with in the present work.

*Fig. 1.* Schematic presentation of the phase diagram of a one-component system with an enantiotropic phase transition.

Q — point of the equilibrium of the low-temperature ( $\alpha$ ) and the high-temperature ( $\beta$ ) modification;

$T_{\alpha}^f$  — hypothetical melting point of the low-temperature modification  $\alpha$  (undeterminable experimentally);

$T_{\beta}^f$  — melting point of the high-temperature modification  $\beta$ .



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The systems of this type are schematically presented in Fig. 1. The melting point of the high-temperature modification,  $T_\beta^f$ , and the corresponding value of the change of the enthalpy of the phase transition " $\beta \rightarrow \text{liq}$ ",  $\Delta H_\beta^f$ , as well as the molar heat capacities,  $C_P^l$ ,  $C_P^\beta$ ,  $C_P^\alpha$ , the transition temperature " $\alpha \rightarrow \beta$ ",  $T_\alpha^f$ , and the corresponding value  $\Delta H_{T_\alpha^f}^{\beta/\alpha}$  can be determined experimentally (further  $\Delta H_{T_\alpha^f}^{\beta/\alpha} = \Delta H^{tr}$ ).

On the other hand, neither the melting temperature,  $T_\alpha^f$ , of the low-temperature modification nor the change of the enthalpy corresponding to the process " $\alpha \rightarrow \text{liq}$ ",  $\Delta H_\alpha^f$ , can be determined experimentally under the equilibrium conditions.

The aim of our considerations is to determine the quantities  $\Delta H_\alpha^f$ ,  $\Delta H_{T_\alpha^f}^{\beta/\alpha}$ ,  $\Delta S_\alpha^f$ ,  $\Delta S_{T_\alpha^f}^{\beta/\alpha}$ , and  $T_\alpha^f$ .

### 1. Determination of $\Delta H_{T_\alpha^f}^{\beta/\alpha}$

For the molar heat capacity the expression  $C_P = (\partial H / \partial T)_P$  holds for both the phase " $2$ ", i.e.  $dH^{(2)} = C_P^{(2)} dT$ , and the phase " $1$ ", i.e.  $dH^{(1)} = C_P^{(1)} dT$ , the difference in these expressions being

$$d(H^{(2)} - H^{(1)}) = d\Delta H^{2/1} = \Delta C_P^{2/1} dT. \quad (1)$$

By the integration in the limits  $(T_a, T_b)$  we obtain

$$\int_{T_a}^{T_b} d\Delta H^{2/1} = \Delta H_{T_b}^{2/1} - \Delta H_{T_a}^{2/1} = \int_{T_a}^{T_b} \Delta C_P^{2/1} dT. \quad (2)$$

The dependence  $H = f(T)$  for the systems of this type is presented in Fig. 2.

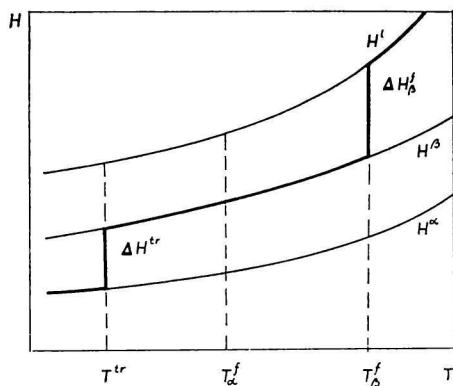


Fig. 2. Temperature dependence of the enthalpy.

$H^l$  — enthalpy of the substance in the liquid state;

$H^\beta$  — enthalpy of the high-temperature modification  $\beta$ ;

$H^\alpha$  — enthalpy of the low-temperature modification  $\alpha$ .

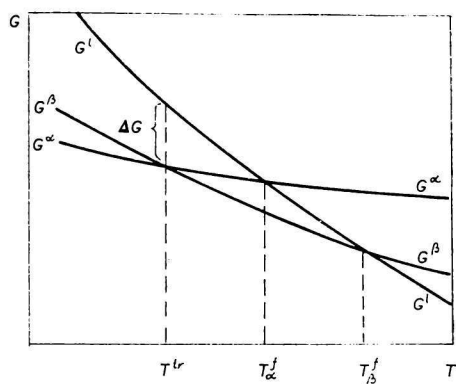


Fig. 3. Temperature dependence of the Gibbs energy.

$G^l$  — Gibbs energy of the substance in the liquid state;

$G^\beta$  — Gibbs energy of the high-temperature solid modification of the substance;

$G^\alpha$  — Gibbs energy of the low-temperature solid modification of the substance.

1.1. Let  $\Delta C_P^{2/1} = 0$ .

The lines  $H^1$ ,  $H^\beta$ ,  $H^\alpha$  are parallel ( $\Delta H^{1/\beta} = \text{const}$ ,  $\Delta H^{\beta/\alpha} = \text{const}$ ); hence independently of temperature it holds

$$\Delta H^{1/\alpha} = \Delta H^{1/\beta} + \Delta H^{\beta/\alpha} = \text{const}. \quad (3)$$

1.2. Let  $\Delta C_P^{2/1} \neq 0$ .

We use relation (3) in the form

$$\Delta H_{T^{\text{tr}}}^{1/\alpha} = \Delta H_{T^{\text{tr}}}^{1/\beta} + \Delta H^{\text{tr}} \quad (4)$$

since it holds

$$\Delta H_{T^{\text{tr}}}^{1/\beta} = \Delta H_\beta^{\text{f}} - \int_{T^{\text{tr}}}^{T_\beta^{\text{f}}} \Delta C_P^{1/\beta} dT \quad (5)$$

and we finally obtain

$$\Delta H_{T^{\text{tr}}}^{1/\alpha} = \Delta H_\beta^{\text{f}} + \Delta H^{\text{tr}} - \int_{T^{\text{tr}}}^{T_\beta^{\text{f}}} \Delta C_P^{1/\beta} dT. \quad (6)$$

The following proceeding can be applied as well:

$$\Delta H_{T^{\text{tr}}}^{1/\alpha} = \Delta H_\alpha^{\text{f}} - \int_{T^{\text{tr}}}^{T_\alpha^{\text{f}}} \Delta C_P^{1/\alpha} dT. \quad (7)$$

Since it holds

$$\Delta H_\alpha^{\text{f}} = \Delta H_{T_\alpha^{\text{f}}}^{1/\beta} + \Delta H_{T_\alpha^{\text{f}}}^{\beta/\alpha}, \quad (8)$$

$$\Delta H_{T_\alpha^{\text{f}}}^{1/\beta} = \Delta H_\beta^{\text{f}} - \int_{T_\alpha^{\text{f}}}^{T_\beta^{\text{f}}} \Delta C_P^{1/\beta} dT, \quad (9)$$

$$\Delta H_{T_\alpha^{\text{f}}}^{\beta/\alpha} = \Delta H^{\text{tr}} - \int_{T_\alpha^{\text{f}}}^{T^{\text{tr}}} \Delta C_P^{\beta/\alpha} dT \quad (10)$$

after substituting into (7) we obtain

$$\Delta H_{T^{\text{tr}}}^{1/\alpha} = \Delta H_\beta^{\text{f}} + \Delta H^{\text{tr}} - \int_{T_\alpha^{\text{f}}}^{T_\beta^{\text{f}}} \Delta C_P^{1/\beta} dT - \int_{T_\alpha^{\text{f}}}^{T^{\text{tr}}} \Delta C_P^{\beta/\alpha} dT - \int_{T^{\text{tr}}}^{T_\alpha^{\text{f}}} \Delta C_P^{1/\alpha} dT. \quad (11)$$

By comparing (7) and (11) and rearranging we obtain the identity

$$\Delta C_P^{1/\alpha} = \Delta C_P^{1/\beta} + \Delta C_P^{\beta/\alpha}. \quad (12)$$

The correctness of this identity may be shown by the transcription

$$C_P^{1/\alpha} = C_P^1 - C_P^\alpha, \text{ etc.}$$

Thus the quantity  $\Delta H_{T^{\text{tr}}}^{1/\alpha}$  can be determined by means of eqn (6). On the other hand, the quantity  $\Delta H_\alpha^{\text{f}}$  cannot be determined in the same way since the temperature  $T_\alpha^{\text{f}}$  remains unknown.

## 2. Determination of $\Delta S_{T^{\text{tr}}}^{l/\alpha}$

According to the differential definition of the enthalpy at  $P = \text{const}$  it holds that  $dH = T dS$ . Let us write this relation for the phases "2" and "1" and make the difference (at the same temperature):

$$d\Delta H^{2/1} = T d\Delta S^{2/1}. \quad (13)$$

From a comparison of (1) and (13) it follows

$$d\Delta S^{2/1} = \Delta C_P^{2/1} d \ln T. \quad (14)$$

Integrating eqn (14) in the limits  $(T_a, T_b)$ , we obtain

$$\Delta S_{T_b}^{2/1} - \Delta S_{T_a}^{2/1} = \int_{T_a}^{T_b} \Delta C_P^{2/1} d \ln T. \quad (15)$$

For the systems of this type, the dependence  $S = f(T)$  is analogous to the dependence  $H = f(T)$ .

2.1. Let  $\Delta C_P = 0$ .

Then it holds independently of the temperature  $T$

$$\Delta S^{l/\alpha} = \Delta S^{l/\beta} + \Delta S^{\beta/\alpha} = \text{const}. \quad (16)$$

2.2. Let  $\Delta C_P^{2/1} \neq 0$ .

In the same way as for the function  $H$ , we obtain relation

$$\Delta S_{T^{\text{tr}}}^{l/\alpha} = \Delta S_{\beta}^f + \Delta S^{\text{tr}} - \int_{T^{\text{tr}}}^{T_{\beta}^f} \Delta C_P^{l/\beta} d \ln T, \quad (17)$$

which can be used for the determination of the quantity  $\Delta S_{T^{\text{tr}}}^{l/\alpha}$ .

Eqn (17) can be transcribed in such a way as to show the sequence of operations by which the affected quantity may be determined. The quantity  $\Delta S_{T^{\text{tr}}}^{l/\alpha}$  can be experimentally determined in the following steps:

a) Transition " $\alpha \rightarrow \beta$ " at  $T^{\text{tr}}$ :  $\Delta S^{\text{tr}}$ .

b) Heating of " $\beta$ " from  $T^{\text{tr}}$  to  $T_{\beta}^f$ :  $\int_{T^{\text{tr}}}^{T_{\beta}^f} C_P^{\beta} d \ln T$ .

c) Melting " $\beta \rightarrow l$ " at  $T_{\beta}^f$ :  $\Delta S_{\beta}^f$ .

d) Cooling of " $l$ " from  $T_{\beta}^f$  to  $T^{\text{tr}}$ :  $\int_{T^{\text{tr}}}^{T_{\beta}^f} C_P^l d \ln T$ .

The required quantity is given by the sum of the above terms. It also holds

$$\Delta S_{T^{\text{tr}}}^{l/\alpha} = \Delta S_{\alpha}^f - \int_{T^{\text{tr}}}^{T_{\alpha}^f} \Delta C_P^{l/\alpha} d \ln T. \quad (18)$$

Relation (18) is analogous to eqn (7). The further proceeding is the same as that reported above (eqns (7–11)).

The quantity  $\Delta S_{\alpha}^f$  cannot be calculated for the same reason as is the case with  $\Delta H_{\alpha}^f$ .

3. Determination of  $T_\alpha^f$ 

The calculation is based on the Gibbs energy  $G$ . According to the differential definition of this function, at  $P = \text{const}$  it holds that  $dG = -S dT$ ; for the process under investigation we get

$$d\Delta G^{2/1} = -\Delta S^{2/1} dT. \quad (19)$$

Integrating eqn (19) from  $T_a$  (the lower limit) to  $T_b$ , and rearranging we obtain

$$\Delta G_{T_a}^{2/1} = \Delta S_{T_b}^{2/1}(T_b - T_a) - \int_{T_a}^{T_b} \int_T \Delta C_P^{2/1} d \ln T dT. \quad (20)$$

It is assumed that at  $T = T_b$  it holds that  $G^2 = G^1$  and hence  $\Delta G_{T_b}^{2/1} = 0$ .

The course of the dependence  $G = f(T)$  for the systems of this type is presented in Fig. 3. As evident, whilst  $T = T^{tr}$ , it holds not only that  $G^\alpha = G^\beta$ , but also that

$$\Delta G_{T^{tr}}^{1/\alpha} = \Delta G_{T^{tr}}^{1/\beta}. \quad (21)$$

$$3.1. \Delta C_P^{2/1} = 0.$$

From eqn (20) it follows

$$\Delta G_{T^{tr}}^{1/\beta} = \Delta S_\beta^f(T_\beta^f - T^{tr}), \quad (22)$$

$$\Delta G_{T^{tr}}^{1/\alpha} = \Delta S_\alpha^f(T_\alpha^f - T^{tr}). \quad (23)$$

By comparing (22) with (23) and rearranging we get

$$T_\alpha^f = \frac{T_\beta^f \Delta S_\beta^f + T^{tr} \Delta S^{tr}}{\Delta S_\beta^f + \Delta S^{tr}}. \quad (24)$$

In this case, the quantities  $\Delta S^{2/1}$  do not depend on temperature and hence  $\Delta S_\beta^f = \Delta S_{T_\alpha^f}^{1/\beta}$ .

$$3.2. \Delta C_P^{2/1} \neq 0.$$

At  $T = T^{tr}$  it holds

$$\Delta G_{T^{tr}}^{1/\beta} = \Delta S_\beta^f(T_\beta^f - T^{tr}) - \int_{T^{tr}}^{T_\beta^f} \int_T \Delta C_P^{1/\beta} d \ln T dT. \quad (25)$$

All the quantities on the right side of this equation can be determined experimentally

$$\Delta G_{T^{tr}}^{1/\alpha} = \Delta S_\alpha^f(T_\alpha^f - T^{tr}) - \int_{T^{tr}}^{T_\alpha^f} \int_T \Delta C_P^{1/\alpha} d \ln T dT. \quad (26)$$

The quantity  $\Delta C_P^{1/\alpha}$  can be determined using relation (12). Thus it remains to determine the quantities  $\Delta S_\alpha^f$  and  $T_\alpha^f$ .

It holds

$$\Delta S_\alpha^f = \Delta S_{T_\alpha^f}^{1/\beta} + \Delta S_{T_\alpha^f}^{\beta/\alpha}, \quad (27)$$

$$\Delta S_{T_\alpha^f}^{1/\beta} = \Delta S_\beta^f - \int_{T_\alpha^f}^{T_\beta^f} \Delta C_P^{1/\beta} d \ln T, \quad (28)$$

$$\Delta S_{T_{\alpha}^f}^{\beta/\alpha} = \Delta S^{\text{tr}} - \int_{T_{\alpha}^f}^{T^{\text{tr}}} \Delta C_P^{\beta/\alpha} d \ln T. \quad (29)$$

Then for the quantity  $\Delta S_{\alpha}^f$  one can write

$$\Delta S_{\alpha}^f = \Delta S_{\beta}^f + \Delta S^{\text{tr}} - \int_{T_{\alpha}^f}^{T_{\beta}^f} \Delta C_P^{\beta/\alpha} d \ln T - \int_{T_{\alpha}^f}^{T^{\text{tr}}} \Delta C_P^{\beta/\alpha} d \ln T. \quad (30)$$

(Thus  $\Delta S_{\alpha}^f$  is a function of  $T_{\alpha}^f$ .)

After substituting from (30) into (26), only one unknown,  $T_{\alpha}^f$ , remains on the right side of eqn (26). This quantity can be calculated by comparing eqns (25) and (26). Subsequently, it is possible to determine also the quantity  $\Delta H_{\alpha}^f$  from eqn (7) and the quantity  $\Delta S_{\alpha}^f$  from eqn (18).

*Application of the derived relations in the calculation of the unknown values of  $T_{\alpha}^f$  and  $\Delta H_{\alpha}^f$  for  $\text{Na}_3\text{AlF}_6$ ,  $\text{BaCl}_2$ , and  $\text{CaF}_2$*

For practical purposes, for the calculation of  $C_P$  most frequently the empirical expansion of the type

$$C_P = a + bT + cT^{-2}$$

is used. By substituting into the relations (2), (15), and (20), we obtain after rearranging equations

$$\Delta H_{T_a}^{2/1} = \Delta H_{T_b}^{2/1} - \Delta a^{2/1}(T_b - T_a) - \frac{\Delta b^{2/1}}{2}(T_b^2 - T_a^2) + \Delta c^{2/1}[1/T_b - 1/T_a], \quad (31)$$

$$\Delta S_{T_a}^{2/1} = \Delta S_{T_b}^{2/1} - \Delta a^{2/1} \ln(T_b/T_a) - \Delta b^{2/1}(T_b - T_a) + \frac{\Delta c^{2/1}}{2}[1/T_b^2 - 1/T_a^2], \quad (32)$$

$$\begin{aligned} \Delta G_{T_a}^{2/1} = & \Delta S_{T_b}^{2/1}(T_b - T_a) + \Delta a^{2/1}[T_a \ln(T_b/T_a) - T_b + T_a] + \\ & + \frac{\Delta b^{2/1}}{2}(T_b - T_a)^2 - \frac{\Delta c^{2/1} T_a}{2}[1/T_b - 1/T_a]^2. \end{aligned} \quad (33)$$

#### a) $\text{Na}_3\text{AlF}_6$

The required thermochemical parameters for cryolite were reported by O'Brien and Kelley [2], Frank [3], and recently by JANAF [4]. All these three groups of data were applied in the calculation in the case when  $\Delta C_P = 0$  (Table 1).

For the exact determination of the required values (for  $\Delta C_P \neq 0$ ) the data proposed by JANAF [4] were accepted. For the expansion of  $C_P$  and  $C_P = f(T)$ , the data reported by O'Brien and Kelley [2] and the value of  $C_P^l$  proposed by JANAF [4] were used:

$$C_P^{\alpha} = (45.95 + 29.46 \times 10^{-3} T - 2.78 \times 10^5 T^{-2}) \text{ gibbs mol}^{-1},$$

$$C_P^{\beta} = (52.15 + 15.86 \times 10^{-3} T) \text{ gibbs mol}^{-1},$$

$$C_P^l = 94.7 \text{ gibbs mol}^{-1}.$$

The results of the calculation are listed in Table 2.

Table 1

Thermochemical parameters of the melting process of the low-temperature modification of  $\text{Na}_3\text{AlF}_6$  calculated on the basis of the initial data presented by different authors on the presumption that  $\Delta C_P^{2/1} = 0$

Author	$T_\beta^f$ [K]	$T^{\text{tr}}$ [K]	$\Delta H_\beta^f$ [kcal mol <sup>-1</sup> ]	$\Delta H^{\text{tr}}$ [kcal mol <sup>-1</sup> ]	$T_\alpha^f$ [K]	$\Delta H_\alpha^f$ [kcal mol <sup>-1</sup> ]
<i>O'Brien et al.</i> [2]	1300	845	27.64	2.16	1251.16	29.80
<i>Frank</i> [3]	1279	833.5	26.71	2.22	1228.61	28.93
<i>JANAF</i> [4]	1285	838	25.64	1.97	1237.88	27.61

Table 2

Thermochemical parameters of the melting process of the low-temperature modifications of  $\text{Na}_3\text{AlF}_6$ ,  $\text{BaCl}_2$ , and  $\text{CaF}_2$

Sub- stance	Ref.	$C_P = 0$				$C_P \neq 0$			
		$T_\beta^f$ [K]	$T^{\text{tr}}$ [K]	$\Delta H_\beta^f$ [kcal mol <sup>-1</sup> ]	$\Delta H^{\text{tr}}$ [kcal mol <sup>-1</sup> ]	$T_\alpha^f$ [K]	$\Delta H_\alpha^f$ [kcal mol <sup>-1</sup> ]	$T_\alpha^f$ [K]	$\Delta H_\alpha^f$ [kcal mol <sup>-1</sup> ]
$\text{Na}_3\text{AlF}_6$	[4]	1285	838	25.64	1.97	1237.9	27.61	1266	23.83
$\text{BaCl}_2$	[5]	1233	1193	3.90	4.10	1212.2	8.00	1212.3	8.01
$\text{CaF}_2$	[8]	1691	1424	7.10	1.14	1648.2	8.24	1637	9.428

#### b) $\text{BaCl}_2$

The thermochemical parameters of this substance were determined by *Dworkin* [5] and *Janz* [6]. With respect to the attitude of *Lumsden* [7], the data presented by *Dworkin* were accepted for this calculation.

$$C_P^\alpha = 23.1 \text{ gibbs mol}^{-1},$$

$$C_P^\beta = 25.5 \text{ gibbs mol}^{-1},$$

$$C_P^l = 26.3 \text{ gibbs mol}^{-1}.$$

The remaining initial parameters and the results of the calculations are listed in Table 2.

#### c) $\text{CaF}_2$

The thermochemical parameters were presented by *Naylor* [8].

$$C_P^\alpha = (14.30 + 7.28 \times 10^{-3} T + 4.69 \times 10^5 T^{-2}) \text{ gibbs mol}^{-1},$$

$$C_P^\beta = (25.81 + 2.5 \times 10^{-3} T) \text{ gibbs mol}^{-1},$$

$$C_P^l = 23.88 \text{ gibbs mol}^{-1}.$$

The remaining initial parameters and the results of the calculations are listed in Table 2.

In Table 2, two sets of values of the parameters  $T_\alpha^f$  and  $\Delta H_\alpha^f$  are listed, one of which was calculated on the simplified assumption that  $\Delta C_P^{2/1} = 0$ , and the other one was determined exactly, for  $\Delta C_P^{2/1} \neq 0$ . In the case of  $\text{BaCl}_2$  it is evident that, because of the small differences  $T_\beta^f - T^{\text{tr}}$ , the results obtained by both methods are practically identical. When the differences  $T_\beta^f - T^{\text{tr}}$  are great, the method of calculation for  $\Delta C_P^{2/1} \neq 0$  appears to be mathematically more exact. In the calculation it is assumed that the relation for  $C_P^f$ , determined for temperatures  $T \leq T^{\text{tr}}$ , can be extrapolated up to the temperature  $T_\alpha^f$ ; this assumption need not be generally valid from the physical aspect.

In the case of  $\text{Na}_3\text{AlF}_6$ , the calculation for  $\Delta C_P^{2/1} \neq 0$  furnishes a value  $\Delta H_\alpha^f$  inferior to that of  $\Delta H_\beta^f$  which is rather a seldom case.

The parameters  $T_\alpha^f$  and  $\Delta H_\alpha^f$  find a practical application mainly in the case of the binary and higher systems. This will be treated in a subsequent paper.

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