Calculation of thermodynamic excess functions in binary systems on the basis of isobaric phase equilibria and calorimetric measurements of changes in enthalpy

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Dedicated to Professor M. Gregor, DrSc, Corresponding Member
of the Slovak Academy of Sciences, on his 75th birthday

The general procedure of calculation of mixing parameters ΔS^E_{mix} and ΔG^E_{mix} in binary systems the components of which do not form compounds is presented. The excess functions can be calculated in this way assuming that the phase diagram of the system in question is known and that the corresponding enthalpies of mixing and of phase transitions are known in the chosen temperature range as well.

В работе дан общий ход вычисления функций смешивания ΔS^E_{mix} и ΔG^E_{mix} в бинарных системах компоненты которых не образуют соединения. Избыточные функции можно рассчитать этим способом только в случае известной фазовой диаграммы данной системы и известных соответствующих теплот смешения и теплот фазовых превращений в избранном температурном интервале.

On the basis of thermodynamic excess functions ΔH^E_{mix}, ΔS^E_{mix} (and therefore also ΔG^E_{mix}) of a binary system and from their isobaric temperature functions the values of some energetic and structural properties of the system can be calculated [1, 2] and compared with those of model solutions [3].

Knowing the isobaric temperature functions of heats of mixing and isobaric phase diagram of the studied system the thermodynamic molar excess functions can be calculated as follows.

1. Calculation of excess entropy of a binary solution which coexists with crystals of component *A* or *B*. It is assumed that the concentration of the second component in the crystals is very low and that the components do not form compounds.

Let us have two phases α and β which coexist in equilibrium. The components A and B are present in both phases. Then it holds

$$\mu_{A,\alpha}(x, T_{eq}(x, y)) = \mu_{A,\beta}(y, T_{eq}(x, y)) \tag{1}$$

and

$$\mu_{B,\alpha}(x, T_{eq}(x, y)) = \mu_{B,\beta}(y, T_{eq}(x, y)) \tag{2}$$

x and y are equilibrium mole fractions of component B in the phase α and β, respectively, and $T_{eq}(x, y)$ is the temperature at which both phases are in equilibrium (Fig. 1). The phase α is a solution for which in the concentration range 0—x_{eut} and at coexistence of both phases $x \gtrless y$ and in the concentration range x_{eut}—1 $y \gtrless x$ (x_{eut} being the mole fraction of component B in the eutectic solution).

If the concentration y of component B in the phase β is very low, the equilibrium between the almost pure crystal of the component A and the solution may be approximately described by the relation (for $x \leqq x_{eut}$)

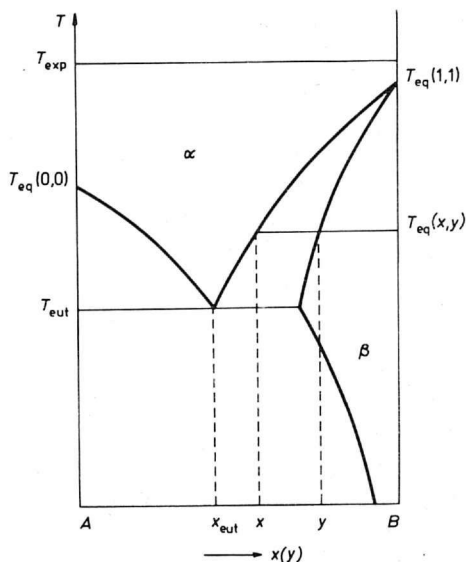$$\mu_{A,\alpha}(x, T_{eq}(x, 0)) = \mu_{A,\beta}(0, T_{eq}(x, 0)) \tag{3}$$

Fig. 1. Phase diagram of a binary system A—B.

This relation can be used for calculation of excess entropy of a solution at the temperature T_{exp} (the temperature for which the experimental data are known). From eqn (3) it follows

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$$\bar{H}_{A,\alpha}(x, T_{eq}(x, 0)) - T_{eq}(x, 0)\,\bar{S}_{A,\alpha}(x, T_{eq}(x, 0)) =$$
$$= H_{A,\beta}(0, T_{eq}(x, 0)) - T_{eq}(x, 0)\,S_{A,\beta}(0, T_{eq}(x, 0)) \tag{4}$$

or

$$\bar{S}_{A,\alpha}(x, T_{eq}(x, 0)) = \frac{\bar{H}_{A,\alpha}(x, T_{eq}(x, 0)) - H_{A,\beta}(0, T_{eq}(x, 0))}{T_{eq}(x, 0)} +$$
$$+ S_{A,\beta}(0, T_{eq}(x, 0)) \tag{5}$$

The value of the partial molar entropy of component A in the solution at the temperature T_{exp} equals

$$\bar{S}_{A,\alpha}(x, T_{exp}) = \frac{\bar{H}_{A,\alpha}(x, T_{eq}(x, 0)) - H_{A,\beta}(0, T_{eq}(x, 0))}{T_{eq}(x, 0)} + S_{A,\beta}(0, T_{eq}(x, 0)) +$$
$$+ \int_{T_{eq}(x, 0)}^{T_{exp}} \frac{\bar{C}_{A,\alpha}(x, T)}{T}\,dT \tag{6}$$

and thus for the partial molar entropy of mixing it follows

$$\Delta \bar{S}_{mix,A,\alpha}(x, T_{exp}) = \bar{S}_{A,\alpha}(x, T_{exp}) - S_{A,\alpha}(0, T_{exp}) =$$
$$= \frac{\bar{H}_{A,\alpha}(x, T_{eq}(x, 0)) - H_{A,\beta}(0, T_{eq}(x, 0))}{T_{eq}(x, 0)} + S_{A,\beta}(0, T_{eq}(x, 0)) +$$
$$+ \int_{T_{eq}(x, 0)}^{T_{exp}} \frac{\bar{C}_{A,\alpha}(x, T)}{T}\,dT - \left[S_{A,\beta}(0, T_{eq}(x, 0)) + \int_{T_{eq}(x, 0)}^{T_{eq}(0, 0)} \frac{C_{A,\beta}(0, T)}{T}\,dT + \right.$$
$$\left. + \frac{\Delta H_{tr,A}(T_{eq}(0, 0))}{T_{eq}(0, 0)} + \int_{T_{eq}(0, 0)}^{T_{exp}} \frac{C_{A,\alpha}(0, T)}{T}\,dT \right] \tag{7}$$

The term in brackets equals $S_{A,\alpha}(0, T_{exp})$. $\Delta H_{tr,A}(T_{eq}(0, 0))$ is the change in enthalpy at the phase transition of β in α at equilibrium temperature. After rearranging eqn (7) we obtain (for $x \le x_{eut}$)

$$\Delta \bar{S}_{mix,A,\alpha}(x, T_{exp}) = \frac{\bar{H}_{A,\alpha}(x, T_{eq}(x, 0)) - H_{A,\beta}(0, T_{eq}(x, 0))}{T_{eq}(x, 0)} +$$
$$+ \int_{T_{eq}(x, 0)}^{T_{exp}} \frac{\bar{C}_{A,\alpha}(x, T)}{T}\,dT - \int_{T_{eq}(x, 0)}^{T_{eq}(0, 0)} \frac{C_{A,\beta}(0, T)}{T}\,dT - \frac{\Delta H_{tr,A}(T_{eq}(0, 0))}{T_{eq}(0, 0)} -$$
$$- \int_{T_{eq}(0, 0)}^{T_{exp}} \frac{C_{A,\alpha}(0, T)}{T}\,dT \tag{8}$$

The right side of eqn (8) can be expanded by adding zero differences of the quantities; then

$$\Delta \bar{S}_{\text{mix},A,\alpha}(x, T_{\text{exp}}) =$$

$$= \frac{\bar{H}_{A,\alpha}(x, T_{\text{eq}}(x, 0)) - H_{A,\beta}(0, T_{\text{eq}}(x, 0)) + H_{A,\alpha}(0, T_{\text{eq}}(x, 0)) - H_{A,\alpha}(0, T_{\text{eq}}(x, 0))}{T_{\text{eq}}(x, 0)}$$

$$+$$

$$+ \int_{T_{\text{eq}}(x, 0)}^{T_{\text{exp}}} \frac{\bar{C}_{A,\alpha}(x, T)}{T} \, dT + \int_{T_{\text{eq}}(x, 0)}^{T_{\text{exp}}} \frac{C_{A,\alpha}(0, T)}{T} \, dT - \int_{T_{\text{eq}}(x, 0)}^{T_{\text{exp}}} \frac{C_{A,\alpha}(0, T)}{T} \, dT -$$

$$- \int_{T_{\text{eq}}(x, 0)}^{T_{\text{eq}}(0, 0)} \frac{C_{A,\beta}(0, T)}{T} \, dT + \int_{T_{\text{eq}}(x, 0)}^{T_{\text{eq}}(0, 0)} \frac{C_{A,\alpha}(0, T)}{T} \, dT - \int_{T_{\text{eq}}(x, 0)}^{T_{\text{eq}}(0, 0)} \frac{C_{A,\alpha}(0, T)}{T} \, dT -$$

$$- \frac{\Delta H_{\text{tr},A}(T_{\text{eq}}(0,0))}{T_{\text{eq}}(0, 0)} - \int_{T_{\text{eq}}(0, 0)}^{T_{\text{exp}}} \frac{C_{A,\alpha}(0, T)}{T} \, dT \qquad (9)$$

After arithmetic operations we obtain the final relationship

$$\Delta \bar{S}_{\text{mix},A,\alpha}(x, T_{\text{exp}}) = \frac{\Delta \bar{H}_{\text{mix},A,\alpha}(x, T_{\text{eq}}(x, 0)) + \Delta H_{\text{tr},A}(T_{\text{eq}}(x, 0))}{T_{\text{eq}}(x, 0)} +$$

$$+ \int_{T_{\text{eq}}(x, 0)}^{T_{\text{exp}}} \frac{\Delta \bar{C}_{\text{mix},A,\alpha}(x, T)}{T} \, dT + \int_{T_{\text{eq}}(x, 0)}^{T_{\text{eq}}(0, 0)} \frac{\Delta C_{\text{tr},A}(0, T)}{T} \, dT -$$

$$- \frac{\Delta H_{\text{tr},A}(T_{\text{eq}}(0, 0))}{T_{\text{eq}}(0, 0)} \qquad (10)$$

In the same way we can calculate the partial molar entropy of mixing of component B in the range $x \geqq x_{\text{eut}}$ and at the temperature T_{exp}. (The same assumption about coexistence of almost pure substance B with melt as in the former case has to be fulfilled.)

$$\bar{S}_{\text{mix},B,\alpha}(x, T_{\text{exp}}) = \frac{\bar{H}_{B,\alpha}(x, T_{\text{eq}}(x, 1)) - H_{B,\beta}(1, T_{\text{eq}}(x, 1))}{T_{\text{eq}}(x, 1)} +$$

$$+ \int_{T_{\text{eq}}(x, 1)}^{T_{\text{exp}}} \frac{\bar{C}_{B,\alpha}(x, T)}{T} \, dT - \int_{T_{\text{eq}}(x, 1)}^{T_{\text{eq}}(1, 1)} \frac{C_{B,\beta}(1, T)}{T} \, dT - \frac{\Delta H_{\text{tr},B}(T_{\text{eq}}(1, 1))}{T_{\text{eq}}(1, 1)} -$$

$$- \int_{T_{\text{eq}}(1, 1)}^{T_{\text{exp}}} \frac{C_{B,\alpha}(1, T)}{T} \, dT \qquad (11)$$

or

$$\Delta \bar{S}_{\text{mix},B,\alpha}(x, T_{\text{exp}}) = \frac{\Delta \bar{H}_{\text{mix},B,\alpha}(x, T_{\text{eq}}(x, 1)) + \Delta H_{\text{tr},B}(T_{\text{eq}}(x, 1))}{T_{\text{eq}}(x, 1)} +$$

$$+ \int_{T_{\text{eq}}(x, 1)}^{T_{\text{exp}}} \frac{\Delta \bar{C}_{\text{mix},B,\alpha}(x, T)}{T} \, dT + \int_{T_{\text{eq}}(x, 1)}^{T_{\text{eq}}(1, 1)} \frac{\Delta C_{\text{tr},B}(1, T)}{T} \, dT - \frac{\Delta H_{\text{tr},B}(T_{\text{eq}}(1, 1))}{T_{\text{eq}}(1, 1)} \qquad (12)$$

At the eutectic temperature both almost pure crystal components A and B coexist in equilibrium with a eutectic solution and therefore it is possible to calculate partial molar entropies of mixing for both components $(\Delta \bar{S}_{\text{mix},A,\alpha}(x_{\text{eut}}, T_{\text{exp}})$ and $\Delta \bar{S}_{\text{mix},B,\alpha}(x_{\text{eut}}, T_{\text{exp}})$. The values $\Delta \bar{S}_{\text{mix},B,\alpha}(x, T_{\text{exp}})$ for $x \leqq x_{\text{eut}}$ and $\Delta \bar{S}_{\text{mix},A,\alpha}(x, T_{\text{exp}})$ for $x \geqq x_{\text{eut}}$ are calculated using relevant integrated Gibbs—Duhem equations.

For $x \leqq x_{\text{eut}}$

$$\Delta \bar{S}_{\text{mix},B,\alpha}(x, T_{\text{exp}}) = \Delta \bar{S}_{\text{mix},B,\alpha}(x_{\text{eut}}, T_{\text{exp}}) -$$

$$- \int_{\Delta \bar{S}_{\text{mix},A,\alpha}(x_{\text{eut}}, T_{\text{exp}})}^{\Delta \bar{S}_{\text{mix},A,\alpha}(x, T_{\text{exp}})} \frac{1-x}{x} \, d\Delta \bar{S}_{\text{mix},A,\alpha}(x, T_{\text{exp}}) \qquad (13)$$

and for $x \geqq x_{\text{eut}}$

$$\Delta \bar{S}_{\text{mix},A,\alpha}(x, T_{\text{exp}}) = \Delta \bar{S}_{\text{mix},A,\alpha}(x_{\text{eut}}, T_{\text{exp}}) -$$

$$- \int_{\Delta \bar{S}_{\text{mix},B}(x_{\text{eut}}, T_{\text{exp}})}^{\Delta \bar{S}_{\text{mix},B}(x, T_{\text{exp}})} \frac{x}{1-x} \, d\Delta \bar{S}_{\text{mix},B,\alpha}(x, T_{\text{exp}}) \qquad (14)$$

The excess entropy of a solution of components A and B at the temperature T_{exp} is given by the relation

$$\Delta S^{\text{E}}_{\text{mix},\alpha}(x, T_{\text{exp}}) = \Delta S_{\text{mix},\alpha}(x, T_{\text{exp}}) - \Delta S_{\text{mix(id)},\alpha}(x, T_{\text{exp}}) =$$

$$= (1-x) \, \Delta \bar{S}_{\text{mix},A,\alpha}(x, T_{\text{exp}}) + x \Delta \bar{S}_{\text{mix},B,\alpha}(x, T_{\text{exp}}) +$$

$$+ R[(1-x) \ln (1-x) + x \ln x] \qquad (15)$$

2. Approximate calculation of excess entropy at the formation of liquid phase α in a binary system A—B the components of which in the phase β form solid solutions with limited solubility but do not form any compounds.

The equilibrium between phases α and β is described precisely by eqns (1) and (2) from which the following relationships can be derived

$$\bar{H}_{A,\alpha}(x, T_{\text{eq}}(x, y)) - T_{\text{eq}}(x, y) \, \bar{S}_{A,\alpha}(x, T_{\text{eq}}(x,y)) = H_{A,\beta}(0, T_{\text{eq}}(x,y)) -$$

$$- T_{\text{eq}}(x,y) \, S_{A,\beta}(0, T_{\text{eq}}(x,y)) + RT_{\text{eq}}(x,y) \ln a_{A,\beta}(y, T_{\text{eq}}(x,y)) \qquad (16)$$

and

$$\bar{H}_{B,\alpha}(x, T_{\text{eq}}(x,y)) - T_{\text{eq}}(x,y) \, \bar{S}_{B,\alpha}(x, T_{\text{eq}}(x,y)) = H_{B,\beta}(1, T_{\text{eq}}(x,y)) -$$

$$- T_{\text{eq}}(x,y) \, S_{B,\beta}(1, T_{\text{eq}}(x,y)) + RT_{\text{eq}}(x,y) \ln a_{B,\beta}(y, T_{\text{eq}}(x,y)) \qquad (17)$$

If the value of y in the phase β with prevailing component A (resp. B) is near to zero (resp. to one) the activity coefficient may be considered in both cases as unit and the activity of component A (resp. B) in the phase β with prevailing component A (resp. B) may be replaced by mole fraction of the component. Then treating eqns (16) and (17) in the same way as described in the previous paragraph we obtain for $x \lesseqgtr x_{\text{eut}}$

$$\Delta\bar{S}_{\text{mix}(\beta s),A,\alpha}(x, T_{\text{exp}}) \doteq \frac{\bar{H}_{A,\alpha}(x, T_{\text{eq}}(x,y)) - H_{A,\beta}(0, T_{\text{eq}}(x,y))}{T_{\text{eq}}(x,y)} +$$

$$+ \int_{T_{\text{eq}}(x,y)}^{T_{\text{exp}}} \frac{\bar{C}_{A,\alpha}(x, T)}{T} \, dT - \int_{T_{\text{eq}}(x,y)}^{T_{\text{eq}}(0,0)} \frac{C_{A,\beta}(0, T)}{T} \, dT - \frac{\Delta H_{\text{tr},A}(T_{\text{eq}}(0,0))}{T_{\text{eq}}(0,0)} -$$

$$- \int_{T_{\text{eq}}(0,0)}^{T_{\text{exp}}} \frac{C_{A,\alpha}(0, T)}{T} \, dT - R \ln z(T_{\text{eq}}(x,y)) \qquad (18)$$

where $z = 1 - y$. For $x \gtreqless x_{\text{eut}}$

$$\Delta\bar{S}_{\text{mix}(\beta s),B,\alpha}(x, T_{\text{exp}}) \doteq \frac{\bar{H}_{B,\alpha}(x, T_{\text{eq}}(x,y)) - H_{B,\beta}(1, T_{\text{eq}}(x,y))}{T_{\text{eq}}(x,y)} +$$

$$+ \int_{T_{\text{eq}}(x,y)}^{T_{\text{exp}}} \frac{\bar{C}_{B,\alpha}(x, T)}{T} \, dT - \int_{T_{\text{eq}}(x,y)}^{T_{\text{eq}}(1,1)} \frac{C_{B,\beta}(1, T)}{T} \, dT - \frac{\Delta H_{\text{tr},B}(T_{\text{eq}}(1,1))}{T_{\text{eq}}(1,1)} -$$

$$- \int_{T_{\text{eq}}(1,1)}^{T_{\text{exp}}} \frac{C_{B,\alpha}(1, T)}{T} \, dT - R \ln y(T_{\text{eq}}(x,y)) \qquad (19)$$

The quantities having the index (βs) denote the system in which a solution with low solubility of components is formed. Further treatment is similar as in the paragraph 1. Eqns (18) and (19) can be written in the simplified form; *e.g.* for $\Delta\bar{S}_{\text{mix}(\beta s),B,\alpha}(x, T_{\text{exp}})$

$$\Delta\bar{S}_{\text{mix}(\beta s),B,\alpha}(x, T_{\text{exp}}) \doteq \Delta\bar{S}_{\text{mix},B,\alpha}(x, T_{\text{exp}}) - R \ln y(T_{\text{eq}}(x,y)) \qquad (20)$$

3. Calculation of $\Delta G_{\text{mix}}^{\text{E}}$.

The values of $\Delta G_{\text{mix}}^{\text{E}}$ are calculated using the definition equation ($T_{\text{exp}} = \text{const}$)

$$\Delta G_{\text{mix}}^{\text{E}} = \Delta H_{\text{mix}}^{\text{E}} - T_{\text{exp}} \Delta S_{\text{mix}}^{\text{E}} = \Delta H_{\text{mix}} - T_{\text{exp}} \Delta S_{\text{mix}}^{\text{E}} \qquad (21)$$

Eqns (8, 10—12, 15, 18—20) can be derived also from the temperature dependence of the changes in Gibbs energy, or more efficiently, from the Planck function Φ

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$$\left[\frac{\partial\left[-\dfrac{\Delta\bar{G}_{\text{mix},\alpha}(x,T)}{T}\right]}{\partial T}\right]_x = \left[\frac{\partial\Delta\bar{\Phi}_{\text{mix},\alpha}(x,T)}{\partial T}\right]_x = \frac{\Delta\bar{H}_{\text{mix},\alpha}(x,T)}{T^2} \tag{22}$$

and

$$\left[\frac{\partial\Delta\Phi_{\text{tr}}(T)}{\partial T}\right]_{\text{eq}} = \left[\frac{\partial\left[-\dfrac{\Delta G_{\text{tr}}(T)}{T}\right]}{\partial T}\right]_{\text{eq}} = R\left[\frac{\partial\ln\dfrac{a_\alpha}{a_\beta}}{\partial T}\right]_{\text{eq}} = \frac{\Delta H_{\text{tr}}(T)}{T^2} \tag{23}$$

The second relationship is a special case of the van't Hoff reaction isobar (the LeChatelier—Shreder equation).

4. Measurements of ΔH_{mix}.

The excess quantities $\Delta S^{\text{E}}_{\text{mix}}$ and $\Delta G^{\text{E}}_{\text{mix}}$ ($\Delta H^{\text{E}}_{\text{mix}} = \Delta H_{\text{mix}}$) can be calculated using eqns (15—21) assuming that the phase diagram of the system, heats of mixing and heats of phase transitions are known in the studied temperature range.

4.1. For the systems in which mixing of pure components is sufficiently fast ΔH_{mix} can be measured directly at chosen temperature using calorimetry for mixing.

4.2. Dealing with the systems which do not obey the condition of sufficiently fast mixing ΔH_{mix} must be determined using the following relation

$$\Delta H_{\text{mix},\alpha}(x,T_{\text{exp}}) = H_\alpha(x,T_{\text{exp}}) - (1-x)\,H_{A,\alpha}(0,T_{\text{exp}}) - xH_{B,\alpha}(1,T_{\text{exp}}) =$$
$$= H_{\text{rel},\alpha}(x,T_{\text{exp}}) - (1-x)\,H_{\text{rel},A,\alpha}(0,T_{\text{exp}}) - xH_{\text{rel},B,\alpha}(1,T_{\text{exp}}) \tag{24}$$

where all quantities H_{rel} are increments in enthalpy measured with respect to the convenient reference state (which is the same for all phases).

4.2.1. Dealing with the systems in which equilibrium is quickly achieved after cooling the convenient reference state can be the mechanical mixture of crystals of pure components at laboratory temperature. This condition is fulfilled e.g. in the case of some systems consisting of inorganic salts. The values H_{rel} can be measured in this case using drop calorimetry.

4.2.2. For the systems in which equilibrium after cooling is not achieved in reasonable time (e.g. metal alloys, systems known from silicate technology) as

standard state can be recommended the state of the system in an appropriate solution or in a mixture of its combustion products at chosen temperature, *etc.* In this case the values H_{rel} in eqn (*24*) must be replaced by the quantities

$$H_{rel} = -(\Delta H_{cool} + \Delta H_{sol(comb)}) \tag{25}$$

ΔH_{cool} is the change in enthalpy measured at cooling the sample in drop calorimeter and $\Delta H_{sol(comb)}$ is heat of dissolution (or combustion) of the sample which was cooled up to laboratory temperature in the drop calorimeter. In this experimentally most complicated case heat of mixing can be obtained by the method of "double calorimetry of the same sample", *i.e.* using drop calorimetry and subsequently determining heat of solution or combustion.

References

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