A DISCUSSION ON EQUATIONS OF PHASE EQUILIBRIUM BETWEEN TWO REGULAR BINARY PHASES

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The conditions of the existence of extreme on the concentration dependences of absolute temperature (x are mole fractions) $T = T^{\alpha}(x_k^{\alpha})$ and $T = T^{\beta}(x_k^{\beta})$ denoting equilibrium between two binary regular solutions are generally developed under two assumptions: *1*) Free enthalpy change of pure components $k = i, j$ at transition from phase α to β is a linear function of temperature. *2*) Concentration dependence of excess free enthalpy (identical with enthalpy) of solutions α and β, respectively, is described in regular model by one concentration and temperature independent parameter for each individual phase.

Experimental results show that the regular solution model is in many cases suitable (at least in zero approximation) for the description of the temperature and composition dependence of thermodynamic properties of individual phases, especially in metallic systems. The possibility to use this model for phase equilibrium calculations was discussed *e.g.* in papers[1-6]. These papers have not discussed the influence of parameters of pure components (transition temperatures $T_k^{\alpha \to \beta}$, and transition enthalpies $H_k^{\alpha \to \beta}$) and of phases (parameters of regular solutions w^{α}, w^{β}) on the form of individual equilibrium lines. On the other hand, similar problem has been solved by Galová[9] and Malinovský, but not for the regular model. The conditions for the existence of extremes in the $T = T^{\alpha}(x_k^{\alpha})$ – and $T = T^{\beta}(x_k^{\beta})$ – dependences in binary system with two regular solutions in equilibrium therefore has been found in this work. The derivation is limited by two assumptions:

1) Free enthalpy change of pure components at the phase transition $\alpha \to \beta$ is a linear function of temperature $(\Delta G_k^{\alpha \to \beta} = G_k^{0,\beta} - G_k^{0,\alpha} = a_k + b_k T)$, where $k = i, j$ denotes the components of solution (a_k, b_k are constants).

2) Concentration dependence of excess free enthalpy of individual phase (solution), identical with the excess enthalpy concentration dependence, is characterized by one parameter for each individual phase: w^{ρ}, $\varrho = \alpha, \beta$, $(G^{E,\rho} = H^{E,\rho} = w^{\rho} x_k^{\rho} \,.\, (1 - x_k^{\rho}))$. Parameters w^{α}, w^{β} are independent on temperature and on composition of solution.

THEORETICAL

At equilibrium conditions of phases α and β for partial molar mixing free enthalpy of components k it holds[2]:

$$\bar{G}_k^{\alpha} = \bar{G}_k^{\beta} . \tag{1}$$

The equilibrium condition in binary system has the form of two equations for non--ideal solution at a temperature T:

$$G_k^{0,\alpha} + \boldsymbol{R}T \ln x_k^{\alpha} + \bar{G}_k^{E,\alpha} = G_k^{0,\beta} + \boldsymbol{R}T \ln x_k^{\beta} + \bar{G}_k^{E,\beta} , \quad (k = i, j) . \tag{2}$$

We can write further under the assumptions introduced above for equilibrium values of mole fractions x_i^{α}, x_i^{β} at a temperature T:

$$\begin{gathered} \ln (x_i^{\beta}/x_i^{\alpha}) - (\Delta H_i^{\alpha\to\beta}/\boldsymbol{R}) [(1/T_i^{\alpha\to\beta}) - (1/T)] - \\ - [w^{\alpha}/(\boldsymbol{R}T)] (1 - x_i^{\alpha})^2 + [w^{\beta}/(\boldsymbol{R}T)] (1 - x_i^{\beta})^2 = 0 , \\ \ln [(1 - x_i^{\beta})/(1 - x_i^{\alpha})] - (\Delta H_j^{\alpha\to\beta}/\boldsymbol{R}) [(1/T_j^{\alpha\to\beta}) - (1/T)] - \\ - [w^{\alpha}/(\boldsymbol{R}T)] (x_i^{\alpha})^2 + [w^{\beta}/(\boldsymbol{R}T)] (x_i^{\beta})^2 = 0 , \end{gathered} \tag{3}$$

where for temperature dependence of $\Delta G_k^{\alpha\to\beta}$ it is written: $\Delta G_k^{\alpha\to\beta} = \Delta H_k^{\alpha\to\beta} - T(\Delta H_k^{\alpha\to\beta}/T_k^{\alpha\to\beta})$ and $\boldsymbol{R}$ is the gas constant. The set of equations (*3*) has the analytical solution in the case $w^{\alpha} = w^{\beta} = 0$ (equilibrium of ideal solutions)[8]. The solution of the equations of the type (*3*) was found and discussed in the case of non-ideal solutions of electrolytes in the paper[9].

In the present work implicitely defined functions $T = T^{\alpha}(x_i^{\alpha})$ and $T = T^{\beta}(x_i^{\beta})$ are analyzed in a similar way as in the work[8]. The terms in equations (*3*) dependent only on the temperature are separated (for the sake of simplicity we will further write x instead of x_i):

$$f(x^{\alpha}, x^{\beta}, T) = M(T) , \quad g(x^{\alpha}, x^{\beta}, T) = Q(T) , \tag{4}$$

where the functions f, g, M and Q are defined by following expressions:

$$\begin{gathered} f(x^{\alpha}, x^{\beta}, T) = \{x^{\beta} \exp [w^{\beta}(1 - x^{\beta})^2/(\boldsymbol{R}T)]\}/\{x^{\alpha} \exp [w^{\alpha}(1 - x^{\alpha})^2/(\boldsymbol{R}T)]\} , \\ g(x^{\alpha}, x^{\beta}, T) = \{(1 - x^{\beta}) \exp [w^{\beta}(x^{\beta})^2/(\boldsymbol{R}T)]\}/\{(1 - x^{\alpha}) \exp [w^{\alpha}(x^{\alpha})^2/(\boldsymbol{R}T)]\} , \\ M(T) = \exp \{(\Delta H_i^{\alpha\to\beta}/\boldsymbol{R}) [(1/T_i^{\alpha\to\beta}) - (1/T)]\} , \\ Q(T) = \exp \{(\Delta H_j^{\alpha\to\beta}/\boldsymbol{R}) [(1/T_j^{\alpha\to\beta}) - (1/T)]\} . \end{gathered}$$

Mole fractions x^α, x^β are temperature dependent. A necessary conditions of the existence of extreme of implicitely defined functions $T = T^\alpha(x^\alpha)$ and $T = T^\beta(x^\beta)$ is the validity of relations $\partial T/\partial x^\alpha = 0$ and $\partial T/\partial x^\beta = 0$, respectively. With the aim to find this condition we differentiate equations (4) and obtain a set of linear algebraic equations, which will be solved by Cramer's rule:

$$(\partial f/\partial x^\alpha)(\partial x^\alpha/\partial T) + (\partial f/\partial x^\beta)(\partial x^\beta/\partial T) + \partial f/\partial T = M(\Delta H_i^{\alpha\to\beta}/[RT^2]),$$

$$(\partial g/\partial x^\alpha)(\partial x^\alpha/\partial T) + (\partial g/\partial x^\beta)(\partial x^\beta/\partial T) + \partial g/\partial T = Q(\Delta H_j^{\alpha\to\beta}/[RT^2]). \quad (5)$$

For unknown derivatives $\partial T/\partial x^\alpha$ and $\partial T/\partial x^\beta$ we get directly with the help of Jacobi's functional determinants:

$$\partial T/\partial x^\alpha = D/D_x \quad \text{and} \quad \partial T/\partial x^\beta = D/D_y, \quad (6)$$

where

$$D = \begin{vmatrix} \partial f/\partial x^\alpha & \partial g/\partial x^\alpha \\ \partial f/\partial x^\beta & \partial g/\partial x^\beta \end{vmatrix} =$$

$$= fg\{(-1)/[x^\alpha x^\beta(1 - x^\alpha)(1 - x^\beta)] + 2w^\alpha/[RTx^\alpha(1 - x^\alpha)] +$$
$$+ 2w^\beta/[RTx^\beta(1 - x^\beta)] - 4w^\alpha w^\beta/(RT)^2\}(x^\alpha - x^\beta),$$

$$D_x = -\begin{vmatrix} \partial f/\partial x^\beta & [M(\Delta H_i^{\alpha\to\beta}/[RT^2]) - \partial f/\partial T] \\ \partial g/\partial x^\beta & [Q(\Delta H_j^{\alpha\to\beta}/[RT^2]) - \partial g/\partial T] \end{vmatrix}$$

$$D_y = \begin{vmatrix} \partial f/\partial x^\alpha & [M(\Delta H_i^{\alpha\to\beta}/[RT^2]) - \partial f/\partial T] \\ \partial g/\partial x^\alpha & [Q(\Delta H_j^{\alpha\to\beta}/[RT^2]) - \partial g/\partial T] \end{vmatrix}.$$

Further it holds:

$$\partial f/\partial x^\alpha = f\{[2w^\alpha(1 - x^\alpha)/(RT)] - [1/x^\alpha]\},$$
$$\partial f/\partial x^\beta = f\{[1/x^\beta] - [2w^\beta(1 - x^\beta)/(RT)]\},$$
$$\partial g/\partial x^\alpha = g\{[1/(1 - x^\alpha)] - [2w^\alpha x^\alpha/(RT)]\},$$
$$\partial g/\partial x^\beta = g\{[2w^\beta x^\beta/(RT)] - [1/(1 - x^\beta)]\},$$
$$\partial f/\partial T = f\{[w^\alpha(1 - x^\alpha)^2 - w^\beta(1 - x^\beta)^2]/[RT^2]\},$$
$$\partial g/\partial T = g\{[w^\alpha(x^\alpha)^2 - w^\beta(x^\beta)^2]/[RT^2]\}.$$

From equations (6) it is evident that the necessary condition for the existence of extreme of the functions $T = T^\alpha(x^\alpha)$ and $T = T^\beta(x^\beta)$ is fulfilled (in the case of $x^\alpha, x^\beta \neq 0$ and $x^\alpha, x^\beta \neq 1$) when $x^\alpha = x^\beta$ in accordance with the paper[9]. We shall discuss only this case. A sufficient condition for the existence of the extreme is then the validity of relation $\partial^2 T/\partial(x^\alpha)^2 \neq 0$ and $\partial^2 T/\partial(x^\beta)^2 \neq 0$, respectively, for $x^\alpha = x^\beta$.

From the equations (*6*) we get by differentiation:

$$\partial^2 T/\partial(x^\alpha)^2 = (D/D_x)' = \{[D'D_x - DD'_x]/[D_x]^2\}$$

and (*7*)

$$\partial^2 T/\partial(x^\beta)^2 = (D/D_y)' = \{[D'D_y - DD'_y]/[D_y]^2\}\,,$$

respectively. In the first equation in equations (7) symbol ′ denotes $\partial/\partial x^\alpha$ and in the second equation in equations (7) it denotes $\partial/\partial x^\beta$. With respect to the fact that $D = 0$ for $x^\alpha = x^\beta = x_E$ we get from equations (7):

$$\begin{aligned}(\partial^2 T/\partial(x^\alpha)^2)_E &= ([-D_y/D_x]\,[\partial^2 T/\partial(x^\beta)^2])_E = \\ &= [1/(-D_x)]\,\{[1/(x_E[1 - x_E])] - [2w^\alpha/(RT_E)]\}\,\{[1/(x_E[1 - x_E])] - \\ &- [2w^\beta/(RT_E)]\}\,\exp\{[w^\beta - w^\alpha]\,[(1 - x_E)^2 + x_E^2]/[RT_E]\}\,,\end{aligned} \qquad (8)$$

where T_E is the temperature corresponding to x_E. It is evident, that there is $\partial^2 T/\partial(x^\alpha)^2 \neq 0$ and $\partial^2 T/\partial(x^\beta)^2 \neq 0$ for all $x_E(0 < x_E < 1)$, when $w^\alpha < 2RT_E$ and $w^\beta < 2RT_E$ are fulfilled simultaneously.

DISCUSSION

We will discuss the values of parameters in phase equilibrium equations (*3*) in the case of existence of an extreme on the dependences $T = T^\alpha(x^\alpha)$ and $T^\beta(x^\beta)$, respectively. In the case $x^\alpha = x^\beta = x_E$ equations (*3*) have the form:

$$\begin{aligned}&\Delta H_i^{\alpha\to\beta} - (\Delta H_i^{\alpha\to\beta}/T_i^{\alpha\to\beta})\,T_E + (w^\beta - w^\alpha)\,(1 - x_E)^2 = 0\,,\\ &\Delta H_j^{\alpha\to\beta} - (\Delta H_j^{\alpha\to\beta}/T_j^{\alpha\to\beta})\,T_E + (w^\beta - w^\alpha)\,(x_E)^2 = 0\,.\end{aligned} \qquad (9)$$

By eliminating the temperature of extreme T_E from the equations (*9*) we get:

$$\begin{aligned}&[(T_i^{\alpha\to\beta}/\Delta H_i^{\alpha\to\beta}) - (T_j^{\alpha\to\beta}/\Delta H_j^{\alpha\to\beta})]\,x_E^2 - (T_i^{\alpha\to\beta}/\Delta H_i^{\alpha\to\beta})\,x_E + \\ &+ [(T_i^{\alpha\to\beta}/\Delta H_i^{\alpha\to\beta}) + ([T_i^{\alpha\to\beta} - T_j^{\alpha\to\beta}]/[w^\beta - w^\alpha])] = 0\,.\end{aligned} \qquad (10)$$

The solution of the quadratic equation (*10*) is a function of 3 parameters:

$$(x_E)_{1,2} = \{[I \pm ([IJ] + A[J - I])^{1/2}]/[I - J]\}\,, \qquad (11)$$

where $I = T_i^{\alpha\to\beta}/\Delta H_i^{\alpha\to\beta}$, $J = T_j^{\alpha\to\beta}/\Delta H_j^{\alpha\to\beta}$ and $A = (T_i^{\alpha\to\beta} - T_j^{\alpha\to\beta})/(w^\alpha - w^\beta)$.

The extreme on the phase equilibrium lines exists $(0 < x_E < 1)$ when it holds: for

$$I > 0\,, \quad J > 0: \quad -I < A < J\,,$$
$$I < 0\,, \quad J < 0: \quad J < A < -I\,,$$
$$I < 0\,, \quad J > 0: \quad [IJ/(I-J)] < A < [-I, J]_{\min}\,,$$
$$I > 0\,, \quad J < 0: \quad [-I, J]_{\max} < A < [IJ/(I-J)]\,, \qquad (12)$$

where $[-I, J]_{\min}$ denotes the minimum value and $[-I, J]_{\max}$ the maximum value from $(-I)$, J.

These conditions determine in the binary system $i - j$ the values of $(w^{\alpha} - w^{\beta})$ allowing the existence of extreme. The regions of the existence of extreme are shown in the Fig. 1 for various values of parameters I and J.

Example. We should illustrate these results by an example. In the paper[7] the solid–liquid equilibrium in the systems Ni–Cu ($I = 0{\cdot}098$ K/J, $J = 0{\cdot}103$ K/J) and Ni–Co ($I = 0{\cdot}098$ K/J, $J = 0{\cdot}104$ K/J) at constant temperature was studied at simplification $\ln \gamma_i = \alpha_{ij}(1 - x_i)^2$ (α_{ij} temperature independent). In the present paper we get for the existence of extreme on the $T = T^{\alpha}(x^{\alpha})$ — and $T^{\beta} = T(x^{\beta})$ — dependences the conditions: $(w^{\alpha} - w^{\beta}) > 3\,590$ J/mol and $(w^{\alpha} - w^{\beta}) < -3\,760$ J/mol in the case of the Ni–Cu system and $(w^{\alpha} - w^{\beta}) > 405$ J/mol and $(w^{\alpha} - w^{\beta}) < -426$ J/mol in the case of the Ni–Co system (α denotes liquid and β denotes solid). The reverse inequalities denote the monotonous course of these dependences $T = T^{\alpha}(x^{\alpha})$ and $T = T^{\beta}(x^{\beta})$. For 1 500 K it means in terms of α_{ij} the limits $0{\cdot}29 > (\alpha^{\alpha}_{ij} - \alpha^{\beta}_{ij}) > -0{\cdot}30$ for Ni–Cu and $0{\cdot}033 > (\alpha^{\alpha}_{ij} - \alpha^{\beta}_{ij}) > -0{\cdot}034$ for Ni–Co in the case of monotonous course of $T = T^{\alpha}(x^{\alpha})$ — and $T = T^{\beta}(x)^{\beta}$ — lines. This results agree with those of paper[7].

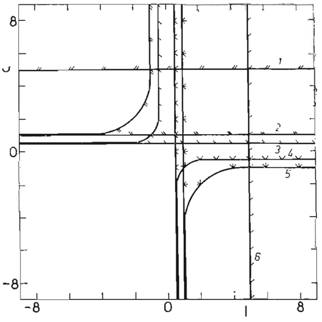

FIG. 1

The Regions of Existence of Extreme on the Lines of Phase Equilibrium $T = T(x)$ for Components Characterized by the Parameters I and J (in K/J)

Short lines denote the part of the plane, where extreme exists. The second part of solutions, with respect to central symmetry (Eq. (*11*) gives $X(I, J, A) = X(-I, -J, -A)$), is not shown; A (in K mol/J). *1* 5, *2* 1, *3* 0·5, *4* −0·5, *5* −1, *6* −5.

In special cases we see, that no extreme exists for the case $w^{\alpha} = w^{\beta} = 0$ ($A \rightarrow \infty$). The same situation (no extreme) will occur for $w^{\alpha} = w^{\beta} \neq 0$, in accordance with the work[9].

No extreme exists also for $I = J = 0$ and $I = J \neq 0$ and further at $T_i^{\alpha\rightarrow\beta} = T_j^{\alpha\rightarrow\beta}(w^{\alpha} \neq w^{\beta})$ for $I = 0$ or $J = 0$ or for sign $I \neq$ sign J.

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