MODELLING OF PHASE DIAGRAM BOUNDARIES AT EQUILIBRIUM OF TWO BINARY REGULAR PHASES

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The conditions of occurrence of extremes on the solidus and liquidus curves in a binary isobaric phase diagram are specified. The solid and liquid phases are regarded as regular solutions in equilibrium. Two simplifying assumptions are made: (i) the Gibbs function of melting of the pure components is a linear function of temperature; (ii) the two phases in equilibrium are regular solutions with a temperature-dependent regular solution parameter. The conditions of occurrence of inflexion points on the solidus and/or liquidus curves are obtained by modelling.

Detailed knowledge of the dependence of the shape of solidus and liquidus curves on the values of the regular solution parameters for the two phases in equilibrium is of crucial importance for phase diagram calculations on the thermodynamic basis. Therefore, attempts were made to gain more information about the correlation of the shape of the solidus and liquidus curves with the regular solution parameters. Phase diagram calculations are based on the condition of identical chemical potentials of the components in all phases in equilibrium[1]. In particular, the equations characterizing the heterogeneous equilibrium in an ideal binary system between the solid (s) and liquid (l) phases (Eqs (*1*) and (*2*), respectively) can be written for one mole of solution as:

$$G_i^{0(\mathrm{s})} + RT \ln (x_i^{(\mathrm{s})}) = G_i^{0(\mathrm{l})} + RT \ln (x_i^{(\mathrm{l})}) \;, \qquad (1)$$

where R and T have their usual meaning and $x_i^{(p)}$ is the molar fraction of component i (i = 1, 2 for phase p = s, l, respectively). The standard molar Gibbs function $G_i^{0(p)}$ (index m is omitted) of component i in phase p is expressed with respect to the standard state of the pure components at the temperature of solution and in the state of solution[2,3]. Equation (*1*) can be modified to the form

$$\Delta G_{fi} = \Delta H_{fi} - T\Delta S_{fi} = RT \ln (x_i^{(s)}/x_i^{(l)}) \ , \tag{2}$$

where ΔG_{fi} is the Gibbs function of fusion of pure component i and ΔH_{fi} and ΔS_{fi} denote the molar enthalpy and molar entropy of fusion of component i, respectively, neglecting their temperature dependence. The system of Eqs (*1*) for the case of an ideal two-component solution ($i = 1, 2$; $x_2 = 1 - x_1$) can be solved algebraically[4]:

$$x_2^{(s)} = (Q - 1)/(Q - N) \ , \qquad x_2^{(l)} = N(Q - 1)/(Q - N) \ , \tag{3}$$

where $Q = \exp(-\Delta G_{f1}/RT)$, $N = \exp(-\Delta G_{f2}/RT)$.
In this case no extreme appears on the solidus or liquidus curve in the phase diagram. In the phases of a non-ideal solution, the excess Gibbs function G^E should be included and generally regarded as temperature and composition dependent. The simplest mathematical description of this concentration dependence, using the statistical background[5], is the regular solution model proposed by Hildebrand[6]:

$$G^{E(p)}/RT = w^{(p)}x^{(p)}(1 - x^{(p)}) \tag{4}$$

for phase p = s, l. In our previous paper[7] dealing with the phase equilibrium between two regular binary phases, parameter $w^{(p)}$ in Eq. (*4*) was supposed to be temperature and composition independent. The following conclusion emerged from the discussion in ref.[7]: an extreme occurs on the solidus and liquidus curves if:

$$-(T_{f2}/\Delta H_{f2}) < A < (T_{f1}/\Delta H_{f1}) \ , \tag{5}$$

where $A = (T_{f2} - T_{f1})/(w^{(l)} - w^{(s)})$ and T_{f1}, T_{f2} are the temperatures of melting of the pure components 1 and 2, respectively. In the present paper, the previous considerations[7] are extended by taking into account the temperature dependence of the regular solution parameters $w^{(p)}$. This means that the enthalpic $w_H^{(p)}$ and entropic $w_S^{(p)}$ terms (concentration and temperature independent) of the regular solution parameter for phase p are included in Eq. (*4*):

$$w^{(p)} = (w_H^{(p)} - w_S^{(p)}T) \ . \tag{6}$$

The aim of this paper is to show how the shapes of the liquids and solidus curves $T = T^{(l)}(x^{(l)})$ and $T = T^{(s)}(x^{(s)})$ in a binary phase diagram depend on the values of the parameters $w_H^{(p)}$ and $w_S^{(p)}$ in the two phases (s and l) in equilibrium. (The considerations applied here to the solid and liquid phases are also valid for any other phases obeying Eqs (*4*) and (*6*).)

THEORY

Equations for the Phase Equilibrium Between Two Regular Binary Phases Including Temperature-Dependent Regular Solution Paramaters

From the two assumptions made in our previous paper[7], only the first, viz. that the Gibbs function of melting of the pure components is a linear function of temperature (*2*), was retained. The second assumption, viz. that the concentration dependence of the excess Gibbs function of an individual phase obeys Eq. (*4*), is modified in this work, namely so that Eq. (*6*) is included. The phase equilibrium equations (*2*) can be then rewritten[8] in the form ($x = x_2$):

$$\ln [(1 - x^{(l)})/(1 - x^{(s)})] - (\Delta H_{f1}/R)\,(1/T_{f1} - 1/T) - [(w_H^{(s)} - w_S^{(s)}T)/RT]\,(x^{(s)})^2 + \tag{7}$$

$$+ [(w_H^{(l)} - w_S^{(l)}T)/RT]\,(x^{(l)})^2 = 0$$

and similarly for component 2 (with subscript 2 instead of 1, and $(1 - x^{(p)})$ instead of $x^{(p)}$). It follows from the Gibbs phase rule that the compositions of the two phases at the temperature of extreme are identical ($x^{(s)} = x^{(l)} = x_e$ at $T = T_e$). By multiplying both equations by $RT_e \neq 0$ and rearranging, we get for the equilibrium in the point of extreme:

$$(-\Delta H_{f1}/T_{f1})T_e + (\Delta H_{f1}) + (x_e)^2\,(-w_H^{(s)} + w_S^{(s)}T_e + w_H^{(l)} - w_S^{(l)}T_e) = 0\ . \tag{8}$$

Denoting $W_H = w_H^{(l)} - w_H^{(s)}$ and $W_S = w_S^{(l)} - w_S^{(s)}$ and rearranging Eq. (*8*) we obtain:

$$\Delta H_{f1} + T_e[(-\Delta H_{f1} - T_{f1}W_S(x_e)^2)/T_{f1}] + (x_e)^2 W_H = 0\ . \tag{9}$$

Multiplication of Eq. (*9*) by $[T_{f1}/-\Delta H_{f1} - T_{f1}W_S(x_e)^2] \neq 0$ gives

$$(\Delta H_{f1}T_{f1} + (x_e)^2 W_H T_{f1})/(-\Delta H_{f1} - T_{f1}W_S(x_e)^2) + T_e = 0\ . \tag{10}$$

Equations similar to (*8*)–(*10*) are obtained for component 2 by using subscript 2 instead of 1 and $(1 - x_e)$ instead of x_e. By eliminating T_e we get:

$$[(\Delta H_{f1} T_{f1} + (x_e)^2 W_H T_{f1})/(-\Delta H_{f1} - T_{f1} W_S (x_e)^2)] + [-(\Delta H_{f2} T_{f2} - (1 - x_e)^2 W_H T_{f2})/(-\Delta H_{f2} - T_{f2} W_S (1 - x_e)^2)] = 0 \ . \qquad (11)$$

As the next step, multiplication of this equation by

$$[-\Delta H_{f1} - T_{f1} W_S (x_e)^2]\,[-\Delta H_{f2} - T_{f2} W_S (1 - x_e)^2] \neq 0 \ ,$$

rearrangement and multiplication by $1/[\Delta H_{f1} \Delta H_{f2} (W_H - W_S T_{f1})] \neq 0$ finaly yields:

$$[(T_{f1}/\Delta H_{f1})\,(W_H - W_S T_{f2})/(W_H - W_S T_{f1}) - (T_{f2}/\Delta H_{f2})](x_e)^2 + {} + 2\,(T_{f2}/\Delta H_{f2}) x_e - (T_{f2} - T_{f1})/(W_H - W_S T_{f1}) - (T_{f2}/\Delta H_{f2}) = 0 \ . \qquad (12)$$

Denoting

$$K = (T_{f2}/\Delta H_{f2})$$

$$L = (T_{f1}/\Delta H_{f1})\,(W_H - W_S T_{f2})/(W_H - W_S T_{f1})$$

$$M = (T_{f2} - T_{f1})/(W_H - W_S T_{f2}) \ , \qquad (13)$$

we obtain the solution of Eq. (*12*) in the form

$$(x_e)_{1,2} = [K \pm (KL + M(L - K))^{1/2}]/(K - L) \ . \qquad (14)$$

An extreme occurs on the phase equilibrium lines $(0 < x_e < 1)$ if

$$-K < M < L \qquad (15)$$

for $K > 0$ and $L > 0$.

For $W_S = 0$ the conditions expressed by Eqs (*13*)–(*15*) are identical with those expressed by Eq. (*5*) in our previous work[7]. In the case of inflexion points the explicit expressions for $T = T^{(l)}(x^{(l)})$ and for $T = T^{(s)}(x^{(s)})$, fulfilling the conditions $(d^2T^{(l)}/dx^{(l)2}) = 0$ or $(d^2T^{(s)}/dx^{(s)2}) = 0$ are complicated. Therefore, thermodynamic modelling was applied to find the parameter values at which the inflexion points appear.

Modelling the Shape of the Solidus and Liquidus Curves Taking into Account the Temperature Dependence of Regular Solution Parameters

Computer modelling offers a complex view upon the influence of the regular solution parameters of the shape of the solidus and liquidus curves. The equilibrium compositions $x^{(s)}$ and $x^{(l)}$ for a binary system 1–2 at chosen temperatures were calculated by Eq. (*7*) by means of the programme DIAGRAM (ref.[9]). Values for the pure components (the enthalpy of fusion at the melting point) and for solutions in equilibrium (coefficients of regular solutions) were entered as the input data. The shapes of the solidus and liquidus curves were observed on the screen.

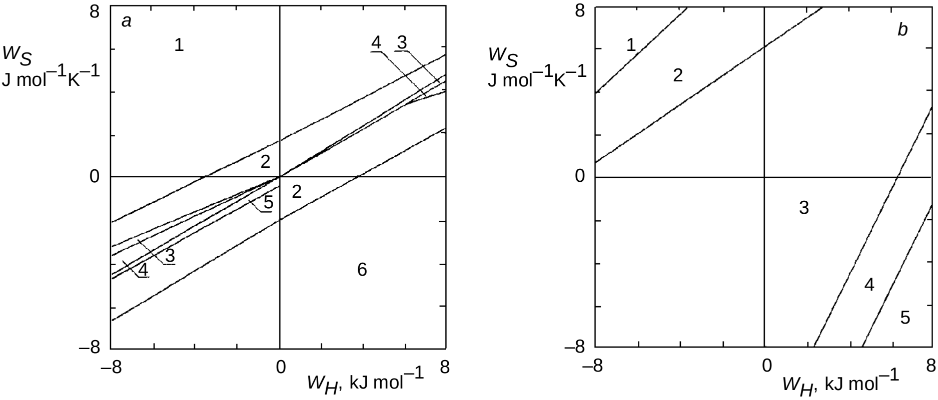

FIG. 1

Fields of occurrence of extremes on isobaric phase diagrams in dependence on the values of W_H and W_S parameters. *a* Fe–Cr system in the solidus–liquidus region. Thermodynamic parameters: H^0_{fFe} = 14 545 J mol^{-1}, T_{fFe} = 1 811 K, H^0_{fCr} = 18 409 J mol^{-1}, T_{fCr} = 2 180 K. The region of equilibrium of three phases (eutectics) lies to the right from the line $W_S = (8 . 10^{-4} W_H - 19)$ and is not shown in Fig. *1a*. 1 maximum, 2 without extreme, 3 inflexion point on the liquidus, 4 inflexion point on the liquidus and on the solidus, 5 inflexion point on the solidus, 6 minimum. *b* Hypothetical system of components 1 and 2 in the solidus–liquidus region. Thermodynamic parameters: H^0_{f1} = 10 000 J mol^{-1}, T_{f1} = 500 K, H^0_{f2} = 15 000 J mol^{-1}, T_{f2} = 800 K. 1 maximum, 2 inflexion point on the solidus, 3 without extreme, 4 minimum, 5 equilibrium of three phases (eutectics)

RESULTS AND DISCUSSION

A simple computer program was written[8] for the solution of Eq. (*12*), i.e. Eq. (*14*). A range of W_H and W_S values was chosen, and the program marked pairs of W_H and W_S values for which Eq. (*15*) was satisfied. This enabled us to show graphically the region of W_H and W_S values for which some extreme exists. Examples of results of this procedure are shown in Figs *1a* and *1b*. Regions where inflexion points occur were obtained by modelling and are also shown in the figures. The results of modelling are important for assessments of thermodynamic and phase data, demonstrating the influence of changes in thermodynamic parameters on the shape of the solidus and liquidus curves in a phase diagram. The same type of solidus and liquidus curves in a phase diagram can be found for various values of the regular solution parameters. In contrast to what is commonly believed[10,2], liquidus and solidus curves without extremes also appear if the W_H and W_S quantities possess relatively large values of the same sign.

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