Computer modelling of the phase diagrams of nonideal systems with the formation of solid solutions

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In the solution of the set of equations describing the liquidus and solidus curves, the presumption of the nonideality was introduced in the most simple way, analogously as for the regular solutions. Various interaction parameters both for the liquid and solid phases have been considered. The influence of these parameters as well as of the values of the enthalpy of fusion of pure components on the resulting shape of the phase diagram has been systematically investigated. At low values of the interaction parameters, a minimum or a maximum appears on the liquidus and solidus curves first. With increasing values of the interaction parameters, the phase diagrams achieve gradually the shape typical for limited solubility including metastable area and, in the limit for the interaction parameter in the solid phase approaching infinity, the shape corresponding to the immiscibility in the solid phase. The slopes of tangents to the liquidus and solidus curves in the limiting points have been determined analytically.

В решение системы уравнений, описывающих линии ликвидуса и солидуса, введено предположение неидеальности, причем сделано это наиболее простым способом, аналогично случаю регулярных растворов. Приняты во внимание различные параметры взаимодействий как в жидкой, так и в твердой фазах. Подробно изучено влияние этих параметров, а также величин энтальпий слияния чистых компонентов на окончательный вид фазовой диаграммы. При низких значениях интеракционных параметров на линиях ликвидуса и солидуса сначала появляется минимум или максимум. С увеличением значений интеракционных параметров фазовые диаграммы приобретают вид, типичный для случая ограниченной растворимости, включая область метастабильности, и в пределе, при интеракционных параметрах в твердой фазе стремящихся к бесконечности, приобретает вид, соответствующий несмешиваемости в твердой фазе. Углы наклона касательных к линиям солидуса и ликвидуса в предельных точках были определены аналитически.

The phase diagrams of systems with solid solutions are conventionally divided into two groups:

1. with an unlimited solubility in the solid phase,
2. with a limited solubility in the solid phase.

Characteristic shapes of both groups of phase diagrams are shown in Figs. 1a and 1b. A subgroup of the second group includes systems with a great difference between the melting temperatures of the pure components (Fig. 1c). In most textbooks [1, 2], the phase diagrams of the 2nd group are presented in the form shown in Figs. 1b and 1c. *Malinovský* [3] investigates these phase diagrams by
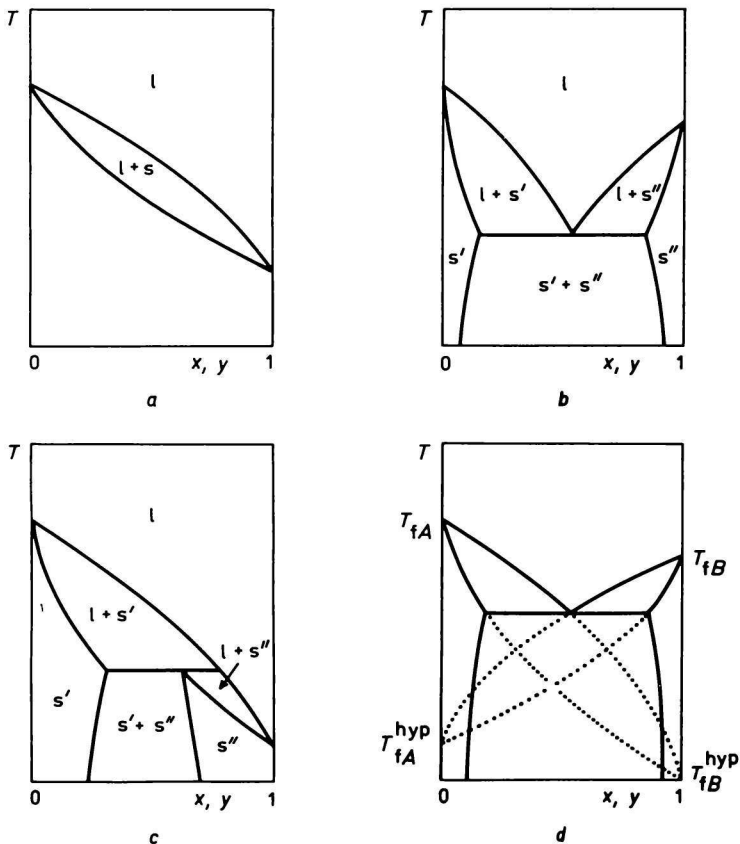

Fig. 1. *a*) Phase diagram with an unlimited miscibility of components. *b*) Phase diagram with a limited solubility of components. *c*) Phase diagram with a limited solubility of components and a great difference between the melting temperatures of components. *d*) Interpretation of a phase diagram with a limited miscibility of components according to *Reisman* [5].

16

treating each part independently. *Seward* [4] also deals with the metastable phase diagrams, however, without giving a continuous solution over the entire concentration range.

Reisman [5] assumes the phase diagram with a limited solubility in the solid phase as formed by superposition of two phase diagrams with unlimited solubility (Fig. 1*d*). Though formally partly convenient, this approach is entirely erroneous because of the following reasons:

a) It is based on the premise of hypothetical phase transitions in the solid phase. There exist, however, components which do not exhibit any phase transition between 0 K and the melting temperature still forming solid solutions;

b) A phase diagram with a limited solubility which demonstrates the nonideality of the system is interpreted through the mediation of two "ideal" phase diagrams;

c) The neglect of the nonideality makes it impossible to determine the curve of solubility of components in the solid phase which is an integral part of the phase diagram.

Theoretical

The equilibrium between a liquid and a solid phase in a system with the formation of solid solutions is described by the general form of the LeChatelier—Shreder equation [6], for $\Delta C_p = 0$

$$\ln (a_{1,i}/a_{s,i}) = (\Delta H_{t,i}/R)(1/T_{t,i} - 1/T) \qquad (1)$$

where $a_{1,i}$ and $a_{s,i}$ are the activities of the i-th component in the liquid and solid phases, respectively, and $T_{t,i}$ and $\Delta H_{t,i}$ are temperature and the heat of fusion, respectively.

For a binary system, two such equations are to be considered, one for each component. If we denote

$$\Delta H_{t,1}/R = H_1, \quad \Delta H_{t,2}/R = H_2, \quad T_{t,1} = F_1, \quad T_{t,2} = F_2$$

we obtain a system of two equations

$$\ln a_{1,1} - \ln a_{s,1} = H_1/F_1 - H_1/T \qquad (2a)$$

$$\ln a_{1,2} - \ln a_{s,2} = H_2/F_2 - H_2/T \qquad (2b)$$

When expressing the activities of components in the liquid and solid phases, we presume the validity of the relation $a_i = x_i \cdot \gamma_i$ (the so-called classical model).

The expression of the activity coefficients is based on the most simple relation for the Gibbs excess energy

$$\Delta G^E = Lx_1x_2 = Lx(1-x) \qquad (3)$$

For the so-called interaction parameter L a relation to the difference of energies between the particles can be derived according to a simple lattice model [7]: $L \sim (2e_{12} - e_{11} - e_{22})$. If we assume simultaneously the validity of relation

$$\Delta G^E = RT[(1-x) \ln \gamma_1 + x \ln \gamma_2] \qquad (4)$$

we can express the activity coefficients of the individual components (ψ is a dimensionless quantity $\Delta G^E/RT$)

$$\ln \gamma_1 = \psi - x(\partial \psi / \partial x) = (L/RT) x_2^2 \qquad (5a)$$

$$\ln \gamma_2 = \psi + (1-x)(\partial \psi / \partial x) = (L/RT) x_1^2 \qquad (5b)$$

Consequently, we have generally used the relation

$$\ln \gamma_i = (\lambda/T)(1-x_i)^2 \qquad (5c)$$

where $\lambda = L/R$.

When expressing activities, the mole fractions in the liquid and solid phase in relations ($2a, 2b$) were denoted as x and y, and the interaction parameters as A and B, respectively

$$\ln a_{l,1} = \ln (1-x) + (A/T) x^2 \qquad (6a)$$

$$\ln a_{s,1} = \ln (1-y) + (B/T) y^2 \qquad (6b)$$

$$\ln a_{l,2} = \ln x + (A/T)(1-x)^2 \qquad (6c)$$

$$\ln a_{s,2} = \ln y + (B/T)(1-y)^2 \qquad (6d)$$

By introducing relations ($6a$—$6d$) into eqns ($2a, 2b$) we obtain the final set of equations which was solved

$$\ln (1-x) + (A/T) x^2 - \ln (1-y) - (B/T) y^2 = H_1/F_1 - H_1/T \qquad (7a)$$

$$\ln x + (A/T)(1-x)^2 - \ln y - (B/T)(1-y)^2 = H_2/F_2 - H_2/T \qquad (7b)$$

If the system is ideal in both phases, *i.e.* if $A = B = 0$ K, based on eqns ($7a, 7b$) x as well as y can be expressed explicitly as a function of temperature. In the opposite case, both equations are transcendent with respect to x and y. From both equations, however, temperature can be expressed (on presumption that $\Delta C_p = 0$)

$$T = (H_1 + Ax^2 - By^2)/(H_1/F_1 - \ln (1-x) + \ln (1-y)) \qquad (8a)$$

$$T = (H_2 + A(1-x)^2 - B(1-y)^2)/(H_2/F_2 - \ln x + \ln y) \qquad (8b)$$

By subtracting both equations we eliminate temperature and obtain an implicit relation of variables x and y: f(x, y) = 0. For the proper modelling of phase diagrams it is more advantageous to choose a constant y, *i.e.* the mole fraction of the second component in the solid phase and to supplement the corresponding x.

18

The fastest numerical method was found to be the Newton's iteration method [8]: $x(2) = x(1) - f/(df/dx)$, where $x(i)$ is the i-th estimate of the variable x. It is merely x which must be prevented to deviate from the interval $\langle 0, 1 \rangle$. If this happens, it must be brought back, *e.g.* by means of random numbers.

Solubility in the solid phase

Beside the liquidus and solidus curves, the curve of the solubility or mutual miscibility of components in the solid phase also appears to be an integral part of the phase diagrams with formation of solid solutions. This curve is determined by the condition of equality of the activities of components in both the solid phases

$$a_{s',1} = a_{s'',1} \quad \text{or} \quad a_{s',2} = a_{s''.}$$

Inevitable condition of the solvability of these equations appears to be the temperature dependence of the activity coefficients as, *e.g.*, in relations (*6b, 6d*). Then it must hold

$$\ln(1-y) + (B/T)y^2 = \ln y + (B/T)(1-y)^2 \tag{9}$$

Hence for T it holds

$$T = B(2y - 1)/\ln[y/(1-y)] \tag{10}$$

For $y = 0.5$ this relation gives an indeterminate expression of the type $0/0$. Applying the L'Hospital's rule [8], however, for $y = 0.5$ we obtain $T = B/2$. The curve $T = \text{fce}(y)$ corresponding to the selected shape of the temperature and concentration dependence of the activity coefficients exhibits a maximum at $B/2$ and it is symmetrical on both sides.

Limiting relations

The relations for the slopes of tangents to the liquidus and solidus curves in the proximity of pure components can be derived utilizing the well-known relations

$$dT/dx = \partial T/\partial x + \partial T/\partial y \cdot dy/dx \tag{11a}$$

$$dT/dy = \partial T/\partial y + \partial T/\partial x \cdot dx/dy \tag{11b}$$

By calculation of the above derivatives and limitation of both x and y to zero, we obtain the final expressions

$$\lim_{x,y \to 0} dT/dx = (F_1^2/H_1)(1 + (A - B)/H_1)(q - 1) \tag{12a}$$

$$\lim_{x,y \to 0} dT/dy = (F_1^2/H_1)(1 + (A - B)/H_1)(q - 1)/q \tag{12b}$$

where $q = \exp\left[(H_2 + A - B)/F_1 - H_2/F_2\right]$.

The limiting expressions for $x, y \to 1$ can be obtained from relations (12a, 12b) by an exchange of indices 1 and 2. It should be mentioned that the difference between the interaction parameters A and B only plays a role in these equations. The relations for $A = B$ are identical with those derived by *Malinovský* [6].

Results and discussion

For an ideal system with $A = B = 0$ K, the solution of the set of eqns (7a, 7b) affords the familiar lens-like shape of the liquidus (upper) and solidus (lower) curves constituting the phase diagram of a system with continuous solid solutions. If we select fixed values of the melting temperatures of components of the model
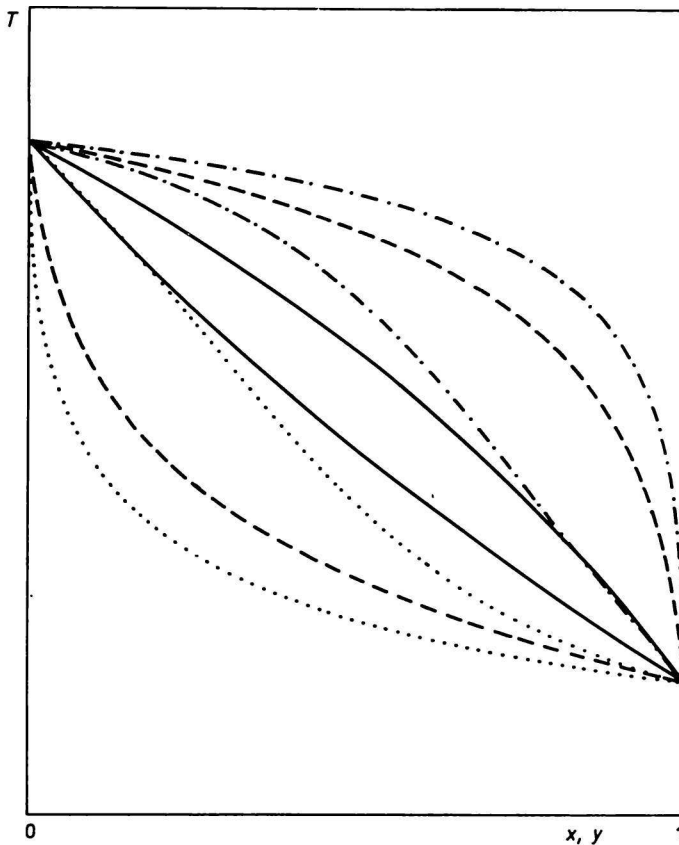

Fig. 2. The influence of ΔH_t of pure components ($A = B = 0$ K). $H_1(H_2) = 10\,000$ K (10 000 K) ——————, 50 000 K (50 000 K) — — —, 10 000 K (50 000 K) —·—·, 50 000 K (10 000 K)

system (*e.g.* $T_{t,1} = 1200$ K, $T_{t,2} = 1100$ K), then the values of ΔH of fusion of both components are the sole parameters which can change the shape of the diagram. The influence of ΔH_t of the components on the shape of the phase diagram is shown in Fig. 2.

In the successive modelling also fixed values of ΔH_t of pure components have been selected ($\Delta H_{t,1}/R = \Delta H_{t,2}/R = 10\ 000$ K). On assumption that the system behaves either in the solid or in the liquid phase as an ideal one, *i.e.* one of the parameters A, B equals zero, we obtain four basic model situations shown in Fig. 3. From their comparison it follows that there is only little difference between the phase diagrams of systems with an equal $A - B$ difference. As it will be stressed later, in the comparison of the model and real phase diagrams also the solubility
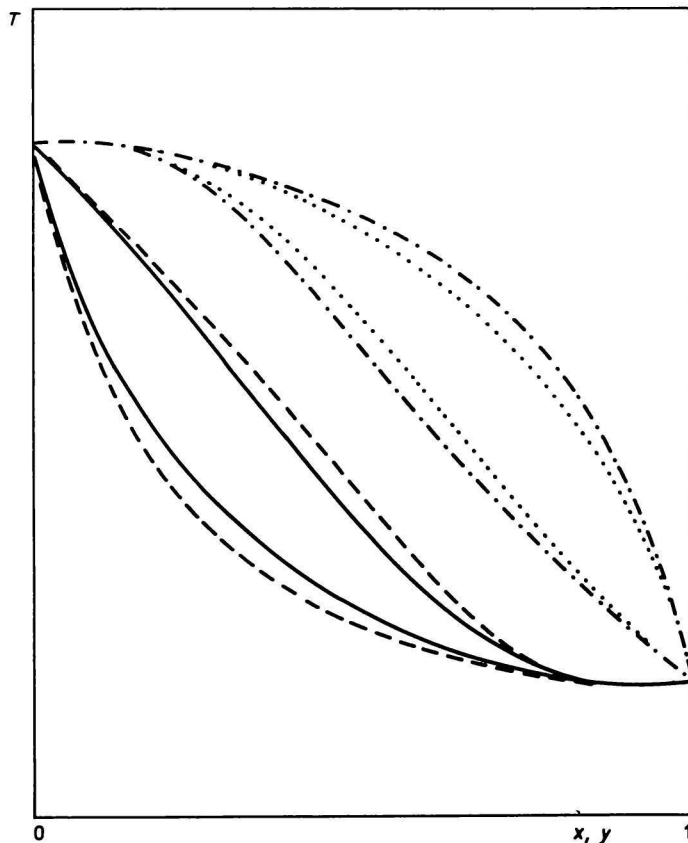

Fig. 3. The influence of parameters A, B ($H_1 = H_2 = 10\ 000$ K).
$A(B) = -1000$ K (0 K) ———, 0 K (1000 K) — — —, 1000 K (0 K) —·—·, 0 K (−1000 K)

curve in the solid phase, which is determined solely by the parameter B, is to be considered.

The influence of signs in the case of the equality of absolute values of the parameters A, B is shown in Fig. 4. Beside expansion and contraction also a rise of a maximum or a minimum can be observed in the phase diagram, similarly to the phase diagrams of the real systems.

When selecting the diagram with a minimum on the solidus and liquidus curves' as the most interesting variant in Fig. 4, we can model the rise of a minimum by gradually increasing the absolute value of the parameter (Fig. 5). An inter-step in this trend was found to be the case when both curves have a common tangent in the
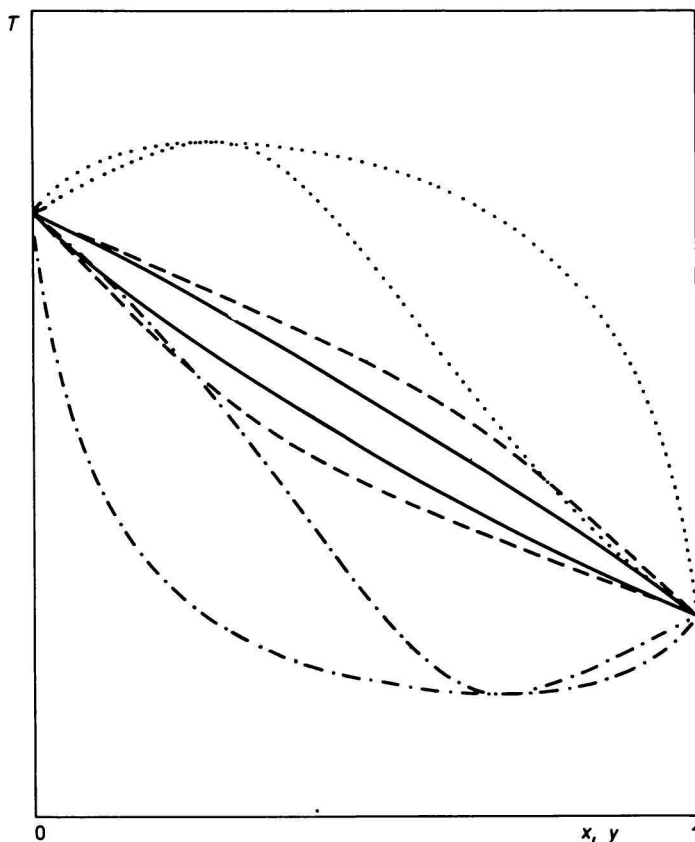

Fig. 4. The influence of parameters A, B ($H_1 = H_2 = 10\ 000$ K).
$A(B) = -1000$ K (-1000 K) ————, 1000 K (1000 K) — — —,
-1000 K (1000 K) —·—·, 1000 K (-1000 K)

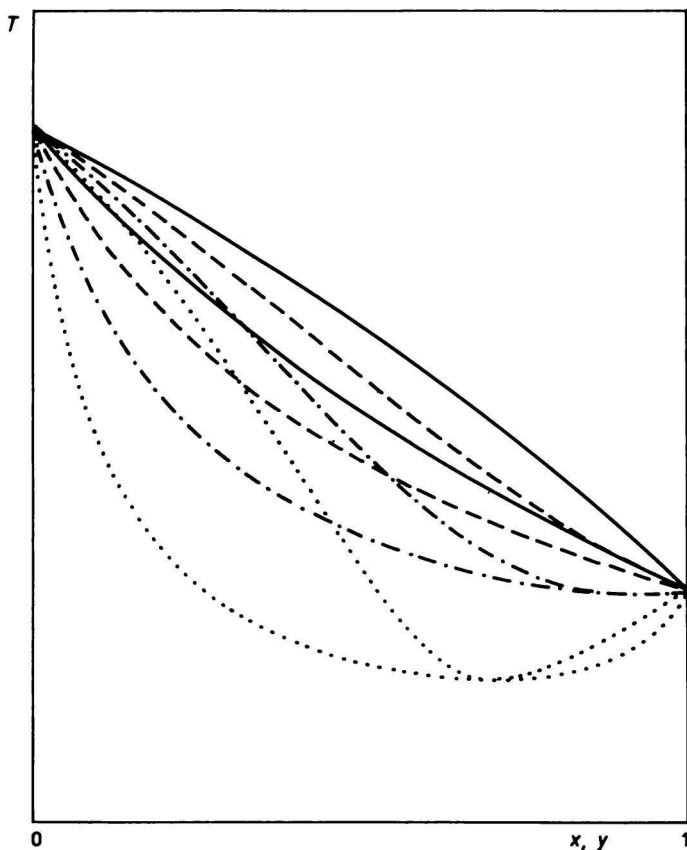*Fig. 5.* The rise of a minimum on the liquidus and solidus curves ($H_1 = H_2 = 10\ 000$ K).
$A(B) = 0$ K (0 K) ——— , -200 K (200 K) — — —,
-500 K (500 K) —·—· , -1000 K (1000 K)

point $x = 1$. In all the modelled cases, the solubility curve occurs in the range of low temperatures ($T_{max} = B/2$) and does not reach into the area of liquidus and solidus curves. When increasing the value of the parameter B, the solubility curve will approach the solidus curve till the intersection (Fig. 6). Then also the liquidus curve is intersected. A typical illustration of such a phase diagram is shown in Fig. 7. It is evident that the liquidus and solidus curves have a common tangent in one point. The connecting line of the intersections of the solubility curve in the solid phase with the solidus curve also passes through intersections on the liquidus curve, which otherwise can be proved by means of eqns (*7a, 7b*) and (*9*). This connecting line delimits the equilibrium part of the phase diagram. The course of the liquidus and
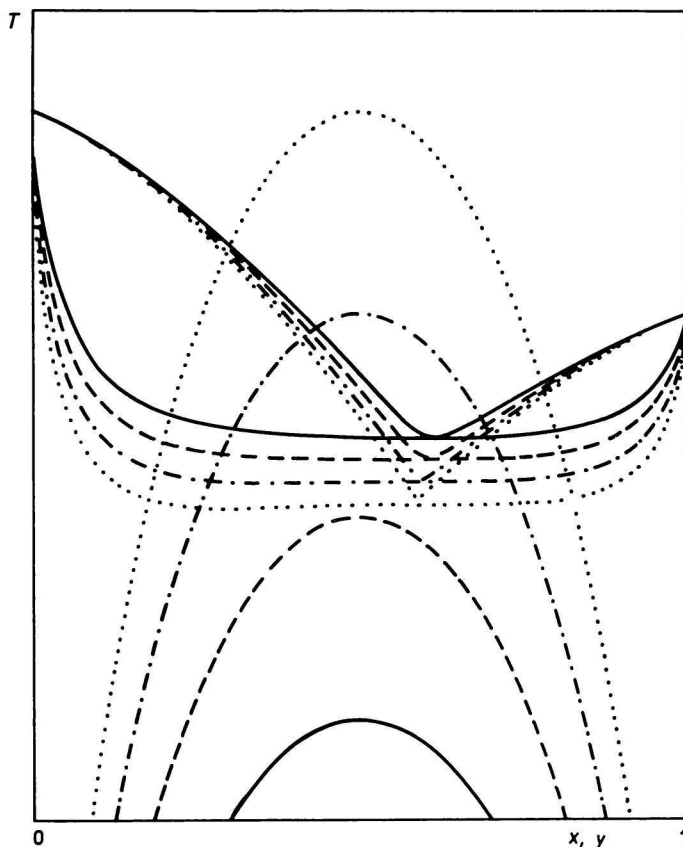
Fig. 6. Formation of the phase diagram with a limited solubility of components.
$A(B) = -1800$ K (1800 K) ———, -2000 K (2000 K) — — —,
-2200 K (2200 K) —·—·, -2400 K (2400 K)

solidus curves below this temperature is to be considered as a metastable one and their interpretation can be inspired by an analogy in the physical chemistry: the continuous course of the van der Waals' isotherm for the liquid—vapour equilibrium.

It is evident that the phase diagram of systems with a limited solubility has been obtained by solving the same set of equations as for the systems with an unlimited solubility, the difference being merely quantitative following the degree of the nonideality of the system. This approach is clearly more justified than the one assumed by Reisman. The obtained solution is continuous within the entire concentration range and it makes the mapping of the metastable area possible which is open to study if admitting the possible undercooling.
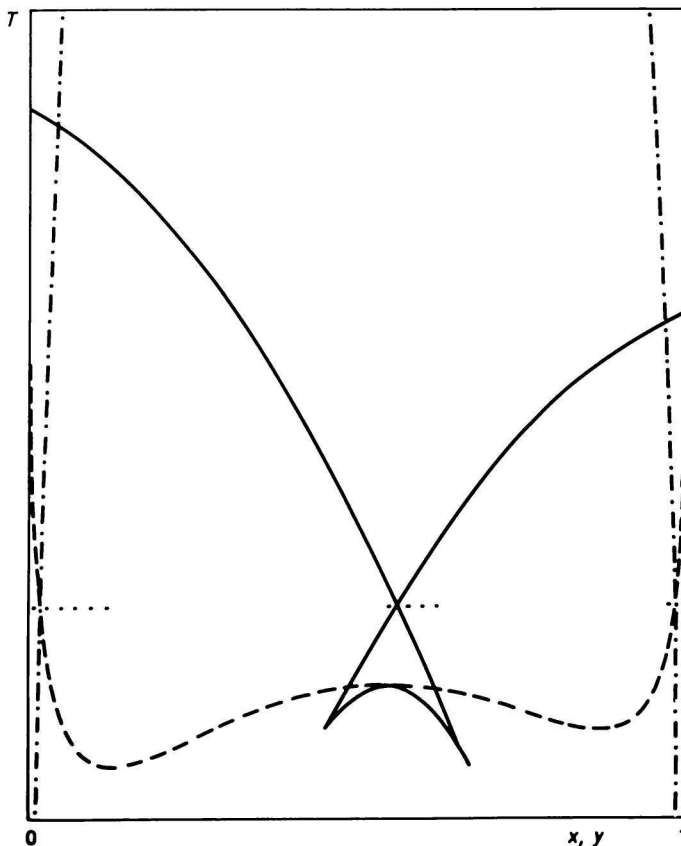
Fig. 7. Typical phase diagram with a limited solubility of components.
$H_1(H_2) = 10\ 000$ K $(10\ 000$ K$)$, A $(B) = -4000$ K $(4000$ K$)$.
Liquidus curve ———— ; solidus curve — — — ; solubility curve in solid phase —·—· ;
connecting line

   A similar shape of the phase diagram is obtained also on assumption of an ideal behaviour in the liquid phase $(A = 0$ K, B positive$)$. With increasing B, the metastable part of the phase diagram moves towards lower temperatures (Fig. 8) and the liquidus curve gradually approximates the liquidus curves of the phase diagram with a zero solubility of components in the solid phase (simple eutectic systems). Thus the phase diagram of a simple eutectic system may be considered to be a limiting case of the general shape of a phase diagram with solid solutions for $B \rightarrow \infty$. The value of the interaction parameter B expresses the readiness of the system to form solid solutions. A high positive value of B indicates that the
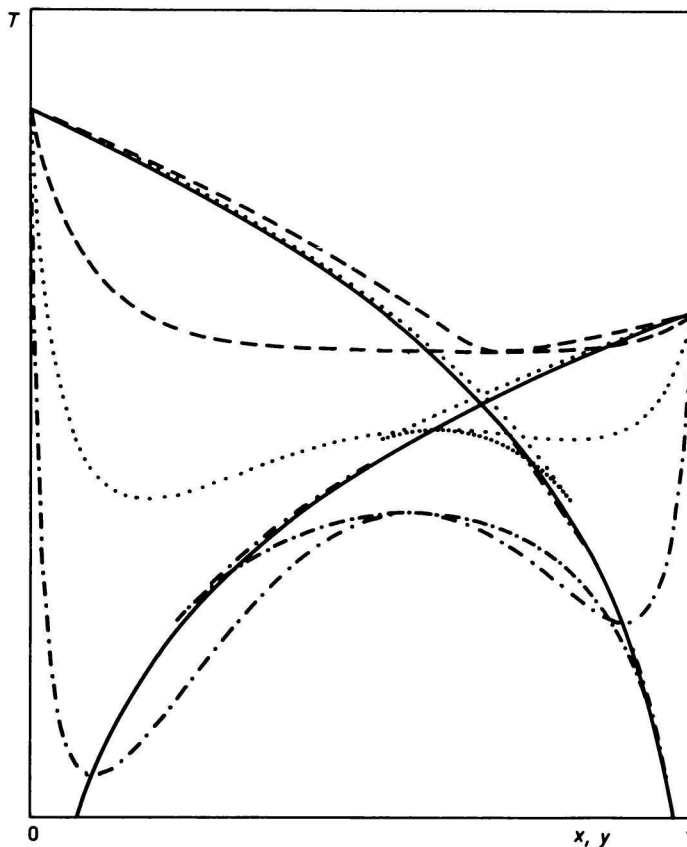
Fig. 8. Formation of a simple eutectic phase diagram ($H_1 = H_2 = 10\ 000$ K).
A $(B) = 0$ K (2000 K) — — —, 0 K (3500 K) · · · · ·, 0 K (5000 K) —·—·, 0 K (∞ K) ———.

components will segregate on transition into the solid phase because of the higher energy of a solid solution compared to that of the individual components.

The phase diagram with a limited solubility in the solid phase, mentioned in the introduction (Fig. 1c), also can be modelled when choosing appropriate values A, B, and of ΔH_f of the pure components. The composition of such a phase diagram by gradually decreasing the value of $T_{t,2}$ while preserving the other parameters is shown in Fig. 9. It is only the curvature of the left-hand branch of the solidus curve which does not correspond to the one shown in the textbooks, however, it is to be taken into consideration that when employing only two interaction parameters, it is difficult to compare in detail the modelled and the real phase diagrams.
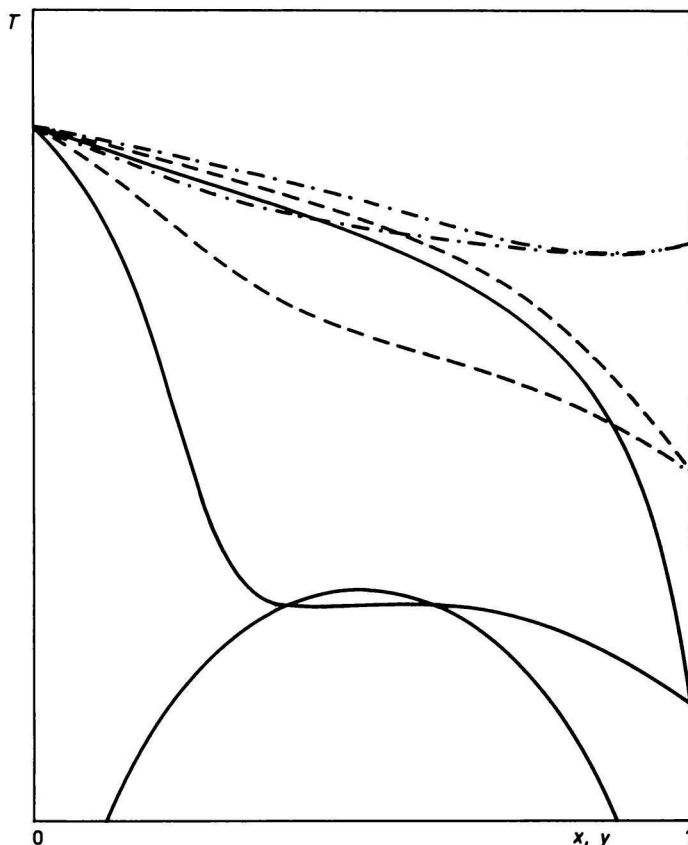
Fig. 9. Formation of a phase diagram of the type 1*c*.
H_1 $(H_2) = 5000$ K (1000 K), A $(B) = 1000$ K (1600 K).
$T_2 = 700$ K ———, 900 K — — —, 1100 K —·—·.

Conclusion

Based on the generally valid relations for the phase equilibria in a system capable to form solid solutions and on the wide-spread method for expressing the nonideality of a system, we have been successful in:

1. Proving that even the phase diagrams with a limited solubility in the solid phase can be composed as a continuous solution of the above equations;

2. Mapping the metastable area of the phase diagram;

3. Combining the solution of the liquidus and solidus curves with the solution of the solubility curve in the solid phase;

4. Proving that the phase diagram of a simple eutectic system is only a limiting case for a great value of B;

5. Revealing the influence of the interaction parameters A and B (for the liquid and solid phase, respectively): the dominant influence of B on the solubility curve in the solid phase and of the difference $A - B$ on the liquidus and solidus curves;

6. Deriving the relations for the slopes of tangents to the liquidus and solidus curves in the proximity of pure components.

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