Computer construction of ternary phase diagrams

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Dedicated to Corresponding Member M. Zikmund, in honour of his 65th birthday

Algorithms for calculation of ternary phase diagrams using the so-called "network method" are presented. As an example of application, the systems immiscible in solid phase both without compounds formation and with compounds formation have been considered. In the second case the influence of the magnitude of equilibrium constant of the reaction leading to the formation of a compound upon the shape of isotherms has been studied.

Приводятся алгоритмы расчета тройных фазовых диаграмм с помощью так называемого «сетевого метода». В качестве примера использования приводятся системы, не смешивающиеся в твердой фазе, как образующие, так и не образующие соединения. В первом примере изучается влияние величины константы равновесия реакции образования соединений на вид изотерм.

Computer construction of phase diagrams is a very important branch in the so-called "material science" (see *e.g.* Ref. [1]). On one hand it is possible by means of computer-aided method to construct phase diagrams on the basis of the experimental data with experimental errors [2—4]. On the other hand, we are able *e.g.* to construct the phase diagram of the ternary system on the basis of the knowledge of the binary phase diagrams [5]. By means of such "extrapolation" we can obtain an estimation of the ternary phase diagram the accuracy of which can be sufficient for a number of applications and the reduction of the laborious experimental work is obvious.

If we restrict ourselves to systems immiscible in the solid phase, then the subject in construction of phase diagrams is the calculation of the liquidus areas (or their sections — isotherms), and their intersections, the so-called eutectoids and eutectics. Such problem is possible to solve analytically but serious complications arise if some compounds are formed in the system. These compounds may be binary or ternary and in the case of a greater number of these compounds the final phase diagram can be so complicated that it is very difficult to choose a general strategy of the analytical method calculation. In such cases the so-called "network method" proved to be useful. This method is based on the

division of the triangle, which restricts the ternary system composition, by a sufficiently dense network. In each point of the network intersections first the equilibrium composition of the system and then the liquidus temperature for each component (both for three original ones and for the new ones formed in the reaction) is calculated. Liquidus temperatures thus obtained are then analyzed with the aim to determine the isotherms, eutectoids, and ternary eutectic points.

This formal approach (algorithms translated into the computer language) enables us to solve the problems of the influence of the magnitude of equilibrium constant of the reaction leading to the compound formation upon the shape of the phase diagram. This influence is well known in the case of binary systems [6]. But in the case of ternary systems topological considerations [7—9] were directed only to the case of the equilibrium entirely shifted in the direction of the compound formation (otherwise equilibrium constant limiting to $+\infty$). Intuitively can be guessed that for the real values of the equilibrium constant isotherms will be more curved. This work should confirm this prediction.

Equilibrium composition calculation

Assuming the equilibrium reaction in the ternary system A—B—C for the formation of the component D

$$p\text{A} + q\text{B} + r\text{C} \overset{K}{\rightleftharpoons} \text{D} \qquad (A)$$

the equilibrium composition of the system can be expressed as

$$K = (c_r)_\text{D}/[(c_r)_\text{A}^p (c_r)_\text{B}^q (c_r)_\text{C}^r] \qquad (1)$$

where K is the apparent equilibrium constant and $(c_r)_i$ are the relative concentrations of the components i in equilibrium. Denoting y as the mole fraction of the component D in the system and x_1, x_2, x_3 as the starting mole fractions of components A, B, C ($x_1 + x_2 + x_3 = 1$ must be valid at the same time) we can modify the relation (1)

$$K = \frac{y[1 + (p + q + r - 1)y]^{p+q+r-1}}{(x_1 - py)^p (x_2 - qy)^q (x_3 - ry)^r} \qquad (2)$$

In the equilibrium composition calculation y must be determined fulfilling the equation (2) for the given starting concentration x_i and the chosen equilibrium constant. Newtonian method proved to be useful in the proper calculation. Relation (2) was rewritten into the form: $F = f(y) - K$. Derivative of F can be most simply executed numerically, e.g. $F' = (f(y + 0.001) - K - F)/0.001$. The

iterative refining of y estimation runs then according to the scheme: $y^{(2)} = = y^{(1)} - F/F'$

Liquidus temperature calculation

The basic equation for the phase equilibrium in the case that solid phase is a pure component is the so-called Le Chatelier—Shreder equation (for $\Delta H_{fus,i} = = const$) [10] (index fus denotes fusion)

$$\ln a_i = (\Delta H_{fus,i}/R)(1/T_{fus,i} - 1/T) \tag{3}$$

From this equation for the liquidus temperature holds

$$T = (\Delta H_{fus,i}/R)/((\Delta H_{fus,i}/RT_{fus,i}) - \ln a_i) \tag{4}$$

In the case of temperature-dependent $\Delta H_{fus,i}$ but with $\Delta C_p = const$ the basic equation has a more complicated form

$$\ln a_i = (\Delta H_{fus,i}/R)(1/T_{fus,i} - 1/T) + (\Delta C_p/R)((T_{fus,i}/T) - 1 - \ln(T_{fus,i}/T)) \tag{5}$$

From this equation, liquidus temperature cannot be explicitly expressed. For practical liquidus temperature calculation it proved to be useful to transfer eqn (5) into the recursive form

$$T = (\Delta H_{fus,i}/R)/((\Delta H_{fus,i}/RT_{fus,i}) - \ln a_i - (\Delta C_p/R)((T_{fus,i}/T) - 1 - - \ln(T_{fus,i}/T))) \tag{6}$$

As the first temperature estimation that value was used which corresponds to $\Delta C_p = 0$ (according to eqn (4)). Iterative application of eqn (6) results in refining of the liquidus temperature and for the termination the criterion that the difference between two following temperature values should be lesser than 0.01 K can be used. In the case of the temperature dependence of ΔC_p, the basic equation is still more complicated [11] but the same procedure for solving liquidus temperatures can be used.

In the case of the calculation of liquidus temperature of the components which are formed in the reaction, the quantity T_{fus} can be regarded as the so-called hypothetical fusion temperature which is related to the unit activity of corresponding component. The equilibrium constant according to eqn (1) is defined for compound formation; its reciprocal value is, therefore, related to the reverse reaction — compound dissociation. If this value is different from zero, dissociation takes place near the fusion temperature and the real fusion temperature value is lesser than the hypothetical which would correspond to the undissociated compound.

Further problem is in expressing of the nonideality of the system. The component activity may be expressed e.g. according to the Haase conception as

a product of the ideal mixture activity and the activity coefficient: $a = a^* \ \gamma$. The ideal mixture activity may be often taken for the mole fraction. Differences occur only in the case of more complicated ionic systems [12] and then $a^* = f(x)$. Proper expressing of the nonideality of the system is in the determination of the dependence $\gamma = f(x)$ which must correspond to the relation for the excess Gibbs energy of the system ΔG^E and comply with the Gibbs—Duhem relation. However, in the systems which will be used in this work as an example ideal behaviour will be deliberately assumed.

Construction of the ternary phase diagram

If the liquidus temperatures of all components in question in all points of the triangle network have been calculated, we can analyze them with the aim to find out the significant curves or points of the phase diagram. The process proceeds in two stages: in the first stage the position of a small triangle is looked for on the basis of the defined conditions, in the second stage the position of the point on the small triangle side is precised by means of the interpolation formulas. Let us designate the vertices of the triangle the left vertex of which has the coordinations I, J by letters S, U, and P (Fig. 1.).
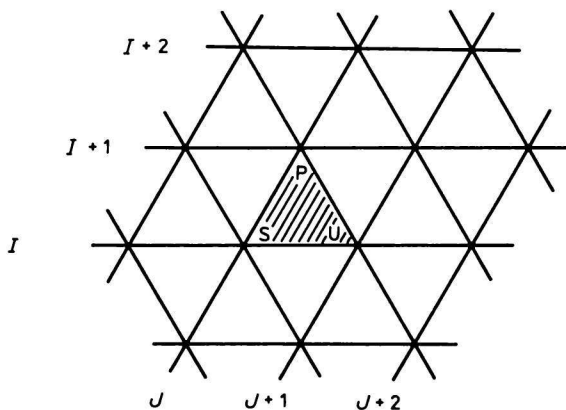

Fig. 1.

Construction of isotherms

In constructing isotherms we are looking for the intersection of liquidus area with the plane of T_i hight. We analyze, therefore, the calculated liquidus temperatures of one component only (e.g. A). If the isotherm intersects the small triangle with the vertices S, U, P, two of the three conditions must be fulfiled

$$(T(S, A) - T_i)(T(U, A) - T_i) < 0 \qquad (7a)$$

$$(T(\text{S}, \text{A}) - T_\text{i})(T(\text{P}, \text{A}) - T_\text{i}) < 0 \qquad (7b)$$

$$(T(\text{U}, \text{A}) - T_\text{i})(T(\text{P}, \text{A}) - T_\text{i}) < 0 \qquad (7c)$$

If *e.g.* the first condition is fulfilled it means that somewhere between the points S and U one point of the isotherm of A component at the temperature T_i occurs. Its position may be precised by means of the relation

$$Z = (T_\text{i} - T(\text{S}, \text{A}))/(T(\text{U}, \text{A}) - T(\text{S}, \text{A})) \qquad (8)$$

where Z is the distance between the isotherm point and the point S related to the length of the small triangle side. The accuracy of such an interpolation method with sufficiently dense network is sufficient and by connecting of all points of one isotherm almost smooth curve is obtained. This outlined procedure must be executed for all components in the system and for all chosen isotherms temperatures.

Construction of eutectoid

In constructing of the eutectoid, which are the curves originated by the intersection of two liquidus areas, we analyze the sets of calculated liquidus temperatures always for the couples of components and in all points of the network. We choose as an example the eutectoid between the components A and B. If the eutectoid intersects just the analyzed small triangle with vertices S, U, P, two of the three conditions must be fulfilled

$$(T(\text{S}, \text{A}) - T(\text{S}, \text{B})).(T(\text{U}, \text{A}) - T(\text{U}, \text{B})) < 0 \qquad (9a)$$

$$(T(\text{S}, \text{A}) - T(\text{S}, \text{B})).(T(\text{P}, \text{A}) - T(\text{P}, \text{B})) < 0 \qquad (9b)$$

$$(T(\text{U}, \text{A}) - T(\text{U}, \text{B})).(T(\text{P}, \text{A}) - T(\text{P}, \text{B})) < 0 \qquad (9c)$$

If the eutectoid point lies somewhere between the vertices S and U, its correct position and temperature coordinates are precised by means of the relations

$$T = T(\text{S}, \text{B}) + Z.(T(\text{U}, \text{B}) - T(\text{S}, \text{B})) \qquad (10a)$$

$$Z = (T(\text{S}, \text{A}) - T(\text{S}, \text{B}))/(T(\text{S}, \text{A}) - T(\text{S}, \text{B}) + T(\text{U}, \text{B}) - T(\text{U}, \text{A})) \qquad (10b)$$

where Z is the distance between eutectoid point and the point S with respect to the side length of the small triangle. This procedure must be repeated for all points of the network and for all couples of the components in the system. For each eutectoid a set of the triads of the values is obtained: the temperature and the coordinates I, J (precised by means of Z). Before constructing of the eutectoid these triads must be classified according to the descendent temperature

values. Then the first triad determines the position of the binary eutectic point of the corresponding couples of the components.

In the ternary system where no compound is formed only one ternary eutectic point can be found. The number of the ternary eutectic points is generally determined by the number of the triads which can be arranged by means of trivial combinatoric rules from all components (some triads can be metastable). These ternary eutectic points may be determined either directly, *i.e.* by means of similar but more complicated conditions as the isotherms or eutectoids points, or indirectly as the intersections of eutectoids triads. The eutectoid of the equilibrium phase diagram is then limited either by binary and ternary eutectic points or by two ternary eutectic points. The extension of the eutectoid under the temperature of the ternary eutectic point belongs to the metastable phase diagram. Unless we need that extension for some special purpose and we draw the equilibrium diagram only, we allow to connect the eutectoid points only between the eutectic points.

Similarly we allow to connect the isotherms points so as they were limited by the side of the small triangle A—B—C or by the corresponding eutectoid.

Examples of the application of the phase diagram construction

System without compound formation

As a first example we consider a hypothetical system of A, B, C components. As the values of temperatures of fusion and of the enthalpies of fusion we choose

$$\theta_{fus,A} = 800\,°C; \quad \Delta H_{fus,A}/R = 3366\,K$$

$$\theta_{fus,B} = 670\,°C; \quad \Delta H_{fus,B}/R = 2838\,K$$

$$\theta_{fus,C} = 990\,°C; \quad \Delta H_{fus,C}/R = 4041\,K$$

The values of ΔC_p of all components have been considered to equal zero. Although we use in our system real values we call it the hypothetical one for the reason of the ideal behaviour assumption. In the phase diagrams of the ideal system isotherms are namely parallel with the opposite side of the triangle and consequently most useful for testing the method because any error or inaccuracy can be recognized in the deviation from the straight line. In Fig. 2 the density of the chosen network as well as the points of some isotherms including their metastable parts can be seen. In Fig. 3 the points of the eutectoids including also their metastable parts are depicted in the same network. In Fig. 4 the final phase diagram formed by connecting of the eutectoids points and isotherms points in corresponding limits and with omitting the network can be seen.
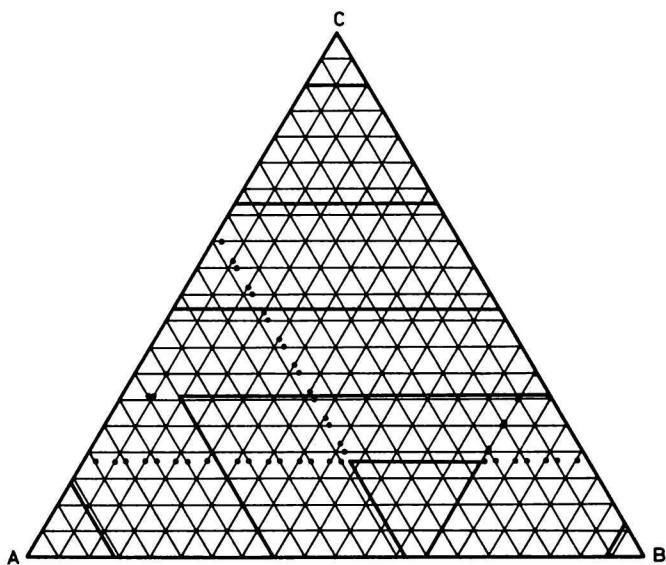
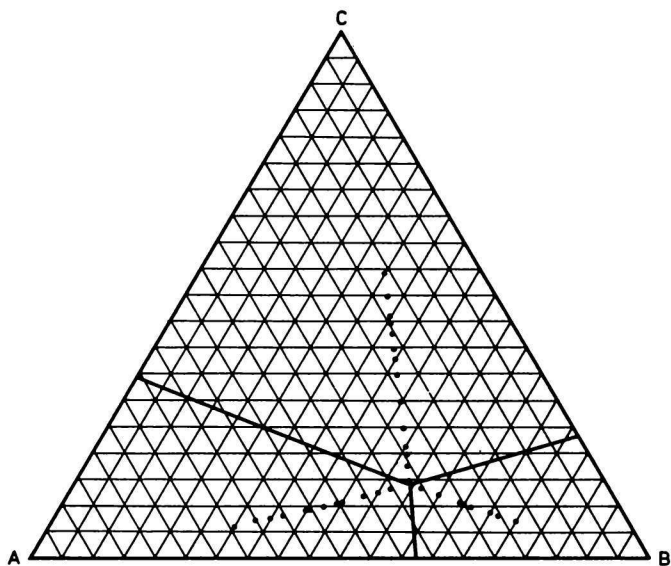*Fig. 2.* Construction of the isotherms of the phase diagram of the A—B—C system (550 K, 650 K, 750 K, 850 K, 950 K).

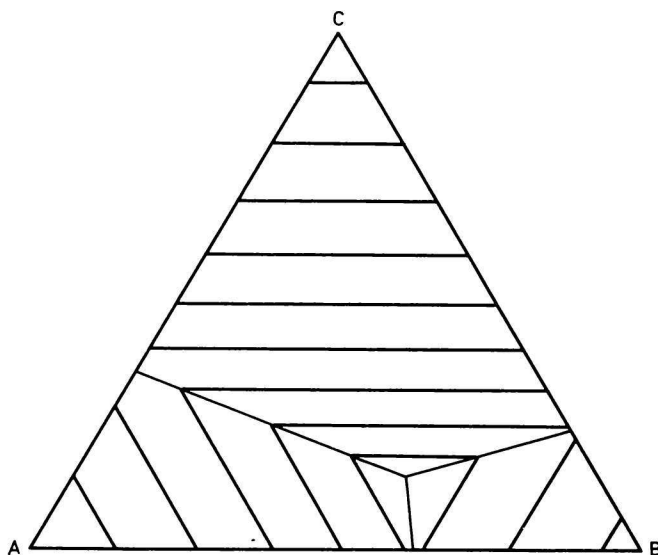*Fig. 3.* Construction of the eutectoids of the phase diagram of the system A—B—C.

Fig. 4. Final phase diagram of the system A—B—C with 50 K isotherms.

System with a compound

If we use again our hypothetical system A—B—C but in addition we assume that among the components A, B, and C the equilibrium reaction A + B + C $\rightleftharpoons$ D takes place then the point corresponding to the stoichiometric composition of the compound lies in the centre of gravity of the triangle.

First of all we shall assume that the equilibrium is shifted entirely to the right. In such case it is not necessary to calculate the equilibrium composition by means of the procedure described in the paragraph after eqn (2) but it is sufficient to put the smallest value of the concentrations x_1, x_2, x_3 for y. The phase diagram obtained by means of this procedure is in Fig. 5. It is apparent that the isotherms have sharp breaks in places where they intersect the connecting lines A—D, B—D, and C—D. Along these connecting lines the phase diagram could be divided into three separate ones and after corresponding geometrical transformations each one could be solved separately.

The other case is when the equilibrium (*A*) is not shifted entirely to the right and the equilibrium constant *K* has a real value (*K* = 100). The equilibrium composition must then be determined point after point (for all points of the network) so that it complies with eqn (2). The compound D concentration can then be represented by means of a space function having vertex in the centre of gravity of the triangle. The final phase diagram is in Fig. 6. In comparison with
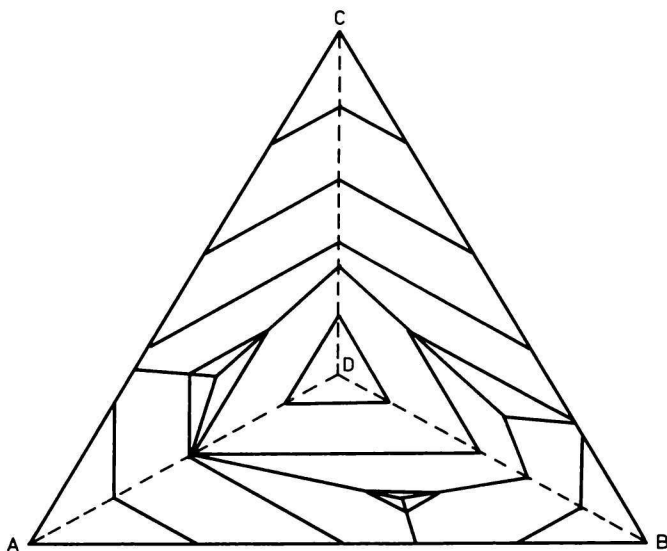
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Fig. 5. Phase diagram of the system A—B—C with the compound D formed in the equilibrium reaction (A) with the equilibrium entirely shifted in the D formation direction ($p = q = r = 1$, $K = +\infty$).
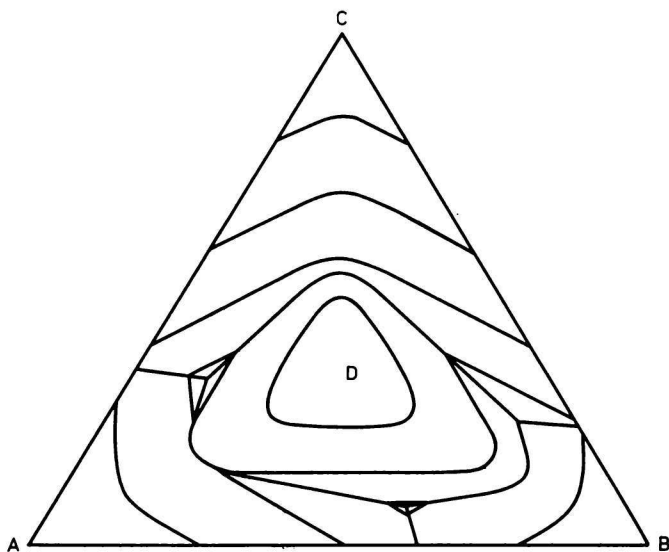

Fig. 6. Phase diagram of the system A—B—C with the compound D formed in the equilibrium reaction (A) with $K = 100$.

Fig. 5 it can be seen that the breaks on the isotherms are changed into gentle transitions and the isotherms have the general shape of the curves similarly like in the real systems, though we still assume the ideal behaviour of all components (also component D) in the system.

Finally, in Fig. 7 is the phase diagram of the system with a compound which in contrast to the foregoing one is formed in the equilibrium reaction of only two components ($K = 100$)

$$A + C \rightleftharpoons E \qquad (B)$$

The point corresponding to the stoichiometric composition of the compound lies in the middle of the side AC of the triangle. In comparison with Fig. 6 three eutectoids and one ternary eutectic point are absent.
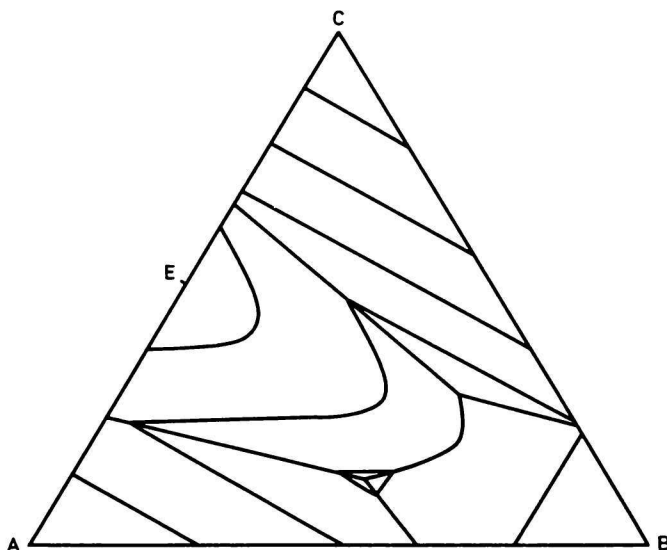

Fig. 7 Phase diagram of the system A—B—C with the compound E formed in the equilibrium reaction (*B*) with $K = 100$.

In conclusion it can be again reminded that the calculation of such phase diagram by means of direct method with respect to its variety of forms would be difficult to transform into the algorithm. But by means of the method proposed here the calculation of the ternary phase diagram with arbitrary number of equilibria and types of reactions can be performed. Further question is then the clear arrangement of the final phase diagram. Modern computer--aided technique allows to distinguish the isotherms of individual components with different colours. However, the contemporary printing technique of this journal does not allow to document it.

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