

§ 211 NON-IDEAL SYSTEMS - GEOMETRICALLY

The correspondence between Gibbs energy and phase diagram is studied by means of qualitative, graphical representations of isobaric-isothermal cross-sections of the Gibbs energy space.

non-ideal systems

In the last three sections of this volume systems are considered where at least one of the forms, in which the two components mix, deviates from ideal-mixing behaviour. Again, a restriction is made to isothermal or isobaric conditions. And even so, and for most of the cases, the equilibrium equations do not lead to explicit formulae for the relation between mole fraction variables and temperature or pressure. In other terms, for given temperature or pressure the compositions of the coexisting phases have to be calculated in a non-analytical manner, that is to say geometrically or numerically. The geometric approach, with a key role for *Gibbs energy versus mole fraction diagrams*, is the subject of this section. In the following section the problem-of-two-composition-variables is reduced to a 'one-mole-fraction-problem'; that is to say, a problem that can be tackled in an analytical manner. The numerical approach, at the level of a pocket calculator, is the subject of the last section.

As a matter of fact, the Gibbs energy versus mole fraction diagram, the *GX diagram* is a pre-eminent tool for the understanding of binary equilibrium. Sketches of *GX* diagrams are extremely useful vehicles for thinking and talking about phase diagrams. Moreover and most importantly, the *GX* diagram surpasses the notions of ideality and non-ideality: it is free from any theoretical model whatever. Therefore, the true purpose of this section is to demonstrate the power of *GX* diagrams.

Gibbs energy versus mole fraction diagrams

Let α and β be two forms, such as liquid and vapour, in which the two substances A and B, system $\{(1 - X) \text{ mole of A} + X \text{ mole of B}\}$, are completely miscible. Then, the *molar Gibbs energies* of mixtures of A and B in each of the two forms are generally represented by

$$G^{\alpha}(T, P, X) = (1 - X)G_A^{*\alpha}(T, P) + XG_B^{*\alpha}(T, P) + RT \ln(X) + G^{E\alpha}(T, P, X) + C \cdot X; \quad (1)$$

$$G^{\beta}(T, P, X) = (1 - X)G_A^{*\beta}(T, P) + XG_B^{*\beta}(T, P) + RT \ln(X) + G^{E\beta}(T, P, X) + C \cdot X. \quad (2)$$

The first two members at the right-hand side of Equations (1) and (2) represent the Gibbs energy contributions of the pure components A and B before mixing. The third term

$$RT \ln(X) \equiv RT \{ (1-X) \ln(1-X) + X \ln X \}, \quad (3)$$

which represents the Gibbs-energy effect of *ideal mixing*, is the same for α and β . The deviation from ideal-mixing behaviour is given by the fourth term; the *excess Gibbs energy*, which is different for α and β . The last term, where the value of C is arbitrary, but necessarily the same for α and β , is referred to as *the linear contribution* ($\leftarrow 205$).

Whenever, for a given T and P , the two curves representing the two Gibbs functions have one or more points in common, there will be the possibility of equilibrium between phases ($\leftarrow 203$; in particular Figure 203:3). Equilibrium between an α -phase of composition X_e^α and a β -phase of composition X_e^β ; and only so if the *overall composition* of the system (X^o) satisfies the condition $X_e^\alpha < X^o < X_e^\beta$. In the *GX diagram*, the compositions of the coexisting phases are given by the points of contact of the *common tangent line*. In terms of *chemical potentials*, the equilibrium compositions of the phases are the solution of the set N of equilibrium conditions ($\leftarrow 203$)

$$N[\mu_A^\alpha = \mu_A^\beta; \mu_B^\alpha = \mu_B^\beta]. \quad (4)$$

Purely mathematically (i.e. if one would ignore the existence of chemical potentials), as follows from Figure 1, the two conditions (two signs of equality) for the points of contact of the common tangent line are

$$N\left[\left(\frac{\partial G^\alpha}{\partial X}\right) = \left(\frac{\partial G^\beta}{\partial X}\right) = \frac{\Delta_e G}{\Delta_e X}\right]. \quad (5)$$

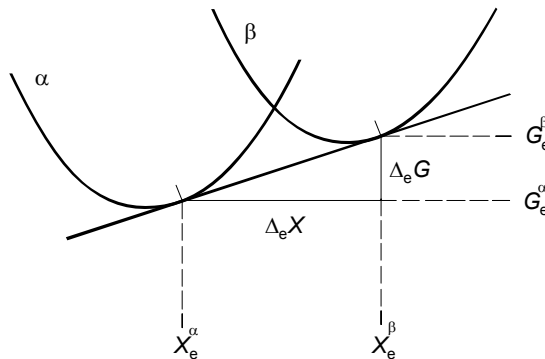


FIG. 1. Towards a 'more mathematical' formulation of the two conditions for the common tangent

The operator Δ_e has the function of indicating that the difference is taken between the value of a property in β and the value of the same property in α , and such that α and β have taken their equilibrium compositions. In the following the operator Δ without the subscript 'e' is used for a difference property such that α and β have the same composition.

Under *isobaric conditions* the difference between $G_A^{*\beta}$ and $G_B^{*\alpha}$ can be given as

$$G_A^{*\beta}(T) - G_A^{*\alpha}(T) \equiv \Delta G_A^*(T) = \Delta G_A^*(T = T_r) + \int_{T_r}^T \left(\frac{\partial \Delta G_A^*}{\partial T} \right)_P dT, \quad (6)$$

where T_r is a reference temperature. If T_r is taken as T_A^o , the temperature at which for pure A there is equilibrium between a phase α and a phase β , then the first term at the right-hand side of Equation (6) will vanish, because

$$\Delta G_A^*(T = T_A^o) = 0. \quad (7)$$

Hence, and because $(\partial \Delta G_A^* / \partial T)_P = -\Delta S_A^*$,

$$\Delta G_A^*(T) = -\int_{T_A^o}^T \Delta S_A^*(T) dT \approx -\Delta S_A^*(T - T_A^o); \quad (8)$$

similarly for pure B

$$\Delta G_B^*(T) \approx -\Delta S_B^*(T - T_B^o). \quad (9)$$

equilibrium between liquid and vapour

As a first example of the relation between Gibbs energy cross-sections and phase diagram, the case is considered where β = vapour and α = liquid, and where the excess parts of the Gibbs functions are negligible (ideal-mixing behaviour in vapour as well as in liquid), see Figure 2. At temperatures above B's boiling point (T_B^o) the G -curve for the vapour is entirely below the one for the liquid: for all compositions the whole amount of matter is gaseous. Similarly, at temperatures below T_A^o the G -curve for the liquid is below the one for the vapour: the whole amount of matter is liquid, no matter the composition of the system. For temperatures between T_A^o and T_B^o the two curves intersect, and, for overall compositions between the points of contact, there will be equilibrium between liquid and vapour. The matter divides itself over a liquid and a gaseous phase, respecting the *lever rule*. Note that in Figure 2 the distances between the G -curves for $X = 0$ are indicated. These distances are given by Equation (8).

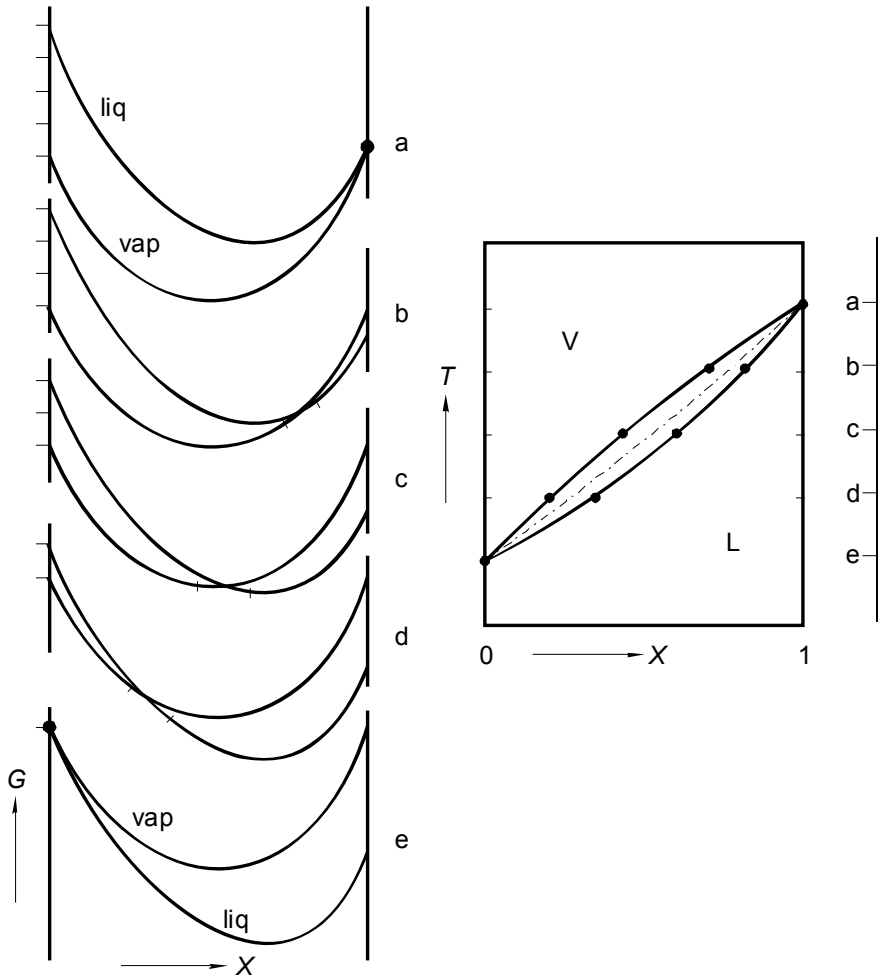


FIG. 2. Relation between Gibbs-energy-versus-mole-fraction cross-sections and phase diagram for the isobaric equilibrium between liquid and vapour

In the case of Figure 3, and compared with Figure 2, the G -curve of the liquid has a greater curvature - caused by a negative excess Gibbs energy, characteristic of an attractive interaction between A and B. The phase diagram has a maximum, a *stationary point* ($\leftarrow 005$) where the *liquidus* and *vaporus* touch one another.

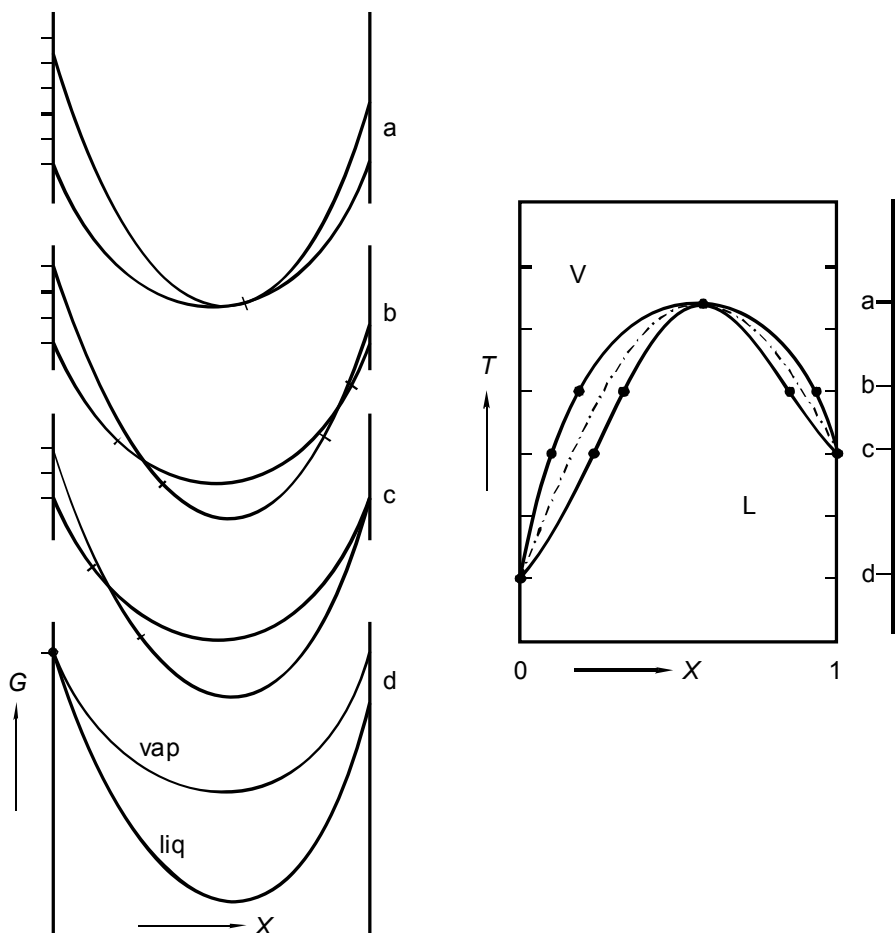


FIG. 3. Isobaric equilibrium between liquid and vapour. Relation between Gibbs-energy-versus-mole-fraction cross-sections and phase diagram-with-maximum

the equal-G curve

The *liquidus* and *vaporus* curves in the TX plane are the loci of the points of contact of the common tangent lines drawn to the G -curves; see Figures 3 and 4. The dash-dotted curves, which are drawn in the phase diagrams, are the *equal-G curves*, *EGC* for short. In a TX or PX diagram, the EGC is the locus of the points of intersection of the G -curves. Or, in other words, the EGC is the solution of the equation

$$\Delta G(T, X) = 0. \quad (10)$$

After substitution of Equations (1) and (2), the EGC equation reads

$$(1-X)\Delta G_A^*(T) + X\Delta G_B^*(T) + \Delta G^E(T, X) = 0; \quad (11)$$

the $\ln(X)$ terms of α and β have cancelled one another, and so have the linear contributions $C \cdot X$. In the theory of equilibrium between phases, the EGC is a powerful tool: it permits a considerable simplification of the thermodynamic description of equilibria between two mixed, or solution phases. In §212 the EGC is one of the means to circumvent the problem-of-two-composition-variables.

equilibrium between three phases – two liquid phases and vapour

As a next step, and as an example of the use of the *equal-G curve*, we consider the equilibrium between vapour and liquid for the case where the liquid mixtures have a positive excess Gibbs energy. Just like the negative excess Gibbs energy in the case of Figure 3 is giving rise to an EGC, which is above the line connecting T_A^o with T_B^o , a positive G^E will produce an EGC below the line $T_A^o T_B^o$. Moreover, a positive G^E may give rise to equilibrium between two liquid phases – the appearance in the phase diagram of a *region of demixing*; see Figure 4 ($\leftarrow 206; \rightarrow 212$).

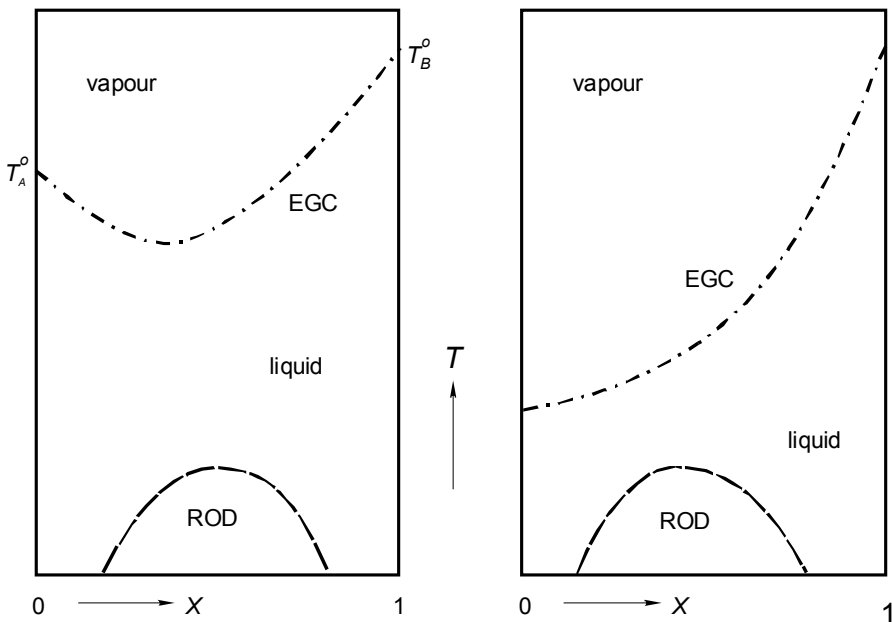


FIG.4. Isobaric equilibrium between liquid and vapour. Positive excess Gibbs energies of liquid mixtures i) make that the equal-G curve is bent down, and ii) give rise to a region of demixing

At this place we consider the case where a large positive G^E makes that the (liquid + vapour) equilibrium interferes with the region of demixing. If so, there is room for a situation of *equilibrium between three phases* ($L_I + L_{II} + V$), for which the *system formulation* is

$$f = M[T, X^{L_I}, X^{L_{II}}, X^{vap}] - N[\mu_A^{L_I} = \mu_A^{L_{II}} = \mu_A^{vap}, \mu_B^{L_I} = \mu_B^{L_{II}} = \mu_B^{vap}] = 0. \quad (12)$$

And from this expression it follows that the isobaric equilibrium between the three phases is invariant: a unique situation with fixed values for the four quantities of the set M, say, indicated as T_3 , $X_3^{L_I}$, $X_3^{L_{II}}$, X_3^{vap} , see Figure 5 with its *three-phase equilibrium line*.

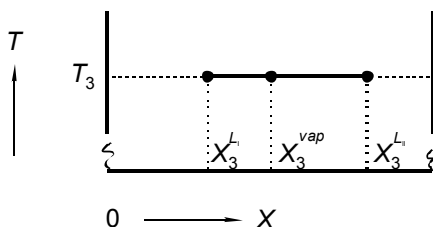


FIG. 5. Three-phase equilibrium line connecting the points that represent the compositions of the phases

From the three points on the line, three pairs of *two-phase equilibrium curves* are emanating. One pair for the equilibrium ($L_I + L_{II}$); another pair for ($L_I + V$); and the third pair for ($L_{II} + V$). In Figures 6 and 7 it is shown how the phase diagram straightforwardly follows from the combination of *binodal* (the boundary of the region of demixing) and equal- G curve. The important things to keep in mind are i) the three-phase equilibrium line has two points on the binodal, and ii) the EGC invariably is situated between liquidus and vaporus - for ($L_I + V$) and ($L_{II} + V$).

Sketches of the GX sections for the three-phase equilibrium temperatures, corresponding to Figures 6 and 7, are shown in Figure 8. The fact that *linear contributions* do change nothing in the world of phase equilibria, makes that the common tangent lines can be given no matter what slope - e.g. slope zero as is done in the case of Figure 8.

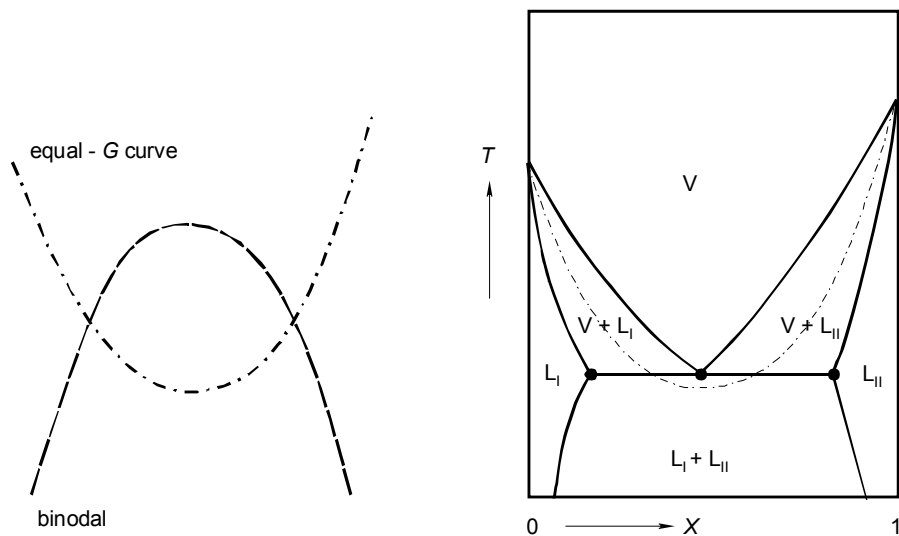


FIG. 6. The equilibrium between liquid and vapour interferes with the equilibrium between two liquid phases. The correspondence between diagram with equal-G curve and binodal (left) and phase diagram with three-phase equilibrium (right)

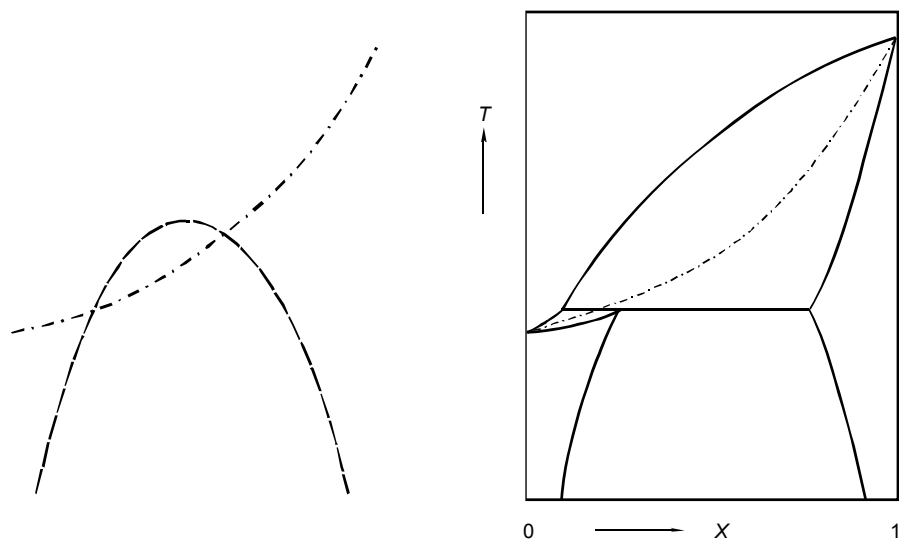


FIG. 7. Analogous to Figure 6 - with the distinction, however, that this time the EGC's minimum is absent

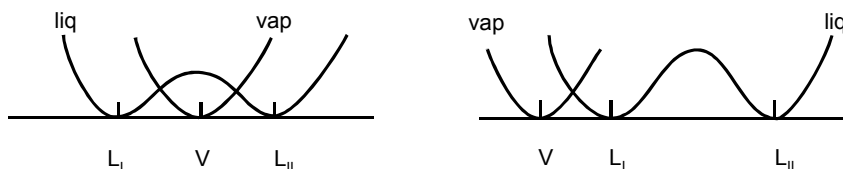


FIG. 8. Sketches of the GX sections for the three-phase equilibrium temperatures in Figure 6 (left) and Figure 7 (right)

types of phase diagram

The phase diagrams Figures 2, 3, 6, 7, and also the one with a minimum in the (L + V) two-phase region, implied in Figure 5 left-hand side, are the basic types of TX phase diagram in the case of two mixed forms. Not only for the equilibrium between liquid and vapour, but also for the equilibrium between liquid and mixed crystalline solid, and any other combination of two forms in which the components are miscible. The issue of *types of phase diagram* is readdressed in the following section.

solids of fixed composition in equilibrium with liquid

The Figures 9, 10, and 11 pertain to systems where solids of fixed composition are in equilibrium with liquid mixtures. In the case of Figure 9 the solid phases just are the component solids; the phase diagram is the *simple eutectic phase diagram*. The symmetrical phase diagram in Figure 10 is characteristic of systems where a *pair of optical antipodes* gives rise to a *racemic compound*, a *racemate*.

In Figure 11 the relative positions of the Gibbs energies are such that the 1:1 compound is a so-called *incongruently melting compound*: on heating the compound changes into (liquid P + solid B) at the three-phase (compound + liquid P + solid B) equilibrium temperature (isothermal section b). In the GX diagram for section c, a (dashed) line can be drawn for the *metastable equilibrium* between solid B and liquid; the point of contact corresponds to a point on the *metastable extension* of the (L + S_B) liquidus in the phase diagram.

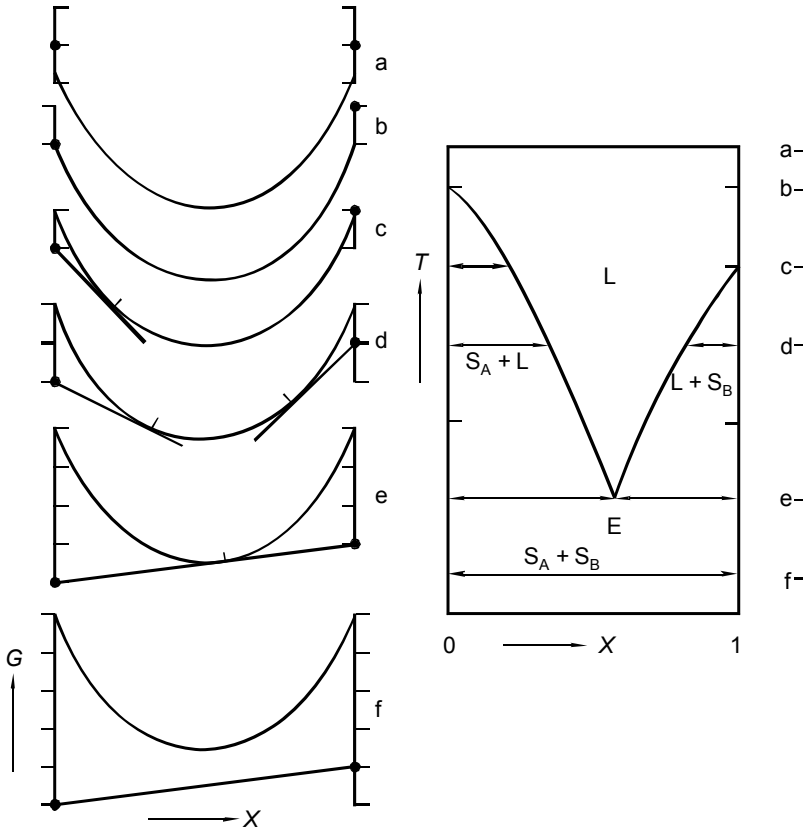


FIG. 9. Isobaric equilibrium between liquid mixtures and solids of constant composition. Relation between GX sections and phase diagram for the case of a simple eutectic: the only solid phases are the pure component ones

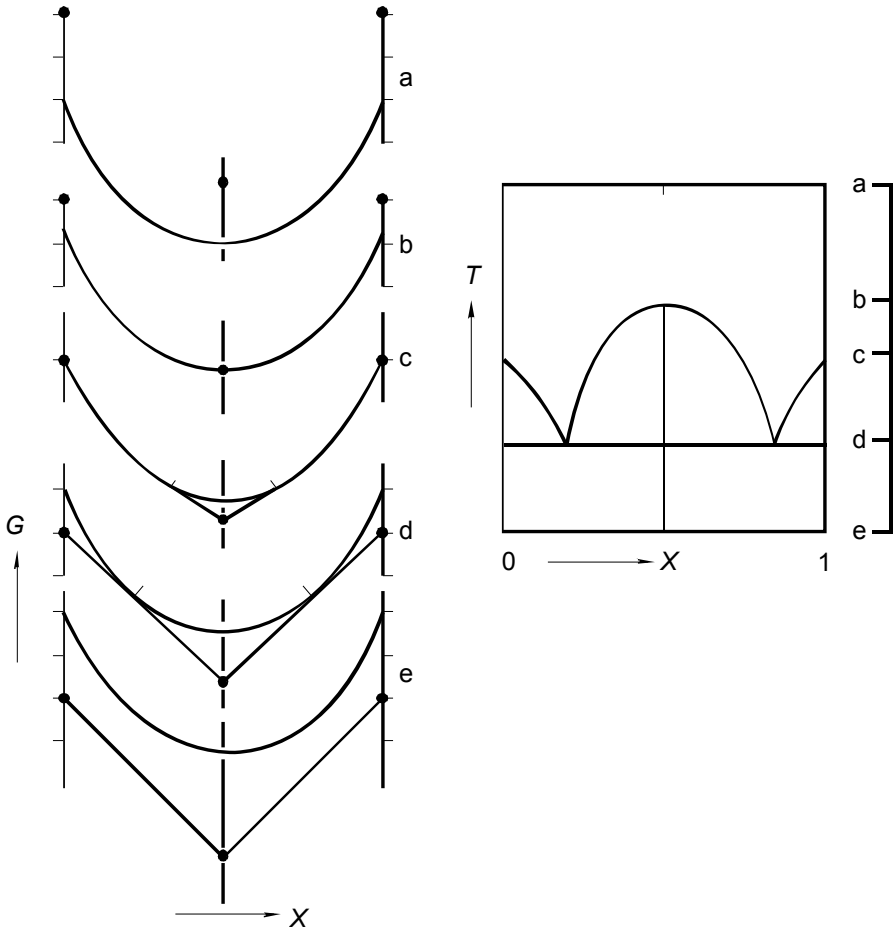


FIG. 10. Isobaric equilibrium between liquid mixtures and solids of constant composition. The latter are the two pure component solids and a 1:1 compound which fully dissociates on melting. The relative positions of the G-points for the solids in the GX sections are such that the compound is congruently melting

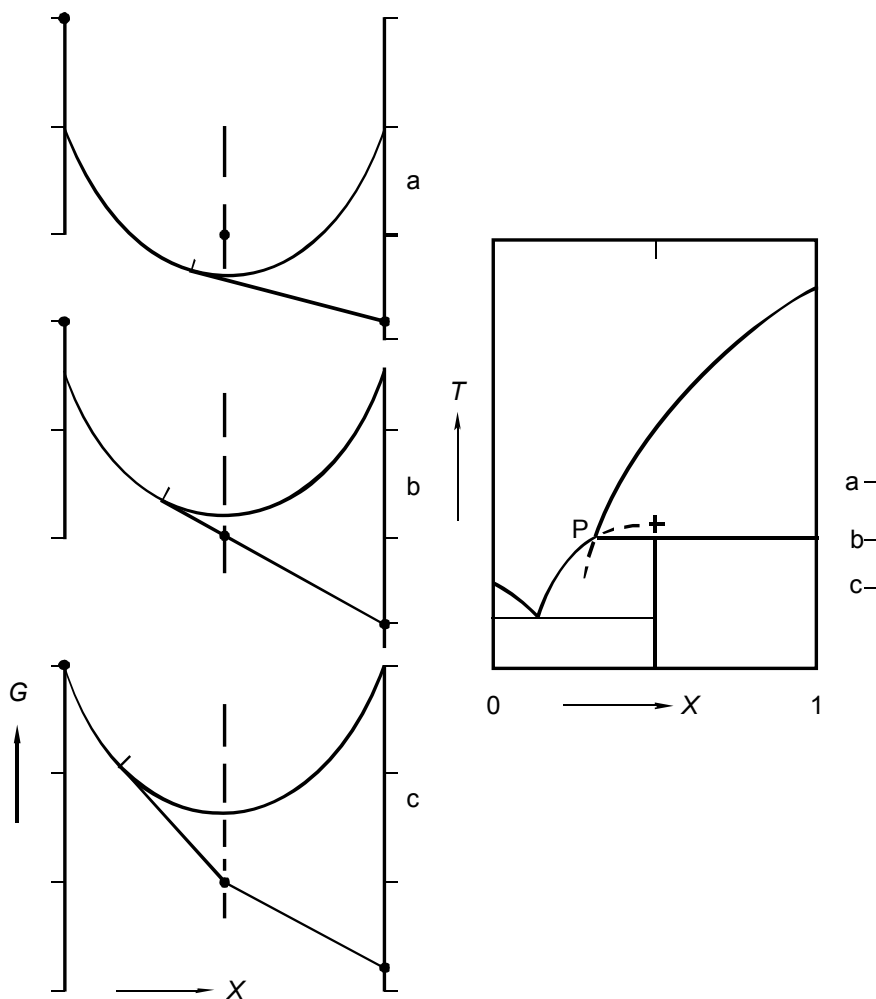


FIG. 11. Analogous to Figure 10 - will the distinction, however, that this time the relative positions of the G -points make that the compound is incongruently melting

crossed isodimorphism

Finally, Figures 12 and 13 are for systems where the molecules of A and B can replace one another in the crystal lattice; the two components, however, having different crystal structures. The phase diagram in Figure 12 shows a *eutectic type of three-phase equilibrium*, and the one in Figure 13 a *three-phase equilibrium of the peritectic type*. Owing to the fact that the phase diagrams in Figures 12 and 13 can be regarded as the stable result of two, each other crossing, *solid-liquid loops*, the term *crossed isodimorphism* is used to refer to this situation.

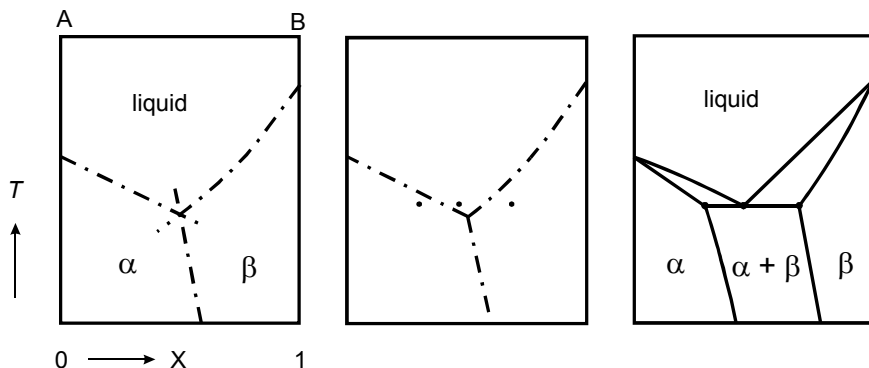


FIG. 12. From EGC diagram to phase diagram with a eutectic three-phase equilibrium. Two, each other crossing (solid + liquid) Equal-G curves invariably involve a phase diagram showing incomplete solid-state miscibility

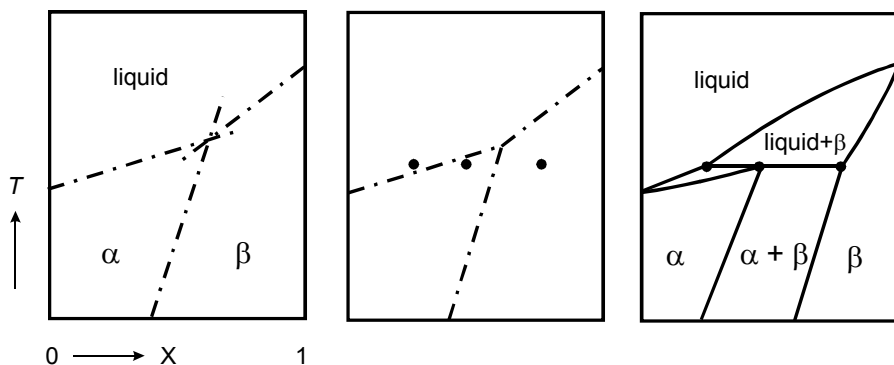


FIG. 13. The peritectic analogue of Figure 12

The qualitative GX diagram is a powerful tool for grasping the ins and outs of binary phase diagrams. Unlike theoretical and empirical models, it has the advantage of being free from any limitations.

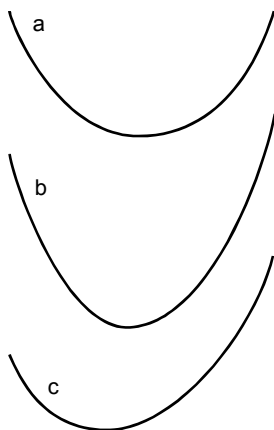
EXERCISES

1. validation of linear contributions

For the case of Figure 1, the equilibrium conditions in N, Equation (5), are satisfied for $X^\alpha = X_e^\alpha$ and $X^\beta = X_e^\beta$.

- Prove that the two conditions are satisfied for the same X values, when equal linear contributions are added to each of the two G functions; i.e. when G^α is replaced by $G'^\alpha = G^\alpha + C X^\alpha$; and similarly for G^β .

2. from G-curves to phase diagram



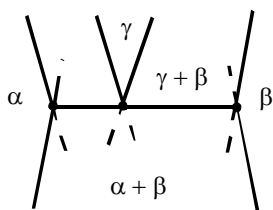
Using transparent paper, or otherwise, construct (liquid + vapour) phase diagrams for a number of combinations of the G-curves given here, and labeled a, b, and c.

Some suggestions

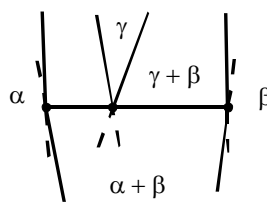
PX or TX	liquid	vapour
PX	a	c
PX	b	c
TX	a	a

3. metastable extensions

Prove, with the help of G-curves, that the condition of minimal Gibbs energy requires that the *metastable extensions of equilibrium curves* - in PX and TX phase diagrams - fall inside the two-phase regions.

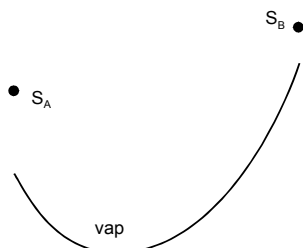


correct



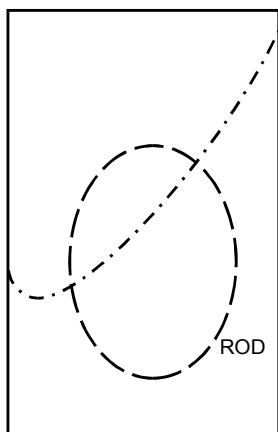
wrong

4. isothermal solid+vapour equilibrium



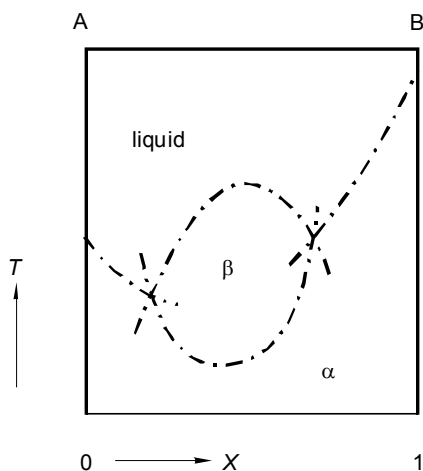
The system is considered in which, at constant temperature, two pure solid components, either individually or together, are in equilibrium with a gaseous mixture of the two components. For the relative positions of the Gibbs energies shown here, construct the PX phase diagram.

5. phase diagram for given ROD and EGC



Construct the TX (liquid + vapour) phase diagram corresponding to the figure with the boundary of a closed region of demixing (ROD) in the liquid state and the equal- G curve for the liquid to vapour transition.

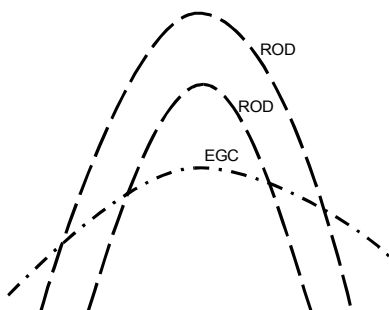
6. from EGC diagram to phase diagram



The two substances A and B are isomorphous in form α . From a certain moment (temperature) on, and for intermediate compositions, the form β makes its appearance (is stabilized).

- Transform this EGC diagram into the corresponding phase diagram.
- Make sketches of the GX sections for the two three-phase equilibrium temperatures.

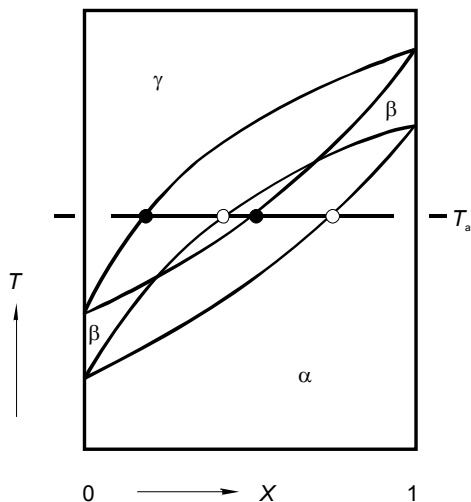
7. phase diagram for EGC and two ROD's



For the purely hypothetical case implied in the sketch, the region of demixing (ROD) in the solid state is below the ROD in the liquid, the solid-liquid equal- G curve having a maximum inside the ROD's.

- Make a sketch of the corresponding TX phase diagram.

8. overlapping two-phase regions



The individually correct $(\alpha + \beta)$ and $(\beta + \gamma)$ two-phase regions are partly overlapping.

- Work out the consequences of this situation by constructing one or more GX diagrams, and thereby revealing the true stable phase diagram.

Clue. For $T = T_a$ draw the G -curve for β and mark on it the points corresponding to the equilibrium with α and the one with γ ; and so on.

9. the system formulation for a symmetrical binary system

Generally, the equilibrium between four phases in a binary system is invariant. This is e.g. the case for the equilibrium between two liquid phases and two solid phases, the latter being the two pure solid components A and B.

- For the case that A and B are a pair of optical antipodes, D and L, the equilibrium between the four phases is monovariant, due to symmetry.
- To demonstrate this, first, construct the GX diagram for the four-phase situation and, next, write down the system formulation such that the conditions are given in terms of G and $(\partial G / \partial X)$.

10. azeotropy and Gibbs-Duhem

Along the liquidus and the vaporus in the TX plane, the liquid and the vapour phase, in combination, satisfy the equilibrium conditions in chemical potentials; and, on its own, each of the two phases respects the Gibbs-Duhem equation (\leftarrow 203):

$$(1 - X^\alpha) d\mu_A^\alpha + X^\alpha d\mu_B^\alpha + S^\alpha dT = 0; \quad \alpha = \text{liq, vap.}$$

- Demonstrate that $dT = 0$, for $X^{\text{liq}} = X^{\text{vap}} = X$: equality of composition goes together with a stationary point, an extremum in the phase diagram (\leftarrow Exc 003:2).

Clue. To get started, subtract the Gibbs-Duhem equation for the liquid from the one for the vapour.

<http://www.springer.com/978-1-4020-6123-3>

Equilibrium Between Phases of Matter
Phenomenology and Thermodynamics

Oonk, H.A.J.; Calvet, M.T.

2008, XII, 404 p., Hardcover

ISBN: 978-1-4020-6123-3