

§ 004 PURE SUBSTANCES

Pure substances are materials that are characterized by a molecule when they are molecular materials like *n*-butane (molecule $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$) and in all other cases by a chemical formula like NaCl for sodium chloride, common salt. Pure substances can take different forms, all having their own stability conditions in terms of temperature and pressure.

phases and forms

The three opening phrases, written by Gibbs under the heading "On Coexistent Phases of Matter" (p. 96 in the 1906 edition of The Scientific Papers of J. Willard Gibbs, Vol I, Thermodynamics) read

"In considering the different homogeneous bodies which can be formed out of any set of component substances, it will be convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its quantity or form. We may call such bodies as differ in composition or state different phases of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase. Phases which can exist together, the dividing surfaces being plane, in an equilibrium which does not depend upon passive resistances to change, we shall call coexistent"

And (p. 97), after the appearance of $n + 2 - r$ (our $c + 2 - p$; ←003)

"Hence, if $r = n + 2$, no variation in the phases (remaining coexistent) is possible. It does not seem possible that r can ever exceed $n + 2$. An example of $n = 1$ and $r = 3$ is seen in the coexistent solid, liquid, and gaseous forms of any substance of invariable composition".

In the case of the first quotation the matter considered (any set of component substances) is (brought to equilibrium in an experimental set-up under certain conditions and subsequently) analyzed as for its homogeneous parts, which correspond to one or more phases (numbered I, II, III, ..., or labelled $\alpha, \beta, \gamma, \dots$). In the case of the second quotation the matter considered is a substance of invariable composition, and the phases are specified by their forms.

Following Gibbs, we will use term 'phase' in the general context of equilibrium between phases of matter. The word phase is present in compound words, having a general nature. Compounds like phase diagram, Phase Rule, two-phase equilibrium curve, single-phase field, three-phase equilibrium.

The term 'form' will be used primarily in the context of materials science. The determination of the form is the first step to the identification of a homogeneous material (phase). A form is characterized by a certain molar volume - which is a

continuous function of temperature and pressure - by a certain crystal structure (when it is crystalline solid), and so on. And whenever, within a given form, two or more substances can form homogeneous mixtures of variable composition, the properties of the mixtures like molar volume will be continuous functions of the composition variables. Two phases in equilibrium can have the same form; and if so, their compositions necessarily are different.

the PT phase diagram

The basic structure element of the PT phase diagram for a pure substance is composed of three two-phase equilibrium curves emanating from the triple point, Figure 1.

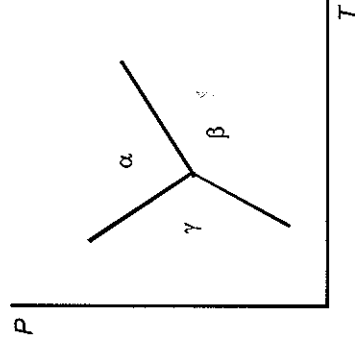


FIG. 1. Basic structure element of a pure substance's phase diagram

A two-phase equilibrium curve has a double function: the $(\alpha + \beta)$ two-phase equilibrium curve i) represents the PT circumstances for which equilibrium can be realized between the α - and the β - forms; and ii) divides the PT plane into two parts, such that at the α side the form β can change spontaneously into α , whereas α never will change into β (at the β -side these things are the other way round).

volume changes and heat effects

In terms of pressure, and for the situation sketched in Figure 1, α can be referred to as the high-pressure form and β as the low-pressure form of the two. The change of the material (at the two-phase equilibrium curve) from the high-pressure form to the low-pressure form is accompanied by a change in volume. This change, no matter how small, is always positive:

$$V^\alpha < V^\beta; \text{ or } \Delta_a^\beta V (= V^\beta - V^\alpha) > 0. \quad (1)$$

In terms of temperature, β is the *high-temperature form* and α the *low-temperature form* of the two. The change from the low-temperature to the high-temperature form is accompanied by a *heat effect*, $Q^{\alpha \rightarrow \beta}$. This effect, no matter how small, is always positive and it means that heat is needed to change α into β .

$$Q^{\alpha \rightarrow \beta} > 0$$

In the case of Figure 1, β is the high-temperature form and at the same time the low-pressure form; the slope of the two-phase equilibrium curve is positive. For the substance water, on the other hand, liquid water is the high-temperature form and at the same time, the high-pressure form: the slope of the two-phase equilibrium curve (the melting curve) is negative; see Figure 001:6. The change from ice to water at 0 °C, 1 atm is accompanied by a decrease in volume ($-19.63 + 18.00 = -1.63 \text{ cm}^3 \cdot \text{mol}^{-1}$) and a heat effect of $6008 \text{ J} \cdot \text{mol}^{-1}$.

As a matter of fact, the thermal counterpart of ΔV is not the heat effect Q itself, but a quantity related to it. The volume change ΔV is a property which is expressed in $\text{m}^3 \cdot \text{mol}^{-1}$, and $\text{J} \cdot \text{mol}^{-1}$ is equal to joule-per-mole-per-pascal; $\text{J} \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$. It means that when ΔV is multiplied by the *mechanical potential*, the pressure P , a property obtained in $\text{J} \cdot \text{mol}^{-1}$ - like the heat effect Q . Analogously, the thermal counterpart of ΔV is a property expressed in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. This property is obtained when the heat effect (of the change $\alpha \rightarrow \beta$) is divided by, the *thermal potential*, the *thermodynamic temperature* at which the change takes place. It is the *change in molar entropy* ΔS (see below; $\rightarrow 106$, in particular).

Summarizing, in a PT phase diagram of a pure substance the *single-phase fields* are positioned such that i) on increasing pressure the changes are in decreasing volume, and ii) on increasing temperature the changes are in increasing entropy.

Clapeyron's equation ($\rightarrow 110$)

The volume change, ΔV , and the heat effect, $Q^{\alpha \rightarrow \beta}$, not only (by their signs) determine the sign of the slope of the equilibrium curve, they also, by their magnitudes, determine the magnitude of the slope:

$$\frac{dP}{dT} = \frac{Q^{\alpha \rightarrow \beta}}{T \cdot \Delta V} \quad (3a)$$

In this equation, T is the thermodynamic temperature, for which the slope is taken. The relationship is referred to as *Clapeyron's equation*, after Emile Clapeyron (1799-1864). Replacing the quotient of heat effect and temperature by

$$dP/dT = \Delta S/\Delta V. \quad (3b)$$

The Clapeyron relation is of general validity; its thermodynamic derivation is given in the Appendix. Equation 3, a special equation is obtained for the case that β is the high-temperature form of a solid or liquid, and moreover, if β is taken as an ideal gas, and β is the high-temperature form of a solid or liquid. For this special case ΔV reduces to RT/P , and with $(1/P)$ as a function of T , the equation changes into

$$\frac{d \ln P}{dT} = \frac{Q^{\alpha \rightarrow \text{vap}}}{RT^2}. \quad (4)$$

As a next step, with $d(1/T) = -(1/T^2) dT$,

$$\frac{d \ln P}{d(1/T)} = -\frac{Q^{\alpha \rightarrow \text{vap}}}{R}. \quad (5)$$

This special equation suggests a linear relationship between $\ln P$ and $1/T$. In reality the relationship is only roughly linear - owing to the fact that Q , along the equilibrium curve, becomes smaller with increasing temperature. In any case, it has become a common practice to represent vapour pressure data - the pressure of vapour in equilibrium with solid or liquid - in a $\ln P$ vs $1/T$ diagram. Such a representation of vapour pressure data is referred to as *Clausius-Clapeyron plot*; see Figure 2.

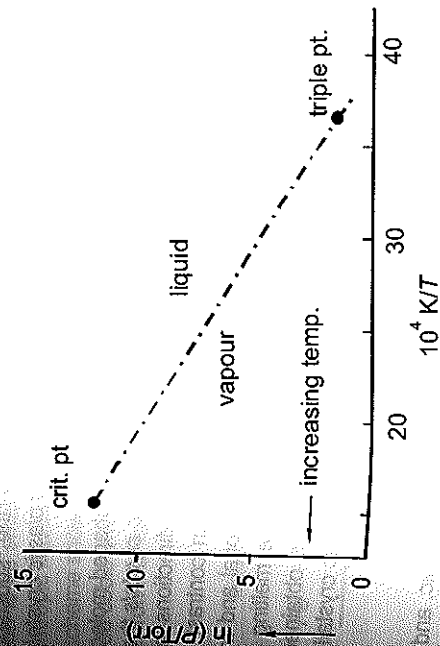


FIG. 2. Clausius-Clapeyron plot of the boiling curve for water, from below the triple point up to its end point, the *critical point* where the distinction between liquid and vapour comes to an end ($\rightarrow 206$)

One of the experiments described in § 001 was carried out - under atmospheric pressure - with an amount of water having a temperature of -5°C , i.e. experimental circumstances under which liquid water may change spontaneously into ice. Circumstances that correspond to a point in the phase diagram lying in the single-phase field for ice.

In itself, water having a temperature of -5°C is not less stable than water having a temperature of $+5^{\circ}\text{C}$. The only thing is that at -5°C liquid water may change spontaneously into ice, whereas at $+5^{\circ}\text{C}$ it never will do. For these reasons liquid water at 1 atm and -5°C is said to be *metastable*.

It is (even) possible to experimentally study the equilibrium between *supercooled water* and gaseous water (\rightarrow Exc 3). It is customary to refer to this equilibrium between phases as an example of *metastable equilibrium*. Accordingly, the extension (beyond the triple point) of the (liquid + vapour) equilibrium curve is referred to as *metastable extension*.

Metastability is a fascinating and, at the same time, a complicating phenomenon. Complicating, because spontaneity (irreversibility) does not go well with controllability (reversibility). Diamond and graphite are two forms of the substance carbon. One is inclined to think that diamond is the stable one of the two forms, but it is not (\rightarrow 109).

polymorphism

In the realm of crystalline materials *polymorphism* is a common phenomenon - it is the fact that many substances give rise to more than one crystalline form. A speaking example is found in the substance carbon tetrachloride, especially so because of the occurrence of *plastic crystalline forms*.

Substances, like carbon tetrachloride, having spherically shaped molecules, often manifest themselves in a plastic crystalline form. In *plastic crystals* the individual molecules occupy crystallographic positions whereas their directions in space are arbitrary: they have (a dynamical) *orientational freedom*. In contrast to 'normal' crystalline materials - where the molecules obtain orientational and *translational freedom* (no fixed positions) at the same time, i.e. at the melting point - for materials like carbon tetrachloride orientational freedom is obtained first and translational freedom in a second step. This is why the plastic crystalline state is referred to as a *mesostate* between 'normal' solid and liquid.

In the case of carbon tetrachloride the normal solid is monoclinic, and at 225.4 K it changes into a rhombohedral plastic-crystalline form. The latter subsequently changes into liquid at 250.3 K . The curious thing about carbon tetrachloride is that it can take a second plastic crystalline form - face-centred cubic (fcc) - which, invariably, is metastable. The form can be obtained by crystallization from the liquid, and, when it is heated, it melts at 244.8 K ; see Figure 3.

The rhombohedral plastic crystalline form and the low-temperature monoclinic form stand to each other in, what is called, and *enantiotropic relationship*: the two crystalline forms can exist at the same time, in equilibrium with one another; a phenomenon referred to as *enantiotropism*. The relationship between the two plastic crystalline forms, on the other hand, is a *monotropic relationship*: the two plastic crystalline forms never coexist - the only thing is that the invariably metastable fcc-form can change spontaneously into the other; the phenomenon is referred to as *monotropism*.

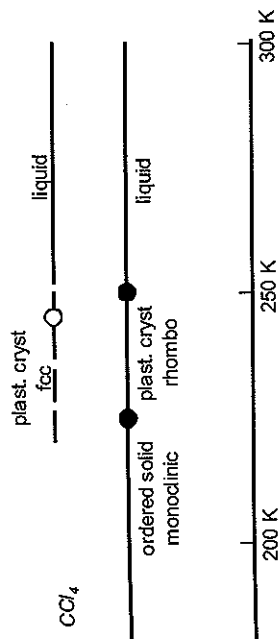


FIG. 3. Carbon tetrachloride's polymorphic relationships. Top: metastable sequence; bottom: stable sequence

Occasionally, a form, which is stable in a certain span of temperature, re-enters as the stable form in another span. *Re-entrant behaviour* is rather frequently observed for forms belonging to the mesostate of *liquid crystals* (van Hecke 1985). Re-entrant behaviour becomes a possibility when the heat effect of the transition is so small that it can change sign (before the form changes into liquid, or isotropic liquid in the case of liquid crystals).

The scheme shown in Figure 4 pertains to iron, whose re-entrant form is the body-centred cubic one. At 1184 K an amount of heat of $900\text{ J}\cdot\text{mol}^{-1}$ is needed to change bcc iron into fcc - at 1665 K , $837\text{ J}\cdot\text{mol}^{-1}$ is needed to realize the opposite change!

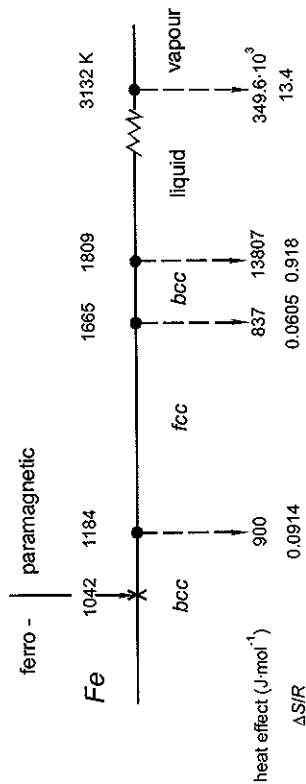


FIG. 4. Sequence of iron's forms. Heat effects of the transitions; increases in entropy divided by the gas constant

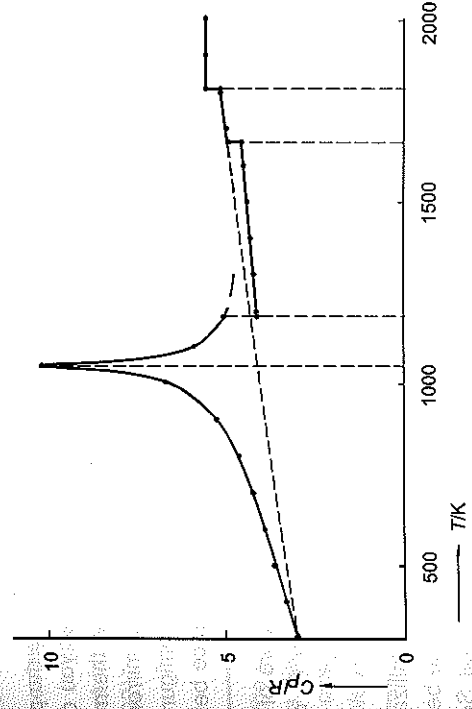


FIG. 5. Heat-capacities-divided-by-the-gas-constant of iron's forms (Barin 1989); see also Figure 4

a glass transition

In the scheme for iron, the cross on the temperature line represents the Curie temperature (1042 K): the temperature at which iron changes from a ferromagnetic to a paramagnetic material. The magnetic susceptibility of a ferromagnetic material decreases with temperature, and very rapidly so in the vicinity of the Curie point - where it falls down to a paramagnetic level (virtually zero). At the Curie temperature there is neither a change in crystal structure, which remains bcc, nor an (isothermal) heat effect.

The heat effect involved in the change is spread out over a range in temperature. It manifests itself in the form of an extra heat capacity ($\rightarrow 103$), increasing with temperature, and falling down at the Curie point. The heat-capacity plot resembles the Greek letter lambda - it explains the use of the term lambda transition, see Figure 5.

Unlike the transition from bcc to fcc at 1184 K - where during the transition a bcc phase is in equilibrium with an fcc phase and where ΔS has a finite, non-zero value - the transition at 1042 K has $\Delta S = 0$, and it has nothing to do with an equilibrium between two phases. In the classification of transitions by Ehrenfest (1933), the transition at 1184 K is referred as a first-order transition, and the one at 1042 K as a second-order transition.

The molecule which is pictured, Figure 6, has a rather planar structure: the carbon atoms 1, 2, 3, 5 and 6 and the oxygen atom are about in the same plane (the plane of the paper); carbon atom 4 is below the plane, and the isopropylidene group originates from it in an upward direction. The molecule is a chiral molecule (cannot be superimposed on its mirror image) and, therefore, it is characteristic of a substance which is optically active (rotates the plane of polarization of polarized light); that substance is laevorotatory carvone. The mirror image of the molecule (C atom 4 above the plane and the isopropylidene group downward) is characteristic of the substance dextrorotatory carvone.

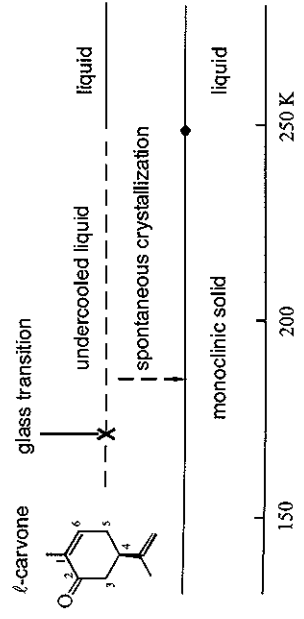


FIG. 6. Laevorotatory carvone - its forms and its behaviour

In the scheme, Figure 4, the row labelled $\Delta S/R$ stands for the change in entropy (see above) divided by the gas constant. ΔS and R are expressed in $J \cdot K^{-1} \cdot mol^{-1}$, their quotient being a dimensionless quantity. The advantage of using (here) ΔS over using Q , the heat effect, is that, for certain classes of change, the former, unlike the latter, has a more or less constant value. As an example, for metallic sodium, melting at 370.98 K, the heat of melting is $2603 J \cdot mol^{-1}$, as distinct from 1809 K and $13807 J \cdot mol^{-1}$ for iron. Notwithstanding these large differences, the values of ΔS are quite comparable: $0.84 R$ for Na and $0.92 R$ for Fe. This observation finds expression in Richards' rule, stating that the entropy of melting of (the outspoken) metals (excluding metals like Sb) is represented by $\Delta S \approx R$. For the ionic alkali halides the entropy of melting is $\Delta S \approx 3 R$.

For the change from liquid to vapour at 1 atm pressure Trouton's rule states that $\Delta S \approx 11 R$; and it is known that the rule is reasonably well respected by non-polar liquids having boiling points in the range 0 to 300 °C, and consisting of small molecules. For Fe, far outside the 0 \rightarrow 300 °C temperature range (see Figure 4), the entropy of vaporization is about $13 R$ - still in the vicinity of the rule.

a lambda type of transition

Besides, *l*-carvone and *d*-carvone have the same thermo-physical properties, such as melting point and heat of melting (imagine that you can see the individual molecules in a beaker with boiling *l*-carvone, the thermometer indicating $t = 231\text{ }^\circ\text{C}$; then turn your back to the beaker and use a mirror to see what is going on in it; in the mirror you see molecules having the configuration of *d*-carvone; the thermometer indicates $t = 231\text{ }^\circ\text{C}$, the only difference being that the numbers on the thermometer are written backwards).

Nota bene, these observations certainly do not mean that a mixture of *d*- and *l*-carvone will manifest the same phase behaviour as *d*- or *l*-carvone individually ($\rightarrow 005$).

Liquid carvone can be supercooled easily, i.e. prevented from crystallization at, or below its melting point. Figure 7 is a *thermogram* which depicts the behaviour of a supercooled *l*-carvone sample, when heated in a Differential Scanning Calorimeter (DSC). In a DSC, the sample to be studied and a reference (e.g. an empty sample pan) are mounted on a metal block that can be heated at a certain rate. In simple terms, the thermogram represents the heat to be added or withdrawn from the sample, in order to keep it at the same temperature as the reference. The events, registered in *l*-carvone's thermogram in order of increasing temperature, are the so-called *glass transition* ($\sim 171\text{ K}$); a crystallization process ($\sim 193\text{ K}$ to 208 K); followed by a recrystallization phenomenon ($\sim 210\text{ K}$ to 218 K); and, finally, the melting of the sample ($\sim 248\text{ K}$).

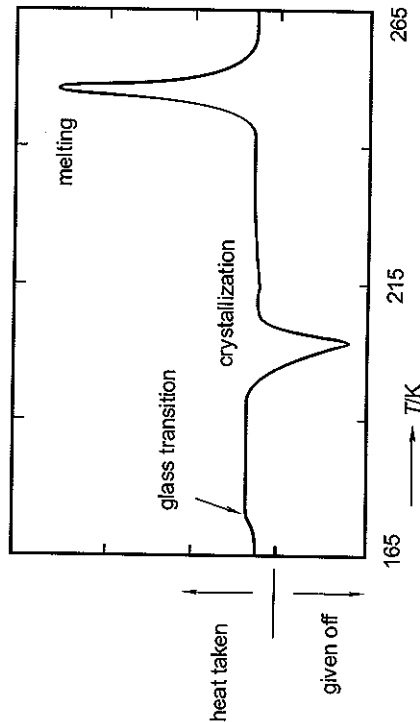


FIG. 7. Thermogram of a supercooled liquid sample of laevorotatory carvone (Gallis et al. 1996)

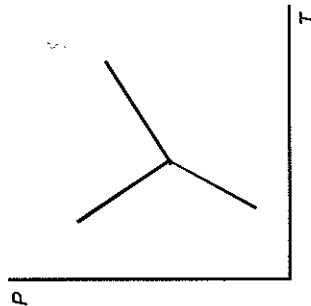
Like the magnetic transition in the bcc form of iron, the glass transition in a supercooled liquid can be regarded as a continuous, non-isothermal transition within a given form. Unlike the former, the latter has, for a given material, not a fixed position on the temperature scale: the glass transition temperature depends

on the cooling conditions to which the liquid is subjected. Below the glass transition temperature the positions of the molecules are fixed: any molecular movement is suppressed by the viscosity, which has become too high (Papon et al. 2002).

Each of the stable forms taken by a pure substance has its own stability field in the PT phase diagram. Forms can appear under conditions outside their stability fields, in which case they are said to be metastable. Frequently forms are seen that are metastable whatever the circumstances.

EXERCISES

1. the position of phase symbols



The figure is part of the phase diagram of a pure substance, including the forms, α , β and γ , of which the molar volumes increase in the order β , γ , α .

- Provide each of the single-phase fields with the correct (phase) symbol.
- Arrange the (form) symbols in order of increasing molar entropy.

2. zero Celsius and zero Celsius

The rounded difference in temperature between the triple point and normal freezing point of water is 0.01 K. This 10 mK (millikelvin) difference has been used to redefine the zero point of the Celsius temperature scale ($\leftarrow 002$).

- To appreciate this, apply Clayperon's equation to calculate, as an integer in mK, the difference in temperature between the two point's.
- The necessary data are given in the text.

3. water's triple point pressure

The table gives for the pure substance water the equilibrium vapour pressure over solid (ice) as well as over metastable liquid for six temperatures from -5 °C to 0 °C.

$t/^\circ\text{C}$	$P(\text{solid})/\text{Torr}$	$P(\text{liquid})/\text{Torr}$
-5	3.013	3.163
-4	3.280	3.410
-3	3.568	3.673
-2	3.880	3.956
-1	4.217	4.258
0	4.579	4.579

- In terms of Equation (5), think up a method in which linear least squares is used to calculate - from the given set of data - water's triple-point coordinates.
- Next, carry out the calculation - temperature in two decimal places and pressure as an integer in Pa.

4. carbon dioxide's metastable normal boiling point

Carbon dioxide is not an everyday substance as far as the positions of its triple point (216.8 K; 5.1 bar) and critical point (304.2 K; 73.9 bar) are concerned.

- Use the data to make an estimate of i) its heat of vaporization, and ii) its (metastable) normal boiling point.
5. the substance water under high pressure

The triple point data for the substance water shown here (see Tonkov 1992) involve, apart from the liquid, seven solid forms/phases - indicated by Roman numerals.

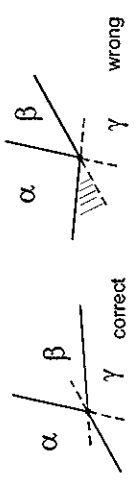
- Use the information to construct the PT phase diagram; mark the single-phase fields with the appropriate symbol.
- Estimate the pressure which is needed to solidify water at 100 °C.
- Estimate the coordinates of the metastable triple point (II + V + ℓ).

triple point	$t/^\circ\text{C}$	P/GPa
I + III + ℓ	-22	0.207
I + II + III	-34.7	0.213
III + IV + ℓ	-17	0.346
II + III + V	-24.3	0.344
V + VI + ℓ	0	0.625
V + VII + ℓ	81.6	2.15
VI + VII + VIII	-3	2.12
II + V + VI	-60	0.6

NB. GPa = gigapascal = 10^9 Pa

6. a rule to be respected by metastable extensions

At the ($\alpha + \beta + \gamma$) triple point, the metastable extension of a two-phase equilibrium curve has to run into the field bounded by the stable parts of the other two equilibrium curves.



The negation of this statement can be reduced to an absurdity, i.e. is giving rise to contradictory conclusions.

- Demonstrate this for the shaded field, remembering that at the α side of the ($\alpha + \beta$) equilibrium curve β can change spontaneously into α .
7. a phase diagram acts as a thermometer

The PT phase diagram of aluminium silicate (Al_2SiO_5) with its three solid forms - sillimanite (I), andalusite (II) and kyanite (III) plays an important part in geology - thermobarometry in particular. The diagram is given in Tonkov's (1992) compilation, the equations for the (I + II) and (II + III) equilibrium lines being $t/^\circ\text{C} = -415 P/\text{GPa} + 848$, and $t/^\circ\text{C} = 920 P/\text{GPa} + 114$, respectively. According to Althaus (1969), for the change from I to III at 600°C, the heat effect is $-9.08 \text{ kJ} \cdot \text{mol}^{-1}$ (heat given off) and the volume effect $-5.51 \text{ cm}^3 \cdot \text{mol}^{-1}$ (decrease).

- Calculate the coordinates of the (I + II + III) triple point.
- For $300 \leq t/^\circ\text{C} \leq 800$ and $0 \leq P/\text{GPa} \leq 1.0$, construct the complete phase diagram, and mark the single-phase fields with the right phase symbol.

8. superposition of stable and metastable

For a "monotropic" substance, construct a PT phase diagram, such that the metastable phase relationships (dashed lining) are superimposed on the stable ones (solid lining) and the phases/forms involved are α (stable solid), β (metastable solid), liquid and vapour.

9. Antoine's equation for vapour pressures

Five data pairs are given for the equilibrium vapour pressure over liquid 1-aminopropane ($\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$), taken from the twelve pairs by Osborn and Douslin (1968).

nr	$t/^\circ\text{C}$	P/Torr
1	22.973	289.13
2	32.564	433.56
3	47.229	760.00
4	62.235	1268.0
5	77.587	2026

- Use the pairs 1, 3, and 5 to calculate the constants A, B, and C of the "Antoine equation"
- $\ln(P/\text{Torr}) = A - \frac{B}{\{(T/K) - C\}}$
- Examine the significance of the result by (re)calculation of the vapour pressures for the five experimental temperatures.

10. supercritical fluid

A 'supercritical fluid' is characterized, let's say, by the following (twofold) property.

- "When at constant pressure (or temperature) its temperature (pressure) is continuously lowered, it will not undergo a sharp transition - at the liquid + vapour equilibrium curve - from vapour (liquid) to liquid (vapour)".
- Draw a (S + L + V) PT phase diagram, and, in it, shade the field that corresponds to supercritical conditions.

11. iron: the heat effect of magnetic change

From Figure 5, estimate the heat effect involved in iron's change from ferromagnetic to paramagnetic.

- How much heat is needed to heat one mole of iron from 1500 K to 2000 K?

12. boiling water altimeter

Demonstrate that one degree per 300 m amounts to a reasonable estimate of the lowering of the boiling point of water resulting from an increase in altitude. First, use Figure 2 for water's heat of vaporization.

§ 005 BINARY AND TERNARY SYSTEMS

The multiplicity of phase diagrams shown by binary systems is reviewed, starting from the isobaric equilibrium between two forms, liquid and vapour, in each of which the component substances are completely miscible. Subsequently, two limiting cases of ternary phase behaviour are derived from the phase diagrams of the binary subsystems.

A and B are completely miscible in α and β

To start with, in the binary system $\{(1 - X) \text{ mol A} + X \text{ mol B}\}$, the case is considered where A and B mix in all proportions in each of the two forms α and β , β being the high-temperature form. For the equilibrium between an α -phase and a β -phase the system formulation is

$$f = M [T, P, X^\alpha, X^\beta] - N [\mu_A^\alpha = \mu_A^\beta; \mu_B^\alpha = \mu_B^\beta] = 4 - 2 = 2. \quad (1)$$

There are two degrees of freedom: the mathematical solution of the combination of equations and variables can be expressed as

$$X^\alpha = X^\alpha(T, P); X^\beta = X^\beta(T, P). \quad (2)$$

and it corresponds to two surfaces in $P-T-X$ space. A surface for the α -phases and another one for the β -phases. For every point on the α surface there is a companion point on the β surface, such that the line connecting the two points is parallel to the X axis.

For the greater part, binary equilibria are studied under either isobaric circumstances (constant pressure) or isothermal circumstances (constant temperature). One could say that the investigator, before starting the experimental work, has 'consumed' one of the two degrees of freedom. As a result, the outcome of the investigation is depicted in either a TX or a PX phase diagram.

As a first example, Figure 1 represents the isobaric equilibrium between $\alpha = \text{liquid}$ and $\beta = \text{vapour}$ in the system A = 1-decanol and B = 1-dodecanol, under the pressure of $P = 20 \text{ Torr}$.

Before going on, it is worthwhile to say a few words about the way in which the interaction between molecules, A and B, is reflected in phase diagrams. The cigar-type of phase diagram, Figure 1, to start with, is typical of systems where the interaction between the two molecular species has a neutral character. 'Neutral' is to say that for the A molecules it makes no difference whether they are surrounded by other A molecules or by B molecules - and vice versa for the B molecules.

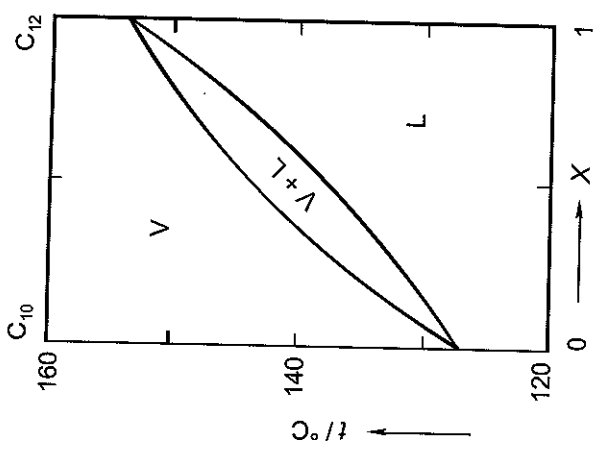


FIG. 1. Isobaric equilibrium between liquid and vapour in the system (1-decanol + 1-dodecano) at $P = 20$ Torr (Rose et al. 1958). Liquidus and vaporus divide the TX plane into three regions: the two single-phase fields L and V, and the two-phase field (V + L)

A non-neutral behaviour is displayed, as an example, by liquid mixtures of chloroform (C) and acetone (A). The isothermal and isobaric (liquid + vapour) phase diagrams for this combination of substances are shown in Figure 2. From the two phase diagrams it follows that the two (C and A) together prefer the liquid state over the gaseous state:

- from the TX diagram: on heating (at increasing temperature) the molecules remain together in the liquid state for a longer time than would be the case for neutral behaviour;
- from the PX diagram: the amount of matter in the gaseous state is lower than it would be for neutral behaviour, as follows from the lower (vapour) pressure.

Therefore, and ignoring the interaction of the molecules in the gaseous state, the two diagrams are evidence of an extra interaction, having an attractive character.

Incidentally, an attractive extra interaction is the exception rather than the rule; at least for liquid mixtures of molecular substances (see the compilation by One 1989). In most of the cases molecular substances give rise to TX (liquid + vapour) diagrams that either have a minimum – evidence of a repulsive extra interaction – or look like Figure 1.

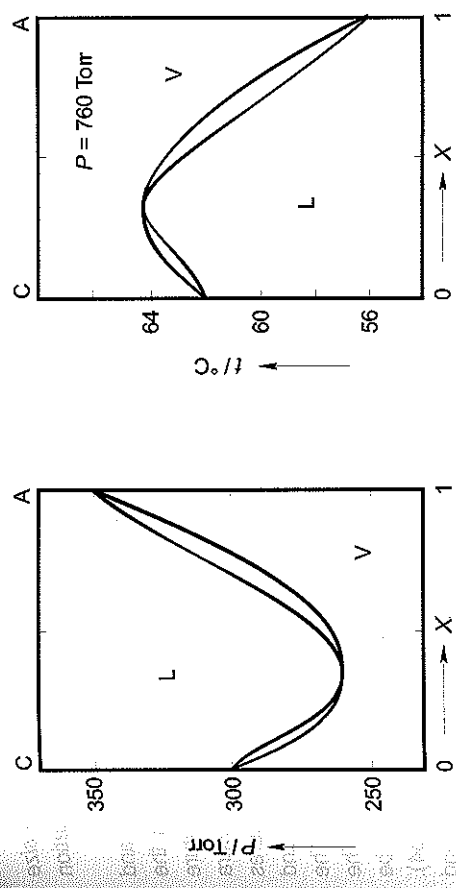


FIG. 2. For the (liquid + vapour) equilibrium in the system {chloroform (C) + acetone (A)}, a minimum in the isothermal diagram ($t = 35.2$ °C, left, Apelblat et al. 1980), goes together with a maximum in the isobaric diagram (right, Reinders and de Minjer 1940)

A repulsive extra interaction is also generally found for solid mixtures, i.e. mixed crystals. A beautiful, speaking example is the combination of sodium chloride (NaCl) and potassium chloride (KCl), whose phase diagram is shown in Figure 3.

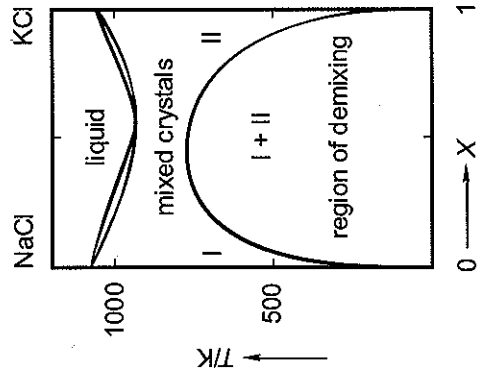


FIG. 3. The TX phase diagram of the NaCl + KCl system, at 1 atm pressure

Crystalline NaCl and KCl both have the so-called NaCl-type of structure. In mixed crystals of the two, the Cl⁻ ions take all the sites for the negative ions, while the Na⁺ and K⁺ ions are randomly distributed over the sites for the positive ions.

The repulsive deviation from neutral behaviour is caused by the mismatch in size between the Na^+ and K^+ ions. The ionic radii of Na^+ and K^+ , for coordination number VI, are 1.02 Å and 1.38 Å, respectively (Shannon 1976).

In the phase diagram the repulsive character is expressed in two ways. First, and assuming a rather neutral interaction in the liquid state, by the minimum in the (solid + liquid) two-phase region: the liquid state is taken up at a lower temperature than would correspond to neutral behaviour. Secondly, the repulsive extra interaction is responsible for a separation of the Na^+ and K^+ ions - at temperatures below 780 K. An equimolar mixed crystal cooled down from 800 K to 650 K, and kept there, will split up into two phases in equilibrium, I and II, see Figure 3. The two phases have the same form, which has the NaCl-type of structure. The compositions of the coexisting phases, and the very fact of separation, can be determined and demonstrated by X-ray diffraction (see Barrett and Wallace 1954). At $T = 650$ K the compositions of the coexisting phases are $X^I = 0.07$, and $X^{II} = 0.80$.

The two-phase field in the lower part of Figure 3 is referred to as region of demixing, or miscibility gap.

limited to negligible miscibility of A and B in α

For the combination of NaCl and RbCl (instead of KCl) the mismatch between Na^+ and Rb^+ (radius 1.52 Å) is so high, that the region of demixing is no longer separated from the (solid + liquid) two-phase region. A like situation is sketched in Figure 4.

The consequence of the overlap is the possibility of a three-phase equilibrium: equilibrium between two solid phases (I and II) and a liquid phase (liq); corresponding to the system formulation

$$f = M [T, X^I, X^{II}, X^{liq}] - N [\mu_A^I = \mu_A^{II} = \mu_A^{liq}; \mu_B^I = \mu_B^{II} = \mu_B^{liq}] = 4 - 4 = 0. \quad (3)$$

From this expression it follows that the equilibrium between the three phases is invariant: it is a unique situation with fixed values for all four quantities of the set M. In the phase diagram the situation is represented by a line, the three-phase equilibrium line, which is parallel to the X-axis and has three points on it, representing the compositions of the coexistent phases, see Figure 4, right-hand side.

For NaCl + RbCl the values of the four variables at the three-phase equilibrium are $T = 788$ K; $X^I = 0.008$; $X^{II} = 0.94$; and $X^{liq} = 0.56$ (Short and Roy 1964).

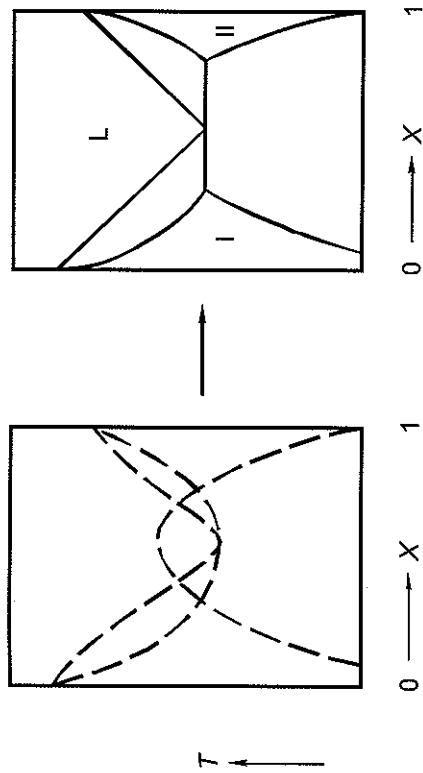


FIG.4. The (solid + liquid) loop and the solid-state region of demixing interfere with one another: the result is a phase diagram with a three-phase equilibrium line, which is the lower boundary of two (solid + liquid) two-phase regions, and the upper boundary of a (solid + solid) two-phase region

For the combination of LiCl and KCl, with Li^+ (0.76 Å) and K^+ (1.38 Å), there is hardly any solid-state miscibility: the TX (solid + liquid) phase diagram is of the simple eutectic type (\rightarrow Exc 3). The term eutectic is from the Greek ευτέκτος, and it means readily melting: a eutectic mixture melts at a temperature lower than the melting points of the pure components. Besides, a three-phase equilibrium, such as in Figure 4 right-hand side, with a liquid phase and two solid phases in the succession solid-liquid-solid, is referred to as a eutectic three-phase equilibrium.

Figure 5c is another example of a simple eutectic phase diagram; it is for the combination of dextrorotatory isopropylsuccinic acid (IPSA) and dextrorotatory methylsuccinic acid (MSA); succinic acid is butanedioic acid ($\text{HOOCCH}_2\text{CH}_2\text{COOH}$).

initial slopes (\rightarrow 208)

The TX phase diagrams Figures 1,2b,3,4 all have ($\alpha + \beta$) two-phase regions, limited by two equilibrium curves - one for the compositions of the α -phases, and the other for the β -phases. An equation for the initial slopes of the two equilibrium curves is the equation named after Jacobus Henricus Van 't Hoff (1852-1911) - an equation similar to the one named after Clapeyron, Equation (004:4). The equation states that for small $\Delta T = T - T_A^0$, where T_A^0 is the temperature at which pure A changes from the form α to the form β , the difference between the initial slopes of the equilibrium curves is given by the expression

$$dX^\beta/dT - dX^\alpha/dT = -(\Delta H_{\alpha \rightarrow \beta} / RT_A^{02}) \quad (4a)$$

In this equation Q is the heat effect of the change, and R the gas constant. Otherwise formulated, with $\Delta X = X^\beta - X^\alpha$, the equation reads

$$\Delta X = -(Q^{\alpha \rightarrow \beta} / RT_A^{\circ 2}) \Delta T. \quad (4b)$$

In terms of the *entropy change*, ΔS (←004), the two equations change into

$$dX^\beta / dT - dX^\alpha / dT = -\Delta S / RT_A^\circ; \quad (4c)$$

$$\Delta X = (-\Delta S / RT_A^\circ) \Delta T. \quad (4d)$$

According to Equation (4b), and all other things being equal, the greater the heat effect is, the greater the difference is between the compositions of the two phases.

NB. If A and B do not mix at all in the low-temperature state α , the addition of A to B, and the addition of B to A, as follows from Equation (4c), inevitably will lower the equilibrium temperature. This is the case for the three systems implied in Figure 5.

The PX counterparts of the Equations (4), i.e. the equations for the initial slopes in PX phase diagrams, are

$$dX^\beta / dP - dX^\alpha / dP = \Delta V / RT; \quad (5a)$$

$$\Delta X = (\Delta V / RT) \Delta P. \quad (5b)$$

For the case that $\beta =$ ideal gas, and $\alpha =$ liquid or solid, and neglecting the molar volume of α with respect to the molar volume of the gas, the Equations (5) change into

$$dX^{vap} / dP - dX^\alpha / dP = 1/P_A^\circ; \quad (6a)$$

$$\Delta X = (1/P_A^\circ) \Delta P. \quad (6b)$$

P_A° represents the equilibrium vapour pressure of pure A.

The last two equations are two of the various expressions of Raoult's Law, the relationship named after François-Marie Raoult (1830-1901).

NB. The Equations (4c,d) and their counterparts Equations (5a,b) are expressions of the close relationship between *entropy* and *volume*. The role played by *entropy changes* in TX equilibria is similar to the role of *volume changes* (be it with opposite sign) in PX equilibria. The two come together for equilibria where P and T are the leading variables - an example is given by Clapeyron's equation, Equation (004:3b).

stationary points

The difference between the initial slopes - of the equilibrium curves in the phase diagrams shown above - is a *pure-substance property*. In the case of Figure 2 right-hand side, the difference between the slopes at the chloroform side is determined by the properties of its change from liquid to vapour - heat of vaporization and boiling point. That difference does not change if the second component, acetone is replaced by another substance, say methanol. Unlike their difference, the *individual* slopes themselves are determined by the combination of the components of the system. The combination chloroform+acetone displays a TX phase diagram with a maximum - at both sides of the system liquidus and vaporus have an upward start. Chloroform+methanol, on the other hand, have a TX phase diagram with a minimum - at both sides downward start of liquidus and vaporus.

Generally, for TX equilibria between liquid and vapour, and starting from neutral interaction, an *attractive* extra interaction has the effect of lifting up the (liquid+vapour) two-phase region. Plausibly, the smaller the difference is between the boiling points of the components, the greater the probability is of producing, for a given extra attraction, a phase diagram with a maximum. In the case of chloroform+methanol there is a *repulsive* extra interaction; the difference in boiling-point temperatures is just 3 K; the phase diagram has a minimum.

Maxima and minima are *stationary points*: liquid mixtures having the composition of the stationary point change - when boiled - completely into vapour at constant temperature, the temperature of the maximum/minimum (←006). At the extremum, liquid and vapour have the same composition. The other way round, if, for a given temperature, liquid-and-vapour-in-equilibrium have the same composition, the equilibrium state necessarily is an extremum in the phase diagram.

In the context of this passage, reference should be made to the Konowalow Rules (Konowalow 1881). For TX liquid+vapour equilibria the rules are

(I) The boiling point as a function of composition shows a stationary point only if liquid and vapour have the same composition;

(II) The boiling point is raised by the addition of that component whose mole fraction in the vapour phase is lower than the mole fraction in the coexisting liquid phase;

(III) The compositions of the coexisting vapour and liquid phases change in the same sense with temperature.

compound formation

Figure 5b is the phase diagram shown by the combination of laevorotatory and dextrorotatory isopropylsuccinic acid (IPSA). The diagram is typical of a *pair of optical antipodes*, of which the two different *chiral molecules* (←004) cocrystallize in a (1:1) centrosymmetrical structure. The crystalline (1:1) combination is referred

The noun 'compound', in racemic compound, is generally used for an intermediate solid phase having a fixed, or a more or less fixed composition. A *stoichiometric compound* has a fixed composition, whereas the composition of a *non-stoichiometric compound* can vary between certain limits.

An example of a non-stoichiometric compound is wustite ($\approx \text{FeO}$) in the system $\text{Fe} + \text{O}$. In the $(\text{Fe} + \text{O})$ TX phase diagram, wustite's single-phase field has the shape of a capital V; at the bottom ($t = 560^\circ\text{C}$) the composition can be written as $\text{FeO}_{1.06}$; at the top ($t = 1360^\circ\text{C}$) $\text{FeO}_{1.03}$, and ($t = 1424^\circ\text{C}$) $\text{FeO}_{1.20}$ (Vasyutinski 1984).

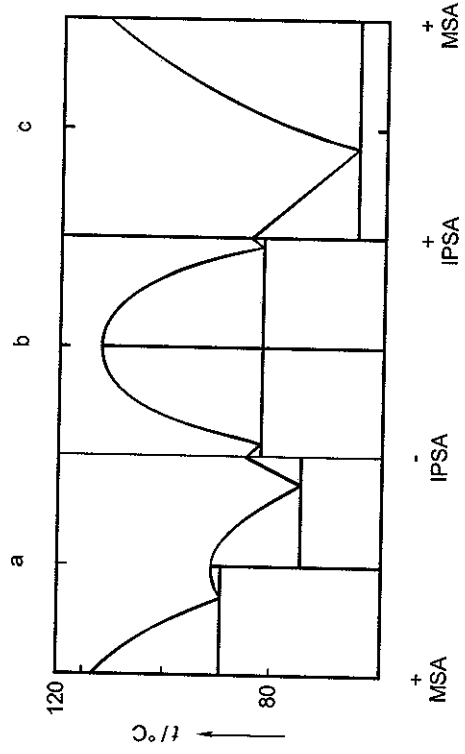


FIG. 5. The determination of (solid + liquid) phase diagrams is a means to establish the configurative relationships between optically active substances. The compound formed by (-) and (+) IPSA is a racemate. A quasicrystal is formed between (-) IPSA and (+) MSA (Fredga and Miettinen 1947)

isodimorphism, isopolymorphism

Mutual *solid-state miscibility* of two substances A and B in the first place is related to the degree of similarity between the A and B molecules ('molecules' in the sense of building units of the crystal lattice). That similarity regards chemical nature, size and shape. Solid-state miscibility is the exception rather than the rule (Kitaigorodskii 1984).

NaCl and KCl are soluble in one another; in all proportions, however, only above 780 K (see above); they show what is called complete *subsolidus miscibility*. Complete *subsolidus miscibility* is also found for combinations like gold and palladium (Okamoto and Massalsky 1985) and 1,4-bromochlorobenzene and 1,4-dibromobenzene (Calvet et al. 1991). Naphthalene and 2-fluoronaphthalene

would also show complete *subsolidus miscibility*, if it were not that they do not crystallize in the same form (van Duijneveldt et al. 1989).

To illustrate these things, we take two solid forms α and β and examine three different situations for their equilibrium with liquid, see Figure 6. In the case of Figure 6a the two substances A and B are isomorphous in such a manner that there is, for each of the solid forms, a single-phase field extending over the full composition range (there is complete *subsolidus miscibility*, and so in the form β). The dashed curves in Figure 6a represent the boundaries of the metastable ($\alpha + \text{liquid}$) two-phase region. Generally, the position of the metastable two-phase region can be calculated from the positions of the stable regions and the heats of transition of the α to β and β to liquid changes. Exceptionally, a full-range *metastable melting loop* is observed in experimental reality - a beautiful example is shown by 1,1,1-trichloroethane (Cl_3CCH_3) + carbon tetrachloride ($\text{Cl}_4\text{CCl} = \text{CCl}_4$) (Pardo et al. 1999). For the situations depicted by Figures 6b and c, substance A's β -form invariably is metastable, and the same goes for B's α -form. The important thing to note is, that there necessarily are three-phase equilibria (eutectic, Figure 6b, and peritectic, Figure 6c) and that, inevitably, there is incomplete solid miscibility (one speaks of *crossed isodimorphism*: two solid-liquid loops cross one another).

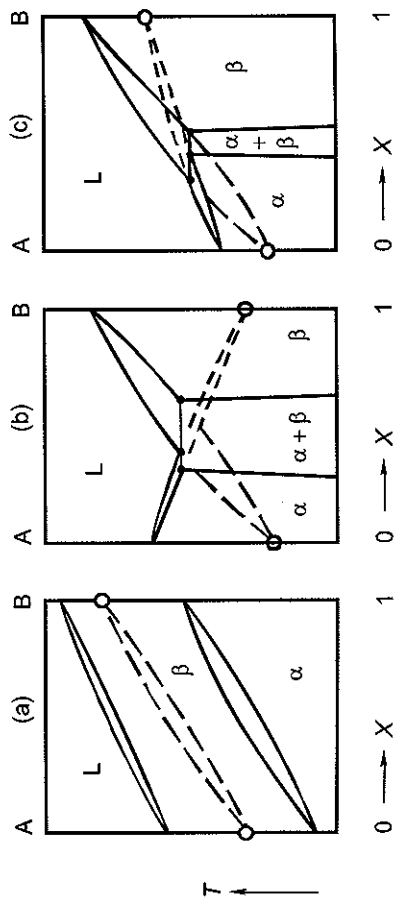


FIG. 6. Isodimorphism (a) and crossed isodimorphism (b and c). α and β are two crystalline forms in which A's molecules and B's molecules can replace one another. Open circles represent metastable melting points

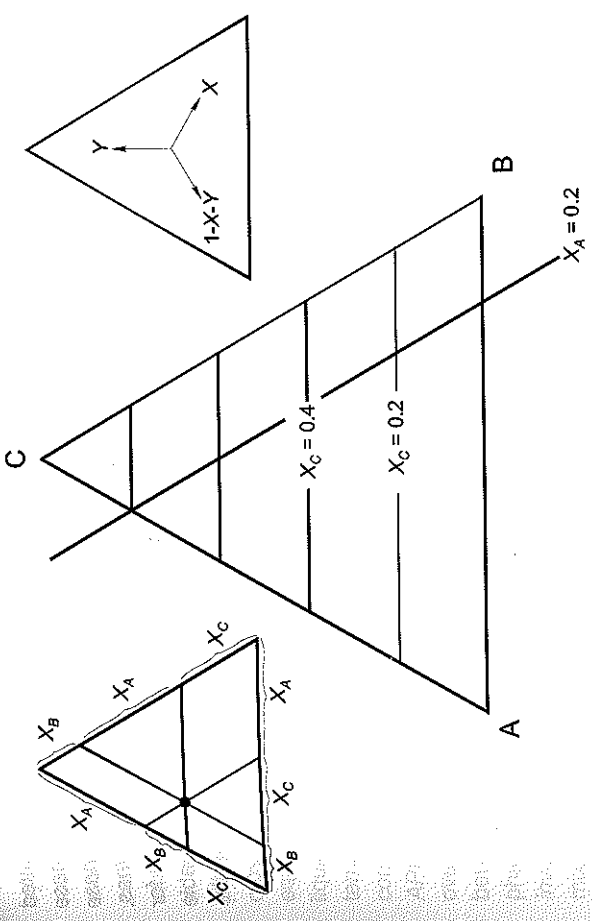


FIG. 8. Gibbs' composition triangle

$$f = M \left[T, X^{\alpha}, Y^{\alpha}, X^{\beta}, Y^{\beta} \right] - N \left[\mu_A^{\alpha} = \mu_A^{\beta}; \mu_B^{\alpha} = \mu_B^{\beta}; \mu_C^{\alpha} = \mu_C^{\beta} \right] = 2. \quad (8)$$

There are two degrees of freedom: the values of, e.g., Y^{α} , X^{β} , and Y^{β} are fixed after the choice of T and X^{α} . The solution of the set of equations corresponds to two surfaces in TXY space.

For the isobaric equilibrium between three phases, α , β , and γ , the formulation is

$$f = M \left[T, X^{\alpha}, Y^{\alpha}, X^{\beta}, Y^{\beta}, X^{\gamma}, Y^{\gamma} \right] - N \left[\mu_A^{\alpha} = \mu_A^{\beta} = \mu_A^{\gamma}; \mu_B^{\alpha} = \mu_B^{\beta} = \mu_B^{\gamma}; \mu_C^{\alpha} = \mu_C^{\beta} = \mu_C^{\gamma} \right] = 1. \quad (9)$$

After the choice of T , the compositions of all three phases are fixed. In the composition triangle, the three-phase equilibrium for given T corresponds to a triangle whose vertexes represent the compositions of the coexistent phases. The area inside the *invariant triangle* is empty: an overall composition given by a point inside the triangle will split up into the three phases. The fact that the three-phase equilibrium is monovariant implies that for each of the three coexistent phases there is a trajectory in TXY space.

nomenclature

The two basic types of three-phase equilibria in isobaric binary systems are the *eutectic* - and *peritectic* type, Figure 7.

More specifically, a eutectic type is named

- eutectic, for $\alpha = \text{solid I}$ $\gamma = \text{liquid}$ $\beta = \text{solid II}$;
- eutectoid, for $\alpha = \text{solid I}$ $\gamma = \text{solid III}$ $\beta = \text{solid II}$;
- monotectic, for $\alpha = \text{solid I}$ $\gamma = \text{liquid I}$ $\beta = \text{liquid II}$; and
- metatectic, for $\alpha = \text{solid I}$ $\gamma = \text{solid II}$ $\beta = \text{liquid}$.

A peritectic type is named

- peritectic, for $\gamma = \text{liquid}$ $\alpha = \text{solid I}$ $\beta = \text{solid II}$
- peritectoid, for $\gamma = \text{solid III}$ $\alpha = \text{solid I}$ $\beta = \text{solid II}$

NB! It is imperative that the so-called *metastable extensions*, in Figure 7 indicated by dashes, run inside two-phase fields.

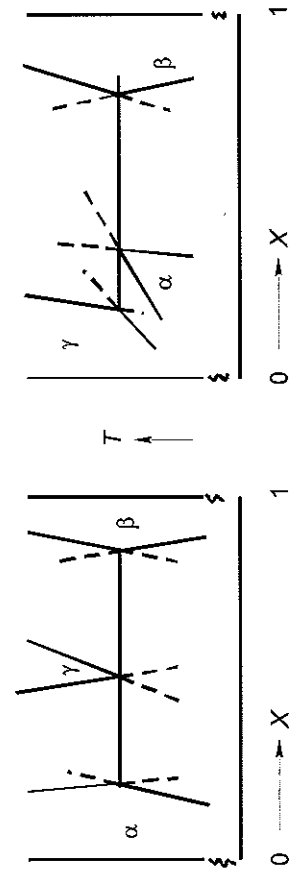


FIG. 7. Parts of TX phase diagrams around three-phase equilibrium lines: a) eutectic type and b) peritectic type of three-phase equilibrium

ternary systems

In ternary systems, defined by

$$\{X_A \text{ mol A} + X_B \text{ mol B} + X_C \text{ mol C}\} \text{ or } \{(1 - X - Y)A + XB + YC\}, \quad (7)$$

compositions are conveniently represented in an equilateral triangle - the *Gibbs triangle*, see Figure 8.

For the isobaric equilibrium between two mixed phases α and β - taken as an example - the system formulation is

An isothermal section of the isobaric equilibrium states, as a result, is represented by a Gibbs triangle that may show one or more *single-phase fields*, *two-phase fields*, *three-phase triangles*, and (only for the temperature of a *four-phase equilibrium*) one *quadrangle*. In isobarothermal representations the use of *tie lines* connecting the positions of two coexistent phases, is much more common than for binary TX or PX representations. More than that, for ternary phases of variable composition, the tie lines are an essential part of the representation of the equilibrium states, see Figure 9.

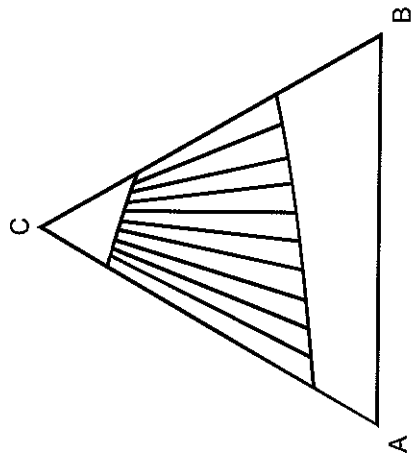


FIG. 9. The system methylcyclohexane (A) + n-hexane (B) + methanol (C) at 1 atm, 30 °C. Phase diagram showing the boundaries of the region of demixing and tie lines connecting the positions of the two coexisting liquid phases (Schuberth 1986)

Like liquidus and vaporus curves in TX and PX diagrams, liquidus and vaporus surfaces in TXY or PXY space can have a maximum or a minimum – at which the coexistent phases have the same composition. In addition to the maximum and the minimum, ternary surfaces have the possibility of a third type of stationary point: the *saddle point*, where a minimum in one direction is a maximum in the other. Saddle points are favoured by the combination of two binary subsystems having a minimum (or maximum) with a third subsystem having a maximum (or minimum). A TXY example is found in the combination of chloroform, acetone, and methanol (Haase 1950). Two of the subsystems were mentioned above; the third, acetone+methanol, has a minimum.

from binary to ternary

The three *binary subsystems*, (A + B), (A + C), and (B + C), are part of the ternary system (A + B + C), or, in other words, the equilibrium states in the binary

systems are part of the equilibrium states in the ternary systems. The other way round, a substantial part of the equilibrium states in a ternary system are already available in the binary subsystems. Or, somewhat exaggerated, ternary equilibrium can be predicted from the information offered by the binary subsystems. Two examples, Figures 10 and 11, are now discussed, to make these things clear. In the case of Figure 10, the equilibrium considered is between solid and liquid phases, and the binary subsystems are of the simple eutectic type. For the ternary cross-section the temperature is selected such that it is above the surface for the equilibrium between liquid and solid C. The isothermal section of the other two liquidus surfaces is represented by the curves PR and RQ inside the triangle. The ternary phase diagram now consists of four fields: i) the *single-phase field* PRQC; it corresponds to conditions where all of the material is liquid; ii) the *two-phase field* APR; iii) the *two-phase field* BQR; iv) the *three-phase triangle* ABR. A mixture of overall composition represented by a in the field APR will give rise to equilibrium between pure solid A and liquid mixture represented by point b on PR; the two phases are connected by the *tie line* through a. Overall compositions inside the *invariant triangle* ABR give rise to equilibrium between solid A, solid B, and liquid mixture represented by R.

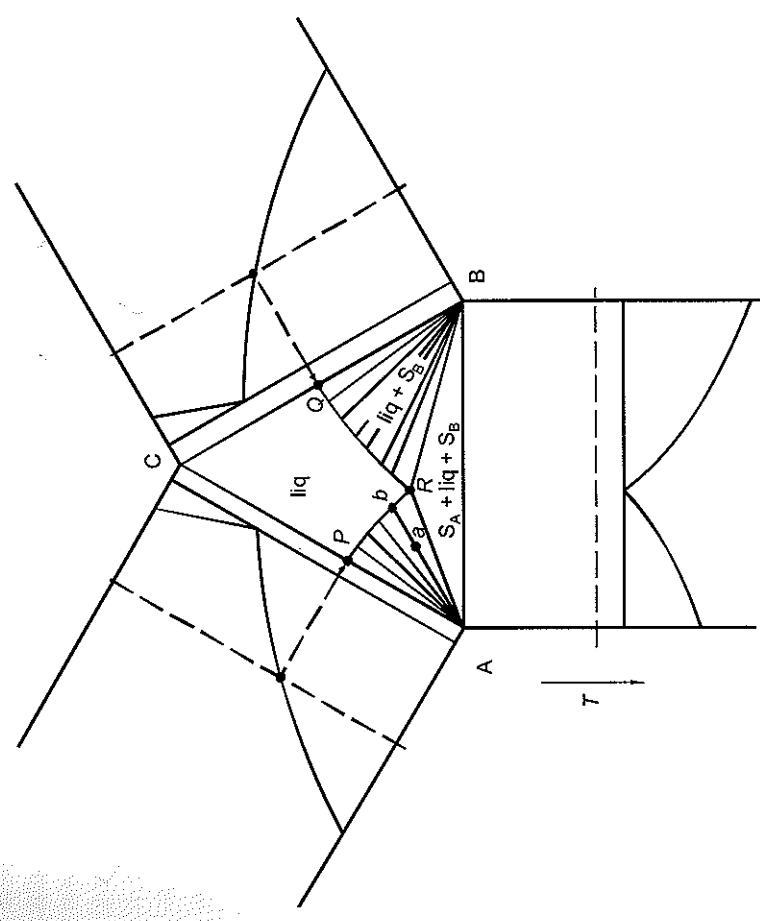


FIG. 10. Isothermal section showing the phase equilibrium relationships of a ternary system composed of three eutectic binary subsystems under isobaric circumstances

Figure 11 pertains to the equilibrium between (mixed-crystalline) solid and liquid in the system 1,4-dichlorobenzene + 1,4-bromochlorobenzene + 1,4-dibromobenzene. This time the coexisting solid and liquid ternary phases have been calculated, using the information provided by the three binary phase diagrams and the thermochemical properties of the pure components (Moerkens et al. 1983). The result of the calculation, including tie lines, is shown for the isothermal section at 70°C. Note that the difference between the tie lines in Figure 10 and the ones in figure 11 is that, unlike the latter, the former - which emanate from one point - can be drawn without doing any special calculations (one has to be sure, of course, that the solid phase is made of pure B!).

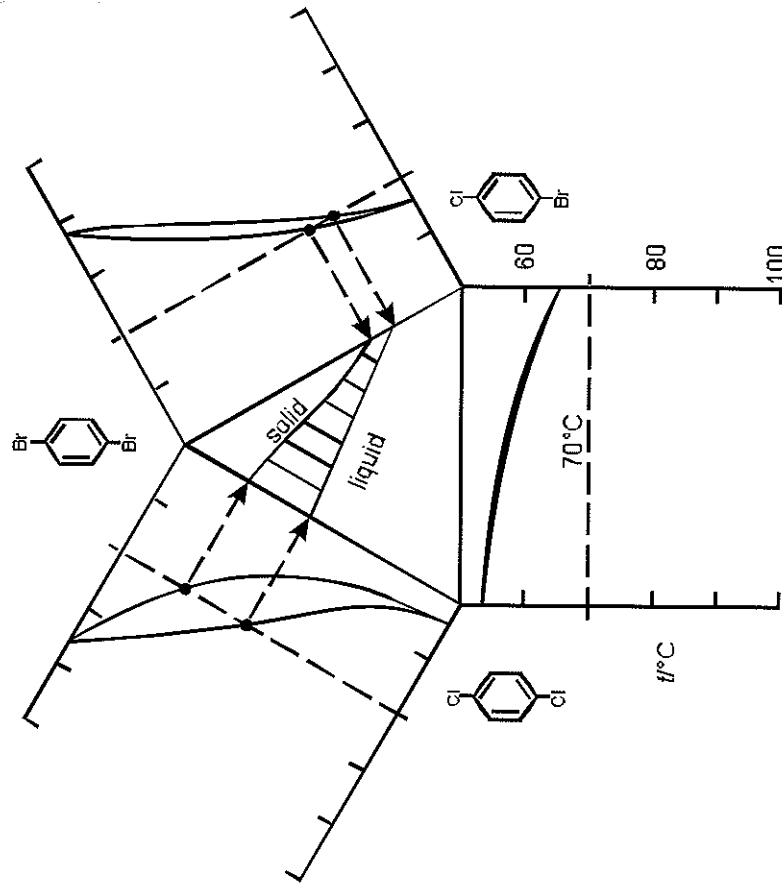


FIG. 11. Ternary system composed of three 1,4-dihalobenzenes forming mixed crystals. Isothermal section ($t = 70^\circ\text{C}$) of ternary (solid-liquid) equilibrium, calculated from the information available for the binary subsystems Moerkens et al. 1983)

imperfections in phase diagrams

The phase diagrams that are shown in textbooks and scientific publications not all, and not at all, have the same history. A phase diagram shown in a text can range from the outcome of a thermodynamic calculation, via a (subjective) interpretation of experimental observations, to a diagram drawn in a freehand manner.

Calculated phase diagrams that satisfy the laws of thermodynamics always combine correctness with beauty. Diagrams in the other categories occasionally show imperfections that could have been avoided.

Two examples of incorrect phase diagrams are the ones already shown in Exc 003:2. The diagram labelled a) is supposed to represent a vaporus and its companion liquidus. The diagram does not respect the obvious rule that for every point on the vaporus there should be a corresponding point on the liquidus. In the case of the diagram labelled b) the 'obvious rule' is satisfied; however, and for thermodynamic reasons (\rightarrow Exc 211:10), two phases in equilibrium can have the same composition, but only for a stationary point (first of the Konowalov Rules, see above).

Unintentionally, a phase diagram drawn in a freehand manner may show a (thermodynamic) inconsistency (Nývlt 1977). A PT phase diagram for a pure substance may have a region that looks like Figure 12, but not for the case that $\beta = \text{liquid}$, and $\gamma = \text{vapour}$. According to the Clapeyron equation, Equation (004:3), a minimum in the boiling curve would imply that, along the boiling curve, and starting from the triple point, the heat of vaporization would change from a negative property to a positive one!

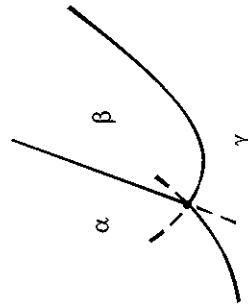


FIG. 12. Region of a PT phase diagram for a pure substance, showing a two-phase equilibrium curve with a minimum

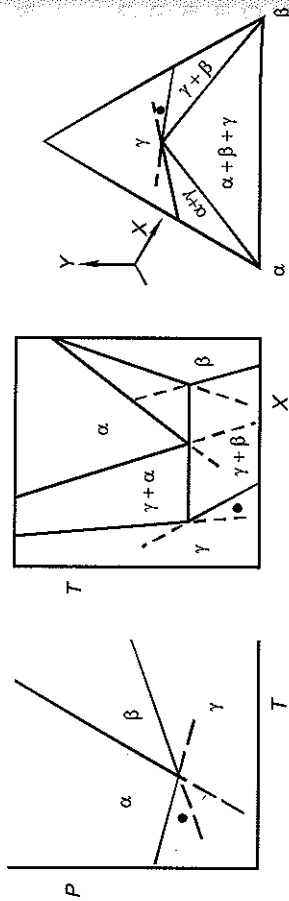


FIG. 13. Three diagrams incompatible with the principles of stability

The three diagrams shown in Figure 13 all have the same kind of imperfection - expressed by the edges of the γ single-phase fields, with their angle of more than 180° . The bullet, in each of the diagrams is positioned in the γ field, which would mean that γ is stable and should not undergo a spontaneous change. However:

- i) in the PT diagram the bullet is at the β side of the $(\beta + \gamma)$ two-phase equilibrium curve, and it means that γ might spontaneously change into β ;
- ii) in the TX diagram the bullet is in (the metastable extension of) the $(\alpha + \gamma)$ two-phase region: the material might split up in a γ part (of another composition) and an α part;
- iii) in the XY diagram the position of the bullet is such that the material, likewise, might split up in a γ part and an α part.

In other words, all of the three diagrams are evidence of a misapplication of the stability principles.

The three diagrams in Figure 13 - to put it in other terms - do not comply with the rules for metastable extensions. To start with the PT diagram for a pure substance, these rules can be detailed as follows.

In a correct PT phase diagram, around the triple point, the metastable extensions alternate with the stable parts of the two-phase equilibrium curves (as shown by Figure 12; ←Exc 004:6). In a TX or PX phase diagram for a binary system, at the three-phase equilibrium, the metastable extensions must fall inside two-phase fields (as shown by Figure 7; →Exc 301:3). In an isobarothermal section for a ternary system, and for the case implied in the XY diagram in Figure 13, the two metastable extensions must fall either both in the $(\alpha + \beta + \gamma)$ invariant triangle or one in the $(\alpha + \gamma)$ field and the other in the $(\beta + \gamma)$ field (rule named after Francisus Antonius Hubertus Schreinmakers (1864-1945); (Schreinmakers 1911, see also Hillert 1998).

Valuable guiding principles in understanding phase behaviour are: the notion of interaction between different molecules, the nature of which is ranging from repulsive via neutral to attractive; the knowledge that much of the properties of ternary systems is already present in the binary subsystems; and the necessity to consequently apply the principles of stability.

EXERCISES

1. a unary diagram made to look like a binary one

The two-phase equilibrium curves of a pure substance's PT phase diagram can be 'opened up' to show two-phase regions - by replacing P by a property which is not necessarily equal for the two phases in equilibrium.

- Draw a $(S + L + V)$ PT phase diagram - melting curve with positive slope; boiling curve up to critical point - and translate it into a diagram in which molar volume is plotted against temperature.

2. the amounts of the phases during an experiment

For the phase behaviour depicted in Figure 6c: a homogeneous sample - whose composition is between the compositions L and α at the three-phase equilibrium - is heated under constant pressure "from a position in the α field to a position in the L field".

- Make a scheme, in which for each part of the route, it is indicated - for each of the possible phases - whether the amount of substance of substance of the phase remains unchanged (=), increases (>), decreases (<), or is equal to zero.

The parts of the route are i) through the α field; ii) through the $(L + \alpha)$ field; iii) at the three-phase equilibrium; iv) through the $(L + \beta)$ field; and v) through the L field.

3. phase diagram and cooling curve

Lithium chloride (LiCl ; melting point 606°C) and potassium chloride (KCl ; m.p. 770°C) are miscible in all proportions when liquid. Their solid state miscibility is negligible. A liquid mixture, having KCl mole fraction $X = 0.1$, will start to crystallize, when cooled, at $t = 566^\circ\text{C}$. The onset temperatures of crystallization for a number of other composition are ($X = 0.2$; $t = 515^\circ\text{C}$); (0.3 ; 452); (0.4 ; 370); (0.5 ; 443); (0.6 ; 541); (0.7 ; 618); (0.8 ; 685); and (0.9 ; 733).

- Construct the (solid + liquid) TX phase diagram.

In an experiment, heat is withdrawn at a constant rate from a sample having $X = 0.2$.

The initial and final temperatures are 600°C and 200°C , respectively.

- Make a graphical representation of the sample's temperature as a function of time (cooling curve: →006)

4. a reciprocal system

The four substances NaCl, KCl, NaBr, and KBr share four structural units which are the two anions and the two cations. A system composed of such four substances is referred to as a reciprocal (salt) system.

- What is the number of independent variables necessary to define the composition of a like system?
- What geometrical figure would you use to represent the compositions of a reciprocal system?

5. increasing repulsive interaction and the phase diagram

In the system $\{(1 - X)A + XB\}$ the interaction in the liquid state between A and B is neutral, the (solid + liquid) TX phase diagram is eutectic. The melting points of A and B are 900 K and 450 K, respectively; the eutectic point has $T = 400$ K and $X = 0.90$.

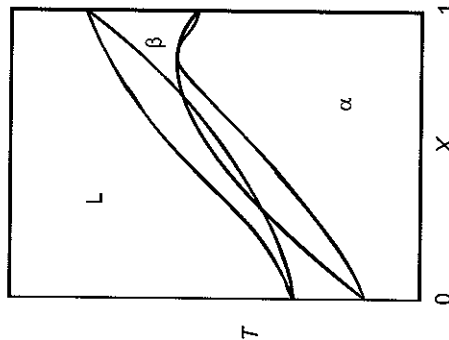
- Make a series of sketch drawings of phase diagrams to demonstrate what happens when the interaction between A and B in the liquid state is going to show an increasing, repulsive deviation from neutral mixing behaviour.

NB. The properties of the pure components remain the same and so do the initial slopes (at $X = 0$, and $X = 1$) of the two liquidus curves (say over the first 10% of the X axis).

6. overlapping two-phase regions

The two (on their own correct) two-phase regions, $(\alpha + \beta)$ and $(\beta + L)$, are partly overlapping. As a consequence, the true phase diagram must have an $(\alpha + L)$ two-phase region.

- Guided by the rule for metastable extensions, make a sketch of the true phase diagram (first locate the two $(L + \beta + \alpha)$ three-phase equilibrium situations).



7. the construction of ternary phase diagrams

The three optically active substances (-) IPSA (A), (+) IPSA (B), and (+) MSA (C), acting in Figure 5, are rather alike, and for that reason it can be assumed that the interaction between their molecules in the liquid state has a nearly neutral character.

As a result, their ternary phase behaviour can be predicted from the binary data with fair accuracy. The fact is that for neutral mixing behaviour, and for given, constant T , the equilibrium

solid C plus (liquid mixture containing C)

simply satisfies the relationship $X_C = \text{constant} = K_C$ (likewise for A and B); and the equilibrium

compound AB plus (liquid mixture containing A and B)

satisfies the relationship $X_A \cdot X_B = \text{constant} = K_{AB}$.

- Use the binary phase diagrams, Figure 5, to construct isothermal sections of the ternary system; for i) $t = 100$ °C; ii) the temperature of the upper eutectic in the system (+) MSA + (-) IPSA; and iii) $t = 80$ °C.

Clue. For each of the solids, stable at the temperature considered, determine the value of the equilibrium constant - like the above K_C or K_{AB} - and use it to construct the complete ternary liquidus. Use the ensemble of liquidus lines to allocate the single- and two-phase fields, and the invariant triangles.

NB. If an invariant triangle involves a liquid phase, then its "liquid vertex" is the intersection of two (of the constructed) liquidus lines.

8. the appearance of an incongruently melting compound

In Figure 5a the left-hand liquidus (the A liquidus) intersects the liquidus pertaining to the 1:1 compound (the AB liquidus) at the left of the equimolar composition - the point of intersection being a eutectic point. When, in such a case, component A is given a higher melting point - all other things remaining the same - the situation may arise that the intersection is a peritectic point, at the right of the equimolar composition. When that is the case, AB's melting point becomes metastable: on heating, AB will, at the peritectic temperature, split up in solid A and liquid having the peritectic composition. The congruently-melting compound, Figure 5a, has changed into an incongruently-melting compound.

- Construct the TX solid-liquid phase diagram for a system involving an incongruently melting compound AB.

9. ternary compositions having a constant ratio of the mole fractions of two components

In the ternary composition triangle ABC, the locus of the compositions that have the same ratio of the mole fractions of A and B is a straight line ending in vertex C.

- Prove the validity of this statement - making use of the properties of similar triangles.

Clue. On AB take a point P; on PC take a point Q; similar triangles ABC and RSQ, R and S being points on AB.

§ 006 DISTRIBUTION AND SEPARATION

An elementary characteristic of equilibrium between phases in systems of two or more components is the fact that the phases as a rule have different compositions. This property holds the possibility that substances can be separated from one another by means of phase changes.

saturation

When a drop of water is brought in an empty space, say a 200 m³ tank kept at 25°C, it will evaporate rapidly and completely. And free water molecules will be present in every cubic micrometer of the space. Similarly a few sugar crystals will dissolve rapidly and completely in a cup of water. Water is a good solvent for sugar (molecules), and an empty space, or vacuum if you like, is a good 'solvent' for water (molecules).

The amount of foreign molecules - solute molecules - a solvent can accommodate, however, is limited: at a certain 'moment' the solvent is saturated - and this moment differs from case to case. The moment of saturation, for water in a space, is reached when the chemical potential of gaseous water ($\mu_{H_2O}^{vap}$) has become equal to the chemical potential of liquid water ($\mu_{H_2O}^{liq}$). Water added after saturation has been reached will not evaporate anymore: there is equilibrium between a liquid and a gaseous phase, governed by the condition

$$\mu_{H_2O}^{liq} = \mu_{H_2O}^{vap} \quad (1)$$

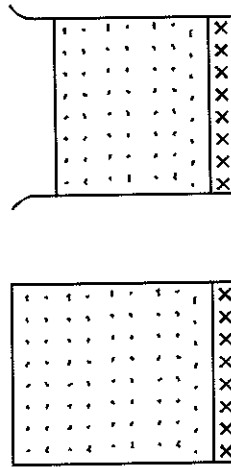


FIG. 1. Two analogous cases: left, the saturation of an empty space by a volatile substance; right, the saturation of a liquid medium by a soluble substance

And this condition is such that the amount of water in the gaseous phase will correspond to a vapour pressure of 23.756 Torr, for $t = 25^\circ\text{C}$.

10. cyclohexane with aniline - mixing and demixing

{(1-X) mole of cyclohexane + X mole of aniline}, in spite of the fact that aniline (aminobenzene) is a nasty substance, is a superior system to demonstrate phenomena of mixing and demixing. The following description of actions and observations - representative of a classroom experiment - may make this clear.

Eight test tubes provided with screw caps are filled - using a 10 ml measuring cylinder - with varying amounts of cyclohexane and aniline; see table. After filling, the tubes 0, 6, and 7 show a single liquid; the tubes 2, 3, 4, and 5 show two, clearly separated liquids; and the content of the remaining tube, tube 1, looks milky.

In a next step the tubes 2, 3, 4, and 5 are immersed in water with a temperature of 40 °C, contained in a plastic beaker. As a result of this action the two liquids, in all of the four tubes, change into a clear single liquid. Thereupon, the water and the tubes are allowed to cool to room temperature. Meanwhile the tubes are shaken every now and then; and for each sample the onset temperature of turbidity is registered, see table.

A similar procedure is followed for the tubes 0, 1, 6, and 7. The tubes are immersed in water having a temperature of 25 °C; and the whole is subsequently cooled by means of ice cubes. The samples undergo a change to a two-liquid situation; with the exception of tube 7, whose content is still homogeneous at 1 °C.

Tube	cyclohexane (ml)	aniline (ml)	X	at room temperature	onset of turbidity
0	7.4	0.4	0.06	one liquid	6.0
1	7.9	0.9	0.12	milky	19.5
2	6.9	1.4	0.19	two liquids	26.0
3	5.8	2.8	0.36	two liquids	30.7
4	4.3	3.5	0.49	two liquids	30.5
5	3.0	5.0	0.66	two liquids	27.7
6	1.9	6.3	0.80	one liquid	14.4
7	1.0	7.1	0.89	one liquid	<1.0

- What is the temperature of the room where the experiments are carried out?
- For $t > 0^\circ\text{C}$, make a graphical representation - temperature versus mole fraction - of the binodal curve (the boundary of the region of demixing), and from the curve derive the coordinates of the critical point.
- Sketch a plausible TX phase diagram for the system over the range from -50°C to 200°C . In more detail: use the region-of-demixing data; calculate the initial slopes of the two liquids emanating from the melting points (mp) of the pure components; and consult Exc 212:12 for a rule of thumb, concerning the change from liquid to vapour.

Cyclohexane: 84 g mol⁻¹; 108 cm³ mol⁻¹ (25 °C); mp 6.6 °C; bp 81 °C; heat of melting 2.66 kJ mol⁻¹.

Aniline: 93 g mol⁻¹; 91 cm³ mol⁻¹ (25 °C); mp -6.3 °C; bp 185 °C; heat of melting 10.54 kJ mol⁻¹.