

Consider a liquid of composition a , largely composed of the component B, but contaminated by some A. When the liquid is cooled to a_1 , a solid of composition b_1 appears, and according to the diagram the solid is a solution of A in B, but it is richer in B than the liquid. Removing the solid gives a slightly purified material, but not much of it (lever rule). Further conventional cooling of the original system delivers more B-rich solid (b_2), and leaves B-depleted liquid (a_2). Finally the whole sample freezes just beneath a_3 to give a sample of the same composition (a) as the original, dirty liquid. Conventional freezing has left us with a material no purer than the initial sample.

We could strain off the early crystals, and then repeat the procedure on them. This *fractional crystallization* would, in each cycle, step the system towards pure B, in the manner of fractional distillation. But the procedure is very slow and wasteful.

The modern procedure is based on the recognition that our interpretation of Fig. 10.13 is idealistic. It assumes that the freezing is so slow that the composition of the solid phase is uniform, and has throughout the equilibrium composition demanded by the phase diagram. For example, it assumes that the composition of the solid shifts uniformly from b_2 to b_3 when the system is cooled from a_2 to a_3 . In any real process this will not be the case because the solute A does not have the time to disperse in and out of the solid at the demand of the slope of the chemical potential. We must think about what happens in a real, non-equilibrium situation.

Consider a dirty liquid of composition a , and let it be cooled to a_1 . Solid of composition b_1 is deposited and dirtier liquid of composition a_1 remains. Now let this liquid be cooled without permitting the system to come to overall equilibrium. The first solid deposited remains at its composition b_1 and the new deposit, if the temperature is dropped to a_2 , is of composition b_2 leaving an even dirtier liquid of composition a_2 . Cooling along the isopleth a_2' without equilibrating with the solids b_1 , b_2 deposits solid b_3 , and leaves dirtier a_3' . The process continues until the last liquid to solidify is heavily contaminated with A.

There is some everyday evidence that the freezing of impure liquids proceeds as we have described. An ice cube is clear near the surface, but misty in the core. This is because the water used to make ice normally contains dissolved air. Freezing normally proceeds from the outside, and the air is accumulated in the retreating liquid phase. It cannot escape from the interior of the cube, and so when that finally freezes it occludes the air in a mist of tiny bubbles.

In the technique of zone refining the sample is normally in the form of a narrow cylinder. This is heated in a narrow, disc-like zone which is swept from one end of the sample to the other. The advancing liquid zone accumulates the contaminants as it passes, for they are preferentially partitioned into the liquid phase. One pass may have the effect of reducing the impurity content only slightly, because a really dirty liquid phase cannot accumulate much more dirt. For this reason it is normal in zone refining to devise a multiple passage system, and a train of hot and cold zones are swept repeatedly from one end of the sample to the other. The zone right at the end of the sample is the impurity dump: when the

heater has passed its position, cooling occurs, and the dirty liquid simply cools to dirty solid, which can be discarded.

A modification of the technique, *zone levelling*, is used to introduce controlled amounts of impurity (for example, indium into germanium). A rich sample of the desired impurity is put at the head of the sample, and made molten. This zone is then dragged through the length of the sample. If the solute is very insoluble in the major component, the liquid zone deposits a uniform distribution of impurity into the pure material, and the final sample is the uniformly doped material.

Zone refining has found application in fields other than the semiconductor industry. Ultrapure materials often have markedly different properties from conventionally pure samples. For instance, bismuth is normally regarded as a hard, brittle metal, yet when it has been zone refined it forms rods which can be bent without fracture. We have already seen how a few per cent of carbon produces brittle cast iron: when all traces of impurity are removed from iron it retains its ductility down almost to absolute zero. Organic chemicals may be refined, and substances thought to have a foul odour have been rendered odourless by purification.

10.4 Three-component systems

Three-component systems have a variance that may reach 4. Even imposing constant temperature and pressure constraints still leaves three variables, and the representation of phase equilibria is on the verge of being absurdly complicated. We shall examine only the very simplest type of three-component systems in order to acquire some familiarity with their representation in terms of triangular diagrams.

Sorting out triangular coordinates. If the system is composed of the components A, B, and C, their mole fractions must sum to unity: $x_A + x_B + x_C = 1$. We need a diagram that automatically ensures that this condition is fulfilled. The equilateral triangle has the required property. It follows from elementary geometry that the sum of the vertical heights of a point from the three edges is equal to the height of the triangle. Fig. 10.14 illustrates the three edges is equal to the height l . If the mole fractions x_A , x_B , and x_C are represented by the three vertical distances, then a mixture of any composition can be represented by a point on the interior of the triangle.

Fig. 10.14 shows how this works in practice. Imagine the triangle marked off by lines parallel to each side, and let the height above the base represent the mole fraction of one component (the component at the opposite apex). In the figure the point P indicates a mole fraction $x_A = 0.50$. A similar grid can be imagined for the B mole fraction, with zero lying along the AC line, and unity at the B apex. Point P corresponds to $x_B = 0.10$. The concentration of C, $x_C = 0.4$, is ensured by the geometry of the triangle.

The edge AB corresponds to $x_C = 0$, and likewise for the other two edges. Therefore the three edges refer to the three binary systems (A, B), (B, C), and (C, A).

An important property of a triangular diagram is the significance of a straight line joining an apex to a point on the opposite edge, Fig. 10.14.

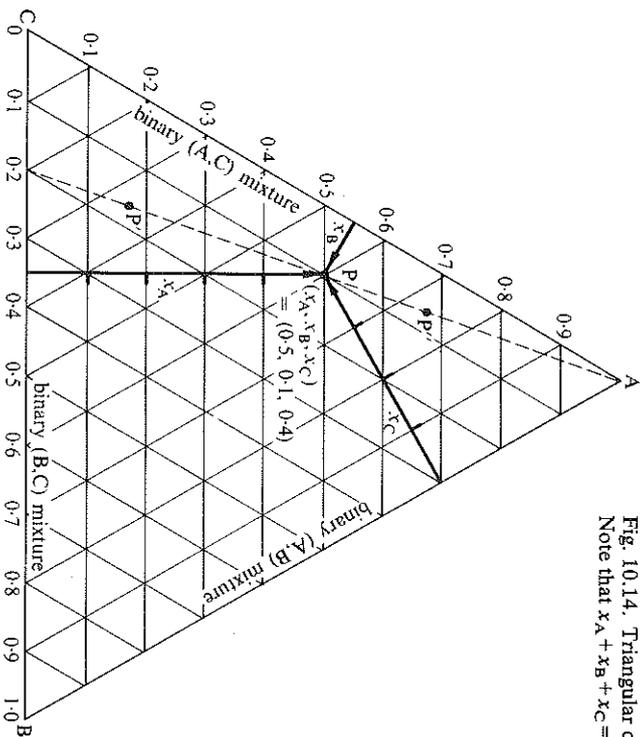


Fig. 10.14. Triangular coordinates. Note that $x_A + x_B + x_C = 1$.

Any point along the indicated line represents a composition that is progressively richer in A as it passes from P' through P to P'' , but the significant point is that B and C remain present in the same initial proportion. The validity of this observation depends on the properties of similar triangles, and on showing that $x_B/x_C = x_B''/x_C''$. Therefore, if we wish to represent the changing composition of a system as A is added, all that is necessary to do is to draw the line from the apex A to the point on BC representing the initial binary system. Any ternary system formed by adding A lies at some point on this line.

Example (Objective 11). Mark the following points on a triangular coordinate system:

- $x_A = 0.20$, $x_B = 0.80$, $x_C = 0.00$.
- $x_A = 0.42$, $x_B = 0.26$, $x_C = 0.32$
- $x_A = 0.80$, $x_B = 0.10$, $x_C = 0.10$
- $x_A = 0.10$, $x_B = 0.20$, $x_C = 0.70$
- $x_A = 0.20$, $x_B = 0.40$, $x_C = 0.40$
- $x_A = 0.30$, $x_B = 0.60$, $x_C = 0.10$

Method. The vertical distance above the line opposite the apex labelled A corresponds to x_A , likewise for B. The mole fraction of C will always take care of itself.

Answer. The points are plotted in Fig. 10.15.

Comment. Note that points (d), (e), and (f) have x_A/x_B in constant ratio and fall on a straight line, as stated in the text.

Partially miscible liquids. A good example of a 3-component system is water/chloroform/acetic acid. Water and acetic acid are completely miscible in all proportions, and so are chloroform and acetic acid. Water and

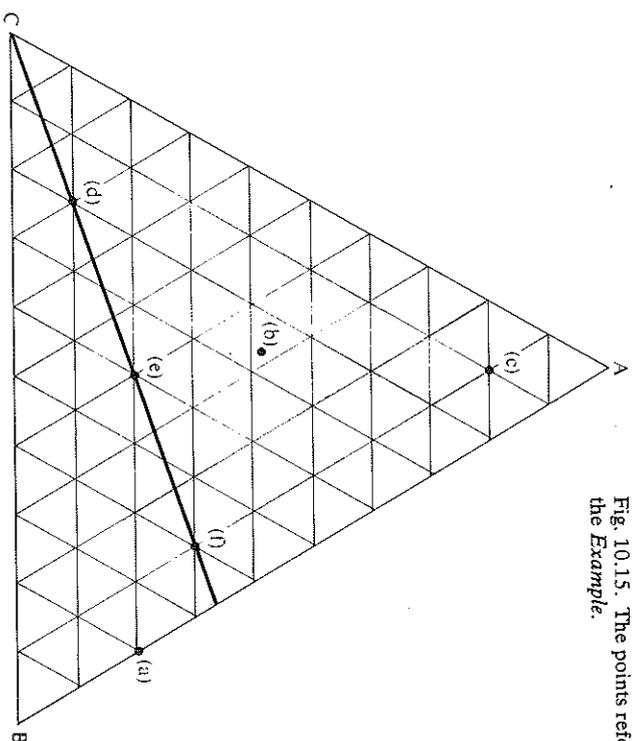


Fig. 10.15. The points referred to in the Example.

chloroform are only partially miscible. What happens when all three are present together?

The 3-component phase diagram for room temperature (and pressure) is shown in Fig. 10.16. This shows that $\text{CHCl}_3/\text{CH}_3\text{CO}_2\text{H}$ and $\text{CH}_3\text{CO}_2\text{H}/\text{water}$ binary mixtures form 1-phase systems, but $\text{CHCl}_3/\text{water}$ (the bottom edge of the triangle) has a 1-phase region at the ends and a 2-phase region at intermediate concentrations. The latter behaviour is analogous to what we saw in more detail in Fig. 10.5.

We might expect that a 1-phase system will be formed from a 2-phase $\text{CHCl}_3/\text{H}_2\text{O}$ mixture if acetic acid is added. Fig. 10.16 confirms that this is so, because at high enough initial acid concentration the system enters a 1-phase region whatever the initial proportions of chloroform and water. Following the line $a_1a_2a_3a_4$ shows this in more detail. We begin with a binary mixture of composition a_1 . The amounts and compositions of the two phases can be read off in the normal way (use the lever rule for the former). Adding acetic acid takes the system along the line joining a_1 to the apex. At some point a_2 the solution still has two phases, but there is more water in the chloroform phase (the phase at a_2') and more chloroform in the water (the phase at a_2'') because the acetic acid assists both to dissolve. Note, however, that there is more acetic acid in the water-rich phase than in the chloroform-rich phase (a_2'' is nearer the acetic acid apex than is a_2') and also note that the tie lines have to be drawn in if the diagram is to be interpreted quantitatively (we have to know which points on the phase boundary, representing the compositions of the two phases, relate to the overall composition a_2). At a_3 two phases are present, but the chloroform-rich layer is there only as a trace. Further addition of acid (e.g., to a_4) makes the whole system a single phase.

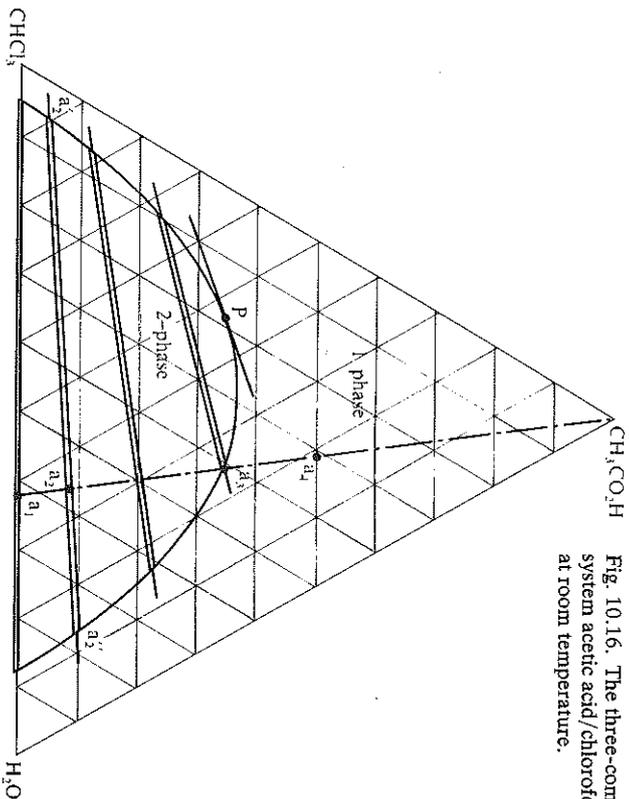


Fig. 10.16. The three-component system acetic acid/chloroform/water at room temperature.

Example (Objective 12). A mixture is prepared consisting of a mole fraction 0.60 of chloroform and 0.40 of water. Describe the changes that occur when acetic acid (ethanoic acid) is added to the mixture.

Method. We can base the discussion on Fig. 10.16. The relative proportions of chloroform and water remain constant, and so the addition of acetic acid corresponds to motion along the line from the acetic acid apex to the point $x_c = 0.60$ on the opposite base line. The tie lines give the phase compositions, the lever rule their proportions.

Answer. Initially, the composition is $x_c = 0.60$, $x_w = 0.40$, $x_a = 0.00$: we shall denote this (0.60, 0.40, 0.00). This composition lies in the two-phase region, the phase compositions being (0.95, 0.05, 0.00) and (0.12, 0.88, 0.00) with relative proportions $5.2/11.5 = 0.45/1$. Addition of acetic acid takes the system along the line mentioned. When sufficient acetic acid has been added such that its mole fraction is 0.18 the overall composition is (0.49, 0.33, 0.18) and the system consists of two phases, one of composition (0.82, 0.06, 0.12) and the other of composition (0.17, 0.60, 0.23) in relative abundance $6.2/6.2 = 1/1$. When enough acid has been added to bring x_a to 0.35, the system consists of a trace of a phase with composition (0.64, 0.11, 0.25) and a dominating phase of composition (0.35, 0.28, 0.37). Further addition of acid takes the system into the single-phase region, where it remains right to the point of pure acetic acid.

The role of added salts. Ammonium chloride is soluble in water. Ammonium sulphate is soluble in water. What is the solubility of a mixture of the two salts?

Fig. 10.17 illustrates the room-temperature phase diagram. The tie lines have been indicated to guide the interpretation. (In fact, there should be a solid mass of tie lines, but that would defeat the object of the

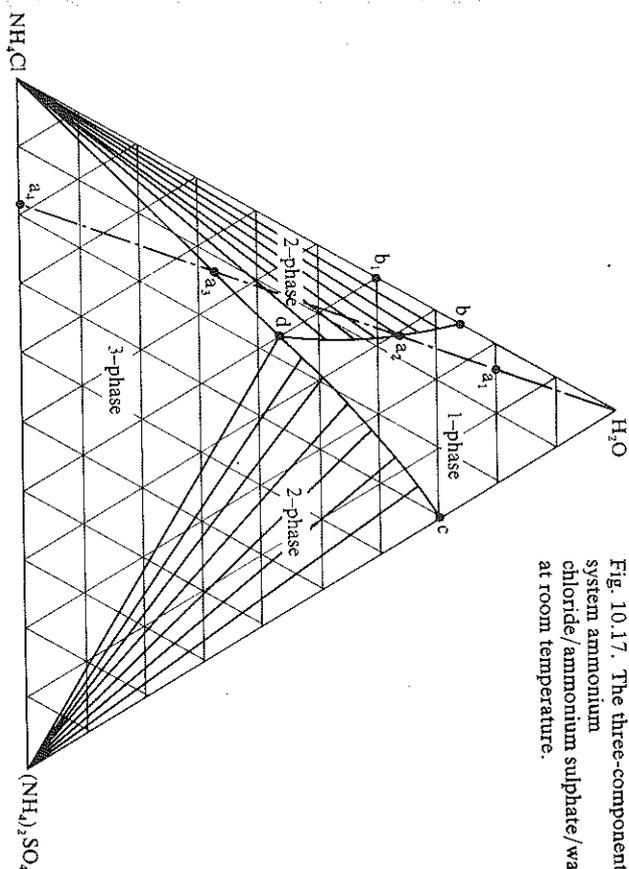


Fig. 10.17. The three-component system ammonium chloride/ammonium sulphate/water at room temperature.

illustration.) The point b indicates the solubility of ammonium chloride in water: a binary mixture of composition b_1 consists of the undissolved solid and the supernatant, saturated solution of composition b. The point c indicates the solubility of the sulphate.

Consider a ternary solution of composition a_1 . This is unsaturated, and is a single phase. Now evaporate the water: the composition moves along line a_1-a_4 . At a_2 it strikes the 2-phase region, and according to the tie lines (all of which have an apex in common) some solid chloride will crystallize out of the solution. The liquid gets relatively richer in sulphate, and its composition moves towards d. When enough water has been removed the overall composition a_3 is reached and the saturated solution of composition d, solid chloride, and solid sulphate (see where the two tie lines go) are in equilibrium. There are three phases, and three components, and so $F = 2$. Both pressure and temperature are fixed, and so this is an invariant point ($F'' = 0$). From this point on the evaporation of the water diminishes the amount of saturated solution, and deposits solid chloride and sulphate. When point a_4 has been reached, the whole of the solvent has disappeared, and we have the binary mixture of two solids.

The composition of the saturated ternary solution (d) corresponds to a smaller mole fraction of water than either of the two binary solutions (b and c). This indicates that the two salts form a more concentrated solution overall than either does alone: this is the *common-ion effect*, where the presence of one salt alters the solubility of the other.

Example (Objective 12). A solution of 50 g ammonium chloride in 30 g water is prepared at room temperature. 45 g of ammonium sulphate is then added. Describe the states of the initial and final systems.

Method. Fig. 10.17 can be used if the masses are converted to mole fractions. Compositions of phases and their abundances can be read off the phase diagram with use of the lever rule.

Answer. The molecular masses of the three components are water: 18 g mol^{-1} ; ammonium chloride: 53.5 g mol^{-1} ; ammonium sulphate: 132 g mol^{-1} . It follows that 30 g water is 1.67 mol , 50 g ammonium chloride is 0.93 mol , and 45 g ammonium sulphate is 0.34 mol . The initial mole fraction composition is therefore (0.64, 0.36, 0.00) and the final (0.57, 0.31, 0.12) for (water, ammonium chloride, ammonium sulphate). From Fig. 10.17 we see that the initial system consists of ammonium chloride with a saturated solution of composition (0.64, 0.36, 0.00) in relative proportion $2.7/12.2 = 0.22/1$. After addition of sulphate there is only one phase.

Further reading

- Phase diagrams.* A. Alper; Academic Press, New York, 1970.
The phase rule and its applications. A. Findlay, A. N. Campbell, and N. O. Smith; Dover, New York, 1951.
The phase rule and heterogeneous equilibria. J. E. Ricci; Van Nostrand, New York, 1951.
High pressure chemistry. R. S. Bradley and D. C. Munro; Pergamon, Oxford, 1965.
Geochemistry. W. S. Fyfe; Clarendon Press, Oxford, 1974.

Problems

- 10.1. The compound p-azoxyanisole forms a liquid crystal. 5 g of the solid was put into a tube which was then evacuated and sealed. Use the phase rule to prove that the solid will melt at a definite temperature, and that the liquid crystal phase will make a transition to a normal liquid phase at a definite temperature.
- 10.2. State how many *components* there are in the following systems. (a) NaH_2PO_4 in water in equilibrium with water vapour, but disregarding the possibility that the salt ionizes in solution; (b) the same, but taking into account the possibility of complete ionization into all possible ions; (c) AlCl_3 in water, noting that hydrolysis and precipitation of $\text{Al}(\text{OH})_3$ occur.
- 10.3. We began the chapter by seeing that two phases were in equilibrium if the chemical potentials of the species present were the same in each phase. By the same type of argument, show that two phases are in thermal equilibrium only if their temperatures are the same, and that they are in mechanical equilibrium only if they are at the same pressure.
- 10.4. Blue copper sulphate crystals decompose and release their water of hydration when heated. How many phases and components are present in an otherwise empty heated vessel?
- 10.5. Ammonium chloride also dissociates when it is heated. How many phases and components are present when the salt is heated in an otherwise empty vessel?
- 10.6. A saturated solution of sodium sulphate, with excess of the salt, is at its boiling point in a closed vessel. How many phases and components are present? How many degrees of freedom are there, and what are they?

10.7. Now suppose that the solution referred to in the last Problem was not saturated. How many components, phases, and degrees of freedom are there at the boiling point, and what are the degrees of freedom?

10.8. Both MgO and NiO are highly refractory materials. Nevertheless, when the temperature is high enough they do melt, and the ceramics industry. Draw the temperature-composition diagram for the MgO/NiO system on the basis of the data below, where x is the composition of the solid, and y that of the liquid (as a mole fraction).

$t/^\circ\text{C}$	1960	2200	2400	2600	2800
$x(\text{MgO})$	0	0.35	0.60	0.83	1.00
$y(\text{MgO})$	0	0.18	0.38	0.65	1.00

10.9. On the basis of the MgO/NiO phase diagram just constructed, state (a) the melting point of composition $x(\text{MgO}) = 0.30$; (b) the composition of the system, in terms of the nature, composition, and proportions of the phases, when a solid containing $x(\text{MgO}) = 0.30$ is heated to 2200°C ; (c) the temperature at which a liquid of composition $y(\text{MgO}) = 0.70$ will begin to solidify.

10.10. The bismuth-cadmium system is of interest in metallurgy, and we can use it to illustrate several points made in the chapter. In fact the solid-liquid phase diagram calculated on the basis of the Clausius-Clapeyron equation is very close to the experimental phase diagram throughout the composition range, and so we begin by constructing it. Use the information that $T_f(\text{Bi}) = 544.5 \text{ K}$, $T_f(\text{Cd}) = 594 \text{ K}$, $\Delta H_{\text{fus}}(\text{Bi}) = 10.88 \text{ kJ mol}^{-1}$, $\Delta H_{\text{fus}}(\text{Cd}) = 6.07 \text{ kJ mol}^{-1}$, and the knowledge that they are insoluble in each other in the solid state.

10.11. On the basis of the phase diagram constructed in the last Problem, state what you would observe when a liquid containing $x(\text{Bi}) = 0.70$ is cooled slowly from 550 K . What relative amounts of solid and liquid are present at (a) 460 K , (b) 350 K ? What would the solid be if the cooling took place very rapidly?

10.12. Plot a graph of the number of phases in equilibrium *and*, on the same diagram, the variance of the system, as the $x(\text{Bi}) = 0.70$ mixture is cooled from 550 K to 450 K .

10.13. Sketch the cooling curve for the mixture treated in the last Problem.

10.14. Now we move on to more familiar liquid mixtures, and begin by constructing the phase diagram for *m*-toluidine and glycerol. In the experiments on which the data below were obtained, solutions of *m*-toluidine were made up in glycerol, and then warmed from room temperature. The mixture was observed to lose its turbidity at the temperature t_1 , and then on further heating, to become turbid again at t_2 . Plot the phase diagram on the basis of the data, and find the upper and lower consolute temperatures.

$100w$	18	20	40	60	80	85
$t_1/^\circ\text{C}$	48	18	8	10	19	25
$t_2/^\circ\text{C}$	53	90	120	118	83	53

$100w$ is the percentage by weight of *m*-toluidine in the mixture.

10.15. Now use the phase diagram drawn in the last Problem to say what happens as *m*-toluidine is added dropwise to glycerol at 60°C . State the number of phases present at each concentration, their composition, and their relative amounts.

10.16. In Fig. 10.7a is shown the phase diagram for two partially miscible liquids, and the water/isobutanol (2-methylpropan-1-ol) system resembles it