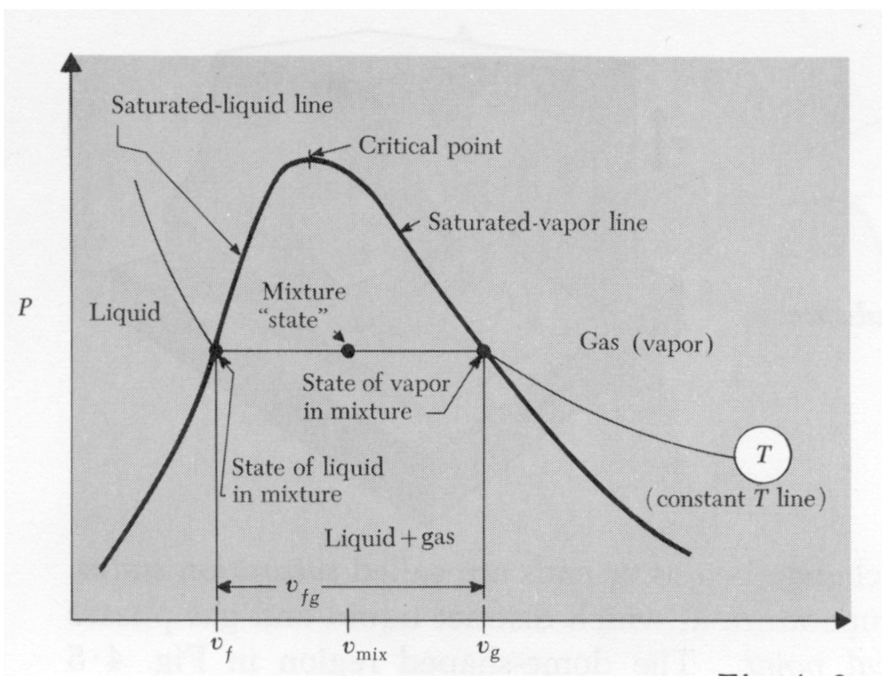
Related Sections of the textbook: 4.4.8; 4.5; 4.6

- **Learn to use the lever rule with phase diagrams.**
- **Become familiar with vapour-liquid phase diagrams of binary mixtures**

So far we have been focussing mainly on which phases will exist under what conditions.

– When two phases coexist, it is often important to know how much is in one or the other phase and the properties of each coexisting phase.
– The P-v phase diagram provides a method for determining this.
– To determine the size of individual phases from the P-v diagram, you need to know the pressure and the specific volume of the system.
– The procedure uses the so-called lever rule.

Let us look at a typical P-v diagram.



– The specific volume of the two-phase mixture is v_{mix}.
– You know that the pressure would remain constant during phase change, therefore the isotherm in the two-phase region would be at constant pressure.
– The point where this isotherm crosses the boundary between the liquid region and the two-phase region represents the state of the liquid under two-phase conditions.
– The point where this isotherm crosses the boundary between the gas region and the two-phase vapour-liquid region represents the state of the equilibrium gas.

– We can read the specific volumes of the liquid and the gas from the chart.

According to the liver rule, **mass fraction** of vapour phase is given by

Mass fraction of vapour = $\dfrac{v_{mix} - v_l}{v_g - v_l}$

Mass fraction of liquid $= \dfrac{v_g - v_{mix}}{v_g - v_f}$

The name comes from analogy with a liver. If the mixture condition is taken as a fulcrum, the mass fraction of each phase is proportional to the length of the liver arm on the opposite side.

You can derive these relationships mathematically with a simple analysis.

Basis = 1 kg of mixture.
Mass fraction of vapour = X. –> mass of vapour = X and mass of liquid = 1-X
Total volume of mixture = $X.v_g + (1\text{-}X).v_f$

Since we have only 1 kg of mixture, this volume is equal to the specific volume of the mixture.
$X.v_g + (1\text{-}X).v_f = v_{mix}$

Solve for X
$X.(v_g - v_f) = v_{mix} - v_f$

Or

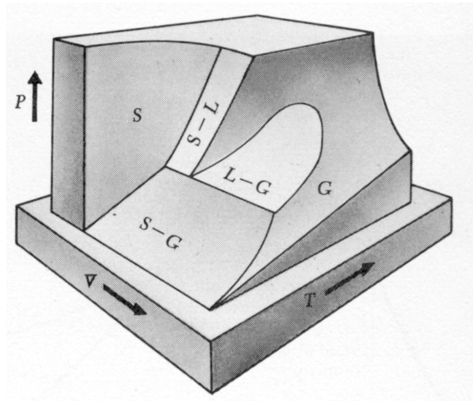
$$X = \frac{v_{mix} - v_f}{v_g - v_f}$$

This gives the mass fraction of vapour phase. The mass fraction of the liquid phase would be 1-X.

$$1 - X = 1 - \frac{v_{mix} - v_f}{v_g - v_f} = \frac{v_g - v_f - (v_{mix} - v_f)}{v_g - v_f} = \frac{v_g - v_{mix}}{v_g - v_f}$$

4.4.9 The PVT Surface:

The P-T diagram and the P-v diagram can be combined into one to get a three-dimensional picture called the PVT surface.



P is in vertical direction. T and v are in the horizontal direction. Note that the PV diagram is a projection of this surface on the P-v plane and the P-T diagram is a projection on the P-T plane.

Systems with Two Independent Components

Application of the phase rule with C = 2, gives

F = 4 - P

The degrees of freedom depend on the number of phases present at equilibrium.

P = 1 ==> F = 3; You can vary three intensive variables (eg. T, P and Composition) without changing the number of phases present at equilibrium.

P=2 ==> F = 2; Only two intensive variables can be changed independently without changing the equilibrium number of phases.

P=3 ==> F = 1; Only one intensive variable can be changed independently.

P = 4 ==> F = 0; The state of the system is fixed.

4.5.1 Binary Phase Diagrams.

- Binary phase diagrams are meant to summarise the information regarding the phase-behaviour of mixtures of two substances that may be fully or partially miscible. The mixture may form one, two, three or even four phases.
- When only one phase is formed, there would be three degrees of freedom.
- Therefore, the presentation of the entire phase behaviour would require a three-dimensional picture in which the x, y, and z co-ordinates will represent three intensive variables.

- It is somewhat difficult to draw three-dimensional figures and relatively more difficult to visualise what is going on in three-dimensions.
- Therefore, it simplifies things to present the data in 2-dimensions at a fixed value of one of the parameters.
- If the three intensive variables representing the three degrees of freedom are temperature, pressure and mass fraction of component A, one can look at what happens to the system at a specified pressure.
- Once the pressure is fixed, you can look at what types of phases are formed at different temperatures and compositions.

Note that in a binary system, the composition represents only one degree of freedom.
If the composition is expressed in terms of mole fractions, fixing the mole fraction of one component automatically fixes the mole-fraction of the other component.

$X_A + X_B = 1$

Therefore,

$X_A = 1 - X_B$

Of course, you could also look at the system in another way by fixing the temperature to see the effects of pressure at a fixed temperature. One could also fix the composition and make a P-T diagram for a pre-set composition, much like the single component P-T diagrams that we saw earlier. **To keep things simple, we will use only T-X diagrams in the remainder of this chapter. We will look at some examples of T-X diagrams.**

4.6 Vapour-Liquid Binary Systems

- In two component vapour liquid systems, depending on the temperature and composition, you may have a gas phase present along with one or two liquid phases.
- The vapour phase is guaranteed to be homogeneous since all gases mix together completely. However, the liquids may or may not mix.
- If we have two pure components A and B that are mixed together as pure liquids, three different situations can arise.

1. Liquids miscible in all proportions: If the liquids are similar in molecular structure, they are likely to be completely miscible. For example, alcohol and water can be mixed in all proportions.
2. Liquids only partially miscible: If the molecules some similarities and some strong differences, you may find that the two liquids are not miscible in all proportions but there is some mutual solubility. A will dissolve in B to some limited extent and B will dissolve in A to limited extent. For example isobutyl alcohol and water.

3. If the molecules are radically different, they may remain completely immiscible. For example water and octane.

Actually there will always be some solubility but it can be so small that you may consider them totally immiscible. We will now examine some examples of such binary systems.