Phase Transformations

Sections: 5C 11th Ed. 5.3 10th Ed.

5.6-5.9, 9th Ed.; 6.1-6.3, 8th Ed.

Phases, Components and Degrees of Freedom

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Phases, Components and Degrees of Freedom

Phase diagrams are extremely useful for systems with multiple components, and serve to describe physical and chemical equilibria over a range of different compositions, as well as points where substances are mutually miscible, or even when a system has to be brought to a specific set of conditions for equilbrium to exist (e.g., pressure, temperature and composition)

Phase diagrams are very important in the development of:
- alloys
- steels
- plastics
- cosmetics
- food products
- ceramic materials
- semiconductors
- superconductors
- petroleum product separations
- glasses

All phase diagrams are developed around one relationship, **the phase rule**, which was derived by J.W. Gibbs - it can be applied to a wide variety of systems

Phase diagrams: pictorial way of understanding the properties of a system

Some Definitions

Phase: Signifies a form of matter that is uniform throughout, not only in chemical composition but also in physical state

Number of phases is denoted by *P*:
P = 1 for gas, gaseous mixture, crystal, two miscible liquids, ice
P = 2 for slurry of ice and water, immiscible metal alloys
Sometimes it is not easy to decide how many phases there are - for example, a **solid solution** of A in solid B - homogeneous on molecular scale - A atoms are surrounded by B atoms, representative of composition on the whole (example a)
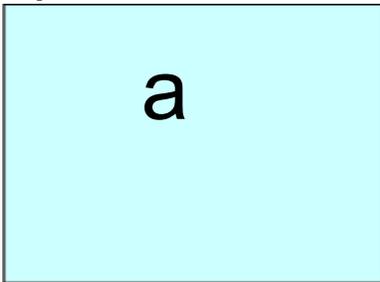
(a)
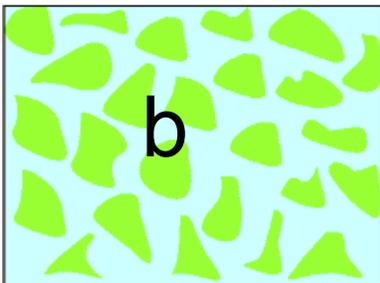
(b)

A **dispersion** (example b) is uniform macroscopically, but not on the microscopic molecular level - for example, regions of A are embedded withing a matrix of B, still uniform composition - **very important in materials synthesis**, especially production of steels, tailoring materials mechanical and electrical properties

Some Definitions, 2

Constituent: A chemical species that is present in a system. For example, a mixture of water and ethanol has 2 consituents

Component: A chemically independent component of the system. The number of components in a system, C, is the minimum number of independent species needed to define the composition of all of the phases present in the system

- When no reaction takes place, Constituents = Components
- When a reaction can occur, the **number of components** is **the minimum number of species which specifies the composition of all of the phases** (or: smallest number of independently variable chemical species to describe the composition of each phase)

$$CaCO_3(s) \quad \rightleftarrows \quad CaO(s) \quad + \quad CO_2(g)$$

Phase 1   Phase 2   Gas Phase

- Number of Phases, $P = 3$
- Number of Constituents = 3
- Number of Components, $C = 2*$

*$CaCO_3$ can be expressed in terms of 2 components in two different phases from the stoichiometry of the reaction

Components Example

Consider the thermal decomposition of ammonium chloride:

$$NH_4Cl \ (s) \quad \rightleftarrows \quad NH_3 \ (g) \quad + \quad HCl \ (g)$$

- Number of Phases, $P = 2$
- Number of Constituents = 3
- Number of Components, $C = 1$*

*NH_3 and HCl are fixed in stoichoimetric proportions by the reaction, and compositions of both phases can be specified by NH_4Cl

N.B., if additional HCl or NH_3 were added to the system, decomposition of the NH_4Cl would not give the correct gas phase compositions, and either HCl or NH_3 would be invoked as a 2nd component

$$H_2O \ (l) \quad \rightarrow \quad \tfrac{1}{2}O_2 \ (g) \quad + \quad H_2 \ (g) \ (at \ room \ temp)$$

- Number of Phases, $P = 2$
- Number of Constituents = 3
- Number of Components, $C = 3$*

*At room temperature, O_2 (g) and H_2 (g) do not react to form water, so they are **not in equilibrium**: regarded as independent constituents

Variance and Degrees of Freedom

The **variance**, F, is the number of intensive variables in a system that can be changed independently without disturbing the number of phases in equilibrium.

In a single-component, single-phase system ($C=1$, $P=1$) the pressure and temperature may be changed independently without disturbing the number of phases in equilibrium:

$F = 2$, system is **bivariant**, or has **two degrees of freedom**

If two phases are in equilibrium in a single-component system ($C=1$, $P=2$) (e.g., a liquid and its vapour), the temperature (or pressure) can be changed, but there must be an accompanying dependent change in pressure (or temperature) to preserve the phases in equilibrium

$F = 1$, system has **one degree of freedom**

If three phases are in equilibrium ($C=1$, $P=3$) (e.g., s, l and g), neither the T nor p can be changed, otherwise the equilibrium is not preserved.

$F = 0$, system has **no degrees of freedom**

Phase Rule

J.W. Gibbs, regarded as America's first theoretical scientist and the father of chemical thermodynamics, wrote that the number of components, C, and the number of phases at equilibrium, P, for a system of any composition:

$$F = C - P + 2$$

1. Count the number of intensive variables (p and T count as 2)
2. Specify composition of the phase by mole fractions of C - 1 components (need C - 1, not C, since sum of all mole fractions = 1, all mole fractions are known if all but one is specified)
3. Since there are P phases, total number of composition variables is $P(C$ - 1), and total number of intensive variables is $P(C$ - 1) + 2
4. At equilibrium, chemical potential of J must be same in every phase

    $$\mu_{J,\alpha} = \mu_{J,\beta} = \ldots \quad \text{for } P \text{ phases}$$

    There are P - 1 equations of this kind for each component J. If there are C components, total number of equations is $C(P$ - 1)
5. Each equation reduces our freedom to vary any of the $P(C$ - 1) + 2 intensive variables, so the number of degress of freedom is

$$F = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

Josiah Willard Gibbs

Josiah Willard Gibbs was born in New Haven, Connecticut, February 11, 1839, and died in the same city, April 28, 1903. He graduated from Yale College in 1858, received the degree of doctor of philosophy in 1863 and was appointed a tutor in the college for a term of three years. After his term as tutor he went to Paris (winter 1866/67) and to Berlin (1967), where he heard the lectures of Magnus and other teachers of physics and mathematics.
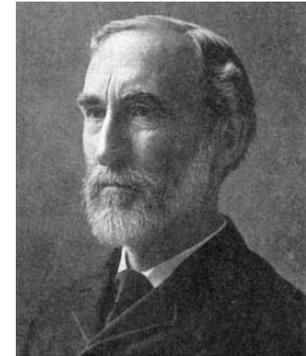
In 1868 he went to Heidelberg where Kirchhoff and Ostwald were then stationed returning to New Haven in June 1869. Two years later he was appointed Professor of mathematical physics in Yale College, a position he held until the time of his death.

In 1876 and 1878 he published the two parts of the paper "On the Equilibrium of Heterogeneous Substances", which is generally considered his most important contribution to physical sciences. It was translated into German in 1881 by Ostwald and into French in 1889 by Le Chatelier.

Outside his scientific activities, J.W. Gibbs's life was uneventful; he made but one visit to Europe, and with the exception of those three years, and of summer vacations in the mountains, his whole life was spent in New Haven. His modesty with regard to his work was proverbial among all who knew him; there was never any tendency to make the importance of his work an excuse for neglecting even the most trivial of his duties, and he was never too busy to devote, at once, as much time and energy as might be necessary to any of his students who sought his assistance.

One Component Systems

Phase diagrams are extremely useful for systems with multiple components, and serve to describe physical and chemical equilibria over a range of different compositions, as well as points where substances are mutually miscible, or even when a system has to be brought to a specific set of conditions for equilbrium to exist (e.g., p, T and composition). For a **one-component system**, $F = 3 - P$:
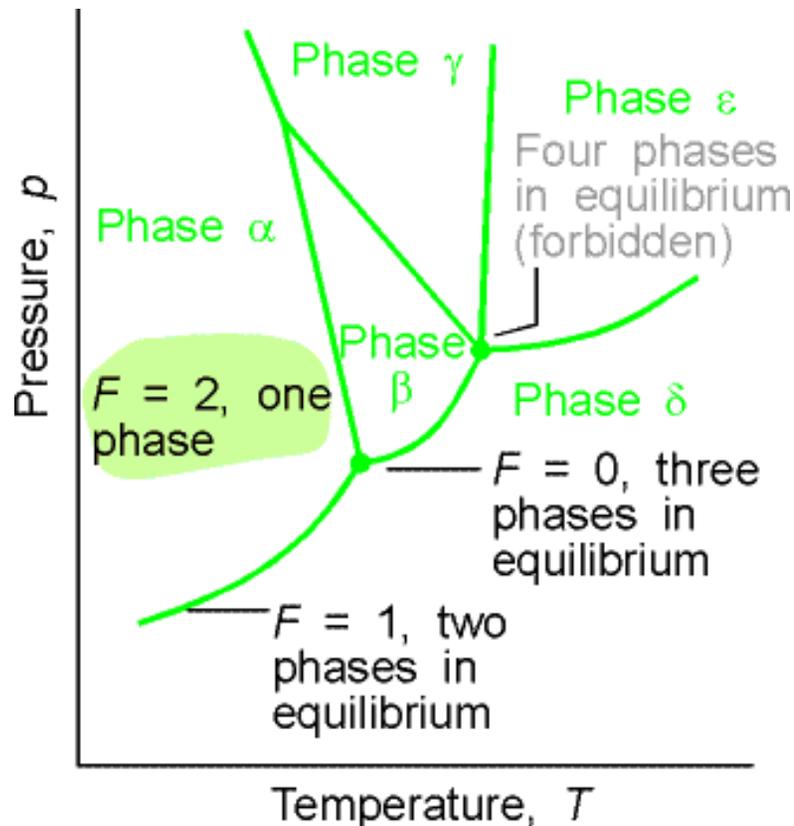
If **1 phase** present, $F = 2$, and p and T can be varied without changing the number of phases (single phase is an **area** on the phase diagram)

If **2 phases** in eqb, $F = 1$, implying the pressure is not freely variable if the temperature is set

If **3 phases** in eqb, $F = 0$, and the system is invariant - this condition can only be established at a definite p and T

4 phases cannot exist in a one component system, since F cannot be negative

Phases, Components and Degrees of Freedom

Consider pure water:
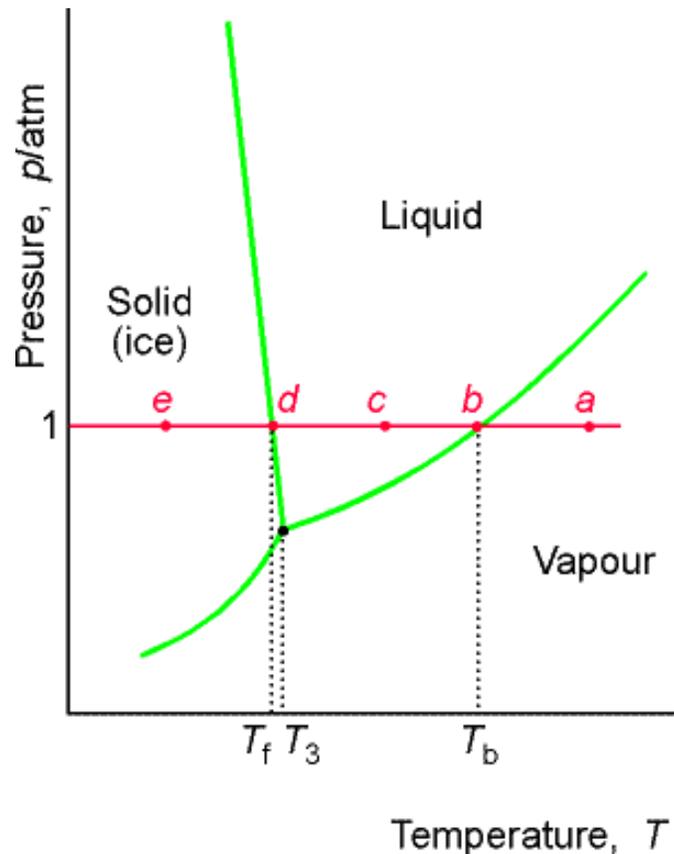
a   In gas phase, cooled at constant p, $F = 2$

b   Liquid appears at the phase transition (the boiling temperature), and $F = 1$. We have specified constant p (single degree of freedom), so equilibrium T is not under our control

c   Lowering T takes liquid to single phase liquid region, $F = 2$, T can be varied at will

d   Liquid-solid phase transition at T_f, with $F = 1$, and at constant p, T is not under our control

e   Lowering T further results in single solid phase with $F = 2$, where p and T can be varied

Experimental Procedures

Detecting phase transitions is tricky, requiring special techniques

Thermal analysis: technique which takes advantage of the enthalpy change during a first order phase transition:
- sample is allowed to cool and the temperature is monitored
- at a 1st-order transition, heat is evolved and cooling stops until the transition is complete
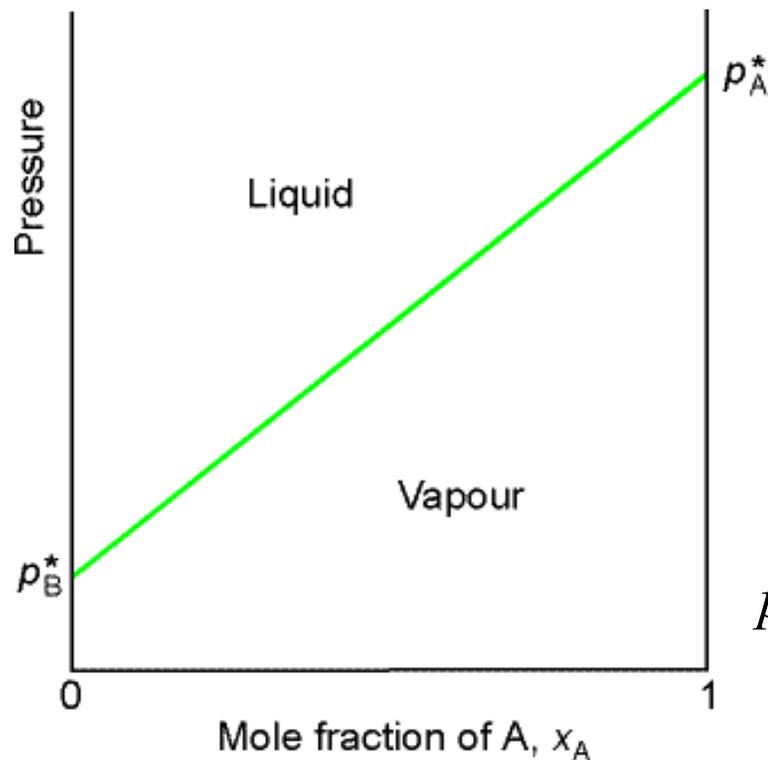- **cooling curve** for the isobar *cde* in the water phase diagram is:

High pressure phase transitions can be observed in the **diamond-anvil cell**, in which pressure can be exerted by turning a screw (1 Mbar pressures) and the phase transition is monitored **spectroscopically** by shift in lines from small ruby pieces added to the sample
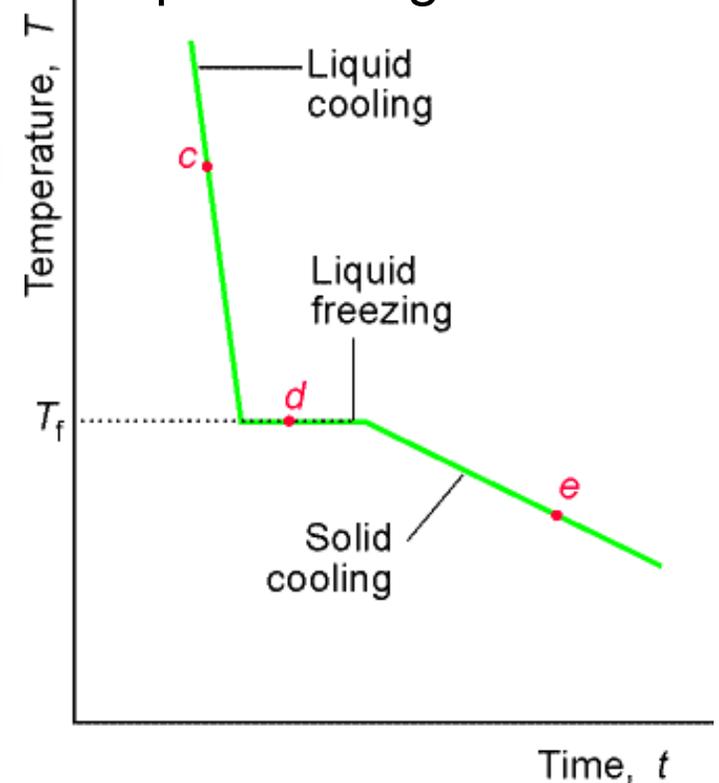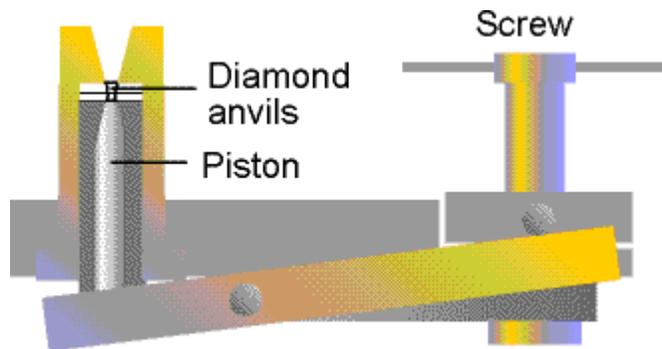
Two Component Systems

When there are two components in a system, $C = 2$, and $F = 4 - P$, so if the temperature is held constant, remaining variance is $F' = 3 - P$, which has a maximum value of 2 for a single phase. The remaining degrees of freedom are assigned normally to p and the composition (mole fraction).

- Phase diagrams of **pressures** & compositions for stable phases
- Phase diagrams of **temperatures** & compositions for stable phases

Pressure (y-axis), Mole fraction of A, x_A (x-axis), regions labelled Liquid and Vapour, with p_A^* at top right and p_B^* at left.

Vapour pressure diagrams: Partial pressures of components of an ideal solution of two volatile liquids are related to the composition of the mixture by Raoult's Law

$$p_A = x_A p_A^* \qquad p_B = x_B p_B^*$$

where * signifies the vapour pressures of pure A and B. Total vapour pressure is

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A$$

i.e., linear variation of vapour pressure at fixed T with changed composition

Composition of the Vapour

Compositions of liquid and vapour in equilibrium are not necessarily the same, vapour should be richer in the more volatile component

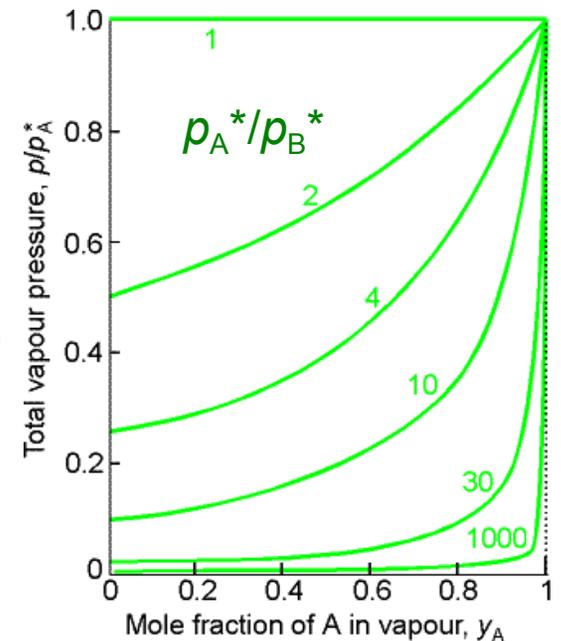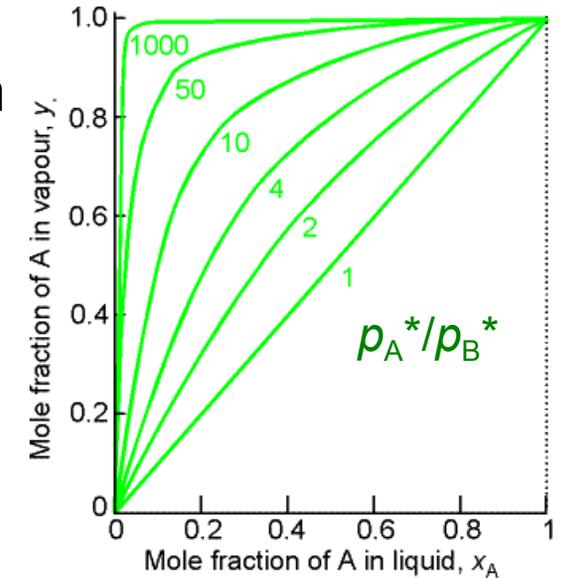For mole fractions of a gas y_A and y_B

$$y_A = \frac{p_A}{p} \qquad y_B = \frac{p_B}{p}$$

For an ideal mixture, partial pressures may be expressed in terms of mole fractions in the liquid (see equations on previous page)

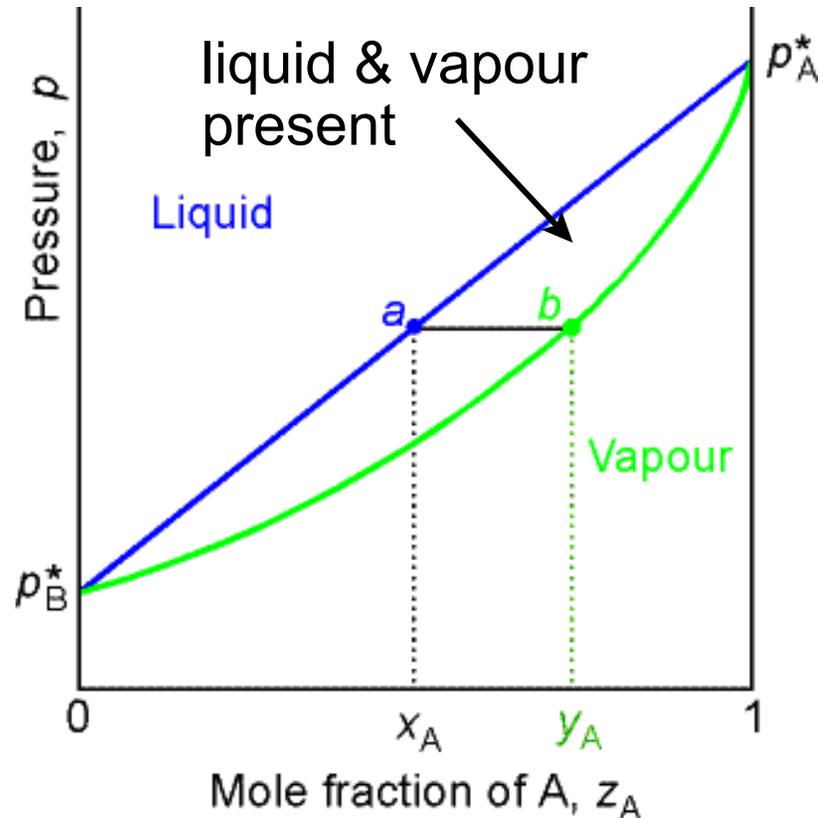$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \qquad y_B = 1 - y_A$$

In all cases, $y_A > x_A$ (vapour richer in more volatile component). If B is non-volatile, $p_B^* = 0$, $y_B = 0$. The total vapour pressure as composition of the vapour:

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}$$

Interpretations of the Diagrams

For distillations, both vapour and liquid contributions are of interest, so we combine the two previous diagrams into one
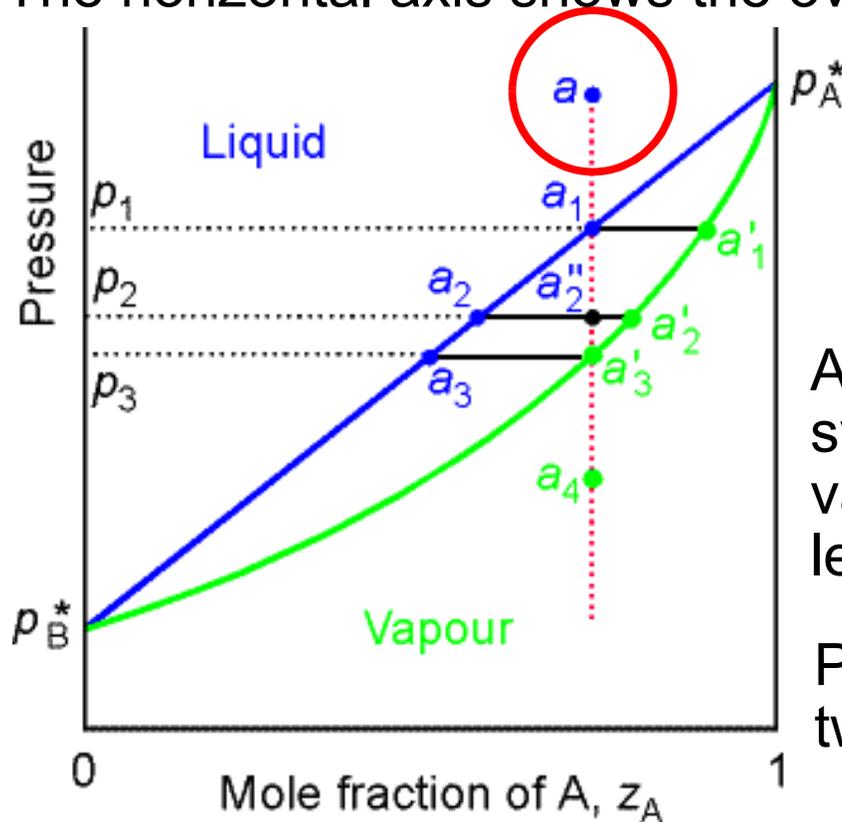

Point a: vapour pressure of mixture of composition x_A
Point b: composition of vapour in equilibrium with liquid at that pressure
At equilibrium, $P = 2$, $F' = 1$, so if composition specified, pressure at which equilibrium exists is fixed

Interpretations of the Diagrams, 2

The horizontal axis shows the overall composition, z_A, of the system:

All points down the **solid diagonal** correspond to a system under high pressure where there is only a liquid phase ($z_A = x_A$, composition of liquid)

All points on **lower curve** correspond to a system with low pressure where only the vapour phase exists (applied pressure is less than the vapour pressure, so $z_A = y_A$)

Points between lines are systems where two phases exist: 1 liquid & 1 vapour

Lowering the pressure on a liquid by drawing out a piston: start at point **a**: Here, $F' = 2$ and $P = 1$; only the liquid phase exists; changes to system <u>do not affect overall composition</u>, so system moves down vertical line that passes through a (vertical line called an **isopleth**), until point **a_1** is reached (pressure reduced to **p_1**)

Interpretations of the Diagrams, 3
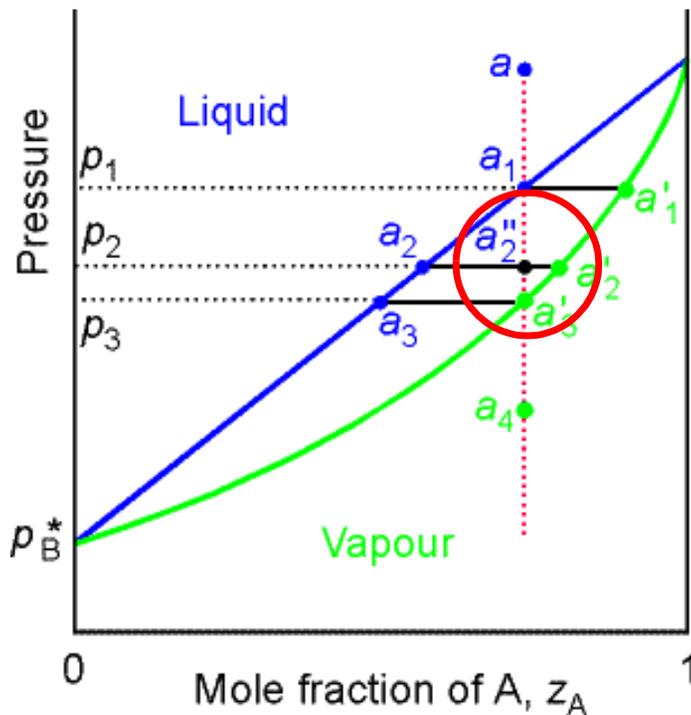
a_1: Liquid is in **equilibrium** with its vapour (composition of vapour phase given by a_1', horizontal line is called a **tie line**) Composition same at the lower pressure, at this pressure, virtually no vapour pressure

a_2'': Pressure is lowered to p_2, new pressure is below the vapour pressure of the liquid, so it vapourizes until the vapour pressure of the remaining liquid becomes p_2.
- Two phases are at **equilibrium**, $F' = 1$ for all points between the two curves
- For a given pressure p_2 (all points on this horizontal line), $F' = 0$

a_3': Pressure is further dropped to p_3, and now the composition of the vapour is the same as the overall composition, so the amount of liquid present must be negligible, with tiny composition a_3 (still in **equilibrium**)

a_4: Pressure drops to p_4, and now only the vapour phase exists, same composition as the overall composition of the system

Interpretations of the Diagrams, 4

The previous diagram can be viewed more generally below, considering pressure reduction via a piston

In (a), the liquid and vapour phase are in equilibrium, the compositions and abundances of the two phases can be predicted.

In (b) compositions of phases are determined from the **tie lines**.
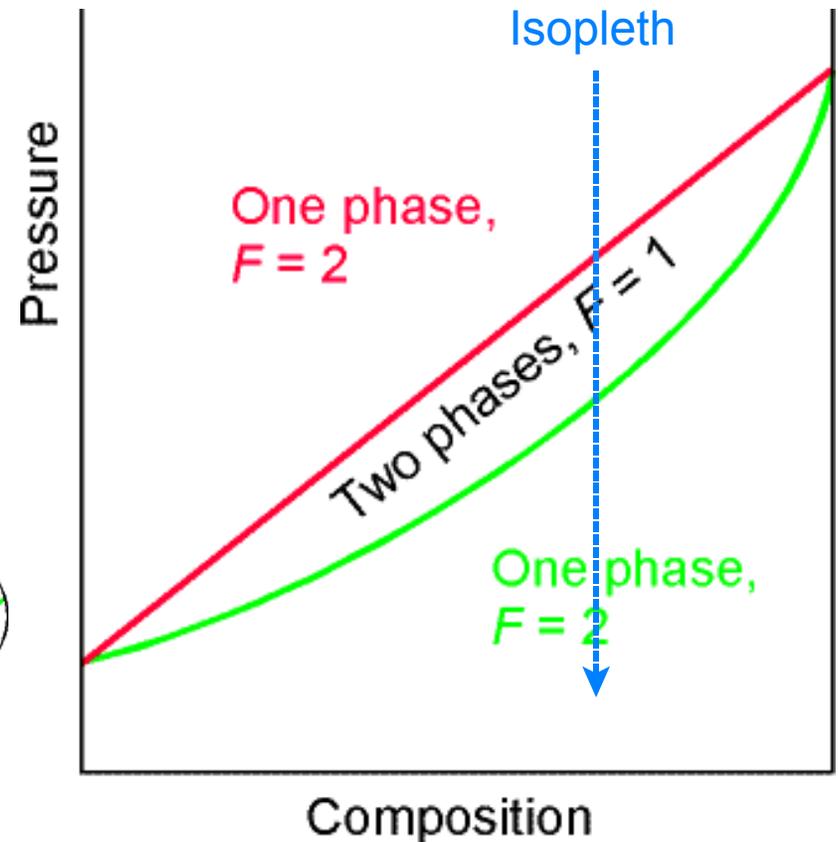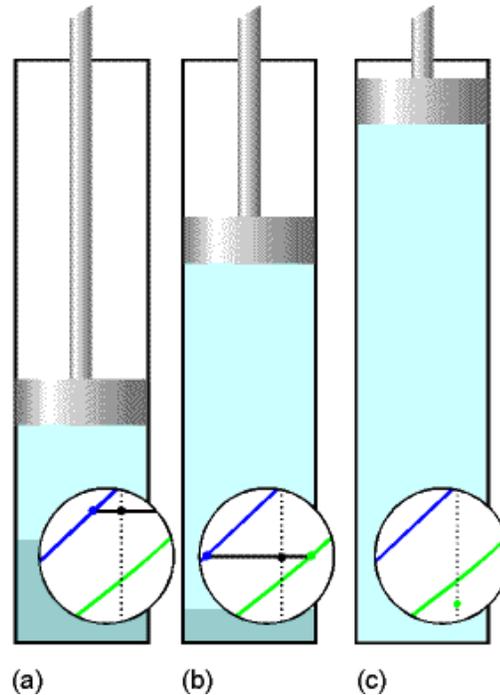
In (c), the applied pressure is much less than the vapour pressure, so all of the liquid has vapourized, and we are in a one phase region

The Lever Rule

The point in a two-phase region of a phase diagram indicates not only qualitatively if both liquid and vapour are present, but also quantitatively tells us the relative amounts of each.

Composition
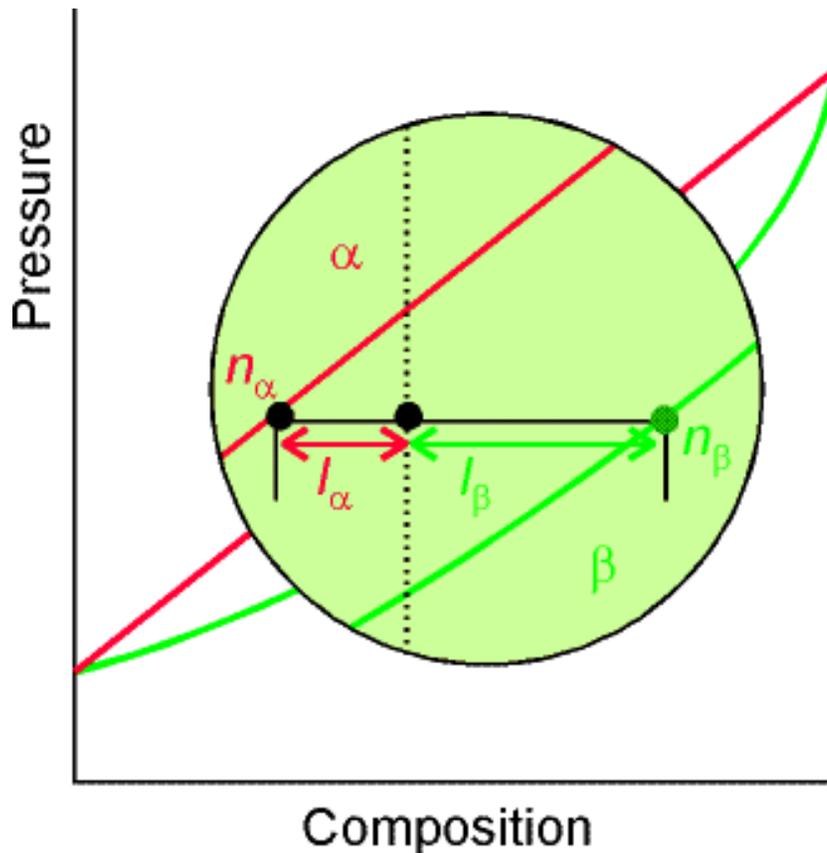
Above, $l_\beta \approx 2l_\alpha$, the amount of phase α is 2x that of phase β

To find the relative amounts of phases α and β in equilibrium, measure distances l_α and l_β along the tie lines, and use the **lever rule**:

$$n_\alpha l_\alpha = n_\beta l_\beta$$

Proof: If $n = n_\alpha + n_\beta$ and the overall amount of A is nz_A, then the overall amount of A is the sum of its two phases:

$$nz_A = n_\alpha x_A + n_\beta y_A$$
$$nz_A = n_\alpha z_A + n_\beta z_A$$

Then equating the sides:

$$n_\alpha(x_A - z_A) = n_\beta(z_A - y_A)$$