Lecture 3: Solutions: Activities and Phase Diagrams

27-10-2009

- Lecture plan:
  - activities
  - Debye-Hückel limiting law
  - Gibbs phase rule
  - vapour composition
  - two-component phase diagrams
  - problems

Activities

- The aim: to modify the equations to make them applicable to real solutions

chemical potential of the solvent:

vapour pressure of A above solution

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

vapour pressure of A above pure A

standard chemical potential for pure A

Solvent activity

chemical potential of the solvent:

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

For ideal solution

$$\mu_A = \mu_A^* + RT \ln x_A$$

(Raoult's law)

For real solution

$$\mu_A = \mu_A^* + RT \ln a_A$$

activity of A

$$a_A = \frac{p_A}{p_A^*}; \quad a_A \to x_A \ \text{as} \ x_A \to 1$$

$$\mu_A{}^* = \mu_A{}^* + RT \ln x_A + RT \ln \gamma_A$$

activity coefficient of A

Solute activity

- Ideal-dilute solution (solvent obeys Roult’s law, solute obeys

  Henry’s law $p_B = K_B x_B$

$$\mu_B^{\ *} = \mu_B^{\ *} + RT\ln\frac{p_B}{p^*_{\ B}} = \underbrace{\mu_B^{\ *} + RT\ln\frac{K_B}{p^*_{\ B}}}_{\mu_B^{\ \ominus}} + RT\ln x_B$$

standard chemical potential of the solute

$$\mu_B^{\ *} = \mu_B^{\ \ominus} + RT\ln x_B$$

- Real solutes $\mu_B^{\ *} = \mu_B^{\ \ominus} + RT\ln a_B$ $\qquad a_B = \frac{p_B}{K_B}$

- Concentration are usually defined as **molality,** the same equation but different standard potential:

dimensionless activity

$$\mu_B = \mu_B^{\ \ominus} + RT\ln b_b \quad ⇨ \quad a_B = \gamma_B\frac{b_B}{b^{\ominus}};\quad \mu = \mu^{\ominus} + RT\ln a$$

Activity

$$\mu = \mu^{\theta} + RT \ln a$$

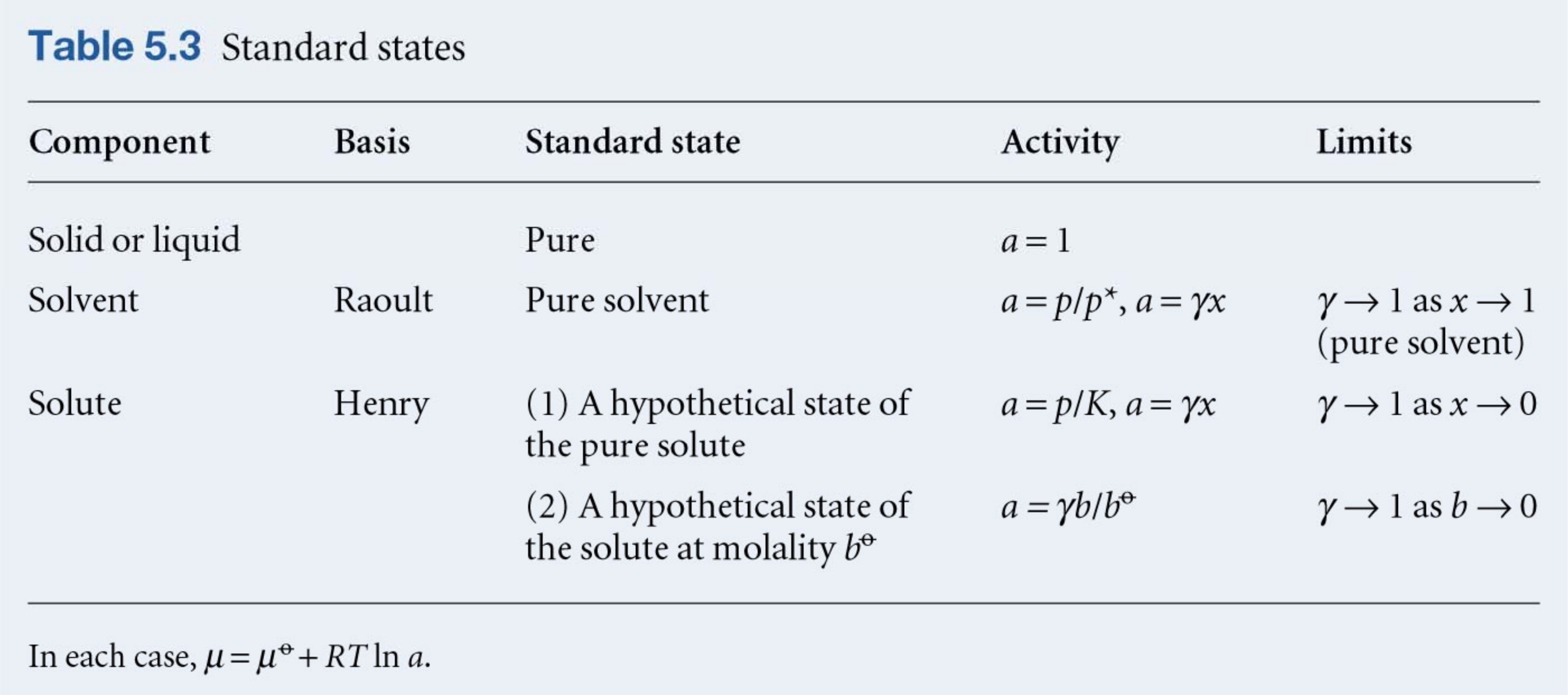


Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^{*}$, $a = \gamma x$	$\gamma \to 1$ as $x \to 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K$, $a = \gamma x$	$\gamma \to 1$ as $x \to 0$
		(2) A hypothetical state of the solute at molality $b^{\ominus}$	$a = \gamma b/b^{\ominus}$	$\gamma \to 1$ as $b \to 0$

In each case, $\mu = \mu^{\ominus} + RT \ln a$.

Example: Biological standard state

- Biological standard state: let’s define chemical potential of hydrogen at pH=7

$$\mu_{H^+} = \mu_{H^+}{}^{\ominus} + RT \ln a_{H^+}$$

$$\mu_{H^+}^{\oplus} = \mu_{H^+}{}^{\ominus} - 7RT \ln(10) = \mu_{H^+}{}^{\ominus} - 40 kJ / mol$$

Ion Activities

- Ions strongly interact to each other due to Coulomb forces, activities can be replaced by molalities anly for sub-mM concentrations

$$\mu = \mu^{\theta} + RT\ln a \leftarrow \boxed{a = \gamma \frac{b}{b^{\theta}}}$$

standard state: ideal solution at molality b^0=1mol/kg

Alternatively:

$$\mu = \mu^{\theta} + RT\ln b + RT\ln\gamma = \mu^{ideal} + RT\ln\gamma$$

ideal solution of the same molality b

In ionic solution there is no experimental way to separate contribution of cations and anions

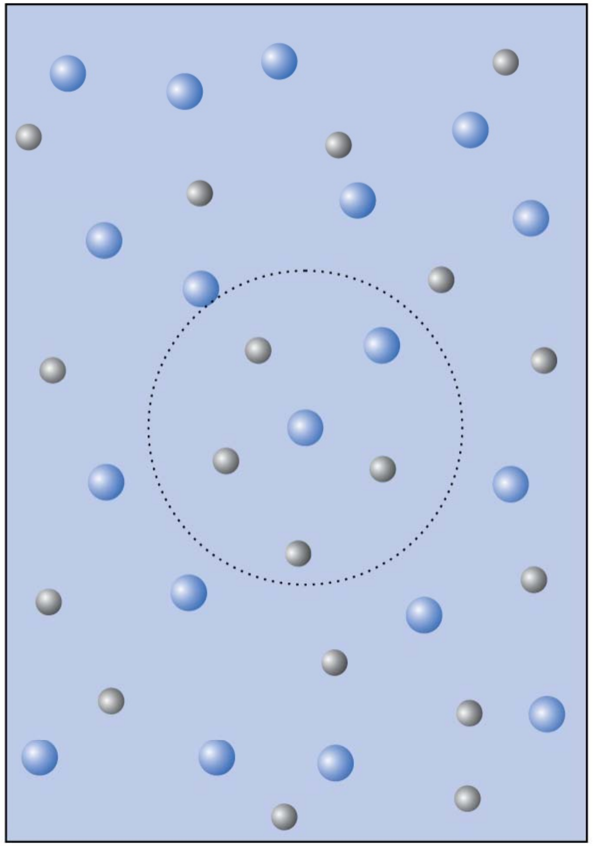
$$G_m = \mu_+ + \mu_- = \mu_+^{ideal} + \mu_-^{ideal} + RT\ln\gamma_+\gamma_- \leftarrow \boxed{\gamma_\pm^{\;2}}$$

$$\mu_+ = \mu_+^{ideal} + RT\ln\gamma_\pm;\ \mu_- = \mu_-^{ideal} + RT\ln\gamma_\pm$$

In case of compound M_pX_q: $G_m = p\mu_+ + q\mu_- = G_m^{ideal} + RT\ln\gamma_+^{\,p}\gamma_-^{\,q}$

Debye-Hückel limiting law

- Coulomb interaction is the main reason for departing from ideality
- Oppositely charged ions attract each other and will form shells (***ionic atmosphere***) screening each other charge
- The energy of the screened ion is lowered as a result of interaction with its atmosphere



Debye-Hückel limiting law

In a limit of low concentration the activity coefficient can be calculated as:

$$\boxed{\log \gamma_{\pm} = -\left|z_{+}z_{-}\right| A I^{1/2},} \quad A = -0.509 \ \text{for water}$$

where: $I = \frac{1}{2}\sum_i z_i{}^2 (b_i / b^{\ominus})$ Ionic strength of the solution

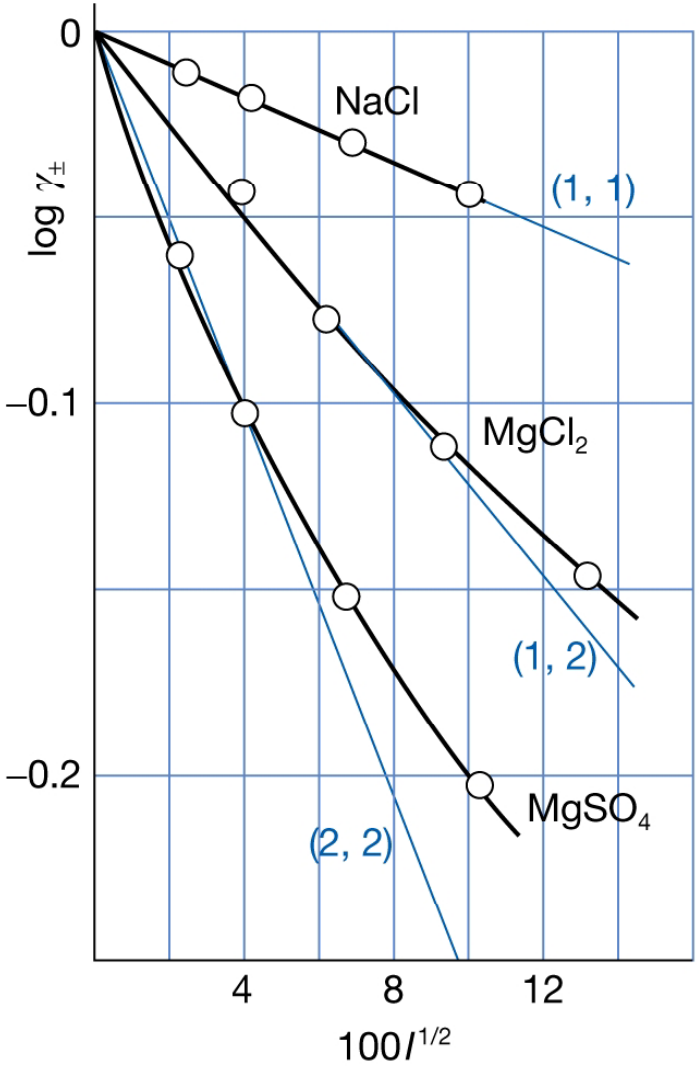
Example: calculate mean activity coefficient of 5 mM solution of KCL at 25C.

$$I = \frac{1}{2}(b_{+} + b_{-})/b^{\ominus} = b/b^{\ominus} = 5 \bullet 10^{-3}$$

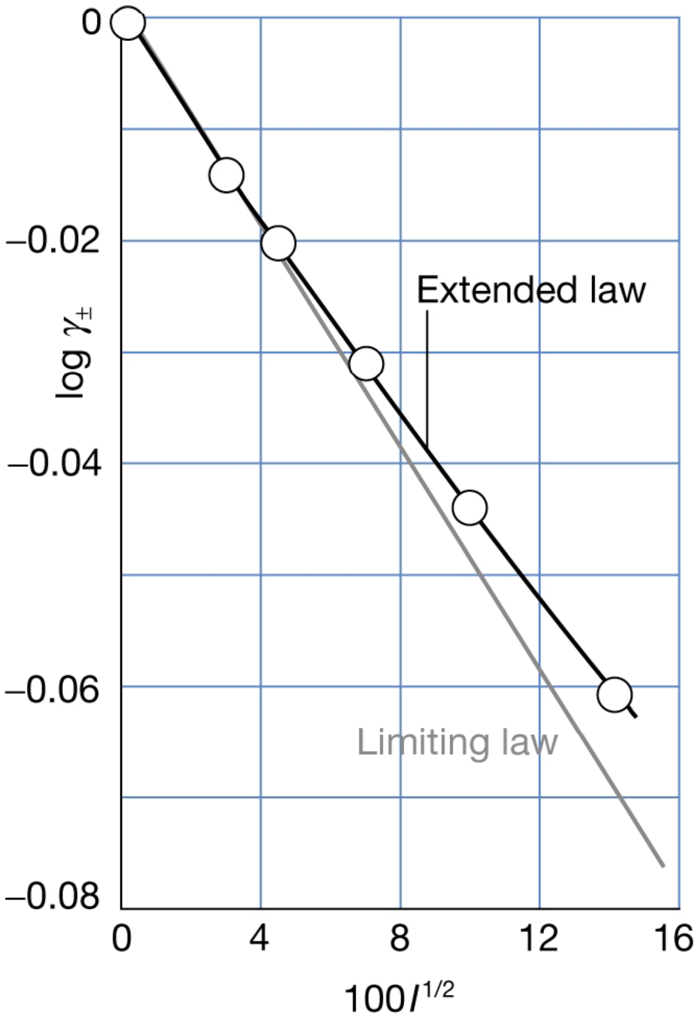
$$\log \gamma_{\pm} = -\left|z_{+}z_{-}\right| A I^{1/2} = -0.509 * (5 \bullet 10^{-3})^{1/2} = -0.036$$

$$\gamma_{\pm} = 0.92$$

Debye-Hückel limiting law



$$\log \gamma_\pm = -|z_+ z_-| A I^{1/2}$$



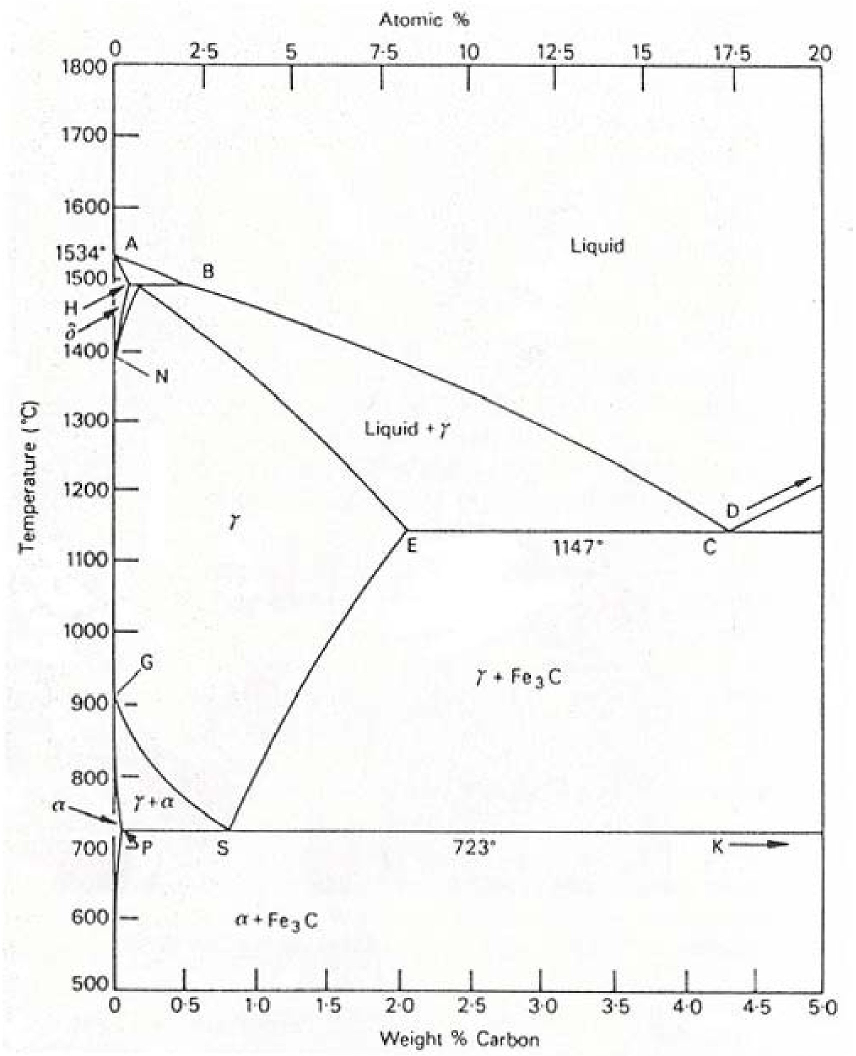
Extended D-H law:

$$\log \gamma_\pm = -\frac{|z_+ z_-| A I^{1/2}}{1 + B I^{1/2}}$$

PHASE DIAGRAMS

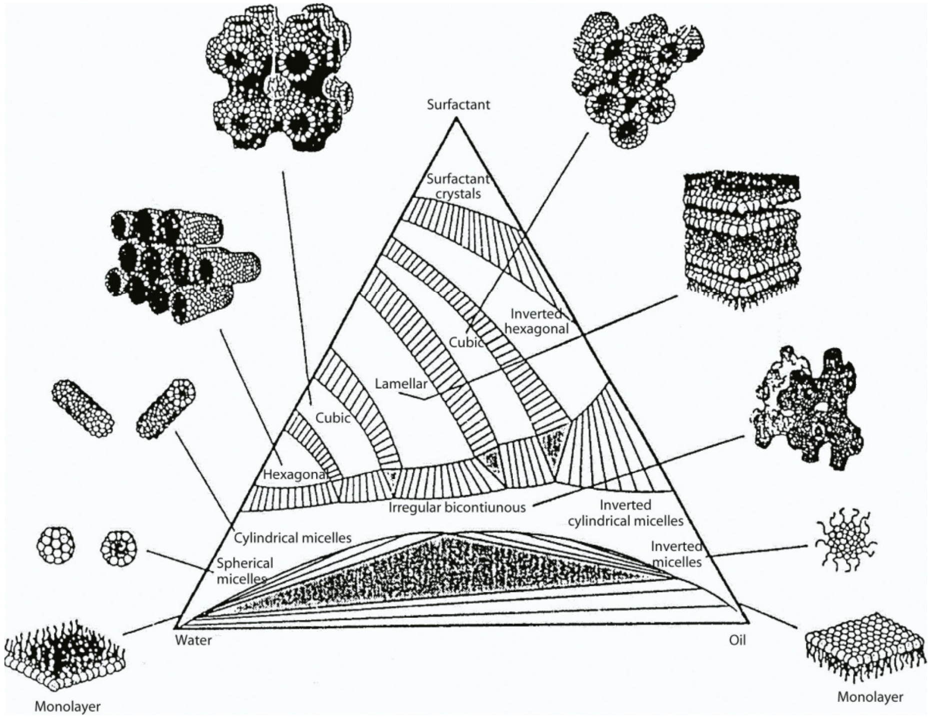
Phase diagrams

- what is the composition (number of phases and their amount and composition) at equilibrium at a given temperature;
- what happens to the system when is cools down/heats up
- we can predict the structure and the properties of the system at low temperature.
- we can understand development and preservation of non-equilibrium structures
- design materials of required properties

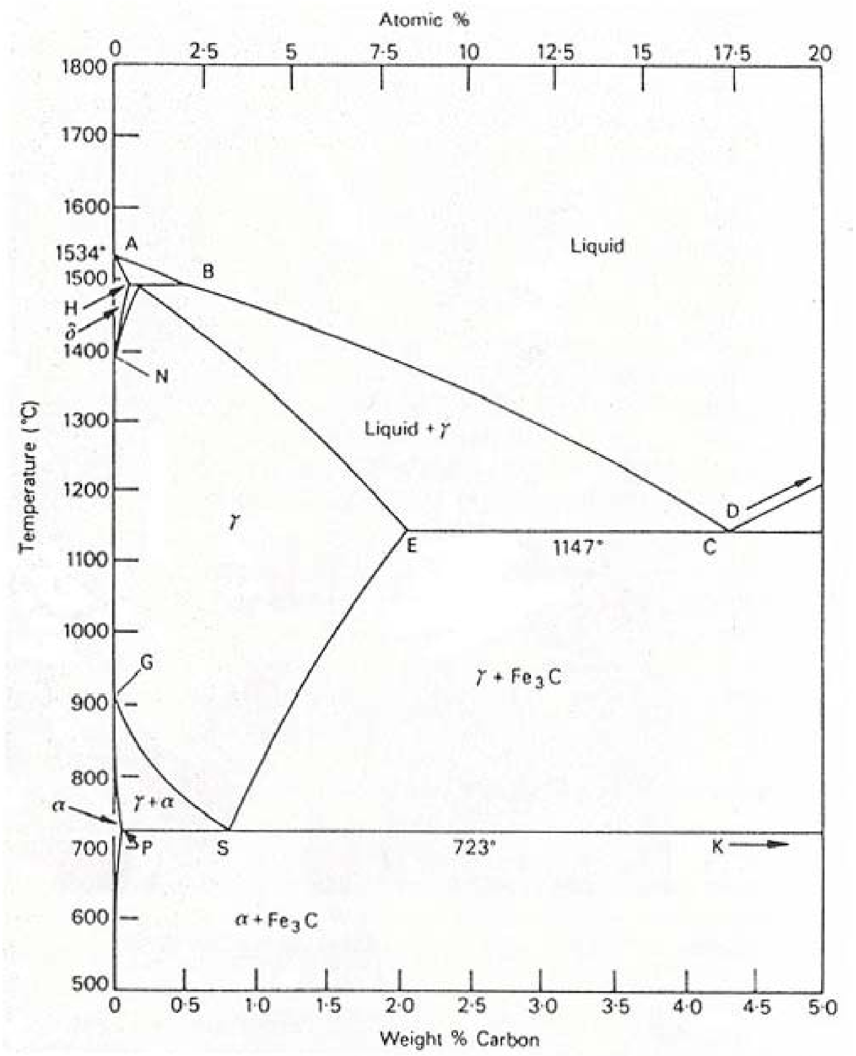


iron-carbon diagram

Phase diagrams



water-surfactant-oil



That’s the base of all modern engineering from swiss knife to food and cosmetics!

iron-carbon diagram

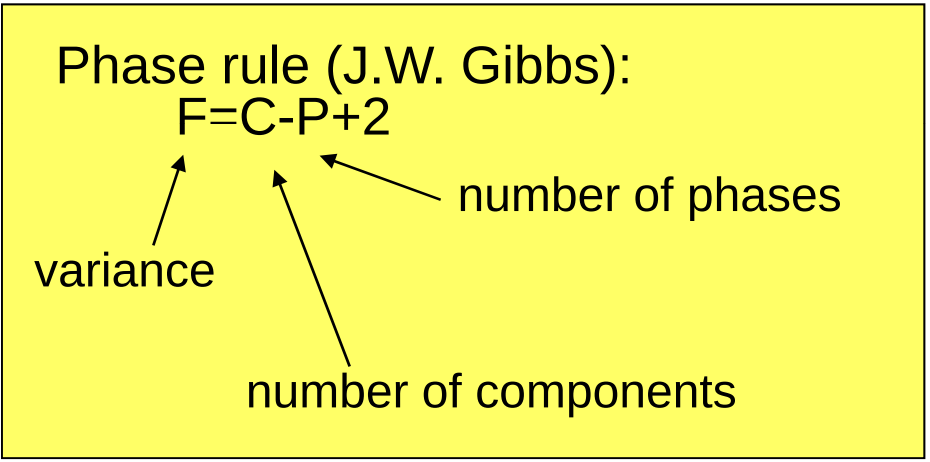
Phase diagrams

- **Constituent** – a chemical species that is present
- **Component** – a **chemically independent** constituent of the system (i.e. not connected by a chemical reaction)

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g) \qquad \underline{C = 2}$$

Phase1 Phase2 Phase3

- **Variance** – the number of intensive variables that can be changed independently without disturbing the number of phases at equilibrium.



- Phase rule (J.W. Gibbs):

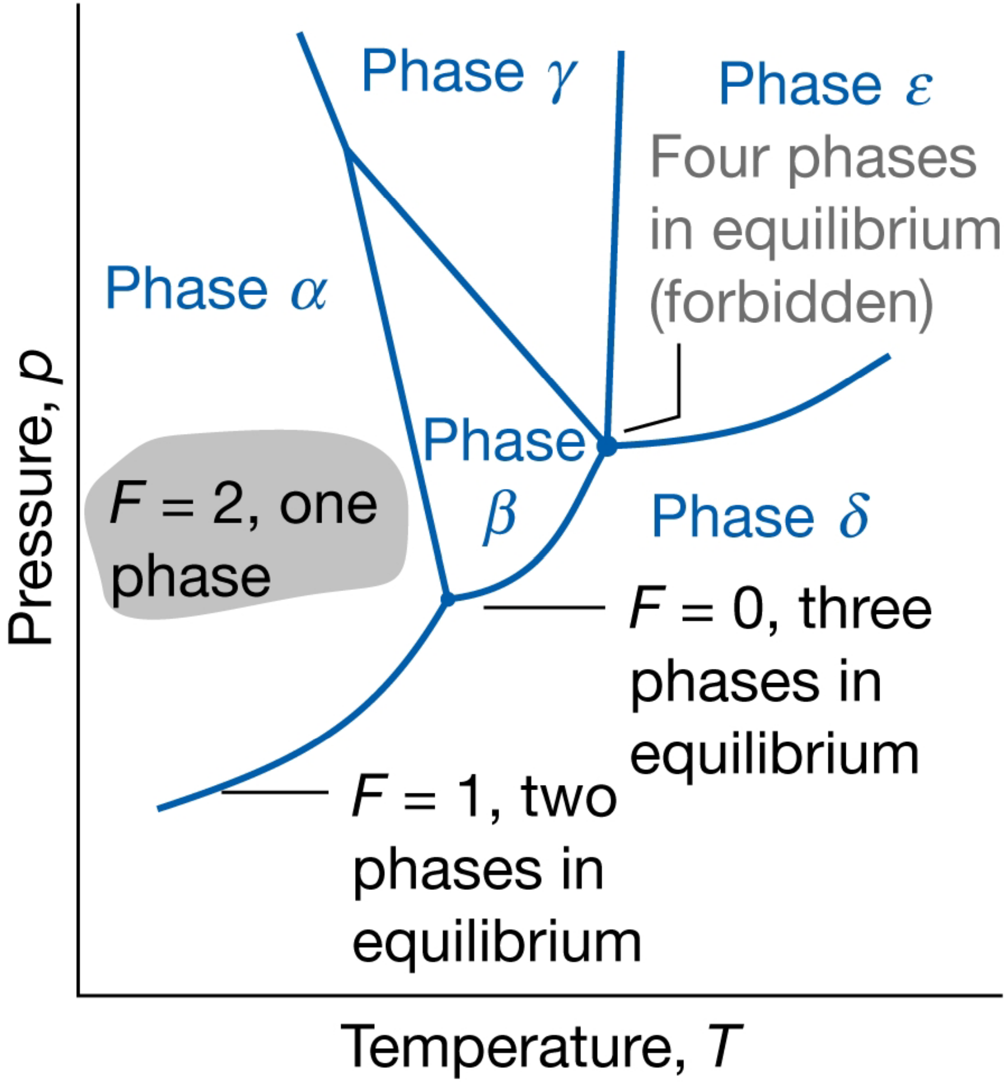
  $F=C-P+2$

Indeed: number of variables would be: $P*(C-1)+2$

number of equations: $C*(P-1)$

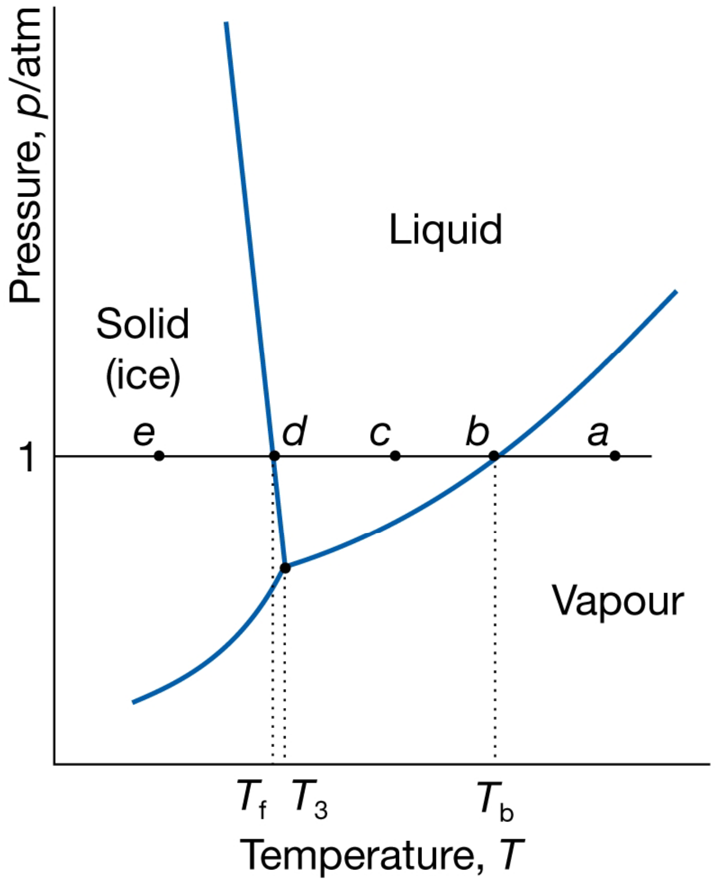
One component diagrams

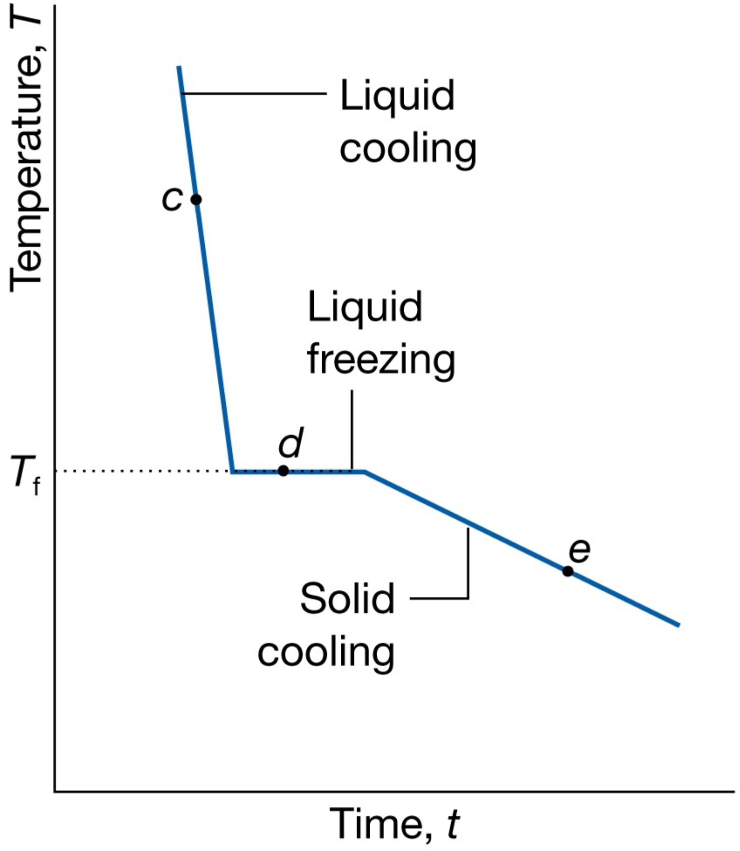
C=1 therefore F=C-P+2=3-P



One component diagrams

Detection of phase transitions and building a phase diagram is based on calorimetry measurements





Two-components diagrams

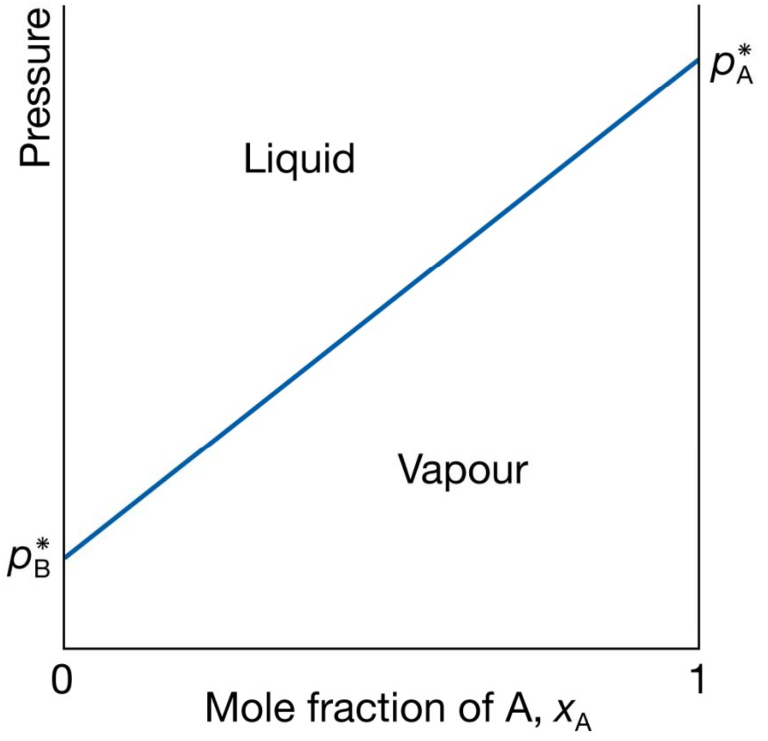
C=2 therefore F=4-P.
We have to reduce degree of freedom e.g. by fixing T=const

- **Vapour pressure diagrams**

Raoult's Law

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

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



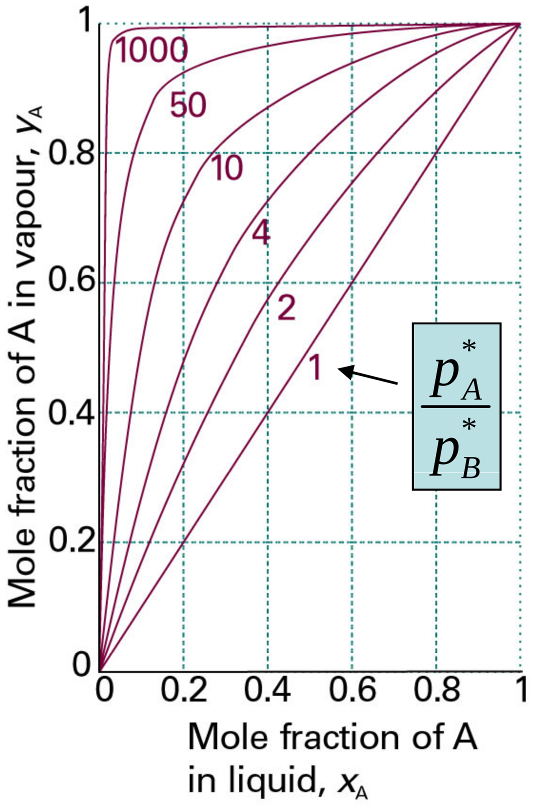
Two-components diagrams

- The composition of vapour

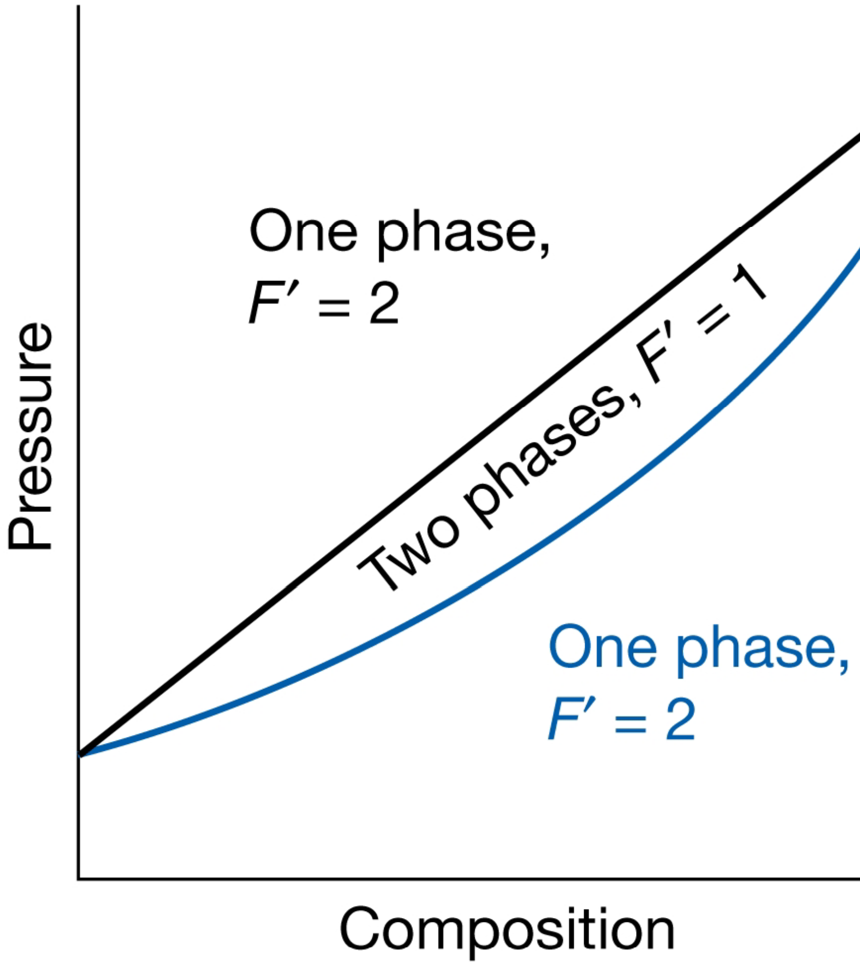
From Dalton's law: $y_A = \frac{p_A}{p}; \qquad y_B = \frac{p_B}{p}$

From Raoult's law: $p_A = x_A p_A{*}; \qquad p_B = x_B p_B{*}$

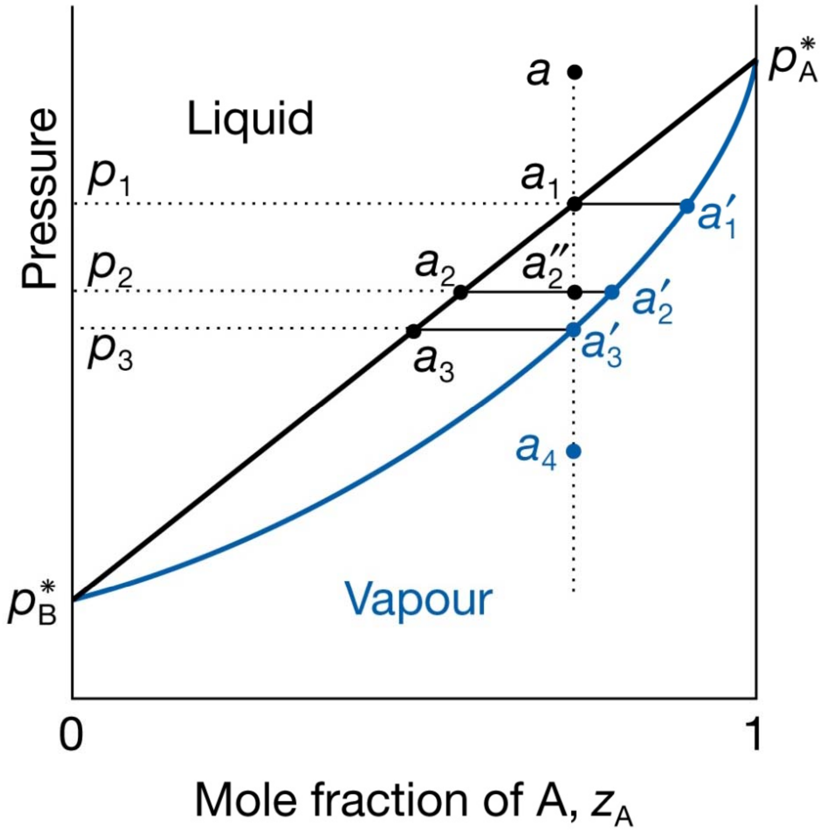
$$y_A = \frac{p_A{*}}{p_B{*} + (p_A{*} - p_B{*})x_A}; \qquad y_B = 1 - y_A$$

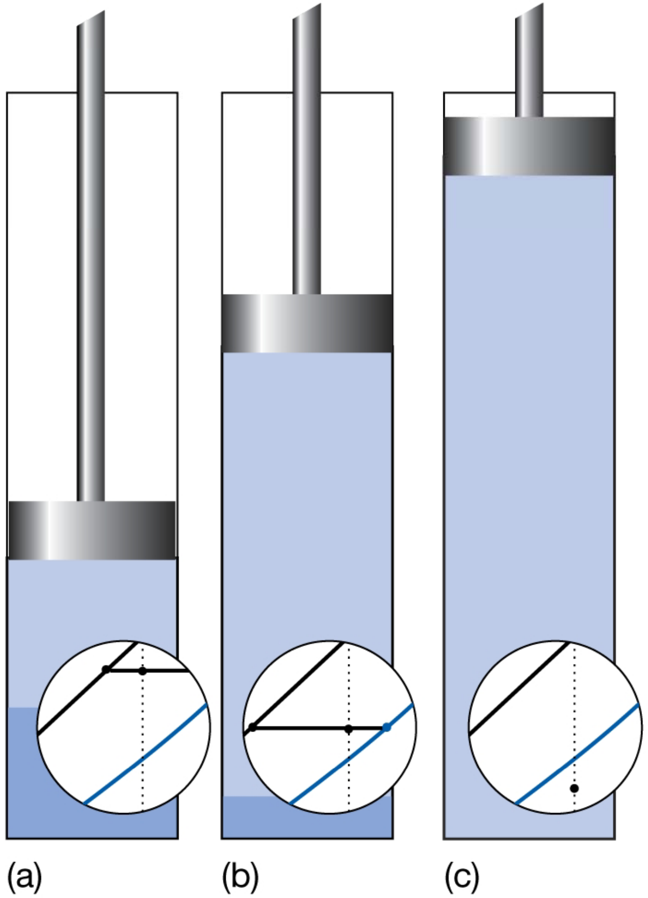


Two components diagrams



Two components diagrams

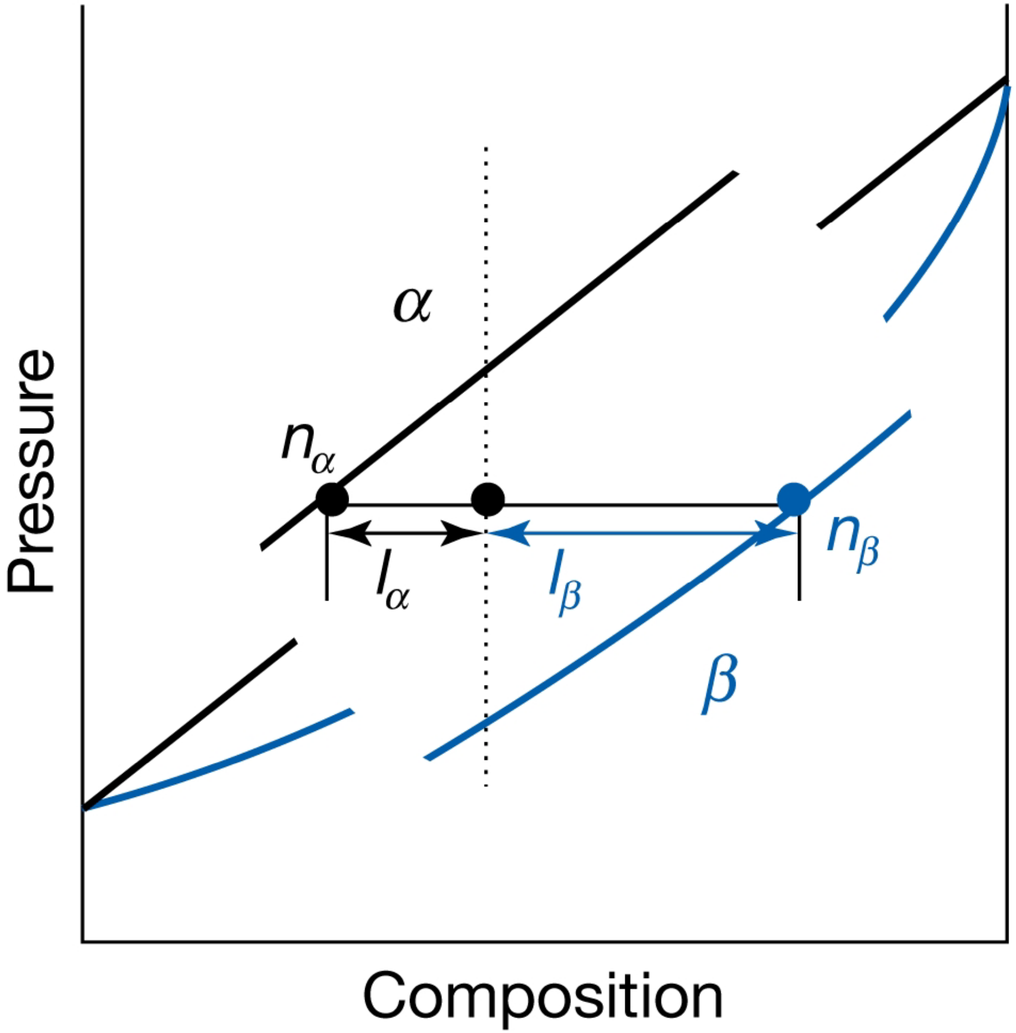




Two components diagrams

The lever rule

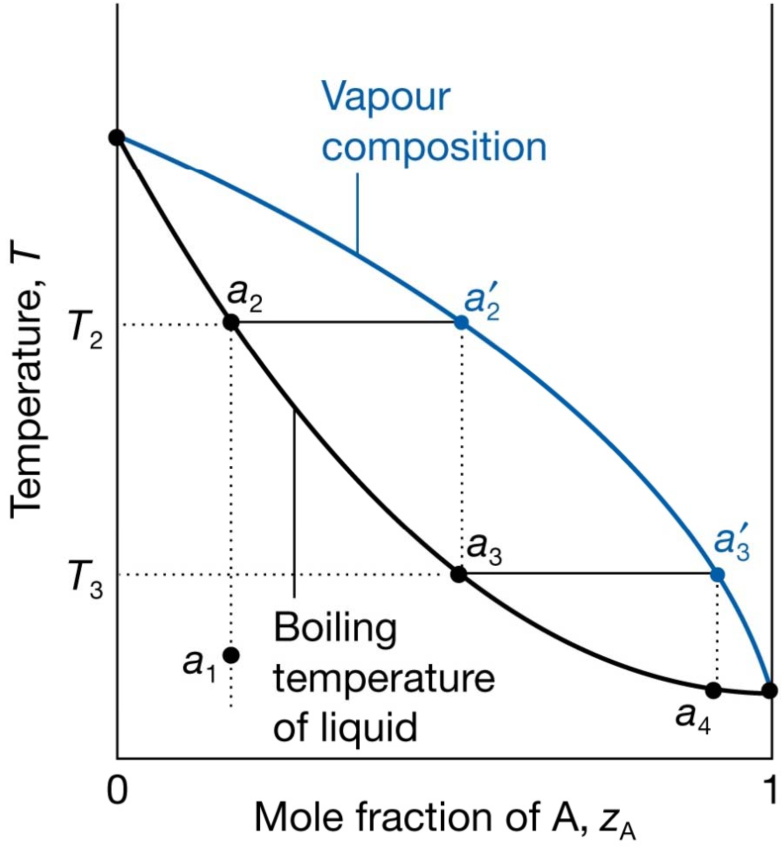
$$n_\alpha l_\alpha = n_\beta l_\beta$$

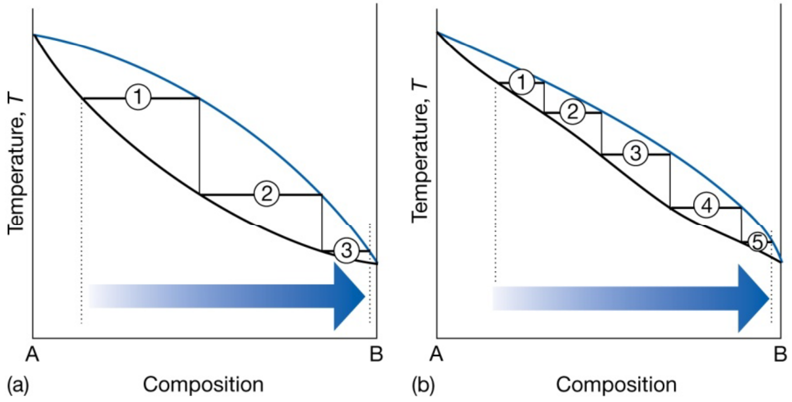


Two-components diagrams

Temperature-composition diagrams

- **Distillation of mixtures**



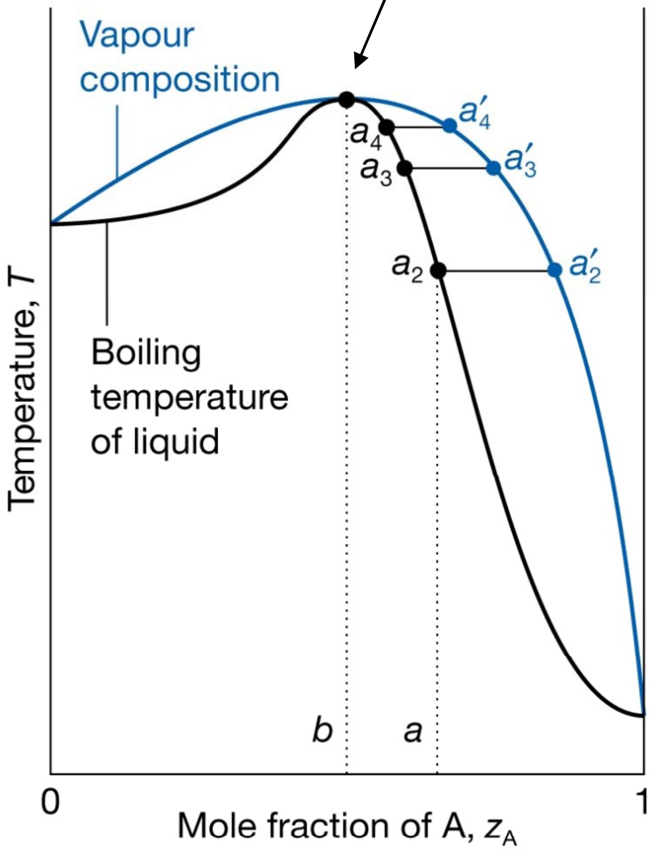


Two-components diagrams

Temperature-composition diagrams

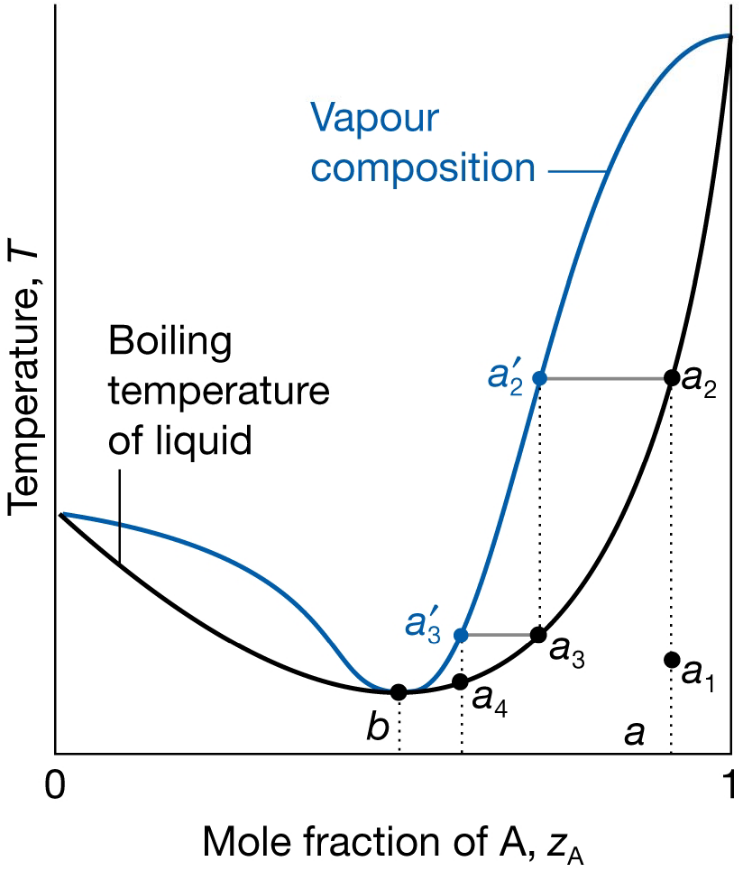
- **Azeotropes**

Azeotrope, evaporation w/o change in composition



A-B interacation stabilize the mixture

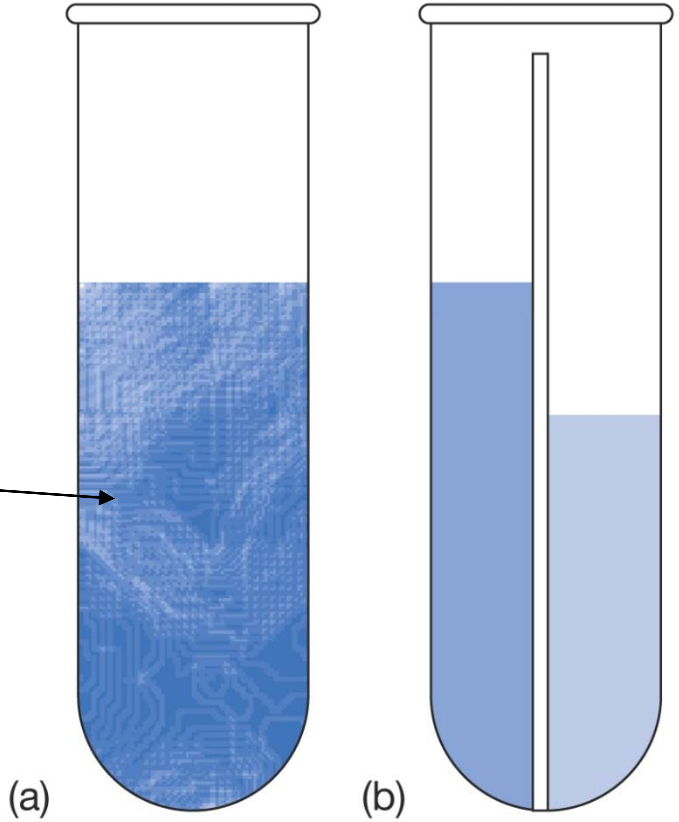
$n_\alpha l_\alpha$



A-B interacation destabilize the mixture

Two components diagrams

- Immiscible liquids

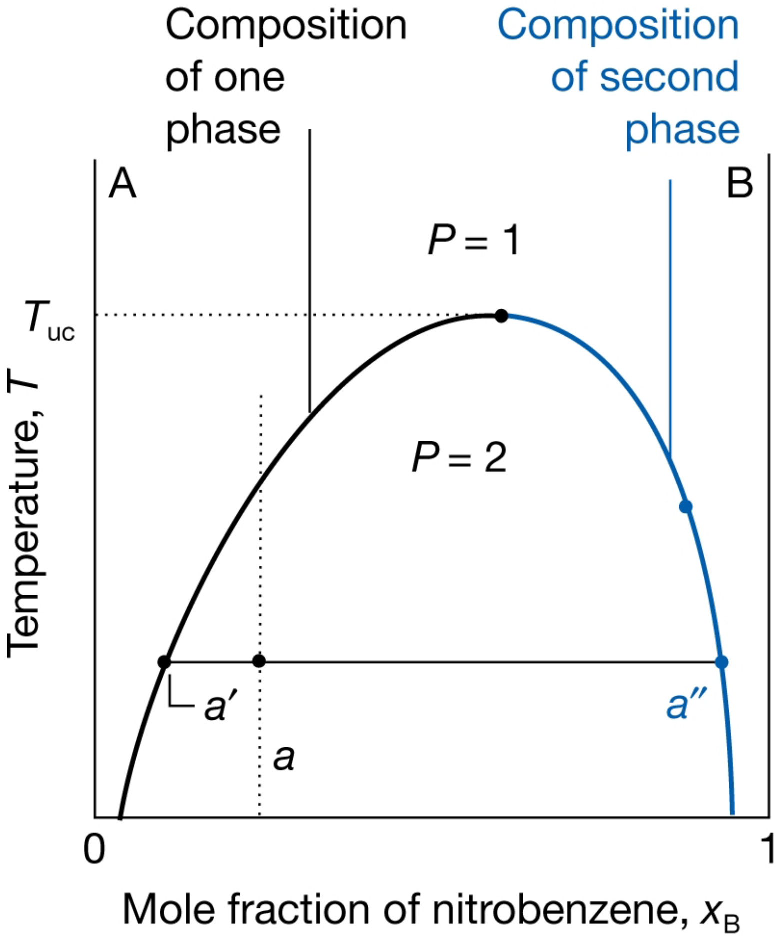


Will boil at lower temperature!

$$p = p_A + p_B$$

Two components diagrams

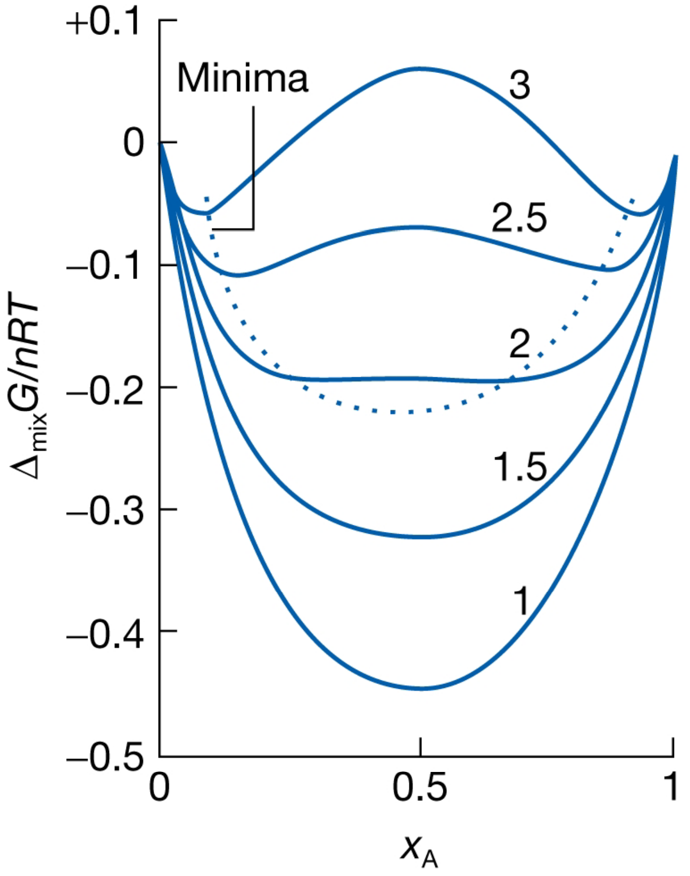
- Liquid-liquid phase diagrams

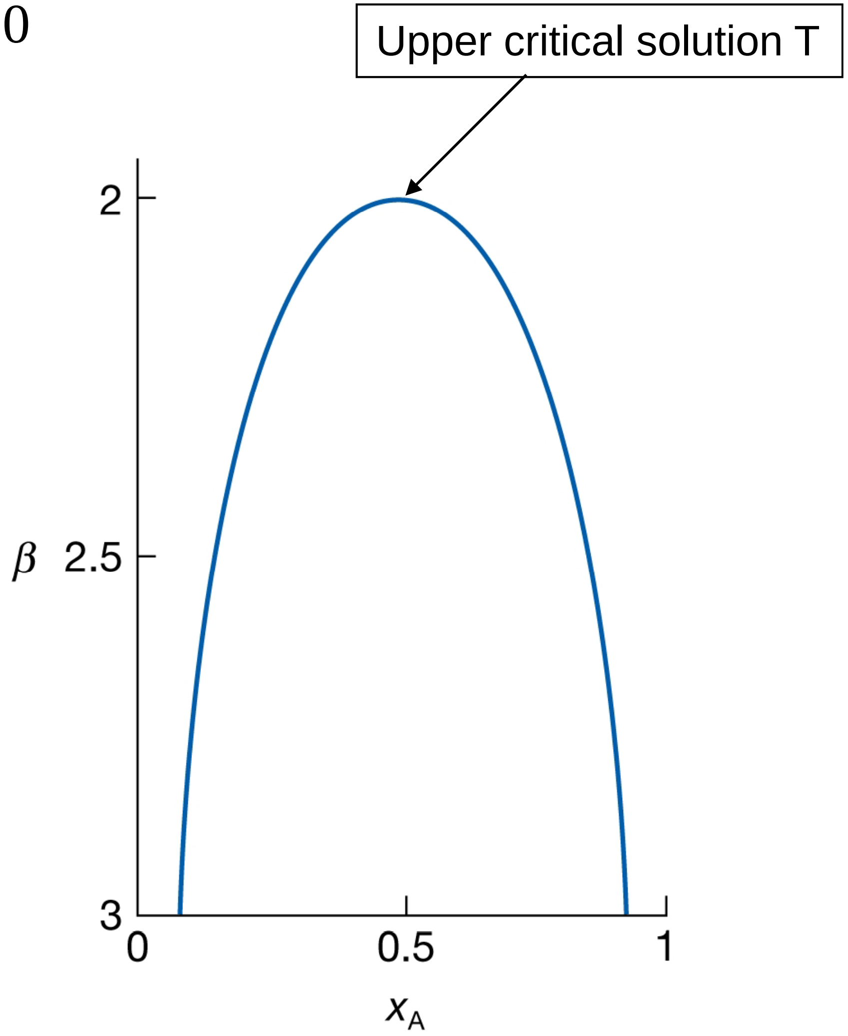


Two components diagrams

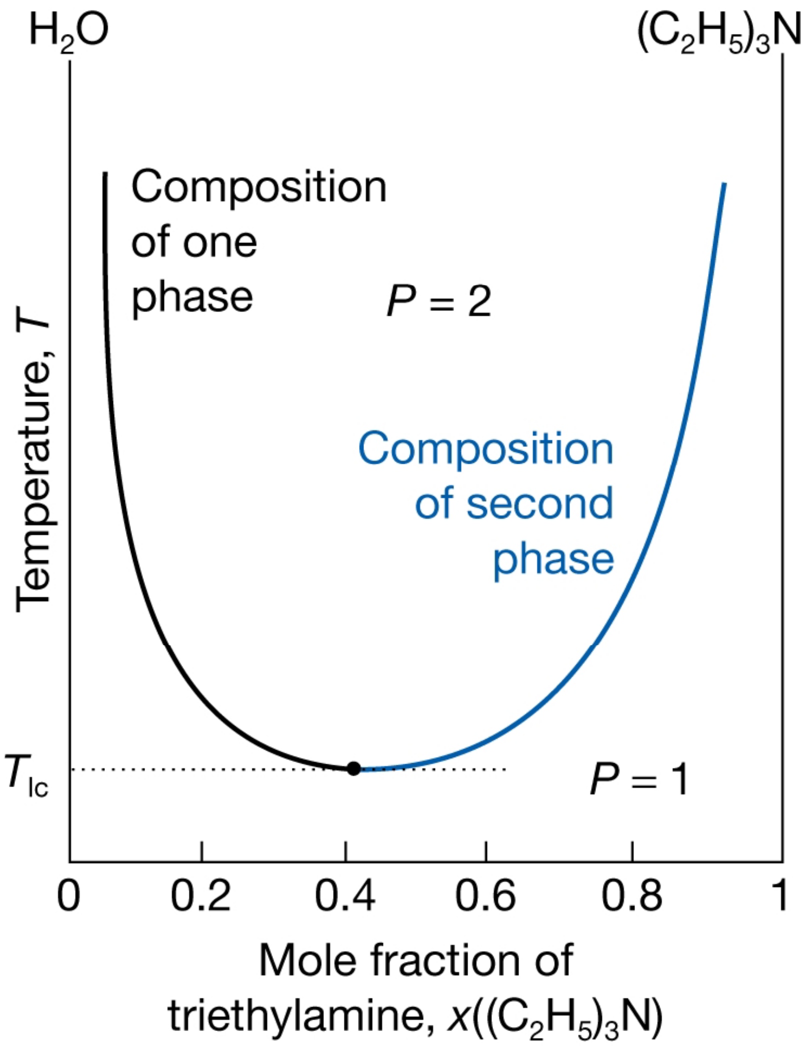
$$\Delta_{mix}G = nRT(\kappa_A \ln \kappa_A + \kappa_B \ln \kappa_B + \beta \kappa_A \kappa_B)$$

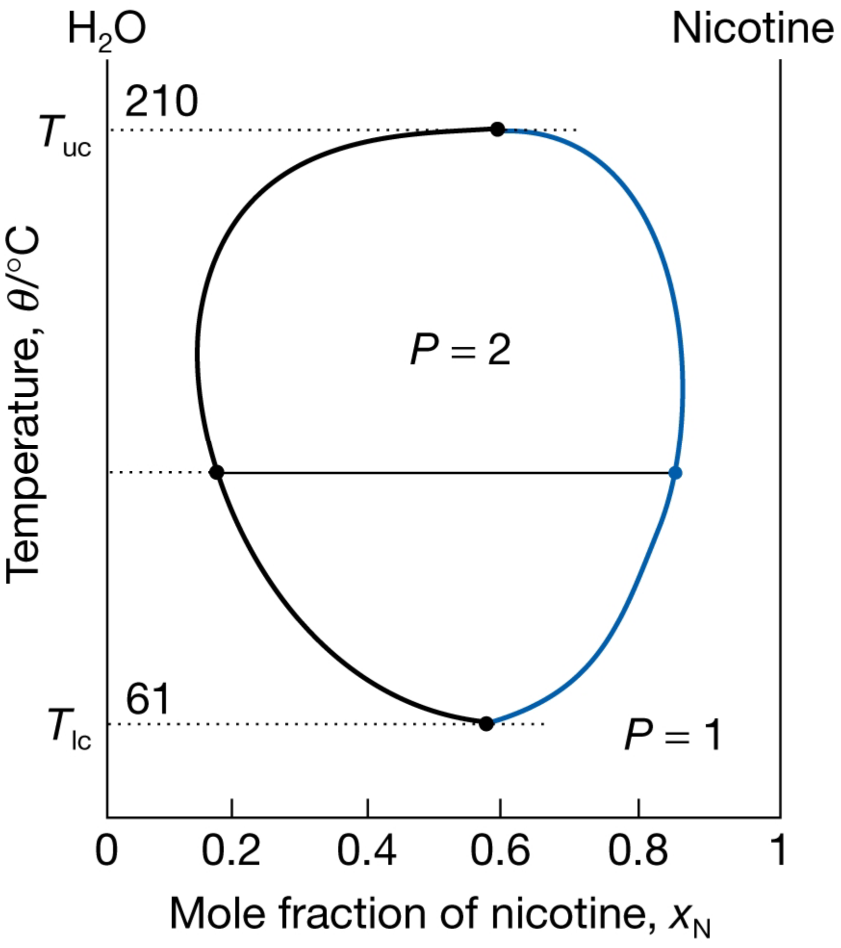
$$\frac{\partial}{\partial \kappa}\Delta_{mix}G = 0 \quad \ln \frac{\kappa}{1-\kappa} + \beta(1-2\kappa) = 0$$




Upper critical solution T

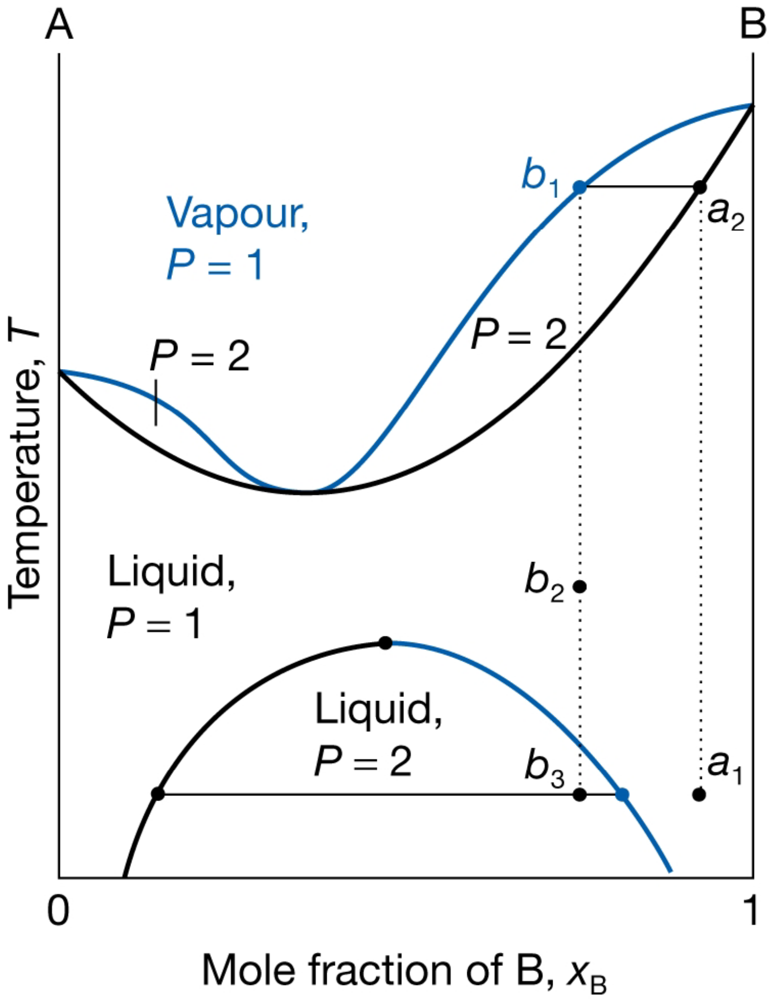
Two components diagrams



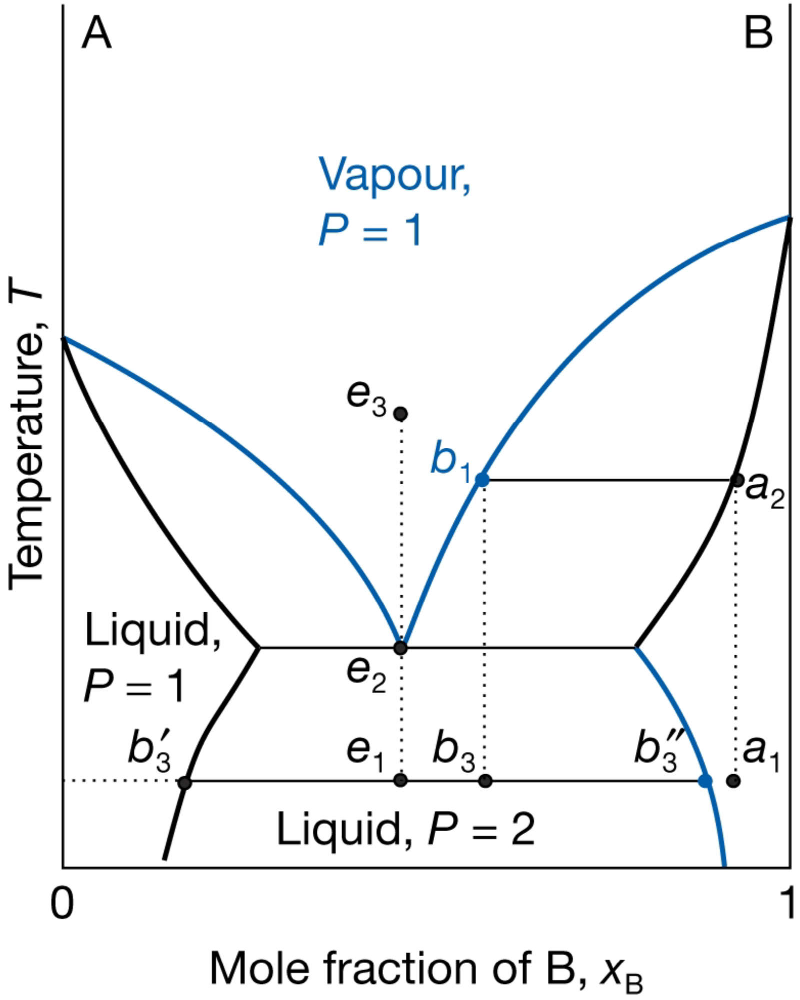


Lower critical temperature is usually caused by breaking a weak complex of two components

Two components diagrams

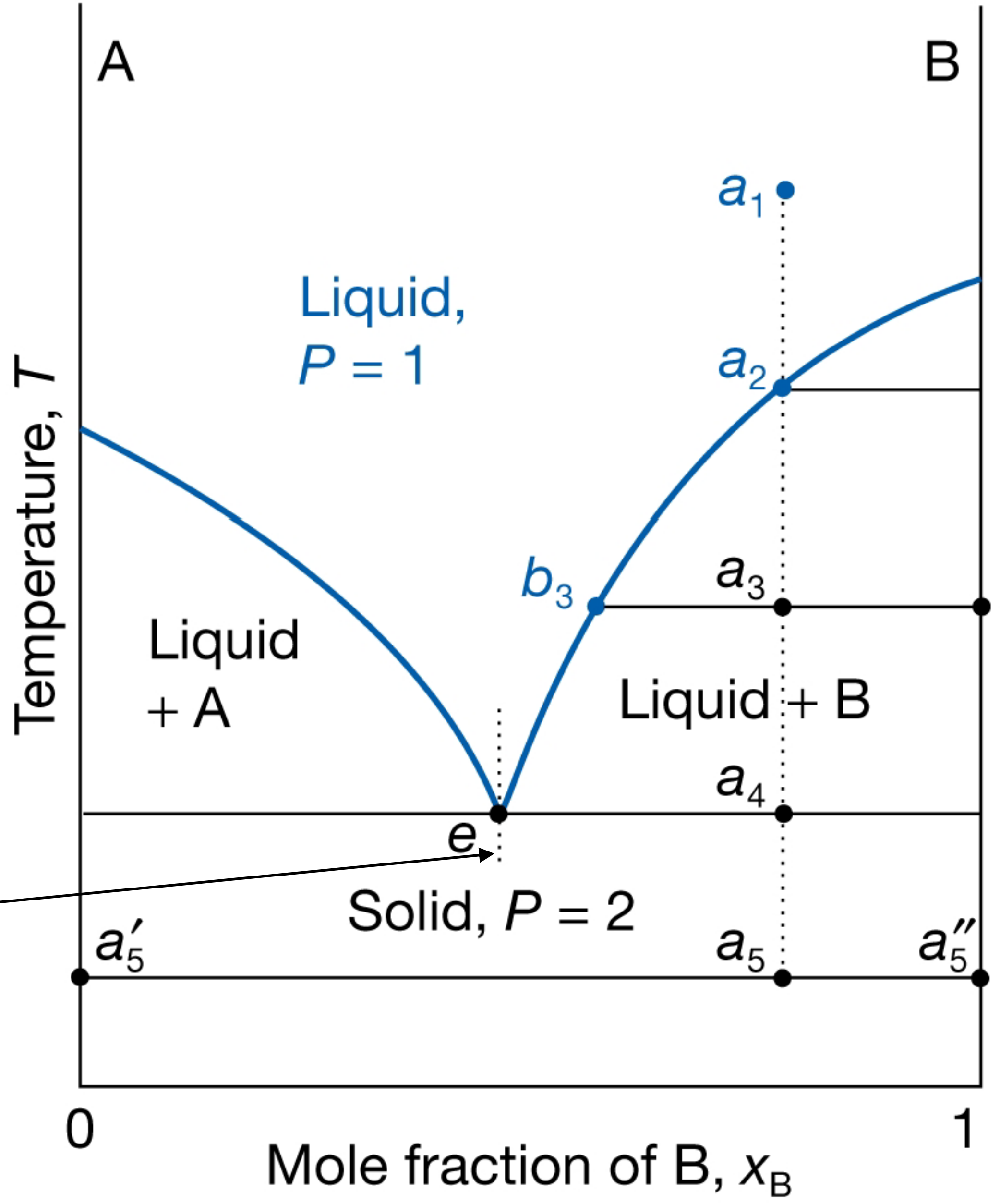


Upper critical temperature is less than the boiling point



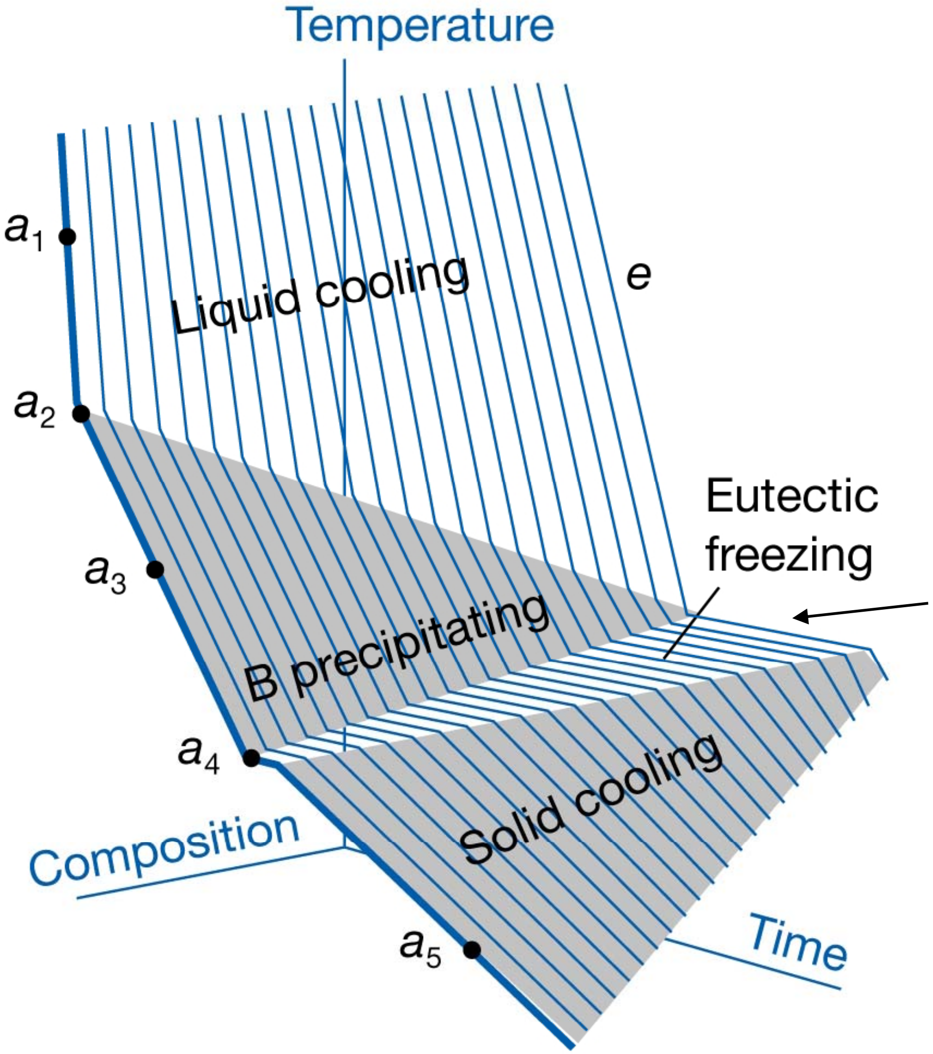
Boiling occur before liquids are fully miscible

Liquid-solid phase diagrams

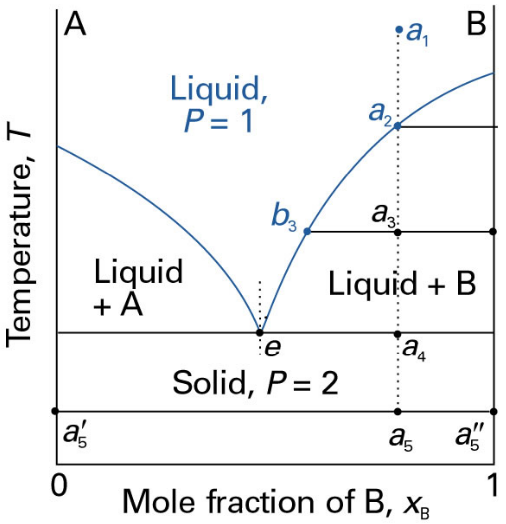


Eutectic composition

Liquid-solid phase diagrams

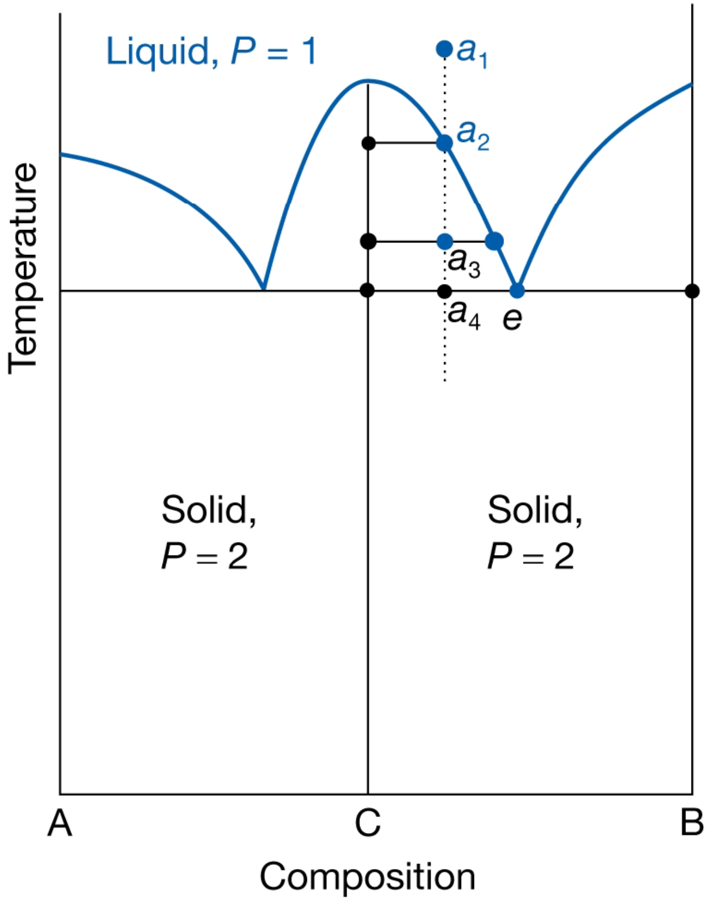


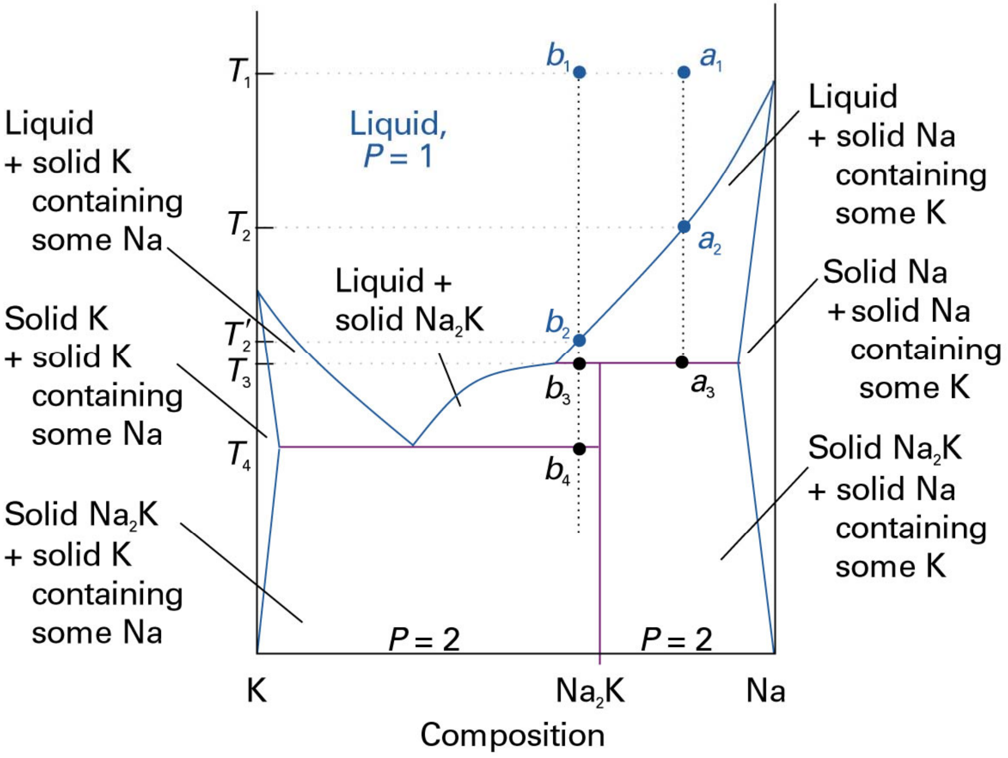
Eutectic halt



Liquid-solid phase diagrams

- Reacting systems



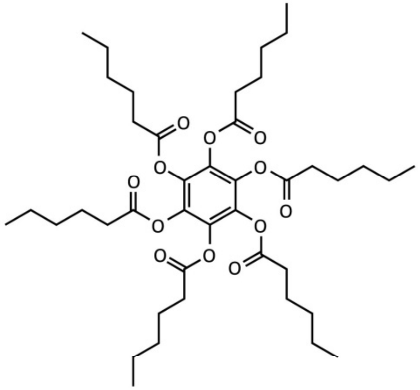


<u>Incongruent melting</u>: compounds melts into components

Liquid crystals

- Mesophase – an intermedediate phase between solid and liquid. Example: liquid crystal
- Liquid crystal – substance having a liquid-like imperfect order in at least one direction and long-range positional or orientational order in at least on another direction

1



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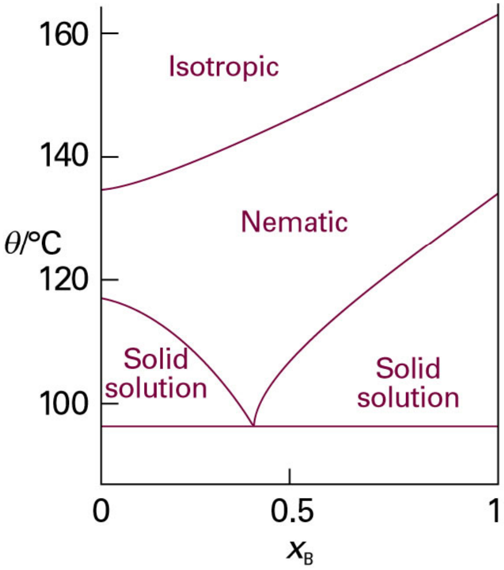
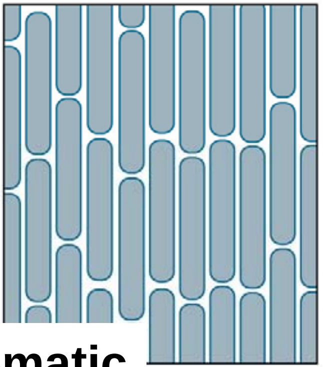
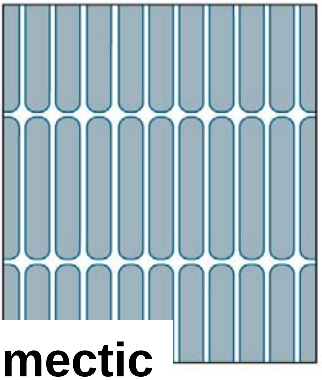




Nematic



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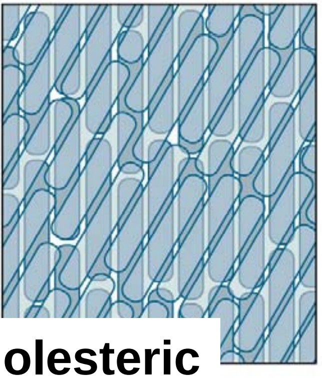
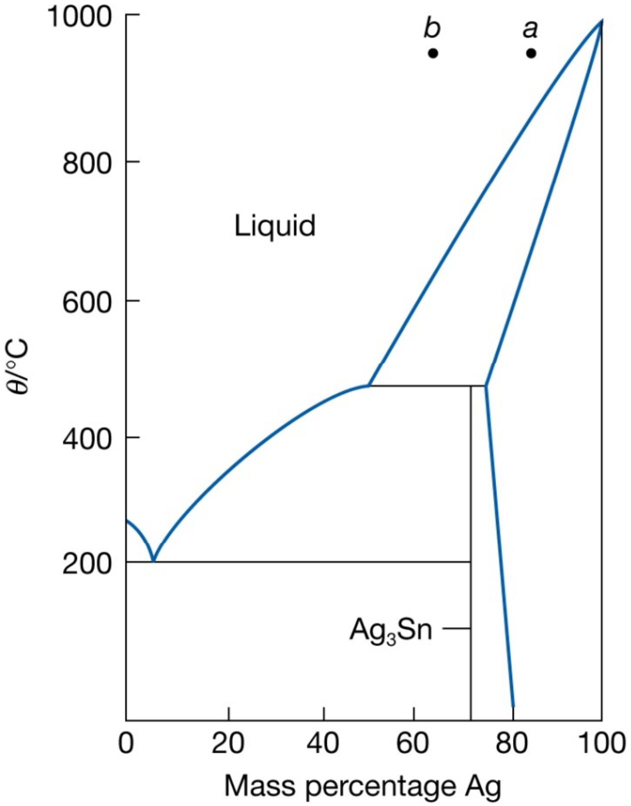


Cholesteric

Problems (to solve in the class)



- **5.20(a)** Estimate the mean ionic activity coefficient and activity of a solution that is 0.010 mol kg^{-1} $CaCl_2$(aq) and 0.030 mol kg^{-1} NaF(aq).
- **6.1a:** At 90ºC the vapour pressure of methylbenzene is 53.3kPa and that of 1.2-dimethylbenzene is 20kPa. What is the composition of a liquid mixture that boils at 90ºC when the pressure is 0.5 atm. What is the composition of the vapour produced. down
- **6.9b**: sketch the phase diagram of the system NH_3/N_2H_4 given that the two substances do not form a compound and NH_3 freezes at -78C, N_2H_4 freezes at +2C, eutectic formed with mole fraction of N_2H_4 0.07 and melts at -80C.
- **6.10b** Describe the diagram and what is observed when **a** and **b** are cooled down

Assignment problems III

- **E6.4b** Benzene and toluene form nearly ideal solutions. Consider equimolar solution of benzene and toluene. At 20°C the vapour pressures of pure benzene and toluene are 9.9kPa and 2.9kPa, respectively. The solution is boiled by reducing the external pressure below the vapour pressure. Calculate:
  (a) the pressure when the boiling begins;
  (b) the composition of vapour
  (c) the vapour pressure when only few drops of liquid remain. Assume that the temperature remain constant at 20°C.

- **P6.6** Consider the phase diagram which represents a solid-liquid equilibrium.
  (a) Label all regions off the diagram according to the chemical species that exist in that region and their phases.
  (b) Indicate the number of species and phases present at the points **b,d,e,f,g,k**;
  (c) Sketch cooling curves for compositions x_b=0.16, 0.23, 0.57, 0.67 and 0.84.