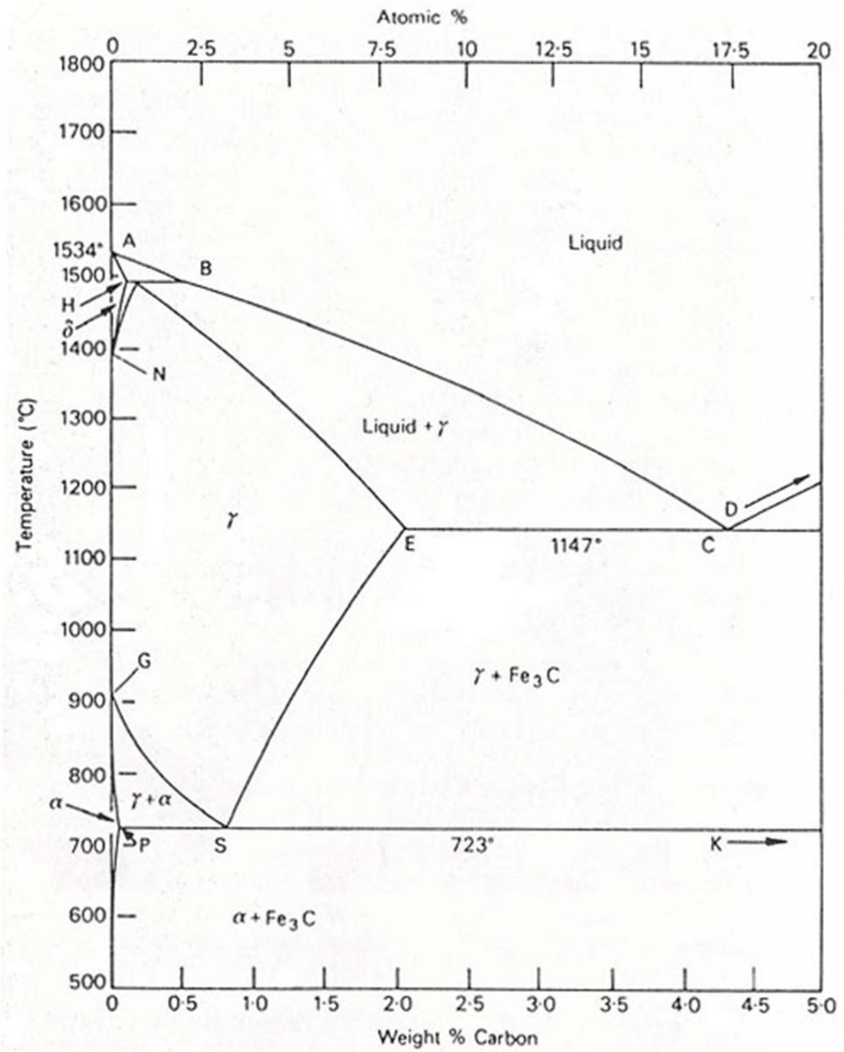
# Lecture 3: Solutions: Activities and Phase Diagrams

*21-09-2010*

- Lecture plan:
  - Gibbs phase rule
  - vapour composition
  - two-component phase diagrams
  - phase diagrams in material science:
    - microstructures in isomorphous binary systems
    - microstructures in eutectic alloys
    - liquid crystals
  - problems

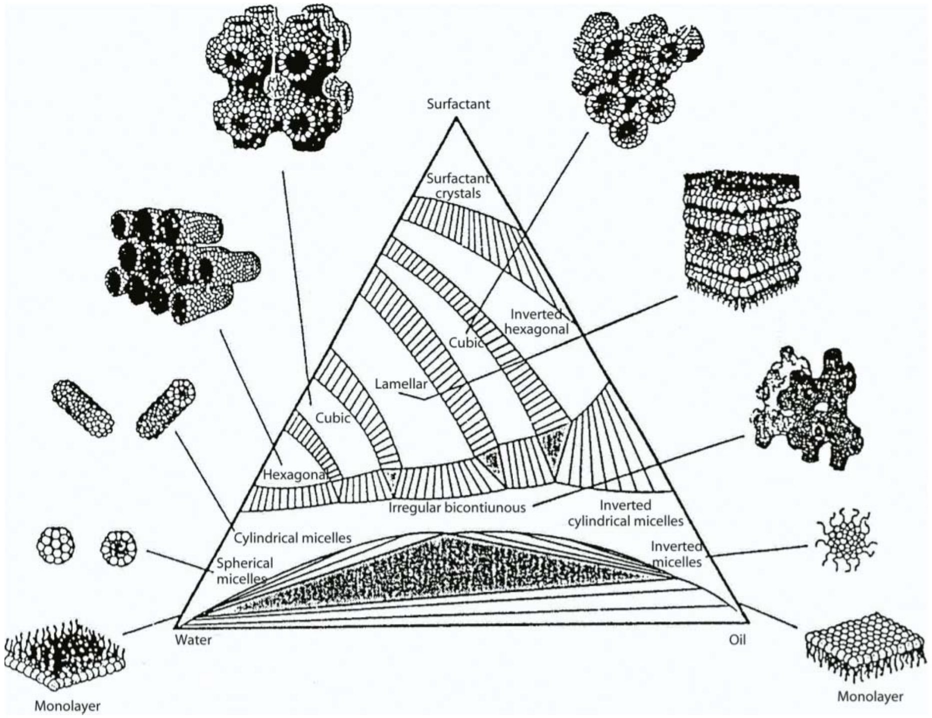
# Phase diagrams

- 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

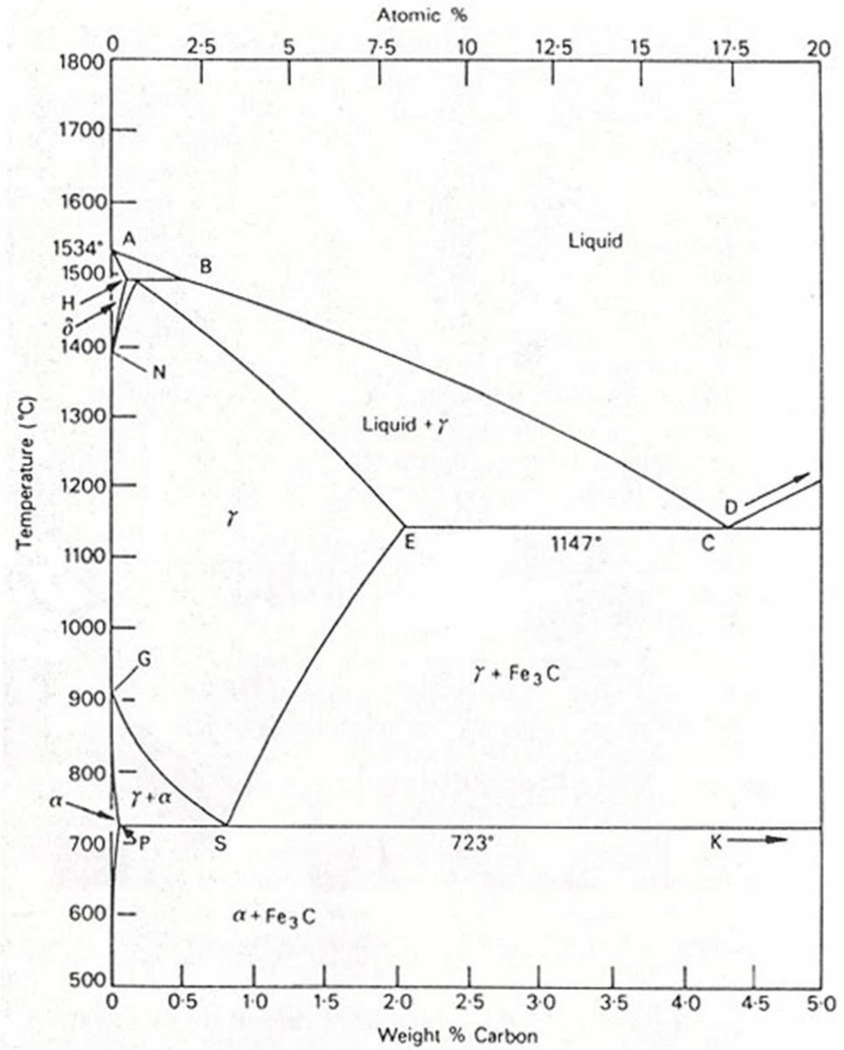



**iron-carbon diagram**

# Phase diagrams




**water-surfactant-oil**




**iron-carbon diagram**

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

# 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)

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

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

  number of phases

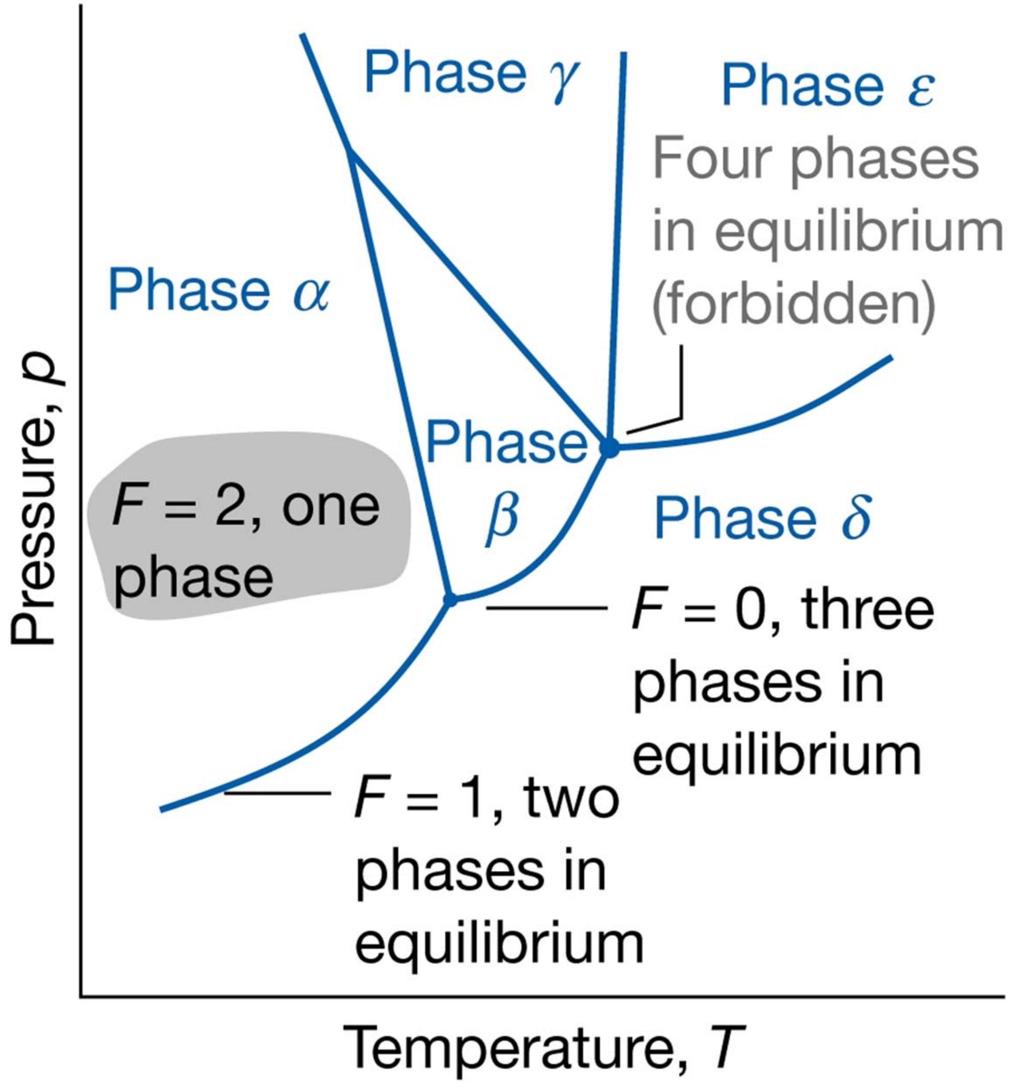
  variance

  number of components

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

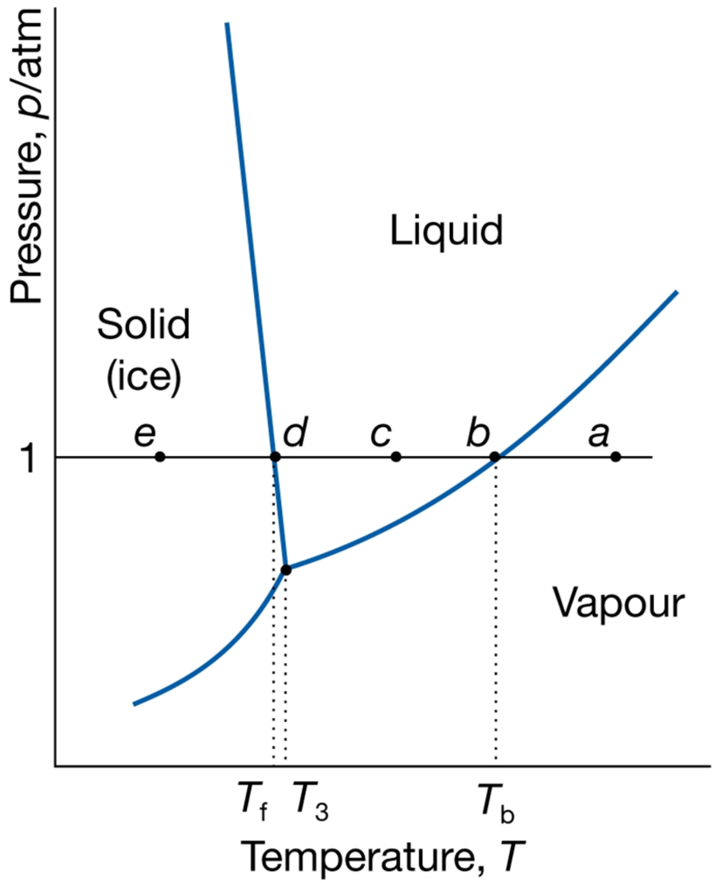
# One component diagrams

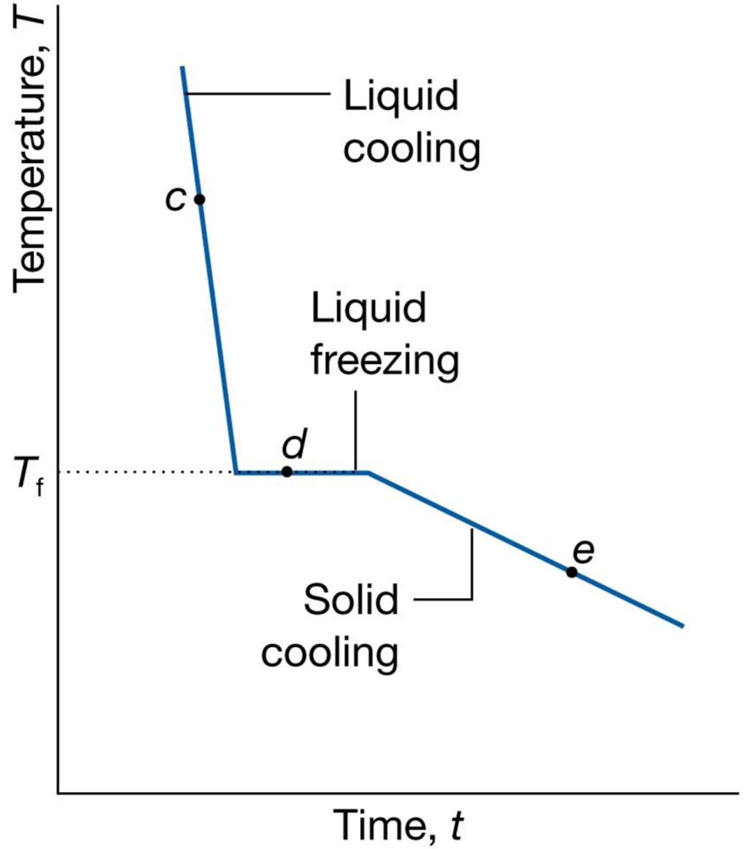
C=1 therefore F=C-P+2=3-P



# One component diagrams

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



# Two-components diagrams

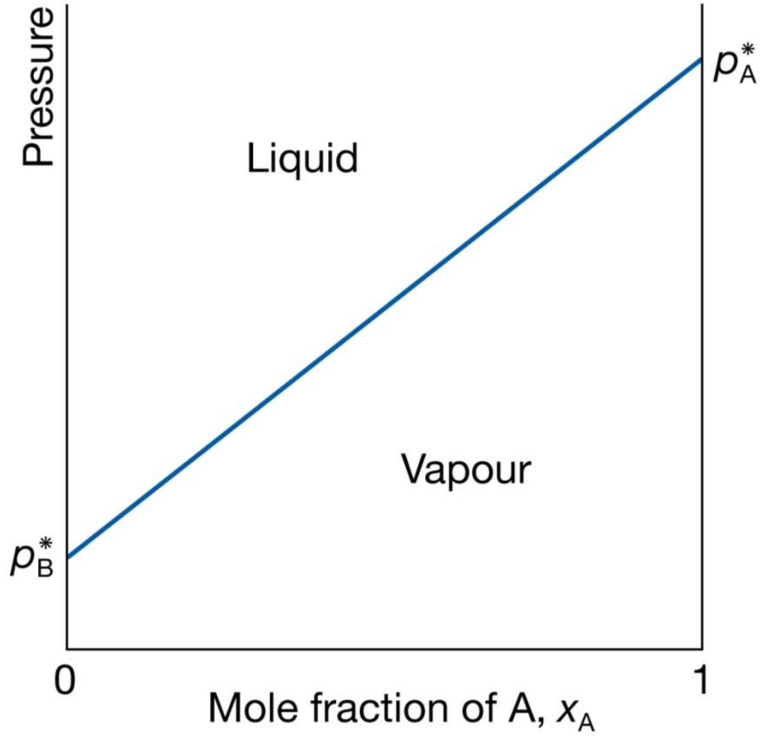
C=2 therefore F=4-P.
We have to reduce degree of freedom e.g. by fixing T=const

- **Vapour pressure diagrams**

Raoult's Law

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

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



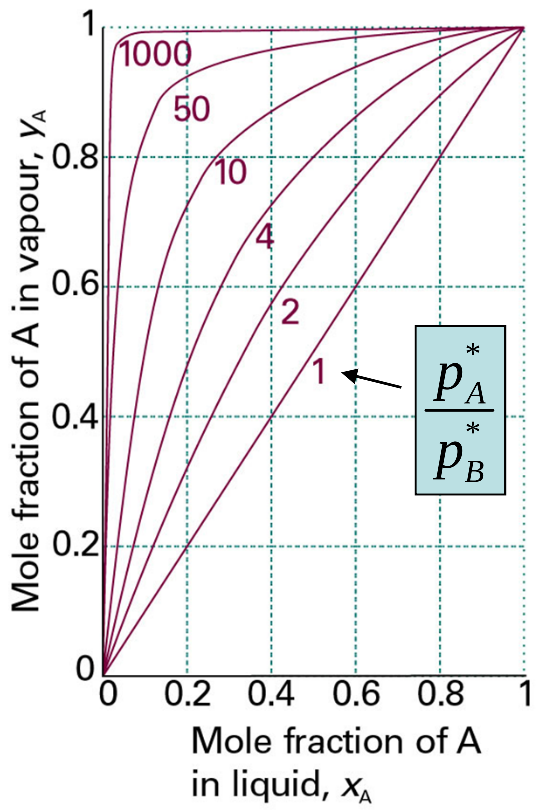
# Two-components diagrams

- The composition of vapour

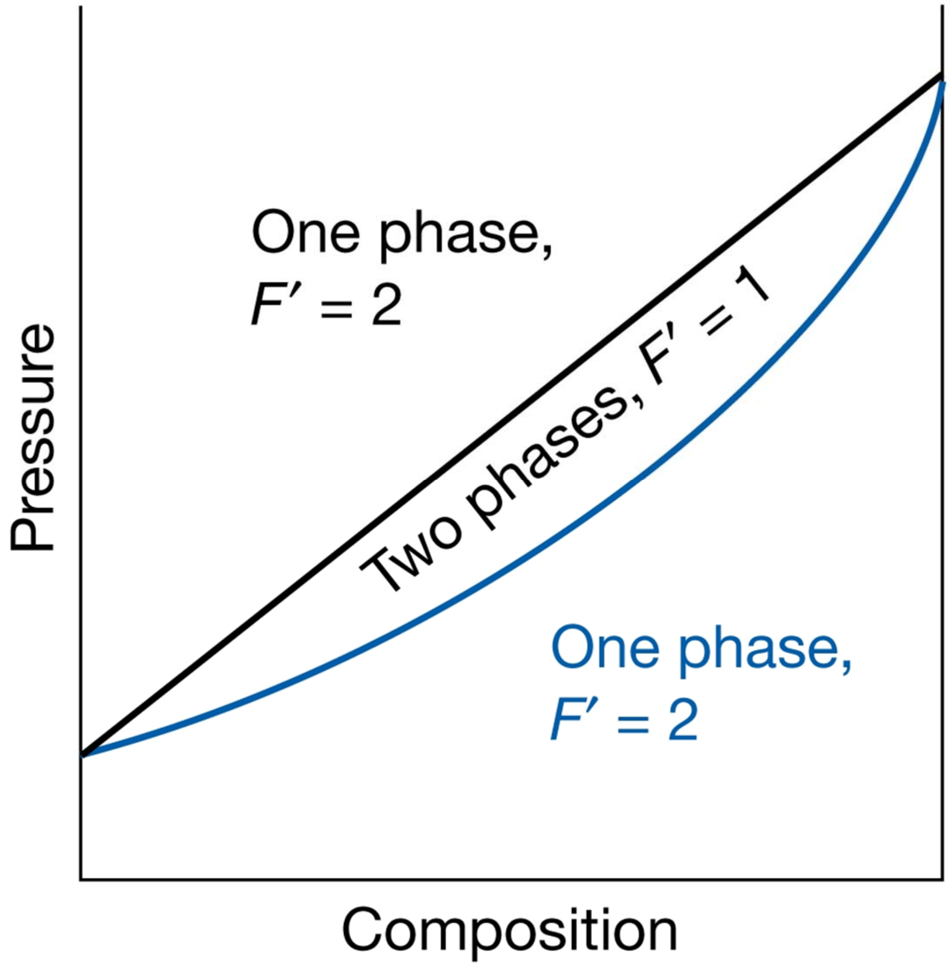
From Dalton's law: $y_A = \dfrac{p_A}{p}$; $\quad y_B = \dfrac{p_B}{p}$

From Raoult's law: $p_A = x_A p_A*$; $\quad p_B = x_B p_B*$

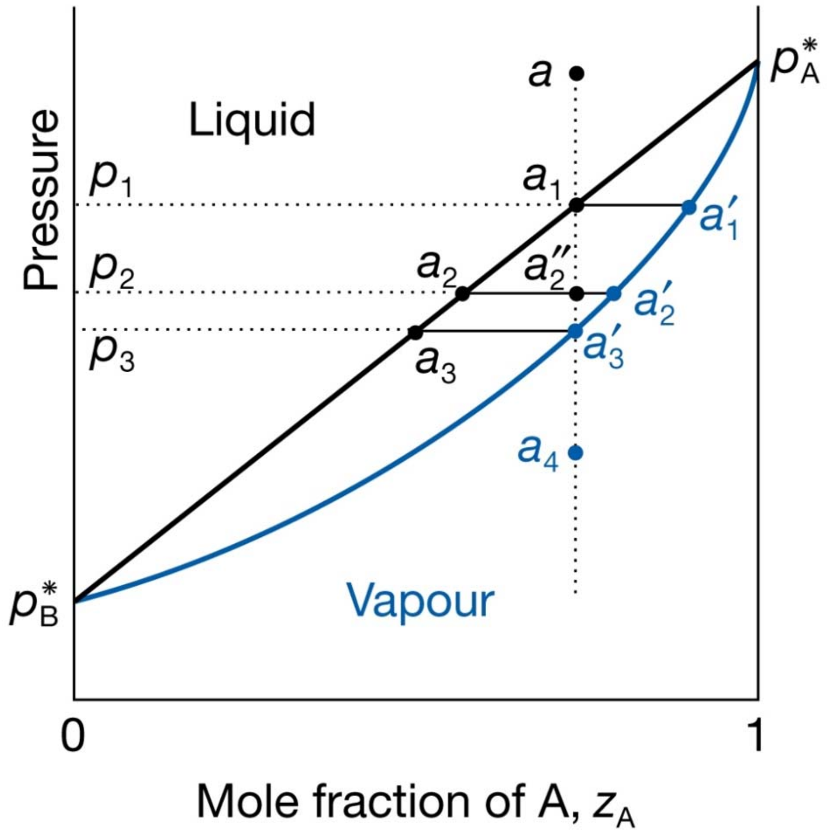
$$y_A = \frac{p_A*}{p_B*+(p_A*-p_B*)x_A}; \qquad y_B = 1 - y_A$$

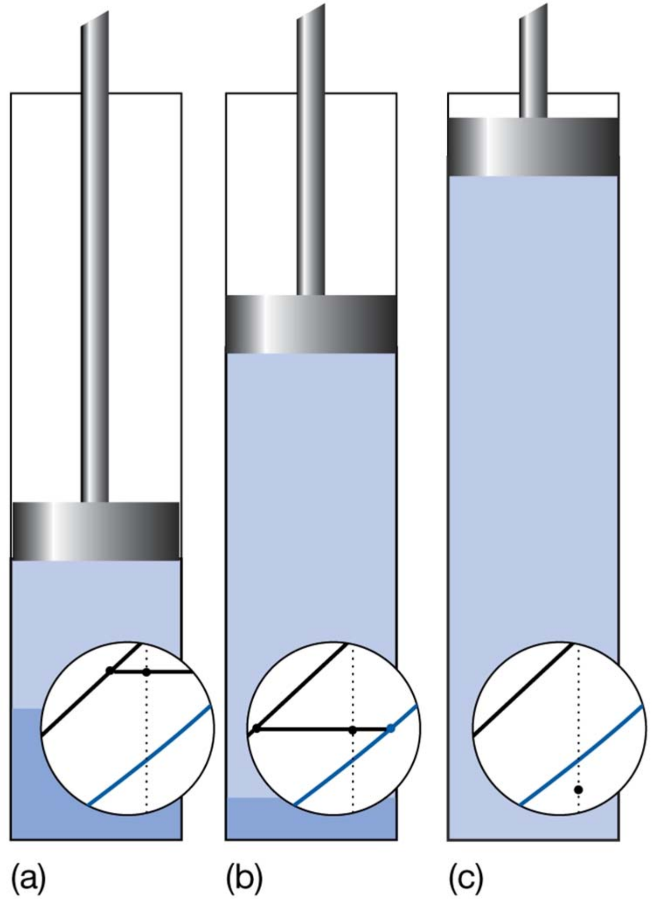


# Two components diagrams



# Two components diagrams



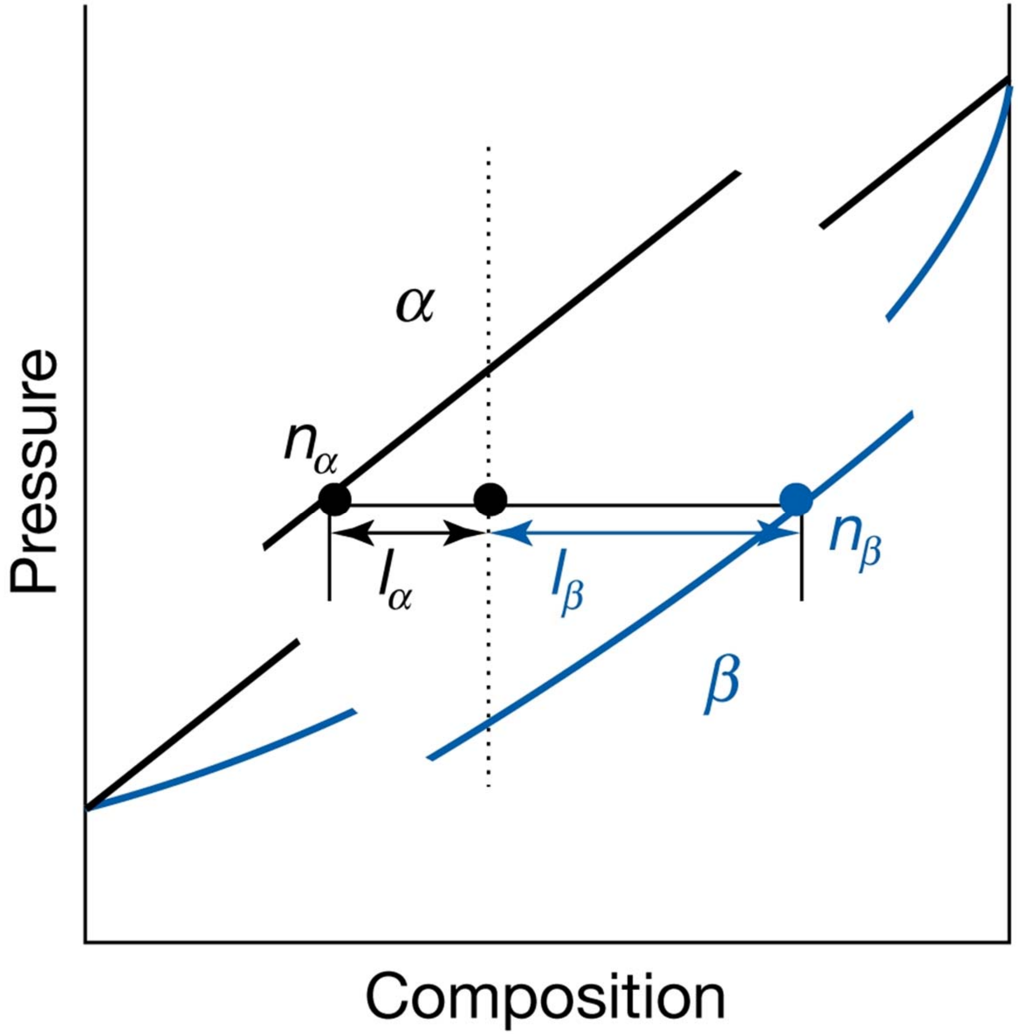



# Two components diagrams

Relative amount and the composition of phases in equilibrium can be found on the phase diagram

**The lever rule**

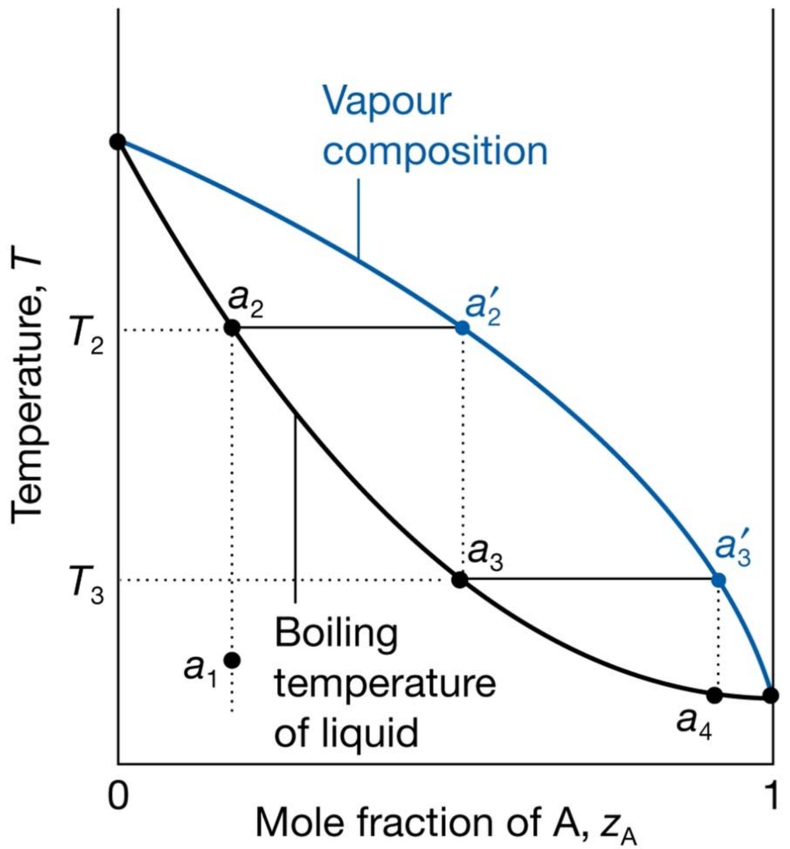
$$n_\alpha l_\alpha = n_\beta l_\beta$$



# Two-components diagrams

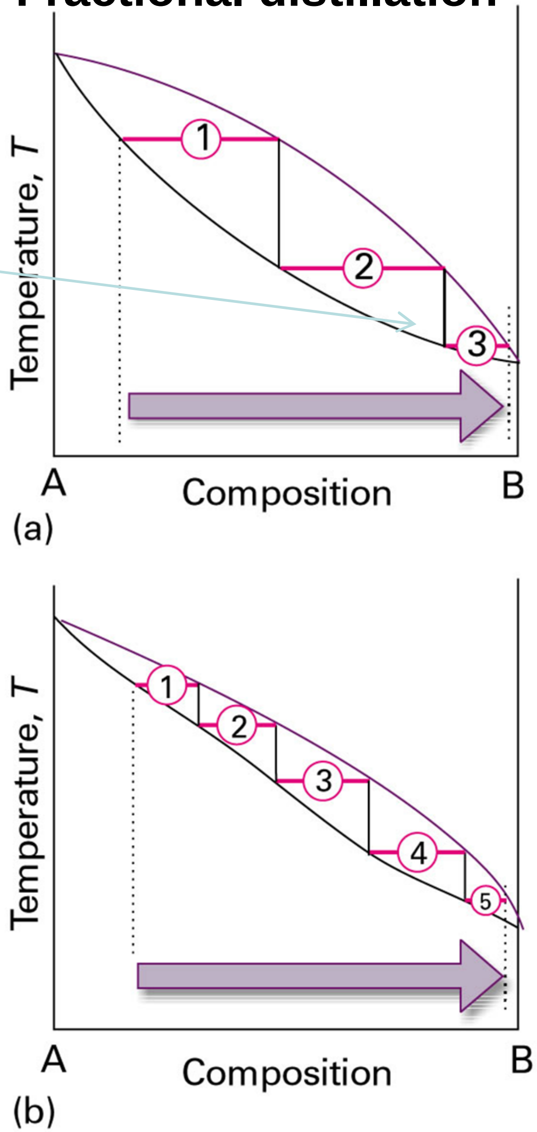
## Temperature-composition diagrams

- **Distillation of mixtures**




**Fractional distillation**

number of theoretical plates

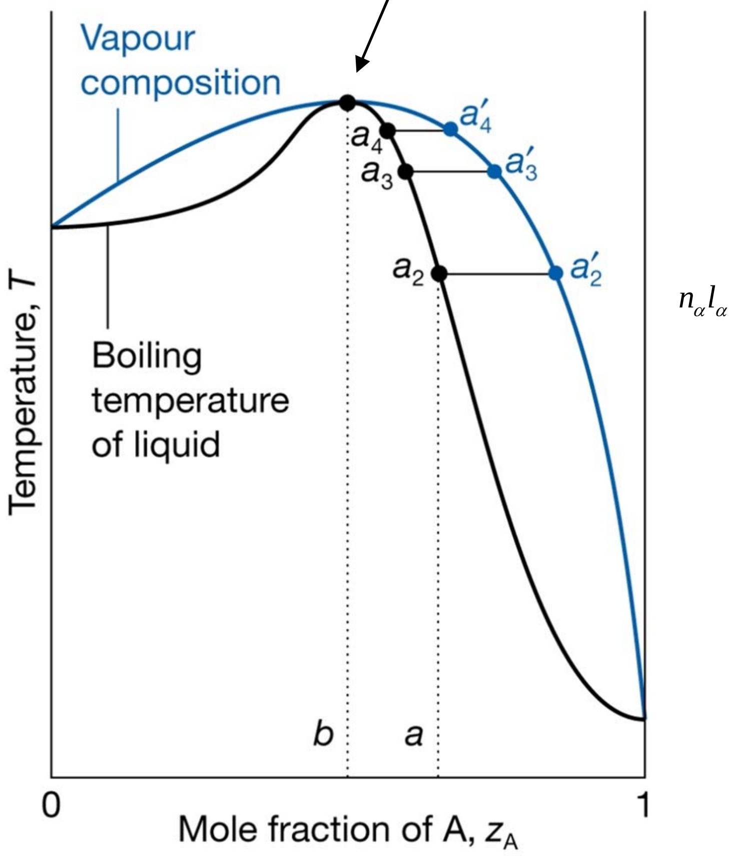


# Two-components diagrams

## Temperature-composition diagrams

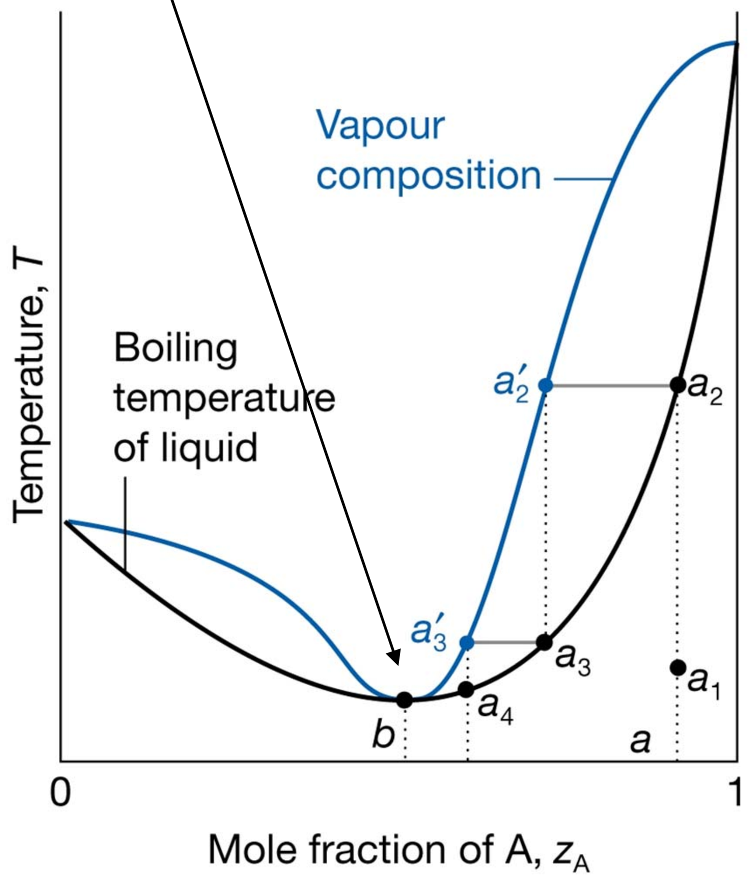
- **Azeotropes**

Azeotrope, evaporation w/o change in composition




A-B interacation stabilize the mixture

$n_\alpha l_\alpha$




A-B interacation destabilize the mixture

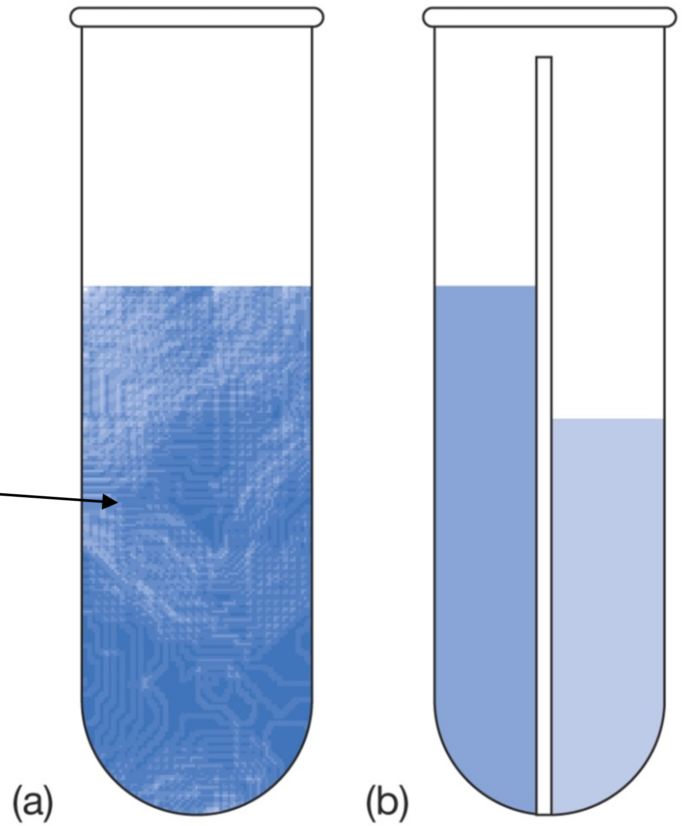
# Two components diagrams

- Immiscible liquids

Will boil at lower temperature!

boiling condition

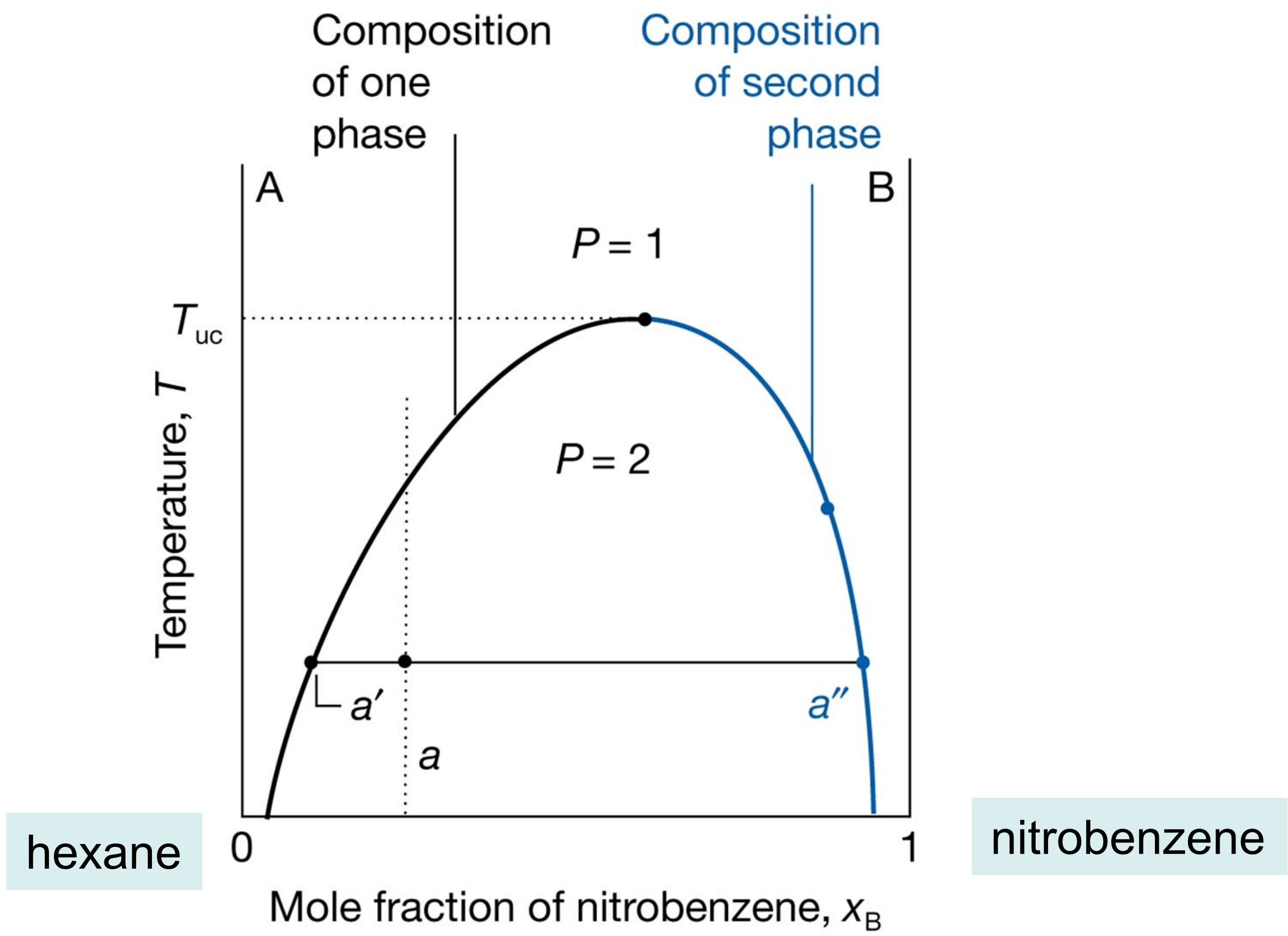
$$p = p_A + p_B = 1atm$$




- can be used for **steam distillation** of heat sensitive components

# Two components diagrams

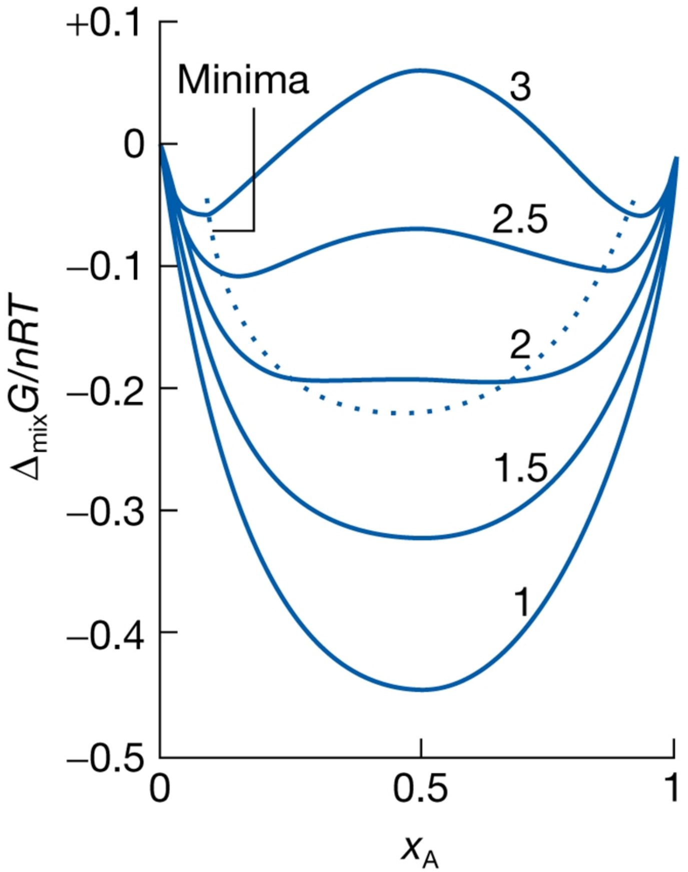
- Liquid-liquid phase diagrams: partially miscible liquids

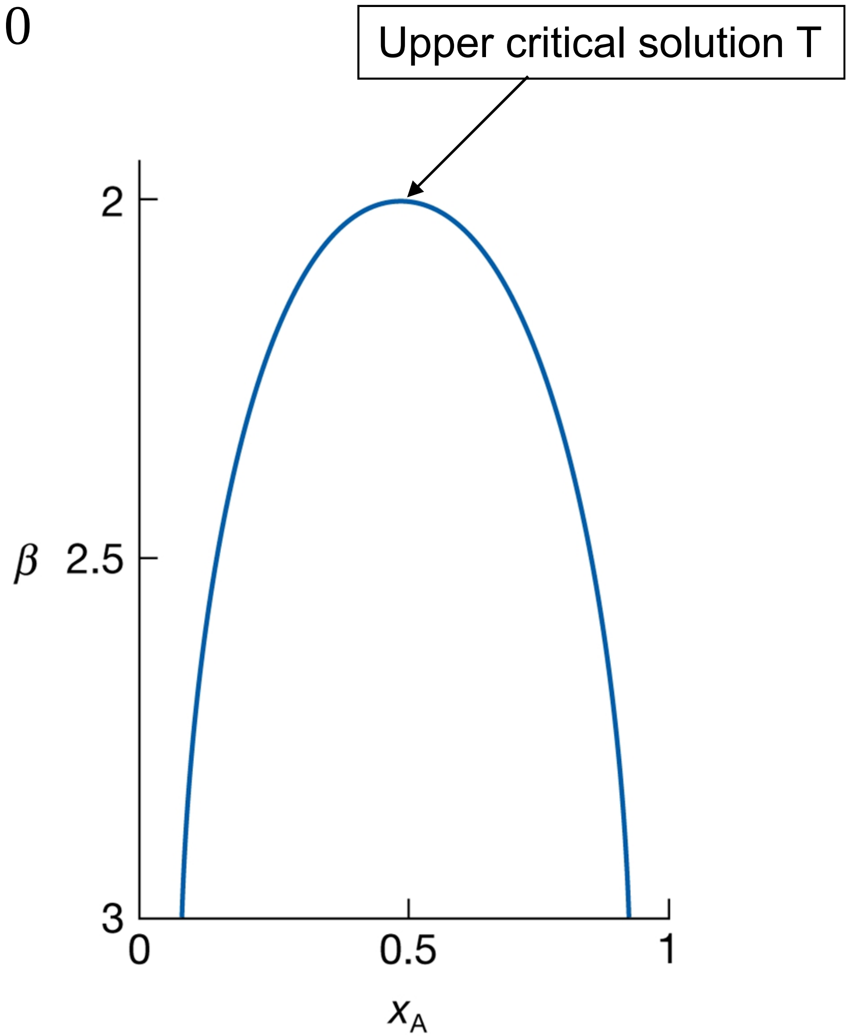


# Two components diagrams

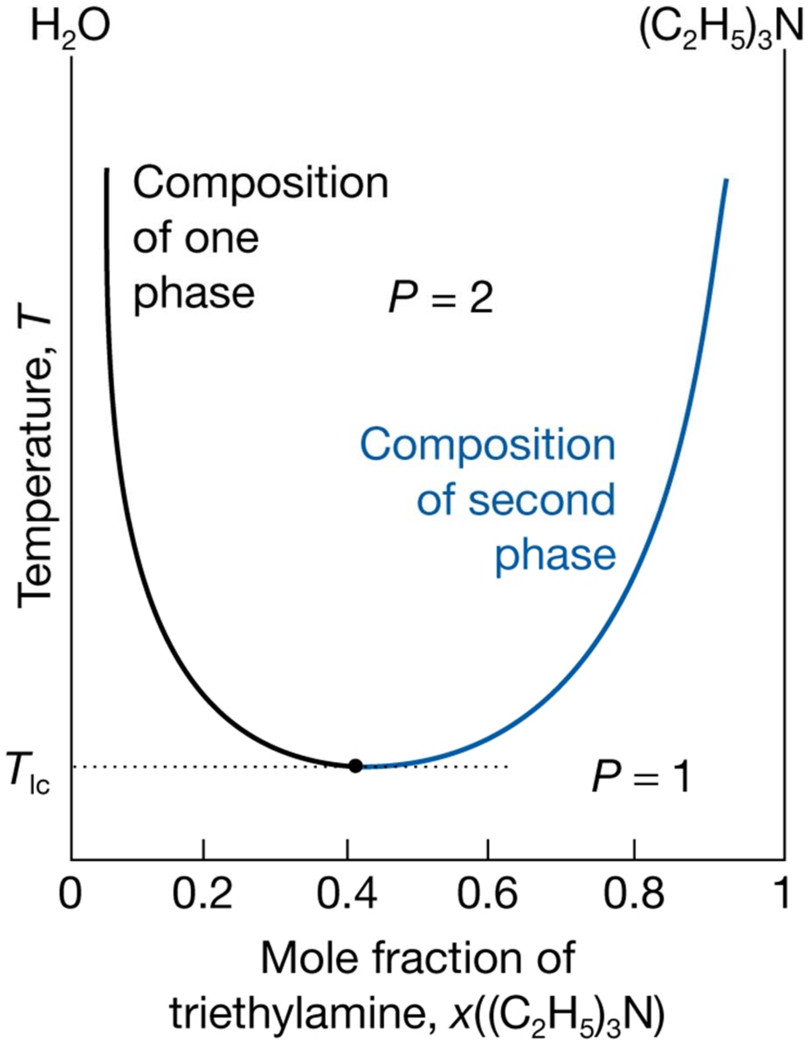
$$\Delta_{mix} G = nRT(\kappa_A \ln \kappa_A + \kappa_B \ln \kappa_B + \beta \kappa_A \kappa_B)$$

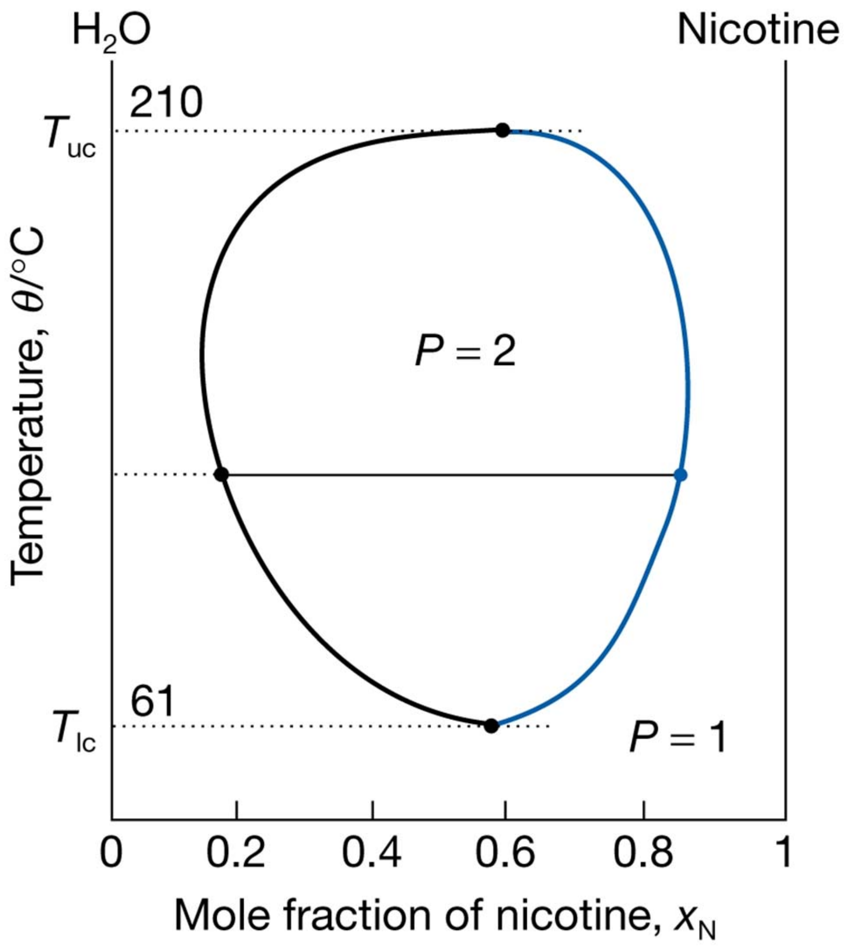
$$\frac{\partial}{\partial \kappa} \Delta_{mix} G = 0 \quad \ln \frac{\kappa}{1-\kappa} + \beta(1-2\kappa) = 0$$



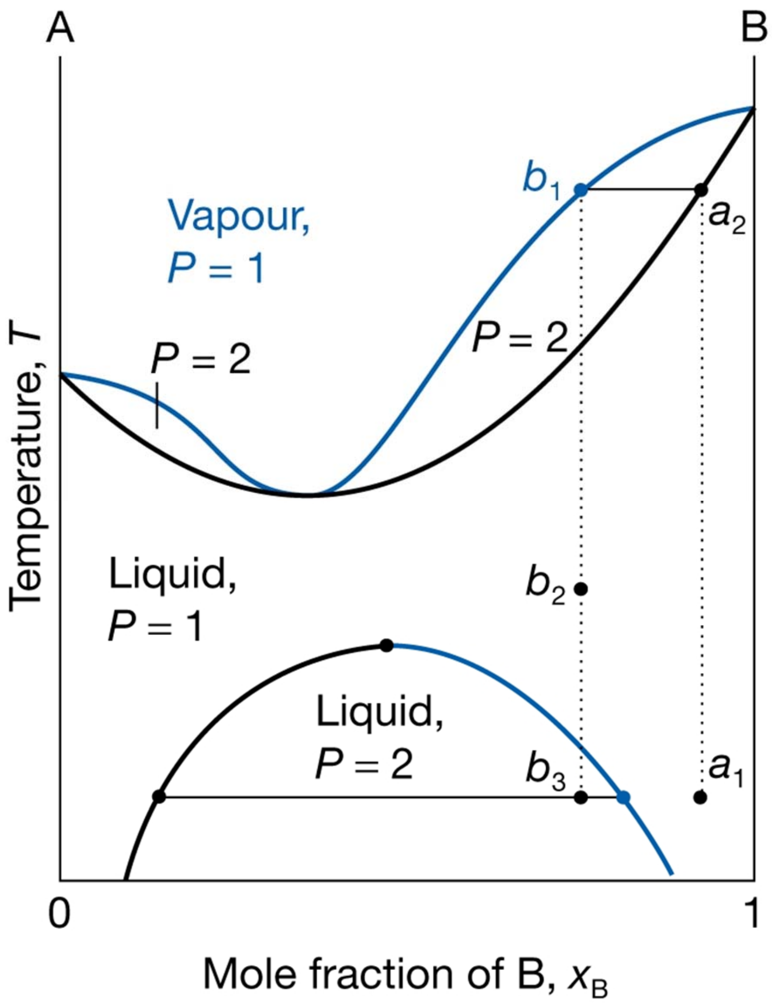
# Two components diagrams



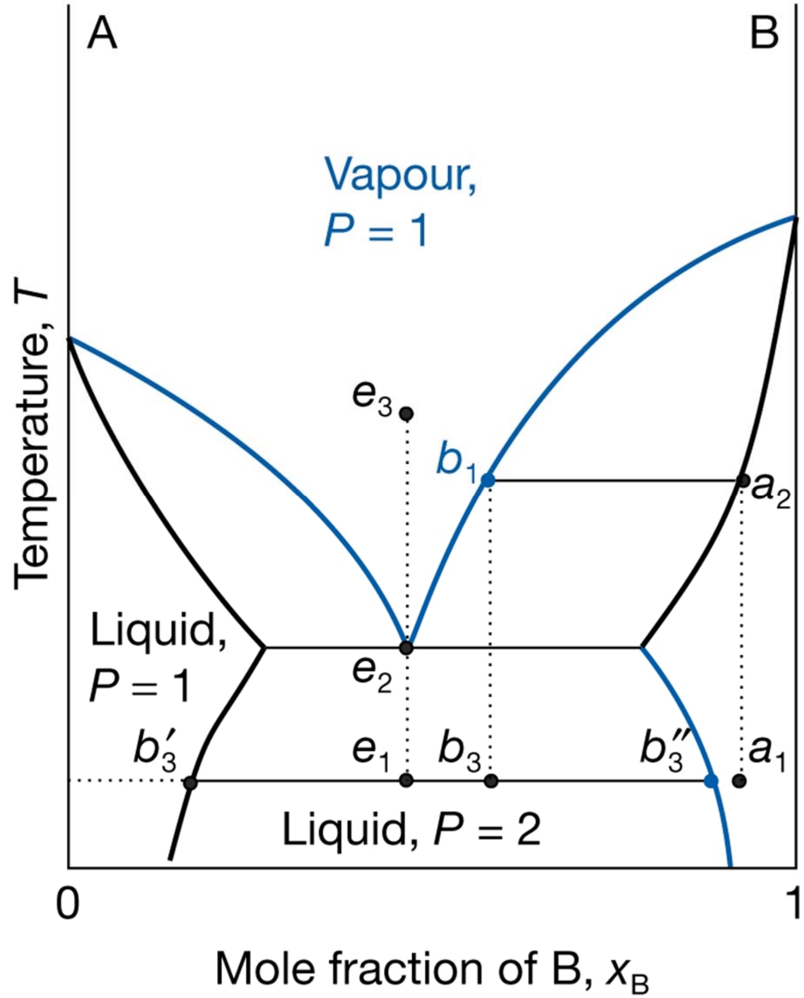




Lower critical temperature is usually caused by breaking a weak complex of two components

# Two components diagrams

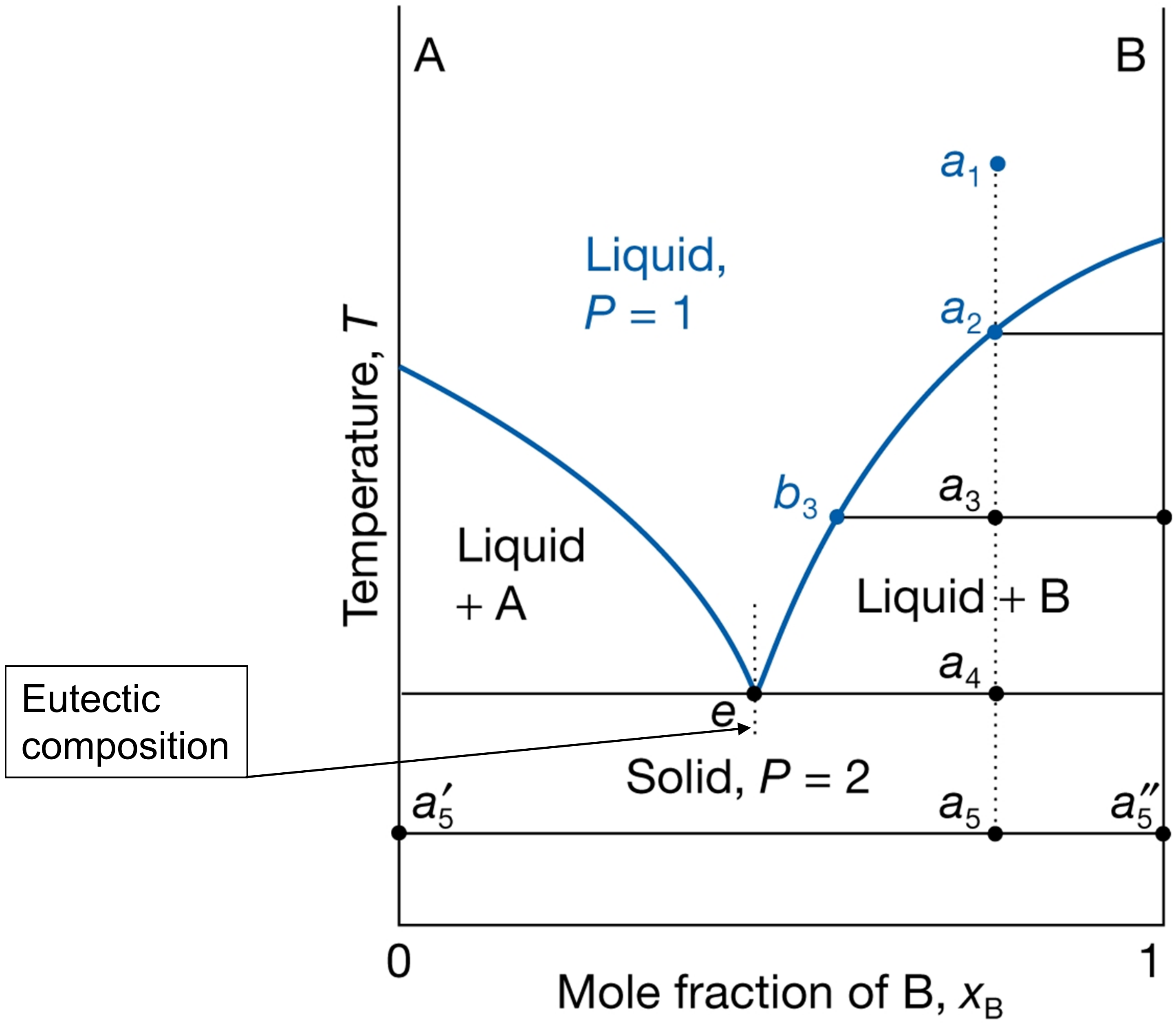



Upper critical temperature is less than the boiling point

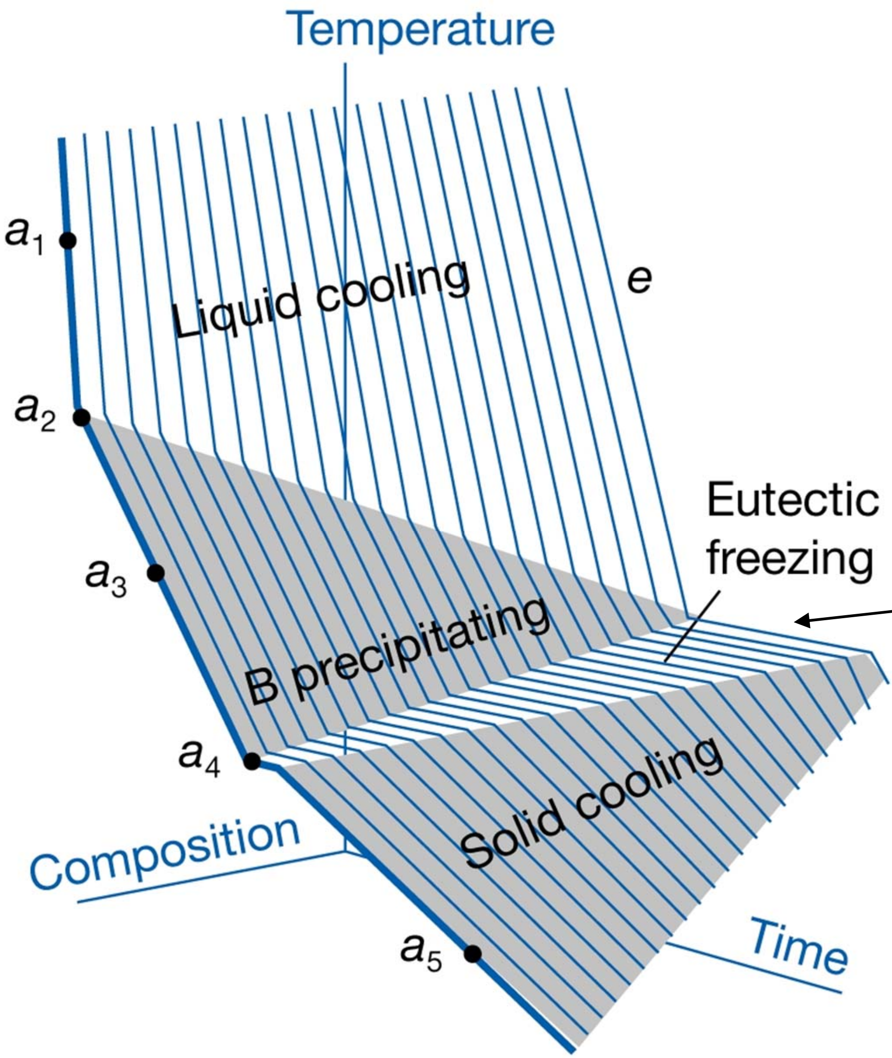



Boiling occur before liquids are fully miscible

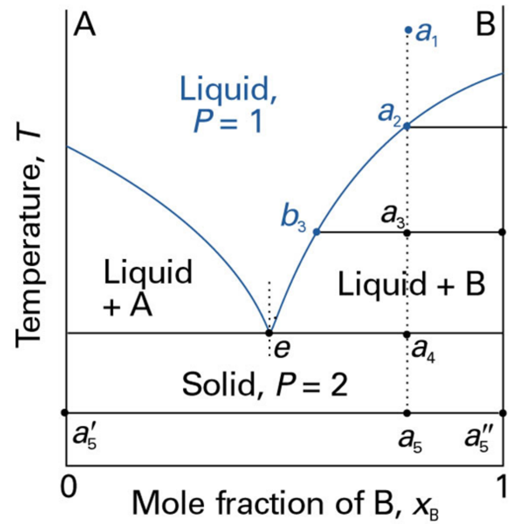
# Liquid-solid phase diagrams



# Liquid-solid phase diagrams



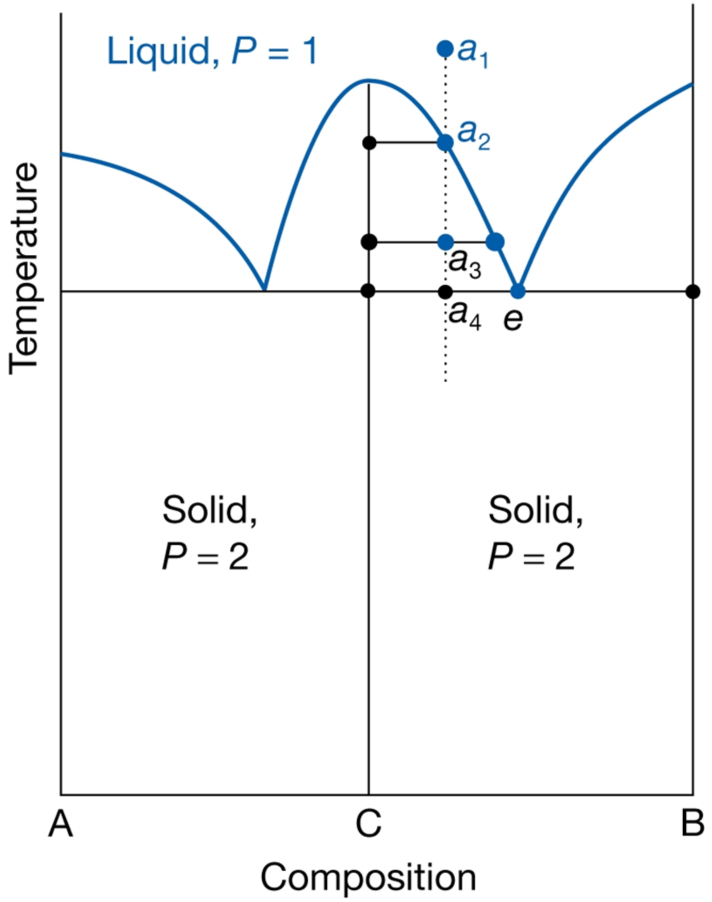

**Eutectic halt**

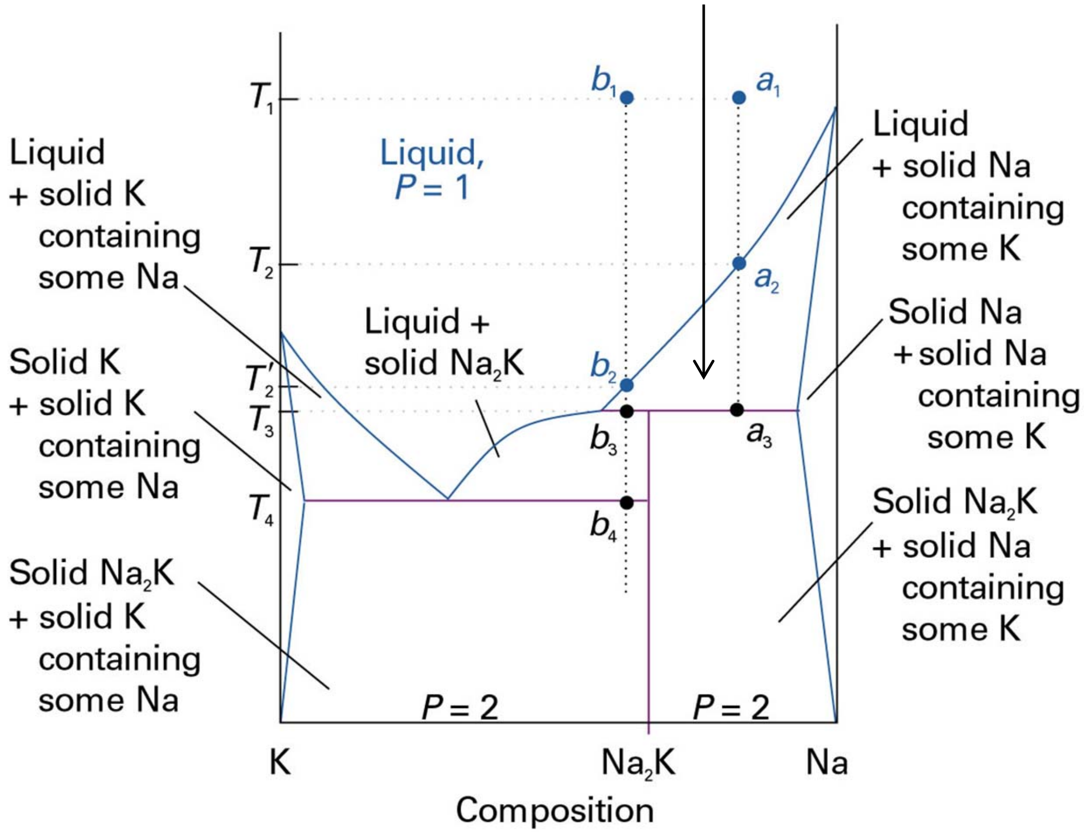


# Liquid-solid phase diagrams

- Reacting systems

peritectic line:
3 phases are in equilibrium



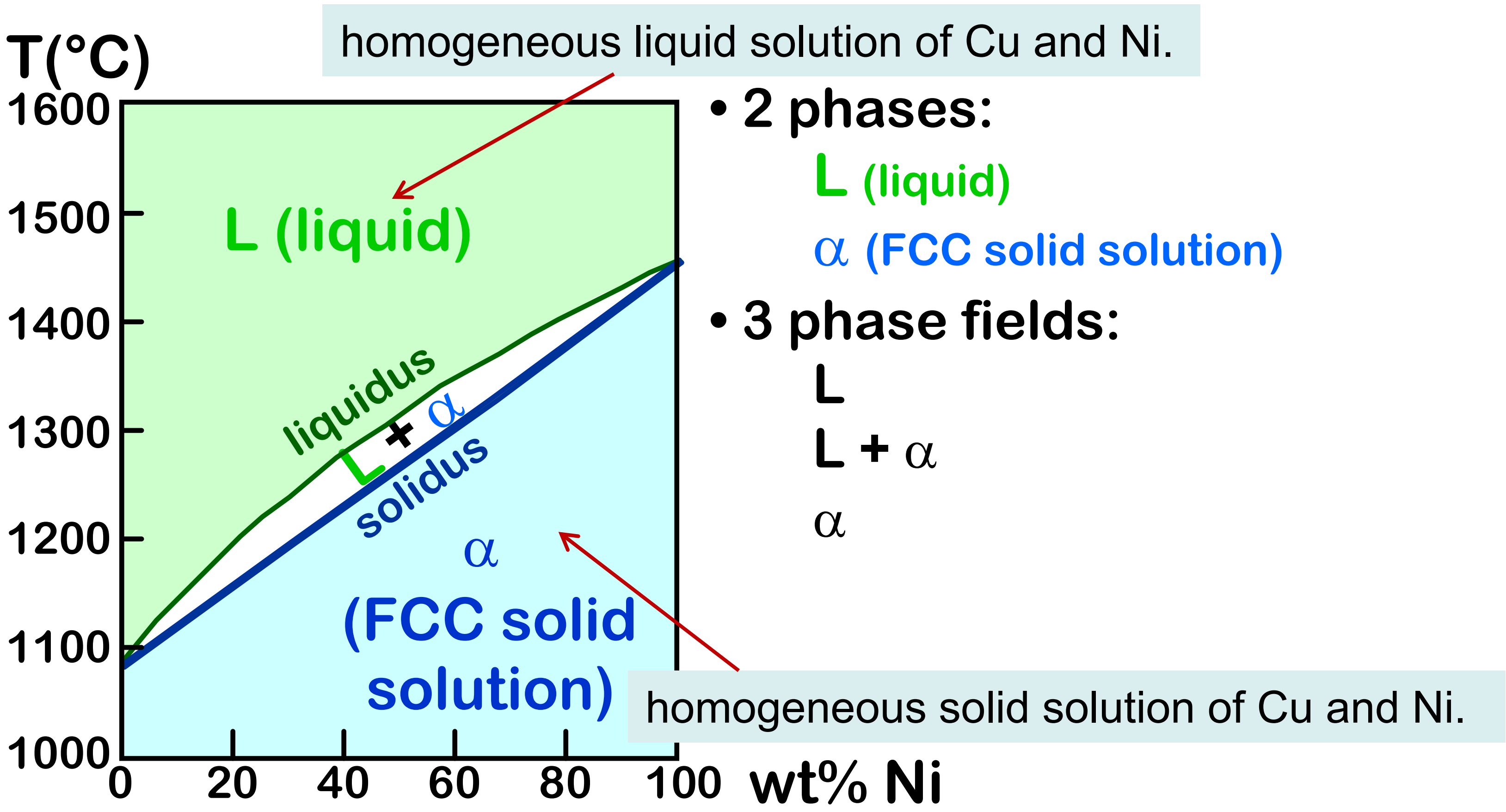




<u>Incongruent melting</u>: compounds melts into components

# Phase diagrams and Microstructure

# Binary phase diagrams

- Phase diagram with total solubility in both liquid and solid state: **isomorphous** system




**Cu-Ni phase diagram**

- **2 phases:**
  - **L (liquid)**
  - **α (FCC solid solution)**
- **3 phase fields:**
  - **L**
  - **L + α**
  - **α**

# Cu-Ni phase diagram

Information we can extract from the diagram:

- the phases present;
- composition of the phases
- percentage of fraction of the phases

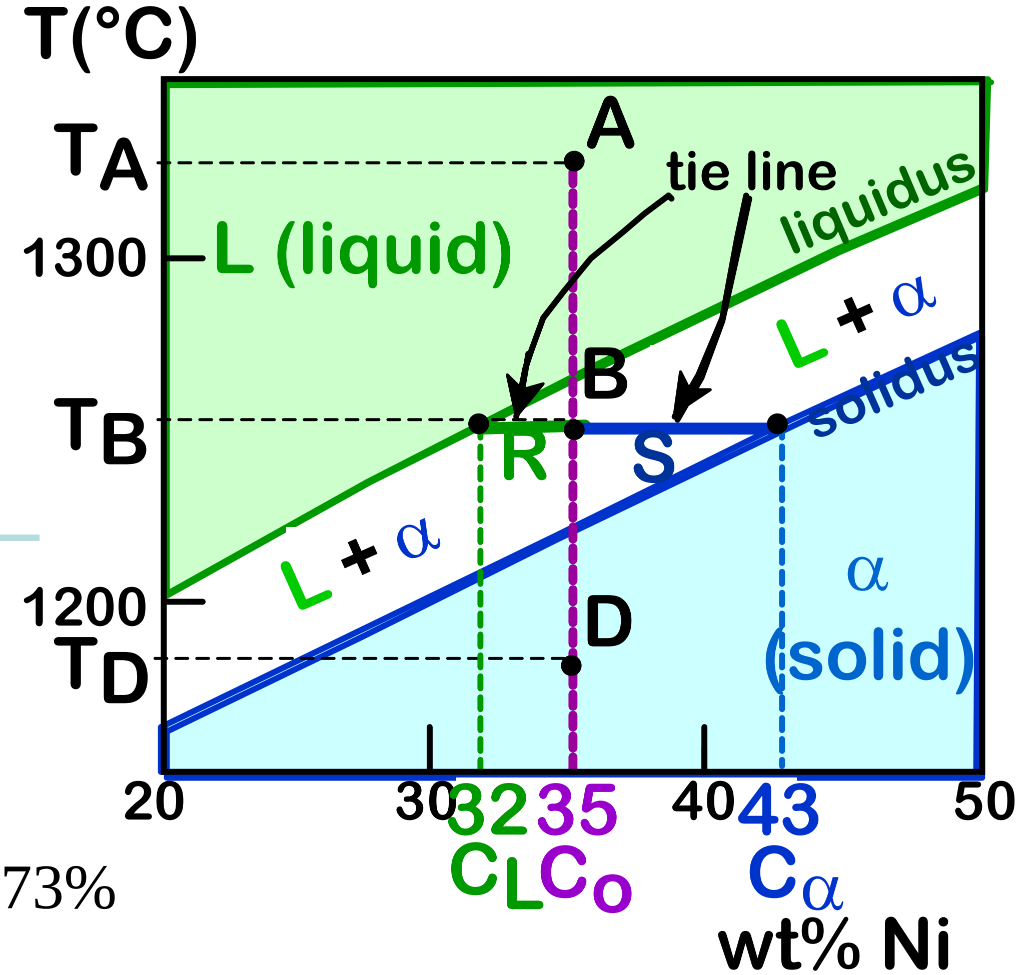
**$C_0$=35 wt% Ni**

**at $T_A$:** Only liquid, composition of liquid is given by the overall composition ($C_0$=35 wt% Ni)
**at $T_D$:** Only liquid, composition of liquid is given by the overall composition ($C_0$=35 wt% Ni)
**at $T_B$:** Both L and α are present

Composition at $T_B$:

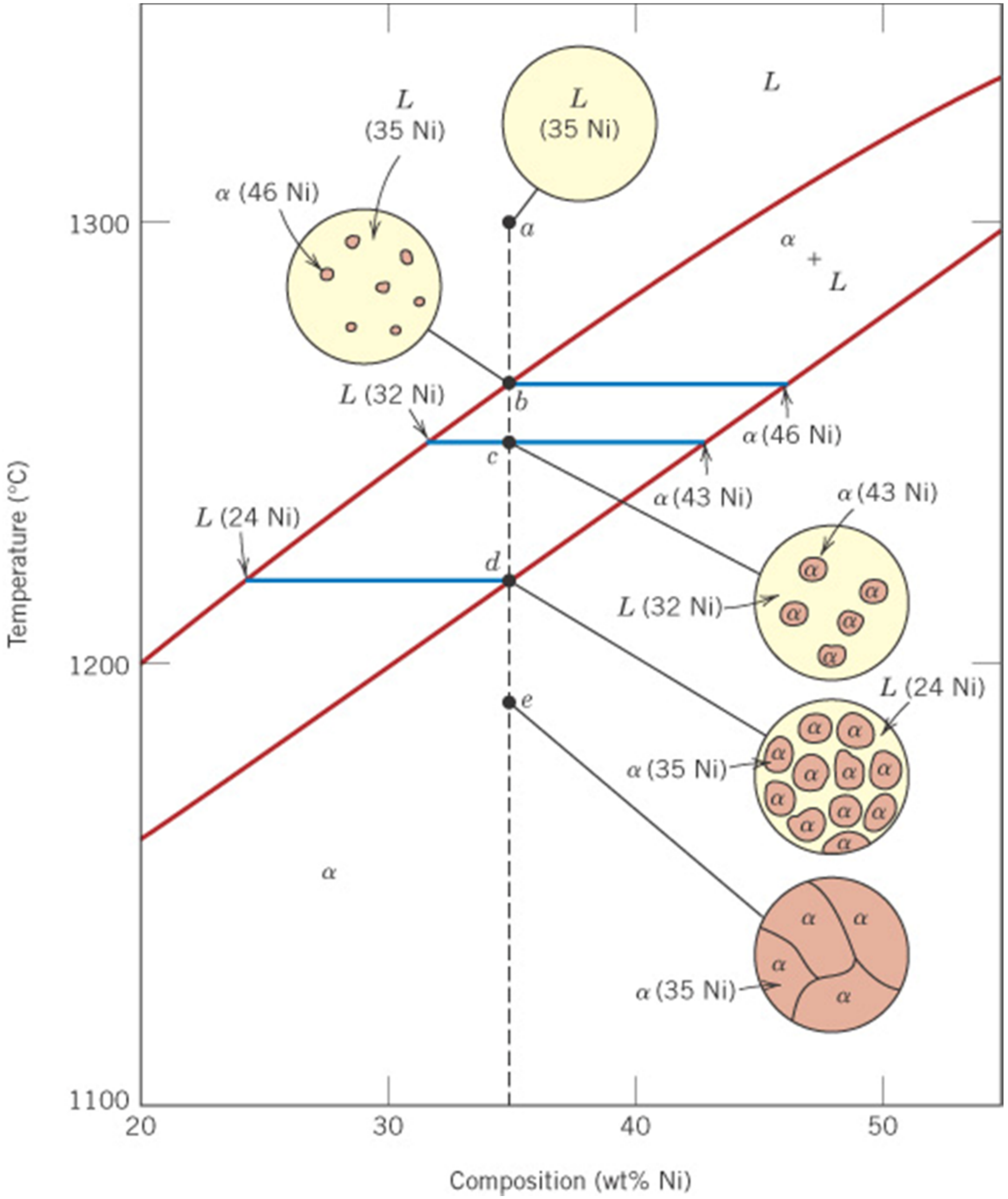
- Liquid phase (L) of 32% Ni
- Solid phase (α) of 43% Ni
- Weight ratio:

$$\frac{W_L}{W_\alpha} = \frac{S}{R}; W_\alpha = \frac{R}{S+R} = \frac{(43-35)}{(43-32)} = 73\%$$



# Development of microstructure in a Cu-Ni alloy

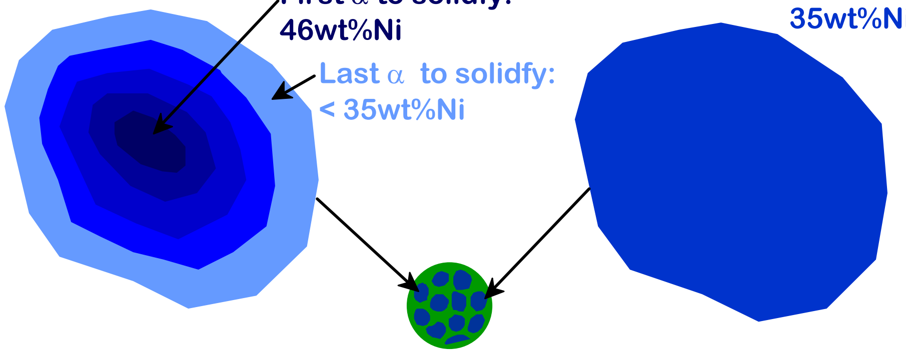
**Equilibrium case**
**(very slow cooling)**

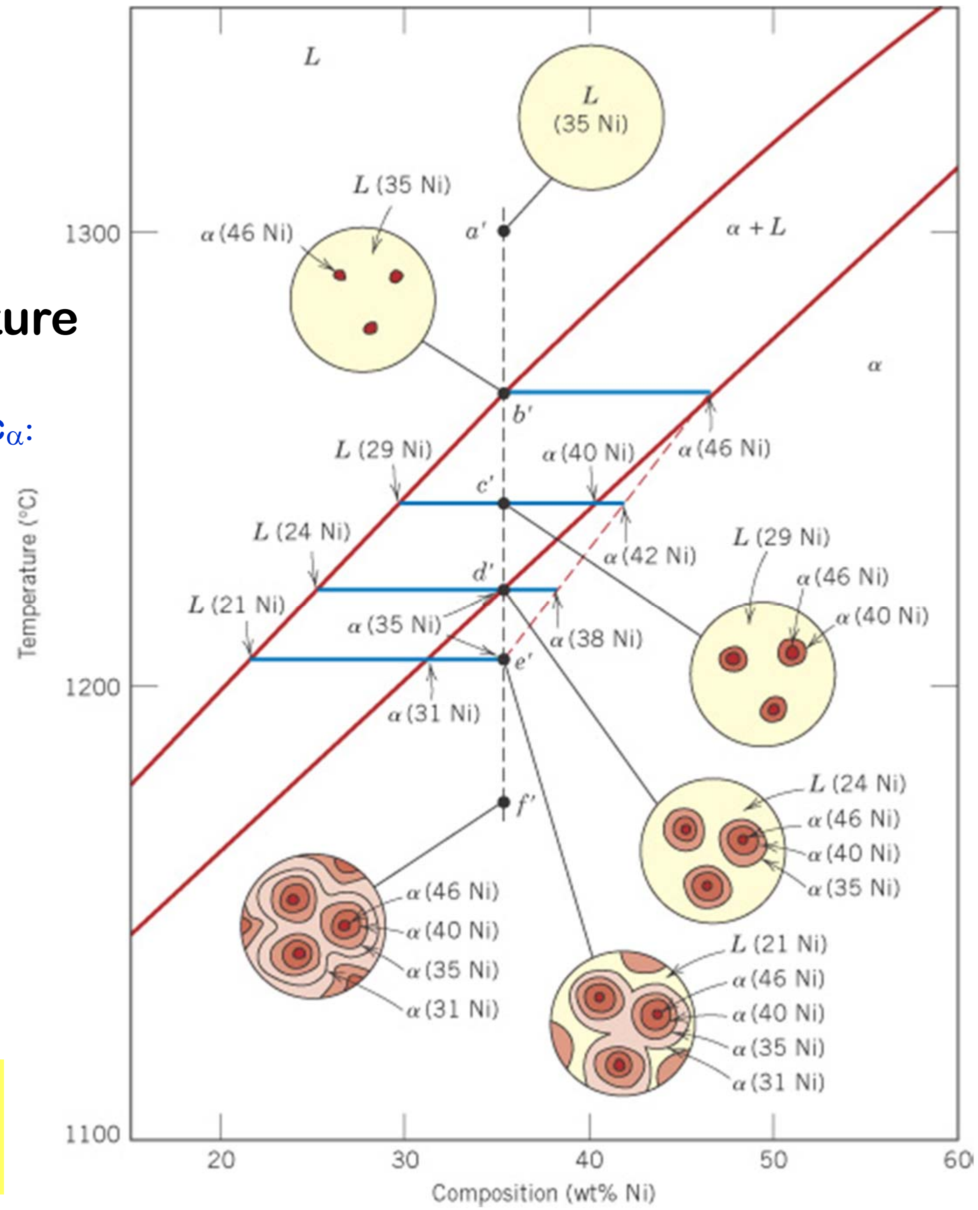


# Development of microstructure in a Cu-Ni alloy

**Non-Equilibrium case**
**(real)**

- **Fast cooling:** **Cored structure**
- **Slow cooling:** **Equilibrium structure**




**How we can prevent coring and get equilibrium structure?**

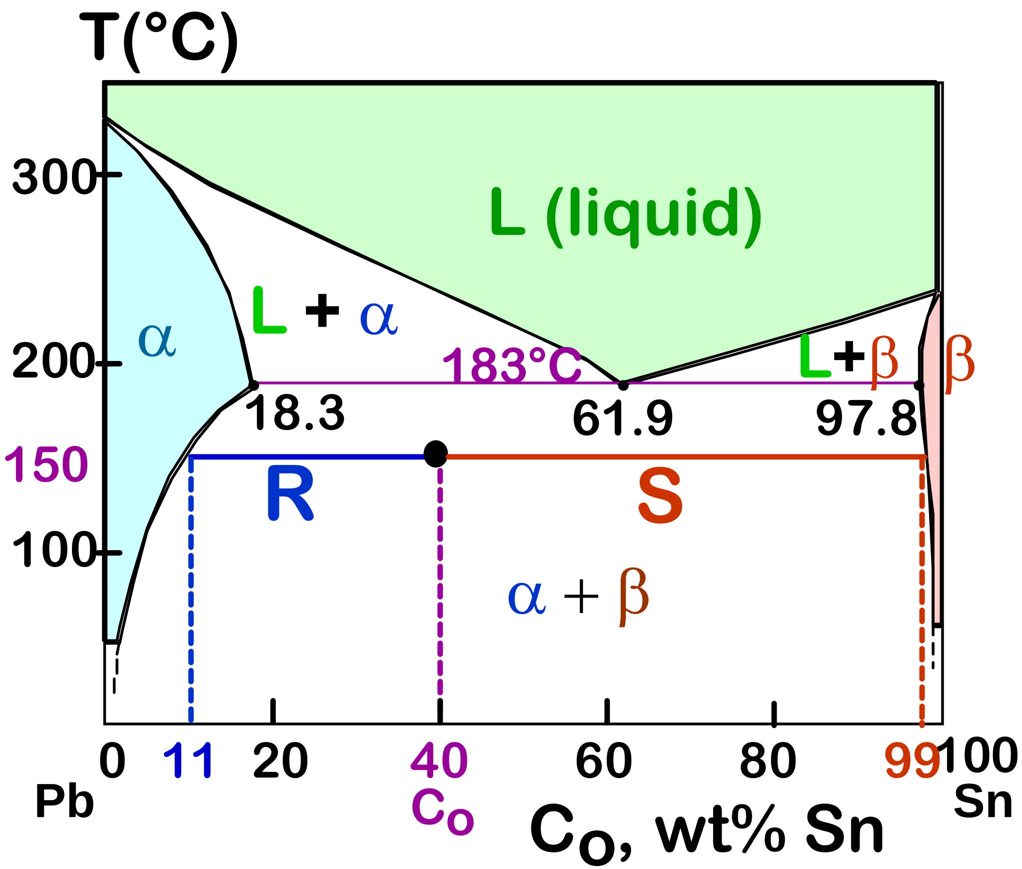
# Binary Eutectic Systems: Sn-Pb

<u>Sn-Pb system:</u>

- limited solubility in solid state
- 3 single phase regions (L, a, b);
- $T_E$=183 $^0$C, no liquid below $T_E$.
- Eutectic composition 61.9%

At the eutectic temperature:

$$L(C_E) \rightleftarrows \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$



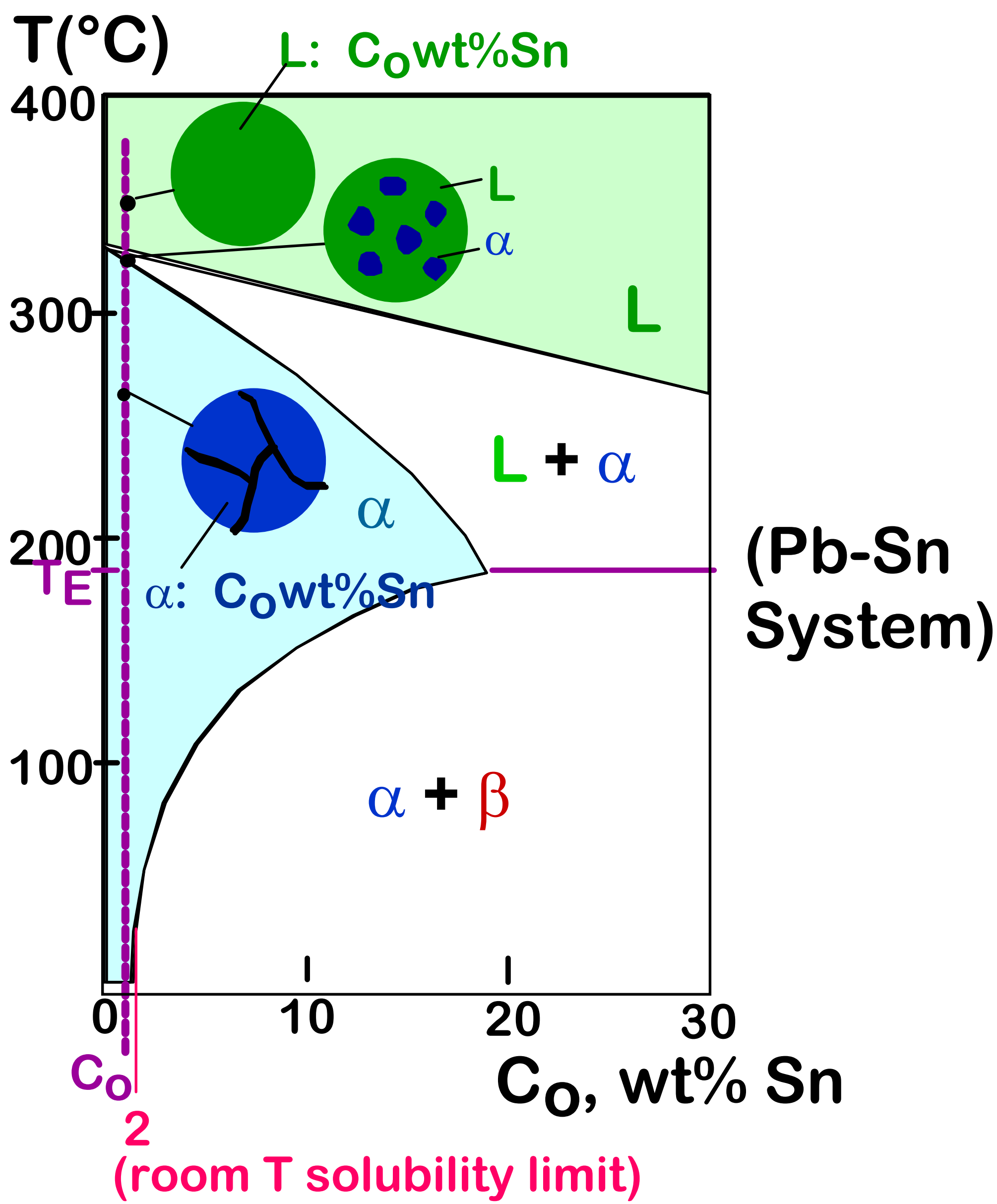

- For a 40wt%Sn-60wt%Pb alloy at 150C, find...
  --the compositions of
  the phases:
  $C_a$ = 11wt%Sn
  $C_b$ = 99wt%Sn

$$W_\alpha = \frac{59}{88} = 67\text{wt\%}$$

$$W_\beta = \frac{29}{88} = 33\text{wt\%}$$

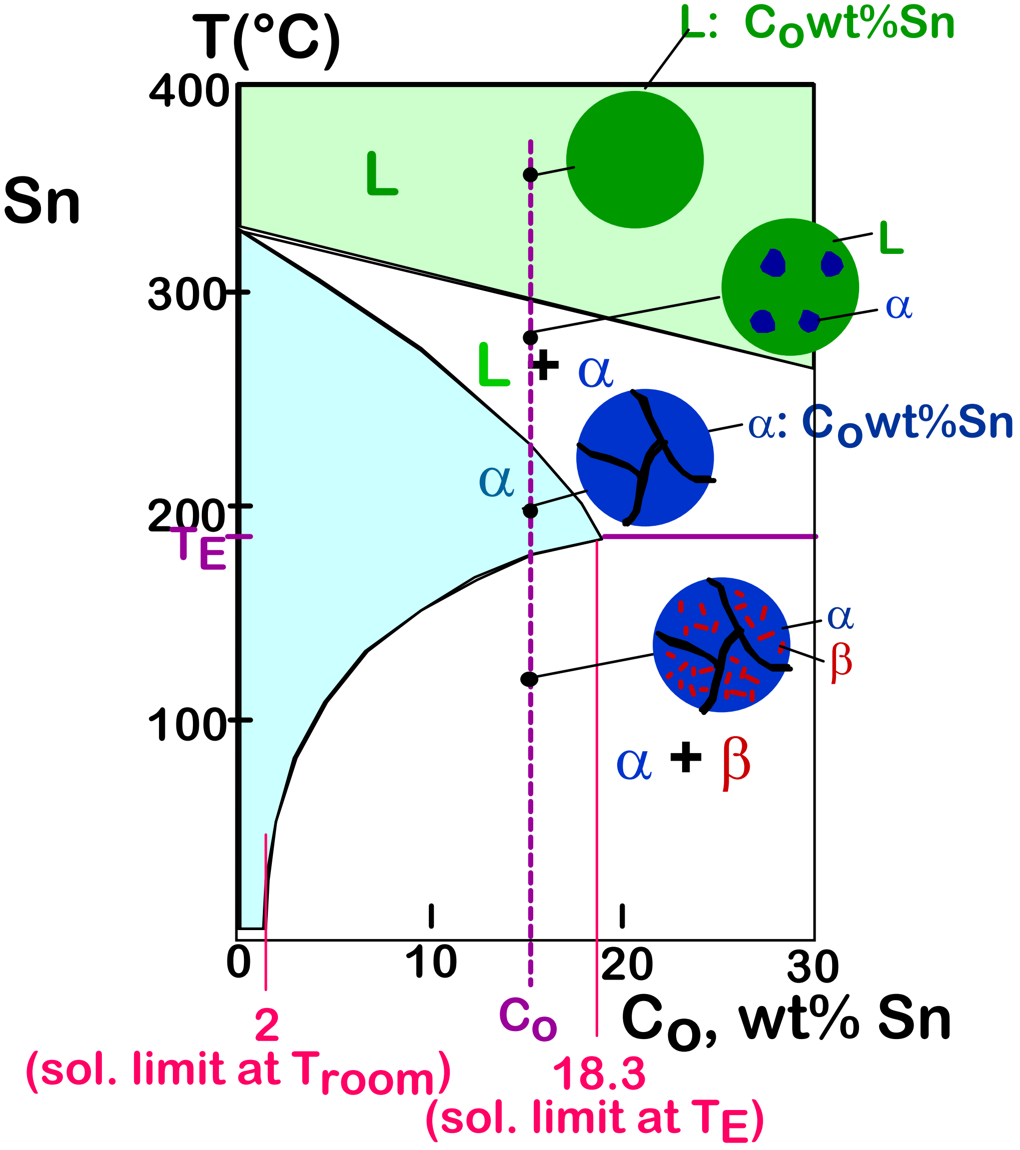
# Microstructures in binary systems

- $C_o$ < 2wt%Sn
- Result:
  --polycrystal of $\alpha$ grains.



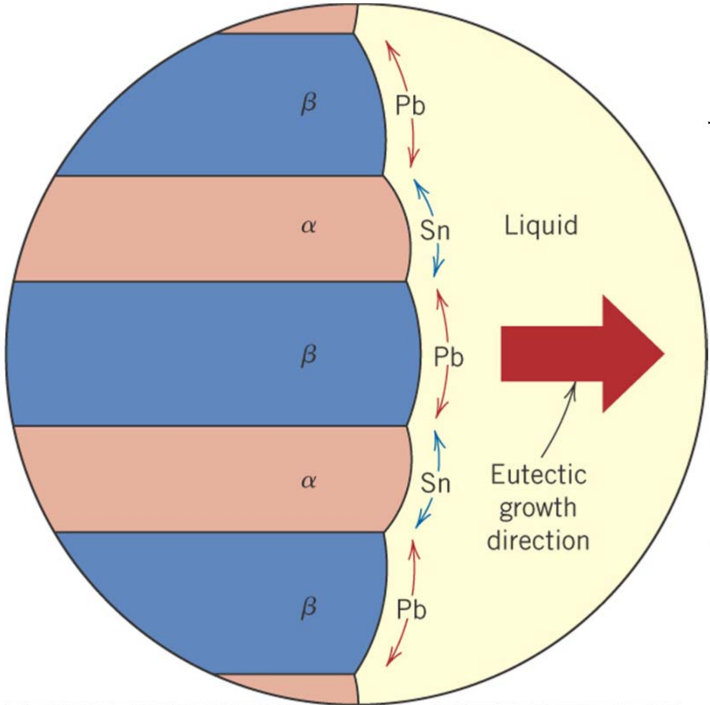
# Microstructures in binary systems

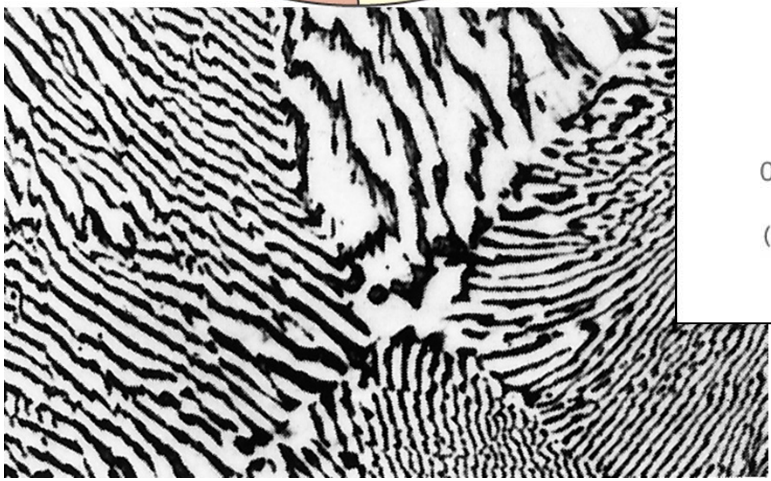
- 2wt%Sn < $C_o$ < 18.3wt%Sn
- Result:
  --α polycrystal with fine
  β crystals.

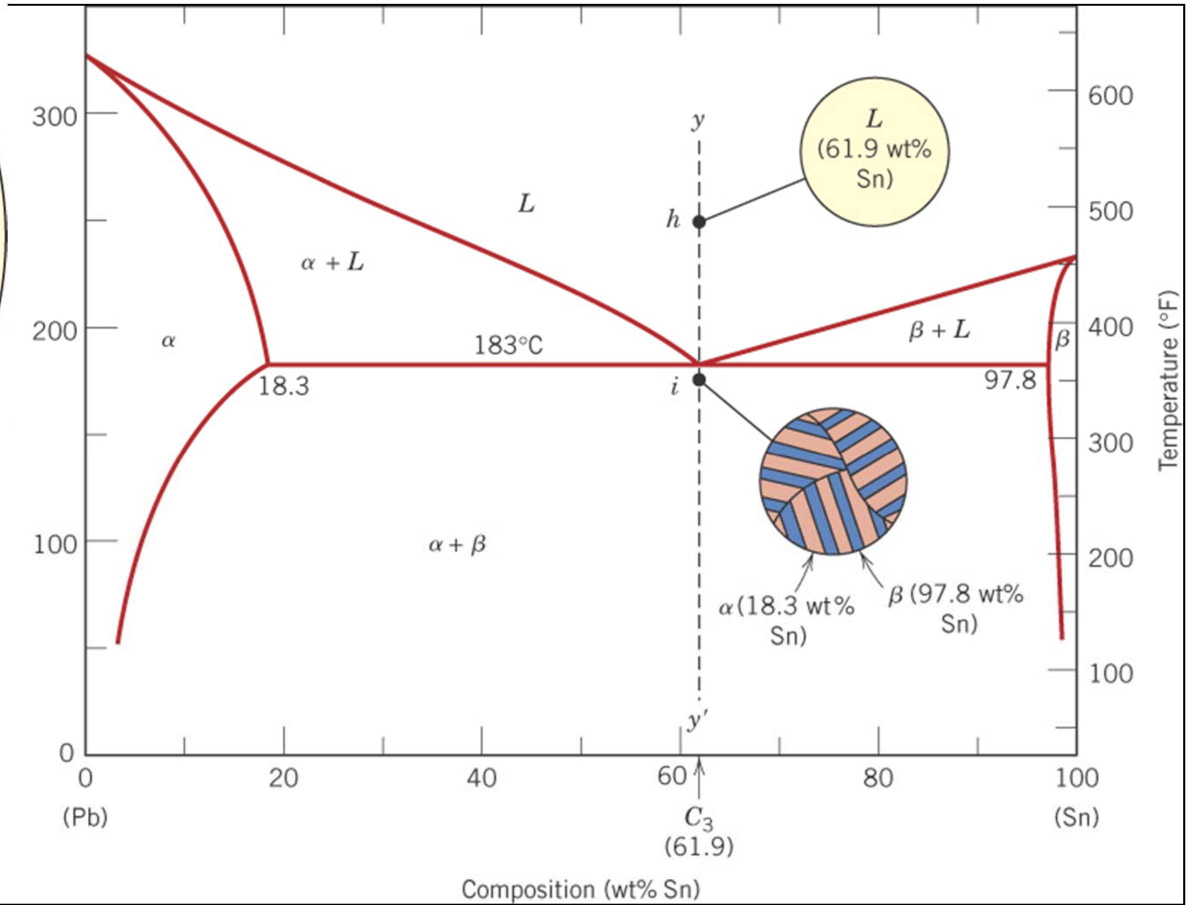


# Microstructures in binary systems

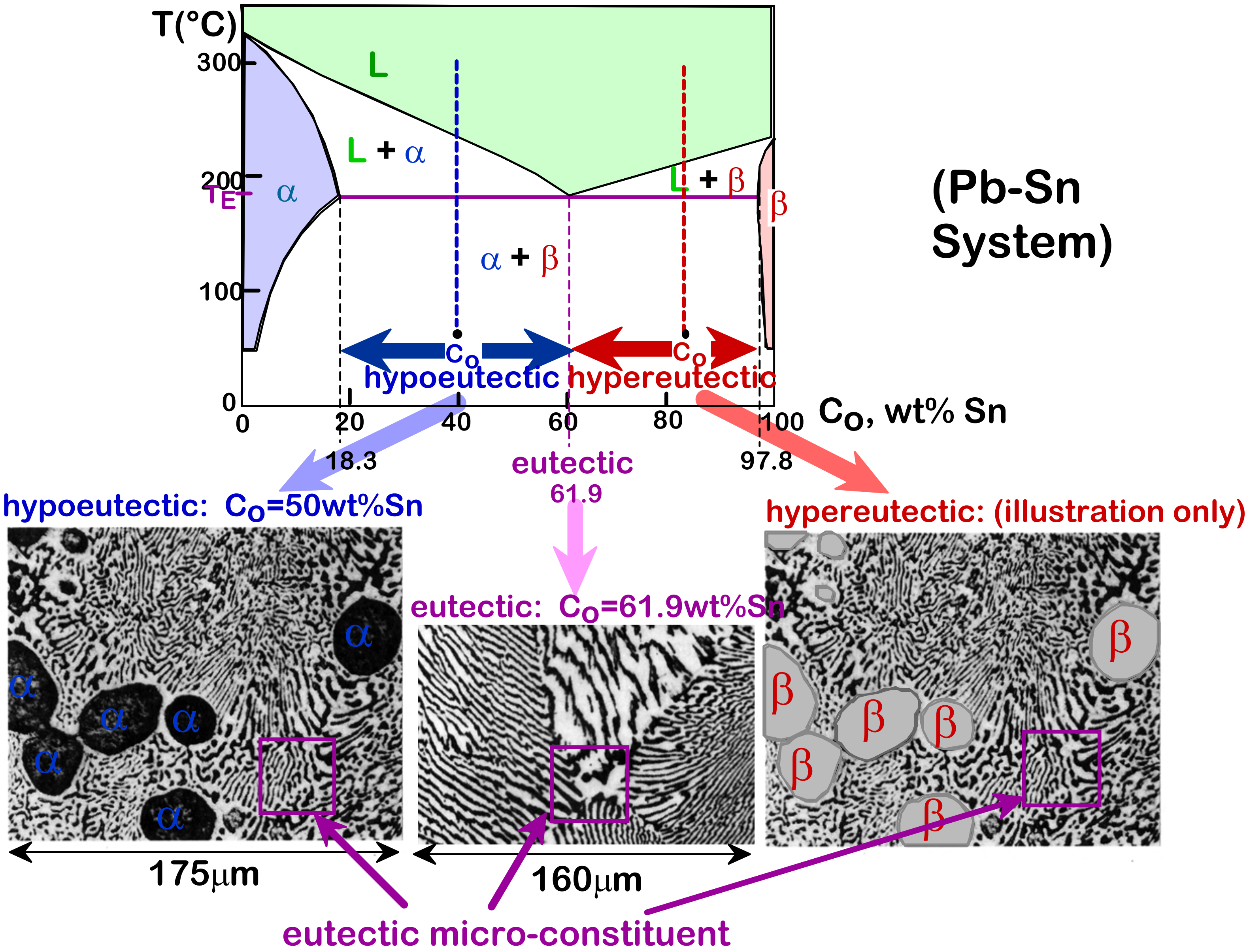
- **Eutectic composition**





# Microstructures in binary systems: eutectic and around




*From: W.D. Callister, "Materials Science and Engineering: An Introduction", 6e.*

# IRON-CARBON (Fe-C) PHASE DIAGRAM

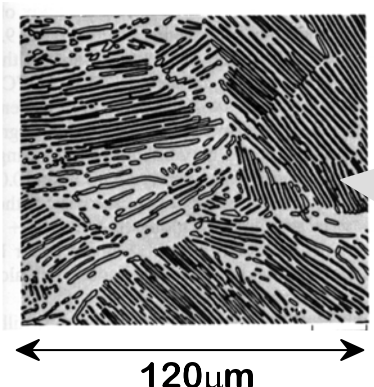
- 2 important points

  -Eutectic (A):

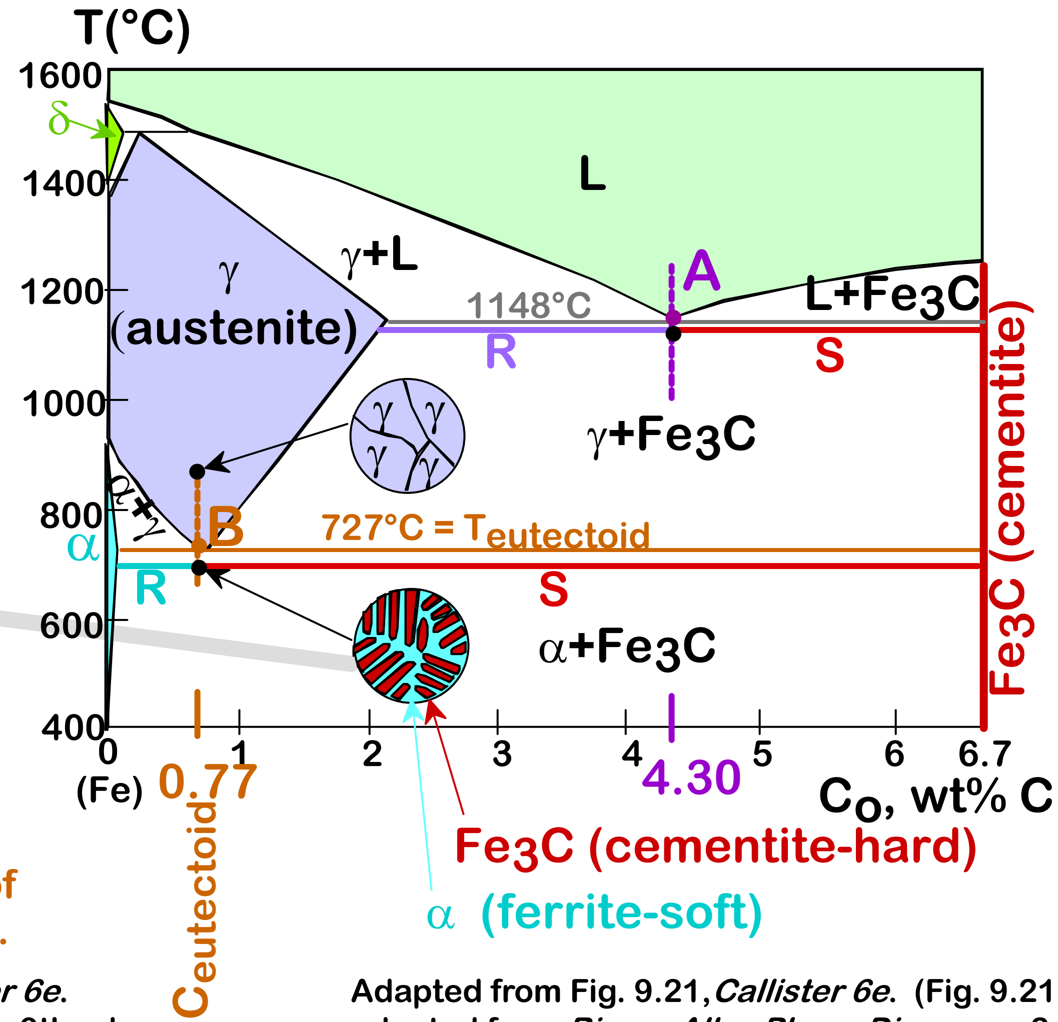
  $L \Rightarrow \gamma + Fe_3C$

  -Eutectoid (B):

  $\gamma \Rightarrow \alpha + Fe_3C$



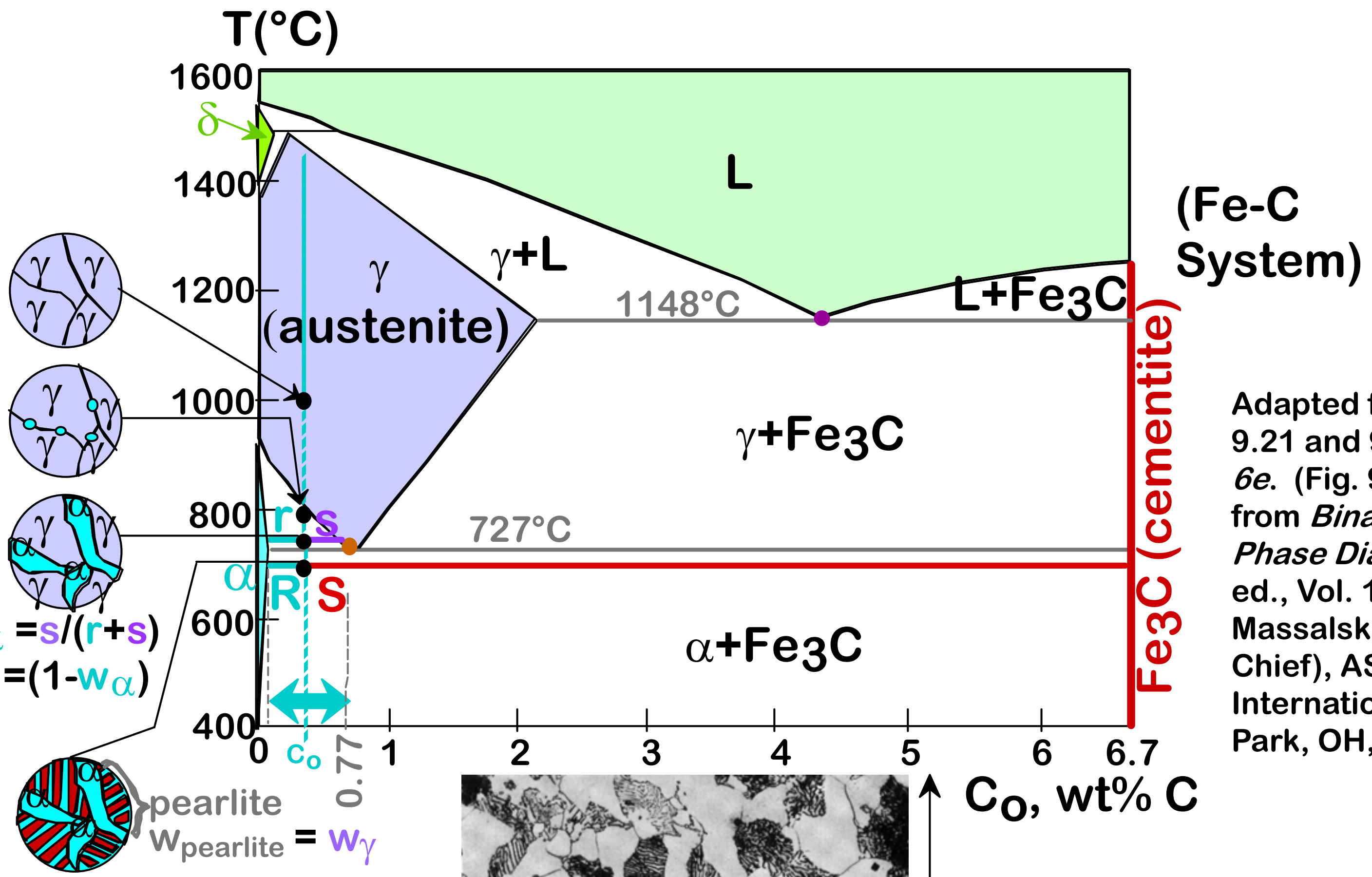

Result: Pearlite = alternating layers of $\alpha$ and $Fe_3C$ phases.




(Adapted from Fig. 9.24, *Callister 6e*. (Fig. 9.24 from *Metals Handbook*, 9th ed., Vol. 9, *Metallography and Microstructures*, American Society for Metals, Materials Park, OH, 1985.)

Adapted from Fig. 9.21, *Callister 6e*. (Fig. 9.21 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

# HYPOEUTECTOID STEEL




$w_{\alpha} = s/(r+s)$

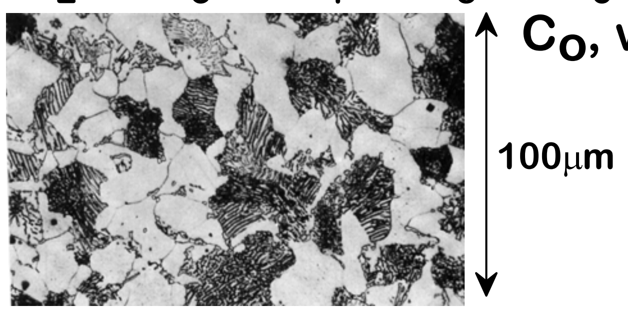
$w_{\gamma} = (1 - w_{\alpha})$

$w_{pearlite} = w_{\gamma}$

$w_{\alpha} = S/(R+S)$

$w_{Fe3C} = (1 - w_{\alpha})$

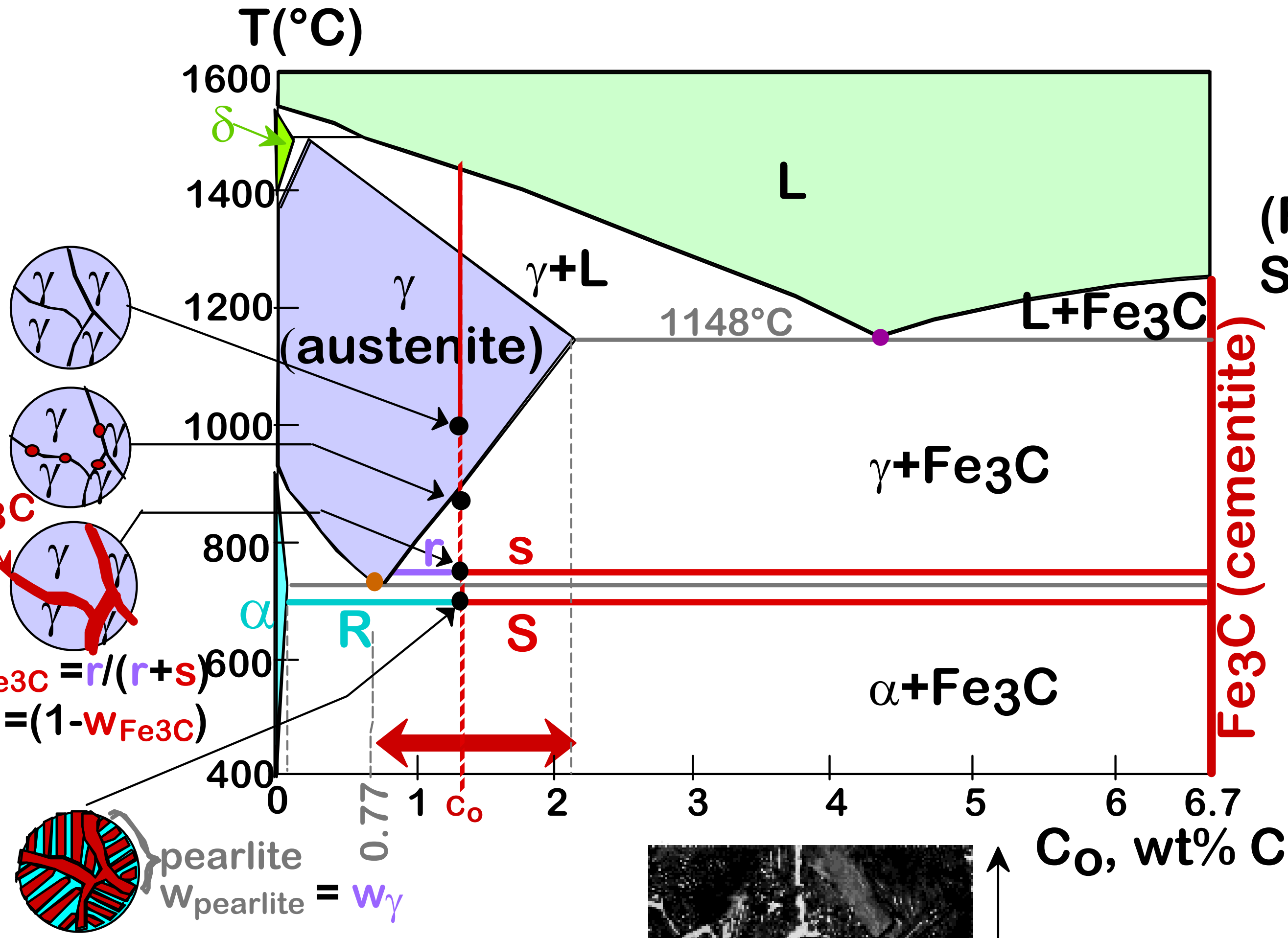
Adapted from Figs. 9.21 and 9.26, *Callister 6e*. (Fig. 9.21 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)




Hypoeutectoid steel

Adapted from Fig. 9.27, *Callister 6e*. (Fig. 9.27 courtesy Republic Steel Corporation.)

# HYPEREUTECTOID STEEL




(Fe-C System)

$w_{Fe3C} = r/(r+s)$

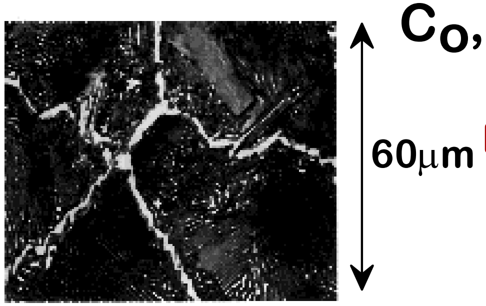
$w_{\gamma} = (1 - w_{Fe3C})$

$w_{pearlite} = w_{\gamma}$

$w_{\alpha} = S/(R+S)$

$w_{Fe3C} = (1 - w_{\alpha})$

Adapted from Figs. 9.21 and 9.29, *Callister 6e*. (Fig. 9.21 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



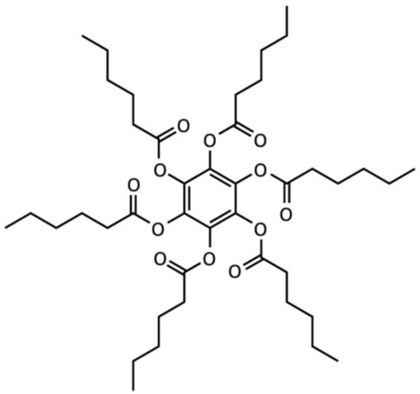

Hypereutectoid steel

Adapted from Fig. 9.30, *Callister 6e*. (Fig. 9.30 copyright 1971 by United States Steel Corporation.)

# 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

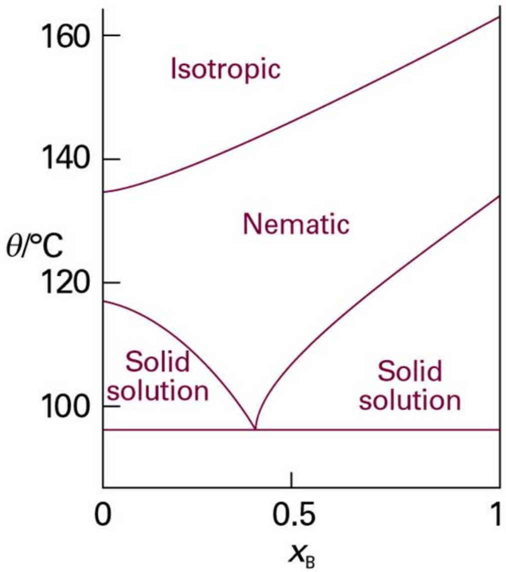

1

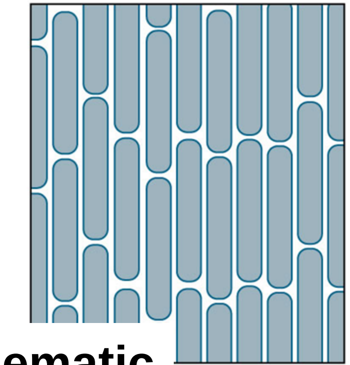



2

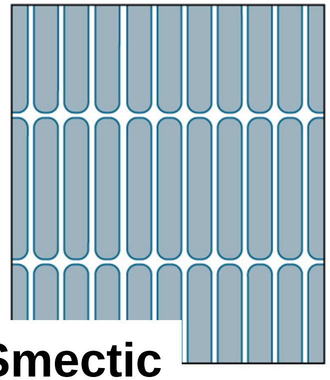
calamitic (rod-like)

discotic

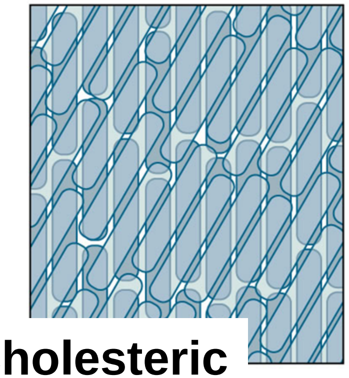


**Nematic**

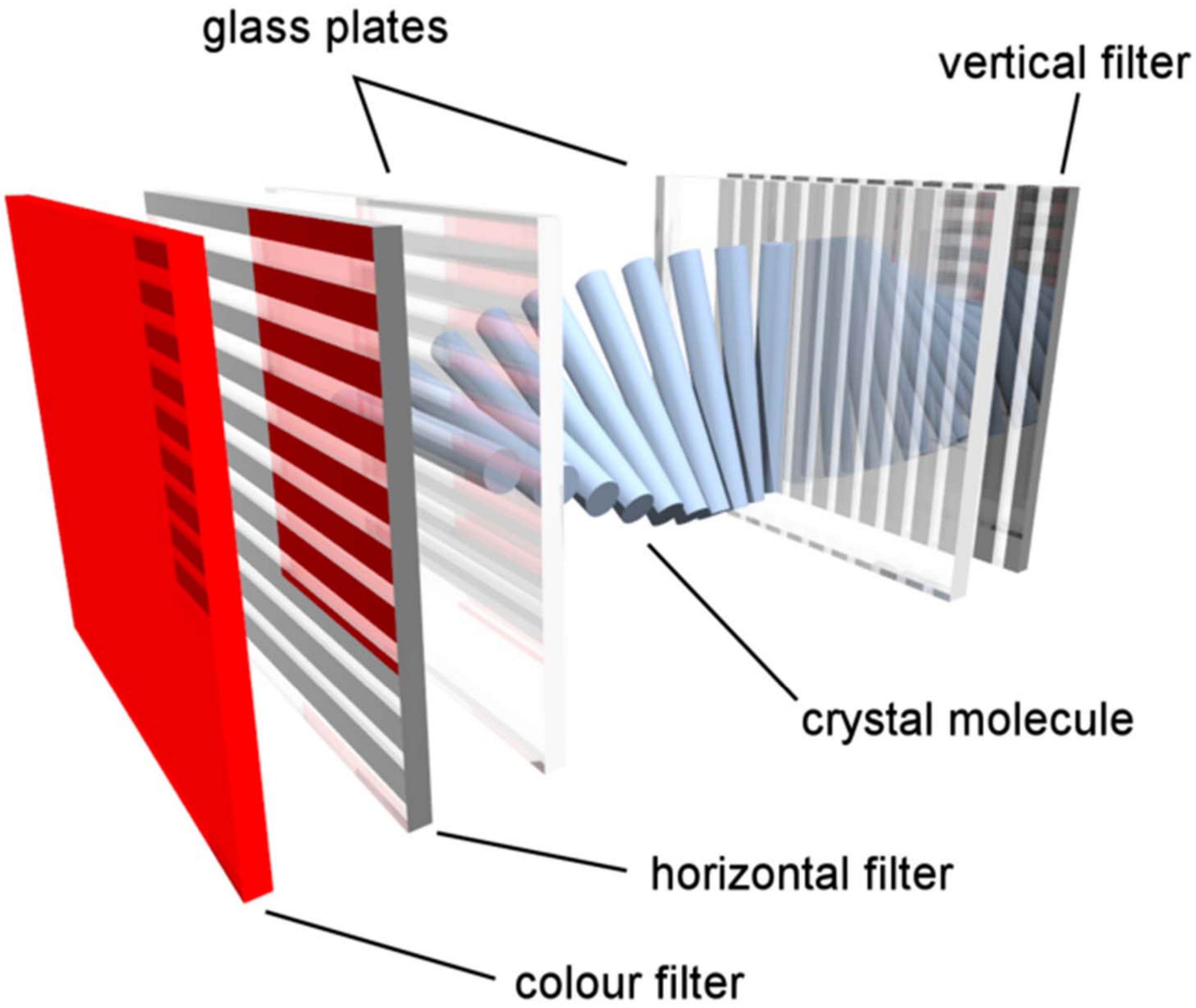


**Smectic**



**Cholesteric**

# Nematic crystals in LCD



# Problems (to solve in the class)

- **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