Lecture 4: Phase diagrams in Material Science. Equilibrium

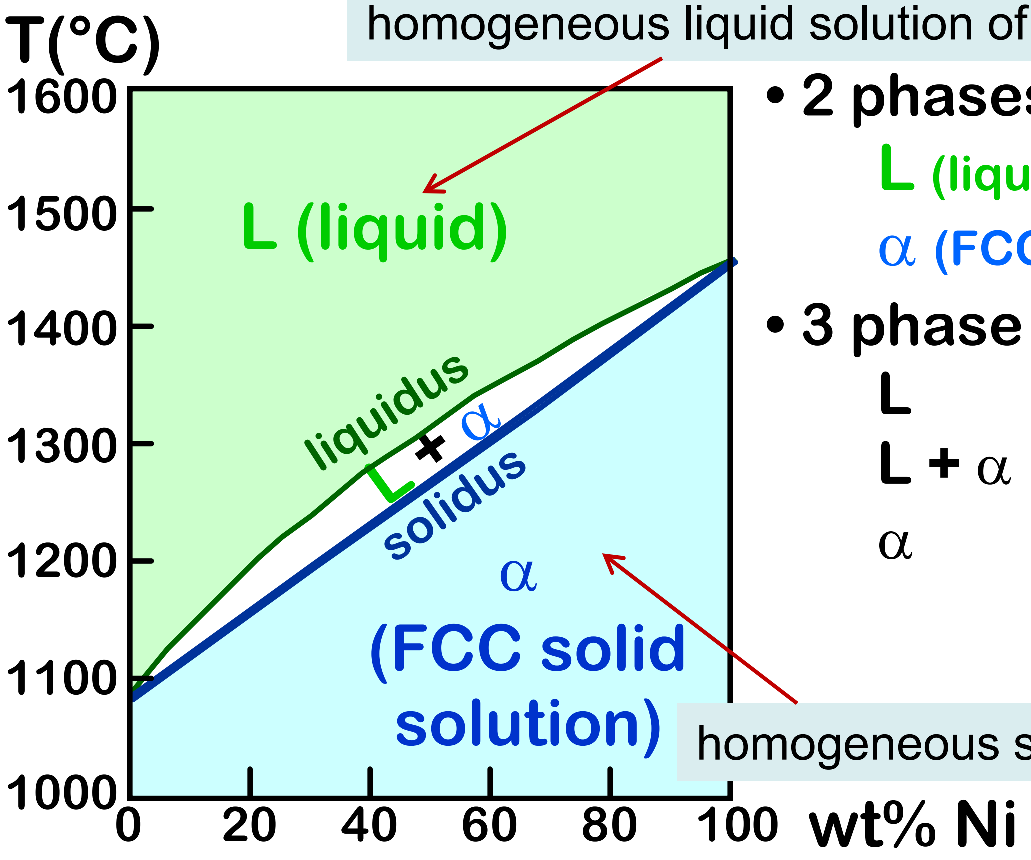
3-11-2009

- Lecture plan:
  - phase diagrams in material science:
    - microstructures in isomorphous binary systems
    - microstructures in eutectic alloys
    - liquid crystals
  - equilibrium
    - equilibrium and Gibbs free energy
    - description of equilibrium
    - response of equilibrium to conditions (P, T, pH)
  - problems

Phase diagrams and Microstructure

Binary phase diagrams

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



homogeneous liquid solution of Cu and Ni.

homogeneous solid solution of Cu and Ni.

Cu-Ni phase diagram

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

Cu-Ni phase diagram

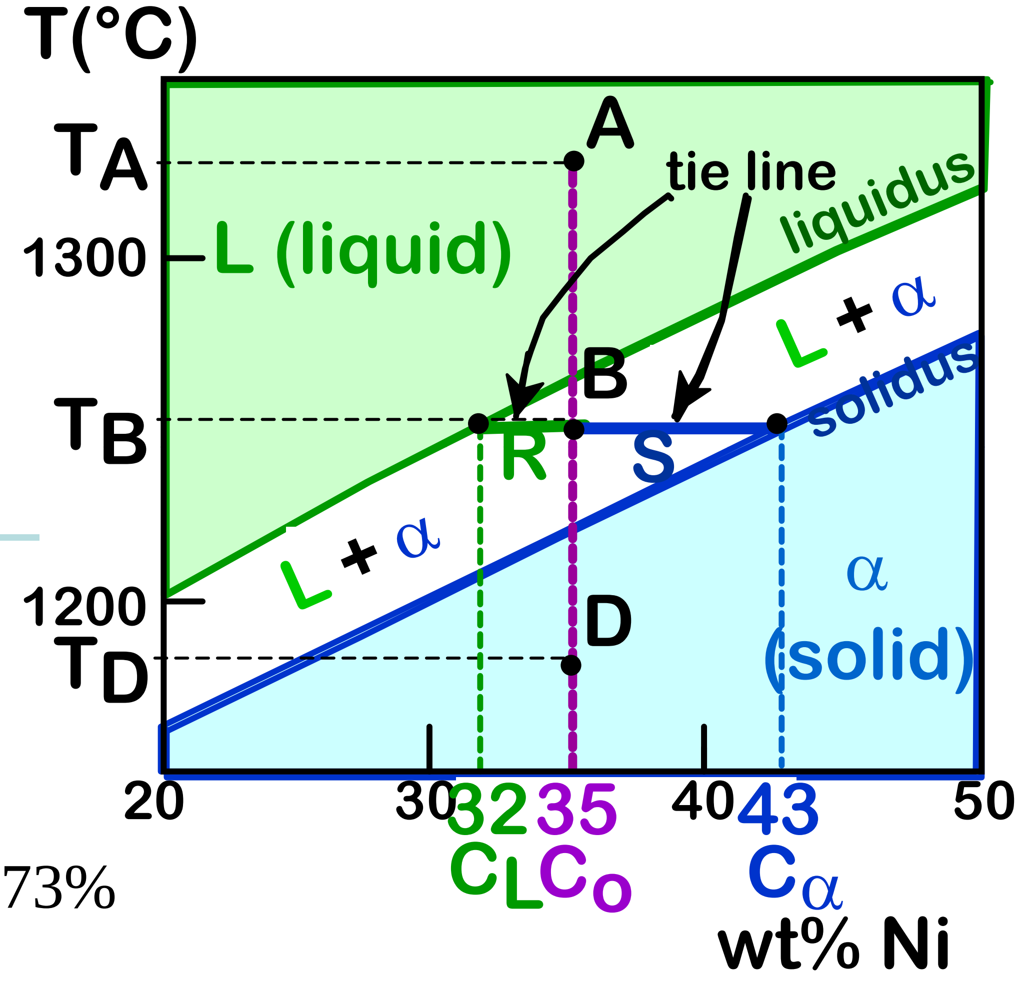
Information we can extract from the diagram:
- the phases present;
- composition of the phases
- percentage of fraction of the phases

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

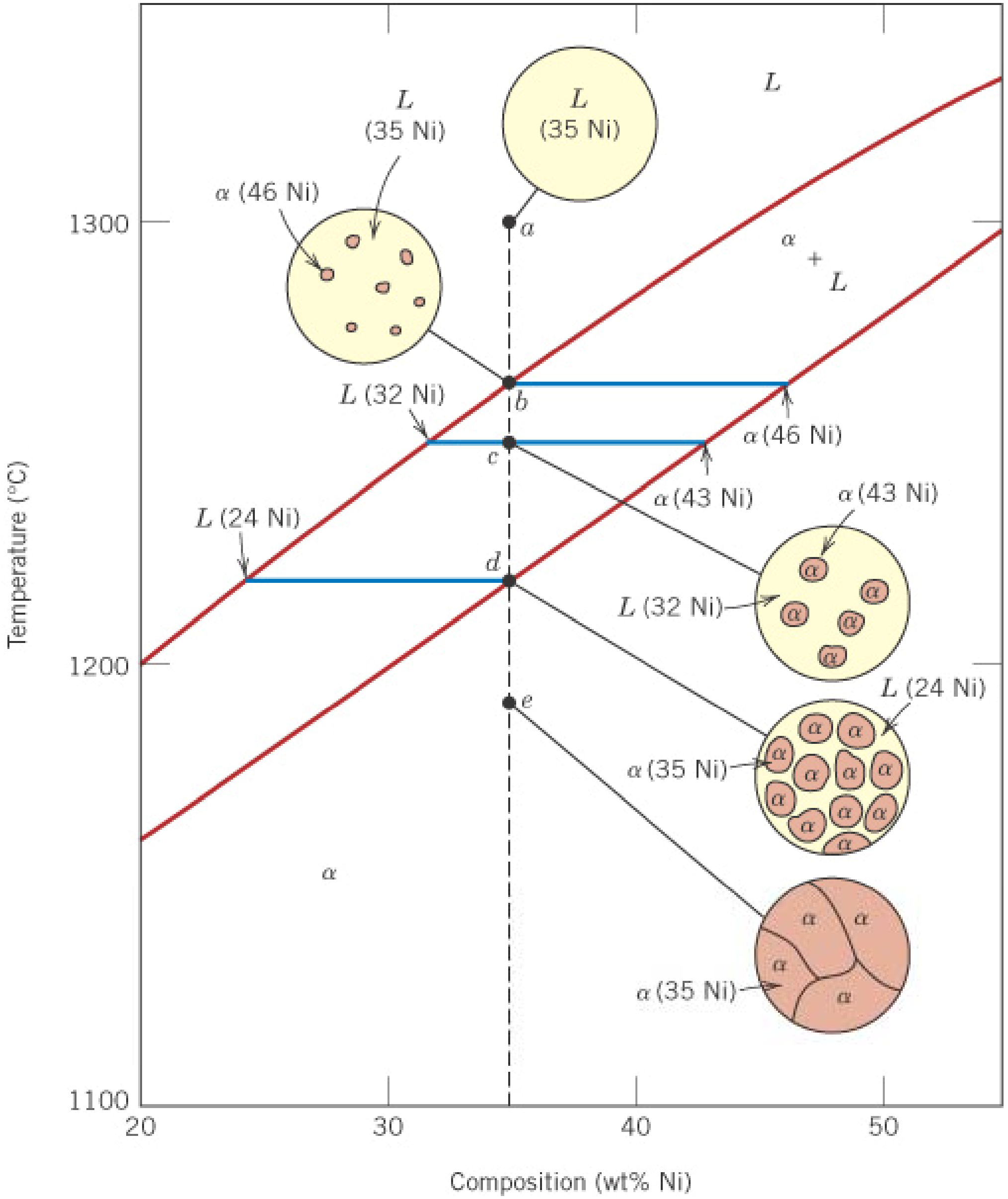
Composition at T_B:
- Liquid phase (L) of 32% Ni
- Solid phase (α) of 43% Ni
- Weight ratio:

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



Development of microstructure in a Cu-Ni alloy

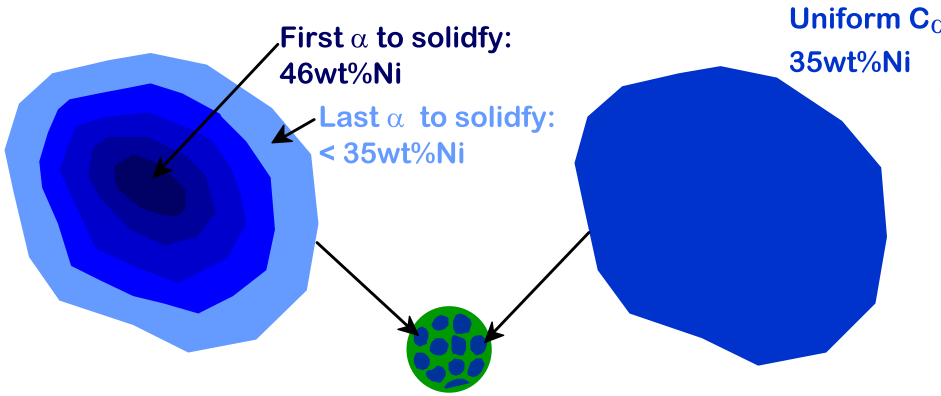
Equilibrium case
(very slow cooling)

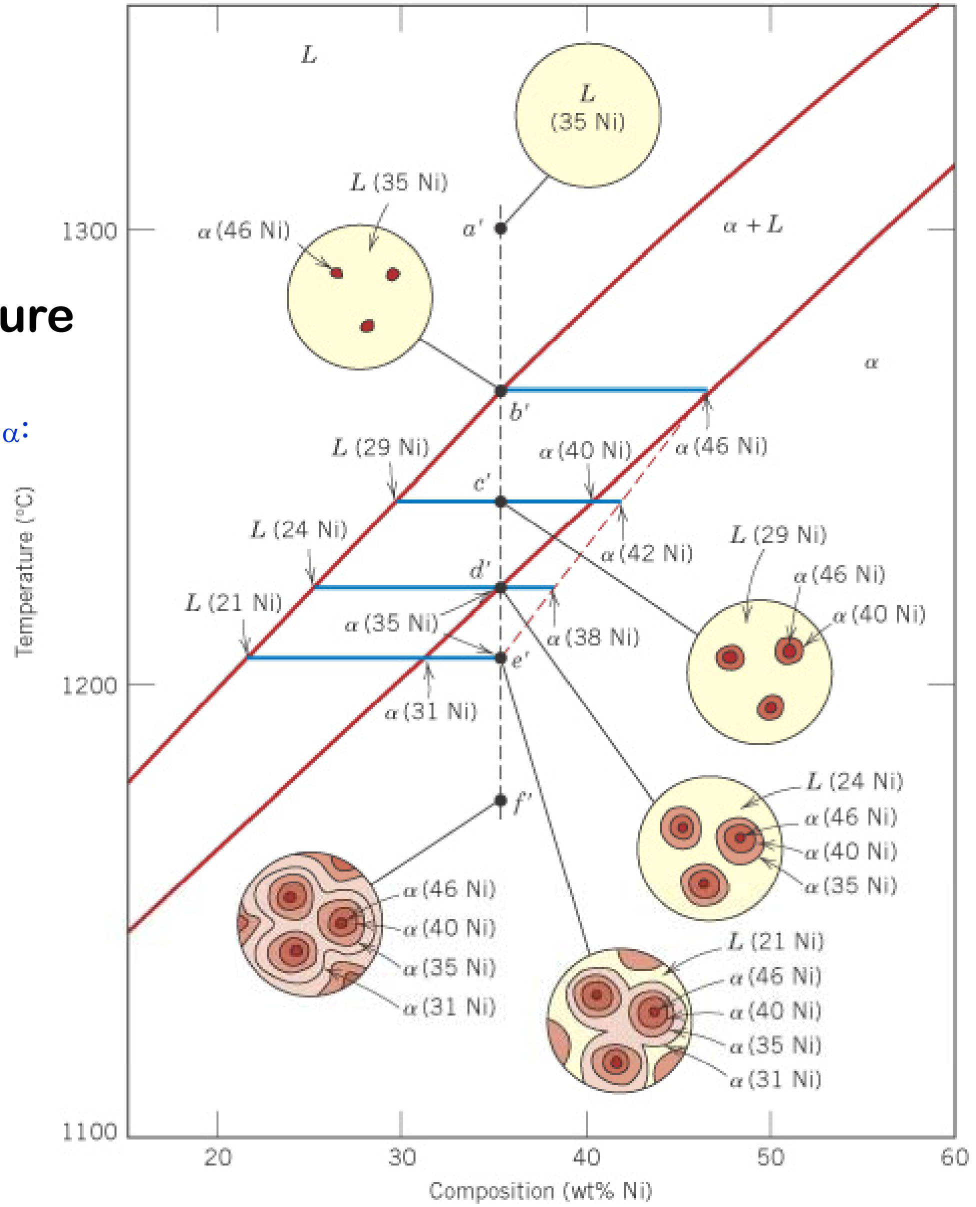


Development of microstructure in a Cu-Ni alloy

Non-Equilibrium case
(real)

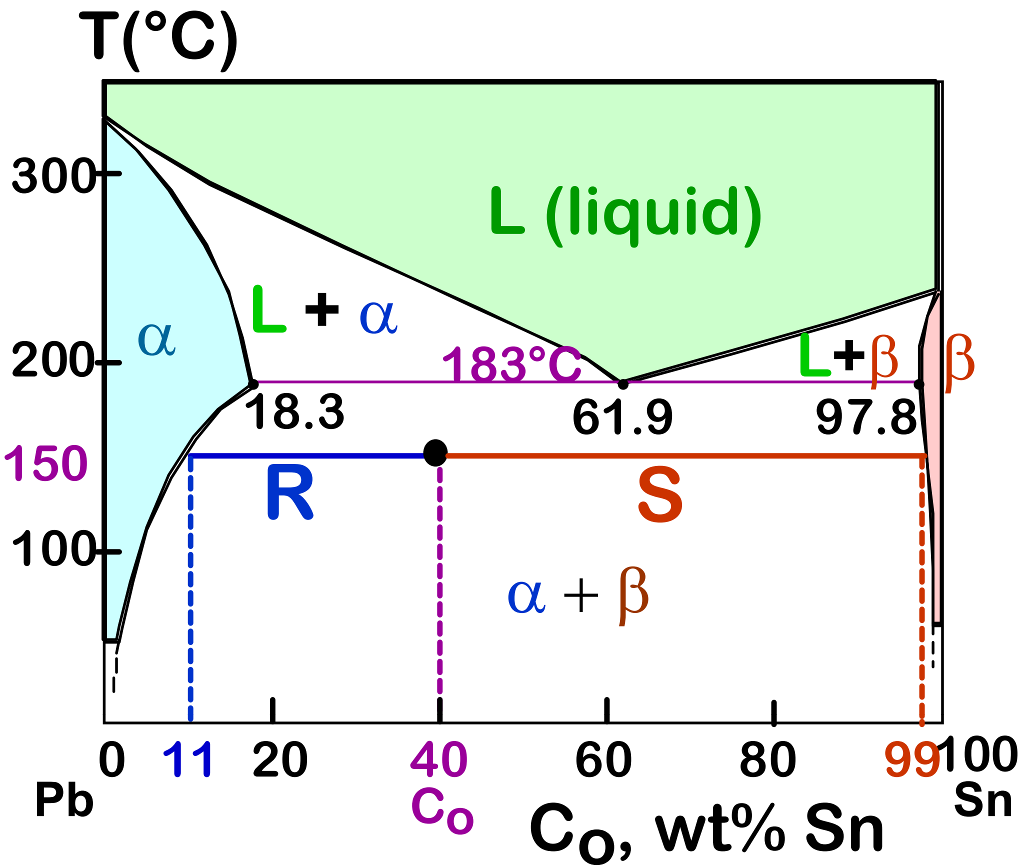
- **Fast cooling:**
  Cored structure
- **Slow cooling:**
  Equilibrium structure





How we can prevent coring and get equilibrium structure?

Binary Eutectic Systems: Sn-Pb



Sn-Pb system:

- 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

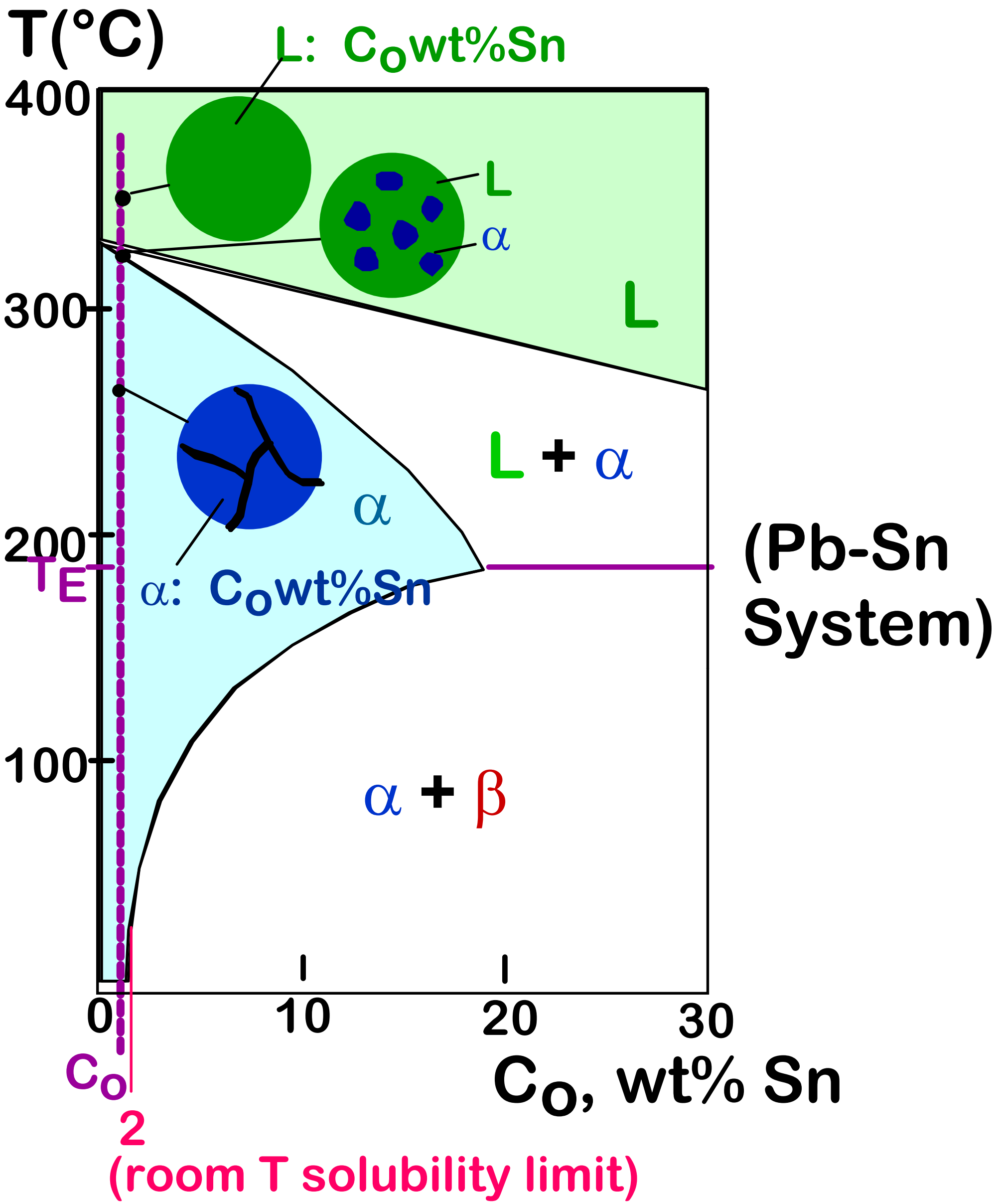
  C_b = 99wt%Sn

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

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

Microstructures in binary systems

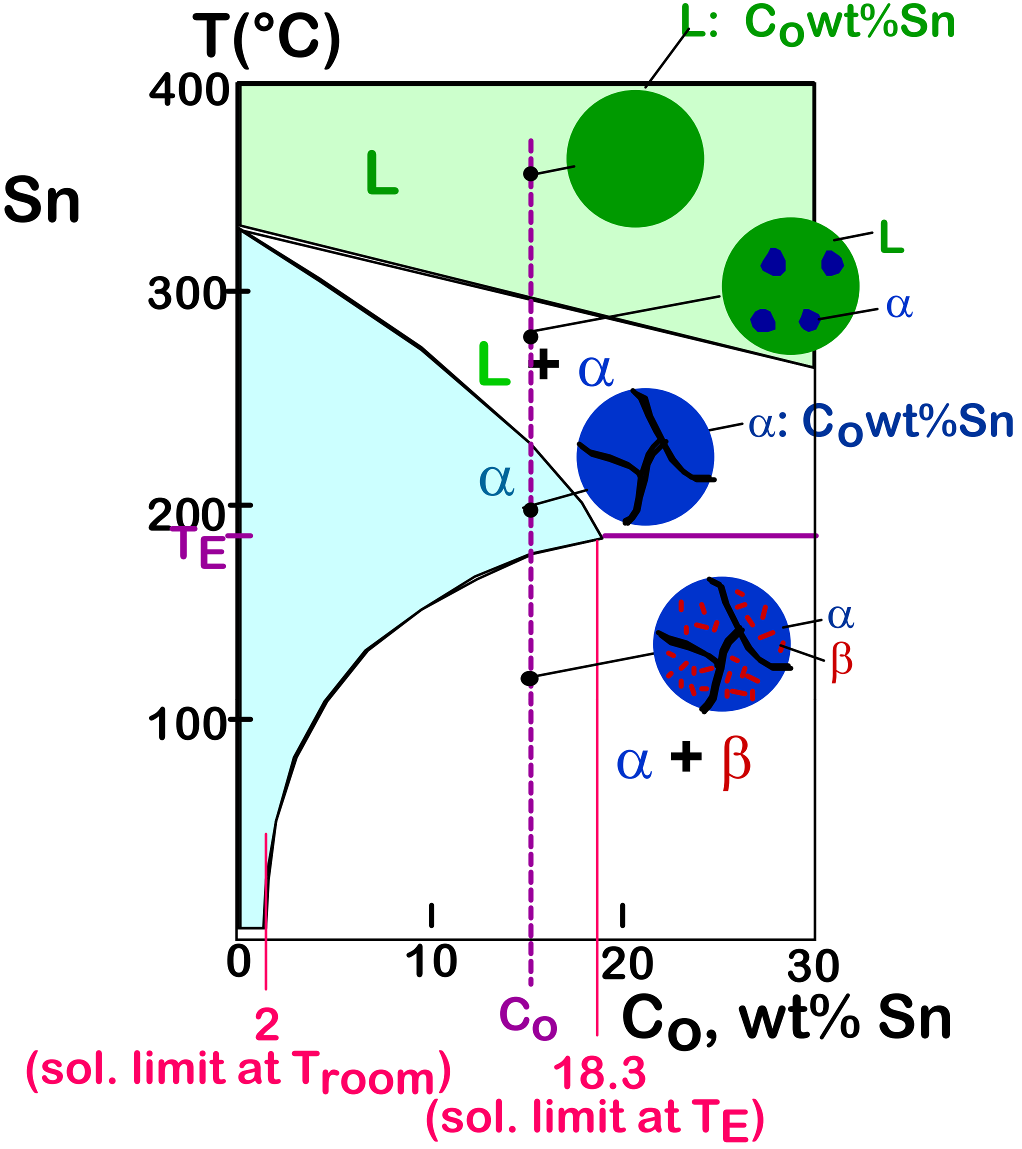
- C_o < 2wt%Sn
- Result:
  --polycrystal of α grains.



Microstructures in binary systems

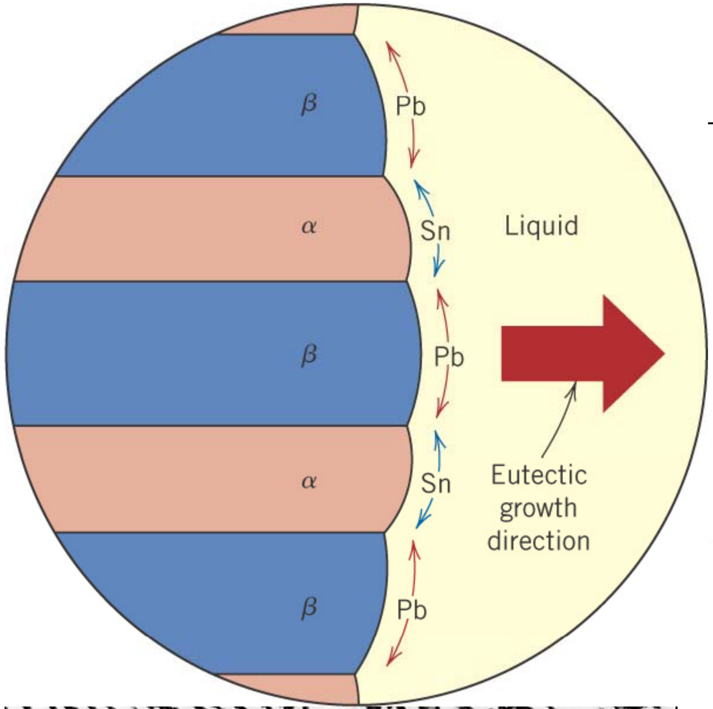
- **2wt%Sn < C_o < 18.3wt%Sn**
- **Result:**

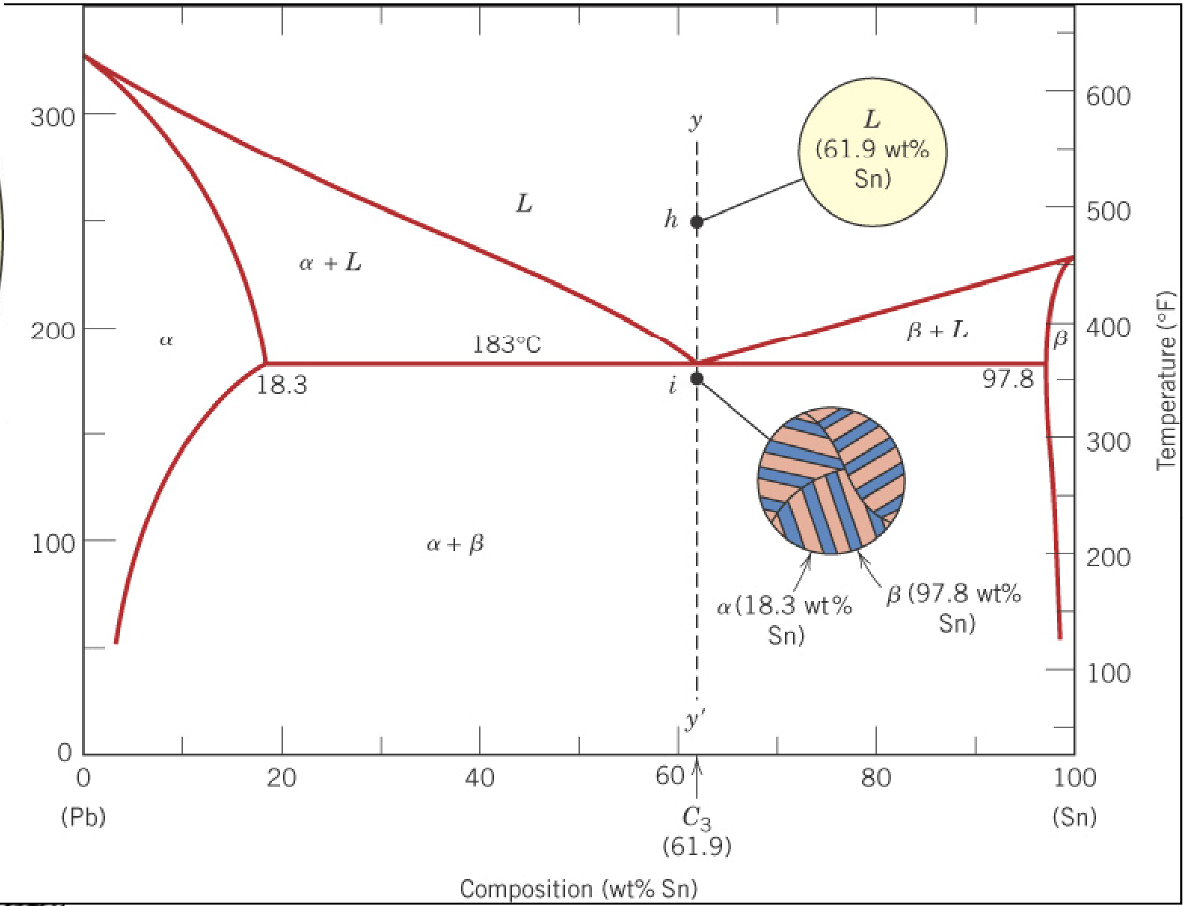
  --α polycrystal with fine β crystals.

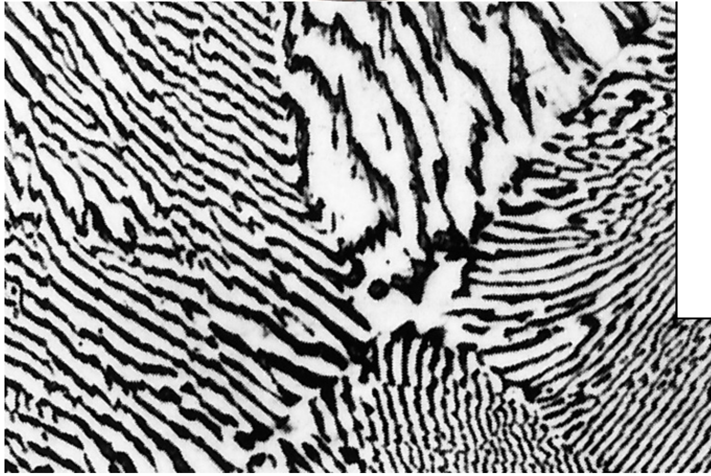


Microstructures in binary systems

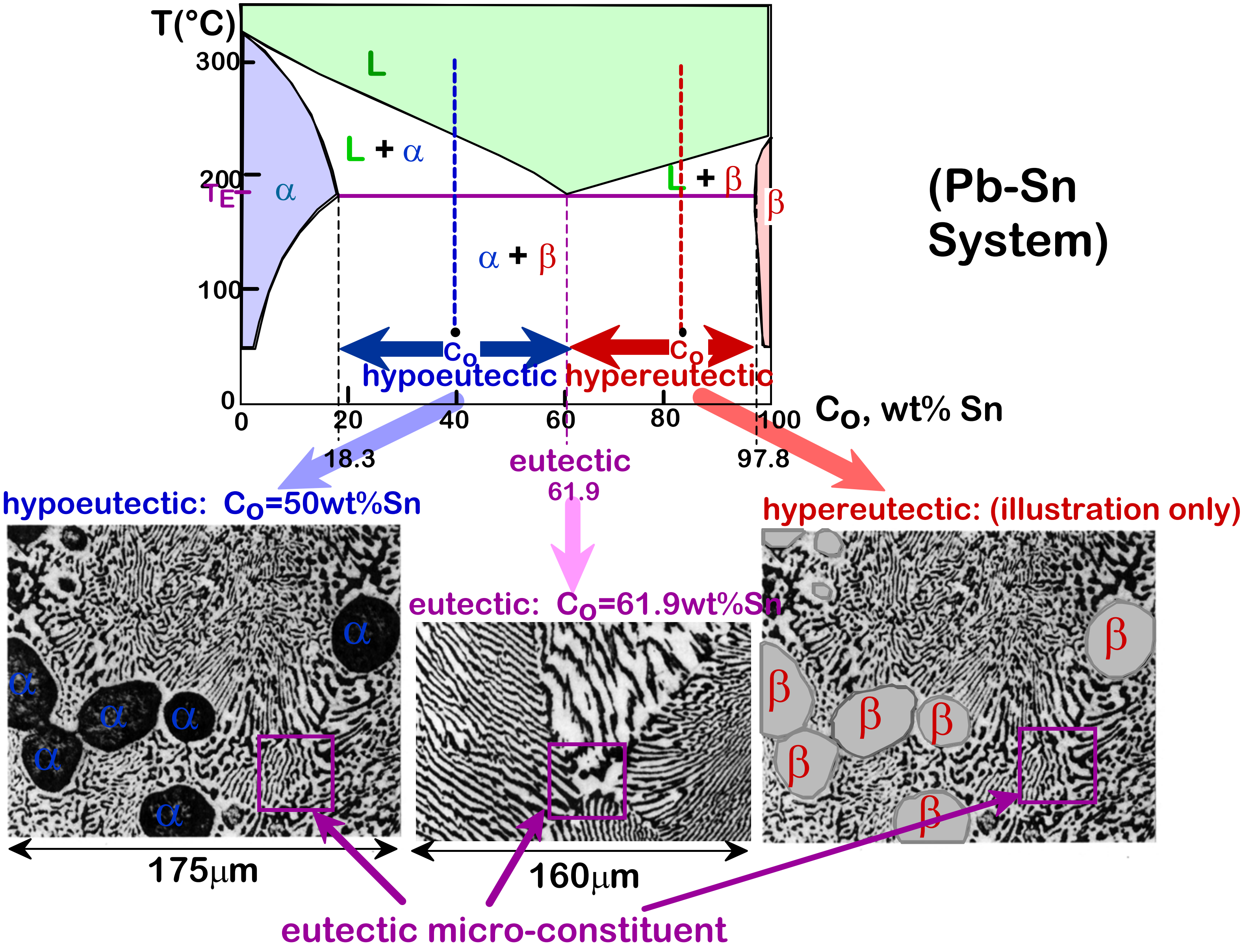
- **Eutectic composition**







Microstructures in binary systems: eutectic and around



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

IRON-CARBON (Fe-C) PHASE DIAGRAM

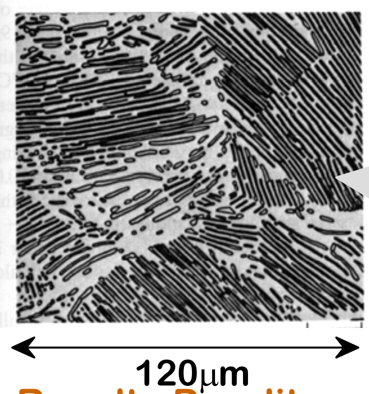
- **2 important points**

-Eutectic (A):

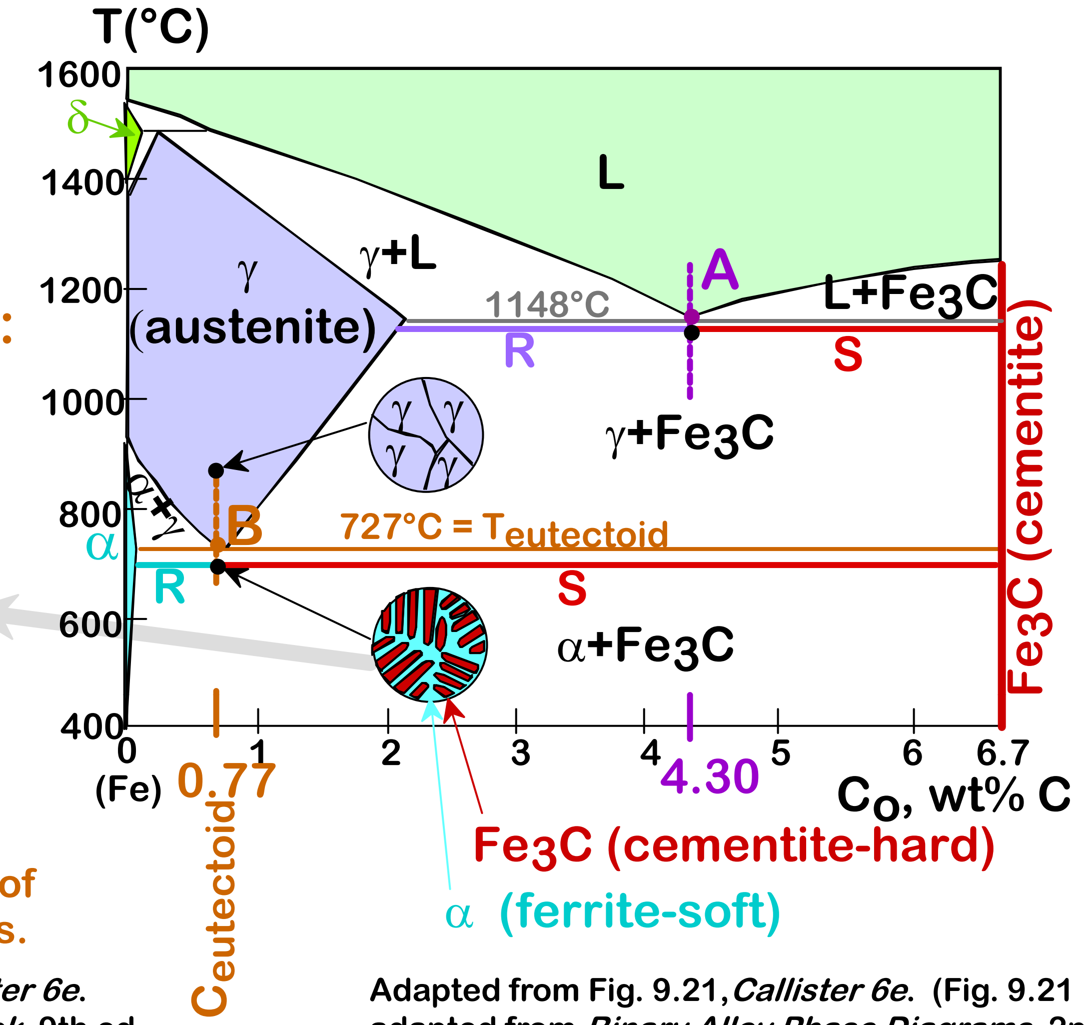
$$L \Rightarrow \gamma + Fe_3C$$

-Eutectoid (B):

$$\gamma \Rightarrow \alpha + Fe_3C$$



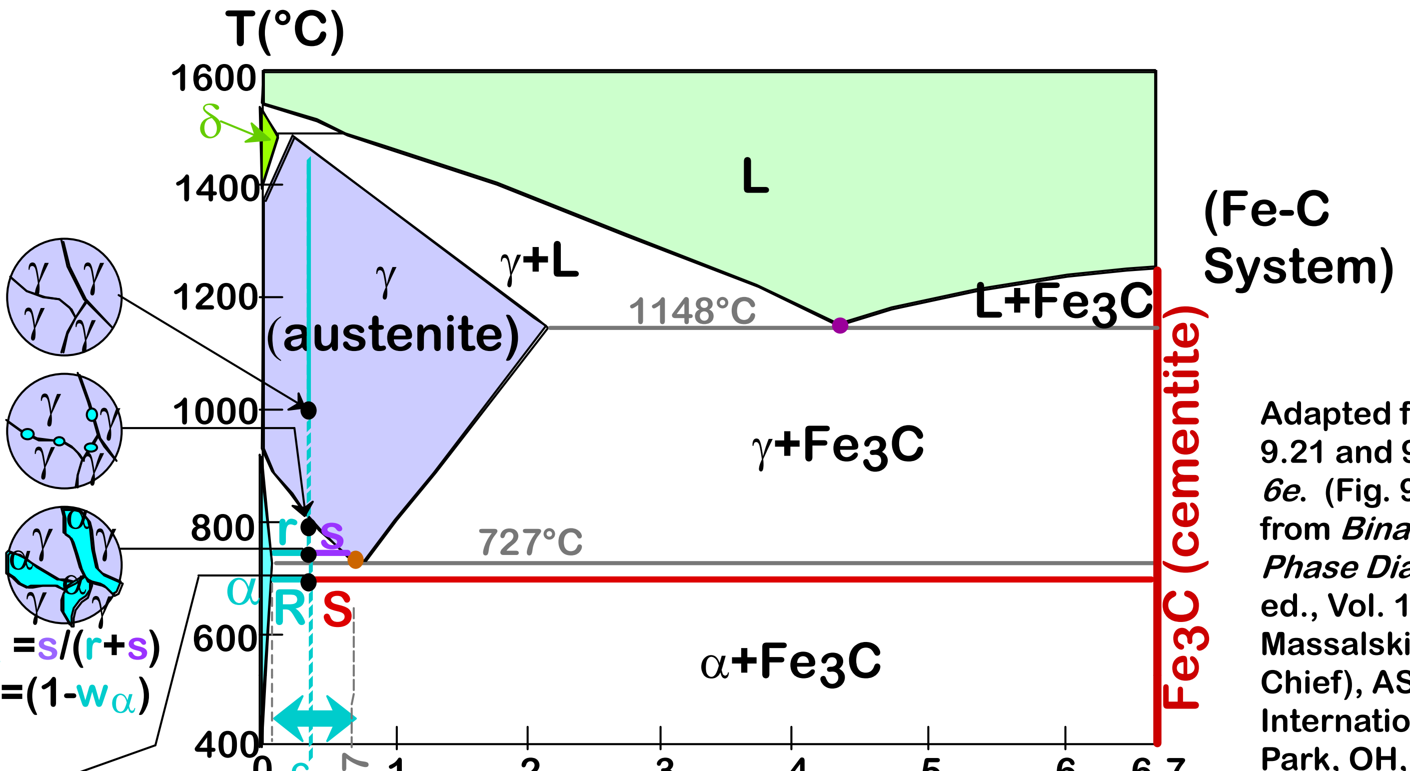
Result: Pearlite = alternating layers of α and Fe_3C phases.



(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



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

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

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

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

$w_{Fe_3C} = (1-w_{\alpha})$

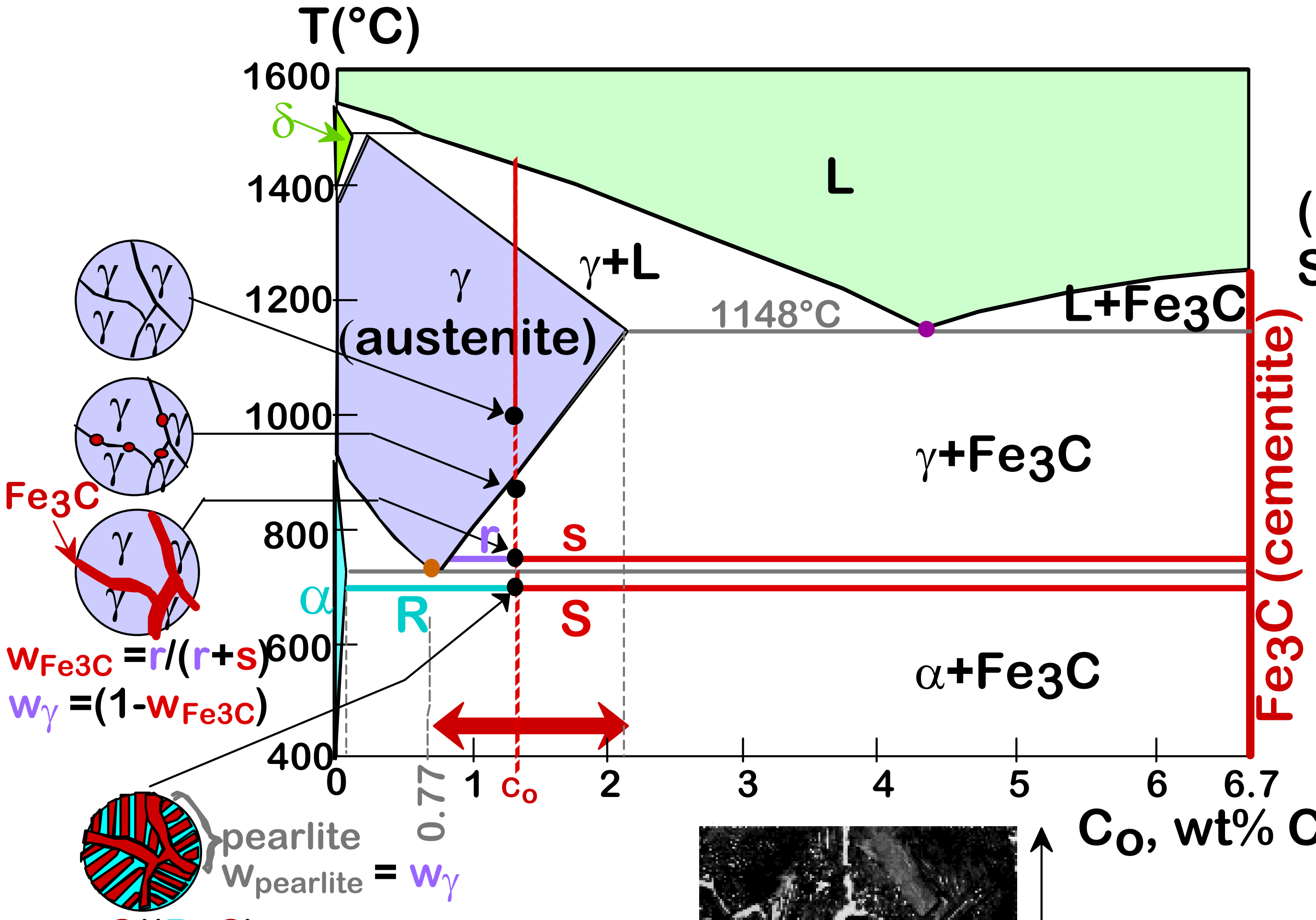
C$_o$, wt% C

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



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

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

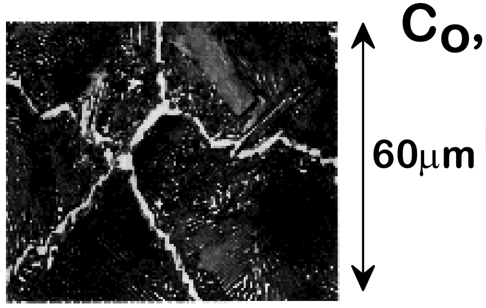
$w_{pearlite} = w_\gamma$

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

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

(Fe-C System)

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.)



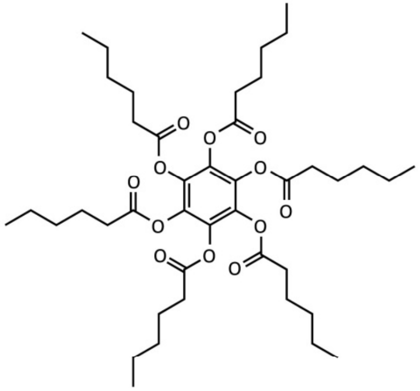
Hypereutectoid steel

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

Liquid crystals

- Mesophase – an intermededediate 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

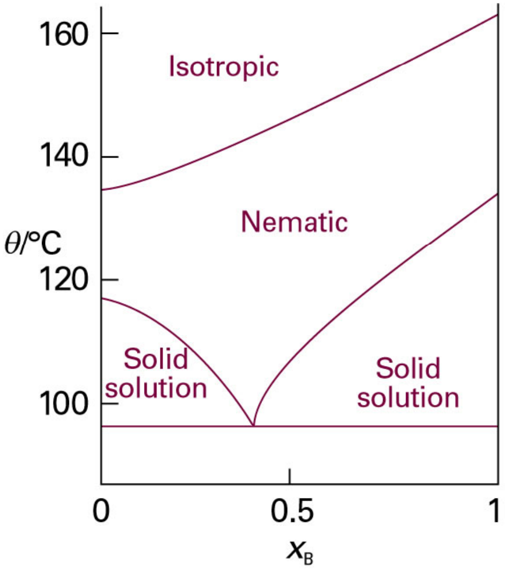
1

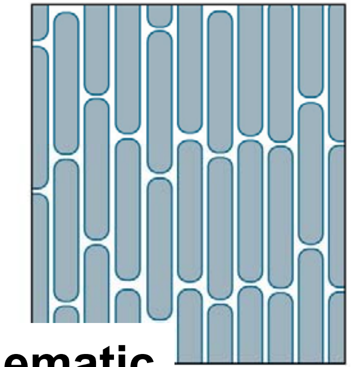


2

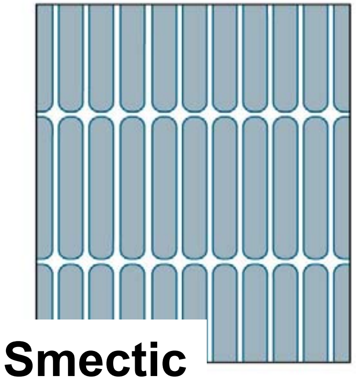
calamitic (rod-like)

discotic

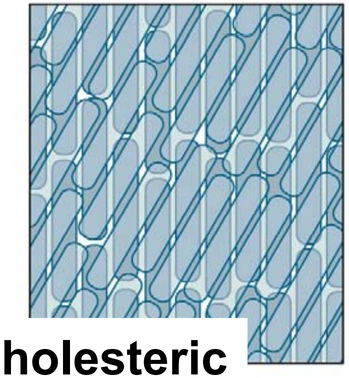




Nematic

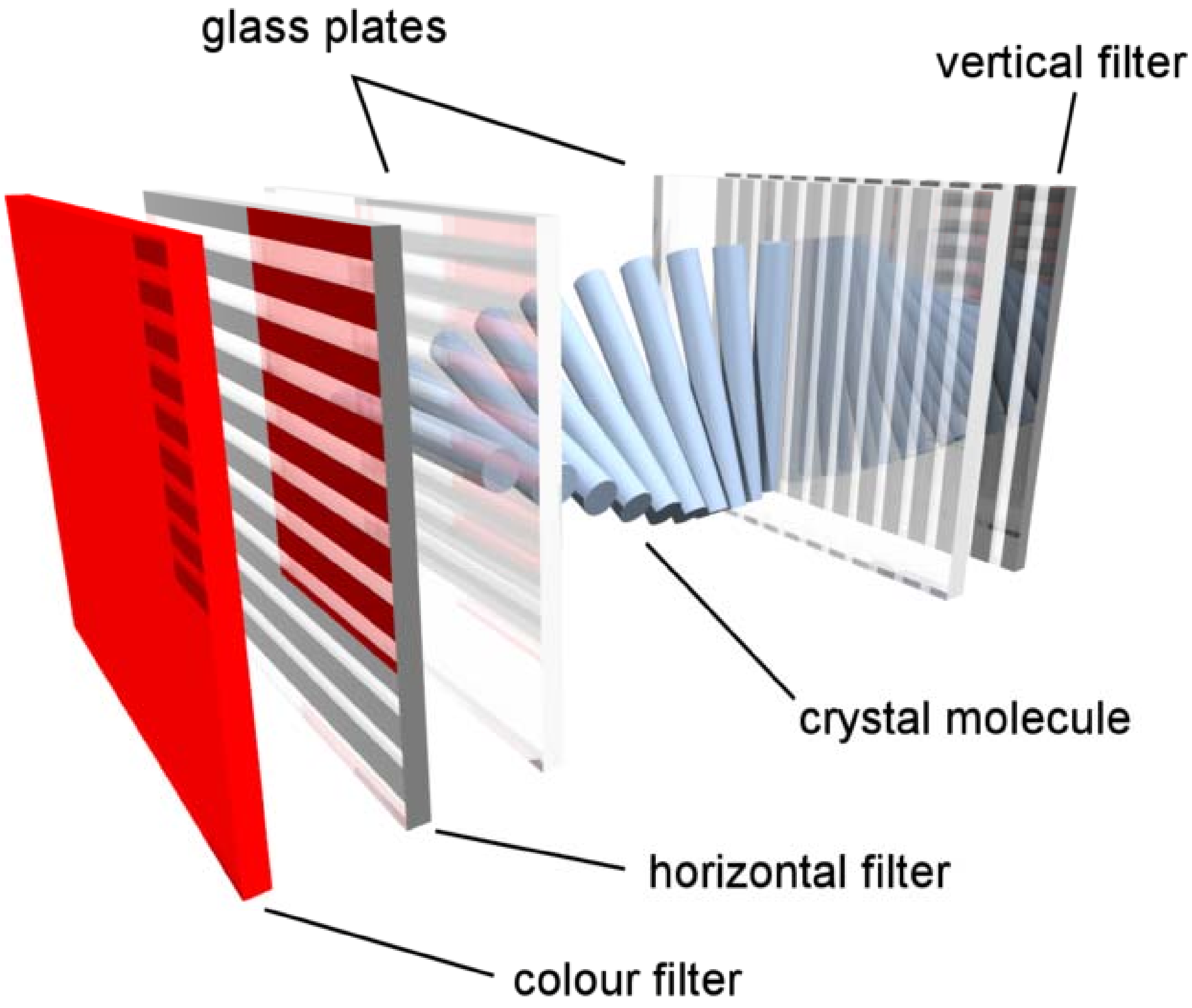


Smectic



Cholesteric

Nematic crystals in LCD



EQUILIBRIUM

Chemical Equilibrium

$$A + B \rightleftarrows C + D$$

- Chemical reaction tend to move towards a dynamic equilibrium in which both reactants and products are present but have no tendency to undergo net change

<u>The question</u>: How to predict the composition of mixture at various condition

The Gibbs energy minimum

- Spontaneous change at const P and T happens towards lower values of the Gibbs energy
- Let's consider reaction $A \rightleftharpoons B$

extent of the reaction

If some amount $d\xi$ of A changed into B: $dn_A = -d\xi$

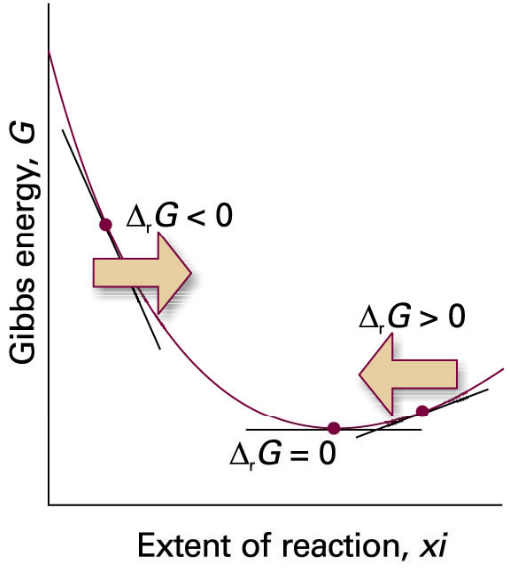
$$dn_B = +d\xi$$

Reaction Gibbs energy (definition): $\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T}$

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

$$\boxed{\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \mu_B - \mu_A}$$

Difference between chemical potentials of the products and the reactants at the composition fo the reaction mixture

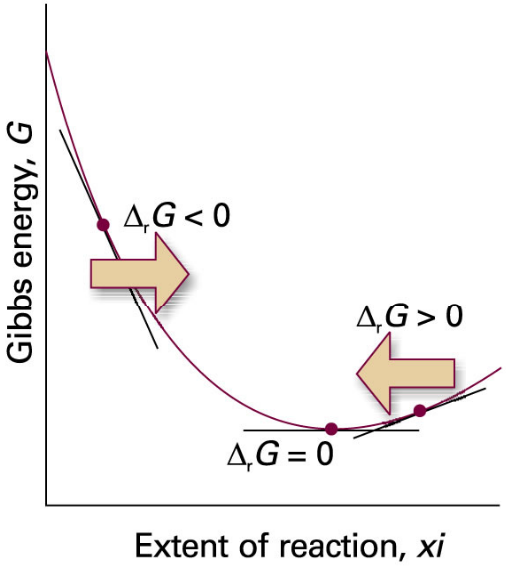


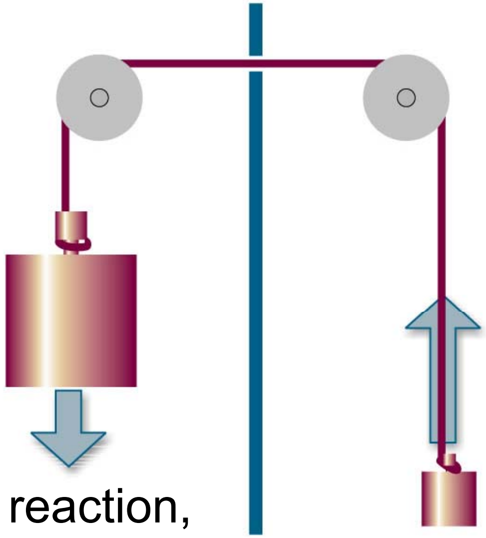
At equilibrium $\Delta_r G = 0$

The Gibbs energy minimum

- Spontaneity reaction at const P, T

$\Delta_r G < 0$	Forward reaction is spontaneous, reaction *exergonic* (work-producing)
$\Delta_r G = 0$	Reaction at equilibrium
$\Delta_r G > 0$	Reverse reaction is spontaneous, reaction *endergonic* i.e. required work to go in forward reaction





Exergonic reaction, e.g. glucose oxidation

Endergonic reaction, e.g. protein synthesis

The description of equilibrium

- Perfect gas equilibrium

$$\Delta_r G = \mu_B - \mu_A = (\mu_B{}^{\theta} + RT\ln p_B) - (\mu_A{}^{\theta} + RT\ln p_A) =$$

$$= \Delta_r G^{\theta} + RT\ln\frac{p_B}{p_A}$$

Q – reaction quotient

K- equilibrium constant

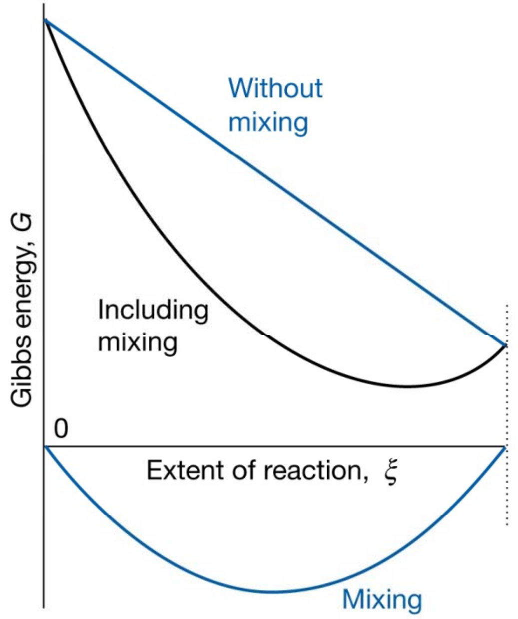
At equilibrium:

$$\Delta_r G = 0 = \Delta_r G^{\theta} + RT\ln\frac{p_B}{p_A}$$

$$RT\ln K = -\Delta_r G^{\theta}$$

Why reaction doesn't go till the end:

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



The description of equilibrium

- General case of a reaction $2A+B \longrightarrow 3C+D$

$$0 = 3C + D - 2A - B$$

$$\Delta_r G = \Delta_r G^{\theta} + RT\ln Q$$

$$\Delta_r G^{\theta} = \sum_{\text{products}} \nu \Delta_f G^{\theta} - \sum_{\text{reactants}} \nu \Delta_f G^{\theta}$$

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}} \qquad Q = \prod_j a_j^{\nu_j}$$

For example, for the reaction above: $Q = \dfrac{a_C^{\ 3} a_D}{a_A^{\ 2} a_B}$

The description of equilibrium

At equilibrium:

$$K = \left(\prod_j a_j^{\nu_j} \right)_{equilibrium}$$

$$RT \ln K = -\Delta_r G^{\theta}$$

Example: Find degree of dissociation of water vapour at 2300K and 1 bar if standard Gibbs energy for decomposition is 118 kJ/mol

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g)$$

$$\ln K = -\frac{\Delta G^{\theta}}{RT} = \frac{118*10^3}{8.3*2300} \qquad K = 2.08*10^3$$

$$K = \frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}} \quad \Longrightarrow \quad \alpha = 0.0205$$

The description of equilibrium

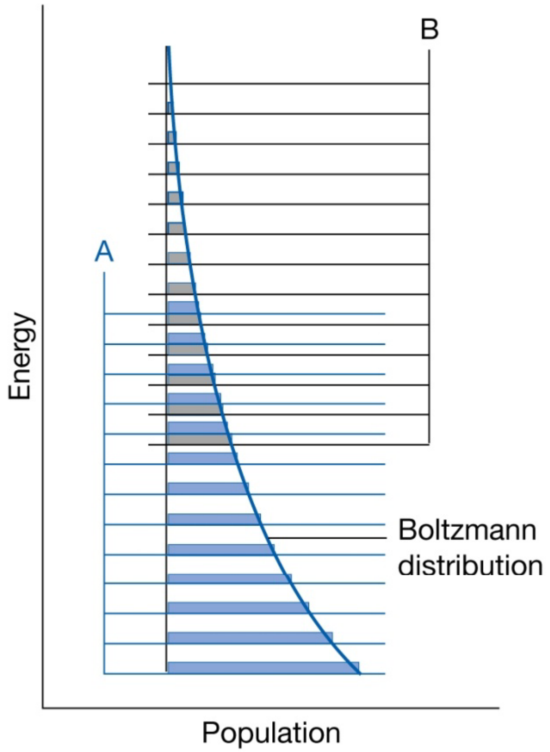
$$RT \ln K = -\Delta_r G^\ominus \qquad K = e^{-\Delta_r G^\ominus / RT} = e^{-\Delta_r H^\ominus / RT} e^{\Delta_r S^\ominus / R}$$

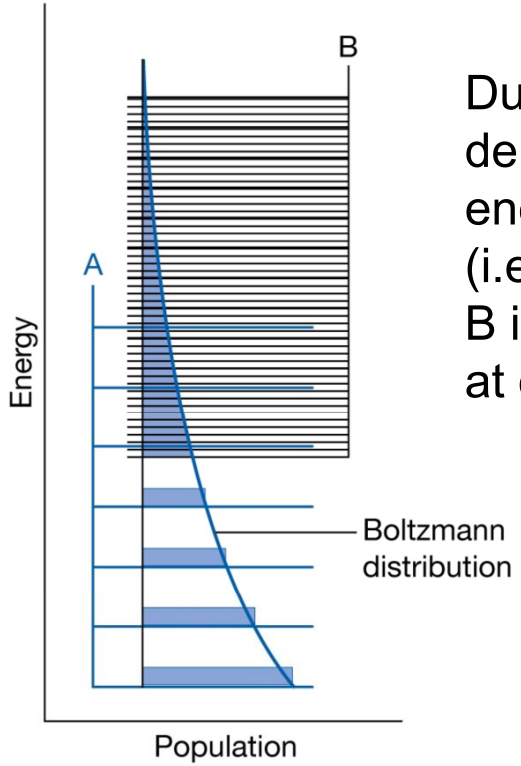
Increase with reaction entropy

decrease with reaction enthalpy

Boltzmann distribution interpretation:

$$p_i = N \frac{e^{-E_i / kT}}{\sum_i e^{-E_i / kT}}$$





Due to higher density of energy levels (i.e. higher S), B is dominant at equilibrium

The description of equilibrium

- Relation between equilibrium constants

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{b_C b_D}{b_A b_B} = K_\gamma K_b$$

At low concentration: $K \approx K_b$

- Using biological standard state

If a biological reaction involves H+ ions, we have to take into account that standard biological condition is at $pH = -\log a_{H^+} = 7$

$$NADH(aq) + H^+(aq) \rightleftarrows NAD^+(aq) + H_2(g)$$

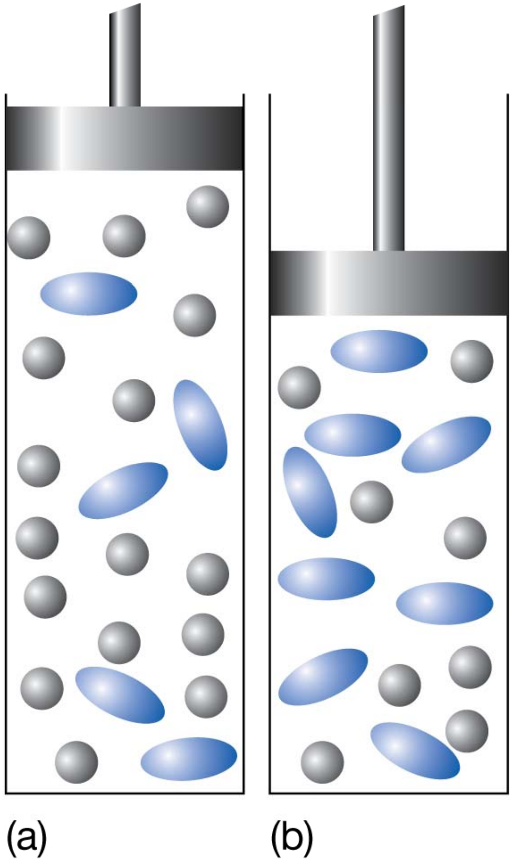
$$\Delta_r G^{\oplus} = \Delta_r G^{\theta} + 7 \ln 10 \times RT =$$

$$= -21.8 kJ / mol + 16.1 \times 8.3 \times 10^{-3} kJ / K\,mol \times 310 K = 19.7 kJ / mol$$

The response of equilibria to the conditions

- Equilibria will respond to temperature, pressure and concentration changes

$$RT \ln K = -\Delta_r G^{\theta}$$



Pressure dependence:

Depends on standard $\Delta_r G^{\theta}$ (standard pressure)

$$\left(\frac{\partial K}{\partial P}\right)_T = 0$$

$$A(g) \rightleftharpoons 2B(g) \qquad K = \frac{p_B{}^2}{p_A p^{\theta}}$$

- Pressure increase by injecting inert gas: no change as partial pressures of reactants and products stay the same .
- Pressure increase by compression: system will adjust partial pressures so the constant stays the same.

The response of equilibria to the conditions

- Le Chatelier principle:
  A system at equilibrium, when subjected to disturbance responds in a way that tends to minimize the effect of disturbance

Extent of dissociation, **α**:

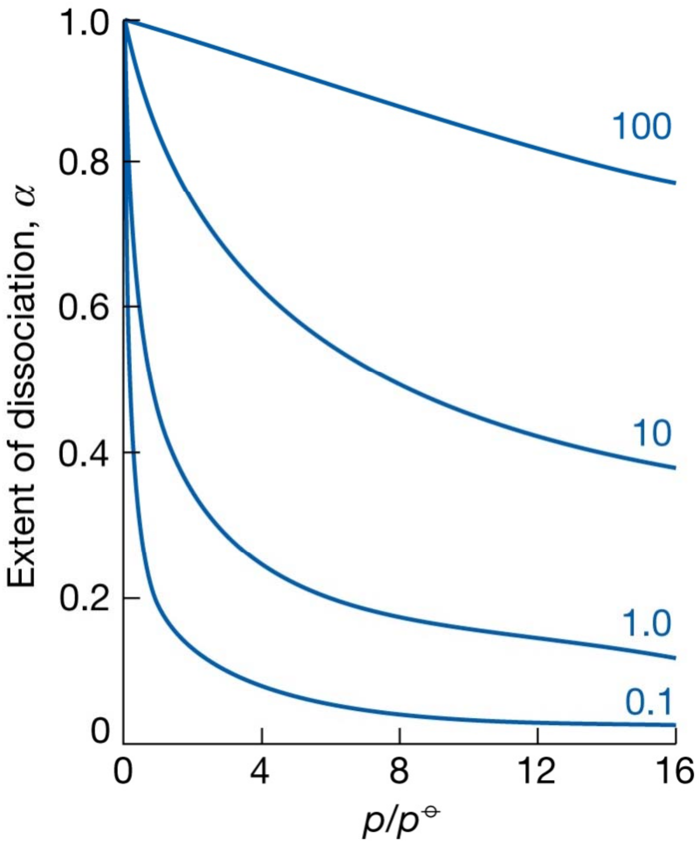
$$\underset{(1-\alpha)n}{A(g)} \rightleftharpoons \underset{2\alpha n}{2B(g)} \qquad K = \frac{p_B{}^2}{p_A p^\theta}$$

Mole fractions at equilibrium:

$$\kappa_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \frac{1-\alpha}{1+\alpha} \qquad \kappa_B = \frac{2\alpha}{1+\alpha}$$

$$K = \frac{p_B{}^2}{p_A} = \frac{\kappa_B{}^2 p^2}{\kappa_A p} = \frac{4\alpha^2 p}{1-\alpha^2}$$

$$\alpha = \left(\frac{1}{1+4p/Kp^\theta}\right)^{½}$$



The response of equilibria to the conditions

- Temperature response

Equilibrium will shift in endothermic direction if temperature is increased and in exothermic direction if temperature is lowered.

Van’t Hoff equation:

$$RT\ln K = -\Delta_r G^{\ominus}$$

Gibbs-Helmholtz equation

$$\frac{d\ln K}{dT} = -\frac{1}{R}\frac{d(\Delta_r G^{\ominus}/T)}{dT} \qquad \frac{d(\Delta_r G^{\ominus}/T)}{dT} = -\frac{\Delta_r H^{\ominus}}{T^2}$$

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2} \qquad \frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^{\ominus}}{R}}$$

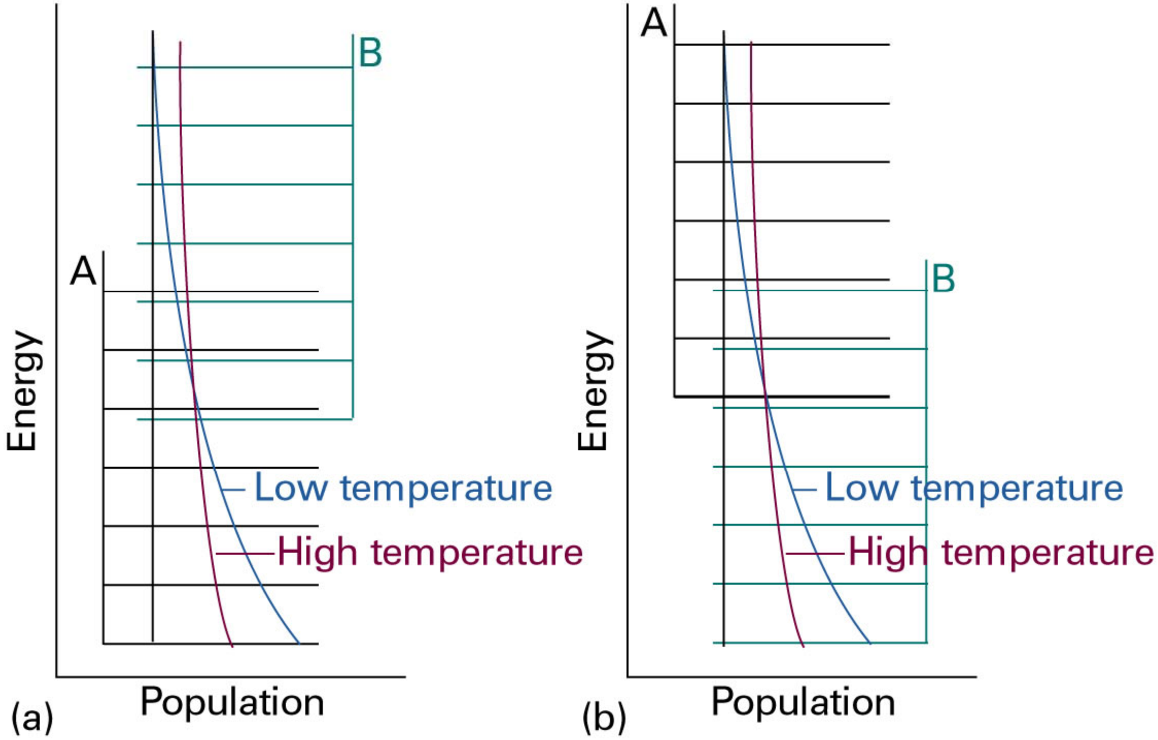
i.e. for exothermic reaction:

$$\Delta_r H^{\ominus} < 0 \qquad \frac{d\ln K}{dT} < 0$$

So, we can predict the equilibrium constant at another temperature: $\ln K_2 - \ln K_1 = -\frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

The response of equilibria to the conditions

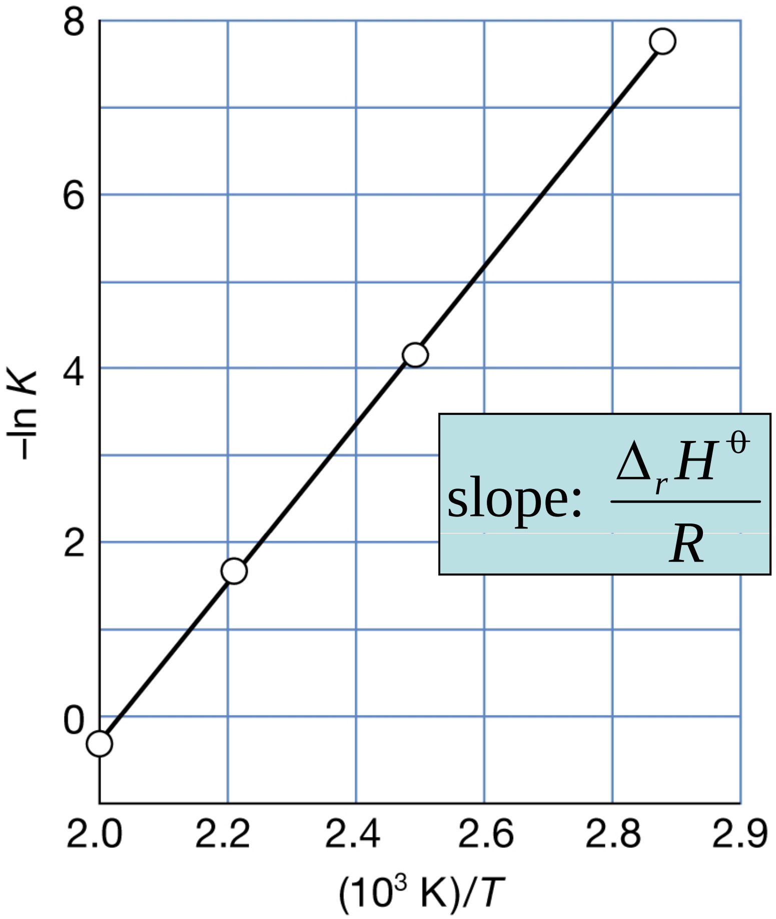
- Boltzmann distribution interpretation



The response of equilibria to the conditions

- Noncalorimetric measuring reaction enthalpy

$$\frac{d\ln K}{d(1/T)} = \frac{\Delta_r H^\theta}{R}$$



The response of equilibria to the conditions

- Value of K at different temperatures

$$\frac{d\ln K}{d(1/T)} = \frac{\Delta_r H^{\theta}}{R}$$

$$\ln K_2 - \ln K_1 = \frac{1}{R}\int_{1/T_1}^{1/T_2} \Delta_r H^{\theta} d(1/T) = \frac{\Delta_r H^{\theta}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Equilibria and pH

- Dissociation of water (autoprotolysis)

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_w = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_2O}{}^2} = a_{H_3O^+} a_{OH^-} = 10^{-14} \ \ at\,298K$$

Ionic dissociation constant of water

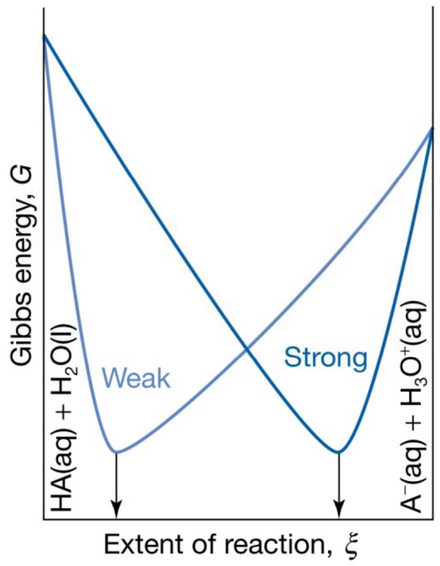
For pure water: $a_{H_3O^+} = a_{OH^-} = 10^{-7}$

$$pH = -\log a_{H_3O^+}$$

at low concentration equal to molarity

The response of equilibria to pH

- Arrhenius acid: increases concentration of H_3O^+ in solution
  Arrhenius base: increases concentration of OH^- in solution



Can be done via donation of OH^- or removing of H^+.

$$NaOH(aq) \rightleftharpoons Na^+(aq) + OH^-(aq)$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Acidity constant, $K_{a:}$

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} \qquad pK_a = -\log K_a$$

Conjugate base

Basicity constant, $K_{b:}$

Conjugate acid

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \qquad K_b = \frac{a_{HB^+} a_{OH^-}}{a_B} \qquad pK_b = -\log K_b$$

Example: dissociation of formic acid

- Example: pK of formic acid is 3.77 at 298K. What is pH of 0.01M solution? What would happen if it were strong acid?

$$HCOOH + H_2O(l) \rightleftharpoons HCOO^- + H_3O^+$$

$$K_a = \frac{\left[H_3O^+\right]\left[HCOO^-\right]}{\left[HCOOH\right]} = 1.695\times10^{-4} \Rightarrow x^2 + 1.695\times10^{-4}x - 1.695\times10^{-6} = 0 \xrightarrow{x_\pm = \frac{-b\pm\sqrt{b^2-4ac}}{2a}} x = 1.22\times10^{-3}$$

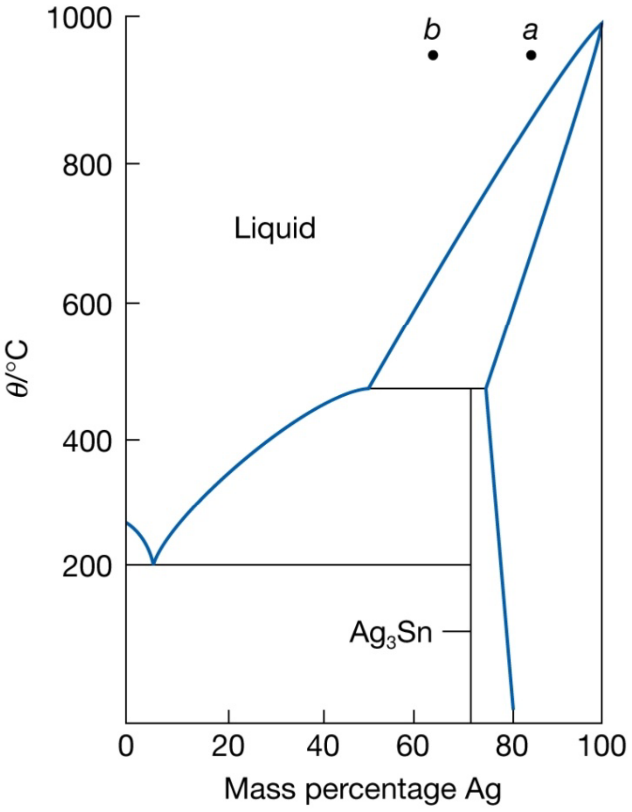
Answer: $[H_3O^+] = 1.22\times10^{-3}$

$$pH = 2.91$$

- What would be dissociation degree at pH=4 and pH=10?

Class problems: Last lecture

- Atkins 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.
- Atkins 6.10b Describe the diagram and what is observed when a and b are cooled down



Class problems:

- **Atkins 7.2b**: Molecular bromine is 24% dissociated at 1600K and 1 bar. Calculate K, $\Delta_r G^0$ at 1600K and predict K at 2000^0C, given $\Delta_r H^0$=+112kJ/mol over the temperature range
- **Atkins 7.4b**: In the gas phase reaction A+B=C+2D it was found that when 2mol A, 1mol B and 3 mol D were mixed and allowed to come to equilibrium at 25C, the mixture contained 0.79mol of C at 1 bar. Calculate mol fraction of every species at equilibrium, K_x, K and $\Delta_r G^0$.