EMA5001 Lecture 7
Short-Circuit Diffusion, &
Reaction Diffusion

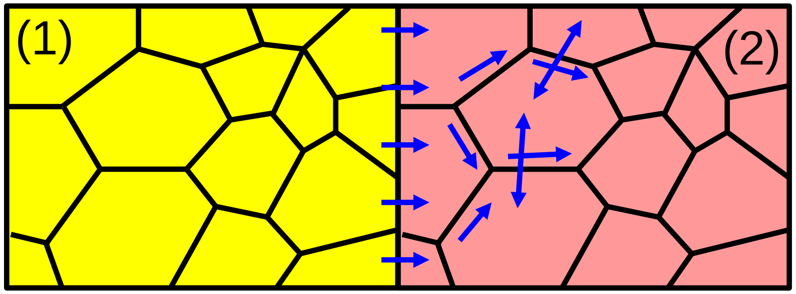
FLORIDA INTERNATIONAL UNIVERSITY

Diffusion Along Grain Boundaries (1)

- **Diffusion along grain boundaries or surface also follow Arrhenius Equation**

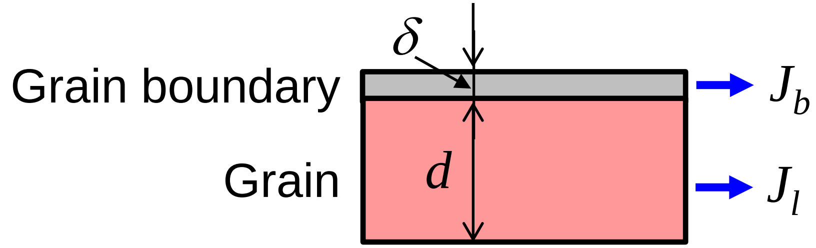
$$D_b = D_{b0} \exp\left(-\frac{Q_b}{RT}\right)$$

$$D_s = D_{s0} \exp\left(-\frac{Q_s}{RT}\right)$$

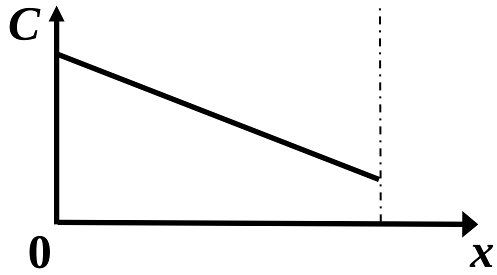


- **Relationship of lattice (bulk), grain boundaries, and surface diffusion**

$$D_s > D_b > D_l$$



- **Example**
  - Steady state diffusion through a thin polycrystalline sheet
  - Grain boundary perpendicular to sheet
  - Concentration gradient identical in grain boundaries and in lattice



Diffusion Along Grain Boundaries (2)

❑Continue from p.10

Flux through lattice: $J_l = -D_l \frac{dC}{dx}$

Flux through the grain boundary $J_b = -D_b \frac{dC}{dx}$

If grain size of d,

If grain boundaries has effective thickness of δ, and $\delta << d$

Total flux

$$J = \frac{J_l d + J_b \delta}{d + \delta} \approx \frac{J_l d + J_b \delta}{d} = \frac{1}{d} \cdot \left(-D_l \frac{dC}{dx} d - D_b \frac{dC}{dx} \delta \right)$$

Therefore,

$$J = -\left(D_l + \frac{\delta}{d} D_b \right) \cdot \frac{dC}{dx}$$

For diffusion through such a polycrystalline film, the apparent diffusion coefficient

$$D_{app} = D_l + \frac{\delta}{d} D_b$$

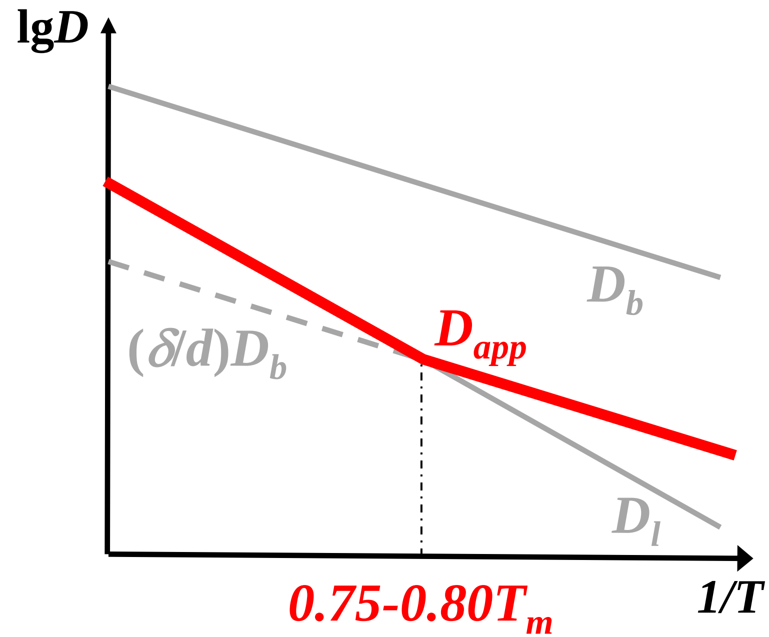
Diffusion Along Grain Boundaries (3)

❑ **Continue from p.11**

$$D_{app} = D_l + \frac{\delta}{d} D_b$$

Or

$$\frac{D_{app}}{D_l} = 1 + \frac{\delta D_b}{d D_l}$$



- The relative importance of lattice and grain diffusion depends on ratio of $\delta D_b / d D_l$
- Normally
  - $D_b > D_l$
  - $Q_b \cong 0.5\, Q_l$
- Temperature effect
  - Grain boundary diffusion dominates at low T;
  - Lattice diffusion dominates at high T
  - Transition temperature of 0.75-0.80 T_m
- More pronounced for material w/ small grains
- Grain boundary diffusion depends on specific boundary and even direction

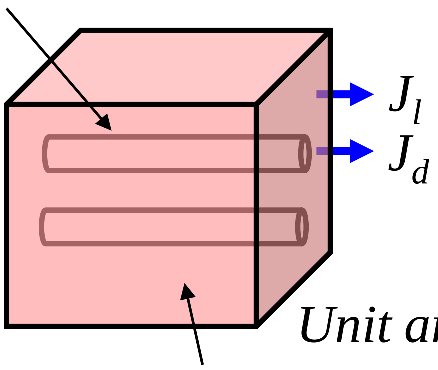
Diffusion Along Dislocations

❑Diffusion along dislocation is often also faster than lattice diffusion

- $Q_d \cong 0.5\ Q_l$

Flux through lattice: $J_l = -D_l \dfrac{dC}{dx}$

Flux through the dislocation $J_d = -D_d \dfrac{dC}{dx}$



If area fraction of total dislocation is g, ($g \sim 10^{-7}$)

Total flux

$$J = J_l + J_d g = -D_l \frac{dC}{dx} - gD_d \frac{dC}{dx} = -(D_l + gD_d)\frac{dC}{dx}$$

$$D_{app} = D_l + gD_d$$

$$\frac{D_{app}}{D_l} = 1 + g\frac{D_d}{D_l}$$

Diffusion Involving Two Phases - with Interfacial Reactions

❑ In binary system involving 2 phases, if

- Slow diffusion process
- Fast interfacial process → local equilibrium
- Fast phase transformation at the phase boundary

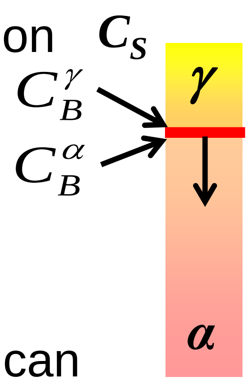
❑ Phase analysis

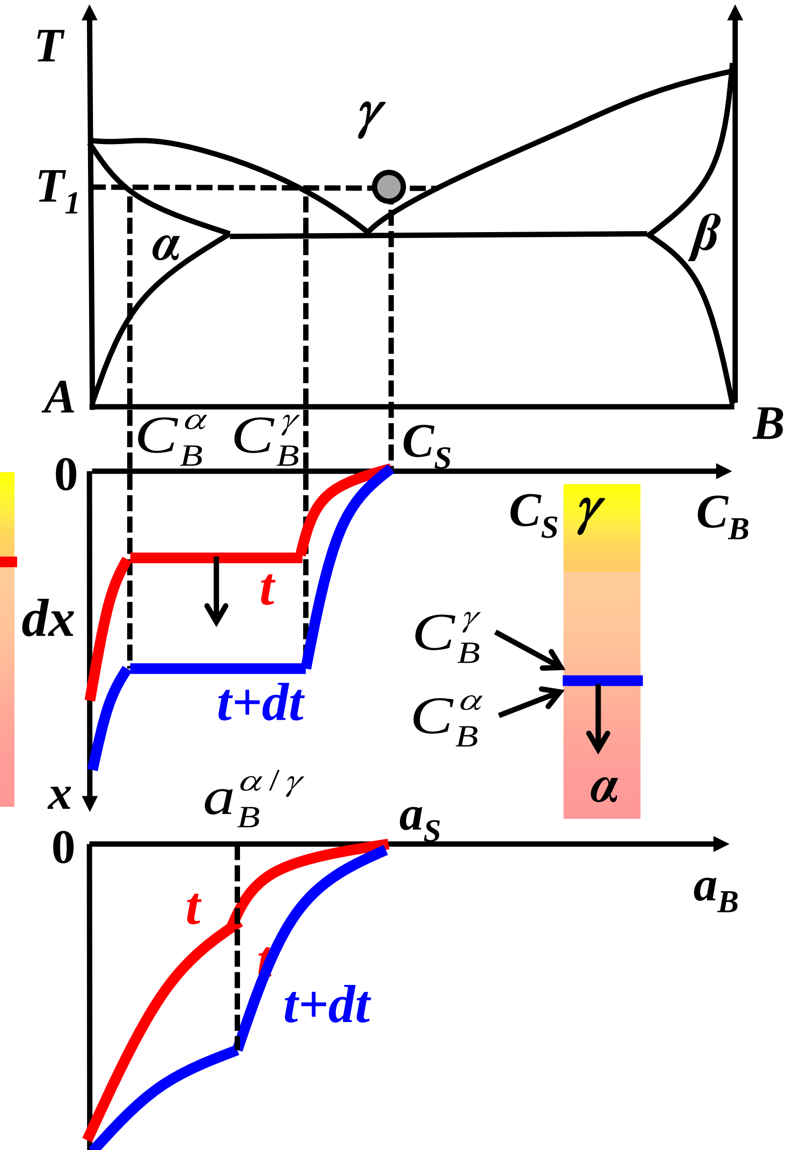
Binary alloy, fixed surface concentration of C_S The number of phases can be present:

$$f = c - p + 2$$

At constant temperature of T_1,

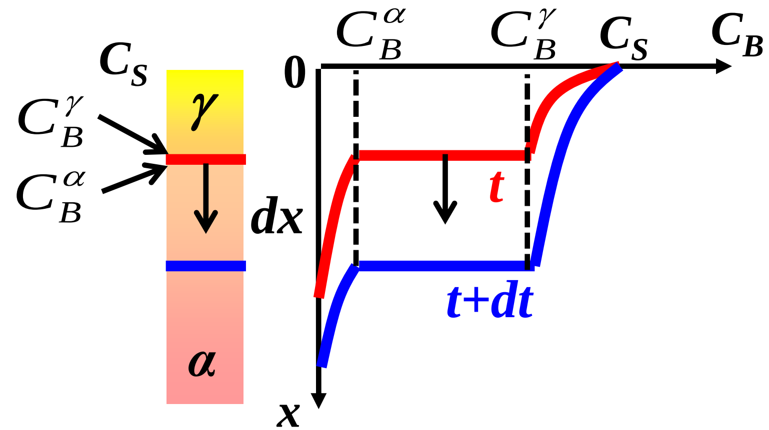
- Single phase region: composition can change
- At two phase boundary, composition will be fixed





Rate of Interface Movement if Controlled by Diffusion

❑For reaction diffusion



In a very short time dt, interface between α and γ moves from x to $x + dx$.

The change in B within dx is

$$\delta_B = \left(C_B^\gamma - C_B^\alpha\right)dx$$

From flux point of view, the change in B is

$$\delta_B = \left(-\tilde{D}_\gamma \frac{\partial C}{\partial x}\bigg|_{C_B^\gamma} dt\right) - \left(-\tilde{D}_\alpha \frac{\partial C}{\partial x}\bigg|_{C_B^\alpha} dt\right) = \left[\tilde{D}_\alpha \frac{\partial C}{\partial x}\bigg|_{C_B^\alpha} - \tilde{D}_\gamma \frac{\partial C}{\partial x}\bigg|_{C_B^\gamma}\right]dt$$

Therefore, $$\frac{dx}{dt} = \frac{1}{C_B^\gamma - C_B^\alpha} \cdot \left[\tilde{D}_\alpha \frac{\partial C}{\partial x}\bigg|_{C_B^\alpha} - \tilde{D}_\gamma \frac{\partial C}{\partial x}\bigg|_{C_B^\gamma}\right]$$

Introduce $$\lambda = \frac{x}{\sqrt{t}}$$

$$\frac{\partial C}{\partial x} = \frac{dC}{d\lambda} \cdot \frac{\partial \lambda}{\partial x} = \frac{dC}{d\lambda} \cdot \frac{\partial\left(\frac{x}{\sqrt{t}}\right)}{\partial x} = \frac{1}{\sqrt{t}} \cdot \frac{dC}{d\lambda}$$

Rate of Interface Movement if Controlled by Diffusion

❑**Continue from p. 15**

$$\frac{\partial C}{\partial x} = \frac{1}{\sqrt{t}} \cdot \frac{dC}{d\lambda}$$

Because the concentration in each phase at the interface are constant, $\frac{dC}{d\lambda}$ is a constant depending on concentration

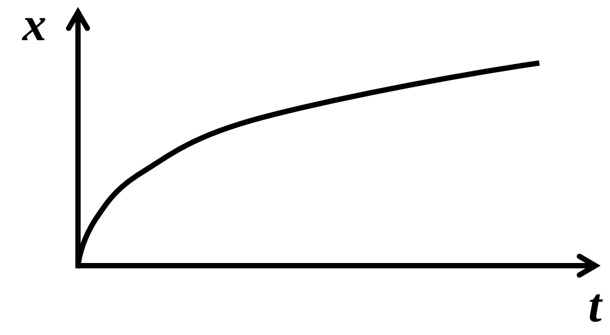
$$\frac{dx}{dt} = \frac{1}{C_B^\gamma - C_B^\alpha} \cdot \left[\tilde{D}_\alpha \left.\frac{\partial C}{\partial x}\right|_{C_B^\alpha} - \tilde{D}_\gamma \left.\frac{\partial C}{\partial x}\right|_{C_B^\gamma} \right]$$

Therefore,

$$\frac{dx}{dt} = A'(C)\frac{1}{\sqrt{t}}$$

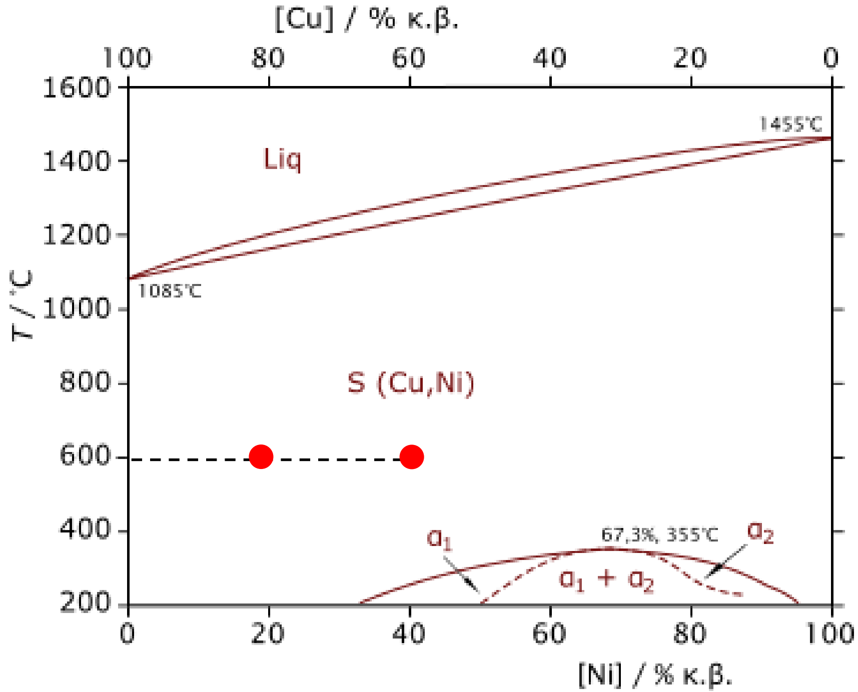
Integrate on both sides, we have $x = B'(C)\sqrt{t}$

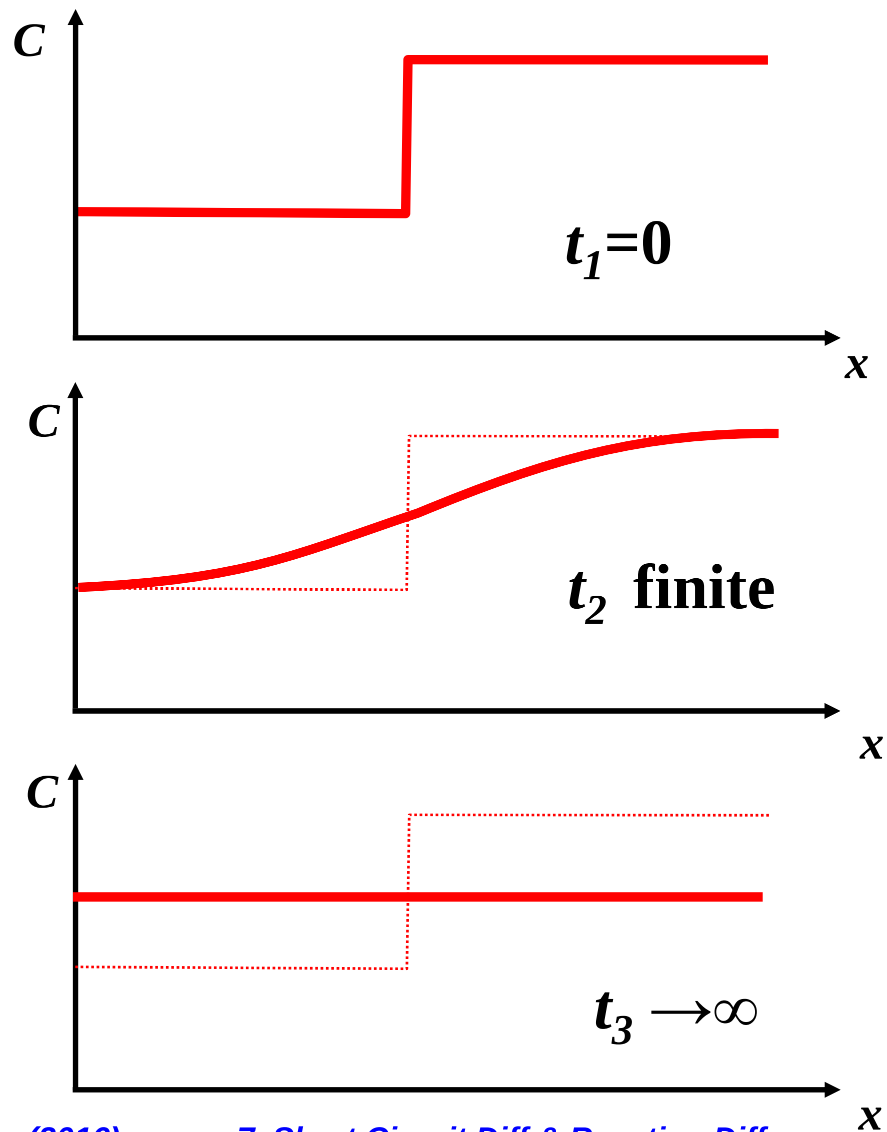
$$x^2 = B(C)t$$



Concentration Profile Change for Diffusion involving Single Phase

- Two piece of Ni-Cu alloys with different initial compositions put in close contact at elevated temperature, plot the change of concentration profile for i) $t_1 = 0$, ii) t_2 finite, iii) $t_3 \rightarrow \infty$



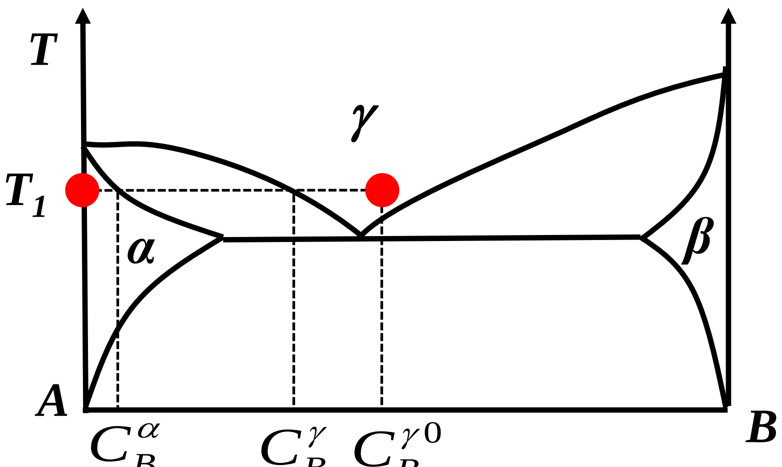


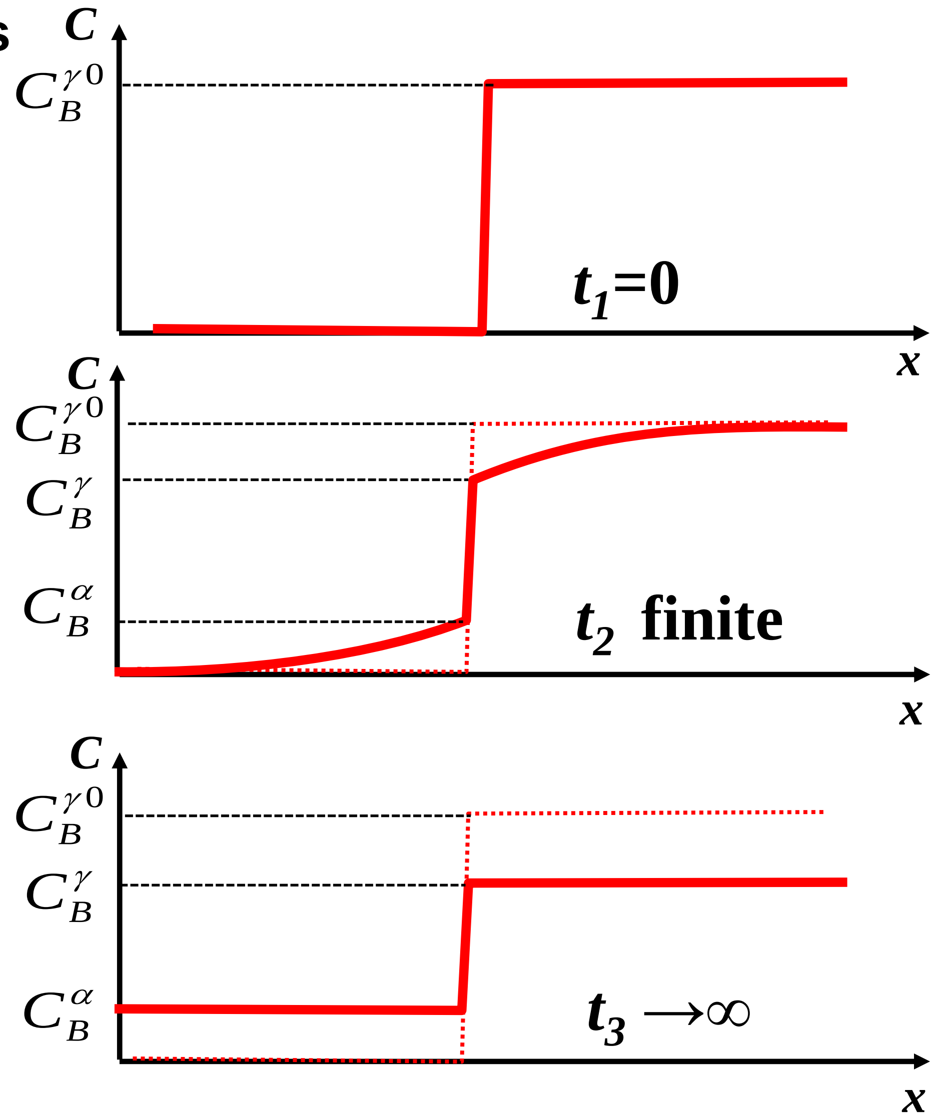
Concentration Profile Change for Diffusion involving Two-Phases (1)

- Two pieces of <u>similar sized</u> alloys with different composition and phases (one is α with pure A and the other is γ) are put in close contact at elevated temperature, as below.

  Assuming slow diffusion and local equilibrium at interface

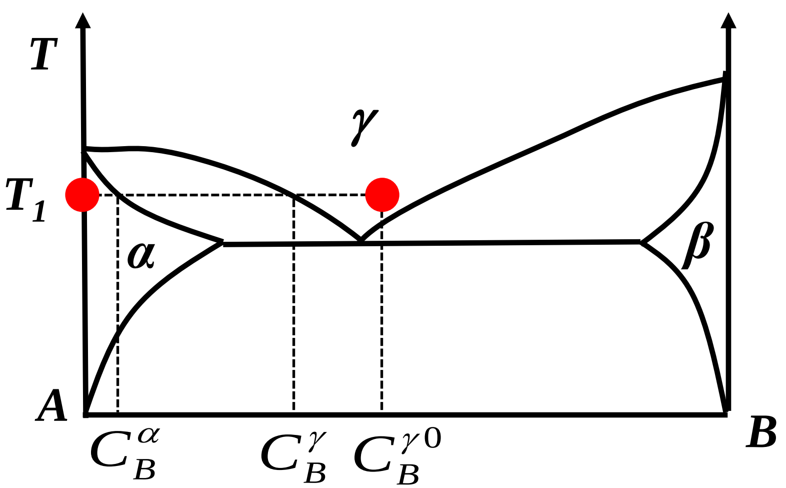
  Please plot concentration profile for i) t_1 = 0, ii) t_2 finite, iii) $t_3 \rightarrow \infty$

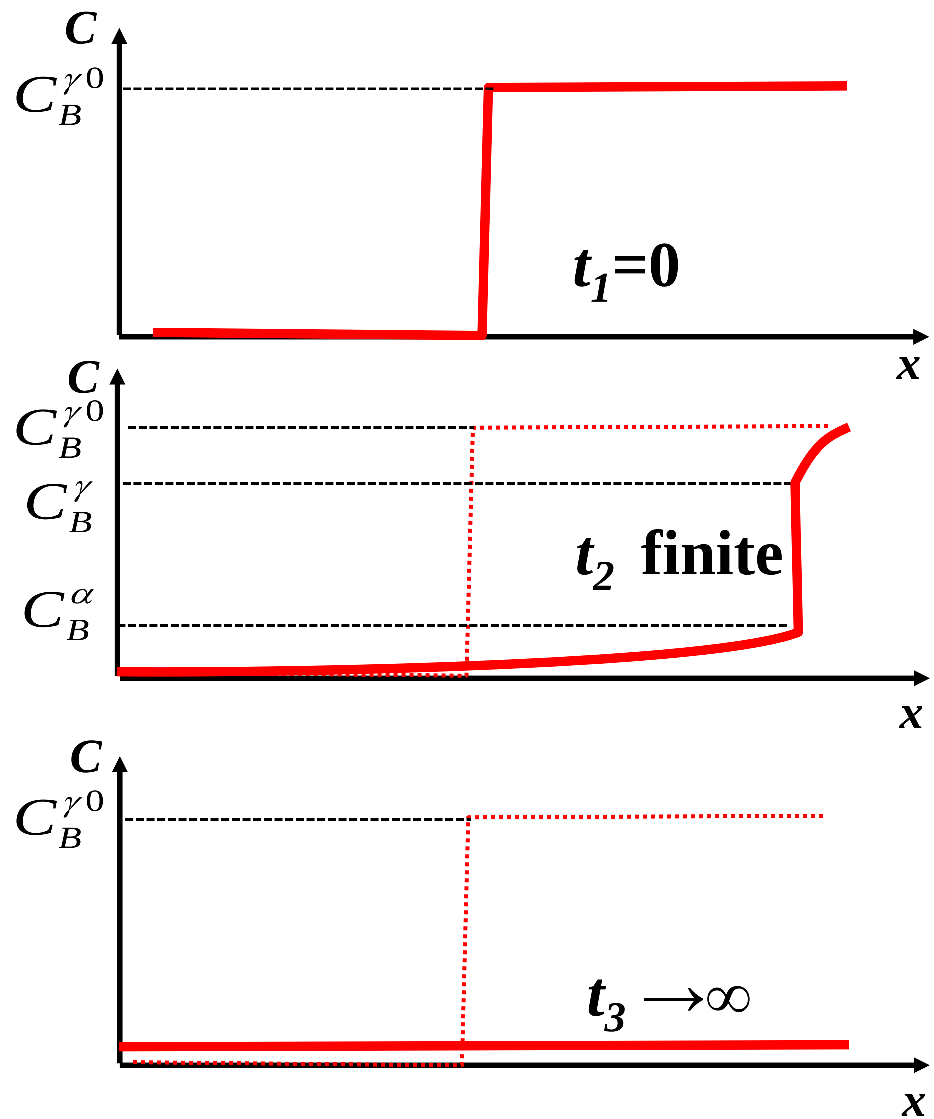




Concentration Profile Change for Diffusion involving Two-Phases (2)

- A very large pieces of one is α with pure A and a very small piece of γ are put in close contact at elevated temperature, as below.
  Assuming slow diffusion and local equilibrium at interface
  Please plot concentration profile for i) t_1 = 0, ii) t_2 finite, iii) $t_3 \rightarrow \infty$





Homework

- **Porter 3rd Ed, Exercise 2.7**
- **Due Feb 29 class**