Dynamic Behaviour of the Interface between Molten and Solidified Salt

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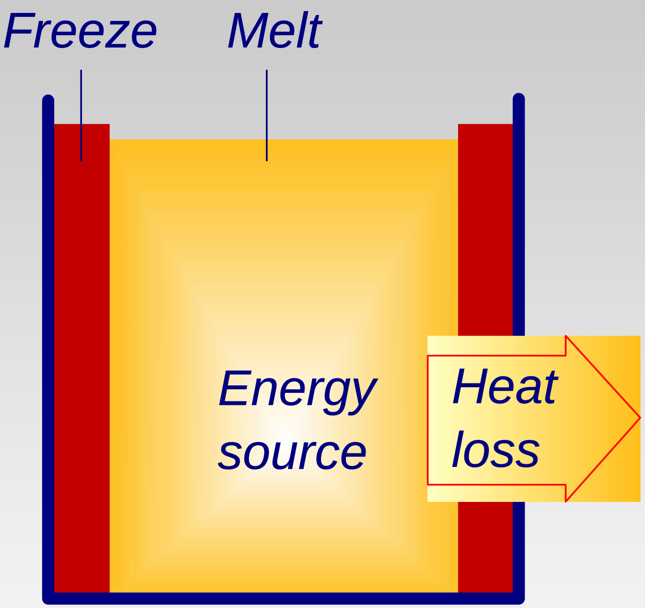
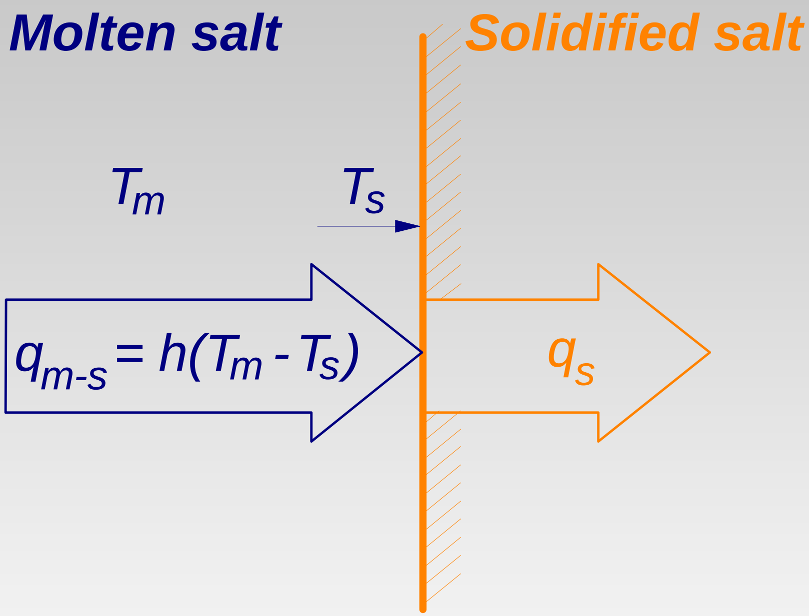
Background and Purpose



- ☐ Some processes have container walls frozen out from melt
- ☐ This may be the only way to protect the lining
- ☐ Example: Aluminium electrolysis

Purpose: To analyse heat and mass transfer at the solid-liquid interface

Heat Balance at Interface



Molten salt

Solidified salt

T_m T_s

$q_{m-s} = h(T_m - T_s)$

q_s

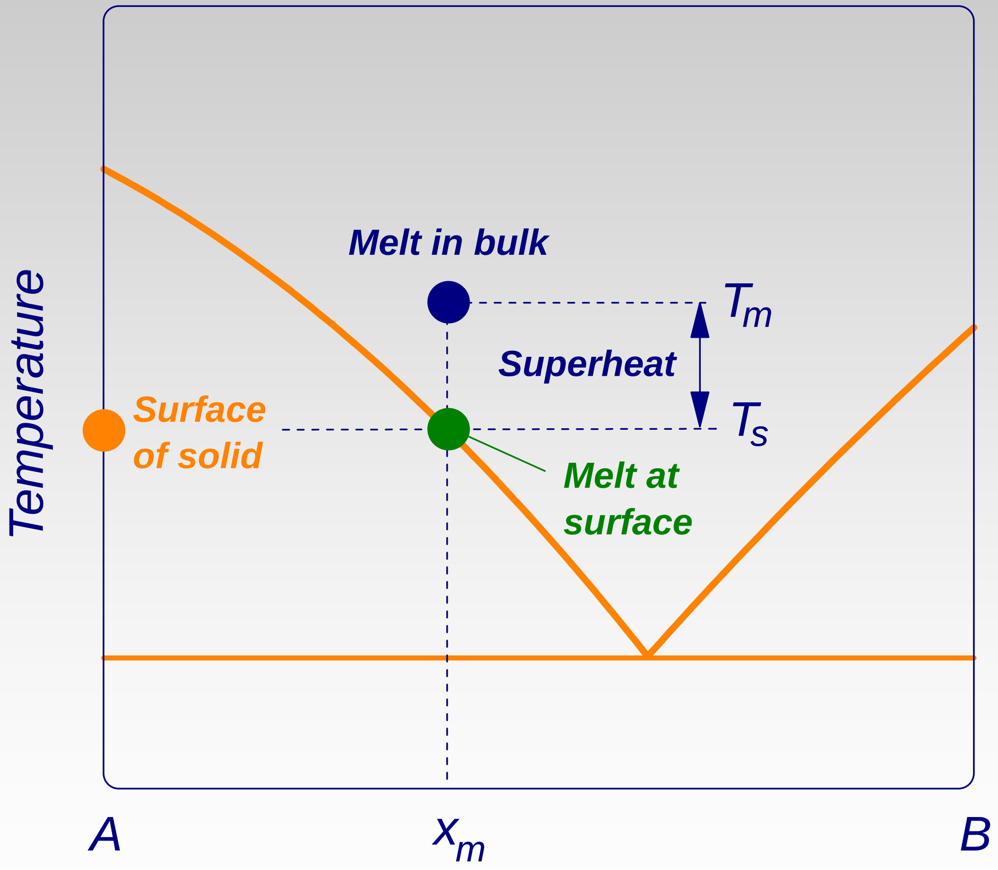
Rate of freezing:

$$j_{freeze} = \frac{q_s - h(T_m - T_s)}{\Delta H_m}$$

- ☐ Heat flux q_{m-s} depends on superheat (T_m-T_s) and heat transfer coefficient h
- ☐ Heat flux q_s depends on thickness of solidified salt layer and container wall insulation
- ☐ If $q_{m-s} = q_s$, neither freezing nor melting occurs (“thermal equilibrium”)

Simple Eutectic Phase Diagram

At equilibrium



- ☐ Neither melting nor freezing occur
- ☐ No mass flux at interface (only heat flux)
- ☐ Melt in bulk and melt at interface have the same composition
- ☐ Interface is at the liquidus temperature of the bulk melt

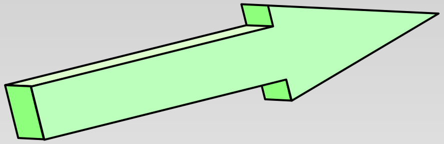
During freezing, an observer *) located at the interface would describe:

- A flow of salt mixture from the bulk of the melt towards the interface (global flow)
- Component B is drifting towards the interface with the global flow
- Since B is not incorporated in the frozen layer (according to the phase diagram) it will be concentrated at the surface
- Due to higher concentration, B diffuses back to the bulk, and the net flux of B is zero

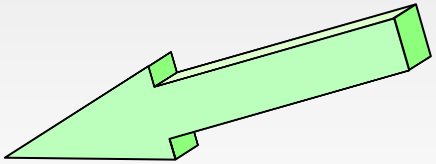
*) The observer would have to be very short and heat-resistant

Analogy

The water flows
in this direction



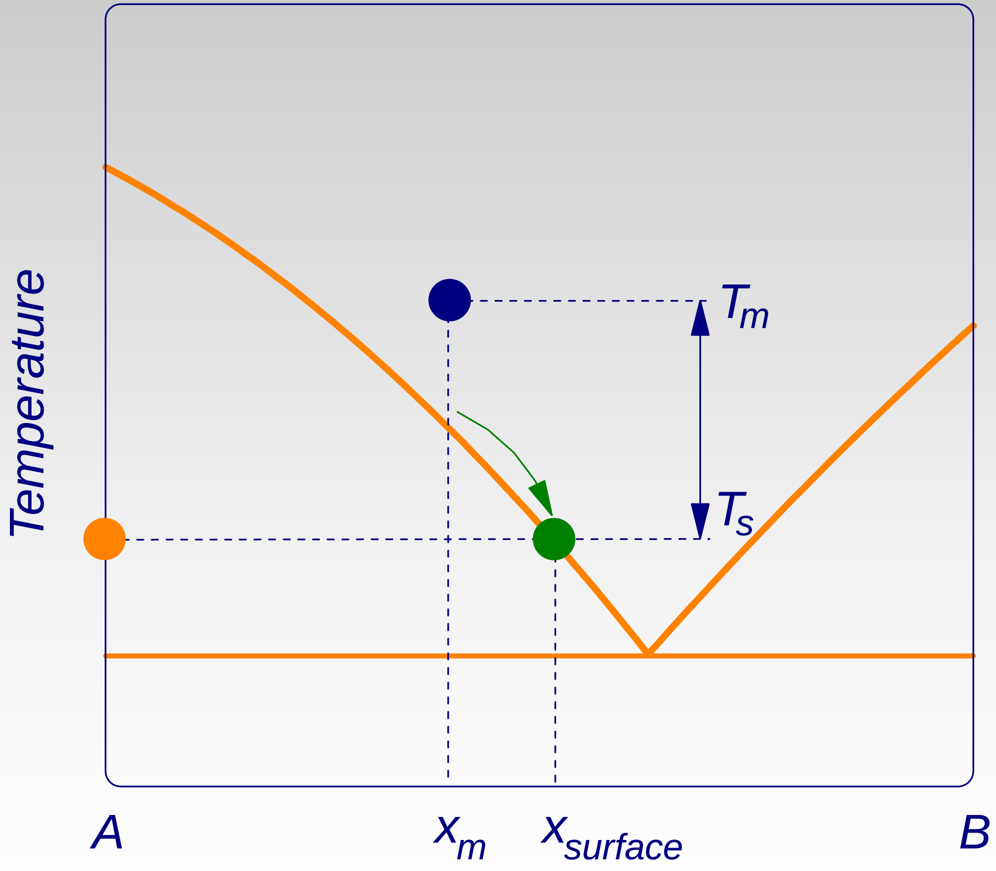
But the duck swims
in that direction



No net "duck motion" observed from the river bank

Simple Eutectic Phase Diagram

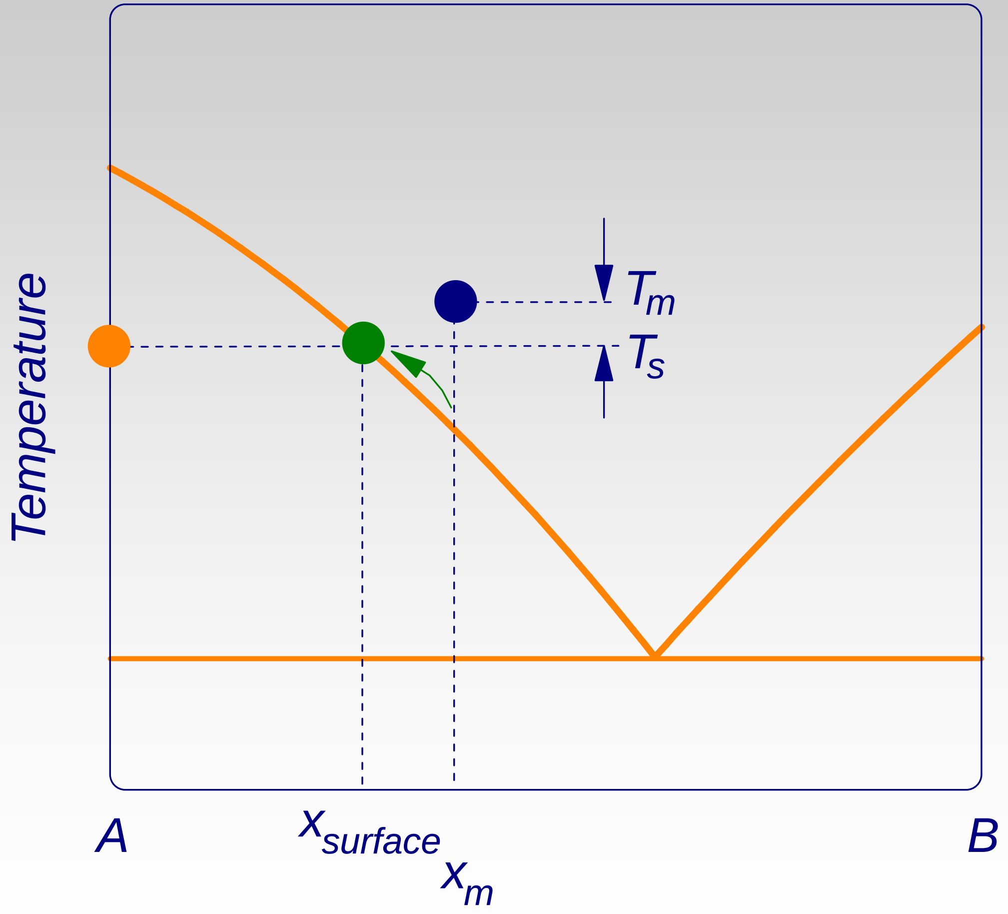
During freezing



- ❑ Only component A is incorporated in solid; B must diffuse back into bulk
- ❑ Concentration of B increases at interface
- ❑ Temperature and composition follow liquidus line): the superheat increases

Simple Eutectic Phase Diagram

During melting



- ☐ Solid contains only component A. Melt at surface enriched in A
- ☐ Temperature and composition follow liquidus line): the superheat decreases

Consequences

- From above qualitative arguments only:
  - Since T_s decreases during freezing (increased superheat), freezing becomes slower than when T_s is constant
  - Since T_s increases during melting (decreased superheat), melting becomes slower than when T_s is constant
  - **A frozen layer made from a salt mixture will therefore be more stable than a layer formed from a pure salt**
  - It may be difficult to form a frozen layer if the liquidus curve is too steep

- **This must be taken into account in dynamic process models**

Solution

- Binary system: Analytical solution possible
- Multi-component system: Must use the Stefan-Maxwell equation,

$$\nabla x_i = \sum_{j=1}^{n} \frac{1}{c_{tot} D_{ij}} \cdot \left(x_i N_j - x_j N_i \right)$$

x_i	Molar fraction, component *i*
c_{tot}	Total concentration [molm^{-3}]
D_{ij}	Binary diffusion coefficient of *i* in *j* [m^{2}s^{-1}]
N_i	Flux of component *j*

…. and solve numerically

- Both cases: Need a model for turbulent diffusivity

Turbulent Heat- and Mass Diffusivities

For mass: $D_{ij} = D_{c(ij)} + D_t$

For heat: $\alpha = \alpha_c + \alpha_t$

where $\lambda / \rho C_p$

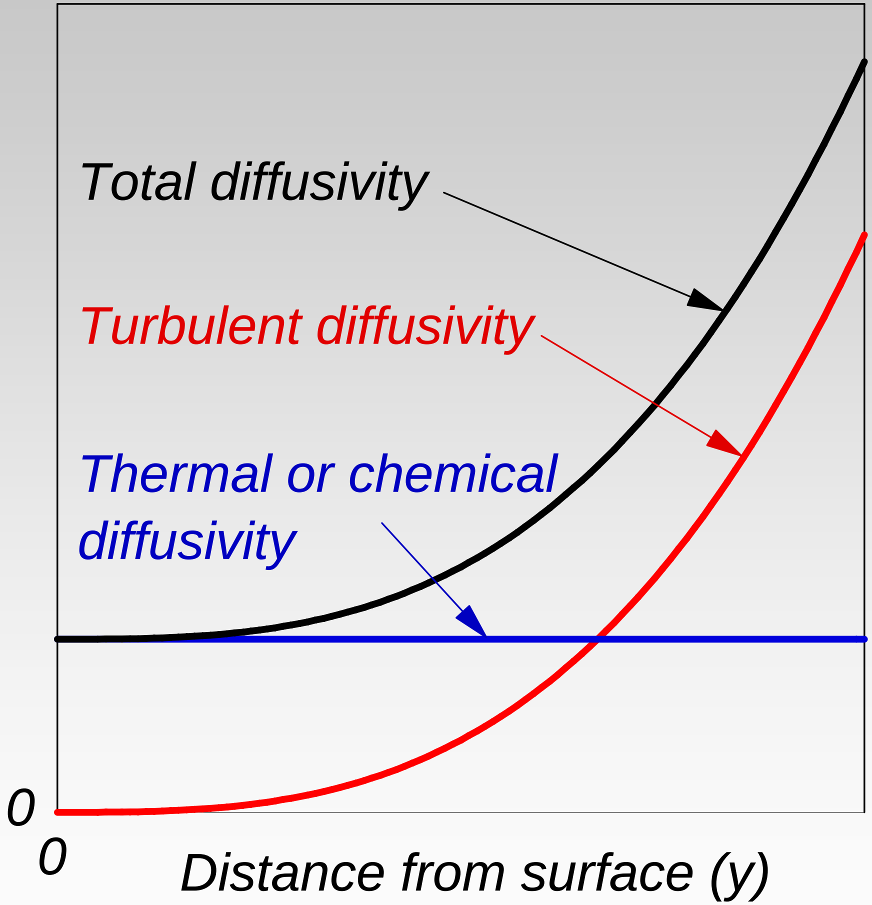
Using boundary layer theory,

$$D_t = \alpha_t = C \cdot y^3$$

Integration

$$k_{(i)} = 0.827 C^{1/3} \cdot D_{c(i)}^{2/3}$$

$$h = 0.827 C^{1/3} \rho C_p \alpha_c^{2/3}$$



Life is not always so easy….

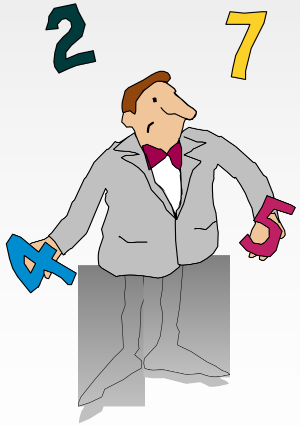
In a 4-component system:

$$\Delta x_1 = \frac{\Delta y}{\bar{c}_{tot}} \cdot \left(\frac{\bar{x}_1 N_2 - \bar{x}_2 N_1}{D_{12} + \bar{D}_t} + \frac{\bar{x}_1 N_3 - \bar{x}_3 N_1}{D_{13} + \bar{D}_t} + \frac{\bar{x}_1 N_4 - \bar{x}_4 N_1}{D_{14} + \bar{D}_t} \right)$$

$$\Delta x_2 = \frac{\Delta y}{\bar{c}_{tot}} \cdot \left(\frac{\bar{x}_2 N_1 - \bar{x}_1 N_2}{D_{21} + \bar{D}_t} + \frac{\bar{x}_2 N_3 - \bar{x}_3 N_2}{D_{23} + \bar{D}_t} + \frac{\bar{x}_2 N_4 - \bar{x}_4 N_2}{D_{24} + \bar{D}_t} \right)$$

$$\Delta x_3 = \frac{\Delta y}{\bar{c}_{tot}} \cdot \left(\frac{\bar{x}_3 N_1 - \bar{x}_1 N_3}{D_{31} + \bar{D}_t} + \frac{\bar{x}_3 N_2 - \bar{x}_2 N_3}{D_{32} + \bar{D}_t} + \frac{\bar{x}_3 N_4 - \bar{x}_4 N_3}{D_{34} + \bar{D}_t} \right)$$

$$\Delta x_4 = \frac{\Delta y}{\bar{c}_{tot}} \cdot \left(\frac{\bar{x}_4 N_1 - \bar{x}_1 N_4}{D_{41} + \bar{D}_t} + \frac{\bar{x}_4 N_2 - \bar{x}_2 N_4}{D_{42} + \bar{D}_t} + \frac{\bar{x}_4 N_3 - \bar{x}_3 N_4}{D_{43} + \bar{D}_t} \right)$$



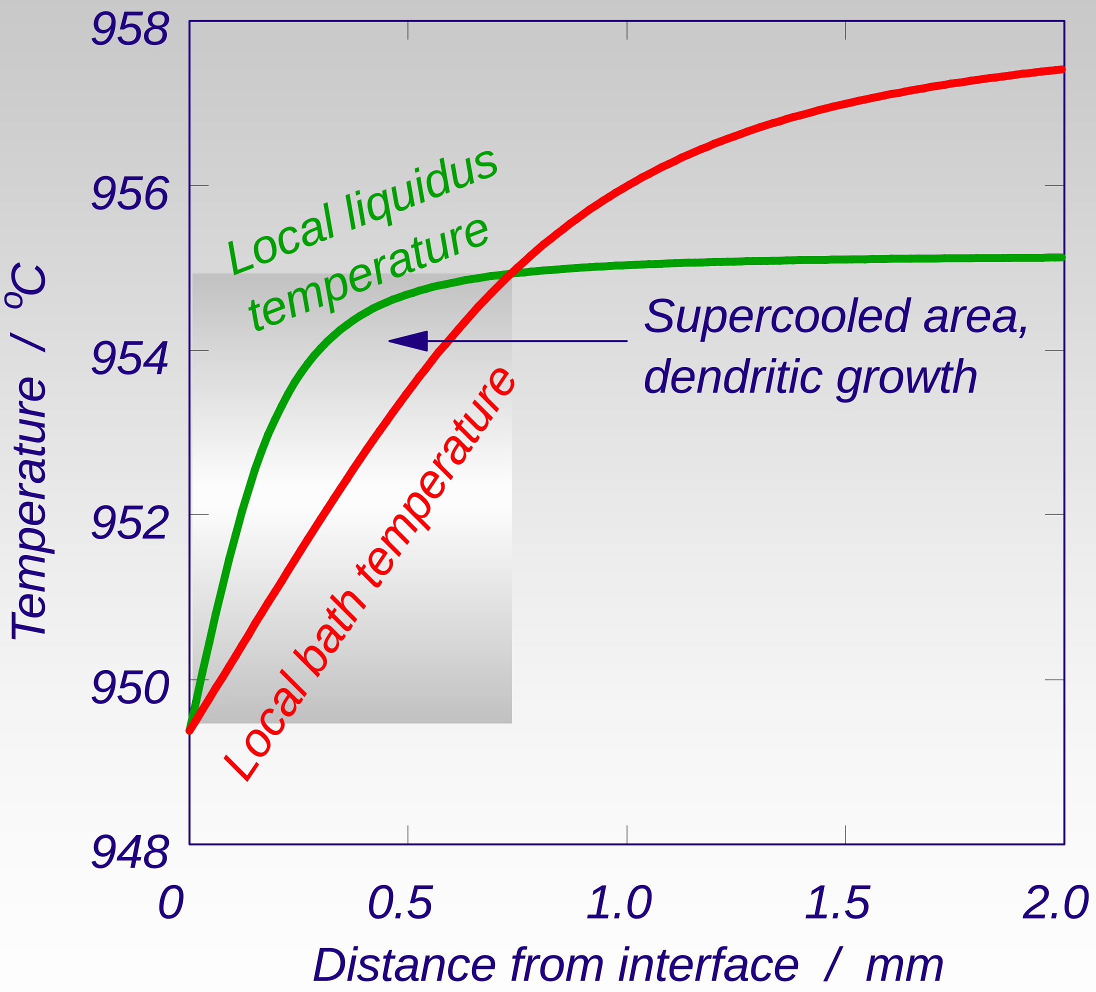
…..but these equations:

- … are easily programmable (*e.g.*, in a spreadsheet)
- … converge very rapidly by using “old” molar fractions as a basis for computing “new” molar fractions
  - 5-10 iterations is usually sufficient
  - Can divide interesting field (near boundary) into very many elements, *e.g.*, 1000
  - … and still get a solution within few seconds
- The main problem is to assess the binary (chemical) diffusion coefficients

Boundary Layer Thickness

- Coefficient of thermal diffusivity is normally much higher than chemical diffusion coefficients
- Turbulent mass diffusivity and turbulent thermal diffusivity are the same
  - Have to be, since mass (concentration) and temperature “experience” the same intensity of convection
- As a consequence (not proven here), the thermal boundary layer is normally thicker than the diffusion boundary layer

Dendritic Crystal Growth

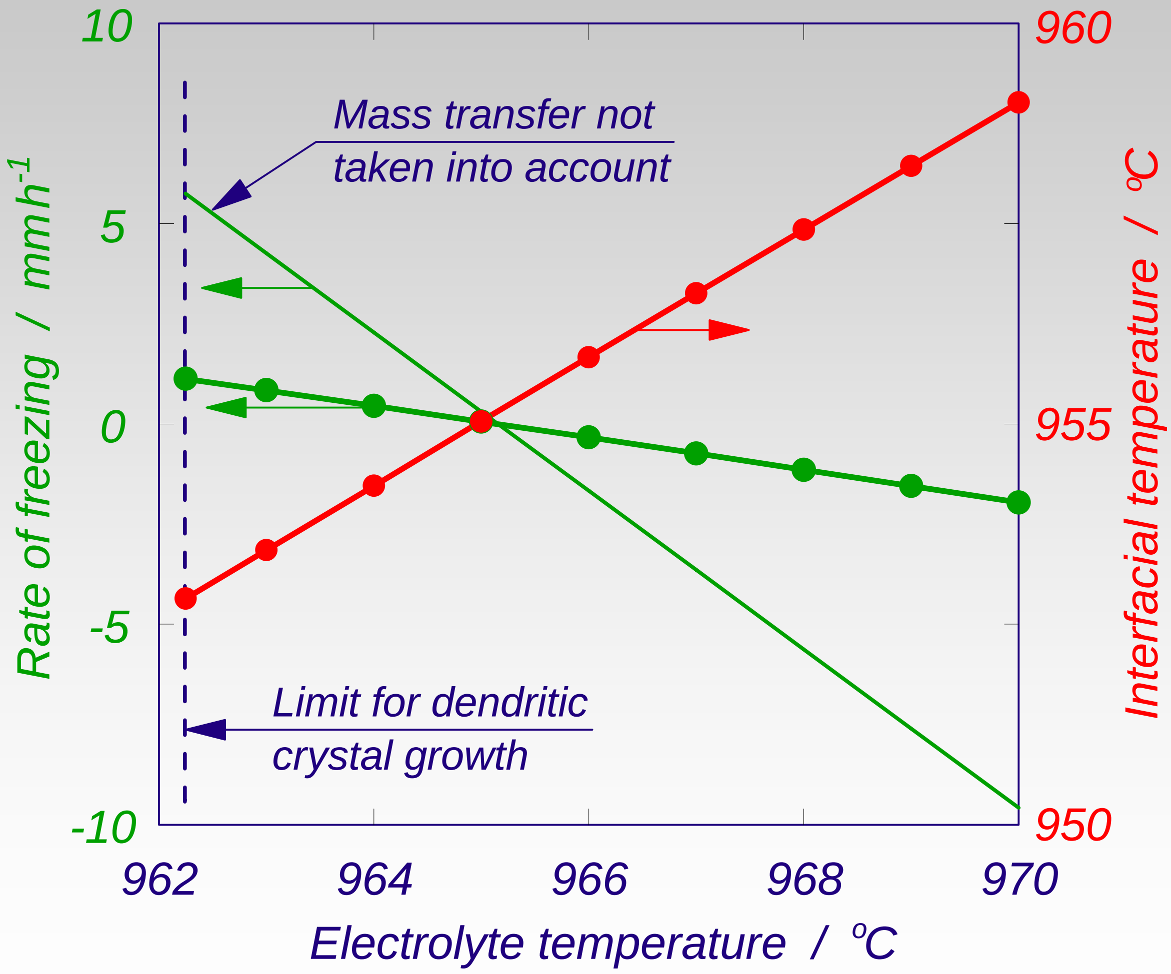


- ❑ Occurs when the local liquidus temperature becomes lower than actual temperature close to the interface
- ❑ Model explains observed structure of freeze samples taken from industrial cells

Example: Aluminium Electrolysis Cell

- Depends heavily on having a freeze on the inner side lining (“sideledge”)
  - High temperature (960 ^{o}C)
  - Strongly oxidizing conditions at top of side (CO_2)
  - Fluoride electrolyte; dissolves any oxide
  - Strongly reducing conditions at bottom of side (Al, dissolved Na)
  - Only frozen electrolyte can withstand all conditions
- The electrolyte is a 4-component mixture
  - NaF, AlF_3, CaF_2, Al_2O_3
- … but the solid phase normally consists of pure cryolite ($3\ NaF \cdot AlF_3$)

Results Obtained for Aluminium Electrolysis Cell



Inner side walls covered by freeze to protect lining

Thank you for your attention