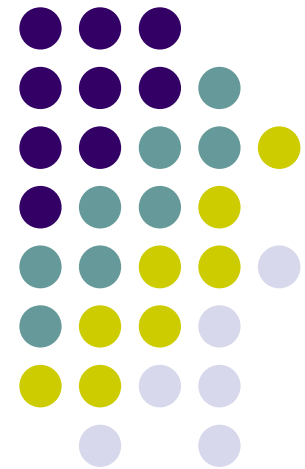
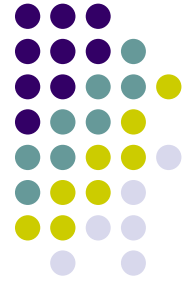


# Difusão



# Sumário

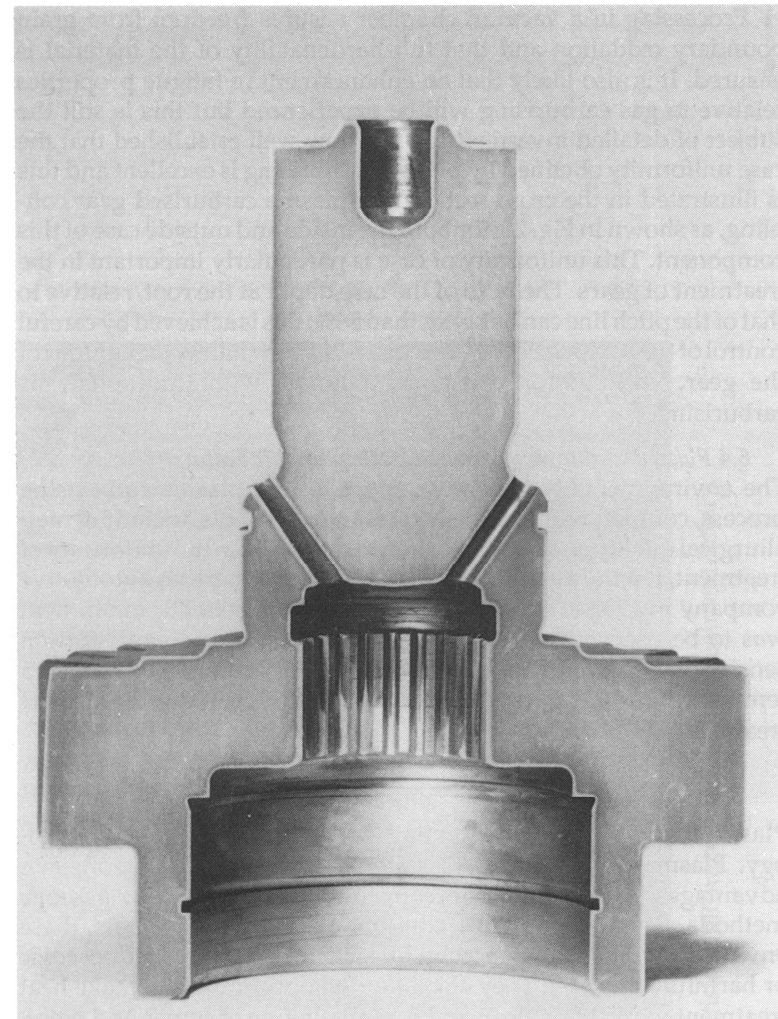
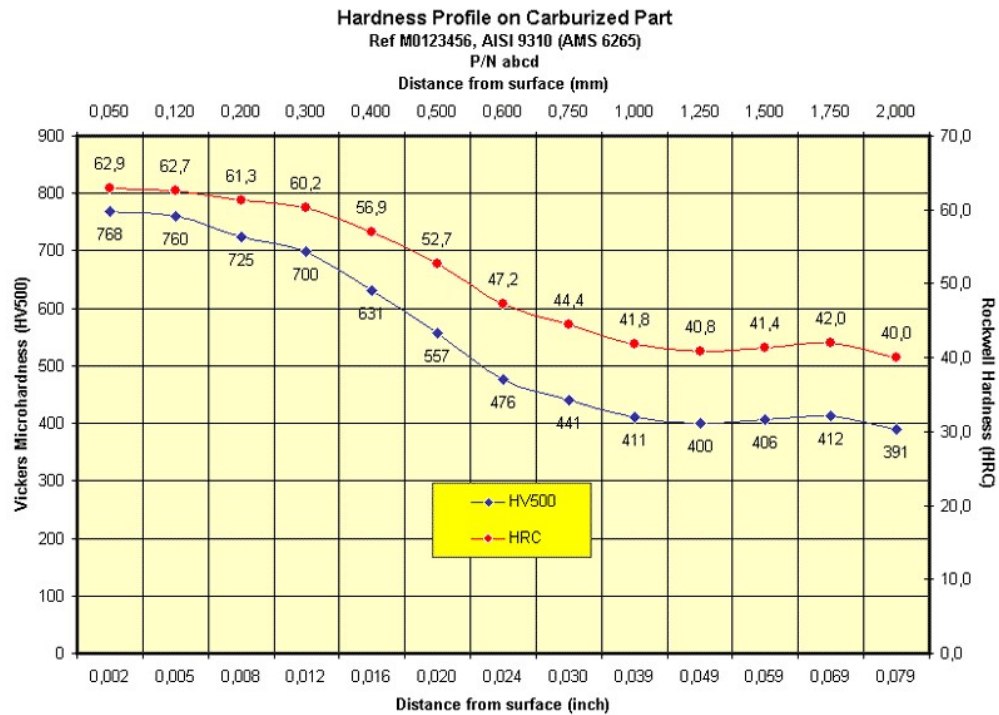


- Difusão de Intersticiais
  - Movimento dos átomos
  - Regime estacionário (1ª lei de Fick)
  - Exemplo de uso
  - O coeficiente de difusão
  - Regime transiente (2ª lei de Fick)
  - Solução para um sólido semi-infinito
  - Exemplo de uso
- Autodifusão
  - Mecanismo
- Difusão de Substitucionais
  - Criação e aniquilação de vacâncias
  - Efeito Kirkendall
  - Equações de Darken (coeficiente de interdifusão)
  - Análise de Matano
- Referências

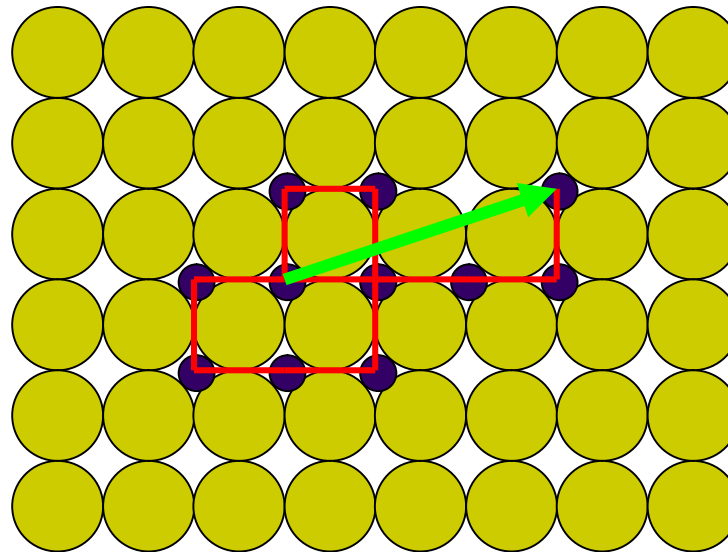
# Exemplo



## Cementação de aços



# Movimentação de átomos nos materiais

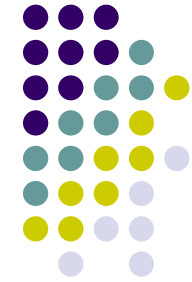


**Movimento aleatório**

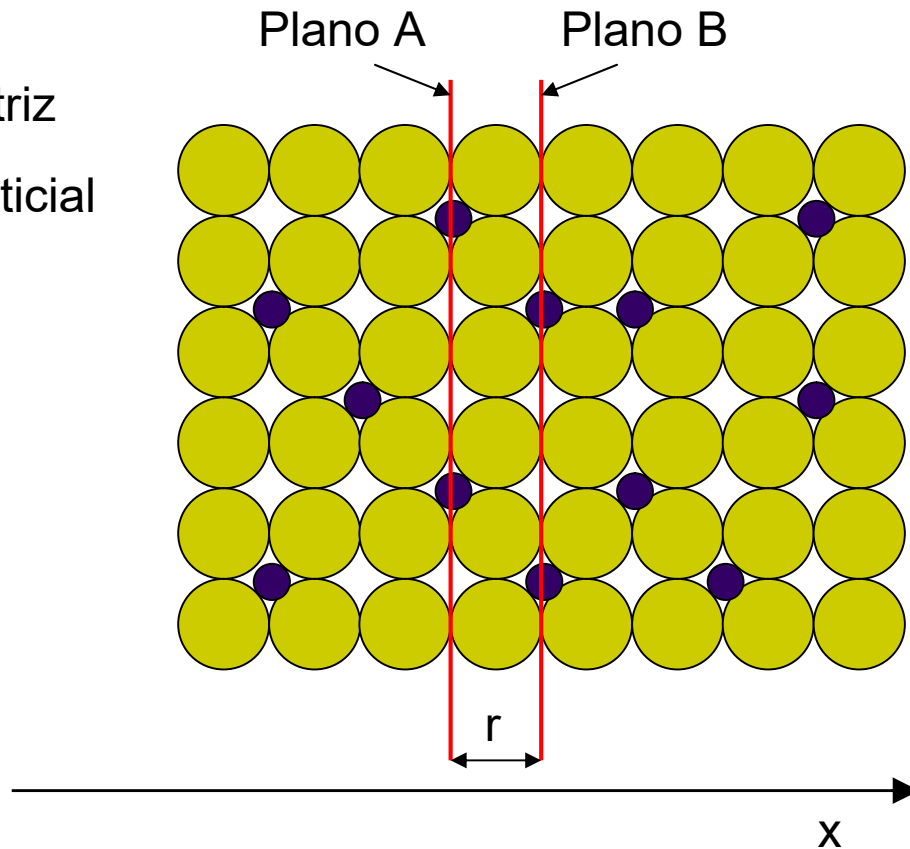
## Exemplo: C em Fe

- 35°C - 1 salto/s - 0,25 nm
- 700°C – 5,9 bilhões de saltos/s – 1,46 m percorridos –  $\Delta S$  de 19  $\mu\text{m}$

# Difusão de Intersticiais



-  Matriz
-  Intersticial



Número de Intersticiais no plano  
 Área do Plano  
 Saltos/segundo

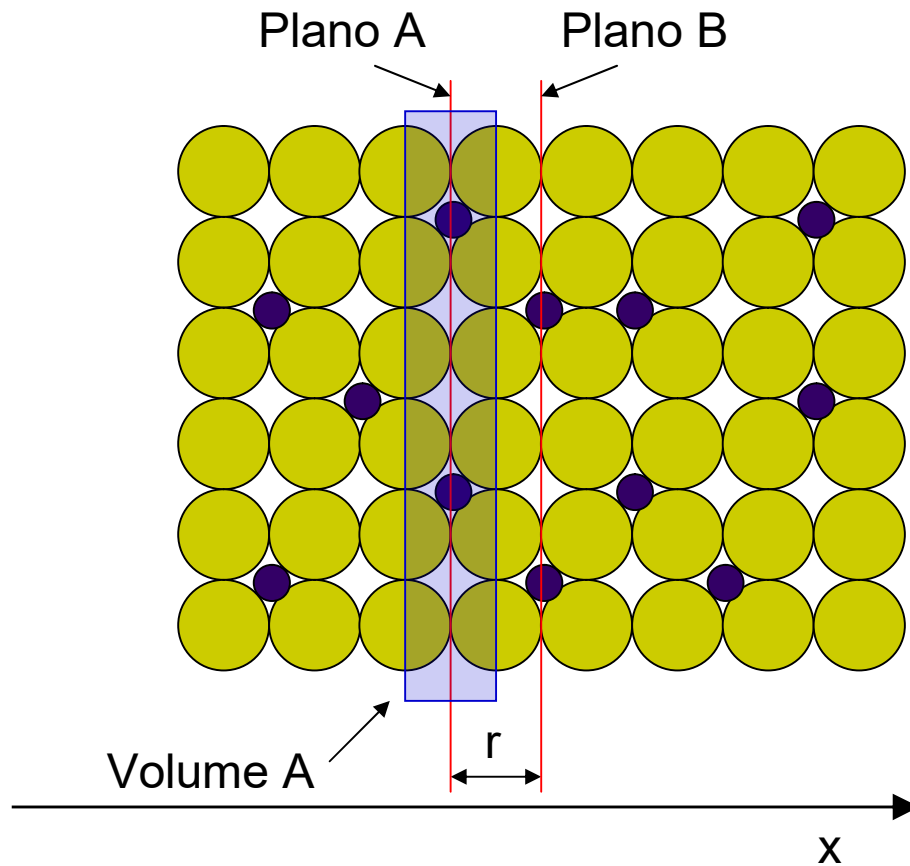
$$\vec{J}_x = \frac{1}{6} \Gamma \frac{n_A}{A}$$

$$\vec{J}_x = -\frac{1}{6} \Gamma \frac{n_B}{A}$$

$$J_x = \frac{1}{6} \Gamma \frac{(n_A - n_B)}{A}$$

(átomos/m<sup>2</sup>/s)

# Difusão de Instersticiais



$$C_A = \frac{n_A}{V_A} = \frac{n_A}{r \cdot A}$$

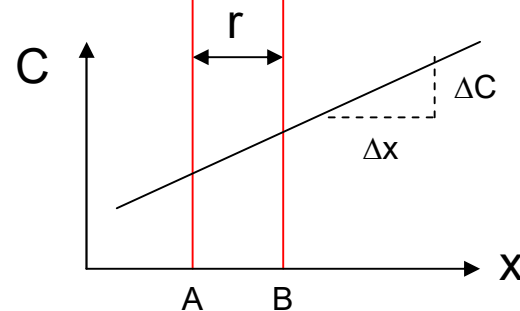
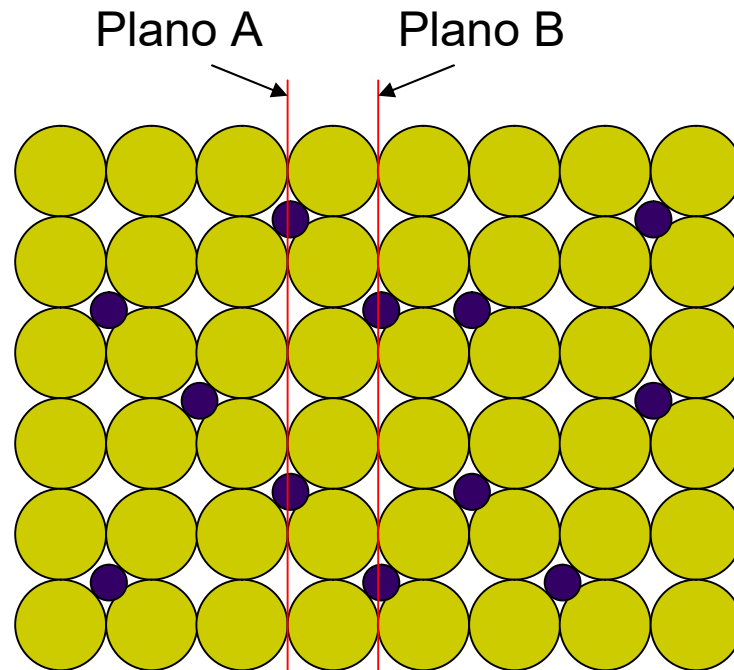
$$C_B = \frac{n_B}{r \cdot A}$$

$$J_x = \frac{1}{6} \Gamma \frac{(n_A - n_B)}{A}$$

$$J_x = \frac{1}{6} \Gamma r A \frac{(C_A - C_B)}{A}$$

$$J_x = \frac{1}{6} \Gamma r (C_A - C_B)$$

# Difusão de Instersticiais

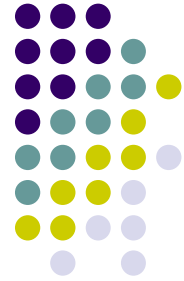


$$\frac{\Delta C}{\Delta x} = \frac{C_B - C_A}{r}$$

$$C_A - C_B = -r \cdot \frac{\Delta C}{\Delta x}$$

$$J_x = \frac{1}{6} \Gamma r (C_A - C_B)$$

$$J_x = -\frac{1}{6} \Gamma r^2 \frac{\Delta C}{\Delta x}$$



# 1ª lei de Fick

$$J_x = -\frac{1}{6} \Gamma r^2 \frac{\Delta C}{\Delta x}$$

$$\Delta x \rightarrow 0 \quad J_x = -\frac{1}{6} \Gamma r^2 \frac{\partial C}{\partial x}$$

↖  
D

$$J_x = -D \frac{\partial C}{\partial x}$$

$$J = -D \left( \frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} + \frac{\partial C}{\partial z} \right)$$

$$J = -D \nabla C$$

A força motriz para a difusão é o gradiente de concentração



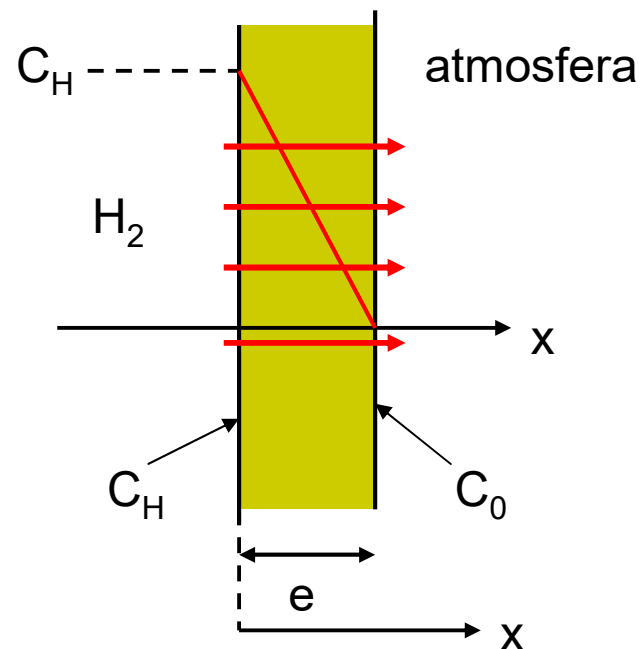


# Aplicação da 1ª lei de Fick

- Regimes estacionários

$$\frac{\partial C}{\partial t} = 0 \quad \frac{\partial C}{\partial x} = \text{constante} \quad J_x = \text{constante}$$

- Exemplo



$$C_H = \underline{cte}$$

$$C_0 = 0$$

$$\frac{\partial C}{\partial x} = \underline{cte} = \frac{\Delta C}{\Delta x} = \frac{C_0 - C_H}{e} = \frac{-C_H}{e}$$

$$J_x = -D \frac{\partial C}{\partial x} = -D \frac{-C_H}{e}$$

$$J_x = D \frac{C_H}{e}$$

# O coeficiente de difusão



$$D = \frac{1}{6} \Gamma r^2$$

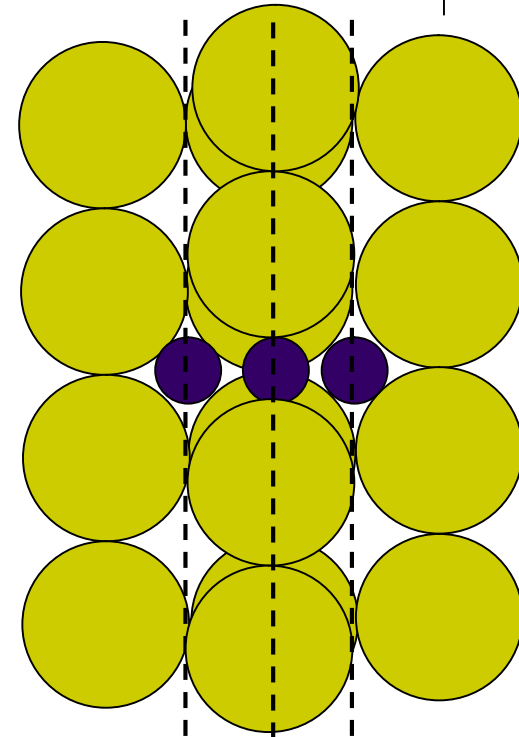
$$\Gamma = z \nu \exp\left(\frac{-\Delta G_m}{RT}\right) \quad \Delta G = \Delta H - T\Delta S$$

Configuração do interstício  
 Freqüência de vibração atômica  
 Probabilidade de sucesso

$$D = \frac{1}{6} r^2 z \nu \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(\frac{-\Delta H_m}{RT}\right)$$

$$D = D_0 \exp\left(\frac{-\Delta H_m}{RT}\right)$$

A temperatura ativa a difusão

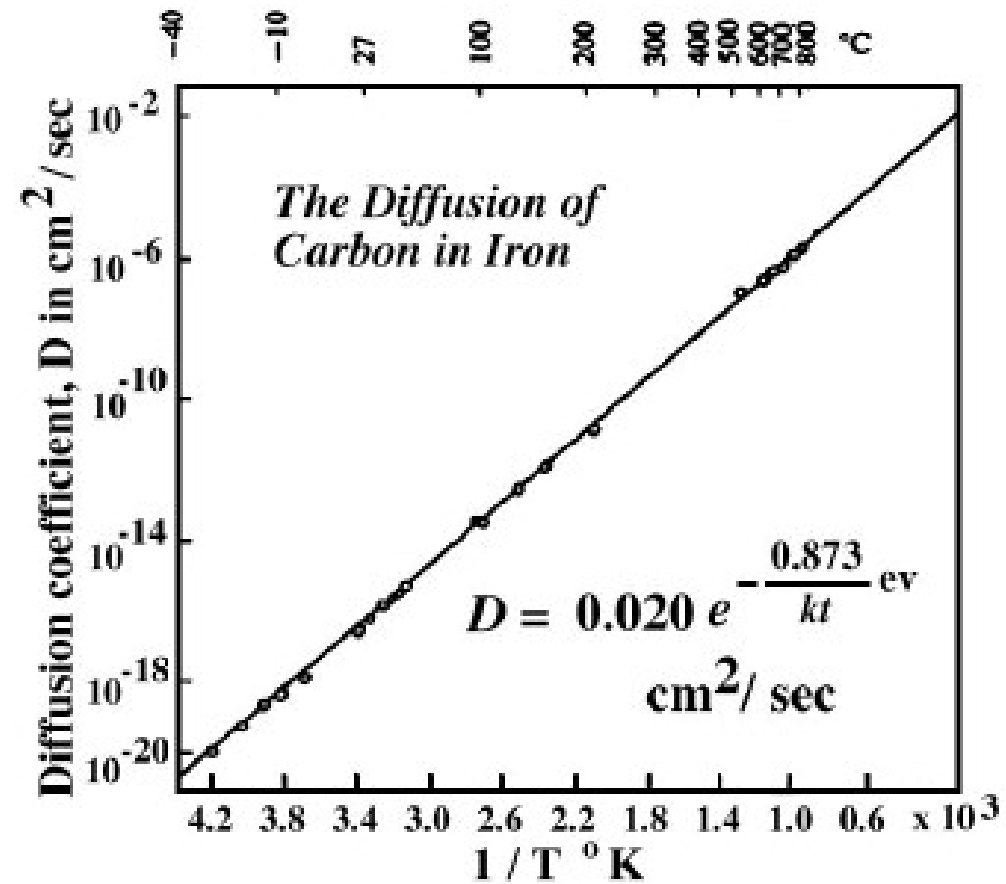


# O coeficiente de difusão

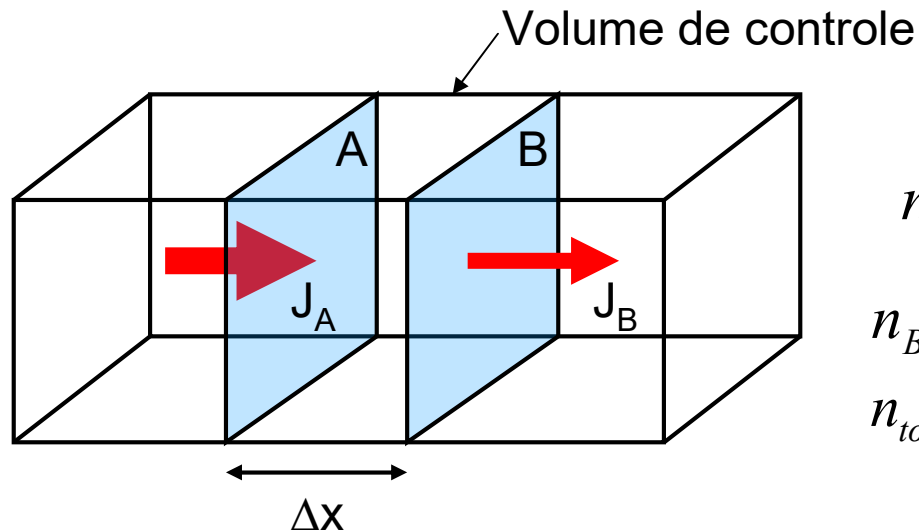


$$D = D_0 \exp\left(\frac{-\Delta H}{RT}\right)$$

$$\ln D = \ln D_0 - \frac{\Delta H}{RT}$$



# Difusão em regime transiente



$$n_A = J_A \cdot A \cdot \Delta t$$

$$n_B = J_B \cdot A \cdot \Delta t$$

$$n_{total} = n_A - n_B = (J_A - J_B) \cdot A \cdot \Delta t$$

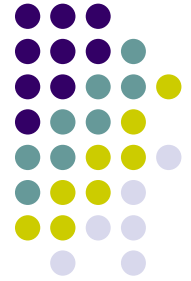
$$\Delta C = \frac{n_{total}}{V}$$

$$\frac{\Delta C}{\Delta t} = - \frac{\Delta J}{\Delta x}$$

$$\Delta x \rightarrow 0$$

$$\Delta t \rightarrow 0$$

$$\frac{\partial C}{\partial t} = - \frac{\partial J}{\partial x}$$



## 2ª lei de Fick

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} \quad J = -D \frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)$$

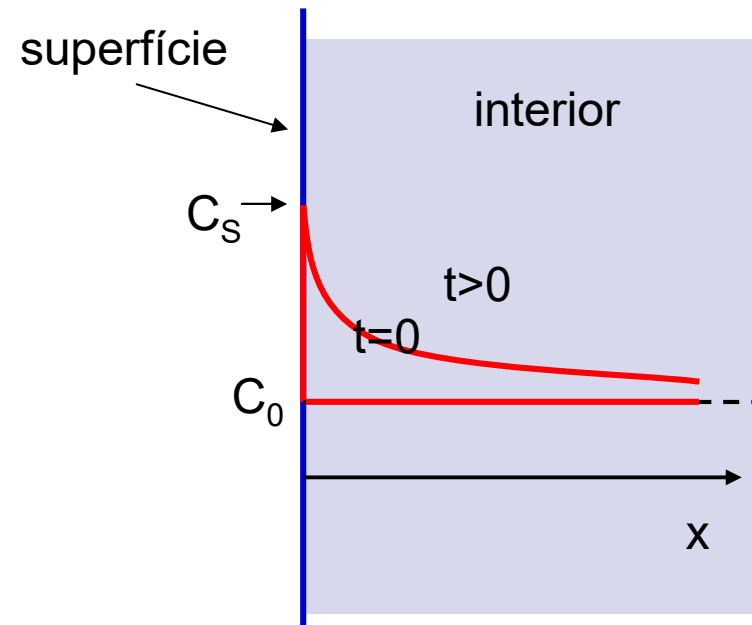
$$\frac{\partial C}{\partial t} = D \nabla^2 C$$



# Uma solução da segunda lei

- Sólido semi-infinito de superfície plana
- $C_s = \text{cte}$
- $C_{(x)} = C_0$  para qualquer  $x > 0$  quando  $t = 0$
- Para  $t > 0$ ,  $C_{(\text{infinito})} = C_0$

$$\frac{C_{(x,t)} - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$



# Função erro



<b>z</b>	<b>erf(z)</b>	<b>z</b>	<b>erf(z)</b>	<b>z</b>	<b>erf(z)</b>
<b>0</b>	0.0000	<b>0.55</b>	0.5633	<b>1.3</b>	0.9340
<b>0.025</b>	0.0282	<b>0.60</b>	0.6038	<b>1.4</b>	0.9523
<b>0.05</b>	0.0564	<b>0.65</b>	0.6420	<b>1.5</b>	0.9661
<b>0.10</b>	0.1125	<b>0.70</b>	0.6778	<b>1.6</b>	0.9763
<b>0.15</b>	0.1680	<b>0.75</b>	0.7111	<b>1.7</b>	0.9838
<b>0.20</b>	0.2227	<b>0.80</b>	0.7421	<b>1.8</b>	0.9891
<b>0.25</b>	0.2763	<b>0.85</b>	0.7707	<b>1.9</b>	0.9928
<b>0.30</b>	0.3286	<b>0.90</b>	0.7969	<b>2.0</b>	0.9953
<b>0.35</b>	0.3794	<b>0.95</b>	0.8209	<b>2.2</b>	0.9981
<b>0.40</b>	0.4284	<b>1.00</b>	0.8427	<b>2.4</b>	0.9993
<b>0.45</b>	0.4755	<b>1.1</b>	0.8802	<b>2.6</b>	0.9998
<b>0.50</b>	0.5205	<b>1.2</b>	0.9103	<b>2.8</b>	0.9999



# Aplicação da segunda lei

- Cementação

- $C_0 = 0,2\%$
- $C_S = 1\%$
- $T = 900^\circ\text{C}$
- $t = 6$  horas
- C a 1 mm da superfície?

$$\frac{C_{(x,t)} - C_0}{C_S - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C_{(x,t)} - 0,2}{1 - 0,2} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C_{(x,t)} = 1 - 0,8 \cdot \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$z = \frac{x}{2\sqrt{Dt}} = \frac{0,1\text{cm}}{2\sqrt{3,55 \times 10^{-6} \frac{\text{cm}^2}{\text{s}} \cdot 6.3600\text{s}}} = 0,255$$

$$\operatorname{erf}(0,255) \cong 0,28$$

$$C_{(x,t)} \cong 1 - 0,8 \cdot 0,28 \cong 0,77\%$$





# Solução numérica

- Pode-se usar qualquer algoritmo que solucione numericamente equações do tipo:

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$

- A equação de condução de calor é um exemplo, portanto qualquer programa que solucione a transferência de calor por condução pode ser usado para difusão.

$$\frac{\partial T}{\partial t} = \alpha\nabla^2 T$$

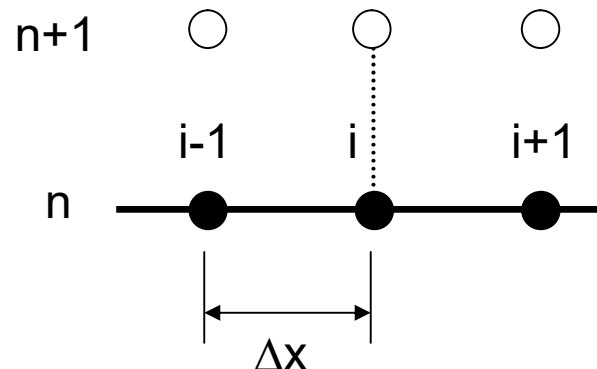
# Exemplo mais simples de solução numérica



- Método das diferenças finitas
- Esquema FTCS (*Forward in Time and Centered in Space*)
  - Em uma direção:

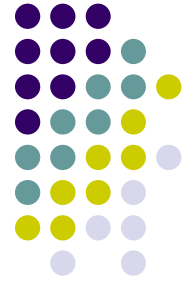
$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \Rightarrow \frac{C_i^{n+1} - C_i^n}{\Delta t} = \frac{D}{(\Delta x)^2} (C_{i+1}^n - 2C_i^n + C_{i-1}^n)$$

n – posição no tempo (passo)  
i – posição no espaço



Estabilidade:  $\Delta t \leq \frac{(\Delta x)^2}{2D}$

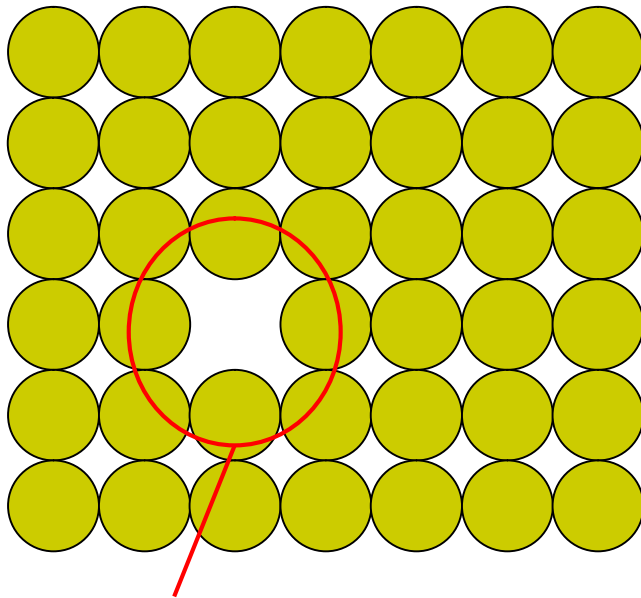
Erro de truncagem:  $\frac{\Delta t}{2} \frac{\partial^2 C_i^n}{\partial t^2} + D \frac{(\Delta x)^2}{4!} \frac{\partial^4 C_i^n}{\partial x^4}$



# Exemplo de uso do FTCS

- Difusão de carbono para o interior de uma lâmina fina de ferro com concentração constante na superfície
- [Implementado em uma planilha de Excel](#)

# Autodifusão



Átomos que podem mudar de posição



$$D = \frac{1}{6} \Gamma r^2$$

$$\Gamma = z \nu \cdot C_v \cdot \exp\left(\frac{-\Delta G_m}{RT}\right)$$

Concentração de vacâncias

$$C_v = \exp\left(\frac{-\Delta G_v}{RT}\right)$$

$$\Gamma = z \nu \cdot \exp\left(\frac{-\Delta G_v}{RT}\right) \cdot \exp\left(\frac{-\Delta G_m}{RT}\right)$$

$$D = \frac{1}{6} r^2 z \nu \exp\left(\frac{-\Delta G_m - \Delta G_v}{RT}\right)$$

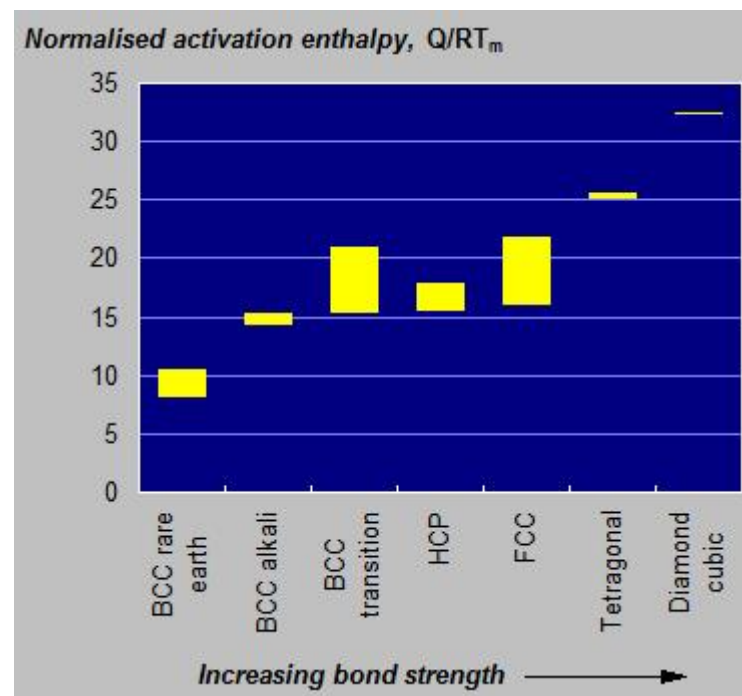


# Autodifusão

$$D = \frac{1}{6} r^2 z \nu \exp\left(\frac{-\Delta G_m - \Delta G_v}{RT}\right)$$

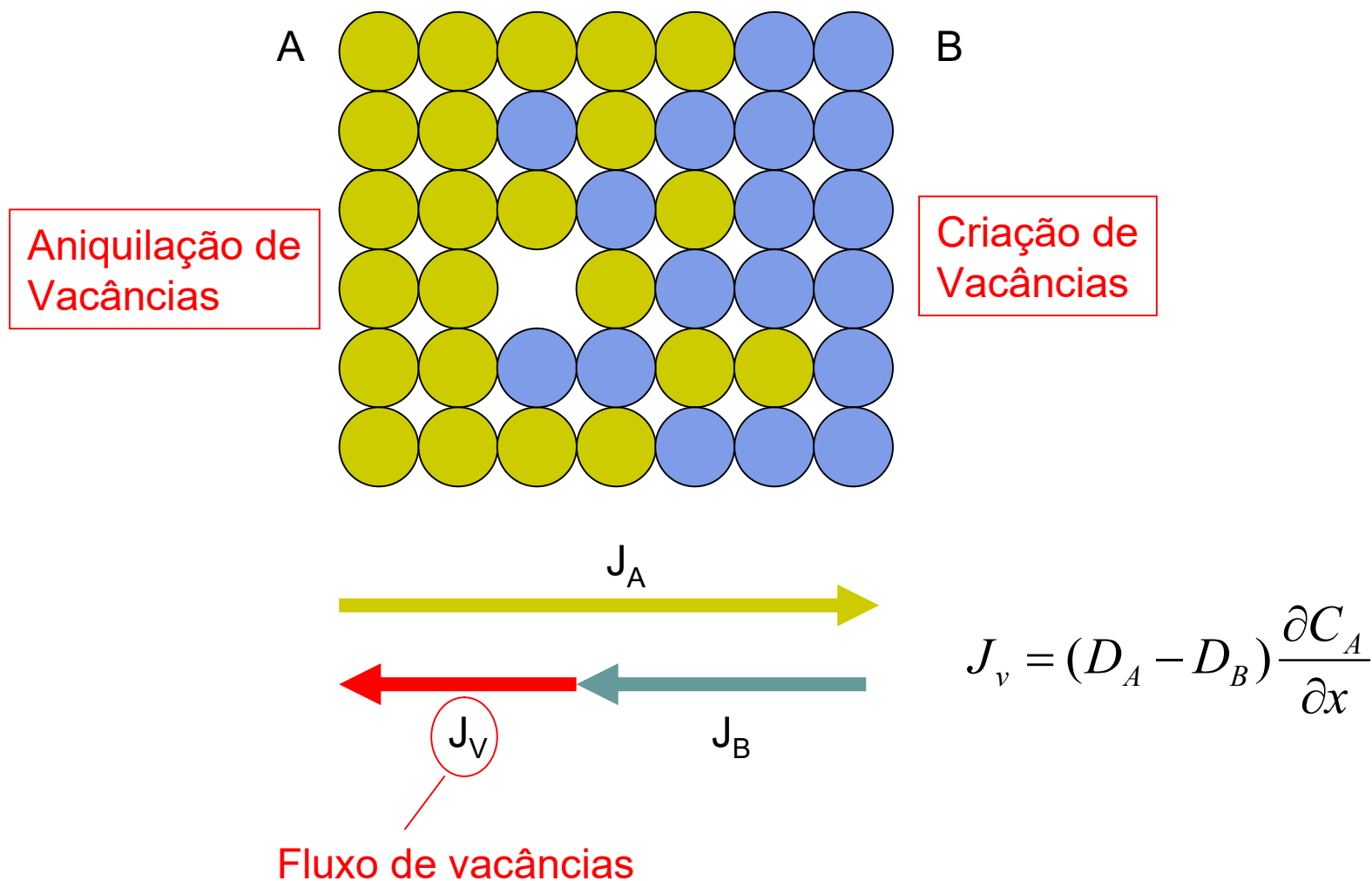
$$D = \frac{1}{6} r^2 z \nu \exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right) \exp\left(\frac{-\Delta H_m - \Delta H_v}{RT}\right)$$

$$D = D_0 \exp\left(\frac{-\Delta H_A}{RT}\right)$$

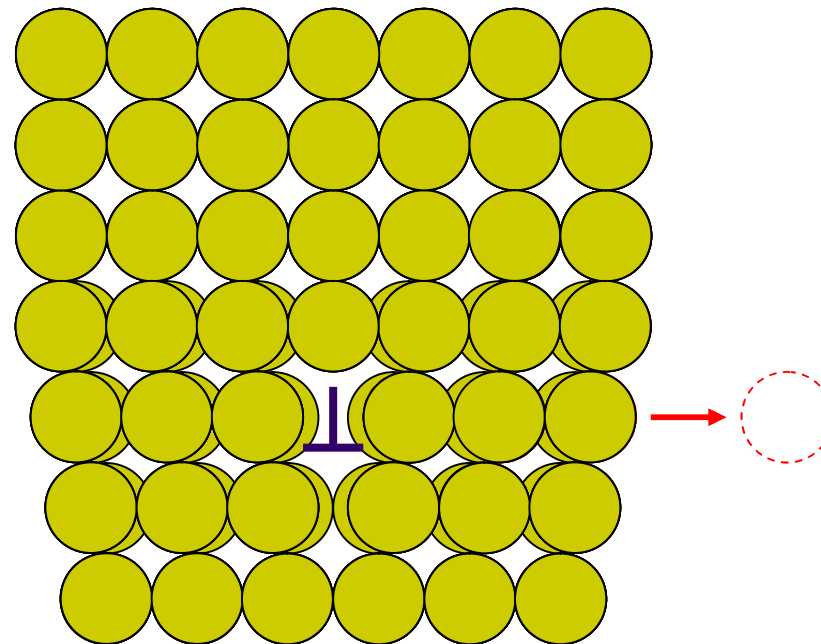




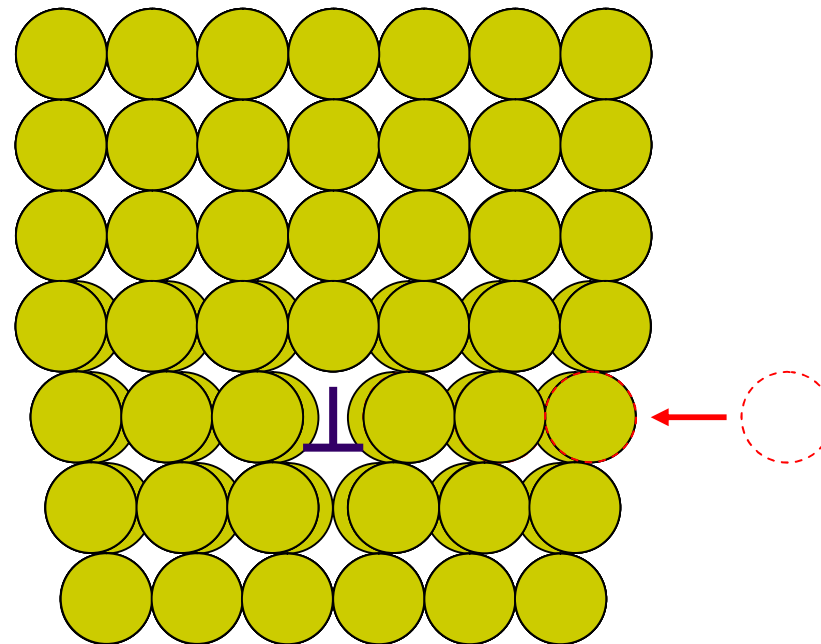
# Difusão de Substitucionais



# Criação de Vacâncias

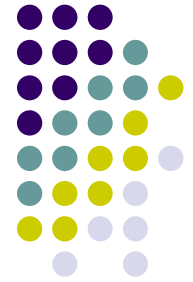


# Aniquilação de Vacâncias

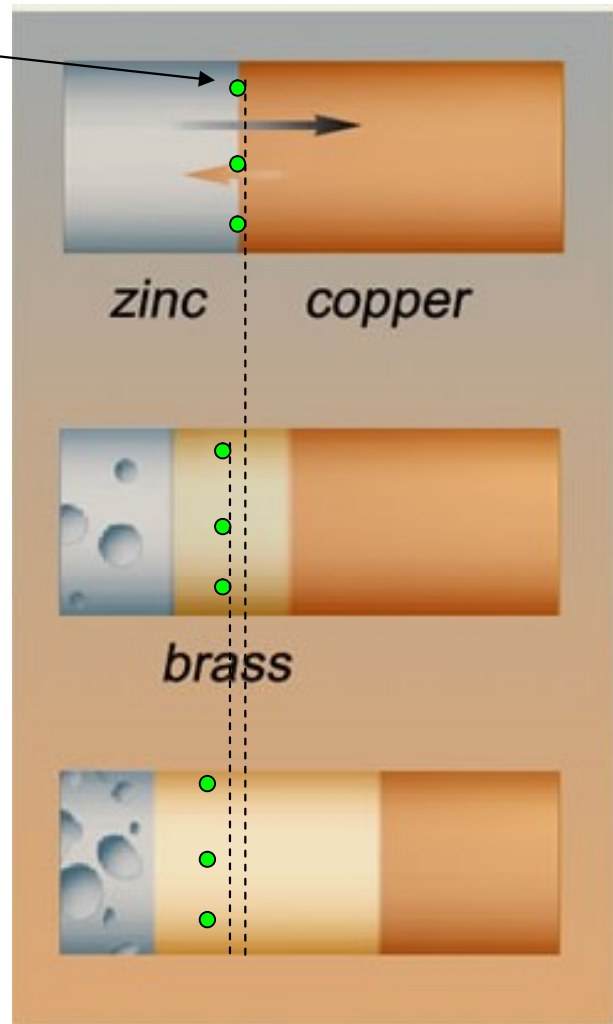




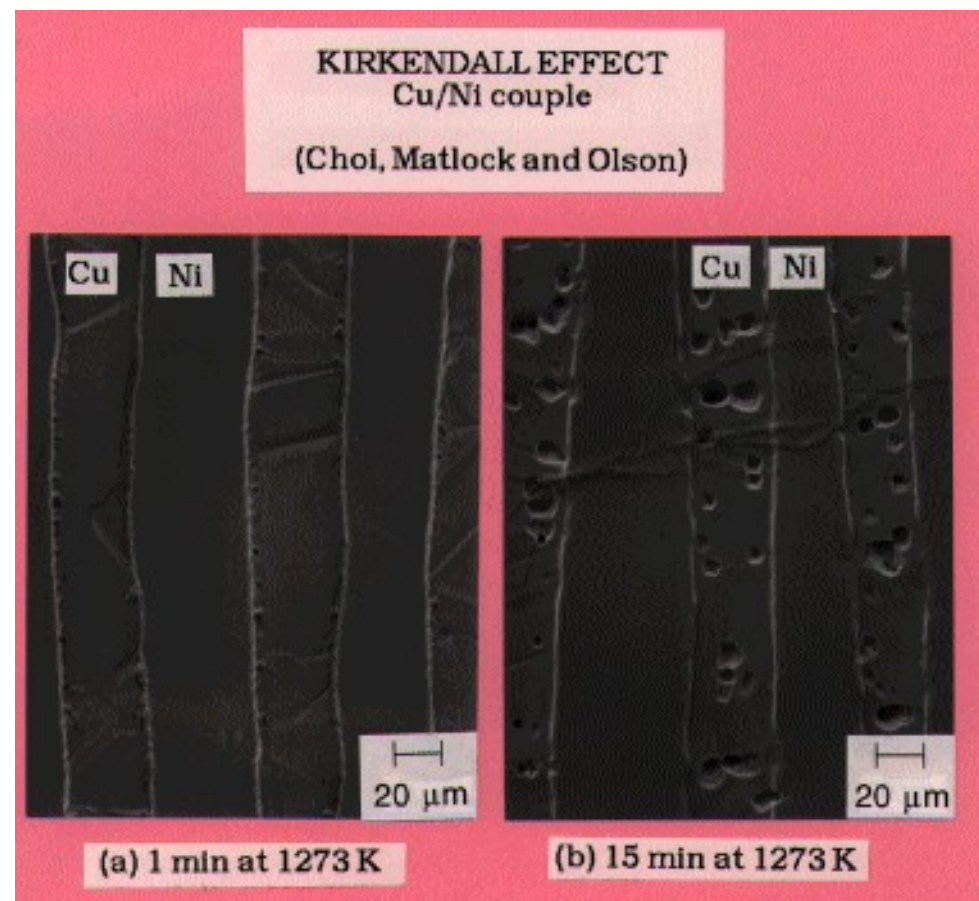
# Efeito Kirkendall



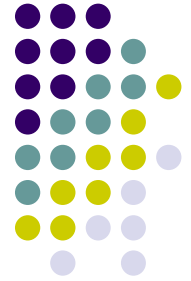
Marcadores



# Efeito Kirkendall



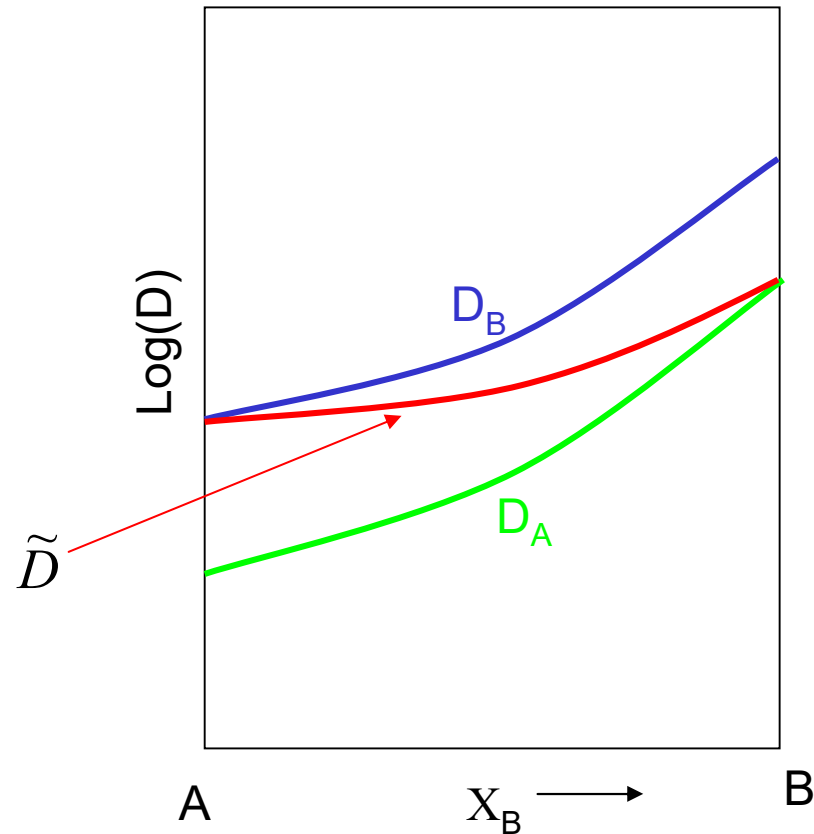
# Equações de Darken



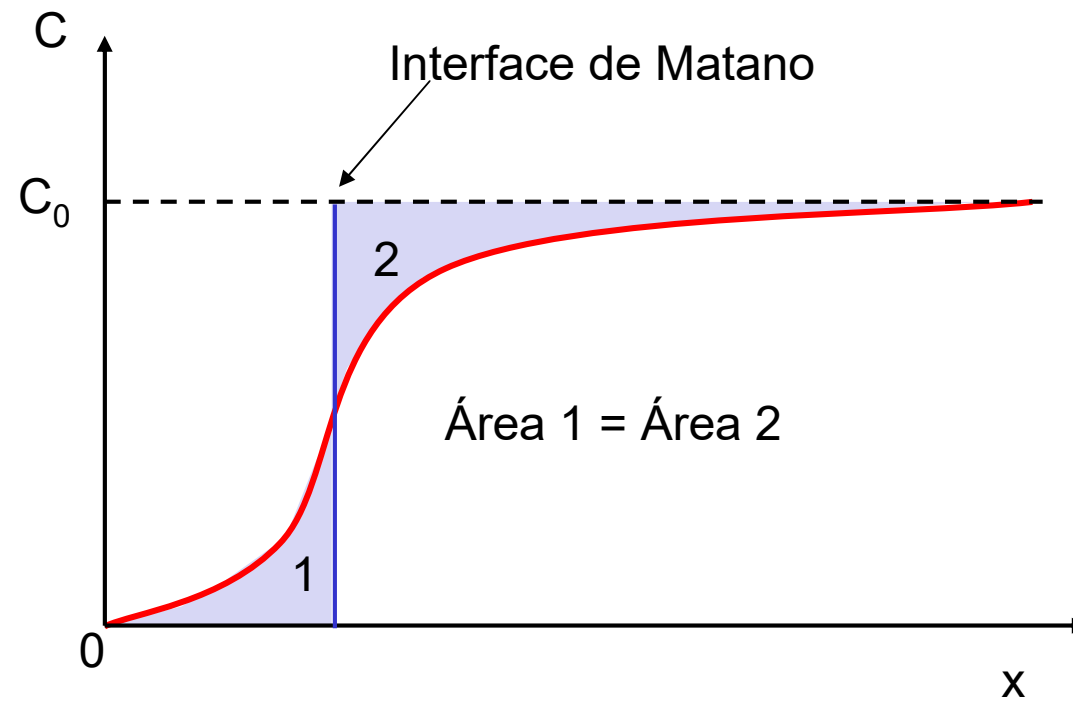
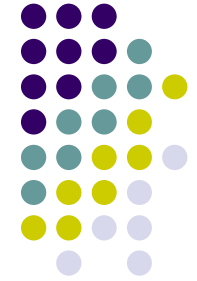
$$J_A = -(\chi_A D_A + \chi_B D_B) \frac{\partial C_A}{\partial x}$$

$$J_A = -\tilde{D} \frac{\partial C_A}{\partial x}$$

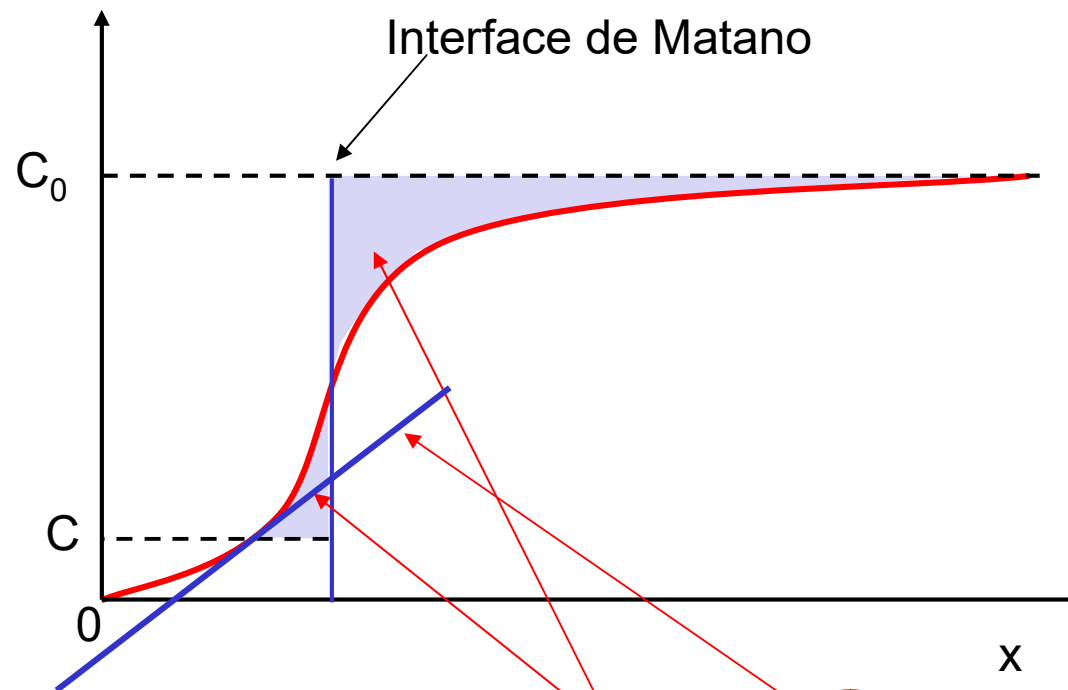
$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left( \tilde{D} \frac{\partial C_A}{\partial x} \right)$$



# Análise de Matano



# Análise de Matano



$$\tilde{D} = -\frac{1}{2t} \int_{C_0}^C x dC \left( \frac{dx}{dC} \right)$$



# Referências

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- Abbaschian, R.; Abbaschian L. e Reed-Hill, R.E. – Physical Metallurgy Principles, 4<sup>a</sup> ed., Cengage Learning, 2009.
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- MATTER – Materials Science on CD-ROM, Liverpool University Press, 1997.