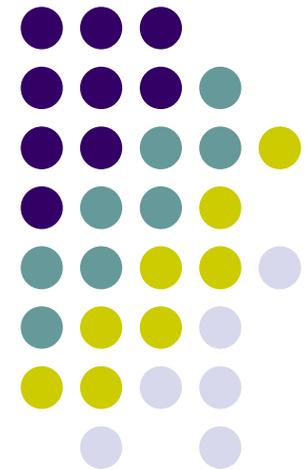


Difusão



Sumário

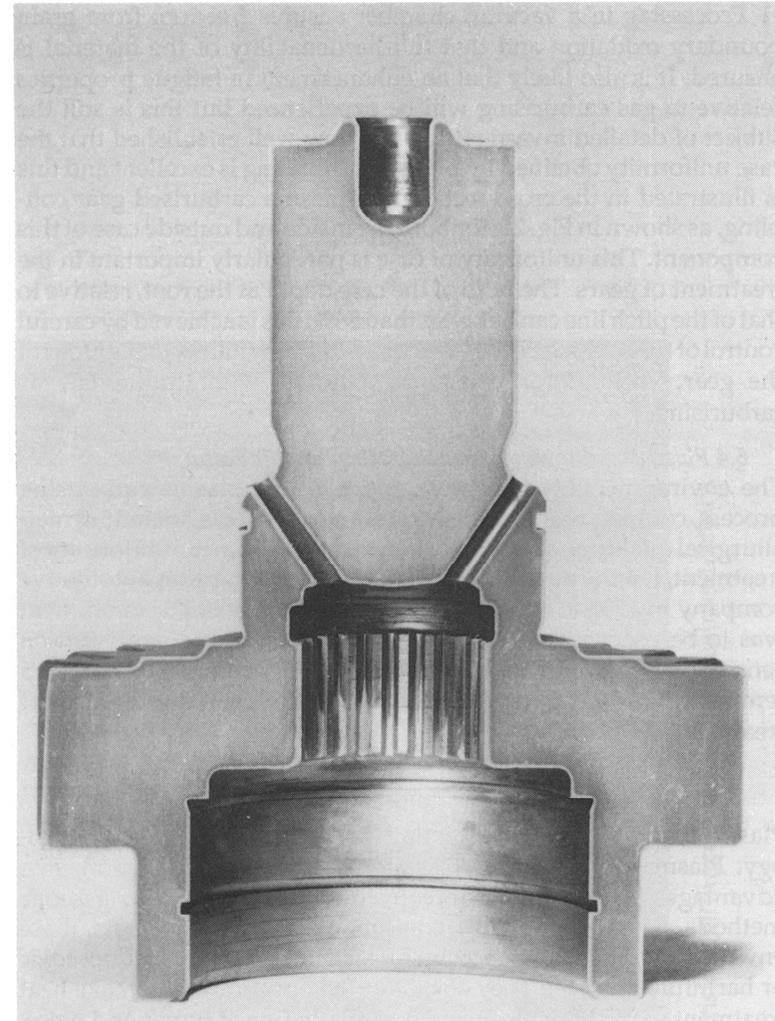
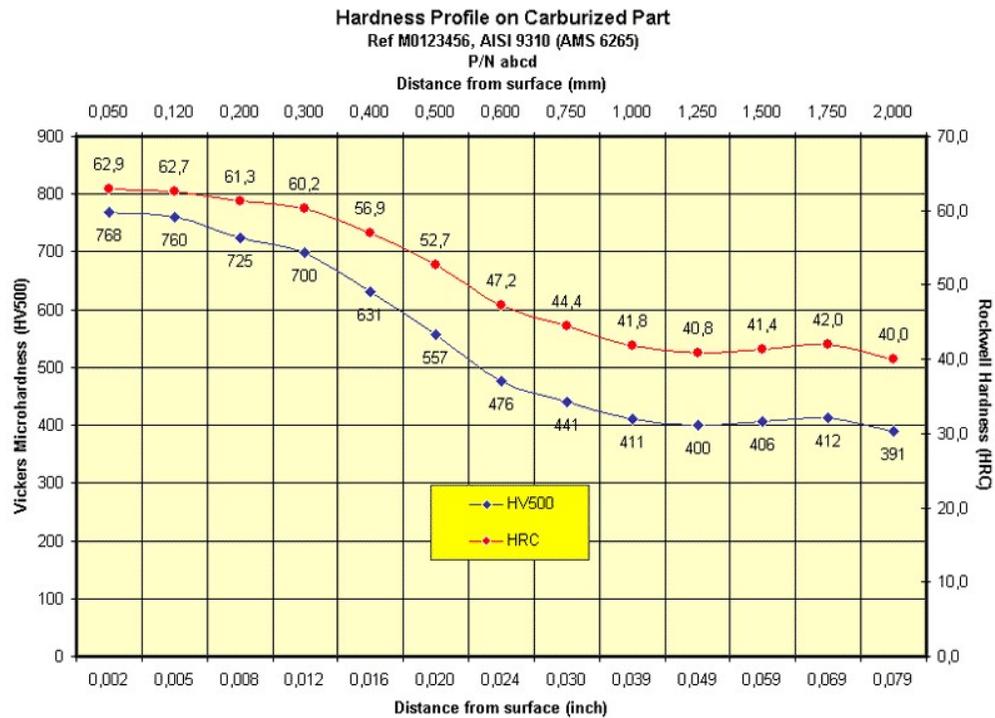


- Difusão de Intersticiais
 - Movimento dos átomos
 - Regime estacionário (1ª lei de Fick)
 - Exemplo de uso
 - O coeficiente de difusão
 - Regime transiente (2ª lei de Fick)
 - Solução para um sólido semi-infinito
 - Exemplo de uso
- Autodifusão
 - Mecanismo
- Difusão de Substitucionais
 - Criação e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

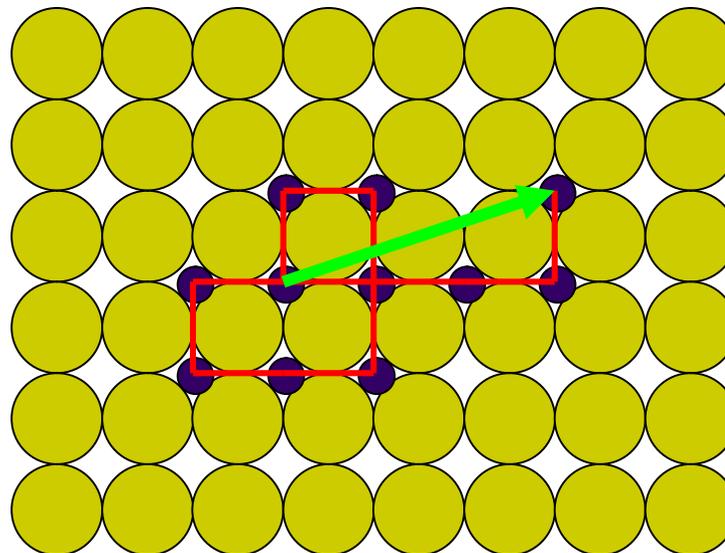
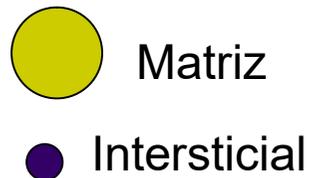
Exemplo



Cementação de aços



Movimentação de átomos nos materiais

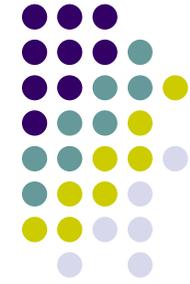


Movimento aleatório

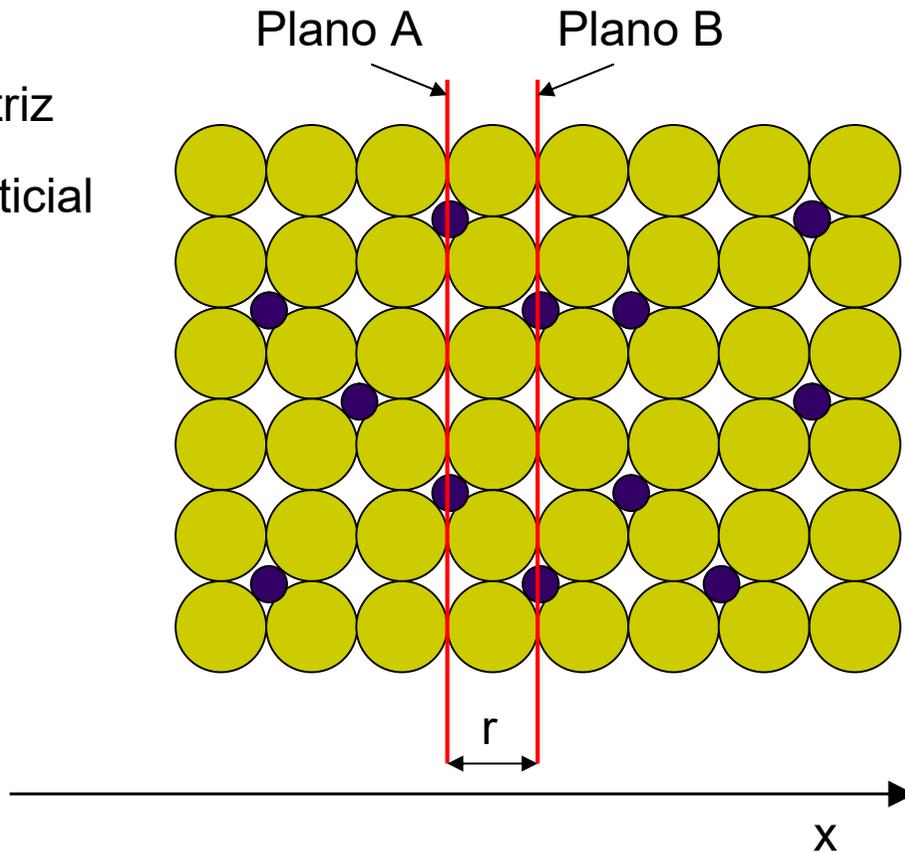
Exemplo: C em Fe

- 35°C - 1 salto/s - 0,25 nm
- 700°C – 5,9 bilhões de saltos/s – 1,46 m percorridos – ΔS de 19 μm

Difusão de Intersticiais



-  Matriz
-  Intersticial



Número de Intersticiais no plano
 Área do Plano
 Saltos/segundo

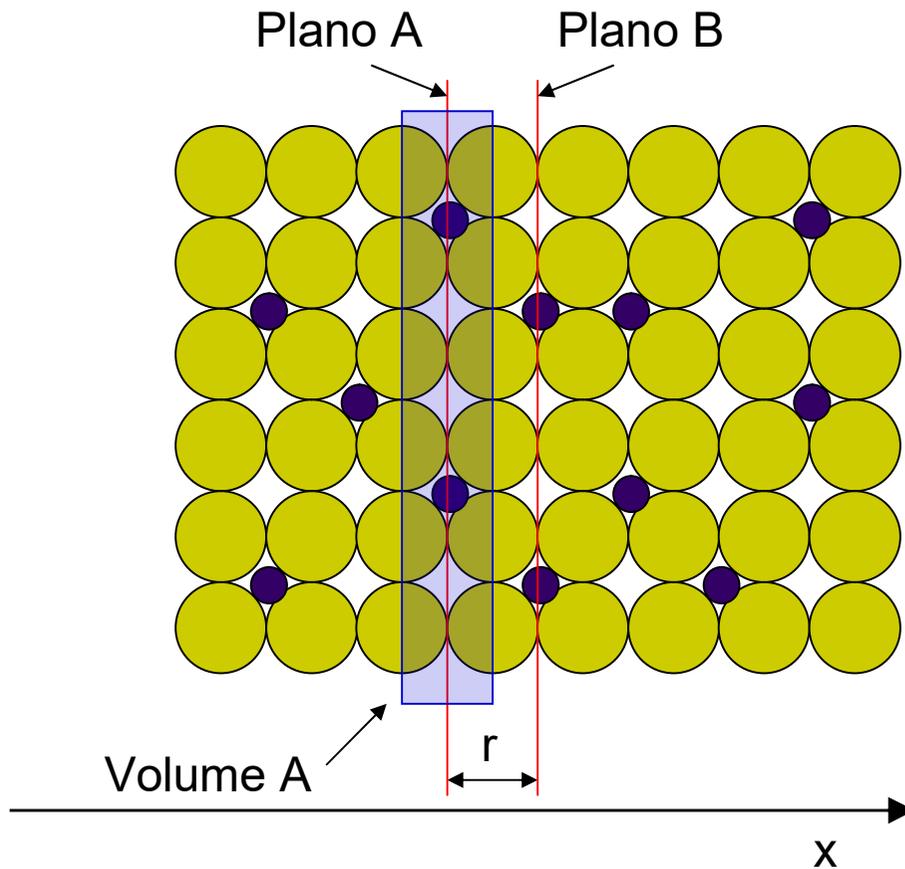
$$\vec{J}_x = \frac{1}{6} \Gamma \frac{n_A}{A}$$

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

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

(átomos/m²/s)

Difusão de Instersticiais



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

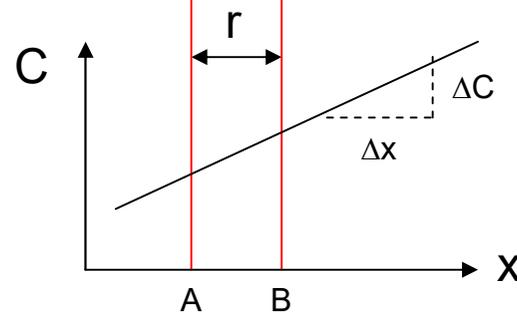
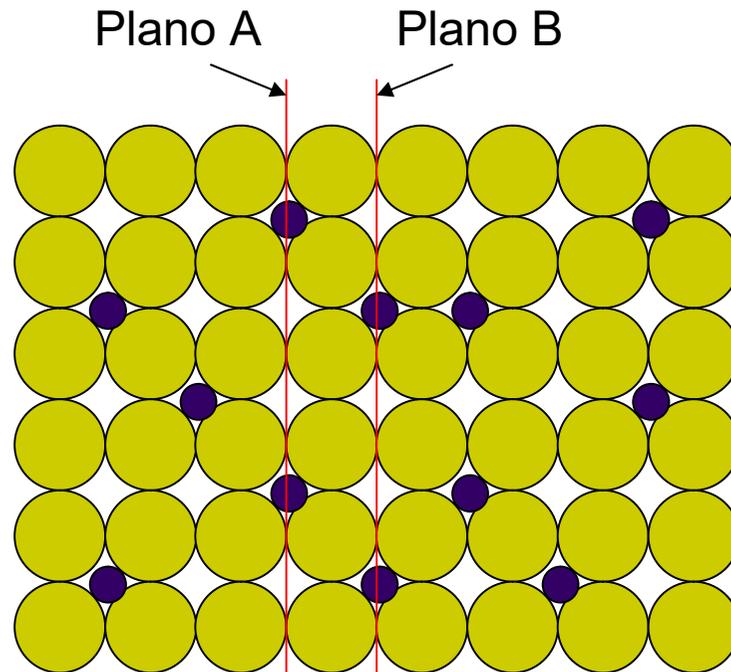
$$C_B = \frac{n_B}{r \cdot A}$$

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

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

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

Difusão de Instersticiais

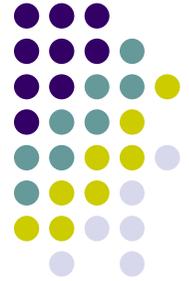


$$\frac{\Delta C}{\Delta x} = \frac{C_B - C_A}{r}$$

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

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

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



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

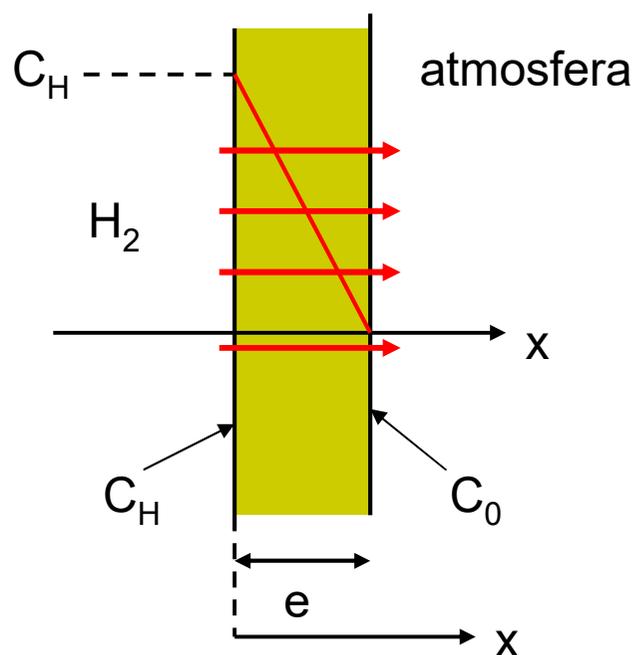


Aplicação da 1ª lei de Fick

- 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



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

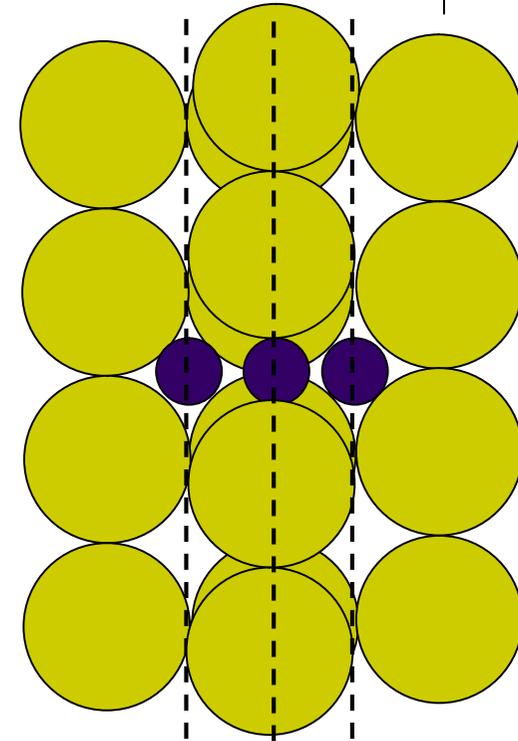
$$\Gamma = z \nu \exp\left(\frac{-\Delta G_m}{RT}\right) \quad \Delta G = \Delta H - T\Delta S$$

Configuração do interstício
 Freqüência de vibração atômica
 Probabilidade de sucesso

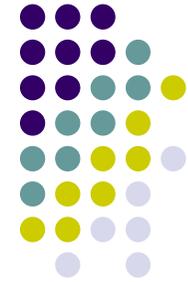
$$D = \frac{1}{6} r^2 z \nu \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(\frac{-\Delta H_m}{RT}\right)$$

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

A temperatura ativa a difusão

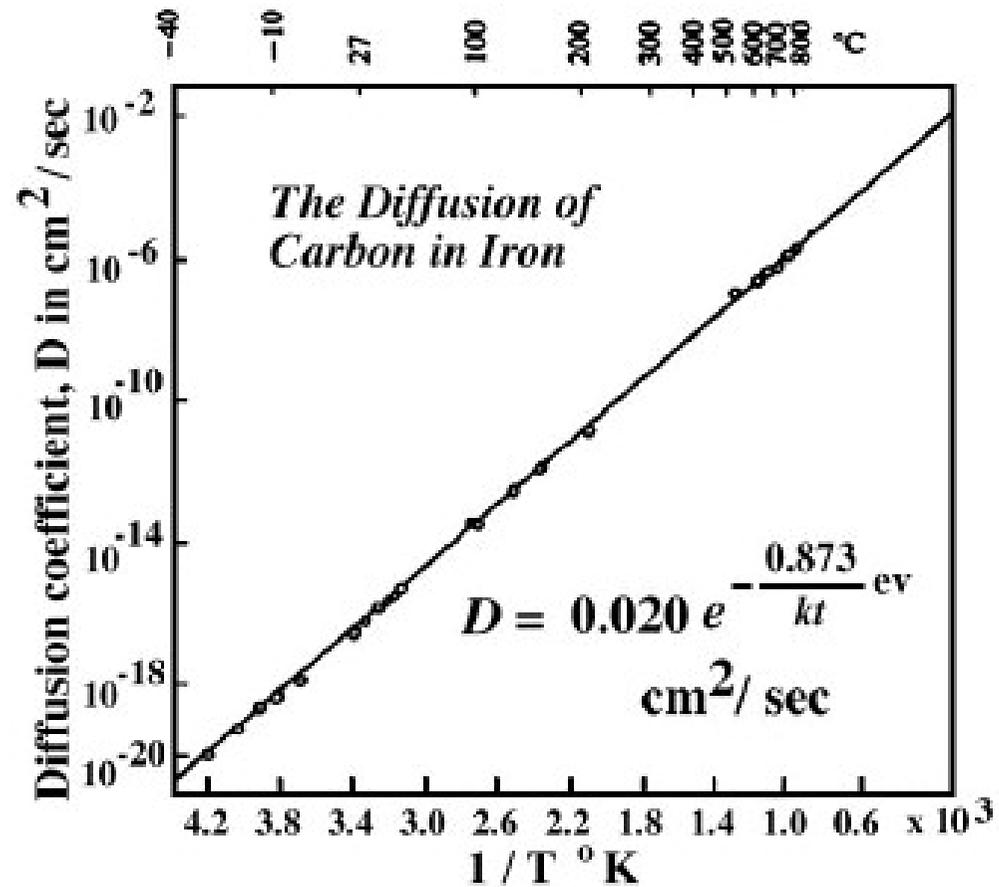


O coeficiente de difusão

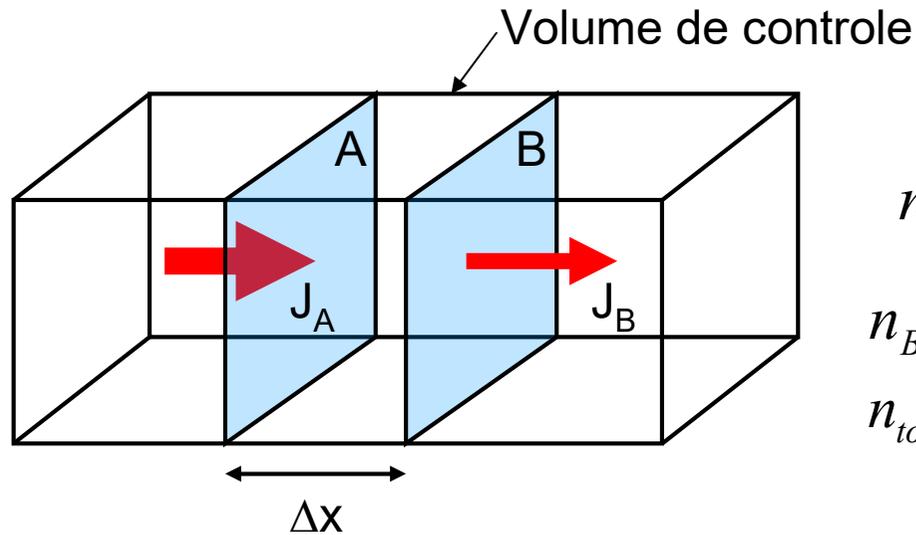
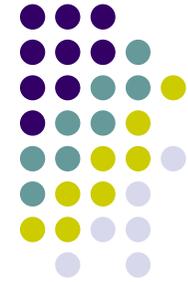


$$D = D_0 \exp\left(\frac{-\Delta H}{RT}\right)$$

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



Difusão em regime transiente



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

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

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

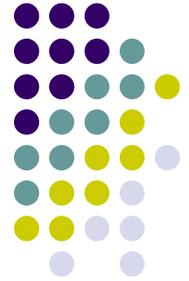
$$\Delta C = \frac{n_{total}}{V}$$

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

$$\Delta x \rightarrow 0$$

$$\Delta t \rightarrow 0$$

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



2ª lei de Fick

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

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

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

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

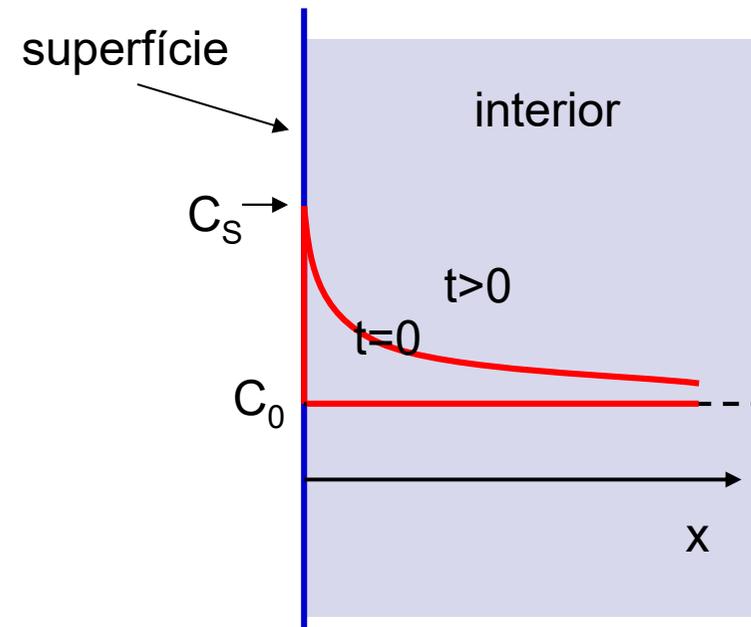
$$\frac{\partial C}{\partial t} = D \nabla^2 C$$



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



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

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

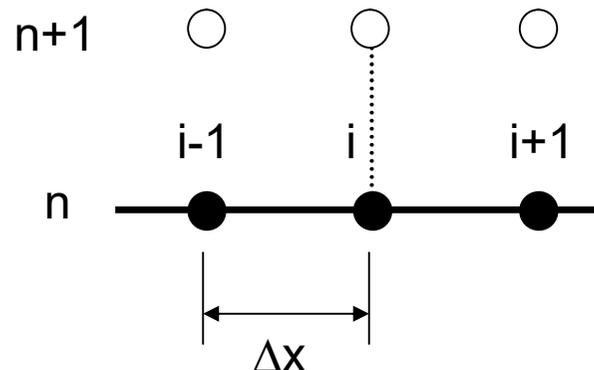
Exemplo mais simples de solução numérica



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

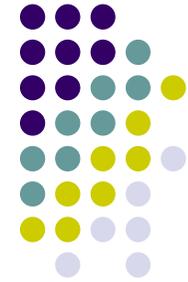
$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \Rightarrow \frac{C_i^{n+1} - C_i^n}{\Delta t} = \frac{D}{(\Delta x)^2} (C_{i+1}^n - 2C_i^n + C_{i-1}^n)$$

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



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

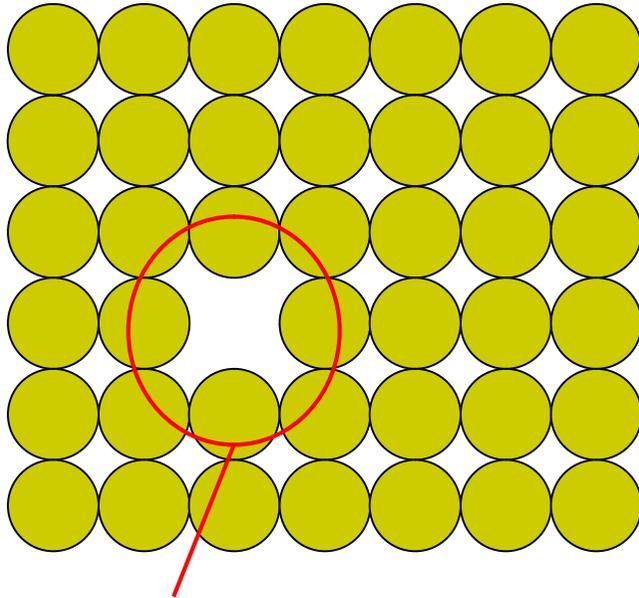
Erro de truncagem: $\frac{\Delta t}{2} \frac{\partial^2 C_i^n}{\partial t^2} + D \frac{(\Delta x)^2}{4!} \frac{\partial^4 C_i^n}{\partial x^4}$



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

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

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

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

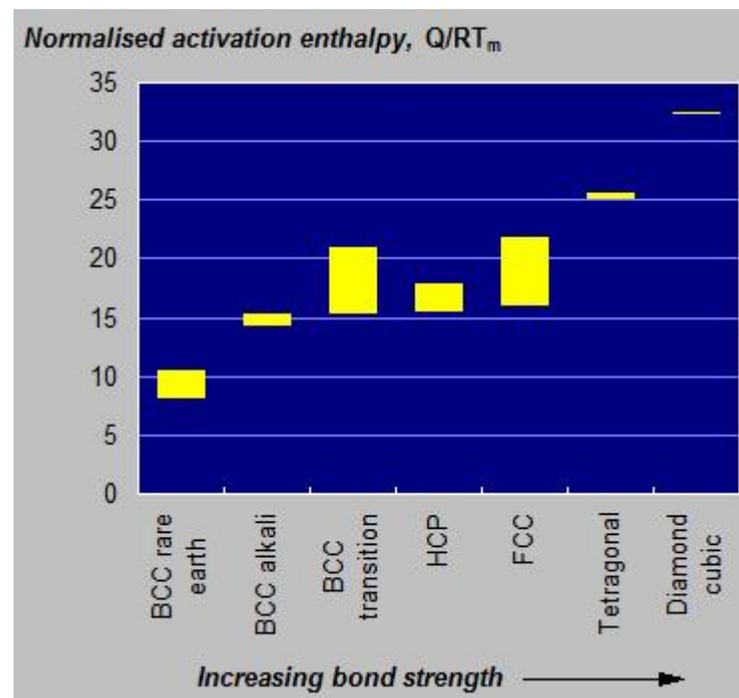


Autodifusão

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

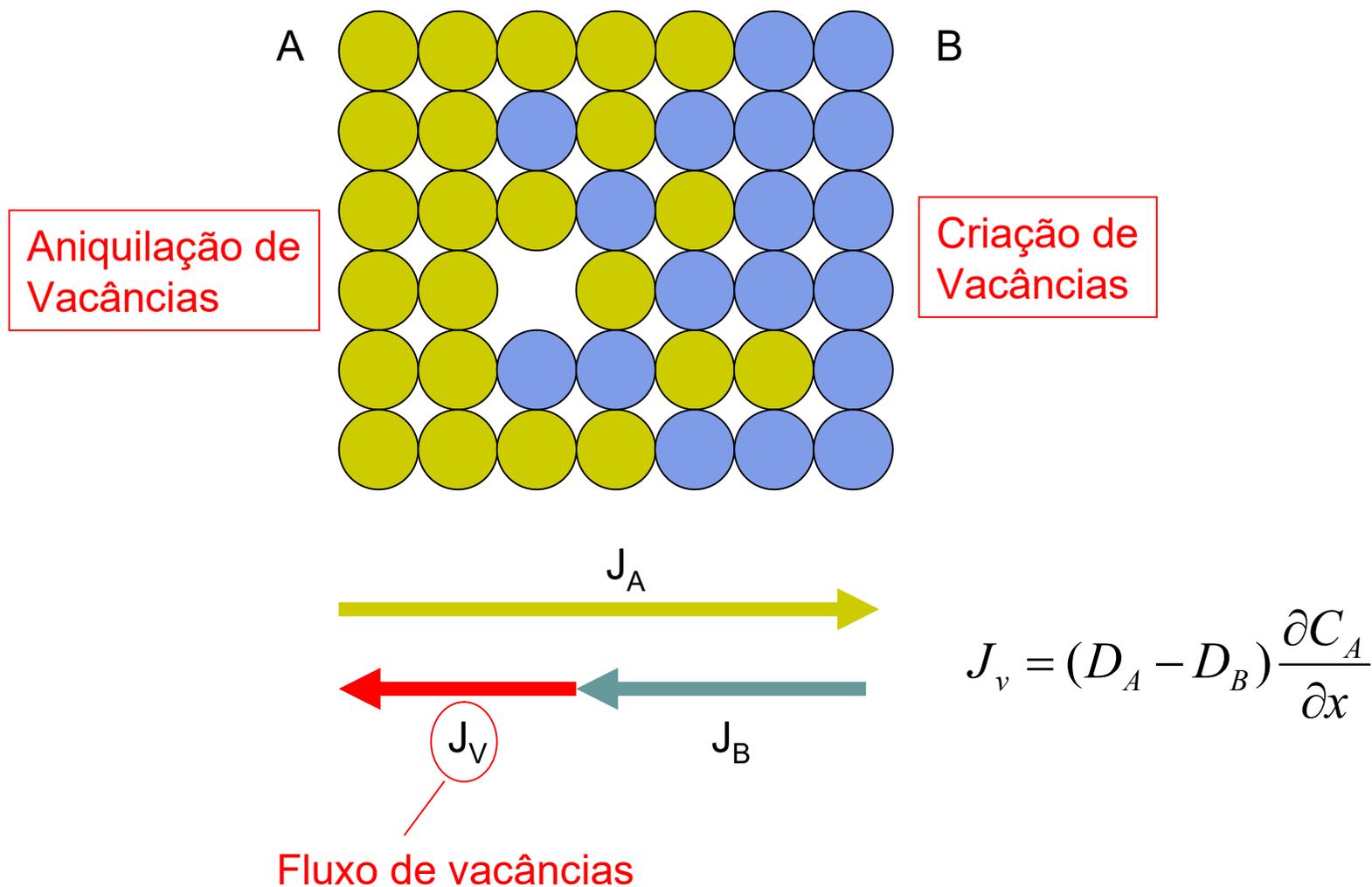
$$D = \frac{1}{6} r^2 z \nu \exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right) \exp\left(\frac{-\Delta H_m - \Delta H_v}{RT}\right)$$

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

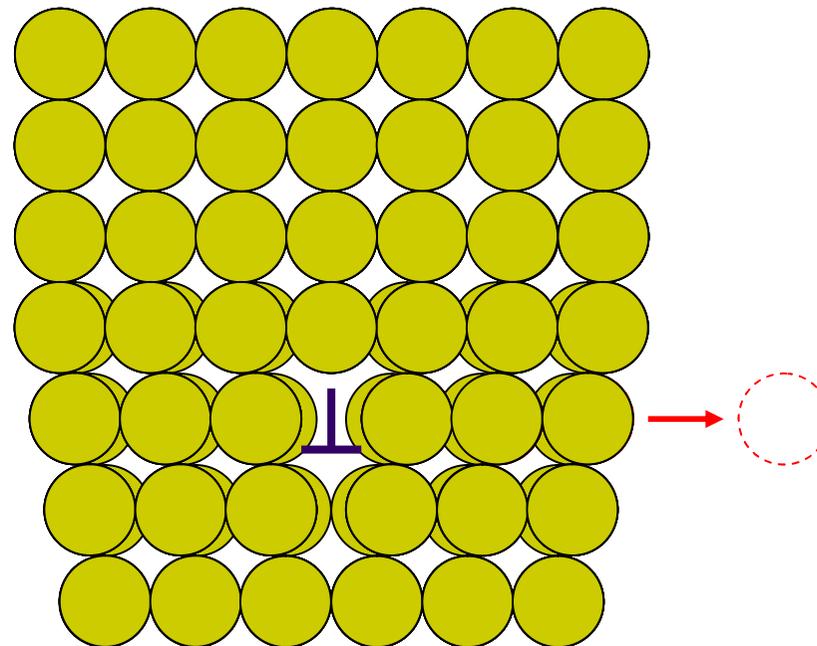
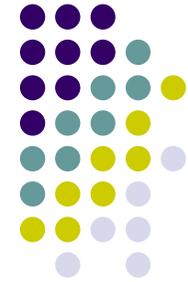




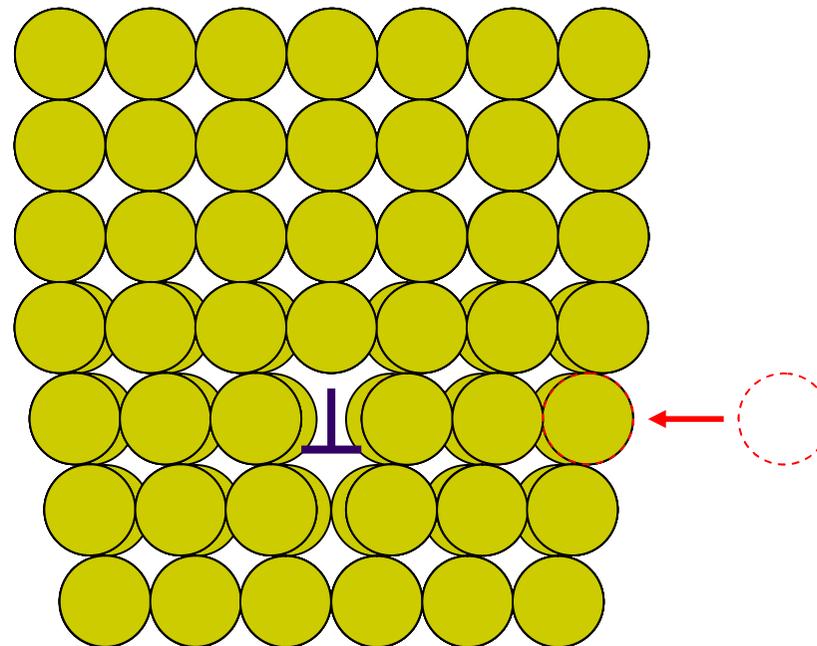
Difusão de Substitucionais



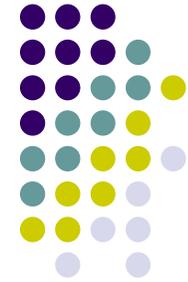
Criação de Vacâncias



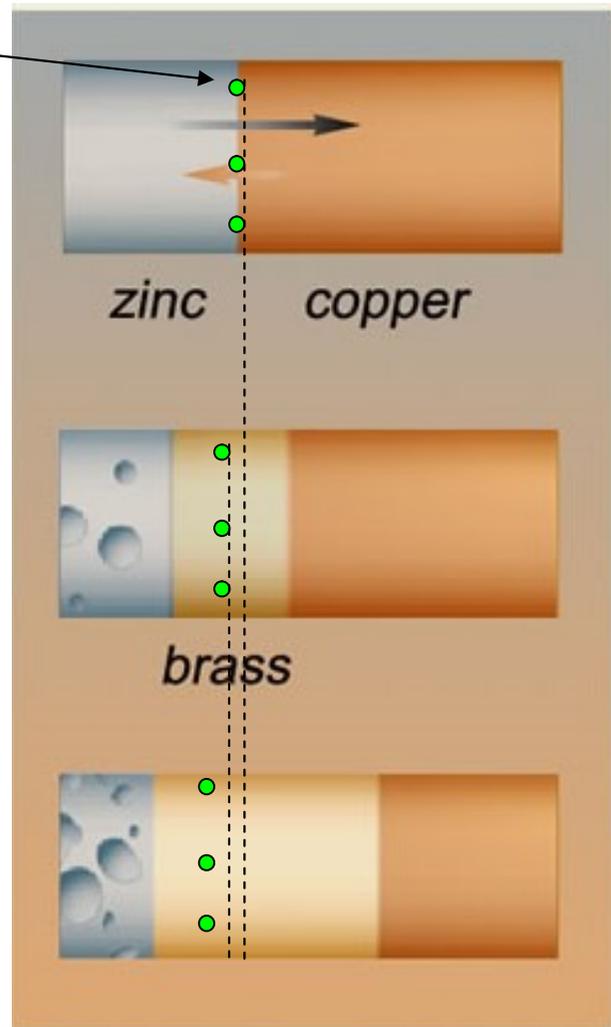
Aniquilação de Vacâncias



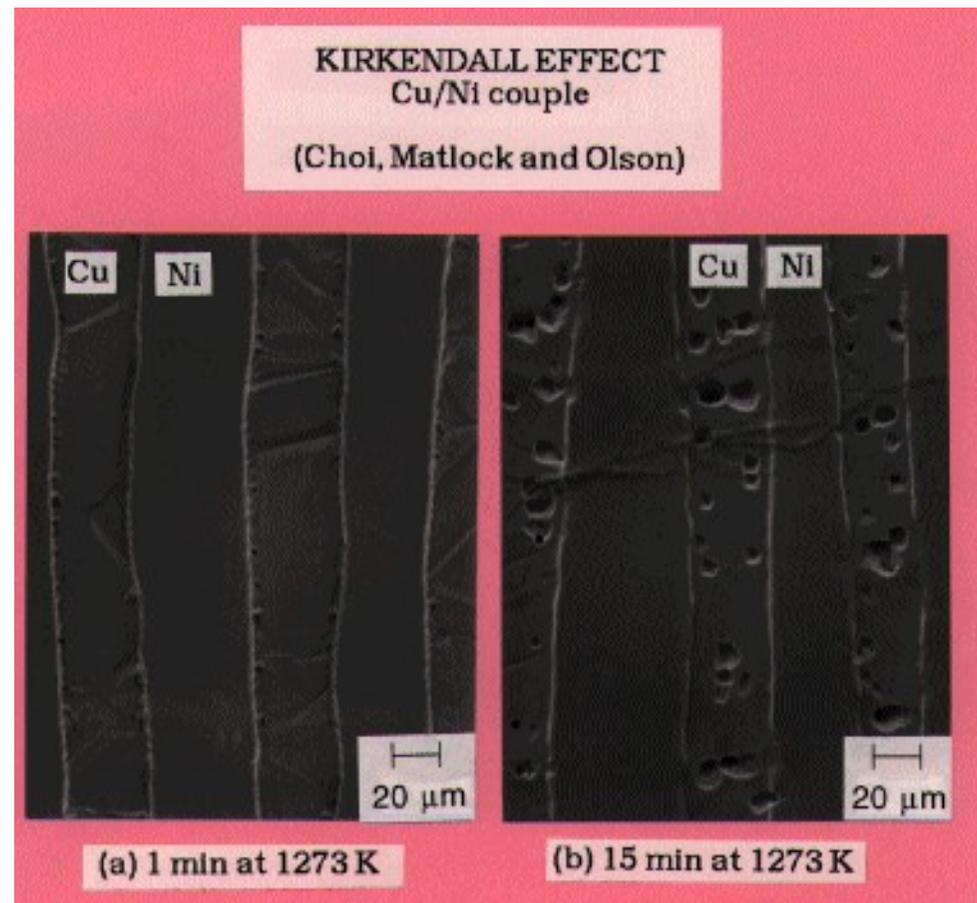
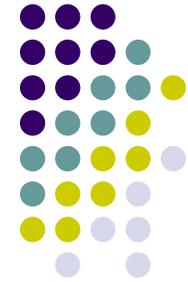
Efeito Kirkendall



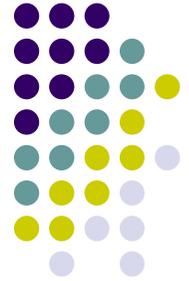
Marcadores



Efeito Kirkendall



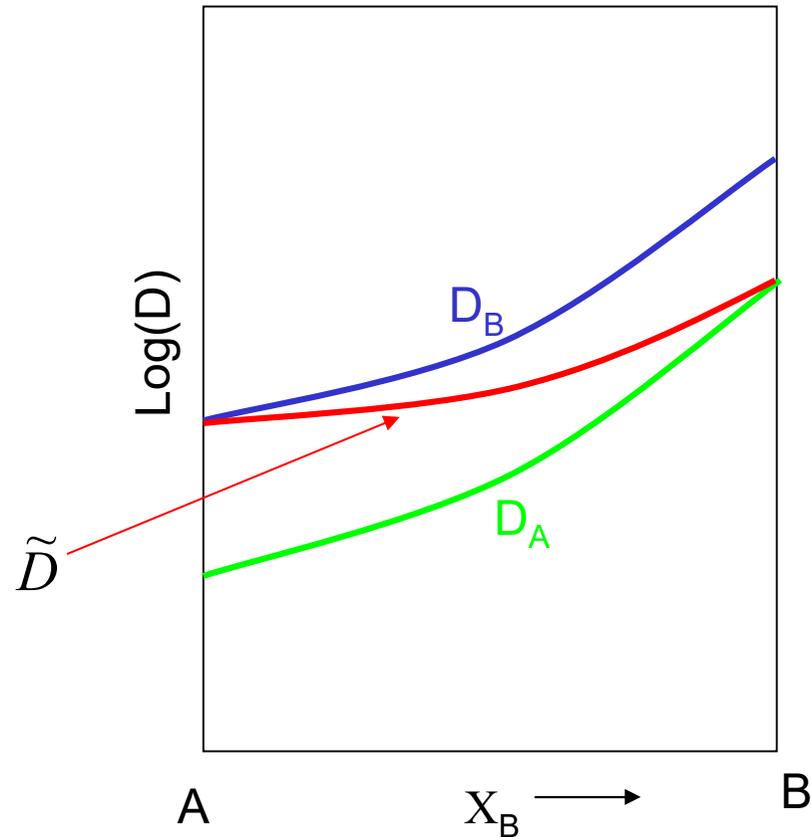
Equações de Darken



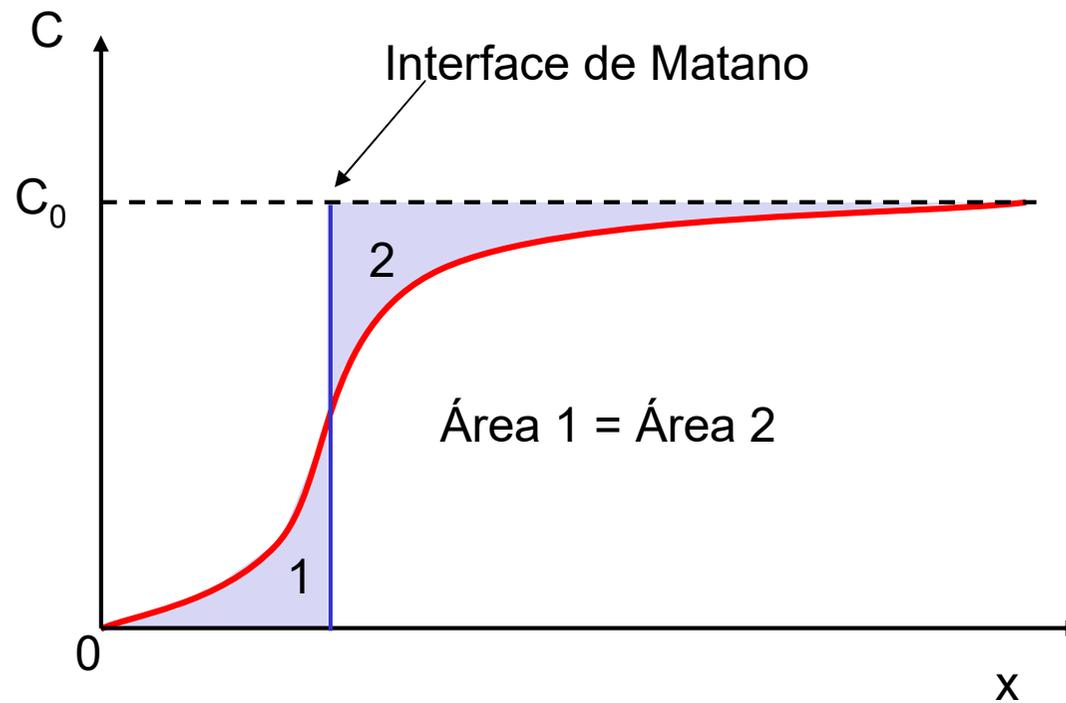
$$J_A = -(\chi_A D_A + \chi_B D_B) \frac{\partial C_A}{\partial x}$$

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

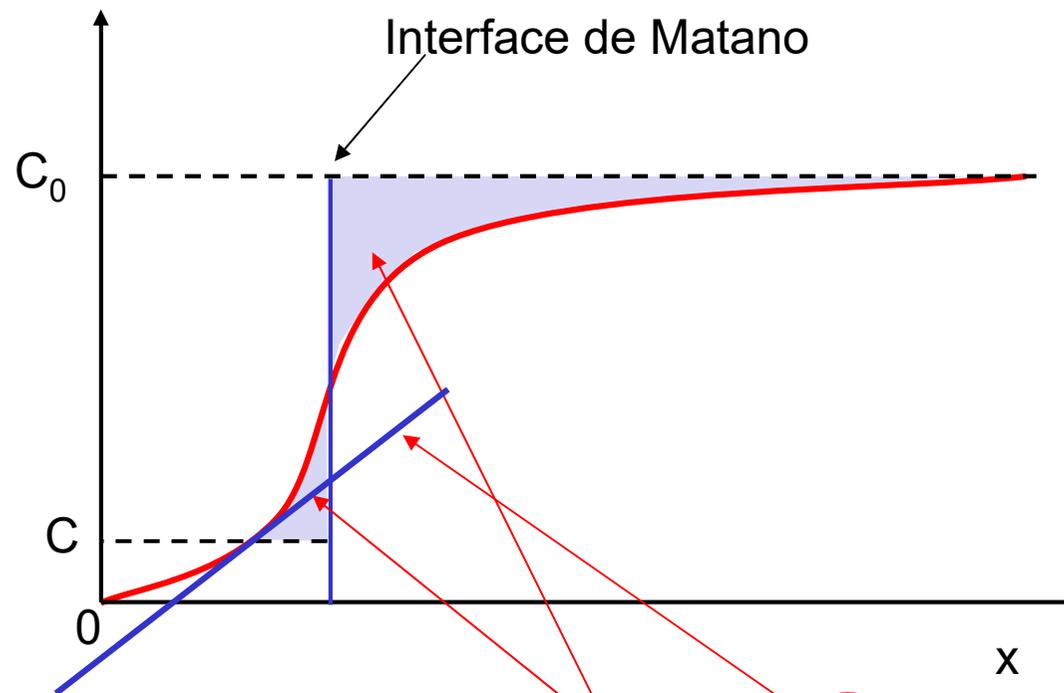
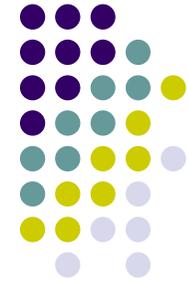
$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_A}{\partial x} \right)$$



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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