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THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Mass Transfer-I

Mass Diffusivity

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Diffusivity, D_{AB} of Gases

Gas phase diffusion Co-efficient (Diffusivity)

Table 2.1 Experimental diffusivity values for selected gas pairs at 1.013 bar pressure

Gas pair A-B	Temperature (K)	$D_{AB} \times 10^5$ (m ² /s)	Gas pair A-B	Temperature (K)	$D_{AB} \times 10^5$ (m ² /s)
Air-CH ₄	273	1.96	Air-C ₂ H ₅ OH	273	1.02
Air-CO ₂	276.2	1.42	Air-H ₂	273	6.11
Air-H ₂ O	298.2	2.6	Air-O ₂	273	1.775
Air-Benzene	298.2	0.9	Air-NH ₃	333	2.53
Air-n-Butanol	299.1	0.87	CH ₄ -Ar	298	2.02
CH ₄ -He	298	6.75	CH ₄ -H ₂	298	7.26
CO-N ₂	295.8	2.12	CO-H ₂	295.6	7.43
CO ₂ -H ₂	298	6.46	CO ₂ -N ₂	298.2	1.65
CO ₂ -O ₂	273	1.39	CO ₂ -CO	273	1.37
CO ₂ -H ₂ O	307.5	2.02	H ₂ -N ₂	297.2	7.73
H ₂ -N ₂	297	7.79	H ₂ -O ₂	273.2	6.97
H ₂ -He	298.2	11.32	H ₂ -SO ₂	285.5	5.25
H ₂ -H ₂ O	307.1	9.15	H ₂ -NH ₃	298	7.83
N ₂ -SO ₂	263	1.04	O ₂ -H ₂ O	308.1	2.82
O ₂ -CO	273	1.85	He-H ₂ O	298.2	9.08
He-Benzene	298.2	3.84	Ar-NH ₃	295.1	2.32

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Gas Diffusivity (correlation)

One of the most common method to estimate the binary gas diffusivity D_{AB} in low pressure system was proposed by **Wilke and Lee (1955)**.

D_{AB} = diffusion coefficient, cm²/s
 M_A, M_B = molecular weights of A and B, respectively
 T = temperature, K
 P = pressure, bar
 σ_{AB} = "collision diameter," a Lennard-Jones parameter, angstrom
 Ω_D = diffusion collision integral, dimensionless

In this equation: $M_{AB} = 2 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{-1}$

$$D_{AB} = \frac{\left[3.03 - \left(\frac{0.98}{M_{AB}^{1/2}} \right) \right] (10^{-3}) T^{3/2}}{PM_{AB}^{1/2} \sigma_{AB}^2 \Omega_D}$$

For a binary system of nonpolar molecular pair, the **Lennard-Jones parameters** can be obtained from the pure components by the following expression:

$$\sigma_{AB} = 0.5(\sigma_A + \sigma_B); \quad \epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2} \quad \sigma = 1.18(V_b)^{1/3} \quad \epsilon_A/\kappa = 1.15T_b$$

$$\Omega_D = \frac{a}{(T^*)^b} + \frac{c}{\exp(dT^*)} + \frac{e}{\exp(fT^*)} + \frac{g}{\exp(hT^*)} \quad V_b = 0.285(V_c)^{1.048}$$

$T^* = \kappa T / \epsilon_{AB}$	$a = 1.06036$	$b = 0.15610$
$c = 0.19300$	$d = 0.47635$	$e = 1.03587$
$f = 1.52996$	$g = 1.76474$	$h = 3.89411$

Source: Wilke, C. R., and C. Y. Lee, Ind. Eng. Chem., 47, 1253 (1955)

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An empirical relation to determine the diffusivity for mixtures of non-polar gaseous or polar with non-polar gas

$$D_{AB} = \frac{10^{-4} \left(1.084 - 0.249 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \right) T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{\left[P_i (r_{AB})^2 f \left(\frac{KT}{\varepsilon_{AB}} \right) \right]}$$

where

D_{AB} is the diffusivity, m^2/s

T is the absolute temperature, K

M_A, M_B is the molecular weight of A and B respectively, kg/kmol

P_i is the absolute pressure, N/m^2

r_{AB} is the molecular separation at collision = $\frac{r_A + r_B}{2}$, nm

ε_{AB} is the energy of molecular attraction = $\sqrt{\varepsilon_A \varepsilon_B}$

K is the Boltzmann's constant

$f \left(\frac{KT}{\varepsilon_{AB}} \right)$ is the collision function

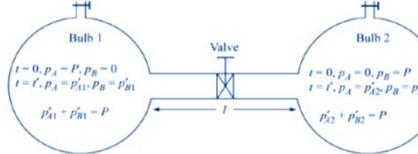
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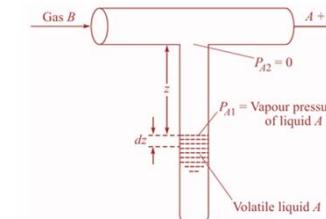
Gas phase diffusion coefficient (Diffusivity) measurement

Gas phase diffusion coefficient can be determined by several experimental methods

➤ Twin bulb method



➤ Stefan tube method



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Twin bulb method

Assumptions:

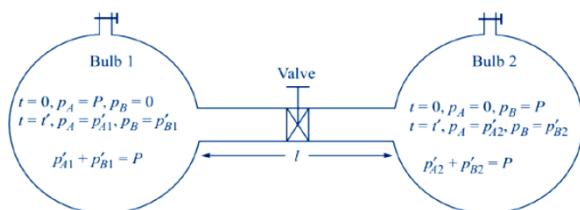
- Negligible Capillary volume
- Each bulb is always a uniform concentration
- Pseudo-steady state diffusion in the capillary

a = tube cross sectional area (inner)

l = length of the capillary tube

v_1, v_2 = volume of the bulbs

p_{A1}, p_{A2} = partial pressures of component A in bulb 1 and bulb 2 ($p_{A1} > p_{A2}$)



Two bulbs are connected by a narrow or capillary tube.

The diffusion will occur for component A from bulb 1 to bulb 2.

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➤ The mixture is kept uniform at a constant temperature T .

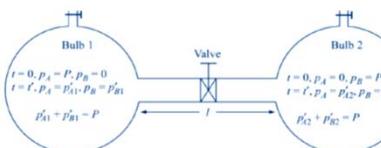
➤ The two bulbs were filled with pure A and pure B while the valve at the middle of tube were closed.

➤ The middle of the tube were opened to allow diffusion to start.

➤ At the end the middle valve is closed and the samples were collected from the bulbs and analysed.

➤ When Valve of bulb 1 is opened, it is filled with pure A at a total pressure of P . and valve of the Bulb2 remain closed. Same for other bulb filled of B. So the total pressure in the bulbs remains constant.

➤ At total pressure in the bulbs remain constant and equal, equimolar counter current diffusion through the connecting tube occurs.



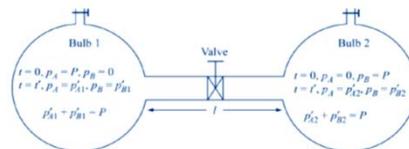
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Pseudo-steady state diffusion in the capillary

- The pseudo steady state approximation is that at any instant the diffusion through the connecting tube occurs at steady state.
- As the concentration in the bulbs change a little, a new steady state of diffusion is attained simultaneously.
- This assumption would be valid or correct if the time scale for change of concentration in the bulbs is considerably larger than the time scale for attainment of the steady state of diffusion through the connecting tube.



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$$\begin{aligned} -\frac{d}{dt}(p_{A1} - p_{A2}) &= aRT \left(\frac{1}{V_1} + \frac{1}{V_2} \right) N_A = \frac{aD_{AB}(p_{A1} - p_{A2})}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \\ \Rightarrow -\frac{d(p_{A1} - p_{A2})}{(p_{A1} - p_{A2})} &= \frac{aD_{AB}}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) dt \end{aligned}$$

We use the following conditions:

$$t = 0, p_{A1} - p_{A2} = P - 0 = P \quad \text{and} \quad t = t', p_{A1} - p_{A2} = p'_{A1} - p'_{A2} \text{ (say)}$$

Upon integration of the above equation within the above limits

$$\ln \frac{P}{p'_{A1} - p'_{A2}} = \frac{aD_{AB}}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) t'$$

This is the working equations for the calculations of D_{AB}

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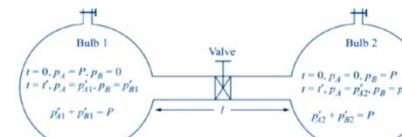
Steady-state diffusion of component A from bulb 1 to bulb 2

$$aN_A = \frac{aD_{AB}(p_{A1} - p_{A2})}{RTl} = -aN_B$$

C_{A1} and C_{A2} are the concentrations of A in the bulbs

$$\begin{aligned} -V_1 \frac{dC_{A1}}{dt} &= aN_A \quad \Rightarrow \quad -\frac{V_1}{RT} \frac{dp_{A1}}{dt} = aN_A \\ V_2 \frac{dC_{A2}}{dt} &= aN_A \quad \Rightarrow \quad \frac{V_2}{RT} \frac{dp_{A2}}{dt} = aN_A \end{aligned}$$

$$C_{A1} = p_{A1}/RT \text{ and } C_{A2} = p_{A2}/RT$$

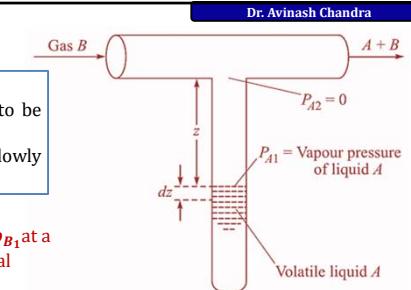


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The Stefan tube method

Assumptions:

- Gas B is not soluble in liquid A. Hence considered to be non-diffusing in B.
- The liquid level in the vertical tube will drop very slowly and pseudo-steady state condition can be assumed



Let at any time t , the partial pressure of component B is p_{B1} at a distance h from the top of the vertical tube and the partial pressure at the top of the tube is p_{B2} .

a = Tube cross sectional area (inner)

z = Height of the capillary tube above liquid level

p_{A1}, p_{A2} = partial pressures of component A

p_{B1}, p_{B2} = partial pressures of component B

p_t = Total pressure

p_{BM} = Log mean pressure difference of B

$$N_A = \frac{D_{AB}}{RTz} \frac{p_t}{p_{B,M}} (p_{A1} - p_{A2})$$

$$p_{BM} = \frac{p_{B1} - p_{B2}}{\ln \left(\frac{p_t - p_{B2}}{p_t - p_{B1}} \right)}$$

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If the fall in the liquid level is dz in a small time dt , the number of moles of A that diffuse out is $a dz (\rho_A / M_A)$. By a material balance over the time dt ,

$$\frac{a dz \rho_A}{M_A} = a N_A dt = \frac{a D_{AB} P (p_{A1} - p_{A2})}{RT p_{BM} z} dt$$

Here a is the inner cross-section of the vertical tube, ρ_A and M_A are the density (of the liquid) and molecular weight of A respectively. If at time $t = 0$, the liquid level is at z_0 from the top, and at time t' (i.e. at the end of the experiment) the liquid level is at z' , integration of the above equation and rearrangement gives

$$D_{AB} = \frac{RT p_{BM} \rho_A (z'^2 - z_0^2)}{2 P M_A (p_{A1} - p_{A2}) t'}$$

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Diffusivity, D_{AB} of Liquids

Diffusivity of Liquids

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Table 2.3 Liquid diffusivities

Solute	Solvent	Temperature, K	Solute concentration, kmol/m ³	Diffusivity, m ² /s × 10 ⁹
Cl ₂	Water	289	0.12	1.26
HCl	Water	273	9	2.7
		283	2	1.8
			9	3.3
			2.5	2.5
NH ₃	Water	289	0.5	2.44
		278	3.5	1.24
		288	1.0	1.77
CO ₂	Water	283	0	1.46
		293	0	1.77
NaCl	Water	291	0.05	1.26
			0.2	1.21
			1.0	1.24
			3.0	1.36
			5.4	1.54
Methanol	Water	288	0	1.28
Acetic acid	Water	285.5	1.0	0.82
			0.01	0.91
Ethanol	Water	291	1.0	0.96
		283	3.75	0.50
			0.05	0.83
n-Butanol	Water	289	2.0	0.90
CO ₂	Ethanol	290	0	0.77
Chloroform	Ethanol	293	2.0	3.2

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Wilke and Chang recommended the following correlation

$$D_{AB}^0 = \frac{(117.3 \times 10^{-18})(\varphi M_B)^{0.5} T}{\mu v_A^{0.6}}$$

D_{AB}^0 = Diffusivity of A in very dilute solution in solvent B, m²/s

M_B = Molecular weight of solvent

T = temperature, K

μ = Solution viscosity

v_A = solute molar volume at normal boiling point in m³/kmol
= 0.0756 meter for water as solvent.

φ = Association factor for solvent

= 2.26 for water

= 1.90 for methanol

= 1.50 for ethanol

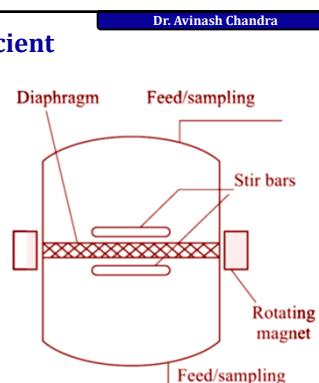
= 1.00 for non associated solvent

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Measurement of liquid phase diffusion Co-efficient

- A very dilute solution is taken in compartment 1
- A solution of slightly higher concentration in compartment 2 molecular diffusion takes place through the narrow pores of the diaphragm cell. There is a diaphragm at the middle from through the molecular diffusion takes place of the components.
- The pores inside the diaphragm are not a straight channel it is a tortuous channel and the length that is not equal to the thickness of the diaphragm



$$N_A = -D_{AB} \frac{dC_A}{dz}$$

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Cont...

$$N_A = \frac{D_{AB}(C_{A1} - C_{A2})}{l\tau}; \quad C_{A1} > C_{A2}$$

From the pseudo-steady state approximation

$$-V_1 \frac{dC_{A1}}{dt} = a\varepsilon N_A \quad \text{and} \quad V_2 \frac{dC_{A2}}{dt} = a\varepsilon N_A$$

$$-\frac{d}{dt}(C_{A1} - C_{A2}) = a\varepsilon \frac{D_{AB}(C_{A1} - C_{A2})}{l\tau} \left(\frac{1}{V_1} + \frac{1}{V_2} \right)$$

If $C_{A1,0}$ and $C_{A2,0}$ are the initial concentrations and $C_{A1,f}$ and $C_{A2,f}$ are the final concentrations in the compartments at time t_f , integration and rearrangement of Eq.

$$D_{AB} = \frac{l\tau}{a\varepsilon t_f} \left(\frac{1}{V_1} + \frac{1}{V_2} \right)^{-1} \ln \left(\frac{C_{A1,0} - C_{A2,0}}{C_{A1,f} - C_{A2,f}} \right)$$

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Diffusivity, D_{AB} of Solids

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Diffusivity of porous solid (media)

- Collision of the diffusing molecules offers resistance to diffusion.
- If the gas diffusion occurs in a very fine pore when the diffusion occurs inside the fine pores particularly at low pressure, the mean free path of the molecules may be larger than the diameter of the passage.
- The collision with wall becomes important and diffusion arising from the collision is called known Knudsen diffusion

Knudsen diffusivity can be determined by using an empirical relation,

$$D_{K,A} = \left(\frac{d}{3} \right) \left(\frac{8 g_c RT}{\pi M_A} \right)^{1/2}$$

The mean free path λ can be estimated by

$$\lambda = \left(\frac{3.2\mu}{P_i} \right) \left(\frac{RT}{2\pi g_c M_A} \right)^{1/2}$$

If $0.2 < d/\lambda < 20$, both molecular and Knudsen diffusion take place

where
 $D_{K,A}$ is the Knudsen diffusivity, cm^2/s
 l is the length of the pore, cm
 P_A is the partial pressure of diffusing substance, cmHg

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Thermally activated Diffusion

Atom needs enough thermal energy to break bonds and squeeze through its neighbors.

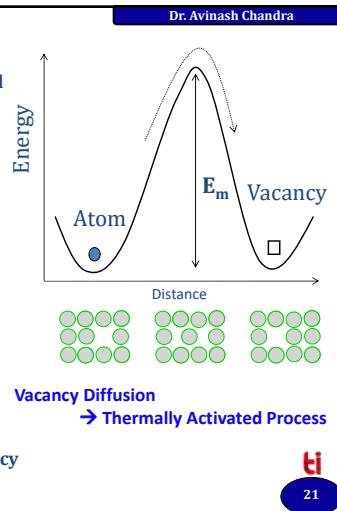
Energy needed → energy barrier
→ Called the activation energy E_m (like Q)

Typical activation energy E_m (~ 1 eV/atom) (like Q_v)

Therefore, a large fluctuation in energy is needed for a jump.

Probability of a fluctuation or frequency of jump, R_j →

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$



R_0 = Attempt frequency proportional to vibration frequency

Swedish chemist Arrhenius

k_B = Boltzman constant (8.62×10^{-5} eV/atom-K)

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$$P = \text{Const.} \exp\left(-\frac{Q_v}{k_B T}\right)$$

2. Probability of thermal fluctuation

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

The diffusion coefficient = Multiply

$$D = \text{Const.} \exp\left(-\frac{E_m}{k_B T}\right) \exp\left(-\frac{Q_v}{k_B T}\right)$$

$$D = D_0 \exp\left(-\frac{Q_d}{k_B T}\right)$$

Arrhenius dependence.

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Diffusion and Temperature

Diffusion coefficient increases with increasing T .

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

$$= D_0 \exp\left(-\frac{Q_d}{kT}\right)$$

D = diffusion coefficient [m^2/s]

D_0 = pre-exponential [m^2/s]

Q_d = activation energy [J/mol or eV/atom]

R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

k_B = Boltzman constant (8.62×10^{-5} eV/atom-K)

Diffusion coefficient is the measure of mobility of diffusing species.

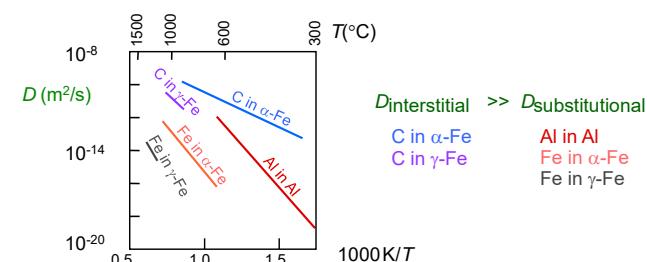
$$\ln D = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T}\right) \quad \text{or} \quad \log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T}\right)$$

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D has exponential dependence on T

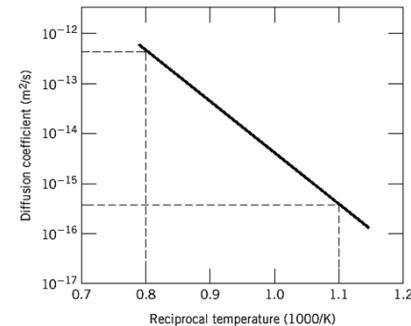


Source: William D. Callister, David G. Rethwisch, Materials Science and Engineering: An Introduction, (8th Ed). 2009;
E.A. Brandes and G.B. Brook, Smithells Metals Reference Book, 7th ed, Butterworth-Heinemann, Oxford, (1992)

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Arrhenius Plots
 $(\ln D)$ vs. $(1/T)$
 Or
 $(\log D)$ vs. $(1/T)$

Graph of $\log D$ vs. $1/T$ has slope of $-Q_d/2.3R$, intercept of $\ln D_0$,

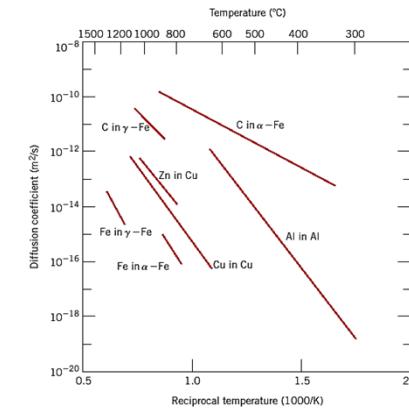
$$\log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T} \right) \quad Q_d = -2.3R \left[\frac{\log D_1 - \log D_2}{1/T_1 - 1/T_2} \right]$$

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Arrhenius plot: Diffusivity for metallic systems



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Factors that Influence Diffusion/ Diffusivity

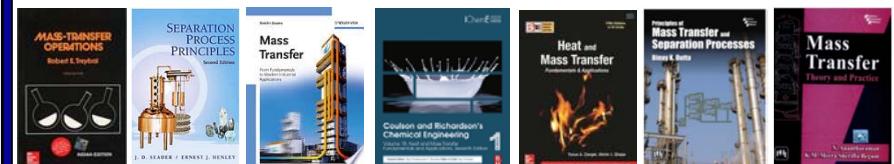
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- **Temperature** - Diffusion rate increases very rapidly with increasing temperature
- **Diffusion mechanism** - Interstitial is usually faster than vacancy
- **Diffusing and host species** - D_o , Q_d is different for every solute, solvent pair
- **Microstructure** - Diffusion faster in polycrystalline vs. single crystal materials because of the rapid diffusion along grain boundaries and dislocation cores.
- **Smaller atoms diffuse more readily**
- **Diffusion faster in open lattices or in open directions**
- **Self-diffusion coefficients for Ag** Depends on diffusion path
- **Grain boundaries and surfaces less restrictive**

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References



ETH
Mass Transfer
Theories for Mass Transfer Coefficients
Lecture 9, 15.11.2017, Dr. K. Wegner

- Lecture notes/ppt of Dr. Yahya Banat (ybanat@qu.edu.qa)

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