



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

# Mass Transfer-I

## Mass Diffusivity



**DEPARTMENT OF CHEMICAL ENGINEERING**  
Thapar Institute of Engineering & Technology  
Patiala (Punjab), INDIA-147004

**Dr. Avinash Chandra**  
(Ph.D., IIT Kanpur)  
Associate Professor

Web: <http://www.thapar.edu/faculties/view/Dr-Avinash-Chandra/ODU=/Mg==>

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

### 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)**.

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

$D_{AB}$  = diffusion coefficient, cm<sup>2</sup>/s  
 $M_A, M_B$  = molecular weights of A and B, respectively  
 $T$  = temperature, K  
 $P$  = pressure, bar  
 $\sigma_{AB}$  = "collision diameter," a Lennard-Jones parameter, angstrom  
 $\Omega_D$  = diffusion collision integral, dimensionless

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

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

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

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

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

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

## Cont...

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

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

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<sup>2</sup>

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

$\epsilon_{AB}$  is the energy of molecular attraction =  $\sqrt{\epsilon_A \epsilon_B}$

$K$  is the Boltzmann's constant

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

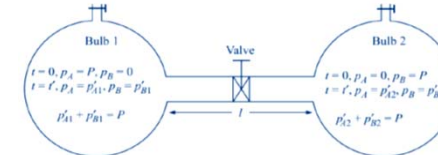
ti

5

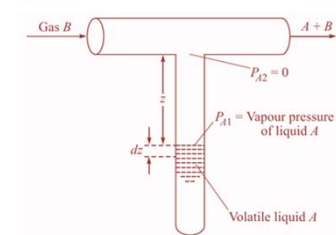
## Gas phase diffusion coefficient (Diffusivity) measurement

Gas phase diffusion coefficient can be determined by several experimental methods

### > Twin bulb method



### > Stefan tube method



ti

6

## Twin bulb method

### Assumptions:

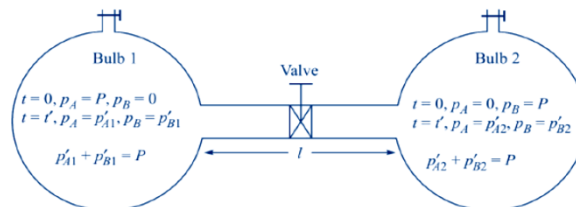
- > Negligible Capillary volume
- > Each bulb is always a uniform concentration
- > Pseudo-steady state diffusion in the capillary

$a$  = 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.

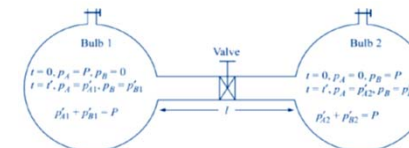
The diffusion will occur for component A from bulb 1 to bulb 2.

ti

7

## Cont...

- > 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.



ti

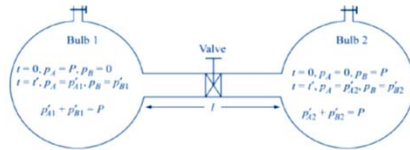
8

## Cont...

Dr. Avinash Chandra

## 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.



ti

9

## Cont...

Dr. Avinash Chandra

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

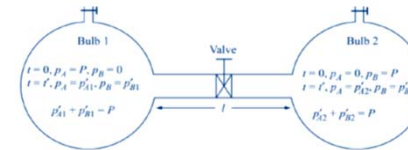
$$aN_A = \frac{aD_{AB}(p_{A1} - p_{A2})}{RTl} = -aN_B$$

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

$$-V_1 \frac{dC_{A1}}{dt} = aN_A \Rightarrow -\frac{V_1}{RT} \frac{dp_{A1}}{dt} = aN_A$$

$$V_2 \frac{dC_{A2}}{dt} = aN_A \Rightarrow \frac{V_2}{RT} \frac{dp_{A2}}{dt} = aN_A$$

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



ti

10

## Cont...

Dr. Avinash Chandra

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

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

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  $D_{AB}$

ti

11

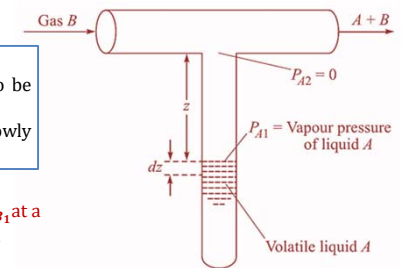
## The Stefan tube method

Dr. Avinash Chandra

## 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

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

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

ti

12

## Cont...

Dr. Avinash Chandra

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

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

ti

13

Diffusivity,  $D_{AB}$  of Liquids

## Diffusivity of Liquids

Dr. Avinash Chandra

Table 2.3 Liquid diffusivities

Solute	Solvent	Temperature, K	Solute concentration, kmol/m <sup>3</sup>	Diffusivity, m <sup>2</sup> /s × 10 <sup>9</sup>
Cl <sub>2</sub>	Water	289	0.12	1.26
HCl	Water	273	9	2.7
		283	2	1.8
			9	3.3
			2.5	2.5
		289	0.5	2.44
NH <sub>3</sub>	Water	278	3.5	1.24
		288	1.0	1.77
CO <sub>2</sub>	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
		291	1.0	0.96
Ethanol	Water	283	3.75	0.50
			0.05	0.83
		289	2.0	0.90
n-Butanol	Water	288	0	0.77
CO <sub>2</sub>	Ethanol	290	0	3.2
Chloroform	Ethanol	293	2.0	

ti

15

## Cont...

Dr. Avinash Chandra

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, m<sup>2</sup>/s

$M_B$  = Molecular weight of solvent

$T$  = temperature, K

$\mu$  = Solution viscosity

$v_A$  = solute molar volume at normal boiling point in m<sup>3</sup>/kmol

= 0.0756 meter for water as solvent.

$\varphi$  = Association factor for solvent

= 2.26 for water

= 1.90 for methanol

= 1.50 for ethanol

= 1.00 for non associated solvent

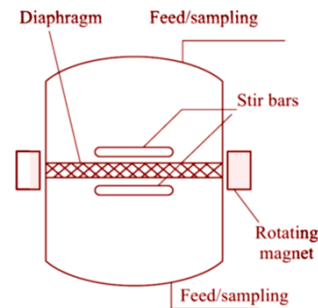
ti

16

## Measurement of liquid phase diffusion Co-efficient

Dr. Avinash Chandra

- 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



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

ti

17

## Cont...

Dr. Avinash Chandra

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

From the pseudo-steady state approximation

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

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

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.

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

$a$  = tube cross sectional area (inner)  
 $l$  = length of the capillary tube  
 $v_1, v_2$  = volume of the solutions in the two cells  
 $C_{A1}, C_{A2}$  = Concentration in the cells at time  $t$   
 $l\tau$  = Effective length of diffusive path

ti

18

## Diffusivity, $D_{AB}$ of Solids

## Diffusivity of porous solid (media)

Dr. Avinash Chandra

- 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  $\lambda$  can be estimated by

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

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

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

ti

20

## 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.

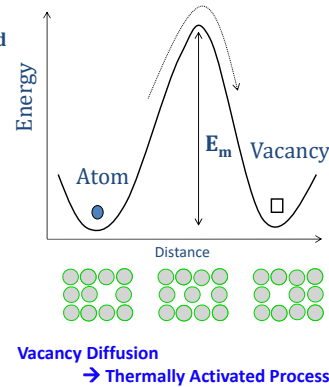
Probability of a fluctuation or frequency of jump,  $R_j$  →

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

$R_0$  = Attempt frequency proportional to vibration frequency

Swedish chemist Arrhenius

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



21

## Cont...

1. Probability of finding a vacancy in an adjacent lattice site at particular **times**

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

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.

22

## 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 [ $\text{m}^2/\text{s}$ ]

$D_0$  = pre-exponential [ $\text{m}^2/\text{s}$ ]

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

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

$T$  = absolute temperature [K]

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

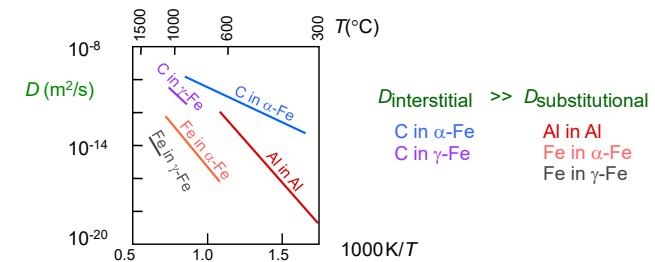
Diffusion coefficient is the measure of mobility of diffusing species.

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

23

## Cont...

$D$  has exponential dependence on  $T$



$D_{\text{interstitial}} \gg D_{\text{substitutional}}$

C in  $\alpha$ -Fe

C in  $\gamma$ -Fe

Al in Al

Fe in  $\alpha$ -Fe

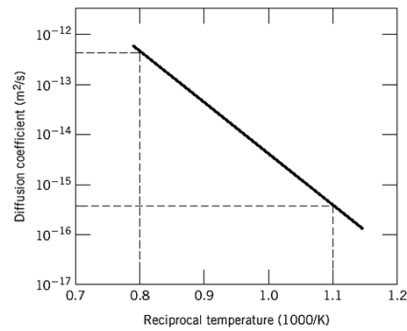
Fe in  $\gamma$ -Fe

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)

24

Cont...

Dr. Avinash Chandra

**Arrhenius Plots****(lnD) vs. (1/T)****Or****(logD) vs. (1/T)**

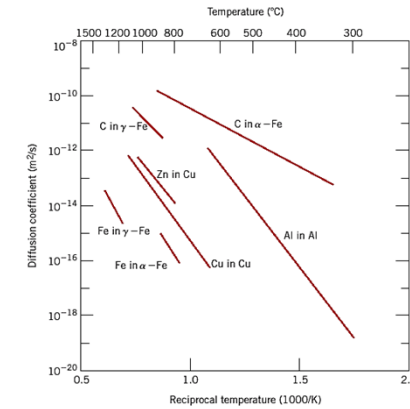
$$\log D = \log D_0 - \frac{Q_d}{2.3R} \left( \frac{1}{T} \right) \quad Q_d = -2.3R \left[ \frac{\log D_1 - \log D_2}{1/T_1 - 1/T_2} \right]$$

ti

25

Cont...

Dr. Avinash Chandra

**Arrhenius plot: Diffusivity for metallic systems**

ti

26

**Factors that Influence Diffusion/ Diffusivity**

Dr. Avinash Chandra

- **Temperature** - Diffusion rate increases very rapidly with increasing temperature
- **Diffusion mechanism** - Interstitial is usually faster than vacancy
- **Diffusing and host species** -  $D_0$ ,  $Q_d$  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**

ti

27

**References**

Dr. Avinash Chandra



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)

ti

28