MODULE Ⅱ：

MOLECULAR DIFFUSION

Dr. Dong-Guang Wang

2.1 FICK'S LAW

Adolf Fick in 1955 first described the molecular diffusion in an isothermal, isobaric binary system of components A and B. According to his idea of molecular diffusion, the molar flux of a species relative to an observer moving with molar average velocity is proportional to the concentration gradient in a certain direction..

$$J_A = -D_{AB}\frac{dC_A}{dZ}$$

Where, J_A is the molar flux of component A in the Z direction. C_A is the concentration of A and Z is the distance of diffusion. The proportionality constant, D_{AB} is the diffusion coefficient of the molecule A in B. This is valid only at *steady state condition of diffusion*. The diffusivity of A in B equals the diffusivity of B in A, i.e., $D_{AB}=D_{BA}$

2.2 Diffusion coefficient

The proportionality factor of Fick's law is called diffusivity or diffusion coefficient which can be defined as the ratio of the flux to its concentration gradient and its unit is m^2/s. It is a function of the temperature, pressure, nature and concentration of other constituents.

Relationship between diffusivity and pressure

Diffusivity decreases with increase in pressure ($D_{AB} \propto 1/p$ for moderate ranges of pressures, up to 25 atm) because number of collisions between species is less at lower pressure. But the diffusivity is hardly dependent on pressure in case of liquid.

Relationship between diffusivity and temperature

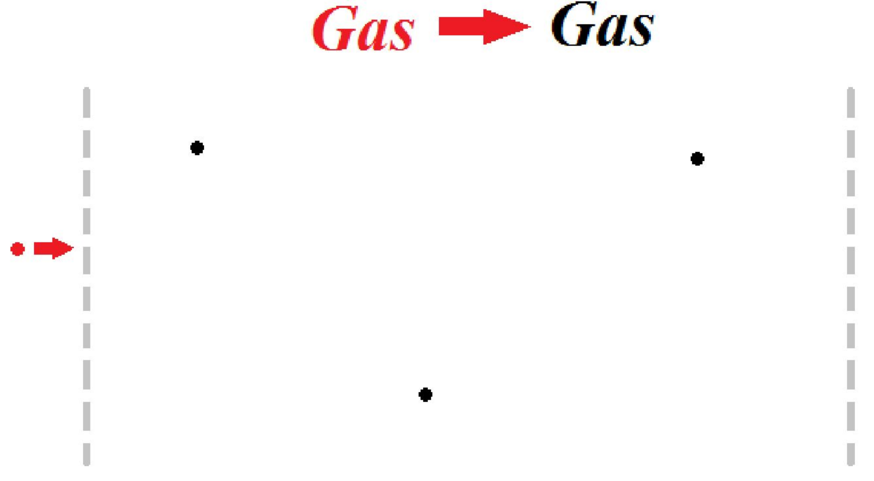
The diffusivity increases with increase in temperature ($D_{AB} \propto T^{1.5}$) because random thermal movement of molecules increases with increase in temperature.

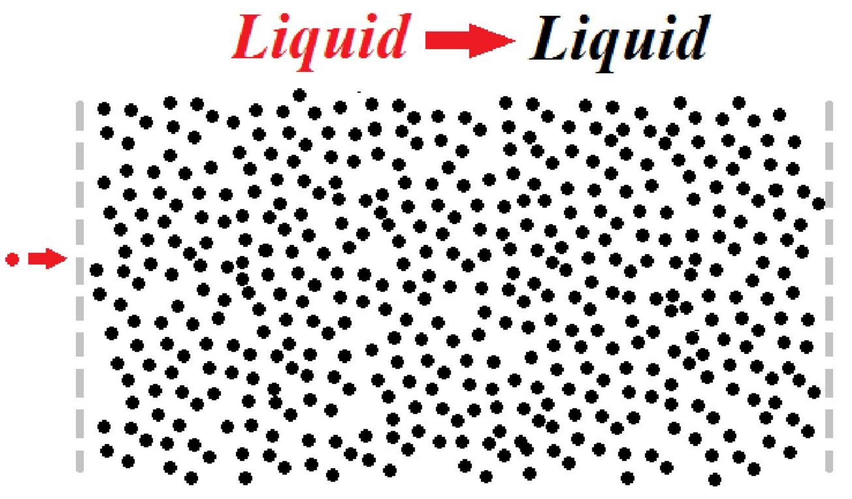
Diffusivity of gas, liquid, and solid

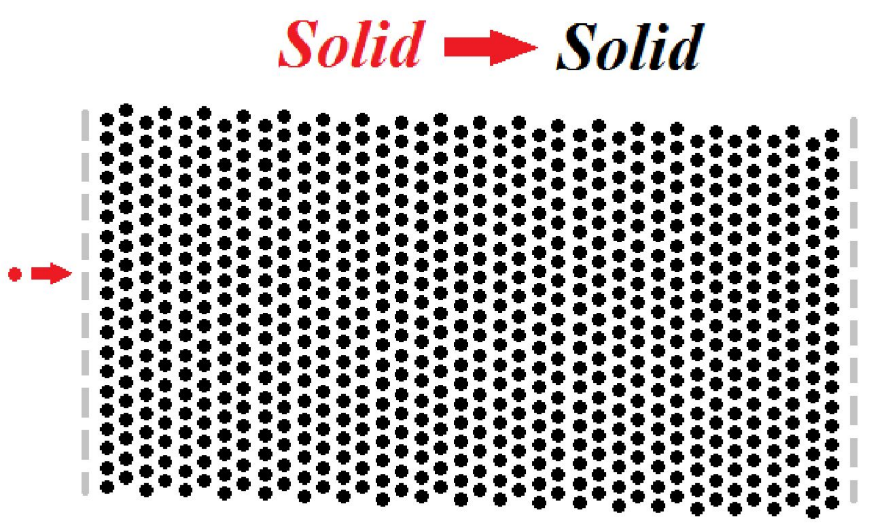
The diffusivity is generally higher for gases (in the range of 0.5×10^{-5} to 1.0×10^{-5} m^2/s) than for liquids (in the range of 10^{-10} to 10^{-9} m^2/s).

Diffusion is almost impossible in solids (in the range of 10^{-13} m^2/s) because the particles are too closely packed and strongly held together with no ‘empty space’ for particles to move through. Solids diffuse much slower than liquids because intermolecular forces in solid are stronger enough to hold the solid molecules together.

Three models of diffusion process in gas, liquid, and solid phase







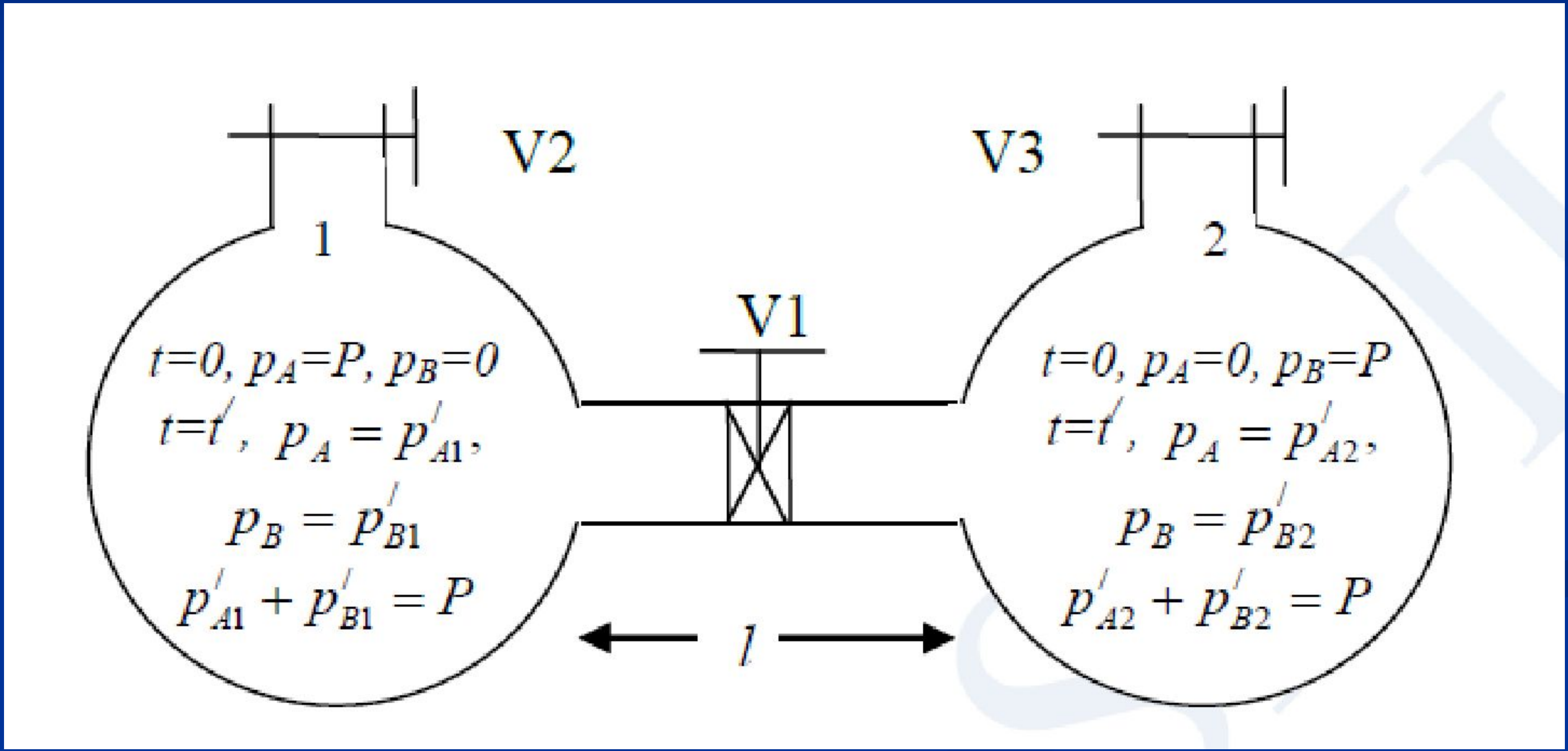
The density of gas is three orders of magnitude lower than that of liquid or solid.

2.3 Ratio between heat and molecular diffusivity (*Le*)

The *Le* number of gas is generally about 1. This means that when gas undergoes transient heat and molecular diffusion, the variations of heat and molecular diffusion distribution are approximately the same. However, for liquid and solid, thermal conductivity is much faster than molecular diffusion.

2.3 Measurement of gas-phase diffusion coefficient

(a) Twin-bulb method



Two bulbs are connected by a narrow tube. In the beginning two bulbs are evacuated and all the three valves [V1, V2 and V3] are kept closed. Then V2 is opened and bulb 1 is filled with pure A at a pressure P. After that V3 is opened and bulb 2 is filled with pure B at the same pressure P. Finally, V1 is opened. At steady state

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

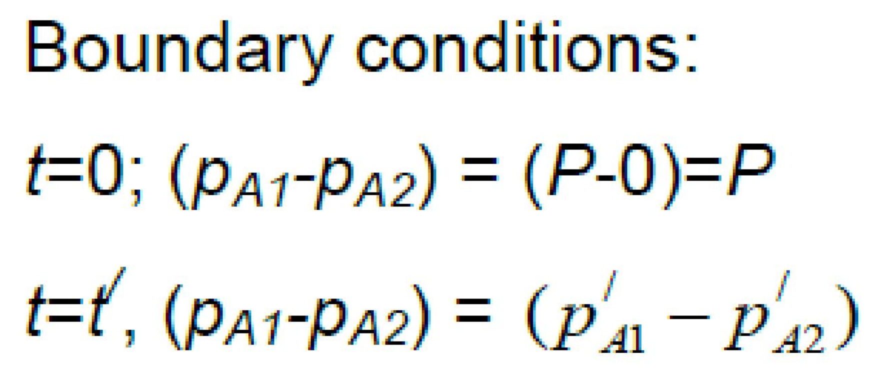
where, *a* is cross sectional area of the connecting tube. If p_{A1} and p_{A2} are partial pressures of *A* in two bulbs at any time, then

$$-\frac{V1}{RT}\frac{dp_{A1}}{dt} = aN_A$$

and $$\frac{V2}{RT}\frac{dp_{A2}}{dt} = aN_A$$

From the above three equations, we have

$$-\frac{d(p_{A1}-p_{A2})}{dt} = \frac{aD_{AB}(p_{A1}-p_{A2})}{l}\left(\frac{1}{V1}+\frac{1}{V2}\right)$$

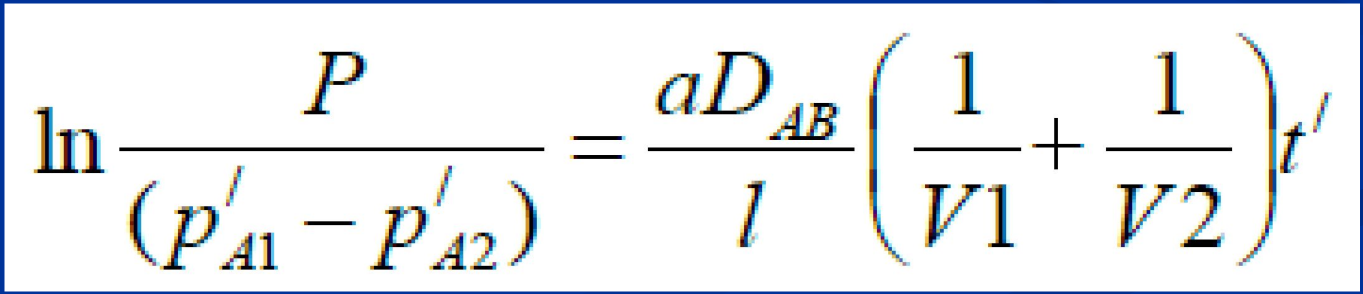


Boundary conditions:

$t=0; (p_{A1}-p_{A2}) = (P-0)=P$

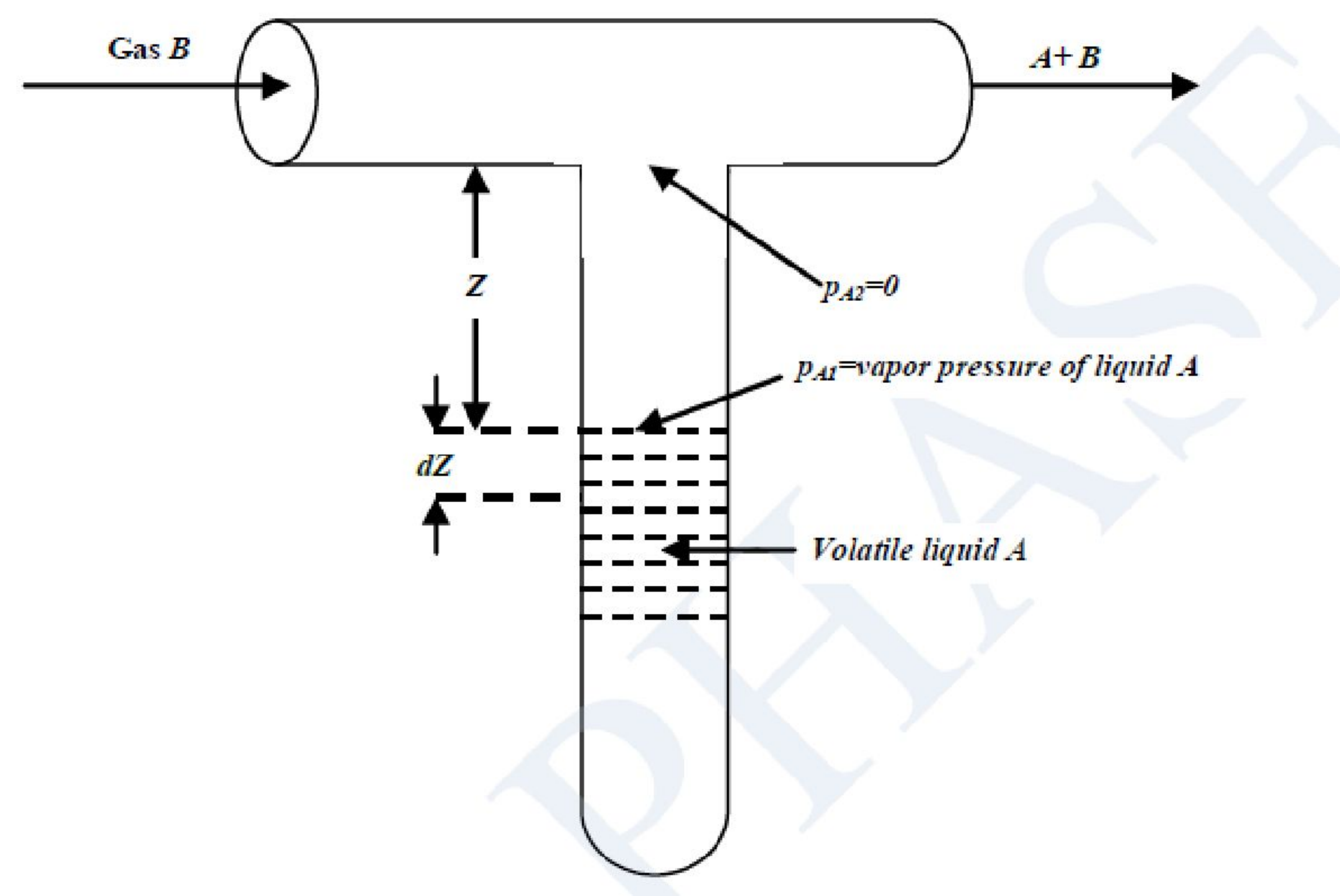
$t=t', (p_{A1}-p_{A2}) = (p'_{A1}-p'_{A2})$

Applying the above boundary conditions, the Equation is integrated to obtain the expression of D_{AB} as follows:



$$\ln \frac{P}{(p'_{A1}-p'_{A2})} = \frac{aD_{AB}}{l}\left(\frac{1}{V1}+\frac{1}{V2}\right)t'$$

(b) Stefan tube method (Diffusion coefficient of steam)



Stefan tube consists of a T-tube, placed in a constant temperature bath. Air pump supply air, passed through the T-tube. Volatile component (A) is filled and change in the level is observed by a sliding microscope. At any time *t*, partial pressure of *A* at the top of the vertical tube is p_{A1} and that at the liquid surface is p_{A2}. The diffusional flux of *A* is given as:

$$D_{AB} = \frac{RTp_{B,lm}(Z'^{2} - Z_0^2)}{2PM_A(p_{A1} - p_{A2})t'}$$

where, partial pressure of A at liquid surface, p_{A1} is equal to vapor pressure at the same temperature. The partial pressure of *A* at the top of the vertical tube, p_{A2} is zero due to high flow rate of *B*.

2.4 Estimation of gas diffusion coefficient

Empirical equation by Fuller, Schettler and Giddings:

$$D_{AB} = \frac{1.00 \times 10^{-7} T^{1.75} \left(\dfrac{1}{M_A} + \dfrac{1}{M_B} \right)^{0.5}}{P \left[\left(\sum v_A \right)^{1/3} + \left(\sum v_B \right)^{1/3} \right]^2}$$

where, T is temperature in K

M_A, M_B are molecular weights of A and B

P is total pressure in bar

v_A, v_B are atomic diffusion volume in m³.

Atomic diffusion volume

C	16.5
H	1.98
O	5.48
N	5.69
S	17.0
Cl	19.5

Molecular diffusion volume

H_2	7.07	Kr	22.8	H_2O	12.7
He	2.88	Xe	37.9	Cl_2	37.7
N_2	17.9	CO	18.9	Br_2	67.2
O_2	16.6	CO_2	26.9	SO_2	41.1
Air	20.1	N_2O	35.9		
Ar	16.1	NH_3	14.9		

Please calculate the molecular diffusion coefficient of n-butanol $C_4H_{10}O$ (B) diffusing through air (A) at 298.9K and 1.0 atm. (The measured value is 8.60×10^{-6} m^2/s.)

The known data : $M_A = 74.1;\quad M_B = 29;$

$$\sum v_B = 4(16.5) + 10(1.98) + 1(5.48) = 91.28$$

$$\sum v_A = 20.1(air)$$

$$D_{AB} = \frac{1.00\times10^{-7}(298.9)^{1.75}\left(\frac{1}{74.1}+\frac{1}{29}\right)^{0.5}}{(1.0)\left[(91.28)^{1/3}+(20.1)^{1/3}\right]^2} = 9.05\times10^{-6}\ m^2/s$$

The deviation between the measured and calculated values is 4%

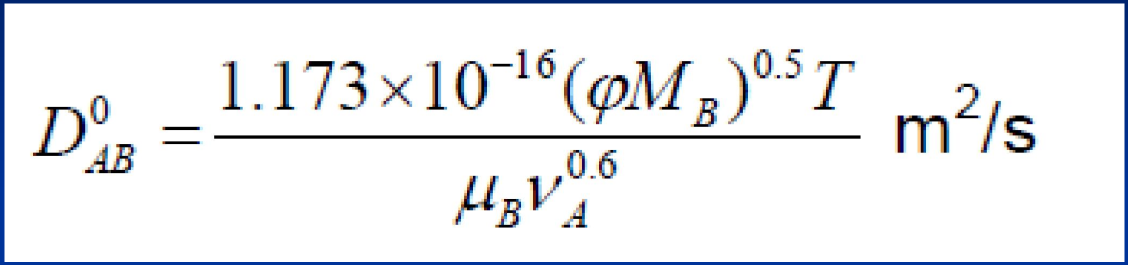
2.5 Estimation of liquid-phase diffusion coefficient

- **Stokes-Einstein Equation**

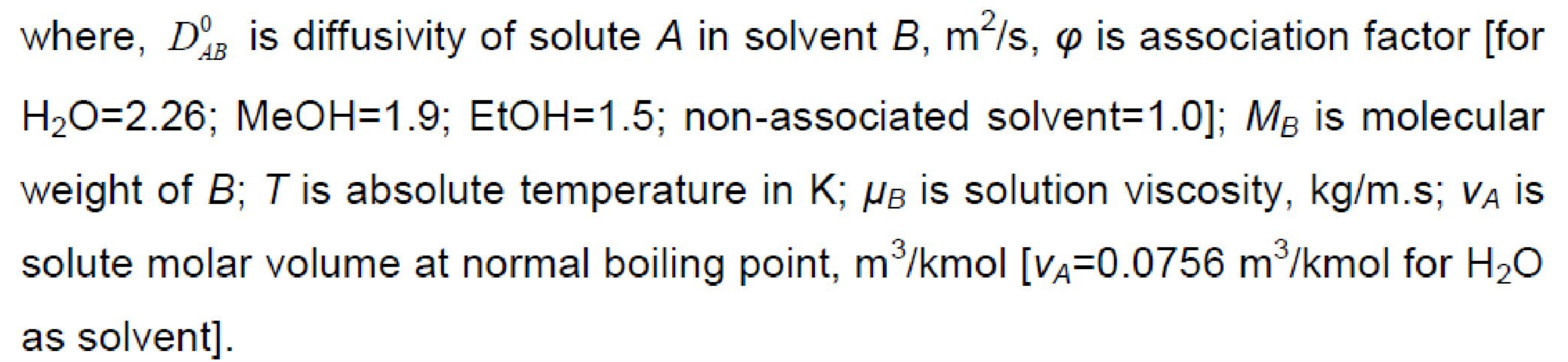
Liquid diffusivity varies linearly with absolute temperature and inversely proportional to viscosity of the medium. Hence,

$$\frac{D_{AB}\mu}{T} = Constant$$

Semi-empirical Equation: Wilke-Chang Equation



$$D^0_{AB} = \frac{1.173\times10^{-16}(\varphi M_B)^{0.5}T}{\mu_B v_A^{0.6}} \text{ m}^2\text{/s}$$



where, D^0_{AB} is diffusivity of solute *A* in solvent *B*, m^2/s, φ is association factor [for H_2O=2.26; MeOH=1.9; EtOH=1.5; non-associated solvent=1.0]; M_B is molecular weight of *B*; *T* is absolute temperature in K; μ_B is solution viscosity, kg/m.s; v_A is solute molar volume at normal boiling point, m^3/kmol [v_A=0.0756 m^3/kmol for H_2O as solvent].

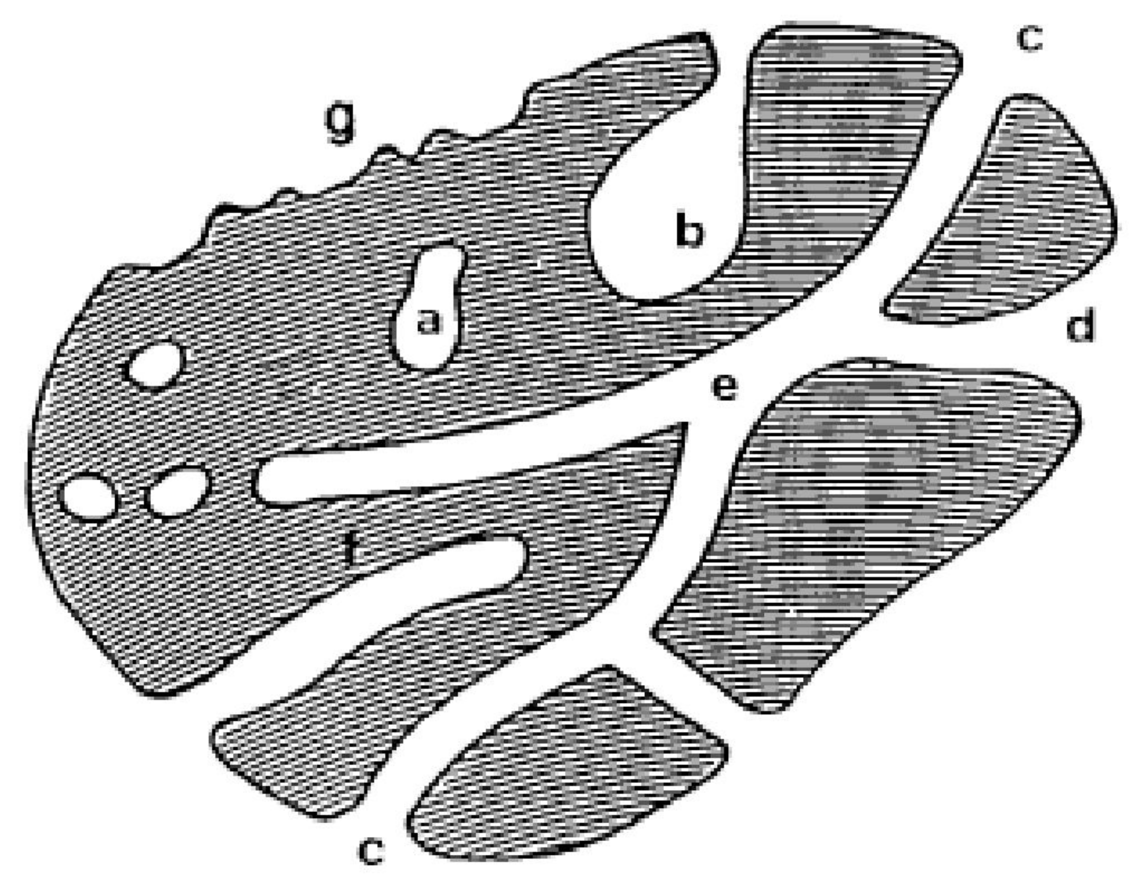
2.6 Diffusion in porous media

- *Porous materials in nature and industry: sand stone, porous rock, filter paper, nano tubes….*
- *main feature: cavities in a solid matrix, cavities are partly or fully connected, and accessible for probe molecules.*
- *porosities are often desired and of importance in medicine, membranes, sorbents, ceramics, and catalysts.*

- types of pores

–open pores: surface ~, column ~, hollow ~

–isolated pores: inclusion ~



- ***Pore size*: (generally pore width): the distance between two opposite walls of the pore**
- **–*Micropores* (< 2 nm)**
- **–*Mesopores* (2-50 nm)**
- **–*Macropores* (> 50 nm)**

Diffusion phenomena in porous solids

- Molecular diffusion
- Knudsen diffusion
- Surface diffusion

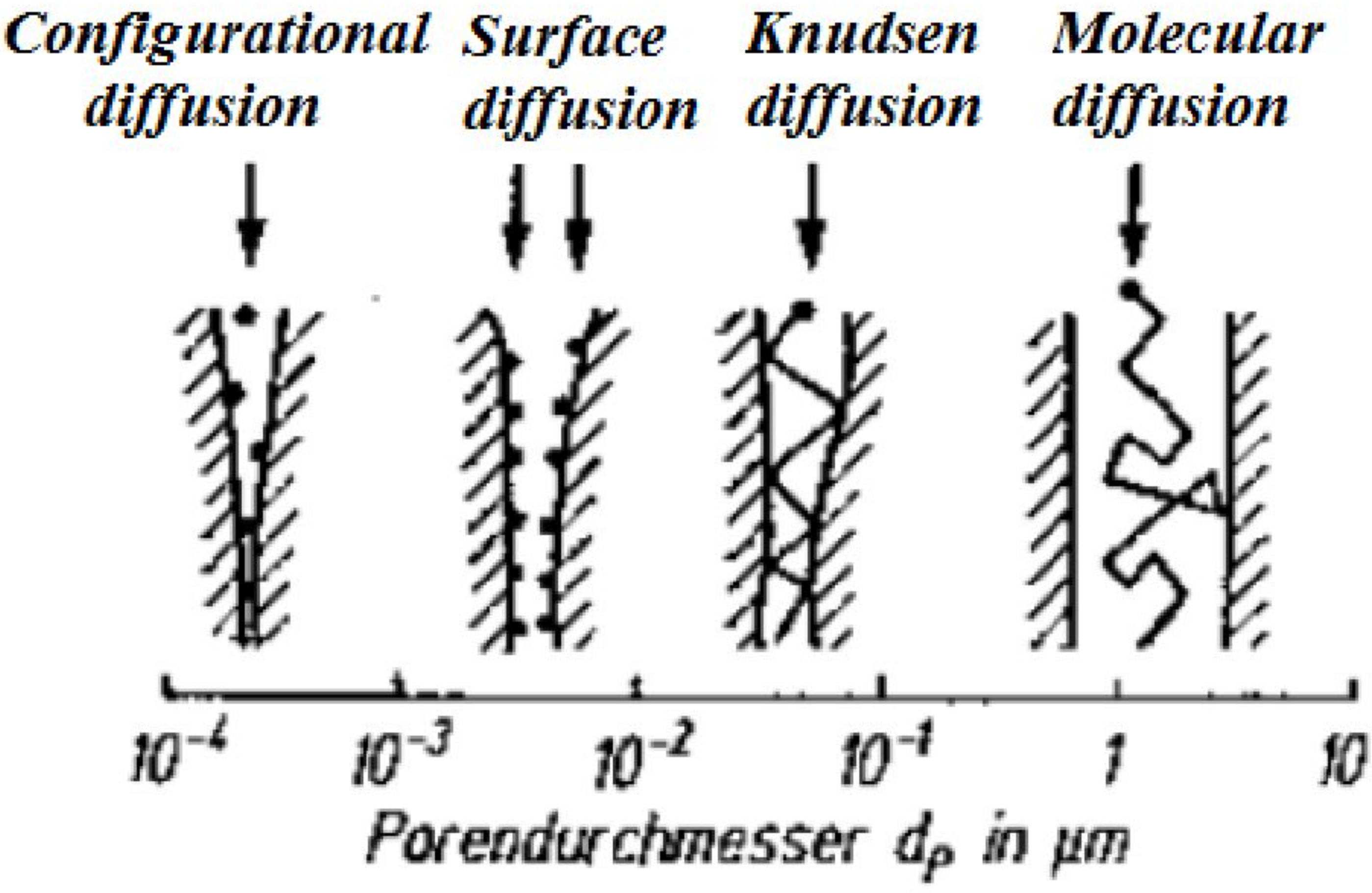
–not of technical importance

- Configurational diffusion

–pore diameter within molecular dimensions (0.3-1 nm) as for zeolites

–diffusion coefficients are smaller by some orders of magnitude

Transport mechanisms in porous solids



Pore diffusion depending on pore diameter

1. Molecular diffusion (Collision principle)

The probability of collision between molecules and molecules is very high, while that between molecules and walls is very low.

$$D_M = \frac{1}{3} v\lambda \quad ;v\text{...average velocity}; \lambda\text{...mean free path length}$$

In physics, the **mean free path** is the average distance traveled by a moving particle (such as an atom, a molecule, a photon) between successive impacts (collisions), which modifies its direction or energy or other particle properties.

The following table lists some typical values for air at different pressures at room temperature.

Vacuum range	Pressure in mbar	Molecules / cm^3	Molecules / m^3	Mean free path
Ambient pressure	1013	2.7×10^{19}	2.7×10^{25}	68 nm
Low vacuum	300 – 1	$10^{19} – 10^{16}$	$10^{25} – 10^{22}$	0.1 – 100 μm
Medium vacuum	$1 – 10^{-3}$	$10^{16} – 10^{13}$	$10^{22} – 10^{19}$	0.1 – 100 mm
High vacuum	$10^{-3} – 10^{-7}$	$10^{13} – 10^{9}$	$10^{19} – 10^{15}$	10 cm – 1 km
Ultra-high vacuum	$10^{-7} – 10^{-12}$	$10^{9} – 10^{4}$	$10^{15} – 10^{10}$	1 km – 10^5 km
Extremely high vacuum	$<10^{-12}$	$<10^{4}$	$<10^{10}$	$>10^5$ km

2. **Knudsen diffusion** (Collision principle)

collision of gas with pore wall > collision of gas with gas

mean free path length of molecule > pore diameter

$$D_{K,i} = \frac{d_p}{3}\sqrt{\frac{8RT}{\pi M}} \approx 10^{-6}\frac{m^2}{s}(at\,293K, 0.01MPa)$$

3. Surface diffusion (Adsorption principle)

Adsorption balance is established in the walls. The diffusion rate with adsorption is much higher than that without adsorption.

4. Configurational diffusion

- –pore diameter within molecular dimensions (0.3-1 nm) as for zeolites
- –diffusion coefficients are smaller by some orders of magnitude

Effective diffusion coefficients

- diffusional flow in the pores may be described by an *effective diffusion coefficient*

--pores are not ideally cylindrical

--pores are connected by a network

- for heterogeneous reactions in a porous solid, the conditions of pressure or pore diameter may be such that the system is between Knudsen and molecular diffusion

$$\boxed{\frac{1}{D^*} = \frac{1}{D_M} + \frac{1}{D_{Kn}}}$$