Transport 2

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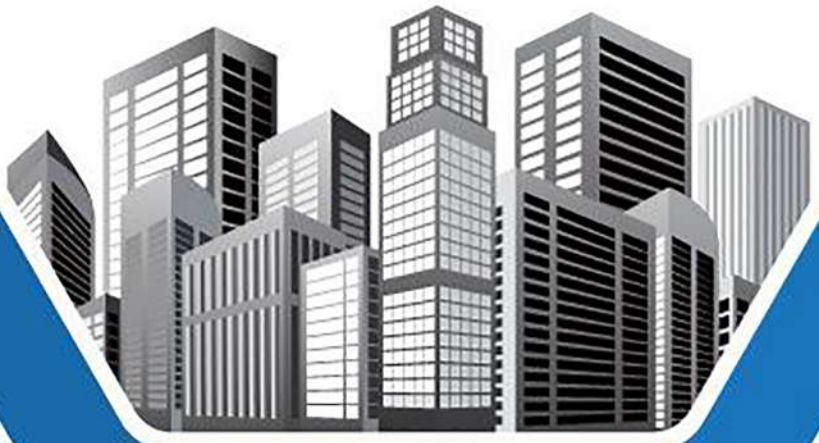


Dr. Ali Al-Mater

Mass transfer Mechanism :

← طيب هلا انا كيف تنتقل الكتلة :

1- Molecular Diffusion (انتشار جزيئي)
2- Eddy Diffusion - convection - (الحمل الحراري)
a. Natural b- forced

Mass transfer Can occur within :
- same phase in a fluid Mixture
- across a phase boundary

يعني الانتقال للمادة يصير اما بالجزيئات نفسها بالخليط نفسه او من خلال ال (boundary)

* Molecular trans port is always present in mass transfer (النقل الجزيئي دائماً موجود بنقل المادة)

fluxes always Contain a molecular term plus a convection term .

Fluxes = molecular + convection

لهلأ منتوسع بالموضوع .

هلا في عنا ٣ مصطلحات بدة :

1- Diffusion : the net transport of substances in a stationary solid or in a stagnant fluid or in a fluid which are moving only in laminar flow , due to a concentration gradient . It may also be present even in highly developed turbule flow but near the solid surface

طيب شو معناة هالحكي هو طريقة لنقل المادة (الانتشار)
والـ diffusion يصير في المادة الصلبة او السوائل
سواء الـ (stagnant) يعني الراكدة او الـ (moving)
المتحركة هلا في شرط للسوائل المتحركة بتكون laminar
واذا صار لل turbulent بتكون على (solid surface)
طبعاً هاد الانتقال يصير تبعاً على
الـ (concentration gradient) اختلاف التراكيز

2- Advection : the net transport of substances by the moving fluid, and so it can not happen in solids. It does not include transport of substances by simple diffusion.
هون انا بحكي عن طريقة نقل بس تتم عن طريق السائل المتحرك
ولا يمكن ان يحدث في المواد الصلبة بما انه
ما بشمل نقل المواد عن طريق (diffu)

3. Convection The net transport of substance caused by both advective transport and diffusive transport in fluid.

Convection = Advection + ~~Conde~~ Diffusion

Molecular Diffusion

- Caused by random microscopic movement of individual molecules in gas/liquid/solid as a result of thermal motion.
- Extremely slow.
- Occurs in solids and fluids that are stagnant or in laminar flow.
- Mass transfer under turbulent-flow but across an interface or near solid surface, the conditions near surface can be assumed laminar.
- Mathematically described by Fick's law:

$$J^*_{AZ} = -D_{AB}\frac{dc_A}{dz}$$

- يصير بسبب الحركة العشوائية لـ (molecules) في غاز - سائل - صلب نتيجة الحركة الحرارية (thermal motion)

- يصير لـ fluid (سائل، غاز) او الصلب بحالة Stagnant

- laminar flow

- زي ما حكينا انه يصير لـ turbulent flow بس وين؟

اما على interface او near solid surface وفي حالة الحالة بتعتبر اجبره (laminar)

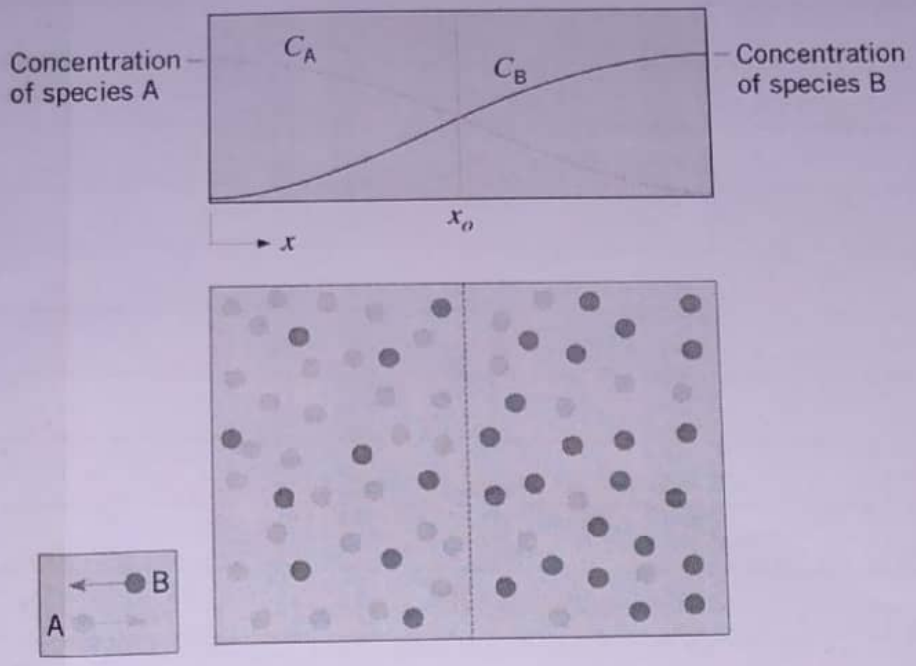
Convective Mass Transfer

- Caused by random macroscopic fluid bulk motion (dynamic characteristics).
- *Orders of magnitude* greater than molecular diffusion.
- Involves transport of materials at the interface between moving fluids (liquid-gas) or at interface between a moving fluid and a solid surface (liquid-solid, gas-solid).
- Mathematically described in a manner analogous to Newton's law :

$$N_{AZ} = k_C \Delta C_A$$

- هاد النوع ميال اكتر للخواص الديناميكية وبرضو الحركة هون عشوائية بس هون نتبه انه (macroscopic) عكس ال (micro) كان Diffusion

- Orders of magnitude < diffusion الحجم اكبر من ال (diff)
  - نقل المواد (interface) بين (moving fluid)
  - (interface) بين ال (solid surface) ⇐ (moving Fluid)
    - liq - solid
    - gas - solid



- هلا هون في مادتين A و B نفس (T و P)
- اتجاه الـ diffusion بكون في اتجاه نقصان التركيز يعني A رح تنتقل للبين اما B للسيار بضل بينتقل من التركيز الاعلى للمنخفض لحدما يصير عندي توازي و بين يصير تركيز الحادتين A , B موحد هون بوقف الـ diffusion .
- A and B (approached) .

Diffusion kind :

Ordinary → Due to concentration (Chemical potential) gradient

Thermal → Due to temperature gradient (Clusius - Dickel column)

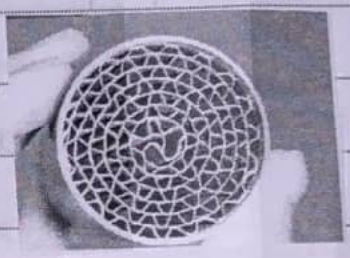
pressure → Due to pressure gradient (centrifuges)

Forced → Due to unequal external forces acting on the chemical species eg ions or charged particles in an electrical field (Nernst - planck equation)

Importance of mass Transfer (Applications)

- Industrial (gas, liq)

1. Dispersion of flue gases
2. pollutant sequestration and mitigation
3. Catalysis
4. Distillation | absorption | extraction | adsorption | SCF
5. Air conditioning



• Daily life (بتشكل حاجات عند الشهيق والزفير)

1. Inhaling / exhaling / oxygen absorption in the lungs

2. Drug release and absorption
3. Sugar dissolution in tea or coffee
4. Moth balls (naphthalene)
5. Sweating

* Typically 50 to 90 percent of capital investment in chemical plant is for **Separations equipment**

← مجرد معلومة انه الرأسمال اغلبه بروح على مواد الفصل

Mass and Molar Notation

. Concentration

- mass concentration ρ_A : is the mass of speacies A per unit volume of solution
- molar concentration $C_A = \rho_A / M_A$ — number of moles of A / unit volume of solution

Fractions (الكسور)

mass Fractions $w_A = \rho_A / \rho$

mole Fraction $x_A = C_A / C$

$\rho = \Sigma \rho_A$ total mass of all speacies / unit volume of sol[illegible]

$C = \Sigma C_A$ total # of moles of [illegible]

Table 24.1 Concentrations in a binary mixture of A and B

Molar Liquid Concentrations	Molar Gas Concentrations	Mass Concentrations (Gas or Liquid)
$c = n/V$	$c = n/V = P/RT$	$\rho = m/V$
$c_A = n_A/V$	$c_A = n_A/V = p_A/RT$	$\rho_A = m_A/V$
$c_B = n_B/V$	$c_B = n_B/V = p_B/RT$	$\rho_B = m_B/V$
$x_A = c_A/c$	$y_A = c_A/c = p_A/P$	$w_A = \rho_A/\rho$
$x_B = c_B/c$	$y_B = c_B/c = p_B/P$	$w_B = \rho_B/\rho$
$c = c_A + c_B$	$c = c_A + c_B, P = p_A + p_B$	$\rho = \rho_A + \rho_B$
$1 = x_A + x_B$	$1 = y_A + y_B$	$1 = w_A + w_B$

هاد الجدول فيه كل قانون ممكن احتاجه سواء liquid Or gas

هنا ال Molar قوانينه تختلف بين gas or liquid بس لما بدي احسب mass concentration ثابته القوانين للشيئين

ليش لانه ال liquid (V) في عنا بس الغازات $PV = RT$

Ex 1. A gas mixture from a hydrocarbon reforming process contain 50% H_2, 40% CO_2 and 10% Methane (CH_4) by volume at 400 C (673 K) and (1.5) atm total system pressure.

Determine the Molar Concentration① and mass Fraction② of each species in the Mixture as well as the density of③ mixture.

Soln:

بدي اريح حالي واحطي رموز لكل عنصر او مركب مثلاً

let $A = H_2$ $B = CO_2$ $C = CH_4$

(ideal gas) وانا بدي افترض انه هم بتعامل مع

① molar concentration.

$C = \frac{P}{RT}$ من الجدول 24.1 بطلع القانون

$C = \frac{1.5\ atm}{(0.08206\ m^3 \cdot atm/kg\ mol \cdot K)(673\ K)} = 2.72 \times 10^{-2}$ kg mol/m^3

بدي اعرف في (ideal gas) تركيب الحجم المئوي (volume percent)

بكافي لـ (mole percent) مشان هيك انا بدي استخدم هاد القانون

لكل مادة $C_x = y_x C$ <= طلعنا هاد C (y_x)

هي السنة

$C_A = y_A C \rightarrow 0.50 * 2.72 \times 10^{-2}$ kg mol/$m^3 = 1.36 \times 10^{-2}$

$C_B = y_B C \rightarrow 0.40 * 2.72 \times 10^{-2} = 1.10 \times 10^{-2}$ kg mole/m

$C_C = y_C C \rightarrow 0.10 * 2.72 \times 10^{-2} = 2.72 \times 10^{-3}$ kgmole/m^3

② mass Fraction

$w_x = y_x M_x / y_x M_x + y_B M_B + y_C M_C$

So, $w_A = \frac{y_A M_A}{y_A M_A + y_B M_B + y_C M_C}$

$$w_A = \frac{(0.50)(2)}{(0.50)(2) + (0.40)(44) + (0.10)(16)}$$

$$= 0.0495 \ g \frac{H_2}{\text{total } g}$$

$$w_B = \frac{(0.40)(44)}{(0.50)(2) + (0.40)(44) + (0.10)(16)}$$

$$= 0.871 \ \frac{g\,CO_2}{\text{total } g}$$

$$w_C = \frac{(0.10)(16)}{(0.50)(2) + (0.40)(44) + (0.10)(16)}$$

$$= 0.0793 \ \frac{g \text{ Methan}}{\text{total } g}$$

(3) density

$$\rho = \rho_A + \rho_B + \rho_C$$

$$= c_A M_A + c_B M_B + c_C M_C$$

$$= 1.36 * 10^{-2} \frac{kg\,mol}{m3} * \frac{2g}{g\,mol} + 1.10 * 10^{-2} \frac{kg\,mol}{m3} * \frac{44\,g}{g\,mol} + 2.72 * 10^{-3} \frac{kg\,mol}{m3} * \frac{16\,g}{g\,mol}$$

$$= 0.555 \ \frac{kg}{m3} \quad \#$$

Ex. 2 A waste water stream is contaminated with 200 mg/L of dissolved trichloroethylene (TCE) at 20 C, which is below its solubility limit in water. What are the molar concentration (in SI unit) and the mole Fraction of TCE in the wastewater, assuming a dilute solution? At 20 C, the mass transfer of liquid water is 998.2 kg/m³ (Appendix 1). The molecular weight of the TCE is 131.4 g/g mole and the molecular weight of water is 18 g/g mol (18.1 kg/kg mol)

Soln:

let A = TCE (solute), B = water (solvent)

The molar concentration of TCE in the wastewater C_A?

ρ_A (Mass concentration) بدي احسبها من خلال ال

① $$C_A = \frac{\rho_A}{M_A} = \frac{200\ mg\ A/L * 1\ g * 1\ kgmol * 1000\ L}{131.4\ g/g\ mole * 1000\ mg * 1000\ g\ mole * 1\ m^3}$$

$$= 1.52 * 10^{-3}\ \frac{kg\ mole}{m^3}$$

(A solute) هون، بس، TCE ال dilute solution ال

$$C \approx C_B = \frac{\rho_B}{M_B} = \frac{998.3\ kg/m^3}{18\ kg/kg\ mol}$$

$$= 55.5\ \frac{kg\ mole}{m^3}$$

ليش اخترت تركيز B لانه احاكي التركيز بميل لـ تركيز ال (solvent) كونه الاكثر عمقية حتى

② Mole Fraction $x_A = \frac{C_A}{C} = \frac{1.52 * 10^{-3}\ kg\ mole/m^3}{55.5\ kg\ mol/m^3}$

$$= 2.74 * 10^{-5}$$

Notation for velocities

* In diffusing mixture, the various Chemical species are moving at different velocity, (velocities).

شو يعني هالحكي !

الخليط الموجود عندي فيه مواد هاي المواد بتكون عندي بسرعات مختلفة بس . يعني مثلا عندي وعاء فيه A, B, C سرعة A غير عن B وغير عن C كل مادة الها سرعتها الخاصة فيها .

- V_α → the velocity of species α relative to stationary coordinates

هي سرعة الـ species يلي عندي بالنسبة لاحداثيات ثابتة .

- Diffusion velocity : the difference between the species velocity and mixture velocity v.

يعني مسافة في عندي سرعة للخليط وسرعة للـ (species)

الفرق بين سرعة الخليط كامل (Mixture) - سرعة الـ species هاد بسميه Diffusion velocity .

(Mixture velocity)

- Mass average
- Molar average — جدول يلي بتعامل معاهم
- Volume average

Ex 2.1

Estimation of mass average, Molar average velocity, volume average velocity.

A gas mixture containing 65% NH_3 8% N_2, 24% H_2, 3% Ar is flowing through a pipe 25 mm in a diameter at a total pressure of 4.0 atm

The velocity of components are:

$NH_3 = 0.03$ m/s

$N_2 = 0.03$ m/s

$H_2 = 0.035$ m/s

$Ar = 0.02$ m/s

مثال على الحسابات الموجودة

for NH_3

$y_i = 0.65$ Given

$M_i = 3*1 + 1*14 = 17$

$v_i = 0.03$ Given

$y_i v_i = 0.65 * 0.03 = 0.0195$

$y_i M_i = 0.65 * 17 = 11.05$

w_i

v, v^* } كيفية حساب القانون وذا الصيغة هاي

name	i	yi	Mi	vi (m/s)	yivi (m/s)	yiMi	wi	wivi	vi-v	vi-v*	wi(vi-v*)	yi(vi-v)
H3	1	0.65	17	0.03	0.0195	11.05	0.73814	0.02214	0.00064	-0.0009	-0.00066	0.000417
2	2	0.08	28	0.03	0.0024	2.24	0.14963	0.00449	0.00064	-0.0009	-0.00013	5.13E-05
2	3	0.24	2	0.035	0.0084	0.48	0.03206	0.00112	0.00564	0.0041	0.000131	0.001354
	4	0.03	40	0.02	0.0006	1.2	0.08016	0.00160	-0.00936	-0.0109	-0.00087	-0.00028
	S	1	87		0.0309	14.97	1	0.02936	-0.00243	-0.00860	-0.00154	0.00154

$$v^* = \frac{\sum_{i=1}^{s} c_i v_i}{\sum_{i=1}^{s} c_i} = \frac{\sum_{i=1}^{s} c_i v_i}{c} = \sum_{i=1}^{s} x_i v_i$$

$$v = \frac{\sum_{i=1}^{s} \rho_i v_i}{\sum_{i=1}^{s} \rho_i} = \frac{\sum_{i=1}^{s} \rho_i v_i}{\rho} = \sum_{i=1}^{s} w_i v_i$$

v-v* | v*-v

-0.00154 | 0.00154

$$v = \frac{\sum_{\alpha=1}^{N} \rho_\alpha v_\alpha}{\sum_{\alpha=1}^{N} \rho_\alpha} = \frac{\sum_{\alpha=1}^{N} \rho_\alpha v_\alpha}{\rho} = \sum_{\alpha=1}^{N} \omega_\alpha v_\alpha$$

* mass avg velocity

* molar avg velocity

$$v^* = \frac{\sum_{\alpha=1}^{N} c_\alpha v_\alpha}{\sum_{\alpha=1}^{N} c_\alpha} = \frac{\sum_{\alpha=1}^{N} c_\alpha v_\alpha}{c} = \sum_{\alpha=1}^{N} x_\alpha v_\alpha$$

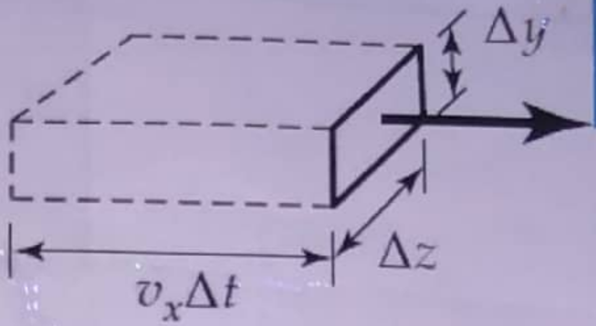
Table 17.7-2 Notation for Velocities in Multicomponent Systems

Basic definitions:	
v_α	velocity of species α with respect to fixed coordinates
$v = \sum_{\alpha=1}^{N} \omega_\alpha \mathbf{v}_\alpha$	mass average velocity
$v^* = \sum_{\alpha=1}^{N} x_\alpha \mathbf{v}_\alpha$	molar average velocity
$v_\alpha - v$	diffusion velocity of species α with respect to the mass average velocity $\mathbf{v}$
$v_\alpha - v^*$	diffusion velocity of species α with respect to the molar average velocity $\mathbf{v}^*$
Additional relations:	
$v - v^* = \sum_{\alpha=1}^{N} \omega_\alpha (\mathbf{v}_\alpha - \mathbf{v}^*)$ (F)	$\mathbf{v}^* - \mathbf{v} = \sum_{\alpha=1}^{N} x_\alpha (\mathbf{v}_\alpha -$

Ex 2.1 هون شرح لكل قانون و كل رمز استخدمناه بـ #

One-Dimensional Convective Fluxes

Fluxes for a flow in which the fluid is flowing in the x direction only.



one dimens هلاهون انا عم بحكي عن
بفي حركة ال flow فقط في
(X) direction

* Mass (or Molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar unit

هلا ال Mass or Molar هو الكمية متجهة (vector) بتدل على كمية الانواع سواء وحدة Mass او Molar.
مابتفرق معي.

that passes per given increment of time through a unit area normal to the vector.

Area طبعاً بدي اعرف انه هاد المتدفق flow بدو يمر عبر
وبده يكون (normal) على ال vector (Mass / Molar)

* هلا ال flux بقدر اعرفه عن طريق

- reference to coordinates that are fixed in space.
- coordinates that are moving with the mass avg velocity.
- Or that moving with the molar avg velocity

Flux of mass: $\rho v_x \, [=] \, \frac{M}{L^2 t}$

Flux of momentum: $\rho v_x v_x \, [=] \, \frac{M}{L t^2}$

Flux of kinetic energy: $\frac{1}{2}\rho v_x^2 v_x \, [=] \, \frac{M}{t^3}$

Flux of internal energy: $\rho \hat{U} v_x \, [=] \, \frac{M}{t^3}$

بناءً على الرسمة يلي اول الصفحة

onvective Flux = (Quantity/volume) (Characteristic Velocity)

← انا هون رح اتعامل فقط مع Diffusion ورح اتعرف على convection

الفرق بين هدول التنين :

- Diffusion → السائل هون ثابت تقريبًا
- convection → هون في velocity عم بتأثر عليه

mass trasfer في عندي driving Force طبعًا هيك

عبارة عن concentration graidient ← اختلاف التراكيز هو يلي

خلقت عندي mass transfer وطبعاً بتتمثل بـ

high concentration → low concentration

وطبعًا بيصير الـ mass transfer كلما بيصير عندي

equilibrium يعني التركيز في كل مكان بيساوي وقتها بلغي (driving Force) .

$$\text{Molecular flux} = \frac{\text{Driving Force}}{\text{Resistance}}$$

$$= (\text{Diffusivity}) * (\text{Gradient of quantity / volume})$$

$$= (\text{Diffusivity}) * \frac{(\text{quantity / volume})}{(\text{Characteristic length})}$$

$$j_{Ay} = -\rho D_{AB} \frac{d\omega_A}{dy}$$

One-dimensional Form of fixed One dimensional Form of fick's first law of diffusion.

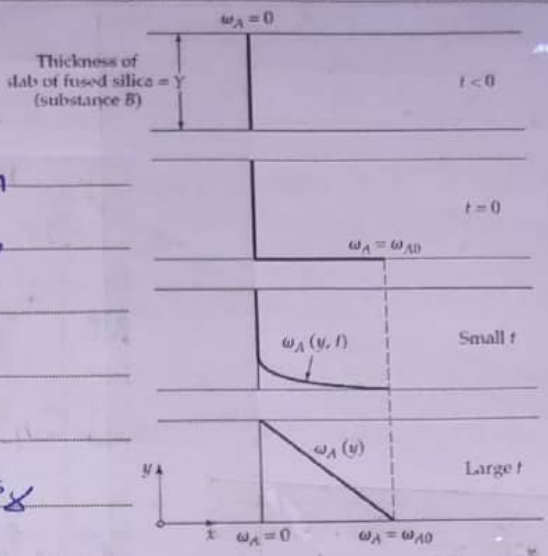


Fig. 17.3-1. Buildup to the steady-state concentration profile for the diffusion of helium (substance A) through fused silica (substance B). The symbol ω_A stands for the mass fraction of helium, and ω_{A0} is the solubility of helium in fused silica, expressed as the mass fraction. See Figs. 1.1-1 and 9.2-1 for analogous momentum and heat-transport situations.

هاي المعادلة انا بقدر استخدمها لاي (binary) سواء كان solid, liq, gas solution.

شرط ان j_{Ay} تم تعريفه على انه mass flux بالنسبة لـ mass avg velocity للخليط.

الشرح:

اول اشي $\omega_A = 0$ هذا لما ما طار عندي Diffusion الوقت $t < 0$ يعني وصرفي عندي diffusion من قليل تدخل نقطة الجبر وصير تكبر شوي شوي وتنتشر بس لما ما طار عندي linear curve لما هاي الحالة بعمل unsteady state وانا بعمل مسايات بعمل بتنتشر كما يطير linear زي اخر شكل هنا انا بقدر اطبق Fick's law • عند large t

An empirical relation for molar flux, First postulated by Fick (accordingly often referred to as Fick's First law) can written as follows for an isothermal, isobaric binary mixture of A and B in stagnant Media Or laminar Flow regimes.

$$J^*_{Az} = -C_T D_{AB} \frac{dx_A}{dz} \quad (1)$$

Mixture A + B

يعني انا طبق هاد القانون بفرض حتى

طبعاً شرط ضغط متساوي و حرارة متساوية

isothermal, isobaric

سواء كانت Stagnant او حتى laminar Flow

تطبق هاي المعادلة .

J^*_A is the **molar flux** of component A in the z direction relative to the molar-average velocity in kmol A/s.m² (fluxes of molecules)

تدفق للمادة A باتجاه z بالنسبة لسرعة المتوسطة المولية

D_{AB} is the molecular diffusivity of the molecule A in B in m²/s

انتشار A في B

C_T is the total concentration in kmol (A +B) /m³.

التركيز الكلي A+B

Z is the distance of diffusion in m

مسافة الـ diffusion

X_A is mole fraction of A in the mixture of A and B

Transport Of	Driving Force	Flux Equation	Phenomenological Coefficient	Flux Unit	Common Name
Mass	Concentration gradient	$J_m = -D \cdot \frac{dc}{dx}$	Diffusion coefficient D [m^2/s]	$\left[\frac{kg}{m^2 \cdot s}\right]$	Fick's law of diffusion
Energy/heat	Temperature gradient	$J_h = -k \cdot \frac{dT}{dx}$	Thermal conductivity k [$J/(s \cdot K \cdot m)$]	$\left[\frac{J}{m^2 \cdot s}\right]$	Fourier's law of heat conduction
Momentum	Velocity gradient	$J_n = -\mu \cdot \frac{dv}{dx}$	Dynamic viscosity μ [$Pa \cdot s$]	$\left[\frac{kg \cdot (m/s)}{m^2 \cdot s}\right]$	Newton's law of viscosity
Volume	Pressure gradient	$J_v = -L_p \cdot \frac{dP}{dx}$	Permeability coefficient L_p [$m^2/(Pa \cdot s)$]	$\left[\frac{m^3}{m^2 \cdot s}\right]$	Darcy's law
Electrical	Voltage gradient	$J_e = -\sigma \cdot \frac{dE}{dx}$	Electrical conductance σ [$C^2/(s \cdot J \cdot m)$]	$\left[\frac{C}{m^2 \cdot s}\right]$	Ohm's law

Ex. A mixture of He and N_2 gas is contained in a pipe at 298 K and 1 atm total pressure which is constant throughout. At one end of the pipe at point (1) the partial pressure P_{A1} of He is 0.6 atm and at the other end 0.2 m $P_{A2} = 0.2$ atm. Calculate the flux of He at steady state if D_{AB} of the He-N_2 mixture is $0.687 * 10^{-4}$ m^2/s

For steady state the flux J^*_{Az} is constant. Also D_{AB} for gas is constant, rearranging

$$J^*_{Az} \int_{z_1}^{z_2} dz = -D_{AB} \int_{c_{A1}}^{c_{A2}} dc_A$$

(2) ---

$$J^*_{AZ} = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1}$$

From the perfect gas law:

$$P_A V = n_A RT \quad , \quad c_{A1} = \frac{P_{A1}}{RT} = \frac{n_A}{V}$$

(3) ---

$$J^*_{Az} = \frac{D_{AB}(p_{A1} - p_{A2})}{RT(z_2 - z_1)}$$

وهاي هي المعادلة يلي ح نستخدمها

$P_{A1} = 0.6$ atm $= 0.6 * 1.01325 * 10^5$

$= 6.04 * 10^4$ pa

$P_{A2} = 0.2$ atm $= 2.027 * 10^4$ pa

using SI unit

تطبيق معادلة رقم (3) ..

Soln :

$$J^*_{Az} = \frac{(0.687 * 10^{-4})(6.08 * 10^{4} - 2.027 * 10^{4})}{8314\,(298)\,(0.20-0)}$$

$$= 5.63 * 10^{-6} \text{ kg mol A / s . m}^2$$

حال انا بدي استخدم Pressure مع (SI) unit

$$J^*_{Az} = \frac{(0.687 * 10^{-4})(0.60 - 0.20)}{(82.06 * 10^{-3})(298)(0.20-0)}$$

$$5.63 * 10^{-6} \text{ kg mol A / s . m}^2$$

هل بعطي نفس الشي لأنه الأهم بأخذ الفرق :

Type of mass transfer fluxes

- Stationary (Fixed) point
  - mass flux n_i
  - molar flux N_i
- moving point
  - mass flux
    - mass velocity j_i
    - Molar velocity j_i^*
  - molar flux
    - Mass velocity J_i
    - Molar veloc[ity] J_i^*

Diffusivities and Dimensionless Numbers

Dimensions of L^2/t

- Momentum diffusivity (kinematic viscosity)

$$\nu = \frac{\mu}{\rho}$$

- Thermal diffusivity

$$\alpha = \frac{k}{\rho \hat{C}_P}$$

- Mass diffusivity

$$D_{AB}$$

Dimensionless

- Prandtl number

$$\mathrm{Pr} = \frac{\nu}{\alpha} = \frac{\hat{C}_P \mu}{k}$$

- Schmidt number

$$\mathrm{Sc} = \frac{\nu}{D_{AB}} = \frac{\mu}{\rho D_{AB}}$$

- Lewis number

$$\mathrm{Le} = \frac{\alpha}{D_{AB}} = \frac{k}{\rho \hat{C}_P D_{AB}}$$

Driving Force

Dring Force

طيب بدنا نحرف اشي اشي منهم :

C_p → قديش بقدر امتص حرارة

K → قديش انا بنقل حرارة

μ → مقاومة العادة للـ Flow

Total flux = Molecular flux + Convective flux

$\frac{\text{Convective Flux}}{\text{Molecular flux}}$ → dimensionless

$= \frac{(\text{Characterstic length})(\text{characteristic velosity})}{\text{Diffusivity}}$

$= Pe$

$Pe_{MT} = \frac{L_{ch}\ v_{ch}}{D_{AB}}$

$Pe_{HT} = \frac{L_{ch}\ v_{ch}}{\alpha}$

$Pe_{MomT} = \frac{L_{ch}\ v_{ch}}{\nu} = Re$

# Total flux	$Pe << 1$	Molecular flux
	$Pe \simeq 1$	Molecular flux + Convective flux
	$Pe >> 1$	Convective flux

Chapter (2)

Existence of Gradient

* when a concentration gradient exists for one component of a binary Mixture in any direction, there must be a concentration difference for the other component of the mixture in the opposit direction.

شو يعني هاد الحكي!
نتخيل كاسة مي منها نقطة حبر عند نقطة اكبر التركيز اعلى
فاكيد للحبر واصل ما عكس الصبي بالتالي الزيادة في تركيز مادة
الحبر رح يرافقه نقصان في مادة تانية وصلك.

* As a result of these concentration differences, both components of the Mixture diffuse in in the opposite directions.

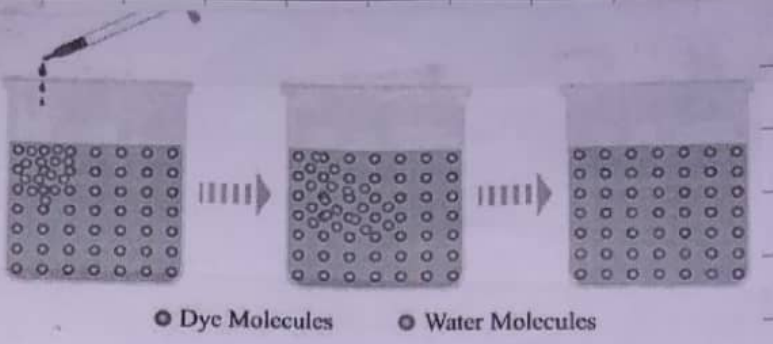
نتيجة لاختلاف التراكيز رح ينتشر كل خليط في اتجاه
معاكس لبعض.

* The rates of these diffusions are not equal in molar units, then the Mixture itself drifts in the direction of the component whose molar diffusional rate is greater

* نتذكر لما طلعوا الشباب وصار كل واحد يتحرك بحرية بالتالي
حركة الشباب الكلية كانت باتجاه الحفلة الاكبر (الوزن الاكثر)
بس بالنسبة للخليط رح يكون باتجاه molar diffusional rate is greater.

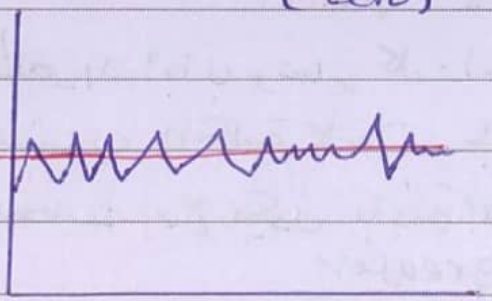
∴ So, it is obvious that total molar flux of each component for a fixed observer will be different than the diffusional fluxes of the components.

باختصار السرعة الكلي مختلف لكل مادة



لكي صوّي عنصاي الصورة الحكي مكرر طبعاً
في عنا مادتين اول ما حطين العادة
A على العادة B تركيز العادة
A كان عالي وتركيز B قليل
طبعاً العادة بلشت بتنتقل mass transfer
من التركيز العالي للمنخفض لحد ما صاروا
متساويين (equal) يعني التركيزين كل مكان
ثابت وصفر كمان (Concentration gradient)
بشو معناه Net Mass transfer
= zero

طب هل صار فعلاً = zero لا لازم اجزء بكل منطقة
لحالها مرة بطلع مرة بنزل بس كل AVG او Net
او يساوي (zero)



في حركة بس الحركة العشوائية
لكن الخط هاد يمثل
Avg يساوي
zero يعني ماني حركة .
بس locally في حركة .

Stefan - Maxwell Formalism

Early experimental investigations of molecular diffusion were unable to verfy Ficks law of diffusion

كان في ناس عملو تجارب و حطو theory وبناء عليها اشتغلو
و التجارب البدائية ماكانت تغطي قانون (Fick)

* Attributed to mass is often transferred simultaneously by two possible means :
- as a result of the concentration differences as postulated by Fick
- and by convection induced by the density differences resulting from the concentration variation.

Stefan and Max using the kinetic theory of gases, showed that the mass flux relative to a fixed coordinate evoves as a result of two contributions:
- the concentration gradient
- the bulk motion

Stefan (1872)

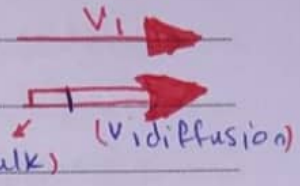
Maxwell (1877)

Total Mass transport = Mass transport by diffusion + mass transport by bulk motion of fluid

The Molar-Average Velocity and Relative velocity :

(bulk velocity

The molar average velocity relative to stationary coordinates) for a multicomponent mixture is defined in terms of the molar concentration of all components by :

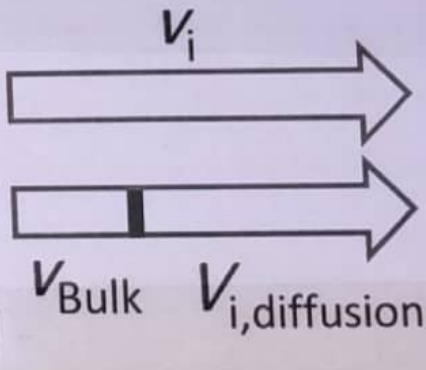


نعبر في الحالة انا باخذ المحصلة بحيث المجموع وباتجاه الاعلى

$$V = \frac{\sum_{i=1}^{n} c_i V_i}{\sum_{i=1}^{N} c_i} = \frac{\sum_{i=1}^{n} c_i V_i}{c} = \sum_{i=1}^{n} x_i V_i$$

V_i → the velocity of each type of molecule in the specified direction.

$V_{i,diffusion} = V_i - V_{Bulk}$



diffusion velocity :

The velocity of particular species relative to the molar avg velocity

The Molar diffusive flux

- The Molar diffusive flux of A in B in a Binary Miature is given by :

$$\dot{J}^{*}_{Az} = - D_{AB} \frac{dc_A}{dz}$$

هاي المعادلة بستخدمها لما بدي اطلع Molar diff flux

لما حاجة معينة داخل مادة اخرى فرضاً عنا A و B . B داخل A وبدي اعرف كم تدفق ماشي انه نوزع (binary Mixture)

- The velocity of the diffusive flux of A in B (diffusion velocity of A) Can Given by

$$v_{A,\text{diffusion}}\,(m/s) = \frac{J^{*}_{A}\,(\text{mol/m}^2.\text{s})}{c_A\,(\text{mol/m}^3)}$$

Flux = $\frac{\text{Flow}}{\text{Area}}$ = mol / $m^2 . s$

velocity = $\frac{\text{mol} / m^2 . s}{\text{mol} / m^3}$ = m/s

(قوانين مهمة للحسابات)

Bulk velocity and Total Molar Flux

. The bulk velocity for a binary Mixture is given by

$$V_{Bulk}\ (m/s) = \frac{(C_A V_A + C_B V_B)\ (mol/m^2 \cdot s)}{C_T\ (mol/m^3)}$$

The total molar flux of components A and B relative to Fixed coordinates

$$N_A = C_A V_A \qquad N_B = C_B V_B$$

The Bulk velocity is:

$$V_{Bulk}\ (m/s) = \frac{(N_A + N_B)}{C_T}$$

(نفس القانون الأول بس بلي فوق حللناه)

هلا ال diffusion يصير للجسم أو للمادة وهي سائلة

مجرد ما صارت velocity يصير اسمه Convection

Convection = (diffusion + advection)

Total Molar flux of Species and Net velocity

→ The total molar flux of species i (N_i) by convection (diff + advection) with respect to a stationary point is defined as the rate of transfer by unit area :

$$N_i \left(\frac{mol}{m^2 \cdot s}\right) = \frac{\overline{\nu_i} \ (mol/s)}{A \ (m^2)}$$

∴ the velocity of the net flux of A in B (relative to stationary coordinates) given by :

$$v_A \ (m/s) = \frac{N_A \ (mol/m^2 \cdot s)}{c_A \ (mol/m^3)}$$

General flux Equation

For species A, :

$$V_A = V_{A\,diffusion} + V_{Bulk}$$

بضرب اطراف المعادلة في C_A

$$C_A V_A = C_A V_{A\,diff} + C_A V_{Bulk}$$

$C_A V_{A\,diff}$ ↓ Molecular Diffusion

$C_A V_{Bulk}$ ↓ Bulk flow Flux

$$C_A = \frac{P_A}{RT}$$ For gass

$$\therefore N_A = J_A^* + C_A \frac{(N_A + N_B)}{CT}$$

اهم معادلة

$$\# \quad N_A = J_A^* + X_A (N_A + N_B)$$

$$\Sigma N_i = \Sigma J_i^\circ + \Sigma X_i N_T$$

حاي المعادلة بتبين علاقة الـ (diffusion coeficent)

Substituting J_A^* for the diffusive flux From Fick's law

$$* \quad N_A = -D_{AB}\frac{dc_A}{dz} + \frac{c_A}{c_T}(N_A + N_B)$$

Molecular Diff flux of A + Bulk flow Flux of f A

وبرجع بتذكر ⇐

Total mass Transported = by diff + by Bulk motion of Fluid

Special Case : $N_A \approx J_A^* = -D_{AB}\frac{dc_A}{dz}$

Z L tearm هاي نفس المعادله بلي فوق بس في

شو البشب ؟؟ (NA + NB) بجون نفس Molar

zero = وعكس الاتجاه

طيب شو بحن ونشرح بشكل مفصل.

$$(-D_{AB} + D_{BA})\, C\, \frac{dy}{dx} = 0$$

A * B * C = zero

zero = D_{AB} = BBA

zero = C

معناته واحد منهم = zero
ممكن
او

zero لو كله zero بصير يستحيل هاد ⇐ $\frac{dy}{dx}$

اصلاً مارح استخدم المعادلة

General Flux Equation
[gases at low pressures]

$$C_A = \frac{n_A}{V} = \frac{P_A}{RT}$$

$$C_T = \frac{n_T}{V} = \frac{P}{RT}$$

∴ The general flux equation becomes :

$$N_A = -\frac{D_{AB}}{RT}\frac{dP_A}{dz} + \frac{P_A}{P}(N_A + N_B)$$

$$N_A = -\frac{D_{AB}}{RT}\frac{dP_A}{dz} + x_A(N_A + N_B)$$

//

Outline

- prelude
- Diffusivity For Gases
- Diffusivity For liquids
- Diffusivity For Solids

← هاد الشابتر ح نقارن بـ diffusivity الـ Solid, liq, gas
وبنشوف الفرقين بكل phase

بشكل عام شو وحدة D_{AB} (Diffusion coeff)
cm^2/s , m^2/s ← يعني تربيع التابعي Area ـال (s)
(m^2/s ↓ SI unit)

* D_{AB} function in T, P, composition
[$D_{AB} = f(T, P, x)$]

* D_{AB} has the dimension L^2/t
indetical to the other transport properties :
Kinematic viscosity $\nu = \mu/\rho$ → in momentum
thermal diffusivity $= \alpha = k/\rho c_p$ → in heat

phase	D_{AB} (m^2/s)
→ Gases	$5 \times 10^{-6} - 1 \times 10^{-5}$
→ liquids	$10^{-6} - 10^{-9}$
→ Gas - Solid	$10^{-12} - 10^{-14}$
solid ~~Gas~~ Solid	$10^{-19} - 10^{-35}$

⇐ شو يعني 10^{-35} ⇐ يعني الانتشار (diffu) بطيء جداً

Dependence of Diffusivity

→ Gases at low density

1- Almost composition independent

at low P ⇐ (x) (composi) الغازات بشكل عام ما بتعتمد على

⇒ ليش؟ لانه حيكون V ↑ يعني المسافات حتكون كبيرة يعني مش عمالة تصادم والانتشار

at low (P) , low density

2- increase with the temperature.

↑ velocity ↑ KE يعني ↑ temp شو السبب

↑ D_{AB} معناته في احتمالية اكبر للحركة يعني

3- Vary inversely with pressure

الضغط عكسي لانه بقرب الجزيئات من بعض يعني المسافة بتقل يعني ال D_{AB} ↓

4- Inversely proportional to molecular weight
اذا زاد الحجم صارت صعبة الحركة والمسافات بين الجزيئات رح تصير قليلة.

→ liquids and solids

1- strongly concentration dependent

2- Increase with tempreture
رح تقيد وتزيد المسافات

* ما بتأثر بشكل ملحوظ بالـpressure لانه
density عالية اصلا

* molecular weight ما بتأثر كثير.

Dependence For Gas phase

- pressure dependence for moderate ranges of pressures up to 25 atm :

$$D_{AB} \propto \frac{1}{P}$$

عكسية مع الضغط

- Temperature dependence :

$$D_{AB} \propto T^{\sim 3/2 - 2}$$

طردية لكن بقوة

$$\left(\frac{3}{2} - 2\right)$$

← تأثير الـ Temp أكثر من تأثير الـ (P)

اذا ضاعفنا T الـ D_{AB} (يضاعف ٤ أضعاف) ح يزيد

اما الـ P نقل للنص .

هيك العلاقات على ضغط UP to 25

حيث لمعنى ضغط قليل وطلعوا على

$$D_{AB}(T,P) = D_{AB}(T_0, P_0)\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{P_0}{P}\right)\left(\frac{\Omega_D T_0}{\Omega(T)}\right)$$

ex (3.4) For the CO - C_2H_4 binary pair with A = CO , B = ethylene (C_2H_4) , the measured diffusion coefficient is $D_{AB} = 0.151\ cm^2/sec$ at $P_0 = 1.0$ atm , $T_0 = 273$ K . what will be the D_{AB} at 2.0 atm and T = 350 k given that ratio of the collision integral at the two conditions is 1.088 ?

$$D_{AB}(T_0, P_0) = 0.151\ \frac{cm^2}{s} \qquad P_0 = 1.0\ atm$$

$$P_1 = 2.0\ atm$$

$$T = 350\ k$$

$$T_0 = 273\ k$$

$$= (0.151) * \left(\frac{1.0}{2.0}\right) * \left(\frac{350}{273}\right)^{3/2} * \left(\frac{1.112}{1.022}\right)$$

$$= 0.119 cm^2/sec \qquad = 1.088 \leftarrow \frac{\Omega_D(T_0)}{\Omega(T)} = 1.088$$

Molecular Diffusion and Kinetic Theory Of Gases :

⟵ بنعرف انه الغازات تتحرك بسرعات عشوائية وفي اتجاهات مختلفة

⟵ منتوقع للجزيئات (diffusion) ⟸ على حرارة اعلى من الصفر المطلق

→ All particles undergo diffusion at temp above absolute zero

$D_{AB} \propto \lambda v$ — $\lambda \to$ mean free path; $v \to$ mean molecular velocity

mean free path → the typical length that a particle travels for before it hits another particle

لو كان عنا جزيئات تنتين وحدة ثابتة والثانية متحركة باتجاه الثابتة الطابة الثابتة رح تضلها مع الطابة المتحركة من الاصطدام رح تضطر تغير اتجاهها لانها اصطدمت رح تخليها تخسر جزء من (KE) يلي عندها.

⟵ كلما λ كانت اكبر الـ diff D_{AB} رح يكون اكبر.

⟵ كلما v كانت اسرع كلما D_{AB} صار اسرع.

$\lambda \Rightarrow$ mean Free path is inversely proportional with . (n) number of molecules

طبعي العلاقة تكون عكسية كل ما كان (n) اكبر بعين λ حتكون اقل

اي اصطدامات حتكون قريبة من بعض بسبب عدد (n)

. Cross-sectional area $A = \pi d^2$

For this molecules

كل ما زاد الحجم بتاع الـ molec ز بقل λ بتاعه Area اكبر

$$\# \quad \lambda = \frac{1}{\sqrt{2}} \left(\frac{1}{nA}\right) = \frac{1}{\sqrt{2}} \left(\frac{1}{\pi n d^2}\right)$$

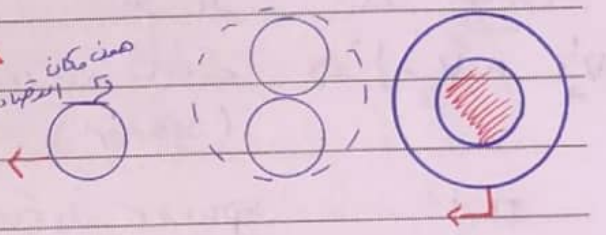
(ideal gas)

$PV = nRT$

$$n \propto \frac{P}{T} \rightarrow \lambda \propto \frac{T}{PA} \rightarrow r \propto \sqrt{\frac{T}{M_{wr}}}$$

نرجع لمصنع $A = \pi d^2$ بدلنا فيه (d) وهو قطر الاصطدام

d → collison diameter (the diameter of a repulsive volume when another molecule is approaching to the First one, it repulses without collision.)



8.8 8.8

Diffusion Coefficient From kinetic theory (Gilliland Equation)

$$D_{AB} \propto \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad \frac{T}{P_{Aavg}}$$

صار عندي مادتين لأنه

$$D_{AB} = \frac{k\, T^{3/2}}{P_{Aavg}} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

$T^{3/2} = T^{\frac{1}{2}} + T$

صفنا احنا عندي (k) (constant) صارت مخادات

Gilliland (1934) للعلماء اخر وطلعوا بـ اثبتت مع

(1) $$D_{AB} = 4.3 * 10^{-9} \frac{T^{3/2}}{P\left(V_A^{\frac{1}{3}} + V_B^{\frac{1}{3}}\right)^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

P → atm

V → Molecular Volume At Normal Boiling (m^3 / kg-mol)

M → Molar Mass Kg / kg-mol

كيف ال A صارت

$\left(V_A^{\frac{1}{3}} + V_B^{\frac{1}{3}}\right)^2 \Rightarrow$ عشان المادة ثابت (spheer)

πd^2 مساحة ال spheer

$\hookrightarrow \sqrt[3]{V}$

← معادلة ممتازة من ناحية كيف تأثر (qualitivly)

P, T, M_{wt} ⇒ (D_{AB}) على variables كيف بأثروا ال

بس مو مش دقيقة.

② Slattery - Bird equation

حلوينا نخلص من (V) (volume) وبربط كل إشي

ب T_c و P_c و ال Constant بتعتمد عليه ← Polarity

$$D_{AB} = a\left(\frac{T}{\sqrt{T_{cA}T_{cB}}}\right)^b \frac{(P_{cA}P_{cB})^{\frac{1}{3}}(T_{cA}T_{cB})^{5/12}\left[\frac{1}{M_A}+\frac{1}{M_B}\right]^{1/2}}{P}$$

where,

D_{AB} = cm^2/sec

P = atm

T = K

- Nonpolar gases Excluding H_2 & He: $a = 2.745 \times 10^{-4}$, $b = 1.823$
- H_2O nonpolar gas: $a = 3.640 \times 10^{-4}$, $b = 2.334$

⇐ اذا قل (V) ال D_{AB} ↑ بزيد

⇐ هاي المعادلة ممتازة at low density

③ Champman - Enskog Equation (For ideal gas)

$$D_{AB} = 1.858 \times 10^{-7}\, T^{3/2} \frac{\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}}{P\,\sigma_{AB}^2\,\Omega_{D\,AB}}$$

m^2/sec ⇐ ب

M_B → kg/kg-mol

$C = \frac{P}{RT}$

$\Omega_{D\,AB}$ → Dimention less

Ω_{DAB} (collision integral) ال molecule كم صارت interaction potential قبل ما يوصلوا

↳ based on the lennard - Jones Potential

$$\Omega_{DAB} = \frac{1.0603}{T^{*0.15610}} + \frac{0.19300}{e^{(0.47635T^*)}} + \frac{1.03587}{e^{(1.52996T^*)}} + \frac{1.76474}{e^{(3.89411T^*)}}$$

لشرح صور الـ molecular Force ⇐ لأنه الجزيئات بين في منطقة ح بتبادو .

attraction ، repulsion 8.8
مسافات بعيدة ↓ قريبة جداً

6. (collision diameter)

Zero = molecules ⇐ بين molecular Force مسافة بين جزيئين

$\sigma_{AB} = \frac{\sigma_{AA} + \sigma_{BB}}{2}$, (Collision diameter)

$\frac{\varepsilon_{AB}}{K_B} = \left(\frac{\varepsilon_{AA}}{K_B} \cdot \frac{\varepsilon_{BB}}{K_B} \right)^{\frac{1}{2}}$, well depth energy minimum

$T^* = \frac{K_B T}{\varepsilon}$, Reduced T
(Dimension less)

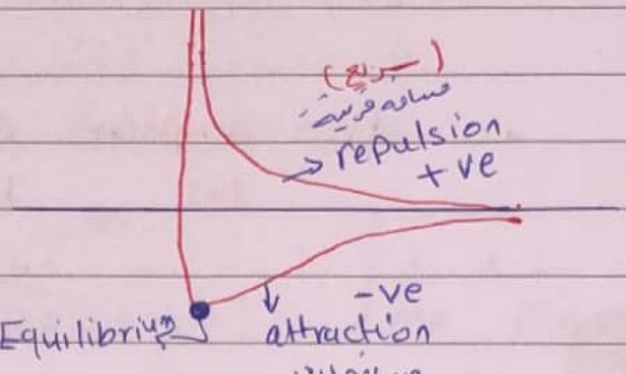


Table E.2
For ε, 6

$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$

repulsive ↓ ↓ attraction

(Lennard-Jones 12-6 Potential)

* $\varepsilon \rightarrow (e.V)$
* $\sigma \rightarrow A^\circ\ 10^{-10}$
* $\frac{\varepsilon}{K_B} (K)$

$K_B = \frac{R}{A_{vog}} = \frac{8.14}{6.023 \times 10^{-23}}$

Table E.2 Collision Integrals for Use with the Lennard-Jones (6–12) Potential for the Prediction of Transport Properties of Gases at Low Densities[a,b,c]

KT/ε or KT/ε_{AB}	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	$\Omega_{D,AB}$ (for diffusivity)	KT/ε or KT/ε_{AB}	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	$\Omega_{D,AB}$ (for diffusivity)
0.30	2.840	2.649	2.7	1.0691	0.9782
0.35	2.676	2.468	2.8	1.0583	0.9682
0.40	2.531	2.314	2.9	1.0482	0.9588
0.45	2.401	2.182	3.0	1.0388	0.9500
0.50	2.284	2.066	3.1	1.0300	0.9418
0.55	2.178	1.965	3.2	1.0217	0.9340
0.60	2.084	1.877	3.3	1.0139	0.9267
0.65	1.999	1.799	3.4	1.0066	0.9197
0.70	1.922	1.729	3.5	0.9996	0.9131
0.75	1.853	1.667	3.6	0.9931	0.9068
0.80	1.790	1.612	3.7	0.9868	0.9008
0.85	1.734	1.562	3.8	0.9809	0.8952
0.90	1.682	1.517	3.9	0.9753	0.8897
0.95	1.636	1.477	4.0	0.9699	0.8845
1.00	1.593	1.440	4.1	0.9647	0.8796
2.00	1.176	1.075	25.0	0.7198	0.6414
2.10	1.156	1.058	30.0	0.7010	0.6235
2.20	1.138	1.042	35.0	0.6854	0.6088
2.30	1.122	1.027	40.0	0.6723	0.5964
2.40	1.107	1.013	50.0	0.6510	0.5763
2.50	1.0933	1.0006	75.0	0.6140	0.5415
2.60	1.0807	0.9890	100.0	0.5887	0.5180

① عشان اطلع ε, σ من الجداول

Ex. (Lennard-Jones) 12-6 Potential

Determine the inter molecular potential energy between two Argon (Ar) atoms separated by a distance of 4.0 A°

K_B → Boltzmann's Const $= 1.38 * 10^{-23} \frac{1}{K}$

N_A → Avogadro's Number $= 6.02 * 10^{23} \frac{\text{Molecule}}{\text{Mole}}$

From table $\varepsilon / k_B = 122.4 K^{-1}$

$\sigma = 3.432$ A°

$$\varepsilon = \frac{\varepsilon}{k_B} * k_B * N_A$$

$$= 122.4 * 1.38 * 10^{-23} * 6.022 * 10^{23}$$

$$= 1017.6 \text{ J/mol}$$

$$= 1.0176 \text{ KJ/mol}$$

$$u = 4 * 1.0176 \left[\left(\frac{3.432}{4} \right)^{12} - \left(\frac{3.432}{4} \right)^{6} \right]$$

$= -0.9761$ KJ/mol ← Attractive energy

Substance	Molecular Weight M	Lennard-Jones parameters σ (Å)	ε/κ (K)	Ref.
Light elements:				
H_2	2.016	2.915	38.0	*a*
He	4.003	2.576	10.2	*a*
Noble gases:				
Ne	20.180	2.789	35.7	*a*
Ar	39.948	3.432	122.4	*b*
Kr	83.80	3.675	170.0	*b*
Xe	131.29	4.009	234.7	*b*
Simple polyatomic gases:				
Air	28.964[i]	3.617	97.0	*a*
N_2	28.013	3.667	99.8	*b*
O_2	31.999	3.433	113.	*a*
CO	28.010	3.590	110.	*a*
CO_2	44.010	3.996	190.	*a*
NO	30.006	3.470	119.	*a*
N_2O	44.012	3.879	220.	*a*
SO_2	64.065	4.026	363.	*c*
F_2	37.997	3.653	112.	*a*
Cl_2	70.905	4.115	357.	*a*
Br_2	159.808	4.268	520.	*a*
I_2	253.809	4.982	550.	*a*
Hydrocarbons:				
CH_4	16.04	3.780	154.	*b*
$CH{\equiv}CH$	26.04	4.114	212.	*d*
$CH_2{=}CH_2$	28.05	4.228	216.	*b*
C_2H_6	30.07	4.388	232.	*b*
$CH_3C{\equiv}CH$	40.06	4.742	261.	*d*
$CH_3CH{=}CH_2$	42.08	4.766	275.	*b*
C_3H_8	44.10	4.934	273.	*b*
n—C_4H_{10}	58.12	5.604	304.	*b*
i—C_4H_{10}	58.12	5.393	295.	*b*
n—C_5H_{12}	72.15	5.850	326.	*b*
i—C_5H_{12}	72.15	5.812	327.	*b*
$C(CH_3)_4$	72.15	5.759	312.	*b*
n—C_6H_{14}	86.18	6.264	342.	*b*
n—C_7H_{16}	100.20	6.663	352.	*b*
n—C_8H_{18}	114.23	7.035	361.	*b*
n C_9H_{20}	128.26	7.463	351.	*b*
Cyclohexane	84.16	6.143	313.	*d*
Benzene	78.11	5.443	387.	*b*
CH_3Cl	50.49	4.151	355.	*c*
CH_2Cl_2	84.93	4.748	398.	*c*
$CHCl_3$	119.38	5.389	340.	*e*
CCl_4	153.82	5.947	323.	*e*
C_2N_2	52.034	4.361	349.	*e*
COS	60.076	4.130	336.	*e*
CS_2	76.143	4.483	467.	*e*
CCl_2F_2	120.91	5.116	280.	*b*

BSL, p.864 for ε and σ.

Ex 5.1-2 use the Champman – Enskog theory to estimate the diffusion of hydrogen in nitrogen at 21°c and 2 atm . The experimental value is 0.38 cm^2/sec

σ_H بوحدة الجول
σ_N

$$\sigma_{AB} = \frac{2.915 + 3.667}{2} = 3.291 A^\circ$$

$$\frac{\varepsilon_{AB}}{K_B} = \left(\frac{\varepsilon_{AA}}{K_B} \cdot \frac{\varepsilon_{BB}}{K_B}\right)^{\frac{1}{2}} = (38 * 99.8)^{\frac{1}{2}} = 61.6 K$$

$$T^* = \frac{K_B T}{\varepsilon} = \frac{294}{61.6} = 4.774$$

$$\Omega_{D_{AB}} = \frac{1.06036}{(4.774)^{0.15610}} + \frac{0.19300}{e^{(0.47635 * 4.774)}} +$$

$$\frac{1.03587}{e^{(1.52996 * 4.774)}} + \frac{1.76474}{e^{(3.89411 * 4.774)}} = 0.85123$$

$$D_{AB} = 1.858 * 10^{-7} * 294.15^{3/2} \frac{\sqrt{\frac{1}{2.016} + \frac{1}{28.013}}}{2.0 * 3.291^2 * 0.85123}$$

$$= 3.707 * 10^{-5} \ m^2/s$$

Ex. Champman and Enskog

Estimate the diffusion coefficient for the system $N_2 - CO_2$ at 590 K and 1 bar. The experimental value reported Ellis and Holsen 1969 is 0.583 cm^2/s.

$\sigma(CO_2) = 3.941\ \mathring{A} \rightarrow$ ~~3.941~~ $3.996\ \mathring{A}$

$\sigma(N_2) = 3.798\ \mathring{A} \rightarrow 3.667\ \mathring{A}$

عطى الأرقام بالحل (Table) عشان ما تلخبط

$\varepsilon\ CO_2/k = 195.2\ k \rightarrow 190\ k$

$\varepsilon\ N_2/k = 71.4\ k \rightarrow 99.8\ k$] من الجدول

$M_{(CO_2)} = 44.0$ $\quad M_{(N_2)} = 28.0$

١- اول خطوة بطلع من الجدول الاشياء

٢- بطلع σ_{AB} , ε_{AB}

$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \rightarrow \frac{3.941 + 3.798}{2} = 3.8695$

arithmatical

لعلاقة نطلع النص

$\varepsilon_{AB} = (\varepsilon_A \cdot \varepsilon_B)^{\frac{1}{2}} \rightarrow [(195.2)(71.4)]^{1/2} = 118 K$

Geometrical

٣- بطلع T^*

$T^* = \frac{kT}{\varepsilon} = \frac{590}{118} = 5.0$

٤- بطلع M_{AB}

$M_{AB} = 2[(1/M_A) + (1/M_B)]^{-1}$

$= 2\left(\frac{1}{44.0} + \frac{1}{28.0}\right)^{-1} = 34.22$

هاي الخطوة اختياري

$$\Omega_D = \frac{1.06036}{5.0^{0.15610}} + \frac{0.19300}{e^{(0.47635*5.0)}} + \frac{1.03587}{e^{(1.52996*5)}} + \frac{1.76474}{e^{(3.89411*5)}}$$

$$= 0.8247 + 0.17827 + 4.93218*10^{-4} + 6.176*10^{-9} = 0.8430$$

$$D_{AB} = \frac{1.858*10^{-7} * T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P \sigma^2 \Omega}$$

$$= \frac{1.858*10^{-7} * (590)^{3/2} \sqrt{\frac{1}{44} + \frac{1}{28}}}{1 * (3.8695)^2 * 0.842}$$

$$= \frac{2.6627*10^{-3} * 0.241}{1*(3.8695)^2 * 0.842} = 0.52 \ cm^2/s$$

(4) Fuller et al Correlation

(use atomic diffusion volume)

Σv → sum atomic diffusion volume

$v = \Sigma n_i v_i$

وفي الكتاب جدول

$$D_{AB} = \frac{10^{-3} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}} * T^{1.75}}{P \left[(\Sigma v_A)^{\frac{1}{3}} + (\Sigma v_B)^{\frac{1}{3}}\right]^2}$$

where,

$D_{AB} = cm^2/s$

$P = atm$

$T = K$

Atomic and Structural Diffusion-Volume Increments, v

C	16.5	Cl*	19.5
H	1.98	S*	17.0
O	5.48	Aromatic ring	–20.2
N*	5.69	Heterocyclic ring	–20.2

Diffusion Volumes for Simple Molecules, Σv

H_2	7.07	CO	18.9
D_2	6.70	CO_2	26.9
He	2.88	N_2O	35.9
N_2	17.9	NH_3	14.9
O_2	16.6	H_2O	12.7
Air	20.1	CCl_2F_2*	114.8
Ar	16.1	SF_6*	69.7
Kr	22.8	Cl_2*	37.7
Xe*	37.9	Br_2*	67.2
		SO_2*	41.1

Ex 5.1-2

Use Fuller's correlation to estimate the diffusion of hydrogen in nitrogen at 21°c and 2 atm, The experimental value is 0.38 cm^2/sec

+ اول اشي بدي جيب الحجوم الذرية (V)

$V_{H_2} = 7.07$, $V_{N_2} = 17.9$

$M_{H_2} = 2.02$ $M_{N_2} = 28.0$

+ بعدين بعوض بالمعادلة

$$D = \frac{10^{-3} T^{1.75} \left(1/M_{H_2} + \frac{1}{M_{N_2}}\right)^{1/2}}{P\left[V_H^{1/3} + V_N^{1/3}\right]^2}$$

$$= \frac{10^{-3} * (21+273)^{1.75} \left(1/2.02 + 1/28.0\right)^{\frac{1}{2}}}{2\left[(7.07)^{1/3} + (2.02)^{1/3}\right]^2}$$

$$= 0.37 \ cm^2/sec$$

Ex. Normal butanol ($C_4H_{10}O$) is diffusing through air at 1 atm abs. Using the Fuller et al. method estimate the diffusivity D_{AB} at 0°c.

$V_C = 16.5$ $V_H = 1.98$ $V_O = 5.48$

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

$V_{air} = 20.1$ # العشرة ان اطلع (V) لمركب من اكثر

$T = 273$ k $M_{butanol} = 74.1$

$M_{air} = 29$

$$D_{AB} = \frac{1.0 * 10^{-7} (273)^{1.75} \left(1/74.1 + 1/29\right)^{\frac{1}{2}}}{1.0\left[(91.28)^{1/3} + (20.1)^{1/3}\right]^2}$$

$$= 7.73 * 10^{-6} \ m^2/s$$

Polar Gases at low pressures

(lennard - Jones - Stockmayer)

(nonpolar). كل اللي اخدناه قائم على مواد

attractive ← (polar) هلا القانون

Force by nature

متى نستخدم (Stockmayer) !

* if one or both components of a gas Mixture are polar often used.

① Brokaw Method : using a different set of collision diameters and ② well depth + ③ the dipole moment for the molecules concerned μ_p in (Debye)

لـ الوحدة ثابتة

$$\delta = \frac{1.94 \times 10^3 \mu_p^2}{V_b T_b}$$

μ_p → dipole moment (debyes)

T_b → normal boiling point (k)

V_b → liquid molar volume at the normal boiling point cm³/mol

$$\frac{\varepsilon}{K_B} = 1.18 (1 + 1.3 \delta^2) T_b$$

$$\sigma = \left[\frac{1.585 V_b}{1 + 1.3\delta^2}\right]^{1/3}$$

ما بروح ع جداول اطلع σ و $\frac{\varepsilon}{KB}$ من هون * هون كلهم [Geometric avg]

$$\sigma_{AB} = (\sigma_{AA} \cdot \sigma_{BB})^{\frac{1}{2}}$$

$$\frac{\varepsilon_{AB}}{k} = \left(\frac{\varepsilon_{AA}}{k} \cdot \frac{\varepsilon_{BB}}{k}\right)^{\frac{1}{2}}$$

$$\delta_{AB} = (\delta_{AA} \cdot \delta_{BB})^{1/2}$$

$\Omega_D = \Omega + \frac{0.19\,\delta_{AB}^2}{T^*}$

$D_{AB} = \frac{1.858 \times (10^{-7}) 3/2 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P\,\sigma_{AB}^2\,\Omega}$

Ex Modified Chapman - Enskog theory for polar gases:

estimate the diffusion coefficient for a mixture of methyl cloride MC (CH_3Cl) and sulfur dioxide SD SO_2 at 1bar and 323k

	MC	SD
Dipol moment debyes	1.9	1.6
Liquid Molar (V) at T_b cm^3/mol	50.1	44.03
Normal boiling temp (K)	248.95	263.13

Soln: $\delta = \frac{1.94 \times 10^3 M_p^2}{VT}$

$\delta_{MC} = \frac{1.94 \times 10^3 \times 1.9^2}{(50.1)(248.95)} = 0.56$

$\delta_{SD} = \frac{1.94 \times 10^3 \times 1.6^2}{44.03 \times 263.13} = 0.43$

$\delta_{MC-SD} = (0.56 + 0.43)\frac{1}{2} = 0.49$

$$\frac{\varepsilon}{k_B} = 1.18\,(1+1.3\,\delta^2)\,T_b$$

$$\frac{\varepsilon_{MC}}{k_B} = 1.18\,(1+1.3\times 0.56^2)\,(248.95) = 414\ K$$

$$\frac{\varepsilon_{SD}}{k_B} = 1.18\,(1+1.3\times 0.43^2)\,(263.13) = 385\ K$$

$$\frac{\varepsilon_{MC-SD}}{k_B} = (414\times 385)^{1/2} = 399\ K$$

$$\sigma = \left(\frac{1.585\,V_b}{1+1.3\delta^2}\right)^{\frac{1}{3}} \qquad \delta_{MC} = \left[\frac{1.585\times 50.1}{1+1.3\times 0.56^2}\right]^{1/3} = 3.84\ A^\circ$$

$$\delta_{SD} = \left[\frac{1.585\times 44.03}{1+1.3\times 0.43^2}\right]^{1/3} = 3.83\ A^\circ$$

$$\delta_{MC-SD} = (3.84\times 3.83)^{1/2} = 3.84\ A^\circ$$

$$T^* = \frac{k_B T}{\varepsilon_{MC-SD}} = \frac{323}{399} = 0.810$$

$$\Omega_{MC-SD} = \frac{1.06036}{0.810^{0.15610}} + \frac{0.19300}{e^{(0.47635\times 0.810)}} + \frac{1.03587}{e^{(1.52996\times 0.810)}} + \frac{1.76474}{e^{(3.89411\times 0.810)}} = 1.60$$

$$\Omega_D = \Omega_{D_{MC-SD}} + \frac{0.19\,\delta^2_{MC-SD}}{T^*} = 1.60 + \frac{0.19\times 0.49^2}{0.810} = 1.66$$

$$D_{MC-SD} = 1.858 \times 10^{-7} \times T^{3/2} \times \frac{\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P \sigma^2 \Omega}$$

$$= 1.858 \times 10^{-7} \times 323^{3/2} \times \frac{\sqrt{\frac{1}{50.49} + \frac{1}{64.06}}}{1 \times 3.842^2 \times 1.66}$$

$$= 8.40 \times 10^{-6} \ m^2/s$$ #

Multi component Diffusion

(فاشوحه الكتور) !!

(qualitative point about Diffusivity in liquids)

- Diffusivity in liquids is about ten times lower than those in dilute gases
- This lower value of diffusivity limit the overal rates For processes taking place in liquids e.g reaction between two Components.
  - Diffusivity limits the rate of acid-base reaction
  - Responsible for the rates of liq-liq (solvent) extractio
- Certain Molecules diffuse as molecules, while others which are designated as electrolytes ionize in Solutions and diffuse as ions
  - Sodium Chloride NaCl diffuses in water as ion Na^+ and Cl^-
  - Though each ions has a different mobility, the electrical neutrality of the solution implies that ions must diffuse at the same rate accordingly it is possible to speak of a diffusion coefficient- Fro molecular electrolytes such as NaCl
  - However, if Several ions are present, the diffusion rates of the individual cations and anions must be considered and molecular diffusion Coefficient have no meaning.

← الاتن بعض العمليات تحتاج عملية تسريع للـ (diffusion) كيف افعل تسريع (للـ diffusion rates) من خلال طريقتين اما زيادة الحرارة او التحريك بسبب انه الانتشار يصير بكل مكان وبتوزع اسرع من الوضع الطبيعي ...

← كلما زادت اللزوجة (N) قلت الـ (diffusion) وصار احتي طبيعي لان الجزيئات بتكون قريبة ع بعض وصعب تحركها.

→ Diffusivity varies inversely with viscosity when the ratio of solute to solvent ratio exceeds five.

• طلاخر انا بدي اعمل extraction (liq-liq) (reaction) وبتدرج يصير الـ (reaction) على (interface) مثل نسبة وفي شغل عشان اشتغل الـ (reaction) تحكم بالتالي رح يصير عندي (droplate) عندي بالتالي المساحات الطبقية رح تزيد ويصير اعلى من الـ (interface) وطالما زيد المساحة طبعا انه D_{AB} رح يزيد: وبتزيد الـ (mass traster rate) بس المشكلة ما بقدر تتحكم بحجم الـ drop يعني عندي بقدر اتحكم بـ Area يعني بقدر اتحكم بـ (mass transfer rate).

→ Diffusivity varies inversely with viscosity when the ratio exceeds five.

→ In viscous materials diffusion becomes independent of viscosity.

$$\left(\frac{D_{AB}\,M}{T}\right)_{T_2} = \left(\frac{D_{AB}\,M}{T}\right)_{T_1} \rightarrow D_{AB}(T_2)$$

$$= D_{AB}(T_1)\,\frac{T_2}{T_1}\,\frac{M\,T_2}{M\,T_1} \rightarrow$$ (عدلوهم)

Ex خارجي

D_{AB} at 25° $= 1*10^{-9}$

$M = 100$ cp

D_{AB} at 100° $= ?$

$M = 10$ cp

$$D_{AB}(100) = 1*10^{-9}\,(25+273)\,\frac{373}{298}*\frac{10}{100}$$

$$= 1.2*10^{-10}$$

(M For liq ⇐ نقلوع الكارة)

Diffusion Coefficient in liquids

Stokes – Einstein Equation

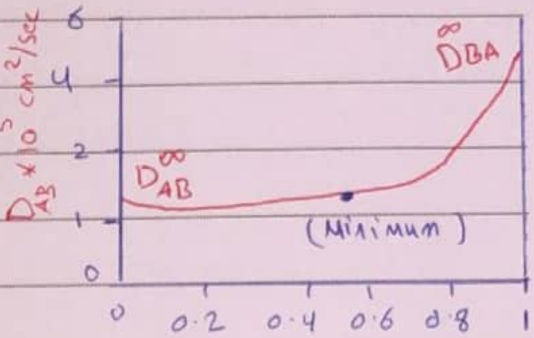
- Based on hydrodynamics of creeping flow
- Applies for solute molecules larger than solvent
- Derived for infinitely dilute solution A in solvent B

$$D_{AB} = \frac{RT}{6\pi \mu_B R_A} \quad , \quad R_A = \left(\frac{3v}{4\pi}\right)^{1/3}$$

- D_{AB} → diffusivity of solute A in solvent B
- T → in K
- μ_B → viscosity for solvent
- R_A → radius of the solute molecule $= R_A = \frac{\sigma_A}{2}$

(مشتقة من sphere)

Table (2.8)



- العلاقة not linear
- صعب في اعتماد عل composition

in gas $D_{AB} = D_{BA}$

- لكن في liquid

$D_{AB} \neq D_{BA}$

- على composition معين (Minimum) في هنا 0.5 هاد اشي مش موجود بالغازات.

D^{∞}_{AB} → zero = A تركيز

المادة المخففة هي A

D^{∞}_{AB} → Diffusion coefficient for solute A in solvent B at ∞ dutution for solute A

D_{BA} → zero = B تركيز

المادة المخففة هي B

Table 2.8
Molecular and van der Waals Volumes of Some Liquids

Substance	v_M (Å^3)	v_W (Å^3)
Benzene	148.6	80.4
Cyclohexane	179.4	102.0
Ethylene glycol	92.4	60.8
Glycerol	121.3	88.5
Methanol	67.0	36.1
n-Pentane	192	96.4

Source: (Edward, 1970)

(Ex 2.11) Diffusion coefficient of lactalbumin, ovalbumin and bovine serum albumin (BSA) in 0.1 M phosphate buffered Salin (PBS) solution at 298 K are reported by Pluen et al. (1999) as $1.14 * 10^{-6}$, $7.8 * 10^{-7}$ and $6.4 * 10^{-7}$ cm^2/s respectivly. if the viscosity of the solvent = 0.8705 Calculate the radius of these macromolecules.

$$R_A = \frac{kT}{6\pi N_B D_{AB}^{\infty}}$$

$N_B = 0.8705$

$T = 298$

$k = 1.3806 * 10^{-23}$

D_{AB} (A) $= 1.14 * 10^{-6}$

D_{AB} (B) $= 7.8 * 10^{-7}$

D_{AB} (C) $= 6.4 * 10^{-7}$

lactalbumin :

$$R_A = \frac{1.3806 * 10^{-23} * 298}{6\pi * 0.8705 * 1.14 * 10^{-6} * 10^{-4}}$$

$= 2.199 * 10^{-9}$ m

$= 2.199$ nm

ovalbumin :

$$R_A = \frac{1.3806 * 10^{-23} * 298}{6\pi * 0.8705 * 7.8 * 10^{-7} * 10^{-4}}$$

$= 3.215 * 10^{-9}$ m

$= 3.215$ nm

BSA : //

$= 3.918$ nm

(Wilke – Chang Correlation)

- Empirical in nature
- For infinitely dilute solute in solvent
- based primarily on data with solvent viscosities 0.4 – 1.5 centipoise (Cp)
- More accurate than stokes – Einstein equation, in particular when solute and solvent are similar in size.

$$D_{AB} = \frac{7.4 \times 10^{-8} (\Phi_B M_B)^{1/2} T}{M_B V_A^{0.6}}$$

- D_{AB} ← Diffusivity solute A in solvent B
- Φ_B → Association Factor for solvent
- M_B → Molar Mass of Solvent (g/mol)
- T → in K
- μ_B ← viscosity for solvent (cp)
- V_A → liquid molar volume of the solute at (nbp) ↓ normal boiling Point

Φ_B =
- Water = 2.6 H_2O
- Methanol = 1.9 CH_3OH
- Ethanol = 1.5 C_2H_2OH
- benzene, ether, heptane, other unassociated solvent = 1

cm^3/mol

table 3.3

Table 3.3 Molecular Volumes of Dissolved Light Gases and Atomic Contributions for Other Molecules at the Normal Boiling Point

	Atomic Volume $(m^3/kmol) \times 10^3$		Atomic Volume $(m^3/kmol) \times 10^3$
C	14.8	Ring	
H	3.7	Three-membered, as in ethylene oxide	−6
O (except as below)	7.4	Four-membered	−8.5
Doubly bonded as carbonyl	7.4	Five-membered	−11.5
Coupled to two other elements:		Six-membered	−15
In aldehydes, ketones	7.4	Naphthalene ring	−30
In methyl esters	9.1	Anthracene ring	−47.5
In methyl ethers	9.9		
In ethyl esters	9.9		Molecular Volume $(m^3/kmol) \times 10^3$
In ethyl ethers	9.9		
In higher esters	11.0	Air	29.9
In higher ethers	11.0	O_2	25.6
In acids (—OH)	12.0	N_2	31.2
Joined to S, P, N	8.3	Br_2	53.2
N		Cl_2	48.4
Doubly bonded	15.6	CO	30.7
In primary amines	10.5	CO_2	34.0
In secondary amines	12.0	H_2	14.3
Br	27.0	H_2O	18.8
Cl in RCHClR′	24.6	H_2S	32.9
Cl in RCl (terminal)	21.6	NH_3	25.8
F	8.7	NO	23.6
I	37.0	N_2O	36.4
S	25.6	SO_2	44.8
P	27.0		

Source: G. Le Bas, *The Molecular Volumes of Liquid Chemical Compounds*, David McKay, New York (1915).

Ex 5.2-1

Estimate the diffusion at 25°C For Oxygen dissolved in water using the Stokes-Einstein equation and the wilke-chang correlation. compare your result with experimental value of 1.8×10^{-5} cm^2/sec

[1] Stokes-Einstein

$$R = \frac{1}{2}\sigma_1 = 1.73 \cdot 10^{-8}\ cm$$

$$D = \frac{K_B T}{6\pi\mu R} = \frac{1.38 \times 10^{-16}\ g\,cm^2/sec^2\ K \times 298\ K}{6\pi(0.01\ g/cm\,sec)\,1.73 \times 10^{-8}\ cm}$$

$$= 1.3 \times 10^{-5}\ cm^2/sec$$

[2] wilke-change

$$D = \frac{7.4 \times 10^{-8}\,(\phi_{H_2O})^{1/2}\,T}{\mu_{H_2O}\,V_{O_2}^{0.6}}$$

$$= 7.4 \times 10^{-8} \times \frac{2.8\,[(18\ cm^3/mol)]^{1/2} \times 298\ K}{1\ cp\ (25\ cm^3/mol)^{0.6}}$$

$$= 2.2 \times 10^{-5}\ cm^2/sec$$

more accurate ✓

Ex (wilke - change diffusivity for liquid)
use the wilke change correlation to estimate For ethylbenzene (A) diffusing into water (B) at 293 k. The viscosity of water at thiss tempreture is 1.0 cp

(V) بدنا اطلع ال density و Mw عشان اقدر اطلع

Ethylbenzene $C_6H_5C_2H_5$
→ C_8H_{10}

density = 0.761 g/cm³ C_8H_{10}
Mwt = 106.17
Association Factor For H_2O = 2.6

$$V_A = \frac{Mwt}{\rho} = \frac{106.17}{0.761} = 139.5 \ cm^3/mol$$

$$D_{AB} = 7.4 \times 10^{-8} \frac{((2.6)(18.01))^{1/2} \times 293}{1.0 \times (139.5)^{0.6}}$$

$= 0.77 \times 10^{-5}$ cm²/sec

Tyn and Calus

$0^{0^{0}}$

Invokes the ratio of surface tensions of the solute and solvent as

$$D_{AB} = 8.93 * 10^{-8} \frac{V_B^{0.267}}{V_A^{0.433}} \frac{T}{\mu_B} \left(\frac{\sigma_B}{\sigma_A}\right)^{0.15}$$

$\sigma \rightarrow$ the surface tension in dyn/cm $= 10^{-3}$ N/m

$\frac{\sigma_B}{\sigma_A}$ تقريباً مساوية لـ 1 إذا كان σ

$$D_{AB}^{\circ} = 8.93 * 10^{-8} \frac{V_B^{0.267}}{V_A^{0.433}} \frac{T \rightarrow k}{\mu_B \rightarrow \text{viscosity for solvent}}$$

Ex. Use Tyn and Calus correlation for ethyl benzene (A) diffusing in water (B) at 293 k $\mu_B = 1.0$ cp

(C_8H_{10}) ... (A) H_2O ... (B)

↳ density $= 0.761$ g/cm^3 ↳ $\mu = 1$ cp

Mwt $= 106.17$

$V_B = 18 \cdot 1 = 18$ cm^3/mol

$V_A = 106.17 / 0.761 = 139.5$ cm^3/mol

$$D_{AB} = 8.93 * 10^{-8} \frac{(18)^{0.267}}{(139.5)^{0.433}} * \frac{293}{1}$$

$$= 0.66 * 10^{-5} \text{ cm}^2/\text{sec}$$

TABLE 11-5 Diffusion Coefficients in Liquids at Infinite Dilution

Solute A	Solvent B	T, K	Experimental $D^{\circ}_{AB} \times 10^5$, cm²/s	Ref.**	Percent error*			
					Wilke and Chang	Tyn and Calus	Hayduk and Minhas	Nakanishi
Acetone	Chloroform	298	2.35	5	42	8.2	5.8	−8.8
		313	2.90		38	5.1	3.2	−11
Benzene		288	2.51	10	1.3	−21	−22	−15
		328	4.25	20	−0.7	−23	−23	−17
Ethanol		288	2.20	10	47	12	8.3	−29
Ethyl ether		298	2.13	20	29	7.4	4.5	4.4
Ethyl acetate		298	2.02	18	36	12	9.4	15
Methyl ethyl ketone		298	2.13	18	37	9.3	6.9	−11
Acetic acid	Benzene	298	2.09	4	28	−9.4	−10	−7.0
Aniline		298	1.96	17	0.4	0.1	0.1	−11
Benzoic acid		298	1.38	4	28	0.6	0.8	−10
Bromobenzene		281	1.45	22	−8.8	−6.4	−6.0	2.4
Cyclohexane		298	2.09	20	−11	−6.9	−7.5	−3.5
		333	3.45		−8.1	−4.2	−5.0	−0.7
Ethanol		288	2.25	10	−1.8	−5.2	−7.0	−39
Formic acid		298	2.28	4	53	−4.2	−4.2	13
n-Heptane		298	2.10	3	−27	−16	−17	−6.2
		353	4.25		−20	−7.1	−8.9	3.6
Methyl ethyl ketone		303	2.09	1	8.7	10	9.0	−8.5
Naphthalene		281	1.19	22	−2.1	5.2	5.6	18
Toluene		298	1.85	20	0.1	4.1	3.5	10
1,2,4-Trichlorobenzene		281	1.34	22	−13	−8.5	−7.7	−0.8
Vinyl chloride		281	1.77	22	8.7	0.1	−0.2	12
Acetic Acid	Acetone	288	2.92	2	35	3.2	−3.2	4.2
		313	4.04	25	33	2.1	−3.7	3.1
Benzoic acid		298	2.62	4	13	−3.5	−8.2	−13
Formic acid		298	3.77	4	56	5.5	0.1	21

TABLE 11-5 Diffusion Coefficients in Liquids at Infinite Dilution (*Continued*)

Solute A	Solvent B	T, K	Experimental $D^{\circ}_{AB} \times 10^5$, cm^2/s	Ref.**	Percent error*			
					Wilke and Chang	Tyn and Calus	Hayduk and Minhas	Nakanishi
Nitrobenzene	Acetone	293	2.94	19	−2.4	8.7	3.0	−6.2
Water		298	4.56	16		5.6	3.7	−19
Bromobenzene	*n*-Hexane	281	2.60	25	16	17	12	26
Carbon tetrachloride		298	3.70	6	12	8.6	4.6	18
Dodecane		298	2.73	23	−17	8.1	−6.7	7.9
n-Hexane		298	4.21	15	−18	−9.0	−4.0	1.3
Methyl ethyl ketone		303	3.74	1	23	23	17	−0.2
Propane		298	4.87	7	3.4	0.6	20	1.3
Toluene		298	4.21	4	−9.0	−6.3	−11	−3.1
Allyl alcohol	Ethanol	293	0.98	9	22	9.7	14	30
Isoamyl alcohol		293	0.81	9	9.8	10	14	15
Benzene		298	1.81	14	−39	−3.0	2.8	−18
Iodine		298	1.32	4	2.4			12
Oxygen		303	2.64	11	−3.2	32	34	47
Pyridine		293	1.10	9	−1.0	−14	−9.1	3.3
Water		298	1.24	12		1.7	11	6.9
Carbon tetrachloride		298	1.50	14	−30	11	18	−6.7
Adipic acid	*n*-Butanol	303	0.40	1	1.1	16	29	8.0
Benzene		298	1.00	14	−52	5.3	20	−23
Butyric acid		303	0.51	1	1.5	7.4	19	2.5
p-Dichlorobenzene		298	0.82	14	−52	13	29	−22
Methanol		303	0.59	14	51	37	50	51
Oleic acid		303	0.25	1	−8.4	26	41	−4.4
Propane		298	1.57	2	−65	−23	−13	−47
Water		298	0.56	14		7.2	26	22
Benzene	*n*-Heptane	298	3.40	3	8.4	1.2	−1.2	13
		372	8.40		1.6	−5.0	−5.9	6.0
Acetic acid	Ethyl acetate	293	2.18	21	69	12	8.5	21
Acetone		293	3.18	21	3.2	−6.8	−9.6	−15
Ethyl benzoate		293	1.85	21	9.0	16	13	−3.9
Methyl ethyl ketone		303	2.93	1	14	8.1	4.8	−5.4
Nitrobenzene		293	2.25	21	10	6.4	4.2	−2.8
Water		298	3.20	12		16	17	−4.2
Methane	Water	275	0.85	26	10	−3.6	0.0	14
		333	3.55		15	0.7	−2.6	19
Carbon dioxide		298	2.00	24	1.6	−22	−13	−19
Propylene		298	1.44	24	−7.7	−13	−13	−6.2
Methanol		288	1.26	10	5.4	−8.7	−5.4	−9.6
Ethanol		288	1.00	9	5.3	−1.6	−2.7	−8.7
Allyl alcohol		288	0.90	9	5.5	0.5	−2.0	−7.4
Acetic acid		293	1.19	13	2.6	−5.0	−4.7	−24
Ethyl acetate		293	1.00	13	−10	−9.4	−16	−0.9
Aniline		293	0.92	13	−2.5	−5.9	−8.9	−10
Diethylamine		293	0.97	13	−8.6	−7.3	−15	−21
Pyridine		288	0.58	9	49	37	38	31
Ethylbenzene		293	0.81	26	−8.9	−0.2	−18	8.0
Methylcylopentane		275	0.48	26	−2.5	0.3	−14	7.0
		293	0.85		−1.7	1.1	−9.0	7.8
		333	1.92		6.3	9.4	8.5	17
Vinyl chloride		298	1.34	8	3.6	−7.6	−3.3	4.3
		348	3.67		4.2	−7.1	3.0	4.9
ave. abs. % dev.					17	9	11	13

*Percent error = [(calc. - exp.)/exp.] × 100

**References: 1, Amourdam and Laddha (1967); 2, Bidlack and Anderson (1964); 3, Calus and Tyn (1973); 4, Chang and Wilke (1955); 5, Haluska and Colver (1971); 6, Hammond and Stokes (1955); 7, Hayduk, et al. (1973); 8, Hayduk and Laudie (1974); 9, Int. Critical Tables (1926); 10, Johnson and Babb (1956); 11, Krieger, et al. (1967); 12, Lees and Sarram (1971); 13, Lewis (1955); 14, Lusis and Ratcliff (1971); 15, McCall and Douglas (1959); 16, Olander (1961) 17, Rao and Bennett (1971); 18, Ratcliff and Lusis (1971); 19, Reddy and Doraiswamy (1967); 20, Sanni and Hutchinson (1973); 21, Sitaraman, et al. (1963); 22, Stearn, et al. (1940); 23, Vadovic and Colver (1973); 24, Vivian and King (1964); 25, Wilke and Chang (1955); 26, Witherspoon and Bonoli (1969)

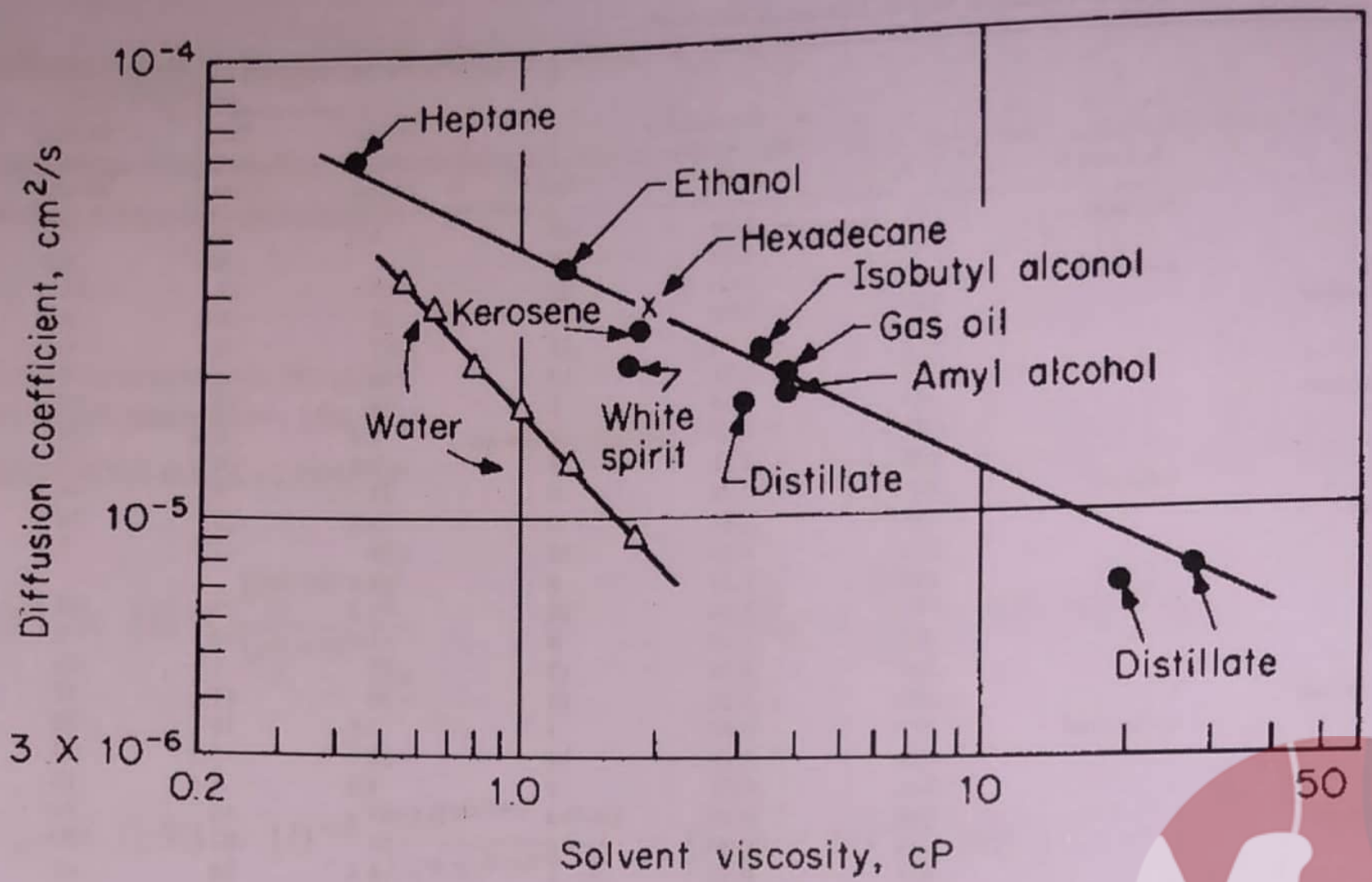
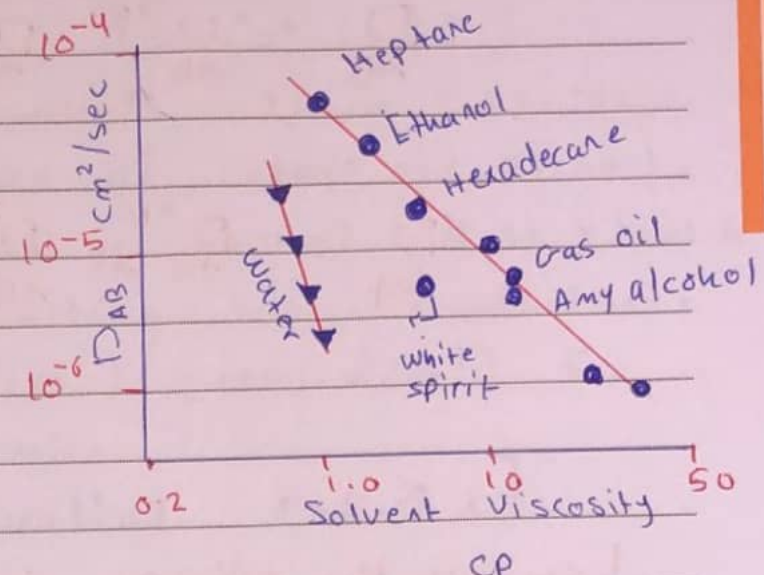


FIGURE 11-8 Diffusion coefficients of carbon dioxide in various solvents. ● Davies et al. (1967); × Hayduk and Cheng (1971); △ Himmelblau (1964)

Table 11.5

Figure (11-8)



اغلب المواد العلاقة ⇐ D_{AB} و N_{cp} بين
linear علاقة
(Water) باستثناء الـ

تفسير ⇐ H_2O تختلف عنهم لان باقي الاشياء Polar.
(مواد عضوية) (Polar) تماثل (H_2O)

المرحة تفسر ان Viscosity هي التي تعيق حركة
(solvent) الـ

Composition Dependence of D_{AB}

Vigens's equation except for strongly associated binary mixtures

$$D_{AB} = D_{AB\infty}^{x_B} \; D_{AB\infty}^{x_A} \left[1 + \frac{\partial \ln \gamma_A}{\partial \ln \alpha_A} \right]_{T,P}$$

$$D_{BA} = D_{AB\infty}^{x_B} \; D_{AB\infty}^{x_A} \left[1 + \frac{\partial \ln \gamma_B}{\partial \ln x_B} \right]_{T,P}$$

at constant T, P

Ex 5.2-3 Diffusion in an acetone – water Mix

Estimate the diffusion coefficient in a 50-mole % mixture of acetone (1) and water (2). This solution is highly nonideal so that $\frac{\partial \ln \gamma}{\partial \ln c_1} = 0.69$ in pure acetone, the diffusion coefficient is 1.26×10^{-5} cm²/sec in pure water it is 4.68×10^{-5} cm²/sec

$$D_0 = [D_0]_{x_1=1}^{x_1} + [D_0]_{x_2=1}^{x_2}$$

$$(1.26 \cdot 10^{-5})^{0.5} + (4.86 \times 10^{-5})^{0.5}$$

$$= 2.43 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$D = D_0 \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} \right)$$

$$= 2.43 \times 10^{-5} (1 - 0.69)$$

(D_{AB} أقل من أقل) $= 0.75 \times 10^{-5}$ cm²/sec

(Diffusion in Electrolytes)

Nernest - Haskell equation for diffusion at infinite dilution

$$D_{AB} = \frac{RT}{F^2}\left[\frac{1/z_+ + 1/z_-}{1/\lambda_+^\circ + 1/\lambda_-^\circ}\right]$$

F: Faraday's constant = 96500 C/g-equiv

z_+ & z_- (valence of cation and anion)

R = universal gas constant 8.31 J/mol·K

$+\lambda$ & $-\lambda$ limiting ionic conductance (A/cm²)(V/cm) g-equiv/cm³) For cation and anion

table 3.7

(effect of salt Normality on D_{AB})

Table 3.7 Limiting Ionic Conductances in Water at 25°C, in $(A/cm^2)(V/cm)(g\text{-equiv}/cm^3)$

Anion	λ_-	Cation	λ_+
OH^-	197.6	H^+	349.8
Cl^-	76.3	Li^+	38.7
Br^-	78.3	Na^+	50.1
I^-	76.8	K^+	73.5
NO_3^-	71.4	NH_4^+	73.4
ClO_4^-	68.0	Ag^+	61.9
HCO_3^-	44.5	Tl^+	74.7
HCO_2^-	54.6	$(\frac{1}{2})Mg^{2+}$	53.1
$CH_3CO_2^-$	40.9	$(\frac{1}{2})Ca^{2+}$	59.5
$ClCH_2CO_2^-$	39.8	$(\frac{1}{2})Sr^{2+}$	50.5
$CNCH_2CO_2^-$	41.8	$(\frac{1}{2})Ba^{2+}$	63.6
$CH_3CH_2CO_2^-$	35.8	$(\frac{1}{2})Cu^{2+}$	54
$CH_3(CH_2)_2CO_2^-$	32.6	$(\frac{1}{2})Zn^{2+}$	53
$C_6H_5CO_2^-$	32.3	$(\frac{1}{3})La^{3+}$	69.5
$HC_2O_4^-$	40.2	$(\frac{1}{3})Co(NH_3)_6^{3+}$	102
$(\frac{1}{2})C_2O_4^{2-}$	74.2		
$(\frac{1}{2})SO_4^{2-}$	80		
$(\frac{1}{3})Fe(CN)_6^{3-}$	101		
$(\frac{1}{4})Fe(CN)_6^{4-}$	111		

Source: Poling, Prausnitz, and O'Connell [2].

Nernest - Haskell equation for diffusion at infinite dilution

$$D_{AB} = \frac{RT}{F^2}\left[\frac{1/z_+ + 1/z_-}{1/\lambda_+^\circ + 1/\lambda_-^\circ}\right]$$

F: Faraday's constant = 96500 C/g-equiv

z_+ & z_- (valence of cation and anion)

R = universal gas constant 8.31 J/mol·K

$+\lambda$ & $-\lambda$ = limiting ionic conductance (A/cm²)(V/cm) g-equiv/cm³) For cation and anion

table 3.7

(Effect of salt Normality on D_{AB})

لما يكون عندي ملح عينة معينة وبزداد ⇐ D_{AB} ج بتناقص بسرعة كبيرة وبعدين برجع بيرتفع وبصير أكتر مما كان في مستواه الطبيعي بطريقة علمية :

As the salt concentration becomes finit (محدد) and increases the diffusion coefficient decreases (repidly) and usually rises, often becoming greater than at high normalities

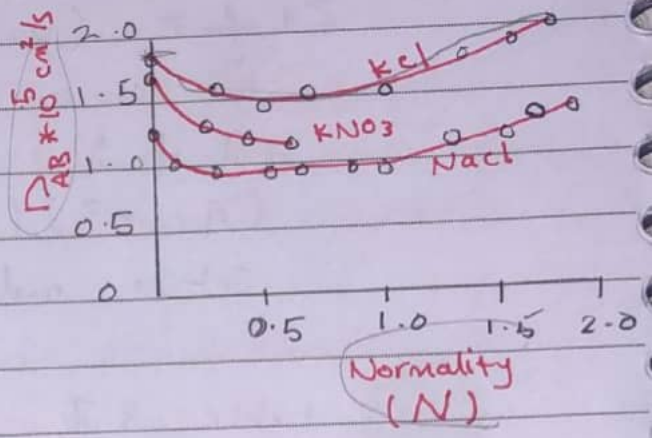
يمكن تطلب تشتقها

Use Gordan's equation up to 2N

$$D_{AB} = D^{\circ}_{AB} \frac{\mu_B}{\mu} (\rho_B \bar{V}_B)^{-1} \left[1 + m \frac{\partial \ln \gamma_\pm}{\partial m}\right]$$

- D°_{AB}: at ∞ dilution = 1
- $\bar{V}_B$: partial Molar volume
- $\frac{\partial \ln \gamma_\pm}{\partial m}$: تصحيح لفانون

كمل باقي معلومات بالسؤال.



effect of concentration on D_{AB} of electrolytes in aqueous solution at 18.5°C.

Normality = Molarity

حال كان الإلكتروليت 1:1 فقط

اما اذا يكون 2:1 مثلاً

نتصير Normality فقط

Ex 11.11

Estimate the diffusion coefficient NaoH in a 2 N aqeous solution.

→ From data on densities of aqueous solution of ($\overset{+}{Na}\overset{-}{OH}$)

صابح

① 12 weight % → $\frac{mol}{L}$ $\frac{mass}{mass}$

. من خلال الضرب بـ MW و الـ solution اعتبره (H_2O)

② 3 N

③ تركيز الماء في aqeous solution حوالي (55.5)

. اذا كان الـ solution شوي dulute كثافته داخل solution = 1

$55.5 = \frac{1000}{18}$

④ $\gamma_\pm$ For NaOH = 1950 at 298 k

⑤ $m = 2 = 0.698$

⑥ value are plotted vs molality m the slope at 2 m = 0.047

$$m \frac{\partial \ln \gamma_\pm}{\partial m} = \frac{m}{\gamma_\pm} \frac{\partial \gamma_\pm}{\partial m} = \frac{2}{0.698}(0.047) = 0.135$$

The vescositiess of water and 2N NaoH solution at 298 K = 0.894 and 1.42 cP

→

$$D^{\circ}_{AB} = \frac{(2)(8.314)(298)}{(1150)(1)(149B)(96.500)^2}$$

$$= 2.12 * 10^{-5} \ cm^2/s$$

$$D_{AB} = (2.12 * 10^{-5}) \frac{0.894}{1.42} \cdot \frac{55.5}{55.5} [1+(2)(0.135)]$$

$= 1.70 * 10^{5} \ cm^2/s$ ← هاي المعنية at ∞ dulution

at 288 k the viscosity of water = 1.144 cp

so the D_{AB} at 288 k is

$$1.70 * 10^{-5} \frac{288}{(334)(1.144)} = 1.28 * 10^{-5} \ cm^2/s$$

هاي فيمة بعد التصحيح

نزلت بعد التصحيح لانه زاد ال (ion)

at dulution one (ion)

D_{AB} زاد وتركيز ⇐ يعني زاد ال ion يعني قلت

mean ⇐ λ قلت لانه

Free Path

(Solid)

هون انا بعني الـ structure
هون الـ D_{AB} افتراضي
لانه الجزيئات مرتبة
كثير حك بحصل
اقل بـ 10000 مرة من الغاز
اقل بـ 1000 مرة من السائل

(Examples)

1- leaching of metal ores.
مثل الشاي في المي

2- Drying of timber and food.
الخشب، والحليب المجفف

3- adsorption of solutes.

4- Diffusion and catalytic reaction in solid catalysts.

5- Separation of fluid by membranes → حيوية / صناعية

6- Treatment of metals at high temperature by gases.

Modes of diffusion in solid

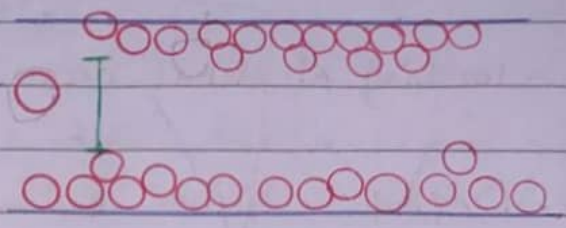
follow Fick's law : does not depend on the structure of the solid.

اذا كان يعتمد على الـ(structure) معناته ما بنطبق عليه (Fick's law)

→ an example is the diffusion of gasses into Polymeric membranes

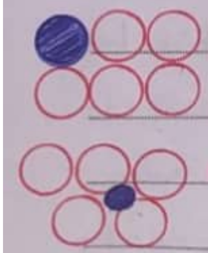
→ solubility of gas is described by Henry's law

Diffusion in porous solid : depends on the actual structure and void channels in the solid



← جزئ الـ solute سواء كان (gas / liq)
جزء من الغاز رح يحلق على الـ سطح
وتركيزه يصير عالي مع الوقت المساحة
ينتقل الى مساحة بين باللون الاخضر

Diffusion Mechanism in solids
- bulk
  - interstitialcy mechanism
  - Vacancy mechanisim
- surface
  - → interstitalcy
  - → vacancy
  - → may accur at (solid - liq) or (solid - gas) interface and grain - boundary



vacancy → تقريبا نفس الحجم

interstitaly → اصغر من الحجم

الـ surface يشمل الـ (bulk)

Knudsen Diffusion

لـ حوالي (50nm)

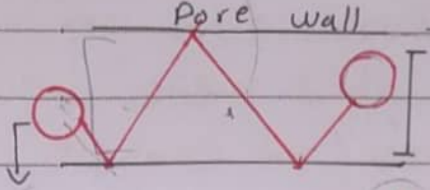
بصير لما متوسط قطر المسام (Pore diameter mean) > متوسط مسار الحر (mean Freepath)

- يحدث في (low permeability porous) => يلي تحتوي على اعداد اقطار صغيرة ↓ (pore diameter)

وعند (low Pressure) ← لما يكون (λ ↑)

← الاصطدام بين ال جزيئ والجدار أهم من الاصطدام بين الجزيئات نفسها.

← بحيث لما (pores) يكون حجمها اقل من (50nm)



لازم (Solute Diameter) > من d pore

(Knudsen number) :

$$Kn = \frac{\lambda}{d}$$ λ → mean Free path, d → d pore

$$\lambda = \frac{K_B T}{\sqrt{2}\pi \sigma_{AB}^2 P}$$ 1.38×10^{-23}

(Kn) is used to indentify :

1- Kn < 0.001 leads to the application of the no-slip boundary condition (continuum)

لـ سرعة الـ molecules على الـ سطح = zero

انا رح اشتغل ال (Kn) (Ficks)

Kn = λ/d مثلا انا كبير (Kn) اذا كان صغير (d كبير)

معناه انا بشتغل (Ficks) law

← في هاي الحالة

ال(structure) مالها دور فقط يلي يلعب دور ال (concentration gradiant)

Ex 3.3 Knudson diffusion in Porous Solid

A Mix of O_2 (A) and N_2 (B) diffuses through the pores of a 2 mm - thick piece of (unglazed) → غشاء porcelain at a total pressure of 0.1 atm and a temp of 293 K. The avg pore diameter is 0.1 μm the porosity is 30.5 %. and the tortuosity is 4.39. Estimate the diffusion fluxes of both components when the mole Fractions of O_2 are 80 %. and 20 %. On either side of the porcelin, the collision diameters for oxygen and nitrogen ~~are~~ are 3.467 and 3.798 Å respectively.

2 layers طبقتين

$$\sigma_{AB} = \frac{(3.467 + 3.798)}{2} = 3.632 \text{ Å}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p} = \frac{1.38\times10^{-23}(293)}{\sqrt{2}\pi(3.632\times10^{-10})^2(0.10\times1.013\times10^5)}$$

$$= 6.81\times10^{-7}$$

$$\lambda = 6810\ ^\circ A$$

$K_n = \lambda/d$

$6810/1000 = 6.81 > 0.05$

$$D_{KA} = \frac{d}{3}\left(\frac{8RT}{\pi M_i}\right)^{1/2}$$

$$D_{KA} = \frac{10^{-7}}{3}\left(8 \times \frac{8.314}{\pi} \times 293 \times \frac{1}{32}\right)^{1/2}$$

$$= 1.47\times10^{-5}\ m^2/s$$

$$= 0.147\ cm^2/s$$

$$D_{KAeff} = \frac{\varepsilon D_{KA}}{t}$$

$$= \frac{0.305 \times 0.147}{4.39}$$

$$= 0.0102\ cm^2/s$$

2- $0.001 < Kn < 0.1$ leads to the application of the slip boundary condition

← سرعة الـ molecule ≠ zero الملاصقة

3- $Kn > 0.1$ leads to the inapplicability of the continuum assumption and most of the gas flow must be characterized using statistical methods.

هون نشتغل على (molecular level)

effective diffusivity

$$D_{A\,eff} = \frac{\varepsilon}{\tau} D_{AB}$$

τ → tortuosity (corrects for the path longer than linear diffusion path)

$(\tau = 1.5 - 5)$

Knudsen diffusivity

$$D_K = \frac{d}{3}\left[\frac{8RT}{\pi M_i}\right]^{1/2}$$