DIFFUSION THROUGH A VARYING CROSS-SECTIONAL AREA

Diffusion through a varying cross-sectional area

- **In some cases, the area A may vary. Then, it is convenient to define N_A as:**

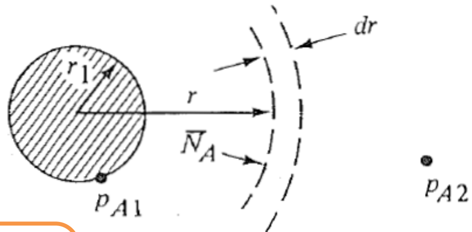
Constant at steady state condition

$$N_A = \frac{\bar{N}_A}{A} \frac{[\text{kgmol/s}]}{[\text{m}^2]}$$

- **Examples**

Diffusion from a sphere

  - Evaporation of a drop of liquid
  - Evaporation of ball of naphthalene



Stagnant medium B "air"

Diffusion from a sphere

$$N_A = \frac{\bar{N}_A}{A} = \frac{\bar{N}_A}{4\pi r^2}$$

- But as given before

$$N_A\left(1 - \frac{p_A}{P}\right) = -\frac{D_{AB}}{RT}\frac{dp_A}{\boxed{dz}}$$

Or

$$N_A = \frac{\bar{N}_A}{4\pi r^2} = -\frac{D_{AB}}{RT}\frac{dp_A}{(1 - p_A/P)\boxed{dr}}$$

- Rearranging and integration

$$\frac{\bar{N}_A}{4\pi}\int_{r_1}^{r_2}\frac{dr}{r^2} = -\frac{D_{AB}}{RT}\int_{p_{A1}}^{p_{A2}}\frac{dp_A}{(1 - p_A/P)}$$

$$\frac{\bar{N}_A}{4\pi}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{D_{AB}P}{RT}\ln\frac{P - p_{A2}}{P - p_{A1}}$$

- Since $r_2 >> r_1$, $\therefore$ $1/r_2 \approx 0$, hence previous eq. becomes

$$\frac{\bar{N}_A}{4\pi r_1^2} = N_{A1} = \frac{D_{AB}P}{RTr_1}\ln\frac{(P - p_{A2})}{(P - p_{A1})}$$

- Or

$$\frac{\bar{N}_A}{4\pi r_1^2} = N_{A1} = \frac{D_{AB}P}{RTr_1}\frac{p_{A1} - p_{A2}}{p_{BM}}$$

NOTE

If p_{A1} is small compared to P (a dilute gas phase), $p_{BM} \cong P$. Also, setting $2r_1 = D_1$, diameter, and $c_{A1} = p_{A1}/RT$, we obtain

$$N_{A1} = \frac{2D_{AB}}{D_1}(c_{A1} - c_{A2})$$

This equation can also be used for liquids, where D_{AB} is the diffusivity of A in the liquid.

Time for complete evaporation or dissolution of the sphere is:

$$t_F = \frac{\rho_A r_1^2 RT}{2M_A D_{AB} P} \frac{1}{\ln \frac{(P - p_{A2})}{(P - p_{A1})}}$$

Example 1

- **Evaporation of a Naphthalene Sphere**

A sphere of naphthalene having a radius of 2.0 mm is suspended in a large volume of still air at 318 K and 1.101325 x 10^5 Pa. The diffusivity of the naphthalene at 318 K is 6.92 x10^{-6} m^2/s.

(1) Calculate the rate of evaporation of naphthalene from the surface.

(2) Estimate the time after which the sphere will completely evaporate.

Solution

(1) $$\boxed{\frac{\bar{N}_A}{4\pi r_1^2} = N_{A1} = \frac{D_{AB}P}{RTr_1} \ln \frac{(P - p_{A2})}{(P - p_{A1})}}$$

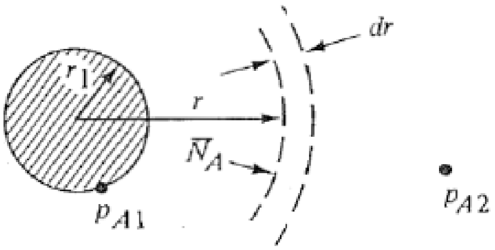
D_{AB} = 6.92 x 10^{-6} m^2/s.

P = 101325 Pa.

The vapor pressure of Naphthalene at 318 K is p_{A1} = 0.555 mm Hg = 0.555/760×101325=74 Pa. [From Tables].

p_{A2} = 0 [Evaporation to a large volume of Air to a large distance].

$r_1 = 2\ mm = 2\times10^{-3}\ m.$



$$\boxed{\frac{\bar{N}_A}{4\pi r_1^{\,2}} = N_{A1} = \frac{D_{AB}P}{RTr_1}\ln\frac{(P-p_{A2})}{(P-p_{A1})}}$$

$$N_{A1} = \frac{(6.92\times10^{-6})(101325)}{(8314)(318)(2\times10^{-3})}\ln\frac{(101325-0)}{(101325-74)}$$

$$= 9.68\times10^{-8}\ \text{kg mol A/s.m}^2$$

Solution

Data

From tables

ρ = 1140 kg/m^3

M_A = 128 g/mol

(2)

$$\boxed{t_F = \frac{\rho_A r_1^{\,2} RT}{2M_A D_{AB} P}\,\frac{1}{\ln\dfrac{(P-p_{A2})}{(P-p_{A1})}}}$$

$$t_F = \frac{(1140)(2\times10^{-3)^{2}}(8314)(318)}{2(128/1000)(6.92\times10^{-6})(101325)}\,\frac{1}{\ln\dfrac{(101325-0)}{(101325-74)}}$$

$$t_F = 91931758\ \ \text{s} = 2.9\ \ \text{yr}$$

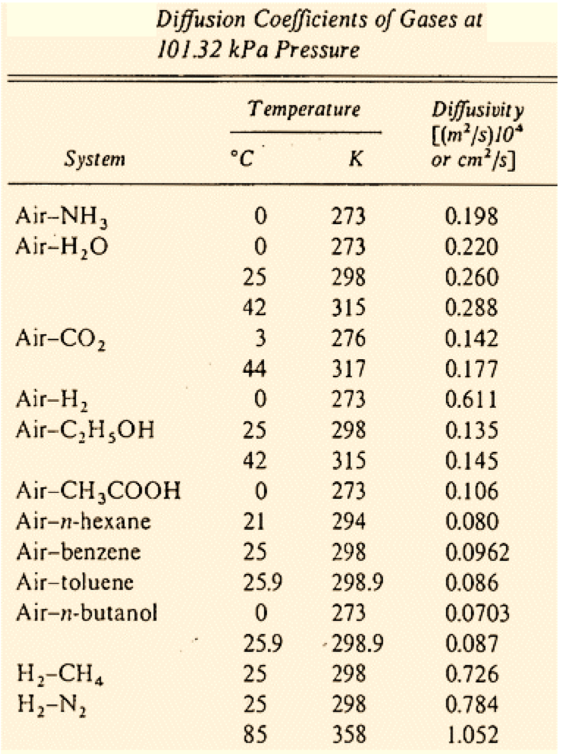
Diffusion coefficients for gases

Usually, the diffusion coefficients are tabulated, as shown in the Table.

A number of experimental methods have been used to determine the diffusion coefficient.

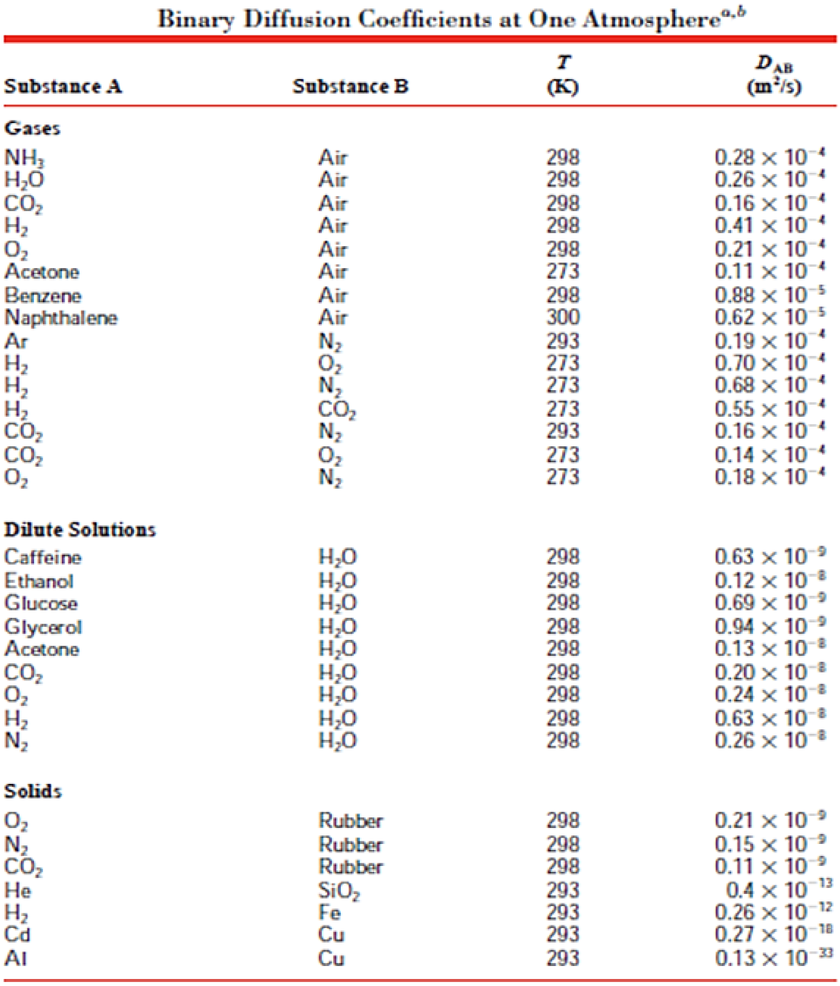
From the given table we can conclude,

↑ T ↑ D_{AB}



Diffusion Coefficients of Gases at 101.32 kPa Pressure

System	Temperature °C	Temperature K	Diffusivity [$(m^2/s)10^4$ or cm^2/s]
Air–NH_3	0	273	0.198
Air–H_2O	0	273	0.220
	25	298	0.260
	42	315	0.288
Air–CO_2	3	276	0.142
	44	317	0.177
Air–H_2	0	273	0.611
Air–C_2H_5OH	25	298	0.135
	42	315	0.145
Air–CH_3COOH	0	273	0.106
Air–*n*-hexane	21	294	0.080
Air–benzene	25	298	0.0962
Air–toluene	25.9	298.9	0.086
Air–*n*-butanol	0	273	0.0703
	25.9	298.9	0.087
H_2–CH_4	25	298	0.726
H_2–N_2	25	298	0.784
	85	358	1.052



Binary Diffusion Coefficients at One Atmosphere^{a,b}

Substance A	**Substance B**	***T* (K)**	**D_{AB} (m^2/s)**
Gases			
NH_3	Air	298	0.28×10^{-4}
H_2O	Air	298	0.26×10^{-4}
CO_2	Air	298	0.16×10^{-4}
H_2	Air	298	0.41×10^{-4}
O_2	Air	298	0.21×10^{-4}
Acetone	Air	273	0.11×10^{-4}
Benzene	Air	298	0.88×10^{-5}
Naphthalene	Air	300	0.62×10^{-5}
Ar	N_2	293	0.19×10^{-4}
H_2	O_2	273	0.70×10^{-4}
H_2	N_2	273	0.68×10^{-4}
H_2	CO_2	273	0.55×10^{-4}
CO_2	N_2	293	0.16×10^{-4}
CO_2	O_2	273	0.14×10^{-4}
O_2	N_2	273	0.18×10^{-4}
Dilute Solutions			
Caffeine	H_2O	298	0.63×10^{-9}
Ethanol	H_2O	298	0.12×10^{-8}
Glucose	H_2O	298	0.69×10^{-9}
Glycerol	H_2O	298	0.94×10^{-9}
Acetone	H_2O	298	0.13×10^{-8}
CO_2	H_2O	298	0.20×10^{-8}
O_2	H_2O	298	0.24×10^{-8}
H_2	H_2O	298	0.63×10^{-8}
N_2	H_2O	298	0.26×10^{-8}
Solids			
O_2	Rubber	298	0.21×10^{-9}
N_2	Rubber	298	0.15×10^{-9}
CO_2	Rubber	298	0.11×10^{-9}
He	SiO_2	293	0.4×10^{-13}
H_2	Fe	293	0.26×10^{-12}
Cd	Cu	293	0.27×10^{-18}
Al	Cu	293	0.13×10^{-33}

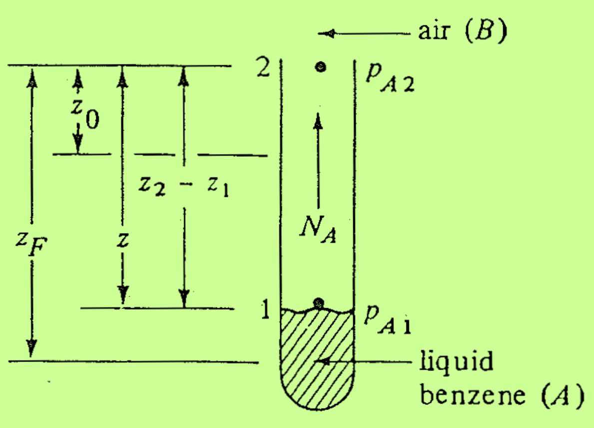
Diffusion coefficients for gases

A number of experimental methods have been used to determine the diffusion coefficient for binary gas mixtures.

One method is to evaporate a pure liquid A in a narrow tube with a gas passed over the top.

The fall in the liquid level is measured with time and the diffusivity is calculated.

$$t_F = \frac{\rho_A (z_F^2 - z_0^2) R T p_{BM}}{2 M_A D_{AB} P (p_{A1} - p_{A2})}$$

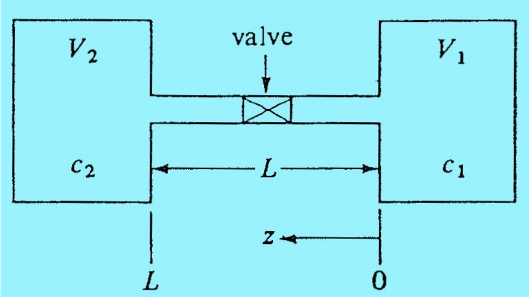


Diffusivity measurement

Pure gas A is added to V_1 and pure B to V_2 at the same pressures. The valve is opened, diffusion proceeds for a given time, and then the valve is closed and the mixed contents of each chamber are sampled separately. Assuming quasi-steady-state diffusion

$$J_A^* = -D_{AB}\frac{dc}{dz} = -\frac{D_{AB}(c_2 - c_1)}{L} \quad \text{....(a)}$$

where c_2 is the concentration of A in V_2 at time t and c_1 in V_1. The rate of diffusion of A going to V_2 is equal to the rate of accumulation in V_2.



Diffusivity measurement of gases by the two-bulb method.

$$AJ_A^* = -\frac{D_{AB}(c_2 - c_1)A}{L} = V_2\frac{dc_2}{dt} \quad \text{...(b)}$$

<u>Material balance</u>: (c_{av} at equilibrium can be calculated using initial composition at t = 0.)

$$(V_1 + V_2)c_{av} = V_1 c_1^0 + V_2 c_2^0 \quad \text{...(c)}$$

Material balance: (at any time t as the previous material balance)

$$(V_1 + V_2)c_{av} = V_1 c_1 + V_2 c_2 \qquad \text{...(d)}$$

From eq. (d) find c_1 then substitute it in eq. **(b)** on rearrangement, integration between t = 0 and t = t, we get

$$\frac{c_{av} - c_2}{c_{av} - c_2^0} = \exp\left[-\frac{D_{AB}(V_1 + V_2)}{(L/A)(V_2 V_1)} t\right] \qquad \text{...(e)}$$

Note

From this eq. (e) we can obtain the diffusivity coefficient D_{AB}, where C_2 is found by sampling.

Diffusion coefficients for gases

Empirical correlations have been developed to calculate the diffusivity. For example, for a binary gas:

1. Chapman& Enskog

$$D_{AB} = \frac{1.8583 \text{x} 10^{-7} T^{3/2}}{P \sigma_{AB}^2 \Omega_{D,AB}} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}$$

T is in K

P is in atm

σ and Ω are parameters

M is the molecular weight in kg mass/kg mol

Based on Boltzmann's kinetic theory of gases, the theorem of corresponding states, and a suitable intermolecular energy potential function.

Diffusion coefficients for gases

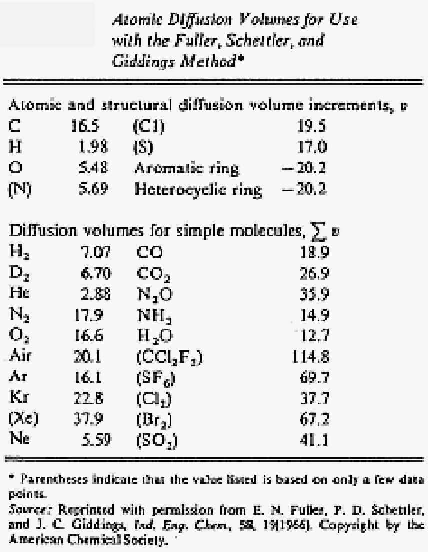
Another empirical correlations is:

2. Fuller et al.

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

atm

$\sum \upsilon$: is called the sum of structural volume increments and is tabulated



*Atomic Diffusion Volumes for Use with the Fuller, Schettler, and Giddings Method**

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, $\sum v$			
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
Ne	5.59	(SO_2)	41.1

* Parentheses indicate that the value listed is based on only a few data points.

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3. Schmidt number of gases

The schmidt number of a gas mixture of dilute A in B is dimensionless and defined as

$$N_{Sc} = \frac{\mu}{\rho D_{AB}}$$

where μ is viscosity of the gas mixture, which is viscosity of B for a dilute mixture in Pa · s or kg/m · s, D_{AB} is diffusivity in m^2/s, and ρ is the density of the mixture in kg/m^3. For a gas the Schmidt number can be assumed independent of temperature over moderate ranges and independent of pressure up to about 10 atm or 10×10^5 Pa.

The Schmidt number is the dimensionless ratio of the molecular momentum diffusivity μ/ρ to the molecular mass diffusivity D_{AB}. Values of the Schmidt number for gases range from about 0.5 to 2. For liquids Schmidt numbers range from about 100 to over 10 000 for viscous liquids.

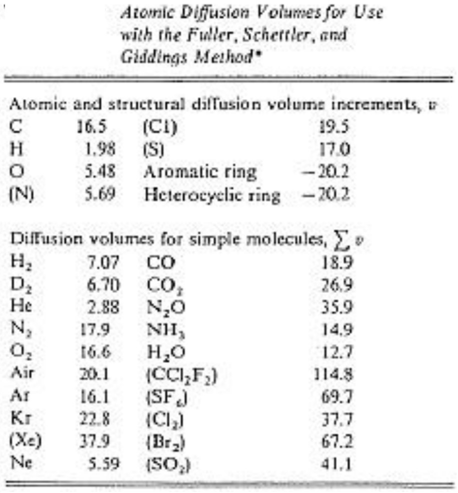
Example 2: Estimation of diffusivity of a gas mixture

Normal butanol $C_4H_{10}O$ (A) is diffusing through air (B) at 1 atm abs. Using the Fuller et al. method, estimate the diffusivity D_{AB} for the following conditions:

(a) For 0°C.
(b) For 25.9°C.
(c) For 0°C and 2.0 atm abs.

Solution

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



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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, $\sum v$			
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
Ne	5.59	(SO_2)	41.1

(a)

P = 1.00 atm
T = 273 + 0 = 273 K
M_A (butanol) = 74.1
M_B (air) = 29

$$\sum v_A = 4(16.5) + 10(1.98) + 1(5.48) = 91.28 \text{ (butanol)} \quad C_4H_{10}O$$

$$\sum v_B = 20.1 \text{ (air)}$$

Solution

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

$P = 1.00$ atm
$T = 273 + 0 = 273$ K
M_A (butanol) $= 74.1$
M_B (air) $= 29$

$$\sum v_A = 4(16.5) + 10(1.98) + 1(5.48) = 91.28 \text{ (butanol)}$$

$$\sum v_B = 20.1 \text{ (air)}$$

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

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

Solution

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

(b) $T = 273 + 25.9 = 298.9$ K

Substituting into the correlation: $D_{AB} = 9.05 \times 10^{-6}$ m^2/s.

(c) Total pressure $P = 2.0$ atm

Using the value predicted in part (a) and correcting for pressure:
$D_{AB} = 7.73 \times 10^{-6}(1.0/2.0) = 3.865 \times 10^{-6}$ m^2/s.