

ME5362: Mass Transport

Home Assignment

Diffusion in Dilute Solutions

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Date of Submission: 10th March 2005

ME6203 Home Assignment
Chapter 2: Diffusion in dilute solutions

Q4.) About 85.6 cm² of a flexible polymer film 0.051 cm thick is made into a bag, filled with distilled water, and hung in an oven at 35⁰C and 75% R.H. The bag is weighed, giving the following data:

| Time (days) | Bag weight (grams) |
|-------------|--------------------|
| 0 | 14.0153 |
| 1 | 13.9855 |
| 4 | 13.9104 |
| 7 | 13.8156 |
| 8 | 13.7710 |
| 12 | 13.6492 |
| 14 | 13.583 |
| 16 | 13.5256 |

What is the permeability (DH) of the polymer film?

From Fick's 1st Law:

$$j_1 = -D \frac{dc_1}{dz}$$

For the steady diffusion across the thin film, the Fick's second law is obtained:

$$0 = D \frac{d^2 c_1}{dz^2}$$

Steady membrane diffusion is subjected to the two boundary conditions stated below:

$$z = 0, c_1 = HC_{1o}$$

$$z = l, c_1 = HC_{1l}$$

H is the partition coefficient = concentration in membrane / concentration in adjacent solution.

The concentration profile is

$$c_1 = HC_{1o} + H(C_{1l} - C_{1o}) \frac{z}{l}$$

The flux across the thin membrane

$$j_1 = \frac{[DH]}{l} (C_{1o} - C_{1l})$$

DH is the permeability of the material.

The equation will be used as a basis of calculation for Q4.

The mass flux, j_1 , can be obtained by linear regression curve of the provided mass weight profile with time. It is just equal to the slope of the fitted curve, as shown in Figure 1 below.

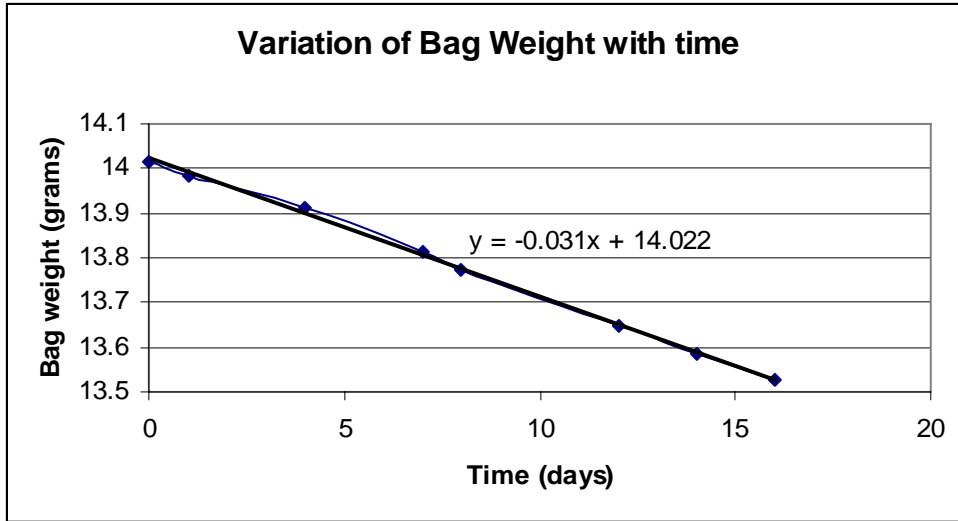


Figure 1: Variation of Bag Weight with time

From Fig. 1, the diffusion rate of water vapor out from the polymer is 0.031 g/day =

$$0.031 \frac{0.001}{24 \times 3600} = 3.588 \times 10^{-10} \text{ [kg / s]}$$

Hence, the mass flux = $j_1 = \frac{3.588 \times 10^{-10} \text{ [kg / s]}}{85.6 \times 10^{-4} \text{ [m}^2\text{]}} = 4.1915 \times 10^{-8} \text{ [kg/m}^2\text{s]}$.

The polymer is wrapped around the distilled water, and put inside the oven of 35°C and 75% RH. Figure 2 shows the diagram of the experiment:

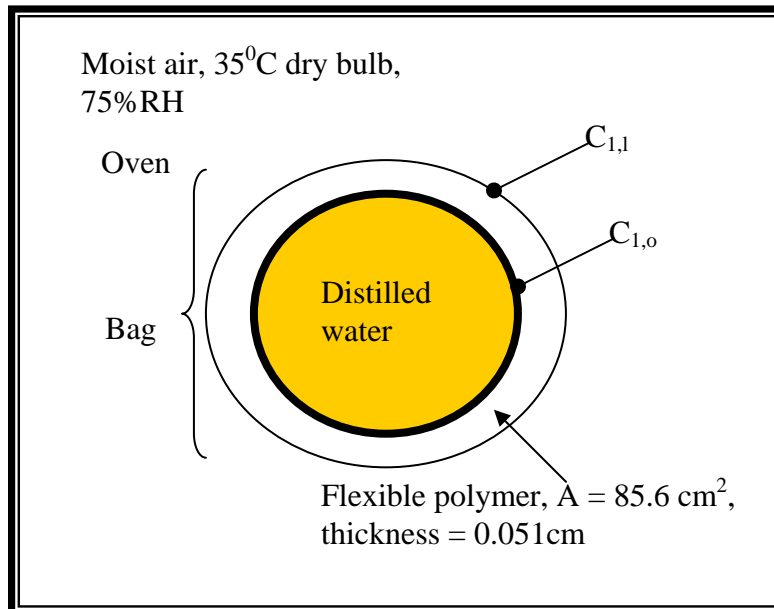


Figure 2: Schematic diagram of the experiment to determine the diffusion coefficient of the flexible polymer

The distilled water is diffused through the polymer into the oven and hence the weight of the bag drops with time. It is assumed the oven is rather big and therefore the water vapor concentration at far stream ($C_{1,\infty}$) (subscript 1 represent water vapor species) is not affected by the diffusion process. Moreover, it is reasonably assumed that at the outer surface of the polymer $C_{1,l} = C_{1,\infty}$.

To determine $C_{1,\infty}$,

By using psychrometric calculator, as shown in Figure 3 below, the air properties can be obtained as:

Dry bulb temperature, $t_{db} = 35^{\circ}\text{C}$

Relative humidity, $\text{RH} = 75\%$

Specific volume, $v = 0.911 \text{ m}^3/\text{kg}$ of dry air

Humidity ratio, $W = 27.03 \text{ g/kg}$ of dry air

Figure 3 Calculated properties of far-field air by using psychrometric calculator

Therefore, the concentration of water vapor, $C_{1,\infty} = \frac{27.03}{0.911} = 29.67 [\text{g} / \text{m}^3]$

And $C_{1,1} = C_{1,\infty} = 29.67 [\text{g}/\text{m}^3] = 29.67 \times 10^{-3} [\text{kg}/\text{m}^3]$.

At the inner interface of the polymer, $C_{1,o}$ corresponds to the saturated condition at $T = 35^{\circ}\text{C}$, on which the relative humidity is 100%.

Similarly, the air properties on the saturated condition are obtained by using psychrometric calculator (Figure 4) as follows:

Dry bulb temperature, $t_{db} = 35^{\circ}\text{C}$

Relative humidity, $\text{RH} = 100\%$

Specific volume, $v_{\text{sat}} = 0.924 \text{ m}^3/\text{kg}$ of dry air

Humidity ratio, $W_{\text{sat}} = 36.57 \text{ g/kg}$ of dry air

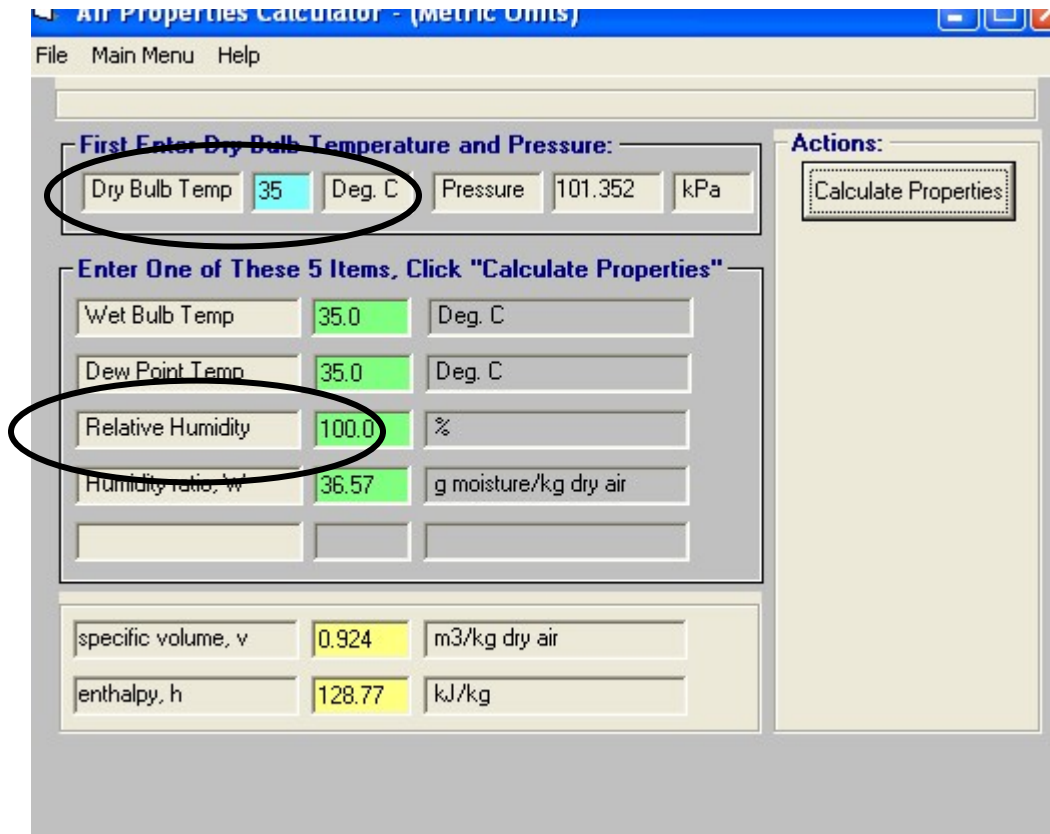


Figure 4 Calculated properties of saturated air at 35°C and 1 atm by using psychrometric calculator

Therefore, the concentration of water vapor at the inner surface,

$$C_{1,o} = \frac{36.57}{0.924} = 39.578 \text{ [g / m}^3\text{]}$$

Since $j_1 = \frac{[DH]}{l} (C_{1o} - C_{1l})$, then

$$4.1915 \times 10^{-8} \text{ [kg / m}^2 \text{ s]} = \frac{[DH]}{0.00051 \text{ [m]}} (39.578 - 29.67) \times 10^{-3} \text{ [kg / m}^3\text{]}$$

It is obtained that

$$[DH] = 2.1575 \times 10^{-9} \text{ [m}^2 \text{ / s]} = 2.1575 \times 10^{-5} \text{ [cm}^2 \text{ / s]}.$$

- Q5.) Diaphragm cells are frequently calibrated by allowing 1-M potassium chloride to diffuse into pure water. The average diffusion coefficient in this case is $1.859 \times 10^{-5} \text{ cm}^2/\text{s}$. Your cell has compartment volumes of 42.3 cm^3 and 40.8 cm^3 ; the diaphragm is a glass frit 2.51 cm in diameter, 0.16 cm thick, and of porosity, ϕ , 0.34 . In one calibration experiment, the concentration difference at 36 hours 6 minutes is 49.2% of that originally present.
- What is the cell's calibration constant, β ?
 - What is the effective length of the diaphragm's pores, $(l/H)\phi$?
 - The current pores are about $2 \times 10^{-4} \text{ cm}$ in diameter. What is the effect of increasing the pore diameter ten times at constant porosity?

Figure 5 below shows a typical diaphragm cell.

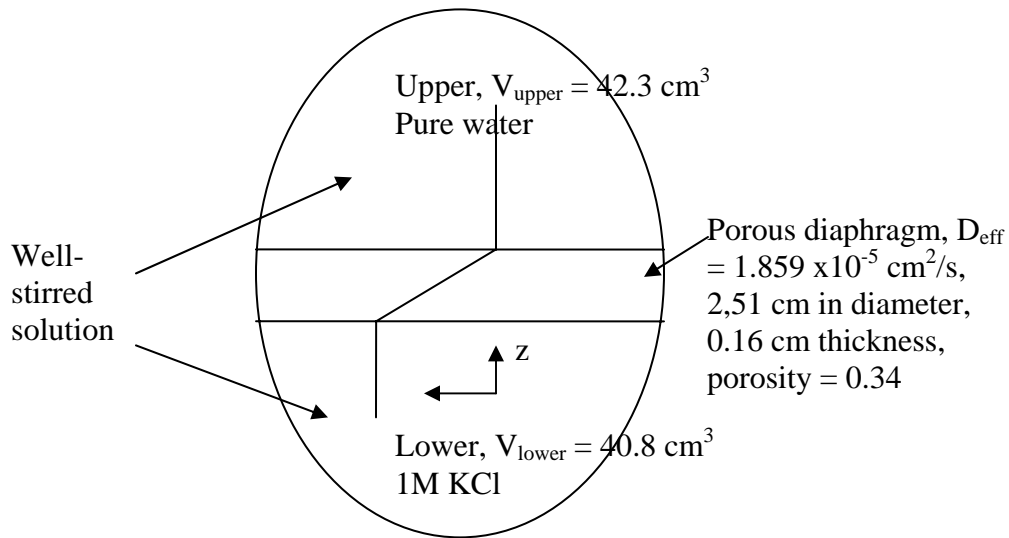


Figure 5 A typical diaphragm cell.

In the pseudo-steady state, the flux across the diaphragm for membrane by diffusion is

$$j_1 = \left[\frac{DH}{l} \right] (C_{1,lower} - C_{1,upper})$$

For overall mass balance on the adjacent components:

$$V_{lower} \frac{dC_{1,lower}}{dt} = -Aj_1$$

$$V_{upper} \frac{dC_{1,upper}}{dt} = +Aj_1$$

$$\frac{d}{dt}(C_{1,lower} - C_{1,upper}) = D\beta(C_{1,upper} - C_{1,lower})$$

$$\beta = \frac{AH}{l} \left(\frac{1}{V_{lower}} + \frac{1}{V_{upper}} \right) - \text{geometrical constant characteristic of particular}$$

diaphragm cell.

$$\text{Initial condition, } t = 0, C_{1,lower} - C_{1,upper} = C_{1,lower}^o - C_{1,upper}^o$$

$$\frac{C_{1,lower} - C_{1,upper}}{C_{1,lower}^o - C_{1,upper}^o} = e^{-\beta Dt}$$

$$D = \frac{1}{\beta t} \ln \left(\frac{C_{1,lower}^o - C_{1,upper}^o}{C_{1,lower} - C_{1,upper}} \right)$$

The porosity ϕ is defined as the ratio of the pore volume to the overall volume of a porous medium. Thus, $(1 - \phi)$ represents the fraction that is occupied by the solid. For this case, $\phi = 0.34$.

In one calibration experiment, the concentration difference at 36 hours 6 minutes is 49.2% of that originally present.

This means at $t = 36 \times 3600 + 6 \times 60 = 129960$ s,

$$\left(\frac{C_{1,lower}^o - C_{1,upper}^o}{C_{1,lower} - C_{1,upper}} \right) = \frac{1}{0.492} = 2.03252$$

The cell calibration constant is

$$\beta = \frac{1}{Dt} \ln \left(\frac{C_{1,lower}^o - C_{1,upper}^o}{C_{1,lower} - C_{1,upper}} \right) = \frac{1}{1.859 \times 10^{-5} \times 129960} \ln(2.03252) = 0.29358 [\text{cm}^{-2}]$$

$$\text{Diffusion length/partition coefficient} = \frac{l}{H} = \frac{A}{\beta} \left(\frac{1}{V_{lower}} + \frac{1}{V_{upper}} \right)$$

$$\frac{l}{H} = \frac{\pi(1.255)^2 [\text{cm}^2]}{0.29358 [\text{cm}^{-2}]} \left(\frac{1}{40.8} + \frac{1}{42.3} \right) \left[\frac{1}{\text{cm}^3} \right] = 0.811542655 [\text{cm}]$$

$$\text{The effective length of diaphragm's length} = \frac{l}{H} \phi = 0.811542655 \times 0.34 = 0.27592$$

$$[\text{cm}] = \mathbf{0.28 [\text{cm}]}.$$

The current pores are about 2×10^{-4} [cm] in diameter. What is the effect of increasing the pore diameter ten times at constant porosity?

What we are looking at is the inter-relationship between diffusion coefficient with pore diameter and porosity. The diffusion coefficient can also be expressed as permeability.

An article had been found from the internet, **Ryoji Takahashi , Satoshi Sato , Toshiaki Sodesawa and Hideyo Nishida, *Phys. Chem. Chem. Phys.*, 2002, 4 (15), 3800 – 3805**

The abstract:

The diffusion coefficient of nickel nitrate dissolved in water in porous silica plates with different pore size was measured to investigate the effect of pore size on the liquid-phase diffusion resistance. The pore-diffusion coefficient of nickel nitrate varied with the pore size of the silica gel. In pores of diameter >5 nm, the diffusion resistance can be ignored, and the pore-diffusion coefficient varies proportionally to the porosity of the silica plates. In pores of diameter <5 nm, however, the diffusion resistance increases rapidly with decreasing pore diameter. A microporous silica shows the largest diffusion resistance: the pore-diffusion coefficient in micropores is less than 0.01 of the diffusion coefficient in an unbounded system.

Hence, for the pore diameter of 2000 nm (> 5 nm), the diffusion resistance can be ignored (means the pore diameter effect can be ignored), and the diffusion coefficient is solely proportional to the porosity of the medium. In this case, **the porosity remains unchanged and hence the diffusion coefficient will be intact, even though the pore diameter is increased by ten times.**

Moreover, A. Buchwald published a paper on “Determination of the Ion Diffusion Coefficient in Moisture and Salt Loaded Masonry Materials by Impedance Spectroscopy” in the 3rd Int. PhD symposium at Vienna in Oct, 2000. Via his efforts, it is verified that the diffusion coefficient are not influenced by the pore diameter as long as the pore structure are similar and a lower content on porosity has also a lower diffusion coefficient.

Q6.) Diffusion coefficients in gases can be measured by injecting a solute gas into a solvent gas in laminar plug flow and measuring the concentration with a thermistor placed downstream. The concentration downstream is given by

$$c_1 = \frac{Q}{4\pi Dz} e^{-r^2 v / 2Dz}$$

where Q is the solute injection rate, z is the distance downstream, r is the distance away from the z axis, and v is the gas flow. One series of measurements involves the diffusion of helium in nitrogen at 25°C and 1 atm. In one particular measurement, the maximum concentration of helium is 0.48 wt% when z is 1.031 cm and Q is $0.045 \text{ cm}^3/\text{s}$. What is the diffusion coefficient?

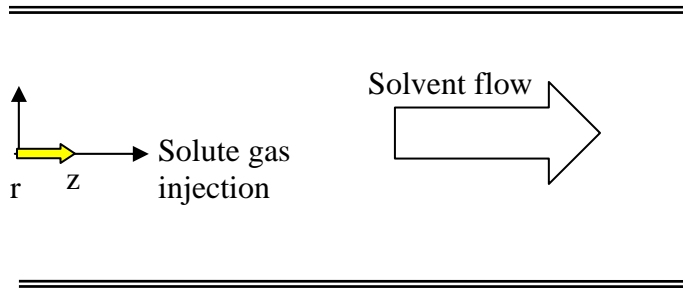


Figure 6 Diagram of a solvent gas in laminar plug flow with solute injection

Solutions:

Figure 6 roughly shows a solvent laminar plug flow with solute injection, as described in the question. The maximum concentration will occur along axial (z) axis, $r = 0$, as the

profile is following Gaussian distribution. Thus, $c_{1,\max} = \frac{Q}{4\pi Dz}$. It is diffusion of

helium in nitrogen at 25°C and 1 atm. In one particular measurement, the maximum concentration of helium is 0.48 wt%. Table 1 below shows the molecular weight and weight proportion of helium and nitrogen respectively.

| | Molecular weight, M | % of weight, m |
|--------------|-----------------------|------------------|
| He | 4 | 0.48 |
| N_2 | 28 | 99.52 |

The ideal gas law applies.

$$\text{Density of helium } \rho_{\text{He}} = \frac{PM_{\text{He}}}{R_{\text{He}}T} = \frac{101325 \times 4}{8314 \times 287} = 0.16359 \text{ kg} / \text{m}^3$$

$$\text{Density of nitrogen } \rho_{\text{N}_2} = \frac{PM_{\text{N}_2}}{R_{\text{N}_2}T} = \frac{101325 \times 28}{8314 \times 287} = 1.14513 [\text{kg} / \text{m}^3]$$

Assume that the total mass is 1 kg.

$$\text{Volume of helium: } V_{He} = \frac{m_{He}}{\rho_{He}} = \frac{0.0048}{0.16359} = 0.02934[m^3]$$

$$\text{Volume of nitrogen: } V_{N_2} = \frac{m_{N_2}}{\rho_{N_2}} = \frac{0.9952}{1.14513} = 0.869[m^3]$$

$$\text{The total volume: } V = V_{He} + V_{N_2} = 0.8984[m^3]$$

Q is the solute (Helium) injection rate (kg/s);

$$Q = 0.045[cm^3 / s](\rho_{He}) = 0.045 \times 10^{-6} [m^3 / s] \times 0.16359 [kg / m^3] = 7.36155 \times 10^{-9} [kg / s]$$

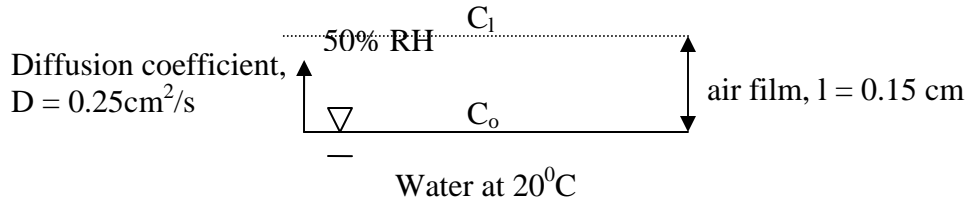
$$\text{Concentration of helium: } c_{He} = \frac{m_{He}}{V} = \frac{0.0048}{0.8984} = 5.3428 \times 10^{-3} [kg / m^3]$$

Since $c_{1,\max} = \frac{Q}{4\pi Dz}$, then the diffusion coefficient, D , is calculated as

$$D = \frac{Q}{4\pi z c_{1,\max}} = \frac{7.36155 \times 10^{-9}}{4\pi \times 0.01031 \times 5.3428 \times 10^{-3}} = 1.063 \times 10^{-5} [m^2 / s] = 1.063 \times 10^{-1} [cm^2 / s] =$$

0.11 cm²/s

Q1.) Water evaporating from a pond does so far as if it were diffusing across an air film 0.15cm thick. The diffusion coefficient of water in 20°C air is about 0.25 cm²/s. If the air out of the film is 50% saturated, how fast will the water level drop in a day?



C_o – concentration of water vapor at liquid surface (saturated condition) in terms of mol/m³

C_l – concentration of water vapor at 0.15cm away from water surface in terms of mol/m³

Water vapor concentration profile; $j = \frac{D}{l}(C_o - C_l)$ Unit for j is mol/m²s

Assume ideal gas law; $pV = nRT$, $C = \frac{n}{V} = \frac{P}{RT}$

$$C_o = \frac{P_o}{RT} = \frac{P_{sat}|_{20^{\circ}C}}{RT} = \frac{2.3388kPa}{8.314kJ/kg.mol.K(293K)} = 9.6 \times 10^{-4} mol/m^3$$

$$C_l = \frac{P_l}{RT} = \frac{0.5P_{sat}|_{20^{\circ}C}}{RT} = \frac{(0.5)2.3388kPa}{8.314kJ/kg.mol.K(293K)} = 4.8 \times 10^{-4} mol/m^3$$

Flux diffusion (in terms of mol/m²s);

$$j = \frac{D}{l}(C_o - C_l) = \frac{0.25 \times 10^{-4} m^2/s}{0.15 \times 10^{-2} m} (9.6 \times 10^{-4} - 4.8 \times 10^{-4}) mol/m^3 = 8 \times 10^{-6} mol/m^2s$$

Flux diffusion (in terms of kg/m²s)

$$= 0.018 kg/mol \text{ (weight of 1 mol liquid water)} \times 8 \times 10^{-6} mol/m^2s$$

$$= 1.44 \times 10^{-7} kg/m^2s.$$

Density of liquid water = 1000 kg/m³

Flux diffusion in terms of volume

$$= 1.44 \times 10^{-7} kg/m^2s / 1000 kg/m^3$$

$$= 1.44 \times 10^{-10} m^3/m^2s = 1.44 \times 10^{-10} m/s$$

$$= 1.44 \times 10^{-10} \times 24 \times 3600 \times 100 \text{ cm/day}$$

$$= 1.24 \times 10^{-3} \text{ cm/day}$$

Q2.)

$$\begin{aligned}\text{Thickness of oil layer} &= 25\text{\AA} \\ &= 25 \times 10^{-10} \text{ m} \\ &= 25 \times 10^{-10} \times 10^2 \text{ cm} \\ &= 2.5 \times 10^{-7} \text{ cm}\end{aligned}$$

$$\text{Resistance of oil layer} = 2\text{s/cm}$$

$$\text{Permeability of oil layer} = \mu = \frac{1}{R} = \frac{1}{2\text{s/cm}} = 0.5\text{cm/s}$$

The Franklin's oil layer can dissolve up to 1.8% water

Solubility of water in oil, $S = 0.018$

Estimate the diffusion coefficient across the oil layer

$$j = \frac{D}{l}(C_o - C_l) \text{ is analog to } I = \frac{V}{R}$$

$$\text{can be modified to become } \mu = \frac{D}{l}S$$

$$D = \frac{\mu l}{S} = \frac{0.5\text{cm/s}(2.5 \times 10^{-7})\text{cm}}{0.018} = 6.944 \times 10^{-6} \text{cm}^2/\text{s}$$