

**ME6203 MASS TRANSPORT
2004-2005**

HOME ASSIGNMENTS

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(5) Estimate the diffusion coefficient of lactic acid ($C_3H_6O_3$) under each of the following conditions:

(a) in air at room temperature and pressure

(b) in milk in the refrigerator

(c) through the wall of a plastic milk bottle

(a) $T = 25^\circ C = 298 K$ $P = 1 \text{ atm pressure}$

$$\tilde{M}_{air} = 29$$

$$\tilde{M}_{C_3H_6O_3} = (12 \times 3) + (1 \times 6) + (16 \times 3) = 90$$

$$V_{air} = 20.1 \text{ (from Table 5.1-4 [4])}$$

$$V_{C_3H_6O_3} = (16.5 \times 3) + (1.98 \times 6) + (5.48 \times 3) = 77.82 \text{ [1] (from Table 5.1-4 [4])}$$

Using Fuller correlation (Eq. 5.1-9 [4]),

$$D = \frac{10^{-3} T^{1.75} \left(\frac{1}{\tilde{M}_{air}} + \frac{1}{\tilde{M}_{C_3H_6O_3}} \right)^{1/2}}{P \left(V_{air}^{1/3} + V_{C_3H_6O_3}^{1/3} \right)^{1/2}}$$

$$= \frac{10^{-3} (298)^{1.75} \left(\frac{1}{29} + \frac{1}{90} \right)^{1/2}}{(1) \left[(20.1)^{1/3} + (77.82)^{1/3} \right]^{1/2}} \Rightarrow D \approx 1.73 \text{ cm}^2 / \text{sec}$$

Alternatively, the diffusion coefficient can be computed with the Chapman-Enskog theory. However, this is only applicable if the values of σ and ϵ are provided or easily found.

(b) Clearly, this is a problem involving diffusion through a liquid solvent and will utilize the Stokes-Einstein equation to estimate a value of the diffusion coefficient.

Stokes-Einstein equation:
$$D = \frac{k_B T}{6\pi\mu R_0}$$

Assuming the lactic acid is introduced into the milk via a gaseous form and solute radius R_0 is half the collision diameter in gas, i.e. $R_0 = 0.5\sigma$.

The difficulty arises here in obtaining the value of σ for lactic acid that is not listed in the table depicting Lennard-Jones potential parameters of different molecules. Thus our team assumes that lactic acid ($C_3H_6O_3$) adopts the properties of methyl acetate ($C_3H_6O_2$) in this case.

From Table 5.1-2 ^[4],

$$\begin{aligned}\sigma &= 4.936 \text{ \AA} \\ R_0 &= 0.5\sigma = 0.5(4.936) \\ R_0 &= 2.468 \times 10^{-8} \text{ cm} \\ \mu_{\text{milk}, T=12^\circ C} &= 0.002302 \text{ Pa.s} \quad [2] \\ \mu_{\text{milk}, T=0^\circ C} &= 0.002898 \text{ Pa.s}\end{aligned}$$

Assuming the temperature is constant at $4^\circ C$ in the refrigerator and viscosity adopts a linear relationship with temperature, we can interpolate to obtain the viscosity at $4^\circ C$.

$$\begin{aligned}\mu_{\text{milk}, T=4^\circ C} &= 0.002898 + \frac{4-0}{12-0} (0.002302 - 0.002898) \\ &= 0.002699 \text{ Pa.s} \\ &= 0.02699 \text{ g/cm s} \\ D &= \frac{k_B T}{6\pi\mu R_0} = \frac{(1.38 \times 10^{-16})(277)}{6\pi(0.02699)(2.468 \times 10^{-8})} \\ &= 3.04 \times 10^{-6} \text{ cm}^2 / \text{sec}\end{aligned}$$

- (c) For lactic acid diffusing through the wall of a plastic milk bottle, we deduced that this falls into the limiting case of low molecular weight solutes (lactic acid) in a concentrated polymer solvent (plastic wall). Based on the theoretical equations provided in *Cussler* ^[4], it is not possible to provide an estimate due to the numerous unknowns such as solute-polymer attractive energy, mass fractions and the free volume parameters.

In this situation, it may be more effective to resort to experimental procedures to obtain the value of the diffusion coefficient. Of the various methods, dynamic light scattering, which involves measuring the Doppler shift in scattered light, is best for polymers. In general, it can be taken that the

diffusion coefficient of lactic acid through the plastic wall will have an order of magnitude $10^{-8} \text{ cm}^2/\text{sec}$.

- (6) *In an experiment to determine the diffusion coefficient of urea in water at 25°C with the diaphragm cell, you find that a density difference of 0.01503 g/cm^3 decays to 0.01090 g/cm^3 after a time of 16 hours and 23 minutes. The cell's calibration constant is 0.397 cm^2 . If the density of these solutions varies linearly with concentration, what is the diffusion coefficient? Compare your answer with the value of $1.373 \times 10^{-5} \text{ cm}^2/\text{sec}$ obtained with the Gouy interferometer.*

Assumption: Density of solutions varies linearly with concentrations, i.e.

$$\rho \propto C.$$

Given parameters:

$$\beta = 0.397 \text{ cm}^2 \quad t = 16 \text{ hours } 23 \text{ minutes} = 58980 \text{ seconds}$$

$$(\rho_{\text{bottom}} - \rho_{\text{top}})_{\text{initial}} = 0.01503 \text{ g/cm}^3$$

$$(\rho_{\text{bottom}} - \rho_{\text{top}})_{\text{final}} = 0.01090 \text{ g/cm}^3$$

Using Eqn 5.5-1 ^[4],

$$\begin{aligned} D &= \frac{1}{\beta t} \ln \left[\frac{(C_{\text{bottom}} - C_{\text{top}})_{\text{initial}}}{(C_{\text{bottom}} - C_{\text{top}})_{\text{final}}} \right] = \frac{1}{\beta t} \ln \left[\frac{(\rho_{\text{bottom}} - \rho_{\text{top}})_{\text{initial}}}{(\rho_{\text{bottom}} - \rho_{\text{top}})_{\text{final}}} \right] \\ &= \frac{1}{(0.397)(58980)} \ln \left[\frac{0.01503}{0.01090} \right] \\ \Rightarrow D &\approx 1.37 \times 10^{-5} \text{ cm}^2 / \text{sec} \end{aligned}$$

Diffusion coefficient using Gouy interferometer, $D_G = 1.373 \times 10^{-5} \text{ cm}^2/\text{sec}$

$$\text{Percentage deviation} = \left| \frac{1.37 \times 10^{-5} - 1.373 \times 10^{-5}}{1.373 \times 10^{-5}} \right| = 0.22\%$$

It can be observed that the percentage deviation of the diffusion coefficient using the two methods is very small. Thus it can be safely suggested that it will be advisable to use the diaphragm cell to obtain an experimental value of the diffusion coefficient rather than the Guoy interferometer in view of the high costs and technical difficulties associated with the later method.

- (8) *Bermer has suggested that bubbles contained in amber represent air trapped 80 million years ago (Amber is a fossilized pine pitch). These bubbles contained thirty-two percent oxygen; Bermer concluded that this was the atmospheric composition at the time. Many objected to this. For example, Issac Asimov pointed out that forest fires would burn everything under these conditions. Hopfenberg objected to these results on other grounds. Bermer had reached his conclusion by crushing amber into 80-micrometer grains “to release the bubbles of air”. Hopfenberg claimed this merely releases oxygen dissolved in the amber in the twenty minutes of crushing. Bermer replied that amber is impermeable. What diffusion coefficient is implied by Hopfenberg’s argument? Is this value reasonable?*

The theory proposed by *Bermer* will indicate that the diffusion coefficient D of the amber has a zero value. *Hopfenberg* argued otherwise, suggesting that amber has the ability to dissolve and transport molecules.

Amber is understood to be a type of amorphous polymer. As illustrated by *Cussler*^[4], three different diffusion limits exist for polymers: namely polymer solute diffusing through a dilute solvent, a low molecular weight solutes in a concentrated polymer solvent and the diffusion of polymer solutes in polymer solvents. In this scenario, the second limiting case is applicable here with the amber serving as the concentrated solvent and air as the low molecular weight solute.

Research work undertaken by *Hopfenberg* also revealed that the diffusion coefficient of propane^[3] in amber falls in the region with magnitude of 10^{-12} cm^2/sec . Since the paper also suggested that the diffusion coefficients for small molecules in amorphous polymers decrease by more than ten orders of magnitude as molecular size of solute increases^[3], the diffusion coefficient of oxygen in amber implied by *Hopfenberg* in this case will be typically 4 orders of magnitude higher than of propane solutes. Thus the diffusion coefficient of oxygen in amber should be of the order 10^{-8} cm^2/sec . Since this value coincides with the general value of diffusion coefficient in the polymer phase

given by *Clusser*^[4], our team unanimously finds it to be reasonable. A more in-depth discussion will be undertaken during the class presentation.

References

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3. Harold B.Hopfenberg, Leonore C. Wilchey, George O. Poinar, etc., Is the Air in Amber Ancient?, Science, New Series, Vol. 241, No. 4866, pp. 717-721
4. Clusser, E. L. (2002). Diffusion, Mass Transfer in Fluid Systems, 2nd edition Cambridge University Press