CBE 548: Advanced Transport Phenomena II
Spring, 2010
Midterm

Problem 1. Basics of Mass Transfer

Consider diffusion in a binary, isothermal system. One can write Fick's law as

$$\mathbf{j}_A = -\rho D \nabla w_A \qquad \mathbf{j}_B = -\rho D \nabla w_B \tag{1.1}$$

where $\mathbf{j}_A = \rho w_A (\mathbf{v}_A - \mathbf{v})$ and $\mathbf{v} = w_A \mathbf{v}_A + w_B \mathbf{v}_B$.

(a) What three assumptions are implicit in this constitutive equation?

Now consider a different constitutive equation

$$\mathbf{J}_\mathbf{A}^* = -cD_{AB}^\circ \nabla w_A \qquad \mathbf{J}_\mathbf{B}^* = -cD_{BA}^\circ \nabla w_B \tag{1.2}$$

where $\mathbf{J*}_A = cx_A (\mathbf{v}_A - \mathbf{v*})$ and $\mathbf{v*} = x_A \mathbf{v}_A + x_B \mathbf{v}_B$.

(b) What is the relationship between D_{AB}° and D_{BA}°?
(c) What is the relationship between D_{AB}° and D?

Problem 1 Solution.

(a) What three assumptions are implicit in this constitutive equation?

1. The diffusive flux is a mass flux.
2. The driving force for diffusion is the gradient in the mass fraction.
3. Diffusion is measured relative to the center-of-mass velocity.

(b) What is the relationship between D_{AB}° and D_{BA}°?

The sum of the diffusive fluxes is zero.

$$\mathbf{J}_\mathbf{A}^* + \mathbf{J}_\mathbf{B}^* = 0$$

$$-cD_{AB}^\circ \nabla w_A - cD_{BA}^\circ \nabla w_B = 0$$

$$-cD_{AB}^\circ \nabla w_A + cD_{BA}^\circ \nabla w_A = 0$$

$$-D_{AB}^\circ + D_{BA}^\circ = 0$$

$$D^{\circ}_{AB} = D^{\circ}_{BA}$$

(c) What is the relationship between D°_{AB} and D?

$$\mathbf{j}_A = \rho w_A w_B \left(\mathbf{v}_A - \mathbf{v}_B\right) = -\rho D \nabla w_A$$

$$\mathbf{J*}_A = c x_A x_B \left(\mathbf{v}_A - \mathbf{v}_B\right) = -c D^{\circ}_{AB} \nabla w_A$$

$$\left(\mathbf{v}_A - \mathbf{v}_B\right) = \frac{-D\nabla w_A}{w_A w_B} = \frac{-D^{\circ}_{AB}\nabla w_A}{x_A x_B}$$

$$D^{\circ}_{AB} = \frac{x_A x_B}{w_A w_B} D$$

Problem 2. Traditional Methods of Estimating Diffusivities

For a single component gas, one can use kinetic theory to estimate the self diffusivity,

$$D_{self,A} = \frac{1}{3}\bar{u}\lambda \tag{2.1}$$

where the mean molecular speed, $\bar{u}$, is

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m_A}} \tag{2.2}$$

and where the mean free path, λ, is

$$\lambda = \frac{1}{\sqrt{2}\,\pi d_A^2 n} \tag{2.3}$$

where k_B is Boltzmann's constant, T is temperature, m_A is the mass of component A, d_A is the collision diameter of component A and n is the number density of component A.

These numbers may be useful:

k_B = 1.38066x10^{-23} J/K/molecule
N_{AV} = 6.02205x10^{23} molecule/mole
R = 8.31441 J/K/mole
1 amu = 1.66056x10^{-27} kg

name	molecular weight	collision diameter (Å)

bromine	159.82	4.268
helium	4.003	2.576

(a) Explain, from a molecular level point of view, the qualitative temperature and density dependence of the self diffusivity.
(b) What is the self-diffusivity of bromine at 400 K and 1 atm?
(c) At the same temperature and density, is the diffusivity of bromine higher or lower than that of helium?
(d) For a 50/50 molar mixture of bromine and helium, use kinetic theory to estimate the Fickian diffusivity at 400 K and 1 atm?

Problem 2 Solution:

(a) Explain, from a molecular level point of view, the qualitative temperature and density dependence of the self diffusivity.

The mean velocity is proportional to the square root of the temperature. This comes from the Maxwell-Boltzmann distribution of velocities. As the velocity (temperature) increases the diffusivity increases.

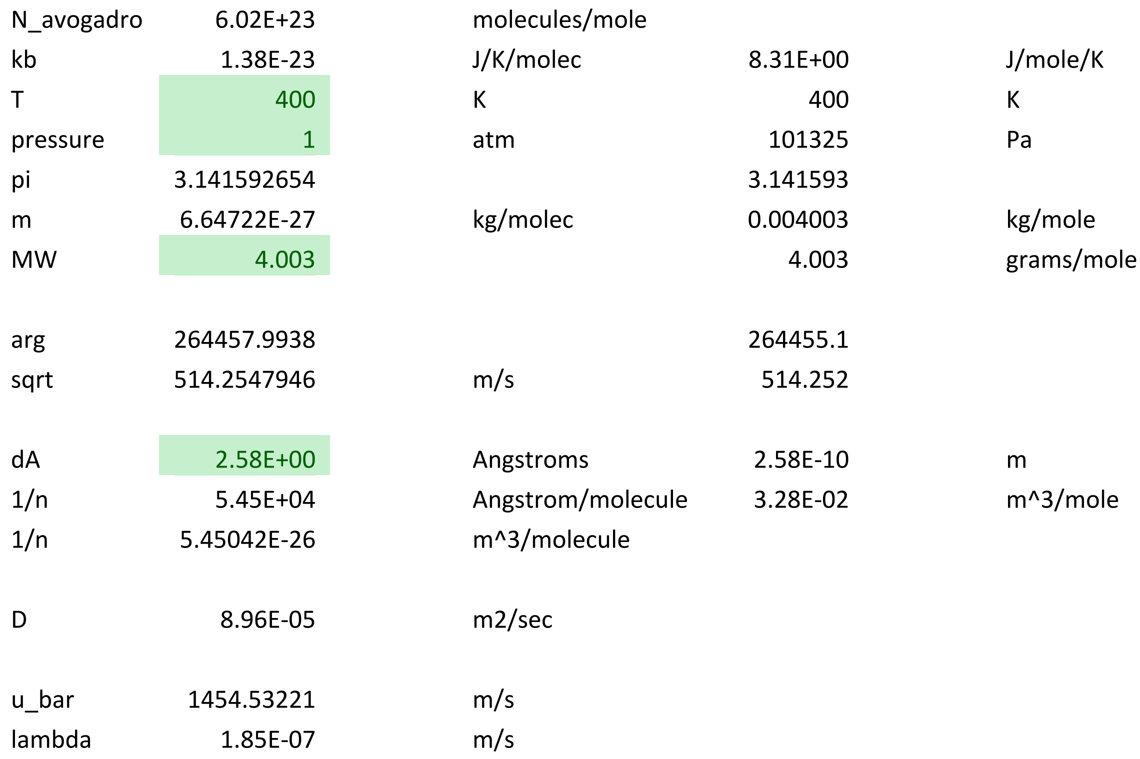
The mean free path is inversely proportional to the density. As the mean free path decreases, the diffusivity decreases.

(b) What is the self-diffusivity of bromine at 400 K and 1 atm?

N_avogadro	6.02E+23	molecules/mole		
kb	1.38E-23	J/K/molec	8.31E+00	J/mole/K
T	400	K	400	K
pressure	1	atm	101325	Pa
pi	3.141592654		3.141593	
m	2.65391E-25	kg/molec	0.15982	kg/mole
MW	159.82		159.82	grams/mole
arg	6623.860275		6623.789	
sqrt	81.38710141	m/s	81.38666	
dA	4.27E+00	Angstroms	4.27E-10	m
1/n	5.45E+04	Angstrom/molecule	3.28E-02	m^3/mole
1/n	5.45042E-26	m^3/molecule		
D	5.17E-06	m2/sec		
u_bar	230.1974852	m/s		
lambda	6.73E-08	m/s		

(c) At the same temperature and density, is the diffusivity of bromine higher or lower than that of helium?

As the molecular weight increases, diffusivity decreases. As collision diameter increases, diffusivity decreases. For both these reasons, bromine will have a lower diffusivity than helium. (Calculation for Helium below.)



N_avogadro	6.02E+23	molecules/mole		
kb	1.38E-23	J/K/molec	8.31E+00	J/mole/K
T	400	K	400	K
pressure	1	atm	101325	Pa
pi	3.141592654		3.141593	
m	6.64722E-27	kg/molec	0.004003	kg/mole
MW	4.003		4.003	grams/mole
arg	264457.9938		264455.1	
sqrt	514.2547946	m/s	514.252	
dA	2.58E+00	Angstroms	2.58E-10	m
1/n	5.45E+04	Angstrom/molecule	3.28E-02	m^3/mole
1/n	5.45042E-26	m^3/molecule		
D	8.96E-05	m2/sec		
u_bar	1454.53221	m/s		
lambda	1.85E-07	m/s		

(d) For a 50/50 molar mixture of bromine and helium, use kinetic theory to estimate the Fickian diffusivity at 400 K and 1 atm?

Several ways to work this problem. For ideal gas, use kinetic theory for self-diffusivity and Darken equation.

$$D_{FICK} = \left(\frac{\partial \ln a_A}{\partial \ln x_A}\right)_{T,p} \left(x_A D_{self,B} + x_B D_{self,A}\right) = \left(0.5 \cdot 8.96x10^{-5} + 0.5 \cdot 0.52x10^{-5}\right) = 4.7\ \mathrm{x}10^{-5}\ \mathrm{m^2/s}$$

The thermodynamic factor is unity for an ideal gas.

Problem 3. Generating Transport Properties from Molecular-Level Simulation

In homeworks 2 and 3, you used molecular dynamics simulation to generate self-diffusivities of pure fluids and mixtures in the gas and liquid states.

(a) In your own words, what are the three most significant weaknesses of using molecular simulation to generate transport properties?
(b) What are the three most significant strengths?

Problem 3 Solution.

(a) In your own words, what are the three most significant weaknesses of using molecular simulation to generate transport properties?

(1) The simulation is only as good as the potential. If the interaction potential used in the simulation is flawed, that flaw will be manifested in the results. IF a physical phenomena is a manifestation of a particular attribute, potentials which fail to include that attribute will not yield the observed phenomena. For example, if aggregation of molecules in the gas phase depends on a dipole moment and you use the Lennard-Jones potential to model the molecules, then you will not observe such aggregation.

(2) Due to computational constraints, molecular simulations are limited to short times. If the relaxation that gives rise to the diffusive process occurs over a timescale greater than a few ns, then molecular simulations cannot capture that behavior.

(3) Like any research technique, molecular simulations must be used carefully. Failure to analyze the results and make sure that physical constraints are satisfied (like energy conservation and momentum conservation) or failure to sufficiently equilibrate the system or run enough data production steps to reach the long-time limit required for diffusion coefficients will lead to unreliable results.

(b) What are the three most significant strengths?

(1) Molecular simulation is the most accurate method for estimating diffusivities, aside from direct experimental measurement. In some cases, it may be more reliable than experiment.

(2) Molecular simulation allows for you to incorporate effects such as the composition dependence of the diffusivity, which based on the information presented in BSL2 is not available from conventional methods for estimating the diffusivity.

(3) There are numerous physical constraints and validation checks that can be done in an MD simulation to make sure that the results that are being obtained conform to physical laws. When checked carefully, this can be used to provide additional reliability for the simulation results.