Uphill Diffusion

David Keffer
Department of Chemical and Biomolecular Engineering
University of Tennessee, Knoxville
April 22, 2010

Our exploration of "uphill diffusion", or diffusion of a species counter to its composition gradient, will take the form of an example. In this example, we will consider a three component fluid described by the van der Waals (vdW) equation of state (EOS).

I. van der Waals' Equation of State

As a reminder, the pressure, p, for the vdW EOS is

$$p = \frac{k_B T}{V_m - b_{mix}} - \frac{a_{mix}}{V_m^2} \tag{1}$$

where k_B is Boltmann's constant, T is temperature, V_m is the molecular volume, b_{mix} is the minimum molecular volume and a_{mix} is a parameter describing the mean field energetic attraction. For the vdW EOS, the mixture parameters are defined in terms of the pure component parameters as

$$b_{mix} = \sum_{i=1}^{N_c} x_i b_i \tag{2}$$

and

$$a_{mix} = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j a_{ij} \tag{3}$$

where N_c is the number of components in the system. Frequently the binary energetic parameters are defined in terms of the pure component energetic parameters

$$a_{ij} = \left(1 - k_{ij}\right)\sqrt{a_i a_j} \tag{4}$$

where k_{ij} is a binary interaction parameter, which is assumed to be zero when unknown. Equation (4) can be replaced by directly providing all a_{ij}. The chemical potential of component i in the vdW EOS is given by

$$\mu_i = -k_B T \ln\left(\frac{V_m - b_{mix}}{x_i \Lambda_i^3}\right) + \frac{k_B T b_i}{V_m - b_{mix}} - \frac{2}{V_m}\sum_{j=1}^{N_c} x_j a_{ij} \tag{5}$$

where we have assumed no internal structure in the molecule and Λ_i is the thermal deBroglie wavelength defined as

$$\Lambda_i \equiv \sqrt{\frac{h^2}{2\pi m_i k_B T}} \tag{6}$$

where h is Planck's constant and m_i is the mass of a molecule of component *i*.

II. Problem Statement

Consider a three component fluid located in an isothermal system between two boundaries. For this example, we will set all of the vdW *b* parameters (all b_i and consequently b_{mix}) to zero. (The conclusions of this example are valid regardless of whether the b parameters are zero or non-zero.) Furthermore, the values of the binary *a* parameters are as follows: $a_{11} = a_{22} = a_{33} = a_{13} = a_{23} = a_{31} = a_{32} = 0$, $a_{12} = a_{21} = 20$ Joules-m^3/mole^2. These a parameters indicate that components 1 and 2 have a attractive interaction with each other. All other pairs of components have no such interaction.

For a three component system, the Gibbs' Phase Rule tells us that we have four degrees of freedom to define the thermodynamic state.

$$\text{DOF} = N_C - N_P + 2 = 3 - 1 + 2 = 4 \tag{7}$$

The thermodynamic state of the boundary at z = 0 is defined by the mole fraction of 1, $x_1 = 0.25$, mole fraction of 2, $x_2 = 0.74$, temperature T = 300 K, and pressure p = 1 bar. The thermodynamic state of the boundary at z = 1 m is defined by the mole fraction of 1, $x_1 = 0.2$, mole fraction of 3, $x_3 = 0.79$, temperature T = 300 K, and pressure p = 1 bar.

III. Problem Analysis

Task 1. Using a finite difference formula, determine the average mole fraction gradients for each component, based on the boundary values.

$$\overline{\left(\frac{\partial x_1}{\partial z}\right)} = \frac{x_1(z=1) - x_1(z=0)}{1} = 0.2 - 0.25 = -0.05\, m^{-1} \tag{8.1}$$

$$\overline{\left(\frac{\partial x_2}{\partial z}\right)} = \frac{x_2(z=1) - x_2(z=0)}{1} = 0.01 - 0.74 = -0.73\, m^{-1} \tag{8.2}$$

$$\overline{\left(\frac{\partial x_3}{\partial z}\right)} = \frac{x_3(z=1) - x_3(z=0)}{1} = 0.79 - 0.01 = 0.78\, m^{-1} \tag{8.3}$$

Task 2. Based on the sign of the mole fraction gradients, in which direction would you expect the diffusive flux of each species to be?

One would expect that species diffuse from high mole fraction to low mole fraction.

Component 1 would move to the boundary at z = 1.
Component 2 would move to the boundary at z = 1.
Component 3 would move to the boundary at z = 0.

Task 3. Using a finite difference formula, determine the average chemical potential gradients for each component, based on the boundary values.

The chemical potential expressions are

$$\mu_1 = -k_B T \ln\left(\frac{V_m}{x_1 \Lambda_1^{\,3}}\right) - \frac{2}{V_m} x_2 a_{12} \tag{9.1}$$

$$\mu_2 = -k_B T \ln\left(\frac{V_m}{x_2 \Lambda_2^{\,3}}\right) - \frac{2}{V_m} x_1 a_{21} \tag{9.2}$$

$$\mu_3 = -k_B T \ln\left(\frac{V_m}{x_3 \Lambda_3^{\,3}}\right) \tag{9.3}$$

To compute the chemical potentials, we will require the molecular volumes. The easiest way to determine the molecular volumes from the vdW EOS is to rearrange the expression for pressure given in equation (1) into a cubic polynomial in the molecular volume.

$$pV_m^3 - \left(k_B T + pb_{mix}\right)V_m^2 + a_{mix}V_m - a_{mix}b_{mix} = 0 \tag{10}$$

Then solve for the three roots of the cubic polynomial. For the simplified case where b_{mix} is zero, one of the roots is zero and the other roots are the solution to the quadratic equation,

$$pV_m^2 - k_B T V_m + a_{mix} = 0 \tag{11}$$

which are

$$V_m = \frac{k_B T \pm \sqrt{\left(k_B T\right)^2 - 4pa_{mix}}}{2p} \tag{12}$$

The stable vapor root corresponds to the root with the positive sign. The roots at the two boundaries are $V_m = 3.515\text{x}10^{-26}$ m^3/molecule at z = 0 and $V_m = 4.082\text{x}10^{-26}$ m^3/molecule at z = 1.

The average chemical potential gradients are

$$\overline{\left(\frac{\partial \mu_1}{\partial z}\right)} = \frac{\mu_1(z=1) - \mu_1(z=0)}{1} =$$

$$= -k_B T \ln\left(\frac{V_m(z=1)}{x_1(z=1)\Lambda_1^{\,3}}\right) - \frac{2x_2(z=1)}{V_m(z=1)}a_{12} + k_B T \ln\left(\frac{V_m(z=0)}{x_1(z=0)\Lambda_1^{\,3}}\right) + \frac{2x_2(z=0)}{V_m(z=0)}a_{12} \qquad (13.1)$$

$$= k_B T \ln\left(\frac{V_m(z=0)x_1(z=1)}{V_m(z=1)x_1(z=0)}\right) + 2a_{12}\left(\frac{x_2(z=0)}{V_m(z=0)} - \frac{x_2(z=1)}{V_m(z=1)}\right)$$

$$\overline{\left(\frac{\partial \mu_2}{\partial z}\right)} = k_B T \ln\left(\frac{V_m(z=0)x_2(z=1)}{V_m(z=1)x_2(z=0)}\right) + 2a_{21}\left(\frac{x_1(z=0)}{V_m(z=0)} - \frac{x_1(z=1)}{V_m(z=1)}\right) \qquad (13.2)$$

$$\overline{\left(\frac{\partial \mu_3}{\partial z}\right)} = k_B T \ln\left(\frac{V_m(z=0)x_3(z=1)}{V_m(z=1)x_3(z=0)}\right) \qquad (13.3)$$

Numerical evaluation yields

$$\overline{\left(\frac{\partial \mu_1}{\partial z}\right)} = 7.509\text{x}10^{-22} \text{ J/molecule/m} \qquad (14.1)$$

$$\overline{\left(\frac{\partial \mu_2}{\partial z}\right)} = -1.081\text{x}10^{-20} \text{ J/molecule/m} \qquad (14.2)$$

$$\overline{\left(\frac{\partial \mu_3}{\partial z}\right)} = 1.748\text{x}10^{-20} \text{ J/molecule/m} \qquad (14.3)$$

Task 4. Based on the sign of the chemical potential gradients, in which direction would you expect the diffusive flux of each species to be?

One would expect that species diffuse from high chemical potential to low chemical potential.

Component 1 would move to the boundary at z = 0.

Component 2 would move to the boundary at z = 1.

Component 3 would move to the boundary at z = 0.

Task 5. Based on your conclusions in Tasks 2 and 4, which fluxes will one actually observe, those given in Task 2 or Task 4? Why?

One will observe the fluxes predicted in Task 4, because Task 4 is based on the thermodynamic driving force for diffusion. Following the chemical potential gradient will lead the system to a lower free energy. Here, because component 1 interacts more favorably with component 2 than it does with component 3, the advantage of the energetic driving force outweighs the disadvantage of the entropic driving force associated with going up a concentration gradient.

Task 6. What is the common term given to the transport phenomena exhibited by one of the components?

Component one will display “uphill diffusion”, where it diffuses up the concentration gradient.

Task 7. Name a chemical engineering unit operation in which this transport phenomena is frequently exploited.

In liquid-liquid extraction, a good solvent is used to extract a solute from a less good solvent. The goodness of a solvent is really an indicator of the chemical potential of the solute in that solvent. Thus, one can extract a solute to a higher concentration in the good solvent than was originally present in the less good solvent, due to the overall reduction in free energy.

Task 8. What is the thermodynamic condition for uphill diffusion in this system.

Uphill diffusion will occur when the gradient for the chemical potential of species 1 is positive. Thus we take equation (13.1) and set it greater than 0.

$$\overline{\left(\frac{\partial \mu_1}{\partial z}\right)} = k_B T \ln\left(\frac{V_m(z=0)x_1(z=1)}{V_m(z=1)x_1(z=0)}\right) + 2a_{12}\left(\frac{x_2(z=0)}{V_m(z=0)} - \frac{x_2(z=1)}{V_m(z=1)}\right) > 0 \tag{15}$$

$$a_{12} > \frac{-\frac{k_B T}{2}\ln\left(\frac{V_m(z=0)x_1(z=1)}{V_m(z=1)x_1(z=0)}\right)}{\left(\frac{x_2(z=0)}{V_m(z=0)} - \frac{x_2(z=1)}{V_m(z=1)}\right)} \tag{16}$$

Remember in this solution that the molar volume that appears on the RHS is a function of the choice of a_{12}. Solving iteratively yields for this example $a_{12} > 11.8$ Jm^3/mole^2.

Matlab Code Used in This Example

```
close all;
clear all;
format long e;
%
%  parameters
%
kB = 1.38066e-23; % J/mol
Nav = 6.022e23;
T = 300; % K
p = 101325; % Pa
a12 = 20.0; % J-m^3/mole^2
a12 = a12/Nav^2; % J-m^3/molecule^2
a21 = a12;
bmix = 0;
%
% boundary one (z=0)
%
x10 = 0.25;
x20 = 0.74;
x30 = 1 - x10 - x20;
amix = x10*x20*a12 + x20*x10*a21;
Vm0 = (kB*T + sqrt( (kB*T)^2 - 4*p*amix) )/(2*p)
%Vm2 = (kB*T - sqrt( (kB*T)^2 - 4*p*amix) )/(2*p)
%
% boundary two (z=1)
%
x11 = 0.2;
x31 = 0.79;
x21 = 1 - x11 - x31;
amix = x11*x21*a12 + x21*x11*a21;
Vm1 = (kB*T + sqrt( (kB*T)^2 - 4*p*amix) )/(2*p)
%Vm2 = (kB*T - sqrt( (kB*T)^2 - 4*p*amix) )/(2*p)
%
%  mole fraction gradients
%
gradx1 = x11 - x10
gradx2 = x21 - x20
gradx3 = x31 - x30
%
%  chemical potential gradients
%
gradmu1 = kB*T*log( (Vm0*x11)/(Vm1*x10) ) + 2*a12*( x20/Vm0 - x21/Vm1 )
gradmu2 = kB*T*log( (Vm0*x21)/(Vm1*x20) ) + 2*a21*( x10/Vm0 - x11/Vm1 )
gradmu3 = kB*T*log( (Vm0*x31)/(Vm1*x30) )
%
%  thermodynamic criteria for uphill diffusion of component 1
%
a12min = -0.5*kB*T*log( (Vm0*x11)/(Vm1*x10) ) / ( x20/Vm0 - x21/Vm1 );
a12min = a12min*Nav*Nav % J*m^3/mole^2
```