Simple Mixtures

Chapter 7 of Atkins: Sections 7.1-7.3

Thermodynamic Description of Mixtures

Partial Molar Quantities
- Partial Molar Volume
- Partial Molar Gibbs Energies
- Significance of Chemical Potential
- Gibbs-Duhem Equation

Thermodynamics of Mixing
- Gibbs Energy of Mixing
- Other Thermodynamic Mixing Functions

Chemical Potentials of Liquids
- Ideal Solutions
- Ideal Dilute Solutions
Simple Mixtures

We now go from the behavior of simple single substance systems to mixtures of substances. In general, these will still be **non-reacting substances** and we will be dealing mostly with the energetics of the mixing process itself and to a lesser extent with the types of nonideal interactions which can take place between different substances. We will also start to learn how to deal with liquid solutions, which will greatly increase our arsenal of systems that we know how to deal with.

Mainly, we will deal with non-reactive **binary mixtures**, which have components A and B, making use of the relation:

\[ x_A + x_B = 1 \]

We have already used such **mole fractions** to describe the partial pressures of mixtures of gases which give rise to a total pressure

\[ p_A + p_B + \phi C = (x_A + x_B + \phi C)p = p \]
The **partial molar volume** is the contribution that one component in a mixture makes to the total volume of a sample.

Add 1.0 mol H₂O

Volume increases by 18 cm³ mol⁻¹

Molar volume of H₂O: 18 cm³ mol⁻¹

Partial molar volume of H₂O in EtOH: 14 cm³ mol⁻¹

The different increase in total volume in the H₂O/ EtOH example depends on the identity of the molecules that surround the H₂O - EtOH molecules pack around the water molecules, increasing the volume by only 14 cm³ mol⁻¹.

Partial molar volume of substance A in a mixture is the change in volume per mole of A added to the large volume of the mixture.
Partial Molar Volume, 2

The **partial molar volume** of components of a mixture vary as the mixture goes from pure A to pure B - that is because the molecular environments of each molecule change (i.e., packing, solvation, etc.)

Partial molar volumes of a water-ethanol binary mixture are shown at 25° C across all possible compositions.

The partial molar volume, \( V_J \), of a substance \( J \) is defined as

\[
V_J = \left( \frac{\partial V}{\partial n_J} \right)_{p,T,n'}
\]

where \( n' \) signifies that all other substances present are constant.
Partial Molar Volume, 3

The **partial molar volume** is the slope of a plot of total volume as the amount of J in the sample is changed (volume vs. composition).

For a binary mixture, the composition can be changed by addition of \( dn_A \) of A and \( dn_B \) of B, with the total volume changing by

\[
dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B
\]

\[
= V_A dn_A + V_B dn_B
\]

If partial molar volumes are known for the two components, then at some temperature T, the total volume \( V \) (state function, always positive) of the mixture is

\[
V = n_A V_A + n_B V_B
\]

Partial molar volumes vary with composition (different slopes at compositions \( a \) and \( b \)) - in example above partial molar volume at \( b \) is negative (i.e., the overall sample volume decreases as A is added)
Partial Molar Volume, 4

The partial molar volume (which can be positive or negative) can be measured by fitting the observed volume (as function of composition) using a curve fitting program (find the parameters that give the best fit of a particular function to the experimental data).

If the function is found, the slope at any point (any composition) can be determined by differentiation; for example, if $V$ has the following functional form:

$$V = A + Bn_A + C(n_A^2 - 1)$$

with constants $A$, $B$ and $C$ then the partial molar volume of $A$ at any composition is

$$V_A = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} = B + 2Cn_A$$

and the partial molar volume of component $B$ is obtained by rearranging

$$V = n_A V_A + n_B V_B$$

so that

$$V_B = \frac{V - n_A V_A}{n_B} = \frac{A - (n_A^2 - 1)C}{n_B}$$
The concept of **partial molar quantity** can be applied to **any extensive state function**. For example, for a pure substance in a mixture, the chemical potential can be defined as the **partial molar Gibbs energy**

$$\mu_J = \left( \frac{\partial G}{\partial n_J} \right)_{p,T,n'}$$

So chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest, $J$

Total Gibbs energy is

$$G = n_A \mu_A + n_B \mu_B$$

where $\mu_i$ are chemical potentials for that particular composition of the mixture

Each individual chemical potential of the substances in a mixture make a contribution to the total Gibbs energy of the substance
Gibbs energy depends on composition, pressure and temperature (so, $G$ may change if any of these variables change - which they may!) For a system with components A, B, ...

$$dG = V dp - S dT + \mu_A dn_A + \mu_B dn_B + \Delta$$

which is the fundamental equation of classical thermodynamics

**At constant temperature and pressure,**

$$dG = \mu_A dn_A + \mu_B dn_B + \Delta$$

In Chapter 4, we saw that under these conditions, $dG = dw_{e,\text{max}}$ (the maximum non-expansion work)

$$dw_{e,\text{max}} = \mu_A dn_A + \mu_B dn_B + \Delta$$

What does this mean? Non-expansion work can happen just from changing system composition at constant pressure and temperature (e.g., **battery**, chemical rxn in two sites called **electrodes**, and the work the battery produces comes from reactants going to products)
More on Chemical Potential

Chemical potential tells us even more than just about variation in $G$

$$G = U + pV - TS$$

so for an infinitesimal change in $U$, we can write

$$dU = -pdV - Vdp + SdT + TdS + dG$$

$$= -pdV - Vdp + SdT + TdS + (Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \mathcal{L})$$

$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \mathcal{L}$$

and at constant volume and entropy

$$dU = \mu_A dn_A + \mu_B dn_B + \mathcal{L}$$

and if that’s not enough...what about $H$ and $A$? These too also depend upon the composition of a mixture! **Chemical potential is IMPORTANT!**

$$\mu_j = \left( \frac{\partial U}{\partial n_j} \right)_{S,V,n'}$$

and

$$\mu_j = \left( \frac{\partial H}{\partial n_j} \right)_{S,p,n'}$$

and

$$\mu_j = \left( \frac{\partial A}{\partial n_j} \right)_{T,V,n'}$$
Gibbs - Duhem Equation

Since \( G = n_A \mu_A + n_A \mu_A \) and \( \mu_j \) depend on composition, for a binary mixture \( G \) may changed by

\[
dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B
\]

But at constant temperature and pressure, since \( G \) is a state function, and we have already shown that

\[
dG = \mu_A dn_A + \mu_B dn_B
\]

so:

\[
n_A d\mu_A + n_B d\mu_B = 0
\]

This special case holds for multiple components, and is the **Gibbs- Duhem equation**

\[
\sum_j n_j d\mu_j = 0
\]

So, for our binary mixture, if one partial molar quantity increases, the other must decrease

\[
d\mu_B = -\frac{n_A}{n_B} d\mu_A
\]

This holds for all partial molar quantities - in binary mixtures, the partial molar quantity of one component can be determined from measurements of the other