# Lecture 5

## Chemical Thermodynamics

Pease read Ch2,Ch3 (White)

- Mixtures
- Chemical Potential
- Non ideality in gasses and aqueous mixtures



# Thermodynamics of Chemical Mixtures

## Partial Molar Quantities and Chemical Potential

Many thermodynamic properties like G depend on composition, which can be expressed in a multi-component system with a *partial molar value*.

The *partial molar value* expresses how that property (volume, pressure, enthalpy, entropy) depends on changes in amount of one component

For example, we can define the partial molar volume of component *a* in phase *ph* as:

$V_a^{ph} = dV/dn_a$ (at constant T, P) such that $V^{ph} = \sum_i V_a/n_a$

## Thermodynamics of Chemical Mixtures

**Partial Molar Volume** is useful for understanding the properties of mixtures.

Let's say we wanted to know how much space is occupied by 1 mole of **calcite**, $CaCO_3$, *versus*
1 mole of **dolomite**, $CaMg[CO_3]_2$, in a limestone formation.

Or we might want to estimate volume changes in a magma if 1 mole of pure forsterite $Mg_2SiO_4$ was turned into 1 mole of 80% forsterite mixed with 20% fayalite, often abbreviated as $Fo_{80} = (Mg_{0.8}Fe_{0.2})_2SiO_4$.

http://commons.wikimedia.org/wiki/File:Forsterite-Olivine-4jg54a.jpg

The **partial molar volumes** of the components in these systems would give us the answer.

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## Thermodynamics of Chemical Mixtures

**Chemical Potential** is ***Partial Molar Gibbs Free Energy***. It is another useful property for understanding mixtures.

**Chemical Potential,** written as **$\mu$,** is change in Gibbs free energy relative to change in a particular component. It is a measure of Free energy change with compositional change.

For all components "i", the finite change version of **$\mu$** is:

$$\boxed{\Sigma\mu_i \cdot \Delta n_i = \Delta G \text{ at constant T, P}}$$

for one component "a" and at $n_{other}$ = constant, this becomes

$$\boxed{\mu_a \cdot \Delta n_a = \Delta G \quad \text{or} \quad \mu_a = \Delta G/\Delta n_a}$$

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## Thermodynamics of Chemical Mixtures

**Chemical Potential** is useful for:

1. *describing open systems*, in which the number moles of at least one component is not fixed due to exchange with the surroundings.

2. *studying mixtures and solutions:*
**$\mu$** provides a means for determining the **G** of a solution relative to the pure components it is made from.

In a closed system at equilibrium, $\boxed{\Sigma\mu_i \cdot \Delta n_i = 0}$



## Thermodynamics of Chemical Mixtures

**Chemical Potential $\mu_i$** applies even when the system lacks "pure" phases:

For example:
a. with minerals that are solid solutions or have substitutions
b. gas phase mixtures
c. liquid mixtures
d. solutes in water

## Thermodynamics of Chemical Mixtures

$\mu_i$ can also be used to look at the exchange of one component between multiple phases of a *closed system.*

*Example 1:* small amounts of Ar in the atmosphere and oceans...

$\boxed{\mu_{Ar}^{atm} \cdot \Delta n_{Ar}^{atm} + \mu_{Ar}^{ocean} \cdot \Delta n_{Ar}^{ocean} = 0}$ (at equilibrium)

Which because $\Delta n_{Ar}^{atm} = -\Delta n_{Ar}^{ocean}$ reduces to

$\mu_{Ar}^{ocean} / \mu_{Ar}^{atm} = 1$, from which we can derive Henry's Law

($K = P_{Ar}^{atm} / conc_{Ar}^{ocean}$)



## Thermodynamics of Chemical Mixtures

$\mu_i$ can also be used to look at the exchange of one component between multiple phases of a *closed system.*

*Example 2:* Rb in plagioclase and clinopyroxene - two minerals typically found in a basalt

$\mu_{Rb}^{plag} \cdot \Delta n_{Rb}^{plag} + \mu_{Rb}^{cpx} \cdot \Delta n_{Rb}^{cpx} = 0$ which rearranges to...

$\mu_{Rb}^{plag} \cdot \Delta n_{Rb}^{plag} = -\mu_{Rb}^{cpx} \cdot \Delta n_{Rb}^{cpx}$

at equilibrium, $\Delta G = \Delta G_{Rb}^{plag} + \Delta G_{Rb}^{cpx} = 0$ and chemical exchange between these two phases should be balanced.

Thus, $\Delta n_{Rb}^{plag} = -\Delta n_{Rb}^{cpx}$ which leads to $\boxed{\mu_{Rb}^{plag} = \mu_{Rb}^{cpx}}$

Which can be used to write something called a partition coefficient equation for Rb exchange between the minerals

## Thermodynamics of Chemical Mixtures

$\mu_i$ can also be used to examine multiple components of a single phase

(i.e., Rb, Sr, Ba and K in a basaltic plagioclase).

Initially, we'd try to treat this system as an ideal mixture…

*ideal mixtures are ones where the components behave in fractional proportions to how they would in pure substances – in other words, there is no energy effect of the interaction of the ideal components.*

In general, for systems of "i" ideal components...

$$\boxed{\mu_i = \mu_i^* + RT\ \ln X_i}$$

where $\mu_i^*$ is the chemical potential at pure i ($X_i$ = 1) and $X_i$ is the mole fraction of component i (e.g., $X_i = n_i/n_{tot}$)



## Non-Ideality in Chemical Mixtures

What if materials in mixtures do not behave ideally?

### Non-Ideality in Solutions of Gasses

Ideal gasses are those whose individual molecules or atoms do not interact with each other in the gas phase.

In this case, the partial pressure of any species i can be related to the total pressure:

$$P_i = X_i P_{Total}$$

Chemical potential for an ideal gas can be expressed as

$$\mu_i = \mu_i^* + RT\ \ln P_i$$

## Non-Ideality in Chemical Mixtures

**Gasses do not behave ideally** in most geologically relevant systems. Instead, they have an effective pressure, known as the ***Fugacity*, F**

Typically $F_i < P_i$

*Fugacity* and pressure are related by a **non ideality factor** known as a fugacity coefficient $\gamma_i$

$$F_i = \gamma_i P_i$$

Typically, $\gamma_i$ gets lower as $P_{total}$ increases (note: $\gamma_i = 1$ in an ideal gas; Many gasses behave close to ideally at low P).



## Non-Ideality in Chemical Mixtures

We deal almost exclusively with F instead of P in geologic settings with high pressure, such as:

- ☛ igneous bodies in the mantle or crust
- ☛ metamorphism of crustal rocks
- ☛ high pressure geothermal fluids

In these systems, the weight of the crust above where bond re-organization and phase change reactions are taking place creates very high *lithostatic pressures*. Experiments in the lab designed to mimic natural systems typically measure F.

We will not discuss the specifics of gas phase non-ideality in this class.

It is important only to know that F is a measure of effective P and that the divergence between F & P is a function of pressure.

## Non-Ideality in Chemical Mixtures

### Non-Ideality in ionic aqueous solutions

Solute activities (apparent concentrations) in aqueous solutions typically differ from their "real" concentrations due to solute-solute and solute-solvent interaction in solution.

Thus, we need to make similar modification to the chemical potential equation for ideal solutes as we made for ideal gasses in equations like:

$$\mu_i = \mu_i^* + RT \ln X_i$$

The effective concentration of a solute is known as ***activity***. It is denoted as $a_i$. ***Activity*** is related to molarity or molality by an activity coefficient, $\gamma_i$, such that:

$$a_i = \gamma_i m_i$$

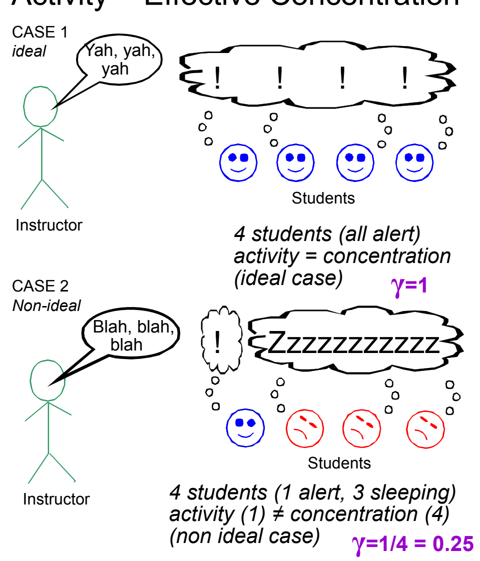


## Non-Ideality in Chemical Mixtures

What do we really mean by "activity", or "apparent concentration"?

This example should help to illustrate the point…

Activity = Effective Concentration



## Non-Ideality in Chemical Mixtures

In aqueous systems, it is relatively easy to develop a theory of non-ideality for ionic species, where **non-ideality** usually results from charge (couloumbic) interactions between different solutes and with the solvent.

We use something called the ***Ionic Strength*** of the solution to help determine the level of couloumbic interactions.

Ionic Strength, **I**, is defined as $\boxed{I = \frac{1}{2} \Sigma m_i z_i^2}$, where

$m_i$ = ion molality of species i $z_i$ = ion charge of species i

e.g., $I_{\text{sea water}} \sim 0.7$ $I_{\text{average rivers}} \sim 0.1$



## Non-Ideality in Chemical Mixtures

Ion interaction at high **I** causes the effective molality or molarity to differ from that expected of the true number of moles of solute in solution.

This has a very real effect of important mineral solubilities in natural waters, such as that of $CaCO_3$.

At low I $K_{sp} = m_{Ca2+} \cdot m_{CO3\ 2-}$
At high I $K_{sp} < m_{Ca2+} \cdot m_{CO3\ 2-}$ because...

$K_{sp} = a_{Ca2+} \cdot a_{CO3\ 2-}$ and $a_i < m_i$

In fact, non-ideality allows there to actually be about 3 times more $Ca^{2+}$ and $CO_3^{2-}$ ions in solution than predicted by $K_{sp}$ and the ideal solute molalities.

## Non-Ideality in Chemical Mixtures

Just what is $\gamma_i$?
It is a quantification of the non-ideality of a solute in a solvent.

In aqueous solutions, non-ideality is a result of:

- ☼ charge interactions/ion charge
- ☼ ion diameter
- ☼ charge stabilizing capability of the solvent (the dielectric constant)
- ☼ other ionic solutes present



## Non-Ideality in Chemical Mixtures

what causes this non-ideality and what is $\gamma_i$ really?

It is a measure of phenomena that take ions **"out of action"** because they are busy doing something else, so that they do not act like a "free" ion.

These phenomena include charge interactions between ions in solution and ion pairing.

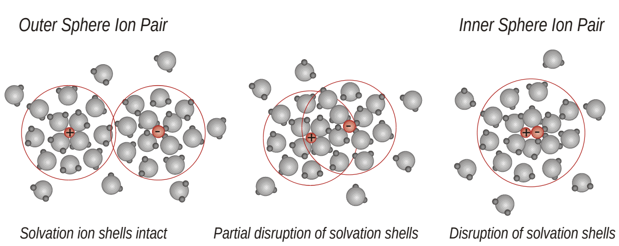



Figure 4.28. In formation of ion pairs, the solvation shells may remain intact or be partially or totally disrupted. The former results in an outer sphere ion pair, the latter results in an inner shere ion pair. *From White, "Geochemistry"*

Ion pairs keep ions busy, lowering the "free" ion activity in high-I aqueous solutions.

## Non-Ideality in Chemical Mixtures

For instance, in a solution of $CaCl_2$ and $MgSO_4$ at high ionic strength, we find...

*a. pure ions*: $Ca^{2+}$, $Cl^-$, $Mg^{2+}$, $SO_4^{2-}$, $HSO_4^-$ (and of course $H^+$ and $OH^-$). – *Remember, these "free" ions are actually hydrated.*

*b. ion pairs*: $MgCl^+$, $CaCl^+$, $MgCl_2^0$, $CaCl_2^0$, $MgSO_4^0$, $CaSO_4^0$ (Plus much lesser concentrations of these ion pairs from the ions of water dissociation: $MgOH^-$, $CaOH^-$, $Mg(OH)_2^0$, $Ca(OH)_2^0$, $HCl^0$, $HSO_4^-$ and $H_2SO_4^0$).

*Note:*
An ion pair such as $Mg(Cl)_2^0$ is different from the ionically bonded compound $Mg(Cl)_2$. In the ion pair, the ions move together as a loosely-affiliated unit but they are not at a close enough interionic distance to be considered a compound.



## Non-Ideality in Chemical Mixtures

$\gamma_i$ is not predicted from thermodynamic theory of ideal solutions.

Instead, $\gamma_i$ is parameterized empirically by matching ion behaviors in known non-ideal solutions.

The simplest parameterization is known as Debye-Hückel theory and is based on the simplest Coulombic electric field arguments.

$$-\log \gamma_i = A z_i^2 I^{1/2}$$

where z = ion charge, I = Ionic Strength and A is a temperature dependent constant related to the solvent dielectric constant. A ~ 0.5 for water at 25°C.

# Non-Ideality in Chemical Mixtures

For <u>ionic solutes in water</u> up to moderate ionic strength, activity is lower than ideal as a result of ion-ion interactions.

At most natural ionic strength, these ions are more soluble than the ideal case.

For <u>neutral (non-charged) molecules in water</u>,

$\log \gamma_i = k_i I$, where k is the dielectric constant.

At most natural ionic strength, these molecules are less soluble than the ideal case.

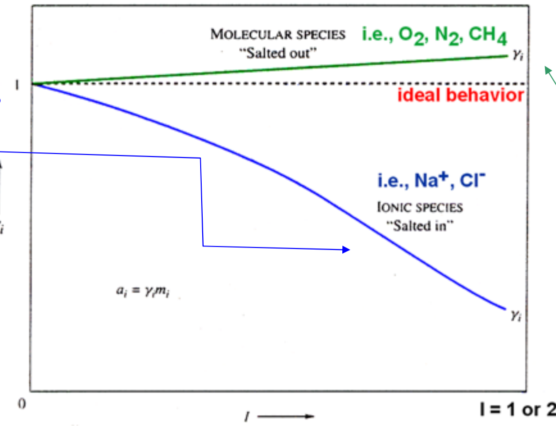



**Figure 4.6** Schematic plot showing the "salting in" ($\gamma < 1$) and "salting out" ($\gamma > 1$) behavior of ionic and molecular species.
*modified from Langmuir, "aqueous environmental chemistry" (1997)*



# Non-Ideality in Chemical Mixtures

ionic solutes in water:.

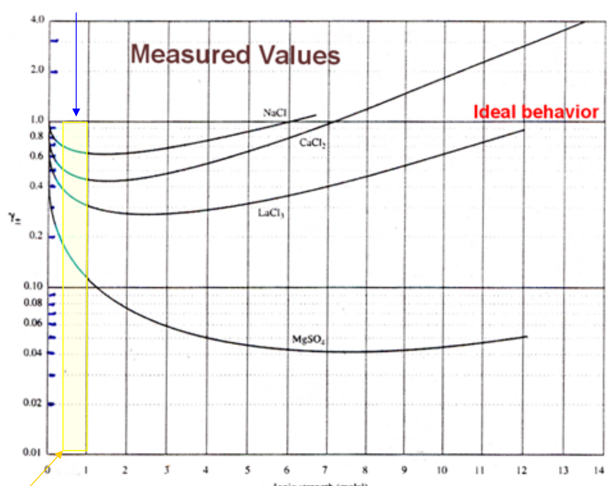



**Figure 4.1** Mean ion activity coefficients of several salts as a function of ionic strength. Data are from Robinson and Stokes (1970).
*from Langmuir, "aqueous environmental chemistry" (1997)*

Range of most rivers and seawater