

Lecture 5

Chemical Thermodynamics

Please read chapter Ch3,Ch4 (McSween et al.)

-or- Ch2,Ch3 (White) – *most detailed*

-or- Ch3 (Brownlow) – *most general*

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

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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 p as:

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

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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** ($\text{CaMg}[\text{CO}_3]_2$) in an outcrop of limestone.

Or we might want to know how volume in a magma chamber might change if 1 mole of pure forsterite Mg_2SiO_4 was turned into 1 mole of forsterite mixed with 20% fayalite ($\text{Mg}_{0.8}\text{Fe}_{0.2}$) $_2\text{SiO}_4$ -- often abbreviated as Fo_{80} .

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 μ , 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 μ is:

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

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

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

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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*:
 μ 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,

$$\sum \mu_i \cdot \Delta n_i = 0$$

Thus μ_i applies even when the system lacks "pure" phases (e.g., minerals with solid solution or substitution, gas phase mixtures, liquid mixtures, solutes in water, etc..).

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Thermodynamics of Chemical Mixtures

μ_i can also be used to look at one component in multiple phases of a *closed system*.

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

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

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

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

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

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

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

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Thermodynamics of Chemical Mixtures

μ_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 abundance-fractional proportions to how they would in pure substances – in other words, there is no energy effect of interaction between ideal components.

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

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

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

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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:

$$P_i = X_i P_{\text{Total}}$$

Chemical potential for an ideal gas can be expressed as

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

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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 γ_i

$$F_i = \gamma_i P_i$$

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

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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 the two is a function of pressure.

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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, γ_i , such that:

$$a_i = \gamma_i m_i$$

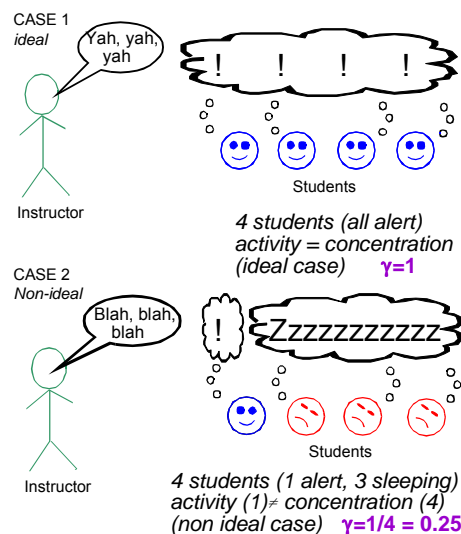
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Non-Ideality in Chemical Mixtures

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

This example should help to illustrate the point...

Activity = Effective Concentration



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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 (coulombic) interactions between different solutes and with the solvent.

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

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

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

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

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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 $K_{\text{sp}} = m_{\text{Ca}^{2+}} \cdot m_{\text{CO}_3^{2-}}$
 At high I $K_{\text{sp}} < m_{\text{Ca}^{2+}} \cdot m_{\text{CO}_3^{2-}}$ because...

$K_{\text{sp}} = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}$ 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.

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Non-Ideality in Chemical Mixtures

Just what is γ_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

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Non-Ideality in Chemical Mixtures

what causes this non-ideality and what is γ_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.

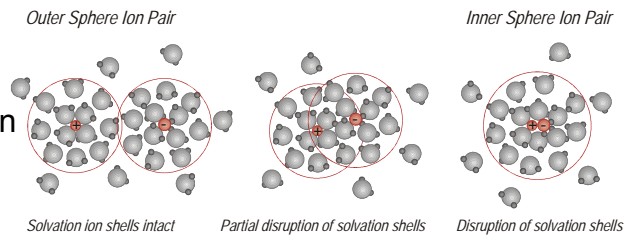


Figure 4.28. In formation of ion pairs, the solvation shells may remain intact or be partially or totally disrupted. The former results in an outer sphere ion pair, the latter results in an inner sphere ion pair.
From White, "Geochemistry"

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

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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^+ , $\text{Mg}(\text{OH})_2^0$, $\text{Ca}(\text{OH})_2^0$, HCl^0 , HSO_4^- and H_2SO_4^0).

An ion pair such as $\text{Mg}(\text{Cl})_2^0$ is different than the ionically bonded compound $\text{Mg}(\text{Cl})_2$. In the ion pair, the ions move together as a loosely-affiliated unit but they are not at close enough inter ionic distances to be considered compounds.

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Non-Ideality in Chemical Mixtures

γ_i is not predicted from thermodynamic theory of ideal solutions.

Instead, γ_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.

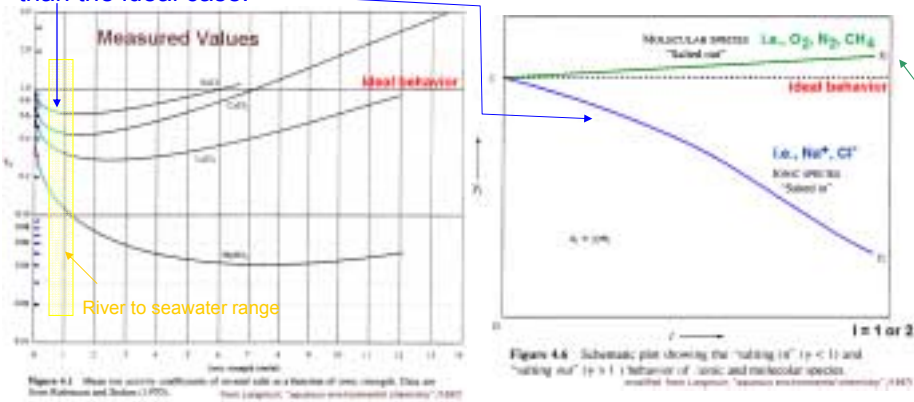
$$-\log \gamma_i = A z_i^2 I^{1/2}$$

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

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Non-Ideality in Chemical Mixtures

For ionic solutes in water, 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 neutral (non-charged) molecules, $\log \gamma_i = k_i I$, where k is the dielectric constant. At most natural ionic strength, these molecules are less soluble than the ideal case.

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