Defining the Standard State

- Common Choices for the **Environment** in the Standard State (the ***Reference Environment*** or ***Reference State***)
  - For ***gaseous*** species: The conditions in an ideal gas at a standard temperature and pressure (typically 20° or 25°C and 1.0 atm)
  - For ***solutes*** in dilute aqueous solutions: Conditions in which each molecule of solute interacts only with water molecules (i.e., infinite dilution in pure water), at the standard *T* and *P*; [marine chemists commonly use "standard seawater" rather than pure water as the background solution]
  - For ***water*** (or, in general, the main component of any liquid phase): The conditions in pure water at the standard *T* and *P*
  - For the major and minor components of ***solids***: The conditions in a pure solid of that constituent at the standard *T* and *P*

Quantifying Activity

- Assume that, if the environment remains constant, the activity of a species is always proportional to its concentration. Then, when comparing the behavior of the same species in two systems, concentration differences account for part of the difference in activity, and any other difference in activity is attributed to the environment, i.e:

$$a_i \equiv \frac{c_i}{c_{i,std.state}} \frac{\text{environ. factor for } i \text{ in system}}{\text{environ. factor for } i \text{ in std. state}} = \frac{c_i}{c_{i,std.state}} \gamma_i$$

- The 'environmental factor' can be considered the reactivity per molecule or per mole. Thus, the product of the numerators or denominators in the middle expression is (mol/L * reactivity/mol), or reactivity/L.

– For **gases** that follow the ideal gas law, $c_{G,i} = P_i/RT$, so:

$$\frac{c_i}{c_{i,std.state}} = \frac{P_i / RT}{1.0 \text{ atm} / RT} = \frac{P_i}{1.0 \text{ atm}}$$

– For **solutes** in aqueous solutions:

$$\frac{c_i}{c_{i,std.state}} = \frac{M \text{ mol/L}}{1.0 \text{ mol/L}}$$

– For **bulk constituent of a liquid** or **any constituent of a solid**:

$$\frac{c_i}{c_{i,std.state}} = \frac{c_i}{c_{i,\,pure\ phase}} = \frac{x_i}{x_{i,\,pure\ phase}} = x_i$$

$$a_i \equiv \frac{c_i}{c_{i,std.state}} \gamma_i$$

- The ***activity coefficient***, γ_i, is the ratio of the activity of a molecule (or mol) of *i* in the actual system to the corresponding activity in the standard state
  - If $\gamma_i = 1.0$, each molecule of *i* is as "active" as it would be in its reference state; commonly called "***ideal behavior***"
  - Molecules in a given system might be either more or less active than in the reference state (γ_i > or < 1.0, respectively)

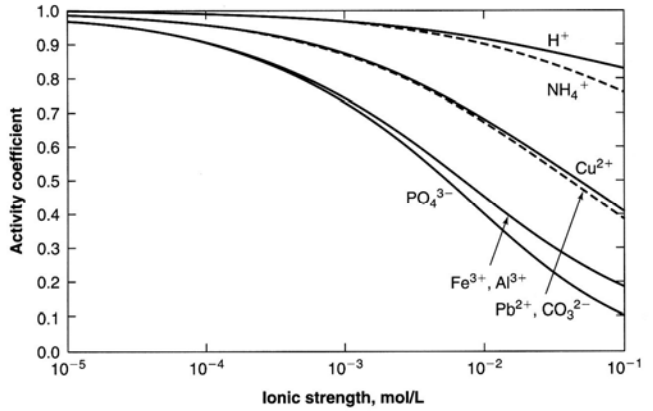
Activity Coefficients of Dissolved Ions

Debye-Hückel $$\log_{10}\left(\gamma_{\text{D-H}}\right) = -Az^2 I^{1/2}$$

Extended Debye-Hückel $$\log_{10}(\gamma_{\text{Ext.D-H}}) = -Az^2 \frac{I^{1/2}}{1 + BaI^{1/2}}$$

Davies $$\log_{10}(\gamma_{\text{Davies}}) = -Az^2 \left\{ \frac{I^{1/2}}{1 + I^{1/2}} - 0.2I \right\}$$

Activity Coefficients of Dissolved Ions



Summary: Chemical Activity

- A quantitative measure of the tendency for molecules to undergo a chemical change that reduces their concentration
- Incorporates factors related to concentration of the molecule of interest and the environment in which it exists
- Quantified based on definition of an arbitrary standard state, comprising a standard concentration and a standard (reference) environment; typically, these conditions are different for species in different phases, and for major vs. minor components of an aqueous solution
- Standard concentration is typically (but not necessarily) a value of 1.0 with units appropriate to the phase; standard environment is typically close to that under normal conditions at earth's surface, albeit somewhat idealized
- Activity coefficients for solutes can be predicted; activity coefficient for water and gases is usually assumed to be 1.0

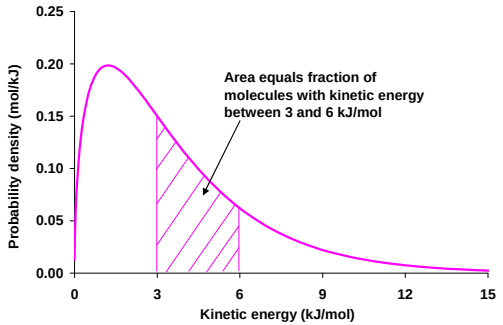
Conventions in this Course

- Activity of species *i*: a_i or $\{i\}$
- Molar concentration of species *i*: c_i or $[i]$
- Activity and molar concentration in systems where $\gamma_i = 1.0$: (*i*)

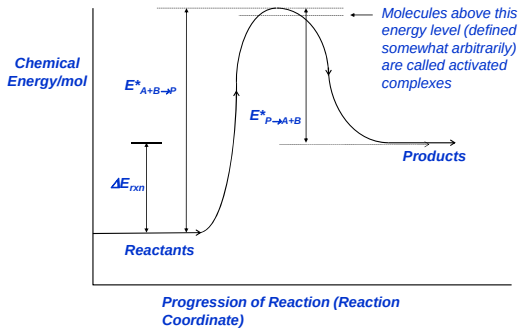
The Kinetic View of Chemical Equilibrium

- Reactions occur by collisions among molecules
  - For molecules in the same (homogeneous) phase, collision frequency should be proportional to the concentrations of the colliding species
  - For molecules in different phases, collision frequency is proportional to the concentrations in the phases (presumed to be proportional to the concentrations at the interface) and the "concentration" of interface
  - Environmental factors also affect the tendency of a species to react, so the proper parameter for characterizing reactivity is a_i; nevertheless, it is common practice to incorporate activity coefficients into other terms and write reaction rates in terms of concentrations (except in one important case, to be shown)
  - All reactions are presumed to be reversible
  - Environmental factors captured in activity coefficient – lower activity coefficient corresponds to more stability, less reactivity

Molecular Energy According to the Boltzmann Distribution



Molecular Energy Changes During a Reaction



Elementary Reactions

- Proceed in a single step, in accord with the reaction stoichiometry
- Follow a rate law that is established by stoichiometry:

$$a\mathrm{A} + b\mathrm{B} \rightarrow p\mathrm{P}$$

$$r_\mathrm{A} = -k_\mathrm{A} c_\mathrm{A}^a c_\mathrm{B}^b \qquad r_B = \frac{b}{a} r_A \qquad r_P = -\frac{p}{a} r_A$$

Note that relationships among r_A, r_B, and r_C apply regardless of whether reaction is elementary.