

Lecture 5: Activity-Concentration Relationships

Review

For a chemical reaction: $aA + bB \rightarrow cC + dD$

1. The energy released from the complete conversion of reactants to products at standard-state conditions (25°C and 1 atm) is a function of changes in enthalpy and entropy:

$$\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$$

2. The energy available from the chemical reaction at any point during the reaction can be calculated as the difference between the free energy of the products and reactants (derived from μ_i – chemical potential):

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT\ln(Q)$$

Here, Q (the reaction quotient) equals the ratio of products to reactants:

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

3. For a reaction at equilibrium ($\Delta G_{rxn} = 0$) at standard-state conditions, $Q = K_{eq}$, the equilibrium constant:

$$\ln K_{eq} = \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right) = \frac{-\Delta G_{rxn}^{\circ}}{RT}$$

I. Equilibrium and Disequilibrium:

How does K_{eq} vary as a function of temperature (25 ± 20°C)?

For a standard-state reaction at equilibrium:

$$\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ} = -RT\ln(K_{eq})$$

The equation is solved for K_{eq} to yield:

$$\ln(K_{eq}) = \frac{-\Delta H_{rxn}^{\circ}}{RT} + \frac{\Delta S_{rxn}^{\circ}}{R}$$

This equation is differentiated with respect to temperature, then integrated from T_1 (the reference temperature; 298 K) to T_2 (the temperature of interest) to yield the Van't Hoff equation:

$$\ln(K_{T_2}) - \ln(K_{T_1}) = \frac{\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

This calculation assumes that ΔH and ΔS do not vary as a function of temperature, a reasonable assumption within $\sim 20^\circ\text{C}$ of standard-state. Increases or decreases in temperature will shift the reaction to favor reactants or products.

How we describe reactions that are not at equilibrium?

Reaction quotient (Q): the ratio of products to reactants present at any given point during a chemical reaction; also called “activity product” or “ion activity product” in the book

Q can be used to represent how far a reaction is from equilibrium; e.g. $Q/K_{eq} = 1$ at equilibrium

If $Q < K_{eq}$, the reaction proceeds towards the right (forms products)

If $Q > K_{eq}$, the reaction proceeds towards the left (forms reactants)

Saturation index (SI) – used for dissolution reactions to describe whether a solution is undersaturated ($Q < K_{eq}$) or oversaturated ($Q > K_{eq}$) with respect to a mineral

$$SI = \log(Q/K_{eq})$$

An equilibrium constant for a dissolution reaction is also referred to as a *solubility product* (K_{sp})

For $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$:

$$K_{eq} = K_{sp} = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} a_{\text{H}_2\text{O}}^2}{a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}}$$

II. Activity-concentration relationships

What is activity?

The effective concentration of a component i in liquid or solid phase

$$\mathbf{a_i = \gamma_i \times m_i}$$

γ_i – activity coefficient;

m_i – concentration in molal units

In an infinitely dilute (ideal) solution, $\gamma_i \rightarrow 1$, so $\mathbf{a_i \rightarrow m_i}$

In reality, activity is usually lower than molality due to intermolecular interactions (e.g., ionic interactions between charged ions in solution)

The activity of pure substances in condensed phases equals unity (e.g. $\mathbf{a_{H_2O} = 1}$; $\mathbf{a_{solid} = 1}$).

$$K_{sp} = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} a_{\text{H}_2\text{O}}^2}{a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}} = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}$$

Activity of a species is affected by:

- 1) Ionic strength of a solution
- 2) Concentration of the species in solution
- 3) Complex formation

1) Ionic strength

Debye-Huckel Theory – ionic interactions lower the free energy of ions in solution and decrease their activity from an ideal solution; thus, $\gamma < 1$ and $a_i < m_i$

Thus, the activity coefficient (γ_i) of a species can be calculated as a function of ionic strength (I), the measure of total charged species in solution:

$$I = \frac{1}{2} \sum m_i z_i^2$$

What is the ionic strength of a solution that contains 0.1 M CaCl_2 ?

$$I = (1/2) \times (0.1 \times 2^2 + 0.2 \times (-1)^2) = 0.3$$

Single-ion activity coefficients (γ_i):

- i. for an uncharged species in solution: $\gamma_i = 10^{0.11}$
- ii. for a charged species in solution (ion), the value for I determines the equation used to calculate γ_i .

For $I < 10^{-3}$ (*0.005 is also suggested*): Debye-Huckel equation:

$$\log \gamma_i = -Az_i^2 \sqrt{I}$$

For $I < 10^{-1}$: Extended Debye-Huckel equation: modified to account for the finite size of ions

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_0 \sqrt{I}}$$

For $I > 10^{-1}$: Davies equation: fits the observation that a_i increases at high I

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_0 \sqrt{I}} + bI$$

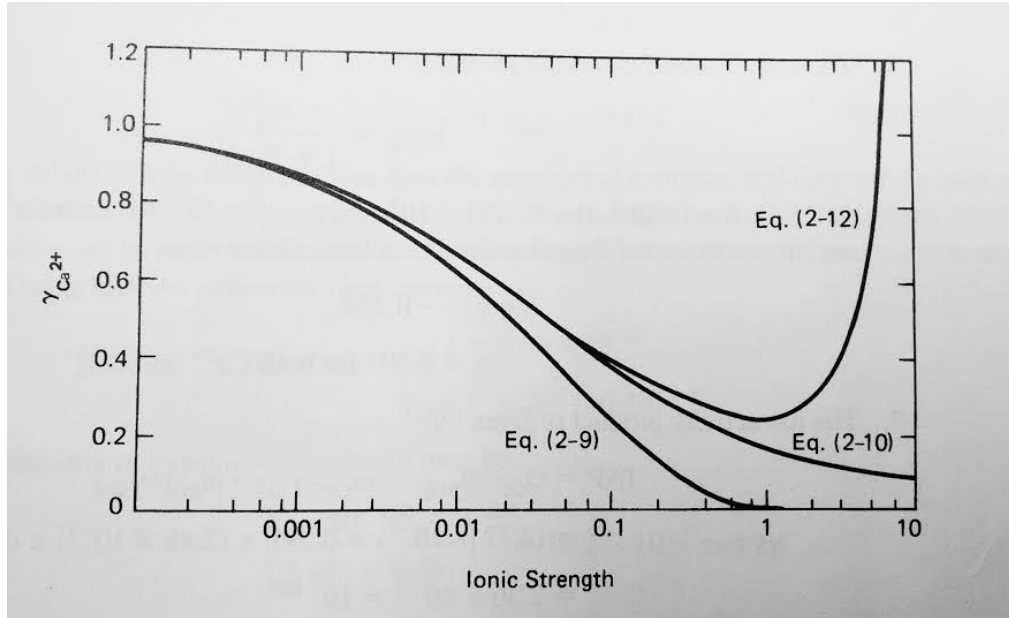
In these equations: z_i = charge on species i I = ionic strength

Fitting parameters (reported in tables):

A = constant B = constant (Refer to Table 4.1 in the textbook); A and B are a function of temperature

a_0 = hydrated radius of i (in practice, chosen to best fit the data; Refer to Table 4.2)

b = general constant ($b = 0.3$ for Davies equation) or constant specific to i



Eqn 2-9: Debye-Huckel

Eqn 2-10: extended Debye-Huckel

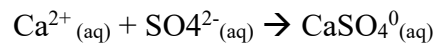
Eqn 2-12: Davies equation

Activity coefficients decrease as a function of increasing ionic strength; ion behavior becomes less ideal.

2) Species concentration

3) Complex formation

Ion pairing – when charged ions in solution interact to form a dissolved, uncharged species



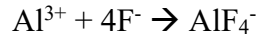
Ion pairing decreases the concentrations of free ions in solution by trapping them in these uncharged species. The concentrations of free ions can be calculated using the *stability constant* K_{stab} , the equilibrium constant for the formation of the ion pair:

$$K_{stab} = \frac{a_{\text{CaSO}_4^0}}{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}$$

The reciprocal of K_{stab} is the dissociation constant K_{diss} .

In brines, *mean ion activity coefficients* are calculated for compounds in solution (e.g., NaCl). These models are more thermodynamically rigorous, but not something we will cover.

Complex – a dissolved species formed from two or more simpler species, each of which can exist in aqueous solution



$$K_{stab} = \frac{a_{\text{AlF}_4^{-}}}{a_{\text{Al}^{3+}} a_{\text{F}^{-}}^4}$$

a_i can decrease due to complexation of i by a *ligand*, an organic or inorganic ion or molecule that binds to a central species to form a coordination complex (complex has well defined structure)

outer-sphere complex – interacting ions retain their hydration shells

inner-sphere complex – ions are not separated by water and directly interact with each other (e.g. ion pairing)

e.g. Fe^{3+} exists as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in solution (H_2O not usually written), and complex formation involves displacement of water molecules by other ligands

- rises in pH deprotonate H_2O to form OH- ligands



Ligands:

unidentate – a ligand with one binding site

multidentate – a ligand with multiple binding site (bidentate, tridentate, etc.)

oxalate: (-OOC-COO-)

chelate – is a complex formed when a ligand binds to a central metal ion at multiple points, creating a ring-like structure.; generally very stable and important for complexing transition metals in the environment. EDTA is a common ligand to form chelates

