Advanced Water Quality

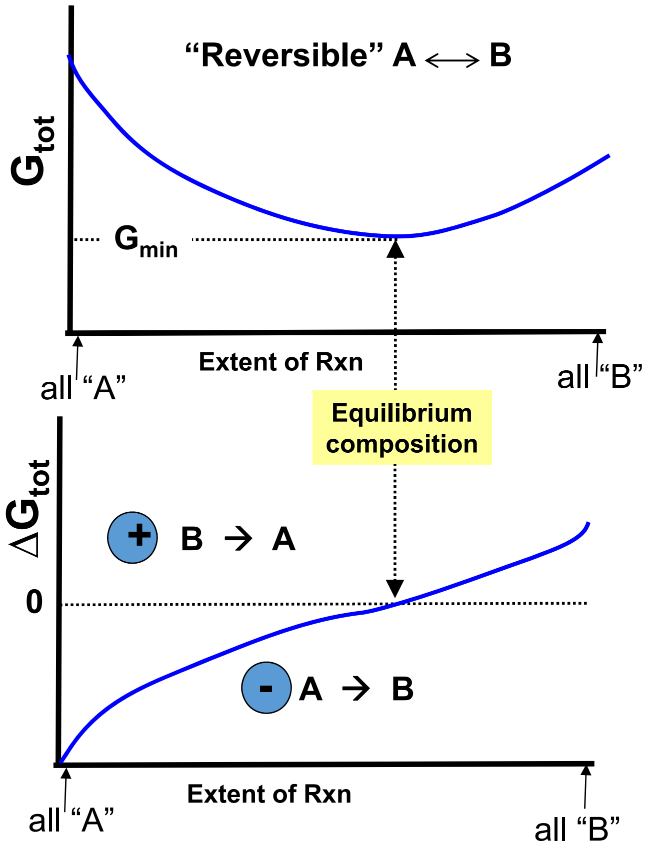
Class 5: Equilibrium and Non-ideal conditions

Today

- Effects of non-ideal conditions on K_{eq}
  - temperature
  - ionic strength

Review

- Reactions proceed spontaneously in direction to lower free energy (G)
- If we know the distribution of reactants and products, we can calculate ΔG,
  - Indicates whether or not reaction is at equilibrium



ΔG vs. ΔG^0

Activity & Standard State

- **{i} = activity** = reactivity of chemical "i" at a given set of real conditions <u>relative</u> to its reactivity at standard state, arbitrarily set equal to1.0
- **Standard State** = conditions describing the standard system
  = {Std Conc.} + {Std. P,T & composition req.}

Table 1.3 Common definitions for the standard state conditions in environmental systems

	Standard State			
		Reference State Conditions		
	Standard Concentration	Temperature	Pressure	Other
Solid	Concentration in pure solid	25°C	1 bar	—
Liquid	Concentration in pure liquid	25°C	1 bar	—
Gas	Concentration in pure gas	25°C	1 bar	Ideal gas behavior
Solute	1.0 *M*	25°C	1 bar	Infinite dilution

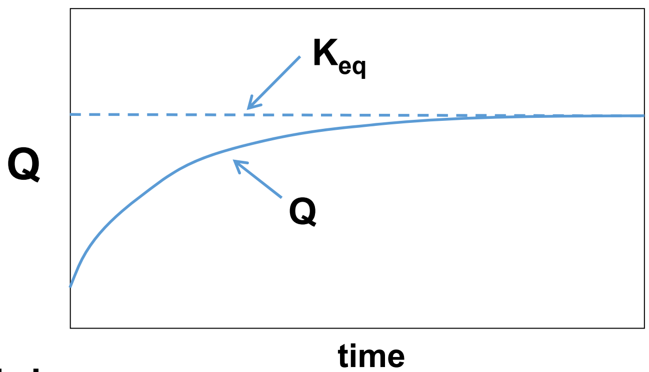
- Aq. solutes: $\{i\} = \gamma_i[i]$
- $\{H_2O\}$, {liquid},{solid} = 1.0
- Gases: $\{i\} = P_i$ (atm)

Reaction Quotient (Q) vs. K_{eq}

- Q = Ratio to products to reactants at any time
- For $H_2CO_3 \longleftrightarrow 2\,H^+ + CO_3^{2-}$

Does not have to be @ equilibrium

$$Q = \frac{\{H^+\}^2\{CO_3^{2-}\}}{\{H_2CO_3\}}$$



- If value of Q = **<u>K_{eq}, rxn is at equilibrium</u>**
- If value of Q ≠ **<u>K_{eq}, rxn is NOT at equilibrium</u>**

Relating K_{eq} to ΔG^0

At equilibrium:

$$\Delta G = 0 = \Delta G^0 + RT\ln Q$$

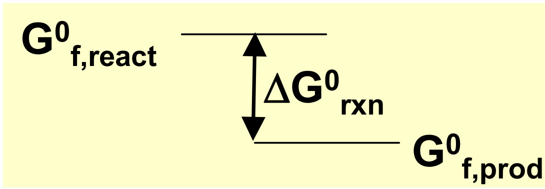
and

$$Q = K_{eq} = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$$

Therefore,

$$\ln K_{eq} = -\frac{\Delta G^0}{RT}$$

The point: K_{eq} values are directly related to fundamental thermodynamic properties of reactants and products:



Problem 1a: Lab analysis indicates that water contains 3×10^{-3} M Ca^{2+}, 4×10^{-5} M Mg^{2+}, 5×10^{-5} M HCO_3^-, and the pH is 8.6 and the temperature is 25 ºC. Are the dissolved ion concentrations in equilibrium with dolomite, undersaturated (i.e., more solid will spontaneously dissolve if added to water), or supersaturated (i.e., some of the dissolved ions will spontaneously precipitate to reach equilibrium)?

-Assume that the solution approximates ideal conditions, so {i} = [i].

$$CaMg(CO_3)_{2(s,\ dolomite)} + 2\ H^+ \longleftrightarrow Ca^{2+} + Mg^{2+} + 2\ HCO_3^-$$

Reactants:	ν_i	$G^0_{i,f}$ (kJ/mol)	$\nu_i\ G^0_{i,f}$ (kJ/mol)
$CaMg(CO_3)_2(s)$		-2161.7	
H^+		0	
		$\Sigma\nu_i G^0_{i,f}$ =	

Products:	ν_i	$G^0_{i,f}$ (kJ/mol)	$\nu_i\ G^0_{i,f}$ (kJ/mol)
Ca^{2+}		-553.54	
Mg^{2+}		-454.8	
HCO_3^-		-586.8	
		$\Sigma\nu_i G^0_{i,f}$ =	

Problem 1b: Lab analysis indicates that water contains $3x10^{-3}$ M Ca^{2+}, $4x10^{-5}$ M Mg^{2+}, $5x10^{-5}$ M HCO_3^-, and the pH is 8.6. Are the dissolved ion in equilibrium with dolomite, undersaturated (i.e., should more solid dissolve), or supersaturated (i.e., should dissolved ions precipitate)? Assume that the solution approximates ideal conditions, so {i} = [i]. **Recalculate using Q vs. K_{eq} comparison.**

Problem 2: What is the activity of Ca^{2+} in pH 9.0 solution in equilibrium with dolomite, if $\{HCO_3^-\}$ = 10^{-4} M and $\{Mg^{2+}\}$ = 10^{-4} M?

Today

- **Effects of non-ideal conditions on K_{eq}**
  - **temperature**
  - ionic strength

Effect of Temperature on K_{eq} Values

- Relationship between K_{eq} and ΔG^0 valid **<u>only</u>** at standard T, P

$$\ln K_{eq} = -\frac{\Delta G^0}{RT}$$

- Cannot use this expression to determine K_{eq} at other Temperatures
  - ΔG^0 is not independent of temp

Need a different approach to correct K_{eq} for non-standard Temp.

Effect of Temp (cont.)

- To correct for temp changes, let's first multiply both sides by the differential (d/dT):

$$\frac{d}{dT}\ln K_{eq} = -\frac{d}{dT}\left(\frac{\Delta G^0}{RT}\right)$$

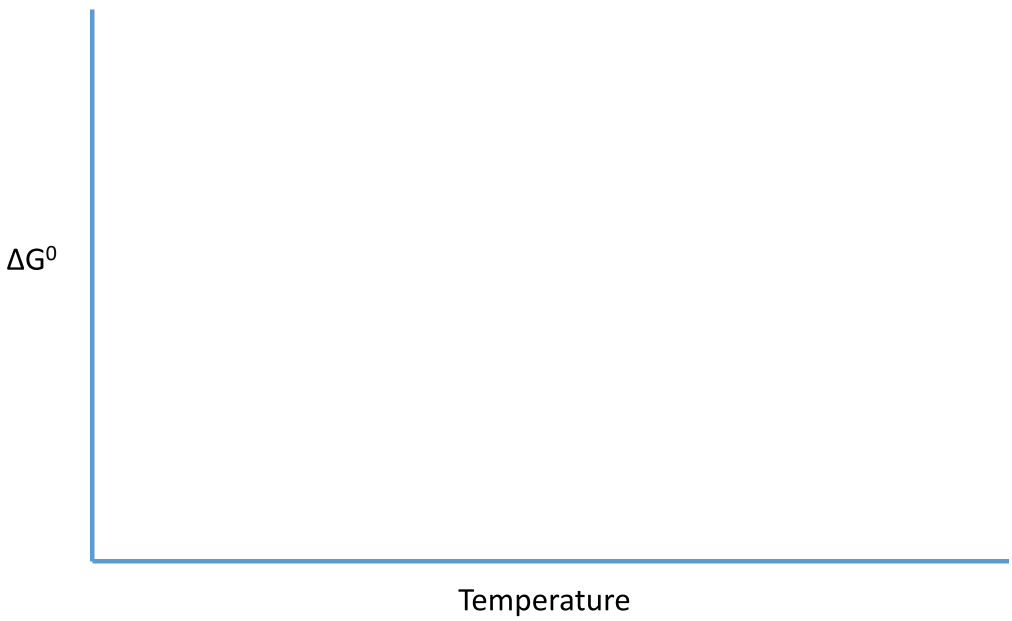
- No fundamental relationship or theoretical approach for predicting a direct relationship between ΔG^0 and T.
- However, we can make some assumptions about major factors that affect ΔG^0.
- for any change in system conditions, we can express ΔG^0 as:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{(Gibbs Relationship)}$$

- Most dramatic effect of T in this eqn is the multiplier of ΔS^0.

Most dramatic effect of temperature changes in this eqn occurs in the multiplier of ΔS^0

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$



Effect of Temp (cont.)

- Relative to this effect, we can assume ΔH^0 and ΔS^0 are approximately constant for small changes in temperature:

$$\Delta H^0_{\text{any T}} \approx \Delta H^0_{25°C} \quad \text{and} \quad \Delta S^0_{\text{any T}} \approx \Delta S^0_{25°C}$$

- Plug the Gibbs relationship into the differential expression:

$$\frac{d}{dT}\ln K_{eq} = -\frac{d}{dT}\left(\frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R}\right)$$

- then add the constant std enthalpy and entropy assumptions:

$$\approx -\frac{d}{dT}\left(\frac{\Delta H^0{}_{25C}}{RT} - \frac{\Delta S^0{}_{25C}}{R}\right)$$

Effect of Temp (cont.)

- Separate the terms:

$$\frac{d}{dT}\ln K_{eq} \approx -\left(\frac{\Delta H^0{}_{25C}}{R}\right)\frac{d}{dT}\left(\frac{1}{T}\right) + \left(\frac{\Delta S^0{}_{25C}}{R}\right)\frac{d}{dT}(1)$$

- Then take the derivatives on the RHS:

$$\frac{d}{dT}\ln K_{eq} \approx \left(\frac{\Delta H^0{}_{25C}}{R}\right)\left(\frac{1}{T^2}\right)$$

- Integrate expression from std temp (T_{std}) to temp of interest (T_2):

$$\int_{Keq,T_{std}}^{Keq,T2} d\ln K_{eq} = \frac{\Delta H^0}{R}\int_{T_{std}}^{T2}\frac{dT}{T^2}$$

Effect of Temp (cont.)

- We end up with:

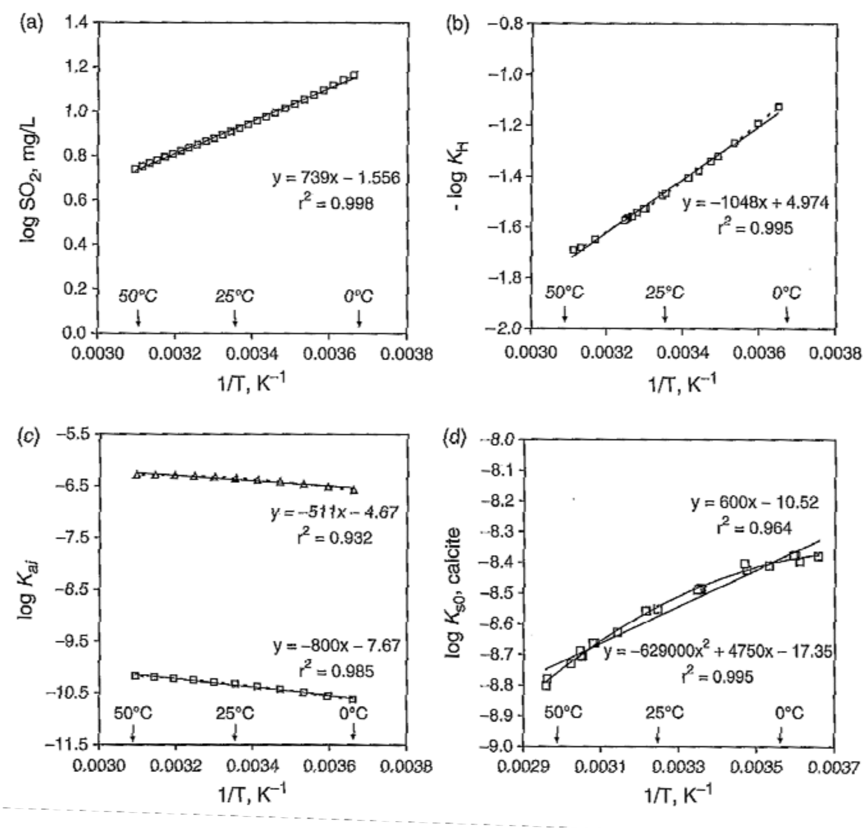
$$\ln K_{eq,T2} = \ln K_{eq,T_{std}} + \frac{\Delta H^0}{R}\left(\frac{1}{T_{std}} - \frac{1}{T_2}\right)$$

- This is called <u>van't Hoff Eqn:</u>

$$\ln\left(\frac{K_{eq,T2}}{K_{eq,T_{std}}}\right) = \frac{\Delta H^0}{R}\left(\frac{1}{T_{std}} - \frac{1}{T_2}\right) = \frac{\Delta H^0 (T_2 - T_{std})}{R T_{std} T_2} \qquad \text{Eq 3.44}$$

- Obtain ΔH^0 similar to ΔG^0, using values in Appendix of your text

$$\Delta H^0 = \left(\sum_i \upsilon_i H^0_{f,i}\right)_{PRODUCTS} - \left(\sum_i \upsilon_i H^0_{f,i}\right)_{REACTANTS}$$



From Brezonik and Arnold (2011) *Water Chemistry*. Van't Hoff plots for (A) O_2 solubility in water, (B) Henry's constant for CO_2, (C) pK_a values for dissolved carbonate species, (D) Solubility constant for calcite.

Example: A chunk of the mineral metacinnabar (HgS) is dropped in a container of acidic water with pH 3.0. Under these conditions, some of the HgS(s) will dissolve according to the following equilibrium reaction ($\log K_{sp}$ = -31.5).

$$HgS(s) + 2\,H^+ \rightleftharpoons Hg^{2+} + H_2S$$

Assuming a well-buffered ideal solution (i.e., I = 0), and that not all of the HgS will dissolve when equilibrium is achieved, determine the equilibrium concentration of dissolved Hg^{2+} at (a) 25 °C, and (b) 50 °C. (c) Does the concentration of dissolved Hg exceed Korean drinking water standards (5×10^{-9} M)?

(a)

$$HgS(s) + 2\,H^+ \rightleftharpoons Hg^{2+} + H_2S$$

Species	G_f^0 (kJ/mol)	H_f^0 (kJ/mol)
$HgS_{(s)}$	-43.3	-46.7
H^+	0	0
Hg^{2+}	164.4	171
H_2S	-27.87	-39.75

(b)

Today

- **Effects of non-ideal conditions on K_{eq}**
  - temperature
  - **ionic strength**

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

I can be estimated from TDS or Specific Conductivity

- Rigorous determination of I can be expensive
  - How do you know you analyzed all ions present?
- Some approximations for rough estimates of I

Langelier:
$I = 2.5\times10^{-5}$ x TDS, where TDS in mg/L

Griffin and Jurinak:
$I = 1.3\times10^{-5}$ x (specific conductance, μS/cm)

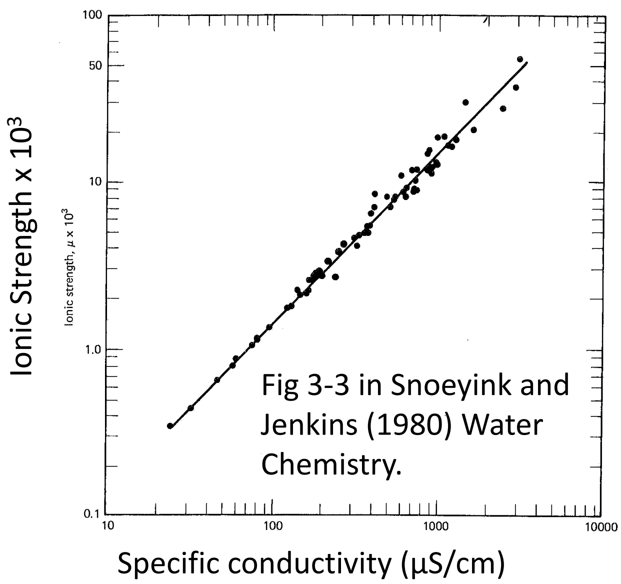
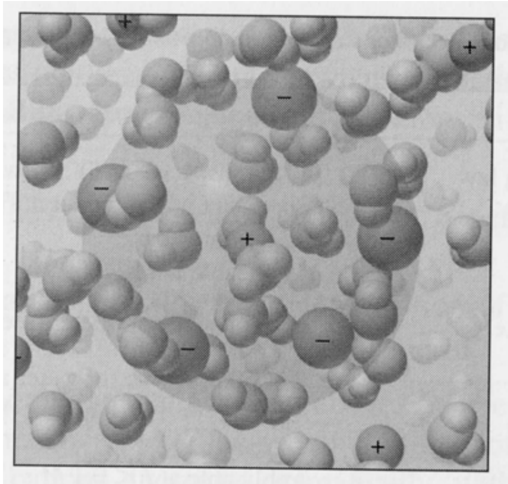


Fig 3-3 in Snoeyink and Jenkins (1980) Water Chemistry.

Non-Ideal Ionic Strength

$$K_{eq} = \frac{\{H_2CO_3\}^1}{\{H^+\}^2\{CO_3^{2-}\}^1} = \frac{(\gamma_{H_2CO_3}[H_2CO_3])^1}{(\gamma_{H^+}[H^+])^2(\gamma_{CO_3^{2-}}[CO_3^{2-}])^1}$$

- Estimate γ_i of dissolved ions from theory
  - *Ionic strength is key variable:* $I = \frac{1}{2}\sum C_i z_i^2$
- **Recall:** standard state conditions for dissolved ions assumes infinitely dilute conditions (ion only surrounded by H_2O; $I \rightarrow 0$)
  - **Real solutions:** other ions present, form diffuse cloud of ions (and H_2O) around the central ion, enriched in ions with opposite charge
  - Oppositely charged ions shield central ion from interactions with other reactants, reducing its intrinsic reactivity per molecule (i.e., its activity {i})
    - Shielding effect of counterions ↑ as I ↑ (water gets saltier), so γ ↓
    - Shielding effect greater for highly charged central ions (attracts "shielding" counterions more effectively)



Non-Ideal Ionic Strength

Table 1.4a Various equations for predicting activity coefficients in aqueous solutions

Name and Equation	Notes and Approximate Range of Applicability
Debye–Huckel limiting law $\log \gamma_{D\text{-}H} = -Az^2I^{1/2}$	$A = 1.82 \times 10^6 (\varepsilon T)^{-3/2}$, where ε is the dielectric constant of the medium. For water at 25°C, $A = 0.51$; z = ionic charge Applicable at $I < 0.005\ M$
Extended Debye–Huckel $\log \gamma_{Ext.D\text{-}H} = -Az^2 \frac{I^{1/2}}{1 + BaI^{1/2}}$	$a \equiv$ ion size parameter (see Table 1.4b) $B = 50.3(\varepsilon T)^{1/2}$; for water at 25°C, $B = 0.33$ Appropriate in solutions where one salt dominates ionic strength Applicable at $I < 0.1\ M$
Davies $\log \gamma_{Davies} = -Az^2\left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.2I\right)$	Applicable at $I < 0.5\ M$
Specific interaction model $\log \gamma_{Pitzer} = \log \gamma_{Ext.D\text{-}H} + \sum_j B_{ij} Im_j$	B_{ij} is specific interaction term between ions i and j; m_j is molality (mol/kg solution) of j Applicable at $I < 1\ M$; additional terms can extend range to higher ionic strengths[a]

[a]See Pitzer (*J. Solution Chem.* 4, 249–265, 1975) or Millero (*Geochim. Cosmochim. Acta* 47, 2121–2129, 1983).

from Benjamin (2002) Water Chemistry

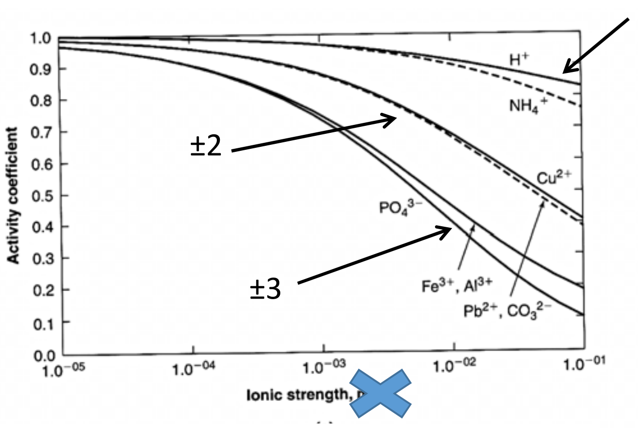
TABLE 2.4 Ion size parameters a for the Extended Debye-Hückel Equation[10]

Ion	a	Ion	a	Ion	a
Ag^+	3	Fe^{2+}	6	Mn^{2+}	6
Al^{3+}	9	Fe^{3+}	9	Na^+	4
Ba^{2+}	5	H^+	9	NH_4^+	3
Be^{2+}	8	HCO_3^-	4	NO_3^-	3
Ca^{2+}	6	HPO_4^{2-}	4	OH^-	3
Ce^{3+}	9	$H_2PO_4^-$	4	Pb^{2+}	5
CH_3COO^-	4	HS^-	3	PO_4^{3-}	4
Cl^-	3	I^-	3	Sn^{2+}	6
ClO_4^-	3	K^+	3	SO_4^{2-}	4
CO_3^{2-}	5	La^{3+}	9	Sr^{2+}	5
Cu^{2+}	6	Mg^{2+}	8	Zn^{2+}	6

From Pankow (1991) Aquatic Chemistry

$A = 1.82 \times 10^6 (\varepsilon T)^{-3/2}$, where ε is the dielectric constant of the medium. For water at 25°C, $A = 0.51$; z = ionic charge

Accounting for Non-Ideal Ionic Strength



- γ_i decreases as I ↑
- Effect of changing I increases dramatically with ↑ charge of central ion
- Different models similar at I < 0.1

$\gamma_i \approx 1.0$ for uncharged species (e.g., H_2CO_3)

Figure 1.6 **(a)** Activity coefficients of various ions according to the extended Debye–Huckel law, based on the infinite dilution reference state. **(b)** The activity coefficient of Ca^{2+} in a solution prepared by dissolution of $CaCl_2$, according to three models. The specific ion interaction (SIT) model (of Pitzer) is the most complex of the three shown, and it fits the experimental data best. However, at low ionic strengths, the other two equations yield satisfactory results.

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from Benjamin (2002) Water Chemistry

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$$HgS(s) + 2\,H^+ \rightleftharpoons Hg^{2+} + H_2S$$

Determine the equilibrium concentration of dissolved Hg^{2+} at 25 °C and I = 0.25, and compare with the dissolved concentration we calculated with I = 0.

Wrap-up

- Often, we assume standard conditions (25°C, 1 atm, infinitely dilute water) where ΔG^0-K_{eq} relationship is valid and $\gamma = 1.0$
- If we wish to apply equilibrium models to non-std conditions, we need to apply corrections:
  - Non-std temperature:
  - Non-std ionic strength: