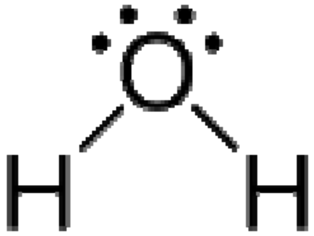
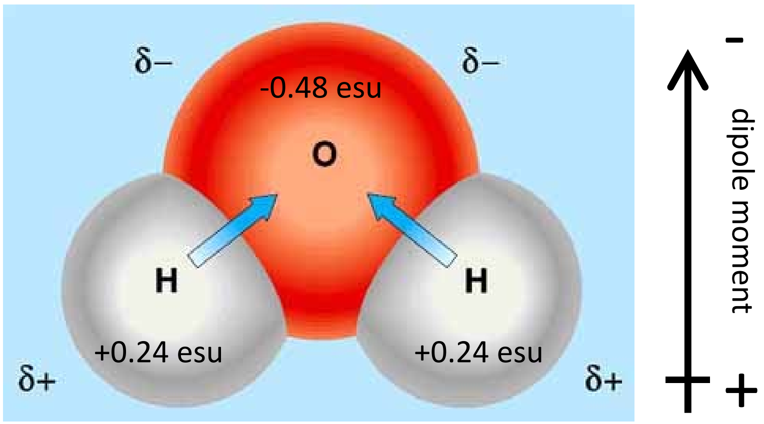
Advanced Water Quality

Class 3: Reaction Model and Thermodynamics

Water



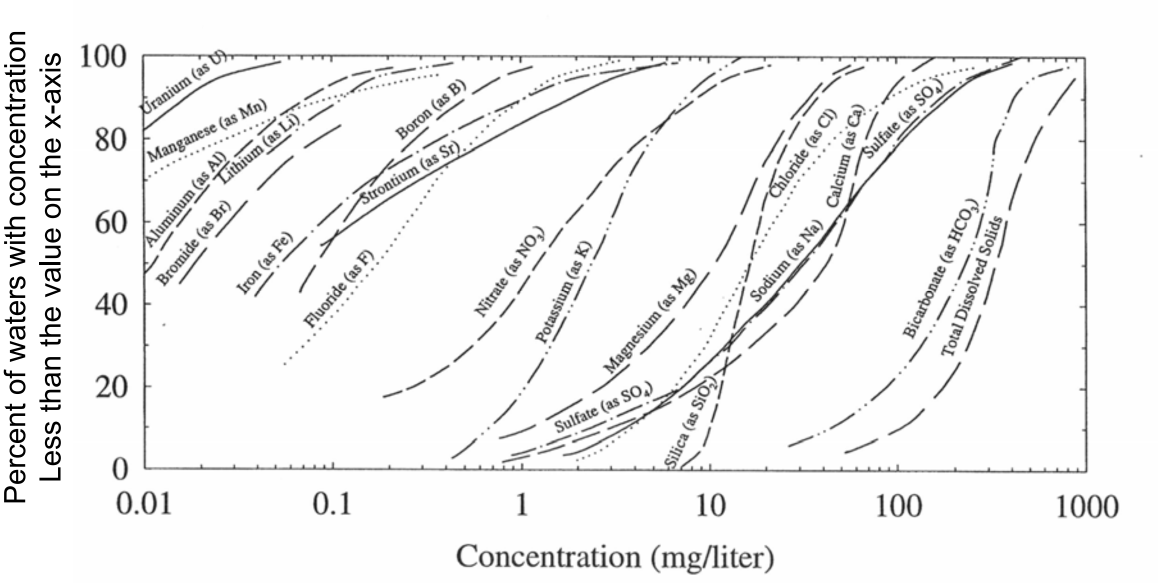


Polar: permanent dipole moment

High dielectric constant (80.1 at 20°C)

- Polar molecules orient in response to local electric fields from other molecules

Constituents in natural waters



Today’s learning objectives

- Describe the major models used to describe aqueous chemical composition and provide examples where each type of chemical model is used.
- Use thermodynamics to explain why chemical “reactants” react to form “products”, and why some reactions reach an “equilibrium” mixture of reactants and products, whereas other reactions proceed from all reactants to all products

Models used to describe aqueous chemical composition

	Reversible or Irreversible?	Fast or slow?
1. Stoichiometric Models		
2. Equilibrium Models		
3. Kinetics Models		

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1. Stoichiometric Models (simple mass balance)

- Irreversible + Fast
- What concentration of hypochlorous acid (HOCl) needs to be dosed to lower the dissolved Mn concentration (12 mg/L) to the secondary MCL (Mn = 0.05 mg/L)?
  - Let's use stoichiometric model to determine this.
  - Known info: HOCl oxidizes dissolved Mn^{2+} to solid phase MnO_2 (and becomes Cl^-)

Review: Balancing chemical reactions

Case A:

If all atoms in reactants do not change their oxidation states as they become product

Step 1: Write the known reactants on the left and known products on the right

Step 2: Adjust stoichiometric coefficients to balance all elements except H and O

Step 3: (If necessary) Add water (H_2O) to balance the element O and add H+ to balance the element H

Ex) $NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + H_2O$

Review: Balancing chemical reactions

Case B:

If atoms in reactants **do** change their oxidation states as they become product

→ This is called redox reaction where electrons are transferred

Step 1. Identify what is oxidized and what is reduced

Step 2. Write unbalanced form of half rxns

Step 3. Balance atoms in the individual half rxns other than H and O

Step 4. Balance oxygens using H_2O

Step 5. Balance hydrogens using H^+

Step 6 (method 1). Balance charge using e^-
(method 2). #e^- could have been determined earlier from changes in formal oxidation state of each half reaction

Step 7. Multiply each half reaction by an appropriate integer so that each contains equivalent e^-

Step 8. Add the balanced half reactions

Ex) $Mn^{2+} + HOCl + H_2O \rightarrow MnO_{2(s)} + Cl^- + 3H^+$

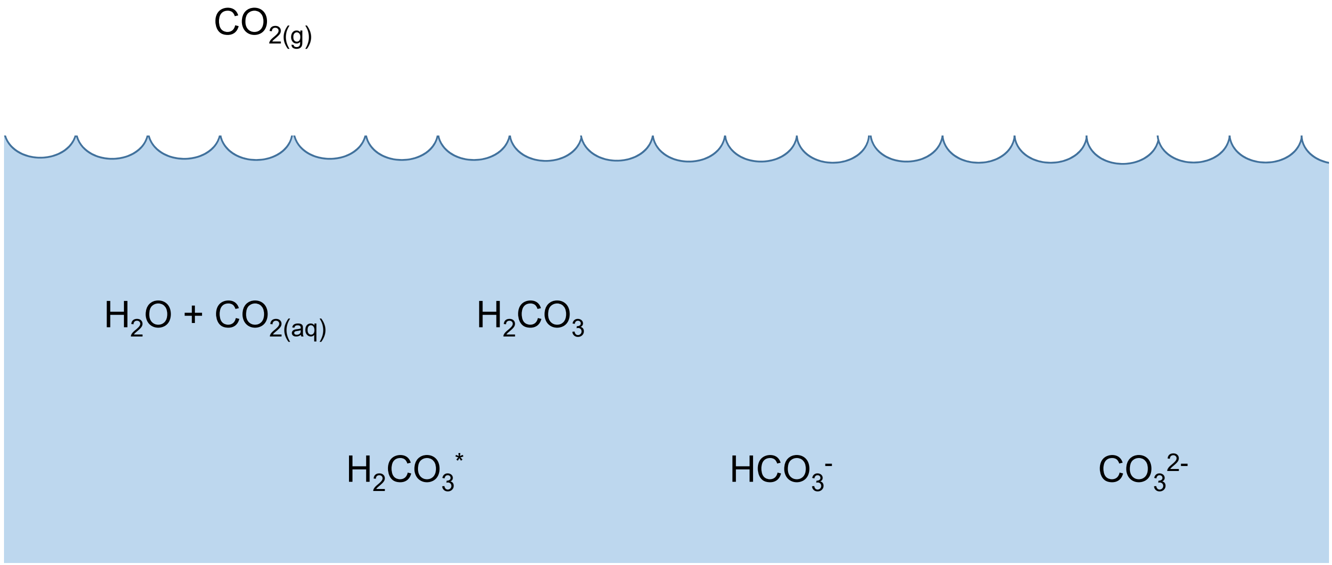
1. Stoichiometric Models (simple mass balance)

- Stoichiometric models tells us there is a 1:1 molar requirement of HOCl to oxidize dissolved Mn^{2+} to solid phase MnO_2.

$$\underset{12\ \text{mg/L}}{Mn^{2+}} + HOCl + H_2O \rightarrow MnO_{2(s)} + Cl^- + 3H^+$$

- Secondary MCL for Mn = 0.05 mg/L

Let's think about carbonate system, what model is adequate for this?



$CO_{2(g)}$

$H_2O + CO_{2(aq)}$

H_2CO_3

$H_2CO_3^*$

HCO_3^-

CO_3^{2-}

2. Equilibrium Models

- Reversible + Fast (e.g., acid-base reactions, metal complexation, adsorption rxns)
- What concentration of strong base (e.g., NaOH) needs to be added to a 10^{-3} M solution of carbonate to raise the pH to 9.5?

$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$

$$K_{a1} = 10^{-6.35} = \frac{\{H^+\}\{HCO_3^-\}}{\{H_2CO_3\}}$$

$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$

$$K_{a2} = 10^{-10.33} = \frac{\{H^+\}\{CO_3^{2-}\}}{\{HCO_3^-\}}$$

$H_2O \leftrightarrow H^+ + OH^-$

$$K_w = 10^{-14} = \{H^+\}\{OH^-\}$$

$NaOH \rightarrow Na^+ + OH^-$

Strong base assumption:
completely dissociates

- What concentration of strong base (e.g., NaOH) needs to be added to a 10^{-3} M solution to raise the pH to 9.5?

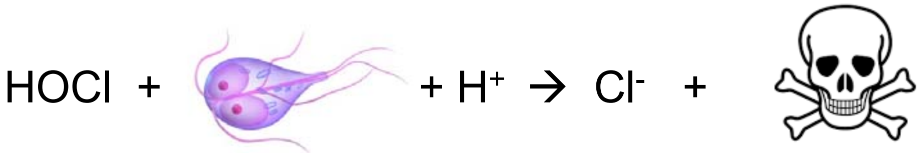
$$C_{NaOH}^{add} = \{Na^+\} = \frac{K_w}{\{H^+\}} + \frac{C_{T,CO3}}{\frac{\{H^+\}}{K_{a1}} + 1 + \frac{K_{a2}}{\{H^+\}}} + \frac{2C_{T,CO3}}{\frac{\{H^+\}^2}{K_{a1}K_{a2}} + \frac{\{H^+\}}{K_{a2}} + 1} - \{H^+\}$$

Review on pX terminology

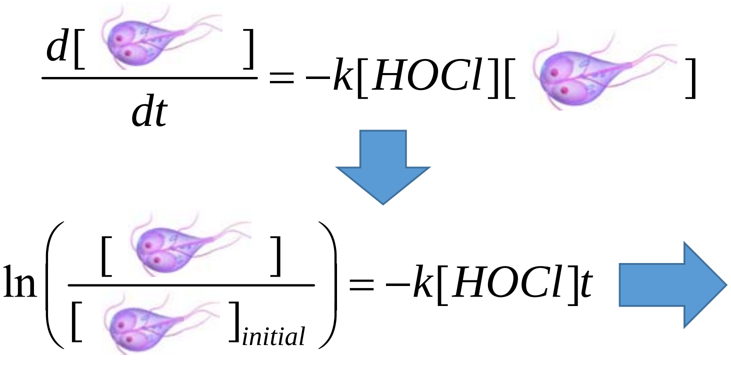
- $pX = -\log_{10}X$
- $pH = pH_a = -\log_{10}\{H_3O^+\}$ or $-\log_{10}\{H^+\}$
  - Note that pH measurements are usually referring to the H_3O^+ molar activity scale, {}, and not molar concentration scale, []
  - However, for dilute solutions (e.g., when ionic strength < 10^{-3} M), you can mostly assume $\{H_3O^+\}=[H_3O^+]$
    - E.g., pH = 4 is equivalent to $[H_3O^+] = 10^{-4}$ M
    - A 1 unit change in pH is equivalent to 10-fold change in $[H_3O^+]$.
- $pK = -\log_{10}X$
  - Often used in acid dissociation constants (K_a) or solubility constant (K_{sp})
  - E.g., acetic acid has $pK_a = 4.76$, which means $K_a = 10^{-4.76}$

3. Kinetics Models

- Irreversible or Reversible + Slow
- How much reactor retention time do I need to to ensure that 99.9% of Giardia Cysts is inactivated by 3 mg/L free chlorine disinfectant?



k = 0.04 (mg/L)$^{-1}$ min^{-1} at 10°C



Assumes ideal plug flow

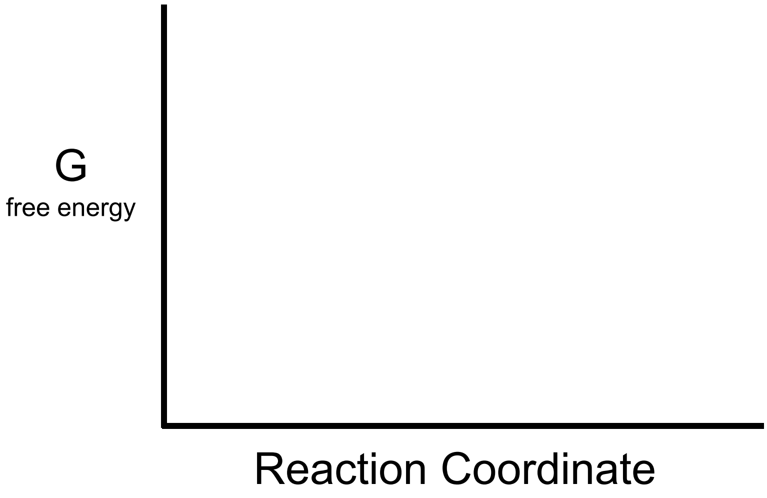
Models used to describe aqueous chemical composition

	Reversible or Irreversible?	Fast or slow?
1. Stoichiometric Models	Irreversible	Fast
2. Equilibrium Models	Reversible	Fast
3. Kinetics Models	Irreversible or reversible	Slow

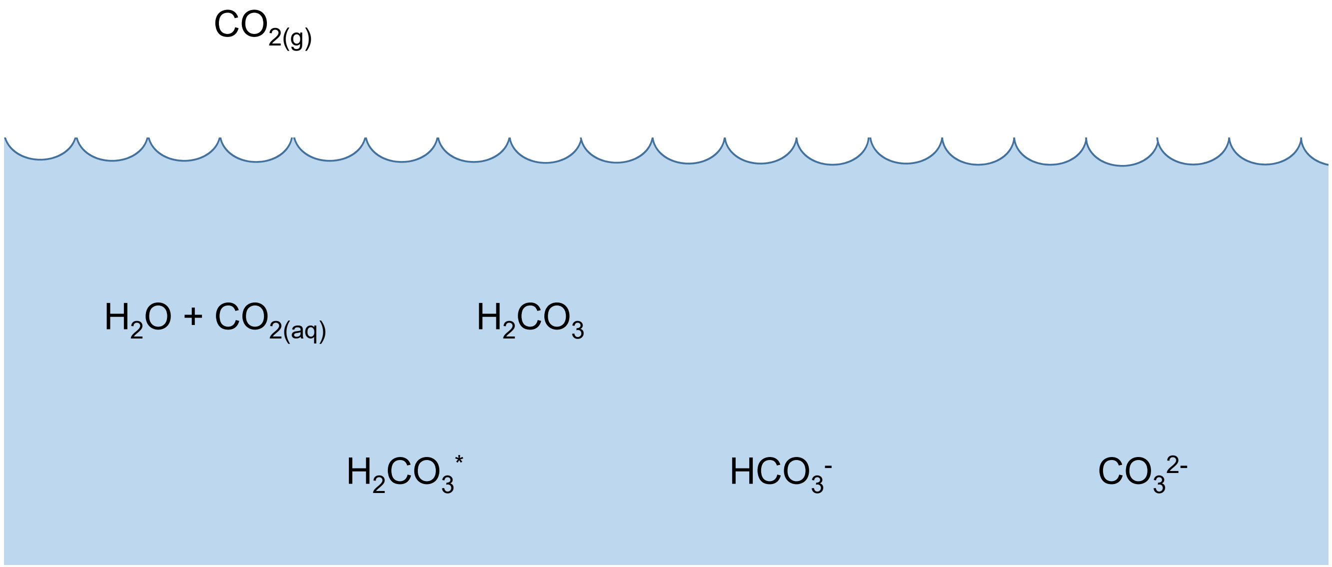
Today’s learning objectives

- Describe the major models used to describe aqueous chemical composition and provide examples where each type of chemical model is used.
- Use thermodynamics to explain why chemical “reactants” react to form “products”, and why some reactions reach an “equilibrium” mixture of reactants and products, whereas other reactions proceed from all reactants to all products

- Thermodynamics provides a basis for predicting whether two substances “A+B” will react spontaneously to “C+D” when they bump into one another



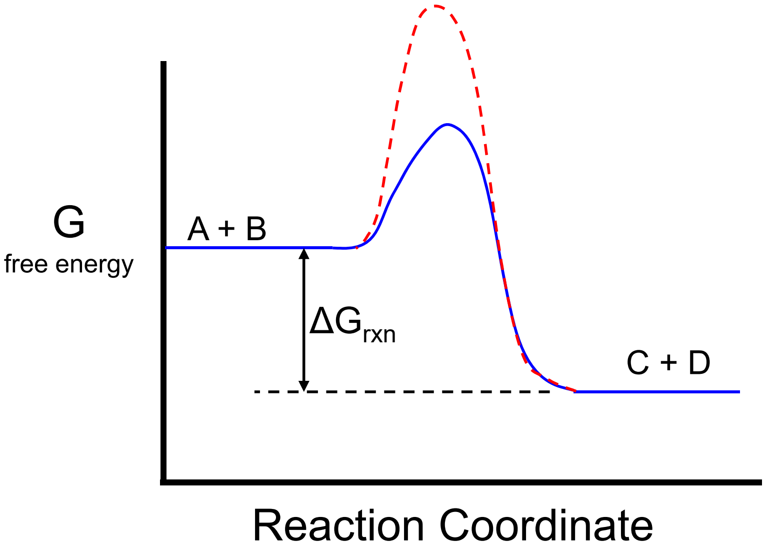
Let’s recall carbonate system and put Thermodynamics into the context



Thermodynamics provides the basis to

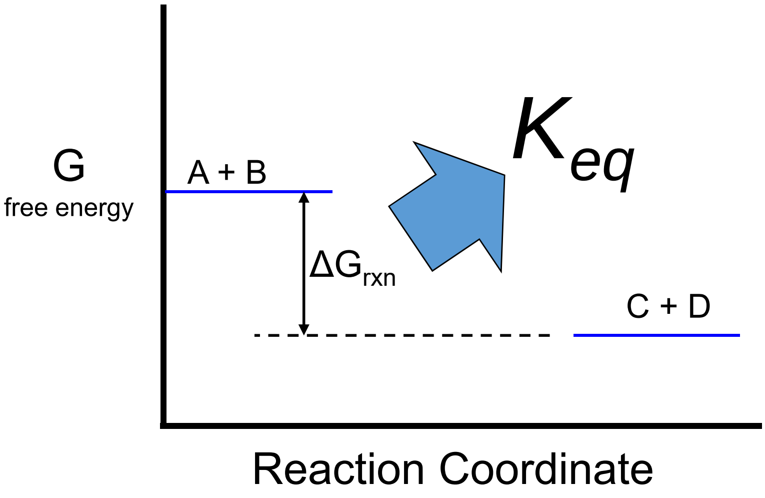
- Calculate equilibrium composition of system
  - Determine composition of CO_2 in seawater in equilibrium with current atmospheric CO_2, and compare to composition if P_{CO2} doubles in the future due to fossil fuel usage
- Determine how far from equilibrium a particular system is
  - Compare measured speciation of dissolved carbonate with predictions for equilibrium with atmospheric levels of CO_2
- Determine how K_{eq} changes as function of temp & pressure
  - How do K_{eq} values for carbonate equilibria change with temp and pressure changes at great depths in ocean
- Determine minimum energy required to make unfavorable processes occur
  - Determine amount of solar energy needed to drive photosynthesis, to create new biomass from CO_2

- Thermodynamics considers change in energy between initial & final states



- Path between states not relevant

- Thermodynamics considers change in energy between initial & final states



- Path between states not relevant

Gibbs Function

- Relates Gibbs free energy (G) to its enthalpic (H) and entropic (S) contributions

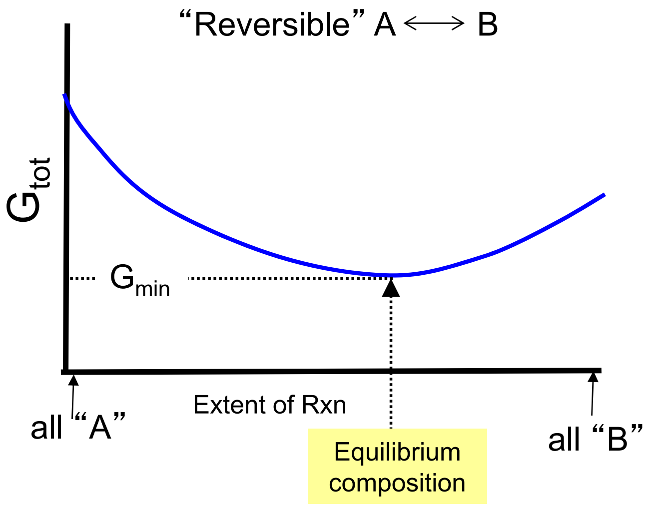
$$G = H - TS$$

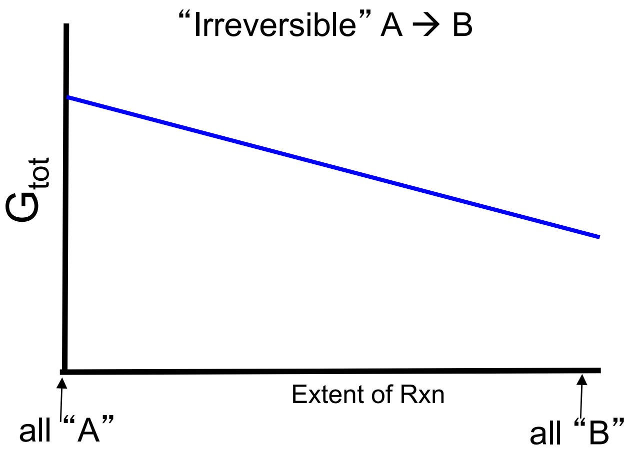
  - Energy (sunlight, heat) needed to drive processes where $\Delta G > 0$

- In principle, we can calculate total free energy of a given mixture of reactants and products:

$$G_{tot} = n_a \bar{G}_a + n_b \bar{G}_b + \ldots$$

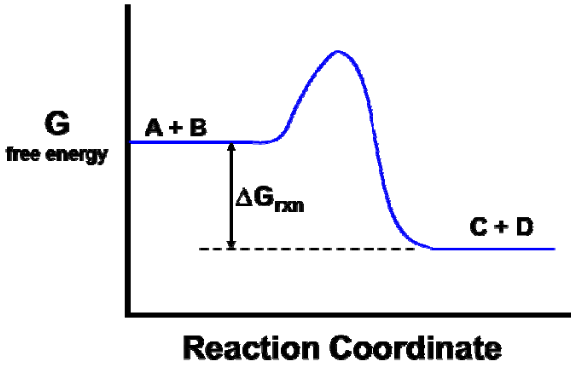
Consider a volume of solution with a collection of "A" and "B" molecules



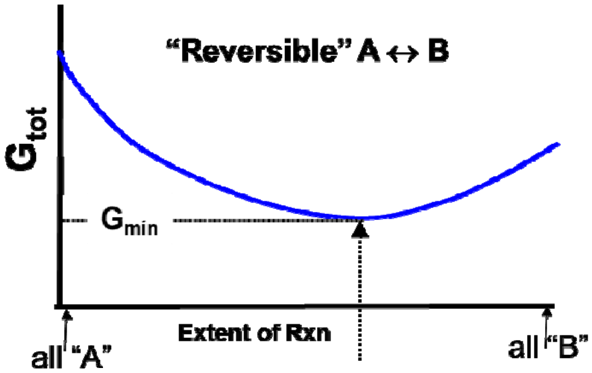


- At equilibrium, G = minimum

Clarification



Vs.

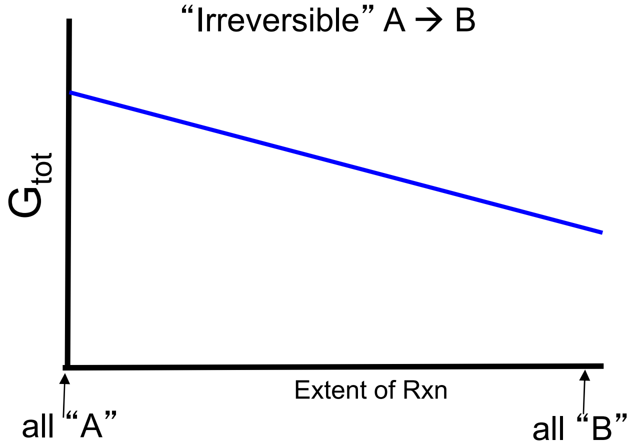


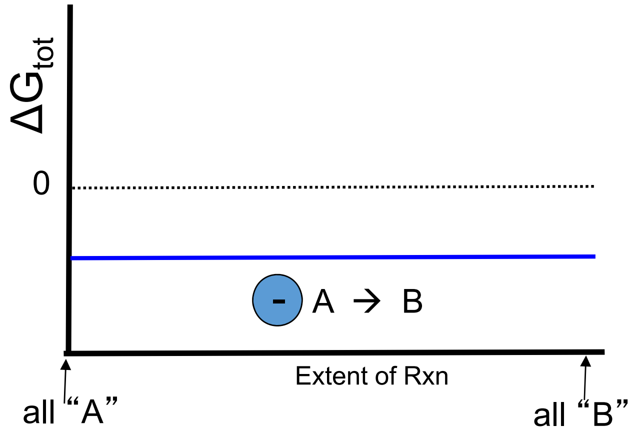
Free energy profile for single set of reactant mCs progressing to a single set of product mCs (conceptual of a single molecular event)

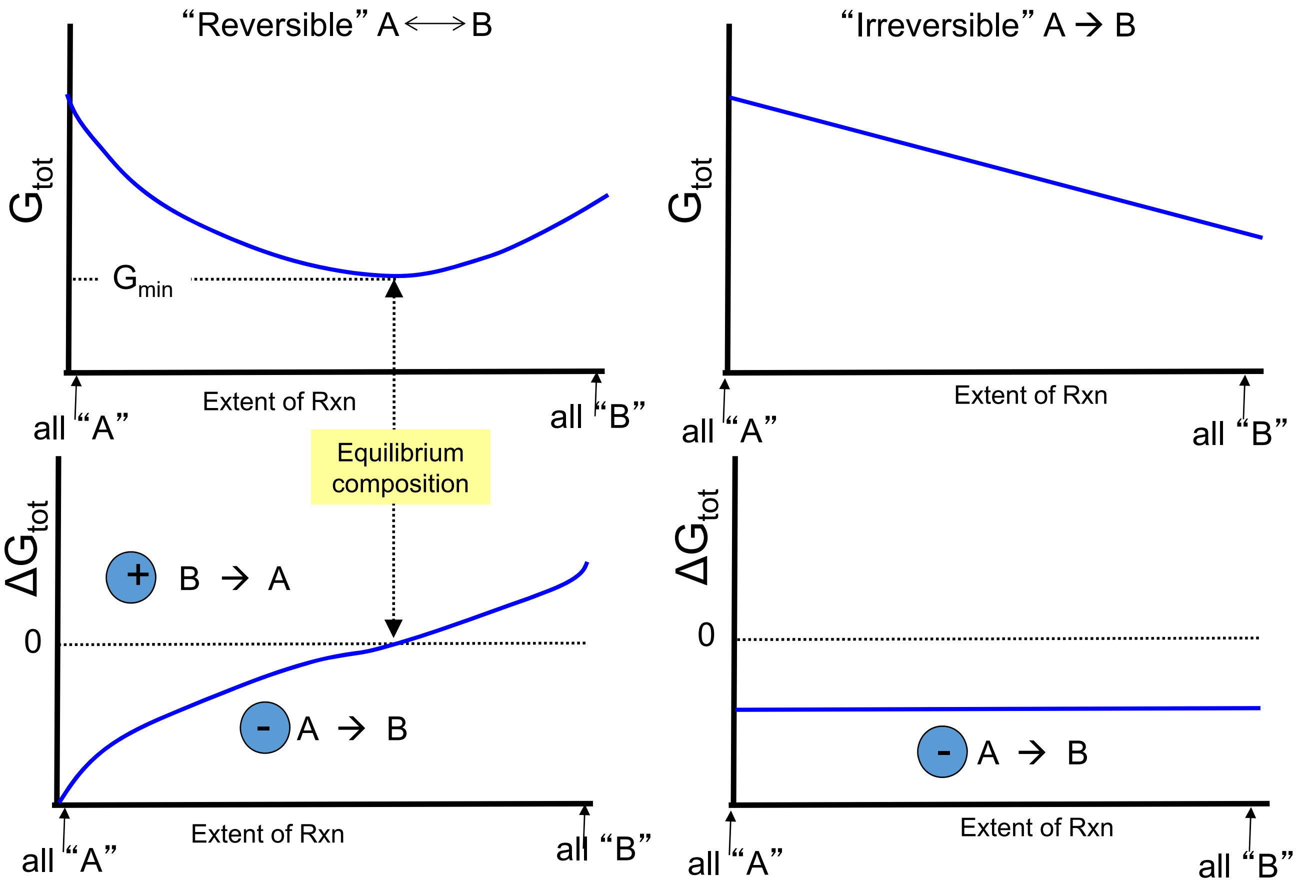
Collective free energy of large population of reactant/product molecules present in varying amounts (*e.g., for example, a small pool of water where an abandoned mine seep mixes with river water*)

- We are more interested in calculating the value for ΔG for any particular point in the reaction.
  - ΔG tells us
  - If ΔG = 0,
  - If ΔG < 0,
  - If ΔG > 0,

“Irreversible” A → B







- At equilibrium, G = minimum, ΔG = 0

- We are more interested in calculating the value for ΔG for any particular point in the reaction.
  - ΔG tells us which side of equilibrium we are on
  - If ΔG = 0, the rxn is at equilibrium
  - If ΔG < 0, rxn will proceed to the right as written
  - If ΔG > 0, rxn will proceed to the left as written
- **Goal:** calculate ΔG for any mix of reactants and products

$$\Delta G = \left(\sum_i \mu_i \nu_i\right)_{products} - \left(\sum_i \mu_i \nu_i\right)_{reactants} \qquad \text{Eq 3.20}$$

μ_i = chemical potential of "i" = free energy per mole of reactant "i"

ν_i = stoichiometric coefficient of reactant "i"

For a given solution composition ([i], [j], [k] known), we can determine whether the system is at equilibrium or not.

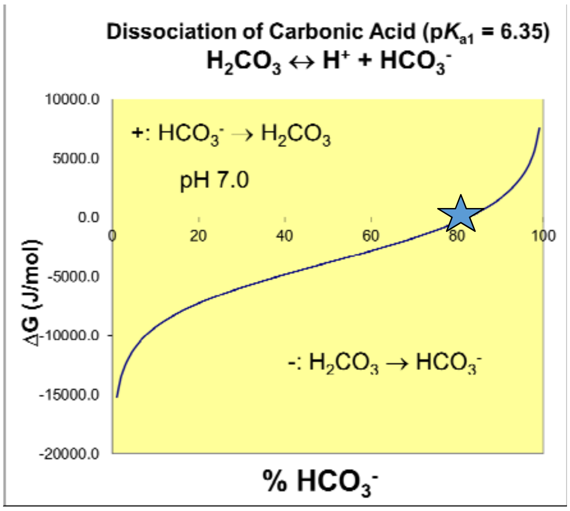
Goal: calculate ΔG for any mix of reactants and products

μ_i under given set of conditions is related to the chemical potential under "standard state" conditions

$$\mu_i = \mu_i^0 + RT\ln\{i\}$$

activity of species "i"

chemical potential of species "i" at "standard state"



Here, we introduce 2 key concepts:

- Activity
- Standard State

Goal: calculate ΔG for any mix of reactants and products

Activity and **Standard State**

- "Thermodynamic" reactivity (activity) of a chemical "A" in any environment is described relative to its reactivity in a "**standard system**", where reactivity is arbitrarily defined as **1.0**
  - **{Activity}** = reactivity of "A" in a particular environment relative to its reactivity in the standard system (unitless)
  - **Standard State** = set of conditions describing the standard system
  - Standard State = {Std Conc.} + {Reference environmental conditions}

    = {Std Conc.} + {Std. P,T & composition req.}

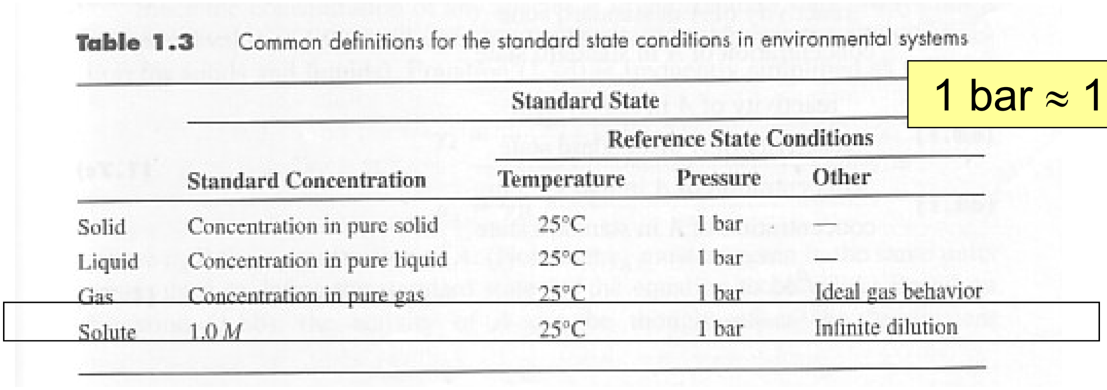


Table 1.3 Common definitions for the standard state conditions in environmental systems

	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

1 bar ≈ 1 atm

Example

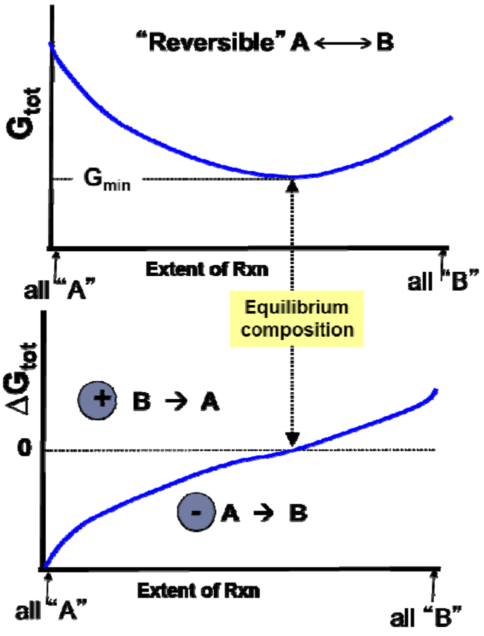
$$Ca^{2+} + HCO_3^- \leftarrow \rightarrow CaCO_{3(s)} + H^+$$

- G^0_f for Ca^{2+} = -553.54 kJ/mol, HCO_3^- = -586.8 kJ/mol, $CaCO_{3(s)}$ = -1128.8 kJ/mol, H^+ = 0 kJ/mol
- At standard state condition, which direction should the reaction go?

Recap

- 3 Models for predicting aqueous chemical composition

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



Thermodynamics

- What is the criteria for reactants "A + B" to spontaneously react to form products "C+D"?
- What is the thermodynamic requirement for equilibrium of a reaction?

Today's Objectives

- Learn to calculate ΔG for a reaction with a given composition of reactants and products.
  - Calculate free energy change of reaction at standard state conditions (ΔG^0)
  - Calculate activities of solutes, H_2O, solids, gases
- Determine if current conditions are at equilibrium or not
- Relate K_{eq} values to thermodynamic properties

We want to calculate ΔG for a given composition of reactants & products

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chemical potential of species "i" at "standard state"

activity of species "i"

Use free energies of formation (G_f^0)
As substitute (Appendix, Pg 758)

Goal: calculate ΔG for any mix of reactants and products

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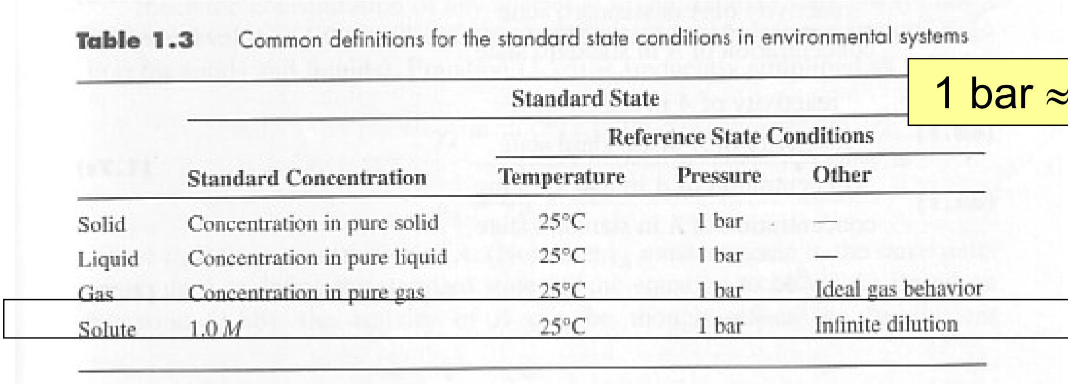

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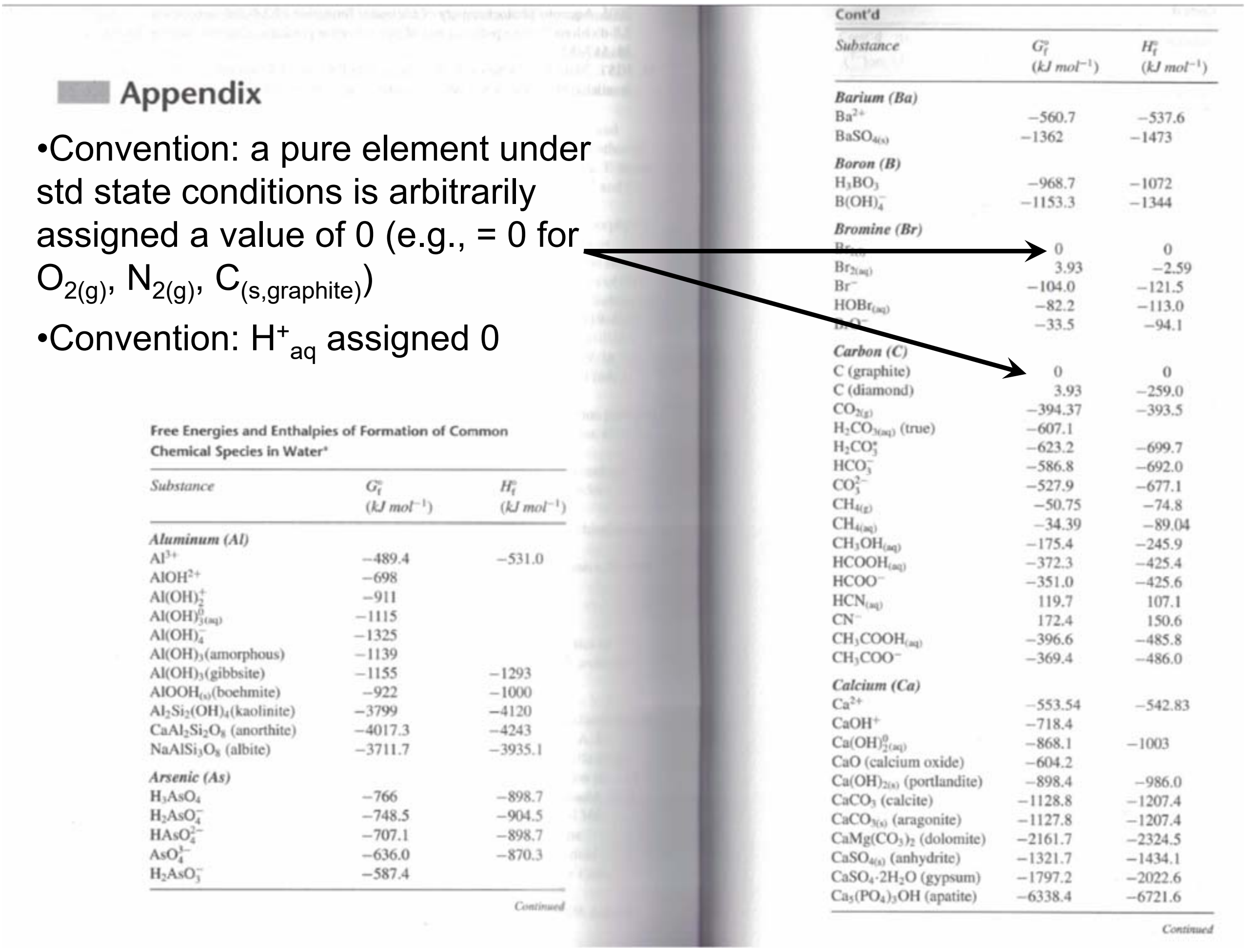

Appendix

- Convention: a pure element under std state conditions is arbitrarily assigned a value of 0 (e.g., = 0 for $O_{2(g)}$, $N_{2(g)}$, $C_{(s,graphite)}$)
- Convention: H^+_{aq} assigned 0

Free Energies and Enthalpies of Formation of Common Chemical Species in Water*

Substance	G_f° (*kJ mol⁻¹*)	H_f° (*kJ mol⁻¹*)
Aluminum (Al)		
Al^{3+}	−489.4	−531.0
$AlOH^{2+}$	−698	
$Al(OH)_2^+$	−911	
$Al(OH)^0_{3(aq)}$	−1115	
$Al(OH)_4^-$	−1325	
$Al(OH)_3$(amorphous)	−1139	
$Al(OH)_3$(gibbsite)	−1155	−1293
$AlOOH_{(s)}$(boehmite)	−922	−1000
$Al_2Si_2(OH)_4$(kaolinite)	−3799	−4120
$CaAl_2Si_2O_8$ (anorthite)	−4017.3	−4243
$NaAlSi_3O_8$ (albite)	−3711.7	−3935.1
Arsenic (As)		
H_3AsO_4	−766	−898.7
$H_2AsO_4^-$	−748.5	−904.5
$HAsO_4^{2-}$	−707.1	−898.7
AsO_4^{3-}	−636.0	−870.3
$H_2AsO_3^-$	−587.4	

Continued

Cont'd

Substance	G_f° (*kJ mol⁻¹*)	H_f° (*kJ mol⁻¹*)
Barium (Ba)		
Ba^{2+}	−560.7	−537.6
$BaSO_{4(s)}$	−1362	−1473
Boron (B)		
H_3BO_3	−968.7	−1072
$B(OH)_4^-$	−1153.3	−1344
Bromine (Br)		
$Br_{2(l)}$	0	0
$Br_{2(aq)}$	3.93	−2.59
Br^-	−104.0	−121.5
$HOBr_{(aq)}$	−82.2	−113.0
BrO^-	−33.5	−94.1
Carbon (C)		
C (graphite)	0	0
C (diamond)	3.93	−259.0
$CO_{2(g)}$	−394.37	−393.5
$H_2CO_{3(aq)}$ (true)	−607.1	
$H_2CO_3^*$	−623.2	−699.7
HCO_3^-	−586.8	−692.0
CO_3^{2-}	−527.9	−677.1
$CH_{4(g)}$	−50.75	−74.8
$CH_{4(aq)}$	−34.39	−89.04
$CH_3OH_{(aq)}$	−175.4	−245.9
$HCOOH_{(aq)}$	−372.3	−425.4
$HCOO^-$	−351.0	−425.6
$HCN_{(aq)}$	119.7	107.1
CN^-	172.4	150.6
$CH_3COOH_{(aq)}$	−396.6	−485.8
CH_3COO^-	−369.4	−486.0
Calcium (Ca)		
Ca^{2+}	−553.54	−542.83
$CaOH^+$	−718.4	
$Ca(OH)^0_{2(aq)}$	−868.1	−1003
CaO (calcium oxide)	−604.2	
$Ca(OH)_{2(s)}$ (portlandite)	−898.4	−986.0
$CaCO_3$ (calcite)	−1128.8	−1207.4
$CaCO_{3(s)}$ (aragonite)	−1127.8	−1207.4
$CaMg(CO_3)_2$ (dolomite)	−2161.7	−2324.5
$CaSO_{4(s)}$ (anhydrite)	−1321.7	−1434.1
$CaSO_4{\cdot}2H_2O$ (gypsum)	−1797.2	−2022.6
$Ca_5(PO_4)_3OH$ (apatite)	−6338.4	−6721.6

Continued

We want to calculate ΔG for a given composition of reactants & products

$$\Delta G = \left(\sum_i \mu_i \nu_i\right)_{products} - \left(\sum_i \mu_i \nu_i\right)_{reac\tan ts}$$

Eq 3.20

μ_i = chemical potential of "i" (J/mol); ν_i = stoichiometric coefficient of reactant "i"

$$\mu_i = \mu_i^0 + RT\ln\{i\}$$

chemical potential of species "i" at "standard state"

activity of species "i"

Use free energies of formation (G_f^0)
As substitute (Appendix, Pg 758)

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How Do we Calculate Activities?

1. Ions and Solute Molecules in Solution

$$\{i\} = \gamma_i[i]$$

[i] = molar concentration (moles/L)

γ_i = activity coefficient

γ = measure of deviation of real environment from the idealized reference-state conditions.

→1.0 as the real environmental conditions approximate reference conditions

- Next class: How to calculate γ_i for ions

  γ_i → 1.0 as solution conditions approach an infinitely dilute state (freshwater)

  [i] → 1.0 as conc. → 1.0 M, the standard concentration (*simplifies our lives*)
- Should use {i} instead of [i] in equilibrium expressions.
- {i} ≈ [i] if we assume infinite dilution conditions
  - good approximation of many freshwater environments
- Activities are **unitless**

for $iA + jB \longleftrightarrow mC + nD$

$$K_{eq} = \frac{\{C\}^m\{D\}^n}{\{A\}^i\{B\}^j} = \frac{(\gamma_C[C])^m(\gamma_D[D])^n}{(\gamma_A[A])^i(\gamma_B[B])^j}$$

2. Solvent Molecules in Solution (the water mCs in themselves)

$$\{i\} = \gamma_i X_i$$

X_i is the mole fraction of solvent molecules

$$X_i = \frac{\text{moles of "i"}}{\text{total moles of all substances}}$$

- γ_i and X_i → 1.0 as solutions become more dilute
  - generally assume that **$\{H_2O\} = 1.0$** because most solutions are so dilute they approximate pure H_2O.
  - if the equilibrium expression has $\{H_2O\}$ in it, we can omit this term from the expression.
- e.g., $H_2O \longleftrightarrow H^+ + OH^-$

$$K_w = \frac{\{H^+\}\{OH^-\}}{\cancelto{1.0}{\{H_2O\}}} = \{H^+\}\{OH^-\}$$

---

3. Pure Liquids or Solids in Equilibrium with a Solution

$\{i\} = 1.0$ ← Not dependent upon the conc. of solid

•Assume unit activity for solid phases that form upon precipitation of ions from solution

•e.g., $CaCO_{3(s)} \longleftrightarrow Ca^{2+} + CO_3^{2-}$

$$K_{sp} = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{\cancelto{1.0}{\{CaCO_{3(s)}\}}} = \{Ca^{2+}\}\{CO_3^{2-}\}$$

4. Gases in Equilibrium with a Solution

$$\{i\} = \gamma_i P_i$$

P_i is the partial pressure of the gas in atm or bar

$$P_i = (n_i/n_{tot}) \times P_{tot}$$

γ_i → 1.0 as the total pressure of the gas (P_{tot}) decreases and ideal gas behavior (PV = nRT) observed

$\{i\} \approx P_i$ at atmospheric pressure levels

$$\Delta G = \left(\sum_i \mu_i \nu_i\right)_{products} - \left(\sum_i \mu_i \nu_i\right)_{reac\tan ts}$$ Eq 3.20

μ_i = chemical potential of “i” (J/mol); ν_i = stoichiometric coefficient of reactant “i”

$$\mu_i = \mu_i^0 + RT\ln\{i\}$$

$$\Delta G = \left(\sum_i \nu_i \left[G_{i,f}^0 + RT\ln\{i\}\right]\right)_{products} - \left(\sum_i \nu_i \left[G_{i,f}^0 + RT\ln\{i\}\right]\right)_{reac\tan ts}$$

Rearranging

$$\Delta G = \underbrace{\left(\sum_i \nu_i G_{if}^0\right)_{products} - \left(\sum_i \nu_i G_{if}^0\right)_{reactants}}_{\Delta G^0} + \underbrace{RTln\left[\frac{\prod\{i\}_{products}^{\nu_i}}{\prod\{i\}_{reactants}^{\nu_i}}\right]}_{RTlnQ}$$

ΔG^0
Std State Contribution
Calculate from Appendix Page 758

RT*ln*Q
Real Conditions Contribution
Calculate from measured or known concentrations

Today’s Objectives

- Learn to calculate ΔG for a reaction with a given composition of reactants and products.
  - Calculate activities of solutes, H_2O, solids, gases
  - Calculate free energy change of reaction at standard state conditions (ΔG^0)
- Determine if current conditions are at equilibrium or not
- Relate K_{eq} values to thermodynamic properties

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].

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

Step 1 - Calculate ΔG^0 :

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	
		$\Sigma\nu_i G^0_{i,f}$ =	

Step 2 - Calculate $\Delta G = \Delta G^0 + RT\ln Q$:

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

How much more dolomite would dissolve before equilibrium is reached

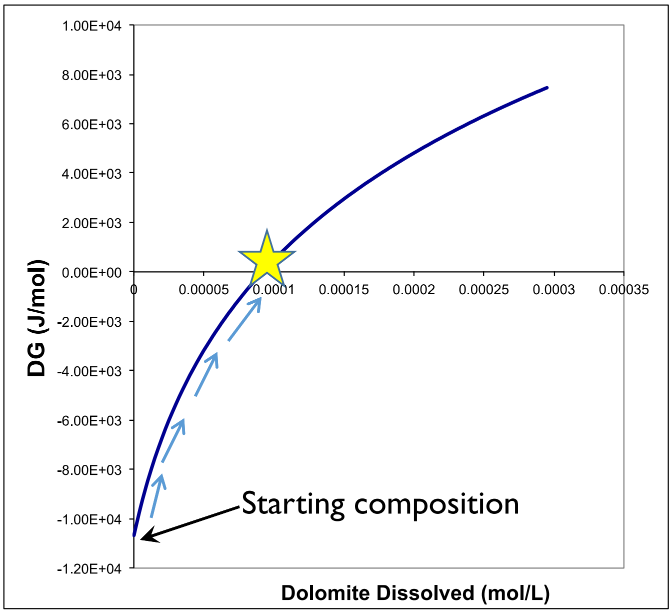
- Use spreadsheet to track how ΔG changes as dolomite incrementally dissolves

- Eqbm reached when 9.2×10^{-5} M more dolomite dissolves
- If more were to dissolve, solution would become supersaturated
    - Too much dissolved; will spontaneously begin to precipitate dolomite

Initial Conditions

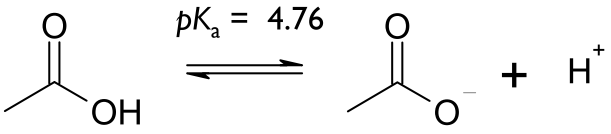
Ca(2+)	3.00E-03
Mg(2+)	4.00E-05
HCO3(-)	5.00E-05
pH	8.6
Keq	3.53E+03

Dolomite dissolved (mol/L)	Q	Q/Keq	ΔG (J/mol)
0	4.75E+01	1.35E-02	-1.07E+04
5.00E-06	7.72E+01	2.18E-02	-9.48E+03
1.00E-05	1.17E+02	3.31E-02	-8.45E+03
1.50E-05	1.68E+02	4.76E-02	-7.55E+03
2.00E-05	2.33E+02	6.58E-02	-6.74E+03
2.50E-05	3.12E+02	8.82E-02	-6.02E+03
3.00E-05	4.07E+02	1.15E-01	-5.36E+03
3.50E-05	5.19E+02	1.47E-01	-4.75E+03
4.00E-05	6.51E+02	1.84E-01	-4.19E+03
4.50E-05	8.04E+02	2.28E-01	-3.67E+03
5.00E-05	9.79E+02	2.77E-01	-3.18E+03
5.50E-05	1.18E+03	3.33E-01	-2.72E+03
6.00E-05	1.40E+03	3.97E-01	-2.29E+03
6.50E-05	1.65E+03	4.68E-01	-1.88E+03
7.00E-05	1.93E+03	5.47E-01	-1.50E+03
7.50E-05	2.24E+03	6.34E-01	-1.13E+03
8.00E-05	2.58E+03	7.31E-01	-7.76E+02
8.50E-05	2.96E+03	8.37E-01	-4.41E+02
9.00E-05	3.37E+03	9.53E-01	-1.19E+02
9.50E-05	3.81E+03	1.08E+00	1.90E+02
1.00E-04	4.30E+03	1.22E+00	4.86E+02
1.05E-04	4.82E+03	1.37E+00	7.71E+02
1.10E-04	5.39E+03	1.53E+00	1.05E+03
1.15E-04	6.00E+03	1.70E+00	1.31E+03
1.20E-04	6.65E+03	1.88E+00	1.57E+03
1.25E-04	7.35E+03	2.08E+00	1.82E+03
1.30E-04	8.10E+03	2.29E+00	2.06E+03
1.35E-04	8.90E+03	2.52E+00	2.29E+03
1.40E-04	9.76E+03	2.76E+00	2.52E+03
1.45E-04	1.07E+04	3.02E+00	2.74E+03



- Can also see why the percentage to which a weak acid dissociates at equilibrium changes with solution pH

Example: Consider the dissociation of 1 mM acetic acid (vinegar), a weak acid



$$HA \leftrightarrow A^- + H^+$$

Compute ΔG as a function of the percent acetic acid dissociated at pH 3.5, 4.5, and 5.5

- We'll assume that all activity coefficients = 1.0, and then can calculate the values of Q, and ΔG from 1 to 99% A^-

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

$$\Delta G^0 = 27155 \text{ J mol}^{-1}$$

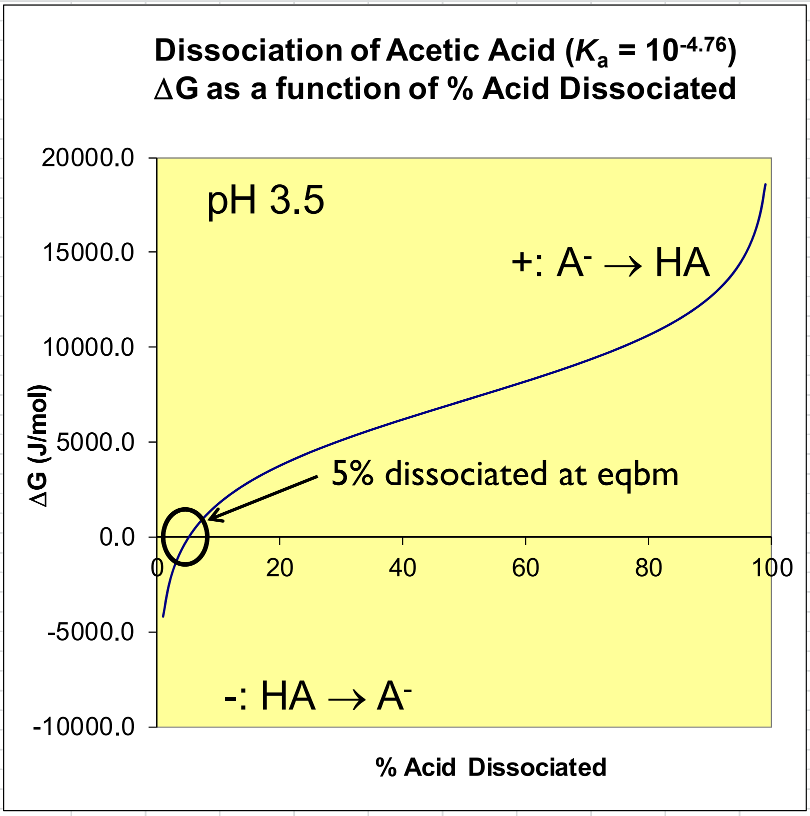
$$\Delta G = 27155 \text{ J mol}^{-1} + (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln \frac{\{H^+\}\{A^-\}}{\{HA\}}$$

@pH 3.5

$$\Delta G = 27155\,Jmol^{-1} + RTln\frac{\{3.2\times10^{-4}\}\{A^{-}\}}{\{HA\}}$$

pH	3.5		Ka	1.7E-05		CT	0.001 mol/L

% Dissociated	{A-} (mol/L)	{HA} (mol/L)	{H+} (mol/L)	Q	Q/Keq	ΔG (J/mol)
1	0.00001	0.00099	3.2E-04	3.2E-06	0.18	-4198.8
2	0.00002	0.00098	3.2E-04	6.5E-06	0.37	-2455.4
3	0.00003	0.00097	3.2E-04	9.8E-06	0.56	-1424.9
4	0.00004	0.00096	3.2E-04	1.3E-05	0.76	-686.1
5	0.00005	0.00095	3.2E-04	1.7E-05	0.96	-107.0
6	0.00006	0.00094	3.2E-04	2.0E-05	1.16	371.1
7	0.00007	0.00093	3.2E-04	2.4E-05	1.37	779.8
8	0.00008	0.00092	3.2E-04	2.7E-05	1.58	1137.6
9	0.00009	0.00091	3.2E-04	3.1E-05	1.80	1456.6
10	0.0001	0.0009	3.2E-04	3.5E-05	2.02	1745.2
11	0.00011	0.00089	3.2E-04	3.9E-05	2.25	2009.1
12	0.00012	0.00088	3.2E-04	4.3E-05	2.48	2252.8
13	0.00013	0.00087	3.2E-04	4.7E-05	2.72	2479.6
14	0.00014	0.00086	3.2E-04	5.1E-05	2.96	2691.9
15	0.00015	0.00085	3.2E-04	5.6E-05	3.21	2891.9
16	0.00016	0.00084	3.2E-04	6.0E-05	3.47	3081.2
17	0.00017	0.00083	3.2E-04	6.5E-05	3.73	3261.2
18	0.00018	0.00082	3.2E-04	6.9E-05	3.99	3432.9
19	0.00019	0.00081	3.2E-04	7.4E-05	4.27	3597.4
20	0.0002	0.0008	3.2E-04	7.9E-05	4.55	3755.3
21	0.00021	0.00079	3.2E-04	8.4E-05	4.84	3907.4
22	0.00022	0.00078	3.2E-04	8.9E-05	5.13	4054.3
23	0.00023	0.00077	3.2E-04	9.4E-05	5.44	4196.5
24	0.00024	0.00076	3.2E-04	1.0E-04	5.75	4334.4
25	0.00025	0.00075	3.2E-04	1.1E-04	6.07	4468.4
26	0.00026	0.00074	3.2E-04	1.1E-04	6.39	4598.9
27	0.00027	0.00073	3.2E-04	1.2E-04	6.73	4726.2
28	0.00028	0.00072	3.2E-04	1.2E-04	7.08	4850.5
29	0.00029	0.00071	3.2E-04	1.3E-04	7.43	4972.2
30	0.0003	0.0007	3.2E-04	1.4E-04	7.80	5091.4
31	0.00031	0.00069	3.2E-04	1.4E-04	8.18	5208.3
32	0.00032	0.00068	3.2E-04	1.5E-04	8.56	5323.2
33	0.00033	0.00067	3.2E-04	1.6E-04	8.96	5436.2
34	0.00034	0.00066	3.2E-04	1.6E-04	9.37	5547.5
35	0.00035	0.00065	3.2E-04	1.7E-04	9.80	5657.2
36	0.00036	0.00064	3.2E-04	1.8E-04	10.24	5765.5
37	0.00037	0.00063	3.2E-04	1.9E-04	10.69	5872.4
38	0.00038	0.00062	3.2E-04	1.9E-04	11.15	5978.2
39	0.00039	0.00061	3.2E-04	2.0E-04	11.63	6082.9


Dissociation of Acetic Acid (K_a = $10^{-4.76}$)
ΔG as a function of % Acid Dissociated

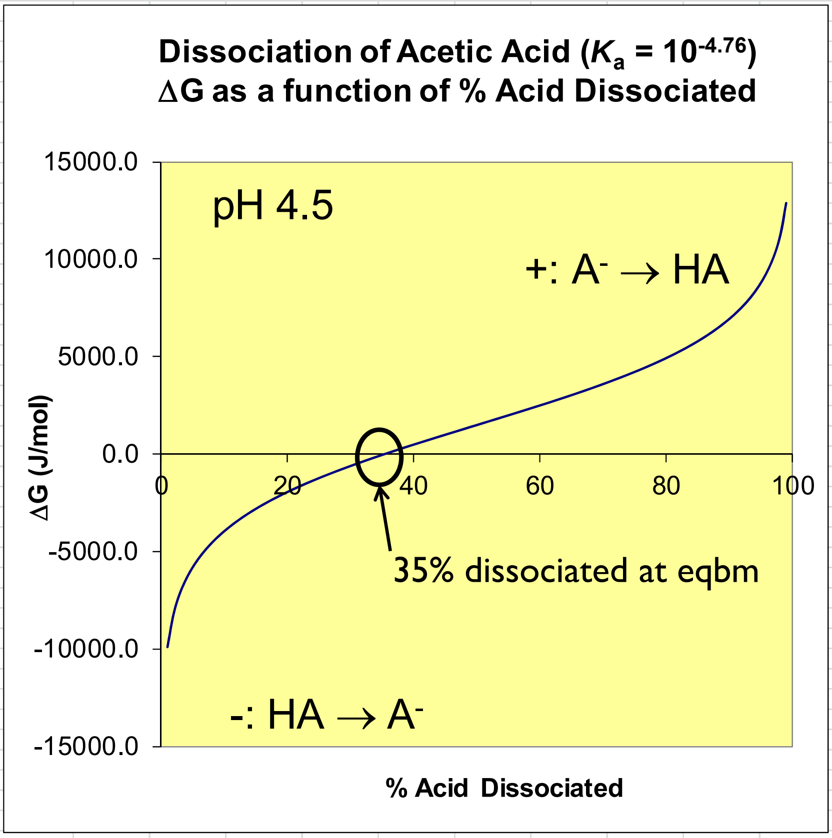
5% dissociated at eqbm

@pH 4.5

$$\Delta G = 27155\,Jmol^{-1} + RTln\frac{\{3.2\times10^{-5}\}\{A^{-}\}}{\{HA\}}$$

pH	4.5		Ka	1.7E-05		CT	0.001 mol/L

% Dissociated	{A-} (mol/L)	{HA} (mol/L)	{H+} (mol/L)	Q	Q/Keq	ΔG (J/mol)
1	0.00001	0.00099	3.2E-05	3.2E-07	0.02	-9906.5
2	0.00002	0.00098	3.2E-05	6.5E-07	0.04	-8163.1
3	0.00003	0.00097	3.2E-05	9.8E-07	0.06	-7132.6
4	0.00004	0.00096	3.2E-05	1.3E-06	0.08	-6393.8
5	0.00005	0.00095	3.2E-05	1.7E-06	0.10	-5814.7
6	0.00006	0.00094	3.2E-05	2.0E-06	0.12	-5336.6
7	0.00007	0.00093	3.2E-05	2.4E-06	0.14	-4927.9
8	0.00008	0.00092	3.2E-05	2.7E-06	0.16	-4570.1
9	0.00009	0.00091	3.2E-05	3.1E-06	0.18	-4251.1
10	0.0001	0.0009	3.2E-05	3.5E-06	0.20	-3962.5
11	0.00011	0.00089	3.2E-05	3.9E-06	0.22	-3698.6
12	0.00012	0.00088	3.2E-05	4.3E-06	0.25	-3454.9
13	0.00013	0.00087	3.2E-05	4.7E-06	0.27	-3228.1
14	0.00014	0.00086	3.2E-05	5.1E-06	0.30	-3015.8
15	0.00015	0.00085	3.2E-05	5.6E-06	0.32	-2815.8
16	0.00016	0.00084	3.2E-05	6.0E-06	0.35	-2626.4
17	0.00017	0.00083	3.2E-05	6.5E-06	0.37	-2446.5
18	0.00018	0.00082	3.2E-05	6.9E-06	0.40	-2274.8
19	0.00019	0.00081	3.2E-05	7.4E-06	0.43	-2110.3
20	0.0002	0.0008	3.2E-05	7.9E-06	0.45	-1952.4
21	0.00021	0.00079	3.2E-05	8.4E-06	0.48	-1800.3
22	0.00022	0.00078	3.2E-05	8.9E-06	0.51	-1653.4
23	0.00023	0.00077	3.2E-05	9.4E-06	0.54	-1511.2
24	0.00024	0.00076	3.2E-05	1.0E-05	0.57	-1373.3
25	0.00025	0.00075	3.2E-05	1.1E-05	0.61	-1239.3
26	0.00026	0.00074	3.2E-05	1.1E-05	0.64	-1108.8
27	0.00027	0.00073	3.2E-05	1.2E-05	0.67	-981.5
28	0.00028	0.00072	3.2E-05	1.2E-05	0.71	-857.1
29	0.00029	0.00071	3.2E-05	1.3E-05	0.74	-735.5
30	0.0003	0.0007	3.2E-05	1.4E-05	0.78	-616.3
31	0.00031	0.00069	3.2E-05	1.4E-05	0.82	-499.4
32	0.00032	0.00068	3.2E-05	1.5E-05	0.86	-384.5
33	0.00033	0.00067	3.2E-05	1.6E-05	0.90	-271.5
34	0.00034	0.00066	3.2E-05	1.6E-05	0.94	-160.2
35	0.00035	0.00065	3.2E-05	1.7E-05	0.98	-50.5
36	0.00036	0.00064	3.2E-05	1.8E-05	1.02	57.8
37	0.00037	0.00063	3.2E-05	1.9E-05	1.07	164.7
38	0.00038	0.00062	3.2E-05	1.9E-05	1.12	270.5
39	0.00039	0.00061	3.2E-05	2.0E-05	1.16	375.2


Dissociation of Acetic Acid (K_a = $10^{-4.76}$)
ΔG as a function of % Acid Dissociated

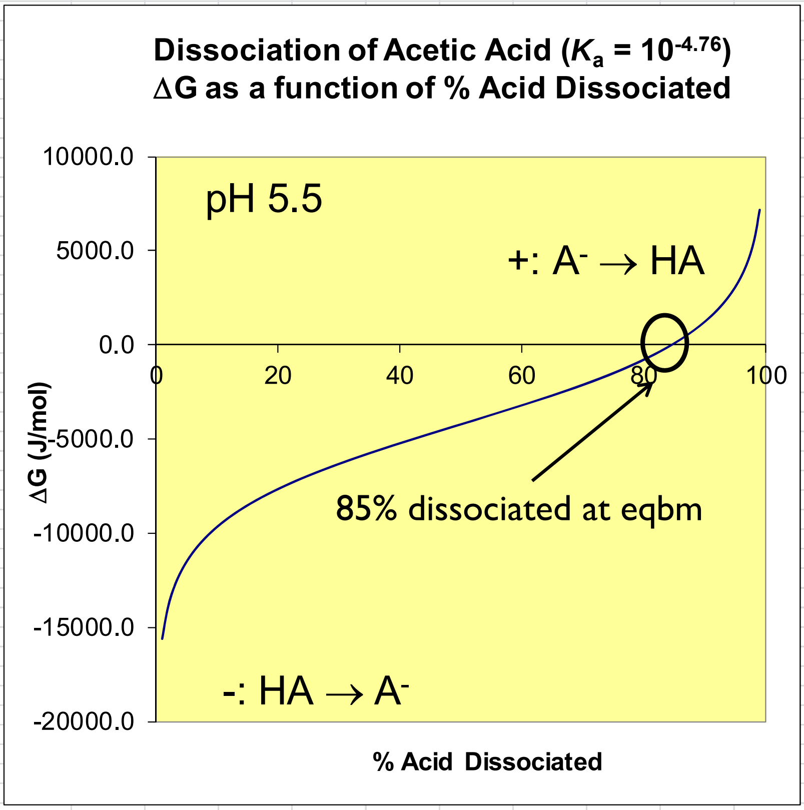
35% dissociated at eqbm

@pH 5.5

$$\Delta G = 27155\,Jmol^{-1} + RTln\frac{\{3.2\times 10^{-6}\}\{A^-\}}{\{HA\}}$$

	pH	5.5		Ka	1.7E-05	
% Dissociated	{A-} (mol/L)	{HA} (mol/L)	{H+} (mol/L)	Q	Q/Keq	ΔG (J/mol)
1	0.00001	0.00099	3.2E-06	3.2E-08	0.00	-15614.2
2	0.00002	0.00098	3.2E-06	6.5E-08	0.00	-13870.8
3	0.00003	0.00097	3.2E-06	9.8E-08	0.01	-12840.3
4	0.00004	0.00096	3.2E-06	1.3E-07	0.01	-12101.5
5	0.00005	0.00095	3.2E-06	1.7E-07	0.01	-11522.4
6	0.00006	0.00094	3.2E-06	2.0E-07	0.01	-11044.3
7	0.00007	0.00093	3.2E-06	2.4E-07	0.01	-10635.6
8	0.00008	0.00092	3.2E-06	2.7E-07	0.02	-10277.8
9	0.00009	0.00091	3.2E-06	3.1E-07	0.02	-9958.8
10	0.0001	0.0009	3.2E-06	3.5E-07	0.02	-9670.2
11	0.00011	0.00089	3.2E-06	3.9E-07	0.02	-9406.3
12	0.00012	0.00088	3.2E-06	4.3E-07	0.02	-9162.6
13	0.00013	0.00087	3.2E-06	4.7E-07	0.03	-8935.8
14	0.00014	0.00086	3.2E-06	5.1E-07	0.03	-8723.5
15	0.00015	0.00085	3.2E-06	5.6E-07	0.03	-8523.5
16	0.00016	0.00084	3.2E-06	6.0E-07	0.03	-8334.1
17	0.00017	0.00083	3.2E-06	6.5E-07	0.04	-8154.2
18	0.00018	0.00082	3.2E-06	6.9E-07	0.04	-7982.4
19	0.00019	0.00081	3.2E-06	7.4E-07	0.04	-7818.0
20	0.0002	0.0008	3.2E-06	7.9E-07	0.05	-7660.1
21	0.00021	0.00079	3.2E-06	8.4E-07	0.05	-7507.9
22	0.00022	0.00078	3.2E-06	8.9E-07	0.05	-7361.0
23	0.00023	0.00077	3.2E-06	9.4E-07	0.05	-7218.9
24	0.00024	0.00076	3.2E-06	1.0E-06	0.06	-7081.0
25	0.00025	0.00075	3.2E-06	1.1E-06	0.06	-6947.0
26	0.00026	0.00074	3.2E-06	1.1E-06	0.06	-6816.5
27	0.00027	0.00073	3.2E-06	1.2E-06	0.07	-6689.2
28	0.00028	0.00072	3.2E-06	1.2E-06	0.07	-6564.8
29	0.00029	0.00071	3.2E-06	1.3E-06	0.07	-6443.2
30	0.0003	0.0007	3.2E-06	1.4E-06	0.08	-6324.0
31	0.00031	0.00069	3.2E-06	1.4E-06	0.08	-6207.0
32	0.00032	0.00068	3.2E-06	1.5E-06	0.09	-6092.2
33	0.00033	0.00067	3.2E-06	1.6E-06	0.09	-5979.2
34	0.00034	0.00066	3.2E-06	1.6E-06	0.09	-5867.9
35	0.00035	0.00065	3.2E-06	1.7E-06	0.10	-5758.2
36	0.00036	0.00064	3.2E-06	1.8E-06	0.10	-5649.9
37	0.00037	0.00063	3.2E-06	1.9E-06	0.11	-5543.0
38	0.00038	0.00062	3.2E-06	1.9E-06	0.11	-5437.2
39	0.00039	0.00061	3.2E-06	2.0E-06	0.12	-5332.5

CT 0.001 mol/L

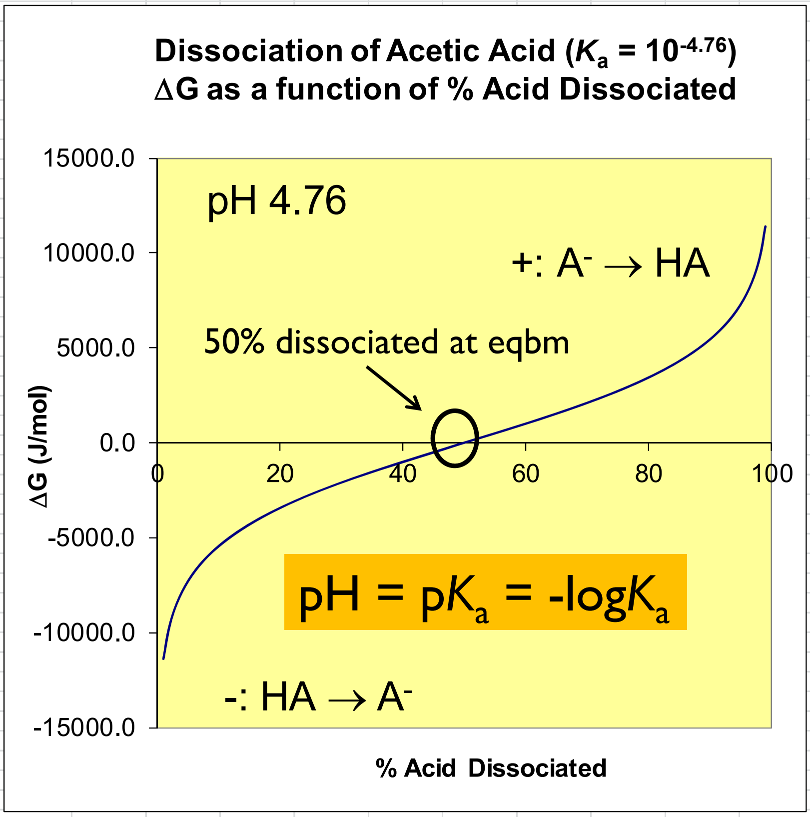


@pH 4.76

$$\Delta G = 27155\,Jmol^{-1} + RTln\frac{\{1.7\times 10^{-5}\}\{A^-\}}{\{HA\}}$$

	pH	4.76		Ka	1.7E-05	
% Dissociated	{A-} (mol/L)	{HA} (mol/L)	{H+} (mol/L)	Q	Q/Keq	ΔG (J/mol)
1	0.00001	0.00099	1.7E-05	1.8E-07	0.01	-11390.5
2	0.00002	0.00098	1.7E-05	3.5E-07	0.02	-9647.1
3	0.00003	0.00097	1.7E-05	5.4E-07	0.03	-8616.6
4	0.00004	0.00096	1.7E-05	7.2E-07	0.04	-7877.8
5	0.00005	0.00095	1.7E-05	9.1E-07	0.05	-7298.7
6	0.00006	0.00094	1.7E-05	1.1E-06	0.06	-6820.6
7	0.00007	0.00093	1.7E-05	1.3E-06	0.08	-6411.9
8	0.00008	0.00092	1.7E-05	1.5E-06	0.09	-6054.1
9	0.00009	0.00091	1.7E-05	1.7E-06	0.10	-5735.1
10	0.0001	0.0009	1.7E-05	1.9E-06	0.11	-5446.5
11	0.00011	0.00089	1.7E-05	2.1E-06	0.12	-5182.6
12	0.00012	0.00088	1.7E-05	2.4E-06	0.14	-4938.9
13	0.00013	0.00087	1.7E-05	2.6E-06	0.15	-4712.1
14	0.00014	0.00086	1.7E-05	2.8E-06	0.16	-4499.8
15	0.00015	0.00085	1.7E-05	3.1E-06	0.18	-4299.8
16	0.00016	0.00084	1.7E-05	3.3E-06	0.19	-4110.4
17	0.00017	0.00083	1.7E-05	3.6E-06	0.20	-3930.5
18	0.00018	0.00082	1.7E-05	3.8E-06	0.22	-3758.8
19	0.00019	0.00081	1.7E-05	4.1E-06	0.23	-3594.3
20	0.0002	0.0008	1.7E-05	4.3E-06	0.25	-3436.4
21	0.00021	0.00079	1.7E-05	4.6E-06	0.27	-3284.3
22	0.00022	0.00078	1.7E-05	4.9E-06	0.28	-3137.4
23	0.00023	0.00077	1.7E-05	5.2E-06	0.30	-2995.2
24	0.00024	0.00076	1.7E-05	5.5E-06	0.32	-2857.3
25	0.00025	0.00075	1.7E-05	5.8E-06	0.33	-2723.3
26	0.00026	0.00074	1.7E-05	6.1E-06	0.35	-2592.8
27	0.00027	0.00073	1.7E-05	6.4E-06	0.37	-2465.5
28	0.00028	0.00072	1.7E-05	6.8E-06	0.39	-2341.1
29	0.00029	0.00071	1.7E-05	7.1E-06	0.41	-2219.5
30	0.0003	0.0007	1.7E-05	7.4E-06	0.43	-2100.3
31	0.00031	0.00069	1.7E-05	7.8E-06	0.45	-1983.4
32	0.00032	0.00068	1.7E-05	8.2E-06	0.47	-1868.5
33	0.00033	0.00067	1.7E-05	8.6E-06	0.49	-1755.5
34	0.00034	0.00066	1.7E-05	9.0E-06	0.52	-1644.2
35	0.00035	0.00065	1.7E-05	9.4E-06	0.54	-1534.5
36	0.00036	0.00064	1.7E-05	9.8E-06	0.56	-1426.2
37	0.00037	0.00063	1.7E-05	1.0E-05	0.59	-1319.3
38	0.00038	0.00062	1.7E-05	1.1E-05	0.61	-1213.5
39	0.00039	0.00061	1.7E-05	1.1E-05	0.64	-1108.8

CT 0.001 mol/L



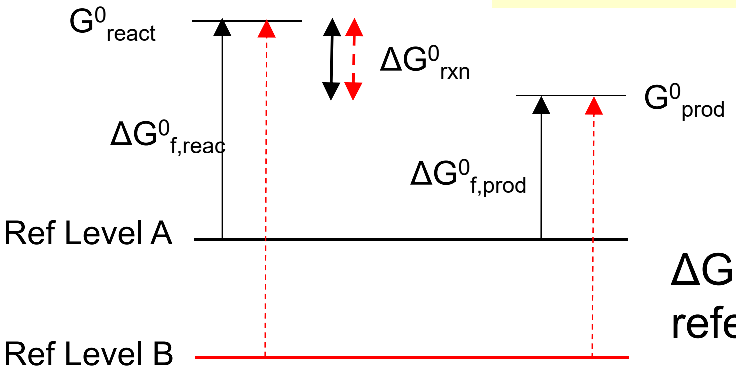
$\bar{G}_{i,f}^{0}$

- Why do we calculate ΔG^0 from G_f^0 values?
- **Problem:** cannot measure absolute values of $\bar{G}_i^0$ directly, but can measure changes in free energy
- To get ΔG^0, we use the values of $\bar{G}_{i,f}^0$, the free energy released (-) or added (+) to produce 1 mole of "i" from its component elements at standard state conditions

-works because products & reactants built from the same component elements, so the energy "level" of the component elements will cancel out.

$$\Delta G^0 = \left(\sum_i \upsilon_i \bar{G}_i^0\right)_{PRODUCTS} - \left(\sum_i \upsilon_i \bar{G}_i^0\right)_{REACTANTS} \qquad \text{(eq. 3-11)}$$

$$= \left(\sum_i \upsilon_i \Delta \bar{G}_{i,f}^0\right)_{PRODUCTS} - \left(\sum_i \upsilon_i \Delta \bar{G}_{i,f}^0\right)_{REACTANTS} \qquad \text{(eq 3-13)}$$



ΔG^0_{rxn} independent of chosen reference energy level

Today's Objectives

- Learn to calculate ΔG for a reaction with a given composition of reactants and products.
    - Calculate activities of solutes, H_2O, solids, gases
    - Calculate free energy change of reaction at standard state conditions (ΔG^0)
- Determine if current conditions are at equilibrium or not
- Relate K_{eq} values to thermodynamic properties

Relating K_{eq} to ΔG^0

At equilibrium:

$$\Delta G = 0 = \Delta G^0 + RT\ln\frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$$

and

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

Therefore,

$$\Delta G^0 = -RT\ln\frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b} = -RT\ln K_{eq}$$

Rearrange

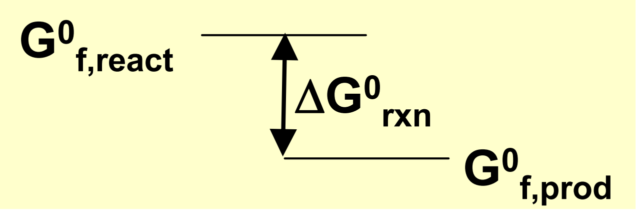
$$\ln K_{eq} = -\frac{\Delta G^0}{RT} \qquad K_{eq} = e^{\left(-\frac{\Delta G^0}{RT}\right)}$$

And

$$\Delta \mathrm{G} = RT\ln\frac{\mathrm{Q}}{K_{eq}}$$

Relating K_{eq} to ΔG^0

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



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

What is K_{eq} for dolomite dissolution?

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

$$\Delta G = \Delta G^0 + RT\ln\frac{\{Ca^{2+}\}\{Mg^{2+}\}\{HCO_3^-\}^2}{\{CaMg(CO_3)_2(s)\}\{H^+\}^2}$$

$$\Delta G = -20{,}240\ \mathrm{J\ mol^{-1}} + (8.314\ \mathrm{J\ mol^{-1}\ K^{-1}})(298\ \mathrm{K})\ln\frac{\{Ca^{2+}\}\{Mg^{2+}\}\{HCO_3^-\}^2}{\{CaMg(CO_3)_2(s)\}\{H^+\}^2}$$

At equilibrium $-\dfrac{\Delta G^0}{RT} = \ln K_{eq}$

$$-\frac{\Delta G^0}{RT} = -\frac{-20{,}240\ \mathrm{J\ mol^{-1}}}{(8.314\ \mathrm{J\ mol^{-1}\ K^{-1}})(298\ \mathrm{K})} = +8.17 = \ln K_{eq}$$

$$K_{eq} = e^{+8.17} = 3.53 \times 10^3$$

Problem 1b: 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. 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.**

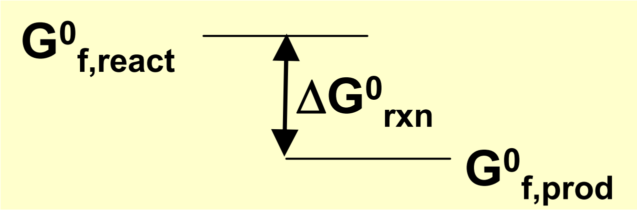
Problem 2: What is the activity of Ca^{2+} in pH 9.0 solution in equilibrium with dolomite, if $\{HCO_3^-\} = 10^{-4}$ M and $\{Mg^{2+}\} = 10^{-4}$ M?

Recap

- Procedure for calculating ΔG and determining degree of (dis)equilibria

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

- How we calculate activities {i}
- How we calculate ΔG^0
- Relationship between K_{eq} values and ΔG^0 of a reaction



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