CH 302 Exam Review

PHYSICAL EQUILIBRIUM, INTRO TO CHEMICAL EQUILIBRIUM

Exam One Breakdown

20 Q's → 12 concept,
8 calc

Last Minute Studying Playlist
Jimmy Wadman on Spotify

Equilibrium

Unit One Learning Outcomes

1. Demonstrate mastery of and compound and reaction stoichiometry (mole-to-mole conversion and grams to mole conversions).
2. Predict the sign of ΔG, ΔH, and/or ΔS for physical change
3. Understand the concept of spontaneous change and equilibrium in the context of phase changes, including calculating phase transition temperatures from standard thermodynamic data.
4. Interpret heating curves and calculate heat required for phase transitions and temperature changes.
5. Describe phase transitions (macroscopically and microscopically).
6. Understand phase in the context of Boltzmann distribution.
7. Understand how intermolecular forces, temperature, and solute concentration affect vapor pressure.
8. Interpret phase diagrams and identify normal boiling and melting point, critical point, and triple point.
9. Describe the factors that favor the dissolution process in terms of intermolecular forces and thermodynamics (eg.: enthalpies of solution, hydration, lattice energy, entropies of solution, free energy of solution, and temperature).
10. Describe how T and P (Henry's Law) each affect solubility.
11. Define and perform calculations for common concentration units: molarity, molality, and mole fraction.
12. Perform calculations and understand the concepts of the four colligative properties: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.
13. Describe the dissociation of ionic compounds in solution and the effects on colligative properties (van't Hoff factor, i).
14. Describe the relationship between free energy and equilibrium
15. Know the importance of the activity of a species and how it relates to concentration, pressure, and equilibrium.
16. Write the mass action expression for homogeneous and heterogeneous equilibria.
17. Determine new values for K when combining multiple reactions.
18. Know the difference between K_p and K_c ~~and be able to convert between the two.~~

Unit One Road Map

1. Quantifying phase changes using enthalpy, entropy, and free energy
2. Vapor Pressure: concepts, calculations, and its relationship to boiling and IMFs
3. Phase Diagrams: identifying the most stable phase of a substance at a given temperature and pressure
4. Thermodynamics associated with creating a solution
   - Does it dissolve?
   - Temperature dependence of dissolution
5. Colligative Properties: the increased stability of a solution changes the physical properties accordingly
   - Vapor pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure
   - Concentration units and conversions
6. **Intro to Chemical Equilibrium: A reaction proceeds in relation to the activities of the products and reactants**
   - Create mass action expressions
   - Modify K based on modifying a chemical reaction
   - Solve problems based on the mass action expression (solve for K, Q, or unknown concentrations at equilibrium)

Exam One - Sources of Error

1. Forgetting or misusing *i* (van't Hoff Factor) in colligative property calculations, concepts
2. Not knowing how to convert between concentration units
3. Mixing different units without converting (particularly with osmotic pressure, CC equation)
4. Forgetting to study the underlying thermodynamics of phase changes, dissolution ✓
5. Forgetting to study the importance of stoichiometry: conversions between concentration units, moles, and molecular weight
6. Learn application questions: past exams - Koofers
7. **MUST DO: Gchem Concentration worksheet (physical equilibrium chapter)**

Thermodynamics of Phase Changes

STATE FUNCTIONS, PHASE DIAGRAMS, VAPOR PRESSURE

Free Energy - Phase Changes

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

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

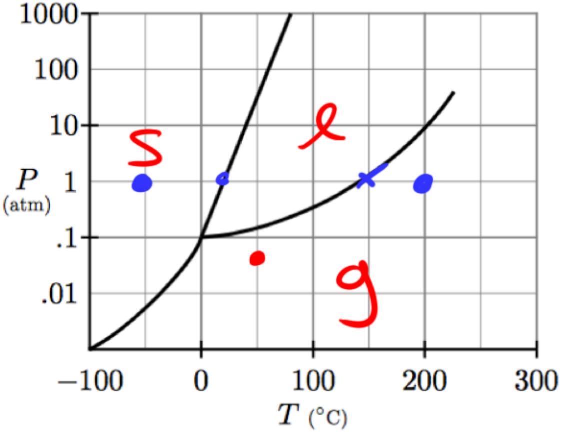
Freezing, condensation, deposition

Energy OUT = lower entropy, energy state
Exothermic, so the phase change gives its energy to the surroundings

Fusion (melting), boiling, sublimation

Energy IN = Higher entropy, energy state
Endothermic, so we get the energy to do this phase change from the surroundings

Phase Diagram Concept Check



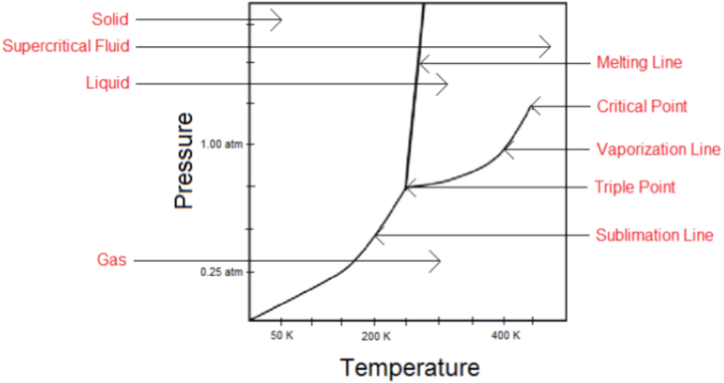
- What is the lowest free energy state at 0.05 atm and 50˚C?
  - I. Solid
  - II. Liquid
  - [✓ III.] Gas
  - IV. Supercritical Fluid
- What phase transition(s) occur when you cool the substance from 200˚C to -50˚C at 1 atm?

Condensation

Freezing

Phase Diagram Checklist

- Phase diagrams show the lowest free energy phase of a substance at a given temperature and pressure.



- Identify the key features of the diagram:
  - What is the stable phase at a certain temperature and pressure?
  - Identify the normal boiling point, melting point, etc.
  - Identify the triple point
  - Identify the critical point
  - What phase transition does a specific line represent?
- Moving along the diagram:
  - What phase transitions do you go through if you go from point A to point B on the graph?

Understand phase in the context of Boltzmann distribution.

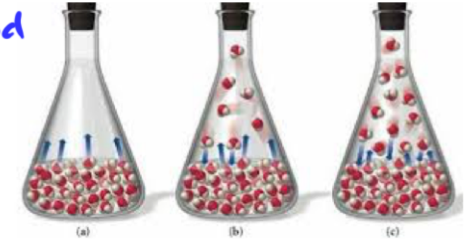
Vapor Pressure

- For any given liquid sample in a closed container, a certain amount of that sample exists is the gas phase. This is what is known as the **vapor pressure**.
- **These molecules have enough kinetic energy to "escape" the attractions of other molecules on the surface.**
- Vapor pressure is a function of dynamic equilibrium between the gas and the surface molecules of a liquid.

Identity of liquid

IMFs

Solution



T ↑ VP ↑

exponential

- The Vapor Pressure is a function of **the IMF's of the liquid (identity of liquid)** and the temperature.
- The normal boiling point of a liquid is where the VP = 1 atm

Vapor Pressure and IMF's

- If Vapor Pressure is the pressure of gas above a liquid in a closed container at a given temperature, we can easily determine that a sample with High IMF's will have a Low VP (less molecules able to overcome the IMFs and be "lifted into the gas phase).

Strong IMF - > low VP (and high boiling point, high ΔH_{vap})

Weak IMF -> high VP (and low boiling point, low ΔH_{vap})

IMF Review

Dispersion Forces < Dipole Forces < Hydrogen-Bonding

Dispersion forces:

C_nH_{n+2}, CCl_4, $C0_2$, F_2 etc.

Dipole-Dipole:

CH_2O, CH_3COCH_3, $AsCl_3$, etc.

H-bonding:

CH_3OH, H_2O, HF, NH_3, etc.

Vapor Pressure Conceptual Question

Consider the vapor pressures from a data table shown below at 20°C:

Benzaldehyde, 1.27 mmHg low VP

Formaldehyde, 3284 mmHg High VP

Both substances are in identical closed containers. Compared to a one mole sample of formaldehyde, you can conclude that a one mole sample of benzaldehyde...

[✓ I.] has a higher ΔH_{vap}

[✓ II.] has a higher boiling point

III. has a lower ΔH_{vap}

[✓ IV.] has a greater number of molecules in the condensed phase

Which of the following has a higher vapor pressure at room temperature?

Same VP

- 10 mL water in a 20 mL container
- 10 mL water in a 50 mL container
- 20 mL water in a 10 mL container
- 10 mL water in an extra wide 50 mL container

Which of the following has the highest number of gas moles?

- 10 mL water in a 30 mL container
- 10 mL water in a 50 mL container → more gas moles

Vapor Pressure Calculations

- Mathematically, the vapor pressure for a given liquid is only dependent on a change in temperature.

Higher Temperature = Exponentially Higher Vapor Pressure

$$P_{vap} = K \cdot e^{\frac{-\Delta H^{\circ}_{vap}}{R \cdot T}}$$

- **Changing the surface area, size of the container, amount of water, and so on does not change the pressure.**
- Of all the derivations used to model this relationship, the most important equation to you will be the Clausius-Clapeyron Equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \boxed{\frac{\Delta H_{vap}}{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Kelvin

Note: the order of P_2 / P_1 and $(1 / T_1 - 1/T_2)$ is important. If you forget the order, remember that as you increase temperature, you are increasing vapor pressure. You are taking the difference of the inverse temperature, so you need to switch the order.

Solutions

DEFINITIONS, CONCENTRATION UNITS, LIKE-DISSOLVES-LIKE, ENTHALPY OF A SOLUTION

Thermodynamics of Solution

Salt Dissolving in Water

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{solvation}} \approx \mathbf{0^*}$$

$(+)$ $(-)$

$$\Delta S_{\text{solution}} = S_{\text{(aqueous)}} - S_{\text{(solid)}} = \textbf{Positive}$$

entropy driven

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \textbf{Negative}$$

$$\Delta G_{\text{solution}} = (0^*) - T\,(+)$$

Dissolution of salt is typically an entropy-driven process, favored at high temperatures

Gas Dissolving in Water

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{solvation}} = \textbf{Negative}$$

0 $(-)$

$$\Delta S_{\text{solution}} = S_{\text{(aqueous)}} - S_{\text{(gas)}} = \textbf{Negative}$$

enthalpy driven

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \textbf{Negative}$$

$$\Delta G_{\text{solution}} = (-) - T\,(-)$$

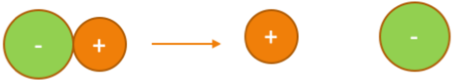
Dissolution of gas is typically an enthalpy-driven process, favored at low temperatures and high pressures

* *ΔH* solution is 0 for an ideal solution. For your typical salts, it is slightly endothermic. There are examples of both endothermic AND exothermic solid dissolution processes

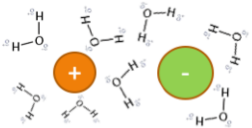
Enthalpy of Salt Solution - Details

$$\Delta H_{solution} = \underset{\text{Always +}}{\Delta H_{lattice}} + \underset{\text{Always -}}{\Delta H_{solvation}}$$

Step one: Lattice Energy breaks apart ionic solute-solute attractions (bonds breaking, endothermic)



+ Step two: Solvation Energy is released when solute-solvent attractions are formed (bonds forming, exothermic)



Theoretically, the value of $\Delta H_{solution}$ should be 0. But what if…

1. $\Delta H_{lattice} > \Delta H_{solvation}$

   ↳ endothermic

2. $\Delta H_{solvation} > \Delta H_{lattice}$

   ↳ exothermic

   NaOH, KOH

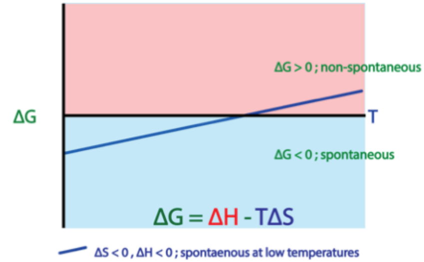
Gas Dissolving in Water - Details

- For a gas dissolving in liquid, the reaction is exothermic ($\Delta H_{solution} < 0$) because there is **no lattice energy** and a negative solvation energy.

- There is a negative change in entropy ($\Delta S < 0$) because you are going from gas to aqueous

- Therefore, dissolution is favored at low temperatures. **Why? Dissolution of a gas is an enthalpy driven process!**

- Henry's Law also states that gas dissolution is favored at high pressures.



$$P_{gas,above} = \overset{atm}{K} X_{gas,dissolved}$$

$$C_{gas,dissolved} = \underset{\frac{M}{atm}}{K} P_{gas,above}$$

Miscibility of Liquids - Like-Dissolves-Like

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process, favored at high temperatures:

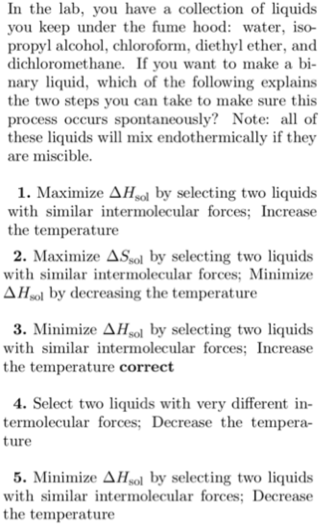
like-dissolves-like

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \textbf{Negative}$$

$$\Delta G_{\text{solution}} = (+) - T(+)$$

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process. There are two important points here:

1. Enthalpy is important when mixing two liquids. Matching the IMF's of two liquids MINIMIZES the ΔH term.
2. Increasing temperature increases solubility



In the lab, you have a collection of liquids you keep under the fume hood: water, isopropyl alcohol, chloroform, diethyl ether, and dichloromethane. If you want to make a binary liquid, which of the following explains the two steps you can take to make sure this process occurs spontaneously? Note: all of these liquids will mix endothermically if they are miscible.

1. Maximize ΔH_{sol} by selecting two liquids with similar intermolecular forces; Increase the temperature

2. Maximize ΔS_{sol} by selecting two liquids with similar intermolecular forces; Minimize ΔH_{sol} by decreasing the temperature

3. Minimize ΔH_{sol} by selecting two liquids with similar intermolecular forces; Increase the temperature **correct**

4. Select two liquids with very different intermolecular forces; Decrease the temperature

5. Minimize ΔH_{sol} by selecting two liquids with similar intermolecular forces; Decrease the temperature

Colligative Properties

DECREASING THE FREE ENERGY RESULTS IN A MORE STABLE LIQUID SOLUTION

Colligative Property Summary

Vapor Pressure Lowering (Raoult's Law):

- Solves for **the *new* vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A)
  - $P_A = X_A P°_A$

Freezing Point Depression:

- Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (m)
  - $\Delta T_f = i\ k_f\ m$

Boiling Point Elevation:

- Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (m)
  - $\Delta T_b = i\ k_b\ m$

Osmotic Pressure:

- Solves for the pressure exerted by a fluid to restore osmotic equilibrium, based on **the molarity of the solute** (M)
  - $\Pi = iMRT$

van't Hoff Factor, $\Delta T_f = i\ k_f\ m$

→ K_f , K_b

Colligative properties depend on the **identity of the solvent** and the **effective solute concentration**, which can be more than just the given concentration.

Compound	van't Hoff Factor
$CaCO_3$	2
Glucosamine	1
$Ca(NO_3)_2$	3
Fe_2O_3	5
CO_2	1

$$CaCO_3(s) \rightarrow \underbrace{Ca^{2+}(aq) + CO_3^{2-}(aq)}_{2 : i}$$

$$Na_2Cr_2O_7$$

$2(+1)$ -2 $i : 3$

Concentration Units

- Some of the concentration units you should know for solutions are (gchem fundamentals chapter):
  - **Molarity (M): moles of solute per liter solution (mol/L)**
  - **Molality: moles of solute per kilogram solvent (mol / kg)**
  - **Mole Fraction: moles of a particular species per total moles of solution / mixture (dimensionless)**
- Remember your fundamentals conversions between moles, mass, and molar mass

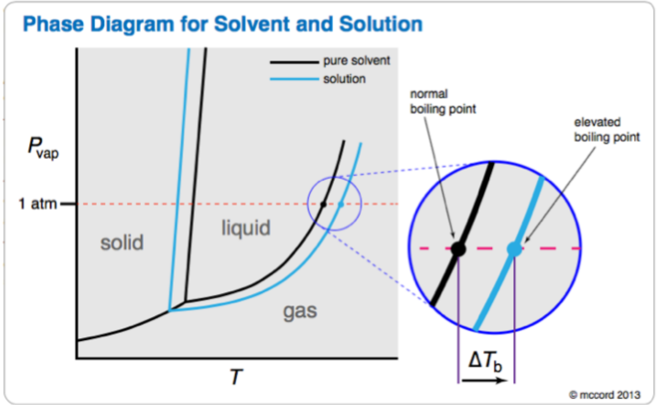
$$M = \frac{mol}{L}$$

$$m = \frac{mol}{kg}$$

$$X_A = \frac{mol_A}{mol_{total}}$$

Stabilizing the Solution - Colligative Properties

- Creating a solution from a pure solvent lowers the free energy of your substance in the liquid phase.
- This has four effects that we call the **colligative properties**
- You can see in the diagram to the right that the liquid phase is favored in a larger range of temperatures
- The point: Colligative properties are a package deal



Boiling Point Elevation, Freezing Point Depression

- Using the following equations, you are solving for the change in the freezing point or boiling point. **Remember: you are solving for a change (ΔT_f is always negative, ΔT_b is always positive) and you are NOT solving for the final temperatures.**

Freezing Point Depression:

Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (m)

$$\Delta T_f = i\ k_f\ m$$

$0°C - \Delta T_f$

Boiling Point Elevation:

Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (m)

$$\Delta T_b = i\ k_b\ m$$

$100°C + \Delta T_b$

Effective Concentration Comparisons

Which of the following aqueous solutions have the same boiling point as 0.6 M sucrose?

$i \cdot m$

a. 0.6 M NaCl

[✓ b.] 0.6 M glucosamine

[✓ c.] 0.3 M KOH

[✓ d.] 0.2 M $\underbrace{Na_2SO_4}_{i=3}$

Which of the following aqueous solutions has the highest boiling point?

[✓ a.] 0.6 M NaCl = 1.2

b. 0.2 M Na_2SO_4 0.6

c. 0.6 M Sucrose 0.6

Follow-up: Which of those solutions has the lowest freezing point?

0.6 M NaCl

Vapor Pressure Lowering

- Vapor Pressure is **lower when a liquid is more stable**. Therefore, it should make sense that when you create a lower free energy solution from a pure solvent, the vapor pressure goes down.
- **Mathematically, vapor pressure lowering looks like this:**

Vapor Pressure Lowering (Raoult's Law):

Solves for the *new* vapor pressure (P_A) of a solution, based on the **mole fraction of the solvent** (X_A) and the vapor pressure of the pure solvent ($P°_A$)

$$P_A = X_A P°_A$$

You WILL have to account for electrolytes in the "total moles" of this mole fraction term, even though you don't see a van't Hoff Factor here.

$$\chi_{\text{Solvent}} = \frac{\text{moles Solvent}}{\text{moles Solvent} + i \cdot \text{moles solute}}$$

Vapor Pressure Lowering - Mixing Volatile Liquids

- The vapor pressure of a binary liquid (A + B) must take into account the vapor pressure of both liquids.
- **Mathematically, this follows Dalton's Law of Partial Pressures:**

Vapor Pressure Lowering (Raoult's Law) + Dalton's Law:

$$P_A = X_A P^\circ_A \qquad P_B = X_B P^\circ_B$$

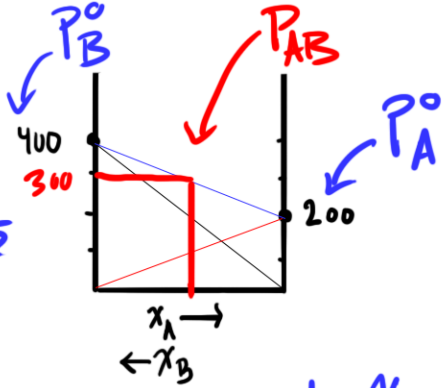
$$P_{total} = P_A + P_B$$

$$P_{AB} = \frac{1}{2}(200) + \frac{1}{2}(400) = 300$$

Vapor Pressure Lowering - Mixing Liquids

Consider two liquids, A and B. Liquid A has a vapor pressure of 200 Torr. Liquid B has a vapor pressure of 400 Torr. Calculate the vapor pressure when the concentrations of A and B are equal.

1:1 $\quad \chi_A = \frac{1}{2}, \chi_B = \frac{1}{2}$



Vapor Pressure Lowering (Raoult's Law):

Solves for **the total vapor pressure**

$$P_A = X_A P^\circ_A$$

$$P_B = X_B P^\circ_B$$

$$P_{total} = P_A + P_B \longrightarrow$$

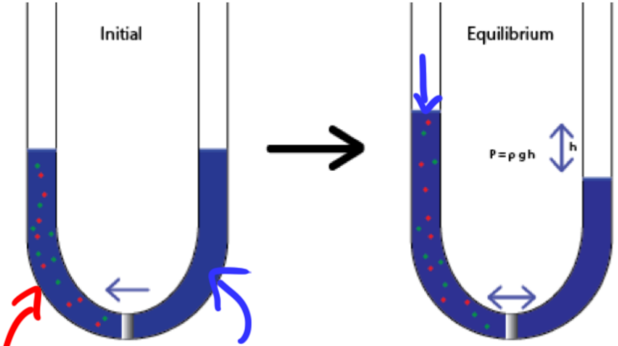
Dalton's Law (CH301)

$$1 = \chi_A + \chi_B$$

$$\frac{1}{2} + \frac{1}{2}$$

Osmotic Pressure

- **Osmotic pressure is the pressure exerted by a fluid to restore osmotic equilibrium.**
- The basic idea is that fluid will flow from the less concentrated to the high concentrated side of a semipermeable membrane (only allows the flow of the solvent; blocks solute).
- The result is a more dilute solution on the left, but an equilibrium is established where there is still pure water left
- Again, this property is due to the fact that the solution is lower in energy. **This is why water flows toward the solution (going from high to low free energy).**



$G_{solution} < G_{solvent}$

$$\Pi = iMRT$$

Chemical Equilibrium

MASS ACTION EXPRESSION, EQUILIBRIUM CONSTANT

Introduction to Chemical Equilibrium

A working definition for equilibrium is the state of a chemical reaction when the rate of the forward reaction and the reverse reaction are equal.

- At this point, there is no net change in the concentrations of your reaction ($\Delta G = 0$)
- We use the equilibrium constant, K, to calculate these exact amounts at equilibrium:

$$aA + bB \rightleftharpoons cC + dD$$

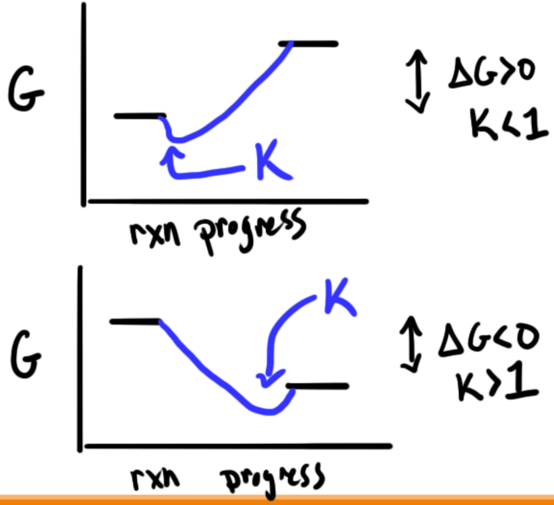
$$K = \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b} \Bigg\} \frac{\text{Products}^{\text{coefficient}}}{\text{reactants}^{\text{coefficient}}}$$

Mathematically, K is equal to the ratio of the action of the products raised to the power of their coefficients divided by the action of the reactants raised to the power of their coefficients.
Conceptually, K is a description of the equilibrium state. Not that a reaction is “spontaneous”/”non-spontaneous”, but what the actual concentrations of the products/reactants are at equilibrium

Key point: Non-spontaneous reactions still can occur to a certain extent. Spontaneous reactions don't always go to 100% products

Interpreting K

- When K is small (less than 1), your reaction is reactant-preferred. A reaction with a small K reacts to a small extent.
- When K is large (greater than 1), your reaction is product-favored. A reaction with a large K reacts to a large extent.



Interpreting K

Acid-Base Reactions all follow the same generic reaction:

$HX(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + X^-(aq)$

K is our method for comparing similar reactions to see which one will net more products. A larger K value corresponds to more products formed.

Challenge: Which chemical will react with water to form the most H_3O^+?

a.	$HA(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + A^-(aq)$	K = 1.8×10^{-5}
[✓ b.]	$HB(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + B^-(aq)$	K = 3.6×10^{-4}
c.	$HC(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + C^-(aq)$	K = 4.2×10^{-11}
d.	$H_3O^+(aq) + D^-(aq) \leftrightharpoons HD(aq) + H_2O(l)$	K = 6.3×10^{12} ←

$HD + H_2O \leftrightharpoons H_3O^+ + D^- \leftarrow K' = \frac{1}{6.3 \times 10^{12}}$

Introduction to Chemical Equilibrium

- We can directly correlate activity to pressure and concentration to create a more sensible relationship.

$$\begin{tikzcd}
 & a_i = \frac{[i]}{[i]^\circ} \arrow[r] & \boxed{K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}} \\
K = \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b} \arrow[ur] \arrow[dr] & & \\
 & a_i = \frac{P_i}{P_i^\circ} \arrow[r] & \boxed{K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}}
\end{tikzcd}$$

REMEMBER: Assume for this example that all species in the K_c example are aqueous. All the species in the K_p example are gases. Remember: the action of any LIQUID or SOLID is 1. These terms will drop out of the mass action expression.

Mass Action Expression

Here are a few chemical reactions. Write the equilibrium expression for each in the proper units:

$2H_2O(l) \leftrightharpoons 2H_2(g) + O_2(g)$

$$K_p = P_{H_2}^{2} \cdot P_{O_2}$$

✓ $Pb(s) + S\,(s) + 2O_2(g) \leftrightharpoons PbSO_4(s)$

$$K_p = \frac{1}{P_{O_2}^{2}}$$

$CH_3COOH(aq) \leftrightharpoons H^+(aq) + CH_3COO^-(aq)$

$$K_c = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Calculations with the Mass Action Expression

$K_c = 2.6 \times 10^8$ at 825 K for the reaction

$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$

$$K_c = \frac{[H_2S]^2}{[H_2]^2[S_2]} = 2.6\times10^8$$

The equilibrium concentration of H_2 is 0.0020 M and S_2 is 0.0010 M. What is the equilibrium concentration of H_2S?

$$2.6\times10^8 = \frac{x^2}{(0.002)^2(0.001)}$$

Consider the reaction below

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

At 1000 K the equilibrium pressures of the three gases in one mixture were found to be 0.562 atm SO_2, 0.101 atm O_2, and 0.332 atm SO_3. Calculate the value of K_p for the reaction.

$$K_p = \frac{(0.332)^2}{(0.562)^2(0.101)}$$

2 Ways to Manipulate K

Reverse the reaction

$2A + B \rightleftharpoons 3C + 2D$, K = 4

$3C + 2D \rightleftharpoons 2A + B$, K = 0.25

$K' = K^{-1}$

Multiply the coefficients by a factor, x

$2A + B \rightleftharpoons 3C + 2D$, K = 4

$4A + 2B \rightleftharpoons 6C + 4D$, K = 16

$K' = K^{x}$