CH 302 – Unit 2 Review 1

INTRODUCTION TO CHEMICAL EQUILIBRIUM

Conceptual Pillars of Equilibrium

1. Many spontaneous chemical reactions reach the lowest free energy state at some point where your reaction mixture is a combination of both products and reactants. This means that many reactions don’t just move forward 100%. The amount (concentration or pressure) of products and reactants at the lowest free energy state is quantified using K.
2. As written, a reaction can move forward (toward the “products”) or backward (toward the “reactants”), depending on the starting point concentrations (Q) and their relationship to K
3. Equilibrium is simultaneously the lowest free energy state of a reaction and the point in the extent of the reaction in which ΔG is equal to zero.

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:

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

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

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

Introduction to Chemical Equilibrium

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

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

$$a_i = \frac{[i]}{[i]^\circ} \longrightarrow \boxed{K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

$$a_i = \frac{P_i}{P_i^\circ} \longrightarrow \boxed{K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}}$$

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.

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

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

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

$$Al(NO_3)_3\ (aq) + 3NaOH\ (aq) \leftrightharpoons Al(OH)_3(s) + 3NaNO_3(aq)$$

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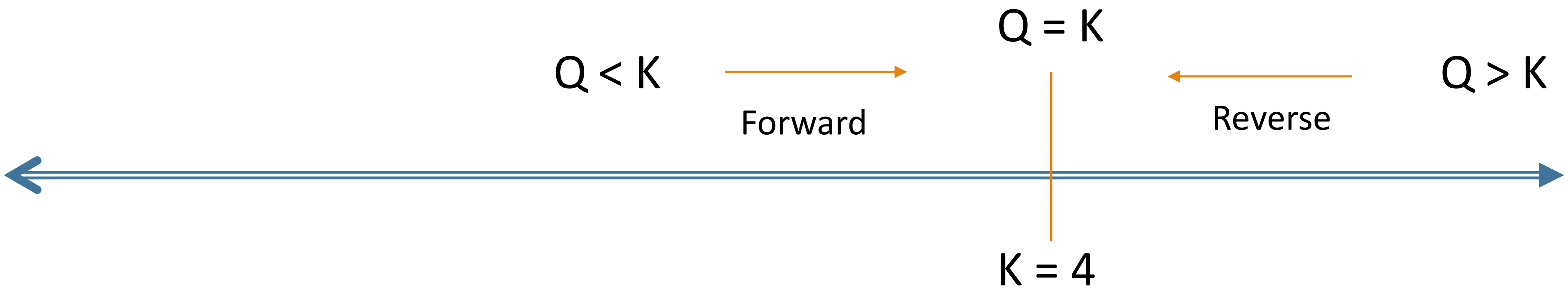
Q vs K: Chemical Equilibrium Terminology

- The purpose of K is to tell you the concentrations at equilibrium.
- The purpose of Q is to tell you the concentrations **at any given starting point.**
- The purpose of comparing Q to K is to tell you how the reaction will proceed at your Q-concentrations.
- **Both expressions are calculated in the exact same way using the mass action expression, but understand that K is the lowest energy state and Q is the starting point**

1. $Q < K$: reaction moves forward toward equilibrium
2. $Q = K$: reaction is at equilibrium (lowest energy state)
3. $Q > K$: reaction moves backward toward equilibrium

Q vs K: Chemical Equilibrium Terminology

1. Q < K : reaction moves forward toward equilibrium
2. Q = K : reaction is at equilibrium (lowest energy state)
3. Q > K : reaction moves backward toward equilibrium



Q = K

Q < K

Forward

Reverse

Q > K

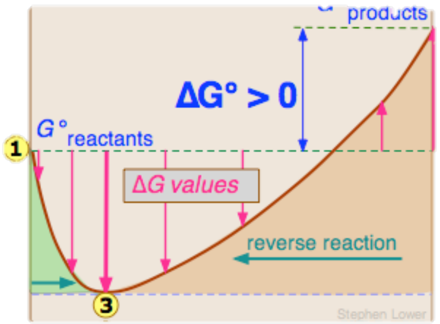
K = 4

The point of these diagrams is to visually depict those three "conceptual pillars of equilibrium"

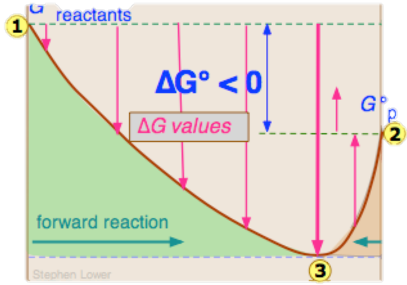
Free Energy vs K

- When K is small (less than 1), only a small fraction of your reactants becomes products. A reaction with a small K reacts to a small extent.
- When K is large (greater than 1), a greater amount of products are formed than reactants remain. A reaction with a large K reacts to a large extent.

When the reactant is favored, the ΔG° is positive.

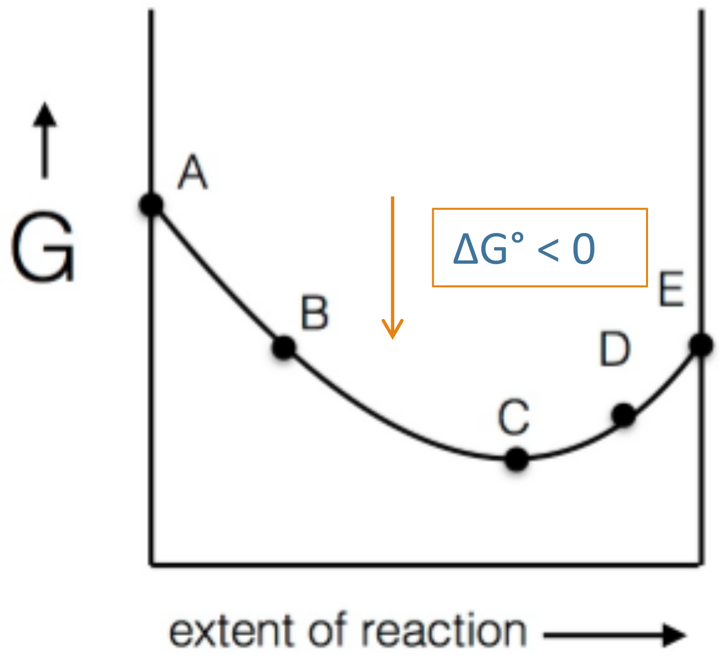


When the product is favored, the ΔG° is negative.



Note: these graphs are an exaggeration of K values. Very large K (think combustion) and very small K (think solubility examples) do not really look like this on a graph

Visualizing Free Energy, K, and Q (Checklist)

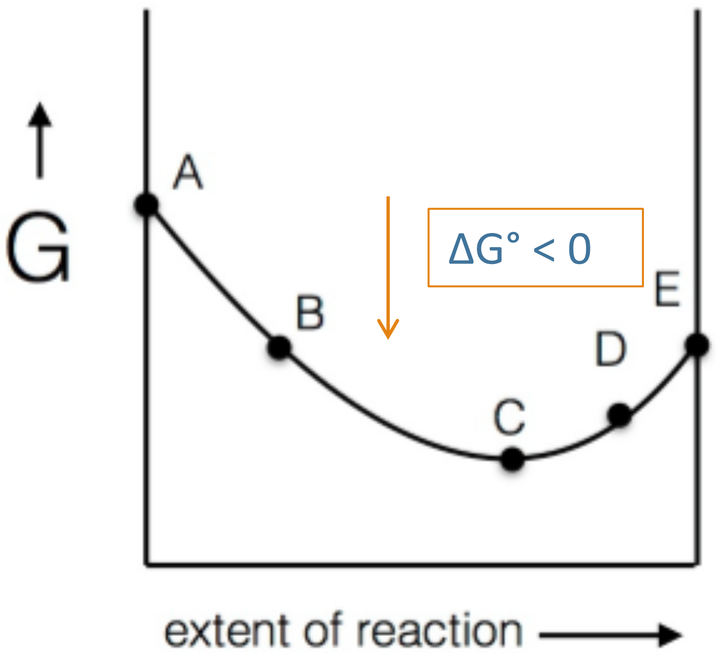


- Identify the relationship between Q and K at any given point on the graph
- Determine whether the reaction is spontaneous or non-spontaneous
- Is ΔG° positive or negative for the reaction?
- Is K greater than or less than 1 on the graph?
- Is ΔG positive or negative at any given point?

Advanced:

- How will the graph change if you compared to another reaction with a ΔG° of greater magnitude?
- How will the graph change if you increase K?

Visualizing Free Energy, K, and Q



A. Q is equal to 0. No matter what K is, Q will be less than K. Reaction will move forward toward equilibrium.
B. Q is less than K. Reaction will move forward.
C. Q is equal to K. Reaction is at equilibrium.
D. Q is greater than K. Reaction will slope back toward the reactants.
E. Q is infinity. No matter what K is, Q will be greater than K. Reaction will move backward toward equilibrium.

Quantifying Free Energy, K, Q

Free Energy, K, and Q are all related based on the following formulas:

$$\Delta G_r = \Delta G_r{}^\circ + RT\ln Q \longrightarrow$$

The free energy of a reaction under any measurable initial conditions

$$\Delta G_r{}^\circ = -RT\ln K \longrightarrow$$

At equilibrium, $\Delta G_r = 0$. Also, Q = K. Therefore, we get a new equation for the relationship between standard free energy and K.

$$K = e^{\frac{-\Delta G_r{}^\circ}{RT}} \longrightarrow$$

We can rearrange this equation to solve directly for a K value at a given temperature given the standard free energy change.

3 Ways to Manipulate K

$K' = K^{-1}$

1. Reverse the reaction

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

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

2. Multiply the coefficients by a factor, x

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

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

$K' = K^{x}$

3. Modify the temperature

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Temperature Dependence of K

- One incredibly important (and sometimes overlooked) relationship is K and Temperature.
- K's dependence on temperature depends on whether the reaction is endothermic or exothermic. The van't Hoff Equation is:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

When you do the math, you will see that for endothermic reactions, increasing temperature increases K. For exothermic reactions, increasing temperature decreases K. It all depends on the sign of ΔH_{rxn}

Play with some values to prove this relationship, then next week I will give you an easier way to figure this out.

Brief overview of Equilibrium Terminology

- We use K and ΔG˚ to express which side of a reaction is “favored”
  - If $K > 1$, the products are favored (ΔG˚ is negative)
  - If $K < 1$, the reactants are favored (ΔG˚ is positive)
- We use the relationship between Q and K to explain which way a reaction will progress toward equilibrium
  - If the starting point of a reaction is $Q < K$, the reaction moves forward toward equilibrium
  - If the starting point of a reaction is $Q > K$, the reaction moves backward toward equilibrium.
- We stress a system at equilibrium to examine how a reaction will “shift” to oppose the stress
  - Stressing equilibrium can either change Q or K, resulting in more products or reactants formed

Application Question

Consider the reaction:

$A(g) \rightleftharpoons 2B(g)$

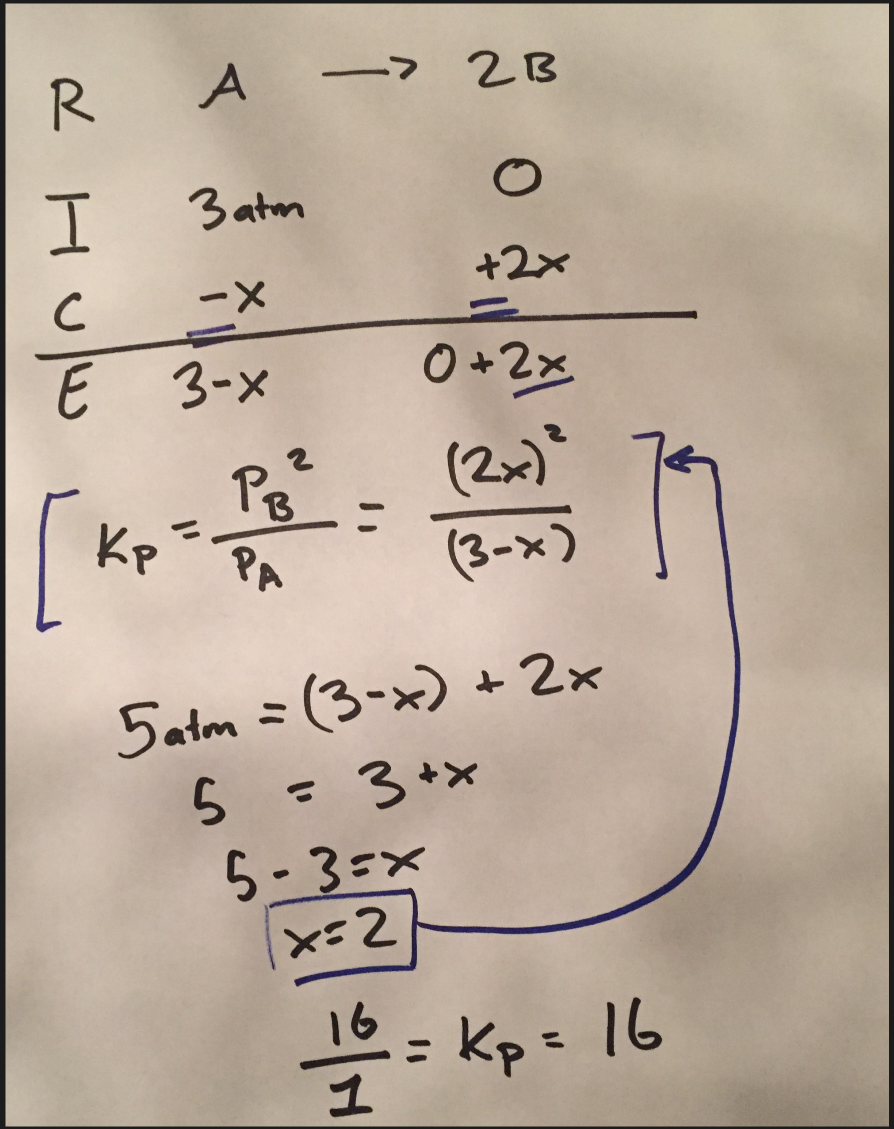
3atm of A is added to an empty chamber. Once the reaction reaches equilibrium, there is 5atm in total. What is the K_p for this reaction?

Final Question

The system

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

is at equilibrium at a fixed temperature with a partial pressure of H_2 of 0.200 atm, a partial pressure of I_2 of 0.200 atm, and a partial pressure of HI of 0.100 atm. An additional 0.26 atm pressure of HI is admitted to the container, and it is allowed to come to equilibrium again. What is the new partial pressure of HI?



R	A	$\longrightarrow$	$2B$
I	3atm		0
C	$-x$		$+2x$
E	$3-x$		$0+2x$

$$\left[K_p = \frac{P_B^2}{P_A} = \frac{(2x)^2}{(3-x)} \right]$$

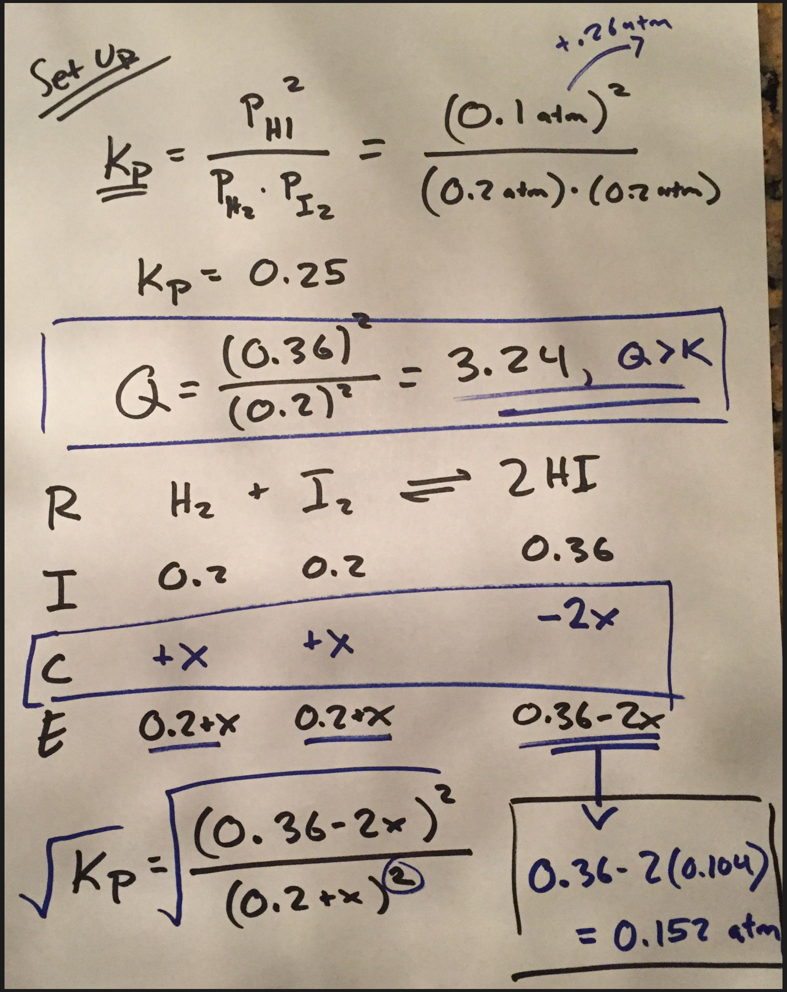
$$5\text{atm} = (3-x) + 2x$$

$$5 = 3+x$$

$$5-3=x$$

$$\boxed{x=2}$$

$$\frac{16}{1} = K_p = 16$$



Set Up

$$\underline{K_p} = \frac{P_{HI}^{\ 2}}{P_{H_2} \cdot P_{I_2}} = \frac{(\overset{+.26\,atm}{0.1}\ atm)^2}{(0.2\ atm) \cdot (0.2\ atm)}$$

$$K_p = 0.25$$

$$\boxed{Q = \frac{(0.36)^2}{(0.2)^2} = \underline{3.24,\ Q > K}}$$

R	H_2	+ I_2	$\rightleftharpoons$ $2HI$
I	0.2	0.2	0.36
C	+x	+x	−2x
E	$\underline{0.2+x}$	$\underline{0.2+x}$	$\underline{\underline{0.36-2x}}$

$$\sqrt{K_p} = \sqrt{\frac{(0.36-2x)^2}{(0.2+x)^{\textcircled{2}}}}$$

$$\boxed{\begin{aligned} &0.36-2(0.104) \\ &= 0.152\ atm \end{aligned}}$$

$$\sqrt{\overset{K_p}{\downarrow}{0.25}} = \frac{0.36-2x}{(0.2+x)\times} = 0.5$$

$$0.1+0.5x = 0.36-2x$$

$$2.5x = 0.26$$

$$x = 0.104$$