

# CH 302 – Unit 2 Review 1

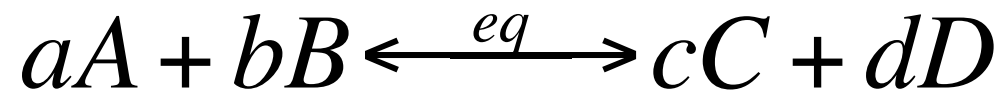
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INTRODUCTION TO CHEMICAL EQUILIBRIUM

# Introduction to Chemical Equilibrium

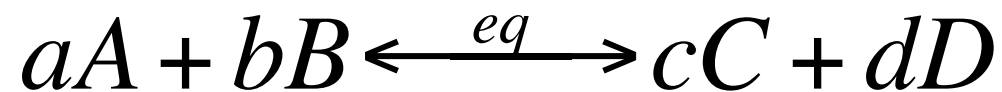
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- A working definition for equilibrium is the state of a chemical reaction when the rate of the forward reaction and the reverse reaction are equal.
- At this point, there is no net change in the concentrations of your reaction
- We use the equilibrium constant,  $K$ , to calculate these exact amounts at equilibrium:



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

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. This is “Mass Action.”



# Introduction to Chemical Equilibrium

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

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

$$a_i = \frac{[i]}{[i]^\circ}$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$a_i = \frac{P_i}{P_i^\circ}$$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

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.

# Easy Question

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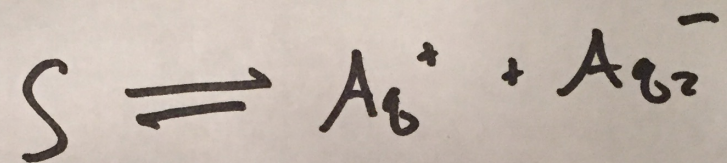
Write the mass action expression in terms of  $K_c$  for the following reaction:



Follow-up Question: What term from Unit 1 is this equal to?

$$K_c = \frac{[Ag^+]^3 [PO_4^{3-}]}{1}$$

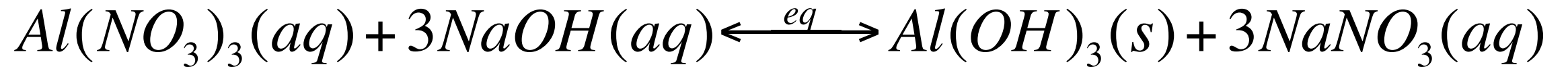
$$K_c = [Ag^+]^3 [PO_4^{3-}] = K_{sp}$$

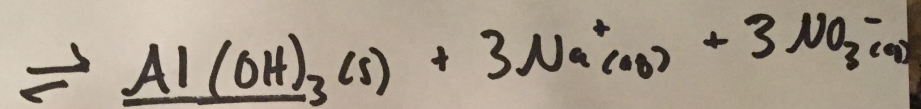
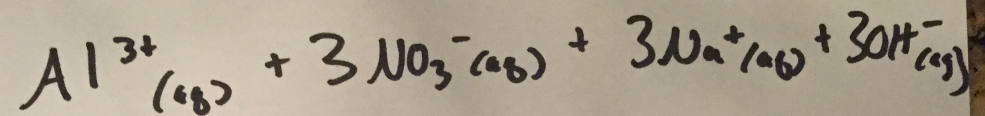


# Challenging Question

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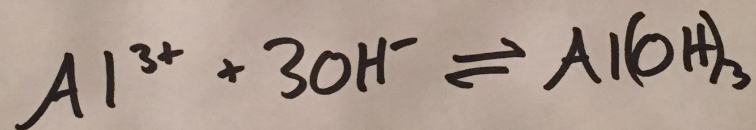
Write the mass action expression in terms of  $K_c$  for the following reaction:





$$K_c = \frac{\cancel{[\text{Na}^+]^3} \cancel{[\text{NO}_3^-]^3}}{[\text{Al}^{3+}] \cancel{[\text{NO}_3^-]^3} \cancel{[\text{Na}^+]^3} [\text{OH}^-]^3}$$

$$K_c = \frac{1}{[\text{Al}^{3+}] [\text{OH}^-]^3}$$



# Q vs K: Chemical Equilibrium Terminology

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- 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.

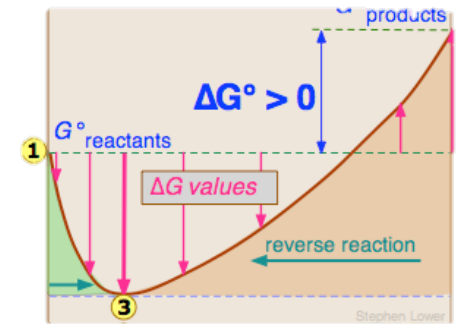
1.  $Q < K$  : reaction moves **forward** toward equilibrium
2.  $Q = K$  : reaction is at equilibrium (just right)
3.  $Q > K$  : reaction moves **backward** toward equilibrium



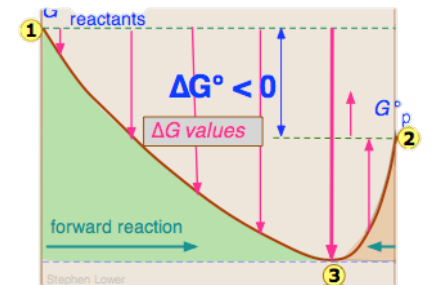
# Free Energy vs K

- 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  $\Delta G^\circ$  is positive.

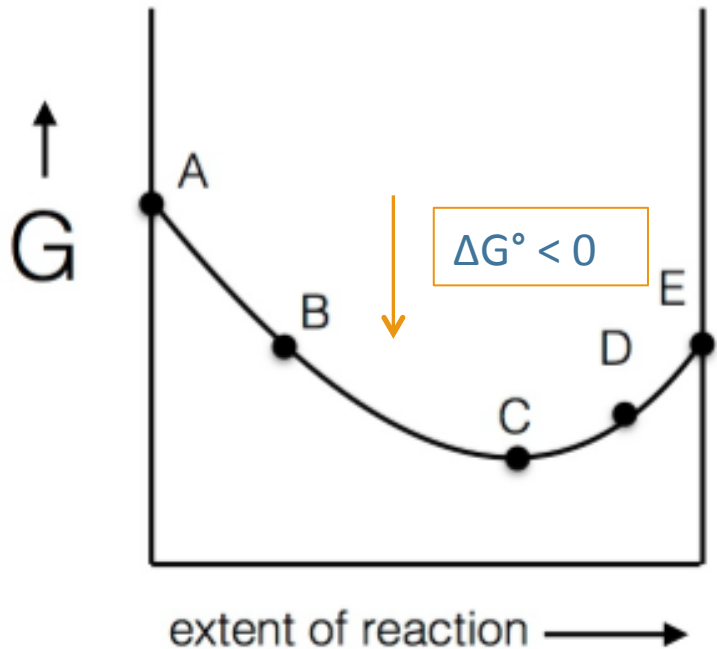


When the product is favored, the  $\Delta G^\circ$  is negative.



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)

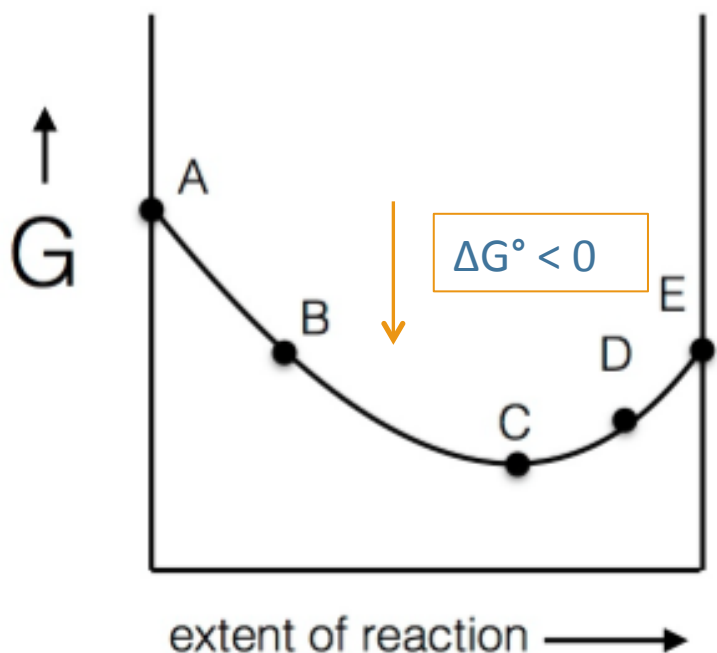


- Identify the relationship between  $Q$  and  $K$  at any given point on the graph
- Determine whether the reaction is spontaneous or non-spontaneous
- Is  $\Delta G^\circ$  positive or negative for the reaction?
- Is  $K$  greater than or less than 1 on the graph?
- Is  $\Delta G$  positive or negative at any given point?

Advanced:

- How will the graph change if you compared to another reaction with a  $\Delta G^\circ$  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

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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.

# Calculation

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For the following reaction



The value of  $K_c = 1.8 \times 10^{-5}$ . What is the  $\Delta G^\circ$  for this reaction at 298K?

$$K = 1.8 \times 10^{-5}$$

$$\Delta G^\circ @ 298\text{K}$$

$$\Delta G^\circ = \boxed{-RT \ln K}$$

$$-0.008314 \frac{\text{kJ}}{\text{mol K}} \times 298\text{K}$$

$$27.31 \frac{\text{kJ}}{\text{mol}} = -2.5 \times \ln(1.8 \times 10^{-5})$$

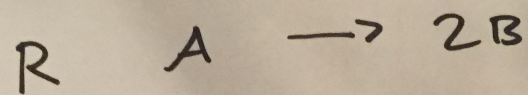
# Application Question

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Consider the reaction:



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?



$$I \quad 3 \text{ atm} \quad 0$$

$$C \quad \underline{-x} \quad \underline{+2x}$$

$$E \quad 3-x \quad 0+2x$$

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

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

$$5 = 3+x$$

$$5 - 3 = x$$

$$x = 2$$

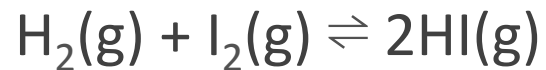
$$\frac{16}{1} = K_P = 16$$



# Final Question (HW Question 15)

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The system



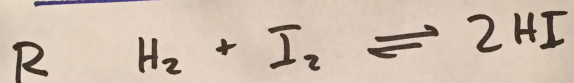
is at equilibrium at a fixed temperature with a partial pressure of  $\text{H}_2$  of 0.200 atm, a partial pressure of  $\text{I}_2$  of 0.200 atm, and a partial pressure of HI of 0.100 atm. An additional 0.26 atm pressure of HI is admitted to the container, and it is allowed to come to equilibrium again. What is the new partial pressure of HI?

Set up

$$K_P = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} = \frac{(0.1 \text{ atm})^2}{(0.2 \text{ atm}) \cdot (0.2 \text{ atm})}$$

$$K_P = 0.25$$

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



$$I \quad 0.2 \quad 0.2 \quad 0.36$$

$$C \quad +x \quad +x \quad -2x$$

$$E \quad \underline{0.2+x} \quad \underline{0.2+x} \quad \underline{0.36-2x}$$

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

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

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

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

$$2.5x = 0.26$$

$$x = 0.104$$

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# Temperature Dependence of K

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- Once 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  $\Delta H_{rxn}$

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