CH 302 Unit 2 Day 1

RICE TABLES, LE CHATELIER'S PRINCIPLE

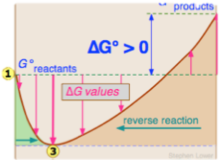
Chemical Equilibria Road Map

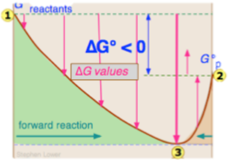
1. Explain equilibrium conceptually using *K, Q, ΔG˚*, and *ΔG* and make calculations between these terms
2. Make calculations using the mass action expression and RICE tables with any given starting conditions (*Q*)
3. Le Chatelier's Principle: Understand how a reaction system at equilibrium shifts in response to stress
    - Add reactants or products, change the pressure/volume, adding an inert gas, changing temperature

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

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

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





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

Quantifying Free Energy, K, Q

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

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

The free energy of a reaction under any measurable initial conditions

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

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

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

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

$$K_p = \frac{P_{NOBr}^2}{P_{NO}^2}$$

Q

Anatomy of a (R)ICE Table

R	$2NO(g)$	$+\ \cancel{Br_2(\ell)}$	$\rightleftharpoons 2NOBr(g)$
I	0.8 atm		0
C	$-2x$		$+2x$
E	$0.8-2x$		$2x$

K

$$K_p = \frac{(2x)^2}{(0.8-2x)^2}$$

Anatomy of a (R)ICE Table

R	$2NO(g) +$	$\cancel{Br_2(\ell)}$	$\rightleftharpoons 2NOBr(g)$
I	0		0.8 atm
C	+2x		-2x
E	2x		0.8-2x

Chemical Equilibria

EQUILIBRIUM CONSTANT, ΔG°, RICE TABLES

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.

} K defines equilibria NOT ΔG directly

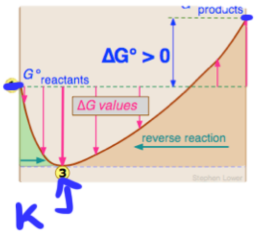
} Q vs K

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

Conceptual - ΔG, ΔG°, K, and Q

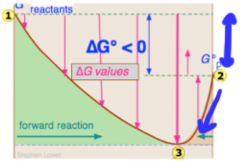
- When *K* is small (less than 1), only a small fraction of your reactants becomes products. A reaction with a small *K* reacts to a small extent.

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



- 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 product is favored, the *ΔG°* is negative.



Q vs K - Chemical Equilibrium Terminology

- The purpose of *K* is to tell you the concentrations (or pressures) 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 starting concentrations.

1. $Q < K$: reaction moves forward toward equilibrium
   - **RICE Table: +x on product side, -x on reactant side**
2. $Q = K$: reaction is at equilibrium (lowest energy state)
3. $Q > K$: reaction moves backward toward equilibrium
   - **RICE Table: -x on product side, +x on reactant side**

$Q > K, \Delta G > 0$

$Q = K, \Delta G = 0$

$Q < K, \Delta G < 0$

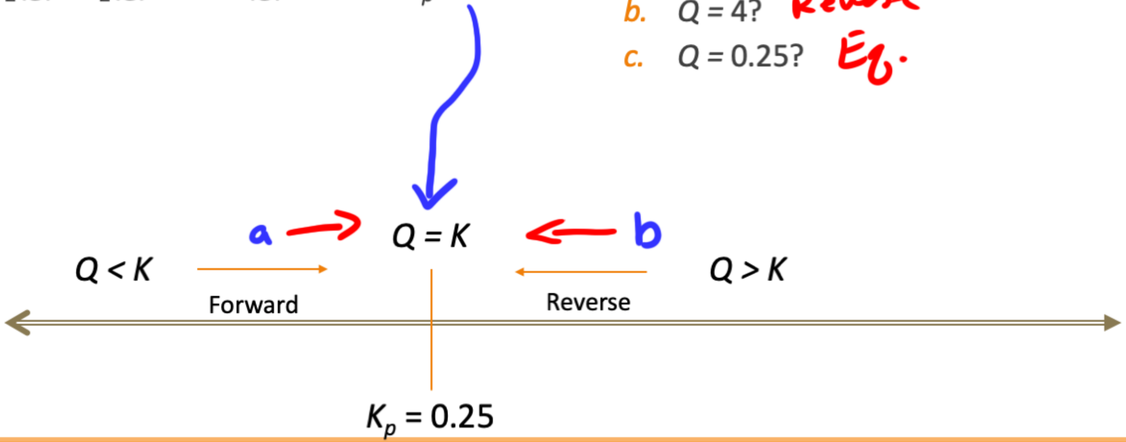
Q vs K - Chemical Equilibrium Terminology

Consider the following reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_p = 0.25$

Conceptually, what will happen if…

a. $Q = 0.1$? Forward
b. $Q = 4$? Reverse
c. $Q = 0.25$? Eq.



a $\rightarrow$ $Q = K$ $\leftarrow$ b

$Q < K$ Forward

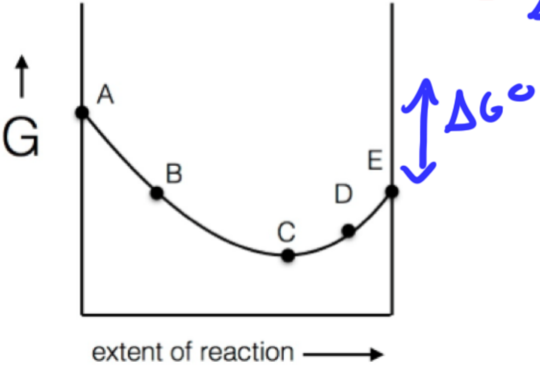
Reverse $Q > K$

$K_p = 0.25$

Visualizing Free Energy, K, and Q

→ 1M prod, 1M react

$\Delta G^\circ < 0$, $K > 1$



A. $Q < K$, $\Delta G < 0$

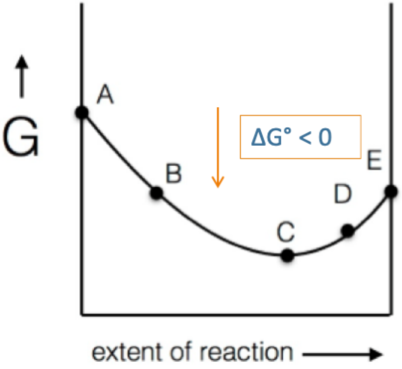
B. $Q < K$, $\Delta G < 0$

C. $Q = K$, $\Delta G = 0$

D. $Q > K$, $\Delta G > 0$ … $\Delta G_{reverse}$ $(-)$

E. $Q > K$, $\Delta G > 0$ … $\Delta G_{reverse}$ $(-)$

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?

Application Question

$$K_p = \frac{P_B^2}{P_A} = \frac{(2x)^2}{3-x} \quad \frac{4^2}{1} = 16$$

Consider the reaction: A(g) $\rightleftharpoons$ 2B(g)

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

R	$A(g) \rightleftharpoons$	$2B(g)$
I	3 atm	0
C	$-x$	$+2x$
E	$3-x$	$2x$

$$5 = (3-x) + 2x$$

$$5 = 3 + x$$

$$x = 2$$

RICE Table Application

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?

1) Solve for Kp:

$$K_p = \frac{(0.100)^2}{(0.200)(0.200)} = 0.25$$

↳ We will use this later

After Stressing Equilibrium, solve for eq. pressures:

$P = 0.360-2x$

2) Af

$P_{HI} =$

$= 0.152$ atm

R	H_2	$+ \; I_2$	$\rightleftharpoons 2HI$
I	0.200	0.200	0.360
C	$+x$	$+x$	$-2x$
E	$0.200+x$	$0.200+x$	$0.360-2x$

$$K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} = \sqrt{0.25} = \sqrt{\frac{(0.360-2x)^2}{(0.200+x)^2}}$$

$$0.50 = \frac{0.360-2x}{0.200+x}$$

$$0.10 + 0.5x = 0.360 - 2x$$

$$2.5x = 0.260$$

$$x = 0.104$$

Exam Question

Consider the following generic reaction:

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

4.18 atm of reactant A and 8.23 atm of product B are introduced to a vacuum chamber. 1/2 of B reacts to reach equilibrium. What is the value of K for this reaction?

$Q > K$

$\Delta G_{reverse}$ happens

R	$A(g)$	$\rightleftharpoons$	$2B(g)$
I	4.18		8.23
C	+2.057		$-4.115 \to -2x$
E	6.2375		4.115

$$4.115 = 2x$$

$$x = \frac{4.115}{2}$$

$$K_P = \frac{P_B^2}{P_A} = \frac{4.115^2}{6.2375} = 2.71$$

Le Chatelier’s Principle

THE RESPONSE TO STRESSING A REACTION SYSTEM AT EQUILIBRIUM

Le Chatelier’s Principle

- Le Chatelier’s Principle creates the guidelines for how a system responds to any disruption of equilibrium
- In other words, a system at equilibrium will respond to stress by directly opposing the stress.
- Factors that might disrupt equilibrium include:
  - Adding or removing species involved in a reaction
  - A change in the volume or pressure
  - Dilution or concentration of the system
  - A change in temperature

Le Chatelier's Principle

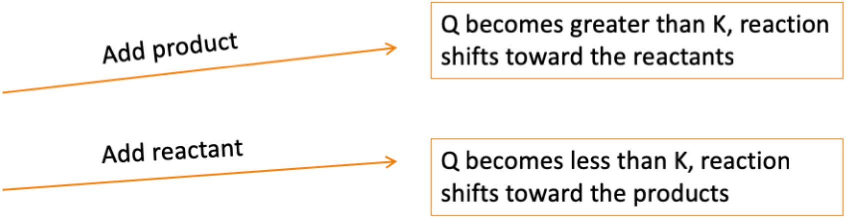
1. Adding or removing species:
   - Adding: reaction shifts toward the opposite side of the addition
   - Removing: reaction shifts toward the same side as the removal
2. Increasing or decreasing the volume (gases):
   - Increasing volume (decreasing pressure): shifts toward the side with the most gas moles
   - Decreasing volume (increasing pressure): shifts toward the side with the least gas moles
3. Diluting or concentration a solution (aqueous):
   - Diluting: shifts toward the side of the most aqueous moles
   - Concentration: shifts toward the side of least aqueous moles
4. Changing the temperature:
   - Endothermic: increasing T shifts toward products ; decreasing T shifts toward reactants
   - Exothermic: increasing T shifts toward reactants ; increasing T shifts toward products

Le Chatelier's Principle - Adding/Removing Stuff

- By adding or removing product or reactant, you are manipulating *Q*
- When you manipulate *Q*, the reaction "shifts" to get you back to *K*

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$K_p = \frac{(P_{HCl})^2}{P_{H_2} P_{Cl_2}}$$



Add product

Q becomes greater than K, reaction shifts toward the reactants

Add reactant

Q becomes less than K, reaction shifts toward the products

Le Chatelier’s Principle - Adding/Removing Stuff

- By adding or removing product or reactant, you are manipulating *Q*
- When you manipulate *Q*, the reaction “shifts” to get you back to *K*

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$K_p = \frac{(P_{HCl})^2}{P_{H_2}P_{Cl_2}}$$

Remove product → Q becomes less than K, reaction shifts toward the products

Remove reactant → Q becomes greater than K, reaction shifts toward the reactants

Le Chatelier’s Principle - Volume and Pressure

- By changing the volume or pressure, you can manipulate *Q* for a gaseous system.
- The reaction shifts based on the number of gas species in the products or reactants

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3 P_{N_2}}$$

Reduce the volume

→

Increase the pressure

If you increase the pressure, you are causing the most stress on the side of the reaction with the most gas species. **The reaction will shift toward the side of the least gas species.**

Le Chatelier's Principle - Volume and Pressure

- By changing the volume or pressure, you can manipulate *Q* for a gaseous system.
- The reaction shifts based on the number of gas species in the products or reactants

$$2A_2(g) + B_2(g) \rightleftharpoons 2C_3(g)$$

$$K_P = \frac{6^2}{3^2 \cdot 1} = 4$$

@ eq → 3 atm , 1 atm 6 atm

6 atm, 2 atm, 12 atm

$$\frac{12^2}{6^2 \cdot 2} = \frac{144}{36 \cdot 2} = 2 \qquad Q < K \qquad \longrightarrow$$

1.5, 0.5, 3

$$\frac{3^2}{1.5^2 \cdot 0.5} = 8 \qquad Q > K \qquad \longleftarrow$$

Le Chatelier’s Principle - Volume and Pressure

- By changing the volume or pressure, you can manipulate *Q* for a gaseous system.
- The reaction shifts based on the number of gas species in the products or reactants

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3 P_{N_2}}$$

Increase the volume

Decrease the pressure

If you decrease the pressure, you are causing the most stress on the side of the reaction with the least gas species. **The reaction will shift toward the side of the most gas species.**

Le Chatelier's Principle - Concentration

Based on the same principle, changing the concentration is changing the volume of the solvent (similar to changing the volume of the container in a gaseous sample).

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

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

Concentrate the solution

$= P\uparrow$

If you concentrate the solution, you are causing the most stress on the side with the most aqueous species. **The reaction will shift in toward the side with the least aqueous species.**

Dilute the solution

$= P\downarrow$

If you dilute the solution, you are causing the most stress on the side with the least aqueous species. **The reaction will shift toward the side of the most aqueous species.**

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.

Le Chatelier's Principle - Temperature

- To simplify the relationship between K and temperature, we can think of temperature like a product or a reactant of a chemical reaction depending on whether the reaction is exothermic or endothermic.
- Endothermic reactions are driven by an input of heat; therefore, heat is like a reactant. Increasing the heat is like adding a reactant. This shifts the equilibrium toward the products.

$$\boxed{\text{Heat + Reactants} \rightleftharpoons \text{Products}}$$

- Exothermic reactions have an output of heat; therefore, heat is like a product. Increasing the heat is like adding a product. This shifts the equilibrium toward the reactants.

$$\boxed{\text{Reactants} \rightleftharpoons \text{Products + Heat}}$$

Le Chatelier's Principle - Questions

Consider the reaction below when it is at equilibrium:

$3NO_2(g) + H_2O(l) \rightleftharpoons 2HNO_3(aq) + NO(g) \qquad \Delta H^\circ = -34\,kJ/mol$

In which direction will the reaction shift when:

a. 3 moles of NO(g) are added ←
b. The temperature is raised to 320 K ←
c. The total pressure is increased (by compression) →
d. An inert gas is added at constant volume NO shift
e. An inert gas is added at constant pressure (in a piston system) ←