Homework #14-4: Le Chatelier’s Principle
(Taken from text book Problems p. 620 #51, 52, 53, 55, 56, 59, 60, 61 and one additional question)

14.51 List four factors that can shift the position of an equilibrium. Only one of these factors can alter the value of the equilibrium constant. Which one is it?
The equilibrium position will shift with a change in concentration, pressure, volume or temperature. Only a change in temperature changes the equilibrium constant.

14.52 Does the addition of a catalyst have any effects on the position of an equilibrium?
No, the addition of a catalyst has no effect on the equilibrium position. (The $E_A$ is lowered by the same absolute amount for both the forward and reverse reactions, so both reaction rates increase by the same factor.)

14.53 Predict how the following equilibrium will change with these changes to the system:

\[ \text{SO}_2(g) + \text{Cl}_2(g) \rightleftharpoons \text{SO}_2\text{Cl}_2(g) \]

(a) Addition of more Cl$_2$(g) would shift the position of equilibrium to the right because the rate of the forward reaction increases, so rate of forward is faster than reverse rxn.

(b) Removal of SO$_2$Cl$_2$(g) would shift the position of equilibrium to the right, because the rate of the reverse reaction decreases, making the forward reaction faster than reverse rxn.

(c) Removal of SO$_2$(g) would shift the position of equilibrium to the left because the rate forward reaction decreases, so the reverse reaction is faster than forward rxn.

14.55 Circle the correct answers for each reaction, to help you to predict the change in the equilibrium constant that would occur if temp is increased:

(a) $A + \text{heat} \rightleftharpoons B \quad \Delta H = 20.0 \text{ kJ/mol}$
- This reaction is (exothermic, endothermic) in the forward direction, so heat acts like a (reactant, product). Write in “heat” appropriately into the equation above.
- Thus, if temperature is increased, the reaction shifts to the (right, left).
- In reality, “heat” is not a reactant or a product, so the real reason the reaction is shifting to the (right, left), is because the equilibrium constant is becoming (larger, smaller).

(b) $A + B \rightleftharpoons C + \text{heat} \quad \Delta H = -5.4 \text{ kJ/mol}$
- This reaction is (exothermic, endothermic) in the forward direction, so heat acts like a (reactant, product). Write in “heat” appropriately into the equation above.
- Thus, if temperature is increased, the reaction shifts to the (right, left).
- In reality, “heat” is not a reactant or a product, so the real reason the reaction is shifting to the (right, left), is because the equilibrium constant is becoming (larger, smaller).

(c) $A \rightleftharpoons B \quad \Delta H = 0.0 \text{ kJ/mol}$
- In this system, heat is neither absorbed nor released. Thus, a change in temperature should have no effect on the value of the equilibrium constant.

14.56 What effect does an increase in pressure have on the following systems at equilibrium? (All at same temp in a cylinder with a movable piston.) Briefly explain each.

(a) $A(s) \rightleftharpoons 2 \text{ B(s)}$ The equilibrium position should shift (right, left, no shift) because…
Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases because liquids and solids are virtually incompressible.

(b) $2 \text{ A(l)} \rightleftharpoons \text{ B(l)}$ The equilibrium position should shift (right, left, no shift) because…
Changes in pressure do not affect the concentrations of liquids.
(c) \( A (s) \rightleftharpoons B (g) \) The equilibrium position should shift \( \textbf{\text{right, left, no shift}} \) because…

an increase in pressure should favor the direction that decreases total moles of gas.

(d) \( A (g) \rightleftharpoons B (g) \) The equilibrium position should shift \( \textbf{\text{right, left, no shift}} \) because…

In this equation there are equal moles of gaseous reactants and products. A shift in either direction will have no effect on the total number of moles of gas present.

(e) \( A (g) \rightleftharpoons 2 B (g) \) The equilibrium position should shift \( \textbf{\text{right, left, no shift}} \) because…

A shift left will have the result of decreasing the total number of moles of gas present.

14.59 \( 2 \text{SO}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2 \text{SO}_3 (g) \quad \Delta H^\circ = -198.2 \text{ kJ/mol} \)

Complete the following statements in order to determine any changes in the concentrations of \( \text{SO}_2 \), \( \text{O}_2 \), and \( \text{SO}_3 \) if the following disturbances occur to the equilibrium system shown above:

(a) \( \text{Increasing the temperature:} \) Equilibrium position shifts \( \textbf{\text{right, left, no shift}} \) because…

Increasing temperature causes rate of endo direction to increase faster than exo direction.

Thus, \([\text{SO}_2]\) and \([\text{O}_2]\) will \( \textbf{\text{inc, dec, not change}} \); \([\text{SO}_3]\) will \( \textbf{\text{inc, dec, not change}} \).

(b) \( \text{Increasing the pressure (by decreasing volume):} \)

- At the instant that pressure is increased, before equilibrium the position shifts, the concentrations of all gaseous substances are increased by the same amount.
- However, the \( Q \) value at that instant is \( \textbf{\text{greater than, less than}} \) the equilibrium constant because….. the reactants have more moles of gas, so the denominator increases more than the numerator.
- Thus, the equilibrium position shifts \( \textbf{\text{right, left}} \) towards \( \textbf{\text{fewer, more}} \) moles of gas, so that \( Q \) will \( \textbf{\text{increase, decrease}} \) until it equals \( K_c \).
- Overall, all concentrations have increased, but which concentration has increased the most? \([\text{SO}_3]\)

(c) \( \text{Increasing the concentration of SO}_2\):

- At the instant that the \( \text{SO}_2 \) is added, the \( Q \) value is \( \textbf{\text{greater than, less than}} \) the equilibrium constant because….. the denominator increases because \( \text{SO}_2 \) (a reactant) was added.

- Thus, the equilibrium position shifts \( \textbf{\text{right, left}} \) towards \( \textbf{\text{reactants, products}} \), so that \( Q \) will \( \textbf{\text{increase, decrease}} \) until it equals \( K_c \).
- Overall, the \([\text{O}_2]\) has \( \textbf{\text{increased, decreased}} \); the \([\text{SO}_3]\) has \( \textbf{\text{increased, decreased}} \).

14.60 In the uncatalyzed reaction, \( \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) \), the pressure of the gases at equilibrium are…

\( P_{\text{N}_2\text{O}_4} = 0.377 \text{ atm}; \quad P_{\text{NO}_2} = 1.56 \text{ atm} \).

What would happen to these pressures if a catalyst were added to mixture? Explain why.

There will be no change in the pressures. A catalyst has no effect on the position of the equilibrium. The rates of the forward and reverse reactions increase by the same amount.

14.61 Consider the reaction, \( 2 \text{CO (g)} + \text{O}_2 (g) \rightleftharpoons 2 \text{CO}_2 (g) \)

Predict and explain the shift in the equilibrium position when helium gas is added to the equilibrium mixture…

(a) \( \text{at constant pressure (no change in temperature):} \)

the volume of the container must necessarily be increased. This will \textbf{\text{decrease the partial pressures of all the reactants and products.}} A pressure decrease will favor the reaction that increases the number of moles of gas. The position of equilibrium will \textbf{\text{shift to the left.}} (Q was greater than \( K_f \))

(b) \( \text{at constant volume:} \) If the volume remains unchanged, the partial pressures of all the reactants and products will remain the same. The reaction quotient \( Q \) will still equal the equilibrium constant, and there will be \textbf{\text{no change}} in the position of equilibrium.
A. The plot below indicates the concentration vs. time for the components of the system \[ \text{CO (g) + Cl}_2 (g) \rightleftharpoons \text{COCl}_2 (g) \] \[ \Delta H = -108 \text{ kJ} \] as it reaches initial equilibration from its reactants and after three applied stresses.

![Concentration Versus Time graph]

1. a) What was stress #1? b) Is Q greater or less than \( K_C \)? c) What direction does the system shift? Explain.
   a) Stress #1 was injection of CO, increasing [CO] from 1.70 M to 2.40 M.
   b) Q is less than \( K_C \) since CO is a reactant.
   c) Thus, the reaction shifts to the right, consuming CO and \( \text{Cl}_2 \) and producing \( \text{COCl}_2 \), so that the Q goes up to the \( K_C \).

2. a) What was stress #2? (Hint: Notice that ALL concentrations decreased.) b) Is Q greater than or less than \( K_C \)? c) What direction does the system shift? Explain. d) Calculate the \( K_C \) before and after stress #2 (at 2nd equil and 3rd equil) to prove that \( K_C \) has not changed.
   a) Stress #2 was an increase in volume, causing concentrations of all components to decrease.
   b) Since the denominator in \( Q \) has two components, the denominator decreases faster than the numerator, and \( Q \) is greater than \( K_C \).
   c) Thus, the reaction shifts to the left to consume \( \text{COCl}_2 \) (a product) and produce CO and \( \text{Cl}_2 \). This causes Q to decrease back to \( K_C \).
   d) \[ K_2 = \frac{(0.91)}{(2.29)(0.59)} = 0.67; \quad K_3 = \frac{(0.34)}{(1.24)(0.41)} = 0.67; \quad K_C \text{ is constant.} \]

3. Notice that there was no initial change in concentration at stress #3. Thus, the only stress possible is a change in temperature. a) Based on the graph, determine what direction the reaction shifted in response to stress #3 and justify. b) Determine whether stress #3 was an increase or decrease in temperature and explain logic. c) Determine whether \( K_C \) must have increased or decreased after stress #3 and justify with a calculation of \( K_C \) at 4th equilibrium.
   a) The reaction shifted to the left since [COCl\(_2\)] decreased as [CO] and [Cl\(_2\)] increased.
   b) Stress #3 was an increase in temperature because the rxn shifted in endothermic direction.
   c) \( K_C \) must have decreased (because shifted left).
   \[ K_4 = \frac{(0.16)}{(1.43)(0.59)} = 0.19 \]