LE CHATELIER'S PRINCIPLE

- What happens to the equilibrium of a system when it is initially disturbed (ie. substances are initially added or taken away, or temperature or pressure is initially changed)?
- Le Chatelier investigated this and found that if a system at equilibrium is subjected to an external stress, the equilibrium will shift to *minimize* the effects of that stress.
- External stresses are factors that will cause the either the forward or reverse rate of reaction to change, thus throwing the system out of equilibrium
- We will examine four factors of external stress
  - concentration
  - pressure and volume
  - temperature
  - catalysts

CHANGES IN CONCENTRATION

- When dealing with any Le Chatelier type problems, ask yourself three questions:
  1) What stress was done to the system?
  2) What is the system going to try and do to minimize the stress?
  3) What reaction (forward or reverse) will achieve this?

- Consider the following equilibrium system

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$

colorless red

1. If more Fe^{3+} is added to the reaction, what will happen?
   - Question #1: Fe^{3+} is added
   - Question #2: System will try and decrease Fe^{3+}
   - Question #3: Since Fe^{3+} is on the reactant side of the reaction, the rate of the *forward* reaction will increase in order to "use up" the additional reactant. Therefore we can say "*the equilibrium shifted to the right or shifted to the product side*" or "*the forward reaction is favoured*"
   - The solution will become a darker red color (a physical observation)
   - How does this change the concentration of the other chemicals involved in the reaction?

[ ] means concentration

$[SCN^-_{(aq)}]$ will decrease

$[FeSCN^{2+}_{(aq)}]$ will increase

2. What happens if we add more $FeSCN^{2+}$?
   - Question #1: $FeSCN^{2+}$ is added
   - Question #2: System will try and decrease $FeSCN^{2+}$
   - Question #3: Since $FeSCN^{2+}$ is on the product side of the reaction, the rate of the *reverse* reaction will increase in order to "use up" the additional product. Therefore we can say "*the equilibrium shifted to the left or shifted to the reactant side*" or "*the reverse reaction is favoured*"
   - How does this change the concentration of the other chemicals involved in the reaction?

Both $[Fe^{3+}_{(aq)}]$ & $[SCN^-_{(aq)}]$ will increase

3. What happens when a SCN^- precipitate forms?
   - Question #1: The concentration of $SCN^-_{(aq)}$ will decrease if a precipitate forms
   - Question #2: try to increase $[SCN^-_{(aq)}]$
   - Question #3: reverse rxn favoured

- The equilibrium constant (K_c) DOES NOT CHANGE when changes in concentration cause a shift in equilibrium. Important!
  - The equilibrium constant does not depend on the initial concentrations of the reactants of products. It only depends on the *equilibrium* concentrations.

EXAMPLE: For the reaction below, predict the direction of the equilibrium shift given the following changes. Temperature and volume are held constant.

$$2\ NO_{2\,(g)} + 7\ H_{2\,(g)} \leftrightarrow 2\ NH_{3\,(g)} + 4\ H_2O_{(g)}$$

a. addition of ammonia (NH_3) left

b. removal of nitrogen dioxide left

c. removal of water vapour right

d. addition of hydrogen right

CHANGES IN VOLUME AND PRESSURE

* • Changing the pressure or volume of a container containing an equilibrium system will *only affect the reaction if gases are present*
    - The moles of any solids, liquids, and aqueous solutions in the reaction will not be affected by a change in pressure/volume

- If you increase the pressure (or reduce the volume) of a system at equilibrium, the stress will be reduced by favouring the side of the reaction with the *fewest* moles of *gas* (fewer moles of gas will occupy a smaller volume, thus reducing pressure)

the coefficients!

- If you decrease the pressure (or increase the volume), the equilibrium will shift to favour the side of the reaction with the *most* moles of *gas* (more moles will occupy a greater volume, thus increasing pressure)

- If both sides of the equation have the same number of moles of *gas*, there will be no change in the position of equilibrium when the pressure changes

- If an inert gas is added to a system, the pressure will increase and the volume remains the same but the concentrations of the gasses will remain the same. Therefore, there will be no shift in the system

EXAMPLES:

1. Predict the effect on the equilibrium when the pressure is increased for the following reactions:

    a. $N_2O_{4(g)} \leftrightarrow 2\ NO_{2(g)}$ shift left
    1 mol 2 mol

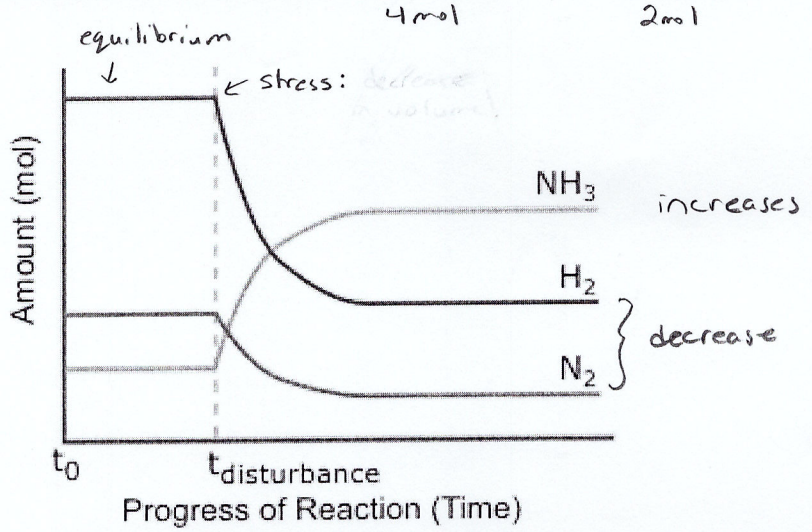
    b. $N_{2(g)} + O_{2(g)} \leftrightarrow 2\ NO_{(g)}$ no shift
    2 mol 2 mol

    c. $4\ NH_{3(g)} + 5\ O_{2(g)} \leftrightarrow 4\ NO_{(g)} + 6\ H_2O_{(l)}$ shift right
    9 mol 4 mol

2. Does the following graph represent an increase or decrease in volume?

Equilibrium System for $3H_{2(g)} + N_{2(g)} \rightleftarrows 2NH_{3(g)}$

4 mol 2 mol



↘ therefor shifting to the right!

∴ increase in pressure / decrease in volume to force a shift to right

Now try Practice Problems, pg. 651 #17 & pg. 655 #8

CHANGES IN TEMPERATURE

- A change in temperature is the only stress that will actually change the equilibrium constant (K_c)
- When determining the way the equilibrium will shift when a temperature change is applied, always write the enthalpy change (ΔH) in the reaction (ie. thermochemical equation) and treat the energy as a "chemical" where the "concentration" can be changed

EXAMPLES:

1. Consider the following equilibrium system, and indicate which way the equilibrium will shift if the temperature is increased.

$N_2O_{4(g)} \leftrightarrow 2NO_{2(g)}$ $\Delta H = +58.0$ kJ (endothermic)

$N_2O_{4(g)} + 58.0\,kJ \rightleftharpoons 2NO_{2(g)}$

   - Question #1: Increase in temperature/energy/heat
   - Question #2: Decrease the temperature/energy/heat
   - Question #3: The forward reaction will be favoured to "use up" the extra energy/heat (ie. shift right)

2. In each of the following equilibria, would you increase or decrease the temperature to force the reaction in the forward direction?

a. $H_{2(g)} + CO_{2(g)} \leftrightarrow H_2O_{(g)} + CO_{(g)}$ $\Delta H = +41.0$ kJ

$H_{2(g)} + CO_{2(g)} + 41.0\ kJ \rightleftharpoons H_2O_{(g)} + CO_{2(g)}$

#1: initial stress was a increase in temp.

#2: shifting right will decrease the amount of heat/energy

#3: shifting right

backwards

b. $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$ $\Delta H = -198$ kJ

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + 198\ kJ$

#1: initial stress was a decrease in temp.

#2: shifting right will increase the amount of heat/energy

#3: shifting right

backward

ADDITION OF A CATALYST

- Recall that a catalyst simply speeds up the reaction by lower the activation energy barrier
- Consider the following reaction:

$$N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$$

  - Adding a catalyst to this system will *not* affect the position of the equilibrium
  - A catalyst speeds up both the forward rate of reaction and the reverse rate of reaction, so there is *no uneven* change in the reaction rates
  - Catalysts will help a reaction reach the point of equilibrium sooner, but will not shift the equilibrium
  - Catalyst will not affect the equilibrium constant

*****Now try pg. 651 #16, 18-20 & pg. 655 #6, 7*****

Practice Problems

1. Consider the following equilibrium reaction.

$$4\ HCl_{(g)} + O_{2(g)} \rightleftarrows 2\ H_2O_{(g)} + 2\ Cl_{2(g)}$$

5 mol 4 mol

Predict the direction of equilibrium shift (ie. forward, reverse, or no change) if the following changes occurred:

a. the pressure is increased shift forward
b. oxygen is added shift forward
c. H_2O is added shift reverse
d. HCl is removed shift reverse
e. Cl_2 is removed shift forward

2. Methanol (CH_3OH) can be manufactured using the following equilibrium reaction.

$$CO_{(g)} + 2\ H_{2(g)} \rightleftarrows CH_3OH_{(g)}$$

3 mol 1 mol

Predict the effect of the following changes on the equilibrium concentration of $CH_3OH_{(g)}$. (ie. will it increase, decrease or remain the same)?

a. The pressure of the system is increased. $[CH_3OH]$ increases
b. More $H_{2(g)}$ is added. $[CH_3OH]$ increases
c. $CO_{(g)}$ is removed. $[CH_3OH]$ decreases

3. Suggest three ways to increase the concentration of SO_3 in the following equilibrium reaction. Changing the concentration of SO_2 and O_2 only counts as one.

3 mol 2 mol

$$2\ SO_{2(g)} + O_{2(g)} \rightleftarrows 2\ SO_{3(g)}$$

→ remove SO_3 as it is formed
→ increase concentration of either SO_2 or O_2
→ increase the pressure (ie. decrease the volume).

Solutions to Questions on page. 655

6. **(a)** right
(b) right
(c) no effect
(d) right
(e) left

7. **(a)** high temperature
(b) low temperature
(c) high temperature
(d) low temperature

8. **(a)** no effect
(b) reaction shifts to the right
(c) reaction shifts to the left