5.5 Factors Affecting Chemical Equilibrium (Qualitative factors)

Many things can change a reaction rate (think about unit 4), but only three things have the potential to change the forward and reverse reaction rates *unequally*. These three things are:

- 1. Change in Concentration
- 2. Change in Temperature
- 3. Change in Pressure (or Volume)

Changes that affect reaction rate but *do not* affect equilibrium are:

- Adding a catalyst (or inhibitor): because it affects the forward and reverse reactions equally.
 It just helps a reaction reach equilibrium sooner.
- 2. Change in surface area: also because it affects the forward and reverse reactions equally.

Le Chatelier's Principle

- The French chemist Henri-Louis Le Chatelier is credited with first discovering ways to change the equilibrium of a chemical system.
- A system at equilibrium represents a delicate balance between the forward and reverse reactions.
- Small changes in external conditions can cause a shift in the equilibrium.
 - o A shift to the right means more products.
 - o A shift to the left means more reactants.
- The system readjusts itself to accommodate the changes forced upon it and the readjustments may alter concentrations.
- Le Chatelier stated that an equilibrium system subjected to an external stress will shift so as to minimize the stress (or remain in equilibrium).
 - A stress is anything changed in a system to upset the equilibrium (concentration, temperature or pressure/volume).

Stresses:

- 1) Changes in Concentration
 - Adding a reactant or product will cause the equilibrium to shift in the opposite direction to use up the extra material.
 - Taking away a reactant or product will cause the equilibrium to shift in the same direction as the removal of material
 - Does not change K_c or K_{eq} (which is a quantitative change)

2) Changes in Volume or Pressure

- Gaseous systems are affected by volume and pressure changes but not solid or liquid systems.
- Volume and pressure changes will only affect equilibrium if the # of moles on the product and reactant sides are different.
- Does not change K_c or K_{eq}

3) Changes in Temperature

- The shift will be to minimize the stress
- Shifts due to changes in temperature are dependent upon whether the system is endothermic or exothermic.
- Does change K_c or K_{eq}

Factors that Affect Equilibrium		
Stress	Shift and Affect	Reason
Concentration :		
↑[reactant]		
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↑[product]		
↓[reactant]		
	·	-
↓[product]		
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Temperature		
↑ T° on endothermic reaction		
		·
↑T° on exothermic reaction		
↓ T° on endothermic reaction		
↓ T° on exothermic reaction		
↓ 1 on exomermic reaction		
-		
Pressure/Volume *ignore for solids and l	liquids ** only has affect if unequal # n	noles on reactant and
product sides		
\uparrow P(\downarrow V) more #moles on reactant side	•	
And In 1		
\uparrow P(\downarrow V) more #moles on product side		
$\downarrow P(\uparrow V)$ more #moles on reactant side		
VI(IV) more minores on reactaint side		
$\downarrow P(\uparrow V)$ more #moles on product side		
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5.5 La Chatelier's Principle Assignment

1. For the following system at equilibrium:

$$H_{2(g)} + Br_{2(g)} \leftrightarrow 2 HBr_{(g)} + 36.4 kJ$$

- a. Predict the shift in equilibrium when more HBr(g) is added to the system.
- b. How will a temperature increase shift equilibrium?
- 2. For the reaction below, predict the direction the equilibrium will shift given the following changes. Temperature and volume are held constant.

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

- a. addition of ammonia
- b. removal of nitrogen dioxide
- c. decrease the temperature
- d. removal of water vapour
- e. addition of hydrogen
- 3. At a particular temperature, the following reaction has an equilibrium constant, K_{eq} of 0.18

$$PCl_{3(g)} + Cl_{2(g)} + 87.9 \text{ kJ} \leftrightarrow PCl_{5(g)}$$

- a) If more PCl₃ is added to the system. Will the value of K_{eq} increase, decrease, or remain the same?
- b) How would the equilibrium shift if a catalyst is introduced?
- c) Explain how you can shift the equilibrium to the products by separately altering the concentration of one of the substances, the temperature, or the pressure.
- 4. For the following reactions, how will equilibrium shift for an increase in pressure?
 - a) $H_{2(g)} + Cl_{2(g)} \leftrightarrow 2HCl_{(g)}$
 - b) $PCl_{3(g)} + Cl_{2(g)} \leftrightarrow PCl_{5(g)}$

5. For the following reactions, how will equilibrium shift if the pressure is decreased?

a)
$$CH_{4(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 3H_2$$

b)
$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

6. Methyl alcohol is produced according to the equation:

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

Predict the effect on the equilibrium species distribution if there was an increase in:

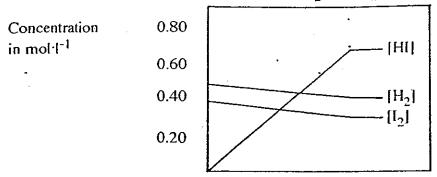
- a) Temperature
- b) Pressure
- 7. List three ways that the following equilibrium reaction could be forced to shift to the right: $2NO_{2(g)}\leftrightarrow 2NO_{(g)}+O_{2(g)}$

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

c)
$$H_{2(g)} + CO_{2(g)} \leftrightarrow H_2O_{(g)} + CO_{(g)}$$
 $\Delta H = +41kJ$

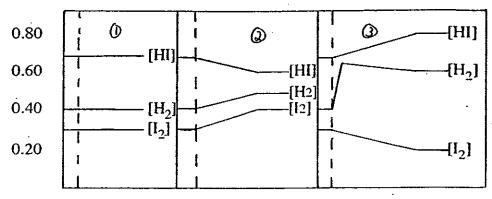
d)
$$2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$$
 $\Delta H = -198kJ$

The following graph show how the concentration of the reactants and product changes until equilibrium is established for the reactions: $H_2(g) + I_2(g) < ---> 2 HI(g) + 12.6 J$



The following graphs begin with the system at equilibrium and then have a stress applied. Select whether graph 1, 2 or 3 best represents the change that would be caused by the stress.

Concentration in mol·l⁻¹



Stresses:

- a) The temperature is increased while the pressure is constant.
- b) The temperature and pressure are increased.
- c) Some hydrogen gas is added.
- d) The pressure is increased while the temperature is constant.
- e) A catalyst is added.