Chemical Equilibrium

•Think of equilibrium as a state of balance.

•Imagine a see-saw that is at rest with a child on each end. This is equilibrium.

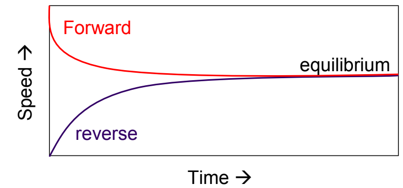
•As soon as one of the children moves, the other child will have to react to keep the seesaw at rest.

•Chemical equilibrium works in a similar fashion

Ref: Merrill Chemistry Textbook

Chemical Equilibrium

- Many reactions are reversible – this means they can go in forward and reverse directions
- Chemical Equilibrium is when the rate forward = rate reverse (NOT when the concentrations are equal)



Equilibrium Constant K_{eq}

- For a reaction at equilibrium, aA+bB ↔ cC + dD
- Or in general, products divided by reactants

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

•Brackets mean molarity

•No units needed on K_{eq}

Equilibrium Constant K_{eq}

- Experimental results show that equilibrium position does not depend on the amounts of pure solids and liquids present (these concentrations cannot change)
- Write them as “1” in the K_{eq} expression

Equilibrium Constant K_{eq}

- Example #1
  $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

- Example #2
  $CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$

$$K_{eq} = \frac{[CO_2][1]}{[1]} \text{ or } K_{eq} = [CO_2]$$

Equilibrium Constant K_{eq}

- What does the equilibrium constant tell us?
- Remember that the equilibrium constant is roughly:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

- A reaction whose equilibrium favors the formation of more products than reactants will have a higher keq than one that favors the reactants.
- In other words, the bigger the K_{eq}, the more the products are favored. The smaller the K_{eq}, the more the reactants are favored.

Le Châtelier's Principle

- Remember that chemical equilibrium is like a see saw.
- Once a reaction has reached equilibrium, if you were to change the pressure, temperature, or concentration of a substance in the system, the system will respond to regain equilibrium.
- As long as temperature is held constant, the K_{eq} value will remain constant in spite of the changes in pressure or concentration

Le Châtelier's Principle and Change in Concentration

- Assume constant pressure and temperature if we're changing concentration
- Increasing concentration shifts equilibrium away from the side where a substance is being added
- Decreasing concentration shifts equilibrium toward the side where a substance is being removed
- Example:
  $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$
  - If we add H_2 which way will equilibrium shift?
  - Away from the left – this means more NH_3 will form and N_2 will be used up (less N_2)

Le Châtelier's Principle and Change in Concentration

- We call equilibrium systems that contain more than one phase "heterogeneous". Consider below a situation where changing concentration does not affect equilibrium…
- Remember how solids and liquids do not appear in the K_{eq} expression? This means they do not affect equilibrium position.
- Example: $NaCl_{(s)} \leftrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$
  - This represents a saturated solution of NaCl (all 3 substances are present, therefore it must be saturated). Adding more NaCl solid will not produce more Na^+ or Cl^- ions.
  - You could, however, get more NaCl by adding either Na^+ or Cl^- ions
- Summary: Changing amounts of solids or liquids will not affect the equilibrium position (in other words, changing a solid or liquid will not change the concentration of any other substances). On the other hand, adding gases or aqueous substances can produce more solid or liquid.

Le Châtelier's Principle and Change in Pressure

- Assume constant concentration and temperature if we're changing pressure
- Increasing pressure shifts equilibrium toward the side that has fewer gas molecules
- Decreasing pressure shifts equilibrium toward the side that has more gas molecules
- Example:
  $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$
  - If we increase the pressure what will happen to the NH_3 concentration?
  - The NH_3 side has 2 gas molecules, the other side has 4
  - Equilibrium will shift toward the right with increased pressure, which means more NH_3 will form.

Le Châtelier's Principle and Change in Temperature

- Assume constant concentration and pressure if we're changing temperature
- K_{eq} value will change with change in temperature
- Treat energy like a substance, then go by the rule for concentration
- Increased temperature = increased energy
- Decreased temperature = decreased energy
- Find the side of the equation that contains the energy (endothermic = energy on the left, exothermic = energy on the right)

Le Châtelier's Principle and Change in Temperature

- Example:
  $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)} + 92kJ$ (exothermic)
- What will happen to the concentration of NH_3 if we heat up the container?
  - Energy is on the right, so it's like we're adding a substance to the right side of the equation → equilibrium will shift left
  - A shift to the left will mean LESS NH_3

Le Châtelier's Principle and Change in Temperature

- Keq will change with temperature change
- Remember: K_{eq} is roughly:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

- A temperature change that shifts equilibrium to the right (products) will increase K_{eq}
- A temperature change that shifts equilibrium to the left (reactants) will decrease K_{eq}

Equilibrium Visualizations

- http://www.chem.arizona.edu/~jpollard/fido/fido.html

Equilibrium Book Problems

- Read Ch. 15 (some parts we won't cover)
- Assigned: 15.2, 15.5,15.9, 15.14, 15.52, 15.56