Chemical Equilibrium

Equilibrium

We've already used the phrase "equilibrium" when talking about reactions.

In principle, every chemical reaction is reversible ... capable of moving in the forward or backward direction.

$$2\ H_2 + O_2 \rightleftharpoons 2\ H_2O$$

Some reactions are easily reversible ...

Some not so easy ...

Equilibrium: the extent of a reaction

In stoichiometry we talk about theoretical yields, and the many reasons actual yields may be lower.

Another critical reason actual yields may be lower is the reversibility of chemical reactions: some reactions may produce only 70% of the product you may calculate they ought to produce.

Equilibrium looks at the *extent* of a chemical reaction.

The Concept of Equilibrium

- Consider colorless frozen N_2O_4. At room temperature, it decomposes to brown NO_2:

$$N_2O_4(g) \rightarrow 2NO_2(g).$$

- At some time, the color stops changing and we have a mixture of N_2O_4 and NO_2.
- Chemical equilibrium is the point at which the rate of the forward reaction is equal to the rate of the reverse reaction. At that point, the concentrations of all species are constant.
- Using the collision model:
  - as the amount of NO_2 builds up, there is a chance that two NO_2 molecules will collide to form N_2O_4.
  - At the beginning of the reaction, there is no NO_2 so the reverse reaction ($2NO_2(g) \rightarrow N_2O_4(g)$) does not occur.

The Concept of Equilibrium

- As the substance warms it begins to decompose:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

- When enough NO_2 is formed, it can react to form N_2O_4:

$$2NO_2(g) \rightarrow N_2O_4(g).$$

- At equilibrium, as much N_2O_4 reacts to form NO_2 as NO_2 reacts to re-form N_2O_4

- The double arrow implies the process is dynamic.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The Concept of Equilibrium

As the reaction progresses

- **[A] decreases to a constant,**
- **[B] increases from zero to a constant.**
- **When [A] and [B] are constant, equilibrium is achieved.**

$$\mathbf{A} \rightleftharpoons \mathbf{B}$$

The Equilibrium Constant

- **No matter the starting composition of reactants and products, the same ratio of concentrations is achieved at equilibrium.**
- **For a general reaction**

$$aA + bB(g) \rightleftharpoons pP + qQ$$

the equilibrium constant expression is

$$K_c = \frac{[P]^p[Q]^q}{[A]^a[B]^b}$$

where K_c is the equilibrium constant.

The Equilibrium Constant

- **K_c is based on the molarities of reactants and products at equilibrium.**
- **We generally omit the units of the equilibrium constant.**
- **Note that the equilibrium constant expression has products over reactants.**

The Equilibrium Constant

The Equilibrium Constant in Terms of Pressure

- **If K_P is the equilibrium constant for reactions involving gases, we can write:**

$$K_P = \frac{(P_{\mathrm{P}})^p (P_{\mathrm{Q}})^q}{(P_{\mathrm{A}})^a (P_{\mathrm{B}})^b}$$

- **K_P is based on partial pressures measured in atmospheres.**

The Equilibrium Constant

The Magnitude of Equilibrium Constants

- The equilibrium constant, *K*, is the ratio of products to reactants.
- Therefore, the larger *K* the more products are present at equilibrium.
- Conversely, the smaller *K* the more reactants are present at equilibrium.
- If *K* >> 1, then products dominate at equilibrium and equilibrium lies to the right.
- If *K* << 1, then reactants dominate at equilibrium and the equilibrium lies to the left.

The Equilibrium Constant

The Magnitude of Equilibrium Constants

- **An equilibrium can be approached from any direction.**

Example:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $2NO_2(g) \rightleftharpoons N_2O_4(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \qquad K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72$$

- **The equilibrium constant for a reaction in one direction is the reciprocal of the equilibrium constant of the reaction in the opposite direction.**

The Equilibrium Constant

Heterogeneous Equilibria

- **When all reactants and products are in one phase, the equilibrium is homogeneous.**
- **If one or more reactants or products are in a different phase, the equilibrium is heterogeneous.**
- **Consider:**

$$CaCO_3(\mathit{s}) \rightleftharpoons CaO(\mathit{s}) + CO_2(\mathit{g})$$

  - **experimentally, the amount of CO_2 does not seem to depend on the amounts of CaO and $CaCO_3$. Why?**

The Equilibrium Constant

Heterogeneous Equilibria

- **Neither density nor molar mass is a variable, the concentrations of solids and pure liquids are constant. (You can't find the concentration of something that isn't a solution!)**
- **We ignore the concentrations of pure liquids and pure solids in equilibrium constant expressions.**
- **The amount of CO_2 formed will not depend greatly on the amounts of CaO and $CaCO_3$ present.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_c = [CO_2]$$

Applications of Equilibrium Constants

Predicting the Direction of Reaction

- We define Q, the reaction quotient, for a reaction at conditions NOT at equilibrium

$$a\text{A} + b\text{B}(g) \rightleftharpoons p\text{P} + q\text{Q}$$

as

$$Q = \frac{[\text{P}]^p[\text{Q}]^q}{[\text{A}]^a[\text{B}]^b}$$

where [A], [B], [P], and [Q] are molarities at any time.

- $Q = K$ only at equilibrium.

Applications of Equilibrium Constants

Predicting the Direction of Reaction

- **If $Q > K$ then the reverse reaction must occur to reach equilibrium (go left)**
- **If $Q < K$ then the forward reaction must occur to reach equilibrium (go right)**

Le Châtelier's Principle

Le Chatelier's Principle: **if you disturb an equilibrium, it will shift to undo the disturbance.**

Le Châtelier's Principle

Change in Reactant or Product Concentrations

- **Adding a reactant or product shifts the equilibrium away from the increase.**
- **Removing a reactant or product shifts the equilibrium towards the decrease.**
- **To optimize the amount of product at equilibrium, we need to flood the reaction vessel with reactant and continuously remove product (Le Châtelier).**
- **We illustrate the concept with the industrial preparation of ammonia**

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

Le Châtelier's Principle

Change in Reactant or Product Concentrations

- Consider the Haber process

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

- If H_2 is added while the system is at equilibrium, the system must respond to counteract the added H_2 (by Le Châtelier).
- That is, the system must consume the H_2 and produce products until a new equilibrium is established.
- Therefore, $[H_2]$ and $[N_2]$ will decrease and $[NH_3]$ increases.

Le Châtelier's Principle

Change in Reactant or Product Concentrations

- **The unreacted nitrogen and hydrogen are recycled with the new N_2 and H_2 feed gas.**
- **The equilibrium amount of ammonia is optimized because the product (NH_3) is continually removed and the reactants (N_2 and H_2) are continually being added.**

Effects of Volume and Pressure

- **As volume is decreased pressure increases.**
- **Le Châtelier's Principle: if pressure is increased the system will shift to counteract the increase.**

Le Châtelier's Principle

- **Consider the production of ammonia**

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

- **As the pressure increases, the amount of ammonia present at equilibrium increases.**
- **As the temperature decreases, the amount of ammonia at equilibrium increases.**
- **Le Châtelier's Principle: if a system at equilibrium is disturbed, the system will move in such a way as to counteract the disturbance.**

Le Châtelier's Principle

Effects of Volume and Pressure

- The system shifts to remove gases and decrease pressure.
- An increase in pressure favors the direction that has fewer moles of gas.
- In a reaction with the same number of product and reactant moles of gas, pressure has no effect.
- Consider

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Le Châtelier's Principle

Effects of Volume and Pressure

- An increase in pressure (by decreasing the volume) favors the formation of colorless N_2O_4.
- The instant the pressure increases, the system is not at equilibrium and the concentration of both gases has increased.
- The system moves to reduce the number moles of gas (i.e. the forward reaction is favored).
- A new equilibrium is established in which the mixture is lighter because colorless N_2O_4 is favored.

Le Châtelier's Principle

Effect of Temperature Changes

- The equilibrium constant is temperature dependent.
- For an endothermic reaction, $\Delta H > 0$ and heat can be considered as a reactant.
- For an exothermic reaction, $\Delta H < 0$ and heat can be considered as a product.
- Adding heat (i.e. heating the vessel) favors away from the increase:
  - if $\Delta H > 0$, adding heat favors the forward reaction,
  - if $\Delta H < 0$, adding heat favors the reverse reaction.
- Removing heat (i.e. cooling the vessel), favors towards the decrease.

How Does Temperature Change the K_c?

The Kc is a mathematical constant that does not change for concentration, volume, and pressure changes. It only changes for temperature.

1. **Exothermic Reactions:**

   A + B ⇋ C + energy

   Increasing the temperature causes the Keq to decrease.

   Decreasing the temperature causes the Keq to increase.

Increasing [A] causes the reaction to shift right and the value of the Kc to remain constant.

2. **Endothermic Reactions:**

   A + B + energy ⇋ C

   Decreasing the temperature causes the Keq to decrease.

   Increasing the temperature causes the Keq to increase.

Decreasing [A] causes the reaction to shift left and the value of the Kc to remain constant.