Chemical Equilibrium Notes (Chapter 18)

So far, we've talked about all chemical reactions as if they go only in one direction. However, as with many things in life, chemical reactions can go both in the forward and reverse directions, depending on the conditions. Though we frequently perform these reactions in conditions that cause the forward direction to be favored, sometimes we don't have that luxury. That's what we'll be discussing in the next few days.

What is equilibrium?

As mentioned before, some chemical reactions can go both in the forward and reverse directions. For example, the reaction for the formation of ammonia from nitrogen and hydrogen occurs in both the forward and reverse directions:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

and

$$2\ NH_3 \rightarrow N_2 + 3\ H_2$$

As we saw in the last few weeks, the rate of a chemical reaction depends on the concentrations of the things that are reacting (i.e. the higher the concentrations, the faster the rate). Let's see what happens when we put N_2 and H_2 into a container and let them react:

- Initially, the reaction proceeds very quickly in the forward direction because the concentration of N_2 and H_2 are very high and the concentration of NH_3 is very low.

- However, after the reaction has been going on for some time, the forward reaction slows down (there is less N_2 and H_2 to react) and the reverse reaction speeds up (there is more NH_3).

- Eventually, the system will stabilize at a point where the forward reaction and the reverse reactions occur at the same rate. When a system operates in such a way that the forward and reverse reactions occur at the same rate, it is said to be at **equilibrium**.

<u>Properties of a system at equilibrium:</u>

- **It can only happen with <u>reversible</u> reactions.**
  - Reversible reactions are chemical reactions that can proceed in both the forward and reverse directions.
    - This is more likely for some reactions than others – combustion reactions don't frequently enter into equilibria.

- **At equilibrium, reactant is still forming product and product is still forming reactant.**
  - The forward reaction and reverse reaction occur at precisely the same speed at equilibrium.

- **At equilibrium, the concentrations of the reactants and products remain constant.**
  - This doesn't mean that the reactions have stopped – only that for every reactant molecule used up to form product, another one is made from a product molecule.
  - The concentrations may be the same, but the molecules are not.

Equilibrium Constants:

As we mentioned earlier, an equilibrium is when the rate of the forward reaction in a chemical process is equal to the rate of the reverse reaction. We're going to examine this a little bit further.

Let's consider the reaction:

$$aA + bB \leftrightarrows cC + dD$$

Using what we know about rate equations, we can write two rate expressions for this process: The expression for the forward reaction and the expression for the reverse reaction.

- For the forward reaction:

$$aA + bB \rightarrow cC + dD$$

The rate equation is: **forward rate = $k_{forward}[A]^a[B]^b$**

- For the reverse reaction:

$$cC + dD \rightarrow aA + bB$$

The rate equation is: **reverse rate = $k_{reverse}[C]^c[D]^d$**

Because the forward rate and the reverse rate are the same in an equilibrium, we can say that:

$$\mathbf{k_{forward}[A]^a[B]^b = k_{reverse}[C]^c[D]^d}$$

Rearranging this equation, we can say that:

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

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Because $K_{forward}$ and $K_{reverse}$ are both constants, we can combine them to create something called K_{eq}, the "**equilibrium constant**". Thus, the equation above is transformed into:

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

- In this expression, [A] stands for "molarity of A", [B] for "molarity of B" and so on.
- **Important note**: If you're working with gases, the terms change to P_A^a and so forth and stand for "partial pressure". Aside from that, there's no difference.

Whenever working with equilibria, this is the big equation that we use to describe it.

Sample problem: What's the equilibrium expression for the equation $H_2CO \leftrightarrows H^+ + HCO^-$?

Answer: Using the equilibrium expression, we find that:

$$K_{eq} = \frac{[H^+][HCO^-]}{[H_2CO]}$$

Another sample problem: What's the equilibrium expression for the equation $H_3PO_4 \leftrightarrows 3\ H^+ + PO_4^{-3}$?

Answer: Using the equilibrium expression, we find that:

$$K_{eq} = \frac{[H^+]^3[PO_4^{-3}]}{[H_3PO_4]}$$

What equilibrium constants mean:

- **The equilibrium constant is useful for determining whether products or reactants are favored in an equilibrium.**
  - Because K_{eq} is a ratio of the products to reactants, the larger the equilibrium constant, the farther the equilibrium lies toward the products (the right) side of the equation.
  - Example: The equilibrium constant for the equilibrium $H_2 + I_2 \leftrightarrows 2\ HI$ is 49.7, meaning that it lies toward the products.

How we determine equilibrium constants:

- **The equilibrium constant can be calculated from the equilibrium concentrations of the products and reactants in a chemical process.**
  - Again, let's consider the equilibrium $A + 2\ B \leftrightarrows C$. If we have the equilibrium concentrations of each compound, we can figure out the value of K_{eq}. Let's take a look at some sample data:

Equilibrium concentration of A (M)	Equilibrium concentration of B (M)	Equilibrium concentration of C (M)
0.25	0.35	0.15

  - First off, we need to find the equilibrium expression for this process. (Walk them through the process to find):

$$K_{eq} = \frac{[C]}{[A][B]^2}$$

  - The only other thing we need to do is to plug our concentrations into this expression and find the equilibrium expression:

$$K_{eq} = \frac{[0.15M]}{[0.25M][B0.35M]^2} = 4.90$$

- Another sample problem: For the equilibrium:

  $N_2 + 3\ H_2 \leftrightarrows 2\ NH_3$

  Find the equilibrium constant from the data below:

$[N_2]$ (M)	$[H_2]$ (M)	$[NH_3]$ (M)
1.25	0.50	0.25

  Answer: 0.400

As we saw before, we can use the concentrations of products and reactants at equilibrium to determine the equilibrium constants. Similarly, we can use the equilibrium constant to determine the concentrations of the products and reactants.

Let's see how this works with an example:

Example:

The equilibrium $H_2 + I_2 \leftrightarrows 2\ HI$ has the equilibrium constant 49.8 at high temperatures. Given this information, what will the equilibrium concentrations of HI be if the equilibrium concentration of H_2 is 0.50 M and the equilibrium concentration of I_2 is 0.25 M?

Solution:

Here's how to solve problems like this:

1) Determine the equilibrium expression

For this reaction, the equilibrium expression is:

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

2) **Plug in the values given to you in the problem.**

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} \text{ or } 49.8 = \frac{[HI]^2}{[0.50M][0.25M]}$$

Solving for [HI], we find the concentration is **2.50 M**

Another example: For the reaction above, determine the equilibrium concentration of H_2 if the equilibrium concentration of HI is 1.50 M and the equilibrium concentration of I_2 is 0.15 M.

Answer: 0.30 M

Important points to remember:

If $k_{eq} = 1$, the system is at equilibrium.

If $k_{eq} > 1$, the right side is favored.

If $k_{eq} < 1$, the left side is favored.

Factors that affect equilbria (Le Châtlier principle):

We saw in the kinetics chapter that we can make reactions go more quickly by doing things such as adding catalysts, increasing the temperature, or by grinding up our reagents. This implies that the mechanics of chemical reactions can be changed by things we do.

This is fortunate because chemists are usually interested in optimizing reaction conditions so that we can get as much of our product as possible. With equilibria, we utilize something called…

Le Châtlier's principle – When you do something to an equilibrium, the equilibrium will change to minimize the effect of whatever it is you did.

Let's see how this works:

1) **Adding reactants pushes the reaction to the right.**

- **The idea**: If we have the equilibrium A $\leftrightarrows$ B, by adding more A to the mixture (increasing its concentration), the equilibrium will try to get rid of some of the A that you added to it by forming more B. As a result, the equilibrium will shift toward products.

- **The proof**: Let's say that the reaction A $\leftrightarrows$ B has an equilibrium constant of 1.50. If we have 1.00 M A at equilibrium, this means that the equilibrium concentration of B will be 1.50 M.
  - However, if we add more A so that the equilibrium concentration of A is 1.50 M, the concentration of B will increase to 2.25 M.

- **When it's used:** Let's say we have the equilibrium:

$$A + B \leftrightarrows C + D$$

  where A is very inexpensive and B is very cheap. If we want to maximize how much C and D are made and waste the least possible amount of B, we can simply add lots and lots of A, pushing the reaction further to the right (and using up the vast majority of the B so it isn't wasted).

2) **Removing products pushes the equilibrium to the right.**

- **The idea:** If you have an equilibrium and pull out some of the B, the equilibrium will shift to make more B so that the amount of B will go back up (minimizing the effect of having taken some away).

- **The proof:** If we have the equilibrium A $\leftrightarrows$ B with a $K_{eq} = 1.50$, the equilibrium might settle such that the concentration of B is 1.50 M and the concentration of A is 1.00 M.

  - If we were to take away the B, the equilibrium will eventually settle such that the equilibrium concentration of B is 0.60 M and the concentration of A will be 0.40 M.

- **When it's used:** If you're doing a chemical reaction and want to get rid of all of your reactants, the best way to do this (if possible) is to remove the products as they form. By doing this you can use Le Châtlier's principle to make nothing by products.

3) Changing the volume of the container in which you're doing the reaction will cause the equilibrium to shift to minimize this effect.

- **The idea:** Let's imagine an equilibrium where:

  $$2\ A_{(g)} \leftrightarrows B_{(g)}$$

  By decreasing the volume of the container you increase the partial pressure of the reactants and products. To cause an offsetting increase in pressure, the equilibrium will shift in the direction that results in the lowest overall pressure (in this case, toward B because doing so replaces two gas molecules with one gas molecule).

  - **Important:** If you had the equilibrium $A_{(g)} \leftrightarrows 2\ B_{(g)}$, you would want to increase the volume (and hence, decrease the pressure) to cause more B to form. When you decrease the pressure, the system will want to increase its pressure by forming more gas molecules.

  - **Important:** If you had an equilibrium with an equal number of gas molecules on both sides of the equilibrium, changing the pressure won't shift the equilibrium at all.

- **When this is used:** Whenever you want to push a reaction with gases in one direction or another and don't feel like either adding or taking away any of the gases in the mixture.

4) Changing the temperature will shift an exothermic reaction to the left and an endothermic reaction to the right.

- **The idea:** This really isn't all that hard to understand if you think of energy as being a product or a reactant. Consider an exothermic reaction (which gives off energy). We can think of the exothermic reaction A + B $\leftrightarrows$ C + D as really looking like:

$$A + B \leftrightarrows C + D + \text{energy.}$$

If you treat energy as a product, you can see that increasing the temperature (i.e. adding energy) will push the equilibrium toward the left just as surely as adding C or D would. Likewise, the endothermic reaction A + B $\leftrightarrows$ C + D can be written as:

$$A + B + \text{energy} \leftrightarrows C + D$$

because energy is required to make the reaction go forward. As a result, increasing the temperature (i.e. adding energy) will push the equilibrium toward products just as surely as adding either A or B would.