

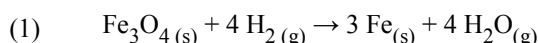
CHEMICAL EQUILIBRIUM

AP Chemistry (Notes)

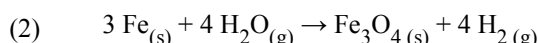
Most chemical processes are reversible. Reactants react to form products, but those products can also react to form reactants.

Examples of reversible reactions:

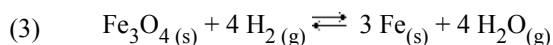
1st - When hydrogen gas is passed over heated iron oxide, iron and steam are produced:



The reverse reaction can occur when steam is passed over red-hot iron:



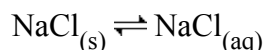
We can write these two equations together as:



As written above in Reaction (3), we would say that in the **forward reaction** iron oxide (multiple oxidation states) and hydrogen gas, the reactants, produce the products iron and steam.

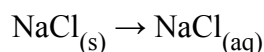
During the **reverse reaction**, iron reacts with steam to produce the products iron oxide and hydrogen gas.

2nd- Here's another example of a reversible reaction - dissolving salt in a beaker of water, described by the following reaction:

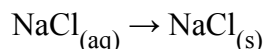


If you keep adding more and more solid salt, eventually you'll reach the point where no more salt dissolves, and the excess sits at the bottom of the beaker. At this point we have a saturated solution. Has the dissolving reaction stopped? It would appear so, but that's not the case.

What happens in our saturated solution, which has reached the point of **equilibrium**, is that both the forward



and reverse



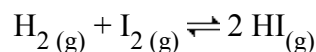
reactions are still going on, but at the same **rate**. This in effect cancels out any observable, or measurable, changes in our system. At the same rate that solid NaCl produces aqueous NaCl (dissolved salt), the dissolved salt is recrystallizing to form more solid NaCl.

Equilibrium is the state at which the rate of the forward reaction equals the

rate of the reverse reaction.

At the point of equilibrium, no more measurable or observable changes in the system can be noted.

For example, the following reaction was allowed to come to the point of equilibrium, and concentrations of all reaction participants were measured at that time:



At equilibrium:	$[\text{H}_2] = 0.022 \text{ M}$
	$[\text{I}_2] = 0.022 \text{ M}$
	$[\text{HI}] = 0.156 \text{ M}$

For this particular reversible reaction, there is more HI at equilibrium (0.156 M) than there is of H_2 and I_2 (both at 0.022M). **We say the product side of the reaction is favored.

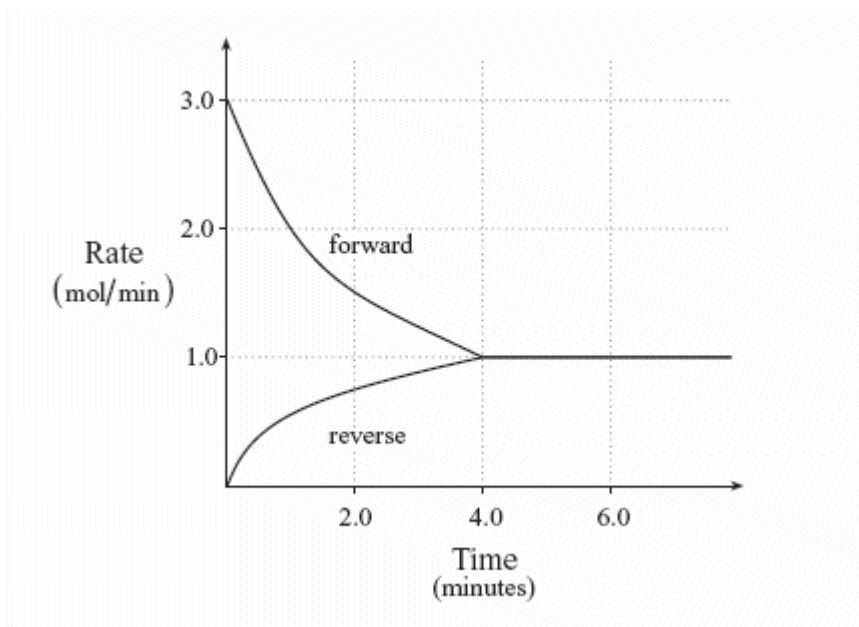
Equilibrium does not mean equal amounts at equilibrium!

In order for a reversible reaction to reach the point of equilibrium, the reaction must be carried out in a **closed system** - no additional reactants can be added or products removed. If, in our last example, the product HI was removed as it formed, the reaction would never reach the point of equilibrium - instead H_2 and I_2 would continue to react to produce HI until one or both of the reactants was used up.

If reactants are constantly being added, and products removed as they form, the system would appear to be at equilibrium because to an outside observer it would appear that the reaction has stopped, but that would not be the case. This situation - with new material constantly being added as products are removed - is called a **steady state system**. A factory with an assembly line is a steady state system - new raw materials are constantly being added; finished products are removed. A campfire with wood being added to the fire is another steady state system. Be careful not to confuse steady state with equilibrium.

How do the rates of the forward and reverse reactions as the reaction heads towards equilibrium (before it reaches equilibrium?)

If we start our above reaction with H_2 and I_2 , and with no HI, the two gases will react at a certain rate. But remember that the rate of a reaction slows down over time, as the reactants get used up (and lower their concentration). Eventually, however, the amount of the product HI increases, and it will begin producing H_2 and I_2 . Thus the rate of the reverse reaction starts out slowly (there is no HI present), but will speed up as the concentration of HI increases. Eventually both rates will level off (not always to the same level as shown by this example, however):



The Equilibrium Constant, K_{eq}

Chemists have found that there is a mathematical relationship that exists between the concentration of the reactants and products once equilibrium has reached that is independent of the initial concentration of the participants.

For any general reaction:



an equilibrium constant expression can be written as:

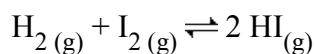
$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

This equation is sometimes called the **mass-action expression**.

This relationship will be very important to us for the next few units, so it is important that you understand how to set this relationship up and what it tells us about an equilibrium system.

The products of the reaction (C and D) are placed in the numerator, and their concentrations are raised to the power of the coefficients from the balanced equation. The reactants (A and B) are placed in the denominator, with their concentrations raised to the power of *their* coefficients.

For the reaction between hydrogen and iodine gas to produce hydrogen iodide:



the equilibrium constant expression will be:

$$K_{\text{eq}} = \frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]}$$

Using the example we examined in our last section, equilibrium concentrations for each substance were measured at equilibrium and found to be:

At equilibrium:	$[\text{H}_2] = 0.022 \text{ M}$
	$[\text{I}_2] = 0.022 \text{ M}$
	$[\text{HI}] = 0.156 \text{ M}$

We substitute these values into our equilibrium expression and solve for K_{eq} :

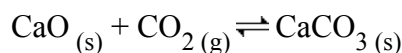
$$K_{\text{eq}} = \frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} = \frac{(0.156)^2}{(0.022)(0.022)} = 50.3$$

The value of K_{eq} , which has no units, is a constant for any particular reaction, and its value does not change unless the temperature of the system is changed. It does not depend on the initial concentrations used to reach the point of equilibrium.- (that is Q)

** K_{eq} relates the concentrations of products to reactants at equilibrium. For aqueous solutions, concentration is often measured as M. For gases, concentration is often measured as partial pressure.

The concentrations of both aqueous solutions and gases change during the progress of a reaction. For reactions involving a solid or a liquid, while the **amounts** of the solid or liquid will change during a reaction, their **concentrations** (much like their densities) will **not** change during the reaction.

Instead, their values will remain constant. Because they are constant, their values **are not included in the equilibrium constant expression**. For example, consider the reaction showing the formation of solid calcium carbonate from solid calcium oxide and carbon dioxide gas:



The Meaning of K_{eq}

What can the value of K_{eq} tell us about a reaction?

- If K_{eq} is very large, the concentration of the products is much greater than the concentration of the reactants. The reaction essentially "goes to completion"; all - or most of - of the reactants are used up to form the products.
- If K_{eq} is very small, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent - most of the reactants remain unchanged, and there are few products produced.
- When K_{eq} is not very large or very small (close to a value of 1) then roughly equal amounts of reactants and products are present at equilibrium.

Le Châtelier's Principle

Chemical systems at equilibrium tend to make these adjustments as well. A French chemist, Henri Louis Le Châtelier developed:

Le Châtelier's Principle

If a system at equilibrium is subjected to an external stress, the equilibrium will shift to minimize the effects of that stress.

Stress: Concentration, Volume & Pressure, Temperature, & Catalyst

Changes in Concentration

When the concentration of a reactant or product is increased, the reaction will proceed in the direction that will use up the added substance.



If N_2 or H_2 is added, the reaction proceeds in the forward direction. If NH_3 is added, the reaction proceeds in the reverse direction.

When the concentration of a reactant or product is decreased, the reaction will proceed in the direction that will produce more of the substance that has been removed.

If N_2 or H_2 is removed, the reaction will proceed in the reverse direction. If NH_3 is removed, the

The value of K_{eq} does not change when changes in concentration cause a shift in equilibrium.

Changes in Temperature

When the temperature is increased, the reaction will proceed in the endothermic direction. When the temperature is decreased, the reaction will proceed in the exothermic direction.



Increasing the temp. causes the equilibrium position to shift in the direction that absorbs heat.

The production of SO_3 is an exothermic reaction. Heat can be considered to be a product and heating the reaction at equilibrium pushes the equilibrium position to the left. This favors the reactants. As a result, the product yield decreases. Cooling pulls the equilibrium to the right, and the product yield increases.

Changes in Volume & Pressure

Changing the pressure or volume of a container enclosing an equilibrium system will only affect the reaction if **gases** are present.

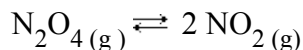
Remember? - equal volumes of gases contain an equal number of particles and, under standard conditions of temperature and pressure (STP), one mole of gas occupies a volume of 22.4 L. This is known as the molar volume of gases. So, two moles of any gas will occupy a volume of 44.8 L and one-half mole would occupy 11.2 L.

How does changing pressure and volume affect equilibrium systems?

- If you increase the pressure of a system at equilibrium (typically by reducing the volume of the container), the stress will best be reduced by reaction favoring the side with the **fewest** moles of gas, since fewer moles will occupy the smallest volume.
- Conversely, if you decrease the pressure (by increasing the volume of the container), equilibrium will shift to favour the side with the **most** moles of gas, since more moles will occupy a greater volume.
- If both sides of the equation have the same number of moles of gas, then there will be no change in the position of equilibrium.

When considering the effect of changing volume or pressure on equilibrium systems, be sure to only count the number of moles **of GASES** on each side of the equation. Solids, liquids, and aqueous solutions will not be affected by changing pressure and volume.

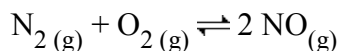
Predict the effect on equilibrium when the pressure is increased for the following reaction:



The reactant side of the equation has 1 mole of a gas; the product side has 2 moles. Increasing the pressure favors the side with the fewest moles of gas, so the equilibrium will shift to the left (the reverse reaction will be favored).

Addition of a Catalyst

The addition of a catalyst to an equilibrium system is our final stress factor. How will adding a catalyst affect the following:



Adding a catalyst to this, or any other equilibrium system, will **not** affect the position of an equilibrium. A catalyst speeds up both the forward and the reverse reactions, so there is no uneven change in reaction rates. A catalyst will help a reaction to reach the point of equilibrium *sooner*,

SUMMARY of Equilibrium constants:

K_c - constant for molar concentration

K_p - constant for partial pressures

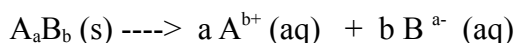
K_{sp} - solubility product; which has no denominator because the reactants are solids.

K_a - acid dissociation constant for weak acids
 K_b – base dissociation constant for weak bases
 K_w – ionization constant for water (1.0×10^{-14})

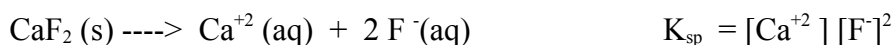
K_{eq} and Gases relationship: $K_p = K_c (RT)^{\Delta n}$
 $R = 0.0821 \text{ (L-atm/mol-K) and } \Delta n = (\text{mol of product gas} - \text{mol of reactant gas})$

K_{sp} Solubility Product

A salt is soluble if more than 1 g of the salt can be dissolved in 100 mL of water.
 Salts that are slightly soluble and insoluble still dissociate in solution to some extent. K_{sp} is a measure of this extent. The greater the value of the solubility product for a salt, the more soluble the salt.



solubility expression: $K_{sp} = [A^{b+}]^a [B^{a-}]^b$



Common Ion Effect

$$K_{sp} = [Ag^{+}] [Cl^{-}] = 1.6 \times 10^{-10}$$

If a block of silver chloride is thrown into a beaker of water, we can tell what the concentrations will be of silver ion and chloride ion at equilibrium.

$$\begin{aligned}
 [Ag^{+}] [Cl^{-}] &= 1.6 \times 10^{-10} \\
 [x] [x] &= 1.6 \times 10^{-10} \\
 x^2 &= 1.6 \times 10^{-10} \\
 x = [Ag^{+}] = [Cl^{-}] &= 1.3 \times 10^{-5} \text{ M}
 \end{aligned}$$

These are very small amounts of Ag^{+} and Cl^{-} in the solution.

Let's say we add 0.10 mole of NaCl to 1L of the AgCl solution. NaCl dissociates completely, so that's the same thing as adding 1 mol of Na^{+} ions and 1 mol of Cl^{-} ions to the solution. The Na^{+} ions will not affect the AgCl equilibrium, so we can ignore them. But the chloride ions must be taken into account. That's because of the common ion effect.

$$[Cl^{-}] = 0.10 \text{ M (0.10 mole of chloride ions/1 L of solution)}$$

$$\begin{aligned}
 [Ag^{+}] [Cl^{-}] &= 1.6 \times 10^{-10} \\
 [Ag^{+}] [0.10] &= 1.6 \times 10^{-10} \\
 [Ag^{+}] &= \frac{1.6 \times 10^{-10}}{0.10}
 \end{aligned}$$

$$[Ag^{+}] = 1.6 \times 10^{-9} \text{ M}$$

**The silver ions have decreased due to the chloride ions introduced by NaCl. The more soluble salt (NaCl) of the 2 solutions mixed can cause the less soluble (AgCl) to ppt. When 2 salt solutions that share a common ion are mixed, the salt with the lower value for K_{sp} will precipitate 1st.