Chemistry 6A F2007

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Wednesday

11/21/07

From the Dictionary:

e·qui·lib·ri·um

Pronunciation: [ee-kwuh-lib-ree-uhm]

–noun, plural -ri·ums, -ri·a

1. A state of rest or balance due to the equal action of opposing forces.

2. Equal balance between any powers, influences, etc.; equality of effect.

3. Chemistry: The condition existing when a chemical reaction and its reverse reaction proceed at equal rates.

Key word: *Rates* ⟶ *Chemical Kinetics or Reaction Rates*

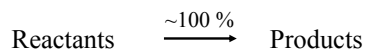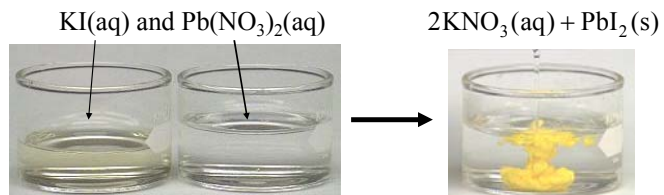
Chemical Reactions:

Some chemical processes react to completion:

Reactants $\xrightarrow{\sim 100\,\%}$ Products

Example: Precipitation Reactions

When solutions of are mixed, a bright yellow ppt forms!

$KI(aq)$ and $Pb(NO_3)_2(aq)$ $\quad\quad 2KNO_3(aq) + PbI_2(s)$

Chemical Reactions:

The reaction:

$$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + PbI_2(s)$$
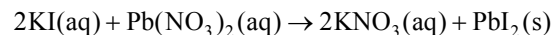
Goes almost to 100% completion: *Forward reaction only*

But when $KNO_3(aq)$ is added to lead (II) iodide:

$$PbI_2(s) + 2KNO_3(aq) \rightarrow \quad \text{No Change!}$$
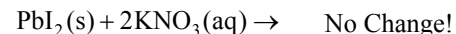
No reverse of the reaction

Many chemical reactions do occur somewhere between the extremes.
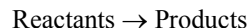
These reactions are governed by "*Equilibrium*"

Chemical Equilibrium:
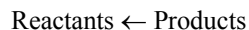
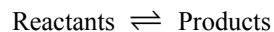Reactions that form only products may be written:

$$\text{Reactants} \rightarrow \text{Products}$$

Reactions that **do not** form products may be written:

$$\text{Reactants} \leftarrow \text{Products}$$

Reactions that are governed by *equilibrium* are written:

$$\text{Reactants} \rightleftharpoons \text{Products}$$

Where the symbol $\rightleftharpoons$ indicates that the reaction proceeds in both directions, *forward* and *reverse*.
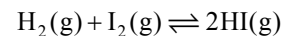

Chemical Equilibrium: Consider the reaction:
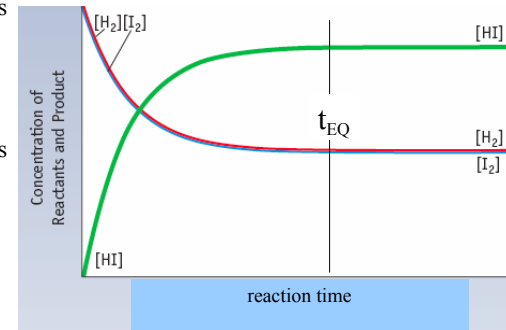
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Initially, only the reactants are present:

$$[HI(g)]_o = 0$$

As the reaction proceeds the reactant concentrations decrease and the product concentration increases.

$$[HI(g)] > 0$$
$$[I_2(g)] < [I_2(g)]_o$$
$$[H_2(g)] < [H_2(g)]_o$$

At some point in time, the concentration of all species remain constant:

When this occurs, *equilibrium* has been established.

The Equilibrium Constant:

In general for a given reaction that exhibits equilibrium, the equilibrium constant expression is given by:

$$aA + bB \rightleftharpoons cC + dD$$

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

Where the concentrations of the product and reactant species are raised to the power of their respective *stoichiometric coefficients*.
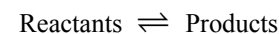

The Equilibrium Constant:

The magnitude of the equilibrium constant K, tells chemists which side of the chemical equation is favored at equilibrium.

$$\text{Reactants} \rightleftharpoons \text{Products}$$

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

If $K \gg 1$, then the numerator (products) concentration dominates at Eq.

The reaction is said to be "*product favored*"

If $K \ll 1$, then the denominator (reactants) concentration dominates at Eq.

The reaction is said to be "*reactant favored*"

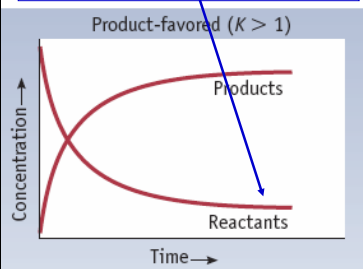If $K \cong 1$ then neither dominates

The Equilibrium Constant:
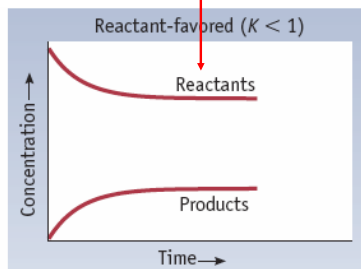

low concentration of reactants at equilibrium

high concentration of reactants at equilibrium.

Product-favored $(K > 1)$

Reactant-favored $(K < 1)$

Product-favored
K >> 1

Reactant-favored
K << 1

Determining the Equilibrium Constant:

Consider the reaction:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$
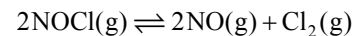
Initially 2.00 mol of NOCl(g) is added to a 1.00 L flask.
At equilibrium you find the concentration of NO(g) to be 0.66 M.
Calculate K for the reaction.

Solution: From the information given, we know that 0.66 mols of NO(g) are present at equilibrium.

$$0.66M \; NO(g) = \frac{0.66 \; mols \; NO(g)}{1L} \times 1.00 \; L \; = 0.66 \; mols \; NO(g)$$

Determining the Equilibrium Constant:

Consider the reaction:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$
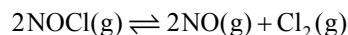
Initially 2.00 mol of NOCl(g) is added to a 1.00 L flask.
At equilibrium you find the concentration of NO(g) to be 0.66 M.
Calculate K for the reaction.

Using stoichiometry, one can calculate the moles and concentration of $Cl_2(g)$ formed at Eq. and the moles of NOCl(g) reacted to get to Eq.

$$0.66 \; mols \; NO(g) \; \times \frac{1mol \; Cl_2(g)}{2mol \; NO(g)} \quad = 0.33 \; mols \; Cl_2(g) \; \times \frac{1}{1.00L} = \boxed{0.33M \; Cl_2(g)}$$

$$0.66 \; mols \; NO(g) \times \frac{2mol \; NOCl(g)}{2mol \; NO(g)} \quad = 0.66 \; mols \; NOCl(g) \; \times \frac{1}{1.00L} =$$
(reacted)

$$\boxed{0.66M \; NOCl(g)}$$

Determining the Equilibrium Constant:

Consider the reaction:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$
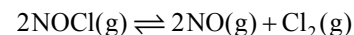
Initially 2.00 mol of NOCl(g) is added to a 1.00 L flask.
At equilibrium you find the concentration of NO(g) to be 0.66 M.
Calculate K for the reaction.

Now we tabulate the results of our calculations:

	[NOCl]	[NO]	[Cl$_2$]
initial concentration	2.00	0	0
change to achieve equilibrium	− 0.66	+ 0.66	+ 0.33
equilibrium concentration	1.34	0.66	0.33

Slide 13

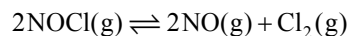|	[NOCl]	[NO]	[Cl$_2$]
initial concentration	2.00	0	0
change to achieve equilibrium	− 0.66	+ 0.66	+ 0.33
equilibrium concentration	1.34	0.66	0.33

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

The equilibrium constant expression for the reaction is:

$$K = \frac{[NO(g)]^2 \times [Cl_2(g)]}{[NOCl(g)]^2} = \frac{(0.66)^2 \times 0.33}{(1.34)^2} = 0.080$$

(reactant favored)

K is always reported as a "unit-less" quantity.

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FACTORS THAT INFLUENCE A SYSTEM AT EQUILIBRIUM
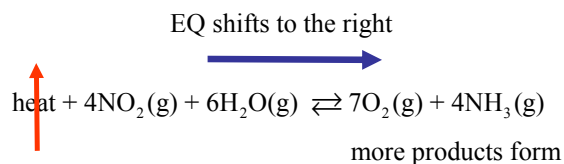
According to Le Châtelier's principle:

"a system at equilibrium will shift in response to stresses placed upon the system at equilibrium".

i.e… (add products/lose reactants and vice versa)

Factors that one must consider are:

•changes in concentration for the reactants or produc

•changes in reaction temperature

•changes in total volume for gas phase equilibrium

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Consider the following endothermic reaction at equilibrium:

EQ shifts to the right

$$heat + 4NO_2(g) + 6H_2O(g) \rightleftharpoons 7O_2(g) + 4NH_3(g)$$

more products form

If an equilibrium mixture was heated, the equilibrium position would shift toward the right to try to use up the added heat.

Slide 16

Consider the following endothermic reaction at equilibrium:

EQ shifts to the right

$$heat + 4NO_2(g) + 6H_2O(g) \rightleftharpoons 7O_2(g) + 4NH_3(g)$$

more products form
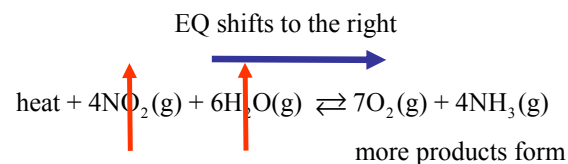
If more $NO_2(g)$ or $H_2O(g)$ are added, the equilibrium position would shift toward the right to try to use up the added reactants.

Consider the following endothermic reaction at equilibrium:

EQ shifts to the right

$$heat + 4NO_2(g) + 6H_2O(g) \rightleftarrows 7O_2(g) + 4NH_3(g)$$

more reactants are
consumed

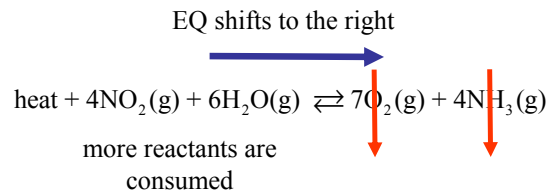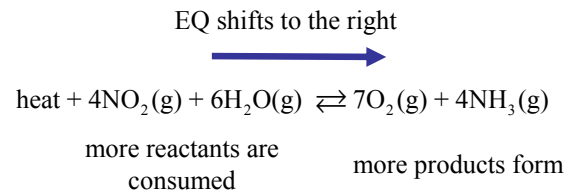If $O_2(g)$ or $NH_3(g)$ are removed, the equilibrium position would shift toward the right and consume more reactants.

Consider the following endothermic reaction at equilibrium:

EQ shifts to the right

$$heat + 4NO_2(g) + 6H_2O(g) \rightleftarrows 7O_2(g) + 4NH_3(g)$$

more reactants are
consumed   more products form

If the volume of the container is increased, the equilibrium position would shift toward the right and which favors more reactants (more moles).

CHAPTER 9:   *Acids, Bases, and Salts*

LEARNING OBJECTIVES

After completing this chapter, one should be able to:
1. Identify Arrhenius and Brønsted acids and bases from written equations.
2. Name common acids based on their formulas.
3. Perform the pH calculations.
4. Write equations that illustrate the characteristic reactions of acids, base and salt reactions.
5. Apply the terms strong and weak to acids and bases.
6. Complete acid/bases titration stoichiometry problems.
7. Explain and write equations that illustrate the hydrolysis of salts.
8. Explain and write equations that illustrate the action of buffers

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ARRHENIUS ACID

An Arrhenius acid is any substance that provides hydrogen ions, H^+, when dissolved in water.

ARRHENIUS BASE

An Arrhenius base is any substance that provides hydroxide ions, OH^-, when dissolved in water.

EXAMPLES OF AN ARRHENIUS ACID AND BASE

HNO_3 is an acid: $HNO_3(aq)$ $H^+(aq) + NO_3^-(aq)$
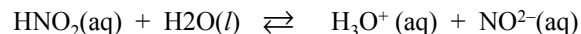
KOH is a base: $KOH(aq)$ $K^+(aq) + OH^-(aq)$

BRØNSTED ACID

A Brønsted acid is any hydrogen-containing substance that is capable of donating a proton (H^+) to another substance.

BRØNSTED BASE

A Brønsted base is any substance capable of accepting a proton from another substance.

EXAMPLE OF A BRØNSTED ACID AND BASE

$$HNO_2(aq) + H2O(l) \rightleftarrows H_3O^+ (aq) + NO^{2-}(aq)$$

In this reaction, HNO_2 behaves as a Brønsted acid by donating a proton to the H_2O.

The H_2O behaves as a Brønsted base by accepting the proton.

CONJUGATE ACIDS AND BASES

The base formed (NO_2^-) when a substance (HNO_2) acts as a Brønsted acid is called the **conjugate base** of the acid. Similarly, the acid formed (H_3O^+) when a substance (H_2O) acts as a Brønsted base is called the **conjugate acid** of the base.

CONJUGATE ACID-BASE PAIRS

A Brønsted acid (such as HNO_2) and its conjugate base (NO_2^-) form what is called a **conjugate acid-base pair**.

The same name is given to a Brønsted base (such as H_2O) and its conjugate acid (H_3O^+).

BINARY ACIDS

Solutions of binary acids such as HCl (aq) are formed by dissolving binary compounds such as HCl (g) in water.

The HCl (g) before being dissolved in water is said to be anhydrous (meaning without water). The anhydrous gas is named hydrogen chloride.

The water solution of the gas is called hydrochloric acid.

Some hydrogen-containing compounds such as HCl, HI, HBr, and H_2S form acidic solutions when they are dissolve in water. The names of the acid solutions, such as the hydrochloric acid given above, can be obtained by following four rules.

RULES FOR NAMING BINARY ACIDS

Rule 1: Drop the word *hydrogen* from the anhydrous compound name.

For example, HI, called hydrogen *iodide* becomes "*iodide*".

Rule 2: Add the prefix *hydro*- to the result of step 1.

Rule 3: Drop the suffix -*ide* from the result of step 2 and replace it with the suffix -*ic*.

HI(g) becomes "*hydroiodic*", HI(aq).

Rule 4: Add the word *acid* to the end of the name as a separate word.

The final name is "*hydroiodic acid*".

RULES FOR NAMING ACIDS CONTAINING POLYATOMIC IONS

Rule 1: All hydrogen atoms that are written as the first part of the formula of the acid are removed. The hydrogens are removed in the form of H^+ ions.

Rule 2: The polyatomic ion that remains after the H^+ ions are removed is named by referring to sources such as *Table 4.7*.

Rule 3: When the remaining polyatomic ion has a name ending in the suffix -ate, the suffix is replaced by the suffix –*ic*, and the word *acid* is added.

Rule 4: When the remaining polyatomic ion has a name ending in the suffix -*ite*, the suffix is replaced by the suffix -ous, and the word *acid* is added.

Rule 5: If the polyatomic ion contains sulfur or phosphorus, the stems -*sulf* or -*phosph* that remain when the suffixes -*ate* or -*ite* are replaced, are expanded to -*sulfur* and -*phosphor* before the –*ic* or –*ous* suffixes are added.

THE AUTO-IONIZATION OF WATER

A sample of absolutely pure water does not contain only H_2O molecules. In addition, small but equal amounts of H_3O^+ and OH^- ions are also present.

The reason for this is that in one liter of pure water 1.0×10^{-7} moles of water molecules behave as Brønsted acids and donate protons to another 1.0×10^{-7} moles of water molecules, which act as Brønsted bases.. The reaction is:

$$H_2O(l) + H_2O(l) \quad \rightleftarrows \quad H_3O^+(aq) + OH^-(aq)$$
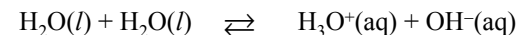
As a result, absolutely pure water contains 1.0×10^{-7} mol/L of both H_3O^+ and OH^-.

The term ***neutral*** is used to describe any water solution in which the concentrations of H_3O^+ and OH^- are equal.

Thus, pure water is neutral because each of the ions is present at a concentration of 1.0×10^{-7} M.