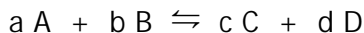


# EQUILIBRIUM

## I. DYNAMIC EQUILIBRIUM

A. Consider the reversible reaction:



At equilibrium:

- Two reactions are occurring simultaneously:  $aA + bB \longrightarrow cC + dD$  and  $cC + dD \longrightarrow aA + bB$ .
- The rate of the forward reaction ( $aA + bB \longrightarrow cC + dD$ ) is equal to the rate of the reverse reaction ( $cC + dD \longrightarrow aA + bB$ ).
- Concentrations of products and reactants are constant but they are not equal (usually).

B. EQUILIBRIUM CONSTANT = K

- K is a constant whose value depends only on temperature.
- Various Equilibrium Constants, K's:

reactions of gases	$K_c$ & $K_p$	solubility	$K_{sp}$
weak acid ionization	$K_a$	ionization of water	$K_w$
weak base ionization	$K_b$	general	$K_{eq}$
hydrolysis	$K_h$		

3. Equilibrium Constant Expression:



the equilibrium constant expression is

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

The brackets [ ] imply molar concentration at equilibrium  
raised to power of coefficient from equation

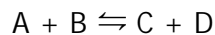
(What about non-equilibrium molar concentrations? We'll use M)

Notice: equilibrium constant expression always has PRODUCTS OVER REACTANTS.

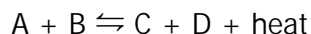
- Meaning of K
  - If the value of K is greater than 1, equilibrium favors the products.
  - If the value of K is less than 1, equilibrium favors the reactants.
  - If  $K = 1$ ,

## C. LE CHATELIER'S PRINCIPLE & CHEMICAL EQUILIBRIUM

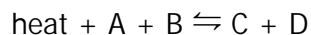
1. Le Chatelier's Principle: if a system in dynamic equilibrium is subjected to a disturbance that upsets the equilibrium, the system changes in such a way as to reduce the disturbance and, if possible, return to equilibrium
2. Effect of Changing the Concentration of a reactant or a product



- a. Increase the concentration of a reactant (A or B)
  - b. Increase the concentration of a product (C or D)
  - c. Decrease the concentration of a product
3. Effect of Changing the Temperature
    - a. Temperature affects the value of K itself
    - b. For a system at equilibrium, addition of heat favors the endothermic process.
      - (1) exothermic reaction:



- (2) endothermic reaction:



4. Effect of Changing Pressure and Volume (gases only)

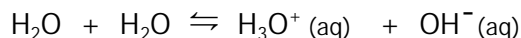
Decreasing the volume (increasing the pressure) of a mixture of gases that are in chemical equilibrium shifts the equilibrium in the direction of the fewest number of molecules (moles) of gas.

5. Effect of Catalyst

## AQUEOUS EQUILIBRIA

### I. Ionization of Water

#### A. Autoionization of H<sub>2</sub>O:



1. The above reaction occurs in pure water as well as any aqueous solution.
2. Equilibrium constant expression:

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

$$\underbrace{K \cdot [\text{H}_2\text{O}]^2}_{K_w} = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \leftarrow \text{Since } [\text{H}_2\text{O}] \text{ is nearly constant in both pure water and dilute aqueous solutions, } [\text{H}_2\text{O}]^2 \text{ can be put with } K, \text{ which is also constant.}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad K_w = \text{Ion Product Constant for Water}$$

$$K_w = 1.0 \times 10^{-14} \quad \text{memorize}$$

3. Concentration of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup>
  - a. Pure water [H<sub>3</sub>O<sup>+</sup>] = [OH<sup>-</sup>]
  - b. Neutral solution:
  - c. Aqueous acid solution\*: [H<sub>3</sub>O<sup>+</sup>] > [OH<sup>-</sup>]
  - d. Aqueous base solution: [H<sub>3</sub>O<sup>+</sup>] < [OH<sup>-</sup>]

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  is always obeyed in any aqueous solution

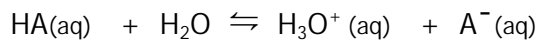
\*Solution of strong or weak acid in water: assume ALL H<sub>3</sub>O<sup>+</sup> comes from the acid and NOT from ionization of water. The amount of H<sub>3</sub>O<sup>+</sup> from the autoionization of water is small enough, compared to the amount produced by the acid, to be considered negligible. (Water ionizes less in acid solution than in pure water.)

The same assumption may be made about aqueous solutions of bases: all the OH<sup>-</sup> present in solution comes from the ionization reaction of the base.

## II. IONIZATION OF WEAK ACIDS AND WEAK BASES

### A. WEAK ACID IONIZATION (monoprotic acids)

1. Reaction of weak monoprotic acid, HA, with water:



2. Weak acid ionization simplified:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

3. Equilibrium constant expression:

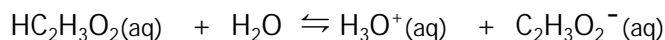
$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}_2\text{O}][\text{HA}]}$$

$$K \cdot [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{p}K_a =$$

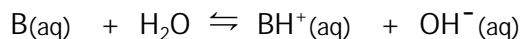
4. Example: acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}$$

### B. WEAK BASE IONIZATION

1. Reaction of weak base, B, with water:



2. Equilibrium constant expression:

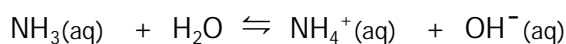
$$K = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{B}]}$$

$$K \cdot [\text{H}_2\text{O}] = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$$\text{p}K_b =$$

3. Example: ammonia,  $\text{NH}_3$

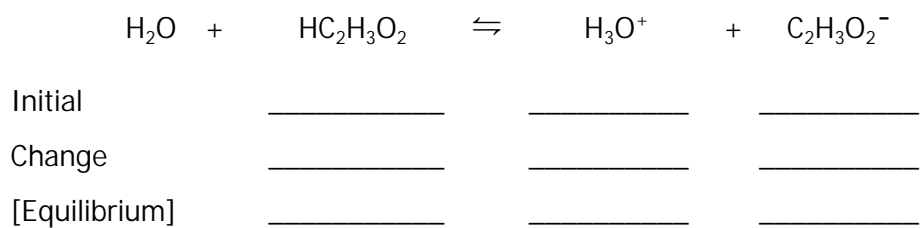


$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

### C. SIMPLE WEAK ACID/BASE EQUILIBRIUM CALCULATIONS

#### 1. Calculation of K given pH

- a. The pH of a 0.100 M  $\text{HC}_2\text{H}_3\text{O}_2$  solution is 2.87. Calculate the  $K_a$ .



- b. The pH of a 0.150 M  $\text{NH}_3$  solution is 11.22. Calculate  $K_b$ .

2. Calculation of K given concentration and percent ionization

a. A 0.200 M solution weak acid, HA, is 1.3% ionized. Calculate  $K_a$ .

3. Calculation of equilibrium concentrations of species in solution (or pH of soln) at equilibrium when K is given.

a. Calculate pH of a 0.150 M HClO solution. ( $K_a = 3.1 \times 10^{-8}$ )

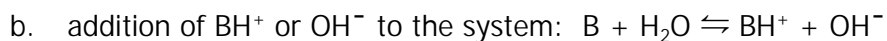
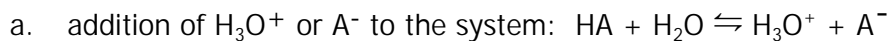
b. Calculate the per cent ionization of the HClO in the above solution.

## D. EFFECT OF ADDITION OF IONS TO WEAK ACID/BASE EQUILIBRIUM

### 1. Common Ion Effect

This is the effect on equilibrium that occurs when an ion common to one of those produced by the ionization of a weak acid or weak base is added to the system.

For example:



Example 1: Weak acid and its salt: Calculate the  $[\text{H}_3\text{O}^+]$  and pH of a 0.200 M HF solution before and after NaF is added to it.  $K_a = 6.9 \times 10^{-4}$

(1) pH of 0.200 M HF solution (no NaF added).

(2) pH of HF solution after adding enough NaF to make soln 0.100 M in NaF. (So solution is now initially 0.200 M HF and 0.100 M NaF).

Example 2: Weak acid and strong acid: What is the pH of a solution that is 0.10 M HCl and 0.10 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.  $K_a = 1.8 \times 10^{-5}$

Example 3: Weak base and its salt: What is the pH of a solution prepared by dissolving 0.020 mole of ammonium chloride, NH<sub>4</sub>Cl, in 100 mL of 0.15 M ammonia? (Assume no volume change upon addition of solid to the solution.)  $K_b$  of ammonia is  $1.8 \times 10^{-5}$

Example 4: Weak base and strong base: What is the pH of a solution that is 0.250 M in trimethylamine,  $(\text{CH}_3)_3\text{N}$  and 0.010 M in NaOH?  $K_b$  of trimethylamine is  $7.4 \times 10^{-5}$

2. Addition of ion that's not common but does react.

Example: 50.0 ml of 0.100 M NaOH is added to 80.0 ml of 0.200 M  $\text{HC}_2\text{H}_3\text{O}_2$ . What is the  $[\text{H}_3\text{O}^+]$  of the resulting solution?  $K_a = 1.8 \times 10^{-5}$

### III. BUFFERS

A. A buffer is a solution that maintains a constant pH (resists change in pH– keeps its own pH) upon addition of  $\text{H}_3\text{O}^+$  (from a strong acid) or  $\text{OH}^-$  (from a strong base) or water (dilution).

A buffer must therefore have two components:

1. a component to react with added  $\text{H}_3\text{O}^+$  to produce a weakly ionized substance (a weak acid or water).
2. a component to react with added  $\text{OH}^-$  to produce a weakly ionized substance (a weak base or water).

B. Some Buffer Systems:

1. Weak acid and its salt (salt that contains conjugate base of the acid)  
example:  $\text{HCN}$  and  $\text{NaCN}$
2. Weak base and its salt (salt that contains the conjugate acid of the base)  
example:  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$
3. "Acid salts": salt containing ion with acidic H  
example:  $\text{NaHCO}_3$
4. Salt of a weak acid & weak base  
example:  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$

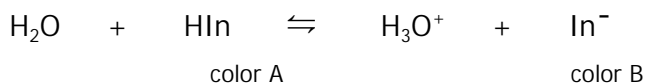
C. SELECTING A BUFFER OF DESIRED pH





#### IV. ACID-BASE INDICATORS

- A. Acid-base indicator is usually a weak organic acid (or base) whose conjugate base (or acid) is a different color than it is:



1. In a more acidic solution, HIn predominates, so solution is color A. Therefore, HIn is called the acid form of the indicator.
  2. In a more basic solution, In<sup>-</sup> predominates, so solution is color B. Therefore, In<sup>-</sup> is called the base form of the indicator.
- B. Acid-base indicator may be used to determine the equivalence point in an acid-base titration.

Equivalence point of a titration occurs when stoichiometrically equivalent amounts of acid and base have been brought together.

Choice of indicator depends on the pH at the equivalence point of the titration.

$$K_{\text{HIn}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$\frac{K_{\text{HIn}}}{[\text{H}_3\text{O}^+]} = \frac{[\text{In}^-]}{[\text{HIn}]} \quad \text{the ratio of acid to base form varies with pH}$$

If [In<sup>-</sup>] is 10 times (or more) larger than [HIn], the base form, In<sup>-</sup>, predominates and only the base color is observed.

If [HIn] is at least 10 times larger than [In<sup>-</sup>], the acid form, HIn, predominates and only the acid color is observed

Henderson Hasselbalch Equation:  $\text{pH} = \text{pK}_a + \log \left[ \frac{[\text{In}^-]}{[\text{HIn}]} \right]$