

## Chem 103 lecture 2b

Strengths of acids and bases

$K_a$  and  $K_b$

pH and pH calculations

## Strengths of acids and bases

Acids and Bases are categorized into two general types:

Strong and weak. Refers to the tendency to donate or accept  $H^+$

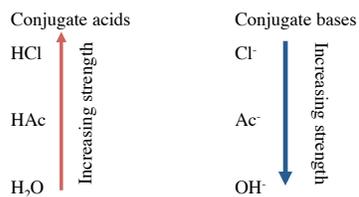
Strong acids and bases dissociate 100%: HCl,  $HNO_3$ ; NaOH, KOH

Weak acids and bases do not dissociate 100%:  $CH_3COOH$ , HF,  $NH_3$

Among weak acids and bases, the rule of thumb is:

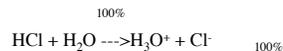
“the stronger the conjugate, the weaker the acid or base”

## Strengths of acids & bases:



## Dissociation of strong acids in water

Strong acids dissociate 100% in water. (Classic example: HCl)



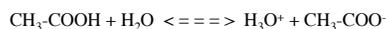
Other examples:  $HNO_3 + H_2O \xrightarrow{100\%} H_3O^+ + NO_3^-$

HBr, HI,  $H_2SO_4$  (remember all these strong acids)

Often we just write:  $HCl \rightarrow H^+ + Cl^-$ ;  $HNO_3 \rightarrow H^+ + NO_3^-$

## Dissociation of weak acids in water

Weak acids do NOT ionize 100% (classic example: acetic acid; contains methyl  $-CH_3$  attached to carboxyl group  $-COOH$ ):



Generic eq'n for weak acid:  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

Called “ $K_a$  equilibrium”.  $K_a$  is “acid dissociation constant”.

What is the expression for  $K_a$ ?  $K_a = [H_3O^+][A^-] / [HA]$

The larger the  $K_a$ , the stronger the weak acid.

Usually  $K_a$  very small, ex:  $K_a$  for acetic acid =  $1.8 \times 10^{-5}$

For  $NH_4^+$  it is  $5.6 \times 10^{-10}$ . Which is the stronger weak acid?

## Weak base equilibrium

For weak bases: “ $K_b$  equilibrium”.  $K_b$  = “base ionization constant: Generic equation



$$K_b = [BH^+][OH^-] / [B]$$

The greater  $K_b$  is, the stronger the base.

Usually  $K_b$  very small, example:  $NO_2^-$  has  $K_b = 2.2 \times 10^{-11}$

$$K_a K_b = K_w = 1.0 \times 10^{-14}$$

Note:  $K_a = [\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$  for acid HA.

For its conjugate,  $\text{A}^-$ , it is:  $K_b = [\text{HA}][\text{OH}^-]/[\text{A}^-]$

So if multiply  $K_a$  of weak acid by  $K_b$  of its conjugate, then :

$$K_a K_b = \left( \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \right) \left( \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \right)$$

$$K_a K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

## pH

Because of wide range of  $[\text{H}_3\text{O}^+]$ , it's convenient to express concentration levels of  $[\text{H}^+]$  by its exponent, using logarithmic scale. This is the "pH scale".

Definition of pH: **pH =  $-\log[\text{H}^+]$  =  $-\log[\text{H}_3\text{O}^+]$**

For example: what's the pH of pure water?

Note: pure water:  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}\text{M}$

$$\text{pH} = -\log \{ [\text{H}_3\text{O}^+] \} = -\log(1.0 \times 10^{-7}\text{M}) = 7.00$$

This is the *neutral* pH

## pH of acidic solutions

If you have an acidic solution with  $[\text{H}_3\text{O}^+] = 2.0 \times 10^{-4}\text{M}$ .  
What's the pH?

$$\text{pH} = -\log(2.0 \times 10^{-4}\text{M}) = 3.70$$

In general, if  $\text{pH} < 7.00$  we say solution is acidic...

If  $\text{pH} > 7.00$  the solution is basic.

What is  $[\text{H}^+]$  if you are given the pH?

$$[\text{H}^+] = 10^{-\text{pH}}$$

## pOH

Definition:  $\text{pOH} = -\log[\text{OH}^-]$

Before:  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

(so if you know  $[\text{H}_3\text{O}^+]$ , you can know  $[\text{OH}^-]$ )

take  $-\log$  of both sides:

$$-\log\{ [\text{H}_3\text{O}^+][\text{OH}^-] \} = -\log\{ 1.0 \times 10^{-14} \}$$

$$-\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] = 14.00$$

$$\text{Or, } \text{pH} + \text{pOH} = 14.00$$

(so if you know pH, you can know pOH)

## Summary

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad \text{and} \quad \text{pOH} = -\log[\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14.00$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$K_a K_b = 1.0 \times 10^{-14}$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

## Calculating pH of a solution

There are at least 5 scenarios we'll encounter involving pH calculations. You are expected to **MASTER** these calculations.

- 1) Strong acid solutions
- 2) Strong base solutions
- 3) Pure Weak acid solutions
- 4) Pure weak base solutions
- 5) Buffer solutions

## Calculations of salt solutions

You are also expected to recognize that salts can have acid or base properties.

E.g.

$\text{NH}_3$  is a weak base. It is NOT a salt.

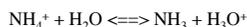
$\text{NH}_4\text{Cl}$  is a salt. Is a solution of  $\text{NH}_4\text{Cl}$  an acidic or basic solution?

Well,  $\text{NH}_4^+$  is the *conjugate acid* of  $\text{NH}_3$  so  $\text{NH}_4^+$  is a weak acid.  $\text{Cl}^-$  is conjugate base of  $\text{HCl}$  a *strong* acid. So,  $\text{Cl}^-$  is so weak as to have a negligible effect.

## Net ionic equations and ICE

You are also expected to know how to write and recognize *net ionic equations*.

e.g. What is the  $K_a$  equilibrium for a  $\text{NH}_4\text{Cl}$  solution?



You are supposed to master ICE type calculations involving  $K_a$  and  $K_b$  equilibria.

I=initial, C=change, E= equilibrium

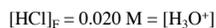
## pH of a strong acid solution

As mentioned earlier, there are at least 5 "scenarios" involving pH calculations. Most simple : pH of a strong acid solution.

For example: What is the pH of a 0.020 M HCl solution?

Answer:

Since HCl is a strong acid, it dissociates completely:



$$\text{So, pH} = -\log [\text{H}_3\text{O}^+] = -\log [\text{HCl}]_F = -\log(0.020) = 1.70$$

## pH of a strong base solution

2nd scenario:

What is the pH of a  $5.2 \times 10^{-4} \text{ M}$  NaOH solution?

Answer: Since NaOH is a strong base, we can write:



It is easier to determine pOH first:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(5.2 \times 10^{-4}) = 3.28$$

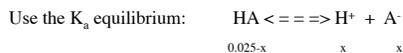
$$\text{pH} = 14.00 - 3.28 = 10.72 \text{ (makes sense?)}$$

Yes because it is a basic pH

## pH of a weak acid solution(stopped here Wed)

What is the pH of a  $2.5 \times 10^{-3} \text{ M}$  acetic acid ( $\text{HA}$ ,  $K_a = 1.8 \times 10^{-5}$ )

Answer:



$$x^2 / (0.025 - x) = 1.8 \times 10^{-5} \Rightarrow x^2 + 1.8 \times 10^{-5} x - 4.5 \times 10^{-7} = 0$$

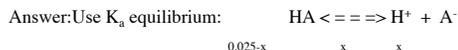
Solve for x by the quadratic equation.  $x = 6.6 \times 10^{-4}$

$$\text{pH} = -\log(6.6 \times 10^{-4}) = 3.18$$

## pH of a weak acid solution

Redo same problem using approximation ( 5% rule):

What's pH of  $2.5 \times 10^{-2} \text{ M}$  acetic acid ( $\text{HA}$ ,  $K_a = 1.8 \times 10^{-5}$ )



$$x^2 / (0.025 - x) = 1.8 \times 10^{-5} \Rightarrow x^2 / (0.025) \approx 1.8 \times 10^{-5}$$

$$\text{Solve for x: } x = \{(0.025)(1.8 \times 10^{-5})\}^{1/2} = 6.7 \times 10^{-4}$$

$$\text{pH} = -\log(6.7 \times 10^{-4}) = 3.17 \text{ (compare with 3.18)}$$

Note:  $6.7 \times 10^{-4} (100\%) / 0.025 = 3\% < 5\%$

## pH of a weak base solution

What is the pH of 0.10 M ammonia? ( $K_b = 1.8 \times 10^{-5} \text{M}$ )

Answer: Use the  $K_b$  equilibrium.  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

$x^2/(0.10-x) = 1.8 \times 10^{-5}$ . Using 5% rule:

$x^2 \approx (1.8 \times 10^{-5})(0.10) \Rightarrow x = 1.3 \times 10^{-3} = [\text{OH}^-]$

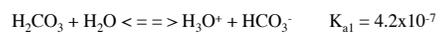
$\text{pOH} = 2.87 \Rightarrow \text{pH} = 14.00 - 2.87 = 11.13$

## Polyprotic acids

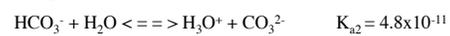
*Polyprotic acids can donate more than 1 proton.*

Examples:  $\text{H}_2\text{CO}_3$  (carbonic acid);  $\text{H}_3\text{PO}_4$  (phosphoric acid).

If you place  $\text{H}_2\text{CO}_3$  in water you will have the following  $K_a$  equilibrium:



If you place  $\text{NaHCO}_3$  in water you have:



There are 2  $K_a$ 's