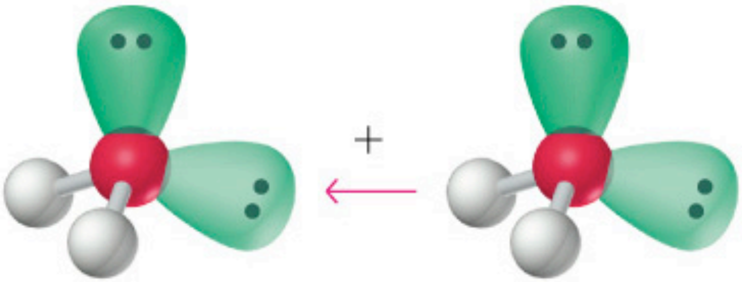
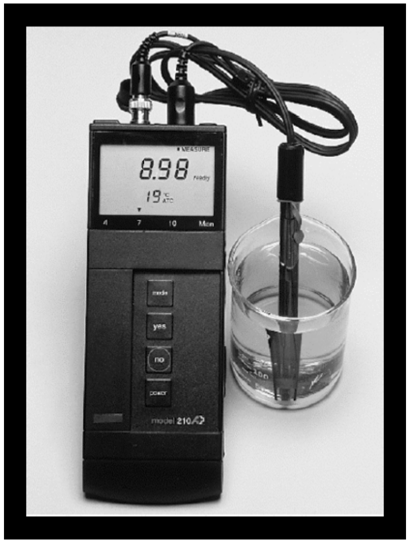
Chapter 16:
Acid-Base Equilibria



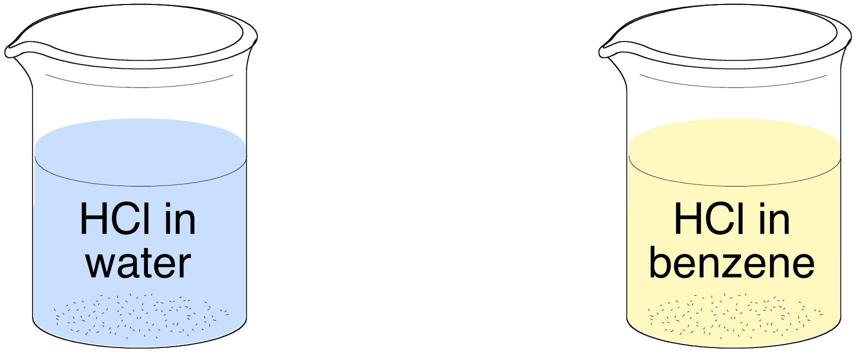


Arrhenius Theory of Acids and Bases

(1859 – 1927)

Svante Arrhenius (1884)

- His theory:
  - Acids: contain H+
  - Bases: contain OH-
- **Key flaws in Arrhenius' theory:**
  - some bases do not contain any OH-
  - assumed the solvent has no effect



conducts electricity

does not conduct electricity

Brønsted-Lowry Theory of Acids and Bases

The most general theory for common aqueous acids and bases is the **BRØNSTED - LOWRY** theory:

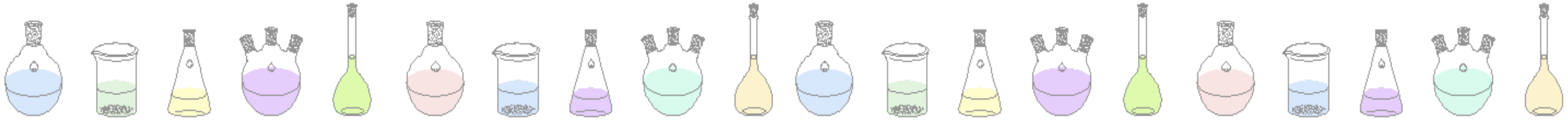
- An acid is a proton donor.
- A base is a proton acceptor.

base acid

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

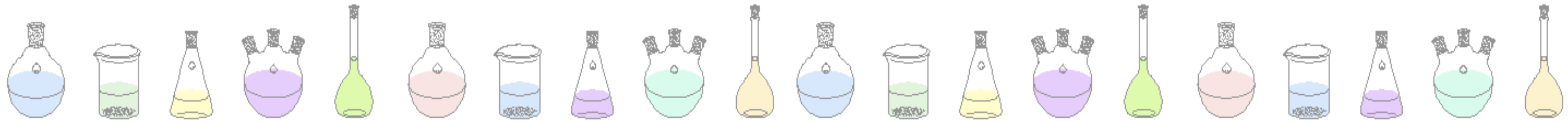
$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

acid base



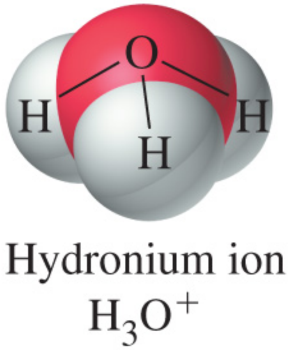
Proton Transfer

- we use curved arrows to show “electron flow” as bonds are broken and formed in the proton transfer



Acids in Chemical Equations

- in water, the proton, $H^+(aq)$, will be actually be associated with at least one water molecule, to form the hydronium ion, $H_3O^+(aq)$
- usually, $H^+(aq)$ and $H_3O^+(aq)$ are used
  - $H^+(aq)$ is more common
  - $H_3O^+(aq)$ is more realistic

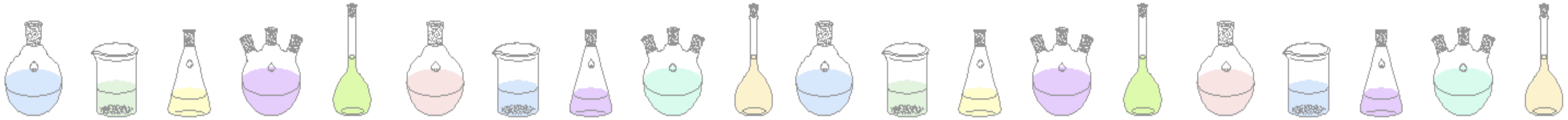


Hydronium ion
H_3O^+

- therefore, the ionization of an acid can be written two ways:

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$



Conjugate Pairs

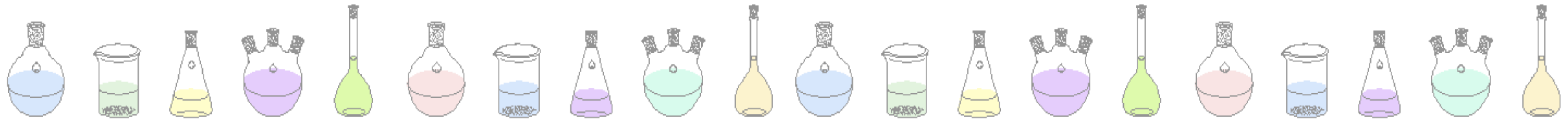
Conjugate acid/base pairs are related through gain or loss of a proton:

$$\underset{\textbf{base}}{NH_3(aq)} + \underset{\textbf{acid}}{H_2O} \rightleftharpoons \underset{\textbf{conj. acid}}{NH_4^+(aq)} + \underset{\textbf{conj. base}}{OH^-(aq)}$$

In this example, NH_3 is a **base** and NH_4^+ is its **conjugate acid.**

Water is an **acid** and OH^- is the **conjugate base.**

EVERY acid has a conjugate base and vice-versa!



Conjugate Pairs

EVERY acid has a conjugate base and vice-versa!

Your Turn…

In the equilibrium system described by:

$$HPO_4^{2-} + H_2O \leftrightarrows H_2PO_4^{-} + OH^{-}$$

Brønsted-Lowry theory would designate:

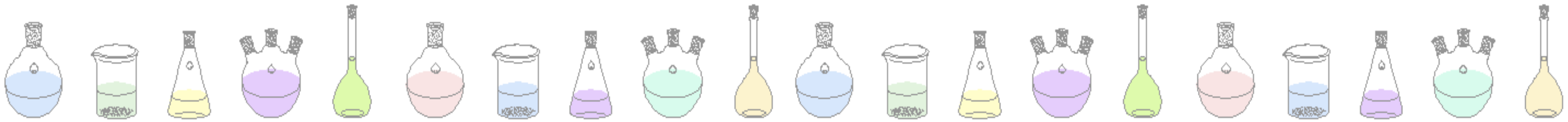
a. HPO_4^{2-} and H_2O as the bases

b. H_2O and OH^- as a conjugate pair

c. $H_2PO_4^-$ and OH^- as the acids

d. $H_2PO_4^-$ and H_2O as a conjugate pair

e. PO_4^{3-} as amphiprotic

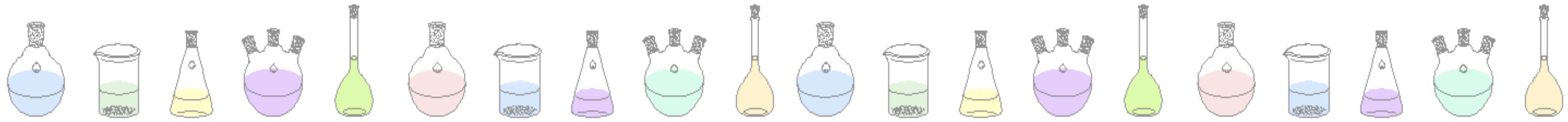


Acid and Base Strength

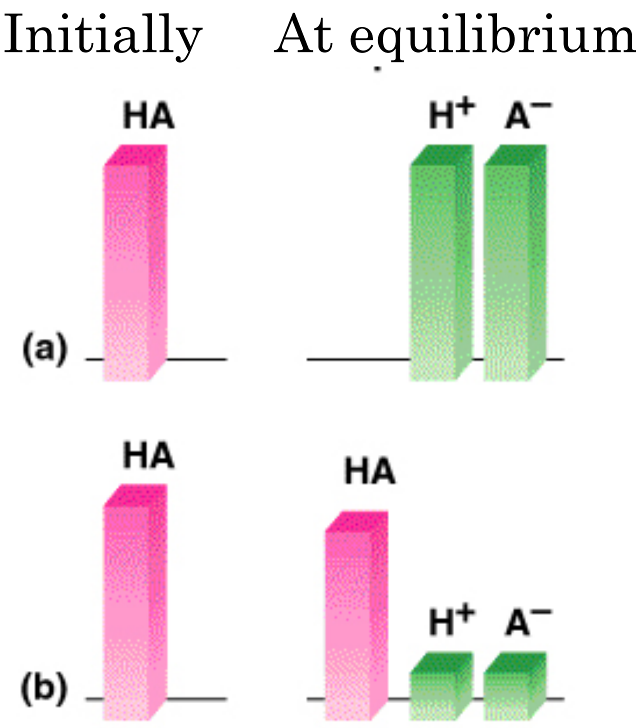
In an acid-base reaction , the favoured direction of the reaction is from the stronger to the weaker member of a conjugate pair

We generally divide acids and bases up into two groups:

strong acids	strong bases
weak acids	weak bases



Acid → H_3O^+ in water



Strong acids: ionize completely in water:

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

Weak acids: only partially ionize:

$$CH_3CO_2H + H_2O \leftrightarrows H_3O^+ + CH_3CO_2^-$$

Acid Ionization Constant

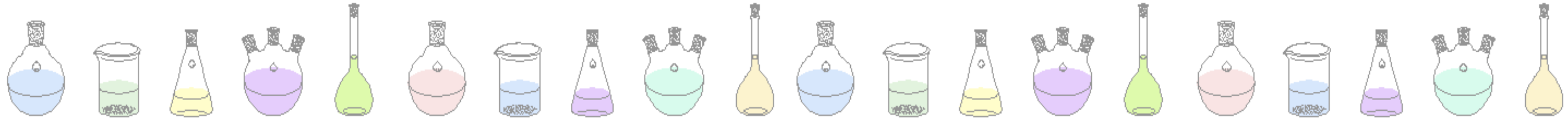
acid **base** **conjugate base** **conjugate acid**

$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$$

$$K_C = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]}$$

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8\text{x}10^{-5}$$

This constant **K_a** follows the rules for equilibrium constants, it has the subscript "a" to indicate that it is the **ionization of an acid**.



Strong Acids

STRONG ACIDS are considered to be 100% ionized in water:

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

$$K_a = \frac{[H_3O^+][NO_3^-]}{[HNO_3]} >>> 1$$

$$pK_a = -\log K_a$$

Weak Acids

WEAK ACIDS are <u>much less than 100%</u> ionized in water.

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} <<< 1$$

$$pK_a = -\log K_a$$

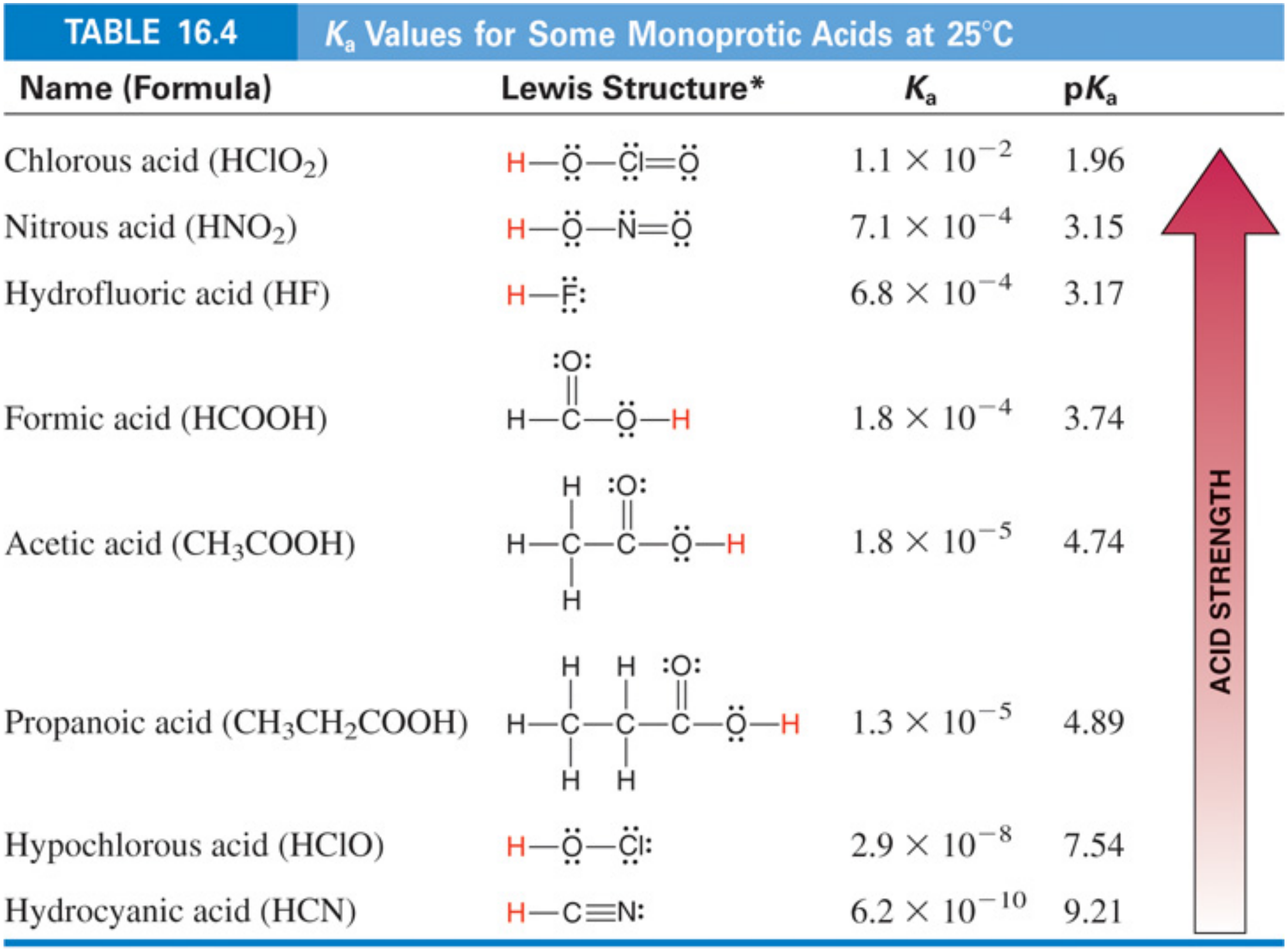


TABLE 16.4 K_a Values for Some Monoprotic Acids at 25°C

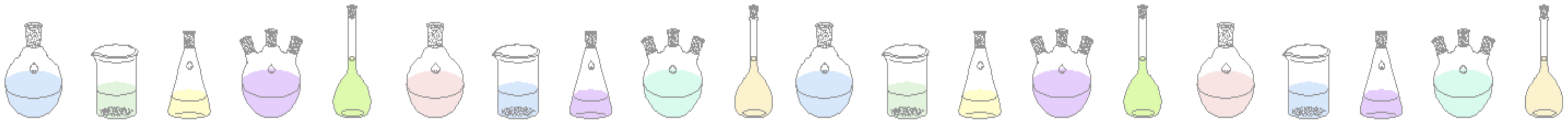
Name (Formula)	Lewis Structure*	K_a	pK_a
Chlorous acid ($HClO_2$)	$H-O-Cl=O$	1.1×10^{-2}	1.96
Nitrous acid (HNO_2)	$H-O-N=O$	7.1×10^{-4}	3.15
Hydrofluoric acid (HF)	$H-F$	6.8×10^{-4}	3.17
Formic acid (HCOOH)	$H-\overset{\overset{O}{\Vert}}{C}-O-H$	1.8×10^{-4}	3.74
Acetic acid (CH_3COOH)	$H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{O}{\Vert}}{C}-O-H$	1.8×10^{-5}	4.74
Propanoic acid (CH_3CH_2COOH)	$H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{O}{\Vert}}{C}-O-H$	1.3×10^{-5}	4.89
Hypochlorous acid (HClO)	$H-O-Cl$	2.9×10^{-8}	7.54
Hydrocyanic acid (HCN)	$H-C\equiv N$	6.2×10^{-10}	9.21

*Red type indicates the ionizable proton; all atoms have zero formal charge.

Strong vs. Weak Acids

$$HA + H_2O \rightleftarrows H_3O^+ + A^-$$

	Strong Acid	**Weak Acid**
K_a	K_a is ________	K_a is ________
pK_a	____________	____________
Dissociation	far to the ________	far to the _________
Eq’m $[H_3O^+]$	$[H_3O^+] \sim [HA]_o$	$[H_3O^+] << [HA]_o$
Strength of conjugate base	A^- much __________ base than water	A^- much ____________ base than water



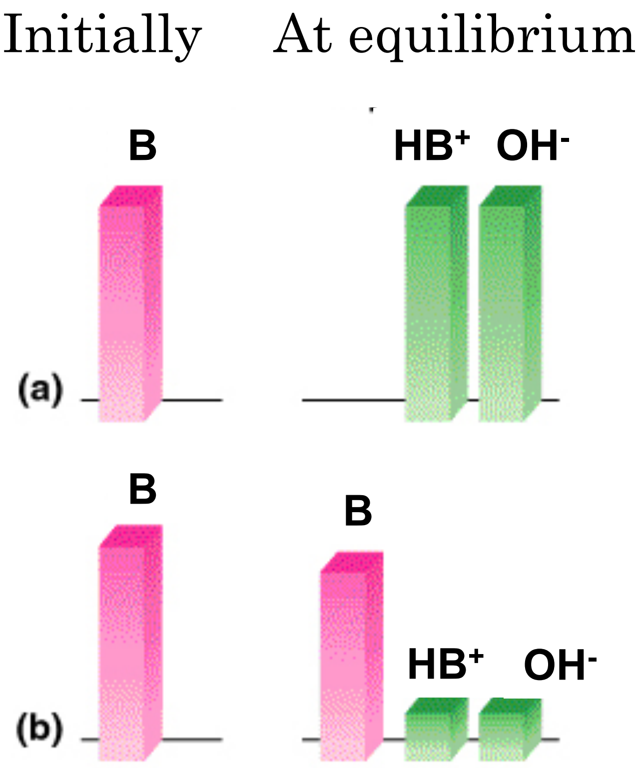
Bases → OH^- in water

<u>Strong bases</u>: ionize completely in water:

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

<u>Weak bases</u>: only partially ionize:

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$



Base Ionization Constant

base **acid** **conjugate acid** **conjugate base**

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_C = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8x10^{-5}$$

This constant K_b follows the rules for equilibrium constants, it has the subscript “b” to indicate that it is the **ionization of an base**.

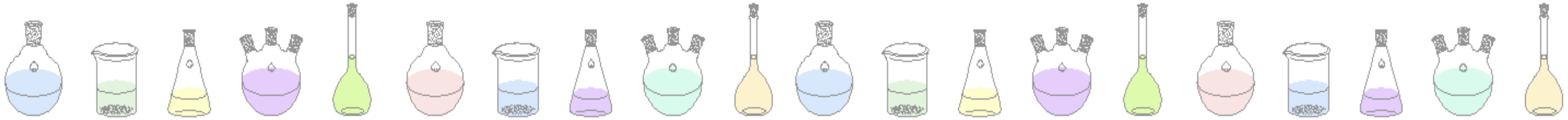
Strong Bases

STRONG BASES are considered to be 100% ionized in water:

$$\mathrm{NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)}$$

$$K_b = \frac{[\mathrm{Na^+}][\mathrm{OH^-}]}{[\mathrm{NaOH}]} >>> 1$$

$$pK_b = -\log K_b$$



Weak Bases

WEAK BASES are much less than 100% ionized in water.

$$NH_3(aq) + H_2O(l) \overset{\rightarrow}{\longleftarrow} OH^-(aq) + NH_4^+(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} <<< 1$$

$$pK_b = -\log K_b$$

Strong vs. Weak Bases

$$\mathbf{B + H_2O \rightleftharpoons HB^+ + OH^-}$$

	Strong Base	**Weak Base**
K_b	K_b is **large**	K_b is **small**
pK_b	**negative**	**positive**
Dissociation	far to the **right**	far to the **left**
Eq’m $[OH^-]$	$[OH^-] \sim [B]_o$	$[OH^-] << [B]_o$
Strength of conjugate acid	HB^+ much **weaker** acid than water	HB^+ much **stronger** acid than water

How do I know if it's a strong acid or base?

Strong Acids

HNO_3, H_2SO_4 (1^{st} H^+)

HCl, HBr, HI

$HClO_4$

Strong Bases

soluble $M_x(OH)_y$

e.g. NaOH, KOH

see Table 16.3

Weak Acids

H_2SO_3, HNO_2

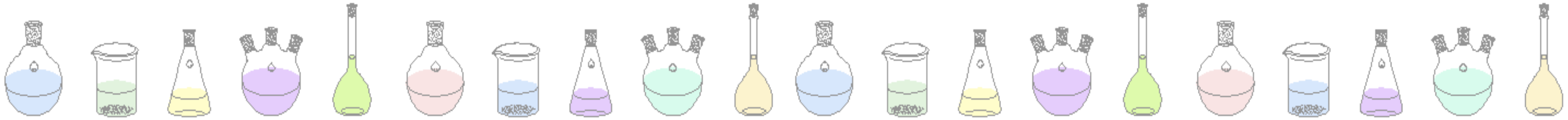
HF, HOCl

CH_3COOH, H_2CO_3

Weak bases

NH_3 and other N compounds (amines)

see Table 16.3



Conjugate Pairs & Direction of Net Change

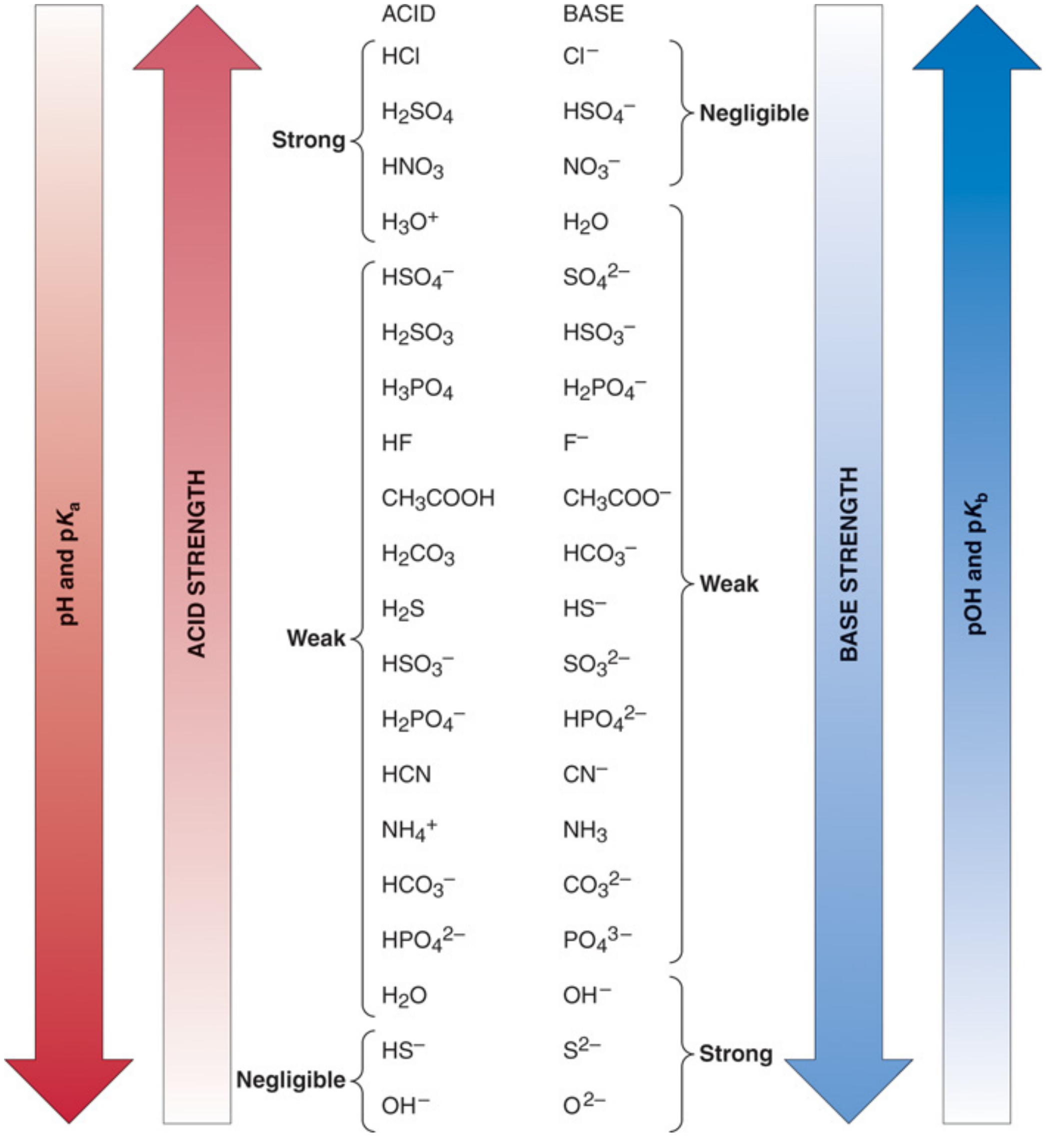
In an acid–base reaction, the favoured direction of the reaction is from the stronger to the weaker member of a conjugate pair

$$\mathrm{HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

$\mathrm{HCl\,(aq)}$	$\mathrm{H_2O\,(l)}$	$\mathrm{H_3O^+\,(aq)}$	$\mathrm{Cl^-\,(aq)}$
acid	base	conjugate acid	conjugate base

In general:

A strong acid will have a weak conjugate base
A strong base will have a weak conjugate acid



	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	Weak
Weak	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	HCN	CN^-	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	Strong
Negligible	HS^-	S^{2-}	
	OH^-	O^{2-}	

Figure 16.3 for the Relative Strengths of Some Acid/Base Pairs

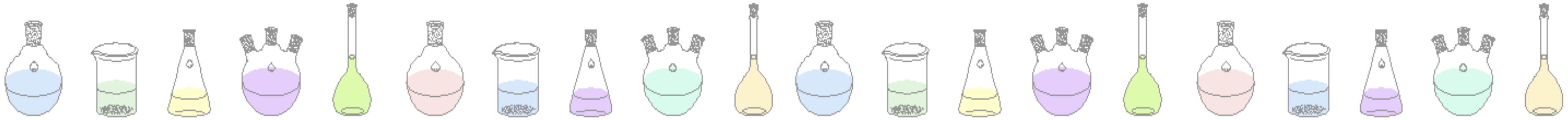
Examples: Predicting the Direction of Change

Predict the products and preferred direction of change for the following acid-base reactions (is K > or < 1?)

1. $CH_3CO_2H \ + \ H_2O$

2. $H_3PO_4 \ + \ F^-$

3. $HCO_3^- \ + \ HSO_3^-$



Your Turn…

Hydrogen cyanide and sulfide ion participate in the following competitive equilibrium in a non-aqueous medium:

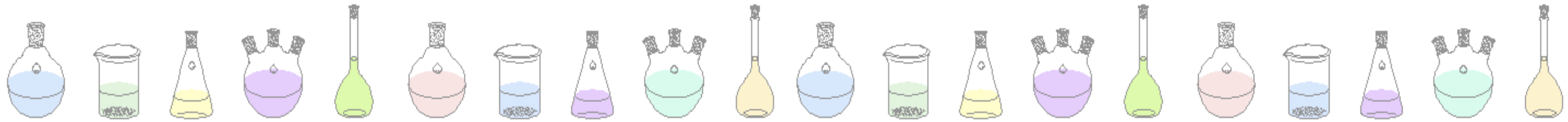
$$\mathrm{HCN} + \mathrm{S}^{2-} \rightleftarrows \mathrm{CN}^{-} + \mathrm{HS}^{-}$$

What is the preferred direction of reaction?

A. Towards reactants

B. Towards products

C. I’m not sure



Your Turn…

Methylamine and ammonia participate in the following competitive equilibrium in a non-aqueous medium:

$$CH_3NH_2 + NH_4^+ \rightleftharpoons CH_3NH_3^+ + NH_3$$

$K_b = 4.4\times10^{-4}$ $K_b = 1.8\times10^{-5}$

What is the preferred direction of reaction?

A. Towards reactants

B. Towards products

C. I’m not sure

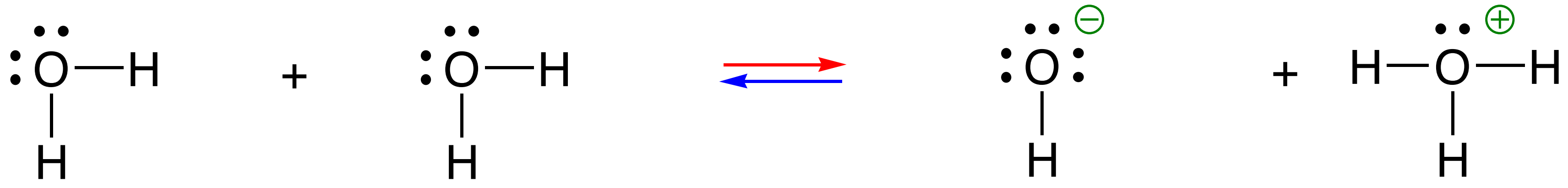
The Self-ionization of Water and the pH Scale

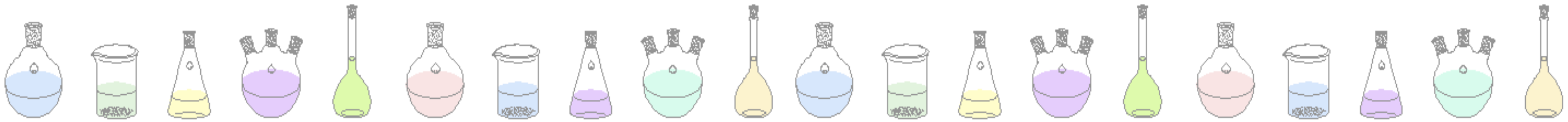
In pure water, water acts as both ***acid and base*:**

This reaction is called ***self-ionization***.

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

acid and base **conjugate acid** **conjugate base**





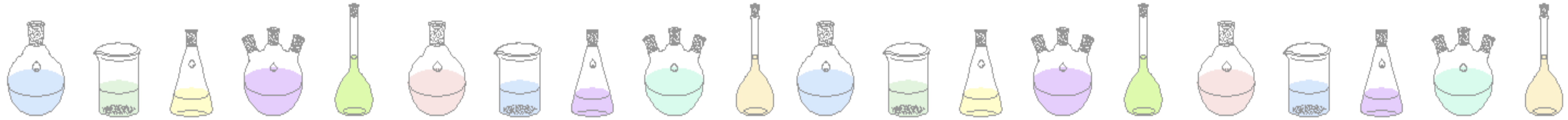
Ion Product of Water

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

- the equilibrium constant at 25°C for the self-ionization is:

$$K = \frac{a_{H_3O^+}\,a_{OH^-}}{a_{H_2O}} = [H_3O^+][OH^-] = 1.0 \times 10^{-14} = K_W$$

- this means that the concentrations of H^+ and OH^- are linked
  - if one value is high, the other must be low!
- in a neutral solution $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M



pH and pOH

- Because the concentrations of H_3O^+ and OH^- are so small we use the following definitions:

$$pH = -\log[H_3O^+] \qquad pOH = -\log[OH^-]$$

$$K_W = [H_3O^+][OH^-] = 1.0\text{x}10^{-14}$$

Using these definitions we can derive the relationship:

$$-\log K_W = -\log[H_3O^+] - \log[OH^-] = -\log(1.0\text{x}10^{-14})$$

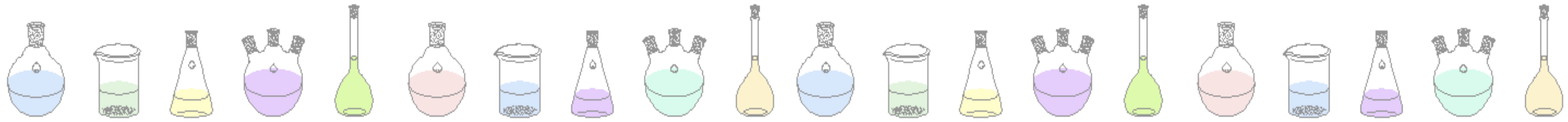
$$pK_W = pH + pOH = -(-14)$$

pH and pOH

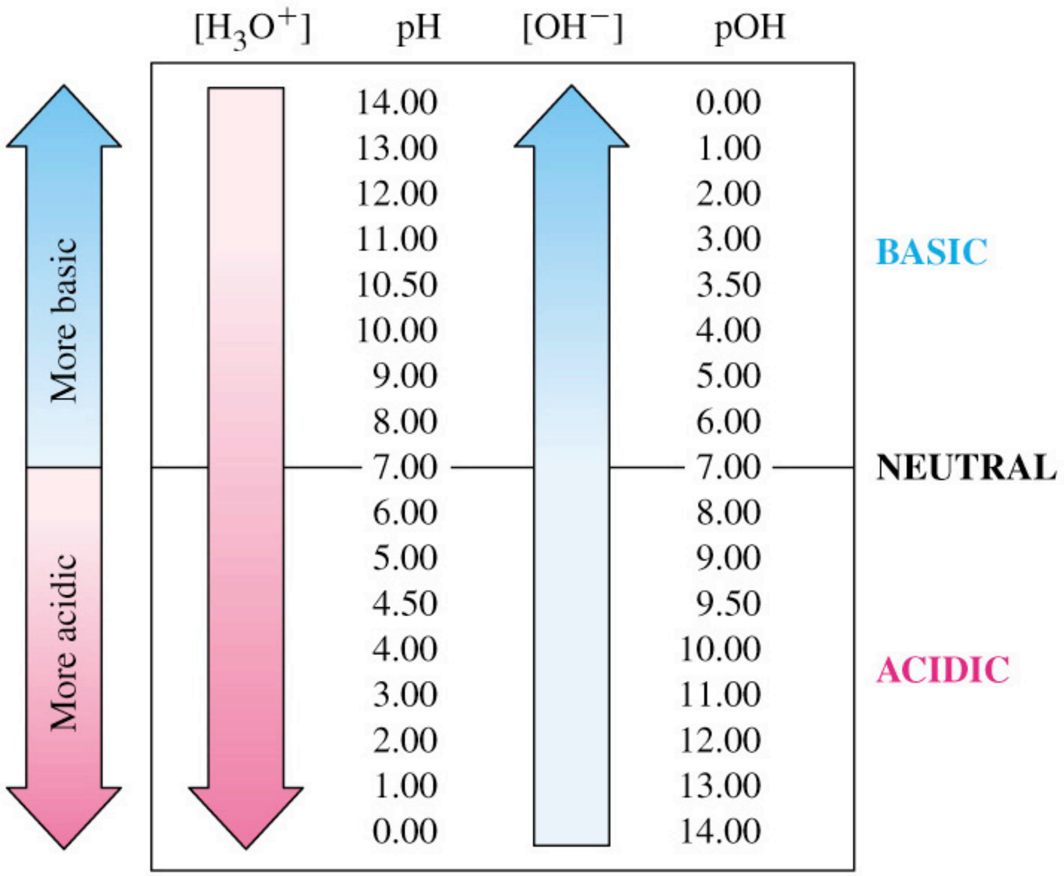
- pH is a shorthand way of stating the concentration of H_3O^+ and has no units

$$\boxed{pH = -\log[H_3O^+]}$$

neutral solution	$[H_3O^+] = [OH^-] = 10^{-7}$	$-\log(10^{-7})$	$pH = 7$
acidic solution	$[H_3O^+] > [OH^-]$	$-\log(>10^{-7})$	$pH < 7$
basic solution	$[H_3O^+] < [OH^-]$	$-\log(<10^{-7})$	$pH > 7$



pH and pOH Scales



$[H_3O^+]$	pH	$[OH^-]$	pOH
	14.00		0.00
	13.00		1.00
	12.00		2.00
	11.00		3.00
	10.50		3.50
	10.00		4.00
	9.00		5.00
	8.00		6.00
	7.00		7.00
	6.00		8.00
	5.00		9.00
	4.50		9.50
	4.00		10.00
	3.00		11.00
	2.00		12.00
	1.00		13.00
	0.00		14.00

household ammonia = pH 11.9

baking soda = pH 8.4

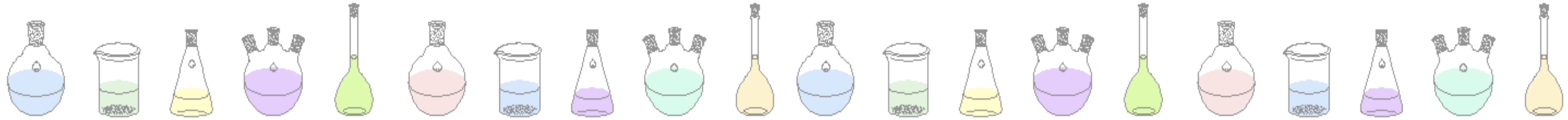
blood = pH 7.4

urine = pH 5 – 7

beer = pH 4 – 4.5

vinegar = pH 2.4 – 3.4

gastric juices = pH 1.0 – 2.0



Your Turn…

The pH values for solutions with H_3O^+ concentrations of $1.0x10^{-1}$, $1.0x10^{-4}$, and $1.0x10^{-9}$ are (no calculators):

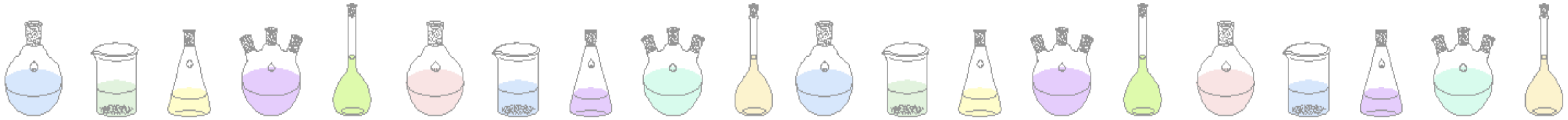
A. 14.0, 12.0, 9.0

B. 13.0, 9.0, 5.0

C. 13.00, 9.00, 5.00

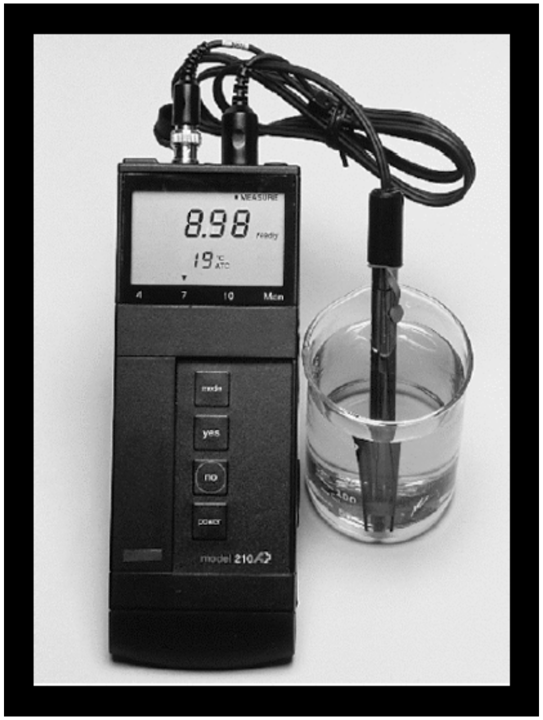
D. 1.00, 4.00, 9.00

E. 1.0, 4.0, 9.0



Your Turn Again…

Which of the following is closest to the concentration of H_3O^+ for the solution depicted to the right (pH=8.98)?



A. 10^{9} M

B. $10^{8.98}$ M

C. 10^{8} M

D. 10^{-8} M

E. 10^{-9} M

Acid-Base Conjugate Pairs

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

base **acid** **conj. acid** **conj. base**

For NH_3: $$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

What would be the K_a expression for the conjugate acid?

$$NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_3O^+\,(aq)$$

For NH_4^+: $$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Acid-Base Conjugate Pairs

Base

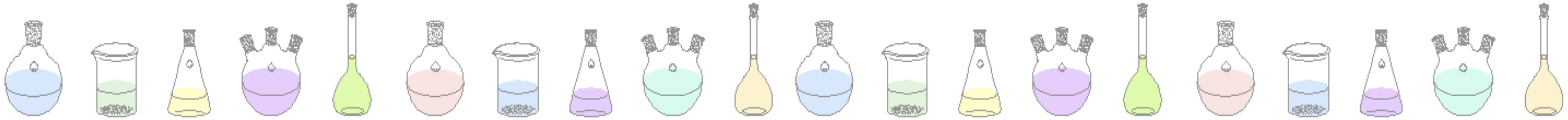
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Conjugate acid

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$K_a \times K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]}$$

for all acid-base conjugate pairs



Acid/base conjugate pairs

For all acid/base conjugate pairs in aqueous solutions:

$$K_a \times K_b = K_w$$

$$pK_a + pK_b = pK_w$$

where $pK_w = 14$ at 25°C

Therefore it's possible to find K_a if K_b is known or *vice versa*...)

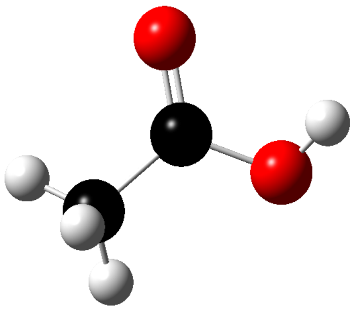
Your Turn…

Given the following reaction:

$$CH_3COOH(aq) + H_2O(l) \leftrightarrows CH_3COO^-(aq) + H_3O^+(aq) \qquad K_a = 1.8 \times 10^{-5}$$

What is the equilibrium constant for:

$$CH_3COO^-(aq) + H_2O(l) \leftrightarrows CH_3COOH(aq) + OH^-(aq)$$



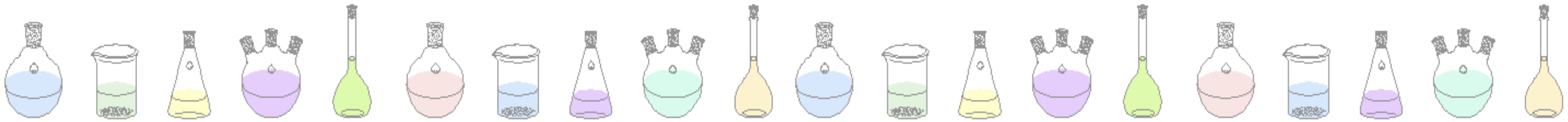
A. $-K_W$

B. $1/K_W$

C. K_W/K_a

D. $-K_a$

E. $1/K_a$

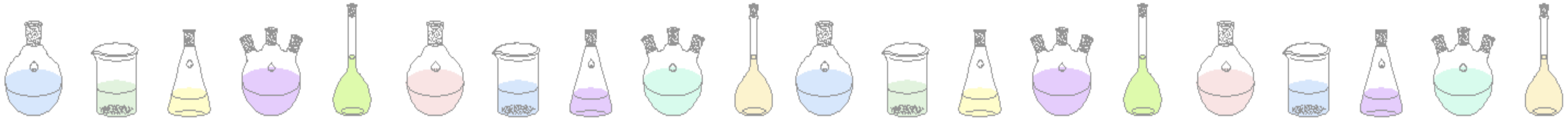


Solving Acid-Base Equilibrium Problems

- to perform equilibrium calculations, we must make the following assumptions:

1. the concentration of H^+ *before* the addition of acid or base (1.0×10^{-7} M) is negligible
2. the quantity of weak acid or base that dissociates is negligible (« x » is very small)

- once x (the quantity of dissociated acid or base) is found, we must verify that it is < 5% of the original concentration of added acid or base
  - if yes, then we may continue with our calculations
  - if no, we must solve the quadratic equation to find x

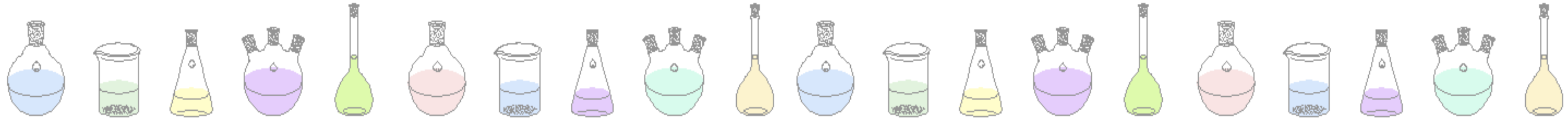


Solving Acid-Base Equilibrium Problems

1. List major species in solution.
2. Write equilibrium expression for dominant equilibrium.
3. List initial concentrations in dominant equilibrium.
4. Define change at equilibrium (as “x”).
5. Write equilibrium concentrations in terms of x.
6. Substitute equilibrium concentrations into equilibrium expression.
7. Solve for x using the assumption that “x is small”
8. Verify assumption.
9. Calculate $[H^+]$ and pH.

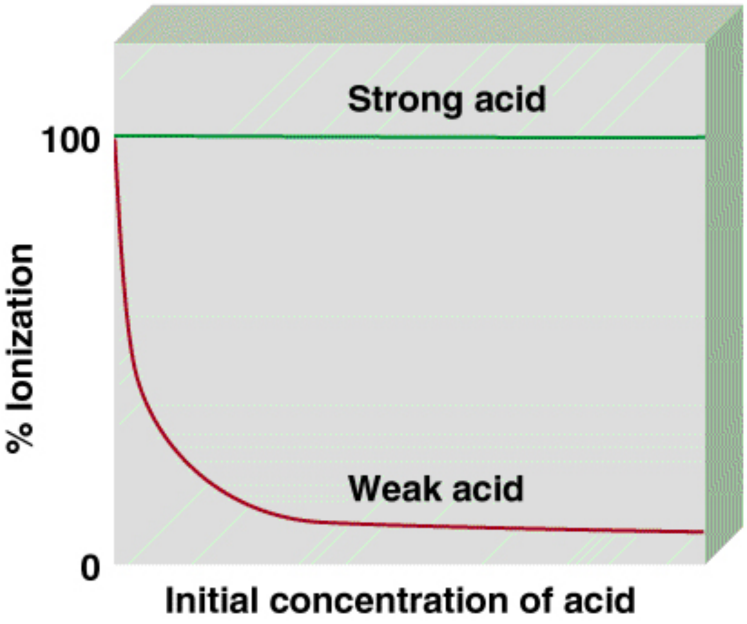
Example: a weak acid at equilibrium

A solution with a total volume of 250.0 mL is prepared by diluting 20.0 mL of glacial acetic acid with water (pure acetic acid, d = 1.05 g/mL). Calculate $[H^+]$ and pH. (K_a= 1.8 x 10^{-5})



Percent Ionization

$$HA(aq) \leftrightarrows H^{+}(aq) + A^{-}(aq)$$



- the percent ionization is defined as:

$$\%\ \text{ionization} = \frac{[A^{-}]\ \text{at equilibrium}}{[HA]\ \text{initial}} \times 100\%$$

- for a monoprotic acid:

$$\%\ \text{ionization} = \frac{[H^{+}]}{[HA]_o} \times 100\%$$

- where $[HA]_o$ is the initial concentration of acid
- note that the percent ionization decreases as the concentration increases

Example: Integrative Problem

15.0 g of formic acid (pKa = 3.75) are added to 100.0 g of pure water. What is the resulting pH of the solution and how much acid remains in its neutral form? You may assume the density of the solution is 1.00 g/mL.

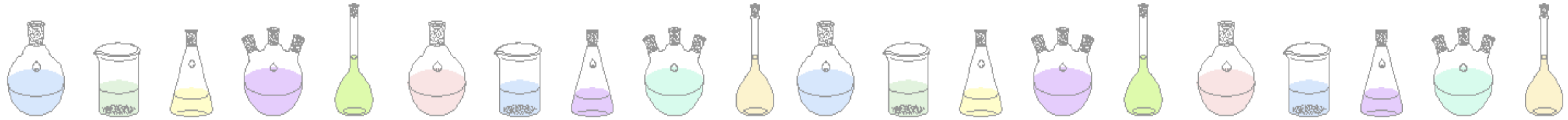
Polyprotic Acids

- Polyprotic acids can furnish more than one proton (H^+) to the solution:

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad K_{a1}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \qquad K_{a2}$$

- Some general features:
  - K_{a1} can be a strong or weak acid
  - subsequent K_{a2} will be relatively weak (i.e. $K_{a2} < K_{a1}$)
- Exact calculations for the resultant simultaneous equilibria can be complex
- In this course, we will ONLY consider examples where the equilibria can be considered sequentially



Polyprotic Acids

Phosphoric acid, H_3PO_3, is a triprotic acid:

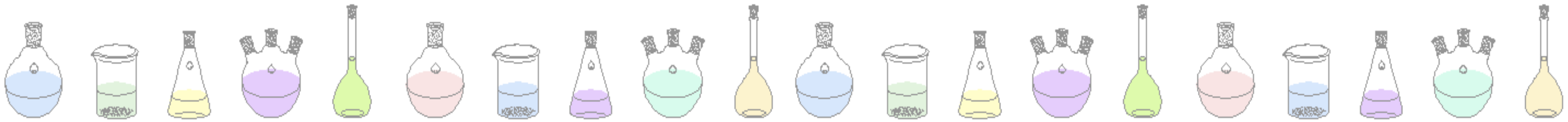
$$H_3PO_4 + H_2O \rightleftarrows H_3O^+ + H_2PO_4^- \qquad K_{a1} = 7.1\text{x}10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftarrows H_3O^+ + HPO_4^{2-} \qquad K_{a2} = 6.3\text{x}10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftarrows H_3O^+ + PO_4^{3-} \qquad K_{a3} = 4.2\text{x}10^{-13}$$

$$K_{a1} >> K_{a2} >> K_{a3}$$

i.e. most of the H_3O^+ is formed in the first ionization step!



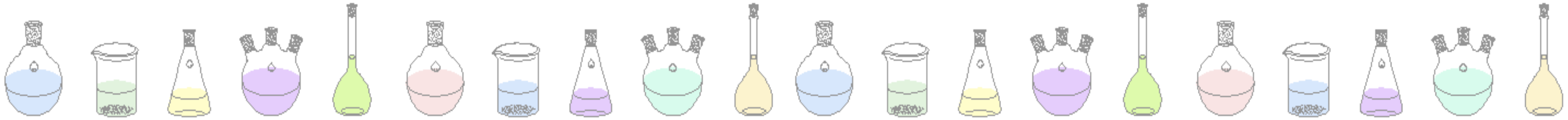
Example: A polyprotic acid

- Consider the dissociation of H_2SO_3 (sulfurous acid):

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \qquad K_{a1} = 1.2\text{x}10^{-2}$$

$$HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-} \qquad K_{a2} = 6.2\text{x}10^{-8}$$

- This acid provides <u>two</u> equivalents of protons per equivalent of acid.
- We can consider the first reaction to be **100% complete** before we consider the second reaction to occur at all.
- Let's look at this mathematically…



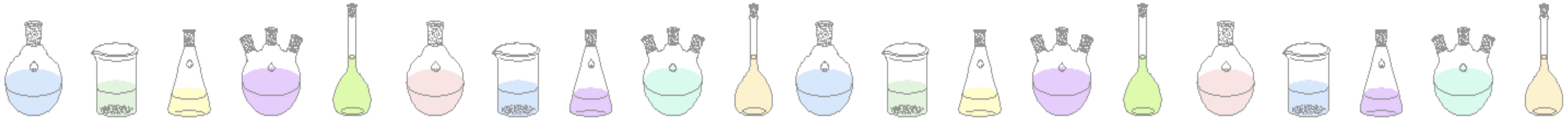
Example: A polyprotic acid at equilibrium

Calculate the pH of a 0.45 M solution of H_2SO_3.

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-}$$

$K_{a1} = 1.2\text{x}10^{-2}$

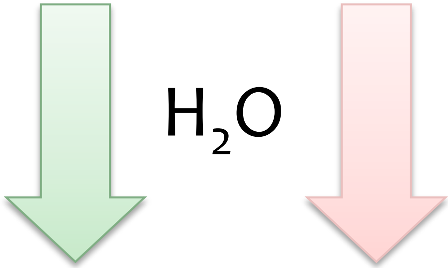
$K_{a2} = 6.2\text{x}10^{-8}$



Hydrolysis

- **hydrolysis:** the reaction between water and a compound causing cleavage of a bond
- in the case of ionic salt, the hydrolysis may produce a change in pH

$$XY\,(s) \rightarrow X^{+}(aq) + Y^{-}(aq)$$



H_2O

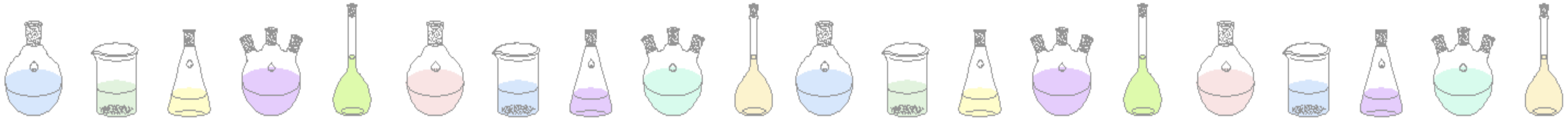
Hydrolysis Rules:

1. Salts of strong bases and strong acids (e.g. NaCl) do not hydrolyze; pH = 7.

2. Salts of strong bases and weak acids (e.g. $NaCH_3COO$) do hydrolyze; pH > 7 because the anion acts as a base.

3. Salts of weak bases and strong acids (e.g. NH_4Cl) do hydrolyze; pH < 7 because the cation acts as an acid.

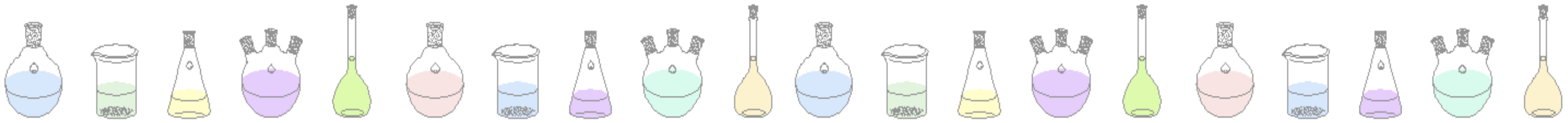
4. Salts of weak bases and weak acids (e.g. NH_4CH_3COO) do hydrolyze; pH will depend on the K_a and K_b of each.



Another way…

- Is the cation the conjugate acid of a weak base?

- Is the anion the conjugate base of a weak acid?



Acid-Base Properties of Salts

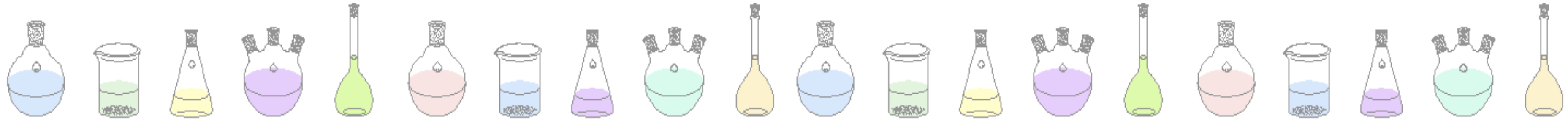
- Example 1: $NaNO_3$

$$NaNO_3\,(s) \rightarrow Na^+(aq) + NO_3^-(aq)$$

$$Na^+(aq) + H_2O \rightarrow \text{no reaction}$$

$$NO_3^-(aq) + H_2O \rightarrow \text{no reaction}$$

- the resulting ions do not react with water
- the pH of a solution of $NaNO_3$ is neutral



Acid-Base Properties of Salts

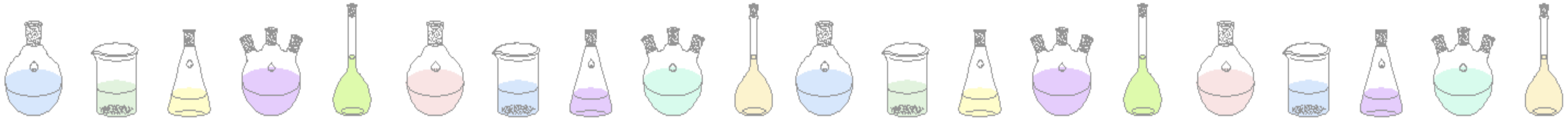
- Example 2: CH_3COONa

$$CH_3COONa\ (s) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$

$$Na^+(aq) + H_2O \rightarrow \text{no reaction}$$

$$CH_3COO^-(aq) + H_2O \rightarrow CH_3COOH(aq) + OH^-(aq)$$

- the anion hydrolyses in water
- the pH of a solution of CH_3COONa is basic



Acid-Base Properties of Salts

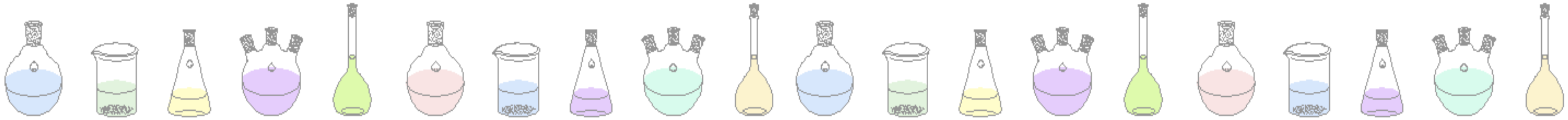
- Example 3: NH_4Cl

$$NH_4Cl\,(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

$$NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$$

$$Cl^-(aq) + H_2O \rightarrow \text{no rxn}$$

- the cation hydrolyses in water
- the pH of a solution of NH_4Cl is acidic



Acid-Base Properties of Salts

Cation	Anion	Acidic or Basic	Example
no rxn	no rxn	no change	NaCl
no rxn	conj base of weak acid	basic	NaF
conj acid of weak base	no rxn	acidic	NH_4Cl
conj acid of weak base	conj base of weak acid	depends on K_a & K_b values	$Al_2(SO_4)_3$

Your Turn…

$NaOCl\ (aq) \rightarrow Na^{+}(aq) + OCl^{-}\ (aq)$

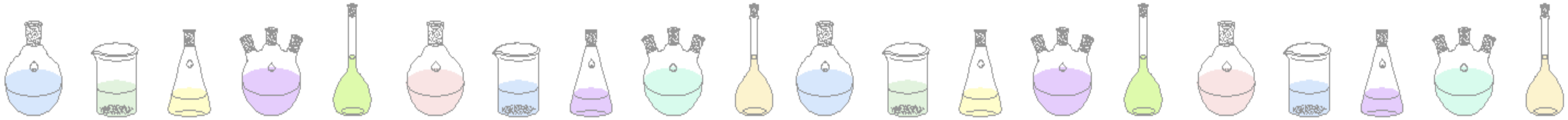
NaOCl is dissolved in water. The pH of the solution will be:

A. Acidic

B. Neutral

C. Basic

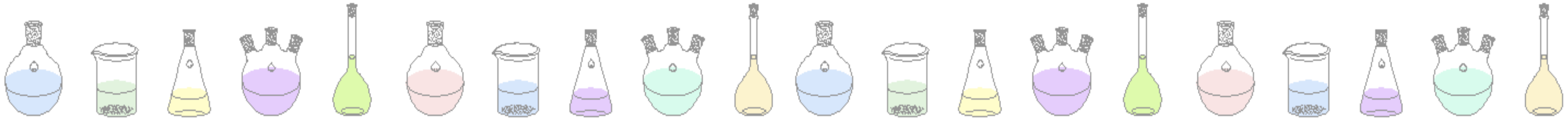
D. I'm not sure



Let’s do some more examples…

Example: a basic salt at equilibrium

Calculate the pH of a 0.10 M solution of Na_2CO_3.



Section 16.5, 16.7, and 16.8: Molecular Properties, the Levelling Effect, Lewis Acids and Bases

REVIEW THIS MATERIAL

ON YOUR OWN

(you'll need it for CHM1321!)

Chapter 16: Key Concepts

1. Arrhenius vs. Brønsted Theory
2. Conjugate Acid/Base Pairs
3. Self-ionization of Water and K_W
4. The pH and pOH Scales
5. Strong Acids and Bases
6. Weak Acids and Bases and K_a/K_b
7. Polyprotic Acids
8. Ions as Acids and Bases

Suggested Chapter 16 Questions

16.4, 16.8, 16.9, 16.11, 16.13, 16.17, 16.19, 16.21, 16.23, 16.29, 16.31, 16.35, 16.44, 16.49, 16.55, 16.58, 16.62, 16.69, 16.76, 16.80, 16.86, 16.102, 16.119, 16.121, 16.125, 16.146, 16.147, 16.151, 16.162, 16.164, 16.170, 16.176, 16.179, 16.182