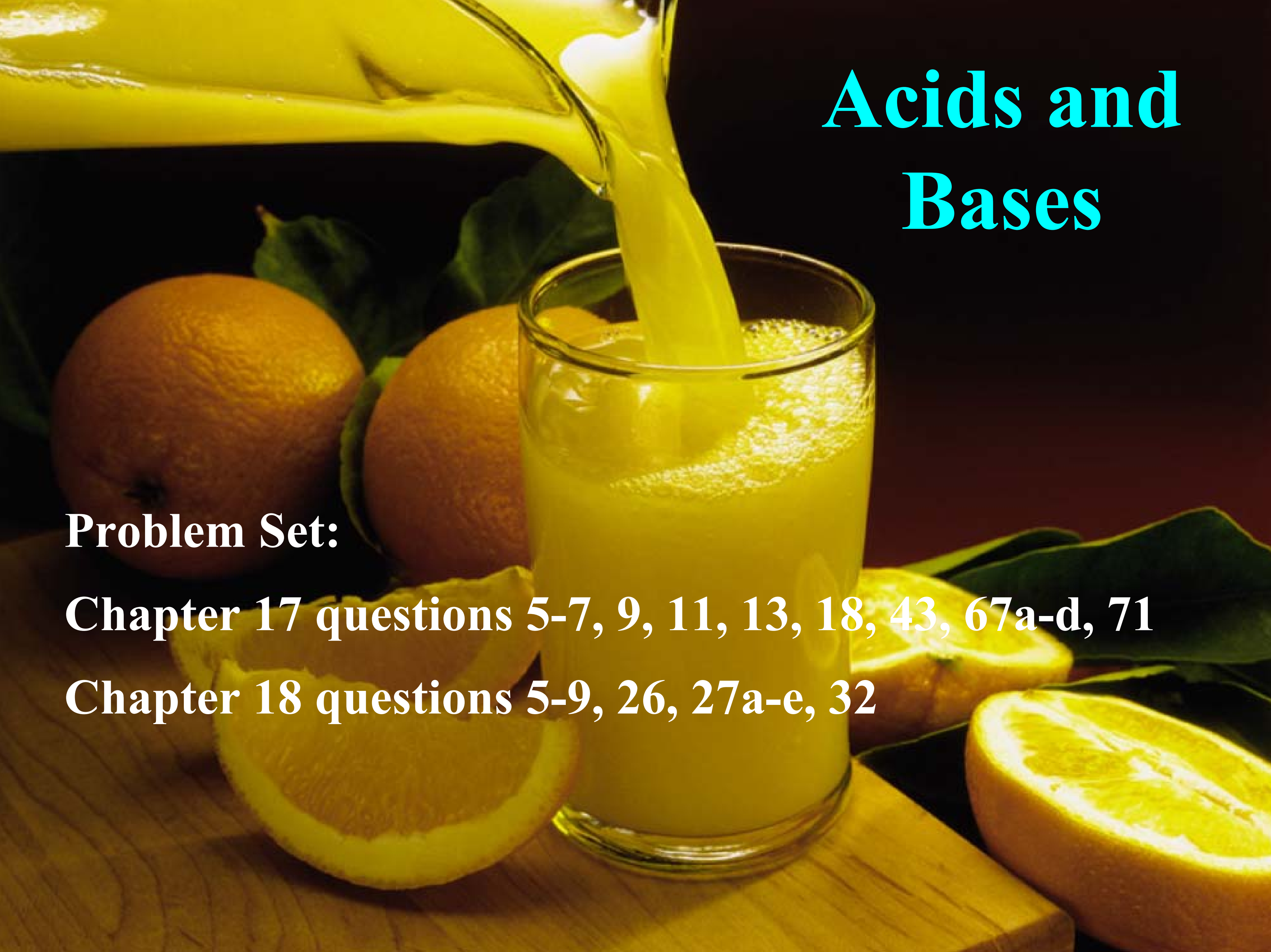


Acids and Bases

Problem Set:

Chapter 17 questions 5-7, 9, 11, 13, 18, 43, 67a-d, 71

Chapter 18 questions 5-9, 26, 27a-e, 32

Arrhenius Theory of Acids

- An acid base reaction involves the reaction of hydrogen ions; and hydroxide ions to form water. All bases contain OH^-. All acids contain H^+:

$$H^+_{(aq)} \quad + \quad OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

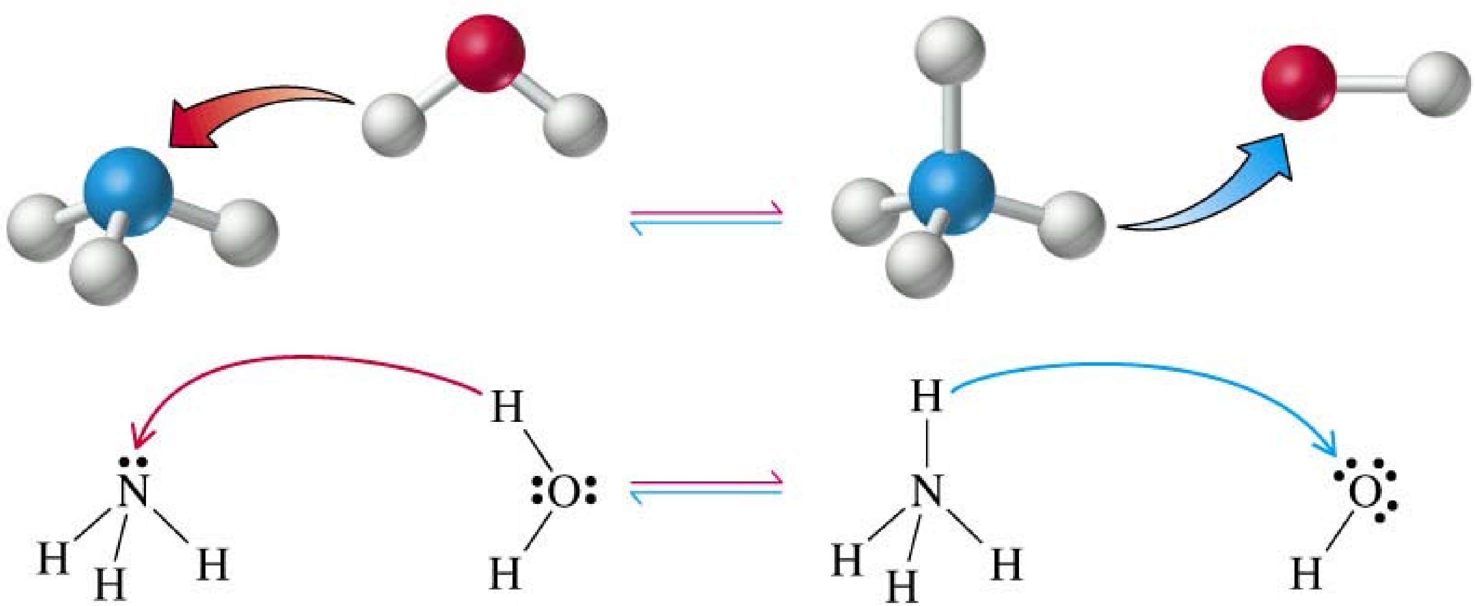
- The problem with this theory is that it requires that base have an OH^- group. Ammonia, NH_3, does not contain OH^-, but is nonetheless a base.

- Another problem of Arrhenius theory is in its not considering the role of the solvent, H_2O.

Bronsted-Lowry Theory

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

- **Both problems with the Arrhenius theory can be now taken care of. We now recognize that NH_3 acts as a base because of it's role as a hydrogen atom acceptor in the reaction. Moreover, we can include the solvent, H_2O in our consideration:**



$$\underset{\text{base(1)}}{NH_3} + \underset{\text{acid(2)}}{H_2O} \rightleftharpoons \underset{\text{acid(1)}}{NH_4^+} + \underset{\text{base(2)}}{OH^-}$$

Base Ionization Constant

• **For the previous reaction, we can write the following equilibrium expression, called the base ionization constant.**

• **Note that water does not explicitly appear in the equilibrium expression because the reaction is taking place in water (pure liquid)**

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

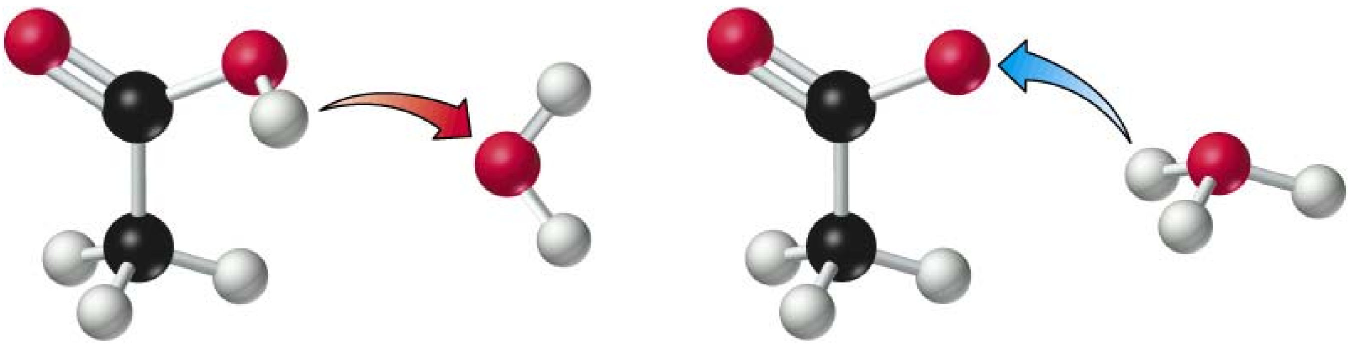
• **In the reaction, NH_3 acts as a base (proton acceptor) and H_2O acts as an acid (proton donator). The *conjugate acid* of NH_3 is NH_4^+. The *conjugate base* of water in the reaction is OH^-. We would refer to NH_4^+/NH_3 as a *conjugate acid/base pair.***

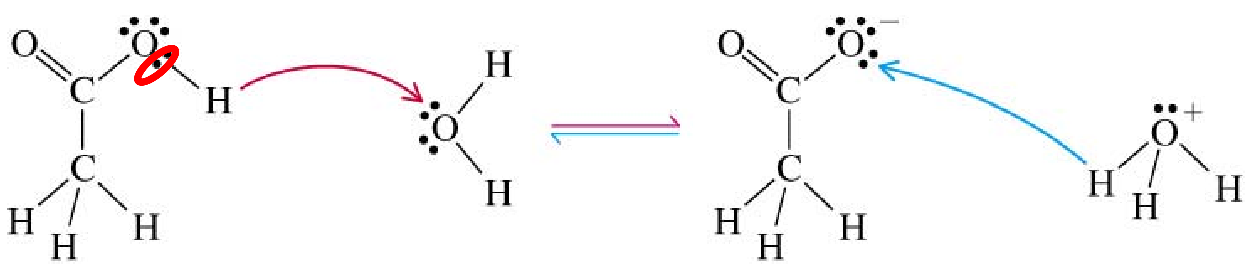
•**Note: The larger the value of K_b, the stronger the base. NH_3 is a weak base, that is there is a reasonable amount of unreacted NH_3**

A Weak Acid

- **Water can also act as base (proton acceptor), when it reacts with an acid such as acetic acid, to form the hydronium ion, H_3O^+**

- **Acetic acid gives up a proton to form the acetate ion. $CH_3CO_2H/CH_3CO_2^-$ form a conjugate acid base pair.**





Hydronium ion

$$\underset{\text{acid(1)}}{HC_2H_3O_2} + \underset{\text{base(2)}}{H_2O} \rightleftharpoons \underset{\text{base(1)}}{C_2H_3O_2^-} + \underset{\text{acid(2)}}{H_3O^+}$$

Acid Ionization Constants

• For the acid reaction we can write the acid ionization equilibrium constant , K_a

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

• The value of K_a is a measure of the strength of the acid in water. The larger the value of K_a, the further the equilibrium lies to the right, the stronger the acid.

•<u>Recall:</u> for a base, the larger the value of K_b, the stronger the base.

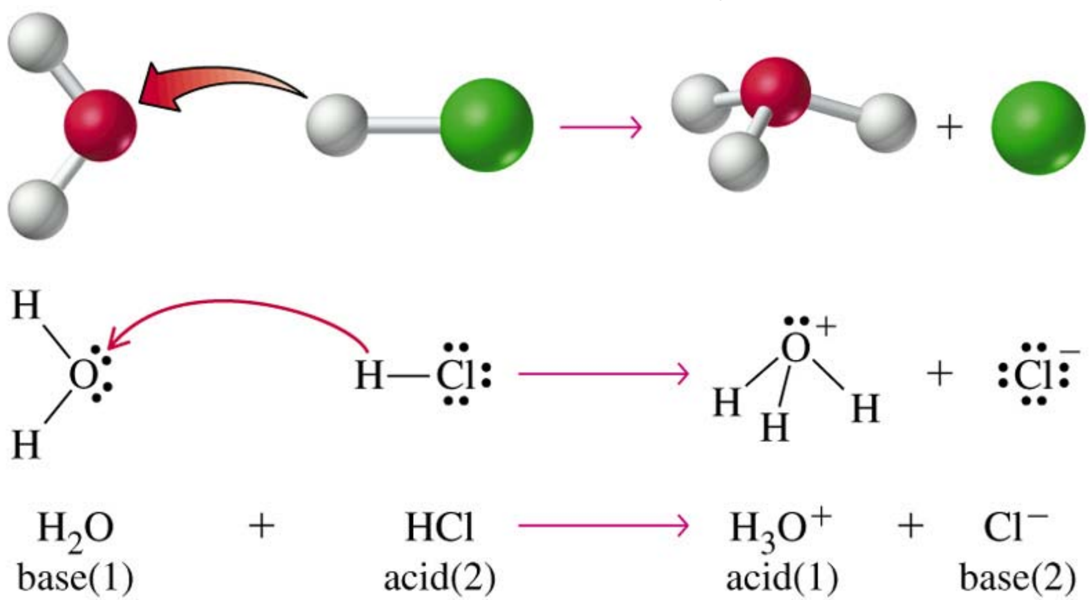
•Regardless of the value of K_a or K_b, if the acid or base ionization reaction does NOT go to completion, we call them ***weak acids*** and ***weak bases***

A Strong Acid

- Hydrochloric acid will react in the following way in water:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

- We write a single arrow for the reaction since the reaction is "complete". The K_a for the reaction is about 10^6. The large value of K_a implies that the equilibrium lies completely to the right. Because the acid dissociates completely, we call this a ***strong acid***.



Comparison of Extent of Ionization of Acetic Acid and HCl

- What does complete dissociation mean? To what extent does HCl dissociate in water, and how does this compare to a weak acid such as acetic acid. Let's calculate the fraction of the acid in the A^- form after the reaction:

$$HA_{(aq)} + H_2O_{(l)} \leftarrow \rightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

	HA	$\leftarrow\rightarrow$	H_3O^+	A^-
I_{nitial} (mol/L)	C_{HA}		0	0
C_{hange} (mol/L)	-x		+x	+x
$E_{quilibrium}$ (mol/L)	C_{HA}-x		+x	+x

C_{HA} is the initial *"formal"* concentration of the acid

Cont'd

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{x^2}{[C_{HA} - x]} \Rightarrow x^2 + K_a x - K_a C_{HA} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a C_{HA}}}{2}$$

$$\text{fraction of ionized acid} = \frac{[A^-]}{C_{HA}} = \frac{x}{C_{HA}}$$

	K_a	x	x/C_{HA}*100%
CH_3CO_2H C_{HA}= 0.01M	1.8 x 10^{-5}	4.15 x 10^{-4} M	4.15%
HCl C_{HA}= 0.01M	~ 1 x 10^{6}	9.99999999 x 10^{-3}M	99.9999999%

Relative Strength of Acids and Bases

Increasing acid strength

Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-
Hydroiodic acid	HI	Iodide ion	I^-
Hydrobromic acid	HBr	Bromide ion	Br^-
Hydrochloric acid	HCl	Chloride ion	Cl^-
Sulfuric acid	H_2SO_4	Hydrogen sulfate ion	HSO_4^-
Nitric acid	HNO_3	Nitrate ion	NO_3^-
Hydronium ion[a]	H_3O^+	Water[a]	H_2O
Hydrogen sulfate ion	HSO_4^-	Sulfate ion	SO_4^{2-}
Nitrous acid	HNO_2	Nitrite ion	NO_2^-
Acetic acid	$HC_2H_3O_2$	Acetate ion	$C_2H_3O_2^-$
Carbonic acid	H_2CO_3	Hydrogen carbonate ion	HCO_3^-
Ammonium ion	NH_4^+	Ammonia	NH_3
Hydrogen carbonate ion	HCO_3^-	Carbonate ion	CO_3^{2-}
Water	H_2O	Hydroxide ion	OH^-
Methanol	CH_3OH	Methoxide ion	CH_3O^-
Ammonia	NH_3	Amide ion	NH_2^-

Increasing base strength

- The stronger an acid, the weaker it's conjugate base
- e.g.: HCl dissociates completely in water. It's conjugate base, Cl^-, has virtually no tendency to take a proton from H_3O^+ (or H_2O).

Non-Aqueous Solvents

- **Note that $HClO_4$, HI, HBr, HCl, H_2SO_4 and HNO_3 are all strong acids. We cannot tell which acid is stronger because they all dissociate completely in water to yield H_3O^+**

- **Water is said to have a levelling effect on the acids…the strong acids all appear to have the same strength.**

- **To differentiate them, we need to use a solvent that is a weaker base then water (acetic acid or diethyl ether)**

$$HClO_4 + C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5 \longrightarrow ClO_4^- + [C_2H_5-\underset{\cdot\cdot}{\overset{\overset{\displaystyle H}{|}}{O}}-C_2H_5]^+$$

$$HCl + C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5 \rightleftharpoons Cl^- + [C_2H_5-\underset{\cdot\cdot}{\overset{\overset{\displaystyle H}{|}}{O}}-C_2H_5]^+$$

$HClO_4$ dissociates completely in diethylether. It is a stronger acid than HCl

What we learned so far:

- Acid is a proton donor, Base is a proton acceptor
- Acids and bases react with H_2O
- Strong acids and strong bases completely ionize when react with H_2O
- Weak acids and bases reach equilibrium with their conjugate bases and acids when react with H_2O:

1) $HA + H_2O \leftarrow \rightarrow A^- + H_3O^+$

Weak acid ionization constant: $$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

2) $B + H_2O \leftarrow \rightarrow BH^+ + OH^-$

Weak acid ionization constant: $$\mathbf{K_b = \frac{[BH^+][OH^-]}{[B]}}$$

Autoprotolysis of Water

- Electrical conductivity measurements indicate that even the purest water has a finite electrical conductivity.

- Electrical conduction in water requires the presence of ions.

- Finite conductivity remains due to the self ionization of water (autoprotolysis) which stems from it's amphiprotic nature (ability to act both as an acid and a base):

$$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

$K_w = [H_3O^+][OH^-] \sim 1.0 \times 10^{-14}$ (25 ^oC)

K_w is referred to as the ion product of water

Definition: $pK_w = -\log(K_w)$

Pure water

- What is the $[H_3O^+]$ in pure water at 25 °C (0 °C, 50 °C, 100 °C)?

$$2\,H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

55M –2x   x   x

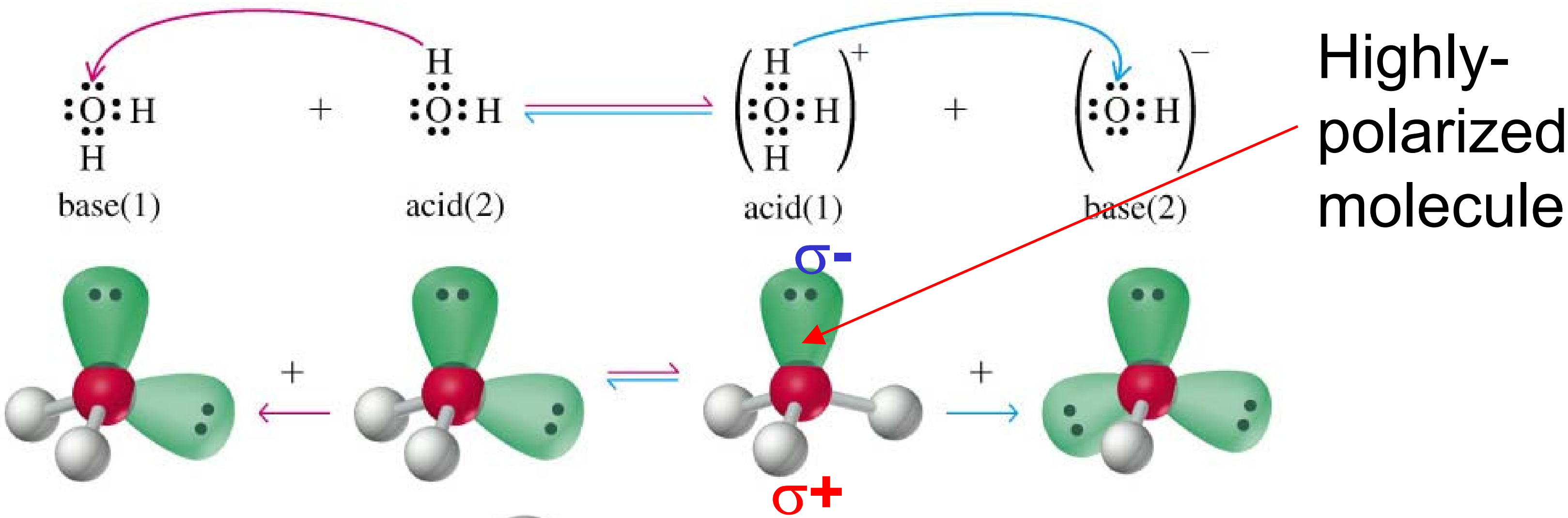
$[H_3O^+] = [OH^-] = x$

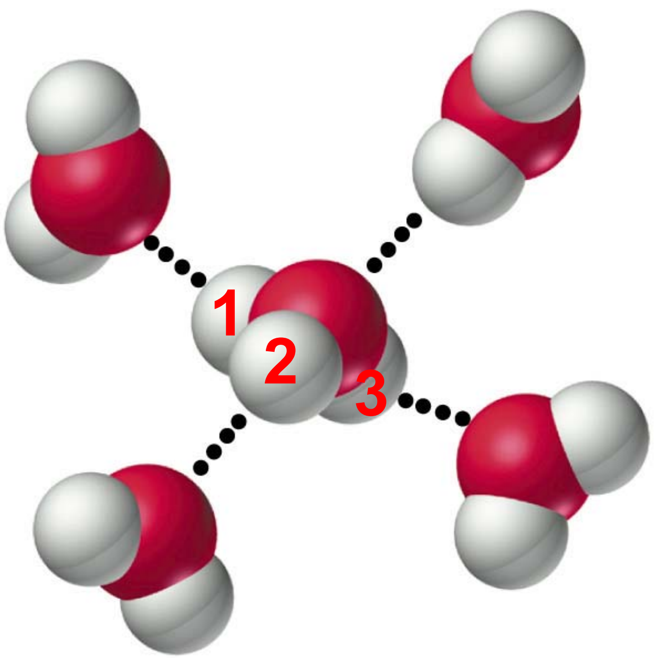
$K_w = [H_3O^+]\,[OH^-] = x^2$

$$x = [H_3O^+] = \sqrt{K_w}$$

T (°C)	K_w	$[H_3O^+] = [OH^-]$
0	0.11×10^{-14}	0.34×10^{-7}
25	1.01×10^{-14}	1.00×10^{-7}
50	5.47×10^{-14}	2.34×10^{-7}
100	49×10^{-14}	7.0×10^{-7}

Hydronium ion in solution





In solution, the hydronium ion is likely highly solvated. This figure shows a H_3O^+ surrounded by 4 water molecules, $H_{11}O_5^+$. Other hydrated species, such as $H_9O_4^+$ are also postulated to exist.

pH

Soren Sorenson defined pH back in 1909. The potential of hydrogen ion, or pH of a solution is defined to be:

pH = -log $[H^+]$ = -log$[H_3O^+]$ *(Strictly pH = -log a_{H3O+})*

pOH = -log $[OH^-]$ *(Strictly pOH = -log a_{OH})*

How are pH and pOH related?

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$-\log K_w = -\log [H_3O^+][OH^-] = -\log 10^{-14}$

$pK_w = -\log [H_3O^+] – \log [OH^-] = 14$

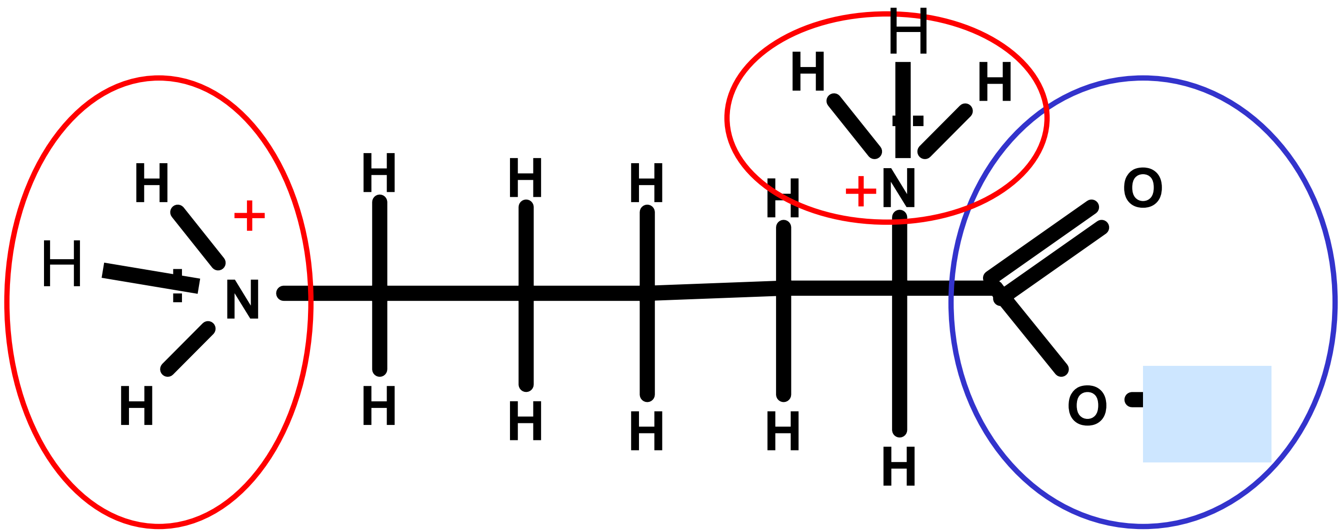
pH + pOH = 14

Note: pOH is not used practically! If you ever need to calculate it, then it is simply: pOH = 14 - pH

Why is pH so Important!

- 1. For reaction in aqueous solutions, reaction rates will typically depend on pH. For example, practically all enzymatic reactions have maximum value at optimal pH. This is important for for biological functioning.
- The electrical charge of most biological molecules will depend on pH due to pH influence on the ionization of weak bases and week acids which are components of those molecules.

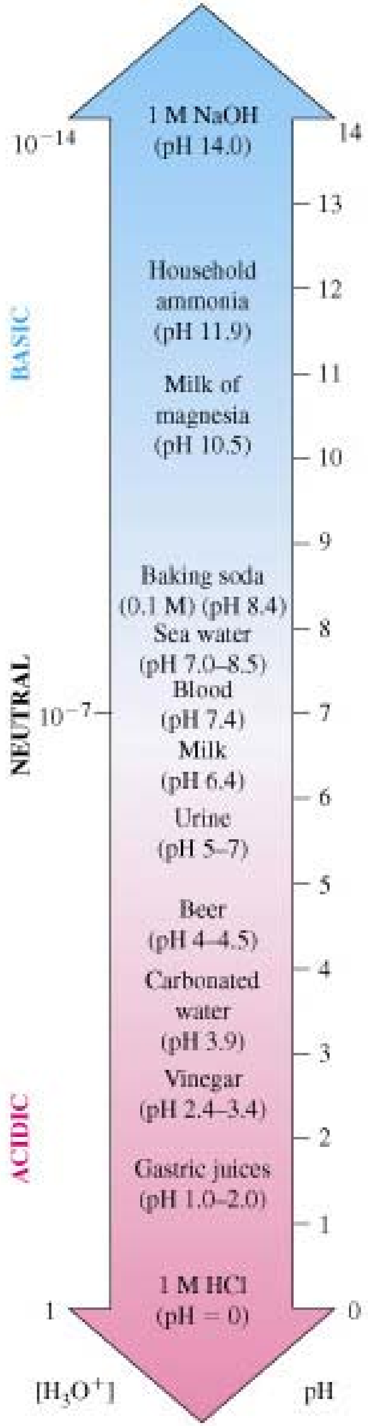
Three ionizable groups in an amino acid, e.g. lysine



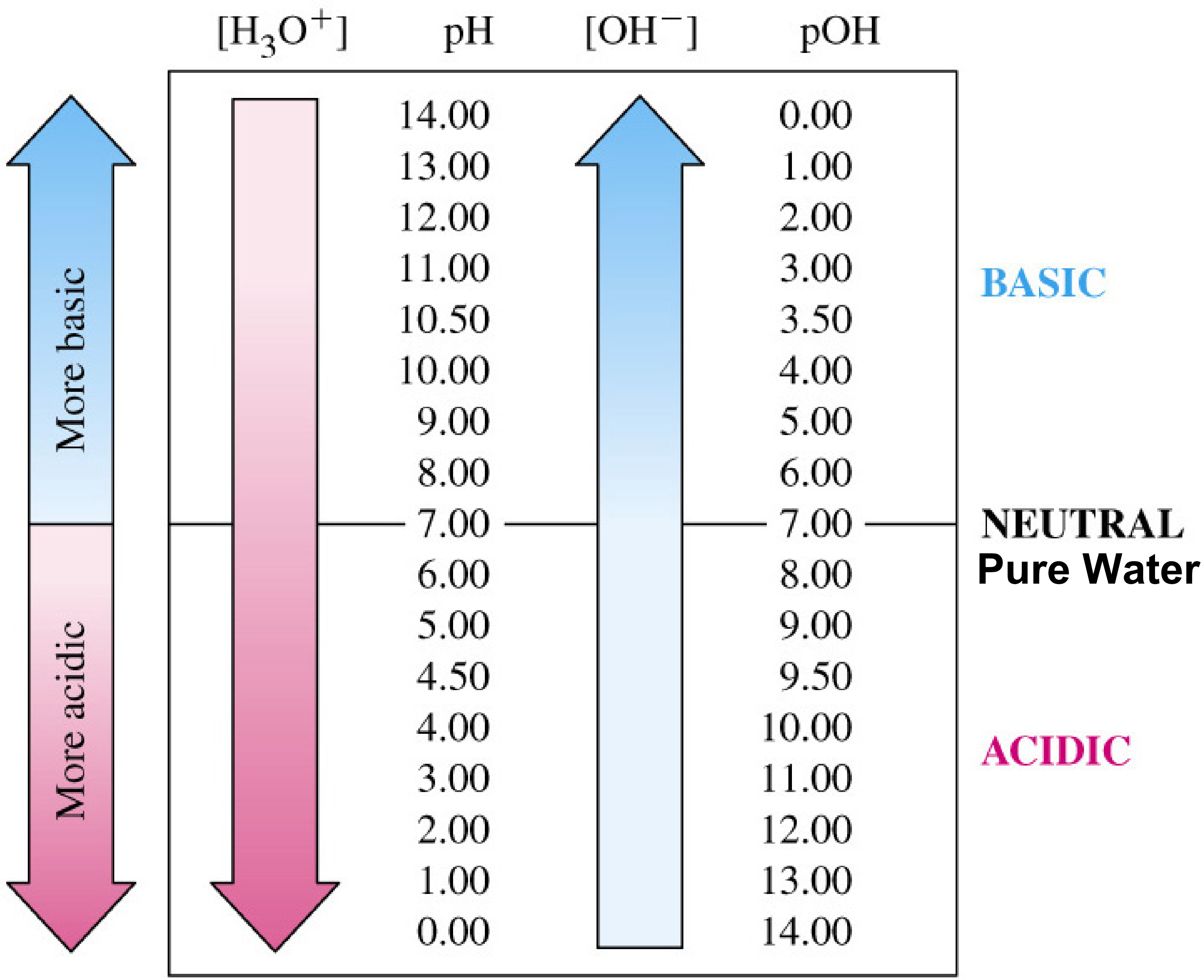
At pH < 9 amino groups are protonated and the molecule acquires +2 charge. At high pH > 3 the carboxyl group deprotonates and the molecule acquires –1 charge. Therefore,

1) for pH < 3 the charge is +2
2) for pH between 3 and 9 the charge is +1
3) for pH > 9 the charge is –1

pH Scale



1 M NaOH
(pH 14.0)
Household ammonia
(pH 11.9)
Milk of magnesia
(pH 10.5)
Baking soda (0.1 M) (pH 8.4)
Sea water
(pH 7.0–8.5)
Blood
(pH 7.4)
Milk
(pH 6.4)
Urine
(pH 5–7)
Beer
(pH 4–4.5)
Carbonated water
(pH 3.9)
Vinegar
(pH 2.4–3.4)
Gastric juices
(pH 1.0–2.0)
1 M HCl
(pH = 0)
BASIC
NEUTRAL
ACIDIC
10^{-14}
10^{-7}
1
$[H_3O^+]$
pH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0



More basic
More acidic
$[H_3O^+]$
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
BASIC
NEUTRAL
Pure Water
ACIDIC

pHs of Strong Acids and Bases

TABLE 17.2
The Common Strong Acids and Strong Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4[a]	$Mg(OH)_2$
	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

[a] H_2SO_4 ionizes in two distinct steps. It is a strong acid only in its first ionization (see page 687).

Strong acids and bases completely dissociate in water.

$$HNO_{3(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$$

$$Mg(OH)_2 \rightarrow Mg^{+2}_{(aq)} + 2\ OH^-_{(aq)}$$

Calculating the pH, pOH, or other quantities is usually trivial in such cases. There are exceptions in dilute solution

Calculations for Strong Acids & Bases using ICE table

What is the pH, pOH, $[H_3O^+]$, $[OH^-]$ and $[NO_3^-]$ for a 0.01 M solution of nitric acid?

	$HNO_{3(aq)}$	$\leftrightarrow$	H_3O^+	$NO_3^-{}_{(aq)}$
I (mol/L)	0.01		0	0
C (mol/L)	-0.01		0.01	0.01
E (mol/L)	0		0.01	0.01

$[H_3O^+] = 0.01M$; $[NO_3^-] = 0.01$, pH = -log 0.01 = $-\log 10^{-2}$ = 2.00

$[OH^-] = K_w/[H_3O^+] = 1 \times 10^{-14}/ 0.01 = 1 \times 10^{-12}$ M

pOH = 14 – pH = 14 - 2 = 12.0

Dilute Solutions

Q: What is the pH of a 0.001 M solution of HNO_3?

A: pH = -log [0.001] = 3.00

Q: What is the pH of a 1 x 10^{-5} M solution of HNO_3?

A: pH = -log [1 x 10^{-5}] = 5.0

Q: What is the pH of a 1 x 10^{-7} M solution of HNO_3?

A: pH = -log [1 x 10^{-7}] = 7.0?? Can this be correct?

Q: What is the pH of a 1 x 10^{-9} M solution of HNO_3?

A: pH = -log [1 x 10^{-9}] = 9.0 ?? ***Definitely incorrect!! A dilute solution of an acid CANNOT be basic. What's the problem?***

Solution to dilute acid problem

Problem: **we ignored the autoprotolysis of H_2O!!**

There are two sources of H_3O^+:

$$HNO_{3(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$$

$$2\,H_2O \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

The total charge should be zero

Information we can use to solve the problems is as follows:

For the 1st equation: $C_{HNO3} = [NO_3^-] = 1.0 \times 10^{-9}$ M

For the 2nd equation: $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (1)

Charge Balance Equation: ***for a neutral solution the number of moles of positive charge must be equal to the number of moles of negative charge.*** **In the current case:**

$[H_3O^+] = [NO_3^-] + [OH^-]$ (2)

Cont'd

***Mass Balance Equation:* there is usually a mass balance that can be written in equilibrium problems.** **In the current case, we could write:**

total $H_3O^+ = H_3O^+$ from nitric acid + H_3O^+ from dissociation of water.

The amount of H_3O^+ from nitric acid is equal to C_{HNO3} since HNO_3 dissociates completely

The amount of H_3O^+ from H_2O dissociation must be equal to $[OH^-]$, since water dissociates 1:1 (1 H^+ for each OH^-),

$$[H_3O^+] = C_{HNO3} + [OH^-] \qquad (3)$$

or $[H_3O^+] = [NO_3^-] + [OH^-]$

***Note:* that in this problem, the charge balance (2) and mass balance equations (3) are identical.**

Solution to problem

Substitute (1) into (3):

$$[H_3O^+] = C_{HNO3} + \frac{K_w}{[H_3O^+]}$$

From the definition: $K_w=[OH^-][H_3O^+]$

$$[H_3O^+]^2 - C_{HNO3}\,[H_3O^+] - K_w = 0$$

$$[H_3O^+] = \frac{C_{HNO3} + \sqrt{C_{HNO3}^2 + 4K_w}}{2}$$

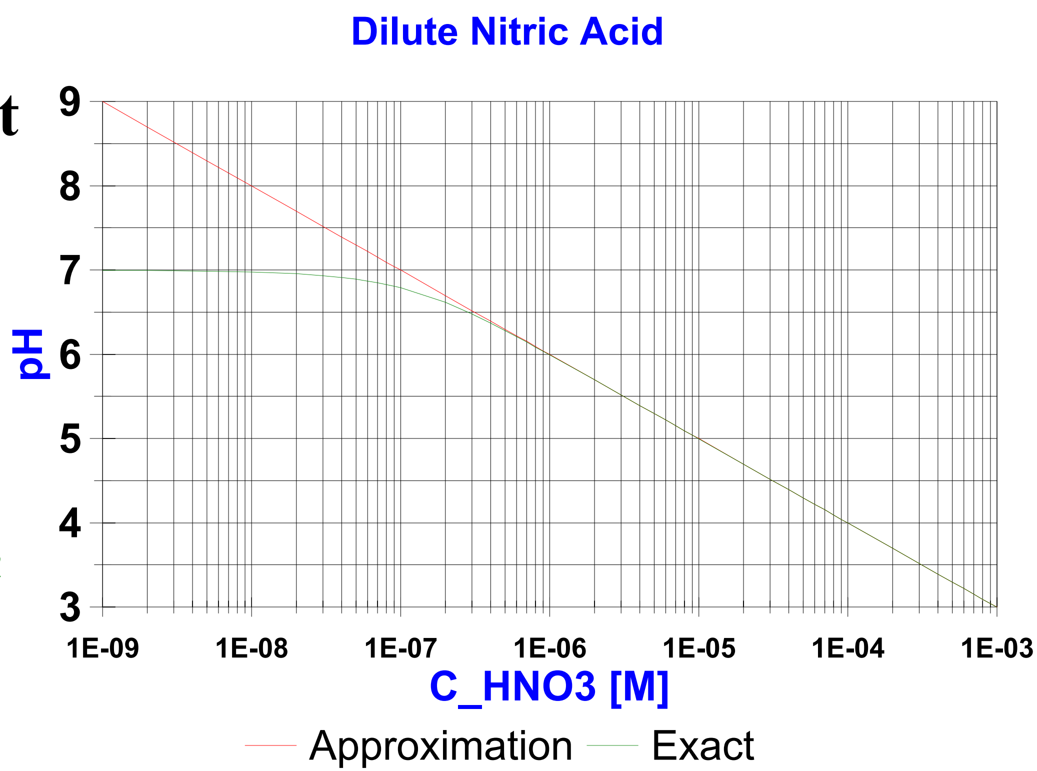
If $C_{HNO3} = 1 \times 10^{-9}$ M, we get

$[H_3O^+] = 1.01 \times 10^{-7}$M

pH = -log [1.01×10^{-7}M]

pH = 6.996

Exact solutions as a function of C_{HNO3} are shown on the following graph.



What we learned so far:

- Strong acids fully dissociate:

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

- pH of strong acids simply depends on their concentrations:

1. High concentration: $C_{HA} >> 2K_w^{1/2}$

$$pH \approx -\log C_{HA}$$

2. Low concentration: $C_{HA} \leq 2K_w^{1/2}$

$$\mathbf{pH} = -\log\left(\frac{\mathbf{C_{HA}} + \sqrt{\mathbf{C_{HA}^2} + \mathbf{4K_w}}}{\mathbf{2}}\right)$$

3. Very low concentration: $C_{HA} << 2K_w^{1/2}$

$$pH \approx -\log\sqrt{K_w}$$

Note: the equation for low concentrations is general and applicable to high concentrations as well

Formulas of Weak Acids

Example: *Chloroacetic acid*

Empirical Formula: $C_2H_3O_2Cl$

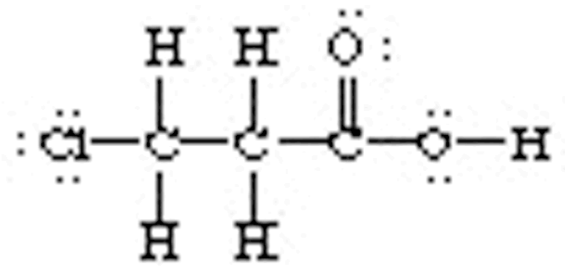
Molecular Formula: $C_2H_3O_2Cl$

Acid Formula: $HC_2H_2O_2Cl$

Carboxyl Group

Condensed Formula: $CH_2ClCOOH$ **or** CH_2ClCO_2H

Lewis Structure:



pK_a and pK_b

The following are general formulas for the K_a's and K_b's of monofunctional weak acids and weak bases

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \qquad K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$B + H_2O \rightleftarrows BH^+ + OH^- \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$pK_a = -\log K_a \qquad\qquad pK_b = -\log K_b$$

The stronger the weak acid, the larger its K_a, and thus the smaller its pK_a. Similar argument is valid for strength of bases: the stronger the weak basis, the larger its K_b, and thus the smaller its pK_b

pK_a = pH at which a half of HA is ionized ($[A^-] = [HA]$)

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = 1$$

$C_{HA} = [HA] + [A^-]$

- $K_a = [H_3O^+]$
- $pK_a = -\log K_a = -\log [H_3O^+] = pH$ by definition

Assignment: Define pK_b in a similar way

K_a's of Weak acids

TABLE 17.3 Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C

	Ionization Equilibrium	Ionization Constant K	pK
Acid		K_a =	pK_a =
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$HC_2H_2ClO_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2ClO_2^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$	1.8×10^{-4}	3.74
Benzoic acid	$HC_7H_5O_2 + H_2O \rightleftharpoons H_3O^+ + C_7H_5O_2^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$HOC_6H_5 + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		K_b =	pK_b =
Diethylamine	$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Acid strength

Base strength

Weak Acid/Weak Base Problems
fall in 3 categories

1. Calculate K_b or K_a for a solution of a known concentration if pH is measured

2. Calculate pH of a solution when the extent of dissociation is minimal

3. Calculate pH of a solution when the extent of dissociation is significant

Finding K_a

Hypochlorous acid, HOCl, is used as a disinfectant in pools and water treatment. A solution of HOCl of concentration C_{HA} (where $C_{HA} >> 2K_w^{1/2}$) has a known pH. *Find K_a*

Create an ICE table

$$HOCl + H_2O \rightleftarrows H_3O^+ + OCl^-$$

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

	HOCl	H_3O^+	OCl^-
Initial	C_{HA}	0	0
Change	-x	+ x	+ x
Equilib	C_{HA}-x	x	x

But, we should know $[H_3O^+]$ from pH

Cont'd

$pH = -\log [H_3O^+] \Rightarrow -pH = \log [H_3O^+] \Rightarrow [H_3O^+] = x = 10^{-pH}$

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{x^2}{C_{HA} - x} = \frac{10^{-2pH}}{C_{HA} - 10^{-pH}}$$

Solve solve the problem if pH = 4.18 for C_{HA} = 0.150 M

$$K_a = \frac{10^{-2\times 4.18}}{0.150 - 10^{-4.18}} = 2.91\times 10^{-8}$$

Finding pH of Weak Acid Solution

Boric acid, $B(OH)_3$, is used as a mild antiseptic. What is the pH of a an aqueous solution of boric acid of concentration C_{HA}? What is the degree of ionization of boric acid in this solution? Assume that K_a of boric acid is known and that water self-ionization is negligible.

Although it's molecular formula does not imply this to be an acid, the hydrogen ion arises principally from the reaction

Note: $B(OH)_3$ is an acceptor of OH^-, that is equivalent to donating H^+

$$B(OH)_3(aq) + 2H_2O \leftrightarrow B(OH)_4^- + H_3O^+ \qquad K_a$$

To solve, create ICE table again.

HBo is symbol for boric acid

Bo^- is the symbol for its conjugate base $B(OH)_4^-$.

Continued

	HBo $\rightleftarrows$	H_3O^+ +	Bo^-
Initial	C_{HA}	0	0
Change	-x	+x	+x
Equilibrium	C_{HA} - x	x	x

$$K_a = \frac{[H_3O^+][Bo^-]}{[HBo]} = \frac{x^2}{C_{HA}-x} \Rightarrow x^2 + K_a x - K_a C_{HA} = 0$$

Where $x=[H_3O^+]=[Bo^-]$

Solution: $x = \dfrac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$ $\quad pH = -\log x = -\log\left(\dfrac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}\right)$

The degree of ionization by definition is $[A^-]/C_{HA}$ $\Rightarrow$ $\dfrac{[A^-]}{C_{HA}} = \dfrac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2C_{HA}}$

Solve solve the problem for C_{HA} = 0.025 M and $K_a = 5.9 \times 10^{-10}$

$$\frac{x}{C_{HA}} = \frac{-5.9\times10^{-10} + \sqrt{5.9^2\times10^{-20} + 4\times5.9\times10^{-10}\times0.025}}{2\times0.025} = 1.5\times10^{-4}$$

Conditions for small degree of ionization

$$\frac{[A^-]}{C_{HA}} = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2C_{HA}}$$

If **K_a/C_{HA} << 1** ($K_a << C_{HA}$) then the degree of ionization is small. Indeed, if $K_a << C_{HA}$ then $K_a^2 << K_aC_{HA}$ and thus $K_a << (4K_aC_{HA})^{1/2}$. Then,

$$\frac{x}{C_{HA}} = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2C_{HA}} = \frac{\sqrt{4K_aC_{HA}}}{2C_{HA}} = \sqrt{K_a/C_{HA}} << 1$$

Important consequence: **K_a/C_{HA} << 1** then

$$x = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2} = \sqrt{K_aC_{HA}}, \quad \text{and } pH = -\log\left(\sqrt{K_aC_{HA}}\right)$$

Conditions for high degree of ionization

$$\frac{[A^-]}{C_{HA}} = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2C_{HA}}$$

If **K_a/C_{HA} >> 1** (C_{HA} << K_a) then the degree of ionization is high. Indeed, if K_a/C_{HA} << 1 then:

$$\text{degree of ionization} = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2C_{HA}} = \frac{-K_a + \sqrt{K_a^2 + K_a^2\frac{4K_aC_{HA}}{K_a^2}}}{2C_{HA}} = \frac{-K_a + K_a\sqrt{1+4\frac{C_{HA}}{K_a}}}{2C_{HA}} =$$

$$= \frac{-1+\sqrt{1+4\frac{C_{HA}}{K_a}}}{2\frac{C_{HA}}{K_a}} = \frac{-1+\sqrt{1+4x}}{2x}, \text{where } x = \frac{C_{HA}}{K_a}$$

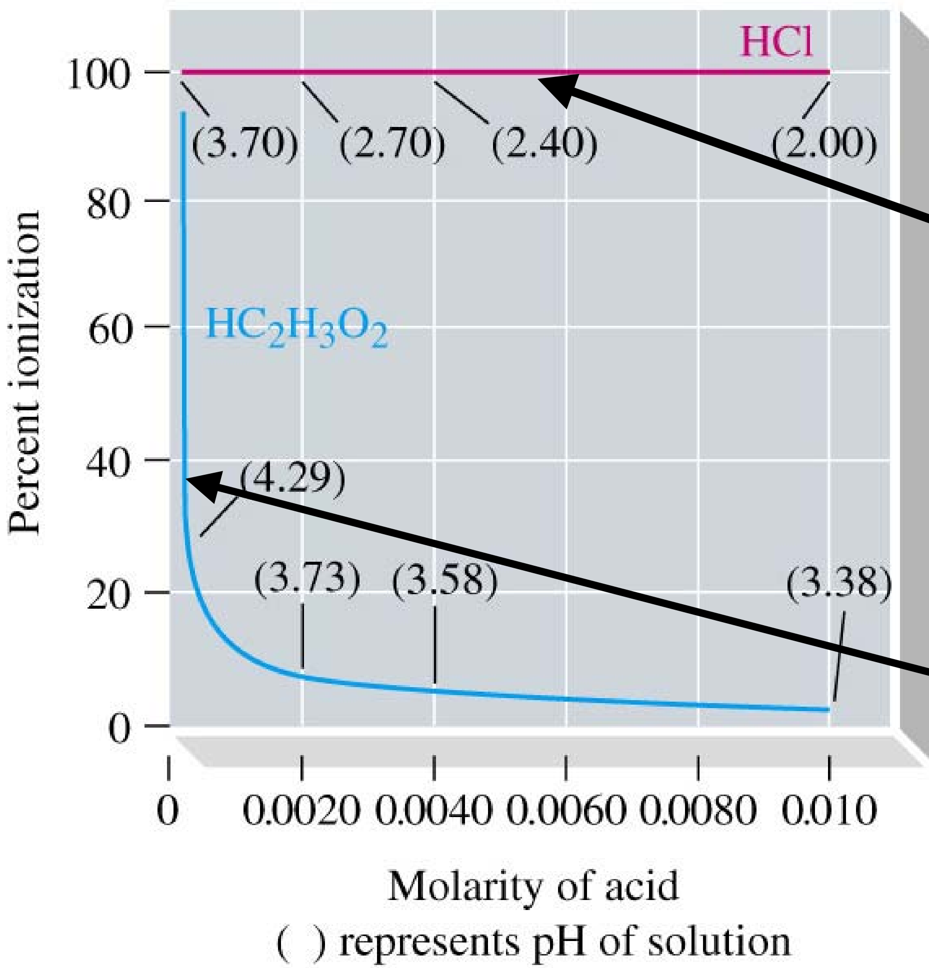
Degree of ionization for C_{HA} << K_a is equal to:

$$\lim_{x\to 0}\frac{-1+\sqrt{1+4x}}{2x} = \lim_{x\to 0}\frac{\sqrt{1+4x}-1}{2x} = \lim_{x\to 0}\frac{\sqrt{1+4x}-1}{2x}\times\frac{\sqrt{1+4x}+1}{\sqrt{1+4x}+1} = \lim_{x\to 0}\frac{\left(\sqrt{1+4x}\right)^2-1^2}{2x\left(\sqrt{1+4x}+1\right)} =$$

$$= \lim_{x\to 0}\frac{1+4x-1}{2x\left(\sqrt{1+4x}+1\right)} = \lim_{x\to 0}\frac{4x}{2x\left(\sqrt{1+4x}+1\right)} = \lim_{x\to 0}\frac{2}{\sqrt{1+4x}+1} = \frac{2}{\sqrt{1}+1} = 1$$

Thus, if C_{HA} << K_a, the degree of ionization is high

Example: Dependence of degree of ionization on C_{HA}



For a strong acid:
K_a is always >> C_{HA} (remember that Ka >> 1, but CHA ≤1)
Therefore, the degree of ionization is always high

For a weak acid K_a >> C_{HA} only at very low concentrations; it is when the degree of ionization may be high

Dissociation of Weak Bases

By analogy, create an ICE table for dissociation of a weak base, B.

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

	B		BH^+	OH^-
Initial	C_B		0	0
Change	-x		+x	+ x
Equilib	C_B- x		x	x

If K_b << [B]

$$[OH^-] = \sqrt{K_b C_B}$$

If K_b $\cancel{<<}$ [B]

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_b C_B}}{2}$$

Polyprotic Acids (and bases)

Acids (or bases) that generate more than one H^+ (OH^-) upon dissolving in aqueous solution typically undergo a series of acid/base equilibria. Consider H_3PO_4:

$$H_3PO_4 + H_20 \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a1} = 7.5 \times 10^{-3}$$
$$H_2PO_4^- + H_20 \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_{a2} = 6.2 \times 10^{-8}$$
$$HPO_4^{2-} + H_20 \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad K_{a3} = 4.8 \times 10^{-13}$$

Intermediate species can act as both an acid and a base. We say they are *amphiprotic*

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \qquad K_{b1} = 2.1 \times 10^{-2}$$
$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \qquad K_{b2} = 1.6 \times 10^{-7}$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \qquad K_{b3} = 1.3 \times 10^{-12}$$

<u>Note:</u> Ions react with water. Earlier we saw only neutral molecules reacting with newtral molecules and ions with ions

Calculating pH for Weak Polyprotic Acids

We can make several assumptions about ionisation of weak polyprotic acids:

1. Essentially all the H_3O^+ is produced in the first ionization step. The acid is weak, thus $K_{a1} << 1$. Thus the extent of ionization is low. Thus, $[H_2PO_4^-] << C_{H4PO4.}$ Thus, the amount of H3O produced in the 2nd and 3rd equilibria is small.

2. $[H_2PO_4^-] \approx [H_3O^+]$. Since $K_{a2} << 1$, then very little of $H_2PO_4^-$ is ionized (unless the concentration of $H_2PO_4^-$ is so low that the level of ionization becomes high).

3. $[HPO_4^{2-}] \approx K_{a2}$. This is the result of assumption 2

$$K_{a_2} = \frac{[HPO_4^{2-}]\cancel{[H_3O^+]}}{\cancel{[H_2PO_4^-]}} = [HPO_4^{2-}] \Rightarrow [HPO_4^{2-}] = K_{a2}$$

4. $[PO_4^{3-}] \approx K_{a2}\,K_{a3}/[H_3O^+]$. This is the result of

$$K_{a_3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} = \frac{[PO_4^{3-}][H_3O^+]}{K_{a2}} \Rightarrow [PO_4^{3-}] = \frac{K_{a2}K_{a_3}}{[H_3O^+]}$$

Calculating pH for Weak Polyprotic Acids Continued

Using the first assumption as conclude that pH of a weak polyprotic acid is determined by the first equilibrium:

$$pH = -\log[H_3O^+] = -\log \frac{-K_{a_1} + \sqrt{K_{a_1}^2 + 4K_{a_1}C_{H_nA}}}{2}$$

where H_nA is a general formula for a plyprotic acid with n protons

Note: the 3 assumptions allow to find not only pH but also the concentrations of all intermediates: $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}

Home assignment: Solve example 17-9 from the text

Other Polyprotic Acids

Acid	Ionization Equilibria	Ionization Constants, K	pK
Hydrosulfuric[a]	$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$	$K_{a_1} = 1.0 \times 10^{-7}$	$pK_{a_1} = 7.00$
	$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$	$K_{a_2} = 1 \times 10^{-19}$	$pK_{a_2} = 19.0$
Carbonic[b]	$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	$K_{a_1} = 4.4 \times 10^{-7}$	$pK_{a_1} = 6.36$
	$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$	$K_{a_2} = 4.7 \times 10^{-11}$	$pK_{a_2} = 10.33$
Phosphoric	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$	$K_{a_1} = 7.1 \times 10^{-3}$	$pK_{a_1} = 2.15$
	$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$	$K_{a_2} = 6.3 \times 10^{-8}$	$pK_{a_2} = 7.20$
	$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$	$K_{a_3} = 4.2 \times 10^{-13}$	$pK_{a_3} = 12.38$
Sulfurous[c]	$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$	$K_{a_1} = 1.3 \times 10^{-2}$	$pK_{a_1} = 1.89$
	$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$	$K_{a_2} = 6.2 \times 10^{-8}$	$pK_{a_2} = 7.21$
Sulfuric[d]	$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$	K_{a_1} = very large	$pK_{a_1} < 0$
	$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	$K_{a_2} = 1.1 \times 10^{-2}$	$pK_{a_2} = 1.96$

Acid strength

Home assignment: Solve example 17-10 from the text

Relationship Between pK_a of an Acid and pK_b of its Conjugate Base

$CH_3CO_2H_{(aq)}$ + $H_2O_{(l)}$ ←→ $H_3O^+_{(aq)}$ + $CH_3CO_2^-{}_{(aq)}$

acetic acid *acetate*

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

But let us also consider the hydrolysis reaction of acetate,

where acetate acts as a base:

$CH_3CO_2^-{}_{(aq)}$ + $H_2O_{(l)}$ ←→ $OH^-_{(aq)}$ + $CH_3CO_2H_{(aq)}$

acetate *acetic acid*

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} = 5.6\times 10^{-10}$$

$$K_aK_b = \frac{\cancel{[CH_3CO_2^-]}[H_3O^+]}{\cancel{[CH_3CO_2H]}} \times \frac{\cancel{[CH_3CO_2H]}[OH^-]}{\cancel{[CH_3CO_2^-]}}$$

$$K_aK_b = [H_3O^+] \times [OH^-]$$

$$K_aK_b = K_w$$

$$pK_a + pK_b = pK_w \qquad \text{OR} \qquad pK_a + pK_b = 14 \text{ at } 25\ ^\circ\text{C}$$

This is a general result, the K_a of an acid and the K_b of it's conjugate base are related. From this we can write three equivalent statements…

The higher the K_a of an acid, the lower the K_b of its conjugate base.

The lower the pK_a of an acid, the higher the pK_b of its conjugate base.

The stronger an acid is, the weaker is it's conjugate base!

Salts

Solutions of salts are very common in chemistry, biological systems, environmental matrices, etc. We can now predict in a qualitative sense (and in some cases quantitatively) the pH of solutions of acids, bases and salts.

Salts of strong acids/strong bases

Example – **solution of $MgBr_2$, salt of strong acid + strong base**

$2HBr_{(aq)} + Mg(OH)_{2\,(aq)} \rightarrow 2\,H_2O_{(l)} + MgBr_{2\,(aq)}$ *formation*

$MgBr_{2\,(aq)} \rightarrow Mg^{2+}_{(aq)} + 2\,Br^{-}_{(aq)}$ *dissolution*

Weak conjugate acid of strong base → $Mg^{+2}_{(aq)} + \cancel{H_2O} \rightarrow$ No *reaction*

Weak conjugate base of strong acid → $Br^{-}_{(aq)} + \cancel{H_2O} \rightarrow$ No *reaction*

Weak conjugate acid and base do not hydrolyze (do not react with water) $\Rightarrow$ pH = 7

Salt of Strong Acid/Weak Base

Salts of strong acids/weak bases

Example **– aqueous solution of NH_4NO_3,**

which is salt of strong acid (HNO_3) and weak base (NH_3):

$HNO_{3(aq)} + NH_{3\,(aq)} \rightarrow NH_4NO_{3\,(aq)}$ ***formation***

$NH_4NO_{3\,(aq)} \rightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$ ***dissolution***

Weak conjugate base of strong acid

$NO_3^-{}_{(aq)} + H_2\cancel{O} \rightarrow$ **No** ***reaction***

Strong conjugate acid of weak base

$NH_4^+{}_{(aq)} + H_2O \rightarrow H_3O^+{}_{(aq)} + NH_{3\,(aq)}$ ***reaction!***

Conjugate acid of the weak base is strong thus it will hydrolyze $\Rightarrow$ pH < 7

Salt of Weak Acid/Strong Base

Salts of weak acids/strong bases

Example **– solution of NaF, salt of weak acid + strong base**

$$NaOH_{(aq)} + HF_{(aq)} \rightarrow H_2O_{(l)} + NaF_{(aq)}$$ *formation*

$$NaF \rightarrow Na^+_{(aq)} + F^-_{(aq)}$$ *dissolution*

Weak conjugate acid of strong base

$$Na^+_{(aq)} + H_2O \cancel{\rightarrow}$$ No *reaction*

Strong conjugate base of weak acid

$$F^-_{(aq)} + H_2O \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$ *reaction!*

Conjugate base of the weak acid is strong, it will hydrolyze $\Rightarrow$ pH > 7

Salt of Weak Acid/Weak Base

Salts of weak acids/weak bases

-conjugate base of the weak acid will hydrolyze, as will the conjugate acid of the weak base. One must look at the pK_a and pK_b to predict the pH of solution.

Example **– solution of $C_2H_5NH_3C_7H_5O_2$,(ethylammonium benzoate), salt of weak acid + weak base**

$C_7H_5O_2H_{(aq)} + C_2H_5NH_{2\,(aq)} \rightarrow C_2H_5NH_3C_7H_5O_{2\,(aq)}$ *formation*

$C_2H_5NH_3C_7H_5O_{2\,(aq)} \rightarrow C_2H_5NH_3^+{}_{(aq)} + C_7H_5O_2^-{}_{(aq)}$ *dissolution*

Strong conjugate acid of weak base

$C_2H_5NH_3^+{}_{(aq)} + H_2O \rightarrow H_3O^+{}_{(aq)} + C_2H_5NH_{2\,(aq)}$ *reaction!*

$C_7H_5O_2^-{}_{(aq)} + H_2O \rightleftarrows C_7H_5O_2H_{(aq)} + OH^-{}_{(aq)}$ *reaction!*

Strong conjugate base of weak acid

How do we predict which wins out in this competition?

Conjugate Acid/Base competition

pK_a of $C_7H_5O_2H$ = 4.20; pK_b of $C_7H_5O_2^-$ = 14 – 4.20 = 9.8

pK_b of $C_2H_5NH_2$ = 3.37; pK_a of $C_2H_5NH_3^+$= 14 – 3.37 = 10.6

Since the pK_b of the basic part of the salt (i.e. benzoate) is lower than the pK_a of the acidic part of the salt (ethylammonium), benzoate's base strength is stronger than ethylammonium's acid strength. The base should win out and we predict the final solution will be basic, pH>7.

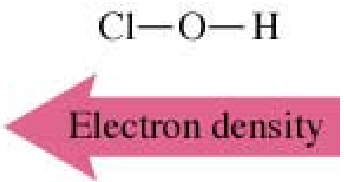
(Another way to look at this is to compare the pK_a and pK_b of the acid and base that form the salt. Since ethylamine is a stronger base than benzoic acid is an acid, then the conjugate base wins the conjugate acid and the resultant solution of the salt must be basic.)

Acid-Base Properties of Salts
Summary

Cation	Anion	Acidic or Basic	Example
neutral	neutral	neutral	$NaCl$
neutral	conj base of weak acid	basic	NaF
conj acid of weak base	neutral	acidic	NH_4Cl
conj acid of weak base	conj base of weak acid	depends on K_a & K_b values	$Al_2(SO_4)_3$

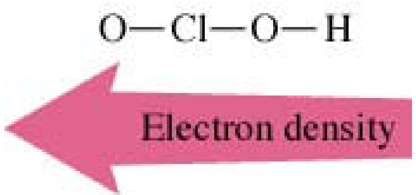
How Does Acidity & Basicity Depend on Structure?

Structure related acidity



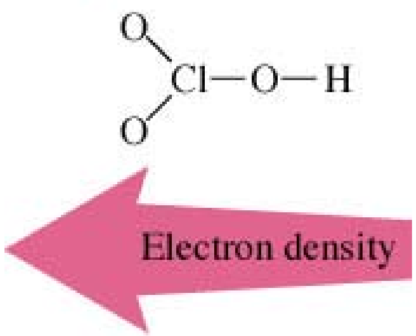
$K_a = 2.9\text{x}10^{-8}$

Hypochlorous acid



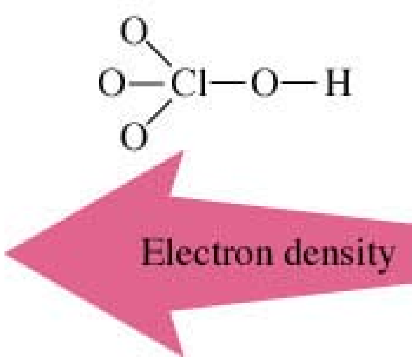
$K_a = 1.1\text{x}10^{-2}$

Chlorous acid



K_a = strong?

Chloric acid

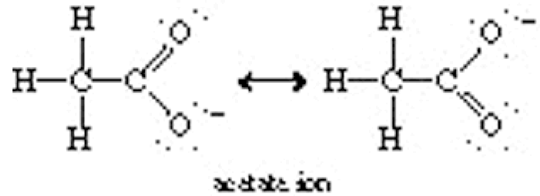


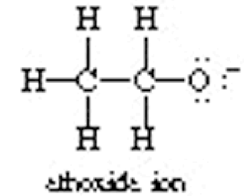
K_a = strong!

Perchloric acid

Very strong oxidizing

Agent, explosive!





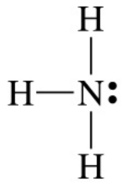
Acetic acid	ethanol
K_a=1.8 x 10^{-5}	K_a=1.3 x 10^{-16}

Acidity is not only related to structure of acid (energy of OH bond), but also to the stability of anion product.

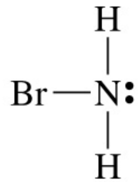
Resonance in acetate ion stabilizes this structure…weak acid.

For ethoxide ion (other alcohols are similar), the charge is localized on –O^-, it behaves as relatively strong base. Ethanol is therefore a very weak acid.

Structure Related Basicity of Amines



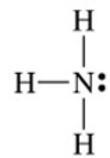
Ammonia, $pK_b = 4.74$



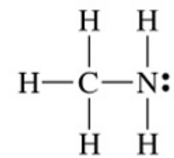
Bromamine, NH_2Br, $pK_b = 7.61$

Lone pair electrons on N are responsible for base behaviour of amines, by binding to H^+. Electronegative groups attached to N lower electron density, reducing strength of base.

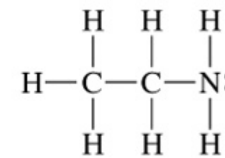
Hydrocarbon attachments have little electron with-drawing ability. Alkyl amines are stronger base than NH_3.



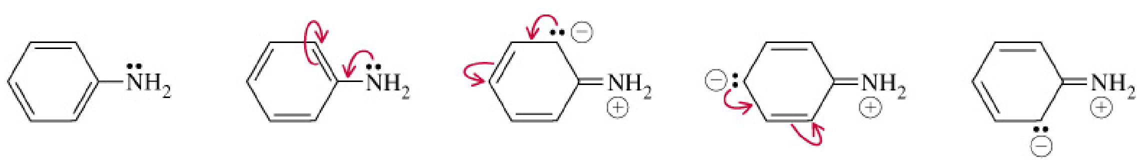
Ammonia
$pK_b = 4.74$



Methylamine
CH_3NH_2, $pK_b = 3.38$

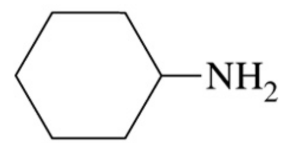


Ethylamine
$CH_3CH_2NH_2$, $pK_b = 3.37$

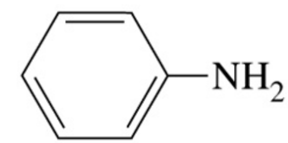


Aromatic amines have additional electron withdrawing effects due to delocalization on aromatic ring.

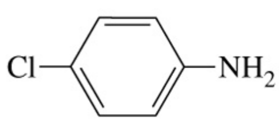
The effect is illustrated when comparing base strength of cyclohexylamine (non-aromatic) and aniline (aromatic).



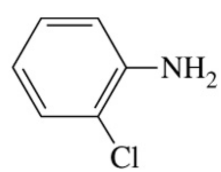
Cyclohexylamine, $pK_b = 3.36$



Aniline, $pK_b = 9.13$



para-Chloroaniline, $pK_b = 10.01$



ortho-Chloroaniline, $pK_b = 11.36$

An additional illustration of the effect of an electron withdrawing group on base strength of an aromatic amine.

Lewis Acids & Bases

	Bronsted-Lowry
Lewis Acid: electron pair acceptor	**(proton donor)**
Lewis Base: electron pair donor	**(proton acceptor)**

To identify Lewis acids, look for species (ions, atoms, etc…) that have valence shells that can accept electron pairs.

Example: H^+ **Lewis acid**

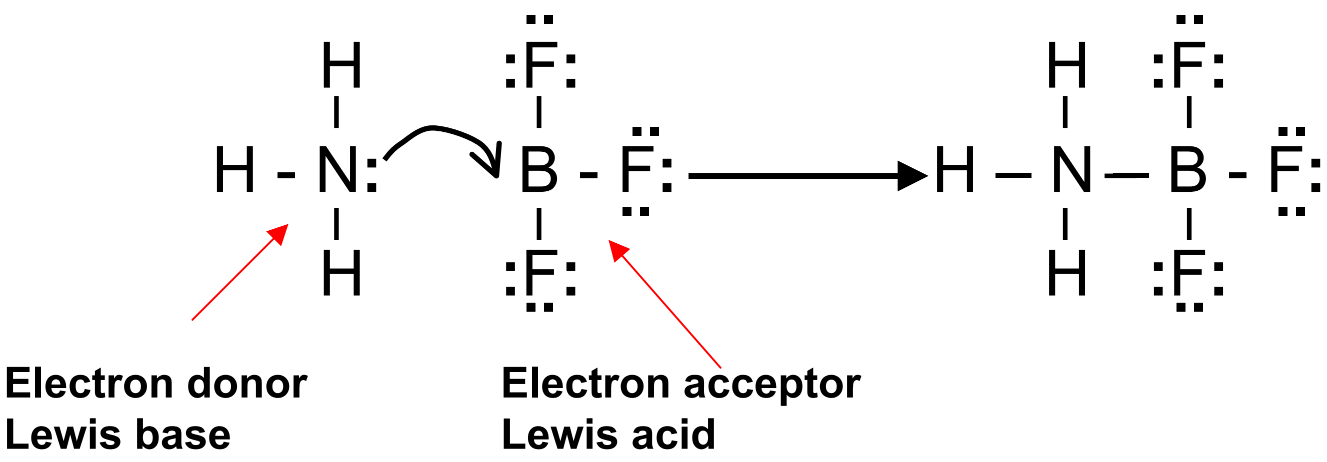
To identify Lewis bases, look for species that have lone pair electrons that can be "donated" to form a covalent bond.

Examples: $:NH_3$ $:\ddot{\underset{..}{O}}H^-$ **Lewis bases**

Identifying Lewis Acids and Bases in Chemical Reactions

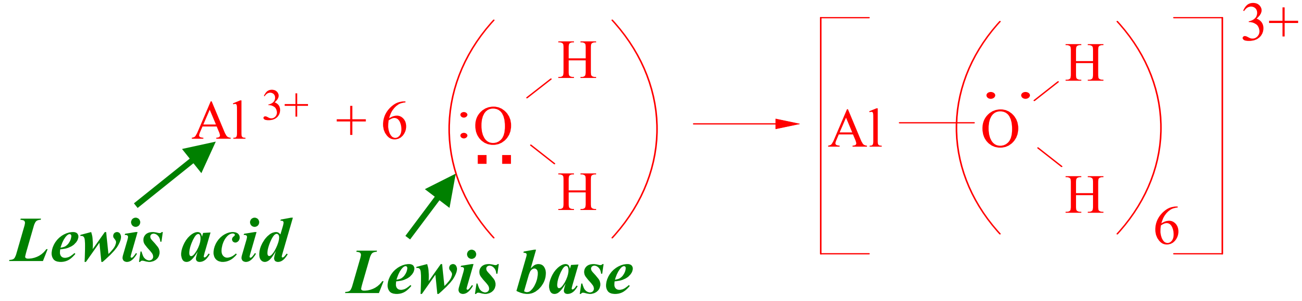
1. Draw the Lewis structures of the reacting molecules
2. Decide on the direction of electrons moving between the molecules
3. The molecule that accepts electron(s) is a Lewis acid, the molecule that donates electron(s) is a Lewis base

Example: $NH_3 + BF_3 \rightarrow NH_3BF_3$

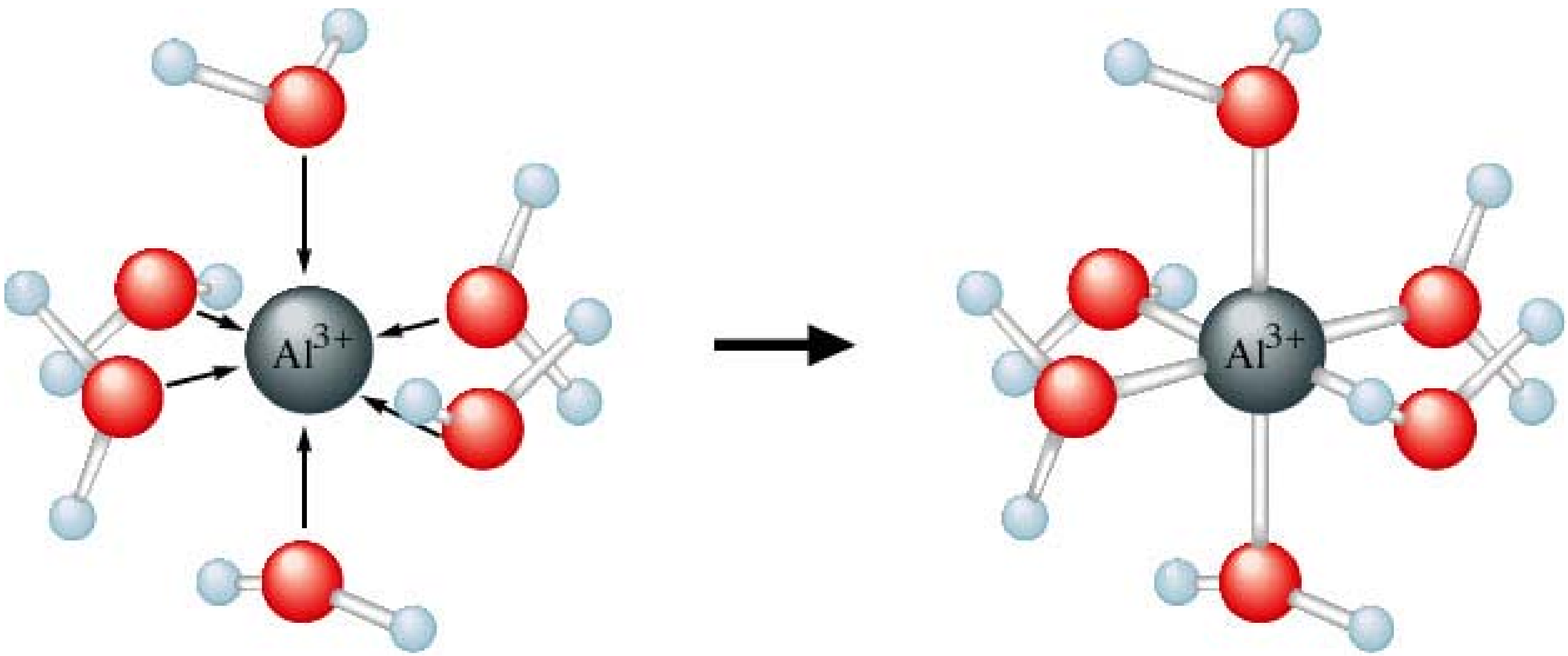


Complex Ions as Lewis Acids

Al^{3+} ions are formed upon dissolving $AlCl_3$ in water. Al^{3+} can form coordinate covalent bonds with water:



Hydrated metal ion in solution is an example of complex ion



Complex Ions as Lewis Acids Continued

$\{Al(H_2O)_6\}^{3+}$ is a Lewis acid; it reacts with water:

$\{Al(H_2O)_6\}^{3+} + H_2O \longleftrightarrow \{Al(OH)(H_2O)_5\}^{2+} + H_3O^+$

Thus, the solution of $AlCl_3$ in water is acidic

Salts of some other metal ions (in particular transition metal ions) hydrolyze and thus express acidic properties

Another example is $FeCl_3$

More Acids and Bases: Buffers

Acids, Bases and the Common Ion Effect

Consider the following acid equilibrium of a weak acid

$$HF + H_2O \rightleftarrows H_3O^+ + F^- \qquad K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

H^+
+
Cl^-

$HCl_{(aq)}$

What happens when we add some strong acid to the mixture?

By LeChatelier's principle, we predict the HF dissociation should be driven left, suppressing the dissociation

HCl completely dissociates, adding free H_3O^+ to solution. This is a common ion to the weak acid equilibrium

More quantitative

a) Determine [F^-] in a solution of 0.500M HF.
b) Determine [F^-] in a solution of 0.500M HF and 0.10M HCl.
K_{HF} = 6.6x10^{-4}.

a) A solution of a weak acid. Let's use the quadratic.

$$[H^+] = [F^-] = \frac{-K_{HF} + \sqrt{K_{HF}{}^2 + 4K_{HF}C_{HF}}}{2}$$

[F^-] = 0.0178M

Continued

b) Use ICE table. Let HF and HCl dissociate separately.

	HF + H_2O ⇄	H_3O^+	+ F^-
Initial			
weak acid	C_{HF}	0	0
strong acid	0	C_{HCl}	0
Change	-x	+ x	+ x
Equilib	C_{HF}-x	C_{HCl} +x	x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$K_a = \frac{\left(C_{HCl} + x\right)x}{C_{HCl} - x}$$

$$K_a C_{HF} - K_a x = C_{HCl} x + x^2$$

$$x^2 + (K_a + C_{HCl})x - K_a C_{HF} = 0$$

$$x = \frac{-(K_a + C_{HCl}) + \sqrt{(K_a + C_{HCl})^2 + 4K_a C_{HF}}}{2} = 3.17 \times 10^{-3}$$

Continued

Comparison

a) no common ion, [F-] = 0.0178 M

b) Common ion, [F-] = 0.0032 M

5 X less!

This is one example of the common ion effect.

When a strong acid supplies the common ion, H_3O^+, the ionization of a weak acid is suppressed.

When a strong base supplies the common ion, OH^-, the ionization of a weak base is suppressed.

What About Adding a Strong Base to a Weak Acid

Consider the following acid equilibrium of a weak acid

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

OH^-
+
Na^+

$NaOH_{(aq)}$

What happens when we add some strong base to the mixture?

By LeChatelier's principle, we predict the HF dissociation should be driven right, suppressing the withdrawal of H_3O^+

NaOH completely dissociates, adding free OH^- to solution. OH- withdraws H_3O^+ forcing the reaction to produce additional H_3O^+

Adding Salt of Weak Acid to Weak Acid

Consider the following acid equilibrium of a weak acid

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

F^- + Na^+ ← $NaF_{(aq)}$

What happens when we add some NaF?

By LeChatelier's principle, we predict the HF dissociation should be driven left, suppressing the dissociation

NaF is a strong electrolyte, therefore it completely dissociates, adding free F^- to the solution. This is a common ion to the weak acid equilibrium. Reaction consumes the excess of F^-

Buffers

Choose the correct answer(s). Definitions of "buffer"in the Cambridge Dictionary of English.

Buffer- something or someone that helps protect against harm

Friends are excellent buffers in times of crisis

Buffer- a foolish old man.

Some old buffer was saying that nothing needed to be changed

Buffer- a nudist, someone that enjoys dressing in the "buff".

Some young buffer was saying that nothing needed to be changed since there was nothing to change into.

Chemical buffer – a chemical system that resists change

Example: any chemical system in equilibrium can be considered as a buffer since it will resist to a change introduced by adding or removing its components. Removing B increases the quotient. The system responses by shifting the equilibrium to the left.

$$aA + bB + cC \rightleftarrows dD + eE + fF$$

$$K_{eq} = \frac{[D]^d[E]^e[F]^f}{[A]^a[B]^b[C]^c}$$

Acid/Base buffer – a system that resists changes to pH caused by addition of excess acid or base

An acid-base equilibrium is a pH buffer

$$HA + H_20 \rightleftarrows A^- + H_30^+$$

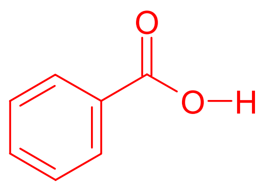
If we add a strong acid (H_3O^+) to this system then, according to the LeChatelier's principle, the equilibrium shifts to the left to resist to the increase of H_3O^+. The system will resist to pH change by the strong acid until it has A^- present.

If we add a strong base (OH^-) to this system then, according to the LeChatelier's principle, the equilibrium shifts to the right to resist to the decrease of H_3O^+. The system will resist to pH change by the strong base until it has HA present.

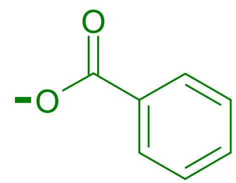
An optimum buffer has to have about equal amounts of HA and A^-. It can not be achieved by simply dissolving the weak acid in water, since its ionization level is low: $[A^-]_{eq} << [HA]_{eq}$

Acid/Base buffer systems can be made by mixing AH and A$^-$ (or B and BH$^+$) were the source of A$^-$ (or BH$^+$) is an appropriate salt

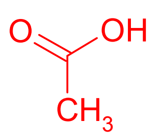
A mixture of a weak acid, HA, and it's conjugate base, A$^-$



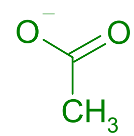
Benzoic acid



benzoate



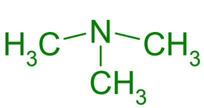
acetic acid



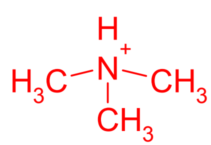
acetate

Add as sodium salts, NaA, for example

A mixture of a weak base, B, and it's conjugate acid, HB



trimethylamine



trimethylammonium

Add as chloride salt, HBCl for example

Weak Acids and Bases Widely Used as Buffers

TABLE 17.3 Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C

	Ionization Equilibrium	Ionization Constant K	pK
Acid		K_a =	pK_a =
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$HC_2H_2ClO_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2ClO_2^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$	1.8×10^{-4}	3.74
Benzoic acid	$HC_7H_5O_2 + H_2O \rightleftharpoons H_3O^+ + C_7H_5O_2^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$HOC_6H_5 + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		K_b =	pK_b =
Diethylamine	$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Acid strength

Base strength

Q: **What is pH of a buffer made of a weak acid, HA, and its conjugate base, A^- in equal concentrations (e.g. 0.1 M)?**

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

	HA	H_3O^+	A^-
Initial			
weak acid	0.10	0	0
conj base	0	0	0.1
Change	-x	+x	+ x
Equilib	0.1-x	+x	0.1+x

$$K_a = \frac{[H_3O^+]_{eq}[A^-]}{[HA]_{eq}} \Leftrightarrow K_a = \frac{[H_3O^+]\cancel{[0.1+x]}}{\cancel{[0.1-x]}} \Leftrightarrow [H_3O^+] = K_a$$

$$\Updownarrow$$

$$pH = pK_a$$

Note: Direct addition of A^- suppresses ionization of HA more than in the case of only HA dissolved. As a result x <<< 0.1

Henderson-Hasselbalch (H-H) Equation

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Solve for $[H_3O^+]$

$$[H_3O^+] = \frac{K_a[HA]}{[A^-]}$$

Take –log of both sides

$$-\log[H_3O^+] = -\log K_a - \log[HA] + \log[A^-]$$

$$-\log[H_3O^+] = -\log K_a + \log\frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

From previous ICE table, we see that in general: $[HA] = C_{HA} - x$ and $[A^-] = C_{A^-} + x$. However, when $x << C_{HA}$, we can assume that $[HA] = C_{HA}$ and $[A^-] = C_{A^-}$

$$\boxed{pH = pK_a + \log\frac{C_{A^-}}{C_{HA}}}$$

Note: In the previous example we had $C_{HA}=C_{A-}$, In general, $C_{HA} \neq C_{A-}$

Buffer Ratio, Buffer Capacity, Buffer Range

Definitions:

1. **Buffer ratio** is C_{A-}/C_{HA}
2. **Buffer capacity** is the amount of strong acid or base the buffer is able to neutralize with pH changing one unit only
3. **Buffer range,** is the pH range over which a buffer effectively neutralizes added acids or bases

Properties:

1. **Buffer capacity increases with proportional increasing the concentrations of buffer components** (keep C_{A-}/C_{HA} = const).
2. **Buffer capacity is maximum when $[A^-]/[HA] = 1$** ($pH = pK_a$)
3. **Buffer capacity is reasonable when $0.1 < C_{A-}/C_{HA} < 10$**
4. Buffer range can be found from the H-H equation by substituting the last constraint ($0.1 < C_{A-}/C_{HA} < 10$) into the H-H equation and using $\log 0.1 = -1$, $\log 10 = 1$:

$$\textbf{Buffer Range} = \mathbf{pKa \pm 1}$$

How to prepare a buffer

1. What is the required pH of the buffer?
2. Find an appropriate HA/A$^-$ system from tables; pK_a for such a system has to be within 1 unit of the required pH

3. Use the H-H equation to find the buffer ratio, $R = C_{A-}/C_{HA}$, you will need for the desired pH.

4. Determine the required buffer capacity = the concentration of strong acid or base that could impact the buffer.

   a) If you expect adding a strong **acid**, choose the total concentration of buffer components as:

$$C_{HA} + C_{A^-} > [\text{strong acid to be added}]\frac{(1+0.1R)(1+R)}{0.9R}$$

   b) If you expect adding a strong **base**, choose the total concentration of buffer components as:

$$C_{HA} + C_{A^-} > [\text{strong base to be added}]\frac{(R+0.1)(1+R)}{0.9R}$$

5. Calculate the concentrations of C_{A-} and C_{HA} in the buffer using known:

C_{A-}/C_{HA} (from 3)

$C_{HA} + C_{A-}$ (from 4)

6. Calculate the masses of components for required volume

7. Wight and dissolve buffer components

Example: Make 1 L of a buffer with pH 3.5 capable of buffering the addition of 0.001 M HCl

1) Required pH = 3.5

2) Pick the buffer HA/A^- system

Acid	pK_a
Citric Acid	3.13
Benzoic acid	4.20
Acetic acid	4.77
Carbonic acid	6.36
Ammonium ion	9.25

Citric acid has pK_a closest to the desired buffer pH.

3) Determine ratio of C_{A^-}/C_{HA} of citric acid needed. Use either HH- equation or equilibrium expression

$$pH = pK_a + \log \frac{C_{A^-}}{C_{HA}}$$

$$\log \frac{C_{A^-}}{C_{HA}} = pH - pK_a$$

$$\frac{C_{A^-}}{C_{HA}} = 10^{pH - pK_a}$$

$$\frac{C_{A^-}}{C_{HA}} = R = 10^{3.5 - 3.13} = 2.34$$

4) Required buffer capacity is 0.001 M of HCl. Lets chose the total concentration of buffer components. When we add a strong acid then,

$$C_{HA} + C_{A^-} > [\text{strong acid to be added}]\frac{(1+0.1R)(1+R)}{0.9R}$$

$$\mathbf{C_{HA} + C_{A^-} > 0.001\,M \times \frac{(1+0.1\times 2.34)(1+2.34)}{0.9\times 2.34} \approx 0.002\,M}$$

Lets take $C_{HA} + C_{A-} = 0.01$ M, which is 5 times more than the required miniumum

5) Calculate the concentrations of buffer components using the results from 3) and 4):

We require:

$C_{A-}/C_{HA} = 2.34$ (1)

and

$C_{A-} + C_{HA} = 0.01M$ (2)

$\left.\begin{matrix} (1) \\ (2) \end{matrix}\right\}$ 2 unknowns

2 equations

from (1) $C_{A-} = 2.34\ C_{HA}$, substitute into (2) to get:

$2.34\ C_{HA} + C_{HA} = 0.01M$ $C_{HA} = 0.003\ M$

$C_{A-} = 2.34\ C_{HA}$ $C_{A-} = 0.007M$

Note: To introduce A^- into the buffer we can:

(i) Use sodium salt of citric acid, NaA, that completely dissociates in water: $NaA \rightarrow Na^+ + A^-$ or

(ii) React citric acid with NaOH: $HA + NaOH \rightarrow Na^+ + A^- + H_2O$

6) Calculate the masses of components

(i) Using Sodium salt of citric acid:

Molar Weight of citric acid, $C_6H_8O_7$:

MW_{HA} = 192.1g/mole

Molar Weight of monosodium citrate, $NaC_6H_7O_7$:

MW_{NaA} = 214.1g/mole

We are preparing V = 1L with final concentrations of HA and NaA equal to 0.003 and 0.007 M respectively, thus:

$$mass_{HA} = C_{HA} \times V \times MW_{HA} =$$
$$= 0.003 \text{ mol/L} \times 1\text{L} \times 192.1 \text{ g/mol} = 0.576\text{g}$$

$$mass_{NaA} = C_{NaA} \times V \times MW_{NaA} =$$
$$= 0.007 \text{ mol/L} \times 1\text{L} \times 214.1 \text{ g/mol} = 1.50\text{g}$$

7) Weigh 0.576g of citric acid and 1.50g of monosodium citrate and dissolve them in 1 L of water. Mix vigorously. The buffer is ready!

6) Calculate the masses of components

(ii) Using reaction of citric acid with NaOH

Since citric acid is in this case a sole source of HA and A^- the concentration of citric acid has to be equal to the total concentration of buffer components chosen:

$$C_{\text{citric acid}} = C_{HA} + C_{A-} = 0.01 \text{ M}$$

The mass of citric acid to be taken to obtain the concentration of 0.01 M in 1 L is:

$$\text{mass}_{HA} = C_{\text{citric acid}} \times V \times MW_{\text{citric acid}} =$$

$$= 0.01 \text{ mol/L} \times 1 \text{ L} \times 192.1 \text{ g/mol} = 1.921\text{g}$$

7) **Weigh 1.921 g of citric acid, dissolve in 1L of water (resulting pH 2.62), and neutralize with NaOH until pH = 3.5. The components in the mixture would be the same as in (i)**

(ADD SUGAR AND ENJOY YOUR BEVERAGE)

Blood as a Buffer

pH of blood is 7.40 +/- 0.05. pH is maintained by a series of buffer systems, in particular: H_2CO_3/HCO_3^-, phosphate, amines and proteins. pH regulation in body is critical since functioning of enzymes is highly pH dependent.

Alkalosis – raising of pH resulting from hyperventilation, or exposure to high elevations (altitude sickness).

Acidosis – lowering of pH in blood by organ failure, diabetes or long term protein diet.

What causes alkalosis at high elevation?…a multiple equilibrium hypothesis.

in the lungs

$CO_{2(g)}$

$\uparrow\downarrow$

At elevation, $P_{CO2(g)}$ is lowered

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)}$$

in blood

$$H_2CO_{3(aq)} + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

pH increases !

The bicarbonate buffer is essential for controlling blood pH

$pK_a = 6.4$

At pH 7.4 from HH eq:

$$\frac{[HCO_3^-]}{[H_2CO_3]} \sim 10$$

Acid/Base Titrations

Acid base titrations are examples of volumetric techniques used to analyze the quantity of acid or base in an unknown sample.

Acid + Base $\rightleftarrows$ H_2O + salt

Lets assume that we need to find the concentration of acid by titration with base. This is done by detecting the point at which we have added an equal number of equivalents of base to the acid. This is the *equivalence point*. For neutralization of an unknown monoprotic acid (A) with a base (B), we have at equivalence:

moles of acid = moles of base $\rightarrow$ $C_A V_A = C_B V_B$

$$C_A = C_B \frac{V_B}{V_A}$$

We detect the equivalence point with a pH meter or by identifying the *end-point* with an acid base indicator.

pH Indicators

Acid-base indicators are highly colored weak acids or bases. When added at low concentrations they do not influence pH but indicate changing pH by changing their color:

$$\text{HIndicator} \rightleftarrows \text{Indicator}^-$$

color 1 color 2

Color transition occurs for 0.1< [Indic$^-$]/[HIndic]<10

$$pH_{transition} = pK_a^{ind} + \log\frac{[In^-]}{[HIn]} = pK_a^{ind} \pm 1$$

In general there are three colors: acid, transition and base

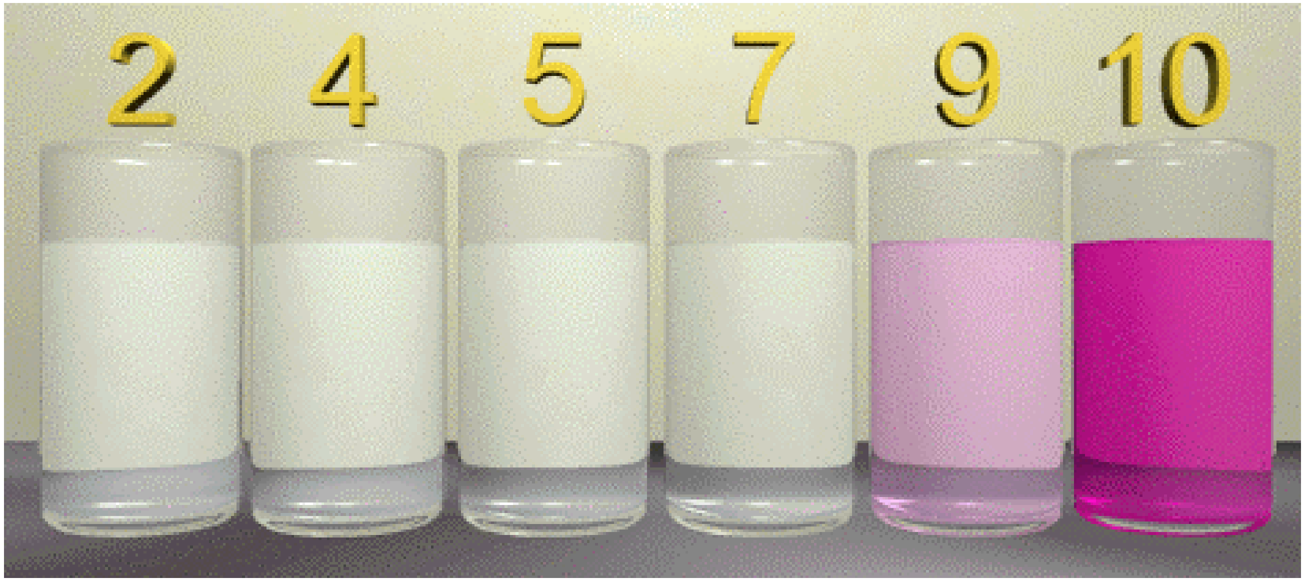
Example. Bromthymol blue

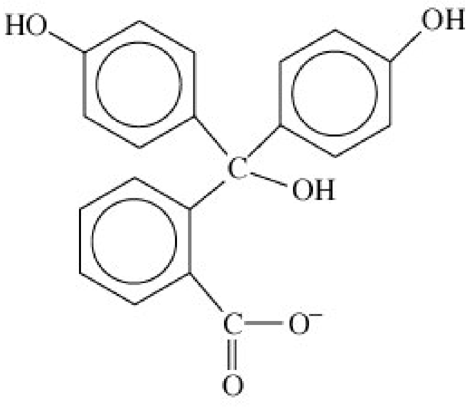
Yellow → Green → Blue

One of the forms may be colorless - phenolphthalein (colorless to pink)

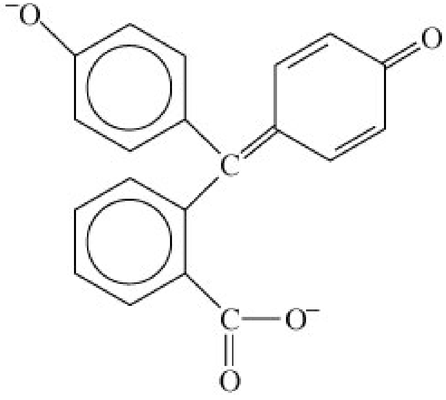
The colour transition range for an indicator is p$K_a \pm 1$

phenolphthalein





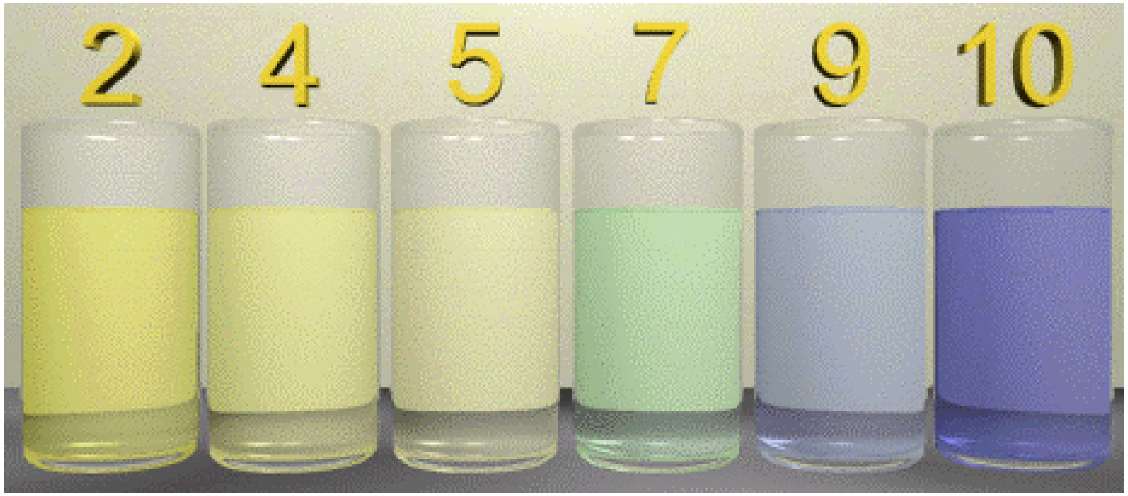
(Colorless acid form, HIn)



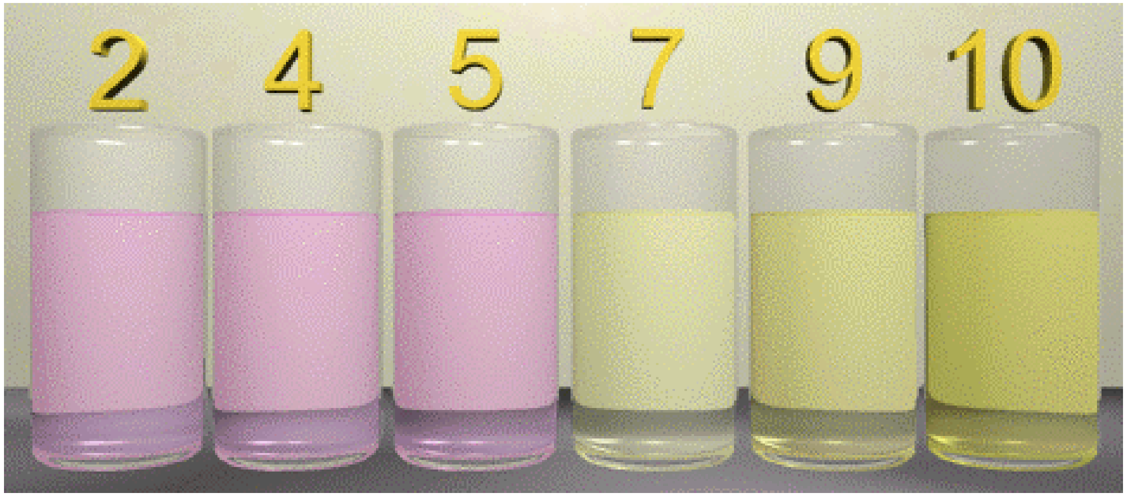
(Pink base form, In⁻)

Indicator Examples

bromthymol blue

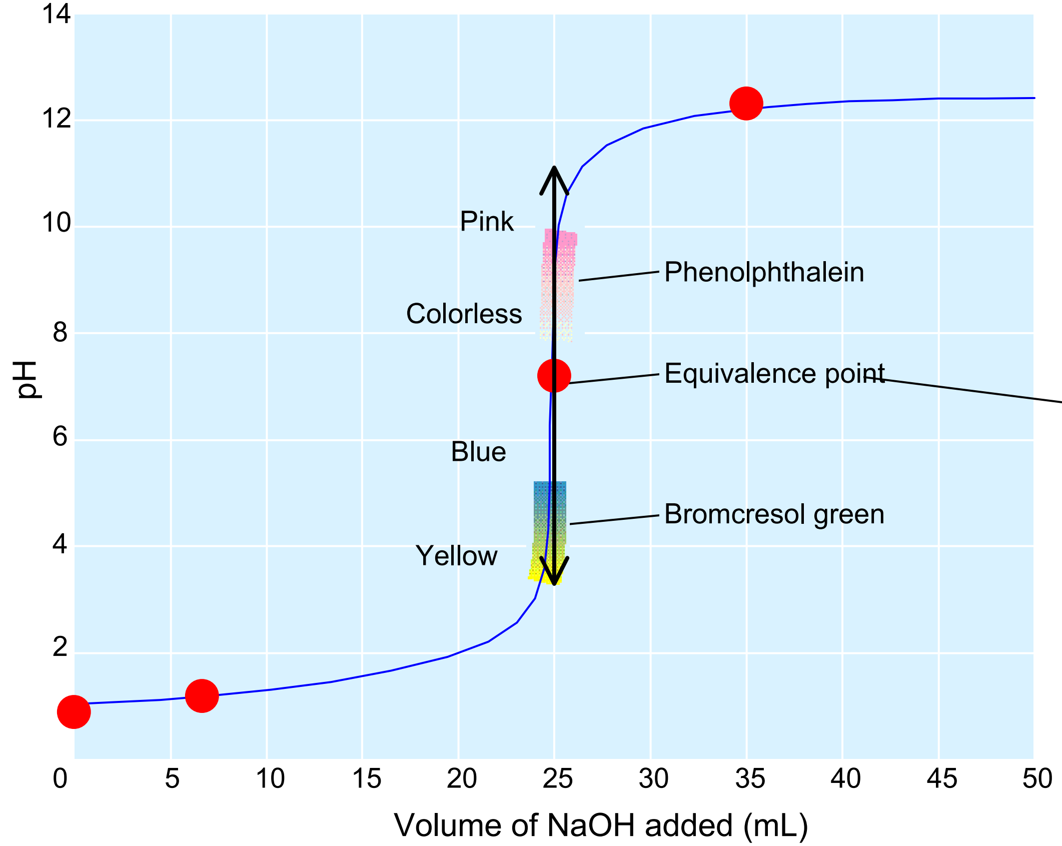


methyl red



Acid Base titrations

Titration of strong acid (0.1 M HCl) with strong base



Volume NaOH added (mL)	pH
0	1.00
5	1.18
10	1.37
15	1.60
20	1.95
21	2.06
22	2.20
23	2.38
24	2.69
25	7.00
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	12.52

Characteristics:

1. Low initial pH
2. Flat initial part
3. Neutral equivalence point!!!
4. Large pH change at equivalence point
5. Flat final part

Example

What is the pH at 0mL, 10mL, 25.0mL and 35mL in titration of 25mL of 0.100 M HCl (strong acid) with 0.100M NaOH.

1) 0 mL $pH = -\log[H_3O^+] = -\log C_{HA} = -\log(0.100M) = 1.00$

2) 10mL (all calculated in moles)

$$HCl_{(aq)} + NaOH_{(aq)} \rightleftharpoons H_2O + NaCl_{(aq)}$$

$HCl_{(aq)} = H_3O^+$

	$HCl_{(aq)}$ (H_3O^+)	$NaOH_{(aq)}$	H_2O	$NaCl_{(aq)}$
Initial				
strong acid	0.0025	0	0	0
strong base	0	0.001	0	0
Change	-0.0010	-0.001	0.001	0.001
Equilib	0.0015	~0	0.001	0.001

Stoichiometric neutrolization

$[H_3O^+]$ = mol H_3O^+ /V_{tot} = 0.0015 /(0.025 + 0.010)L = 0.0429

pH = - log(0.0429) = 1.37

In general, before equivalence is reached in titration:

$$[H_3O^+] = (C_AV_A – C_BV_B) / (V_A+V_B)$$

25.0 mL moles acid = moles base, equivalence point.

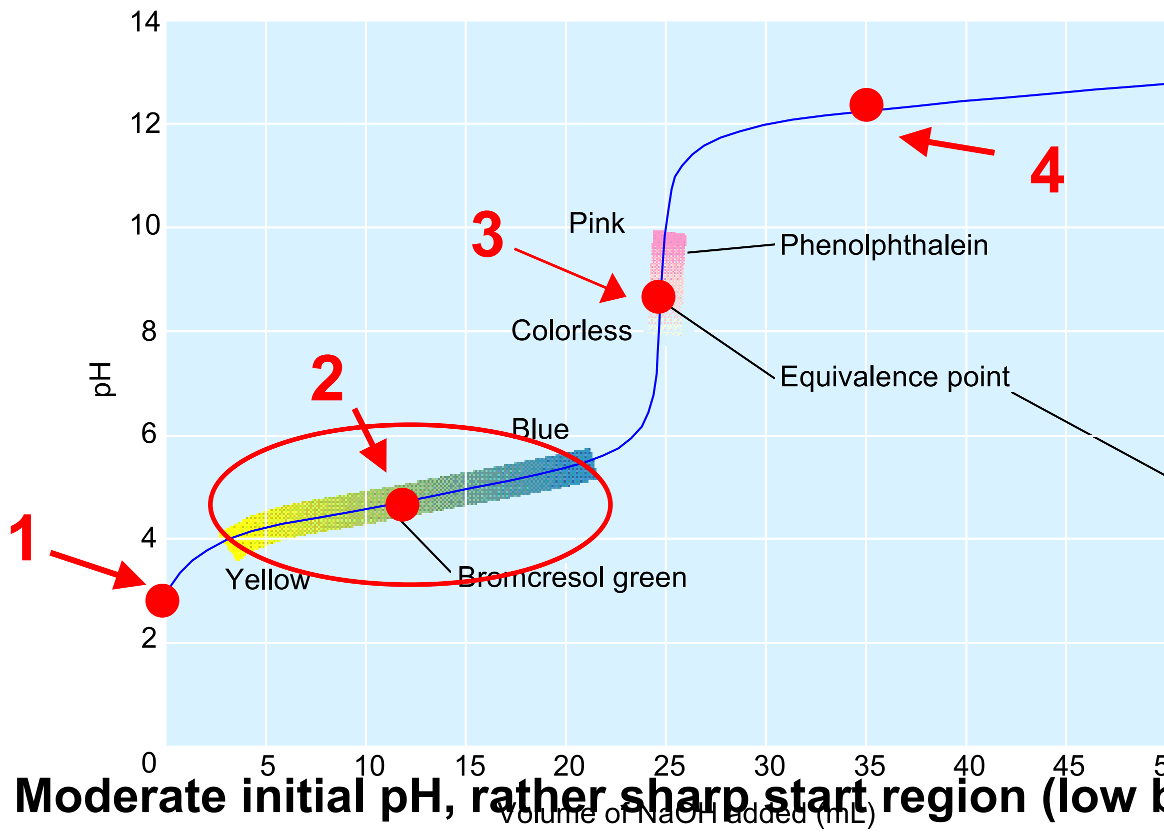
all acid is neutralized, with no excess base
We are left with pure $NaCl_{(aq)}$ solution, **pH = 7.00**

35.0mL pH is determined by amount of excess base

$$[OH^-] = (C_BV_B – C_AV_A) / (V_A+V_B)$$
$$= \{(.1M)(.035L)-(.1M)(.025L)\}/\{.025+.035L\} = 0.0167M$$

pH = 14 – pOH = 14 – (-log [OH^-]) = 14 -1.78 **pH = 12.22**

Titration of weak acid with strong base (making a buffer)



Volume NaOH added (mL)	pH
0	2.92
1	3.47
2	3.79
3	3.98
4	4.13
5	4.25
10	4.67
15	5.03
20	5.45
21	5.57
22	5.72
23	5.91
24	6.23
25	8.78
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	[illegible]

1) **Moderate initial pH, rather sharp start region (low buffer capacity),**

2) **Flat buffer region, the lowest slope is at pH = pK_a, which is the point of half neutralization (remember, by adding a strong base to a week acid we are making a buffer: HA + B $\rightleftarrows$ A^- + BH^+ {buffer components are red})**

3) **Basic equivalence point (the effect of conjugate base formed after complete neutralization), change in pH not as great as with strong acid strong base**

4) **Excess base region is similar to that for titration of strong acid with strong base**

Titration of weak acid with strong base: Calculation of pH for different regions on the titration curve

1. <u>Initial Point:</u> calculate pH of solution of a weak acid.
   use approximation for weak acid or quadratic.
2. <u>Buffer Region:</u> Use the H-H equation to determine pH:
   2.1. moles HA = initial moles HA – moles OH added
   2.2. moles A^- = moles OH added
   2.3. $pH = pK_a + \log([A^-]/[HA])$
3. <u>Equivalence point:</u> a pure solution of a weak base, A^-.
   \# moles A^- = # moles HA we started with.
   Use approximation for weak base or quadratic
4. Excess base: pH is determined solely by the amount of excess strong base added. See strong acid/strong base example.

Example

Q: What is the pH at the equivalence point in the titration of 50 mL (V_{HA}) of a 0.1 M (C_{HA}) solution of acetic acid with 0.1 M (C_{NaOH}) NaOH.

Solution: At equiv. Point (by definition), all acid, HA, is converted to its conjugate base, A^-, in the reaction: $HA + NaOH \rightarrow A^- + Na^+ + H_2O$. After that, new equilibrium is established in the reaction of the conjugate base with water: $A^- + H_2O \leftrightarrow HA + OH^-$. Initial concentrations for the new equilibrium are: $[A^-] = C_{A-} = ?$, $[HA]_{ini} = 0$ and $[OH^-]_{ini} = 0$. The value of pH will be determined by $[OH^-]_{eq}$. To find $[OH^-]_{eq}$ we need to know C_{A-}.
Lets rewrite the statement we already made:
At equiv. Point (by definition) moles A^- = moles HA = $C_{HA} \times V_{HA}$, then:

$$C_{A-} = \text{moles } A^-/V_{tot} = C_{HA}V_{HA}/V_{tot} \qquad (1)$$

To find V_{tot} at equivalence we recall that for a monoprotic acid, at equivalence point (by definition):

moles acid = moles base

$$C_{HA}V_{HA} = C_{NaOH}V_{NaOH} \quad \Rightarrow \quad V_{NaOH} = C_{HA}V_{HA}/C_{NaOH}$$

$$V_{tot} = V_{HA} + V_{NaOH} = V_{HA} + C_{HA}V_{HA}/C_{NaOH} = V_{HA}(1 + C_{HA}/C_{NaOH}) =$$

$$= 50\text{ mL}(1 + 0.100\text{M}/0.100\text{M}) = 50\text{ mL} \times 2 = 100\text{mL}$$

Using (1): $C_{A-} = C_{HA}V_{HA}/V_{tot} = 0.1\text{M} \times 50\text{mL}/100\text{mL} = 0.05\text{M}$

Using $K_b = K_w/K_a$, K_a for acetic acid of 1.8×10^{-5}, and just found C_{A-} we can determine $[OH^-]$ at equivalence:

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_{A^-}}}{2} = \frac{-\frac{K_w}{K_a} + \sqrt{\left(\frac{K_w}{K_a}\right)^2 + 4\frac{K_w}{K_a}C_{A^-}}}{2}$$

$$= \frac{-\frac{1\times10^{-14}}{1.8\times10^{-5}} + \sqrt{\left(\frac{1\times10^{-14}}{1.8\times10^{-5}}\right)^2 + 4\frac{1\times10^{-14}}{1.8\times10^{-5}}0.05}}{2} = 5.27\times10^{-6}$$

pH = 14 – pOH = 14 – (-log (5.27×10^{-6}))

pH = 8.72

When titrating weak acid with strong base, pH at equivalence is always basic!

Which indicator would we use for the previous case?

$$pK_{indicator} = pH_{equivalence} \pm 1$$