Analytical Chemistry

Lecture I

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Equilibrium Constants

Self-ionization of Water

- concentrations or molarities can be written with brackets
- For example:

  concentration of A = [A] = 2.0 M
- K_w:
  - the ionization constant of water
  - the product of $[OH^-]$ and $[H^+]$
- at 25°C

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

K_w

- subject to the same restriction as any other equilibrium constant (T, P)
- Will acidic solutions have more H^+ or OH^-?
  - $[H^+]>[OH^-]$: acidic
  - $[OH^-]>[H^+]$: basic
  - $[OH^-]=[H^+]$: neutral
- can find the $[OH^-]$ or $[H^+]$ from a mole ratio of the dissociation or reaction in the water of the acid or base

Water as an Acid and a Base

Autoionization of water:

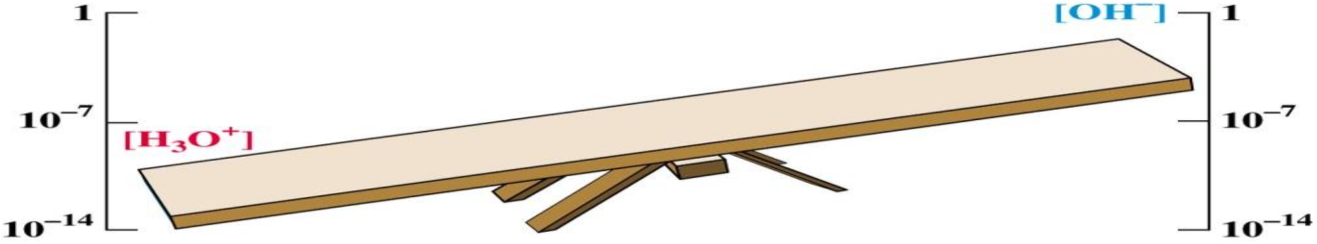
$$\frac{[H_3O^+][OH^-]}{[H_2O(l)]^2}$$

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

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

$$K_w = 1.0 \times 10^{-14}\ (\text{at } 25^oC)$$

In pure water $[H^+] = [OH^-]$



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

$K_a/K_b/K_w$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

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

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

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

$K_a/K_b/K_w$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

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

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

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

$$H_2O \rightleftharpoons OH^- + H^+$$

$$\boxed{K_w = K_a K_b = \frac{[OH^-][H^+]}{(1)}}$$

pH Calculations

Strong Electrolyte

- Acids, HNO_3, HCl, H_2SO_4
- Bases , KOH, NaOH, $Ba(OH)_2$
- Salts, KCl, $AlCl_3$, $BaCl_2$

Weak Electrolyte

- Acid, acetic acid, HCOOH, HCN
- Base, NH_4OH

- **Acid-base theories:-**
- **1) Arrhenius Theory (H^+ and OH^-):-**
- **Acid**:-any substance that ionizes (partially or completely) in water to give hydrogen ion (which associate with the solvent to give hydronium ion H_3O^+):
- $HA + H_2O \leftrightarrow H_3O^+ + A^-$
- **Base**:-any substance that ionizes in water to give hydroxyl ions.

such as metal hydroxides (e.g. NaOH) dissociate as

$M(OH)n \leftrightarrow n\ M^+ + n\ OH^-$

- $NaOH \leftrightarrow Na^+ + OH^-$

2) Bronsted-Lowry Theory (taking and giving protons, H^+):-

Acid:-any substance that can donate a proton.

Base:-any substance that can accept a proton. Thus, we can write a half reaction: Acid = H^+ + Base

3) Lewis Theory (taking and giving electrons):-

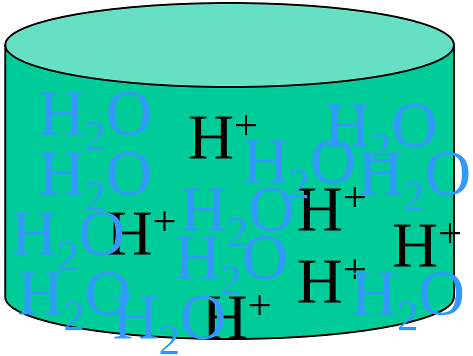
Acid:-a substance that can accept an electron pair.

Base:-a substance that can donate an electron pair.

$H_2O + H^+ \leftrightarrow H_2O{:}H^+ \ (H_3O^+)$

$HO{:}^- + H^+ \leftrightarrow H{:}OH$

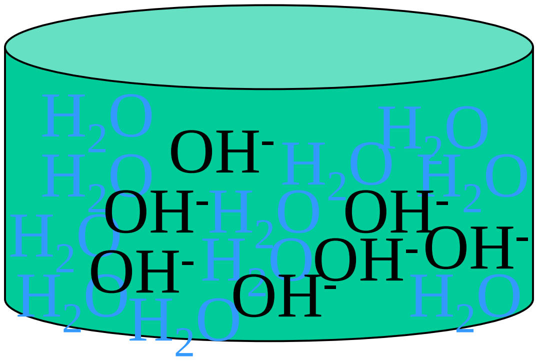
What is an ACID?



- pH less than 7
- Neutralizes bases
- Forms H^+ ions in solution
  - It turns Litmus to Red.

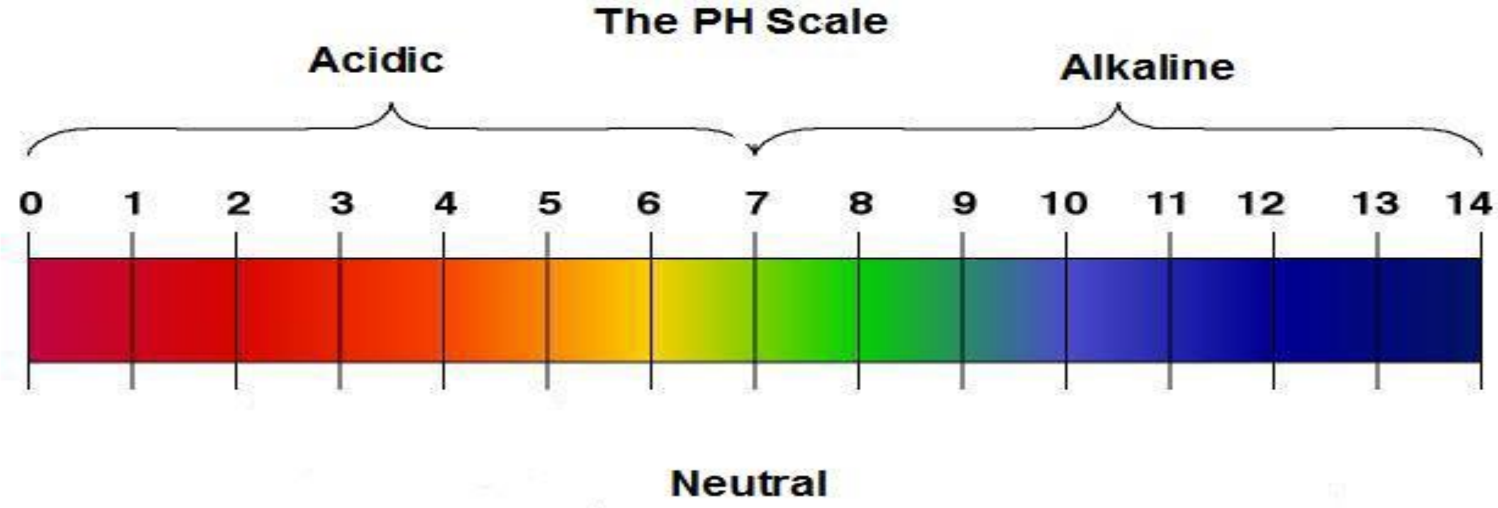
What is a BASE?

- pH greater than 7
- Feels slippery
- Bitter Taste
- Usually forms OH^- ions in solution
- It turns Red Litmus Blue.



What is a BASE?

- pH greater than 7



Strong and weak acids and bases

- Strong acid – fully dissociates in water, i.e. almost every molecule breaks up to form H^+ ions
- Some strong acids are…HCl, H_2SO_4, HNO_3

- Weak acid – partially dissociates in water
- Some weak acids are…carboxylic acids such as CH_3COOH, C_2H_5COOH

- Strong base – fully dissociates in water, i.e. almost every molecule breaks up to form OH^- ions
- Some strong bases are….NaOH, compounds which contain OH^- ions or O^{2-} ions

- Weak base – partially dissociates in water
- Some weak bases…nitrogen-containing compounds, such as NH_3

- Strengths can be determined by the acid or base dissociation constant

pH

- *pH* is a scale in which the concentration of hydronium ions in solution is expressed as a number ranging from 0 to 14.
- Instead of referring to a scale of 1 to 10^{-14}, the pH scale is much easier to use.
- pH is the negative of the exponent of the hydronium concentration.

The pH Scale

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

or

$$[H_3O^+] = 10^{-pH}$$

pH Meter: Laboratory Measurement of pH

pH paper

- pH paper changes color to indicate a specific pH value.

Determining the Basicity of a Solution pOH

- Since acids and bases are opposites, pH and pOH are opposites!
- pOH does not really exist, but it is useful for changing bases to pH
- pOH looks at the perspective of a base:

$$\mathbf{pOH = -\log [OH^-]}$$

- Since pH and pOH are on opposite ends:

$$\mathbf{pH + pOH = 14}$$

pH Equations

You must know the following equations, which are all based on the ionization of water at 25^0 C!

$$H_2O \rightleftarrows H^+ + OH^-$$

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

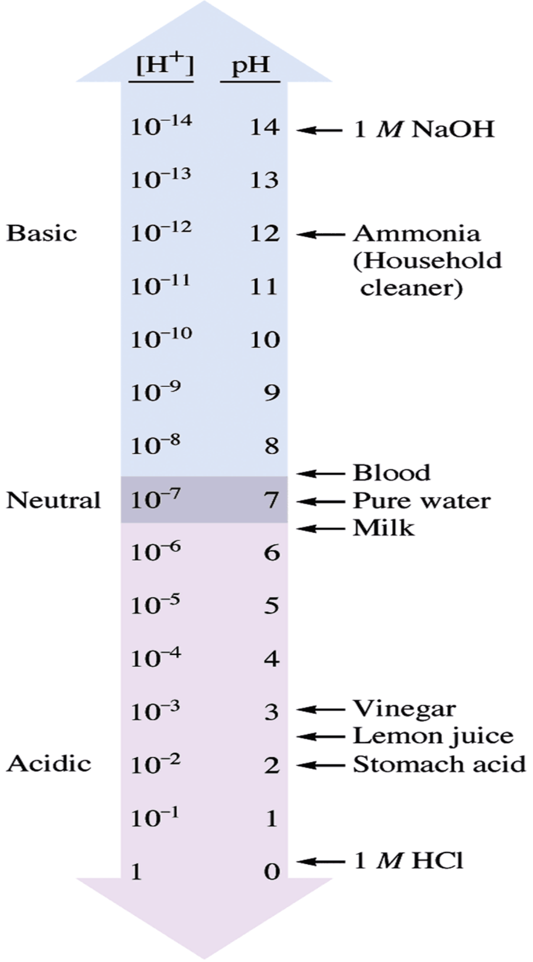
$$pH = -\log[H^+] \qquad pOH = -\log[OH^-]$$

$$[H^+] = 10^{-pH} \qquad [OH^-] = 10^{-pOH}$$

$$pH + pOH = pK_w = 14.000$$

pH scale

- more convenient than using concentrations
- pH=-log $[H^+]$
- pOH=-log $[OH^-]$
- pH increases as $[H^+]$ decreases
- pH < 7: acid
- pH > 7: base
- pH = 7: neutral



1. What is the pH of a solution that has a hydronium ion concentration of $6.5 \times 10^{-5} M$?

2. What is the hydronium ion concentration of a solution with pH 3.65?

1.

$$pH = -\log[H_3O^+]$$

$$pH = -\log[6.54 \ x\,10^{-5}]$$

$$pH = 4.19$$

2.

$$[H_3O^+] = 10^{-pH}$$

$$[H_3O^+] = 10^{-3.65}$$

$$[H_3O^+] = 2.2x10^{-4}$$

1. What is the pOH of a solution that has a hydroxide ion concentration of 4.3×10^{-2} *M*?

2. What is the hydroxide ion concentration of a solution with pOH 8.35?

1.

$$pOH = -\log[OH^-]$$

$$pOH = -\log[4.3 \ x\,10^{-2}]$$

$$pOH = 1.37$$

2.

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

$$[OH^-] = 10^{-8.35}$$

$$[OH^-] = 4.5x10^{-9}$$

Example :-A 1.0×10^{-3} M solution of HCl prepared. What is the hydroxyl ion concentration $[OH^-]$?

$$Kw=[H^+][OH^-]=1.0\times10^{-14}$$

$$1.0\times10^{-3}\times[OH^-]=1.0\times10^{-14}$$

$$[OH^-]=1.0\times10^{-11}\ \mathrm{M}$$

e.g., $Ba(OH)2 \rightarrow Ba^{2+} + 2OH^-$

Given 0.1 *M* Ba(OH)2, the pOH is –log(0.2) = 0.7

Example :- Calculate the pH and pOH of a 2×10^{-3}M HCl ?

$[H^+]= \quad 2\times10^{-3}$

$pH= \quad -\log[H^+] =-\log(2.0\times10^{-3}) =3-\log2.0=2.70$

$pKw = \quad pH + pOH =14$

$pOH = \quad 14\text{-}pH =14 - 2.70 =11.3$

Example :-Calculate the pOH and pH of a 5×10^{-2} M NaOH ?

$[OH^-]=5\times10^{-2}M$

$pOH = -\log[OH^-] =-\log(5\times10^{-2}) =2-\log5 =2-0.70=1.30$

$pH + pOH =14$

$pH=14-pOH \quad =14-1.30= \quad 12.70$

Example

- A shampoo has a pH of 2.53. Calculate the pOH, $[H^+]$ and $[OH^-]$. Is it acidic, basic, or neutral?

$$pOH = 14.00 - pH = 14.00 - 2.53 = 11.47$$

$$[H^+] = 10^{-2.53} = 0.0029M$$

$$[\mathrm{OH}^-] = 10^{-11.47} = 3.42 \times 10^{-12}\ M$$

pH < 7 so acidic

e.g., An aqueous solution of a strong base has pH 12.24 at 25°C. Calculate the concentration of base in the solution (a) if the base is NaOH and (b) if the base is Ba(OH)2.

Answer:

pH = 12.24 means that pOH = 14 – 12.24 = 1.76

Therefore $[OH^-] = 10^{-1.76} = 0.0174$

With NaOH, we must have [NaOH] = 0.017 *M*

With Ba(OH)2, we have [Ba(OH)2] = (0.017 / 2) = 8.7×10^{-3} *M*

pH of mixtures

Strong acids and strong alkalis (either in excess)

1. Calculate the initial number of moles of H^+ and OH^- ions in the solutions
2. As H^+ and OH^- ions react in a 1:1 ratio; calculate unreacted moles species in excess
3. Calculate the volume of solution by adding the two original volumes
5. Divide moles by volume to find concentration of excess the ion in M
6. Convert concentration to pH

If the excess is H^+ $\quad pH = -\log[H^+]$

If the excess is OH^- $\quad pOH = -\log[OH^-]$ then

$pH + pOH = 14$

or use $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ at 25°C therefore

$[H^+] = K_w / [OH^-]$ then

$pH = -\log[H^+]$

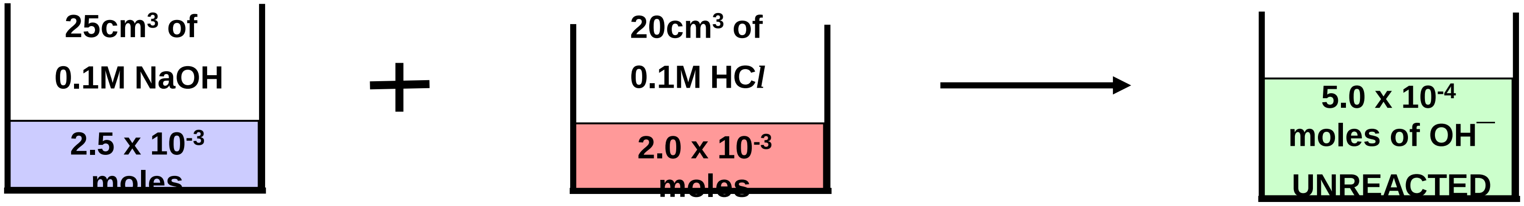
pH of mixtures

Strong acids and alkalis (either in excess)

Calculate the pH of a mixture of 25cm^3 of 0.1M NaOH is added to 20cm^3 of 0.1M HC*l*

1. Calculate the number of moles of H^+ and OH^- ions present

2. As the ions react in a 1:1 ratio, calculate the unreacted moles of the excess species



The reaction taking place is… HC*l* + NaOH ⟶ NaC*l* + H_2O

or in its ionic form $H^+ + OH^- \longrightarrow H_2O$ (1:1 molar ratio)

2.0×10^{-3} moles of H^+ will react with the same number of moles of OH^-

this leaves $2.5 \times 10^{-3} - 2.0 \times 10^{-3} =$ 5.0×10^{-4} moles of OH^- in excess

pH of mixtures

WORKED EXAMPLE

Strong acids and alkalis (either in excess)

Calculate the pH of a mixture of 25cm^3 of 0.1M NaOH is added to 20cm^3 of 0.1M HC*l*

1. Calculate the number of moles of H^+ and OH^- ions present
2. As the ions react in a 1:1 ratio, calculate the unreacted moles of the excess species
3. Calculate the volume of the solution by adding the two individual volumes
4. Convert volume to L (divide cm^3 by 1000)

the volume of the solution is 25 + 20 = 45cm^3

there are 1000 cm^3 in 1L

volume = 45/1000 = 0.045L

pH of mixtures

Strong acids and alkalis (either in excess)

Calculate the pH of a mixture of 25cm^3 of 0.1M NaOH is added to 20cm^3 of 0.1M HC*l*

5. Divide moles by volume to find concentration of excess ion in mol L^{-1}

$[OH^-] = 5.0 \times 10^{-4} / 0.045 = 1.11 \times 10^{-2}$ mol L^{-1}

. As the excess is OH^- use $pOH = -\log[OH^-]$ then $pH + pOH = 14$

or $K_w = [H^+][OH^-]$ so $[H^+] = K_w / [OH^-]$

$[OH^-] = 5.0 \times 10^{-4} / 0.045 = 1.11 \times 10^{-2}$ M

$[H^+] = K_w / [OH^-] = 9.00 \times 10^{-13}$ M

$pH = -\log[H^+] = 12.05$

Example :-Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution (keep track of millimoles) of pH=3.0 and 3.0 mL of a strong base of pH= 10.0 ?

$[H^+]=1.0\times10^{-3}M$ mmol

$H^+=M\times V=1.0\times10^{-3}\times2.0=2\times10^{-3}$ mmol

$pOH=14-pH=14-10=4.0$

$[OH-]=1.0\times10^{-4}M$ mmol

$OH^-=M\times V=1.0\times10^{-4}\times3.0$ mL$=3.0\times10^{-4}$mmol

There is an excess of acid:-

$$\text{mmol } H^+ = 2.0\times10^{-3} - 3.0\times10^{-4}$$
$$= 1.7\times10^{-3} \text{ mmol}$$

$$[H^+] = 1.7\times10^{-3} \text{ mmol} / 5\text{mL } (2+3)$$

$$= 3.4\times10^{-4}\text{M pH}$$

$$= -\log 3.4 \times 10^{-4}$$

$$= 4 - 0.53$$

$$= 3.47$$

Q/ Calculate the pH for the following:

a) 50 ml 0.1M HCl

b) 50 ml 0.1M HCl + 50 ml H_2O

c) 50 ml 0.1M HCl + 50 ml 0.1M NaOH

d) 50 ml 0.1M HCl + 40 ml 0.1M NaOH

e) 40 ml 0.1M HCl + 50 ml 0.1M NaOH

Sol./

a) $HCl \rightarrow H^+ + Cl^-$

$$\begin{array}{ccc} 0.1M & 0.1M & 0.1M \end{array}$$

$pH = -\log 1\times10^{-1} = 1$

b) M1 V1 = M2 V2

$0.1 \times 50 = M2 \times 100$

M2 = 0.05 M

$pH = -\log 5 \times 10^{-2} =$

c) $HCl + NaOH \longrightarrow NaCl + H_2O$

$0.1\times50 \quad 0.1\times50$

m.mole HCl = m.mole NaOH

$0.1\times50 \qquad 0.1\times50$

$5 \qquad 5$

pH = 7 because $\left[OH^-\right]=\left[H^+\right]=\sqrt{K_w}$

d) $HCl + NaOH \rightarrow NaCl + H_2O$

$0.1\times50 \quad 0.1\times40$

Molaity HCl_{excess} = m.mole solution/volume solution

$= (5\text{-}4)/90 = 1/90$

$pH = -\log 1/90$

e) $HCl + NaOH \rightarrow NaCl + H_2O$

$0.1\times40 \quad 0.1\times50$

Molaity $NaOH_{excess}$ = m.mole solution/volume solution

$= (5\text{-}4)/90 = 1/90$

$pOH = -\log 1/90$

$pH = 14 - pOH$