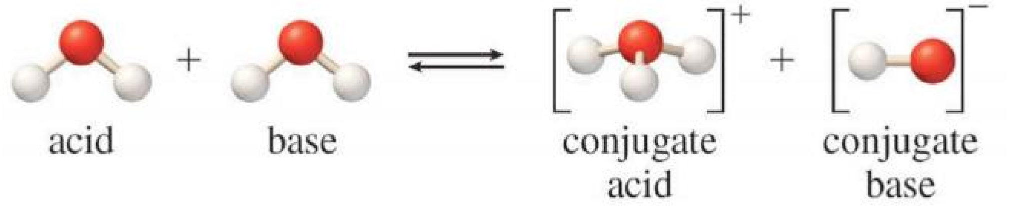
Lecture 3
pH Calculations

Water is **amphoteric**: it can act as an acid or a base.
Water also autoionizes to a very small degree

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



The equilibrium constant Kw does not include the liquid, so

$$\mathbf{Kw = [H^+]\times[OH^-]}\ \textit{or}\ \mathbf{Kw = [H_3O^+]\times[OH^-]}$$

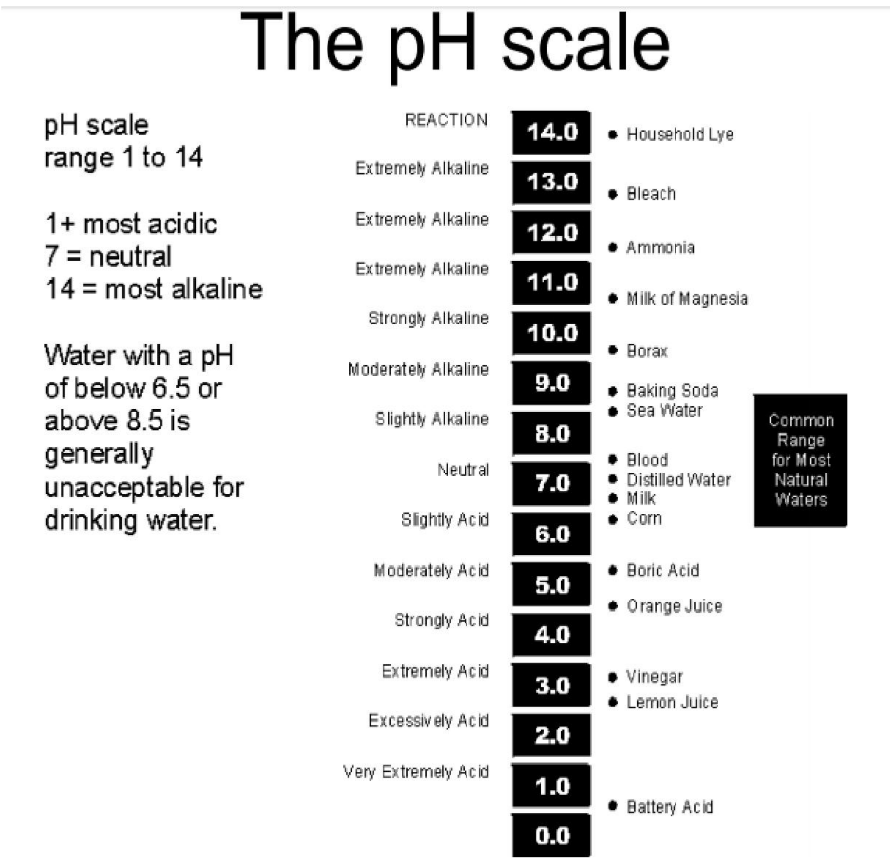
at 25C, $[H^+]=1.0\times10^{-7} = [OH^-]$, **Kw = 1.0×10^{-14}**
For any temperature, pure water is neutral ($[OH^-] = [H^+]$) but the concentrations vary slightly which is reflected in Kw.

- If $[H^+] = [OH^-]$ the solution is **neutral**
- If $[H^+] > [OH^-]$ the solution is **acidic**
- If $[H^+] < [OH^-]$ the solution is **basic**

The pH and pOH Scales

$$pH = -lg[H^+]$$
$$pOH = -lg[OH^-]$$
$$pH+pOH=14$$

For pure water at 25°C, pH = pOH = 7 (neutral).
When pH < 7 - the solution is acidic.
When pH > 7 - the solution is basic.



Strong Acids and Bases

Strong acids and bases ionize / dissociate completely.

Strong acids: $HClO_4$. HI, HBr, HCl, HNO_3, H_2SO_4, H_2SeO_4.
Strong bases: NaOH, KOH, CsOH, RbOH, LiOH, $Ba(OH)_2$, $Sr(OH)_2$.

Therefore the pH is easy to calculate: the concentration of [H+] or [OH–] is just given by the starting concentration of the strong acid or base, and the stoichiometry.
e.g., $HCl \rightarrow H^+ + Cl^-$ Given 0.1 M HCl, the pH= –log(0.1) = 1.
e.g., Ba(OH)2 $\rightarrow Ba^{2+} + 2OH^-$ Given 0.1 M $Ba(OH)_2$, the pOH=–log(0.2) = 0.7
Then pH=14-pOH=14-0.7=13.3

Weak Acids and Acid Ionization Constants

Weak acids do not fully dissociate in water. The extent to which a weak acid ionizes in water depends on^
1. the concentration of the acid
2. the equilibrium constant for the ionization reaction, K_a

-monoprotic acid *(HNO_2, HF, CH_3COOH)*:

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

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

-diprotic acid *(H_2CO_3, H_2SO_3, $H_2PO_4^-$)*:

$$\mathbf{H_2A(aq) \leftrightarrow H^+(aq)+HA^-(aq)}$$

$$K_a = \frac{[H^+]\times[HA^-]}{[H_2A]}$$

K_a is called the ***acid ionization constant***.
$pK_a = -logK_a$

The larger the value of Ka, the stronger the the acid.

Name	Formula	K_a	pK_a
Hydrochloric acid	HCl	1.0×10^{7}	−7.00
Phosphoric acid	H_3PO_4	7.5×10^{-3}	2.12
Hydrofluoric acid	HF	6.6×10^{-4}	3.18
Lactic acid	$CH_3CH(OH)CO_2H$	1.4×10^{-4}	3.85
Acetic acid	CH_3CO_2H	1.8×10^{-5}	4.74
Carbonic acid	H_2CO_3	4.4×10^{-7}	6.36
Dihydrogenphosphate ion	$H_2PO_4^-$	6.2×10^{-8}	7.21
Ammonium ion	NH_4^+	5.6×10^{-10}	9.25
Hydrocyanic acid	HCN	4.9×10^{-10}	9.31
Hydrogencarbonate ion	HCO_3^-	5.6×10^{-11}	10.25
Methylammonium ion	$CH_3NH_3^+$	2.4×10^{-11}	10.62
Hydrogenphosphate ion	HPO_4^{2-}	4.2×10^{-13}	12.38

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

Weak acid: $[H^+]=[A^-]$

$$K_a = \frac{[H^+]^2}{[HA]}$$

$$[H^+]^2 = K_a \times [HA]$$

$$[H^+] = \sqrt{K_a \times [HA]}$$

$$\boxed{pH = -\lg\sqrt{K_a \times [HA]}}$$

Weak Bases and Base Ionization Constants

The pH of a solution of a weak base can be calculated in a way which is very similar to that used for a weak acid. Instead of an acid constant K_a, a base constant K_b must be used. If a weak base B accepts protons from water according to the equation

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

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

Weak base: $[BH^+]=[OH^-]$

$$K_b = \frac{[OH^-]^2}{[B]}$$

$$[OH^-]^2 = K_b \times [B]$$

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

$$pH = 14 - pOH = 14 - (-\lg \sqrt{K_b \times [B]})$$

$$\boxed{pH = 14 + \lg \sqrt{K_b \times [B]}}$$

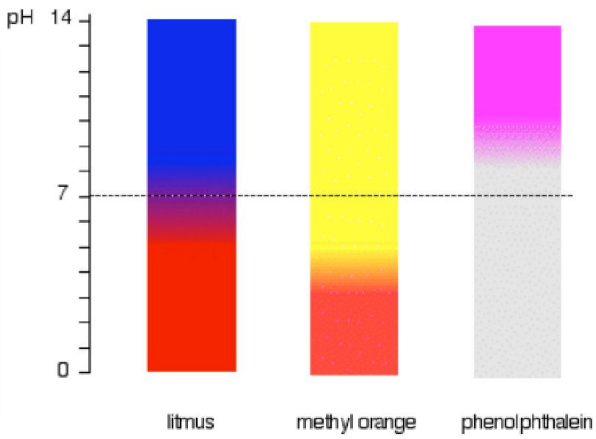
A list of K_b values for selected bases arranged in order of strength is given in the table below.

Base	Formula and Ionization Equation	K_b
Ammonia	$NH_3 + H_2O \rightleftharpoons NH^+_4 + OH^-$	1.77×10^{-5}
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH^+_3 + OH^-$	3.9×10^{-10}
Carbonate ion	$CO^{2-}_3 + H_2O \rightleftharpoons HCO^-_3 + OH^-$	2.1×10^{-4}
Hydrazine	$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$	$K_1 = 1.2 \times 10^{-6}$ $K_2 = 1.3 \times 10^{-15}$
Phosphate ion	$PO^{3-}_4 + H_2O \rightleftharpoons HPO^{2-}_4 + OH^-$	5.9×10^{-3}

Indicators

Common Acid–Base Indicators

Indicator	Approximate pH Range for Color Change	Color Change
methyl orange	3.2–4.4	red to yellow
bromthymol blue	6.0–7.6	yellow to blue
phenolphthalein	8.2–10	colorless to pink
litmus	5.5–8.2	red to blue
bromcresol green	3.8–5.4	yellow to blue
thymol blue	8.0–9.6	yellow to blue



PROBLEMS:

1. Determine the pH of a 0.010 M HNO_3 solution.
2. What is the pH of a 2.5×10^{-6} M solution of HCl?
3. Calculate the pH of a solution of 0.0025M H_2SO_4.
4. Calculate the pH of a 0.0010 M NaOH solution.
5. What is the pH of a 0.020M $Sr(OH)_2$ solution?
6. a) What is the hydrogen ion concentration of an aqueous HCl solution that has a pH of 3.0?

b) What is the hydroxide ion concentration of this same solution?

c) Which ion, H^+ or OH^- , is in greater concentration? ____________

d) Is this solution acidic or basic? _____________

7. Find the $[H^+]$ and the $[OH^-]$ of a solution with a pH of 3.494. Is this solution acidic or basic?_____________________
8. What is the pH of a 0.1 M solution of HNO_2?
9. What is the pH of a 0.05 M solution of NH_4OH?
10. What is the pH of a 0.3 M solution of H_2S?