Lecture 2
pH Calculations
By/ Dr. Ekhlas Q. J.

What is pH?

$$pH = -\log_{10}[H^+_{(aq)}]$$

where $[H^+]$ is the concentration of hydrogen ions in mol dm^{-3}

_____

to convert pH into
hydrogen ion concentration

$$[H^+_{(aq)}] = \text{antilog}(-pH)$$

_____

IONIC PRODUCT OF WATER K_w = $[H^+_{(aq)}][OH^-_{(aq)}]$ mol^2 dm^{-6}

= 1×10^{-14} mol^2 dm^{-6} (at 25°C)

Autoionization of H_2O

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Pairs   1   2   2   1

| acid | base | acid | base |

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

   # 1   # 2

| acid | base | Conjugate acid of H_2O #2 | Conjugate base of H_2O #1 |

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

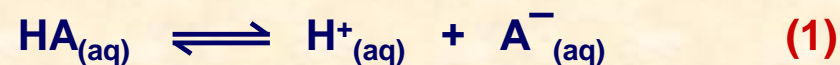| Conjugate acid of OH^- | Conjugate base of H_3O^+ | acid | base |
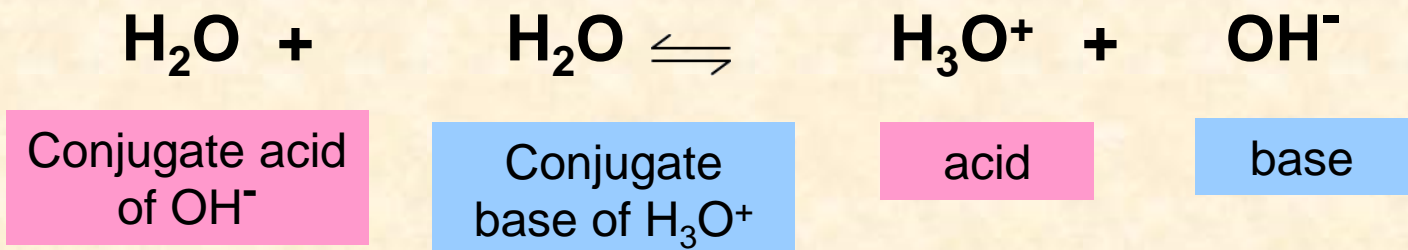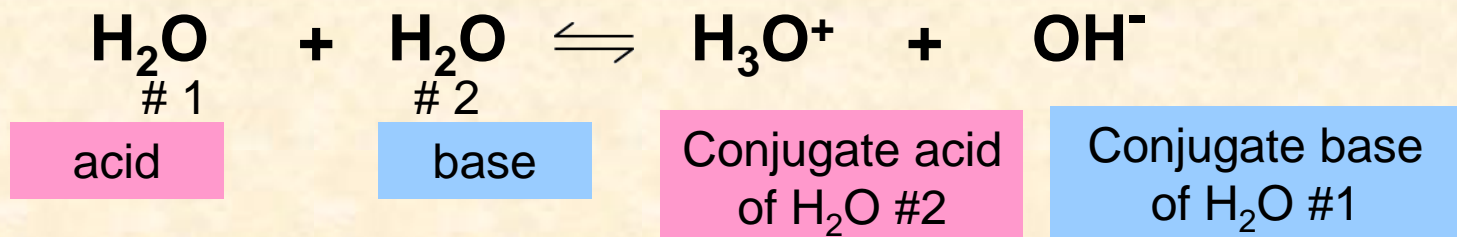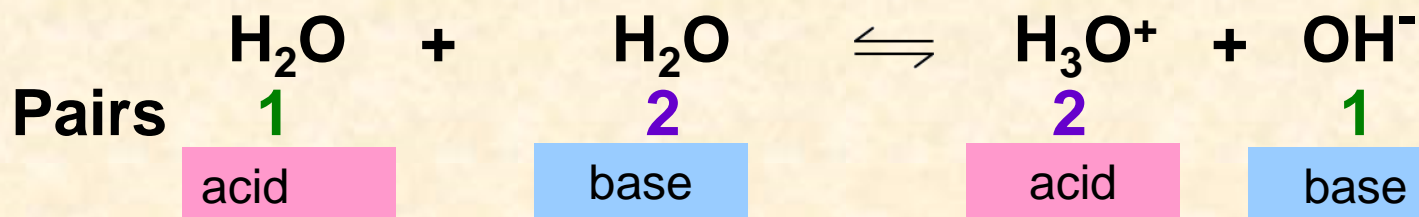
Amphoterism - an ion or molecule can act as an acid or base depending upon the reaction conditions

Calculating pH - weak acids

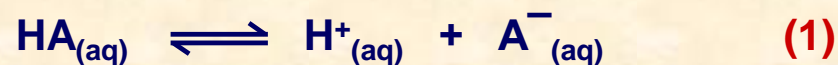**A weak acid is one which only partially dissociates in aqueous solution**

A weak acid, HA, dissociates as follows

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \qquad (1)$$

Calculating pH - weak acids

A weak acid is one which only partially dissociates in aqueous solution

A weak acid, HA, dissociates as follows

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \qquad (1)$$

Applying the Equilibrium Law

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} \quad mol\ dm^{-3} \qquad (2)$$

The ions are formed in equal amounts, so

$$[H^+_{(aq)}] = [A^-_{(aq)}]$$

therefore

$$K_a = \frac{[H^+_{(aq)}]^2}{[HA_{(aq)}]} \qquad (3)$$

Rearranging **(3)** gives

$$[H^+_{(aq)}]^2 = [HA_{(aq)}]\ K_a$$

therefore

$$[H^+_{(aq)}] = \sqrt{[HA_{(aq)}]\ K_a}$$

$$pH = -\log\ [H^+_{(aq)}]$$

Calculating pH - weak acids

Calculate the pH of a weak acid HX of concentration 0.1M (K_a = 4×10^{-5} mol dm^{-3})

HX dissociates as follows
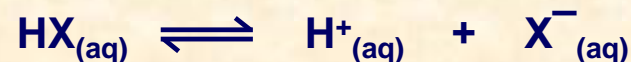
$$HX_{(aq)} \rightleftharpoons H^+_{(aq)} + X^-_{(aq)}$$

Dissociation constant for a weak acid

$$K_a = \frac{[H^+_{(aq)}] [X^-_{(aq)}]}{[HX_{(aq)}]} \text{ mol dm}^{-3}$$

Substitute for X$^-$ as ions are formed in equal amounts and the rearrange equation

$$[H^+_{(aq)}] = \sqrt{[HX_{(aq)}] K_a} \text{ mol dm}^{-3}$$

ASSUMPTION

HA is a weak acid so it will not have dissociated very much. You can assume that its equilibrium concentration is approximately that of the original concentration

$$[H^+_{(aq)}] = \sqrt{0.1 \times 4 \times 10^{-5}} \text{ mol dm}^{-3}$$

$$= \sqrt{4.00 \times 10^{-6}} \text{ mol dm}^{-3}$$

$$= 2.00 \times 10^{-3} \text{ mol dm}^{-3}$$

ANSWER   pH = - log $[H^+_{(aq)}]$ = 2.699

Format for solving problems of weak acids using an equilibrium table

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

	HA(aq)	H$^+$(aq)	A$^-$(aq)
Initial concentration (M):			
Change in concentration (M):			
Equilibrium concentration (M):			

- Fill in initial concentrations
- Determine concentration changes in terms of x
- Determine equilibrium concentrations in terms of initial concentrations (C_i) and x
- Substitute into the K_a expression and solve for x

Percent Ionization

- Another way to measure the strength of an acid is to determine the percentage of acid molecules that ionize when dissolved in water; this is called the **percent ionization**.

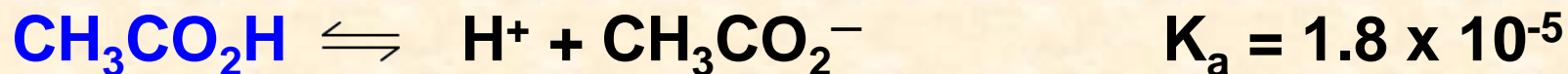 – The higher the percent ionization, the stronger the acid.

$$\text{Percent Ionization} = \frac{\text{molarity of ionized acid}}{\text{initial molarity of acid}} \times 100\%$$

- Because $[\text{ionized acid}]_{equil} = [H_3O^+]_{equil}$

$$\text{Percent Ionization} = \frac{[H_3O^+]_{equil}}{[HA]_{init}} \times 100\%$$

Problem: (a) Calculate pH and (b) the fraction of CH_3CO_2H ionized at equilibrium. The concentration of CH_3CO_2H is 1 M (initial, or total). The K_a for acetic acid is 1.8×10^{-5}

Estimate major species in solution **CH_3CO_2H** (a weak acid) and **H_2O.**

$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$ **$K_a = 1.8 \times 10^{-5}$**

$H_2O \rightleftharpoons H^+ + OH^-$ **$K_w = 1.0 \times 10^{-14}$**

Problem: (a) Calculate pH and (b) the fraction of CH_3CO_2H ionized at equilibrium.

$$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$$

	CH_3CO_2H	H^+	$CH_3CO_2^-$
Initial	1.0M	~ 0	0
Equilibrium	1.0 – x	x	x

Problem: (a) Calculate pH and (b) the fraction of CH_3CO_2H ionized at equilibrium.

$$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$$

Initial	**1.0M**	**~ 0**	**0**
Equilibrium	**1.0 – x**	**x**	**x**

$$K_a = \frac{(x)(x)}{(1.0 - x)}$$

assume $x \ll 1.0$

$$K_a = \frac{(x)(x)}{(1.0)}$$

$$K_a = 1.8x10^{-5} = \frac{(x)(x)}{(1.0)}$$

$$x = \sqrt{1.8x10^{-5}}$$

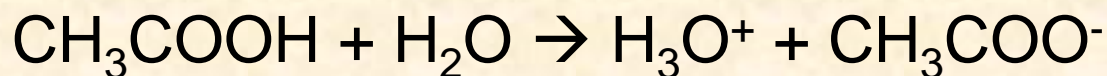$$x = 4.3x10^{-3}$$

$$pH = -\log[4.3x10^{-3}] = 2.3$$

The pH of 0.1M CH_3COOH is 2.87. What is the value of the acid dissociation constant, K_a?

$pH = -log\ [H_3O^+]$ $= 2.87$ $\Rightarrow [H_3O^+] = 1.35 \times 10^{-3}$

$$CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$$

$$K_a = \frac{[H_3O+][CH_3COO^-]}{[CH_3COOH]}$$

	CH_3COOH	H_3O^+	CH_3COO^-
Initial conc	0.1	0	0
Equil. Conc	0.1 – x	x	x

$$K_a = \frac{[1.35\times10^{-3}][1.35\times10^{-3}]}{[0.1]}$$

$$K_a = 1.8 \times 10^{-5}$$

Calculate the pH at 25°C of a 0.18 M solution of a weak acid that has $K_a = 9.2 \times 10^{-6}$.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

	HA(aq)	H$^+$(aq)	A$^-$(aq)
Initial concentration (M):	0.18	0	0
Change in concentration (M):	$-x$	$+x$	$+x$
Equilibrium concentration (M):	$.18 - x$	x	x

$$9.2 \times 10^{-6} = \frac{(x)(x)}{0.18 \ M - x}$$

Use the approximation since K_a is small compared to C_i.

$$9.2 \times 10^{-6} = \frac{x^2}{0.18 \ M}$$

$$9.2 \times 10^{-6} = \frac{x^2}{0.18 \ M}$$
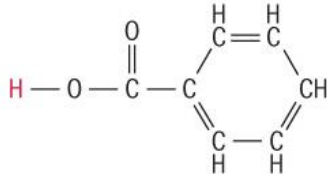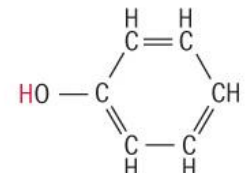
$$1.3 \times 10^{-3} \ M = x$$

Check the approximation:

$$\frac{1.3 \times 10^{-3} \ M}{0.18 \ M} \, x100 = 0.72\%$$

$$0.72\% < 5\%$$

Approximation is valid.

$$pH = -\log(1.3 \times 10^{-3} \ M) = 2.89$$

Acid ionization constants of some monoprotic weak acids at 25 °C

Acid	Formula	Structural Formula	Ionization Reaction	K_a
Chlorous acid	$HClO_2$	$H-O-Cl=O$	$HClO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + ClO_2^-(aq)$	1.1×10^{-2}
Nitrous acid	HNO_2	$H-O-N=O$	$HNO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + NO_2^-(aq)$	4.6×10^{-4}
Hydrofluoric acid	HF	$H-F$	$HF(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + F^-(aq)$	3.5×10^{-4}
Formic acid	$HCHO_2$	$H-O-\overset{\overset{O}{\|\|}}{C}-H$	$HCHO_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + CHO_2^-(aq)$	1.8×10^{-4}
Benzoic acid	$HC_7H_5O_2$		$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.5×10^{-5}
Acetic acid	$HC_2H_3O_2$	$H-O-\overset{\overset{O}{\|\|}}{C}-CH_3$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous acid	$HClO$	$H-O-Cl$	$HClO(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + ClO^-(aq)$	2.9×10^{-8}
Hydrocyanic acid	HCN	$H-C\equiv N$	$HCN(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol	HC_6H_5O		$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons$ $H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

Weak Bases and Base Ionization Constants

To define the base ionization constant K_b we write:

$B(aq) + H_2O(l) \leftrightarrow HB^+(aq) + OH^-(aq)$
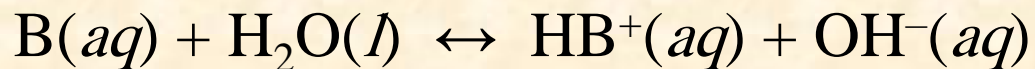
$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

where HB+ is the conjugate acid of base B

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

pK

- A way of expressing the strength of an acid or base is **pK.**

- p$K_a = -\log(K_a)$, $K_a = 10^{-pKa}$

- p$K_b = -\log(K_b)$, $K_b = 10^{-pKb}$

- **The stronger the acid, the smaller the pK_a.**
  - Larger K_a = smaller pK_a
  - Because it is the –log

- **The stronger the base, the smaller the pK_b.**
  - Larger K_b = smaller pK_b

Ionization constants of some weak bases at 25 °C

Name of base	Formula	Structure	K_b
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\ddot{N}-H$ with H below	5.6×10^{-4}
Methylamine	CH_3NH_2	$CH_3-\ddot{N}-H$ with H below	4.4×10^{-4}
Ammonia	NH_3	$H-\ddot{N}-H$ with H below	1.8×10^{-5}
Pyridine	C_5H_5N	ring with $N:$	1.7×10^{-9}
Aniline	$C_6H_5NH_2$	ring $-\ddot{N}-H$ with H below	3.8×10^{-10}
Urea	H_2NCONH_2	$H-\ddot{N}-\overset{\overset{O}{\|\|}}{C}-\ddot{N}-H$ with H below each N	1.5×10^{-14}

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

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

$$K_b = 1.8 \times 10^{-5}$$

Step 1. Define equilibrium concentrations.

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial	0.010	0	0
change	-x	+x	+x
equilib	0.010 - x	x	x

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
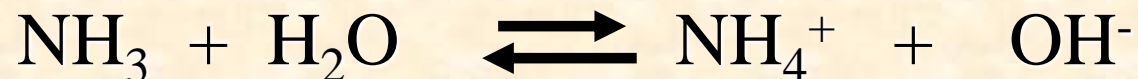
$$K_b = 1.8 \times 10^{-5}$$

Step 2. Solve the equilibrium expression

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.010 - x}$$

Assume x is small ($100 \cdot K_b < C_o$), so

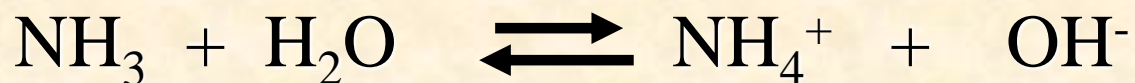$$x = [OH^-] = [NH_4^+] = 4.2 \times 10^{-4} \text{ M}$$

and $[NH_3] = 0.010 - 4.2 \times 10^{-4} = 0.010$ M

The approximation is valid !

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

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

$$K_b = 1.8 \times 10^{-5}$$

Step 3. Calculate pH

$[OH^-] = 4.2 \times 10^{-4}$ M

so pOH = - log $[OH^-]$ = 3.37

Because pH + pOH = 14

pH = 10.63

Calculate the pH at 25ºC of a 0.16 M solution of a weak base with a Kb of 2.9×10^{-11}.

Solution: Since K_b is so small we can make the math simple.

	B (+ H₂O) ⇌	HB⁺ +	OH⁻
Initial	0.16	0	0
Change	-x	+x	+x
Equilibrium	0.16 - x	x	x

$$K_b = \frac{[HB^+][OH^-]}{[B]} = \frac{x^2}{0.16 - x} \approx \frac{x^2}{0.16}$$

which gives $x^2 = (0.16)K_b$ or $x = 2.15 \times 10^{-6} \Rightarrow pOH = 5.67$
Therefore pH = 14 − 5.67 = 8.33

Using pH to Determine K_b
This is very similar the weak acid calculation

e.g., Determine the K_b of a weak base if a 0.35 M solution of the base has a pH of 11.84 at 25°C.

Solution:

pOH = 14 − pH = 2.16 $\Rightarrow$ [OH$^-$] = $10^{-2.16}$ = 6.92 x 10^{-3}

	B (+ H_2O) $\rightleftharpoons$	HB$^+$ +	OH$^-$
Initial	0.35	0	0
Change	- 6.92 x 10^{-3}	+ 6.92 x 10^{-3}	+ 6.92 x 10^{-3}
Equilibrium	0.3431	6.92 x 10^{-3}	6.92 x 10^{-3}

$$K_b = \frac{(6.92 \times 10^{-3})^2}{0.3431} = 1.4 \times 10^{-4}$$

Determine the K_b of a weak base if a 0.50 M solution of the base has a pH of 9.59 at 25°C.
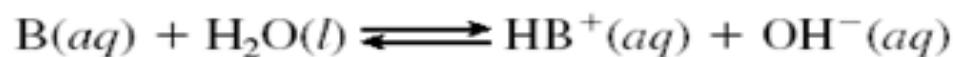
$$pH + pOH = 14.00$$

$$9.59 + pOH = 14.00$$

$$pOH = 4.41$$

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

$$[OH^-] = 10^{-4.41} = 3.89 \text{ x } 10^{-5} M$$

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

Initial concentration (M):	0.050 M		
Change in concentration (M):	-3.89×10^{-5} M	$+3.89 \times 10^{-5}$ M	$+3.89 \times 10^{-5}$ M
Equilibrium concentration (M):	0.050 M*	3.89×10^{-5} M	3.89×10^{-5} M

$$* \; 0.050 \, M - (3.89 \times 10^{-5} \, M) \approx 0.050 \, M$$

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

$$K_b = \frac{(3.89 \times 10^{-5} \, M)2}{0.50 \, M} = 3.0 \times 10^{-9}$$

Equilibria Involving Weak Acids and Bases

1. The pH of a 0.10 M nicotinic acid solution is 2.92. Calculate K_a and the % ionization.

$$1.4 \times 10^{-5} \quad 1.2\%$$

2. A solution of propionic acid, CH_3CH_2COOH, is 0.20 M. $K_a = 1.3 \times 10^{-5}$. Calculate the pH and % ionization.

$$2.79 \quad 0.80\%$$

3. A solution of hydrazine, N_2H_4, is 0.025 M. $K_b = 8.5 \times 10^{-5}$. Calculate the pH and % ionization.

$$11.15 \quad 5.6\%$$