**Acids and Bases II**

**Definitions**
- **Arrhenius**: \( \text{H}^+ + \text{OH}^- \Leftrightarrow \text{H}_2\text{O} \)
- **Brauned - Lowry**: \( \text{H}^+ + \text{A}^- \Leftrightarrow \text{HA} \)
- **Lewis**: \( \text{A}^+ + \text{B}^+ \Leftrightarrow \text{A}^+ \text{B}^+ \)

**Conjugate Acids and Bases**

**Autoionisation of Water**
\[ \text{H}_2\text{O} \Leftrightarrow \text{H}^+ + \text{OH}^- \]
\[ K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ \text{C} \]

**The ‘p’ Convention**
- \( \text{pH} = -\log_{10}[\text{H}^+] \Rightarrow [\text{H}^+] = 10^{-\text{pH}} \)
- \( \text{pH} + \text{pOH} = \text{pK}_w = 14 \text{ at } 25^\circ \text{C} \)

**Temperature Dependence of pH**

**Strong Acids and Bases**
- (HCl, HBr, HI, H\(_2\)SO\(_4\), HNO\(_3\), HClO\(_4\)) completely ionised
- most electronegative elements (except HF)

**Strong Bases**
- (groups 1 & 2 – NaOH, …), least electronegative, also completely ionised (except Be)

**Weak Acids and Bases**
- Any acid or base not on the list of strong ones is weak - it does not completely ionise in water.
  - e.g., acetic (ethanoic) acid, CH\(_3\)CO\(_2\)H (HA for short):
    \[ \text{HA} \Leftrightarrow \text{H}^+ + \text{A}^- \]
  - Acid dissociation constant
  \[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]
  - The more positive the \( pK_a \), the weaker the acid (and the stronger the conjugate base)

**Example**
- Find the pH of 0.1 M acetic acid (CH\(_3\)COOH, HA for short)
  DATA: \( pK_a = 4.7, \quad K_a = 10^{-4.7} \)
  \( K_a \) is very small, reaction favours reactant (more HA than H\(^+\))
  \( \Rightarrow \) not all HA ionised \( \Rightarrow [\text{H}^+] < 0.1 \Rightarrow \text{pH} > 1 \)
Example cont’d

- Find % ionisation of 0.50 M HF ($pK_a = 3.1$)

Example

- The $pK_a$ of formic acid (HCO$_2$H) is 4.1; find the pH of $10^{-2}$ M NaHCO$_2$ – (check: it will be basic, expect pH > 7)

Weak Bases

Ionisation of a weak base:

\[
\text{NH}_3 (aq) + H_2O (l) \rightleftharpoons \text{NH}_4^+ (aq) + OH^- (aq)
\]

\[
K_c = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3] [\text{H}_2\text{O}]} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]}
\]

- Give equilibrium constant special name - Base ionisation constant, $K_b$:

\[
K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]}
\]

Can calculate pOH and hence pH, given $K_b$

Relationship between $pK_a$ and $pK_b$

For conjugate systems (Bronsted-Lowry acid-base pairs)

As acid (HA): \(HA \rightleftharpoons H^+ + A^- \quad K_a = \frac{[H^+][A^-]}{[HA]}\)

As conjugate base (A$^-$):

\(A^- + H_2O \rightleftharpoons HA + OH^- \quad K_b = \frac{[HA][OH^-]}{[A^-]}\)

\[
K_a \times K_b = \frac{[H^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H^+][OH^-] = K_w = 10^{-14}
\]

\[
pK_a + pK_b = 14
\]

Hence only need values of $pK_a$, since $pK_b = 14 - pK_a$

Relative Strengths Of Acids And Bases

- Strongest acids lose their protons easily
  - more polarised the H–X bond the greater the acid strength
  - the larger the X, the weaker the bond, the stronger the acid
- Strongest bases hold on to protons strongly
- An acid-base equilibrium always lies in the direction of the weaker acid and weaker base

\[
\text{HCN} + \text{CH}_3\text{COO}^- \rightleftharpoons \text{CH}_3\text{COOH} + \text{CN}^-
\]

weaker acid & weaker base $\leftrightarrow$ stronger acid & stronger base


Indicators

- Indicator: weak acid $\leftrightarrow$ base
  - each form has a different colour
  - delocalised electrons change energies with protonation
- The pH at which acid $\rightarrow$ base depends on the $pK_a$ of the indicator

\[
\text{e.g. phenol red}
\]

\[
\text{Yellow} \quad \text{Red} \quad \text{pH} \quad 5.5\rightarrow2.5
\]

Silberberg Fig 19.4 p 815

Indicators

- Crystal violet
- Thymol blue
- 2,4-Dinitrophenol blue
- Bromocresol green
- Methyl red
- Alizarin
- Bromthymol blue
- Phenol red
- Phenolphthalein
- Alizarin yellow R