8. Acids and Bases

8.11
Definitions of Acids and Bases

- Bronsted-Lowry acid - Proton Donor \([H^+]\)
- Bronsted-Lowry base - Proton Acceptor \([H^{+}]\)

\[
\text{e.g. } \text{HCl}(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)
\]

The difference between a conjugate base/acid and acid/base is the presence of a \(H^+\) ion.

- Lewis Acid: A lone electron pair acceptor
- Lewis Base: A lone electron pair donor

Lewis theory:
- Includes B.O. acids and alkalis; but excludes those that have a full valence shell, the \(H^+\) can be replaced with an atom with an empty orbital.
- Always involves formation of covalent bonds.
- See the \(\text{NH}_3\) reaction.

An amphiprotic substance is one that can act as a Lewis Acid or Base.

E.g. \(\text{H}_2\text{O}\) - Oxygen has 2 lone pairs [can function as a Lewis base] and has 2 hydrogen atoms attached that can be lost as \(H^+\) ions, hence \(\text{H}_2\text{O}\) would act as a proton donor.

Reactions:
1. \(\text{Acid} + \text{Carbonate} \rightarrow \text{Salt (carbonate)} + \text{Water} + \text{Carbon dioxide}\)
2. \(\text{Acid} + \text{ammonia base} \rightarrow \text{ammonia gas} + \text{Salt}\)
3. \(\text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water} \hspace{5mm} \text{(Cleavage of except NaOH)} \rightarrow \text{NH}_3\text{(aq)} + \text{HCl(aq)} \rightarrow \text{NH}_4\text{Cl(aq)}\)
4. \(\text{Acid} + \text{Metal} \rightarrow \text{Salt} + \text{Hydrogen gas}\)
5. \(\text{Acid} + \text{metal oxide} \rightarrow \text{Salt} + \text{Water} \hspace{5mm} \text{[\(-\Delta H\)]}\)
6. \(\text{Acid} + \text{hydrogen carbonate} \rightarrow \text{Salt} + \text{Water} + \text{CO}_2\)
Strong vs Weak Acid/Base:

- Determined by the extent to which they ionise in solution.
- We can determine this by determining the equilibrium of the reaction, if it lies to the reactants - the acid/base has not fully ionised, ergo it is a weak acid/base.
- There are certain acids and bases whose reactions go to completion:
  - Strong Acids [weaker base]:
    - HCl
    - HNO₃
    - H₂SO₄ [first ionisation]
  - Weak Acids [stronger base]:
    - H₃PO₄
    - CH₃COOH or any organic acids
    - H₂CO₃
  - Strong Bases [weaker acid]:
    - LiOH
    - NaOH
    - KOH and Ba₂(OH)₂
  - Weak Bases [stronger acid]:
    - NH₃
    - ethylene or any amines

Experimental Methods:

1) Electrical Conductivity:
- Higher concentration of mobile ions begets a larger number of charged particles available to carry a charge throughout a solution (for strong base/acids).
- Use electrodes + ammeter → greater electrical conductivity.
- If asked, test conductivity and Motors is a better conductor than the other.

2) Rate of Reaction:
- $\Delta$ [H⁺] / [OH⁻], more collisions per unit time per unit volume, increases the rate. This matches that of a strong acid/base (as $\Delta$ [H⁺]²)
- Use a reaction with a strong metal or acid (e.g., Li salts, strong acid reaction is more vigorous).

3) pH:
- $-\log_{10}[H^+]$: conc of H⁺ ions in mol/dm³.
- The lower this number, the more acidic something is.
- $\Delta$ pH measurement = [H⁺] → delphinium strength.

X: Protonic Acids:
- X = number of protons that can be lost.
- Ionises in X steps and % ionisation decreases with each step because negative charge builds on the conjugate base, more energy needed to remove a H⁺ from it.

E.g.:

- $\text{H}_2\text{SO}_4 + (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{HSO}_4^- (\text{aq})$
- $\text{HSO}_4^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{SO}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$

[Note: The diagram refers to a visual aid in the document, which is not transcribed.]
**pH calculations**

\[ \text{pH (potential hydrogen)} = - \log_{10} [H^+] \text{ and } [H^+] = 10^{-\text{pH}} \]

**Example Question**

1. 10 ml of \( H_2SO_4 \) \([0.1 \text{ mol/dm}^3]\) was added to 5 ml of 0.1 \text{ mol/dm}^3 \text{ NaOH}. What is the pH of the final solution?

- Write the equation
  \[ \text{H}_2\text{SO}_4 \text{(aq)} + 2\text{NaOH} \text{(aq)} \rightarrow \text{Na}_2\text{SO}_4 \text{(aq)} + 2\text{H}_2\text{O} \]

- Determine the limiting reagent:
  
  Moles of \( H_2SO_4 \text{ available} = \frac{10}{1000} \times 0.1 = 0.001 \]
  
  Moles of \( \text{NaOH available} = \frac{5}{1000} \times 0.1 = 0.0005 \): this is the limiting reagent as 0.00025 moles of \( H_2SO_4 \) need to react with it.

- Find the moles of the excess solution left
  \[ \frac{0.0005}{2} = 0.00025 \text{ moles of } H_2SO_4 \text{ needed} \]

- 0.001 - 0.00025 = 0.00075 moles.

- Depending on the protic nature of the solution, find the moles of \( H^+ \)

  \( \text{As this is } H_2SO_4, 0.00075 \times 2 = 0.0015 \text{ mole} \)

- \( \div \) this by total volume of solutions \([\text{VIP}]\)

  \[ \frac{0.0015 \text{ moles}}{0.015 \text{ dm}^3} = 0.1 \text{ mol/dm}^3 \]

6. **Apply pH equation**

   \[ - \log_{10} [0.1] = 1 \]

   \[ pOH = - \log_{10} [OH^-] \]

   \[ k_w = k_c \frac{[H_2O]}{[H_2O]} \]

   \[ k_w = 1 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6} \text{ at } 298 \text{ K} \]

   \[ k_w \uparrow, T \downarrow \text{ because as } T \uparrow, k_c \downarrow \]

   \[ \text{As } T \uparrow, [H^+] \text{ and } [OH^-] \text{ decrease, } [H_2O] \text{ is constant, at } 55 \text{ K} \]

   \[ \downarrow \text{ pH and } \downarrow pOH \]

   \[ - \left[ \log_{10} [H^+] + \log_{10} [OH^-] \right] = 14 \text{ at } 298 \text{ K} \]

   \[ k_w = \left[ H^+ \right][OH^-] \]

   \[ pK_w = - \log_{10} [k_w] \]
And on pH and neutrality.

Note the equation \( 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \)

The \([\text{OH}^-] = [\text{H}^+]\) is 1:1.

Even though pH would change with T, the \([\text{OH}^-] : [\text{H}^+]\) stays at 1:1, this makes a solution

neutral.

\[ \text{FOR NEUTRALITY} \implies [\text{H}^+] = [\text{OH}^-] \]

\[ \text{FOR ACIDITY} \implies [\text{H}^+] > [\text{OH}^-] \]

\[ \text{FOR BASIC NATURE} \implies [\text{H}^+] < [\text{OH}^-] \]

\[ \text{CSEE FINAL PAGE} \]

\(k_a\) (acid dissociation constant) - Expression of the strength of weak acid/base

used for weak acids.

For the equation \( \text{HA} \rightleftharpoons A^- + \text{H}^+ \)

\[ \text{H}_2\text{O} + \text{HA} \rightleftharpoons \text{H}_3\text{O}^+ + A^- \]

\[ k_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

but, we assume \([\text{H}_2\text{O}]\) is constant so at 55 M

\[ k_c [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = k_a \]

\(p_{k_a} = -\log_{10}(k_a)\)

\(p_{k_b} = -\log_{10}(k_b)\)

another assumption we make is that \(\text{HA}J\) does not change, as we know that this is a weak acid

\(k_b\) is identical (-ish)

For 2) \( B + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^- \)

\[ k_b = \frac{[\text{BH}^+][\text{OH}^-]}{[B]} \]

the same story unfolds.

\[ \text{Note: if we flip 1 or 2 around} \]

1' \( \rightarrow \text{A}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{O} + \text{HA} \rightarrow \text{base} \) [base is A^-]

2' \( \rightarrow \text{BH}^+ + \text{OH}^- \rightleftharpoons B + \text{H}_2\text{O} \rightarrow \text{acid} \) [acid is OH^-]

so, their \(k_a / k_b\) become \(k_b / k_a\), with the reciprocal of the old ones.

\[ E.g. 1' \rightarrow \frac{[\text{HA}]}{[\text{H}_3\text{O}^+][\text{A}^-]} \]

\[ \text{monoprotic} \]

Example: The pH of a 0.020 mol dm\(^{-3}\) solution of weak acid is 3.9. Find \(k_a\).

Step 1: Write equation for \(k_a\) - \(\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+]^2}{[\text{HA}]} = k_a \)

\[ k_a = \frac{(10^{-3.9})^2}{0.02} \]

\[ k_a = \]
Buffer solutions

Definition: a solution that resists changes in pH when small amounts of acids or alkalis are added.

Consists of a strong acid/base with its strong conjugate base.

2 Ways of formation:

1) weak acid/base + salt containing conjugate acid/base
   - e.g. \[ \text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^- \]
   - \[ \text{NaCH}_3\text{COO} \text{(aq)} \rightleftharpoons \text{Na}^+ + \text{CH}_3\text{COO}^- \]

2) weak acid/base + strong acid/base holding conjugate base/acid in limited quantity.
   - e.g. \[ \text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{NaCH}_3\text{COO}^- + \text{H}_2\text{O} \]
   - \[ A = \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \]
   - \[ B = \text{NaCH}_3\text{COO} \rightarrow \text{Na}^+ + \text{CH}_3\text{COO}^- \]

Resisting Changes [Acidic Buffers]
Consider the system above.

1) Addition of H⁺ ions \[ \rightarrow \] equilibrium of A shifts to the left, using up the added H⁺ to produce additional CH₃COOH, hence [H⁺] does not change (for calc.) reacts with CH₃COOH to produce CH₃COOH

2) Addition of OH⁻ \[ \rightarrow \] reacts with CH₃COOH to produce H₂O and CH₃COO⁻, no change in [H⁺], by consuming added OH⁻

Resisting Change [Basic Buffers]

- e.g. \[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{NH}_4^+ \]

1) Addition of H⁺ \[ \rightarrow \] react with OH⁻ to form H₂O, enzyme (H₂O) stays constant

2) Addition of OH⁻ \[ \rightarrow \] shift equil to left in order to consume added OH⁻, (H⁺) stays

- \[ \text{OH}^- \] reacts with the H⁺ NH₄⁺ to produce NH₃ and H₂O \[ \rightarrow \] (H⁺) constant

Why do we add more of the conjugate?
- we need high concs of the conjugate base/acid is used in maintaining pH
- weak base/acid only weakly, not enough of conjugate
- hence ionic salt holding it added so it fully dissociate, allowing for sufficient quantity

Factors Affecting Buffers

- Dilution, pH change, buffering capacity: amount of acid/base that can be absorbed
- Temp: affects \[ K_a \] and \[ K_b \], hence affects pH, \[ \text{pH} \] to have constant temp in blood transfusions - due to blood buffers
Why don't we use strong bases?

* e.g. HCl → Cl⁻ + H⁺

No equilibrium to be shifted when H⁺ added, hence CH⁺↑, ↓ pH

Addition of OH⁻ consumes H⁺, hence CH₂⁺↑, ↑ pH

**Henderson-Hasselbalch Equation**

\[ \text{pH} = \text{pKa} - \log \frac{[\text{acid}]}{[\text{salt}]} \]

\[ \text{pOH} = \text{pKb} - \log \frac{[\text{base}]}{[\text{salt}]} \]

**Assumptions**

1) [acid/base] initial = [acid/base] final - assumes weak dissociation zero

2) salt fully dissociated

if [salt] = [acid],

\[ \text{pH} = \text{pKa} \]

\[ \text{pOH} = \text{pKb} \]

because \( \text{pKa} - \log[1] \)

\[ \text{pKb} = \text{pKb} - \frac{[\text{H}_2\text{O}]}{[\text{base}]} \]

**Example**

A buffer has 0.1 mol of CH₃COOH and 0.13 mol of Na CH₃COO in 1 dm³ of solution.

(a) pH of buffer?

(b) pH when 0.02 mol of KOH added?

(c) pH when 0.03 mol of HNO₃ added?

\[ \text{pH} = \text{pKa} - \log \frac{0.10}{0.13} \]

\[ \text{pH} = 4.76 - \log \frac{0.10}{0.13} \]

\[ \text{pH} = 4.87 \]

(b) KOH + CH₃COOH → K⁺ + CH₃COO⁻ + H₂O

I 0.02 0.10 0.13
E 0 0.08 0.15

Note: consideration of c. base and acid

\[ \text{pH} = 4.76 - \log \frac{0.08}{0.13} \]

\[ \text{pH} = 5.03 \]

(c) H⁺ + NO₃⁻ + CH₃COO⁻ → CH₃COOH + NO₃⁻

I 0.01 0.02 0.13 0.10
E 0 0.11 0.12

\[ \text{pH} = 4.76 - \log \frac{0.12}{0.11} \]

\[ \text{pH} = 4.72 \]


pH curves

- with position and volume of acid/base added on the x-axis

Shape 1 (strong acid + strong base)

- Initial pH is 14 - pOH of NaOH
- High rate of decrease and large vertical range because strong acid + strong base
- Low $[H^+]$, small addition of $[OH^-]$ has a large effect on pH given that $\text{pH} \_\text{y}$ is a logarithmic scale

- Equivalence point
  - Molar of Acid = Molar of Base
  - neutral here, as salt is neutral
  - at pH 7
  - can find equivalence volume and pH

Shape 2 (weak acid + strong base)

- Buffer region

- Equivalence point: basic, as salt produced will be basic

Volume of HCl added to NaOH (cm$^3$)

Determined by strength of acid or base depending on x-axis. Use either pK$\alpha$, pK$b$ or full dissociation on to determine.

2) Buffer Region: Consider the salt of $\text{CH}_3\text{COOH} + \text{NaOH}$, $\text{NaCH}_3\text{COO}$. If dissociates into Na$^+$ and $\text{CH}_3\text{COO}^-$, it is a weak conjugate acid. If more H$^+$ is added, it simply reacts with the added H$^+$ to produce $\text{CH}_3\text{COOH}$, consuming added H$^+$ and resisting change.

Buffered system formed by CH$_3$COOH, Na$_2$CO$_3$, H$_2$CO$_3$ at pH 7.
3. Equivalence Point: for Still when moles of acid = moles of base. However, the salt produced here would be basic as \( \text{NaCH}_3\text{COO} \rightarrow \text{Na}^+ + \text{CH}_3\text{COO}^- \). The \( \text{CH}_3\text{COO}^- \) forms a deprotonated covalent bond with a surrounding \( H^+ \), \( \downarrow \text{[H}^+ \text{]} \). \( \uparrow \) pH at equivalence. Say that salt was formed from weak acid + strong base, hence basic salt.

**Shape 2: Weak base + Strong Acid [with worked calculation]**

Consider the titration of \( \text{NH}_3 \) (aq) with \( \text{HCl} \) (aq).

![Diagram of pH changes during titration]

- Volume of \( 0.1 \text{mol dm}^{-3} \ \text{HCl} \) added to \( 0.1 \text{mol dm}^{-3} \ \text{NH}_3 \) 25 cm³

Calculating \( x,y \):

\[
V = 25 \text{cm}^3 \\
C = 0.1 \text{ mol dm}^{-3}
\]

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

\[
\text{K}_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 10^{-4.75} \\
\]

\[
\frac{10^{-4.75}}{0.1} = [\text{OH}^-]^2 \\
\]

\[
[\text{OH}^-] = 0.0013335 \\
p\text{OH}^- = 2.875 \\
p\text{H}^- = 14 - p\text{OH}^- = 11.1 \ (3.5.5)
\]

**Buffer Region**

Ionic salt produced by \( \text{NH}_3 + \text{HCl} \) (\( \text{NH}_4\text{Cl} \)), dissociates into \( \text{NH}_4^+ \) and \( \text{Cl}^- \).

- We have a system in place, once enough \( \text{NH}_4^+ \) is produced, that can act as a buffer

Thus, adding more \( \text{HCl} \) results in limited pH change as added \( H^+ \) is reacted with \( \text{NH}_3 \) to produce \( \text{NH}_4^+ \), consuming added \( H^+ \). This can be proven by the Henderson-Hasselbach Equation.
$Y_3$

- Realistically, $Y_3$ should be $< 7$. This is because NH$_4$Cl is acidic in solution.

**Proof**

\[
\text{NH}_4\text{Cl} (aq) \rightarrow \text{NH}_4^+ (aq) + \text{Cl}^-(aq)
\]

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+
\]

[Correction: Cation hydrolysis, added $\text{H}_3\text{O}^+$, $\downarrow \text{pH}$]

**Half-Neutralisation**

- For pH = PkJ or PkOH = Pk$b$, $[\text{base}/\text{acid}] = [\text{concentration of salt}]$. This can happen when half of the solution being hydrolysed is neutralised, because...

**Calculation**

\[
\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}
\]

Init: 0.00125 0.00125 0

Calc: -0.00125 -0.00125 + 0.00125

End: 0.00125 0 0.00125

pH at this point = pk$b - \log \left( \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3]} \right)

pOH = pk$b = \log \left( \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3]} \right) - 14

= 4.75

pH = 9.25 at $x = 12.5$

**Weak Acid + Weak Base** (Curve 4)

- Low vertical range of equivalence point = hard to calculate.

- Equivalence at pH < 7 → a near equal collision of the salt dissociate to the same extent, hence COH$_3$ = CH$_3$COOH.

- Volume: 35

- $\text{NH}_3$ added to CH$_3$COOH.
**Polyprotic Acids**

\[ \text{H}_2\text{SO}_4 + \text{NaOH} \rightarrow \text{H}_2\text{SO}_4 \text{aq} \rightarrow \text{H}^+ + \text{HSO}_4^- \text{aq} \]

2 equivalence points
- all of \(\text{H}_2\text{SO}_4\) used
- all of \(\text{NaOH}\) fin

\[ \rightarrow \text{NOT ASSESSED} \]

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**Strong vs Weak (Acids)**

- lower equivalence \(\rightarrow\) higher equivalence
- lower start \(\rightarrow\) higher start
- high vertical range of equiv \(\rightarrow\) low vertical range of equivalence

**Salt (consider conjugate)**

- \(\text{s}\.a + \text{s}\.b \rightarrow \text{neutral salt} + \text{water}\)
- \(\text{w}\.a + \text{s}\.b \rightarrow \text{basic salt} + \text{water}\)
- \(\text{s}\.a + \text{w}\.b \rightarrow \text{acidic salt} + \text{water}\)
- \(\text{w}\.a + \text{w}\.b \rightarrow \text{neutral salt} + \text{water}\)

**Indicators**

- Definition: An indicator is a weak acid or base that changes colour when it becomes dissociated
- point at which it changes color = end point
- Equivalence point must match end point; endpoint must be within vertical range of the equivalent
- Special: Especially considered with weak acids/bases as their vertical range is smaller
- Usually weak acids or bases

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**Acidic Indicator**

- Both acidic and basic indicators rely on equilibrium
- \(\text{e.g. } \text{H}\text{Ind} \rightleftharpoons \text{H}^+ + \text{Ind}^-\)

- \(\text{H}^+\) concentration increases, thereby counteracting the increase in \(\text{H}_2\text{O}\)

- \(\text{OH}^-\) concentration decreases, making the indicator less effective

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**Basic Indicator**

- \(\text{e.g. } \text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-\)

- \(\text{OH}^-\) concentration increases, making the indicator more effective

- \(\text{H}^+\) concentration decreases, making the indicator less effective
NOTE
Always write indicator like this

\[ \text{HIn(aq)} \rightleftharpoons \text{H}^+ \text{In}^{(aq)} (\text{color1}) \] (color1)

\[ \text{HIn}^{(aq)} \rightleftharpoons \text{H}^+ + \text{In}^{(aq)} (\text{color2}) \] (color2)

Kind and \( K_{\text{kind}} \): 
\[ \frac{[\text{In}^\text{red}]}{[\text{HIn}]} = \text{halfway through colour change} \] or \( \frac{[\text{H}^+]}{[\text{In}^{(aq)}]} \) = \( \text{HIn}^{(aq)} \) = \( \text{H}^+ \) = \( \text{In}^{(aq)} \)

\( \therefore \) \( \text{Kind} = \frac{[\text{H}^+]}{[\text{In}^{(aq)}]} \)

and \( pK_{\text{kind}} \) word = \( pH \). Only at the halfway point.

However, this does not always happen, so we do \( \pm 1 \) to produce a colour change interval. e.g. for methyl orange \( pK_{\text{kind}} = 3.7 \), but \( 3.1 < pH < 4.4 \)

Must select appropriate range that will be the same range as the equivalence point.

\( \rightarrow \) phrase: "indicator end point within range of pH at equivalence point."

Why is there a change in colour?
The energy gap of undissociated and dissociated will vary, hence different degrees of energy conjugation in each states. Hence different wavelengths of light absorbed and then transmitted.

Table of how different colours affect range of equivalence point

| S.A + S.B | 3 - 7, 7 in middle |
| S.A + S.B | 7 - 11, 9 in middle |
| S.B + W.B | 3 - 7, 5 in middle |
| W.A + W.B | No sig change of pH range, but usually 7 |

\( \pm 2 \) for S.A or S.B

Acid Deposition
Why is rainwater acidic?
- Usually \( pH 5.65 \)
- Dissolved \( CO_2 \) which forms carbolic acid
- Acidic rain = rain with \( pH < 5.60 \)

\( H_2O + CO_2 \rightleftharpoons H_2CO_3 \)

\( H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \)

Acid Deposition: Process by which acidic particles, gases and precipitates leave the atmosphere

Wet Acid Deposition
- Fallout from aerosol precipitates (referring to the acidic material), e.g. snow, rain, hail

Dry Acid Deposition
- Acidifying particles, gases fall to ground as smoke (dust) and later dissolve to form acids.
**Sulfur Oxides**
- $SO_2$ from burning fossil fuels [coal, heavy oil] and smelting [iron from ore]
  
  $S (s) + O_2 (g) \rightarrow SO_2 \ [\Delta H]$

  $SO_2 (g) + H_2O (\ell) \rightarrow H_2SO_3 (g)$ [sulfurous acid]
  
  OR
  
  $2SO_2 + O_2 \rightarrow 2SO_3 \ [\text{in sunlight}]

  $SO_3 + H_2O \rightarrow H_2SO_4$

  $H_2O + SO_2 \rightarrow 2H^+ + SO_3^{2-}$

  $H_2SO_3 \rightarrow H^+ + H_2O + SO_3$ [photooxidation]

**Nitrogen Oxides**
- NOx for instance is formed from the heat of internal combustion engines or from lightning strike
  
  $N_2 + O_2 \rightarrow 2NO \rightarrow \Delta H$, v. high energy needed

  $2N_2O + O_2 \rightarrow 2NO_2$

  $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \leftarrow$ nitric acid

  OR

  $2NO_2 + H_2O + O_2 \rightarrow 4HNO_3$

  $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$

  $H^+ + NO \rightarrow HNO_2$

  $H^+ + NO_2 \rightarrow HNO_3$

  $SO_3$ and $NO$ into $H_2SO_4$, $H_2SO_3$, $NO_2$ and $HNO_3$

  Dry deposition in lakes or teaeying

  Rainfall with acids

**Effects**

**Materials**
- marble and limestone made of $CaCO_3$
- react with $H_2SO_4$, $H_2SO_3$ and $SO_2$ (dry deposition) to form $CaSO_4$

  $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$

  $2CaCO_3 + 2SO_2 + H_2O \rightarrow 2CaSO_4 + 2CO_2$
- Also reacts with nitric acid: $2\text{HNO}_3 + \text{CaCO}_3 \rightarrow \text{Ca(NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2$
- $\text{CaSO}_4$ and $\text{Ca(H}_2\text{O}_2)$ are very soluble, hence washes off the limestone easily.
- $\text{CaSO}_4$ and $\text{Ca(O}_2\text{)}_2$ larger than $\text{CaSO}_2$ in Mr, hence creation caused expansion and cracking

**Metals**
- Dry deposition and wet react with metals, e.g. Iron
- $\text{Fe(O}_2\text{)} + \text{SO}_3 + \text{O}_2 \rightarrow \text{Fe}_2\text{SO}_4$
- $\text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2 + \text{Fe}_2\text{SO}_4$ (Remember ionic conductivity increase in rate of electrochemical corrosion reactions)

**Acid rain can remove protective oxide coatings**
- e.g. $\text{Al}_2\text{O}_3 + 6\text{H}_2\text{SO}_4 \rightarrow 2\text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$
- Causes damage to bridges, roads, tracks, etc.

**Lakes + Water Bodies**
- Causes staining of Important
- Reacts with $\text{Al(OH)}_3$ in rock to form solute, toxic $\text{Al}^{3+}$
- $\text{Al(OH)}_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$
- $\text{Al}^{3+}$ interferes with gill operation → cannot take in $\text{O}_2$
- Cause eutrophication due to nutrients in acid rain → algal blooms rest increases BCO demand, loss of ecosystem.

**Plants**
- $\text{Al}^{3+}$ in the same reaction, damages roots, cannot take in nutrients → stunted growth and yellowing, loss of leaves, thinning of tree tops.
- Acid Rain causes leaching of nutrients like $\text{Ca}^{4+}$ and $\text{Mg}^{2+}$ → needed for chlorophyll, cannot photosynthesize.
- Dry deposition block stomata → no gas exchange

**Humans**
- Fine sulfate and nitrate particles irritate mucous membranes → risk of asthma, bronchitis and emphysema.
- Heavy metal ions like $\text{Al}^{3+}$ in water could cause Alzheimer's.
Salts [overall pH determined by the competitive hydrolysis of cations and anions]

Cation Hydrolysis:

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]

comes about from a salt created by a weak base but strong acid

e.g.

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]

Anion Hydrolysis:

\[ [A^-] + \text{H}_2\text{O} \rightleftharpoons [HA] + [OH^-] \]

from salt by reaction between strong base weak acid

e.g.

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \]

If cations and anions hydrolyse to same extent, pH = 7.

*Note: Group 1 & 2 cations cannot hydrolyse to form H^+ as their charge densities are too low

Metal Cation Hydrolysis

Consider \([\text{Al(H}_2\text{O})_6]^{3+}\)

- Al is a metal cation with a high charge density
- This high charge density allows it to polarise the \(\text{O-H}\) bond in water, weakening it in the process
- Therefore, it allows for a \(\text{H}^+\) ion to leave a \(\text{H}_2\text{O}\) and react with another \(\text{H}_2\text{O}\) to form the hydronium ion

\[ [\text{Al(H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} (l) \rightleftharpoons [\text{Al(H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^+ \]

This reaction goes to completion and loss of \(\text{H}^+\) until the complex ion loses its charge; thus it can no longer dissolve \([\text{CAI(H}_2\text{O})_6\text{OH}]^-\) - Forms a precipitate

Metal Cations form acidic solution by \(\text{H}^+\)

**NOTE:** If you have \(\text{XA}\), where \(X\) is a transition metal ion and \(A^-\) is an anion, you must use the hydrated complex ion of \(X\) and explain from there.

\(\text{X}^{2+}\) for example

\[ [\text{X(H}_2\text{O})_6]^{2+} \]

brackets: charge distributed across molecule
Post Combustion Methods of reducing SO₂ emissions

1) Flue Gas Desulphurisation
   - Ca(OH)₂ + SO₂(g) → CaSO₃(s) + H₂O
     (Calcium Sulfate)
   - 2CaSO₃(s) + O₂(g) + 4H₂O(l) → 2CaSO₄·2H₂O(s)
     (Gypsum)
   - Gypsum or hydrated calcium sulfate can be used to make plaster and cement

2) Catalytic Converter
   - Honeycomb interior to increase S.A for contact with gases
   - Uses porous Al₂O₃ as loading with platinum and other precious metals.
   - Catalyses the reduction of NOₓ into N₂ and O₂
     e.g. 2CO₂(g) + 2NO(g) → 2CO₂(g) + N₂(g)

3) Lower Temperature Combustion
   - Formation of NO reduced at lower temperature
   - Can be accomplished by recirculating exhaust gases into the engine, & NO in emission

Pre Combustion

1) Hydrodesulphurisation = process by which sulfur is catalytically removed from refined petroleum, so that it can react with by reacting it with H₂ to form H₂S, v. toxic, so it is trapped and broken down into elemental sulfur to manufacture H₂SO₄.

2) Alternatives - lower demand for fossil fuels
   - More efficient energy transfer systems
   - Switching to more renewable energy

3) Liming of lakes - neutralizes acid and increases concentration of Ca²⁺ and CO₃²⁻
   - Good for coral

Ka and Kb [Again]
   - Consider the c. base - acid pair HA / A⁻
     - HA + H₂O ⇌ H⁺ + A⁻ → kₐ = \frac{[H⁺][A⁻]}{[HA]}
     - A⁻ + H₂O ⇌ HA⁺ + OH⁻ → kₐ = \frac{[HA⁺][OH⁻]}{[A⁻]}

$$kₐ \cdot kₐ = \frac{[H⁺][A⁻]}{[HA] \cdot \frac{[HA⁺][OH⁻]}{[A⁻]}} = k_W$$

\[ kₐ \cdot kₖ = kₖ = \frac{[H⁺][OH⁻]}{[HA⁺]} \]
This is qualitative proof that stronger acids dissociate have weak bases because, if $pK_a$ is low, $pK_b$ must be high [(i.e., the base is weak)]

**Buffers**

Example Q: Describe how a phosphate buffer $\left[ Q: H_2PO_4^{-}\text{(aq)} \rightleftharpoons HPO_4^{2-}\text{(aq)} + H^+\text{(aq)} \right]$ minimizes the effect of the addition of (a) a strong base, (b) a strong acid.

(a) $OH^-$ reacts with $H_2PO_4^-$ to form $HPO_4^{2-}$ and $H_2O$, minimizing the effect of this addition:

$$H_2PO_4^- + OH^- \rightarrow H_2O + HPO_4^{2-}$$

(b) $H^+$ reacts with $HPO_4^{2-}$ to form $H_2PO_4^-$, minimizing the effect of this addition:

$$H^+(\text{aq}) + HPO_4^{2-}\text{(aq)} \rightarrow H_2PO_4^-\text{(aq)}$$

$K_w$, $K_a$, and $K_b$

Example Q: Why does a buffer solution still have $OH^-$ ions?

$[OH^-]$ cannot go to 0 because there is an equilibrium present such that $COHJ = \frac{K_w}{[H^+]},$

thus $[OH^-] \neq 0$

**General Tips + Notes**

1) **ALWAYS WRITE EQUATIONS**
2) Refer to the reactions in explaining how buffer solutions resist change.
3) Always divide mol by volume for everything.
4) State, in a titration question, the acid-base combo in terms of strength.
5) To find proportions of salt and acid $\rightarrow$ use $K_a$.

**Example:** $9.50\text{ pH Buffer}$ required with $NH_3$ and $NH_4Cl$

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

$$K_b = \frac{[NH_4^+]}{[OH^-]} \rightarrow \text{find ratio, then deduce } v_\text{acid} \text{ needed, can get }$$

directly if concs are already equal.

$$pH = pK_a + \log \left( \frac{\text{salt}}{\text{base}} \right)$$

$$pOH = pK_b + \log \left( \frac{\text{salt}}{\text{base}} \right)$$

$$4.50 = 4.25 + \log \left( \frac{\text{salt}}{\text{base}} \right)$$

$10^{-1.25} = \log \left( \frac{\text{salt}}{\text{base}} \right) = 0.62.$

$= 5.62 \times 10^{-1}.$