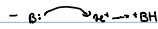- 18.1 Lewis acids and bases - The acid-base concept can be extended to reactions that don't involve proton transfers

  - Lewis Theory (inorganic chemistry)

    - In Brønsted-Lowry acid-base theory, a base is defined as a proton acceptor & an acid as a proton donator.

      - When a base accepts a proton, it donates an electron pair to the proton, shown as:

        - $B: \frown H^+ \rightarrow {}^+BH$

        - $B:$ represents a base (with one or more lone pairs of electrons), $H^+$ represents the proton, $BH^+$ the conjugate acid and the curved arrows represents the movement of an electron pair to form a coordinate covalent bond.

    - Example reaction: $H_3N: \frown H^+ \rightarrow {}^+NH_4$ & $H_2\ddot{O}: \frown H^+ \rightarrow H_3O^+$

    - A Lewis acid is defined as a substance that can accept a pair of electrons from another atom to form a coordinate covalent bond.

    - A Lewis base is defined as a substance that can donate a pair of electrons to another atom to form a dative (coordinate) covalent bond.

    - All Brønsted-Lowry bases are Lewis acid-bases, but not viceversa.

      - Lewis-acid bases are more general than the Brønsted-Lowry.

    - Reactions with no protons involved, water is absent and the reactions frequently occur in a gas phase

      - E.g. $NH_3: \frown BCl_3 \rightarrow NH_3BCl_3$
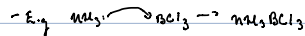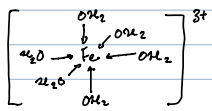
        - Ammonia is the Lewis base, and the Boron trichloride is the Lewis acid (pair acceptor).

        - The reaction occurred because of the fact that Boron (being a Lewis acid (pair acceptor)) wants to have a full shell.

  - Transition metal complexes

    - Lewis bonding is found in complex ions formed by Transition metals. — Explanation of Lewis bonding with complex ions

    - A charged metal ion which is placed in a aqueous solution will be surrounded by $H_2O$ molecules.

    - E.g. $Fe^{3+}$ will be surrounded by 6 $H_2O$ molecules → $[Fe(H_2O)_6]^{3+}$ (hexaaquairon (III) ion).

      - The 6 $H_2O$ molecules each donate a lone pair (Lewis base) from their Oxygen atoms to the empty 3d orbital of the central $Fe^{3+}$ ion.

      - The water molecule is a ligand (an ion/molecule attached to a metal atom by coordinate bonding).

$$\left[ \begin{array}{c} OH_2 \\ H_2O \xrightarrow{\quad} Fe \xleftarrow{\quad} OH_2 \\ H_2O \quad OH_2 \end{array} \right]^{3+}$$

↳ complex ion of $Fe^{3+}$

    - Investigation of Transition metal complexes

      - Ionisation isomers are compounds with the same formula but that differ as to which anions are coordinated and which are present as counter ions.

        - E.g. $[CoBr(H_2O)_5]^+ Cl^- \rightarrow [CoCl(H_2O)_5]^+ Br^-$

        - When dissolved in water, the different isomers will release different ions due to the fact that the $H_2O$ will separate the ion by separating the counter ions & the anion coordinated.

          - E.g: $[CoBr(H_2O)_5]^+ Cl^- + (aq) \rightarrow Cl^- + [CoBr(H_2O)_5]^+$ & $[CoCl(H_2O)_5]^+ Br^- + (aq) \rightarrow Br^- + [CoCl(H_2O)_5]^+$

        - $Cl^-$ & $Br^-$ are the counter ions.

      - Isomers can be distinguished by one another because of the fact that adding a reactant such as $HgCl$ would result in different precipitates occurring.

      - $CrCl_3 \cdot 6H_2O$ also isomers: $[Cr(H_2O)_6]Cl_3$ (violet), $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (green), and the green $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$.

        - The extra $H_2O$ molecules (molecules on the right side of the equation) can be removed with dehydration.

        - Conductivity can be used to see what the exact isomer it is.

          - Ions are 4, 3, 2 for $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$, respectively.

- Lewis Theory (organic chemistry)

  - Nucleophiles and electrophiles

    - like many reactions, an organic reaction results from a process of breaking covalent bonds and forming new ones.

      - This involves electron pair transfers.

    - Ionic mechanisms, such as nucleophilic substitution and electrophilic substitutions, also involve electron transfers, and are therefore Lewis acid-base theory.

      - Nucleophilic substitution is where an electron rich nucleophile (chemical substance that donates an electron pair to form a chemical bond in relation to a reaction) [Lewis base] relatively bonds with or attacks the positive or partially positive charge of an atom or a group of atoms to replace a leaving group.

      - Electrophilic substitution reactions are chemical reactions in which an electrophile (positively charged or neutral species with vacant orbitals that are attracted to an electron rich center (electron pair acceptors)) [Lewis acid] displaces a functional group in a compound.

    - By definition Lewis bases have high presence of electron density while Lewis acids are low electron density centers.

    - The electron pair donated by the Lewis base to the Lewis acid is used to form a single sigma bond to the electron deficient acid center.

    - most Lewis bases contain lone pairs of electrons/non-bonding pairs.

      - $H_2O$ (water) for example is a Lewis base as it has two lone pairs.

    - Lewis acids instead usually contain an incomplete octet, a full positive charge (cation), or partial positive charge (atoms with a lower electro-

negativity compared to the atoms they're bonded with).

- Carbon cations (carbocations) are examples of Lewis acids.

- Example Lewis acid-base reaction:



Why is there a positive sign?
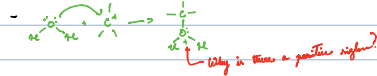
- It can be seen in the diagram above an electron pair from the oxygen is used to form a sigma bond to the central carbon in the carbocation.

- **Basic (Bronsted-Lowry) or nucleophilic behavior**

- A Bronsted-Lowry base is a proton acceptor while a Lewis base (nucleophile) is a electron-pair donator.

- A nucleophile wants to bond with an electron deficient center, protons, or other atoms (commonly carbon) while Bronsted-Lowry bases want to bond with protons/$H^+$ ions.

- In a acid-base reaction, the size of the base rarely matters, while in a nucleophile reaction the size of the base does impact matters.

- The smaller the nucleophile the more effective they are.



methoxide    tertiary-butoxide
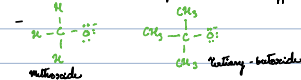
- The methoxide is a more effective nucleophile because it is smaller than the tertiary-butoxide even though the oxygen is the same and they have a similar structure, and are similar bases.

- The larger the ion the harder it is for it to reach the electrophile center, or its usually a carbon which is in the middle of the molecular structures. This doesn't matter for Bronsted bases because acidic protons are usually on the surface of the molecule.

- **Classification of Lewis acids**

- A Lewis acid must have at least one empty orbital in its valence shell in one of its atoms to accept an electron pair from a Lewis base.

- Classified as:

- molecules which contain a central atom with an incomplete octet.

- Usually Lewis acids are electron-deficient molecules such as the halides (compound of a halogen with another element or atom from another groups) of Boron, Beryllium, and aluminum. E.g $BCl_3$, $BeCl_2$, and $AlCl_3$.

- molecules with a central atom with an empty d-orbital.

- These molecules can accept electron pairs in the d-orbital forming adducts (product of an addition between two compounds) with halide ions (halogen ion) and organic bases.

- simple cations

- Theoretically all simple cations are potentially Lewis acids.
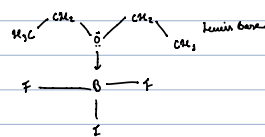
- The Lewis acid strength increases with an increase in the charge and increases when the ionic radius decreases.

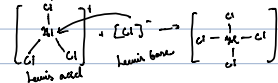- molecules with a multiple bond between atoms of different electronegativity

- E.g $CO_2$, $SO_2$, $SO_3$. Oxygen electronegativity is greater than Carbon so the pi electrons (in pi bond) are pushed away from the carbon or sulfur atoms making them electron deficient, making them able to accept a electron pair from a Lewis base.

- Questions How to write Lewis acid-base equations?

- Boron trifluorine + ethoxyethane $(O(C_2H_5)_2)$.



Lewis base

- $HgCl_3^- + Cl^- \rightarrow HgCl_4$



Lewis acid    Lewis base

- $NH_3 + H^+ \rightarrow [H_3N:\!-\!-\!-\!H \rightarrow :NH_3]^+$

Lewis   Lewis
Base    acid

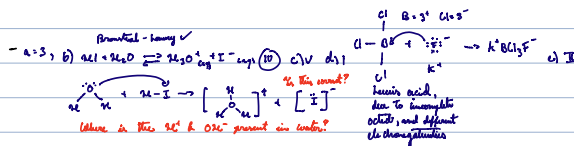- $Li^+ + 4 CH_3OH \rightarrow$

Lewis    Lewis
acid    Base

- molecules other than cations

- The Brønsted - Lowry can be applied to other solvents other than water.
    - Solvents are the liquid in which a solute is dissolved to form a solution.
    - Ammonia is also amphiprotic (can act as a Brønsted-Lowry acid or base).
- As an acid: $NH_3 \rightarrow NH_2^- + H^+$
- As a base: $NH_3 + H^+ \rightarrow NH_4^+$

==In liquid ammonia solution==
- Ammonium chloride, $[NH_4^+ Cl^-]$, behaves as a ==strong== acid, and sodium amide, $[Na^+ NH_2^-]$, behaves as a ==strong== base.
- In liquid ammonia, an acid can be defined as a substance that provides $NH_4^+$ ions. While a base produces amide ions, $NH_2^-$.
    - Generally, in a self-ionising solvent an acid is a substance that produces the cation characteristic of the solvent, and a base is a substance that produces the anion characteristic of the solvent.
- An ==aprotic solvent== is a solvent whose molecules ==don't donate== a proton.
    - <span style="color:red">← What does this do?</span>
- <span style="color:red">Levelling effect ← Explain</span>
    - Non-aqueous solvents that are good proton donors, e.g ==liquid ammonia==, ==encourage acids to ionise in them==.
        - meaning that when a weak acid is put in a basic solvent, it will fully dissociate in the solvent rather than only partially dissociate like where its placed in an aqueous solution. Therefore, in a basic solvent all acids are strong.
    - The solvent is said to show a greater ==levelling effect== on the acid, since the strength of the acid can't be greater than the protonated solvent.
        - E.g in aqueous solution, no acidic species can exist that is a stronger than $H^+/H_3O^+$.
    - In acidic solvents, liquid sulfuric acid, ionisation of bases is promoted.
        - Most acids are relatively weak under these conditions.

- <span style="color:orange">Summary of the various acid and base Theories</span>
    -

| Theory | Basic principles |
|---|---|
| Traditional approach | Acid: a substance that has certain properties (e.g sour taste, turns litmus red) |
| Arrhenius | Acid: $H^+$ present in aqueous solution |
| | Base: $OH^-$ present in aqueous solution ∴ neutrality: $[H^+] = [OH^-]$ |
| Brønsted - Lowry | Acid: $H^+$ donor    conjugate acid - base pairs |
| | Base: $H^+$ acceptor   no concept of neutrality |
| Lewis | Acid: lone pair acceptor |
| | Base: lone pair donator |
| Usanovich | Acid: a substance that donates a cation, or accepts an anion, or an electron |
| | Base: a substance that donates an anion or an electron, or accepts a cation |

- <span style="color:orange">Questions</span>
    - a → 3, b) $HCl + H_2O \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ <span style="color:blue">Brønsted - Lowry ✓</span> c) V d)  <span style="color:blue">Cl B = 3+ Cl = 3-</span>
    
    <span style="color:blue">Cl — Bl⁺ + :F:⁻ → K⁺ BCl₃F⁻   K⁺</span>   c) $\overline{II}$
    
    <span style="color:red">Is this correct?</span>
    
    $\overset{..}{\underset{..}{O}}_H + H-I \rightarrow [\overset{H}{\underset{H}{O}}]^+ + [\overset{..}{\underset{..}{I}}]^-$
    
    <span style="color:red">Where is the $H^+$ & $OH^-$ present in water?</span>
    
    <span style="color:blue">Lewis acid, due to incomplete octets, and different electronegativities</span>
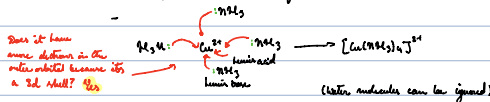
- <span style="color:orange">Applying Lewis' acid- base theory to inorganic and organic chemistry to identify the role of the reacting species</span>
    - Carbon dioxide molecules reacting with hydroxide ions to form hydrogencarbonate ions:
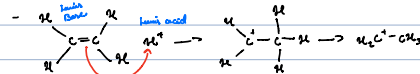    
    $O = \overset{..}{\underset{..}{C}} \overset{..}{\underset{..}{O}} + :\overset{..}{\underset{..}{O}}H \rightarrow$ 
    
    [structure of hydrogencarbonate]
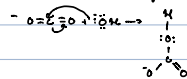
    - Copper (II) ions in aqueous solution reacting with ammonia molecules to form the complex Tetraamminecopper (II) ions:
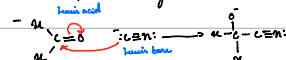    
    <span style="color:red">Does it have some electrons in the outer orbital because its a 3d shell? Yes</span>
    
    $H_3N \underset{NH_3}{\overset{NH_3}{Cu^{2+}}} NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$
    
    Lewis acid / Lewis base
    
    (Water molecules can be ignored)

    - Fluoride ions reacting with a silicon tetrafluoride molecule to form the silicon hexafluorine ion:
    
    $:\overset{..}{\underset{..}{F}}: + SiF_4 + :\overset{..}{\underset{..}{F}}:^- \rightarrow [SiF_6]^{2-}$
    
    Lewis acid   Lewis base
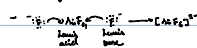
    - The pi bond of an ethene molecule reacting with a proton (electrophile) to form an ethyl carbocation:
    
    $\underset{H}{\overset{H}{C}} = \underset{H}{\overset{H}{C}} \quad H^+ \rightarrow \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} H \rightarrow H_2C^+ - CH_3$
    
    <span style="color:blue">Lewis Base</span>  <span style="color:red">Lewis acid</span>

    - A cyanide ion (nucleophile) reacting with the carbon atom of the carbonyl group of a methanal molecule (to form a tetrahedral intermediate):
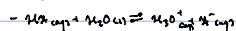    
    $\underset{H}{\overset{H}{C}} = O \quad :C \equiv N: \rightarrow H - \overset{O}{\underset{H}{C}} - C \equiv N:$
    
    <span style="color:blue">Lewis acid</span>   <span style="color:blue">Lewis base</span>

- <span style="color:orange">pKa Calculations involving acids and bases</span>
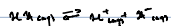    - <span style="color:orange">Acid - Base reactions or equilibria</span>

- most acids & bases are weak.

- the equilibrium law can be used to the extent to which a base or acid ionises or dissociates.

  - A weak acid equilibrium can be represented in either of the following ways, depending on whether the hydrated proton is represented as $H_3O^+$ consuming 5 or $H^+$:

    - $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

      or

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

- water is omitted from the equilibrium expression written as:

  - $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$ or $K_a = \dfrac{[H^+][A^-]}{[HA]}$

- the magnitude of $K_a$ indicates if the acid or base is strong or weak by showing its dissociation level in water.

  - the larger the value of $K_a$, the stronger the acid.

  - $pK_a = -\log_{10} K_a$ is another measure of acid strength. The smaller the value of $pK_a$ the stronger the acid.

- <span>Calculations involving acids and bases</span>

  - <span>The ionic product of water</span>

    - the reason that distilled water is a poor electrical conductor is because of the water not dissociating a lot: $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ or $2H_2O_{(l)} \rightleftharpoons H_3O^+ + OH^-$.

    - $K_w$ represents the ionic product constant of water.

      - At 298K (25°C) the measured concentrations of $H^+_{(aq)}$ & $OH^-_{(aq)}$ in pure water are $1 \cdot 10^{-7}$ mol dm$^{-3}$.
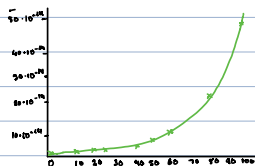
        - $K_w = [H^+][OH^-] = 1 \cdot 10^{-14}$ mol² dm$^{-6}$ ⟶ $K_w = K_a \cdot K_b$

    - Questions: $1.0 \cdot 10^{-11}$ mol dm$^{-3}$

    - $K_w$ changes with temperature.

      - If the temperature increases the pH will decrease even if the solution is chemically neutral since the concentrations of $H^+$ & $OH^-$ are still equal.

      - Graphical representation:



    - the dissociation of water is expected to be an endothermic reaction as energy is required to break bonds between oppositely charged ions.

      - this also shows that the dissociation of water is an endothermic reaction as Le Chatelier's principle will favor the reaction which will lower the temperature (endothermic), meaning more dissociation will occur, shifting equilibrium to the right and dissociating water even more.

        - this increases $K_w$.

    - Question:

      - 60°C $K_w = 9.55 \cdot 10^{-14}$ mol² dm$^{-6}$     $9.55 \cdot 10^{-14} = [H^+][OH^-]$
        $9.55 \cdot 10^{-14} = x^2$
        $x = \sqrt{9.55 \cdot 10^{-14}}$
        $x = 3.09 \cdot 10^{-7}$ mol dm$^{-3}$

    - By definition the pH of an aqueous solution is the measure of its hydrogen ions concentration.

      - It depends on the temp because the degree of dissociation of an acid does, $K_a$ changes.

    - Neutrality of a substance is independent of the pH: a neutral solution is one where the concentration of $H^+$ ions equals the concentration of $OH^-$ ions.

      - Corresponding to 7 at 25°C.

  - <span>The pH and pOH scales</span>

    - pH and pOH is the negative by base 10 of the concentration of $H^+$ ions & $OH^-$ ions in a substance.

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

    - $pH + pOH = 14$

      - $K_w = [H^+][OH^-] \longrightarrow 1 \cdot 10^{-14}$ mol² dm$^{-6}$ = $[H^+][OH^-]$

      - $pK_w = pH + pOH = 14$

    - Questions:

      - $0.01$ mol dm$^{-3}$ HCl$_{(aq)}$  pH = 2

      - pH = 12

- since there are two $OH^-$ ions, the concentration must be doubled. therefore, concentration of $OH^-$ ions in $0.02$ mol dm$^{-3}$ rather than

$0.01$ mol dm$^{-3}$. therefore, $pOH = -Log_{10}[0.02]$ $\quad$ $14-1.7 = \underline{12.3\ pH}$ $\quad$ another method: $\frac{1\cdot10^{-14}}{0.02}$ $\rightarrow [OH^+] \rightarrow [OH^+] = 5\cdot10^{-13}$ $\quad -Log(5\cdot10^{-13}) = \underline{12.3\ pH}$
$\quad pOH = 1.7$

- H ions = 2 therefore $[H^+] = 0.02$ mol dm$^{-3}$ $\quad pH = 1.7$

- To calculate the concentration of $H^+$ & $OH^-$ ions the following formulas are used:

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

- Questions:

- $[H^+] = 10^{-2.8}$
$[H^+] = 1.58\cdot10^{-3}$ mol dm$^{-3}$

- $HNO_3$ aq, $1.82g$, $0.1$ dm$^3$ $\quad c = \frac{m}{v} = \frac{0.02}{0.1} = c = 0.2$ mol dm$^{-3}$ $\quad pH = -Log(0.2)$
$1.01 + 14 + 16\cdot3 = 63.01$ g mol$^{-1}$ $\quad\quad\quad\quad\quad = 0.6990399343$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \simeq \underline{0.70}$

- $v_1 = 0.01$ dm$^3$ $\quad v_2 = 1$ dm$^3$ $\quad$ change $= 10^2 = 100$ times original amount. $\quad \Delta pH = 2$ pH value

- They don't give you any values in the book to calculate the pH value therefore final pH can't be calculated.

- pH scale is used to describe both alkaline & acidic solutions.

- Alkaline solution have a low concentration of $H^+$ ions from the dissociation of $H_2O$.

- pOH can also be used to find acidity of how alkaline a solution is.

- Questions:

- $-Log_{10}(0.1) = 1$ $\quad pH = 13$

- $[OH^-] = 10^{-pOH}$
$\quad = 10^{-2}$
$[OH^-] = 0.01$ mol dm$^{-3}$ ✓

- $[OH^-] = 10^{-1}$ $\quad pH = 14-1$
$\quad = 1$ $\quad\quad\quad = \underline{13}$ ✓

- $[H^+] = 10^{-2}$ $\quad [OH^-] = 10^{-12}$ mol dm$^{-3}$ $\quad p\underline{H = 2}$ ✓
$\quad\quad\quad\quad\quad pOH = 12$ ✓

- <span>Acid dissociation constant</span>

- A weak monobasic (acid with only one $H^+$ ion), $HA$, reacts with $H_2O$:

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

- This will give the acid dissociation constant (strength of an acid in a solution), $k_a$.

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

- The $k_a$ is a measure of the strength of a weak acid.

- The larger the value for $k_a$, the stronger the acid as it dissociates more.

- $k_a$ is usually small, therefore its usually expressed as $pk_a$:

- $pk_a = -Log_{10}\ k_a$

- The lower the value of $pk_a$ the stronger the acid.

- $k_a$ & $pk_a$ aren't affected by concentration but rather only temperature changes.

- Meaning acid strength varies with temp.

- Since $[H^+] = [A^-]$ in a solution with only acid is present:

- $k_a = \frac{[H^+]^2}{[HA]}$ $\rightarrow [H^+] = \sqrt{[HA]\cdot k_a} \rightarrow pH = -Log[H^+]$

- Questions:

- $k_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$ $\quad [H^+] = 10^{-3.1}$ ✓
$\quad\quad\quad\quad\quad\quad\quad\quad\quad [H^+] = 7.94\cdot10^{-4}$
$\quad = \frac{[7.94\cdot10^{-4}]^2}{0.01}$ $\quad [C_6H_5COO^-] = [H^+]$
$\quad = 6.31\cdot10^{-5}$
$\quad$ ( Book $10^{-6}$ is wrong.

- $CH_3COOH$ aq, $k_a = 1.8\cdot10^{-5}$ mol dm$^{-3}$

$1.8\cdot10^{-5} = \frac{[H^+]^2}{0.1}$ $\quad\quad pH = -Log[1.14\cdot10^{-3}]$
$\quad\quad\quad [H^+] = \sqrt{1.8\cdot10^{-6}}$ $\quad\quad\quad = \underline{2.97}$
$\quad\quad\quad [H^+] = 1.34\cdot10^{-3}$ mol dm$^{-3}$

- <span>Base dissociation constant</span>

- A weak base can be either Ammonia (molecule), or an anion, such as ethanoate.

- A weak base, have a weakly basic solution.

- $B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$

- $B^-_{(aq)} + H_2O_{(l)} \rightleftharpoons BH_{(aq)} + OH^-_{(aq)}$
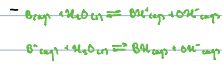
- Base dissociation constant, $K_b$:

  - $K_b = \dfrac{[BH^+][OH^-]}{[B]}$ or $\dfrac{[BH][OH^-]}{[B^-]}$

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

- Question:

  - $[OH^-] = \sqrt{0.5 \cdot 1.8 \cdot 10^{-5}}$    $pOH = -\log[3 \cdot 10^{-3}]$
    $= \sqrt{9 \cdot 10^{-6}}$    $pOH = 2.52$
    $= 3 \cdot 10^{-3}$ mol dm$^{-3}$    $pH = 11.5$

  Book method & answer is wrong

- Questions:

  - $[H^+] = 10^{-6.8}$ ✓    $k_w = (1.58 \cdot 10^{-7})(1.58 \cdot 10^{-7})$
    $= 1.58 \cdot 10^{-7}$ ✓    $k_w = 2.50 \cdot 10^{-14}$ mol$^2$ dm$^{-6}$
    $[OH^-] = 1.58 \cdot 10^{-7}$ ✓

  - $10^{-3.20} = 6.3 \cdot 10^{-4} = [H^+]$, $[OH^-] = 1.56 \cdot 10^{-11}$ mol dm$^{-3}$ ✓    $[OH^-]$

  p.618 ⊙ $v = 0.2$ dm$^3$, $[OH^-] = 1 \cdot 10^{-1}$, mass of NaOH $= (22.99 + 16 + 1.01)$ $n = cv$    $g = 40 \cdot 0.02$
    $= 40$ g mol$^{-1}$    $= 1 \cdot 10^{-1} \cdot 0.2$ mass 0.8 grams
    $= 0.02$ mol

  - ⊙ $[H^+] = 0.1$ mol dm$^{-3}$ ✓    $\dfrac{1 \cdot 10^{-14}}{0.1} = [OH^-]$
    $[OH^-] = 1 \cdot 10^{-13}$

  - $v = 0.05$ dm$^3$, $c = 0.5$ mol dm$^{-3}$    $pOH = -\log_{10} 0.5$    $pH = 13.7$ ✓
    $pOH = 0.3$

  - $pK_a = -\log_{10} K_a$    $[H^+] = \sqrt{(0.125)(1.74 \cdot 10^{-5})}$
    $K_a = 10^{-4.76}$    $[H^+] = 1.48 \cdot 10^{-3}$ mol dm$^{-3}$
    $K_a = 1.74 \cdot 10^{-5}$    $pH = 2.83$

  - $pK_b = -\log_{10} K_B$    $[OH^-] = \sqrt{(7.41 \cdot 10^{-10})(0.5)}$    $14 = pOH + pH$
    $K_b = 10^{-9.13}$    $= 1.93 \cdot 10^{-5}$    $pH = 9.28$
    $= 7.41 \cdot 10^{-10}$    $[H^+] = 5.19 \cdot 10^{-10}$    or
    $pH = 9.28$

  - $0.025$ mol dm$^{-3}$, $pH = 3.74$    $[H^+] = 10^{-3.74}$    $K_a = \dfrac{(1.82 \cdot 10^{-4})^2}{0.025}$
    $[H^+] = 1.82 \cdot 10^{-4}$ mol dm$^{-3}$    $K_a = 1.37 \cdot 10^{-6}$

  - $M_r = 1.01 + 19$    $K_a = 1.8 \cdot 10^{-4}$    $K_a \cdot K_b = K_w$
    $= 20.01$ g mol$^{-1}$    $\dfrac{1 \cdot 10^{-14}}{1.8 \cdot 10^{-4}} = K_b$
    $K_b = 5.56 \cdot 10^{-11}$ ✓

  - $\dfrac{19.23 \text{ g dm}^{-3}}{121.64 \text{ g mol}^{-1}} = 0.158$ mol dm$^{-3}$    $Sr^{+2} = 0.158$ dm$^{-3}$ $OH = 0.316$ mol dm$^{-3}$
    $pOH = -\log 0.316$    $pH = 13.5$
    $= 0.5$

  - $v = 0.025$ dm$^3$ $c = 0.1$ mol dm$^3$ HCl & $0.015$ dm$^3$ of $0.1$ mol dm$^3$ NaOH

  $NaOH + HCl \rightleftharpoons NaCl + H_2O$

  $HCl = 0.0025$ mol & NaOH $= 0.0015$ mol

  1:1 ratio
  $1.5 \cdot 10^{-3} : 1.5 \cdot 10^{-3}$

  $1.5 \cdot 10^{-3}$ mol of HCl will be neutralized

  $1 \cdot 10^{-3}$ mol of HCl remains

  $\dfrac{1 \cdot 10^{-3}}{0.04} = 0.025$ mol dm$^{-3}$   $-\log_{10}(0.025)$
    $pH = 1.6$

- Discussing the relative strengths of acids and bases values of $K_a$, $pK_a$, $K_b$, and $pK_b$

  - The figure shows the relative strength of Brønsted-Lowry acids & bases. It shows there is an inverse relationship between $K_a$ (or $K_b$), and $pK_a$ (or $pK_b$).
  -

    $pK_a$ decreases          $pK_b$ decreases

    strong acid    weak acid    strong base    weak base
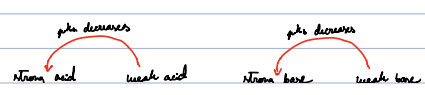
- the graph shows that as the value for $k_a$ increases then the value for $pk_a$ will decrease, the same will occur with a base.
  - the reason that $pk_b$ doesn't decrease is because of the fact that the $pH$ formula is given by: $14 = pH + pOH$, meaning the lower the value for $pOH$, the higher the $pH$
- Base examples: $C_6H_7O_6^-$ $(k_b: 1.3 \cdot 10^{-10})$, $(CH_3)_3N$ $(k_b: 4.8 \cdot 10^{-5})$, $C_5H_5N$ $(k_b: 1.7 \cdot 10^{-9})$
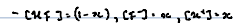  - the conjugate acids for these bases are (arranged in increasing acidity): $(CH_3)_3NH^+ < C_5H_5NH^+ < C_6H_7O_6H$
  - the weaker the base the stronger the conjugate acid. Meaning that the lower the $k_b$ value is the stronger the conjugate acid will be.

- **Assumptions and simplifications**
  - For weak acids approximately 1% of the acid is dissociated.
  - **Worked example**
    - $[HF] = (1-x)$, $[F^-] = x$, $[H^+] = x$
    
    $$7.2 \cdot 10^{-4} = \frac{x^2}{(1-x)}$$
    
    $$0 = x^2 + 7.2 \cdot 10^{-4} - 7.2 \cdot 10^{-4}$$
    
    $$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
    
    $$= \frac{-(7.2 \cdot 10^{-4}) \pm \sqrt{(7.2 \cdot 10^{-4})^2 - 4(-7.2 \cdot 10^{-4})}}{2}$$
    
    $x = 0.0265$  $[H^+] = 2.65 \cdot 10^{-2}$  $-\log_{10}(2.65 \cdot 10^{-2}) = pH$
    $$pH = 1.6$$

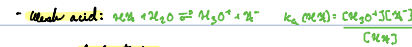- **Relationship between $k_a$ for a weak acid and $k_b$ for its conjugate base**
  - the relationship between $k_a$ for a weak acid $HA$ & $k_b$ for its conjugate base $A^-$ is:
    - $k_a(HA) \cdot k_b(A^-) = K_w (1 \cdot 10^{-14})$
    - $pk_a(HA) + pk_b(A^-) = pk_w (14)$
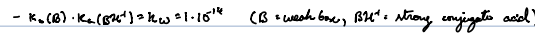  - the stronger the acid, the larger $k_a$ and the smaller $pk_a$. Similarly, larger $k_b$ the smaller $pk_b$.
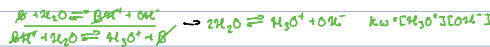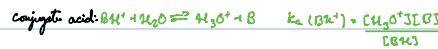  - this equations is proof that the stronger the acid/base the weaker its conjugate base/acid.
  - **Weak acid:** $HA + H_2O \rightleftharpoons H_3O^+ + A^-$    $k_a(HA) = \dfrac{[H_3O^+][A^-]}{[HA]}$
    - **Conjugate base:**
    
    $A^- + H_2O \rightleftharpoons HA + OH^-$    $k_a(A^-) = \dfrac{[HA][OH^-]}{[A^-]}$
    
    $\cancel{HA} + H_2O \rightleftharpoons H_3O^+ + \cancel{A^-}$
    $\cancel{A^-} + H_2O \rightleftharpoons \cancel{HA} + OH^-$
    
    $2H_2O \rightleftharpoons H_3O^+ + OH^-$    $k_w = [H_3O^+][OH^-]$

- **Relationship between $k_b$ for a weak base and $k_a$ for its conjugate acid**
  - $k_b(B) \cdot k_a(BH^+) = k_w = 1 \cdot 10^{-14}$    ($B$ = weak base, $BH^+$ = strong conjugate acid)
  
  $pk_b(B) + pk_a(BH^+) = pk_w (14)$
  
  - **Proving equations:**
  
  **Weak base:** $B + H_2O \rightleftharpoons BH^+ + OH^-$    $k_b(BH^+) = \dfrac{[BH^+][OH^-]}{[B]}$
  
  **conjugate acid:** $BH^+ + H_2O \rightleftharpoons H_3O^+ + B$    $k_a(BH^+) = \dfrac{[H_3O^+][B]}{[BH^+]}$
  
  $\cancel{B} + H_2O \rightleftharpoons BH^+ + OH^-$
  $BH^+ + H_2O \rightleftharpoons H_3O^+ + \cancel{B}$    $\rightarrow 2H_2O \rightleftharpoons H_3O^+ + OH^-$    $k_w = [H_3O^+][OH^-]$
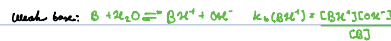
- Acids which release more than one protons per molecule are **polyprotic acids.**

- **Buffer solutions**
  - A buffer solution is an aqueous solution whose $pH$ ($H^+$ ion concentration) remains unchanged by dilutions with water or when small amounts of acids or base are added to it.
    - Essentially, buffers resist changes in $pH$.
  - Buffers are necessary in electrophoresis are used to calibrate $pH$ meters.
    - Other uses are in shampoos & dyes, aswell as physiological systems are always buffered.

- Types of buffers
  - There are three types of buffer:
    - **Acid buffers**, which are prepared from a weak acid and a salt of the acid.
      - E.g ethanoic acid and sodium ethanoate.
    - **Basic or alkaline buffers**, which are prepared from a weak base and a salt of the base, for example ammonia and ammonium chloride.
    - **Neutral buffers**, which are usually prepared from phosphoric acid and its salts.
- Actions of buffer solutions
  - Acid buffers
    - Since ethanoic acid ($CH_3COOH$) is only slightly dissociated & sodium ethanoate ($CH_3COONa$) is completely dissociated, a mixture of the two contains a relatively low concentration $H^+$ ions, [Why is that? the $H^+$ ions are from the weak acid, meaning that not many are released.]
      - $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ & $CH_3COONa \rightarrow CH_3COO^- + Na^+$ [Different buffers or are they mixed together to make a single one? mixed together]
    - If an acid is added to the buffer, the additional $H^+$ ions will be removed by combination with ethanoate ions to form undissociated acid molecules. [coming from new acid.]
      - The large amount of ethanoate ions are used to "get rid" of additional hydrogen ions from an acid due to the presence of sodium ethanoate.
    - If an alkaline is added, then the $OH^-$ ions combine with the $H^+$ ions to form water.
    - Ethanoic acid molecules are there so that when $OH^-$ ions are added they will dissociate to make up for the the $OH^-$ ions being removed.
  - Basic buffers
    - Since ammonia is only slightly dissociated & ammonium chloride is completely dissociated, a mixture of the two contains a relatively low concentration of $OH^-$ ions, but a lot of ammonia molecules & ammonium ions: $NH_4Cl \rightarrow NH_4^+ + Cl^-$ & $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.
    - If an acid is added the $H^+$ ions will combine with $OH^-$ ions to form water.
      - leading to more ammonia molecules reacting with water & releasing $OH^-$ ions.
    - If base added, the $OH^-$ ions react with the ammonium ions from $NH_4Cl$ to form ammonia & water.
- Calculations involving buffer solutions
  - Two assumptions made with buffer solutions:
    - In a buffer solution, the weak base or weak acid won't dissociate, because of the presence of ions from the dissociation of its salts will prevent dissociation of the acid or base molecules.
    - It's assumed that all the ions present in the buffer are produced from the dissociation of the salt: none comes from the acid or base.
  - Acid buffers
    - $pH = pK_a - Log_{10} \dfrac{[salt]}{[H^+]}$ or $pH = pK_a + Log_{10} \dfrac{[salt]}{[HA]}$
    - This is the Henderson-Hasselbalch equation. This indicates:
      - the pH of a buffer solution depends on the $K_a$ of the weak acid
      - the pH of a buffer solution depends upon the ratio of the concentration of the acid and its conjugate base and not on their actual concentrations.
  - Basic buffers
    - $pOH = pK_b + Log_{10} \dfrac{[B^+]}{[BOH]}$
  - Calculating the pH of a buffer system
    - 0.2 moles of sodium ethanoate, 0.5 $dm^3 = V$, $C = 0.1$ $mol\ dm^{-2}$, $k_a = 1.8 \cdot 10^{-5}$
    - $pH = pK_a + log \dfrac{[S^-]}{[HA]}$        $\dfrac{0.2}{0.5} = 0.4$ $mol\ dm^{-3}$
    - $pH = 5.35$ ✓
    - Book method            $ka = \dfrac{[H^+][S^-]}{[HA]}$
      - $[CH_3COO^-] = 0.2 \cdot 2$        $1.8 \cdot 10^{-5} \dfrac{x(0.4)}{0.1}$
        $= 0.4$ $mol\ dm^{-3}$        $x = 4.5 \cdot 10^{-6}$
                 $x = -log(4.5 \cdot 10^{-6})$
                 $x = 5.346767486$
                 $x = 5.35$ ✓
- Calculating the mass of a salt required to give an acidic buffer solution with a specific solution

- sodium propanoate $M_r = 96.07 g mol^{-1}$, $v = 1 dm^3$, $c = 1 mol dm^{-3}$ (propanoic acid) $pka = 4.87$, $pH$ of buffer $= 4.5$

$[H^+] = 10^{-4.5}$          $k_a = 1 \cdot 10^{-4.87}$          $ka = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$          $1.35 \cdot 10^{-5} = \dfrac{(3.16 \cdot 10^{-5})(x)}{1}$

$= 3.16 \cdot 10^{-5} mol dm^{-3}$          $= 1.35 \cdot 10^{-5}$                    $= 1.35 \cdot 10^{-5}$          $x = 0.427 mol dm^{-3}$

$= 1.35 \cdot 10^{-5}$          $= 0.427 mol$

$0.427 \cdot 96.07 = \underline{41.0 g}$

- <span style="color:orange">Characteristics of buffer solutions</span>
  - <span style="color:orange">Dilution</span>
    - The Henderson - Hasselbalch equation ($pH = pka + log_{10}\dfrac{[A^-]}{[HA]}$) shows that the pH of a buffer solution will depend only on the ratio of the concentrations of the acid and their conjugate base, so dilution of the buffer solution should have no effect
      - Due to the fact that when you dilute a buffer with distilled water you will dilute the acidic & alkaline portions equally.
  - <span style="color:orange">Buffering capacity</span>
    - <span style="color:red">The weak acid is used to absorb the additional base added, and the dissociated base is used for acids.</span>
    - Buffer solutions have a limited capacity to resist pH changes.
      - If too much strong acid a base is added to the buffer, no more buffering action is possible.
    - The buffering capacity increases as the concentration of the buffer salt/acid solution increases.
      - The closer the buffered pH is to the pka, the greater the buffering capacity.
    - If HCl is placed in a buffer containing ethanoic acid ($CH_3COOH$) and sodium ethanoate ($CH_3COONa$) the HCl will initially donate its $H^+$ ion to the $CH_3COO^-$ forming $CH_3COOH + Cl^-$.
      - This will lower the pH by lowering the $\dfrac{[CH_3COO^-]}{[CH_3COOH]}$ ratio, but so long as there is a lot of $CH_3COO^-$ present the pH wont decrease significantly. <span style="color:red">Can't more $CH_3COO^-$ be formed by $CH_3COOH$ dissociating to re-establish equilibrium? The reaction is $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. Adding HCl will mean that the equilibrium will shift to the left as there is an excess of products. Therefore, acid buffers are best used for bases rather than acids.</span>
      - The $CH_3COO^-$ is the conjugate base of $CH_3COOH$
    - Once the base has run out the pH will decrease significantly.
      - known as the "breaking the buffer solution".
    - The amount of acid that the buffer can absorb before its breaks is the "buffer capacity of addition of strong acid".
    - The same will occur with a base when all of the weak acid will be used.
    - The ability of a buffer to absorb strong acids & strong bases depends on the individual concentrations of its strong & weak base.
  - <span style="color:orange">Preparation of a buffer</span>
    - To prepare an acidic buffer solution, a weak base would have to be mixed with its own conjugate base which is in its salt.
      - The conjugate base comes from an aqueous salt which dissociates in water giving the base.
    - For a base buffer, a weak base is mixed with its conjugate acid.
    - The base & acid can never be strong because that would mean that the initial solution would be 100% dissociated.
      - Therefore, the acid and base will always have to be weak.
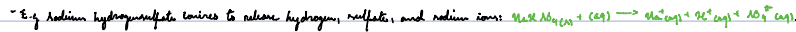
- <span style="color:orange">18.3 pH curves</span>
  - <span style="color:orange">Salt hydrolysis</span>
    - <span style="color:blue">A salt is defined as a compound formed when the hydrogen of an acid is completely or partially replaced by a metal.</span>
      - E.g $HCl + NaOH \rightarrow NaCl + H_2O$ (metal)
    - If all of the hydrogen is replaced then the salt formed is a "normal salt".
    - If only some of the hydrogen is replaced, then the salt formed is an "acidic salt".
    - Acid salts can only be formed diprotic or triprotic acids. Monoprotic acids will always form normal salts.
      - Chart with example acids:

| Acid | Salt | Example(s) | Classification |
|---|---|---|---|
| Hydrochloric acid, HCl | Chlorides | Sodium chloride, NaCl | Normal |
| Nitric acid, $HNO_3$ | Nitrates | Sodium nitrate, $NaNO_3$ | Normal |
| Ethanoic acid | Ethanoates | Sodium ethanoate, $CH_3COONa$ | Normal |
| Sulfuric acid, $H_2SO_4$ | Sulfates and hydrogensulfates | Sodium sulfate, $Na_2SO_4$, and sodium hydrogensulfate, $NaHSO_4$ | Normal and acidic |
| Carbonic acid, $H_2CO_3$ | Carbonates and hydrogencarbonates | Sodium carbonate, $Na_2CO_3$, and sodium hydrogencarbonate, $NaHCO_3$ | Normal and acidic |
| Cyanic acid, HCN | Cyanides | Sodium cyanide, NaCN | Normal |

- If the acid salts are soluble in water, will dissolve to form acidic solutions.
    - E.g sodium hydrogensulfate ionises to release hydrogen, sulfate, and sodium ions: $NaHSO_{4(aq)} + (aq) \rightarrow Na^+_{(aq)} + H^+_{(aq)} + SO_4^{2-}_{(aq)}$.
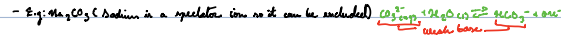    - The dissolved acid salt displays typical acidic properties.
- Normal salts on the other hand if they are soluble will form neutral solutions.
    - E.g $NaCl_{(s)} + (aq) \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$
- Although some normal salts will dissolve in water to form either acidic or alkaline solutions.
    - This is because one of the ions reacts with water to release an excess of either hydroxide or hydrogen ions. This is called salt hydrolysis.
    - E.g: $Na_2CO_3$ ( sodium is a spectator ion so it can be excluded) $CO_3^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^- + OH^-$
        weak base
        - This is an example of hydrolysis of a salt of a weak acid and a strong base. Which is which?
        - $OH^-$ ions are in excess making the solution alkaline.
- Similar reactions will occur between water and the anion of the salt formed from a weak acid and strong base. ⟵ same explained
    - E.g $NH_4^+_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$
- Examples of hydrolysis of a salt of a weak acid and weak base in $CH_3COONH_{4(aq)}$:
    - $NH_4^+_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$ or $CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$
    - Both of these ions ($NH_4^+$ & $CH_3COO^-$) react with water and undergo hydrolysis.
- Other hydrolysis occur with salts that contain metal cations which are small & highly charged.
    - E.g copper (II) sulfate, $CuSO_4$, aluminium sulfate, $Al_2(SO_4)_3$, and iron (III) chloride, $FeCl_3$.
    - These types of hydrolysis occur very readily with trivalent cations ($Fe^{3+}$), much less with $Cu^{2+}$, and not at all with monovalent ions ($Na^+$).
    - The acidity also varies with the ionic radius: the smaller the ion, the greater the hydrolysis.
- <u>Predicting the relative pH of aqueous salt solutions formed by the different combinations of strong and weak acid and base</u>
    - NaF formed by NaOH reacted with HF
        - $NaOH + HF \rightarrow NaF + H_2O \longrightarrow NaF \rightarrow Na^+ + F^-$
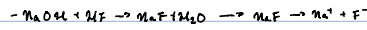        
        Why is it a weak base?
        The reason being that it comes from a strong base, and the stronger the base the weaker the conjugate acid, and vice versa.
        - The pH of NaF will be higher than 7 because of the fact that $Na^+$ is a very weak conjugate acid of NaOH. While $F^-$ ions is a strong conjugate base of HF or its basic enough to remove a $H^+$ ions from water. $F^- + H_2O \rightleftharpoons OH^- + HF$ making the solution alkaline as there will be excess $OH^-$ ions.
- <u>Acid-base titration</u> - titration curves for strong and weak acids & bases
    - <u>Titration of a strong acid against a strong alkali</u>
        - If we have $0.1 mol\,dm^{-3}$ of HCl in a flask initially, then pH will be 1 ($pH = -log_{10}[H^+]$).
        - Once $22.5 cm^3$ of $0.1 mol\,dm^{-3}$ of NaOH is added to $25 cm^3$ of $0.1 mol\,dm^{-3}$ of HCl, the pH will change becoming more alkaline.
        - The amount of HCl which the NaOH removed is given by $v_{removing} = \frac{v_{base}}{v_{acid}} \cdot 100 = \frac{22.5}{25} \cdot 100 = 90\%$ neutralised.
            - 10% of original HCl volume remains unneutralised.
        - The new concentration of $H^+$ ions can be determined by multiplying the original concentration by the new volume: $0.1 mol\,dm^{-3} \cdot 0.1 = 0.01 mol\,dm^{-3}$.
            - Given by the formula: $c_1 \cdot H^+ mole = [H^+]$.
            - The new pH value is now 2.
        - These calculations ignore the dilution effect which follows that the addition of NaOH not only adds $OH^-$ ions, but also increases the volume and therefore the concentration of the resulting solutions.
            - Therefore, the new equation is: new $H^+$ concentration = old $H^+$ ion concentration · unneutralised percentage · dilution effect $\left(\frac{v_1}{(v_1+v_2)}\right)$
            - Therefore, the new $[H^+] = 5.26 \cdot 10^{-3} mol\,dm^{-3}$. Meaning new $pH = -log_{10}(5.26 \cdot 10^{-3}) -> 2.28$
    - Further examples
        - $24.75 cm^3$ of $0.1 mol\,dm^{-3}$ NaOH added to $25 cm^3$ of $0.1 mol\,dm^{-3}$ of HCl    without dilution effect: $0.1 \cdot \left(1 - \frac{24.75}{25}\right)$
            - $[H^+] = 0.1 \cdot \left(1 - \frac{24.75}{25}\right) \cdot \frac{25}{49.75}$    $pH = -log_{10}(4.98 \cdot 10^{-5})$        $[H^+] = 0.001$  pH = 3
            $= 4.98 \cdot 10^{-5} mol\,dm^{-3}$    $= 3.30$
        - $24.975 cm^3$ of $0.1 mol\,dm^{-3}$ NaOH to $25 cm^3$ of $0.1 mol\,dm^{-3}$ HCl.
            - $[H^+] = 0.1 \cdot \left(1 - \frac{24.975}{25}\right)\left(\frac{25}{49.975}\right)$    or $[H^+] = 0.1 \cdot \left(1 - \frac{24.975}{25}\right)$
            $= 5 \cdot 10^{-5} mol\,dm^{-3}$  pH = 4.3    $[H^+] = 1 \cdot 10^{-4}$  pH = 4
        - $24.9999 cm^3$ of NaOH, $0.1 mol\,dm^{-3}$, $25 cm^3$ of HCl, $0.1 mol\,dm^{-3}$
            - $[H^+] = 0.1 \cdot \left(1 - \frac{24.9999}{25}\right) \cdot \frac{25}{49.9999}$    $[H^+] = 0.1 \cdot \left(1 - \frac{24.9999}{25}\right)$
            $= 2 \cdot 10^{-7} mol\,dm^{-3}$  pH = 6.7    $= 4 \cdot 10^{-7} mol\,dm^{-3}$  pH = 6.3
        - These calculations show that the pH rises very quickly near the end-point or equivalence point where the reacting volumes will be equal.
            - The equivalence point is the point at which the reactants are of equal quantities.

- When 25cm³ of NaOH is added to 25cm³ of acid of 0.1moldm⁻³ it gives a pH of exactly 7, since the OH⁻ & H⁺ ions are in a 1:1 ratio.
- If aqueous NaOH is continually added beyond the end-point, there will be excess OH⁻ ions since all of the H⁺ ions were used up in neutralisation.
- The OH⁻ concentration begins to rise as quickly after the end point as the hydrogen ion concentration decreased before the end-point.
  - The pH after 25.5cm³ of 0.1moldm⁻³ sodium hydroxide added to 25cm³ of 0.1moldm⁻³ HCl.
    - reaction factor = $\left(\frac{25.5-25}{25}\right) \cdot \frac{0.5}{25} = 0.02$
    - approx pH (ignoring dilution effect):
      - $0.1 - 0.02 = 0.02\ moldm^{-3}\ [OH^{-1}]$   $pOH = -\log 0.002$   $pH = 14 - pOH$
        $= 2.69$   $= 11.3$

**Titration of a weak acid against a strong alkaline**
- 25cm³ of 0.1moldm⁻³ ethanoic acid requires exactly 25cm³ of 0.1moldm⁻³ of NaOH to reach the equivalence point.
  - when the volumes react, neutralisation occurs and only sodium ethanoate and water will remain.
    - $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O_{(l)}$
  - the resulting solution won't be neutral because ethanoic acid is a weak acid and forms H⁺ ions as well as a conjugate base when dissociating.
    - ==this is why the equivalence point will be higher, because the conjugate base of the ethanoic acid will bond with the sodium ion to form a alkaline salt (products of the neutralisation of a strong base (NaOH) and a weak acid (CH₃COOH)). When this salt is in water (formed from reaction), it will react with the water to form its CH₃COOH and more OH⁻ ions. The Na⁺ & OH⁻ won't react as they are from a strong base and the reaction is always to the right.==
  - At the beginning of the titration the pH will be about 3 since CH₃COOH is a weak acid.
  - adding NaOH will result in OH⁻ ions being added, forming water & shifting the equilibrium for ethanoic acid to the right.
  - ==Titration curve for the titration of 25cm³ of 0.1moldm⁻³ ethanoic acid with 0.1moldm⁻³ sodium hydroxide==
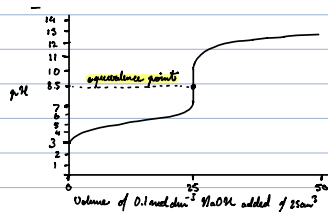


- the CH₃COOH can be seen that its a weak acid because of its relatively high starting pH and its s like shape.
  - this is due to the fact that ethanoic acid being a weak acid will mean that only a small percentage of the substance will dissociate therefore the lack of H⁺ ions will result in a higher pH value.
- the dissociation of CH₃COOH will be gradual since its a weak acid and as more OH⁻ ions are added, more H⁺ ions will be formed from the shift in the equilibrium.
- The reason that the pH at the equivalence point will be higher than 7, is because of the fact that CH₃COONa will dissolve in the water formed from reacting NaOH with CH₃COOH. The ==CH₃COONa is a salt from a strong base and a weak acid, meaning its an alkaline salt==, and when its dissolved in water it will dissolve to form: $CH_3COONa + aq \rightarrow CH_3COO^- + Na^+ \longrightarrow CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
  - the forward reaction is heavily favored (CH₃COO⁻ + H₂O reaction).
- When a base is added to a weak acid (seen in figure above), the steady increase show where the best buffering action occurs. known as buffer regions.
- The titration curve of a weak acid also shows the pKa and in turn the Ka.
  - To do so the ==half-neutralised acid (12.5cm³ of alkali)== corresponds to the pKa of the acid. During the titration of CH₃COOH the NaOH will gradually convert the CH₃COOH into ions, so ==halfway to the end point half of the ethanoic acid molecules will have been converted to ethanoate ions.==
    - meaning [CH₃COOH] = [CH₃COO⁻].
    - therefore $Ka = [H^+]\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$
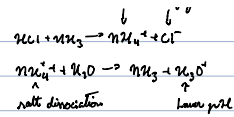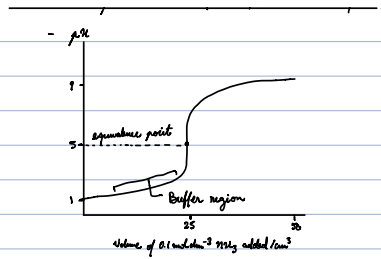      $Ka = [H^+] \cdot 1$
      $Ka = [H^+]$
      $pKa = pH$

**Titration of a strong acid against a weak alkali**
- If 0.1moldm⁻³ of HCl is titrated against 0.1moldm⁻³ of aqueous ammonia (NH₃), then the pH will change by a very small amount until its near the equivalence point, where it changes quickly.
  - the equivalence point will be low (≈ pH 5) since ammonia is a weak base.
  - Titration curve of the titration of 25cm³ of HCl with 25cm³ of NH₃.                                    salt    conjugate base

$$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$

salt dissociation      lower pH



- **titration of a weak acid against a weak alkali**
    - If $0.1 \, mol \, dm^{-3}$ of ethanoic acid is titrated against $0.1 \, mol \, dm^{-3}$ of ammonia the titration curve formed will be much more gradual with no sharp change in pH, meaning no vertical section.
    - No indicator is suitable for this process.
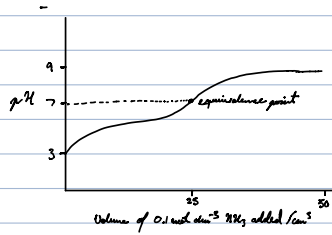


- **Indicators**
    - **Nature of indicators**
        - Acid-base indicators are soluble dyes which change color according to the hydrogen ion concentration, that is, the pH.
        - Indicators are usually weak acids where the acid molecule and its conjugate base are different colors.
            - The wavelength of the light absorbed by the acid changes greatly when a proton is lost to form the conjugate base.
        - Phenophthalein indicator structure.
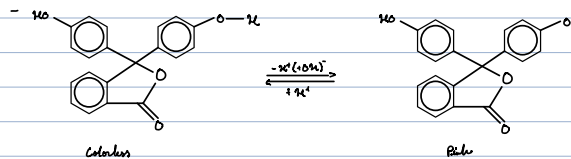


- **Action of indicators**
    - Example indicator. $HIn_{(aq)}$ (acid), $In^-$ (conjugate base), $H^+$ (conjugate acid).
        - $HIn_{(aq)} \rightleftharpoons In^-_{(aq)} + H^+_{(aq)}$    or    $HIn_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}$
    - Bromophenol blue has a yellow color when it's a molecule, and it's blue when it's dissociated.
        - When the indicator is placed in a neutral substance, the color will be yellow because the acid won't dissociate much. Therefore, there will be a relatively high concentration of $HIn$ molecules.
    - **Addition of acid:**
        - If the indicator is placed in a solution with an excess of $H^+$ ions then the equilibrium will shift to the left according to the Le Châtelier's principle. This will increase the concentration of $HIn_{(aq)}$.
    - **Addition of an alkaline.**
        - When there will be an excess of $OH^-$ ions, then the $H^+$ ions that are from the dissociated acid will bond with them to then shift the equilibrium to the right to produce more $H^+$ ions, making the color blue.
    - $\dfrac{[HIn_{(aq)}]}{[In^-_{(aq)}]} = \dfrac{[H^+_{(aq)}]}{[Ka]}$
        - This equation shows that the color of an indicator depends not only on the hydrogen ion concentration, that is the pH, but also on the value of the acid dissociation constant, $Ka$.
    - $pH = pka + \log_{10} \dfrac{[In^-_{(aq)}]}{[HIn_{(aq)}]}$
- **pH range of indicator**
    - In general the color change takes place over a range of 2 pH units, specifically, from $pH = pka - 1$ to $pH = pka + 1$, so from 10% of one form of the indicator to 10% of the other form.
    - A few indicators undergo more than one change. E.g. thymol blue at pH 1.2 - 2.8 & 8.0 - 9.6.

- The reason being that the undissociated acid is in equilibrium with the two coloured forms.

## Indicators as weak bases

- methyl orange is a weak base which can be represented as $BOH_{(aq)}$. Its red when its dissociated, and yellow when its a molecule.
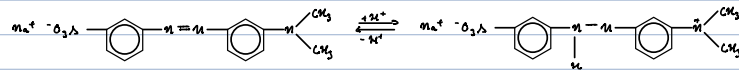- **Addition of acid:**
    - If even acid ($H^+$ ions) is added to a solution of the indicator, the equilibrium will shift to the right because there will be a deficit of $OH^-$ ions, this will increase the concentration of its conjugate acid, meaning the color will become red.
- **Addition of a base**
    - If $OH^-$ ions are added then the equilibrium will shift to the left, because there will be an excess. This will make the solution yellow.
- Structure of methyl orange:

$$Na^+ \; {}^-O_3S - \bigcirc - N=N - \bigcirc - N\begin{matrix}CH_3\\CH_3\end{matrix} \xrightleftharpoons[-H^+]{+H^+} Na^+ \; {}^-O_3S - \bigcirc - N-N - \bigcirc - \overset{+}{N}\begin{matrix}CH_3\\CH_3\end{matrix}$$

- The best indicator to choose is an indicator that changes in the vertical section of the acid equivalence point. This is indicated in section 22 of the booklet.

## Conductometric titrations
- The conductivity can show the end point because as base is added to the acid or vice versa, the $H^+$ and $OH^-$ ions will form water decreasing the conductivity of the solution.
- At the end point the conductivity should be zero or in the case of titration between a weak acid/base with a strong base/acid, there will still be some ions present but it will be the lowest value.