OCR (B) Chemistry A-level

Storyline 8: Oceans
Detailed Notes

Energetics

Solubility

The relative solubilities of a solute in aqueous and nonaqueous solvents are determined by some important factors. With respect to **intermolecular forces**, the stronger the interactions are between the solute and the solvent molecules, the more soluble the solute will be in that particular solvent. Therefore **polar** molecules will be soluble in polar solvent (most prominent intermolecular forces are dipole-dipole interactions between the molecules), **nonpolar** molecules will be soluble in nonpolar solvents (most prominent intermolecular forces are london dispersion/Van der Waals forces). Generally polar molecules and nonpolar molecules do not mix.

Ionic compounds are more soluble in polar solvents like water, as ions are charged and can form strong favourable interactions with the solvents.

Lattice Enthalpy ($\Delta_{LE}H$)

Lattice enthalpies are used for **ionic substances**. Lattice enthalpy is a measure of the strength of ionic bonding in a giant ionic lattice.

Lattice **dissociation** enthalpy is defined as:

> **The enthalpy change when one mole of a solid ionic compound is completely dissociated into its gaseous constituent ions under standard conditions.**

This is an **endothermic process.**

Lattice **formation** enthalpy is defined as:

> **The enthalpy change when one mole of a solid ionic compound is formed from its gaseous constituent ions under standard conditions.**

This is an **exothermic process.**

Lattice enthalpy cannot be measured directly. It is calculated using experimental values for other enthalpy changes in a cycle called a **Born-Haber cycle**.

Enthalpies of Solution ($\Delta_{sol}H$) and Hydration ($\Delta_{hyd}H$)

Enthalpies of solution and hydration can be used as another way of measuring lattice enthalpies **indirectly**. They are combined using a similar idea to Hess's Law.

Enthalpy of **solution** is defined as:

The enthalpy change when one mole of ionic solid is dissolved in water to infinite dilution so that the ions no longer interact under standard conditions.

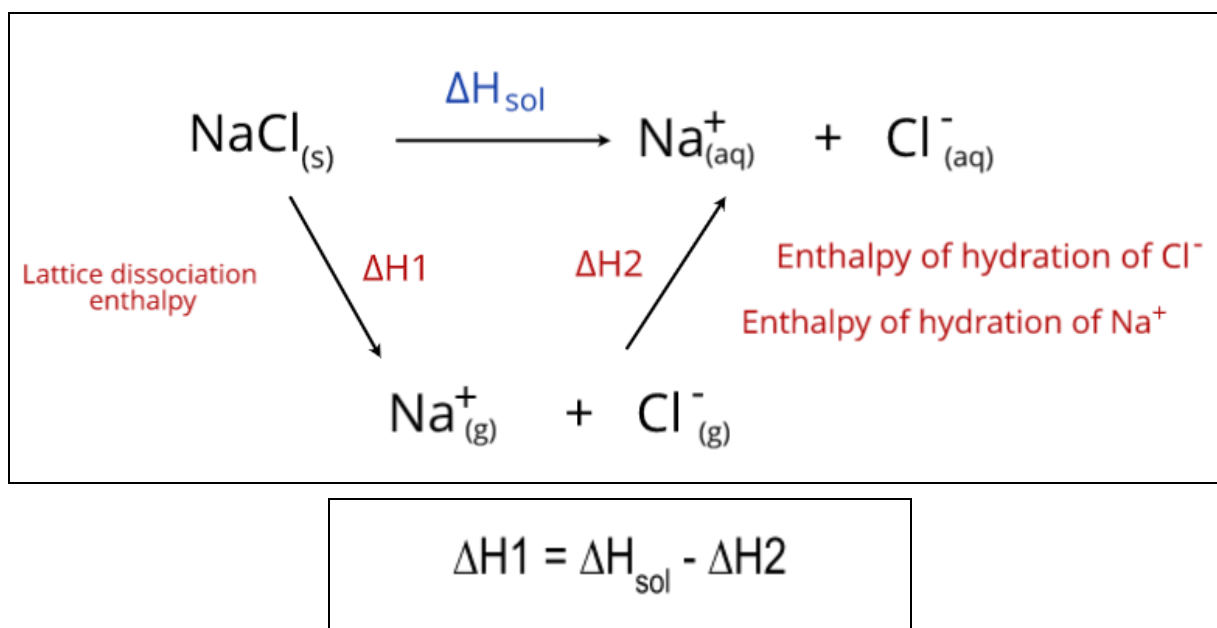Enthalpy of **hydration** is defined as:

The enthalpy change when one mole of gaseous ions is dissolved in water to form one mole of aqueous ions under standard conditions.

Enthalpy of hydration is nearly always **negative** as water molecules have **δ+ regions** that naturally **attract** negative ions.

When a solvated ion is surrounded by solvent molecules that are aligned in a spherical shell, this is a **hydrated ion**.

The enthalpy of solution and the enthalpy of hydration are combined in the following way to form an **energy cycle**.

Example: Calculating the lattice dissociation enthalpy of sodium chloride

$$\Delta H1 = \Delta H_{sol} - \Delta H2$$

Factors Affecting Enthalpy of Hydration and Lattice Enthalpy

Enthalpy of hydration is a measure of the attraction between ions (that were in a lattice) and water molecules in solution. **Positive ions** will be attracted to the **δ- oxygen atoms**, and **negative ions** will be attracted to the **δ+ hydrogen atoms.**

Attractions are stronger with **smaller ions** and with ions of a **greater charge**. This explains why hydration enthalpies **decrease** as you move **down a group** and why Na^+ ions have a lower enthalpy of hydration than Mg^{2+} ions.

Lattice dissociation enthalpy also **increases** in magnitude with **decreasing ionic radius** and **increasing charge**. This is because the ions form **stronger attractions** and so the energy required for dissociation is greater.
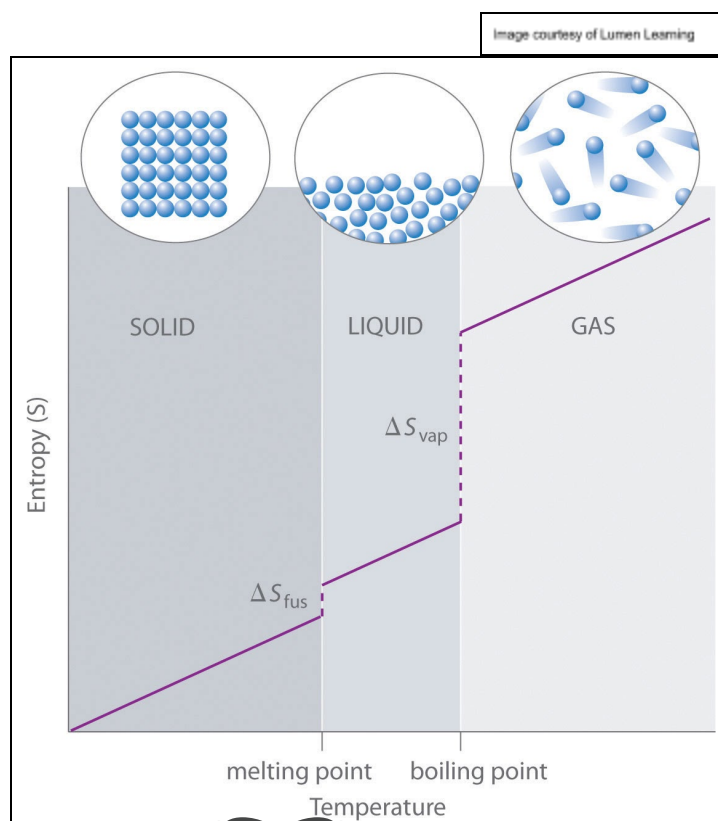
Entropy

In chemistry, things tend towards a state of **disorder**. Entropy, **ΔS**, is a **measure of disorder**. It is a measure of the dispersal of energy in a system, which is greater the more disordered a system is.

Some **endothermic reactions** are able to occur **spontaneously** at room temperature. This shows how enthalpy is not the only driver of chemical reactions. **Entropy** is also key.

Entropy increases as temperature increases because the particles **gain energy** and move **faster and further apart**. In other words, the particles become less ordered.

Gases have the **greatest entropy** compared to solids and liquids.

When a substance melts or evaporates, there is a **sudden increase** in entropy. The entropy change of vaporisation is much greater than that of fusion as a **gas is much more disordered** than a liquid or a solid.

Another case where there is a sudden increase in entropy is in a reaction when there are **more moles of gaseous product** than reactants. In this case there is an **increase in disorder**.

When a **lattice** is **dissolved** in solution, there is an increase in entropy. This is because the ions that make up the lattice are **dissociated** and can **move** in the solution, as opposed to being held in their positions by strong bonds. This freedom of movement causes an **increase in disorder.**

The overall entropy change for a reaction can be calculated. It is measured in **$J\ K^{-1}\ mol^{-1}$**:

The entropy change for a reaction within a system can be calculated by finding the difference between the standard entropies of the **products** and the **reactants**:

$$\Delta S_{total} = \Sigma \Delta S_{products} - \Sigma \Delta S_{reactants}$$

If the entropy change for a reaction is **positive**, the products are **more disordered** than the reactants.

If the entropy change for a reaction is **negative**, the products are **less disordered** than the reactants.

Generally, you will only calculate the entropy change within a system. However, it is important to understand that the **natural direction of change** is towards a more disorderly state overall, which is a **positive change** in entropy. An example of this is the natural and spontaneous spreading of gas throughout a room, or the expansion of the universe.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

Solubility Product, K_{sp}
The solubility constant indicates **how much a compound dissociates in water.** It only applies to saturated compounds. The higher the value, the more soluble the compound.

When an ionic solid dissolves in water, an **equilibrium** is established between the ions and the compound. E.g. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

The equilibrium constant is called the **solubility product**:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$BaSO_4(s)$ isn't present in the equilibrium constant equation because it is a solid in a **heterogeneous equilibrium**. The number of molecules of each substance is used in the K_{sp} equation in the same way as in other equilibrium constant equations (e.g. if there were $2Ca^{2+}(aq)$ in the equilibrium equation, K_{sp} would contain $[Ca^{2+}]^2$).

The **units** for solubility products are worked out using the equation:

- For $BaSO_4$:
  $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
  $(mol\ dm^{-3})$ x $(mol\ dm^{-3})$
  $= mol^2\ dm^{-6}$
- For $Ca_3(PO_4)_2$:
  $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$
  $(mol\ dm^{-3})^3$ x $(mol\ dm^{-3})^2$
  $= mol^5\ dm^{-15}$

The solubility product for a compound will always be **the same under the same conditions** provided that the solution is saturated. If two compounds are mixed together, a precipitate will only form if the ionic concentrations give a value greater than the solubility product (otherwise, the solution won't be saturated).

Example calculations:
- The solubility of magnesium hydroxide, $Mg(OH)_2$, at 298 K is 1.71 x 10^{-4} mol dm^{-3}.
  $Mg(OH)_2(s) \leftrightharpoons Mg^{2+}(aq) + 2OH^-(aq)$
  The concentration of $Mg(OH)_2$ is 1.71 x 10^{-4} mol dm^{-3}, so using the equation:
    - $[Mg^{2+}] = 1.71$ x 10^{-4} mol dm^{-3}
    - $[OH^-] = 2$ x $(1.71$ x $10^{-4}) = 3.42$ x 10^{-4} mol dm^{-3}
  $K_{sp} = [Mg^{2+}][OH^-]^2$
  $= (1.71$ x $10^{-4})$ x $(3.42$ x $10^{-4})^2$
  $= 2.00$ x 10^{-11} mol^3 dm^{-9}

- The solubility product of barium sulfate, $BaSO_4$, at 298K is 1.10 x 10^{-10} mol^2 dm^{-6}.
  $BaSO_4(s) \leftrightharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$
  Using the equation (where y is the unknown solubility):
    - $[Ba^{2+}] = y$
    - $[SO_4^{2-}] = y$
  $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
  1.10 x $10^{-10} = y$ x y
  1.10 x $10^{-10} = y^2$
  $y = \sqrt{(1.10\ x\ 10^{-10})} = 1.05$ x 10^{-5} mol dm^{-3}

Equilibria (Acid–Base)

Brønsted–Lowry Acids and Bases

Acid-base equilibria involve the **transfer of protons** between substances. Therefore, substances can be classified as acids or bases depending on their interaction with protons.

A Brønsted-Lowry **acid** is a **proton donor**. For example, ammonium ions (NH_4^+).
A Brønsted-Lowry **base** is a **proton acceptor**. For example, hydroxide ions (OH^-).

Brønsted–Lowry conjugate acid-base pairs

A **conjugate acid** is the species formed when a **base accepts a proton**. A **conjugate base** is the species formed when an **acid donates a proton**. Conjugate acids and conjugate bases form conjugate acid-base pairs.

Example:
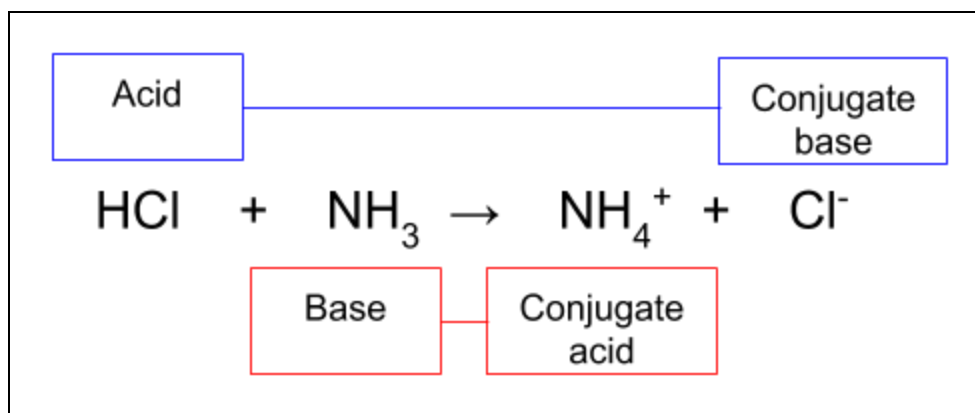
Acid and Base Strength

Acid strength doesn't refer to the concentration of a solution. A **strong acid** is defined as being:

An acid that completely dissociates into its ions when in solution.
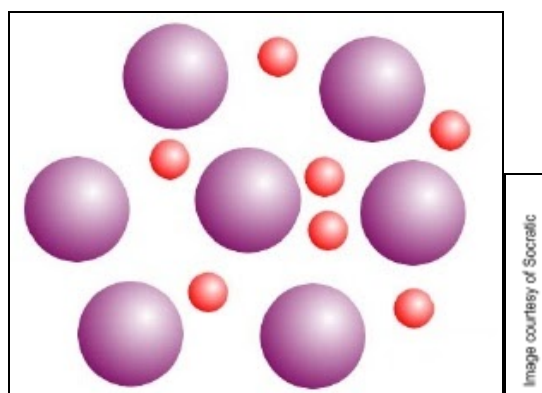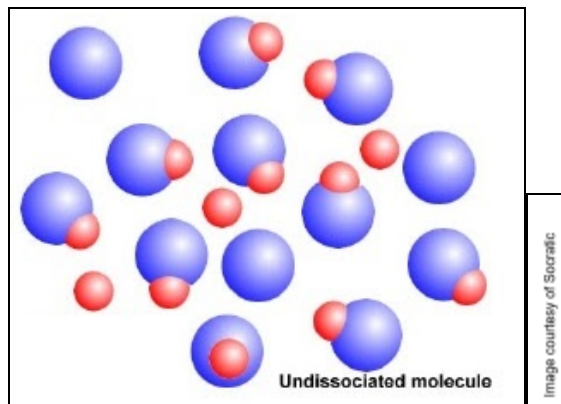
Example:

In comparison, a **weak acid** is defined as being:

An acid that only slightly dissociates into its ions when in solution.

Example:

Undissociated molecule

Image courtesy of Socratic

The same definitions are true for **strong** and **weak bases**.

Strong acids have pH between 0-1 and weak acids have pH between 3-7. Strong bases have pH between 12-14 and weak bases have pH between 7-11.

Ionic Equations
An ionic equation shows the **reacting ions** in a chemical equation. **Spectator ions** are ions that do not change in the reaction and are left out of the ionic equation. It is important to **balance** elements and charge in ionic equations.

In the reactions of acids with carbonates, metal oxides, and alkalis, H^+ is the reacting ion.

Example:

$$2H^+_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)}$$
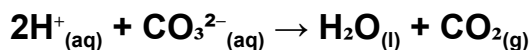
The Acid Dissociation Constant
Weak acids and bases only **slightly dissociate** in solution to form an **equilibrium** mixture. Therefore, the reaction has an acid dissociation constant, **Ka**.
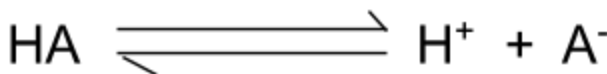
$$HA \rightleftharpoons H^+ + A^-$$

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

The constant Ka can be found using **pKa**:

$$pK_a = -\log_{10}K_a$$

$$K_a = 10^{-pK_a}$$

The value pKa is a logarithmic acid dissociation constant, representing how acidic something is. A **low value** of pK_a, or equivalently a large K_a, indicates a **strong acid**.

Determining pH

pH is a measure of **acidity and alkalinity**. It is a **logarithmic** scale from 0 to 14 that gives the concentration of **H^+ ions** in a solution. 0 is an **acidic** solution with a high concentration of H^+ ions whereas 14 is a **basic** solution with a low concentration of H^+ ions.

pH is a specific example of pK_a for when H^+ ions are present. It can be calculated using the **concentration of hydrogen ions**, $[H^+]$, as follows:

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

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

This equation also allows the concentration of H^+ ions to be determined if the pH is known. When using these equations above, the concentration of H^+ ions is given in **mol dm^{-3}**.

This concentration of H^+ ions is equivalent to the **concentration of a strong acid** as it **completely dissociates** to ions in solution.

Ionic Product of Water

Water **slightly dissociates** to form hydroxide and hydrogen ions in an equilibrium with its own equilibrium constant, **Kw**.

$$K_w = [H^+][OH^-]$$

At **25°C**, room temperature, Kw has a constant value of **1.0×10^{-14}**. However, as temperature changes, **this value changes**.

The **forward** reaction in the equilibrium of water is **endothermic** and is therefore favoured when the temperature of the water is increased. As a result, as temperature increases, **more H^+ ions** are produced meaning the water becomes **more acidic.**

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

In the same way that pKa can be calculated from Ka, **pKw** can be calculated from **Kw**.

$$pK_w = -\log_{10}K_w$$

$$K_w = 10^{-pK_w}$$

The pH of a **strong base** can be calculated using pKw or Kw. For a **strong base**, the concentration of OH^- will be the **same** as the concentration of the base.

$K_w = [OH^-][H^+]$
Rearrange Kw to find $[H^+]$: $[H^+] = \dfrac{K_w}{[OH^-]}$
Use $K_w = 10^{-14}$ and the concentration of the base to find $[H^+]$.

Finally, calculate pH using: $pH = -\log_{10}[H^+]$

Calculations
The relationships of Ka, pKa and $[H^+]$ can be used to find the **pH of weak acids and bases**. Depending on the reaction and the relative concentrations, a different method may have to be used:

HA in excess - Use [HA] and $[A^-]$ along with Ka to find $[H^+]$, then pH.

A^- in excess - Use Kw to find $[H^+]$, then pH.

HA = A^- - In this case, pKa is equal to pH, therefore find pKa.

Calculating the Ka of Weak Acids
Weak acids only **partially dissociate** in solution. Therefore, the **equilibrium** of a weak acid has to be taken into account.

1. The initial concentrations, change in concentrations and equilibrium concentrations of the reactants and products have to be found.
2. The concentration of H^+ ions can then be found using the pH given.
3. This value can be used to find the actual equilibrium concentrations.
4. Finally, these values can be substituted into the expression for Ka.

Example:
A weak acid, HA, with a concentration of 0.25 M has a pH of 3.5. What is its Ka?
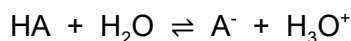
$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$
We assume that 'x' mol of HA dissociates to A^- and H_3O^+.

	HA	A⁻	H₃O⁺
Initial	0.25	0	0
Change	-x	+x	+x
End	0.25 - x	x	x

Using the pH value give, the $[H^+]$ (= x) can be calculated:

$$[H_3O^+] = [H^+] = 10^{-pH}$$

$$[H^+] = 10^{-3.5} = 3.16 \times 10^{-4} \text{ M}$$

$$x = 3.16 \times 10^{-4} \text{ M}$$

Substituting into the expression for Ka and using the equilibrium concentrations:

$$Ka = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.25-x)}$$

We can now substitute in the value of x calculated earlier: x = 3.16 x 10⁻⁴ M

$$Ka = \frac{(3.16 \times 10^{-4})^2}{(0.25 - (3.16 \times 10^{-4}))}$$

$$Ka = 3.99 \times 10^{-7}$$

Approximations
For weak acid calculations, the following approximations are made:

$[HA]_{equilibrium} \sim [HA]_{undissociated}$ i.e. $[HA] \gg [H^+]$

$[HA]_{equilibrium} \sim [A^-]_{equilibrium}$ i.e. negligible dissociation of H_2O

These approximations are limited to calculations for weak acids. For stronger weak acids, the approximations breakdown because the first assumption may no longer be valid.

Buffers

A buffer solution is a system that **minimises pH changes** on addition of small amounts of an acid or a base. It is formed from a **weak acid and its salt** or an excess of a **weak acid and a strong alkali**. This produces a mixture containing **H^+ ions** and a large **reservoir of OH^-** ions which helps to resist any change in pH. Therefore, a buffer solution is defined as:

**A solution which is able to resist changes in pH when
small volumes of acid or base are added.**

The large reservoir of OH^- ions allows the **ratio of acid to base** in the mixture to be kept almost **constant**.

Consider the following buffer solution: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

The **OH^- concentration** will **increase** if a small amount of base is added, making the solution more basic. The extra OH^- ions will react with the NH_4^+ ions, to form the **original reactants**. Therefore, the equilibrium will shift to the left to remove the OH^- ions and stop the pH from changing largely.

Buffer Calculations

Buffer calculations are long calculations that use acid-base calculations. There are two types:

Acid + Base - Find the number of moles of each species.
- Calculate their concentrations when at equilibrium using the total volume.
- Use Ka to find [H^+] and therefore pH.

Acid + Salt - Find the moles of the salt.
- Use Ka to find pH.

Example:
A buffer solution contains 0.35 mol dm^{-3} methanoic acid and 0.67 mol dm^{-3} sodium methanoate. For methanoic acid, Ka = 1.6 x 10^{-4} mol dm^{-3}. Find the pH of this buffer.

We **assume** that the **sodium methanoate completely dissociates** so that the equilibrium concentration of HCOO$^-$ is the same as the initial concentration of HCOO$^-$Na$^+$. Similarly, HCOOH only slightly dissociates so we assume that the **equilibrium concentration** is equal to the **initial concentration**.

1. First, find the expression for Ka for methanoic acid
   $$HCOOH \rightleftharpoons H^+ + HCOO^-$$
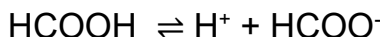
$$Ka = \frac{[H^+] \times [HCOO^-]}{[HCOOH]}$$

2. Rearrange the expression to find [H$^+$]

$$[H^+] = \frac{Ka \times [HCOOH]}{[HCOO^-]}$$

$$[H^+] = 1.6 \times 10^{-4} \times (0.35/0.67) = 8.4 \times 10^{-5}$$

3. Convert [H$^+$] to pH

$$pH = -\log_{10}(8.4 \times 10^{-5}) = 4.08$$

Adding Small Volumes

The pH of a buffer solution doesn't change much but will change in the **order of 0.1 or 0.01 units of pH** when a **small volume** of acid or base is added.

Adding small amounts of **acid (H$^+$) increases the concentration** of the acid in the buffer solution, meaning the overall solution will get slightly **more acidic**.

Adding small amounts of **base (OH$^-$) decreases the concentration** of acid in the buffer solution, meaning the overall solution will get slightly more **basic**.

Uses of Buffers

Buffer solutions are common in **nature** in order to keep systems regulated. This is important as **enzymes** or reactions in living organisms often require a **specific pH**, which can be maintained using a buffer solution.

Another important buffer in nature is found in the human circulatory system. The **pH of human blood** is maintained in a buffer between **carbonic acid and hydrogencarbonate ions**. These ions **neutralise any acidic substances** that enter the bloodstream, converting them to carbonic acid and water. This buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

Energy and Matter

The Greenhouse Effect

The **greenhouse effect** is the process of radiation from the atmosphere (it is usually **UV and visible radiation** that reaches the earth), warming the planet above temperatures that it would have reached without the atmosphere. The planet then radiates energy (often IR radiation) outwards in all directions. Greenhouse gases (e.g. carbon dioxide and methane) in the **troposphere** absorb some of this IR, which increases their kinetic energy alongside their vibrational energy in their bonds. Vibrational energy like this can be passed along to other molecules by **collisions**, increasing their kinetic energy. This causes a general increase of

energy so also causes an **increase in temperature**. An increase in greenhouse gases being emitted into the atmosphere leads to an increase in the greenhouse effect.