

# Edexcel IAL Chemistry A-level

## Unit 4: Rates, Equilibria and Further Organic Chemistry Definitions

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## Definitions and Concepts for Edexcel IAL Chemistry A-level Rates, Equilibria and Further Organic Chemistry

### Topic 11: Kinetics

**Activation energy:** The minimum energy required for a reaction to occur between two colliding particles.

**Arrhenius equation:**  $k = Ae^{-E_a/RT}$ , where  $k$  is the rate constant,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the gas constant and  $T$  is the temperature.

**Catalyst:** Provide a lower activation energy for a reaction to occur by providing an alternative reaction route. A catalyst does not affect the equilibrium constant since it increases the rate of the forward and backward reaction equally.

**Colorimetry:** Method used to calculate the concentration of a specific coloured compound in a solution by measuring the extent to which it absorbs certain wavelengths of light. Measured with a colorimeter.

**Concentration-time graph:** A graph which can be used to deduce the rate of reaction by drawing tangents to the curve.

**First order reactant:** A substance in the reactant mixture where the rate of reaction is directly proportional to the concentration of this substance.

**Half-life ( $t_{1/2}$ ):** The time taken for the initial concentration of the reactants to decrease by half.

**Halogenoalkane:** An organic compound containing a halogen atom attached to an alkyl chain.

**Heterogeneous catalysts:** Catalysts that are in a different phase or state to the species in the reaction.

**Homogeneous catalysts:** Catalysts that are in the same phase or state as the species in the reaction.

**Initial rate:** The rate of a reaction at time  $t=0$ .

**Nucleophile:** An electron pair donor.

**Nucleophilic substitution:** A reaction in which an electron pair donor attacks an electrophilic atom (an atom with a partial or full positive charge) to replace an atom/group of atoms.





**Order of reaction:** Tells you how the reactant's concentration will affect the rate of reaction. In the rate equation, it is the power to which the concentration of the reagent is raised.

E.g. rate =  $k[A]^2[B]$ .

**Primary carbocation:** A molecule in which the carbon with the positive charge is only attached to one alkyl group. This is the least stable carbocation.

**Rate-concentration data:** Rate-concentration data or graphs can be used to deduce the order (0, 1 or 2) with respect to a particular reactant.

**Rate constant:** Relates the rate of a chemical reaction at a given temperature to the product of the concentrations of reactants.

**Rate determining step:** The slowest step in a multi-step reaction. The overall rate is decided by this step. Species present in the rate determining step will also be in the rate equation.

**Rate equation:** Describes the relationship between the rate of chemical reaction and the concentrations of reagents.

$$\text{Rate} = k[A]^m[B]^n,$$

where  $k$  is the rate constant and where  $m$  and  $n$  are the orders of reaction with respect to reactants A and B.

In this example, the reaction is 1st order with respect to B, and 2nd order with respect to A. Therefore increasing the concentration of B by a factor of 2 will increase the rate by the same factor. However, increasing the concentration of A by 3 will increase the rate by a factor of  $3^2 = 9$ .

**Rate of reaction:** The rate at which the reactants are converted into products.

**Second order reactant:** A substance in the reactant mixture where the rate of reaction is directly proportional to the square of the concentration of this reactant.

**Secondary carbocation:** A molecule in which the carbon with the positive charge is attached to two alkyl groups. This is more stable than a primary carbocation but less stable than a tertiary carbocation.

**S<sub>N</sub>1:** A nucleophilic substitution reaction which occurs in two steps. The S<sub>N</sub> stands for it being a nucleophilic substitution reaction, and the 1 means it occurs in two steps.

**S<sub>N</sub>2:** A nucleophilic substitution reaction which occurs in one step.



**Substitution:** A reaction in which one atom/group of atoms replaces another.

**Tertiary carbocation:** A molecule in which the carbon with the positive charge is attached to three alkyl groups. This is the most stable type of carbocation.

**Total order of a reaction:** Sum of all the individual orders of all the reactants in a chemical reaction.

**Zero order reactant:** A substance in the reactant mixture where the rate of reaction is independent of the concentration of this reacting substance.

## Topic 12: Entropy and Energetics

### Topic 12A: Entropy

**Endothermic:** A reaction which takes in energy from the surroundings ( $\Delta H$  is positive). The reaction mixture and surroundings will decrease in temperature as heat energy is absorbed by the reaction.

**Entropy:** A measure of the disorder of a system. The units of entropy are  $\text{JK}^{-1}\text{mol}^{-1}$ . On a molecular level, gases are more disordered than liquids, which are more disordered than solids. A reaction that produces a greater number of molecules than the number of reactant molecules will have a positive entropy change, as more random arrangements of these molecules will exist, in other words, the system will become more disordered.

**Entropy change:** This can be calculated by finding the difference between the standard entropies of the products and the reactants:

$$\Delta S_{\text{total}} = \sum \Delta S_{\text{products}} - \sum \Delta S_{\text{reactants}}$$

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.

**Feasible reaction:** For a reaction to be feasible at a given temperature it must occur spontaneously. This means no extra energy is required for the reaction to occur.



**Gibbs free-energy change:** A measure of the feasibility of a chemical reaction. This equation relates Gibbs free energy to enthalpy change, entropy change and temperature. A non-positive Gibbs free energy change means the reaction is feasible and a positive Gibbs free energy change means it is not feasible.

$$\Delta G = \Delta H - T\Delta S_{\text{system}}$$

## Topic 12B: Energetics

**Atomisation enthalpy ( $\Delta_{\text{at}}H$ ):** The energy required for the formation of one mole of gaseous atoms from an element in its standard state under standard conditions.

**Bond enthalpy:** The amount of energy required to break one mole of the stated bond in the gas phase.

**Born-Haber cycle:** Calculates the lattice enthalpy by applying Hess's law and comparing the standard enthalpy change of formation of the ionic compound to values such as ionisation energy and electron affinity.

**Covalent character:** The partial sharing of electrons between atoms that have an ionic bond.

**Enthalpy of electron affinity ( $\Delta_{\text{ea}}H$ ):** The enthalpy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous 1- ions under standard conditions.

**Enthalpy of hydration:** 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 solution:** The enthalpy change when one mole of solute is dissolved in water to infinite dilution so that the ions no longer interact, under standard conditions.

**Lattice dissociation enthalpy:** 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:** 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.

**Perfect ionic model:** Model which assumes that all ions are perfectly spherical, charge is distributed evenly throughout the ion and that the ions display no covalent character.





## Topic 13: Chemical Equilibria

**Endothermic reaction:** A reaction that takes in energy from the surroundings ( $\Delta H$  is positive). The energy of the products is higher than the reactants.

**Equilibrium:** A chemical state in which the forward and reverse reactions of a process occur at the same rate. This means there is no overall change in the concentrations of the reactants and products.

**Equilibrium constant (K):** A value that relates the amount of products and reactants at equilibrium in a reversible reaction at a specific temperature. K is unaffected by pressure and presence of a catalyst but is affected by temperature.

**Exothermic:** A reaction that releases energy to the surroundings ( $\Delta H$  is negative). The energy of the reactants is higher than the products.

**Heterogeneous equilibrium:** An equilibrium reaction that involves substances in different states (solid, liquid, or gaseous).

**Heterogeneous systems:** A system where the reactants and products are in different phases.

**Homogeneous equilibrium:** An equilibrium reaction that involves substances all in the same state (solid, liquid, or gaseous).

**Homogeneous system:** A system where all the reactants and products are in the same phase.

**$K_c$ :** A value that relates the concentrations of products and reactants present at equilibrium in a reversible reaction at a specific temperature. The equilibrium constant that is equal to the concentration of products raised to their stoichiometric coefficients divided by the concentration of reactants raised to the power of their stoichiometric coefficients. Liquids and solids are not included in heterogeneous  $K_c$  expressions as their concentrations effectively remain constant.

**$K_p$ :** A value that relates the amounts of gaseous products and gaseous reactants present at equilibrium in a reversible reaction at a specific temperature. For example:



$$K_p = \frac{p(C)^2}{p(A) \times p(B)^3}$$

where  $p(X)$  is the partial pressure of each gas at equilibrium.





**Mole fraction:** A value used in the calculation of partial pressure.

$$\text{Mole Fraction} = \frac{\text{Number of moles of a particular gas}}{\text{Total number of moles of all gases in the mixture}}$$

**Partial pressure:** The pressure that would be exerted by one gas in a mixture if it occupied the container alone.

$$P_A = PX_A,$$

where  $P_A$  is the partial pressure of A, P is the total pressure and  $X_A$  is the mole fraction of A.

**Reversible reaction:** A reaction in which the products from the reaction can react together to form the original reactants. The direction of reversible reactions can be changed by changing the conditions.

## Topic 14: Acid-base Equilibria

**Acidic buffer:** A buffer containing a weak acid and its conjugate base, e.g. a solution of acetic acid and sodium acetate.

**Basic buffer:** A buffer containing a weak base and its conjugate acid, e.g. a solution of ammonia and ammonium chloride.

**Brønsted-Lowry acid:** Proton donors. These species release hydrogen ions in solution.

**Brønsted-Lowry base:** Proton acceptors.

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

**Carbonic acid-hydrogencarbonate buffer:** This is the biological buffer system present in blood plasma, it is used to maintain blood pH between 7.35 and 7.45.

**Conjugate acid:** The species formed when a base accepts a proton.

**Conjugate acid-base pair:** A pair of compounds that can be interconverted by the transfer of a proton. Conjugate acid-base pairs are important in the formation of buffers to control pH.





**Conjugate base:** The species formed when an acid donates a proton.

**Diprotic acid:** An acid which can release two  $H^+$  ions upon dissociation, e.g.  $H_2SO_4$ .

**End point:** The point during the titration when the indicator changes colour. A suitable indicator should change colour near the equivalence point (so should have a pH range within the pH change during the equivalence point).

**Equivalence point:** The point when full neutralisation occurs. In acid-base titrations it is the point where all the acid/base has been neutralised and  $[H^+] = [OH^-]$ . This is the vertical section of an acid/base titration curve.

**Indicators:** Indicators are chemical solutions whose colour depends on the pH of the solution they are in. Methyl orange and phenolphthalein are indicators commonly used in titrations. Methyl orange is red in acid and yellow in alkali. Phenolphthalein is colourless in acid and pink in alkali.

**$K_a$ :** Acid dissociation constant, a quantitative measure of the strength of an acid in solution. The larger the  $K_a$  value, the stronger the acid, since it means the acid is largely dissociated into its ions.

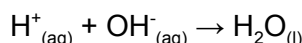
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

**$K_w$ :** Ionic product of water. At 298K,  $K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .

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

**Monoprotic acid:** An acid which can release only one  $H^+$  upon dissociation, e.g. HCl.

**Neutralisation:** A reaction between an acid and a base to form water and a salt. The ionic equation for neutralisation is:



**pH:** A value that represents the acidity or alkalinity of a solution. Acidic solutions have a pH of less than 7, while alkali solutions have a pH of greater than 7. Neutral solutions have a pH of 7.

$$pH = -\log[H^+]$$

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







**pH curve:** A graph of pH against the volume of acid/base that is added to a solution. The curve usually has a vertical part which can be identified as the equivalence point.

**pH meter:** An instrument which measures the pH of a solution. A digital pH meter is preferred to a universal indicator as it can give a more precise value.

**pH scale:** A measure of the hydrogen ion concentration, indicating the acidity or alkalinity of a solution. It can be measured using a universal indicator or a pH probe and has a range of 0-14.

**Polyprotic acid:** An acid which can release more than one  $H^+$  ions upon dissociation, e.g.  $H_3PO_4$ .

**Strong acid:** An acid which dissociates/ionises almost completely in water. This means nearly all the  $H^+$  ions will be released. E.g. HCl.

**Strong base:** A base which dissociates/ionises almost completely in water. E.g. NaOH.

**Titration:** An experimental technique used to determine the concentration of an unknown solution by using a second solution with a known concentration.

**Weak acid:** Acids which only dissociate/ionise very slightly in water so that only a small number of  $H^+$  ions are released. E.g. Ethanoic acid.

**Weak base:** A base which only slightly dissociates/ionises in water. E.g.  $NH_3$ .

## **Topic 15: Organic Chemistry: Carbonyls, Carboxylic Acids and Chirality**

### **Topic 15A: Chirality**

**Chiral centre:** A carbon atom that is bonded to 4 different atoms/groups of atoms.

**Enantiomers:** Molecules that are non-superimposable mirror images of one another. Enantiomers have opposite effects on plane-polarised light.

**Nucleophilic Substitution:** A reaction in which a nucleophile attacks an electrophilic atom to replace an atom/group of atoms.

**Optical isomerism:** A type of stereoisomerism present in compounds that are non-superimposable mirror images of one another, caused by the presence of a chiral centre. They have the same molecular formula with different arrangements in space.





**Racemic mixture (racemate):** A mixture containing equal amounts of enantiomers. It has no rotational effect on plane polarised light.

## Topic 15B: Carbonyl Compounds

**2,4-Dinitrophenylhydrazine:** A compound which forms an orange precipitate in the presence of aldehydes and ketones.

**Aldehyde:** A compound containing the  $\text{-CHO}$  functional group at the end of an alkyl chain. Aldehydes can be oxidised to carboxylic acids by heating them under reflux with  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ .

**Carbonyl:** Compounds containing the  $\text{C=O}$  functional group. Aldehydes and ketones are carbonyl compounds.

**Intermolecular forces:** Interactions between different molecules. Types of intermolecular forces including permanent dipole-dipole interactions, induced dipole-dipole interactions (these are also known as van der Waals forces) and hydrogen bonding.

**Ketone:** A compound containing the  $\text{C=O}$  functional group within an alkyl chain. Ketones cannot be oxidised further.

**Nucleophile:** An electron pair donor.

**Oxidation:** The loss of electron(s), leading to an increase in oxidation number.

**Oxidising agent:** A species which brings about oxidation by gaining electrons. The oxidising agent is itself reduced.

**Primary alcohol:** An alcohol in which the  $\text{-OH}$  is attached to a primary carbon atom (i.e.  $\text{RCH}_2\text{OH}$ ). Primary alcohols can be oxidised with  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$  to form either an aldehyde or a carboxylic acid, depending on the conditions.

**Reducing agent:** A species which brings about reduction by losing electrons. The reducing agent is itself oxidised.

**Reduction:** The gain of electron(s), leading to a decrease in oxidation number.

**Reflux:** The continual boiling and condensing of a reaction mixture. This technique is often used to make sure a volatile liquid reaches a high enough temperature to ensure that the reaction goes to completion.



**Secondary alcohol:** An alcohol in which the -OH is attached to a secondary carbon atom (i.e.  $R_2CHOH$ ). Secondary alcohols can be oxidised under reflux with  $Cr_2O_7^{2-}/H^+$  to form a ketone.

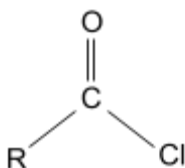
**Tertiary alcohol:** An alcohol in which the -OH is attached to a tertiary carbon atom (i.e.  $R_3COH$ ). Tertiary alcohols cannot be oxidised.

**Tollens' reagent:** Also known as ammoniacal silver nitrate, this reagent forms a silver mirror in the presence of an aldehyde and can be used to distinguish between aldehydes and ketones. An aldehyde is oxidised to a carboxylic acid while silver ions in Tollens' are reduced to silver, forming a silver mirror on the wall of the test tube.

**Van der Waals:** Also known as induced dipole-dipole, dispersion, and London forces, van der Waals forces exist between all molecules. They arise due to fluctuations of electron density within a molecule. These fluctuations may temporarily result in an uneven electron distribution, producing an instantaneous dipole. This dipole can induce a dipole in another molecule, and so on.

## Topic 15C and 15D: Carboxylic Acids and Carboxylic Acid Derivatives

**Acyl chloride:** A compound containing the functional group  $COCl$ . Acyl chlorides are a derivative of carboxylic acids, but the -OH is substituted by -Cl.



**Biodegradable:** A substance that can be broken down by bacteria or another living organism.

**Carboxylic acid:** An organic compound containing the  $-COOH$  functional group. They are weak acids.

**Condensation polymerisation:** A long chain molecule formed when monomers react together with the release of small molecules, such as water. Types of condensation polymers are polyamides (formed from carboxylic acids/acyl chlorides and amines) and polyesters (formed from carboxylic acids/acyl chlorides and alcohols).

**Ester:** A compound containing the  $R-COO-R'$  functional group (where R and R' are alkyl groups). Formed by the condensation reaction between an alcohol and a carboxylic acid.





**Ester hydrolysis:** Esters can either be hydrolysed with hot aqueous acid (forming carboxylic acids and alcohols) or with hot aqueous alkali (forming carboxylate salts and alcohols). Polyesters can be hydrolysed in a similar way.

**Esterification:** The process of making esters. Esters can be made by the reaction between carboxylic acids and alcohols in the presence of an acid catalyst, or by the reaction between acid anhydrides and alcohols.

**Hydrogen bonding:** A type of intermolecular bond formed between a  $\delta^+$  hydrogen atom and the lone pair of electrons on an electronegative atom. These electronegative atoms are either nitrogen, oxygen or fluorine.

**Hydrolysis:** A reaction in which water is used to break down a compound.

**Monomer:** A small molecule that can react to form polymers.

**Nucleophilic addition:** A reaction in which an electrophilic  $\pi$  bond reacts with a nucleophile, breaking the  $\pi$  bond and forming two new  $\sigma$  bonds. Examples include carbonyl compounds reacting with  $\text{NaBH}_4$  to form alcohols or with  $\text{HCN}$  to form hydroxynitriles.

**Nucleophilic addition-elimination:** A reaction in which a nucleophile is added to a molecule by breaking a  $\pi$  bond then a leaving group is removed to reform the  $\pi$  bond.

**Polar bond:** A covalent bond in which there is an unequal distribution of the electrons between the two atoms due to the differing electronegativities of the bonding atoms. One atom will have a partial positive charge while the other will have a partial negative charge.

**Polyester:** A type of condensation polymer formed by the linkage of an alcohol group in one monomer with a carboxylic acid group of another (e.g. Terylene). These polymers can be broken down by hydrolysis and are biodegradable. The bond between each monomer is called an ester linkage.

**Polymer:** A large molecule made from many small monomers that have been bonded together.

**Polymerisation:** The process of making a polymer from its monomers. There are two types: addition polymerisation and condensation polymerisation.

## 15E: Spectroscopy and Chromatography

**Carbon-13 NMR spectroscopy:** A type of NMR spectroscopy which analyses  $^{13}\text{C}$  nuclei. The number of peaks in the spectrum shows the number of different environments and the chemical shifts represent the environments present.



**Chemical shift:** The shift of a carbon or proton environment relative to standard tetramethylsilane (TMS). This chemical shift value ( $\delta$ ) depends on the molecular environment of the proton/carbon atom.

**Chromatography:** A technique used to separate and identify components in a mixture. There are several different types of chromatography, including thin layer chromatography and gas chromatography. Separation during chromatography depends on the balance between each individual compound's solubility in the mobile phase and retention by the stationary phase.

**Coupling:** The interaction between adjacent non-equivalent protons during NMR spectroscopy.

**Deuterated solvent:** A solvent, such as  $\text{CDCl}_3$ , in which all of the hydrogen atoms have been replaced by deuterium ( $^2\text{H}$ ). Deuterated solvents are used so there is no solvent peak on the  $^1\text{H}$  NMR spectrum.

**Doublet:** A signal on a  $^1\text{H}$  NMR spectra made up of two peaks, indicating that there is one adjacent non-equivalent proton.

**Electronegativity:** A measure of the ability of an atom to attract a bonding pair of electrons within a covalent bond. The Pauling scale is often used, with fluorine being the most electronegative element and caesium and francium being the least electronegative elements.

**Elemental analysis:** A sample is analysed to determine the proportion of elements that make up the compound present. This is done by converting a known amount of an unknown sample into simple known compounds.

**Environment:** In NMR spectroscopy, a proton or carbon environment considers the atoms/groups that are adjacent to that hydrogen/carbon atom. If two hydrogen/carbon atoms are surrounded by different groups of atoms, they are in different environments.

**Equivalent protons:** Protons that are in the same environment.

**Gas chromatography (GC):** A type of chromatography in which a column is packed with a solid (or a solid coated in a liquid) and a gas is passed through the column under pressure at high temperature. Mass spectrometry may then be used to analyse the components separated by GC.

**Mass spectrometry:** A technique used to identify compounds and determine their relative molecular mass.

**Mobile phase:** A fluid that moves through a chromatography system to separate a mixture. This may be a gas (GC) or a liquid (TLC). The different components of the mixture have differing affinities to the mobile phase, causing them to be separated.





**Molecular formula:** The total number of atoms of each element in the compound.

**Molecular ion peak:** The peak on a mass spectrum with the highest  $m/z$  value. This is used to determine the molecular mass of a compound.

**M/Z ratio:** The mass to charge ratio on a mass spectrum. For  $1+$  ions, this is equivalent to the mass of the ion.

**Nuclear magnetic resonance (NMR):** A technique that uses the absorption of electromagnetic radiation by an atomic nucleus in an external magnetic field to analyse the structure of a compound. Typically, either  $^{13}\text{C}$  or  $^1\text{H}$  nuclei are analysed.  $^{13}\text{C}$  NMR spectra are generally simpler than  $^1\text{H}$  NMR spectra.

**Proton NMR spectroscopy:** A type of NMR spectroscopy which analyses  $^1\text{H}$  nuclei. The number of peaks on the spectrum shows the number of proton environments and the chemical shifts represent the environments. The area under each peak shows the relative number of protons in each environment. The splitting pattern can be used to work out the number of adjacent protons.

**Quartet:** A signal on a  $^1\text{H}$  NMR spectra made up of four peaks, indicating that there are three adjacent non-equivalent protons.

**Retention time:** The time taken for a sample to travel through the GC column. The recorded retention time can be compared with standards to identify the substances in the mixture.

**$R_f$  value:** In TLC,  $R_f$  values can be calculated as shown below then compared with standards to identify the substances present in a mixture.

$$R_f = \text{Distance moved by substance} \div \text{Distance moved by solvent}$$

**Stationary phase:** A substance over which the mobile phase moves in chromatography. This is typically a solid, although a solid coated in a liquid may be used in gas chromatography (GC).

**Tetramethylsilane (TMS):** The standard for chemical shift measurement in NMR spectroscopy.

**Thin layer chromatography (TLC):** A type of chromatography used to separate mixtures. The stationary phase is a thin layer of alumina or silica fixed to a metal or glass plate. The plate is dotted with the mixture and placed in a beaker of solvent which is allowed to travel up the plate. The mixture separates due to the components having different solubilities in the mobile phase.

**Triplet:** A signal on a  $^1\text{H}$  NMR spectra made up of three peaks, indicating that there are two adjacent non-equivalent protons.

