Cambridge AS & A Level · Chemistry 9701

Chemistry 9701 formulas and definitions: A2

All 151 formulas, facts and definitions to learn, by syllabus topic. Formulas the exam gives you are left out.

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A Level

Chemical energetics

ΔH_{latt}: gaseous ions → 1 mol of ionic solid (always negative)

ΔH_{at}: element in standard state → 1 mol of gaseous atoms (always positive)

EA_1: 1 mol of gaseous atoms + 1 mol of electrons → 1 mol of gaseous 1– ions

ΔH_{hyd}: 1 mol of gaseous ions → aqueous ions (always negative)

ΔH_{sol}: 1 mol of solute → very dilute solution (either sign)

$\Delta H_{\text{f}} = \Delta H_{\text{at}}(\text{metal}) + \Sigma IE + \Delta H_{\text{at}}(\text{non-metal}) + \Sigma EA + \Delta H_{\text{latt}}$

ΔH_{at} of a gaseous diatomic element $= \frac{1}{2}\times$ its bond energy

$\Delta H_{\text{sol}} = \Sigma \Delta H_{\text{hyd}} - \Delta H_{\text{latt}}$

Entropy: the number of possible arrangements of the particles and their energy in a system

$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ (T in K; ΔS in kJ K^{-1} mol^{-1})

Feasible when $\Delta G < 0$

Temperature where feasibility changes: $T = \Delta H / \Delta S$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$0\ ^{\circ}\text{C} = 273$ K, so $25\ ^{\circ}\text{C} = 298$ K

Electrochemistry

$F = Le$

$Q = It$ (Q in C, I in A, t in s)

Moles of electrons $= \frac{Q}{F}$; moles of product $= \frac{\text{moles of electrons}}{\text{electrons per particle}}$

$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{positive}) - E^{\ominus}(\text{negative})$; never multiply $E^{\ominus}$ by a coefficient

Feasible when $E^{\ominus}_{\text{cell}} > 0$

$E = E^{\ominus} + \dfrac{0.059}{z} \log \dfrac{[\text{oxidised species}]}{[\text{reduced species}]}$

$\Delta G^{\ominus} = -nE^{\ominus}_{\text{cell}}F$ (n = moles of electrons in the equation)

Standard conditions: 1.00 mol dm^{-3} ions, 101 kPa gases, 298 K

Standard hydrogen electrode: $E^{\ominus} = 0.00$ V

Equilibria

$K_w = [\text{H}^+][\text{OH}^-]$ (the expression)

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

$\text{pOH} = -\log_{10}[\text{OH}^-]$; pH + pOH = 14.00 at 298 K

$K_a = \dfrac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$, units mol dm^{-3}

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

Weak acid alone: $[\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$

Buffer: $[\text{H}^+] = K_a \times \dfrac{[\text{HA}]}{[\text{A}^-]}$, or $\text{pH} = pK_a + \log_{10} \dfrac{[\text{A}^-]}{[\text{HA}]}$

K_{sp} of $\text{A}_x\text{B}_y = [\text{A}^{y+}]^x[\text{B}^{x-}]^y$, units $(\text{mol dm}^{-3})^{x+y}$

$K_{pc} = \dfrac{[\text{solute in solvent 1}]}{[\text{solute in solvent 2}]}$ at equilibrium, no units

Concentration $= \dfrac{\text{moles}}{\text{volume in dm}^3}$; moles $= \dfrac{\text{mass}}{M_r}$

Reaction kinetics

$\text{rate} = k[\text{A}]^m[\text{B}]^n$; overall order $= m + n$

Order 0: rate unchanged; order 1: rate ∝ [A]; order 2: rate ∝ [A]²

Units of k for overall order n: $\text{mol}^{1-n}\ \text{dm}^{3(n-1)}\ \text{s}^{-1}$ (order 1: s^{-1}; order 2: mol^{-1} dm^3 s^{-1})

First order: $k = \dfrac{0.693}{t_{1/2}}$ ($0.693 = \ln 2$)

Fraction left after n half-lives $= \left(\frac{1}{2}\right)^n$

Rate at time t = gradient of the tangent to the concentration–time graph

First order: gradient of rate against [A] $= k$

Large excess of B: $k' = k[\text{B}]$

Group 2

Thermal stability of nitrates and carbonates **increases** down the group (radius up, charge density down, anion polarised less)

$\mathrm{MCO_3} \rightarrow \mathrm{MO} + \mathrm{CO_2}$

$\mathrm{M(NO_3)_2} \rightarrow \mathrm{MO} + 2\mathrm{NO_2} + \frac{1}{2}\mathrm{O_2}$

$\mathrm{M(HCO_3)_2} \rightarrow \mathrm{MCO_3} + \mathrm{CO_2} + \mathrm{H_2O}$

$\Delta H_{\mathrm{sol}} = \sum \Delta H_{\mathrm{hyd}}(\mathrm{ions}) - \Delta H_{\mathrm{latt}}$

Down the group: ΔH_{latt} and ΔH_{hyd} both become less exothermic

Sulfates (large anion): ΔH_{hyd} falls more, ΔH_{sol} less exothermic, solubility **decreases**

Hydroxides (small anion): ΔH_{latt} falls more, ΔH_{sol} more exothermic, solubility **increases**

$[\mathrm{OH^-}] = 2 \times [\mathrm{M(OH)_2}]$; $\mathrm{pH} = -\log[\mathrm{H^+}]$; $\mathrm{pH} + \mathrm{pOH} = 14.00$ at 298 K

Chemistry of transition elements

Transition element: forms one or more stable ions with incomplete d orbitals

Ions lose 4s electrons before 3d; Cr is $[\mathrm{Ar}]\ 3d^5\ 4s^1$, Cu is $[\mathrm{Ar}]\ 3d^{10}\ 4s^1$

Charge of complex = charge of metal ion + sum of ligand charges

Coordination number = number of dative bonds to the metal (en and $\mathrm{C_2O_4^{2-}}$ count 2, EDTA counts 6)

Linear 180°; square planar 90°; tetrahedral 109.5°; octahedral 90°

Octahedral splitting: 2 higher, 3 lower; tetrahedral: 3 higher, 2 lower

Larger ΔE means higher-frequency light absorbed (no equation needed)

$E^{\ominus}_{\mathrm{cell}} = E^{\ominus}(\mathrm{reduced}) - E^{\ominus}(\mathrm{oxidised})$; feasible if > 0

$\mathrm{MnO_4^-} : \mathrm{Fe^{2+}} = 1:5$; $\mathrm{MnO_4^-} : \mathrm{C_2O_4^{2-}} = 2:5$; $\mathrm{Cu^{2+}} : \mathrm{S_2O_3^{2-}} = 1:1$

$K_{\mathrm{stab}} = \dfrac{[\mathrm{complex}]}{[\mathrm{M}^{n+}][\mathrm{L}]^x}$, no $[\mathrm{H_2O}]$; units $\mathrm{mol}^{-x}\ \mathrm{dm}^{3x}$

K for exchange A $\rightarrow$ B $= K_{\mathrm{stab}}(\mathrm{B}) \div K_{\mathrm{stab}}(\mathrm{A})$

An introduction to A Level organic chemistry

Benzene $\mathrm{C_6H_6}$: planar hexagon, C–C–C and C–C–H angles 120°, every carbon sp^2

σ bond: head-on overlap of orbitals; π bond: sideways overlap of p orbitals; benzene's π electrons are delocalised above and below the ring

Electrophilic substitution: electrophile replaces an H on a benzene ring; addition–elimination: nucleophile adds to C=O of an acyl chloride, then HCl is lost

Amine: 1°, 2°, 3° = 1, 2, 3 carbons on N; amide: $\mathrm{RCONH_2}$ 1°, $\mathrm{RCONHR'}$ 2°, $\mathrm{RCONR'_2}$ 3°

Stereoisomers from n chiral centres $= 2^n$

H count: $2n + 2$ for n carbons, minus 2 for each ring or double bond (benzene ring: minus 8), plus 1 for each N, minus 1 for each halogen

Optically active: rotates the plane of plane-polarised light. Enantiomers: same angle, opposite directions. Racemic mixture: equal amounts of both, no rotation

Hydrocarbons

Benzene: planar, 120°, six sp^2 carbons, σ bonds (head-on overlap) and a delocalised π system (sideways overlap of p orbitals)

Halogenation: $\mathrm{X_2}$ with $\mathrm{AlX_3}$ (or $\mathrm{FeBr_3}$), room temperature, dark → halogenoarene + HX

Nitration: conc. $\mathrm{HNO_3}$ + conc. $\mathrm{H_2SO_4}$, 25–60 °C → nitroarene + $\mathrm{H_2O}$

Alkylation: RCl + $\mathrm{AlCl_3}$, heat; acylation: RCOCl + $\mathrm{AlCl_3}$, heat → + HCl

Electrophiles: $\mathrm{X_2 + AlX_3 \rightarrow X^+ + AlX_4^-}$; $\mathrm{RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-}$;
$\mathrm{HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+}$

Catalyst back: $\mathrm{H^+ + AlX_4^- \rightarrow HX + AlX_3}$

Side-chain oxidation: hot alkaline $\mathrm{KMnO_4}$, then dilute acid; ring carbon's chain → –COOH, extra chain carbons → $\mathrm{CO_2}$

Ring hydrogenation: $\mathrm{H_2}$, Pt or Ni, heat; 3 mol $\mathrm{H_2}$ per benzene ring

Side chain: $\mathrm{X_2}$ in UV light (free radical); ring: $\mathrm{X_2}$ with $\mathrm{AlX_3}$ in the dark (electrophilic)

2,4-directing: –$\mathrm{NH_2}$, –OH, –R; 3-directing: –$\mathrm{NO_2}$, –COOH, –COR

Hybridisation: benzene-ring and C=O carbons sp^2; carbons with four single bonds sp^3; C≡N and C≡C carbons sp

Halogen compounds

Making a halogenoarene: $\mathrm{X_2}$ with $\mathrm{AlX_3}$ (or $\mathrm{FeBr_3}$), room temperature, dark, dry

$\mathrm{X_2 + AlX_3 \rightarrow X^+ + AlX_4^-}$ and $\mathrm{H^+ + AlX_4^- \rightarrow HX + AlX_3}$

$\mathrm{C_6H_6 + X_2 \rightarrow C_6H_5X + HX}$ (electrophilic substitution)

An alkyl group on the ring sends the halogen to positions 2 and 4

Chloroalkane + NaOH(aq), heat → alcohol (nucleophilic substitution); chloroarene: no reaction

Reason: Cl lone pair (p orbital) delocalised into the ring → C–Cl partial double bond → stronger

Ease of hydrolysis: acyl chloride > chloroalkane > chloroarene

$\mathrm{Ag^+ + X^- \rightarrow AgX}$: AgCl white, AgBr cream, AgI yellow

Hydroxy compounds

$\mathrm{ROH} + \mathrm{R'COCl} \rightarrow \mathrm{R'COOR} + \mathrm{HCl}$: room temperature, nucleophilic addition–elimination

Phenylamine $\xrightarrow{\mathrm{NaNO_2 + HCl(aq),\ <10\ ^\circ C}}$ diazonium salt $\xrightarrow{\text{warm with } \mathrm{H_2O}}$ phenol $+\mathrm{N_2}$

$2\mathrm{C_6H_5OH} + 2\mathrm{Na} \rightarrow 2\mathrm{C_6H_5ONa} + \mathrm{H_2}$; $\mathrm{C_6H_5OH} + \mathrm{NaOH} \rightarrow \mathrm{C_6H_5ONa} + \mathrm{H_2O}$

Phenol + $\mathrm{Na_2CO_3(aq)}$: no reaction

$\mathrm{C_6H_5OH} + 3\mathrm{Br_2} \rightarrow \mathrm{C_6H_2Br_3OH} + 3\mathrm{HBr}$: bromine water, room temperature, white precipitate

Dilute $\mathrm{HNO_3}$, room temperature → 2-nitrophenol + 4-nitrophenol

Diazonium salt + phenol in NaOH(aq), below 10 °C → azo dye ($-\mathrm{N{=}N}-$)

OH on a ring is 2,4,6-directing

Acidity: carboxylic acid > phenol > water > alcohol

Reason: O lone pair (p orbital) overlaps with the ring → O–H weakened, anion stabilised, ring electron density increased

Carboxylic acids and derivatives

Alkylbenzene $\xrightarrow{\text{hot alkaline } \mathrm{KMnO_4}\text{, then dilute acid}}$ benzoic acid (one COOH per side chain)

$\mathrm{RCOOH} + \mathrm{SOCl_2} \rightarrow \mathrm{RCOCl} + \mathrm{SO_2} + \mathrm{HCl}$

$\mathrm{RCOOH} + \mathrm{PCl_5} \rightarrow \mathrm{RCOCl} + \mathrm{POCl_3} + \mathrm{HCl}$

$3\mathrm{RCOOH} + \mathrm{PCl_3} \rightarrow 3\mathrm{RCOCl} + \mathrm{H_3PO_3}$ (heat)

$\mathrm{HCOOH} + [\mathrm{O}] \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$ (Tollens', Fehling's, acidified $\mathrm{KMnO_4}$ or $\mathrm{K_2Cr_2O_7}$)

$\mathrm{HOOCCOOH} + [\mathrm{O}] \rightarrow 2\mathrm{CO_2} + \mathrm{H_2O}$ (warm acidified $\mathrm{KMnO_4}$)

$\mathrm{RCOCl} + \mathrm{HX} \rightarrow \mathrm{RCOX} + \mathrm{HCl}$, where HX is $\mathrm{H_2O}$, $\mathrm{R'OH}$, $\mathrm{C_6H_5OH}$, $\mathrm{NH_3}$, $\mathrm{R'NH_2}$ or $\mathrm{R'_2NH}$; room temperature

Mechanism: nucleophilic addition–elimination

Acidity: carboxylic acid > phenol > water > alcohol

Chloro acids: more Cl, Cl nearer COOH, or Cl instead of Br → stronger acid

Ease of hydrolysis: acyl chloride > alkyl chloride > aryl chloride

Nitrogen compounds

$\mathrm{RX} + 2\mathrm{NH_3} \rightarrow \mathrm{RNH_2} + \mathrm{NH_4X}$ (ethanol, sealed tube, heat; excess $\mathrm{NH_3}$)

$\mathrm{RX} + \mathrm{R'NH_2} \rightarrow \mathrm{RNHR'} + \mathrm{HX}$ (ethanol, sealed tube, heat)

$\mathrm{RCN} + 4[\mathrm{H}] \rightarrow \mathrm{RCH_2NH_2}$ ($\mathrm{LiAlH_4}$ in dry ether, or $\mathrm{H_2}$/Ni)

$\mathrm{RCONH_2} + 4[\mathrm{H}] \rightarrow \mathrm{RCH_2NH_2} + \mathrm{H_2O}$ ($\mathrm{LiAlH_4}$ in dry ether)

$\mathrm{RCOCl} + \mathrm{R'NH_2} \rightarrow \mathrm{RCONHR'} + \mathrm{HCl}$ (room temperature)

$\mathrm{RNH_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{RNH_3^+} + \mathrm{OH^-}$

Basicity: secondary amine > primary amine > $\mathrm{NH_3}$ > phenylamine > amide

$\mathrm{ArNO_2} + 6[\mathrm{H}] \rightarrow \mathrm{ArNH_2} + 2\mathrm{H_2O}$ (hot Sn and conc. HCl, then NaOH(aq))

$\mathrm{C_6H_5NH_2} + 3\mathrm{Br_2} \rightarrow \mathrm{C_6H_2Br_3NH_2} + 3\mathrm{HBr}$ (room temperature, white precipitate)

$\mathrm{NaNO_2} + \mathrm{HCl} \rightarrow \mathrm{HNO_2} + \mathrm{NaCl}$

$\mathrm{ArNH_2} + \mathrm{HNO_2} + \mathrm{H^+} \rightarrow \mathrm{ArN_2^+} + 2\mathrm{H_2O}$ (below 10 °C)

$\mathrm{ArN_2^+} + \mathrm{H_2O} \rightarrow \mathrm{ArOH} + \mathrm{N_2} + \mathrm{H^+}$ (warm)

Coupling: $\mathrm{ArN_2^+}$ + phenol in NaOH(aq) → $\mathrm{Ar{-}N{=}N{-}C_6H_4OH}$ (4-position)

Amide hydrolysis: acid → $\mathrm{RCOOH} + \mathrm{R'NH_3^+}$; alkali → $\mathrm{RCOO^-} + \mathrm{R'NH_2}$

Isoelectric point: the pH at which the amino acid is a zwitterion (no overall charge)

Electrophoresis: pH < isoelectric point → cathode; pH = isoelectric point → stays; pH > isoelectric point → anode

Polymerisation

Ester linkage $-\mathrm{CO}-\mathrm{O}-$: diol + dicarboxylic acid (loses $\mathrm{H_2O}$) or dioyl chloride (loses HCl); or one hydroxycarboxylic acid

Amide linkage $-\mathrm{CO}-\mathrm{NH}-$: diamine + dicarboxylic acid (loses $\mathrm{H_2O}$) or dioyl chloride (loses HCl); or one aminocarboxylic acid; peptide link between amino acids

Condensation monomers need two reacting groups each; a molecule with one group ends the chain

Repeat unit from two monomers = one residue of each; from one monomer = one residue; continuation bond at each end

Monomers from a section: cut C(=O)–O or C(=O)–N, add OH to the C=O and H to the O or N

C=C only → addition; two condensing groups → condensation; O or N in the main chain → condensation

Poly(alkenes): inert, non-polar C–C and C–H bonds, cannot be hydrolysed, so they persist

Photodegradable polymers: groups such as C=O absorb UV light and the chain breaks

Polyesters and polyamides: hydrolysed by acid or alkali, so biodegradable

Repeat-unit formula = monomers' formulae – small molecules lost; chain $M_r \approx n \times M_r(\text{repeat unit})$

Organic synthesis

The 24 reactions in the table, with reagents, conditions and types (and the AS ones)

Directing: $-\mathrm{NH_2}$, $-\mathrm{OH}$, $-\mathrm{R}$ to 2, 4; $-\mathrm{NO_2}$, $-\mathrm{COOH}$, $-\mathrm{COR}$ to 3

Reducing agents: $\mathrm{NaBH_4}$ only C=O of aldehydes and ketones; $\mathrm{LiAlH_4}$ also COOH, amides and nitriles; Sn/HCl only $-\mathrm{NO_2}$

$\mathrm{ArNO_2 + 6[H] \rightarrow ArNH_2 + 2H_2O}$; $\mathrm{RCN + 4[H] \rightarrow RCH_2NH_2}$; $\mathrm{RCONH_2 + 4[H] \rightarrow RCH_2NH_2 + H_2O}$

Ease of hydrolysis: acyl chloride $>$ halogenoalkane $>$ aryl chloride

Acidity: alcohol $<$ water $<$ phenol $<$ carboxylic acid; basicity: amide $<$ phenylamine $<$ $\mathrm{NH_3}$ $<$ alkylamine

Percentage yield $= \dfrac{\text{actual mass}}{\text{theoretical mass}} \times 100$

Analytical techniques

$R_f = \dfrac{\text{distance moved by the spot}}{\text{distance moved by the solvent front}}$, both from the baseline

Retention time = time from injection to detection

Percentage of a component $= \dfrac{\text{its peak area}}{\text{total peak area}} \times 100$

TLC: stationary phase aluminium oxide (or silica) on a support; mobile phase a polar or non-polar solvent

GLC: stationary phase a high-boiling non-polar liquid on a solid support; mobile phase an unreactive gas ($\mathrm{N_2}$, He)

n hydrogens on adjacent carbons $\Rightarrow n + 1$ lines: singlet, doublet, triplet, quartet, then multiplet

Relative peak areas = ratio of numbers of hydrogens

TMS, $\mathrm{Si(CH_3)_4}$, defines $\delta = 0$

$\mathrm{ROH + D_2O \rightleftharpoons ROD + HOD}$: O–H and N–H peaks disappear