Chemistry common q&a

Atomic Structure

- The **2p electron** to be removed from B is at a **higher energy level** than the **2s electron** to be removed from Be.
    - Hence **less energy is required** to remove the 2p electron in B than the 2s electron in Be.
    - Hence, the **first ionisation energy of B is less** than that of Be.

- Ba: [Xe]6s2 Tl: [Xe] 4f145d106s26p1 (← state electronic configuration!)
    - Tl has a **higher nuclear charge** than Ba
    - Although Tl has **more shielding electrons** than Ba, these 4f and 5d electrons **exert a poor shielding effect**
    - Thus Tl has a **higher effective nuclear charge** and higher first ionisation energy.

- As the valence orbitals of K are less diffuse/smaller than that of Rb, there is more effective overlap of (4s) orbitals between the K atoms and the bond strength for K_2 is stronger than the bond strength for Rb_2.

- Electron removed from inner 3d subshell which is closer to the nucleus hence requires higher energy to remove it

- Electron removed experiences inter-electronic repulsion as it is removed from one 3d orbital containing a pair of electrons, requiring lower energy to remove it

- State electronic configurations
    - First ionization energy (1st I.E.) of Rb is lower than K as Rb has a **larger number of filled principal quantum shell** and its **valence electron is located in a shell with a larger n.** Hence, its valence electron is **further** from and **less attracted by the nucleus**, thus requiring less energy to remove.

- Mg^{2+} has one less occupied principal quantum shell than that of its parent atom Mg

    - The terms "effective nuclear charge" should not be used here. Effective nuclear charge is used only to explain the trend in IE / atomic radii ACROSS the period.

- Ionisation energy graph
    - Gradual increase
    - Large jump between change in quantum number + subshells (e.g. 4s to 3p)
    - Large jump between 4th and 5th valence electron means element is in Grp IV

Chemistry common q&a

- When electrons are already filled, 3d subshell comes before 4s

Dot and cross, structure (Lewis, etc.)

- Use dots for one atom, crosses for adjacent atom (even if they are the same element)
- For ions, remember to bracket the molecules and add the relevant charges on top right hand corner, outside bracket.
- H-bonds:
    - Illustrate using slanted lines
    - Indicate d+ and d-
    - Indicate lone pair from F, O, N!
- Ionic interactions (e.g. in proteins) : hyphenated line

Chemical Bonding

Structure & Bonding – always state structure before bonding

NaH exists as a **giant ionic lattice**, while GeH4 exist as **simple covalent molecules**. Hence the **strong ionic bonds** between sodium and hydride ions **require a lot of energy to be overcome**, and NaH remains as a solid until 800℃.
In comparison, the **breaking of weak instantaneous dipole-induced dipole forces** (accept van der Waals' forces) between GeH4 molecules require much less energy, hence GeH4 boils at a low temperature.

*The only giant covalent lattices are Diamond, SiO2

Polarity and bonding
(Polarity depends on electronegativity)

GeH4 is **non-polar** and has only **instantaneous dipole-induced dipole interactions**. PH3 has **intermolecular permanent dipole-permanent dipole forces in addition to id-id** (or VDW forces), which are comparable to the id-id forces in GeH4. Hence the overall intermolecular forces overcome when boiling PH3 are comparable/similar in strength to that of GeH4.

The **difference in electronegativity** between Br and F is greater than that between Cl and F. Hence Br-F bond is **more polar** and **stronger** than Cl-F bond, thus **requiring more energy to break.**

IF7 has a lower boiling point than compound than IF5, hence exists as a gas at room temperature. This is because IF7 is a **non-polar molecule** with **no net dipole moment**. The predominant intermolecular forces of interaction is instantaneous dipole-induced dipole**(id-id).** [1] IF5 is a **polar** molecule with predominantly permanent dipole-permanent dipole interaction (**pd-pd)** which is **much stronger** than the id-id interaction.[1]

lone pair–lone pair > lone pair–bond pair > bond pair–bond pair

Chemistry common q&a

Boiling point

- State structure e.g. simple molecular structure
- Explain bonding
  - Larger electron cloud → **more polarizable** → stronger id-id → more energy required to overcome stronger IMF
  - Electron-donating CH3 group → **decreases partial positive charge on C** → makes C-F bond less polar than expected → weaker pd-pd → less energy required

Solubility

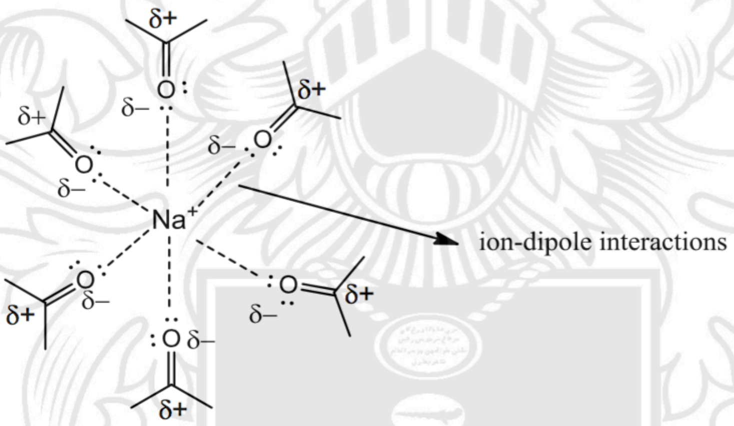
The ions produced form **strong ion-dipole interactions with water molecules**, hence promoting **solubility**.

Formation of solute-solvent interactions can overcome that of solute-solute and solvent-solvent

Factors affecting id-id

- Electron cloud size: larger → stronger id-id
- Straight/branched: straight → stronger id-id

Ionic bonding



Note:

The above diagram shows what it actually looks like in 3-dimensional space i.e. Na^+ is surrounded by six propanone molecules.

Only one Na^+ with one propanone molecule is needed for this answer.

Important features:

- δ^- on O atoms
- interactions (dotted lines) clearly from lone pairs on O to Na^+ ion
- stating type of interactions

- Most students managed to draw the correct diagram. Diagrams with missing dotted lines were NOT accepted as such diagrams did not show clearly the interacting atoms.
- It is also incorrect to label Na^+ as δ+, as it has a +1 charge, not a partial positive charge.

Chemistry common q&a

Hybridization

The **side-to-side overlap** between the 3p orbital of Si and the 2p orbital of O to form a pi bond is **not effective** due to the **larger atomic size** of Si, compared to the overlap between the 2p orbitals of C and O.
The resultant pi-bond is too weak to be formed under normal conditions. Hence SiO2 does not exist as O=Si=O molecules.

C3-C4 bond forms as a result of an sp3-sp3 overlap. The C2-C3 bond forms as a result of an sp2-sp3 overlap. list out the hybrid orbitals and state the type of overlap. OR

Hence the C2-C3 bond is shorter (stronger) as the orbital overlap involves greater s character.

The ?bond in C=O bond of R-N=C=O is made up of sp–sp2 head-on overlap whereas the ?bond in C=O of CH3COCH3 is made up of sp2–sp2 head on overlap.

The sp–sp^2 ?bond in C=O bond of R-N=C=O therefore has a higher s–character, hence leading to more effective overlap of orbitals and shorter bond length.

<u>Ideal Gases</u>

- **Ideal conditions: high temperature, low pressure**
- **Occupy negligible volume as compared to container**
- **Have negligible intermolecular forces of attraction**

Assuming ideal gas behaviour and applying pV = nRT, … [working]
Applying Avogadro's law, V $\propto$ n

$P_T = P_A + P_B$
$X_A = n_a/n_T$
$P_1V_1 = P_2V_2$ (at constant temperature)
$V_1/T_1 = V_2/T_2$ (at constant pressure)

Pressure in Pa
  - 1kPA = 1000 Pa
  - 1 atm = 101 325 Pa
  - 1 bar = 100 kPa = 1000 x 100 Pa

Volume in m^3
  - $1m^3 = 1000dm^3$

Temperature in Kelvin (Celsius + 273)
R=8.31 $J\ K^{-1}\ mol^{-1}$.

C3H8 (gas X) is not an ideal gas. Instantaneous dipole-induced dipole interactions / van der Waals forces are present between C3H8 molecules.

Chemistry common q&a

Deviation from ideal behaviour

Pentanone has a **larger electron cloud** (48 electrons) compared to propanone (32 electrons). [1]

A larger electron cloud is **more easily polarized** hence the **intermolecular instantaneous dipole-induced dipole interactions**/ van der Waals‟ interactions found in pentanone is **stronger**. [1] Hence pentanone will **deviate more from ideal behaviour** in the gaseous state due to the stronger inter-molecular forces.

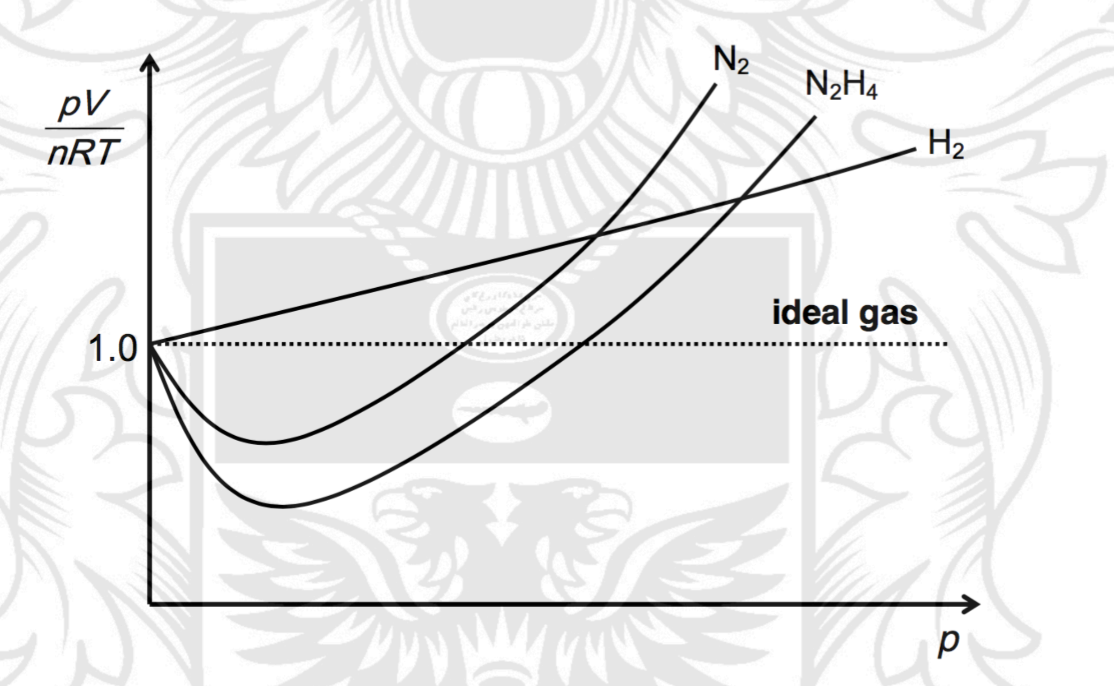
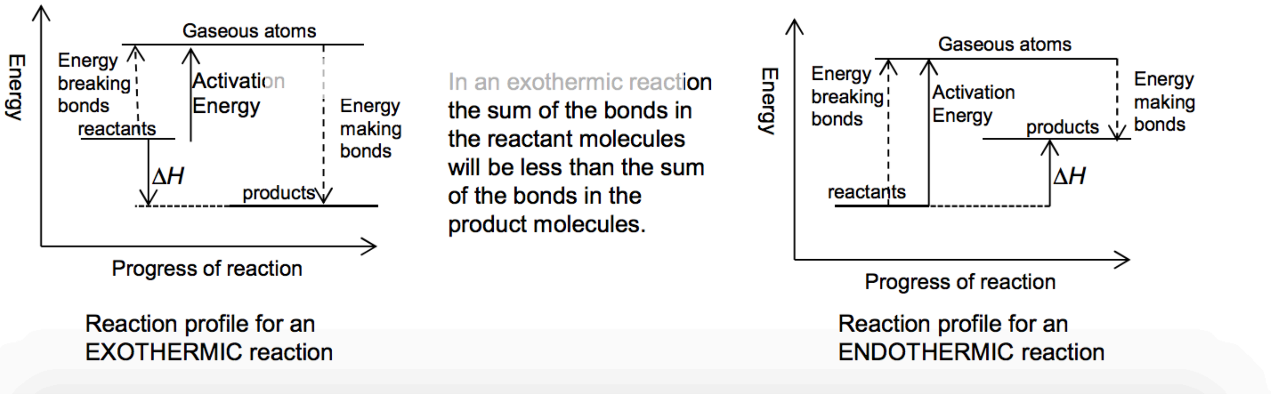


Figure 1: Note, H2 gas has small Mr thus more ideal (id-id, less IMF)

Chemical Energetics

- Energy level diagram
    - Y-axis: ‘E. level’, include ‘0’ at origin
    - Include ΔH values on arrows in cycle
    - Add all values that move in the same direction
- Exothermic: products have less energy than the reactants.
-



In an exothermic reaction the sum of the bonds in the reactant molecules will be less than the sum of the bonds in the product molecules.

Reaction profile for an EXOTHERMIC reaction

Reaction profile for an ENDOTHERMIC reaction

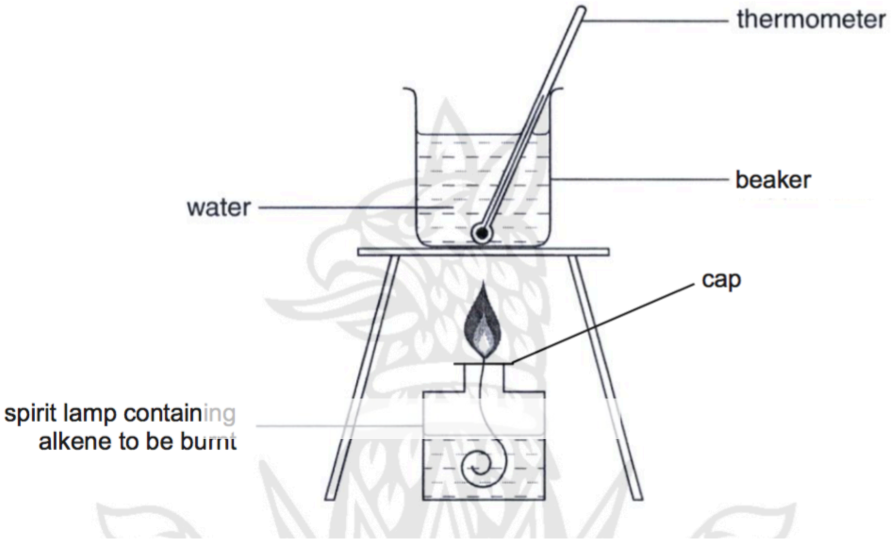
Chemistry common q&a

- ‘By Hess’ Law,…’
- $\Delta H_{hyd} \propto q/r$
    - Ionic radius (Ca$^{2+)}$ < Ionic radius (Ba$^{2+)}$ as **Ba belongs to a higher principal quantum shell and has more inner shell electrons.**
    - Since both ions have the **same ionic charge**, the **charge density** of Ca^{2+} is greater resulting in **greater ion-dipole interactions** and **higher magnitude of hydration energy** than barium ion.
    - Magnitude of hydration energy/exothermic or endothermic
- The energy given out by the C–I bond formed is insufficient to compensate for the energy needed to break the C–Cl bond / the C–I bond formed is weaker than the C–Cl bond broken, hence ΔH is endothermic.

- When given ΔHc → **CR**A**P** (reactants – products)
- When given ΔHf → **FLIP**PE**R** (products – reactants)
- $\Delta H_{rxn} = \sum(\text{total bonds broken}) - \sum(\text{total bonds formed})$
- The bond energy of a X–Y bond is the **average** amount of energy required to break 1 mole of the X–Y bonds in the **gaseous** state to form **X(g) and Y(g) atoms**.

Q (J) = m (g) x c (J g-1K-1) x ΔT (K)

Assuming no heat loss, heat evolved from combustion = heat gained by calorimeter set-up – c [cis–hex–3–ene] × amt of cis–hex–3–ene = C × temperature rise



Experimental set-up

1. **Fill up one spirit lamp with cis–hex–3–ene** (to about **80%** capacity), taking care to avoid getting any cis–hex–3–ene on the outside surface of the lamp.

2. **Set up the apparatus as shown above,** such that the **beaker is about 2-3 cm from the tip of the wick.**

Calibration of calorimeter set-up

3. Using a **250 cm3 beaker**, measure out **200 cm3 of water**.
4. Using an **electronic weighing balance**, weigh the **mass of the spirit lamp filled** with cis–hex–3–ene. **Record** this mass.
5. Using the **thermometer**, read the **temperature of the water** and record it.
6. Use the **lighter** to light the lamp and place it under the beaker of water, **centering the flame under the bottom of the beaker** and ensuring the flame is at an approximately constant distance below it.
7. Using the thermometer, carefully and gently **stir** the water.
8. When the temperature has **risen to about 5 °C**, **blow out** (extinguish) the flame.
9. **Continue to stir the water**, **recording the highest temperature reached.**
10. While the lamp is **cooling**, **clean the soot off from the bottom of the beaker**.
11. **Re-weigh the spirit lamp when it has cooled to room temperature**. Record this mass.
12. **Repeat** Steps 3 to 11, using the same lamp after cleaning it. (For a more accurate estimate of the heat capacity.)

Determining mass and temperature changes using trans–hex–3–ene

13. Repeat Step 1 by filling the other spirit lamp with trans–hex–3–ene.
14. Repeat Steps 3 to 11, using this new spirit lamp, recording the relevant masses and temperatures.
15. For a more accurate estimate of the data, Step 14 can be repeated.

Summary of Key Points / Ideas:

- Spirit lamp and beaker should be **filled more than half** but cannot be completely filled to full capacity (e.g. between 60 to 80%).
    - Beaker should at least be half-filled with water (i.e. 125 cm^3) but not fully filled (i.e. 250 cm^3)
- Styrofoam cups cannot be used since the flame could burn the cup; they should not be seated inside a beaker since this introduces even greater barrier to heat transfer from flame to water.

- **Mass of spirit lamp** before and after the combustion must be recorded.
- **Initial temperature of the water and the highest temperature** reached by the water after the combustion must be recorded.
- Use of **lighter to light the lamp** and placing the lamp under the beaker of water, and ensuring the flame is at an **approximately constant distance** below it.
- **Extinguishing** the flame when a **fixed temperature is reached** (e.g. 5 to 10 °C).
- **Repeating** of experiment (state which steps exactly) with trans–hex–3–ene.

Chemistry common q&a

From 5.0M to 1.0M:

To prepare the stock solution of 1.0 mol dm−3 of propanone, using a burette, introduce 50.00 cm3 of the 5.0 mol dm−3 propanone solution into a 250 cm3 volumetric flask. Top up to 250 cm3 mark with deionised water. Shake well to ensure that the prepared solution is homogeneous.

Safety hazards

- Hexenes are inflammable liquids and are hence a fire hazard.
- Any of the following: Containers of the hexenes should be covered and stored away, when not in use; proper disposal of hexenes;
- the wick should be lit away from any nearby hexenes.
- Propanone is flammable and volatile. The solutions containing propanone should be stoppered and kept away from naked flame
- Or Hexenes are volatile and hence a health hazard, causing respiratory problems.
- Experiment to be carried out in fume cupboard to avoid inhaling toxic vapour of hexene.

Gibbs Free Energy & Entropy

The entropy of a system is a measure of the **disorder** of the system or how probable the system is.

Lattice energy of a compound is the energy evolved to form 1 mole of **pure** solid ionic compound from its constituent gaseous ions, under standard conditions of 1atm and 298K.

As $|L.E.|$ proportional to $|(q_+q_-) / (r_+ + r_-)|$ → Cu2+ is doubly charged and Cu+ is singly charged, CuO will have a more exothermic lattice energy.

ΔG: J mol^{-1}
ΔS: J mol^{-1} K^{-1}
ΔH: kJ mol^{-1}

Common mistake: failure to convert units of ΔS from J mol^{-1} K^{-1} → x10^{-3} → kJ mol^{-1} K^{-1}

Factors affecting entropy

- (Increase/decrease) no. of gas particles
- Change in phase (g > L > s)
- Mixing of compounds
- Temperature
  - Increase temperature → increase KE → increase disorderliness → increase entropy

Chemistry common q&a

Chemical Equilibria

- If K_c is small, POE lies to the left
- Kc only changes with temperature. It does not change if pressure or concentration is altered. A catalyst also has no effect on Kc
- Two features of Dynamic Equilibrium
  - 1. Forward and backward reactions are occurring at equal rates.
  - 2. The concentrations of reactants and products stays constant
- **A catalyst has no effect on the position of equilibrium, but it will speed up the rate at which the equilibrium is achieved.**

When volume of the system increases, the concentration of the reacting species decreases[1] and the position of equilibrium will shift to the left with more gaseous molecules [1] to increase the concentration of the reacting species.

OR

When volume increases, partial pressures of the reacting species decreases. Hence, the position of equilibrium will shift to the left to decrease Qp

But as the temperature of the system remains constant, the Kp value remains constant.

*****Kc values (e.g. Kc, Kp) ONLY AFFECTED BY TEMPERATURE!*****

Acid-Base Equilibria

Why species is able to act as Lewis acid:

Al has a **energetically low-lying empty p-orbital** which can accept a pair of electrons.

Why species is able to act as Lewis base:

Lone pair of electrons; electron pair donor

Strong acids: dissociate completely [H+] = initial [HCl]

Weak acids: partial dissociation

Strength =/= concentration! Concentration – amount of acid per unit volume of solution

Basicity of an acid – no. of H atoms ionizable

Strong bases: ionize completely NaOH → Na+ + OH-

Weak bases: partial ionization

Kw = Ka x Kb = 1 x 10^-14 at 25 deg Celsius

- Value of Kw increases with increasing temperature as self-ionization of water is an endothermic process
- Ka, Kb dependent on temperature
- The stronger the acid, the weaker its conjugate base

pKw = pH + pOH (pKw =14)

pH dependent on concentration of acid/base therefore not good indicator of strength

Chemistry common q&a

Ka is best indicator as it is constant at constant temperature, does not vary with concentration of acid. pH and alpha increases with increasing dilution of acid.

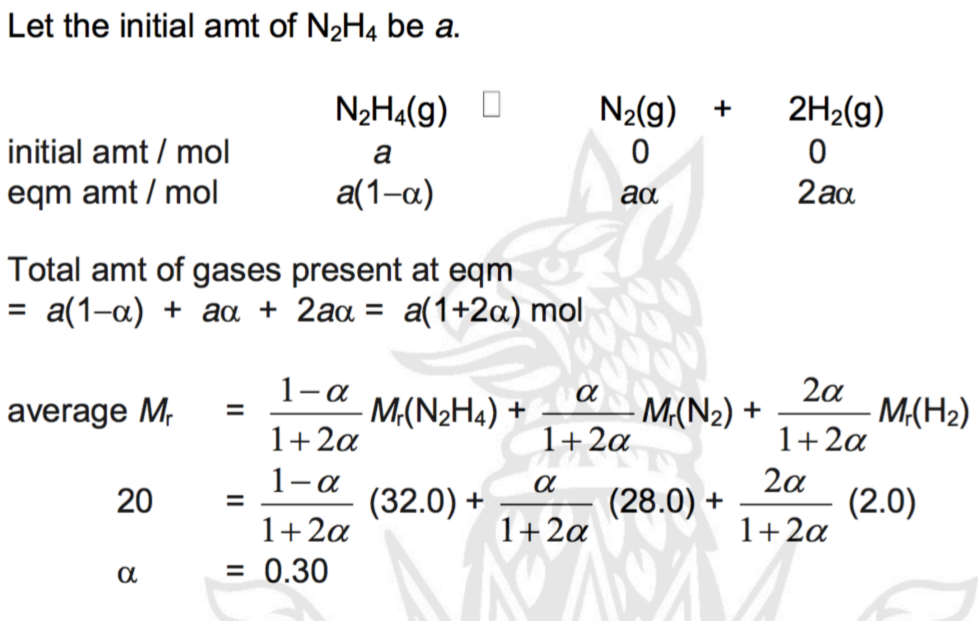
Polyprotic acids

Successive Ka values become smaller (weaker acids) because they involve acidic species that are **increasingly negative charged → making donation of positively charged H+ ion increasingly more difficult.**

i.e. Ka1 > Ka2 > Ka3

Degree of ionization

Alpha = (no. of **moles** of molecules **ionized** at equilibrium)/(no. of **moles** of molecules present initially)



Let the initial amt of N_2H_4 be a.

	$N_2H_4(g)$	□	$N_2(g)$	+	$2H_2(g)$
initial amt / mol	a		0		0
eqm amt / mol	$a(1-\alpha)$		$a\alpha$		$2a\alpha$

Total amt of gases present at eqm

$= a(1-\alpha) + a\alpha + 2a\alpha = a(1+2\alpha)$ mol

$$\text{average } M_r = \frac{1-\alpha}{1+2\alpha} M_r(N_2H_4) + \frac{\alpha}{1+2\alpha} M_r(N_2) + \frac{2\alpha}{1+2\alpha} M_r(H_2)$$

$$20 = \frac{1-\alpha}{1+2\alpha}(32.0) + \frac{\alpha}{1+2\alpha}(28.0) + \frac{2\alpha}{1+2\alpha}(2.0)$$

$$\alpha = 0.30$$

Remember alpha is like proportion so even under 'change amt/mol' should be -alpha(a) (alpha proportion of a)

Alpha increases with increasing dilution (the more dilute the acid, the more it ionizes)

- E.g., a weak acid HA
  HA + H2O <======> H3O+ + A-
  Dilution means adding H2O and here means according to Le Chatelier's Principle will shift equilibrium forward/rightwards, that increases the degree of dissociation.

Salt hydrolysis

Will undergo if:

- Anion is conjugate base of weak acid
- Cation is conjugate acid of weak base
- E.g., NH4Cl is a salt. Anion is Cl-, conjugate acid of strong acid HCl → does not undergo hydrolysis, NH4+ is conjugate acid of weak base NH3 → undergoes hydrolysis
  - Only NH4+ + H2O → NH3 + H3O+ (causes solution to be acidic)

Buffer solution

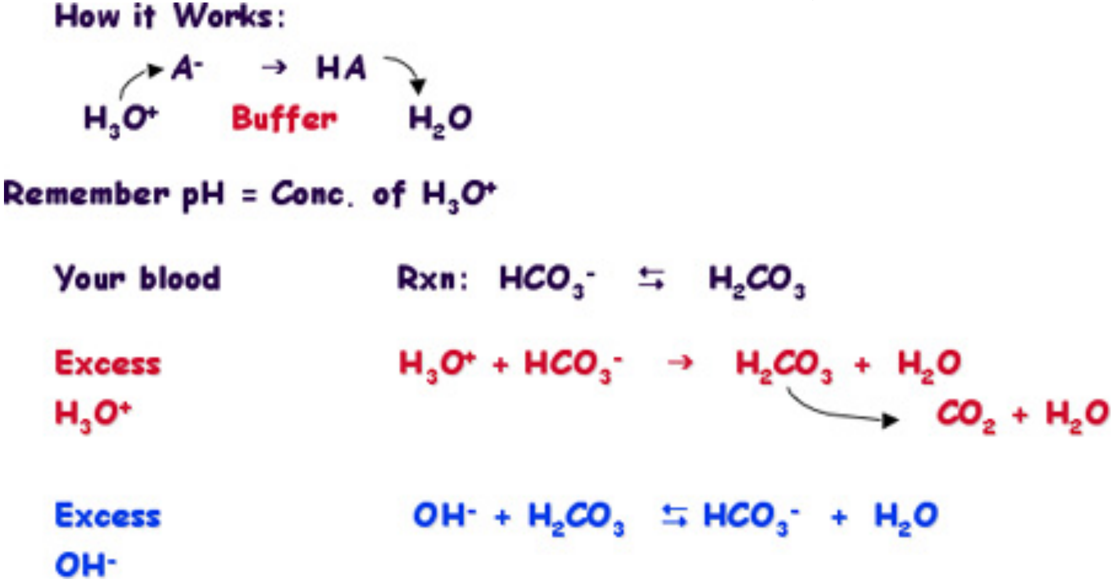
Chemistry common q&a

Able to resist pH change upon addition of small amount of acid or base.

- When small amount of acid/base added, presence of **large reservoir of unionized molecules** ensure that nearly all the added acid/base ions are removed → [acid/base] changes very little, pH kept approximately constant.

In Blood

- When showing individual equation/rxn e.g. HCO3- + H+, use full arrow, NOT REVERSIBLE. → demonstrates effectiveness of buffer system!



Equivalence point

Acid just completely reacted with base

Distinct colour change of suitable indicator

- Methyl orange pH 3.1-4.4: acid red/orange, alkaline yellow, end point orange (SA WB)
- Phenolphthalein 8.3-10: acid colourless, alkaline pink, end point light pink (if titrant is alkali) colourless (if titrant is acid) (SB WA)
- Bromothymol blue pH 6-7.7: acid yellow, alkaline blue, end point green
- Sharp end point – change colour distinctly upon addition of one drop of titrant from burette
- Colour change must occur when correct volume of titrant is added
- pH range coincides with region of rapid pH change in titration curve

Titration curve

- Initial pH
- MBC
- Equivalence point

pH when certain amount of reagent (acid/base) is added

- Find which one is in excess, which one limiting
- Find current amount (initial amount – amount added)
- Remember to find new total volume after adding reagent
- Calculate [H+] or [OH-] to find pH/pOH

**But if salt is present, may be buffer (WA-SB or SA-WB)*

Chemistry common q&a

pH at MBC: pH = pKa because [acid] = [salt]

If WA-SB or SA-WB, pH at equivalence point:

- At equivalence point, only salt is present
- Write equations of salt + H_2O → original acid + OH^-
- Amount of salt = amount of original acid
- New volume: volume of acid + volume of base added at equivalence point
- Concentration of salt = amount of salt / new volume
- Since this is conjugate base, pOH = -lgroot(Ka x c) where c is concentration of salt

Common ion effect

Reduces solubility

Ag^+ → original 0.1

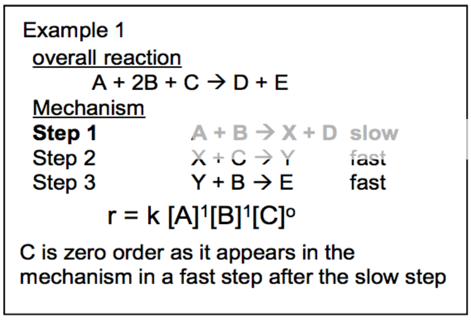
Added Ag^+ → x

New total Ag^+ = 0.1+x, but estimate x<<0.1 therefore still 0.1

Then 0.1x[concentration of other atom] = given Ksp

Reaction Kinetics

- Order of reaction with respect to a reactant is the power to which that reactant's concentration is raised in the experimentally determined rate equation.
- Order of reaction is with respect to a **species**, NOT to a concentration i.e. "order of reaction w.r.t. [NaOH]" is incorrect.
- **Rate constant k: only dependent on temperature**
    - **Increase temp → increase k**
    - (Arrhenius equation)
- The **molecularity** (number of moles of each substance) of the molecules in the slowest step will be the **same as the order of reaction for each substance**. e.g. 0 moles of A in slow step would mean A is zero order. 1 mole of A in the slow step would mean A is first order



Example 1

overall reaction

A + 2B + C → D + E

Mechanism

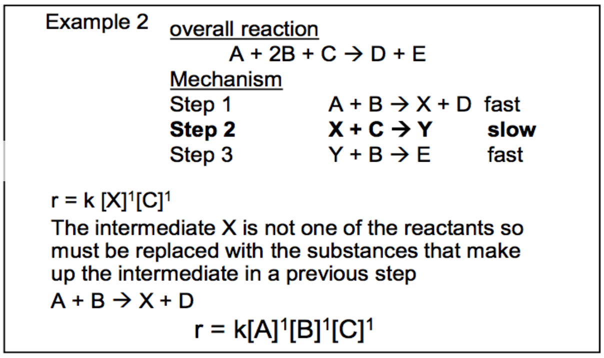
Step 1 A + B → X + D slow

Step 2 X + C → Y fast

Step 3 Y + B → E fast

$r = k[A]^1[B]^1[C]^0$

C is zero order as it appears in the mechanism in a fast step after the slow step



Example 2

overall reaction

A + 2B + C → D + E

Mechanism

Step 1 A + B → X + D fast

Step 2 **X + C → Y** **slow**

Step 3 Y + B → E fast

$r = k[X]^1[C]^1$

The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step

A + B → X + D

$r = k[A]^1[B]^1[C]^1$

- Colorimetry

  - Colour intensity of a chemical is directly proportional to its concentration.
    - As concentration of iodine decreases, the brown colour intensity will also decrease
    - A graph of absorbance against time can be plotted.
    - Rates at various times can be obtained by drawing tangents to the curve and then calculating the gradients
  - $2S_2O_3^{2-}(aq) + I_2(aq)$ yellow brown ◊ $2I^-(aq)$ colourless + $S_4O_6^{2-}(aq)$

Electrochem/Electrolysis

- The white powder formed is $PbSO_4$. Since an ionic compound does not conduct electricity in the solid state, $PbSO_4$ will stop the current from flowing through the electrodes when it coats the electrodes entirely.

Chemical Tests

- $KMnO_4$ (aq), H_2SO_4, heat
  - Observations: (Positive test) decolourization of purple $KMnO_4$

$$RCHO(aq) + 2Ag(NH_3)_2^+(aq) + 3OH^-(aq) \longrightarrow$$

An aldehyde

$$RCOO^-(aq) + 2Ag(s) + 4NH_3(aq) + 2H_2O$$

Free silver

Proteins

- Denaturation
  - **Side chain interactions disrupted**
  - **Secondary, tertiary, quaternary structures modified, protein unfolds into randomly coiled polypeptide chain**
  - **Primary structure remains intact as covalent peptide bonds not broken**
  - **TEMPERATURE**

    - Strong molecular vibrations agitate polypeptide chains → overcome interactions that stabilize protein conformation → disorganized structure, unfolds → denatured. Or even coagulation
  - **CHANGES IN pH**
    - Change ionic charges on aa residues, disrupting electrostatic attractions/ionic interaction
      - Low pH: protonation – CO2- converted to CO2H
      - High pH: de-protonation: -NH3+ converted to –NH2
      - At certain pH, protein isoelectric (equal no. of +ve and –ve charges) → no longer repel one another, coagulate / ppt out of solution
  - **HEAVY METAL IONS**
    - **Ag+, Cu2+, Hg2+ positively charged cations**
    - Compete with positively charged groups –NH3+ for attraction to negatively charged groups → disrupt original ionic interactions
    - Especially Hg2+ → disrupt disulfide linkages by reacting with –SH groups → denatures and ppts out of solution
  - Addition of base: positively charged NH3+ groups undergo acid-base to form uncharged NH2 → causes ionic interactions to break and 3D conformation of protein is disrupted.
- In the zwitterionic form, the equal number of positive and negative charges resulted in **an extensive network of ionic interactions**. [1] Thus, the solubility is at its minimum as the zwitterion **will not readily form ion-dipole interactions with water.** [1]
- Primary structure: sequence of amino acids in polypeptide chain
  - Most important: overall shape, function, properties
- Secondary structure: **ways** in which segments of polypeptide chain **orientate** into **regular pattern** through **H bonding between N-H and C=O** groups of peptide linkages
  - Alpha-helix and Beta-pleated sheet
  - Alpha-helix
    - **Regular coiled spiral** polypeptide chain
    - **Intra-chain H-bond** between C=O group of one aa residue and N-H group of aa four residues away
    - H bonds linear, maximally stable
    - R groups POINT **OUTWARDS** **perpendicular** to axis of helix, stabilizing overall folding of polypeptide chain
  - Beta-pleated sheet
    - Intra-chain H bonding
    - Stabilized by H bond between C=O group of peptide in one strand, N-H group of peptide in **adjacent strand**

- **R groups project ABOVE AND BELOW sheet PERPENDICULARLY**
- **Remember H-C-R group between N-H and next C=O!!!!!**

- Tertiary structure: **3D arrangement** of protein due to folding, which is in turn due **to R group interactions**
    - H bonding between polar groups
    - Ionic interactions between oppositely charged groups CO2- and NH3+
        - Disrupted by pH changes
    - VDWs between non-polar groups
    - Disulfide linkages
        - **-CH2-SH + HS-CH2- + [O] → -CH2-S-S-CH2- + H2O**
- Quaternary structure: **spatial arrangement and association of polypeptide units held together by R group interactions**
    - Haemoglobin: 2 alpha-sub units, two Beta-sub units
        - Considerable side chain interactions (VDWs) to stabilize quaternary structure
        - Each subunit datively covalent bonded to a Haem residue
        - One Hb can bind to 4 O2 molecules → HbO8 (oxyhaemoglobin)
- N-terminal (left) C-terminal (right)
- Peptide bond has partial double bond character due to delocalization of electrons – 120 degrees, reduces flexibility, restricted bond rotation
- Hydrolysis: acid/base, HEAT UNDER REFLUX FOR A FEW HOURS
    - For complete hydrolysis, heat with CONCENTRATED HCl at 100-120 degrees Celsius for 10-36 hours in evacuated tube

Acidity/Basicity

- Base
    - Negative charge delocalized over two electronegative oxygen atoms, making lone pair of electrons on O less available for protonation

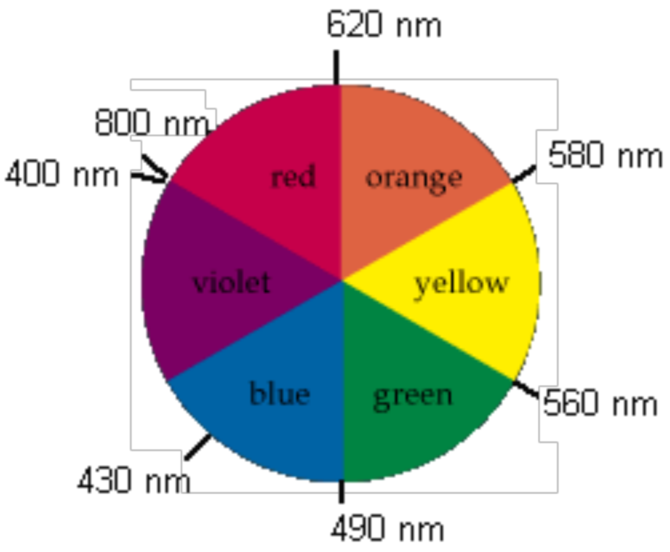
Inorganic Chemistry

- High charge density Al3+ polarizes and weakens O-H bonds of coordinated water molecules, causing H+ to be released
- 8HI + H2SO4 → 4I2 + H2S + 4H2O
- As shown by plot (II), $MgCO_3$ decomposes more readily than $BaCO_3$. Mg^{2+} is smaller than Ba^{2+} and has a higher charge density and polarising power. Hence it distorts the electron cloud of the CO_3^{2-} anion, and weakens the

carbon- oxygen bond within the anion to a greater extent, resulting in $MgCO_3$ requiring less energy for thermal decomposition and thus it decomposes more readily.

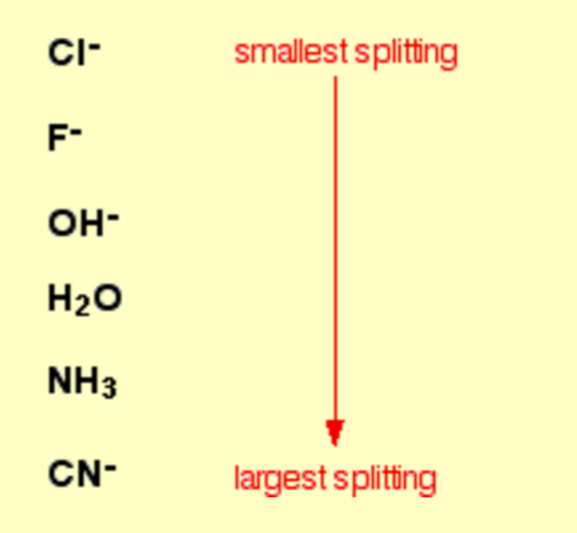
Transition Metals

Nickel is regarded as a transition element because it is able to form **at least one stable ion (e.g. Ni2+) with a partially filled d-subshell.**



- Catalysts
  - Ease of **interconversion between oxidation states** in same physical state provide an alternative reaction pathway of lower activation energy
  - AlCl3 electron deficient. Thus able to accept lone pair of electrons from Cl2 to form Electrophile Cl+. On the other hand, PCl3 has noble gas configuration, thus reacts with Cl2 to form PCl5 which is not an electrophile.
- Bidentate ligand: a molecule or an ion with **two donor atoms**, each of which has at least one electron pair for donation, which can form two coordinate bonds with a central metal atom or ion simultaneously
- Same central metal ion but different colours:
  - The two solutions have different colours despite containing the same nickel(II) ion because of the **presence of different ligands**.
  - Both the H2O and NH3 ligands **split the five 3d-orbitals** of the Ni2+ ion into two sets of slightly **different energy levels** but **to different extents.**
  - Hence [Ni(H2O)6]2+(aq) and [Ni(NH3)6]2+(aq) ions **absorb different wavelengths of light** from the visible spectrum for d-d transitions (i.e. the promotion of electrons from the lower energy d orbitals to the higher energy d orbitals).

  - **Consequently different colours, corresponding to the complements of the different colours absorbed, are observed for the two different complex ions.**



- Why coloured:
  - The presence of ligands split the partially filled d-orbitals of Fe^{2+} into two different sets, resulting in a small energy gap between them. Visible light that has a wavelength which corresponds to the energy gap is absorbed to promote a d-electron from an orbital of lower energy to an orbital of higher energy. The colour observed (red) is complementary to the colour of the visible light which is absorbed (green-blue).
  - The presence of H_2O ligands causes the splitting of the five 3d orbitals in Cu^{2+} ion into two sets of slightly different energy levels. [1] Since these 3d orbitals are partially filled, electrons from the lower-energy d orbitals can absorb energy corresponding to certain wavelengths (OR red/orange/yellow) from the visible spectrum and get promoted to the higher-energy d orbitals [1] The colour observed is the complement of the colour absorbed. [1]
- Heterogeneous catalysts
  - **Partially filled d orbitals** → reactants can be adsorbed onto surface area of metal
- Homogeneous catalysts:
  - Variable oxidation states
  - Ease of conversion between oxidation states

Chemistry common q&a

Others

Acidity

- The conjugate base of the ester is stabilised as the negative charge can be dispersed by delocalisation into the adjacent C=O group.
  - This is a question on the acidity of a compound and the focus should have been on the stability of the conjugate base.

Basicity

- Prove if monobasic or dibasic, etc. by comparing no. of moles of compound and no. of moles of H+ released

Bond energy values – discrepancy

- Data Booklet gives average values
- B.E. defined in terms of gaseous reactants and products. Hence, enthalpy change of vapourization should be included in calculation.

Conditions for Friedel-Crafts Alkylation

- Benzene, anhydrous $AlCl_3$, room temperature

Experiments

- Why lower bp organic product likely to be obtained through distillation
  - B.p. < water bath temperature → product would distill off and not be oxidized further
- Why highest bp organic product likely to be formed through reflux
  - In cooler region of condenser, lowest bp product will condense back into mixture, and further oxidation into higher bp product can take place
- Suggest why flask in which product is collected is surrounded by iced water
  - Propanal is volatile.
  - Hence by reducing temperature, can reduce the loss of propanal.
- Why ZnO rather than H_2SO_4 is used in excess
  - Unreacted ZnO can be removed by filtration but it is difficult to remove excess H_2SO_4
- One way to show that a saturated solution has been obtained
  - **Remove a drop of solution and see if any solid is formed upon cooling.**
  - **If solid formed, saturated**
- Explain why cold distilled water is used to wash crystals
  - Washing with water removes any water-soluble impurities
  - **Cold water: reduce loss of salt**
- One method of drying
  - Dry crystals between filter paper
  - **Place crystals under Infrared lamp**
  - Dry in oven at 120 deg Celsius

Chemistry common q&a

Nitrobenzene to phenylamine

- Sn, conc HCl, heat [1] **then** NaOH(aq)
- Reactions: reduction THEN acid-base

Phenylamine/phenol reactivity

- The –NH2/-OH group activates the benzene ring due to the partial **delocalisation of the lone pair of electrons in N into the pi electron cloud of the benzene ring** [1]. Hence the benzene ring is **more susceptible to electrophilic attack** in phenylamine [1] and only mild conditions are required for reaction.

Electrophiles

Electrophiles are positively charged or neutral species having **vacant orbitals** that are attracted to an electron rich centre. It participates in a chemical reaction by accepting an electron pair in order to bond to a nucleophile.

Nucleophiles

Let's start with "nucleophiles" (from "nucleus loving", or "positive-charge loving"). **A nucleophile is a reactant that provides a pair of electrons to form a new covalent bond. Contains lone-pair of electrons**

Alkenes

Why carbons attached to more alkyl groups are more stable:

- The positively charged carbon, attached to more electron-donating alkyl groups, has its **positive charge dispersed to a greater extent**.
- Presence of EWG e.g. Cl in alkene decreases electron density of C=C bond, thus attracts electrophiles less readily

Oxidation

- =CR(R') → ketone
- =CR(H) → carboxylic acid
- =CH2 → carbon dioxide (terminal alkene)
- *R can be alkyl group or benzene ring!
- KMnO4, NaOH, H.U.R → ketone, carboxylate salt, carbonate anion (CO3^2-)
- VS Cold, KMnO4, NaOH → form diols

Halogenoarenes

P orbital of Halogen overlaps with pi electron cloud of benzene ring → lone pair of electrons in p orbital of halogen delocalizes into benzene ring → **partial double bond character**

Resistant to nucleophilic substitution because C-X bond is very strong; electronic repulsion between electrons in benzene ring and electron-rich nucleophile that is approaching

Testing for Cl, Br, I

Chemistry common q&a

- **Add NaOH(aq) separately to each compound and heat**
- **Cool**
- **Add HNO3**
  - **Cannot use HCl/H2SO4 because they will react to form AgCl or AgSO4, interfering with the observation of this test**
- **Add AgNO3**
  - **White ppt: Cl**
  - **Cream ppt: Br**
  - **Yellow ppt: I**
- **RECAP: Add NaOH separately to each compound, heat. Cool, then acidify with HNO3(aq). Finally, add AgNO3.**

C-F and C-Cl → great stability and non-flammability (high bond strength)
Applications of CFCs:

- fire extinguisher → volatile, inert, non-flammability of CFCs (CBr2ClF)
- Aerosol repellants: propel liquid out of a spray (CFCs inert and non-toxic)

CFCs

- Due to their stability, do not break down when released in atmosphere; C-Cl bond broken, not C-F
- Chlorine atom(radical) combines with ozone molecules to form ClO (radical) and oxygen → destruction of ozone
- Net reaction: O3 + O → 2 O2

Carbonyls

- Sp2 hybridized → nucleophilic attack from either side of plane, forming racemic mixture
- C atom of C=O has partial positive charge because bonded to a more electronegative oxygen atom → electron rich nucleophiles are attracted to this electron-deficient site
- Bulky hydrocarbon groups increase steric hindrance hindering nucleophilic attack
- HCN with trace amount KCN catalyst
  - KCN → K+ + CN-
  - 1st step CN-, 2nd step H-CN (O electrons go to electron deficient H in H-CN) to form the alcohol group
- HCN with trace amount KOH/NaOH as catalyst
  - HCN weak acid → partially dissociates to give CN-
  - Since reaction rate dependent on CN-, low [CN-] means slow reaction
  - Therefore to increase reaction rate, add small amount of strong base like NaOH and KOH
    - OH- + H+ (from H+ + CN-) → H2O form water
    - By LCP, POE of HCN ←→ H+ + CN- shift right, (as H+ decrease to form water) → increase [CN-] → increase reaction rate
  - In essence: HCN + OH- → H2O + CN-
  - OR Add strong electrolyte like NaCN or KCN (complete ionization of electrolyte provides sufficient [CN-] to start reaction)
    - NaCN + aq → Na+ + CN-

Chemistry common q&a

- 2,4-dinitrophenylhydrazine → 2,4-dinitrophenylhrazone (**orange** ppt) + H_2O
  - **Condensation** reaction (elimination of small molecule, water)
- Tollens' reagent and heat – $[Ag(NH_3)_2]^+$ → $R\text{-}CO_2^-$, Ag (silver mirror), NH_3, H_2O
  - Aldehydes (positive) vs ketones
  - Redox: Ag reduced, aldehyde oxidized
- Fehling's solution and heat – Cu^{2+} → $R\text{-}CO_2^-$, Cu_2O (reddish-brown ppt), H_2O
  - Aliphatic aldehydes (positive)
- Iodoform (formation of tri-iodomethane) **3433**
  - 3 I_2 (aq) with 4 NaOH(aq), heat
  - → $R\text{-}CO_2^-$, CHI_3, $3I^-$, $3H_2O$
  - *Product has one less C than reactant

Basic strength

- Availability of lone pair of electrons for coordination with a proton
- Electron-withdrawing on benzene ring decreases electron density on N of NH_2, making lone pair of electrons less available for coordination to a proton
- Compound V is not basic because the lone pair of electrons on the nitrogen atom interacts with the pi-electron cloud of the adjacent C=O bond and is delocalised, and hence not available for co-ordination to a proton.
- In addition, this lone pair of electrons also delocalises into the pi-electron cloud of the benzene ring.

Amides

Why amides are effectively neutral:

- Lone pair on N overlaps with p electrons, gets involving in **delocalized pi bonding between C, O, N**
- The result of this is that the nitrogen lone pair becomes ***delocalised*** - in other words it is no longer found located on the nitrogen atom, but the electrons from it are spread out over the whole of that part of the molecule.

This has two effects which prevent the lone pair accepting hydrogen ions and acting as a base:

- Because the lone pair is no longer located on a single atom as an intensely negative region of space, it isn't anything like as attractive for a nearby hydrogen ion.
- Delocalisation makes molecules more stable. For the nitrogen to reclaim its lone pair and join to a hydrogen ion, the delocalisation would have to be broken, and that will cost energy.
- (Resonance)

Amide hydrolysis

Basic hydrolysis

- Whether 2 deg or 3 deg amide, amine always has 1 extra H (3 bonds total)?

Acidic hydrolysis

Chemistry common q&a

- Amine has 2 extra H, and + (will have 4 bonds)

$-NH_2$ is electron donating to benzene ring → enhances electron density → more susceptible to electrophilic attack

Amides

Resonance stabilized (electrons on N atom) → not available for coordination with proton → neutral

Ammoniacal solution of $AgNO_3$ → Tollens' reagent

*Reduction

$NaBH_4$ in methanol	Reduces carbonyl compounds only
$LiAlH_4$ in dry ether	Reduced carbonyl, R-CN, carboxylic acids and derivatives (including amides, where C=O group reduced to CH_2 group) But NOT Alkenes
H_2 with Ni	Carbonyl, R-CN (to amine), alkenes

*Oxidation

Not "hot acidified $KMnO_4$" be specific:

$KMnO_4$ (aq), dilute H_2SO_4 (aq), heat

$K_2Cr_2O_7$ (aq), dilute H_2SO_4, heat → cannot oxidise alkenes

*Reducing agent

SO_2

Graphs

'emf against lgx' → y-axis: emf, lgx: x-axis

Elucidation/Deduction

- Students need to note that the deductions/reasonings must contain BOTH parts: (i) type of reaction and (ii) functional group in order to gain full credit. Students often give partial deduction missing out either part (i) or (ii) in their answers.
- Students should not use the term, "double bond" to indicate alkene as this could refer to C=O or C=C. Instead, students should clearly state the functional group as C=C or simply alkene.
- Table:

Observation	Deduction

Pink deposit of Copper forms

(1) As it is

F_2 is a supremely reactive, poisonous, pale, yellowish brown gas.

Cl_2 is a pale green gas.

Chemistry common q&a

Br2 is a reddish-brown volatile liquid.
I2 is a violet-dark gray, lustrous solid.

(2) In water

Cl2 solution in water is colourless. Yellow-green in organic solvent.
Br2 solution in water is yellow in colour. Brown in organic solvent.
I2 solution in water is brown in colour. Purple in organic solvent.