

Chemistry PPQ Notes

Organic reagents to remember

Sn1, Sn2: reflux w/ aq. NaOH, 3° > 2° > 1° due to stability, I > Br > Cl due to electronegativity/bond strength.

sn1, sn2 operate via different mechanisms due to steric hindrance in sn1 and the fact that the carbocation is stabilised via + inductive effect.

when halogenating alcohols, use PX—eg PBr3 or PI3. For chlorinating something you can use PCl5 (test for OH) but it's very violent so use HCl instead, or SOCl2 (where SO2 and HCl produced as side products are gases and so easily removed).

sn1/sn2 with H2O just have entire H2O add on and then form hydronium then HBr

If a halogenoalkane is heated under reflux with a solution of sodium or potassium cyanide in ethanol (mutual solvent). This is nucleophilic substitution of CN⁻ into the position of the halide ion, as opposed to the nucleophilic *addition*, where you'd use acidified KCN.

Nucleophilic substitution of ammonia (you'd expect ethanol conditions cause elimination, but with ammonia, they don't): The halogenoalkane is heated with a concentrated solution of ammonia in ethanol. The reaction is carried out in a sealed tube. You couldn't heat this mixture under reflux, because the ammonia would simply escape up the condenser as a gas.

2-bromopropane is heated under reflux with a concentrated solution of sodium or potassium hydroxide in ethanol in an elimination reaction, competing with substitution.

When a haloalkane meets a nucleophile like OH⁻ it can either undergo nucleophilic substitution or elimination, where elimination is favoured in harsher conditions (higher temp and concs, more ethanol, branches chains)

FR substitution (UV light), electrophilic addition happen without anything else being needed

In nucleophilic addition, the aldehyde or ketone is mixed with a solution of sodium or potassium cyanide in water to which a little sulphuric acid has been added. The pH of the solution is adjusted to about 4 - 5, because this gives the fastest reaction.

Aldehydes and ketones can be reduced by NaBH₄ (via H⁻ as nucleophile—simplification) into primary and secondary alcohols, respectively, using conditions 1 or 2 (changes whether H⁺ or H₂O fills H of O in during final step to make OH):

1. The reaction is carried out in solution in water to which some sodium hydroxide has been added to make it alkaline. The reaction produces an intermediate which is converted into the final product by addition of a dilute acid like sulphuric acid.

2. The reaction is carried out in solution in an alcohol like methanol, ethanol or propan-2-ol. This produces an intermediate which can be converted into the final product by boiling it with water.

The solution will contain hydrogen cyanide (from the reaction between the sodium or potassium cyanide and the sulphuric acid), but still contains some free cyanide ions. This is important for the mechanism.

Acyl chlorides are extremely reactive in nucleophilic addition/elimination reactions, and so will react in normal conditions without anything special (with water to give OH, with alcohols to give ester, with ammonia to give amides and NH₄X, with amides to give n-substituted amides elongating total carbon chain)

test for sn1 vs sn2 via:

- investigate how a polar solvent affects the reaction— polar solvent interacts favourably with carbocation made in sn1, whereas in sn2 it just interacts with nu:, hindering reaction
- look to isolate carbocation intermediate to show it's sn1
- keep [everything] constant (incl. OH-) except for haloalkane and plot graph of []/time, take gradients to plot rate/[] to get rate w.r.t. haloalkane, if it's 1 then it's sn2, if 0 then it's sn1

PPQ Notes—Electrolysis

A fuel cell is essentially two chemical equilibria happening in parallel, where one generates more electrons than the other, causing movement of electrons through a wire, which is the energy provided by the fuel. The input materials can be summed in an “overall” reaction, by combining the two redox half equations, to give an equation that tells us what we put in, what we get out, and how much energy we generate (measured in standard electrode potential).

Advantages of fuel cells (hydrogen) in cars:

- Higher efficiency than traditional fossil fuels
- Less noise of cars since less moving parts
- No greenhouse gas emissions, as water is only product

Disadvantages of fuel cells (hydrogen) in cars:

- Shorter driving ranges and slower top speeds.
- Refuelling times are longer.
- Fuel cells are bigger, heavier and more cumbersome than their fossil fuel counterparts.
- Formation of the hydrogen fuel is technically challenging and not necessarily eco-friendly since fossil fuels are often used to generate the hydrogen.

When taking about standard electrodes, always mention the fact that they've been setup at standard conditions: 1M solution, 298K, 1atm.

Sulfuric acid is a great drying/dehydrating agent because it has a high affinity for water. For example, when you're making AlCl₃, you move Cl₂ over hot Al. But you can't have any humidity present as it'll react with the product (group 3 chloride reactions) to give Al(OH)₃ and HCl. Thus, use CaCl₂ and H₂SO₄ in the experimental set-up as drying agents.

Period 3 Elements—Reactions

With Oxygen

Na burns with a bright white flame to give oxide (white) and peroxide (yellow)

Mg burns with a *brilliant* white flame to give oxide (white)

Aluminium burns, but less fiercely due to a protective layer of the oxide that forms

Silicon burns with difficulty to give the (IV) oxide

Phosphorus burns spontaneously to give (P₂O₃) in less oxygen and (P₂O₅) in more—these are empirical formulae

Sulfur burns upon heating to form SO₂.

Chlorine doesn't directly react w/ oxygen, but instead indirectly forms Cl₂O, ClO₂, Cl₂O₂, etc.

With Water (decrease reactivity w/ water going across period)

Na burns fiercely, making the hydroxide.

Magnesium reacts quite little with cold water (to make some hydroxide), but fiercely with steam to make the oxide.

Aluminium reacts somewhat with steam, again inhibited by the protective oxide that forms.

None of the others react with cold water EXCEPT Chlorine, which forms HOCl + HCl.

Oxides with Water

Na oxide is vigorous, making the hydroxide (basic)

Mg oxide is gentle, making the hydroxide (basic)

Al oxide is inert in water—not soluble, but is amphoteric

SiO₂ is inert in water, but weakly acidic so reacts with strong oxides

P₂O₃ w/ cold water to make H₃PO₃

P₂O₅ reacts violently w/ cold water to make H₃PO₄

SO₂ w/ cold water to make H₂SO₃

SO₂ w/ bases makes sodium sulphite (Na₂SO₃)

SO₃ reacts violently w/ water to make H₂SO₄

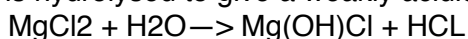
Cl₂O reacts to make 2HOCl (pure chlorine reacts with water to make HOCl AND HCL)

Chlorides with Water

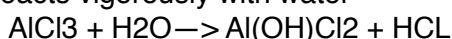
Ease of hydrolysis increases going across period. From NaCl to AlCl₃ the cations get more charge dense, and so pull hydroxide from water more strongly, leaving an increasingly acidic solution behind.

NaCl doesn't react, just dissolves

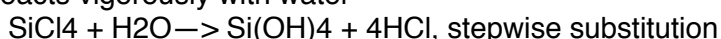
MgCl₂ is hydrolysed to give a weakly acidic solution



AlCl₃ reacts vigorously with water



SiCl₄ reacts vigorously with water



Where Si(OH)₄ decomposes into SiO₂ + 2H₂O

PCl₃ reacts to form H₃PO₃ and HCL

PCl₅ reacts to make PCl₃(OH)₂ via lone pair (octet expansion) which breaks H₂O off to make POCl₃, which then reacts with water to give H₃PO₄ and HCL, which are the two products in the final equation.

P(OH)₅ dehydrates because it's unstable, to give H₃PO₄.

SCl₄ → S(OH)₄ (same octet expansion mechanism, stepwise) → H₂SO₃ → SO₂

SCl₂ disproportionation with water to give SO₂ and S

S₂Cl₂ gives H₂S and SO₂ and HCL, which react to give H₂O and S.

Chlorine reacts to form both HOCl and HCL (disproportionation, like sulfur).

Exam Notes

Calorimeter improvements:

- Add a lid to the can so heat isn't lost via evaporation.
- Add insulation on the top/sides of the can so that heat isn't lost from there.
- Stir the water in the pot so heat is evenly distributed.
- Repeat measurements of dT and take an average.
- Put a cap on the spirit burner when it isn't burning to prevent evaporation.

Ease of lighting/combusting something is proportional to how volatile it is as a liquid.

Diamond is hard because of it's covalent bonds *in all directions/tetrahedral*, where graphite just slips over its own layers.

Graphene is a single layer of graphite; *a 2D sheet of carbon atoms arranged in hexagonal rings.*

When thinking about group 14 oxides, remember that the 2+ ions becomes more stable as you go down (the pair of s₂ electrons are not shielded as much, and so are held surprisingly tighter—see

Lorentz-Fitzgerald relativistic contraction.) Thus, Sn(IV) is more stable than Sn(II), but Pb(IV) is less stable than Pb(II).

D block elements are those in the periodic table that correspond to the *d-subshells being filled*. Transition elements, however, have an *ion* that has a partially filled d-orbital.

The first ionisation energies increase a tiny bit across the transition elements because (stay relatively constant because 4s electrons are removed each time) though electrons inside are shielding outer electrons more (d shell filling), nuclear charge is increasing and outweighs that by attracting the 4s electrons a little more, making them marginally harder to remove each time.

A repeat unit is the *simplest repeating unit of the lattice*, that shows the *full symmetry of the crystal*.

Hydrated molecules are different from complex ions with water as ligands. In hydrated molecules, the entire molecule bonds with water to include it in the structure in some way that's still not clear. In a complex ion, the molecule splits into its constituent ions, with water ligating to the ions individually, instead of forming one giant structure with the entire molecule. For example, Co(II) chloride hydrated is just $.6\text{H}_2\text{O}$, but complex ion is $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

Silver iodide is a yellow solid.

100cm³ volumetric flasks and 10cm³ pipettes exist too, if those numbers are more convenient for your titration calculations.

Ferritin stores iron, as the protein apoferritin binds to Fe²⁺ and stores it as Fe³⁺, and controls its release into the body (for use in haemoglobin, or myoglobin, for example).

Zinc hydroxide is colourless solution (white solid); see solubility rules:

- Nitrates are always soluble, as are potassium, sodium and ammonium salts.
- Halide salts are usually soluble, with the exceptions of silver and lead.
- Sulfates are usually soluble, with the exceptions of barium and lead.
- Carbonates and hydroxides are usually insoluble, with the exceptions of ammonium and G1, G2 from calcium down.

Note that these aren't golden guiding principles, though. For examples, they suggest that Zinc(OH) isn't soluble (which is true). However, when you add a hydroxide to a zinc salt, the compound forms is colour and soluble. How? Because initially Zn(OH)₂ is formed, which is a white ppt, but upon adding more hydroxide, you make this ZnO₂(²⁻), which is soluble. So the "product" of the reaction (in excess) is colourless and soluble, which may not have been predictable from the solubility rules.

P₂O₅ and P₂O₃ don't actually exist as compounds, but P₄O₁₀ and P₄O₆, instead.

If you're doing a titration into a flask which has a load of things inside it, and is more than halfway full, you should shake between addition of burette substance so that you allow everything to mix—in this case, swirling is not enough.

When something that should be reactive isn't reacting, it may be because of high activation energy or steric hindrance of the molecule that wasn't accounted for when calculating the initial reactivity.

Deficiencies of the Van Arkel diagram include:

- Doesn't account for the oxidation number of the atoms in an element, and so doesn't know if a nitrous oxide is NO or NO₂, etc, each of which might have different properties.
- Doesn't take into account the allotropy of a compound, and structure is important because that dictates properties.

- Doesn't take into account what temperature it's at/pressure, and therefore not which state/phase it's in, each of which affects properties.

When you get a question about catalysts in a biological context, make sure you explicitly mention *enzymes*.

The 1 IE of transition elements is relatively constant because you're removing the same 4s electrons each time. There is a slight increase because the small increase in electron shielding of the outer shell (due to filling up the d-subshell) is not quite enough to cancel the increase in nuclear charge attracting the outer electrons.

You have two tetrahedral holes per close-packed atom, and one octahedral hole. By choosing which type of holes the anions fill up, you get the stoichiometry of the compound.

The water of hydration is different to a complex ion with water as the ligands. A water of hydration is simply the original crystal structure with water squeezed into the pores, so it can be expelled without significantly changing the original structure.

Colour in transition metals arises from d-orbital splitting, and electrons moving between orbitals. If all the d-orbitals in the ion are full, or completely empty, this type of d-orbital splitting won't cause colour.

R/S refers to the ordering of the priority groups attached to the chiral carbon, where R—right—is clockwise. +/- simply refers to how the molecule rotates plane-polarised light, unrelated to whether it's R or S. + here is clockwise.

Tetrahedral transition metal complexes form when you have larger ligands, like Cobalt (II) Chloride, and square planar complexes will form when you have smaller ligands that can fit onto one plane, like with platinum compounds (especially with cyanide—think about cis-trans platin).

Less energy is released than theoretically predicted when hydrogenating benzene because more energy is needed to break the bonds in benzene due to pi delocalisation, which makes the structure more stable than other alkenes.

Oxidation states of transition metals initially increase from Sc to Mn because there is an increase number of d electrons that can be removed to form increasingly charged ions, but at Mn increase in nuclear charge counters this effect by binding electrons tightly, and preventing electrons from being removed so then the oxidation states decrease to +2 for Zinc.

Hess' Law states that the enthalpy change for a reaction is independent of the route taken to get to the products *provided that the starting and final conditions are the same*.

The K_c , K_p , etc. constants refer to balance of products/reactants *at equilibrium only*. If there is a shift in equilibrium, K_c does not apply until the system restores equilibrium! This is why you can have shifts in equilibrium due to new species being introduced, but an unchanged K value, which *only changes with temperature!*

You only get the amount of coupling in a proton NMR on a carbon atom that corresponds to how many hydrogens the carbons directly adjacent to that carbon (and ONLY those carbons) have. Labile protons, on groups like -OH, don't couple with anything else, and show up merely as singlets.

Some nucleophilic reactions form enantiomers because at some point in the mechanism, there is a *planar carbonyl that can be attacked from either side, forming two different optical isomers*.

CN groups can be hydrolysed to make COOH by aqueous acids.

Usually write bromine water as just Br₂, since you're just using the water as a solvent. When you add bromine water to phenol until, you get 2,4,6 tribromophenol, which is a white ppt, and the bromine water will decolourise because the bromine reacts away.

When you're working on anything redox, and can't get oxygens to balance, add *water*, as adding anything else containing oxygen disturbs reduction/oxidation.

A fuel cell just has two half equations going on in different parts of it. One is producing electrons that go on to reduce the other. In the process, electrons move, supplying energy to some electrical device.

While the transition elements have a pyramid of oxidation states, starting at +3 with Sc, and peaking at Mn⁷⁺, it's not always that predictable; they have many variable oxidation states, so don't count on using numerical arguments in questions about, say, bonding.

The reason we see colour of transition metals normally is to do with absorption of light, as opposed to emission. The complexes' field splitting causes electrons be excited, and the complementary colour of that absorbed is seen—the energy gap to the electron absorbs corresponds to the *visible range of the EM spectrum*.

“Why does this form an optical isomer?”

Things form optical isomers when they have no plane of symmetry/when they have *non-superimposable mirror images*.

Stereoisomers refer to any time where both the molecular formula and bonding are the same, but you still have two non-superimposable mirror images; and, hence, optical isomerism and geometric isomerism are both types of stereoisomerism.

You can spot a meso compound by looking at when the compound has a plane of symmetry—this way you get to avoid having to visualise/manipulate things/draw them out.

Principles of proton NMR:

- Protons have half integer spin, and so can orient themselves with or against an external magnetic field.

- The energy difference between the two alignment states corresponds to the frequency of radio waves absorbed to flip between them.

- Electrons shield protons from magnetic field. If a proton is next to an electronegative atom, it is de-shielded and thus exposed to the full strength of the external magnetic field, and so there is a large difference in energy between the two states, and a high frequency of radio waves are absorbed, so it shows up as a peak *downstream (to the left), as it has a high chemical shift*.

Lattice energy is exothermic because of bonds forming, and the smaller the ions in the lattice, the closer the ions, more attraction, therefore more exothermic, hence the greater the charge, or smaller the size, the greater the lattice enthalpy.

Cu₂O is a red solid, CuI is a white solid.

The reason that [H₂O] is constant in the Kw expression is because there is negligible dissociation, not because its in excess—it has nothing to be in excess too, in this situation, and if most of it dissociated, the conc. would change no matter how high it was.

A racemate is an *equimolar* mixture of two enantiomers.

Diastereomers are defined as stereoisomers that are not enantiomers.

When describing entropy changes, talk about how energy can be arranged in different ways, and how disorder/randomness can increase/decrease.

Nucleophile is something that *donates a pair of electrons to form a covalent bond*.

Nitrile groups are reduced to amines. You can use Lithal etc. for this, but you can also use hydrogen w/ a metal (nickel) catalyst (*remember that using the latter will also break C=C as it's the catalyst for hydrogenating alkenes*).

NH₂ is labile, as is OH! When you react something with an acyl chloride, you say it's been *acylated*. When explaining where you got certain conclusions by looking at spectra/deducing structures from reaction schemes, make sure you say where each signal came from in the structure you deduced ("triplet at 150 chemical shift comes from CH₂ next to C=O") etc.

In benzene, the reason it forms delocalised electrons is because *p orbitals above and below the ring overlap*. The bonds between carbons aren't quite as short as normal double bonds, and not quite as long as normal single bonds.

The reason that species are negatively charged is because they have an extra electron! This usually forms a lone pair which they use to attack, make sure to *draw the lone pair on* when illustrating mechanisms.

When writing Ecells, use commas for no phase boundary on the same half cell and lines for a phase boundary. Always include state symbols for clarity, and stoichiometry. The species gaining electrons is written closest to the salt bridge. When you have multiples species on either side of the ionic equation (like dichromate with H⁺ on its side), use square brackets to group them.

When you have two electrical equilibria, of one readily losing electrons and the other supplying them, and you let current flow (taking it from an electrode potential joined by a voltmeter and joining them by a wire, or putting the two species together in a test tube) each equilibrium will become one way due to positive feedback, leading to one being oxidised and the other reduced, giving the overall reaction that we normally see.

When trying to find overall Ecell, lay the eq's out in the conventional way (electrons on the left), and compare the E values. Do $E(T) = E(R) - E(O)$ for the alleged reaction after quoting the values laid out conventionally. Do the E-values intuitively tell you the reaction will feasibly happen (to confirm your answer later is correct)?

In the Nernst equation, "n" refers to the small common whole number between the two half equations—the one you use in the overall equation given/derived.

A conjugate acid-base pair is always related just by a difference of one H⁺ is all.

Amine groups get protonated when in acidic environments.

H₂SO₄ catalyses esterification!

REAGENTS/CONDITIONS LIST

Electrophilic substitution of the nitro-group onto benzene takes place with cHNO₃, cH₂SO₄, at 50-60 degrees celsius.

For making a nitro-group into an amine group on a benzene, you can use Sn/HCl because other reducing agents are too strong.

When you want to halogenate something, like an alcohol, use PCl_5 as the standard halogenating agent.

=C= is a planar molecule because the pi bond above AND below plane restricts rotation, forcing it to be planar.

Colours of halogens:

Fluorine—Pale yellow-brown gas, reacts violently with water.

Chlorine—Green gas, green solution.

Bromine—Red-brown liquid, intense yellow-orange in solution.

Iodine—Dark grey solid, pale brown-yellow in solution, purple in organic solvent and as a gas.

Enthalpy definitions:

Reaction: heat change when quantities react in ratio/states specified by the given equation, in standard conditions (1 atm, 1 M, stated temperature—usually 298 K)

Formation: heat change when elements in their standard states (H_2 gas & O_2 gas, say) react to form 1 mol of a compound in its standard state, all in standard conditions.

Combustion: heat change for complete reaction of 1 mol of substance with excess O_2 to produce oxides in standard states, all done in standard conditions.

Neutralisation: heat change for reaction between acid and base producing 1 mol water in standard conditions.

Hydration: heat change when 1 mol of gaseous ions become 1 mol of aqueous ions, all in standard conditions.

Solution: heat change when 1 mol in standard state becomes 1 mol in aqueous ions (so separate lattice via lattice enthalpy, first, and then enthalpy of hydration), all in standard conditions.

Atomisation: heat change when element in standard state becomes 1 mol of element in gaseous atoms, all in standard conditions.

Vaporisation: 1 mol of a substance in liquid state becomes 1 mol in gaseous state, all in standard conditions.

Electronic spectroscopy principles:

In hydrogen, you have three series of light emission spectra: LBP (increasing). From any shell to the first shell, the transition releases a frequency of light corresponding to the Lyman series, and from any shell to the second shell, to the Balmer series, and any shell to the third shell, the Paschen series.

Convergence limit of each series in emission spectra corresponds to the amount of energy that you need to ionise (escape to $n=\infty$) starting an electron from that shell. For example, convergence limit of Balmer series corresponds to electron starting in $n=2$ and being ionised.

Hydrogen sub shells are degenerate *not because they're all 0*, but because there are no electrons in the second, third, and so on shells to shield outer electrons/repel them (which is what leads to them being higher in energy).

Mass spec principles:

We don't need to know about the magnetic field bending molecules! Instead, only time-of-flight mass spec.

1. Ionisation via:

1. Electron impact—electrons emitted from a filament cause ejection of an electron from the molecule

2. Chemical ionisation: for unstable molecules, you add a charge by a chemical reaction. Either way, you make a unipositive ion.

The reason fragmentation happens is because the molecular ion is unstable and so fragments by itself. This is not another entire planned step in the process.

2. Acceleration is via electric field. Heavier ions have a longer time of flight (since they are subject to the same accelerating force, but have a larger mass, and so a lower acceleration). Thus, smaller mass ions reach the detector first and vice versa. Remember that each fragment is given the same kinetic energy (but they have different masses and so different speeds).

3. Detection by production of a small current when the ion reaches the detector. The machine records *when* these currents were produced to get a sense of what fragments hit first vs last.

Dynamic EQM is when the *rate of forward reaction is the same as the rate of backwards reaction*.

Ecell is a powerful tool to predict whether reactions will happen, but it's important to understand that it only applies when the reaction is an aqueous solution and in standard conditions.

Benzene:

- Know evidence for it via hydration and unreactivity.
- Reacts by electrophilic substitution.
- Equal bond lengths show evidence for pi system.

When thinking of electron donating/withdrawing:

- EDG: 2,4 directing & activating.

Two factors to consider when thinking of whether something is or is not electron donating.

- Inductive effect.
- More important: lone pairs/contribution to pi system. Nitrogen (in NO₂—deactivating) doesn't have any lone pairs to contribute to the pi system when it's bonded to two oxygens (one O= and one O-) so is d+ as it attracts and removes electron density from the pi ring. The resonance structures of where the + charge is in the ring. NH₂ is electron donating because N in that compound has a free lone pair, as opposed to in NO₂ where it's net positive (due to dative bond with an oxygen).

When you want to reduce NO₂ to NH₂, use Tin + conc. HCl because LiAlH₄ is too strong.

Bisulfite reaction is nucleophilic addition to an aldehyde (HSO₃⁻) to replace =O w/ OH and H with SO₃⁻. Used in the purification of aldehydes because it's very easy to reverse by adding aqueous acid.

To test for carbonyl groups, use Brady's reagent/2,4 DNP, which gives an orange ppt in the positive case. Use Tollen's/Fehlings for aldehyde in particular (giving silver/red ppt., respectively).

To test for haloalkanes, remove the halide from the hydrocarbon by using a nucleophile like OH⁻, then use nitric acid + AgNO₃ to see if there's a coloured ppt/see if it is soluble in NH₃ (dil)—solubility of silver nitrates in Ammonia decreases as you go down the three.

Use an ox. agent like KMnO₄ or K₂Cr₂O₇ (purple to colourless and orange to green, respectively) to check if things get oxidised at all (a way to test for 1/2/3 alcohols). Or, test for alcohols using

PCl₅ and checking for steamy fumes of HCl. Or, use the Lucas reagent to test for cloudiness (it's ZnCl₂ in conc. HCl), where primary alcohols (they don't really react much in STP) become cloudy slower than secondary alcohols (which take a few minutes), which are, in turn, slower to react than tertiary alcohols (because these have the most stable intermediate state).

Na⁺ can also be used as a test for alcohols (though it's not a great one). It reacts to form hydrogen gas (same mechanistically as how it reacts with water), and to carry this out you have to do it in dry conditions so you're sure the thing you're testing can only be an alcohol, and not water.

To reduce things, use NaBH₄ (in ethanol) or LiAlH₄ (in dry ether to remove any traces of water), and heat the thing you want to reduce with these, making sure to use excess reducing agent.

Separate two different aqueous layers by using a filter funnel.

To purify a product, wash it with cold water, then recrystallise the product from a minimum of hot solvent (like hexane or water, depending on its solubility). This just means dissolve it in a hot solvent and let the solvent cool to aid precipitation of the original product, without any impurities. Check the purity of a product by measuring its melting point against the perfect pure sample, or by separating it via TLC and comparing it to the separation pattern of the pure, original sample.

Decomposition of carbonates not only has a high activation energy, but is also an endothermic reaction in itself.

Covalent character in an ionic bond weakens it, so that as you go down group 2, you get less polarising cations and so less covalent character, and so the electron clouds of the carbonates are less distorted, and thus more energy is needed to break those bonds within the carbonates.

When you're adding two metal/non-metal oxides, the type of reaction they're often looking for is "acid-base".

Hypervalency is when the outer shell electrons exceeds 8—the octet is expanded.

Pre-U really reward symmetry in their organic questions, the answer to a molecular question will never involve a super complicated molecule that you have to work out all the details of.

To avoid flammable things catch fire, heat them using a heating mantle (an electronic water bath, of sorts) as opposed to a bunsen burner—make sure to avoid naked flames so they don't catch on fire.

Alcohols are more soluble in organic solvents than in water, especially for longer chain hydrocarbons.

In fractional distillation, one thing stays in the chamber where the reactants started, and the other (with the higher melting point) *distills over/off*.

Remember that bond angle across a hydrogen that is participating in a hydrogen bond is 180 degrees.

Bond energy is defined as the energy required to break the bonds in 1 mol of gaseous atoms.

When using water to make up solutions (in titrations etc.), make sure to mention that it should be *de-ionised/distilled*.

Parth Notes—Paper 2

The reason that group 2 carbonates become easier to decompose as you go down is because they become less polarising. When the cation is very charge dense, and very polarising, you distort the electron cloud of the carbonate, making the bonds *within* the carbonate weaker and thus it's easier to decompose.

Phosphorus is a larger molecule than nitrogen, and so cannot form pi bonds and so doesn't form P₂ (with a triple bond), but instead forms P₄.

H₂O₂ is a good oxidising agent, but needs H⁺ to accompany it when it gets oxidised (to water, for example).

There are two good ways of removing SO₂ from the atmosphere before it gets there, in factories and stuff—this is called flue gas desulfonation:

- $\text{CaCO}_3 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{CO}_2$, $\text{CaSO}_3 + (1/2)\text{O}_2 \rightarrow \text{CaSO}_4$ (plaster—useful)
- $\text{MgCO}_3 + \text{SO}_2 \rightarrow \text{MgSO}_3$ (which can be heated to regenerate SO₃, useful, when needed)

Sulfuric acid is involatile, oxidising and dehydrating agent, and is important as a catalyst for esterification.

Chlorine and bromine are green and brown-orange in all states—standard, organic, aqueous, whatever. Iodine is a grey solid, brown solution, and purple in organic solvent.

In cold NaOH, halogens disproportionate to make, say, NaCl + NaOCl, and at high temperatures, NaClO becomes NaClO₃—disproportionates further. F₂, however, is always -1, and so doesn't disproportionate. Instead, it forms NaF and F₂O with NaOH, and the F₂O decomposes with water to give HF and O₂.

Fluorine is very small and so lots can fit around a central atom—this often happens around big central atoms, which are forced to become hyper-valent in its presence, forming things like UF₆, etc.

Addition of bisulfite is basically nucleophilic, and happens with aldehydes or methyl ketones (not long chain ketones due to steric hindrance), and is a common reaction used to purify aldehydes as the aldehydes will have an addition reaction to make an insoluble product which can then be separated and then converted back into the reactant using acid. The bisulfites becomes SO₃⁻ and is associated with the original Na⁺ (or whatever cation).

Tollen's reagent can actually be used as an oxidising agent.

Halo-alkane to alcohol you need NaOH (aq), warm gently because substitution competes with elimination.

Halo-alkane to amine is NH₃ in ethanol, high temperature and pressure.

Alcohol to halo-alkane is phosphorus halide (like PCl₃ or PBr₃) in ethanol conditions, under reflux.

Basically, when making alcohols, do it gently, and in (aq), as opposed to in ethanolic/high temperatures.

To make a Grignard, you just heat a halo-alkane with a metal under reflux. You break down the O-MgBr by adding aqueous acid to end up with MgBr(OH).

Atom economy is just $Rm(\text{useful})/Rm(\text{total} - \text{reactants})$. To reduce the impact of chemistry on the environment: find benign alternatives to hazardous chemicals, use renewable feedstocks, use catalysts instead of stoichiometric reagents to reduce waste, run reactions at ambient temp/pressure to increase energy efficiency, minimise chemical products of toxicity.

IR happens because molecules that have covalent bonds have natural frequencies of rotations, stretching, and they absorb different wavelengths of IR according to their natural frequencies, which causes changes in the modes of vibration.

Experimental formation & use of a Grignard:

- Add magnesium metal to a flask containing liquid halo-alkane and ethoxyethane (dry ether).
- Add the thing you want your Grignard to attack dropwise into the flask, and heat under reflux to make the new, desired, product.
- Cool it, and add aqueous acid workup to the solution mixture to make MgBrOH, and an OH, in your desired product.
- Separate and purify your product.

Practical tips:

- Don't tare a beaker to get the mass of what's inside it, only tare at 0. Take a measurement and subtract it from another to get the mass you need.
- Don't just state that a liquid is in XS, find out exactly how much you need, and use a measuring cylinder to measure out 25% more, or something like that.
- For two titres to be concordant, they should be within 0.1cm^3 of each other.

Iodine solution is brown, and it turns blue black in the presence of starch.

Methyl orange is red in acidic conditions and yellow in basic conditions. Use for acidic endpoints.

Litmus is used for neutral endpoints, going from red to blue.

Phenolphthalein is an indicator for basic endpoints, colourless in acidic solution, and pink in basic conditions.

A primary standard is the thing that you make up in volumetric flask, it is very pure and we know its concentration to a high degree of precision. It needs to be: high purity, high stability in air, high solubility in water, low hygroscopicity, high molar mass. Don't want it to react with air as things in volumetric flasks are exposed to them.

Hydrogen has all its sub-shells degenerate, so its 2p has the same energy as 2s, but its quantum level 2 still has a different energy to quantum level 1.

The reason that you don't have just hydrogen forming is because many reactions aren't redox, and forming hydrogen would involve a change in oxidation state on its behalf.

Iodide ions are colourless and so a titration with thiosulfate means that iodine is being removed and so when it is there the solution is BB (with starch indicator present) and when the thiosulfate has removed it all it is colourless (as iodide ions are colourless).

When a *suggest* question is hard, look at the details of the question given, they want you to use a fact that they gave you and relate it to something else.

Parth Notes 3

Make sure you specify that electrochemical eqm calculations are only for standard conditions.

The voltage reading you get when measuring electrode potential is only for the initial condition not letting any current flow; if you let current flow, electrons would move and shift equilibrium such that the pd was 0.

Fuel cells are also better because there are fewer moving parts and so it makes less noise.

The rate constant, k , is a combination of the collision frequency, the steric factor, and the temperature. A , the pre-exponential factor, takes into account how often they collide, and whether its' in the right orientations to result in reaction. Larger size, more collisions, heavier—>slower—> fewer collisions, steric factor encapsulated how the molecules need to collide (orientation for reaction to occur, and A takes these three factors into account, and then the formula contains T/E_a to account for temperature proportion.

Metalloid oxides tend to form amphoteric compounds.

Cu^+ is colourless because it's $4s^1 3d^{10}$ so there are no free d orbitals for electrons to be promoted to, and so it can't have a colour.

Ferritin binds to Fe^{2+} and stores it as Fe^{3+} , thereby storing iron and controlling the release of the ion.

Myoglobin is an emergency store of oxygen in muscle tissue that only releases oxygen at very low partial pressures.

Ligands can affect stability of oxidation states of compounds, for example, in water, Co^{2+} is the most stable, but in ammonia Co^{3+} is more stable.

Lattice enthalpies are calculated via theoretical electrostatics, and so increased degree of covalency (similar electronegativities) mean that the ionic model breaks down.

$NaBH_4$ can reduce aldehydes and ketones to alcohols but no more; $LiAlH_4$ is more powerful can reduce everything we're concerned with; though, sometimes it's too powerful, for example, we choose to use Sn/HCl to reduce a nitro-group into an amine when attached to a benzene ring.

When using rate experiments to find out whether something is SN_1 or 2, keep conc. of everything constant (excess) and plot a $\ln[\]/time$ graph for the OH^- . If it has a constant half life curve, then it's first order and thus SN_2 , if it's linear then it's SN_1 .

The fact that you have interfering nucleophiles reacting in SN_1 , and that you get Markovnikov products (major/minor) is strong evidence that it reacts via a carbocation intermediate.

Nucleophilic addition forms a racemic mixture not because there's a planar carbocation, but just because the CN^- attacking the carbonyl can do so from either side initially.

Make sure your $AlCl_3$ catalyst is *dry*.

Electrophilic addition of nitro groups is important for the production of aryl amines, which have important use industrially as dyes and drugs.

Nitro groups will further react with nitrobenzene (3, 5 directing) in harsh conditions since it's deactivating— CH_2SO_4 and 110 C .

A Zwitter ion is a compound that is neutral overall, but carries formal charges on different atoms.

Chemical shift is just observed frequency - TMS frequency / spectrometer frequency. Labile protons exchange rapidly with other protons in solution, and never couple with anything else.

Coupling refers to interaction between non-equivalent protons on adjacent carbon atoms that manifest as several spikes as part of the same signal on an NMR spectrum.

In d-block elements, 4s electrons are both added and removed first.

When you're looking at (period 3) trends in ionisation energies, know that you get a dip when you first move past the s orbital and when you get 4 electrons in the p orbital.

For the MCQ, if you're not sure a reaction takes place, consult the data booklet! You have it with you in this exam for a reason!

In both absorption and emission spectra, the convergence limit represents *high energy*, not just because it's on the right side of the diagram, which is high frequency by convention, but because the small difference between the energies at the range corresponds to the electrons going from $n=99 \rightarrow n=1$ and $n=98 \rightarrow n=1$ where $n=98, 99$ are almost identical in terms of energy.

On a spectral diagram, the LBP series will all be blobs at separate locations shifted to the right of the diagram as you have energy transitions going to lower levels (and thus giving off more energy).

In MO theory, bond order is not bonds-antibonds all over two, but instead *electrons in bonds - electrons in anti bonds*, all over two.

CuCl_4 complexes are yellow, often giving a green solution because they're mixed with Cu^{2+} atoms/ CuSO_4 , which is blue.

Dichromate is only an oxidising agent when it's *acidified*.

When you're told something is in a ring, it doesn't mean that everything is bonded to each other; for example, there can be hydrogen bonds within the ring structure holding it together. And when you think hydrogen bonds, it must be H on an electronegative group attracted to something that's δ^- .

In an elimination reaction, you set up a good leaving group (like OH_2^+) and then get something to remove an H attached to the carbon so that it can form an extra bond, and the leaving group (on the other carbon) leaves. This is why you can use ethanolic NaOH to cause elimination with $\text{CH}_3\text{CH}_2\text{Br}_3$ but not C_2Br_6 .

To be covalent, they need to have similar electronegativities, but also high average electronegativity.

When looking at questions that make you think about electronegativity, draw out the periodic number line and look at the absolute distance based on charge density and proximity to top right corner.

dG is energy available for useful work, and at a temperature that is for phase change, when there is a phase change, no useful work is done because it's an equilibrium already happening. Therefore, $dG=0$ in these conditions.

Practical Paper Notes

The fat “record these weights/initial data points” in a table and do some simple manipulation have a lot of marks because you get marks for:

- recording all values
- headings/unit on table
- uniform DPs
- correct calculations
- accurate values that strongly agree with teachers

hesitate to give things to 1sf or 2sf, as they usually like 3sf, or more detail (but do this according to the question asked)

values should be 0.2 cm³ apart to be considered concordant titres.

all the marks on long calculations are method marks for using the results you got correctly, not for obtaining some correct answer.

you can never lose marks on qualitative analysis for giving *too much detail*, as long as you have the observation they're looking for, you get the mark.

be quick but methodical when executing quantitative experiments, there's 5/40 marks for getting an answer that matches the teachers, so do it as systematically as a teacher would.

UNIFORM DECIMAL PLACES IN A TABLE, and give decimal places to the precision appropriate to the measuring instrument! It doesn't matter if it's 13cm if it was measured in a burette, write 13.00cm.

when recording results of a chemical test, be super detailed, and give *observations*, as well as deductions (which don't need to be shown in fully, unlike observations).

use precision, reliability, and accuracy often in your answers, as using a burette over a measuring cylinder means you know the volume added to more *precision*, not more “detail”

qualitative analysis

look very carefully during qualitative analysis—the key insight will be faint bubbles produced (say “fizzing” as well as effervescence, or a very pale brown gas, etc.)

when you try to see if a ppt dissolves in excess, really try excess—even take a small sample out to make sure

be very mindful of which solution you're adding to which, label obsessively so you can check on reactions even 10 mins after they occur to see if anything has changed. this way you also don't confuse one solution for another and therefore get a reaction when there shouldn't be one, etc.

when you're testing halides, the solubility in ethanol test is really important to differentiate between chloride and bromide, because often cream and white look quite similar and you can end up fooling yourself.

it's really key to pay attention to get the observations detailed and accurate in the qualitative analysis, even repeating some of the key ones if you have time, as they set up the rest of the questions.

when a gas is given off, you have to test it (for ammonia, CO_2 , hydrogen, etc.), you can't just inspect the answer as there are marks for a correct observation—*especially when it tells you to test and identify any gases given off* (eg: effervescence, followed by making limewater cloudy).

glucose is an aldehyde

when you want to cool something without it absorbing water (such as right after you've heated it to get rid of all the water), then you should cool it in a desiccator to ensure no water gets absorbed.

CO_3^{2-} is pink

lead isn't on syllabus anymore, but its iodide is very yellow, and its chloride is white.

blue is Cu^{2+}

green solution is likely Cr^{3+} or Fe^{2+}

yellow chromate becomes orange dichromate when acid is added to it

when you're decomposing things, using the lid, and opening it periodically, might make it more accurate because then you don't lose contents of what's inside the crucible at any point

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100 Words:

What has been your most rewarding academic experience?

Attending an academically elite school, and participating in Olympiads. At Westminster, I have several friends that are IMO/ISO medallists, so I've been lucky to be exposed to ideas that have slowly taught me rigour. I rarely make it past the second round of the math/physics Olympiad, but I did attend the UK's IBO training camp last year. I really enjoy being surrounded by people who are much smarter than I am. I can't wait to lose myself in Math 25 (maybe even 55), Physics 16, and the like.

What has been your most rewarding extracurricular experience?

Five years ago, I founded CareerFear, what is today an international charity that has over 120 volunteers in 14 cities around the world, and has worked personally with over 6,000 students, as well as impacted 40,000+ more. En route, I've had to pick up random skills like web development, filing taxes, speaking in front of thousands, but, more importantly, it's convinced me that I find most meaning in being able to clearly see the value my work has on society.

What do you imagine will be challenging as you make the transition to college?

Continuing to grapple with the question of where, exactly, I plan on taking my life after Harvard and, indeed, the path I should take en route to getting there. But more immediately, I imagine integrating with US culture might be a bit of a shock, initially, as I've lived abroad my entire life, and am quite accustomed to British culture and norms.

What would you like to be doing 10 years from now?

Working at the intersection of scientific research and industry. For example, at, say, a very small carbon engineering startup that's taking a PhD thesis in physical chemistry and spinning it off to find a better way to absorb CO₂ (an arbitrary example). Or, say, working at a gaming startup that's trying to use deep learning to build a new type of MMORPG. In essence, I'd like to be creating fundamentally new technology in industry. En route, I'd like to apply for the Rhodes/Marshall, and am also considering grad school.

What do you most want your first-year academic adviser, proctor, and peer advising fellow to know about you?

I cannot overstate how much I enjoy being around people that are 1) much more capable than I am (read: I love very hard classes) 2) enjoy discussing academic topics—no matter if they're literary, economical or chemical (read: love classes that build a core group of academic friends). I am not interested in a career in academia, or purely in the physical sciences. I want to apply math/CS to climate science, medicine, urban planning, and a host of other niche fields. Plan on studying some amount of econ/literature, too.