<u>Some question types and answers for paper F335.</u> – some responses based on mark schemes. Questions based on some of these have occurred several times and could do so again.

#### Describe structure of benzene

-each carbon uses 3 electrons to form single bonds

-one electron from each carbon is delocalised

-forms two rings of electron density above and below plane of carbon atoms

-6 electrons delocalised -make ring more energetically stable/ open to electrophilic substitution.

-All C-C bond lengths equal.

-undergo substitution as addition would disrupt the delocalisation and require more energy. (e.g doesn't decolourise bromine water as an alkene would).

### Why does a dye or pigment appear to be colour "X"?

-absorbs <u>visible</u> light
-of correct frequency to excite <u>electrons</u> to higher energy level
-frequency absorbed linked to size of energy <u>gap</u> between levels (ΔE=hv)
-complementary colours not absorbed and transmitted (reflected if solid) = colour seen /colour "X" (<u>NO</u> emission of visible photons involved).
<u>NOT emission – only very hot objects usually emit light!</u>

Why is benzene colourless but dye "X" is coloured? (or similar).

- Dye X contains more extensive region of delocalised electrons
- More extensive delocalisation in dye X **reduces** energy needed to excite electrons as it decreases the <u>size of the gap between energy levels</u>. (Δ**E=hv**)
- So dye X can be excited by absorbing visible light frequencies we see complementary colour (colours <u>not</u> absorbed) to those absorbed.
- Benzene needs **UV** radiation to be able to excite electrons so no visible frequencies absorbed/all visible frequencies transmitted.
- UV radiation has <u>higher</u> energy/frequency than visible radiation.
- (Alternating double bonds allow electrons to be delocalised, as do aromatic rings).
- Emission is **NOT** involved in the colour of dyes at room temp- do NOT use the "E" word in your answers or you will CON earlier marks. Absorbing ONLY.

-

### Colour in transition metal ions in solution.

- 3<u>d</u> or <u>d</u>-subshell (d-orbitals) split into two levels.
- Electrons are excited/ move up to higher energy level
- By absorbing light of frequency corresponding to the gap (delta E)  $\Delta E$  = hv
- See complementary colour to light absorbed.
- Changing the ligand changes the size of the gap  $\Delta E$  and hence changes the frequency of light absorbed causing a colour change.

### How can **emission** spectrum be used to tell difference between 2

## pigments/elements?

-electrons have been e	xcited to higher energy		
levels.		↓	
-they will drop	¥		
<b>down</b> to <u>lower</u>			
<u>energy levels</u> by			
emitting a photon			

(In most cases <u>not</u> falling to "ground state")

- frequency of photon linked to size of gap **between** energy levels (Δ**E=hv**)

-each element will have different energy levels so frequencies emitted will be unique to each element seen as "bright <u>lines</u>" on dark background.

-if diagram needed, remember higher energy levels **<u>closer</u>** together than lower ones.

### What are conditions used in the Haber Process?

Pressure = **25-150atm** temp = **400-500°C**, Iron catalyst. (beware alternatives in some revision guides!)

### Dead easy way to lose marks?

**Not** putting "+" or "-" sign in front of entropy( $\Delta S$ ) or enthalpy ( $\Delta H$ ) changes. Not writing sign for oxidation states in **front** of number (+5 yes, 5+ no, 5 no). Forgetting to convert enthalpy changes (delta H) to <u>JOULES</u> in <u>entropy</u> calculations. ( $\Delta S_{surr} = -\Delta H/T$ )

Writing electron configurations as subscripts and not superscripts  $(1s^2 2s^2 2p^6 YES 1s_2 2s_2 2p_6 NO!!)$ 

**Not** putting the **O**—**H** bond in a "**full** structural formula" of an alcohol, carboxylic acid etc.

### What is a buffer?

<u>Resists changes in pH</u> if <u>small</u> amounts of <u>alkali/acid</u> are added. Weak acid and salt **both** present in **high** concentrations. (may need to add that excess acid/alkali can be barmful to tissues or en

(may need to add that excess acid/alkali can be harmful to tissues or enzyme function).

### How does a buffer work/ maintain pH etc?

Contain weak acid (HA) and salt (A<sup>-</sup>) in equilibrium  $HA \rightleftharpoons H^+ + A^-$ If acid added, extra H<sup>+</sup> ions send equilibrium position to left to restore H<sup>+</sup> levels to original value.

If alkali added,  $OH^{-}$  remove  $H^{+}$ , equilibrium moves to right to replace  $H^{+}$ 

Ka expressions – always write full  $K_a$  expression – even for stated weak acids. (only use Ka =  $[H^+]^2/[HA]$  in calculations)

### Conjugate acid/ base pairs

 $H_2SO_4 / HSO_4^- HNO_3/NO_3^- HCl/Cl^- H_2NO_3^+/HNO_3 CH_3COOH/CH_3COO^- H_3O^+/H_2O H_2O/HO^- HClO_3/ClO_3^-$  in each case losing H<sup>+</sup> creates conjugate base. Make sure you can name the negative ion in each example. Hydrogensulfate (VI), nitrate(V), chloride, ethanoate, hydroxide, chlorate (V).

#### What is a weak acid?

-only partially dissociated in solution/ dissociation equilibrium lies to the left.

Write an equation that shows HCl is a strong acid. HCl  $_{(aq} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$  Forwards arrow only, NO equilibrium sign.

Suggest why a solution of pH 8 is not suitable for use in eye drops. alkali(ne)/ OH- ions damage/harmful to/irritate/sting... the eye

Systematically name : FeCl<sub>2</sub> KClO<sub>3</sub> KNO<sub>2</sub> NO<sub>2</sub> Cu(NO<sub>3</sub>)<sub>2</sub> Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> HNO<sub>2</sub> Iron (II) chloride, potassium chlorate (V), potassium nitrate (III), nitrogen (IV) oxide (or nitrogen dioxide), copper (II) nitrate (V), iron (III) sulfate (VI), nitric (III) acid (nitrous acid).

#### Colour changes :

Potassium dichromate (if oxidises alcohol or aldehyde) <u>Orange</u> to <u>green</u>. Bromine water (reacting with C=C in alkene) <u>yellow/orange/brown</u> to <u>colourless</u>. (Not **red** at start)

Iron (III) chloride (in presence of phenol group) - yellow/brown to purple.

#### Bond angles and shape questions

There are 2/3/4/6 <u>regions of electron density around</u> the <u>central atom</u>. Regions/areas of <u>electron density</u>, <u>repel</u> as <u>far apart as possible</u> to <u>minimise</u> <u>repulsion</u>,

giving bond angles of  $180/120/109/90^{\circ}$ .

(each lone pair counts as a region of electron density, a double or triple bond counts as **one** region).

Names: linear/bent or v-shaped/triangular planar/ tetrahedral/octahedral.

Dot and cross structures cannot account for the bonding in some molecules such as  $B_2H_6$  so why do Chemists continue to use dot and cross structures? -It works effectively/well for the majority of molecules/substances.

#### Ionic structures – properties

High melting point –strong electrostatic attractions between ions need much energy to overcome.

Soluble in water – ions can be hydrated/ form strong ion-dipole bonds to water molecules.

Conduct when molten (or aqueous solution if soluble)- **ions** free to move in liquid/solution and carry charge and create a current. (**NO** <u>delocalised</u> <u>electrons</u> in <u>ionic substances!</u>)

Explain why salts containing large cations and large anions are likely to have low melting points.

Weak <u>ionic bonds</u> OR weak electrostatic forces between <u>ions</u> (NOT intermolecular bonds or ion-dipole)

Small amount of <u>energy</u> needed to separate ions.

#### Explain why calcium oxide has a high melting point.

-reference to ions or ionic structure -strong electrostatic forces **OR** strong attraction forces between ions **OR** strong ionic bonds **OR** a lot of energy needed to break ionic bonds

How does adding  $-SO_3H$ , or  $-SO_3Na^+$  change properties of organic substance? Makes more soluble in water. - ionic  $-SO_3$  groups are strongly hydrated (form strong **ion-dipole** bonds) in water. Ion –dipole bonds formed stronger / similar to H-bonding between water molecules.

#### **IR** questions

Use term **absorbance**, name specific **bond**, state wave numbers e.g absorbance at 1720-1740 cm<sup>-1</sup> for C=O aldehyde.

#### **NMR** questions

Give chemical shift and give the **full** description of the proton type from the table, don't forget relative intensities – e.g methanol contains peaks at  $\delta$  1.0 R-CH<sub>3</sub> and  $\delta$ 4.0 R-OH, intensities in ratio 3:1. (Hs, protons, hydrogens OK to use but not H<sup>+</sup>) **Splitting in nmr.** 

<u>Doublet</u> (split into 2) implies <u>1 H</u> on <u>adjacent</u> (neighbouring) <u>carbon</u>. <u>Triplet</u> (split into 3) implies <u>2 Hs</u> on <u>adjacent</u> (neighbouring) <u>carbon</u>. <u>Quartet</u> (split into 4) implies <u>3 Hs</u> on <u>adjacent</u> (neighbouring) <u>carbon</u>.

#### Mass spectrum questions.

Don't forget **all** ions seen in the mass spectrum have +1 charge! [COOH]<sup>+</sup> this charge must be written.

Remember the ion at the higher end of the spectrum giving the Mr is called the "molecular ion".

#### Carbon dioxide vs. silicon dioxide – structure and bonding/properties.

 $-CO_2$  gas at room temp, SiO<sub>2</sub> = solid with very high melting point -CO<sub>2</sub> = simple molecules, only weak instantaneous dipole-induced dipole bonds between CO<sub>2</sub> molecules- need little <u>energy</u> to overcome.

 $SiO_2 = covalent network$ , vast amounts of <u>energy</u> needed to break network of strong <u>covalent</u> bonds. (<u>NOT</u> "intermolecular bonds" in SiO<sub>2</sub> = common mistake!) SiO<sub>2</sub> insoluble in water, water can't break down network of covalent bonds. CO<sub>2</sub> slightly soluble in water as lone pair on O atoms in CO<sub>2</sub> can form (limited) H-Bonds to H on water molecules.

#### Why is it good to bury CO<sub>2</sub> in deep oceans/ why is it not being done?

-CO<sub>2</sub> responsible for greenhouse effect – melts polar icecap or sea level rise, climate change harming agriculture/ecosystems.

-adding CO<sub>2</sub> to sea water reduces water pH/increases acidity- harms marine life, technology not yet developed or technology very expensive.

#### Give 2 ways of **removing** carbon dioxide from the atmosphere.

increasing photosynthesis / planting more trees (capture and storage )by pumping to the ocean floor or sea bed / pump <u>deep</u> under the sea. (not just pump into sea/ocean) capture and storage in (former) oil / gas wells / porous rock

(de due and storage in (former) <u>off / gas weils</u> / <u>porous</u> rock

(don't confuse with the question on how to reduce  $CO_2$  emissions)

# Why is the shape of molecule X important in a biological context (enzyme, bacteria, medicine)?

-to be effective X must fit the receptor/active site of the bacteria/enzyme = molecular recognition.

-enzyme active site (receptor sites) have specific shapes so only molecules that fit this will react (produce response). –X bonds or forms intermolecular bond to the active site.

#### Write an equation corresponding to the third ionisation enthalpy of Zinc.

 $Zn^{2+}(g) \rightarrow Zn^{3+}(g) + e^{-}$  must have **gas** state symbols and correct charges. Gaseous states for **all** ionisation enthalpies.

# Explain why the second ionisation enthalpy of Calcium is smaller than the third ionisation enthalpy of calcium.

-(2nd IE) removing electron from <u>shell further</u> from <u>nucleus</u> **OR** (3rd IE) removing electron from <u>shell closer</u> to <u>nucleus</u> (If shell is full or not is **NOT** relevant)

-(2nd IE) (electron experiences) less attraction **OR** (3rd IE) (electron experiences) more attraction from nucleus.

#### Define the term electronegativity.

The ability of an atom to attract electrons in a (covalent) bond.

#### Carboxylic acid naming challenges?

Carboxylic acid group dominates and <u>takes carbon number 1</u> and name will end in - oic acid.

CH<sub>3</sub>CH(OH)CH<sub>2</sub>COOH 3-<u>hydroxy</u>butanoic acid.

CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>CH<sub>2</sub>)COOH 2-ethylbutanoic acid (NOT 3-carboxyhexane or other creative ideas!)

What name is given to the functional group in  $H_3C-O-CH_3$ ? -ether

What name is given to the group  $-SO_3H$  and  $-SO_3^-$ -sulfonic acid and sulfonate.

What is meant by unsaturation in fatty acids? The presence of C=C /alkene groups.

#### E/Z (trans/cis) isomerism

-the C=C double bond prevents rotation

-there must be two different groups on each **carbon** of the Carbon –carbon double bond.

Explain why the E(trans) form of an unsaturated fatty acid has a higher melting point than the Z(cis) version.

-molecules/chains can pack/ line up together more <u>closely</u>.
-<u>intermolecular</u> bonds are <u>stronger</u>. (NOT "more" imb's, not covalent bonds)
-<u>more energy</u> required to melt/break i.m.b's. (Not break covalent bonds)

What is an enantiomer (optical isomer)? A non-superimposable mirror image.

#### Explain the meaning of the term "pharmacophore"

<u>part</u>/area/region of the <u>molecule</u>/structure/compound that *either* binds/bonds/fits to a receptor/enzyme/active site *or* is responsible for the medicinal/pharmacological action of the drug

# Explain how inhibitors slow down the rate of an enzyme-catalysed reaction. (inhibitor) binds with / forms bonds with / fits into the active site (of the enzyme)

(inhibitor) blocks the active site/receptor site **OR** competes with the substrate **OR** substrate cannot bind/fit/react (with the active site) **OR** stops substrate being broken down/reacted/catalysed **OR** fewer/less active sites available

# A substance used as an antidote for arsenic poisoning is itself toxic. Suggest a test chemists would do before this drug is allowed to be used.

-Determining a safe dose of the chemical.

-Determining how toxic it is compared to arsenic.

# An insecticide is toxic to people and animals. Suggest 2 arguments that farmers may give to be able to continue using this product.

-no effective alternatives available

-it can be used with suitable care or in low concentrations.

-it is needed to produce a better yield of food or to boost crop profit/keep food price cheap.

# Identify some of the steps involved in going from discovering a substance discovered in fungi to a synthetic statin for medical use.

show that a compound has medicinal properties (identify "lead" compound) analyse/work out structure/ identify pharmacophore synthesise (similar molecules)

clinical trials (may include animal/ethical testing, checking for side effects) (not just "trials")

#### What is an electrophile?

-molecule/ion with partial positive/ **positive** charge -attracted to regions of high electron density/negative charge -**accepts** a pair of electrons to form a covalent bond.

# Give the conditions needed for the coupling reaction between a diazonium salt and an aromatic amine or phenol to make an azo dye.

-alkali(ne) conditions/ NaOH

-low temperature/ below 10  $^{\circ}$ C

### Why is an ionic substance soluble in water?

- <u>Ionic</u> bonds in the lattice have to be broken and <u>hydrogen bonds</u> between water molecules have to be **broken** – requires energy (endothermic).
- Ion-dipole bonds formed between water molecules and ions.
- Forming ion-dipole bonds releases energy (exothermic).
- If more energy released than put in then substance is likely to be soluble (if ion-dipole bonds stronger/similar in strength to the ionic and hydrogen bonding they replace).

Name the forces between Ca<sup>2+</sup> and water molecules in a hydrated calcium ion. -<u>ion-dipole</u> bonds/forces (NOT ionic-dipole)

# Why is a non-polar molecule (e.g octan-1-ol) more soluble in a triglyceride oil than in water?

-main intermolecular bonds between non-polar molecules/hydrocarbon chains = idid (limited pd-pd / Hbonds if polar/OH group present).

Main intermolecular bonds in triglycerides also = id-id

Main intermolecular bonds between water molecules = H bonds

Non-polar molecules only able to form weak id-id bonds to water, much weaker than H-bonds.

Dissolving only favoured if **weaker bonds replaced by stronger/similar ones** – can't happen in water as H-bonds so strong, but possible in oil as id-id bonds similar in strength. (Would disrupt the strong H-bonding between water molecules). -More energy should not be used to break bonds than is released in making bonds if

-More energy should not be used to break bonds than is released in making bonds dissolving is to be favourable.

### Describe a hydrogen bond (or drawing a diagram of H-bonds).

-<u>lone pair</u> on O (N or F) forms attraction to <u>delta-positive H</u>-atom joined to O (N or F). – Hydrogen is delta positive due to large electronegativity difference between H and O (N or F). A <u>diagram</u> often helps to answer this question even when not explicitly asked for

Diagrams of H-bonds: ensure lone pair looking <u>down</u> H-bond, hatched/ dashed lines used to indicate H-bond,

straight line through H-O: ---H-O or H-N: --- H-N , H-O:---H-N etc.

Put in the vital partial (delta) charges on O, N, F (delta minus) and correct H (delta plus) !

#### What is the intermolecular bond between non-polar molecules and how is it formed.

Non-polar molecules only have <u>instantaneous dipole-induced dipole</u> intermolecular bonds. Random <u>movement of electrons</u> in molecule creates <u>uneven dist</u>ribution of charge (=<u>instantaneous dipole</u>).

This <u>induces a dipole</u> in a <u>neighbouring molecule</u> leading to an <u>attraction</u>. <u>Molecules with more electrons</u> will <u>form stronger intermolecular bonds</u>. <u>More energy</u> will needed to <u>overcome/break</u> the stronger intermolecular bonds so <u>boiling</u> <u>point is higher</u>.

<u>NOTE</u> using the initials" id-id" or "pd-pd" without defining what they stand for is <u>NOT</u> acceptable.

# Why would increasing pressure change the equilibrium position in $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ ? Give a reason.

<u>Equilibrium position</u> will move to the <u>right/products</u>. (because) there are <u>more moles/molecules</u> (particles) on the <u>left</u>. ORA (NOT "more reactants than products" without mention of number of particles/moles.)

# Why is very high pressure not used in practice (for an industrial process where raising pressure would increase yield)?

Achieving high pressure **very expensive** as need **thick walled pipes** and powerful pumps / compressors- high energy costs. (Increased risk injury from explosions). Cost saving compensates for fall in yield.

# Why is high pressure used in a reaction where it would not increase equilibrium yield?

Faster rate of reaction. As more successful collisions per unit time / more frequent collisions.

Glycerin is a co-product in the manufacture of biodiesel from vegetable oil. Explain what is meant by the term *co-product* distinguishing it from *by-product*. (June 12) -co-product is formed in the same reaction that makes the main product.

-by-product is formed by side/other/unwanted reactions.

(Usual idea that co-products are useful products that can be sold whereas byproducts are not useful and have to be disposed not credited here but if added *as well* would not be CON.)

#### Le Chatelier Questions.

Talk about the equilibrium position and <u>yield</u> of product. -In the Haber process, increasing the pressure causes the **equilibrium position** to

shift to the right as this side has fewer moles of gas, <u>increasing yield</u> of NH<sub>3</sub>. -When temperature is raised in the Haber process the **equilibrium position** shifts to the left (the <u>endothermic</u> direction), <u>decreasing the yield</u> of NH<sub>3</sub>.

• If you have linked equilibria make sure you mention each equation -

Eg. Adding more  $CO_{2(g)}$  causes equilibrium position in equation "3.1" to move to the right, this causes an increase in  $CO_{2(aq)}$  causing equilibrium position in equation "3.2" to move to the right leading to an increase in  $HCO_3^-$  ion concentration.

# Explain why an exothermic equilibrium process is actually carried out a high temperature.

Must make clear that the <u>increase in rate</u> makes up /compensates for the <u>fall in</u> <u>yield</u>. Idea of "compromise conditions" must mention rate and yield.

#### Why is the molecule CF<sub>3</sub>Cl polar?

C-Cl and C-F bonds have different polarities

The <u>dipoles/charges</u> do <u>not cancel out</u> OR <u>centre of positive and negative charges</u> <u>don't</u> <u>coincide</u>

OR there is a greater (partial) negative charge on the F side of the molecule.

### Describe the stationary and mobile phase in Gas-liquid chromatography (GLC.

Stationary phase = high boiling liquid on solid/silica support. Mobile phase = inert carrier gas such as  $N_2$  or Ar. (don't confuse TLC and GLC!!).

A reaction involves the dehydration of an organic molecule. Give another name for this **type** of reaction.

<u>Elimination</u>. (NOT condensation which involves 2 or more molecules joining together with the elimination of a small molecule eg. Alcohol  $\rightarrow$  alkene +water = elimination, alcohol + carboxylic acid  $\rightarrow$  ester +water = condensation)

#### Disadvantages/advantages of adding N / nitrates to the soil.

-N is essential nutrient for plant growth

-nitrates can be leached/washed out of soil into rivers/lakes where they can cause eutrophication.

#### Hazards of ...

CO – toxic, prevents oxygen uptake by binding to haemoglobin, contributes to photochemical smog. (NOT greenhouse gas). – (CO is made from incomplete combustion of hydrocarbons).

 $CO_2$  – green house gas, absorbs IR radiation, its bonds vibrate more when IR absorbed, increasing kinetic energy of the gas molecules = temperature rise.  $NO_x/SO_x$  – cause acid rain, toxic, irritant to respiratory system.

 $NO_2$  – toxic, causes acid rain (which kills trees, fish/ corrodes buildings ), contributes to photochemical smog and (tropospheric) ozone formation.

 $NH_3$  – is alkaline/ toxic.

Cl<sub>2</sub> – toxic, damaging to respiratory system.

Ozone- toxic, contributes to photochemical smog, respiratory irritant.

N.B **HCI** (aq/g) "hydrochloric acid"= (<u>aq</u>) =corrosive

"hydrogen chloride" (g) = toxic

 $AlCl_3$  – aluminium compounds are toxic. Benzene = a carcinogen.

("harmful" and "polluting" are usually too woolly to get a mark in hazard questions).

Describe the importance to the environment of having industrial reactions with high atom economies.

-little waste/ most atoms or reagents used (Not: toxic or less raw materials needed)

#### What does the "V" in the name Calcium nitrate (V) indicate.

<u>oxidation</u> <u>state</u>/<u>number</u> of nitrogen/N (in the ion) **OR** nitrogen/N has oxidation state/number of (+) 5

#### Why is Calcium nitrate (V) used as a fertiliser?

(contains) N/nitrogen/nitrate which <u>crops/plants</u> need (as a nutrient) **OR** <u>soluble</u> source of nitrogen/nitrate.

### How will feasibility of a reaction with known entropy change of system be affected as temperature rises if the enthalpy change of reaction is exothermic?

State :  $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$   $\Delta S_{surroundings} = -\Delta H / T$  will be <u>positive</u> as  $\Delta H$  is negative. As temp (T) rises the value of - ( $\Delta H / T$ ) decreases (value of  $\Delta H$  is constant) (assume - unless told otherwise- that  $\Delta S$  system is independent of temperature) so  $\Delta S$  total becomes <u>smaller</u> and reaction becomes less feasible. To be feasible  $\Delta S_{total}$  must be greater than zero / positive.