Marks

Question 31 — The Chemistry of Art (25 marks)

(a) (i) Identify the metal ion that will produce a yellow colour in a flame test. **1**

(ii) Explain how some metal ions produce a characteristic colour in a flame. **3**

(b) Using an example from medicine or biological research, describe the bonding in a coordination complex. **4**

(c) (i) Explain what is meant by a reflectance spectrum. **2**

(ii) Outline how infrared light and ultraviolet light are used to determine the chemical composition of pigments. **3**

(d) During your practical work you performed a first-hand investigation to determine the oxidising strength of potassium permanganate.

(i) State the electronic configuration of manganese in terms of subshells. **1**

(ii) Outline the procedure used to determine the oxidising strength of potassium permanganate. **2**

(iii) Using your results from the procedure in part (d) (ii), justify a conclusion about the oxidising strength of potassium permanganate. Use half-equations in your answer. **3**

(e) Analyse trends in the physical properties of the first transition series. **6**

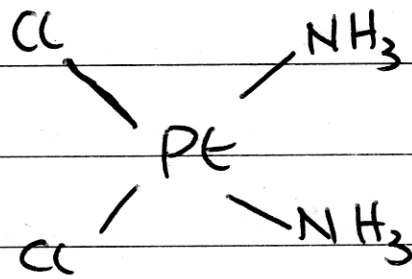
Question 31

Na^{2+} is yellow/orange

(a) i) barium ~~ion~~ ion (Ba^{2+}) is yellow/green

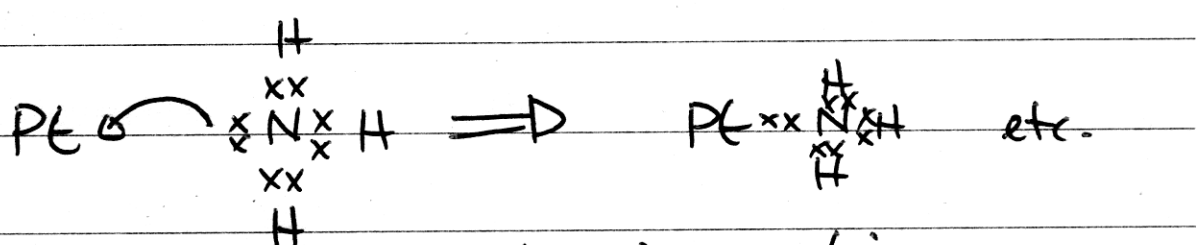
ii) When the metal ion is introduced into the flame, the energy provided by the flame drives a free electron onto the ion (producing an atom) and causes electrons within the atom to jump energy levels whilst absorbing energy (as described by Bohr's 2nd postulate). Each metal has a unique, signature electron configuration with distinct energy levels. ∴ As the electrons cascade down the energy levels again, they emit different amounts of discreet energy (as photons). The energy released means that each photon has a characteristic frequency ($E=hf$) and hence a characteristic wavelength ($c=f\lambda$). It is these characteristic λ's of light that we see emitted from the flame because of the electron transitions in the atoms.

(b)



Cisplatin (shown above) is a coordination complex used in medicine. Each ligand has a lone pair of electrons which are donated to the metal ion, resulting in a coordinate covalent bond. The ligand (e.g. NH_3) is a Lewis Base (i.e. electron pair donor) and the metal is a Lewis Acid (i.e. electron pair acceptor), ∴ the reactions between the metal (Pt) and the ligands (NH_3's and Cl's) are Lewis Acid/Base reactions.

Cisplatin is used as an anticancer drug in medicine as it binds onto the cancer cells, preventing them from dividing. This therefore allows the treatment of a localised tumour.



∴ Lewis reaction.

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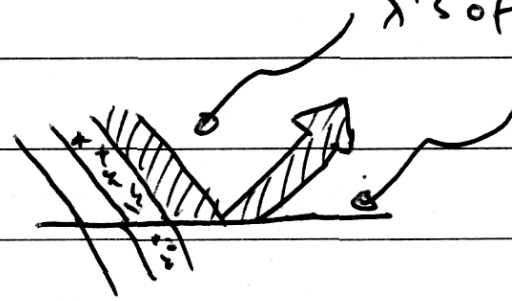
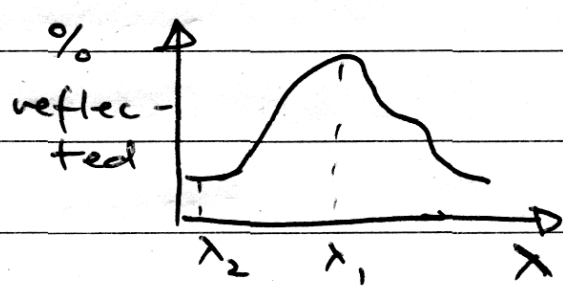
(c) i)



A reflectance spectrum is a spectrum produced by shining white light at an opaque surface, and observing what wavelengths are reflected from the surface. The resulting spectrum will be coloured, but missing some characteristic λ's which have been absorbed by the substance being studied. These have been absorbed because the Energy of the photons corresponds to an electron transition within the substance's atoms. A reflectance spectrum looks like this:



In this case the substance absorbs λ_2 but reflects λ_1.

(ii) IR spectroscopy: A ceramic is heated and the resulting infrared radiation is passed through a sample and a solvent sample. The radiation is collected by a thermocouple and compared. The spectrum is graphed % transmittance against λ. Each atom will absorb diff λ's of energy (infrared energy), ∴ each atom has a characteristic IR spectrum. ∴ by comparing results obtained from a pigment with a database of spectra from known substances, the composition of the pigment can be determined. IR spectroscopy is good for qualitative testing (especially of organic compounds), but not so good for quantitative results.

U.V: a similar process is used, but using energy in the U.V spectrum instead of that in the IR spectrum. A graph of absorbance vs. λ is compiled, and compared with known substances in a similar way.

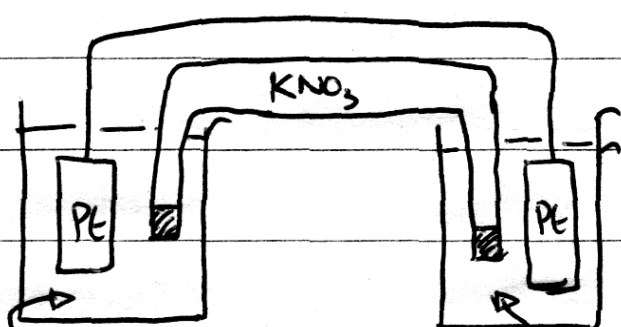
P.T.O.

U·V spectroscopy can provide quantitative insights into the concentration of the pigments also as concentration ∝ absorption.

∴ By comparing known spectra with that of the pigment, it's composition can be determined. An advantage of ~~the~~ IR/U.V - double beam spectroscopy is that it is not destructive, ∴ the painting doesn't get destroyed.

(d) i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

ii)



halide anion. H^+ and MnO_4^-

(1) setup a galvanic cell as shown above. In one beaker put an acidified potassium permanganate solution. In the other beaker put a soluble bromide salt.

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(2) Observe any colour changes in the two beakers.

(3) Repeat using chloride, and then fluoride instead of bromide and observe any colour changes.

(4) Consult the "standard potentials" sheet to explain any changes and make a conclusion about the oxidising strength of MnO_4^-.

(iii) In the cell with bromide, the $KMnO_4$ will decolourise (see eqn ① on next page) and the bromide will turn brown (eqn ②) (Br_2). A similar thing will happen with the chloride (but yellow chlorine gas will result). There will be no change with the fluoride.

∴ $KMnO_4$ is strong enough to oxidise both the two halides (bromide and chloride), but not strong enough to oxidise fluoride.

P.T.O.

Using the table of standard potentials:

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ (+1.51V)

(1) – Mn^{2+} is colourless.

– +1.51V is very high.

(2) $Br^- \rightleftharpoons \frac{1}{2}Br_2(aq) + e^-$ (−1.10v)

– the magnitude of this voltage is very large, indicating that it's hard to oxidise Br^-. But as 1.51 − 1.10 > 0, the reaction occurs (as was witnessed by the reaction).

Similarly with chloride: ($Cl^- \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$) (−1.36v)

1.51 − 1.36 > 0 ∴ this reaction occurs.

But, with fluoride: ($F^- \rightarrow \frac{1}{2}F_2 + e^-$ (−2.89v))

1.51 − 2.89 < 0 ∴ the reaction doesn't happen.

P.T.O.

But, as $KMnO_4$ oxidises two substances (Br^- and Cl^-) which are very hard to oxidise (as shown by their large reduction potentials), it can be shown that potassium permanganate is a very strong oxidising agent (resulting from manganese being in a high oxidation state).

(e) (i) melting point: Melting point increases along the first transition series until manganese (... $3d^5$) and then decreases along the rest of the series. This is because of Hund's rule of maximum multiplicity. Each d orbital fills one e^- at a time before e^- pair up. ∴ Manganese has one e^- in each d-orbital in order to maximise the # of e^- in each orbital with the same spin. The reason M.P. increases to Mn is that there are more unpaired d electrons to

form inter ~~mole~~-atomic bonds with other atoms, ~~4th~~ increasing the energy needed to break them. As e^- begin to pair up ~~fourth~~ (following Mn), melting point decreases because of the ↓ decreased unpaired electrons available for bonding.

(2) atomic radii: atomic radii decreases along the first transition series to Mn, and then increases. This is because up until Mn, there is a significantly higher nuclear charge attracting the outer $4s^2$ electrons (with every extra proton added with the next atom). Following Mn, the greater number of electrons in the 3d subshell shield the $4s^2$ from the nuclear charge, allowing them to move further and further away, increasing the radius.

(3) Density: density can be explained in terms of atomic radii and mass (as d = mass per unit volume). ∴ whilst mass is increasing

constatly (w/ every extra proton), atomic radii exhibit the property mentioned in (2). ∴ density decreases until Mn and then increases as the atomic volume increases.

(4) Magnetism: A substance is paramagnetic if it has paired electrons in it's outer shell, that nears it is attracted (weakly) by magnetic fields. A substance is diamagnetic (repelled by B fields) if it has unpaired e^-. ∴ by Hund's rule, ~~substances~~ metals are diamagnetic up until Mn (b/c of the unpaired d-electrons) and exhibit paramagnetic properties following that (as d electrons begin to pair up.)

(6) Hardness, there is no trend in hardness across the first transition series.

(7) All transition metals display the properties of metals (ie. they are good conductors of

heat and electricity).

(8) Ionization energy: whilst not a physical property, IE (1st) ~~decreases~~ increases along the period as the outer most e^- is further away from the nucleus ~~and more~~ but the nuclear charge (extra b/c of ↑ protons) is so much greater.

∴ the first transition series displays trends in M.P., atomic radii, density, magnetism.