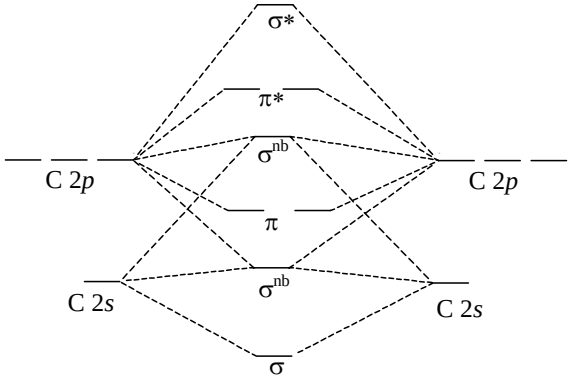
Question 1 Multiple choice and short answer. Complete all questions directly on the examination paper. (21 total points)

Questions (i)-(iv) refer to the molecular orbital of C_2. Below is the empty MO diagram. Fill in the appropriate number of electrons and answer the following questions. (2+2+2+2 points)



(i) What is the bond order of C_2?

(a) 3

(ii) Which of these should be the most stable form of C_2?

(e) C_2^{2-}

(iii) Draw an MO picture for the two non-bonding orbitals.

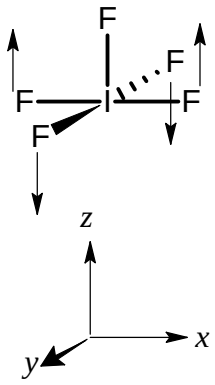
(They will look the same, except with phase difference; these will be *sp* hybrid combinations)



(iv) Valence bond theory predicts ethyne is linear H-CC-H. Based on the MO picture, would the same geometry be predicted? Explain.

The HOMO and LUMO are both pointing outwards at 180° from each other, and in line with the C-C axis. (and these orbitals are the ones most likely to interact with the incoming H atoms) Therefore the geometry will be linear, matching the prediction of valence bond theory.

Questions (v) to (vii) deal with the following bending vibration for the molecule IF_5, shown below (the arrows alternate up and down as you go around the bottom F's). It has point group C_{4v},. Answer the following questions about this system. (2+2+2 points)



C_{4v}	E	C_4	C_2 ($2C_4$)	σ_v	σ_d		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x,y), (R_x,R_y)	(xz,yz)

(v) The vibration has what symmetry?

(d) B_1

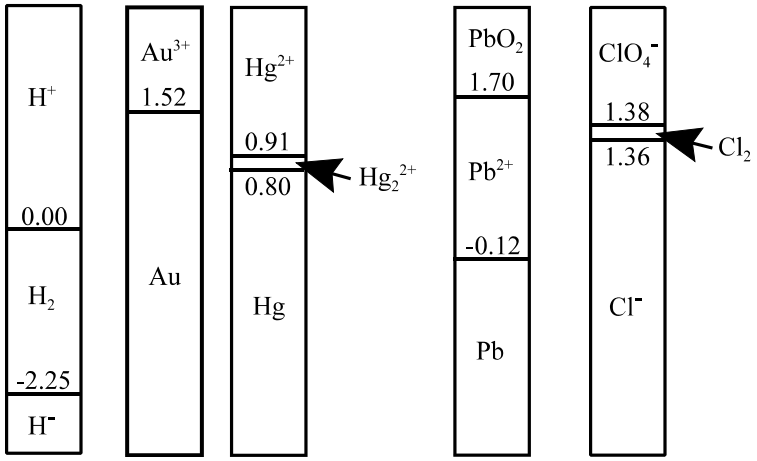
(vi) Therefore, the vibration is

(c) active in Raman only

(vii) If F^- is added to form IF_6^-, what would be the point group?

(d) O_h

Questions (viii) to (xi) use the predominance diagrams given. Your stomach acid can be approximated as 1 *M* HCl. (2+2+1+2 points)



(viii) The neutral metal is the least bioavailable form (and the least toxic). Which metals are more toxic because they are unstable in the stomach (react with Cl^- or H^+ to give a more bioavailable form)?

(c) Pb

(ix) If you chose a reaction in (viii), give a balanced redox equation for the reaction (if not, answer "no reaction").

$Pb + 2\ H^+ \rightarrow Pb^{2+} + H_2$

(x) Give the voltage generated for your reaction in (ix).

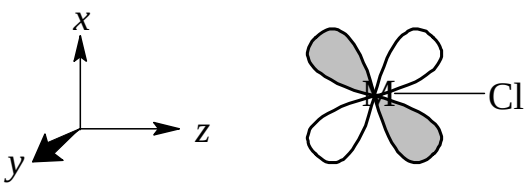
$\Delta E° = 0.12$ V

(xi) Why is Cl_2 unlikely to be generated in ANY reaction that might occur under stomach conditions?

The window for stability of Cl_2 is very small (0.02 V), so there's only a very small chance that a metal would also have a redox potential that falls in that small range, and therefore it's more likely that the metal species will be able to co-exist with Cl^- or oxidize completely to ClO_4^-.

Question 2 More multiple choice. Answer directly on this page (2 points each, 8 total points)

(i) In crystal field theory, I mentioned that the t_{2g} level is for π-bonding orbitals. One of these orbitals (d_{xz}) is shown. Which *one* of the following O orbitals on H_2O would overlap with the d_{xz}?



(a) p_x

(ii) Element 118 was recently discovered (in 2002), and has been given the temproary atomic symbol Uuo. Which is the most likely for Uuo:

(a) It will not easily form any chemical compounds

(iii) What is the point group of dichloromethane, CH_2Cl_2?

(d) C_{2v}

(vii) In the angular overlap model (on which M.O. theory is based), the overlap between any two orbitals depends on

(d) both (a) and (b)

Question 3 More short answer. Answer directly on this page. (9 total points) (NOTE: questions (a) and (b) were on material not covered this year)

(c) Ti^{3+} complexes have a d^1 configuration and a wide variety of colours. The aqueous species $Ti(H_20)_6^{3+}$ has a λ_{MAX} of 470 nm. What is the value of Δ_O? Give the answer in units of kJ/mol. (2 points)

$\Delta_o = \Delta E = h\nu = hc/\lambda = (6.626 \times 10^{-34}$ Js)$(3.00 \times 10^8$ m/s)/470×10^{-9} m $= 4.2 \times 10^{-19}$ J
to get in kJ/mol, multiply by Avagadro's number (6.02×10^{23} /mol) = 255 kJ/mol

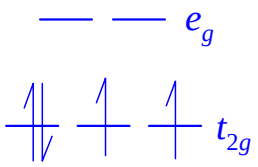
(d) Both paramagnetic and ferromagnetic substances will be attracted to a magnetic field. Explain the difference between them. (2 points)

Both have unpaired electrons, so are attracted to a magnetic field. In ferromagnetism, the magnetic moment on all molecules is pointed in the same direction, in paramagnetism, the molecules are lined up randomly with respect to each other.

Question 4 Do 5 of the following 7. (4 points each, 20 total) (NOTE: (d) was not covered)

(a) The compound ion $[Cr(NH_3)_6]^{2+}$ was found to have a magnetic moment of 2.77 μ_B. Draw the *d*-orbital splitting for this compound, and add the appropriate number of electrons.

solving the quadratic equation $N^2 + 2N - 2.77^2 = 0$ gives one sensible root, which is 1.94, which is closest to 2 unpaired electrons. Therefore:



(b) Explain why ligands with strong σ-donor ability give a large value of Δ_O.

Recall that the e_g set is technically an antibonding (σ*) orbital. Also recall that a strong bond leads to a lowering of the σ level and a raising of a σ* level. If the e_g level is raised (and the t_{2g} level stays the same), the Δ_o will increase.

(c) Explain how a d^9 octahedral complex might distort and justify the energetic reason for it doing so.

A d^9 complex has 3 electrons in the e_g set. A distortion (bond lengthening) along the *z*-axis will also cause a bond shortening along the *x* and *y* axes. Thus, the antibonding d_{z^2} will decrease in energy (less antibonding because bond is longer) and the antibonding $d_{x^2-y^2}$ will increase in energy (more antibonding because bond is shorter). The two formerly e_g orbitals are thus no longer degenerate. Putting the 3 electrons in the new pattern results in one electron being higher in energy but two electrons being lower in energy. Thus, the overall energy is lowered after the distortion.

(e) Explain the chelate effect.

for the two reactions

$6\ L + M^{n+} \rightarrow ML_6^{n+}$ (monodentate ligand)

$3\ LL + M^{n+} \rightarrow M(LL)_3^{n+}$ (bidentate chelating ligands)

both have unfavourable (negative) Δ*S* of reaction, but the lower has a *less unfavourable* entropy change, and thus is overall more favourable in Δ*G* (this is assuming the two Δ*H* are the same, *e.g.* in the case of all N donors like in the difference between six NH_3 *vs.* three 1,2-diaminoethane)

(f) For the following reaction, ΔH_{rxn} = +217 kJ/mol.

$$P_4\,(g) \rightleftharpoons 2\,P_2\,(g)$$

The bond energy of a P-P single bond is 200 kJ/mol (*i.e.*, upon formation of a P-P single bond, -200 kJ/mol is released). If P_4 is a tetrahedron of 4 P atoms (with all single bonds) calculate the bond enthalpy of the P≡P triple bond of the P_2 molecule. Explain why the value is so much lower than that for N≡N (which is 946 kJ/mol).

recall that P_4 has six P-P single bonds (a tetrahedron shape has 4 faces and 6 edges), therefore ΔH for P_4 is approximately 6×(-200) = -1200 kJ/mol. From the formula

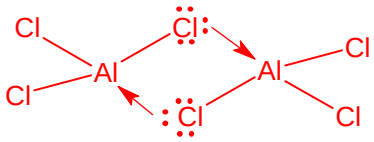
$$\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$$

the ΔH of P_2 must be [217 + (-1200)] / 2 = -492 kJ/mol

This is much smaller than the ΔH for N_2 because 3*p*-3*p* π-bonding is much weaker than 2*p*-2*p* π-bonding. (as discussed in class - *i.e.* because the internuclear distance is increasing faster than the width of the 3*p* orbital)

(g) The compound $Al(CH_3)_3$ dimerises to form $Al_2(CH_3)_6$. $AlCl_3$ also dimerises to Al_2Cl_6, but the bonding is different from the methylated dimer. Explain and compare the bonding in these two aluminium species.

The bonding in $AlCl_3$ is identical to that of BCl_3 (lone pair on Cl donates into the empty Al p_z orbital to complete the Al octet)



$Al(CH_3)_3$ forms a dimer with banana bonds like in B_2H_6 (where the carbon sp^3 orbital is isolobal to the H 1*s* orbital)

