Question 1 Short answer. Answer **6 of the following 8** questions in the space provided. 2 points each (12 total)

(a) Normally, atomic radius decreases left to right. However, Ga is larger than Zn. Explain.

When adding a new subshell, the new orbitals are higher in energy. Therefore, the resulting atom will be bigger. Zn has a electronic configuration [Ar]$3d^{10}4s^2$, while Ga has one electron in a new subshell, the 4p, which makes it larger than Zn.

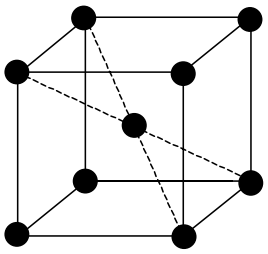
(b) Given that hydrogen-bonding arises from the polarity of the X-H bond (the more polar, the stronger the H-bonding), how would you expect the degree of hydrogen bonding to change as you go down a group? You can assume H will be the most electropositive element.

As you descend a group, electronegativity decreases. If H is the most positive element in the bond, then the bond polarity should decrease as you descend a group (the other element is becoming less negative and therefore more positive). Therefore, H-bonding should become less pronounced/weaker as you go down a group.

(c) Explain the structure of and compare the difference between the two isomorphs of ZnS (sphalerite and wurtzite). Hint: the Zn^{2+} cations are in tetrahedral holes.

In both structures, the S^{2-} anions are close-packed, and the Zn^{2+} cations are in half of the tetrahedral holes. The difference between the two structures is that sphalerite has cubic close packed (ABCABC) layers and wurtzite has hexagonal close packed (ABAB) layers.

(d) Generate the first 2 terms of the Madelung constant for a body-centred cubic unit cell. The unit cell is shown. Remember that the central atom has a different charge than the corner atoms.



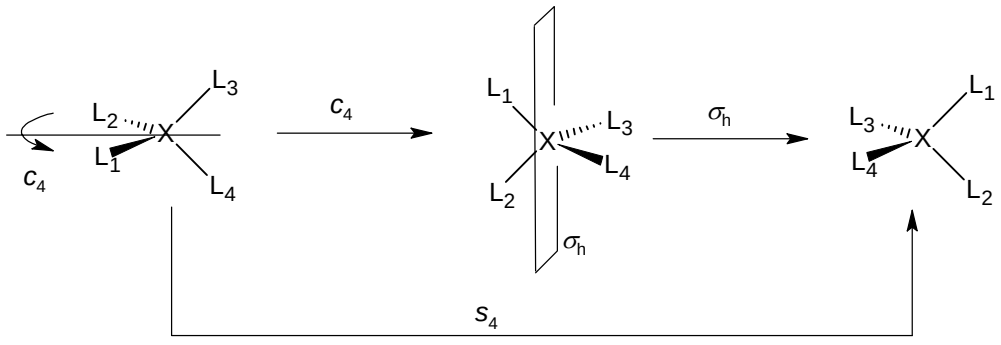
1st term: 8 neighbours (on each corner of the cube) @ distance *d*

2nd term: 6 neighbours (the centre atom of each neighbouring cell, there are 6 neighbouring cells, one on each face of the cube), @ distance????

If the body centre is $\sqrt{3}$ of an edge, then the edge is $1/\sqrt{3}$ of the body diagonal. If we have defined the distance *d* as being 1/2 the body diagonal, then the edge distance is $2/\sqrt{3}$.

Therefore, the first two geometric terms of the Madelung constant are
$8 - 6\sqrt{3}/2$ (or $8 - 3\sqrt{3}$)

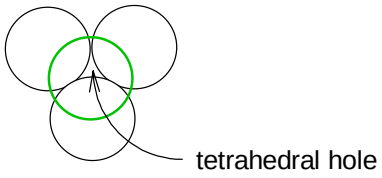
(e) Show the S_4 axis for a tetrahedral molecule.



(f) Explain the origin of the inert pair effect.

s-orbitals spend more time near the nucleus than *p* or *d* orbitals. Therefore, as the nucleus gets larger (more positive), the electrons in the *s*-orbitals are drawn to the nucleus (and therefore stabilised) faster than those electrons in other orbitals. This has the effect of making the *s*-orbitals resistant to oxidation, and eventually (when the 6th period is reached) making the 6th-row element's most stable oxidation state 2 less than elements above it. For example, Pb^{2+} is more stable than Pb^{4+}.

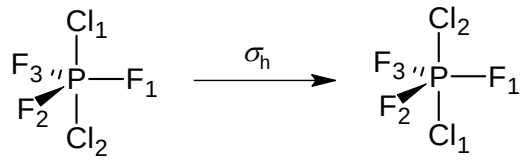
(g) Describe a tetrahedral hole in a close-packed lattice.

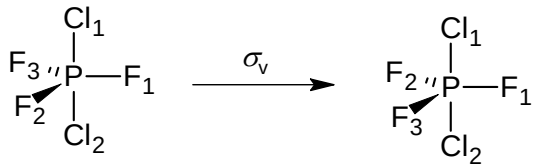


(h) According to the Aufbau principle, Cm (curium, element 96) should have an electronic configuration of [Rn]7$s^2$5f^8. Instead, it has configuration of [Rn]7$s^2$5$f^7$6d^1. Explain.

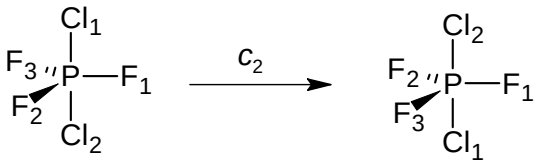
Because there are 7 *f* orbitals, the 8th electron in the Cm *f* shell would be paired. Because the 5*f* and 6*d* orbitals are very close in energy, it costs less energy to promote this electron to the 6*d* orbital rather than suffer the pairing energy penalty associated with putting it into the 5*f* orbital.

Question 2: Perform the following symmetry operations: (2 points)



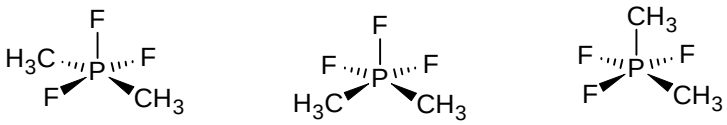


(in plane of paper)



(along P-F_1 axis)

Question 3: Draw all possible isomers of the square-based pyramidal structure $P(CH_3)_2F_3$. (2 points)



Question 4: Briefly describe two potential defects possible in a crystalline lattice. (2 points)

Any two of the following:
- colour centre (anion replaced by electron)
- entire missing formula unit (one cation and one anion missing)
- cation (or anion in fluorite) in the wrong type of hole (T- instead of O-hole)
- extended defect (fault plane)

Question 5 Give the point group for **9 of the following 11** species. Note: in some cases you will have to determine if unshown resonance structures lead to greater symmetry than is present in the one structure shown. 1 point each (9 points total).

(a) T_d (b) D_{3h} (c) C_{2h} (d) D_{6h} (e) D_{3h} (f) C_s

(g) O_h (h) C_{3v} (i) C_{4v} (j) $C_{\infty v}$ (k) C_{2v}

Question 6 (a) Using the Born-Meyer Equation, calculate the theoretical lattice enthalpy (ΔH_L^o) for MgO, which has the rock salt structure (ccp packing of anion, cation fills all the octahedral holes). Note: $r_{Mg^{2+}}$ = 0.86 Å, $r_{O^{2-}}$ = 1.26 Å. (2 points)

d = 0.86+1.26 = 2.12 Å

$$\Delta H_L^o = \frac{N_A z_A z_B e^2}{4\pi\varepsilon_o d}\left(1-\frac{d^*}{d}\right)A = \frac{(6.02\times10^{23})(2)(-2)(1.602\times10^{-19})}{4\pi(8.85\times10^{-12})(2.12\times10^{-10})}\left(1-\frac{0.345}{2.12}\right)(1.74756)$$

therefore, $\Delta H_L°$ = -3836 kJ/mol

(b) Determine the actual (experimental) lattice enthalpy (ΔH_L) using the following data (all values in kJ/mol): (3 points)

$\Delta H_f°$ = -601	ΔH_{vap} (Mg) = 146	$\Delta H_{O=O}$ ($O_2 \rightarrow 2\ O^\bullet$) = 494
ΔH_{IE} ($Mg \rightarrow Mg^+$) = 738	ΔH_{IE} ($Mg^+ \rightarrow Mg^{2+}$) = 1451	ΔH_{IE} ($O^{2-} \rightarrow O^\bullet$) = -603

Both of the negative values must be turned around in this case (note the direction of the reaction for the ionisation energy!), so the "endothermic" part of the cycle is, in fact, 601 + 146 + 494 + 738 + 1451 + 603 = 3786 kJ/mol

Therefore, $\Delta H_L°$ = -3786 kJ/mol

(c) What does the energy match (or lack thereof) say about the nature of the MgO lattice? Note: these are crude calculations, so an error of up to ±20% is not significant. (1 point)

These numbers are very close to each other, so it means that the assumptions built into the Born-Meyer equation are true - the ions do act like hard spheres, and therefore the bonding is best described as ionic.