1. a) **(2 points)** Estimate the concentration of Mg^{2+} in an aqueous solution of $Mg(OH)_2$ if the $K_{sp} = 5.6x10^{-12}$.

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$= x(2x)^2$$

$$= 4x^3$$

$x = [Mg^{2+}]$

$2x = [OH^-]$

$5 \cdot 16 \times 10^{-12} = 4x^3$; $x = 1 \cdot 12 \times 10^{-4}$ M

b) **(2 points)** Suggest two reasons why an experimentally determined K_{sp} might larger than the true value.

- endpoint vs equivalence
- supersaturated
- activity vs concentration
- acidic water sample (CO_2)

Not valid: human error, overshoot endpoint, bad equipmnt

c) **(2 points)**Do you expect $Ba(OH)_2$ to be more or less soluble than $Mg(OH)_2$. Explain briefly

$Ba(OH)_2$

Lattice energy highest for small highly charged cations (Mg^{2+}); high lattice energy means lower solubility (everything else being equal)

2.**(4 points)** When the Schrödinger equation is solved for a hydrogen atom, three quantum numbers are obtained. What are their symbols and possible values? What particular property (size, shape, orientation) does each quantum number indicate? What is the symbol and what are the allowed values for the fourth quantum number?

Quantum number	Possible Values	Characteristic property
n	1, 2, 3	size
l	0, 1, 2 ... $(n-1)$	shape
m_l	$-l$ to l, integers	orientation
m_s	$\pm 1/2$	spin

3. a) **(2 point)** Indicate the smallest and largest species (atom or ion) in the following group: K, Rb, Sr, Ag, I⁻. Explain your answer.

Smallest Ag Largest Rb

Trends: size increases down a column as # shells increase
size decreases left to right across a row as Zeff
ncreases. I⁻ large as it is an anion.

b) **(2points)** Rank the first electron affinity of F, Cl, Br and I from least negative to most negative. Explain briefly.

EA becomes less -ve as atoms get larger (down a column) as
force of attraction between nucleus & incoming electron decreases.
& F are reversed as F is so small coulombic repulsion is
ificant

I Br F Cl

c) **(2 points)** Define first ionization energy and explain why the first ionization energy of thallium (Z=81) is greater than that of indium (Z = 49)

E_1: energy to remove outermost electron from an atom in the gas phase. $A(g) \longrightarrow A^+(g) + e$

generally decreases down a column as atoms get bigger & electron
strongly attracted to nucleus. Tl has higher than expected IE_1
ause e⁻ experiences greater Zeff than expected as it contains 14 poorly shielding f-type electrons.

4. The semiconducting properties of Si can be improved by doping.

a) **(2 points)** If a silicon substrate where doped with B would you be forming an n-type or a p-type semiconductor? Explain.

Si is group 14; B is group 13 (has 1 less electron)
∴ P doping as you are introducing
an absence of -ve charge.

b) **(3 points)** Explain, using band theory, how doping can by used to increase the conductivity of the semiconductor

Semiconductor: band gap not more than 2 or 3eV.

You can create more charge carriers by introducing an impurity (dopant) that adds an impurity band within band gap of host material. P-doping impurity band just above valence band; accepts e⁻ from valence band & introduces more "holes" (which are charge carrier) in valence band.
n-doping, impurity band near conductⁿ band. e⁻ jump into conductⁿ band. Charge carriers are e⁻ in conductⁿ band.

5. a) **(0.5 point)** What is the electronic configuration for yttrium, Y(39)?

$[Kr]\,5s^2 4d^1$

$1s^2 (2s^2 2p^6)(3s^2 3p^6)(3d^{10})(4s^2 4p^6)(4d^1)(5s^2)$

b) **(0.5 point)** Is yttrium paramagnetic or diamagnetic?

1 unpaired ∴ para

c) **(1 point)** Apply Slater's rules and calculate the effective nuclear charge on a 5s electron on Y?

$$Zeff = 39 - \underbrace{0.35(1.0)}_{5s} - \underbrace{0.85(9)}_{4s4p4d} - \underbrace{1.0(28)}_{\text{all others}} = 3$$

d) **(1 point)** Apply Slater's rules and calculate the effective nuclear charge on a 4d electron on y?

$$Zeff = 39 - \underbrace{0.35(\phi)}_{\text{other d}} - \underbrace{1.0(36)}_{\text{anything to left}} = 3$$

e) **(1 point)** Apply Slater's rules and calculate the effective nuclear charge on a 4p electron on Y?

$$Zeff = 39 - \underbrace{0.35(7)}_{4p\text{ or }4s} - \underbrace{0.85(18)}_{3s,3p3d} - \underbrace{1.0(10)}_{\text{all others}} = 11.25$$

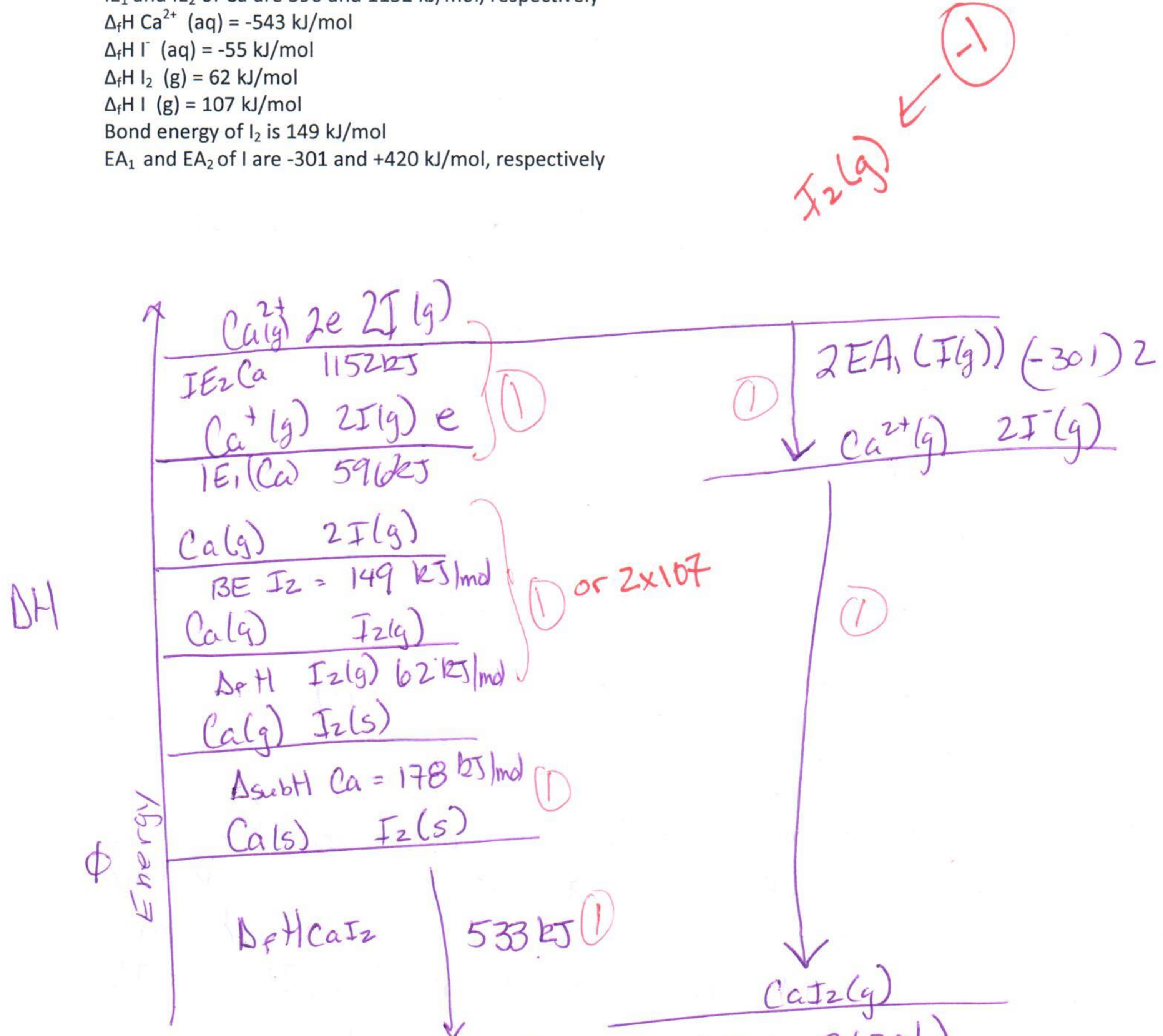
f) **(2 point)** Briefly comment on any trend observed and how it might influence other atomic properties.

Trend: General Zeff increases as you move from valence (5s, 4d) to core (4p, 4s, n=3, n=2, n=1) type electrons.
One would expect, for Y that IE4 would be MUCH greater than IE1, IE2, IE3.
Note: Slaters rules not sufficiently sophisticated to distinguish difference in Zeff on 5s & 4d type electrons so doesn't show clear evidence that 5s electrons removed before 4d.

creasing Zeff indicates cations would be smaller than the
utral atom.

6. **(8 points)** Construct a Born Haber cycle and determine the lattice energy of CaI_2. You **must** draw the cycle and clearly identify each step to receive full marks.
Some relevant (and some not so relevant) information:

$\Delta_f H$ $CaI_2(s)$ = -533 kJ/mol
Enthalpy of sublimation of Ca(s) is $\Delta_{sub}H$ =178 kJ/mol
IE_1 and IE_2 of Ca are 596 and 1152 kJ/mol, respectively
$\Delta_f H$ Ca^{2+} (aq) = -543 kJ/mol
$\Delta_f H$ I^- (aq) = -55 kJ/mol
$\Delta_f H$ I_2 (g) = 62 kJ/mol
$\Delta_f H$ I (g) = 107 kJ/mol
Bond energy of I_2 is 149 kJ/mol
EA_1 and EA_2 of I are -301 and +420 kJ/mol, respectively



533+ 178 +62 +149 +596 +1152 = LE + 2(301) ①

2670 kJ = LE + 602 kJ

LE = 2068 kJ. ①

8. Draw Lewis structures and based on VSEPR theory identify the electron pair geometry around the central atom, the shape of the molecule and approximate bond angle, the polarity and the valence bond hybridization required for the predicted shape. Use the space provided to draw molecule/ion to support your answer.

DRAW LEWIS STRUCTURE FOR MOLECULE HERE

$5 + (7)5 + 2 = 42e^-$

a) (3.5 points) SbF_5^{2-}

(0.5) each

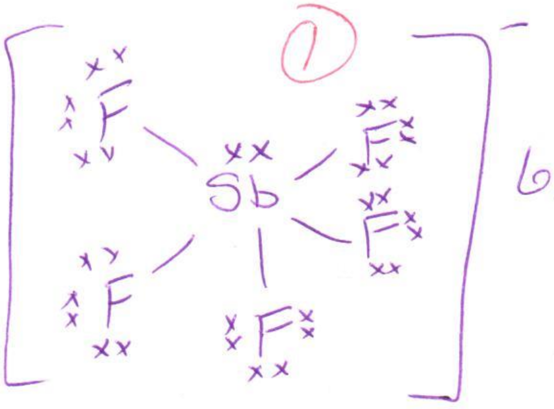
e pair Geometry Octahedral

Shape square based pyramid

Bond angle ~90°

Polar ? Yes

VB hybridization sp^3d^2



6grps

b) **(3.5 points) $AlCl_3$**

0.5 ea.

$3 + 7(3) = 24e^-$

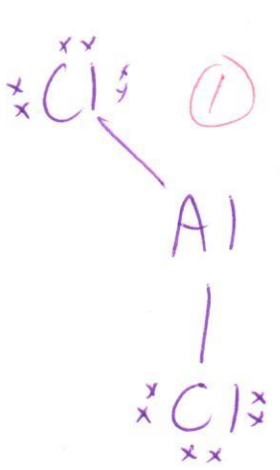
e pair Geometry trigonal planar

Shape trigonal planar

Polar ? No

Bond angle 120°C

VB hybridization sp^2



8. **(8 points)** N_2 and CN^- are isoelectronic (same number of electrons) . Construct MO diagrams for both N_2 and CN^-. Your diagram should show the relative energies of the atomic and molecular orbitals and the molecular orbitals should be labeled as σ σ^*, π and π^* etc. Show the electrons in appropriate orbitals. Indicate clearly any assumptions you make in constructing this diagram. Highlight the differences in the MO diagrams and explain how these diagrams give insight in such properties as bond energy, bond length and polarity.

#AOs = #MOs

MO's form from AO of appropriate energy (i.e. similar) and symmetry

Bonding MO's lower in energy then AOs

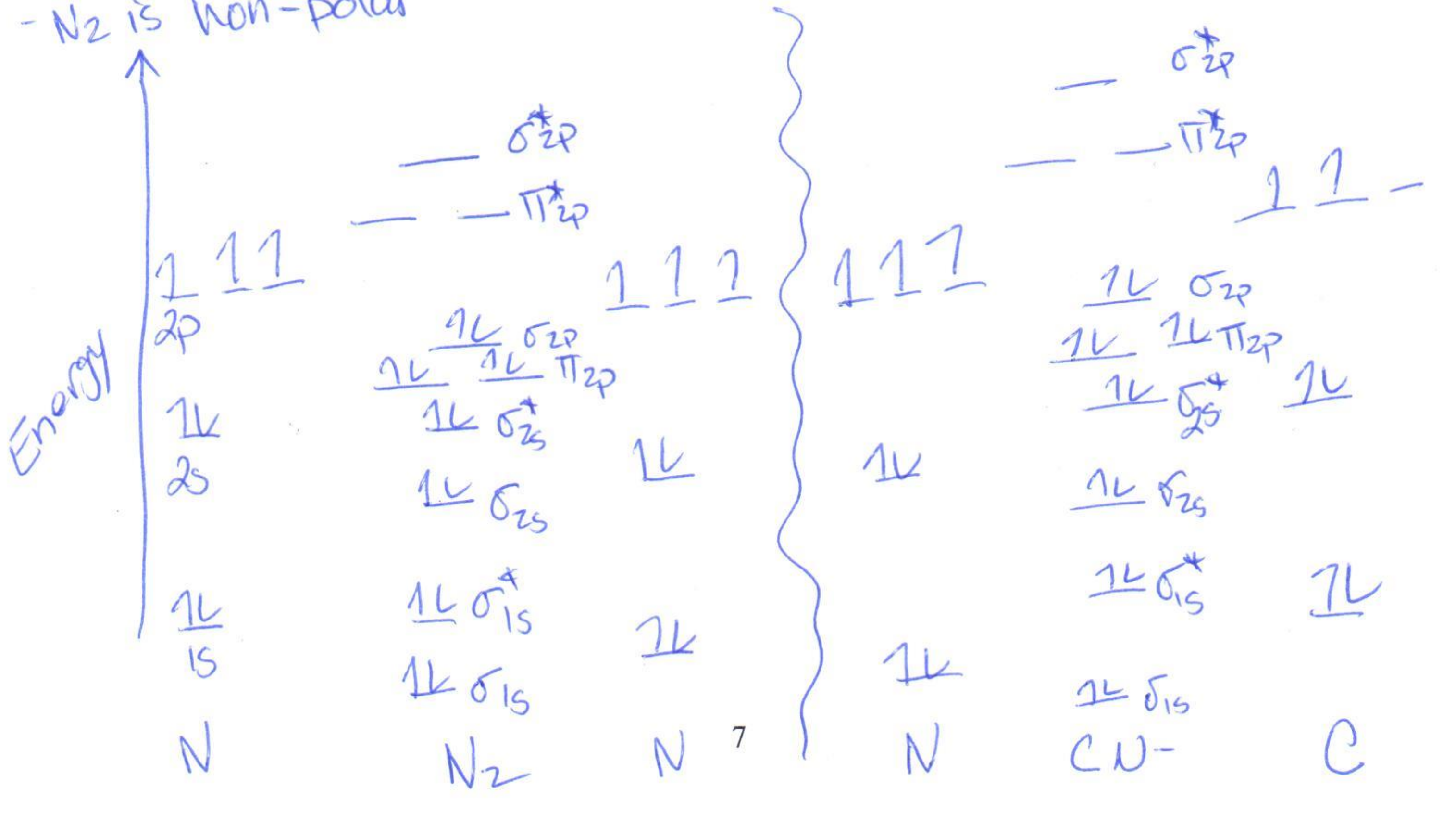
Antibonding MOs higher in energy than AOs

Nonbonding same energy as AOs.

For both N_2 & CN^- π_{2p} MO's lower in energy than σ_{2p} MO's (due to mixing of 2s)

N lower in energy than C because N is more EN.

- Both have Bond order = 3 = $\frac{1}{2}(8-2)=3$ (based on valence electrons only
- In CN^- the bonding orbitals (π_{2p} & σ_{2p}) are closer in energy to the N-AO's; indicates they have more N character & e-density pulled toward N (∴ dipole)
- N_2 is non-polar



9. **(5 points)** Sodium hexafluorantimonate (V), $NaSbF_6$, density 4.37 g cm^{-3}, crystallizes in the sodium chloride lattice. Determine the value for the radius of the hexafluoroantimonate(V) ion. Ionic radii you may (or may not) be interested in include: Na^+ 116 pm; F^- 117 pm; Sb^{5+} 60 pm; Sb^{3+} 76 pm.

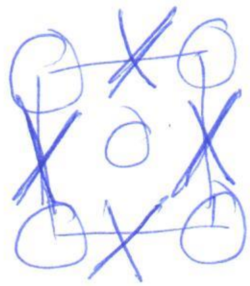
NaCl: Fcc with cations in octahedral holes.

$2r^+ + 2r^- = a$ (= edge length)

1 unit cell includes 4 Na^+ & 4 SbF_6^-

$MM_{NaSbF_6} = 22.99 + 121.56 + (18.998)6 = 258.5$ g/mol

Mass unit cell = $\frac{4 \times 258.5 \text{ g/mol}}{6.023 \times 10^{23}} = 1.718 \times 10^{-21}$ g



O = SbF_6^-
X = Na^+

density = $\frac{\text{mass}}{V} = 4.37 \frac{g}{cm^3} = \frac{1.718 \times 10^{-21} g}{V cm^3}$

$V_{unit\ cell} = 3.931 \times 10^{-22}$ cm^3

$= a^3$

$a = 7.325 \times 10^{-8}$ cm = 733 pm

$= 2(116) + 2(r_{SbF_6^-})$

$r = 250$ pm

10. **(5 points)** The melting point for sodium fluoride is higher than that for sodium chloride while that for carbon tetrafluoride is less than that for carbon tetrachloride. Explain the reasons for the difference in trends.

NaF } Ionic
NaCl

strongest ionic bond formed from small high charge density anions/cations. F^- is smaller then Cl^- so NaF ionic bond stronger NaCl. When you melt an ionic cmpd you are playing with the ionic bonds!

CF_4 } molecular covalent
CCl_4

When you melt molecular covalent compounds you are playing with the intermolecular forces (you are NOT breaking bonds!) These are both non polar compounds therefore you need to consider strength of the dispersion forces. Larger more polarizable CCl_4 will have stronger dispersion (induced dipole) forces & will melt at higher T.