Course: CHEMISTRY | **Number:** 241/2 | **Section:** 01 and 51

Instructors: P.H. Bird & X. Ottenwaelder

Examination: Final | **Date:** 10th Dec, 2011 | **Time:** 09:00 - 12:00 | **# of pages:** 16

Materials Allowed: This is a closed book exam. A periodic table is attached to this paper - *no others are allowed*. You may detach the periodic table if you wish.

Calculators Allowed: Yes

Molecular Models Allowed: Yes

Special Instructions: Please read the instructions at the beginning of each section. Use page 15 for rough work and, if necessary, for extra space. If you do continue an answer on one of these pages, please indicate this clearly.

Be sure to give adequate explanations for your answers where appropriate.

Hints in green, warnings in red, answer checker question numbers in blue.

LAST NAME:

FIRST NAME:

STUDENT NUMBER:

Please also fill in your name and ID number on the scantron sheet in letters/figures, as well as blacking in the appropriate "bubbles". Use a pencil: the scanner cannot read sheets marked in pen.

Please leave blank

Question	23	24	25	26	27	28	29	30	31	32	33
Mark											

The following 22 questions are multiple choice, worth 1 mark each. Identify the choice that best completes the statement or answers the question. You may do rough work on your exam paper, but it will not be marked. Mark your answers on the "scantron" sheet provided *with a pencil*, AND mark your answers on this paper. *Please remember to fill in your name and ID number on the scantron sheet in letters/figures, as well as blacking in the appropriate "bubbles".*

The answer checker will recognize questions 1 to 22.

1. Which elements are the pnictogens?

   a. The elements of group 2.

   b. The elements of group 5.

   c. The elements of group 7.

   d. The 14 elements including and following Lanthanum.

   e. The elements B, Si, As, Te, and At.

   Hint: None – you know it or you don't!

2. The conversion from ${}^{41}_{20}\mathrm{Ca}$ to ${}^{41}_{19}\mathrm{K}$ can occur through:

   a. α-particle emission

   b. β^- emission

   c. β^+ emission

   d. γ emission

   e. neutrino-antineutrino annihilation

   Hint: A proton has been converted to a neutron

3. The Heisenberg Uncertainty Principle tells us that:

   a. we cannot know for certain what is the ground-state configuration of a light atom like sodium.

   b. we cannot exactly solve the Schrödinger equation for a system with more than one nucleus and one electron.

   c. we cannot simultaneously know both the exact position and the exact momentum of a particle such as an electron.

   d. we cannot calculate the wavelength associated with a moving particle such as an electron from its momentum.

   e. we cannot accurately predict the weather in the German town of Heisenberg.

   Hint: None: you should know what the Heisenberg Principle is about.

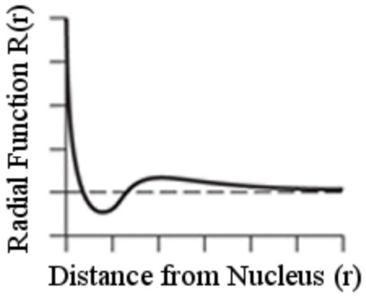
4. How many orbitals have $\ell = 3$?
   a. 1
   b. 3
   c. 4
   d. 7
   e. An infinite number

   Hint: The minimum value of the principal quantum number is 3.

5. Name the orbital which has $n = 4$, $\ell = 2$ and nodes in the xy and xz planes.
   a. $4d_{x^2-y^2}$
   b. $4d_{yz}$
   c. $4d_{z^2}$
   d. $4f_{xyz}$
   e. $4p_x$

   Hint: the orbital has ***two*** planar nodes, not one or three, and “x” should not appear in its name since it is common to the two planes.

6. What could the diagram to the right represent?
   a. The radial function of the 3s orbital of hydrogen.
   b. The radial function of the 4p orbital of hydrogen.
   c. The radial function of the 5d orbital of hydrogen.
   d. Any of the above.
   e. All of the above.



   Hint: It starts a finite (not zero) value of R(r), and has two spherical nodes.

7. In which species does the metal have the configuration: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^6$
   a. Mo(g)
   b. Ru^{2+}(aq)
   c. $PdCl_4^{2-}$(aq)
   d. Fe^{2+}(aq)
   e. None because the 5s orbital is occupied before the 4d.

   Hint: Where are the 5s electrons?

8. For the main-group element antimony (Sb, Z = 51), which orbitals and which electrons must be considered in understanding its chemical bonding using Lewis and valence bond theories, that is, what comprises its valence shell?

   a. $5p^3$

   b. $5s^2\ 5p^3$

   c. $5s^2\ 5p^3\ 5d^0$

   d. $4d^{10}\ 5s^2\ 5p^3$

   e. $4d^{10}\ 5s^2\ 5p^3\ 5d^0$

   Hint: The valence orbitals should be part of the same shell.

9. The highest energy electron of a neutral atom (in its ground state) is all alone in the 6p subshell. Which statement is true?

   a. It is the metal, tellurium (Tl), which forms a chloride, $TlCl_3$.

   b. It is the metal, thallium (Tl), which forms chlorides, TlCl and $TlCl_3$.

   c. It is the non-metal, tellurium (Te), which forms chlorides, $TeCl_2$, $TeCl_4$ and $TeCl_6$.

   d. It is the non-metal, thallium (Tl), which forms the chlorides, TlCl and $TlCl_3$.

   e. No such configuration is possible.

   Hint: The configuration of the neutral atom must be ……$6p^1$.

10. In general, on going left to right across a period:

    a. The effective nuclear charge of the atom decreases and its electronegativity decreases.

    b. The effective nuclear charge of the atom decreases and its electronegativity increases.

    c. The effective nuclear charge of the atom increases and its electronegativity decreases.

    d. The effective nuclear charge of the atom increases and its electronegativity increases.

    Hint: None – you should know the general trends

11. A third-period element has the following first, second, third and fourth ionization energies: 5.98, 18.83, 28.44, and 119.96 eV, respectively. Which element is this?

    a. Na

    b. Mg

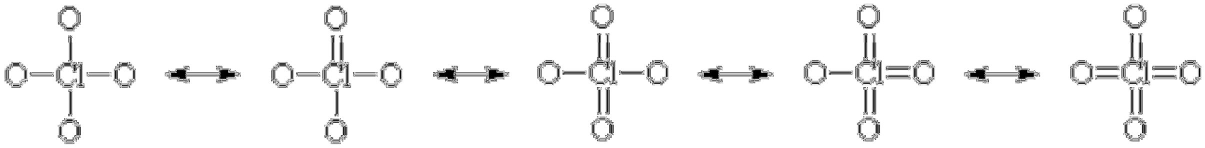
    c. Al

    d. Si

    e. P

    Hint: After how many ionization steps does it suddenly become much harder to remove an electron?

12. Five partial (electrons and partial charges not shown), non-equivalent “resonance” structures of ClO_4^- are shown below. Which one has an average Cl-O bond order of 1.5 and a formal charge on chlorine of 1+?



a. b. c. d. e.

Hint: None. You need to be able to figure out both these properties.

13. Referring to the structures in question 12, where would the *observed* structure of ClO_4^- probably lie in order to comply with Pauling’s principle of electroneutrality?

a. Between a. and b.

b. Between b. and c.

c. Between c. and d.

d. Between d. and e.

Hint: Look for minimum charge separation and charges appropriately placed with respect to electronegativity.

14. The hybridization of the atomic orbitals of the central atom in the square-pyramidal basic electron pair geometry, which is unusual for main group elements, is:

a. sp^2

b. $sp^2d(x^2\text{-}y^2)$

c. $sp^3d(z^2)$

d. $sp^3d(x^2\text{-}y^2)$

e. sp^3d^2

Hint: This is a 5-coordinate geometry, so it uses five atomic orbitals.

15. When building the molecular orbital diagram of diatomic molecules from the second period (Li_2 to F_2, z being the direction of the internuclear axis):

a. Only the 2s-2s and 2p-2p interactions need to be considered.

b. The $2s\text{-}2p_z$ interactions becomes more significant with increasing Z.

c. The $2s\text{-}2p_z$ interactions becomes less significant with increasing Z.

d. The $2p_x\text{-}2p_x$ and $2p_y\text{-}2p_y$ interactions are negligible.

e. The hybridization of the atoms goes from sp^3 in Li_2 to sp^2 in F_2.

Hint: This is about the σ and π molecular orbital energy levels crossing over between N_2 and O_2.

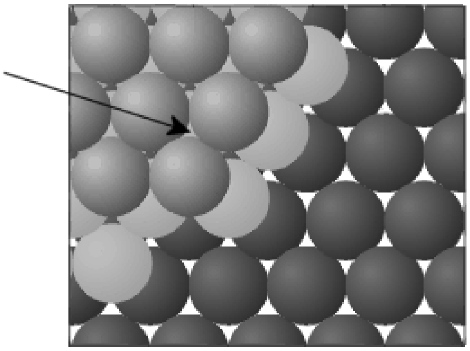
16. The diagram to the right shows a mode of close-packing of spheres. Which statement is true?

a. The arrow points to an octahedral hole in a hexagonal close-packed structure.

b. The arrow points to a tetrahedral hole in a hexagonal close-packed structure.

c. The arrow points to an octahedral hole in a cubic close-packed (face-centred cubic) structure.

d. The arrow points to a tetrahedral hole in a cubic close-packed (face-centred cubic) structure.



Hint: You need to see if the medium grey layer lies directly over the dark grey layer to recognize the type of close-packing, and (independently) what is directly below the tip of the arrow head.

17. Consider the diagram in question 16. If the spheres are the anions, and *all* the tetrahedral holes contain cations, which empirical formula is most likely to have this structure?

a. BaF_2

b. LiI

c. Si_3N_4

d. Na_2S

e. $ScBr_3$

Hint: You need to know the ratio of tetrahedral holes to spheres in a close-packed structure. The required cation to anion ratio is the same.

18. It is possible to calculate lattice energies using the Kapustinskii equation: $\Delta H^o_{latt} = \frac{nZ_aZ_b}{d_o}\left(1 - \frac{d}{d_o}\right)K$ with $K = 1.21 \times 10^5$ kJ pm mol^{-1} and $d = 34.5$ pm. Based on the various influencing factors, which is the correct order of lattice energy, that is from least (on the left) to greatest (on the right) stability?

a. MgO < NaCl < AlN

b. AlN < NaCl < MgO

c. AlN < MgO < NaCl

d. NaCl < MgO < AlN

e. The lattice energies are about the same because the compounds all have a 1:1 stoichiometry.

Hint: Only n, Z_a, Z_b, and d_o could vary, but you need to know what they represent to assign relative values to them (qualitatively in the case of d_o).

19. The lanthanide contraction refers to:

a. The tendency of the lanthanides to have fewer oxidation states than the following transition elements.

b. The tendency of the second and third transition elements of a same group to have similar sizes.

c. The decrease in unit-cell dimensions when a lanthanide replaces the cation in a ionic structure.

d. The short lanthanide-ligand bonds when engaged in complexes.

e. The tendency of the lanthanides to shield electron density efficiently.

Hint: None – you need to know this, and the reason for it.

20. Linkage isomerism is observed between two metal complexes when:

a. The complexes are labile and isomerism occurs via breaking/re-forming the metal-ligand bonds.

b. The complexes have the same formula in the solid state (including counter-ions) but differ in the formula of the inner-sphere complex (first coordination sphere).

c. The complexes have the same ligands but different geometries; for example, one is square-pyramidal and the other is trigonal-bipyramidal.

d. A bidentate ligand occupies *cis* positions in one case and *trans* positions in the other.

e. An ambidentate ligand binds to the metal ion through a different atom in each case.

Hint: None – you need to know the definition of linkage isomerism.

21. To which complex does the term "weak field/high-spin" apply?

a. $[V(H_2O)_6]^{2+}$

b. $[Mn(H_2O)_6]^{2+}$

c. $[Fe(CN)_6]^{4-}$

d. $[Ni(H_2O)_6]^{2+}$

e. $[ZnCl_4]^{2-}$

Hint: You need to know the trends in ligand field splitting with differently charged metal ions, and the different ligands (the spectrochemical series).

22. Crystal-field theory is based on:
   a. The Coulombic attraction between the charge of the metal and the lone pairs of the ligands.
   b. The Coulombic attraction between an electron in a metal d-orbital and the lone pairs of the ligands.
   c. The Coulombic interaction between an electron in a metal d-orbital and the ligands seen as negative point-charges.
   d. The overlap between the d orbitals, all five of different shapes, and the orbitals of the ligands (those containing the lone pair).
   e. The fact that ligands are always positioned along the lobes of the d-orbitals.

   Hint: Check the distinction between crystal field theory and ligand field theory.

The following 11 questions require more complete answers, including explanations. If you need more space, there is a blank page at the end of this paper.

23. (6 marks) Shielding of electrons. (Cannot be checked by the answer checker.)
   a. (2 marks) Briefly describe the underlying principles of Slater's shielding theory. Do *not* give quantitative rules.

      Hint: This question is only asking for general principles: the definition of effective nuclear charge in terms of the shielding effect of certain electrons (which?) on the one under consideration. The answer could include the ordering of orbitals which is used, but no more detail than that.

   b. (2 marks) Using arguments related to the shielding of electrons, explain in detail why the first ionization energy of Be is higher than that of B.

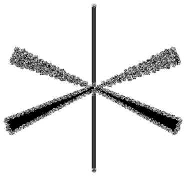
      Hint: Using Slater's rules, $Z_{eff}(Be) = 1.95$ and $Z_{eff}(B) = 2.60$ *: NOT the correct order to explain the IP order. So what does the Slater rules not take account of?

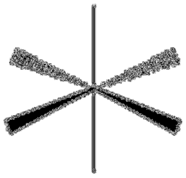
   c. (2 marks) Using arguments related to the shielding of electrons, explain in detail why the first ionization energy of S is lower than that of O.

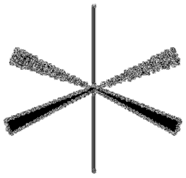
      Hint: Using Slater's rules, $Z_{eff}(O) = 4.55$ and $Z_{eff}(S) = 5.45$ *: NOT the correct order to explain the IP order. So what does the Slater rules not take account of?

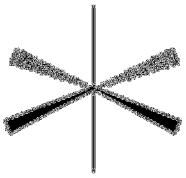
      * Your answer should include the calculations.

24. (5 marks) Draw all possible isomers of the 6-coordinated $[\mathrm{Cr(en)_2Br_2}]^+$ complex where en is ethylenediamine: $\mathrm{H_2N{-}CH_2CH_2{-}NH_2}$. Below each sketch, give descriptive words or symbols for isomerism. Clearly indicate pairs of enantiomers. Not all frameworks may be necessary. (Cannot be checked by the answer checker.)





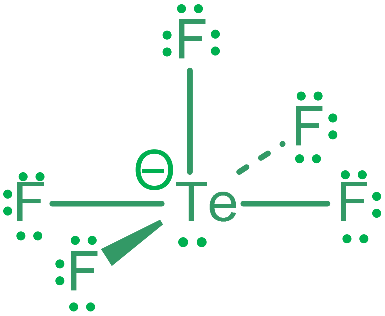




Hint: You will only need 3 of the frameworks. Do not forget to describe each isomer as *cis* or *trans*, and if appropriate, Δ or Λ.

25. (9 marks) For the following species, sketch a Lewis structure, give the “electron pair” (basic) geometry, the associated hybridization of the central atom, and the observed geometry. In each case, show how the bond angles would differ from the ideal angles for the basic shape ("distortions").

a. (3 marks) TeF_5^- Hint: This one is done for you.



Basic geometry: Octahedral ____________

Hybridization: sp^3d^2 ______________

Molecular (observed) geometry: Square-pyramidal _____

Distortions: Te is below the pyramid base due to the lone pair.

b. (3 marks) SF_4

Basic geometry: (25bi)________________

Hybridization: (25bii) _______________

Molecular (observed) geometry: (25biii) ______________

Distortions:

c. (3 marks) XeO_3

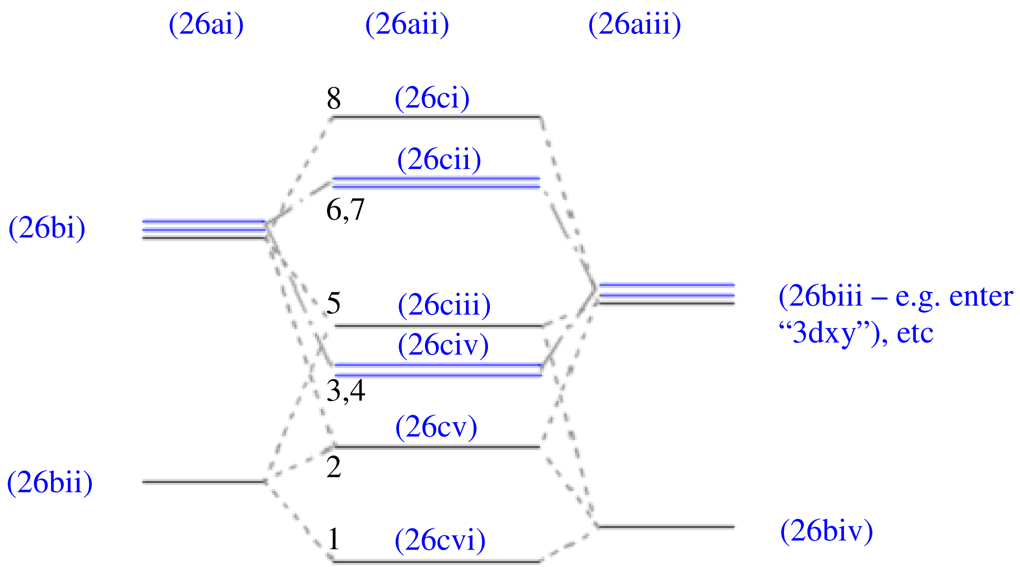
Basic geometry: (25ci)________________

Hybridization: (25cii) _______________

Molecular (observed) geometry: (25ciii)_______________

Distortions:

26. (7 marks) An energy-level diagram of the molecular orbitals for a heteronuclear diatomic molecule or ion appears below. The molecular orbitals (centre) are made by interaction between two fragments (left and right). (1 mark each)



For the molecule-ion CN^-:

a. At the top of the diagram, label which energy levels belong to C and N^- and CN^-.

b. Label the fragment levels with the names of the atomic orbitals.

c. Label the molecular levels σ, σ^*, π or π^*, as appropriate. (enter “sigma” or “sigma*”, etc)

d. Mark in the electrons on the fragment and molecular levels. (not checkable)

e. From this diagram, determine the carbon-nitrogen bond order in CN^- (26e). Explain.

Hint: None – this is similar to CO in the notes.

NB. Make sure you obey Hund’s rule when you place the electrons in part d., especially on the C and N^- atoms.

f. If we were to represent the molecular diagram for the molecule CO on the *same energy scale* as above, how would the energy of the fragment levels change? (Not checkable)

Hint: The C levels would be in the same place, but what would happen to the O levels?

g. Does the carbon character of orbital 8 increase or decrease when going from CN^- to CO? Explain. *Note*: molecular orbitals are expressed as linear combinations of atomic orbitals; the carbon character is the coefficient of carbon-based atomic orbitals in this combination.

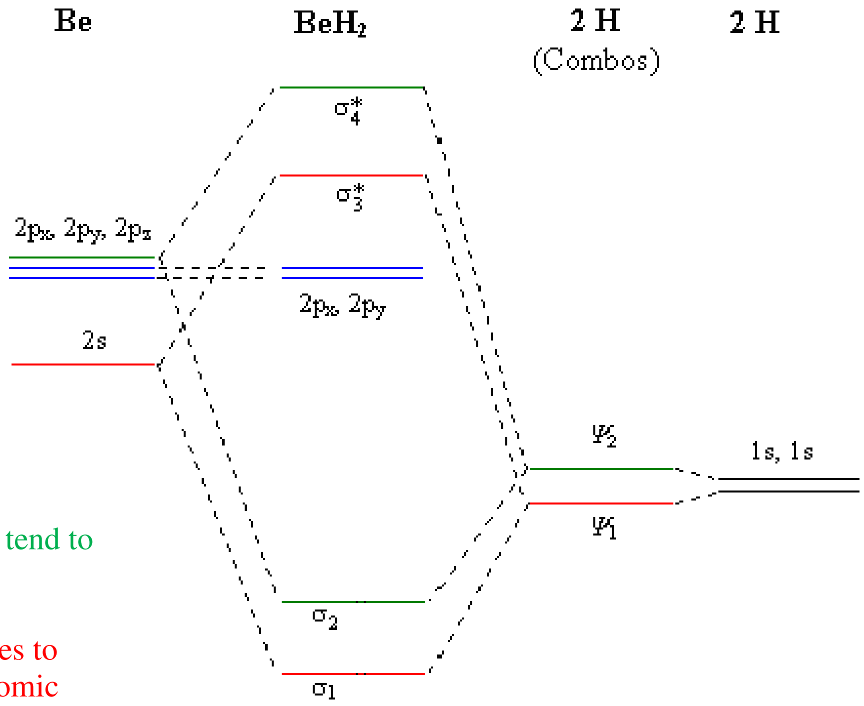
(26g – enter “increase” or “decrease”)

Hint: Orbital 8 has more C 2p character than either N^- or O, but you answer here depends on f.

27. (3 marks) A molecular orbital energy-level diagram for BeH_2 appears below. Also shown are computer-generated molecular orbitals corresponding to the six levels shown for BeH_2. Assume the z axis is defined by the line of atoms, HBeH, and the x axis is vertical on the page (as shown).

   a. (2 marks) Identify the pictures of the orbitals with the corresponding *molecular* energy levels of BeH_2 by labeling them σ_1, σ_2, $2p_x$,… etc.

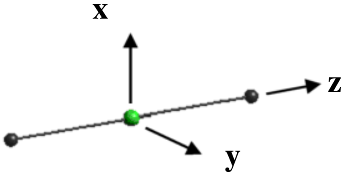
   b. (1 mark) Mark in the valence electrons appropriately on the *molecular* energy levels.

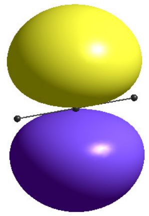


Hint: Orbitals with more nodes tend to be higher in energy.

NB. The aufbau principle applies to molecular orbitals as well as atomic orbitals – don't leave gaps!

27ai to 27avi – enter, e.g., sigma4*





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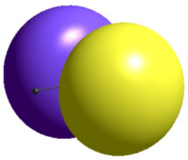
(27ai)



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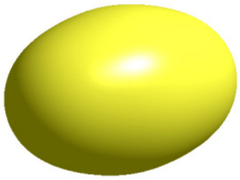

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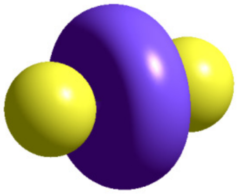

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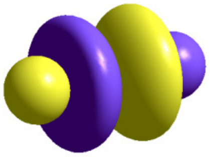
(27aiv)



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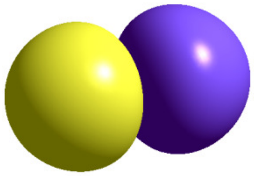
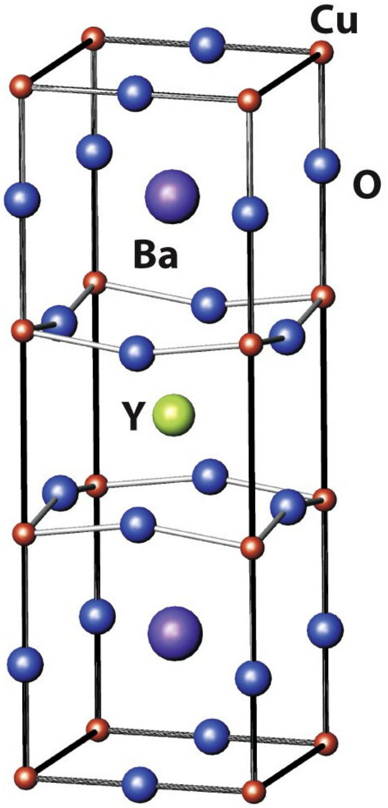
(27av)



Label:
(27avi)

28. (4 marks) The unit cell depicted here is that of a high-temperature superconductor: $YBa_xCu_yO_z$. All the balls representing a particular ion (as labelled) are the same size.



   a. (1 mark) How many O atoms are closest neighbours to a Cu atom sitting at a unit-cell corner? (28a)

   Hint: You need to visualize the adjacent cells around one of the corner Cu's.

   b. (1 mark) How many O atoms are closest neighbours to a Cu atom sitting on a unit-cell edge? (28b)

   Hint: See above.

   c. (2 marks) What is the empirical formula of this material, that is, what are x, y and z? *Do not forget to explain **how** you get your answer.* (28c – enter the formula with your x, y and z values)

   Hint: You have to count the ions or parts of ions in the shown cell, for example, only 1/8 of a corner Cu is in this cell.

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29. (3 marks) The density of crystalline CsCl is 3.99 g/cm^3. Calculate the Cs···Cl distance in this structure. *Data*: atomic weights: Cs = 132.91 g/mol, Cl = 35.45 g/mol; $N_A = 6.022 \times 10^{23}$ mol^{-1}.

   (29 – to check the answer, convert it to Å units 1 Å = 10^{-8} cm.)

   Hint: Draw the unit cell – you should know the structure. Calculate the cell volume from the density. Calculate the cell edge, a (= the $Cl^- – Cl^-$ distance). Calculate the $Cs^+ – Cl^-$ distance = a√3)/2.

30. (4 marks) Consider the following thermodynamic data:

Process	**ΔH° (kJ/mol)**	**Process**	**ΔH° (kJ/mol)**
$Ca^0(g) \rightarrow Ca^+(g)$	+590	$F(g) + e^-(g) \rightarrow F^-(g)$	-328
$Ca^+(g) \rightarrow Ca^{2+}(g)$	+1145	$Ca^+(g) + F^-(g) \rightarrow CaF(s)$	-795 (estimated)
$Ca^0(s) \rightarrow Ca^0(g)$	+178	$Ca^{2+}(g) + 2F^-(g) \rightarrow CaF_2(s)$	-2963 (estimated)
$F_2(g) \rightarrow 2F(g)$	+158		

a. (2 marks) Sketch a labelled Born-Haber cycle for the formation of crystalline CaF from the elements calcium metal and fluorine gas. (not checkable)

NB. This question is asking about the hypothetical CaF, NOT the real CaF_2.

Hint: You should know how to draw the cycle.

b. (1 mark) Calculate the heat of formation ($\Delta H_f°$) of CaF. (30b)

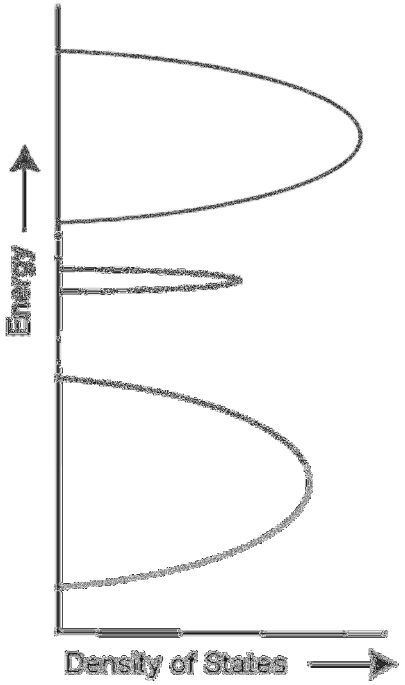
Hint: Make sure this corresponds to part a for CaF, and do the calculation for CaF_2 also: you'll need the numbers for part c.

c. (1 mark) Briefly, what is the main reason why CaF cannot be made experimentally? (Not checkable)

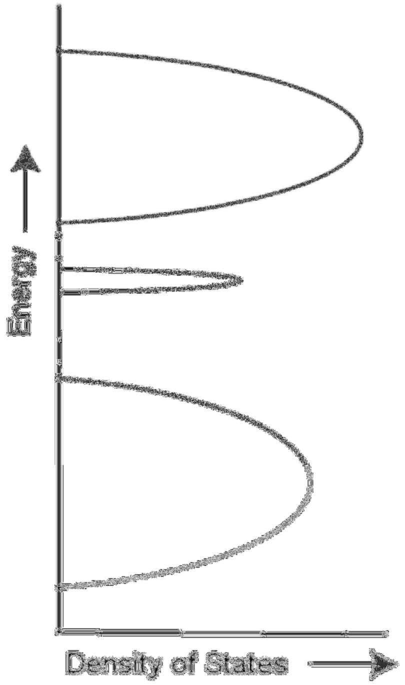
Hint: Focus on the big differences.

31. (6 marks) The diagrams below are frameworks to describe the band structure for an extrinsic n-type semiconductor.

At 0 K:



At 298 K:



a. (1 mark) If the semiconductor is made of doped germanium, which might the dopant be: arsenic or gallium? Explain briefly. (31a)

Hint: You are told it is n-type.

a. (2 marks) On the left diagram, indicate which band(s) is/are filled with electrons at 0 K. Indicate the position of the band gap. Indicate the Fermi level. ? (Not checkable)

Hint: None – all things you should know. Shade the filled bands.

b. (2 marks) On the right diagram, represent the electronic structure (position of the electrons) at a "normal" temperature (example 298 K). Indicate the Fermi level. ? (Not checkable)

Hint: Empty the highest occupied band a little by moving some the electrons to the lowest unoccupied one of the left-hand diagram. Show this with shading.

c. (1 mark) Briefly explain why this semiconductor is a better conductor than pure germanium. ? (Not checkable)

Hint: This should be about the size of the band gaps.

32. (7 marks) Transition metal complexes.

a. (2 marks each) Sketch an energy level diagram for the d-orbitals for each of the following metal complexes. Show the electron configuration in each case. Explain.

Hint: Figure out the configurations first: remember, square-planar is usually found with d^8.

i. $[V(CO)_6]^-$ (32aia – d^n configuration – enter as "dn") and (32aib – geometry*)

Hint: Yes, the formal oxidation state of the metal can be negative!

* Enter "strong field" or "weak field" if appropriate followed by the name of the geometry, e.g "weak field octahedral" or "square planar".

ii. $[PtCl_4]^{2-}$ (32aiia) and (32aiib)

iii. $[FeBr_4]^-$ (32aiiia) and (32aiiib)

b. (1 mark) Identify which complex(es) in part (a) is/are paramagnetic. (32b – enter "i", "ii" or "iii")

Hint: Make sure you have picked the correct state; high-spin or low-spin for the octahedral complexes, if any.

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33. (3 marks) In solution, the ion $[Co(H_2O)_6]^{2+}$ is pale pink, whereas the ion $[CoCl_4]^{2-}$ is intensely blue. Concisely explain this difference in terms of position and intensity of the absorption band. (Not checkable)

Hint: Your answer must show energy level diagrams for these two complexes and then use them in a comparison to explain BOTH the colours and their intensity.

Use this page for extra space if needed. If material on this page needs to be marked, please indicate so in the appropriate question above or I will not look at this page.

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (97.91)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	**La-Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** 208.98	85 **At** 209.99	86 **Rn** 222.02
87 **Fr** 223	88 **Ra** 226.03	**Ac-Lr**	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)									

57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.35	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (245)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)