

**CH101: General Chemistry I**  
**Mid-Term Examination**  
**Fall Semester 2011**  
**Tuesday 25 October. Time: 09.00-11.30 (2.5 hours)**

1. (a) Calculate the maximum wavelength of electromagnetic radiation that can promote ejection of electrons from the surface of tungsten, if its work function is  $7.29 \times 10^{-19}$  J. (4 points)

(b) During an experiment, the maximum kinetic energy of ejected photoelectrons from the surface of tungsten was found to be 11.4 eV. Determine the de Broglie wavelength of an electron with this energy. (4 points)

[Planck's constant  $h = 6.63 \times 10^{-34}$  J s; velocity of  $c = 3.00 \times 10^8$  m/s; electron mass  $m_e = 9.11 \times 10^{-31}$  kg;  $1\text{eV} = 1.60 \times 10^{-19}$  J]

**(a) From Einstein's equation, Work function,  $W = 7.29 \times 10^{-19}$  J**

$$= h\nu_0 = \frac{hc}{\lambda_0} \quad \text{where } \lambda_0 \text{ is the minimum wavelength}$$

$$\text{Hence, } \lambda_0 = \frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{(7.29 \times 10^{-19} \text{ J})}$$

$$= \underline{2.73 \times 10^{-7} \text{ m or } 273 \text{ nm}}$$

**(4 points)**

**(b)**

$$\lambda = \frac{h}{m_e v} = \frac{h}{\sqrt{2m_e KE}} \quad \text{KE is kinetic energy}$$

$$= \frac{(6.63 \times 10^{-34} \text{ Js})}{\sqrt{2 (9.11 \times 10^{-31} \text{ kg})(11.4 \text{ eV} \times 1.60 \times 10^{-19} \text{ J/eV})}}$$

$$= \underline{3.64 \times 10^{-10} \text{ m or } 3.64 \text{ \AA} \text{ or } 0.364 \text{ nm}}$$

**(4 points)**

2. In the Humphreys series of lines in the emission spectrum of atomic hydrogen, the electronic transitions are at the  $n = 6$  level. What is the energy in eV of a photon that results from the longest wavelength transition in this series? (4 points)

[The Rydberg constant is  $2.18 \times 10^{-18}$  J;  $1\text{eV} = 1.602 \times 10^{-19}$  J]

For H (Z = 1)

$$E_n = -\text{constant} \left( \frac{1}{n^2} \right)$$

The constant is the Rydberg constant,  $2.18 \times 10^{-18}$  J or 13.6 eV

For the transition,  $n_7 \rightarrow n_6$  (emission)

$$\Delta E = 13.6 \left( \frac{1}{36} - \frac{1}{49} \right) \text{ eV} = \text{energy of photon}$$

$$= \underline{0.11 \text{ eV}}$$

(4 points)

3. Determine the excited electronic state of  $\text{Li}^{2+}$  that has the same energy as the first excited state of hydrogen. (6 points)

For H, Z = 1 and for  $\text{Li}^{2+}$ , Z = 3.

The energy of electronic levels is given in rydbergs by

$$E_n = -\frac{Z^2}{n^2}$$

For the first excited state of H, n = 2.

Hence

$$\left( -\frac{Z}{n_2^2} \right)_H = \left( -\frac{Z}{n_7^2} \right)_{\text{Li}^{2+}}$$

or

$$-\frac{1}{4} = -\frac{9}{n_7^2}$$

$$n_7^2 = 36$$

(6 points)

**n = 6 ( $\equiv$  5<sup>th</sup> excited state)**

4. (a) The energy of a particle, such as an electron, confined to a one-dimensional box of length L, such that its potential energy is 0 for  $x = 0$ -L and  $\infty$  for all other values of x, is given by

$$E_n = \frac{h^2}{8m_e} \frac{n^2}{L^2}$$

Calculate the energy difference in kJ/mol between the ground state and first excited state for an electron,

(i) in a 1.0 Å box, and

(ii) in a 10 cm box (total 6 points for (i) and (ii)).

(iii) Comment on the result. (4 points)

[Electron mass  $m_e = 9.110 \times 10^{-31}$  kg; Planck's constant  $h = 6.626 \times 10^{-34}$  Js; Avogadro's number is  $6.022 \times 10^{23}$  /mol;  $1 \text{ Å} = 10^{-10}$  m]

(b) Write an equation for the energy of an electron confined to a 3-dimensional box under the conditions described above,

(i) when the box is a cube ( $L_1 = L_2 = L_3$ ), and

(ii) when the box is non-cubic, where  $L_1 \neq L_2 \neq L_3$ . (total 2 points for (i) and (ii))

(iii) Describe how many energy levels exist for the first excited state of cases (i) and (ii) above and state whether these are degenerate. (2 points)

4(a)(ii)  $L=10^{-1}\text{m} \therefore L^2=10^{-2}\text{m}^2$   $1.1 \times 10^{-14}\text{kJ/mol}$

(a)

$$(i) E_2 - E_1 = \frac{3h^2}{8m_e L^2} = \frac{3(6.626 \times 10^{-34}\text{ Js})^2}{8(9.11 \times 10^{-31}\text{ kg})(1.0 \times 10^{-10}\text{ m})^2} = 1.8 \times 10^{-17}\text{ J}$$

$$= \frac{(1.8 \times 10^{-17}\text{ J}) \times (6.022 \times 10^{23}\text{ /mol})}{10^3\text{ (J/kJ)}} = \underline{11,000\text{ kJ/mol}}$$

(ii) Same calculation as above, but  $L^2 = 10^{-4}$ , not  $10^{-20}\text{m}^2$ , so  $E_2 - E_1 = 1.8 \times 10^{-33}\text{ J}$   
 $= \underline{1.1 \times 10^{-12}\text{ kJ/mol}}$  (6 points for (i) and (ii) combined)

(iii) In (i) the electron is confined in a box of atomic dimensions and therefore quantization of energy levels is clear, whereas in (ii), the electron is confined in a very much larger box, is almost classical in its behavior and the energy levels are almost continuous.

(4 points)

(b)

$$(i) E_{n_1 n_2 n_3} = \frac{h^2}{8m_e L^2} (n_1^2 + n_2^2 + n_3^2)$$

$$(ii) E_{n_1 n_2 n_3} = \frac{h^2}{8m_e} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right)$$
 (2 points for (i) and (ii) combined)

(iii) In both cases, there are 3 energy levels, for case (i) they are degenerate, but for case (ii) they are of different energies (non-degenerate).

(2 points)

5. (a) The wave function for one quantum state (orbital) of the hydrogen atom is

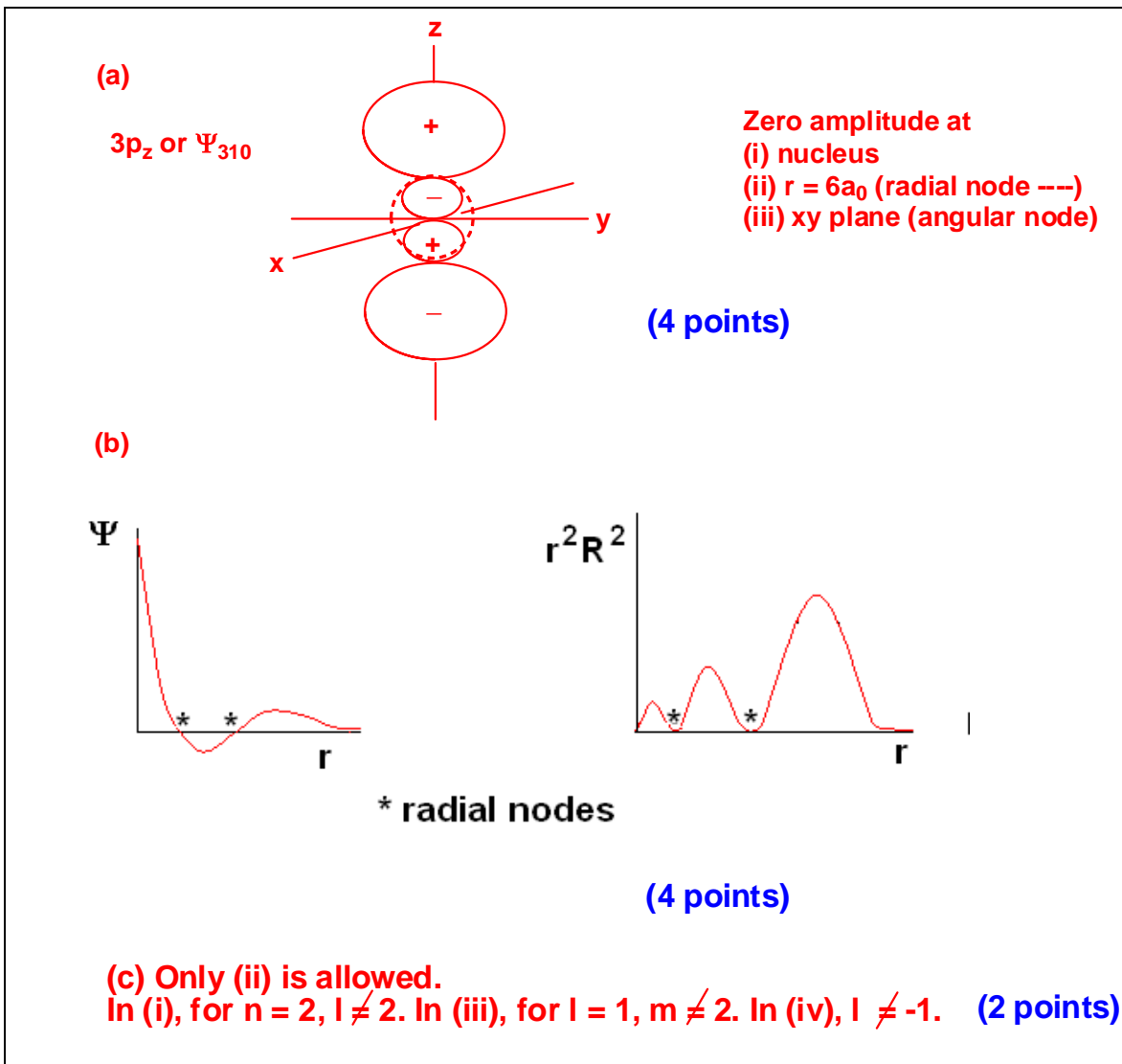
$$\Psi = \frac{\sqrt{2}}{81\sqrt{\pi}} a_0^{-3/2} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos\theta$$

Identify the orbital, sketch its boundary surface, and indicate any regions of space where the amplitude (value of  $\Psi$ ) is zero. (4 points)

(b) Sketch (not to scale) a wave function *versus* distance ( $\psi$  vs.  $r$ ) plot, and a radial probability distribution plot *versus* distance ( $r^2 R^2$  vs.  $r$ ) for the 3s orbital. (4 points)

(c) Determine which of the following combinations of quantum numbers are allowed for an electron in a one-electron atom. (2 points)

- (i)  $n = 2, l = 2, m = 1$
- (ii)  $n = 3, l = 1, m = 0$
- (iii)  $n = 5, l = 1, m = 2$
- (iv)  $n = 4, l = -1, m = 0$



6. The cesium atom has one of the lowest ionization energies of all neutral atoms in the periodic table (375.5 kJ/mol). Calculate the longest wavelength of light that could ionize a cesium atom (in the gas phase) and state the region of the electromagnetic spectrum to which this light belongs. (6 points)

[Planck's constant  $h = 6.626 \times 10^{-34}$  Js; Avogadro's number is  $6.022 \times 10^{23}$  /mol; velocity of light  $c = 2.998 \times 10^8$  m/s]

$$IE = 375.7 \text{ kJ/mol} = \frac{375700 \text{ (J)}}{6.022 \times 10^{23} \text{ (/mol)}} \quad \text{J}$$

$$IE = h\nu = hc/\lambda$$

$$\text{Hence } \lambda = \frac{6.626 \times 10^{-34} \text{ (Js)} \times 2.998 \times 10^8 \text{ (m/s)} \times 6.022 \times 10^{23} \text{ (/mol)}}{375700 \text{ (J/mol)}}$$

$$= \underline{3.184 \times 10^{-7} \text{ m or } 318.4 \text{ nm}}$$

This is in the near ultraviolet region of the electromagnetic spectrum (close to the low wavelength-violet-visible region). (6 points)

7. Determine which of the following beams of atoms or ions would be deflected when passed through an inhomogeneous magnetic field (as in Stern and Gerlach's experiments). Write Y or N against the species symbol, in the box. (4 points)

(i) B (ii) Al<sup>3+</sup> (iii) Cl<sup>-</sup> (iv) Ag

(i) B **Y**  
 (ii) Al<sup>3+</sup> **N**  
 (iii) Cl<sup>-</sup> **N**  
 (iv) Ag **Y**

**(4 x 1 point)**

8. Metal hydrides, like Rb<sup>+</sup>H<sup>-</sup>, can be analyzed with the ionic bonding model. Find the distance  $r_x$ , where the Coulomb attraction equals the energy required to form an ion pair. (8 points) [Electron affinity of H = 0.75 eV; ionization energy of Rb = 4.18 eV]

**Use the "engineering formula" version of the Coulombic equation, that is**

$$PE = \frac{14.4 (\text{eV}\text{\AA})e^2}{r(\text{\AA})}, \text{ where } e \text{ is in units of electronic charge (here } \pm 1)$$

**The PE at the distance  $x$ , where electron transfer takes place, should be the same as the difference between the IE of Rb and the EA of H:**

$$\frac{14.4 (\text{eV}\text{\AA})}{r_x (\text{\AA})} = IE(\text{Rb}) - EA(\text{H}) = 4.18 - 0.75 \text{ eV, from which } r_x = \underline{4.20 \text{ \AA}}$$

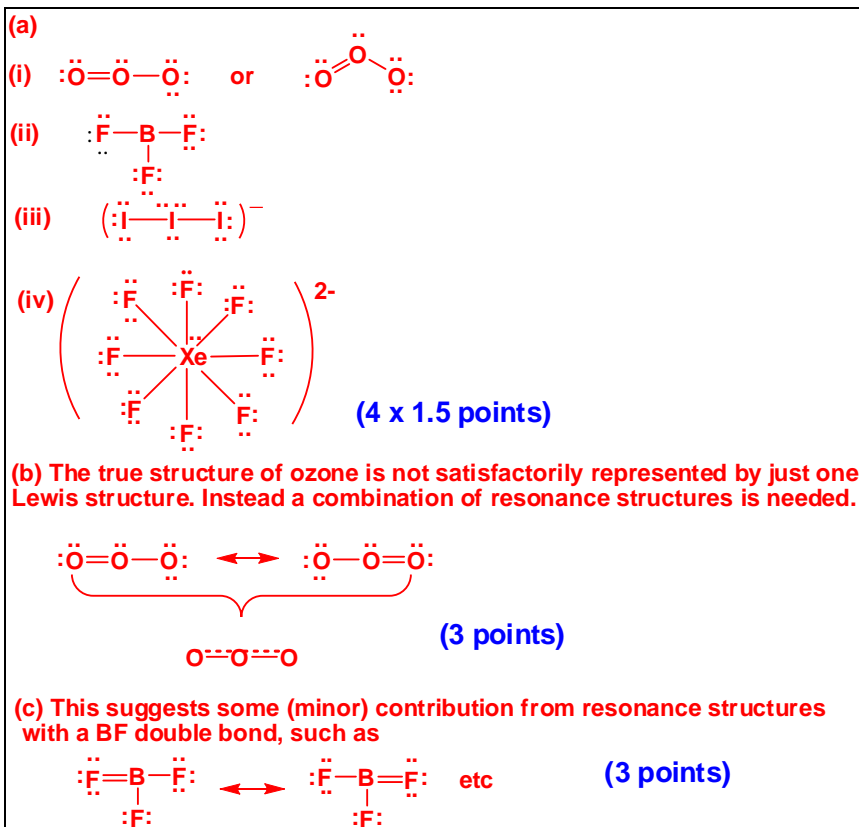
**(4 points for 'engineering formula' + 4 points for its application)**

9. (a) Draw one Lewis structure for each of the following, showing all valence electron pairs.

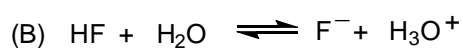
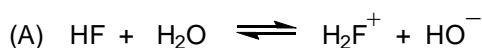
(i) Ozone (O<sub>3</sub>) (ii) Boron trifluoride (BF<sub>3</sub>) (iii) Triiodide ion (I<sub>3</sub><sup>-</sup>) (iv) Xenon octafluoride dianion (XeF<sub>8</sub><sup>2-</sup>). (6 points)

(b) Explain why the observed structure of ozone has O-O bonds that are both identical and intermediate in length between O-O and O=O. (3 points)

(c) Explain why the B-F bonds in BF<sub>3</sub> are rather shorter than expected. (3 points)

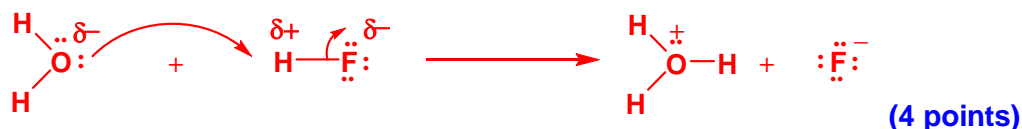


10. With regard to the nonmetal hydrides, consider the reactivity of hydrogen fluoride (HF). Two possible ways that HF may react with water can be postulated as follows (A or B):



Explain which one of the reactions, (A) or (B) is more likely and write a reasonable mechanism for that reaction. (6 points)

**(B) is more likely because the higher electronegativity of F over O (O donates electron pair more easily) and the greater polarity of the H-F bond over the O-H bonds (H-F bond breaks more easily). (2 points)**

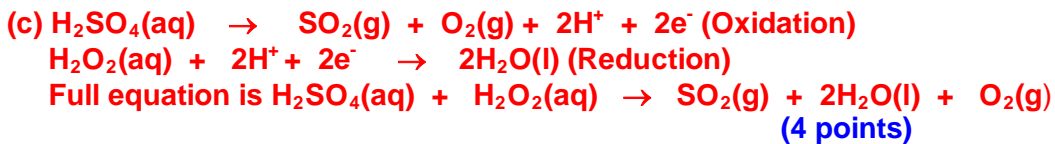
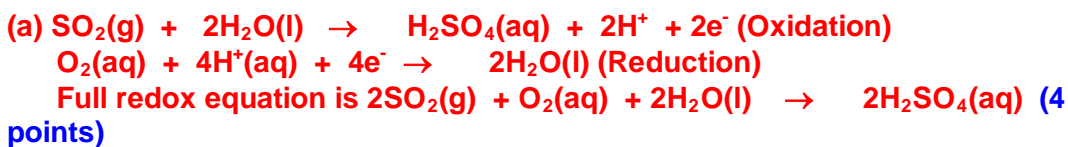


11. (a) Sulfuric acid is produced when  $\text{SO}_2(\text{g})$  dissolves in water droplets and reacts with dissolved oxygen ( $\text{O}_2(\text{aq})$ ) to give  $\text{H}_2\text{SO}_4(\text{aq})$ , which contributes to "acid rain". Write the oxidation and reduction half equations and the full redox equation for this reaction. (4 points)

(b) When potassium nitrite ( $\text{KNO}_2(\text{s})$ ) is dissolved in water, the solution contains only  $\text{K}^+(\text{aq})$ ,  $\text{NO}_2^-(\text{aq})$  and  $\text{H}_2\text{O}(\text{l})$  initially, but it soon becomes slightly alkaline (basic). Write a fully balanced ionic equation that is in accord with this observation. (4 points)

(c) Aqueous mixtures of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  are explosive.

Use the half equation method to determine the full, balanced equation for this reaction, which includes  $\text{SO}_2(\text{g})$  and  $\text{O}_2(\text{g})$  as reaction products. (4 points)



12. (a) Determine the oxidation number of **N** in

(i)  $\text{NH}_2^-$  (ii)  $\text{N}_2\text{H}_4$  (iii)  $\text{NH}_2\text{OH}$  (iv)  $\text{NO}^+$  (v) (4 points)

(b) Write the oxidation and reduction half equations and the full redox equation for the reaction of ammonia with dioxygen to give nitric oxide (NO) (all gaseous) and water (liquid). (6 points)

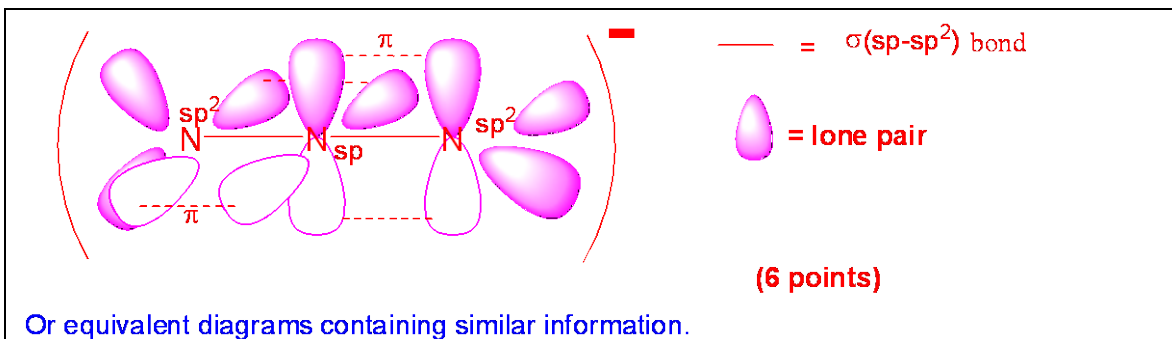
(a) -3 (b) -2 (c) +1 (d) +3 (4 x 1 points)



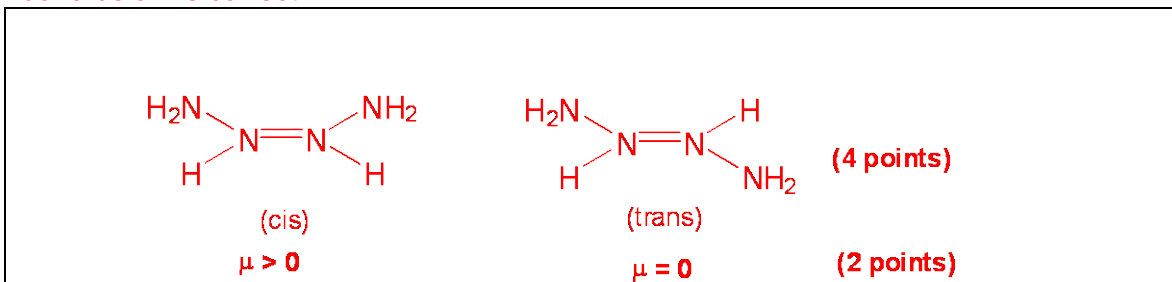
Name.....Student Number.....

**CH101 GENERAL CHEMISTRY I**  
**FINAL EXAMINATION FALL SEMESTER 2011**  
**Tuesday 20 December, 2011: 09.00-11.00 (time allowed: 2 hours)**  
**Attempt all 10 questions, writing your answers in the boxes provided**

1. Sketch a valence bond (VB) model of the azide ion ( $\text{N}_3^-$ ), showing the hybridization on each atom, the  $\sigma$  skeletal structure, lone pair electrons and  $\pi$ -bonding. (6 points)

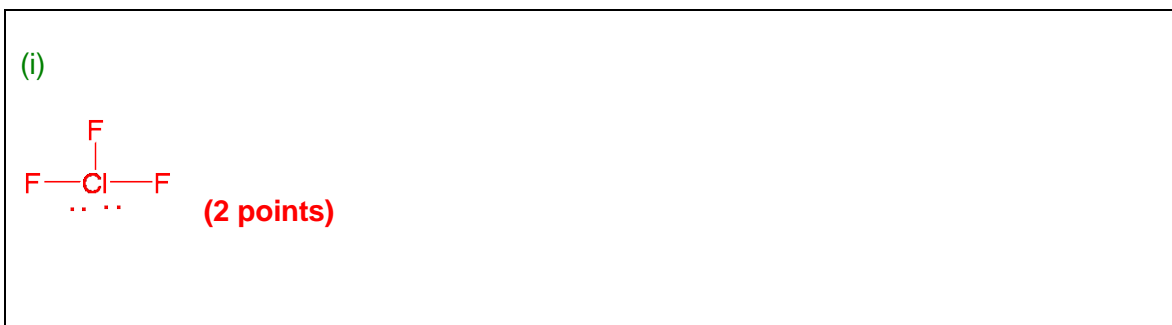


2. Write Lewis structures of the two stereoisomers of tetrazene ( $\text{H}_2\text{N}(\text{NN})\text{NH}_2$ ) (4 points) and predict their molecular dipole moments (that is, whether  $\mu = 0$  or  $\mu > 0$ ) (2 points)  
The structure having lone pair electron at the location of the hydrogen position of N-H bond below is correct.



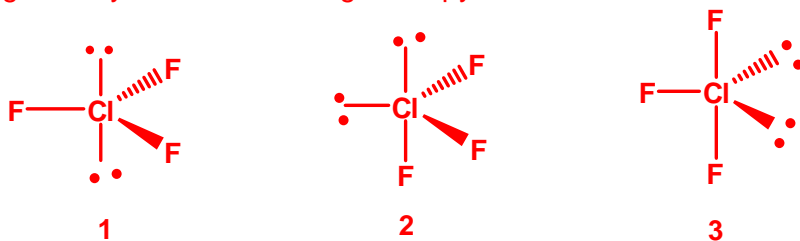
3. Consider the molecule chlorine trifluoride ( $\text{ClF}_3$ ).

- (i) Draw the Lewis diagram of  $\text{ClF}_3$ . (2 points)
- (ii) Draw the three possible structures of  $\text{ClF}_3$ , according to the VSEPR model. (6 points)
- (iii) Select the most stable structure and give reasons for your answer. (4 points)
- (iv) State whether the geometry of the most stable structure is regular or distorted (2 points)
- (v) State whether the most stable structure has a dipole moment (2 points)





(ii) (The Lewis diagram requires 5 electron pairs around the central atom Cl, meaning its geometry is based on a trigonal bipyramid. Hence there are three possible structures.)



(3 x 2 points)

(iii) The most stable structure is the T-shaped geometry (3, as written above) (2 points)

This structure has the lowest number (0) of 90° lone pair-lone pair repulsions, combined with the lowest number of 90° lone pair-bond pair repulsions (4) (2 points)

Structure	1	2	3
90° lone pair-lone pair repulsion:	0	1	0
90° lone pair-bonding pair repulsion:	6	3	4

(iv) Distorted geometry (2 points)

(v) It has a dipole moment (2 points)

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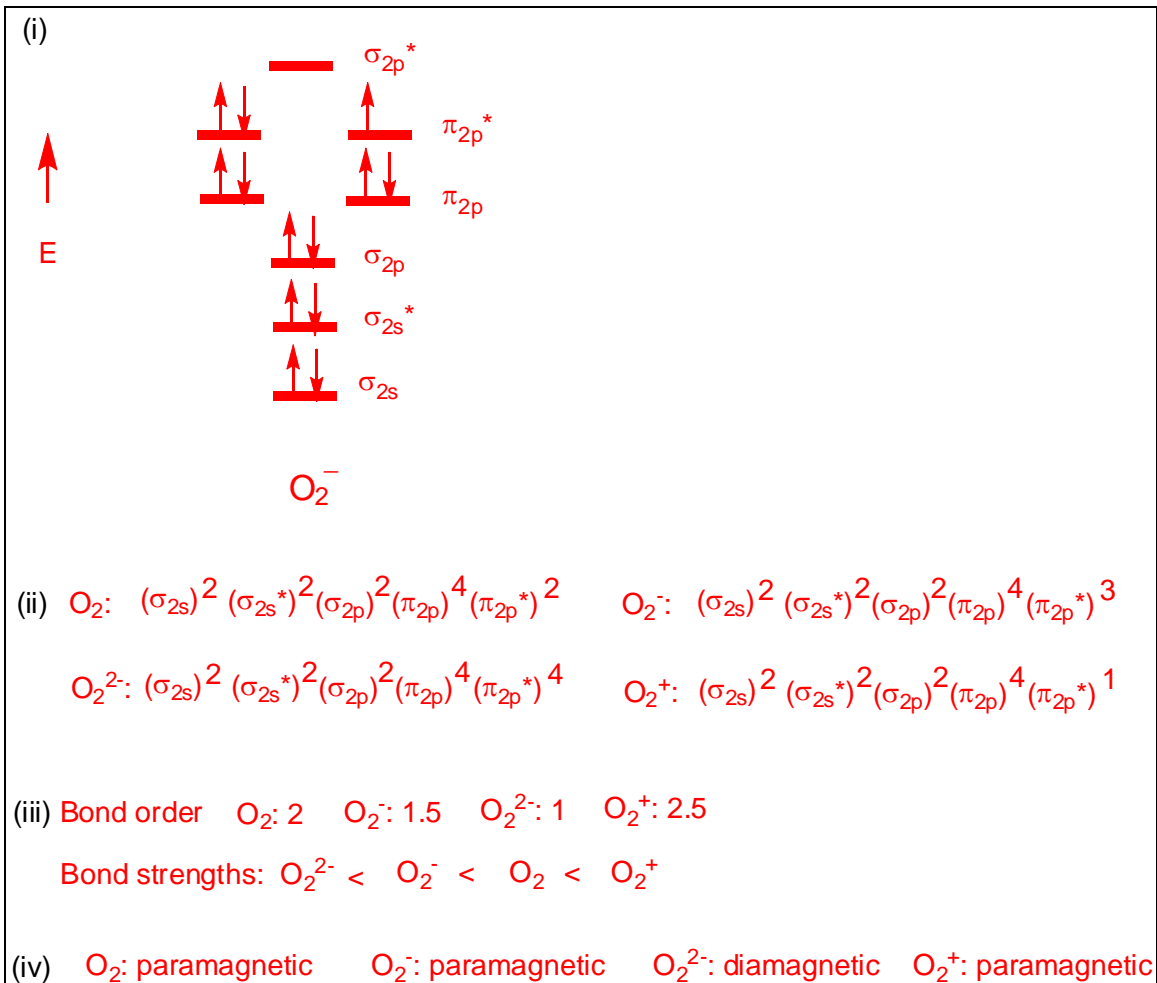
4. Oxygen is able to form the following homonuclear diatomic species: O<sub>2</sub> (dioxygen), O<sub>2</sub><sup>-</sup> (superoxide ion), O<sub>2</sub><sup>2-</sup> (peroxide ion) and O<sub>2</sub><sup>+</sup> (dioxygen cation).

(i) Use the LCAO-MO model to construct an MO energy diagram for O<sub>2</sub><sup>-</sup>. (4 points)

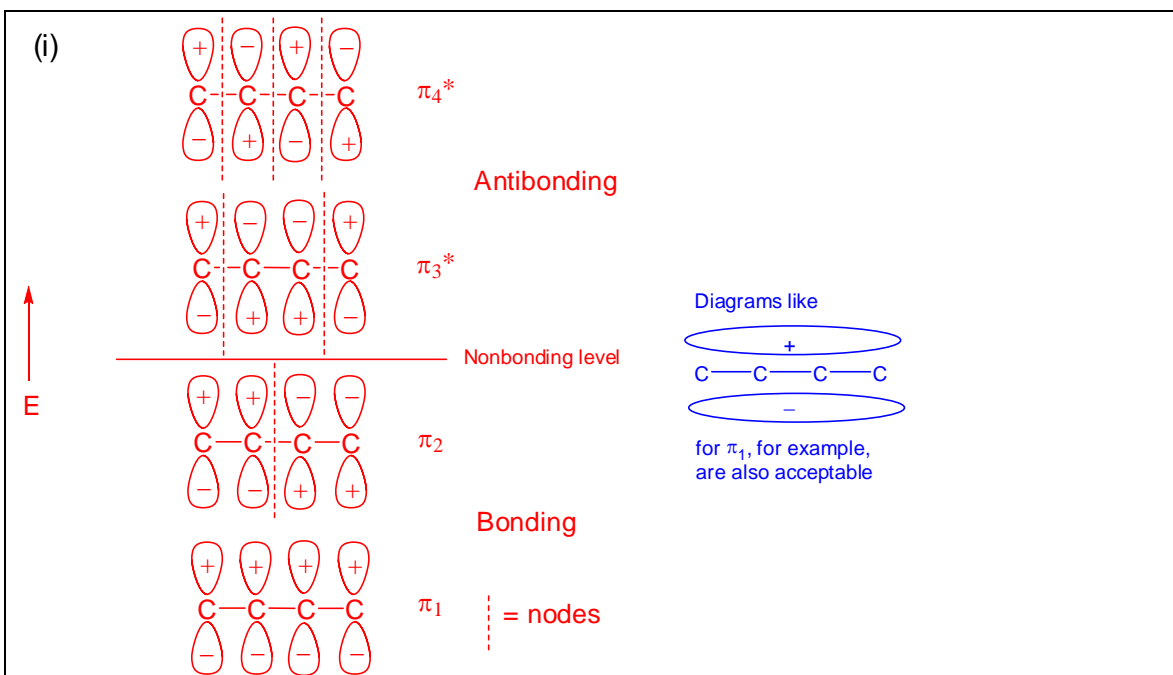
(ii) Write the electron configuration for each of the above species. (4 points)

(iii) Determine the bond order of each of the above species and arrange them in order of bond energy (lowest first). (2 points)

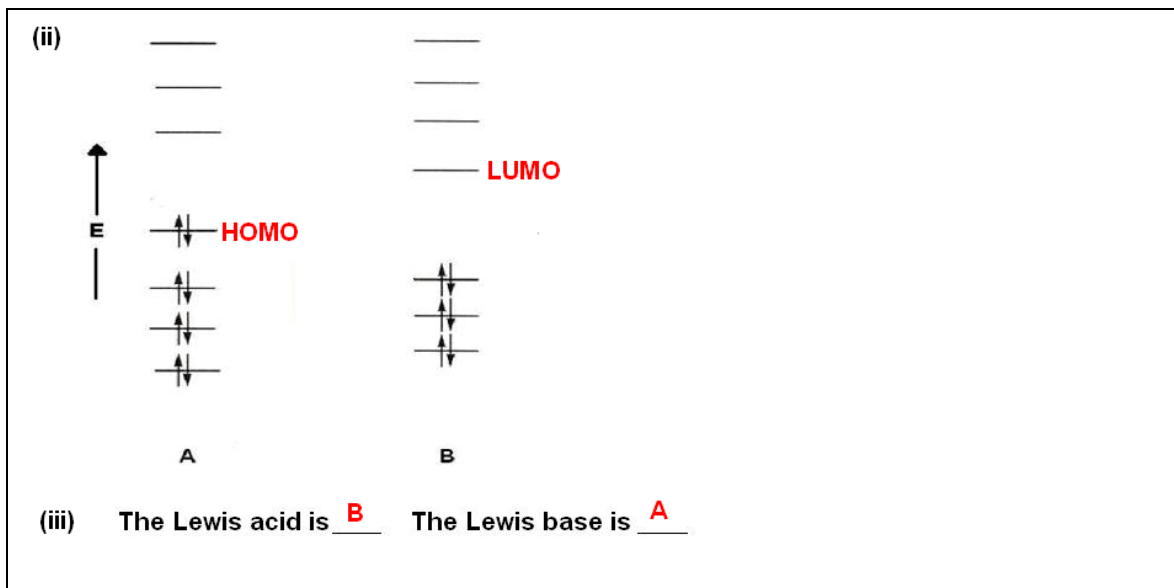
(iv) Predict the magnetic property of each of the species above. (2 points)



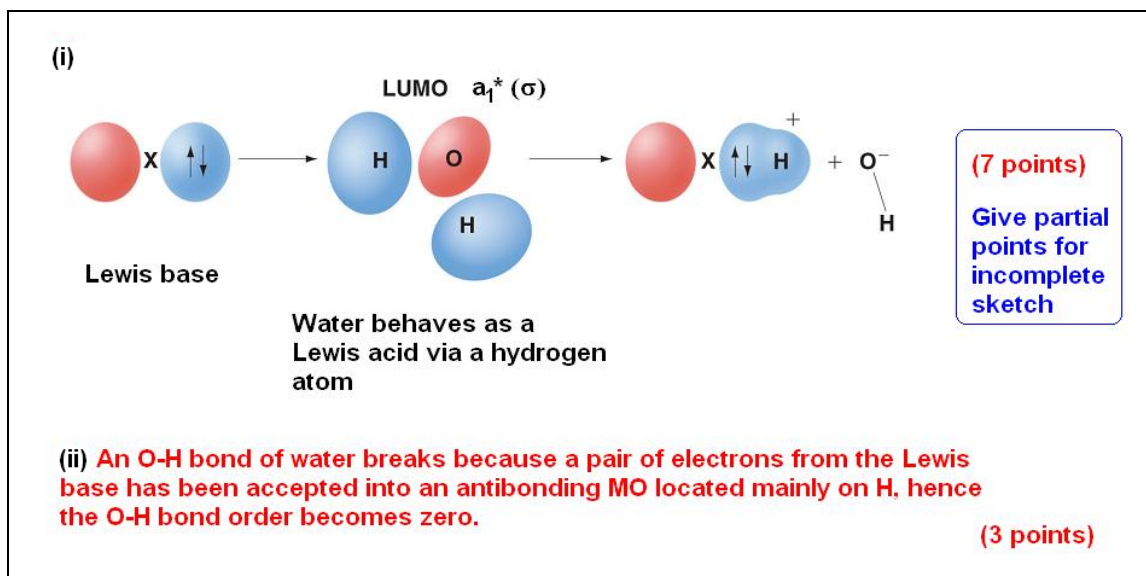
5. (i) Sketch the  $\pi$ -molecular orbitals of the 1,3-butadiene molecule, showing their relative energies and, where appropriate, their nodal planes. Indicate on the sketch the bonding, nonbonding and antibonding energy regions. (6 points)



- (ii) The diagram below indicates the MO energy levels of two molecules, A and B. These molecules react with each other by HOMO-LUMO interaction. Indicate clearly on the diagram the most likely HOMO and LUMO involved in the reaction. (2 points)
- (iii) Which is the Lewis acid and which the Lewis base in this diagram? (2 points)



6. (i) Draw a frontier molecular orbital sketch of a reaction in which water behaves as a Lewis acid. (7 points)
- (ii) Explain briefly why one O-H bond of water must always break during such a reaction (3 points)



7. If the first three lines in the rotational spectrum of  $^1\text{H}^{127}\text{I}$  are 13.18, 26.36, and 39.54  $\text{cm}^{-1}$ , calculate the HI bond length to three significant figures, in Ångströms. (10 points)  
[Planck's constant  $h = 6.626 \times 10^{-34}$  Js; velocity of light  $c = 2.998 \times 10^8$  m/s; Avogadro's number =  $6.022 \times 10^{23}$  amu/g); relative atomic mass of  $^1\text{H} = 1.008$  amu; relative atomic mass of  $^{127}\text{I} = 126.9$  amu]

Allow both "engineering formula" method and "first principle" method (or other method if correct). Partial points can be given.

Engineering formula method

Rotational energy spacing is given by  $\frac{E_{L,j+1}}{hc} = 2Bj$  (B is the rotational constant)

From the data,  $B = 6.59 \text{ cm}^{-1}$

$$\text{Reduced mass } \mu = \frac{(1.008 \text{ amu})(126.9 \text{ amu})}{1.008 \text{ amu} + 126.9 \text{ amu}} = 1.000 \text{ amu}$$

$$r_e(\text{\AA}) = \frac{4.106}{\sqrt{B(\text{cm}^{-1}) \mu(\text{amu})}} \text{ (engineering formula) } = \underline{1.60 \text{\AA}} \quad \text{(10 points)}$$

First Principles method

Rotational energy spacing is given by  $\frac{E_{L,j+1}}{hc} = 2Bj$  (B is the rotational constant)

From the data,  $B = 6.59 \text{ cm}^{-1}$

$$\begin{aligned} \text{Reduced mass } \mu &= \frac{(1.008)(126.9)}{(1.008 + 126.9)} \text{ amu} \left( \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) \\ &= 1.660 \times 10^{-27} \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Since } B &= \frac{h}{8\pi^2 c \mu r_e^2}, \quad r_e = \sqrt{\frac{h}{8\pi^2 c \mu B}} \\ &= \sqrt{\frac{(6.626 \times 10^{-34} \text{ Js})}{8 (3.142)^2 (2.998 \times 10^8 \text{ m/s})(1.660 \times 10^{-27} \text{ kg})(6.59 \times 10^2 \text{ m}^{-1})}} \\ &= \underline{1.60 \times 10^{-10} \text{ m or } 1.60 \text{\AA}} \quad \text{(10 points)} \end{aligned}$$

8. (i) If the force constant for the  $\text{Li}_2$  molecule ( $^7\text{Li}$  isotope) is  $25.5 \text{ N m}^{-1}$  ( $\text{kg s}^{-2}$ ), determine the wavenumber ( $\text{cm}^{-1}$ ) of the line in its vibrational spectrum. (8 points)  
 (ii) State whether you would expect this line to be intense and state briefly the reason for your answer (2 points)

[ $^7\text{Li} = 7.016005 \text{ amu}$ ;  $c = 2.9979 \times 10^8 \text{ m s}^{-1}$ ; Avogadro number =  $6.022 \times 10^{23} \text{ mol}^{-1}$  or  $\text{amu g}^{-1}$ ;  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ ;  $1 \text{\AA} = 10^{-10} \text{ m}$ ]

(i)

$$\Delta E = hc\bar{\nu} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \bar{\nu} \text{ is wavenumber}$$

$$\mu \text{ (reduced mass)} = 3.508003 \text{ amu}$$

$$= (3.508003 \text{ amu}) \left( \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right)$$

$$= 5.8253 \times 10^{-27} \text{ kg}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$= \left( \frac{1}{2 \times 3.142 \times 2.9979 \times 10^8 \text{ m s}^{-1}} \right) \left( \sqrt{\frac{25.5 \text{ kg s}^{-2}}{5.8253 \times 10^{-27} \text{ kg}}} \right)$$

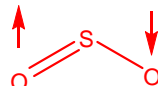
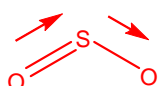
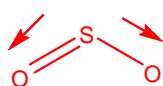
$$= 35100 \text{ m}^{-1}$$

$$= \underline{351 \text{ cm}^{-1}}$$

Allow correct answer using other correct reasoning, such as using  $k(\text{eV}\text{\AA}^{-2}) = 3.667 \times 10^{-6} \mu(\text{amu})[\bar{\nu}(\text{cm}^{-1})]^2$  engineering formula. Can give partial score.

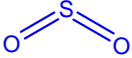
(ii) No, the line will be of low or zero intensity because the vibration of  $\text{Li}_2$  does not involve a change in bond dipole moment.

9. Sketch the vibrations associated with the  $\text{SO}_2$  molecule (6 points) and state which of these vibrations are infrared active (2 points).



(6 points)

They are all IR active (2 points)

Allow other representations of  $\text{SO}_2$  (like ) , as long as they are V-shape.

10. Determine whether the following statements are true or false. Write T or F in the boxes adjacent to the questions. (8 x 1.5 points)

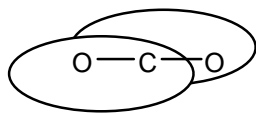
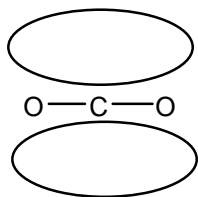
(i) Xenon difluoride is a V-shaped, polar ( $\mu > 0$ ) molecule.

F

(ii) 1,2,3-butatriene is a planar molecule with  $sp$  and  $sp^2$  hybridized carbon atoms.

T

(iii) The diagrams below represent the VB boundary surfaces of the  $\pi$  bonds in  $\text{CO}_2$ .



F

(iv) The ion  $\text{HHe}^-$  has a bond order of zero, according to the LCAO-MO theory and hence should be unstable.

T

(v) Addition of an electron to  $\text{C}_2$  leads to increased stability (higher bond energy), according to the LCAO-MO theory.

T

(vi) A C-D bond (D = deuterium,  $^2\text{H}$ ) will stretch at a higher wavenumber than a corresponding C-H bond.

F

(vii) Iodine ( $\text{I}_2$ ) behaves more like a classical (Newtonian) rotor than  $\text{H}_2$ .

T

(viii) Rotationally,  $\text{CO}_2$  ( $r_e \text{ C=O} = 1.16 \text{ \AA}$ ) behaves like an  $\text{O}_2$  molecule with  $r_e \text{ O-O} = 2.32 \text{ \AA}$ . ( $r_e$  is equilibrium bond distance)

T