uOttawa

Université d'Ottawa | University of Ottawa
Faculté des sciences | Faculty of Science
Département de chimie | Department of Chemistry
Pavillon d'Iorio Hall
10 Marie-Curie Ottawa ON Canada K1N 6N5
☎ 613-562-5728 🖷 613-562-5170 chminfo@uOttawa.ca

MIDTERM 1: CHM 2311 – Introduction to Structure and Bonding

Professor: Jaclyn Brusso

Date: February 13, 2014

Duration: 80 minutes

Name:____

Student Number:______________________________________

Instructions:

- Be sure to print your name and ID number clearly on this test booklet.
- This is a closed book examination.
- Please write legibly and show your work to receive credit for your answers. Partial marks *in some cases* may be awarded for partially correct work.
- For remarking, the exam *must* be written in pen.
- There are 10 questions. You are expected to answer all 10 questions.
- There are 10 pages. Please make sure you have all 10 pages. NOTE: the last page is a DATA SHEET. You may tear it off.
- At the end of the exam, turn in this test booklet and the data sheet.
  GOOD LUCK!

Question	Grade		Question	Grade
1	/5		6	/10
2	/4		7	/6
3	/3		8	/6
4	/6		9	/14
5	/8		10	/10
TOTAL				/72

1. (**5 marks**) Describe the electronic transition that is responsible for the 656.3 nm emission of a hydrogen atom (i.e., determine the initial and final electronic states). For full marks, be sure to show all of your logic and math.

Answer:

Since the 656.3 nm line is in the visible region, we know it is part of the Balmer series, so $n_l = 2$. ✔ Now we just need to determine n_h.

First, determine the energy of 656.3 nm:

$$E = hc/\lambda = (6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m/s})/(656.3 \times 10^{-9}\ \text{m})$$ ✔
$$= 3.027 \times 10^{-19}\ \text{J}$$ ✔

Use Balmer's equation to find n_h:

$$3.027 \times 10^{-19} = (2.179 \times 10^{-18}\ J)\left(\frac{1}{4} - \frac{1}{n^2}\right)$$ ✔
$$n^2 = 9.00$$
$$n = 3$$ ✔

Thus, the electronic transition responsible for the 656.3 nm emission line in the hydrogen atom is the n = 3 to n = 2 transition.

2. (**4 marks**) The energy conservation principle that applies to the photoelectric effect is:

$$E_{photon} = KE_{electron} + W$$

where KE is the kinetic energy of the ejected electron and W is the work function for the metal. The work function is the minimum energy required to eject an electron from the metal surface. If calcium (W = 4.34×10^{-19} J) is irradiated with 325 nm light, what are the speed and de Broglie wavelength of the resulting photoelectron beam?

Answer:

1 mark: $E_{photon} = hc/\text{lambda} = 6.112 \times 10^{-19}$ J

1 mark: $KE = E_{photon} - W = 1.772 \times 10^{-19}$ J

1 mark: $KE = \frac{1}{2} m_e v^2 \rightarrow v = (2\ KE/m_e)^{1/2} = 6.25 \times 10^5$ m/s

I mark: de Broglie lambda = $h/m_e v$ = 1.17 nm

3. (**3 marks**) Define "zero-point energy" and calculate it for an electron in a one-dimensional box with length 26 pm.

Answer:

1 mark: Zero-point energy is the lowest possible energy of a particle (e.g., the particle in a box).

1 mark: For a particle in a 1-D box, the energy is defined as $E_{PIB} = \frac{n^2h^2}{8ma^2}$

1 mark: The zero-point energy for an electron in a 1D box of length 26pm is

$$E = \frac{1^2(6.626\times10^{-34}\,kg\bullet m^2\bullet s^{-1})^2}{8(9.11\times10^{-31}\,kg)(26\times10^{-12}\,m)^2}$$

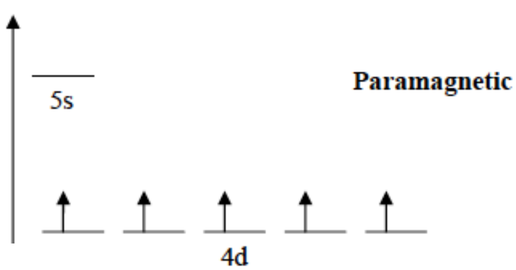
$$E = 8.91 \times 10^{-17}\ \mathrm{kg\ m^2\ s^{-2}}$$

$$E = 8.91 \times 10^{-17}\ \mathrm{J}$$

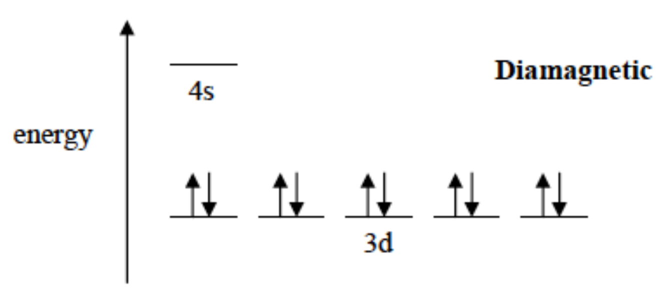
4. (**6 marks**) Complete the following for the ground-state of (a) Ru^{3+} and (b) Ga^{3+}:
   (i) Write the noble gas core electron configuration
   (ii) Draw the orbital energy-level diagram (only show the valence orbitals and electrons)
   (iii) Identify the species as paramagnetic or diamagnetic

Answer:

(a) Ru^{3+}: [Kr] $5s^04d^5$
(electrons are removed from the s orbital, then from the d orbitals).

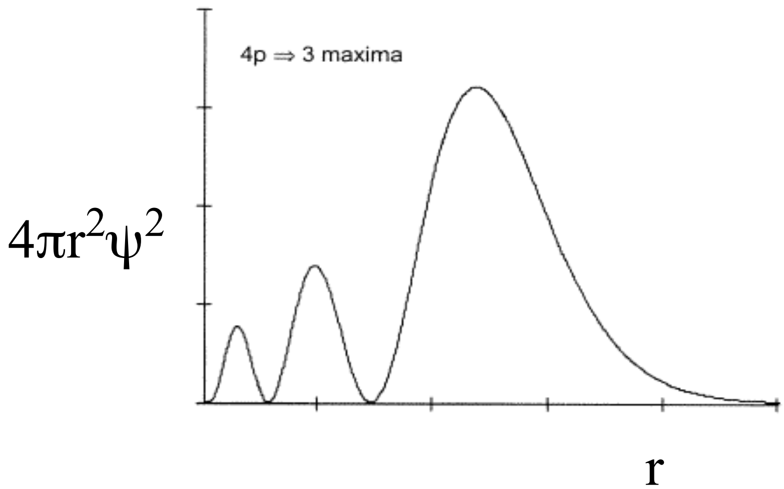


(b) Ga^{3+}: [Ar] $4s^04d^{10}$
(electrons are removed from p, then s orbitals).



5. (**8 marks**) In class we looked at radial and angular wave functions of hydrogen orbitals.

(a) On the axis below, sketch a plot of the radial probability ($4\pi r^2\psi^2$) of finding a 4p electron at distance r from a nucleus. (**1 mark**)



(b) The angular wave function for an orbital is given by:

$$\theta\phi(x, y, z) = (15/4\pi)^{1/2}\ (yz/r^2)\ \text{(r is the radial distance)}$$

Under what conditions do wave functions have nodes? Under what condition does this wave function have an angular node? Which plane or planes correspond to nodes for this orbital (a plane is defined by two coordinates)? What is the value of the quantum number *l* for this orbital? (**4 marks**)

Answer:

Nodes are where the wave function changes sign or where the probability goes to zero. ✔

For this function the following conditions will give nodes:

z = 0 any value of y and x – this is the xy plane ✔

y = 0 any value of x and z – this is the xz plane ✔

Since there are two angular nodes this corresponds to an l value of 2 ✔

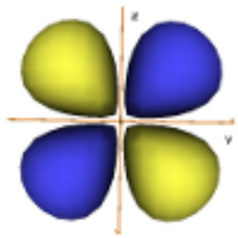
(c) (**3 marks**) Draw the orbital described in part (b). Explain using diagrams whether the orbital is symmetric or antisymmetric with respect to:

i. inversion

ii. reflection in the xy plane (e.g., σ_{xy})

Answer:

1 mark: d_{yz}



1 mark: symmetric with respect to inversion;

1 mark antisymmetric with respect to reflection in the xy plane

6. (**10 marks**) Calculate the effective nuclear charge for an electron in the highest energy level (i.e., furthest from the core) for each of the following species: Na, Na^+ and Na^-. Explain the trend in your results.

Answer:

Z = 11 for Na

Electronic configuration of Na = $1s^2 2s^2 2p^6 3s^1$; thus the slater ordering will be: ($1s^2$) ($2s^2$, $2p^6$) ($3s^1$, $3p^0$)

$Z_{eff} = Z\text{-}\mathbf{S} = 11 – (0.85(8) + 1(2)) = 2.2$

Electronic configuration of Na^+ = $1s^2 2s^2 2p^6$; thus the slater ordering will be: ($1s^2$) ($2s^2$, $2p^6$)

$Z_{eff} = Z\text{-}\mathbf{S} = 11 – (0.35(7) + 0.85(2)) = 6.85$

Electronic configuration of Na^- = $1s^2 2s^2 2p^6 3s^2$; thus the slater ordering will be: ($1s^2$) ($2s^2$, $2p^6$) ($3s^2$, $3p^0$)

$Z_{eff} = Z\text{-}\mathbf{S} = 11 – (0.35 + 0.85(8) + 1(2)) = 1.85$

Based on these calculations, an electron will be more tightly bound, and feel a stronger nuclear attraction in the following order: $Na^+ > Na > Na^-$

BONUS: This is consistent with other properties/trends such as atomic/ionic radii (smaller to larger), ionization potential (higher to lower) and electron affinity (lower to higher).

7. (**6 marks; 2 marks each**) Predict and explain whether:

(a) The boiling point of SO_2 is higher or lower than CO_2.

Answer:
Sulphur dioxide is a polar molecule (bent) while carbon dioxide is nonpolar (linear). The dipole-dipole forces between SO_2 molecules are stronger than the induced dipole-induced dipole forces between CO_2 molecules. Therefore, SO_2 has a higher boiling point.

(b) The bond length of H-Cl is shorter or longer than H-I. Be sure to use valence bond theory concepts in your response.

Answer:
According to valence bond theory, bonding occurs when the outermost orbitals of two atoms overlap. Bond length and strength can be evaluated by considering these orbitals.
Iodine is a larger atom than chlorine, therefore its outermost orbitals are further away from the nucleus, therefore, the H-I bond will be longer than H-Cl.

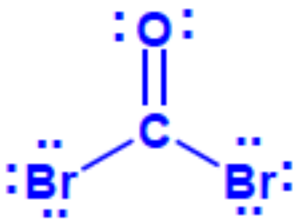
Bond strength results from attraction to the bonding electrons to the nuclei of both atoms. Since the H-I bond is long, the electrons in this bond are far from the nucleus of iodine, therefore their attraction to that nucleus will be weaker. Therefore, H-Cl is a stronger bond than H-I

(c) The first electron affinity of sulphur is more or less negative than oxygen.

Answer:
Natures trick! Special case for oxygen and fluorine due to size of atom – greater degree of electron electron repulsion upon addition of an electron therefore the EA is less negative than S and Cl respectively

8. **(6 marks)** Consider the bonding in $COBr_2$ according to valence bond theory.

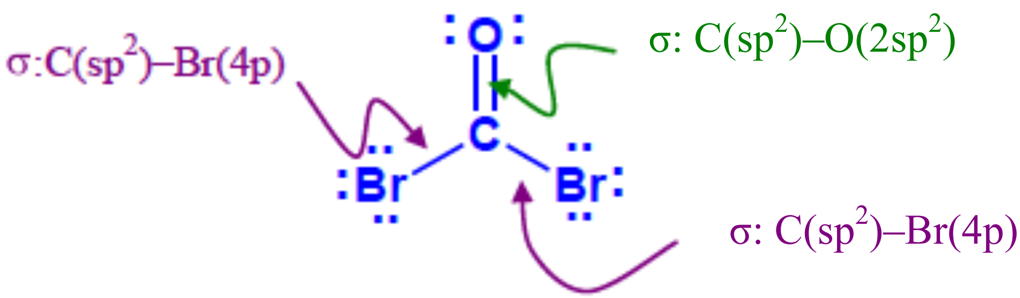
(a) Draw a Lewis structure for $COBr_2$.



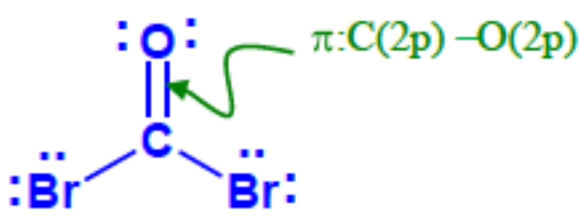
(b) What is the hybridization of the carbon atom?

sp^2

(c) Clearly indicate which atomic orbitals combine to make each σ bond in $COBr_2$.



(d) Clearly indicate which atomic orbitals combine to make each π bond in $COBr_2$.

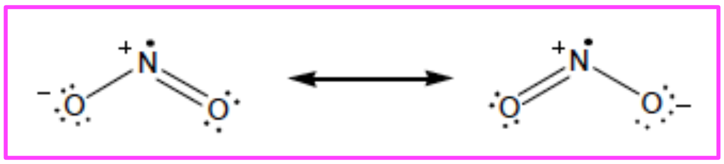


9. **(14 marks; 1 mark per blank; *no partial credit*)** For the following molecules:

i) Draw the Lewis structure. If more than one non-equivalent resonance structure is possible, only draw the most stable structure.
ii) Indicate any non-zero formal charges in the Lewis structure
iii) Determine the VSEPR geometry and shape of the molecule
iv) Draw the three-dimensional representation of the molecule
v) Determine whether the molecule is polar or non-polar
vi) Give the hybridization of the central atom

(a) NO_2

Lewis Structure: **3D Drawing:**

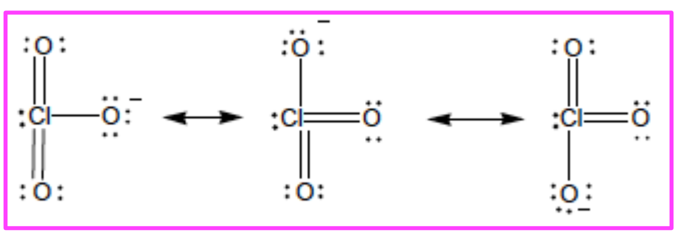


Geometry: _Trigonal Planar______ **Shape:** __Bent or V-shaped_______

Polarity: __Polar ______________ **Hybridization**:____sp^2______________

(b) ClO_3^-

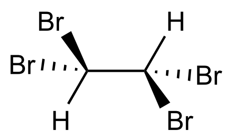
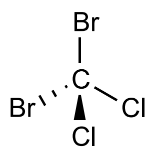
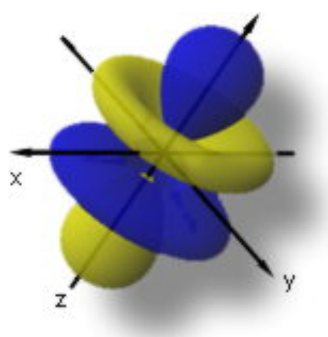
Lewis Structure: **3D Drawing:**



Geometry: ____Tetrahedral ________ **Shape:** _____Trigonal pyramidal_________

Polarity: ____Polar ____________ **Hybridization**:__sp^3______________

10. (**10 marks; 2 marks each**) For each of the following, indicate the highest rotation axis and if there is a plane of reflection. If there is a plane of reflection, indicate what type.

	Compound	**Rotation/Reflection label**
Example	*BF_3*	***C_3, σ_h***
(a)		C_2, σ_h
(b)	ClF_5	C_4, σ_v
(c)		C_2, σ_v
(d)		C_∞ , σ_v
(e)		C_3 , σ_v

DATASHEET

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 H Hydrogen 1.01																	2 He Helium 4.00
2	3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
3	11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
4	19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
5	37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
6	55 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
7	87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)									

58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Key

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

Constants:

$N_A = 6.022\times10^{23}$ mol^{-1}
Rydberg constant = $R_H = 2.179 \times 10^{-18}$ J
Planck's constant = $h = 6.626 \times 10^{-34}$ J s
Speed of light = $c = 2.998 \times 10^{8}$ m s^{-1}
Electron mass = $m_e = 9.11 \times 10^{-31}$ kg
Bohr radius (a_o) = 52.9 pm

Conversion Factors:

1 J = 1 kg m^2 s^{-2}
1 J = 6.241×10^{8} eV

Useful Equations:

$$E_{PIB} = \frac{n^2h^2}{8ma^2} \qquad \psi_{PIB} = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

$$[-(\frac{\mathrm{h}^2}{8\pi^2 m})({\frac{d}{dx^2}}^{2} + {\frac{d}{dy^2}}^{2} + {\frac{d}{dz^2}}^{2}) + V]\Psi = \mathrm{E}\Psi$$

$\psi(r,\theta,\phi) = R(r)Y(\Theta, \Phi)$
The volume element is $r^2\sin\Theta d\Theta d\Phi dr$

$E = ½\, mv^2$
$h = mv\lambda$
$h = \lambda\rho$