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MIDTERM 1: CHM 2311 – Introduction to Structure and Bonding

Professor: Jaclyn Brusso

Date: February 16, 2017

Duration: 70 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 8 questions. You are expected to answer all 8 questions.
- There are 8 pages. Please make sure you have all 8 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	/4		6	/4
2	/6		7	/7
3	/6		8	/12
4	/3		9	/13
5	/6			
TOTAL				/61

1. (**4 marks**) Emissions are observed at wavelengths of 383.65 and 379.90 nm for transitions from excited states of the hydrogen atom to the n = 2 state. Determine the quantum numbers (n) for these emissions.

Answer:

383.65 nm $$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\text{J s})(2.998\times10^{8}\,\text{m/s})}{(383.65\,\text{nm})(\text{m}/10^{9}\,\text{nm})} = 5.178\times10^{-19}\,\text{J}$$ ✔

379.90 nm $$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\text{J s})(2.998\times10^{8}\,\text{m/s})}{(379.90\,\text{nm})(\text{m}/10^{9}\,\text{nm})} = 5.229\times10^{-19}\,\text{J}$$ ✔

$$E = R_H\left(\frac{1}{2^2} - \frac{1}{n_h{}^2}\right);\quad \frac{1}{n_h{}^2} = \frac{1}{4} - \frac{E}{R_H} \text{ and } n_h = \left(\frac{1}{4} - \frac{E}{R_H}\right)^{-\frac{1}{2}}$$

For 383.65 nm: $$n_h = \left(\frac{1}{4} - \frac{5.178\times10^{-19}J}{2.1787\times10^{-18}J}\right)^{-\frac{1}{2}} = 9$$ ✔

For 379.90 nm: $$n_h = \left(\frac{1}{4} - \frac{5.229\times10^{-19}J}{2.1787\times10^{-18}J}\right)^{-\frac{1}{2}} = 10$$ ✔

2. (**6 marks**) Using Slater's rules, determine Z_{eff} for a 4s and a 3d electron of Cu. Which type of electron is more likely to be lost when copper forms a positive ion?

Answer:

Cu	$(1s^2)\,(2s^2\,2p^6)\,(3s^2\,3p^6)\,(3d^{10})\,(4s^1)$ ✔		
4s	$S = 2 + 8 + (8\times0.85) + (10\times0.85) =$	25.3 ✔	$Z^* = 29 - 25.3 = 3.7$ ✔
3d	$S = 2 + 8 + (8\times1.00) + (9\times0.35) =$	21.15 ✔	$Z^* = 29 - 21.15 = 7.85$ ✔

The 3d electron has a much larger effective nuclear charge and is held more tightly; ✔ the 4s electron is therefore the first removed on ionization.

3. **(6 marks; 1 mark each; *no partial credit*)**

(a) At most, how many electrons in an atom can have both $n = 5$ and $l = 3$?

Answer:

The l quantum number limits the number of electrons. For $l = 3$, m_l can have seven values (–3 to +3) each defining an atomic orbital, and for each value of m_l the value of m_s can be $-\frac{1}{2}$ or $+\frac{1}{2}$; there can be two electrons in each orbital. At most, therefore, there can be 14 electrons with $n = 5$ and $l = 3$.

(b) A 5*d* electron has what possible values of the quantum number m_l?

Answer:

A 5*d* electron has $l = 2$, limiting the possible values of m_l to –2, –1, 0, 1, and 2.

(c) What value of quantum number l do *p* orbitals have?

Answer:

p orbitals have $l = 1$

(d) For what values of n do *p* orbitals occur?

Answer:

p orbitals occur for $n \geq 2$.

(e) What is the quantum number l for *g* orbitals?

Answer:

g orbitals have $l = 4$.

(f) How many orbitals are in a *g* subshell?

Answer:

There are 9 possible values of m_l and therefore 9 orbitals.

4. (**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 $E_{PIB} = \frac{n^2 h^2}{8ma^2}$

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

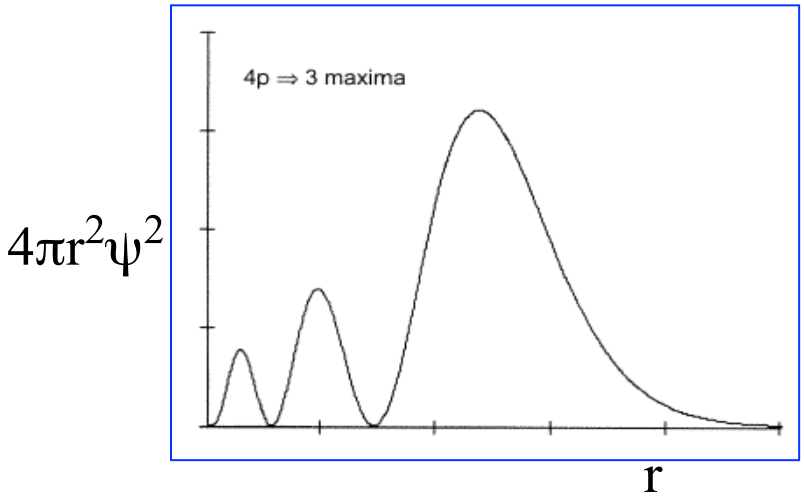
$$E = \frac{1^2(6.626\times10^{-34}\,kg \bullet m^2 \bullet s^{-1})^2}{8(9.11\times10^{-31}\,kg)(26\times10^{-12}\,m)^2}$$

$$E = 8.91 \text{ x } 10^{-17} \text{ kg m}^2 \text{ s}^{-2}$$

$$E = 8.91 \text{ x } 10^{-17} \text{ J}$$

5. (**6 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:

$$Y = \frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$$

Where r is the radial distance. Under what conditions do wave functions have nodes? Under what condition does this wave function have an angular node? What is/are the shape of angular node(s) and where do they occur? What is the value of the quantum number *l* for this orbital? (**5 marks**)

Answer:

Nodes occur when the wave function changes sign and the probability is equal to zero. ✔

For this function, there will be nodes when xz = 0. ✔ In other words when:

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

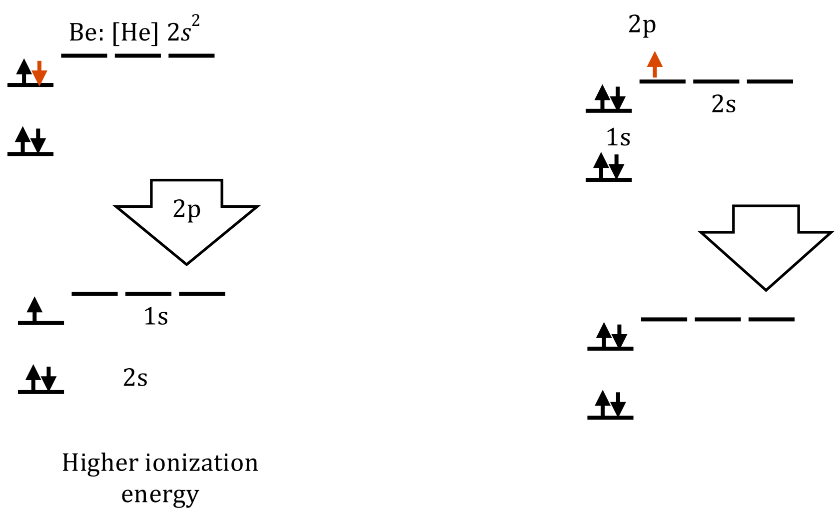
z = 0 any value of x and y – this is the xy ✔ plane

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

6. (**4 marks; 2 marks each**) Predict and explain whether:

(a) The first ionization energy of B is higher or lower than Be.

Answer:
B has a lower first ionization energy because the 2p orbital is higher in energy than the 2s and less energy is required to remove an electron from a higher energy orbital.



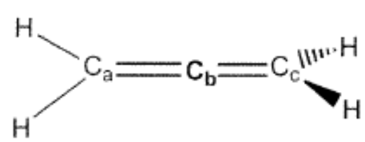
(b) The C–Cl bond length in CCl_4 of is shorter or longer than the C–Br bond length in CBr_4. Be sure to use valence bond theory concepts in your response.

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.
Bromine is a larger atom than chlorine, therefore its outermost orbitals are further away from the nucleus, therefore, the C–Br bond will be longer than C–Cl.

7. **(7 marks)** Consider the allene molecule, $H_2C{=}C{=}CH_2$. Draw the Lewis structure and answer the following questions:
(a) Classify each bond as σ or π and identify the orbitals involved. (**5 marks**)
(b) What is the H-C-C bond angle? What is the C-C-C bond angle? (**1 mark**)
(c) Explain why the four H atoms cannot all lie in the same plane. (**1 mark**)

Answer:

a)

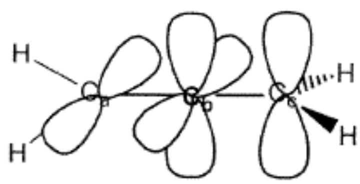


bond	classifcation?	orbitals involved?
H-C	σ	$C(sp^2) – H(1s)$
$C_a{=}C_b$	σ + π	σ: $C_a(sp^2)$-$C_c(sp)$ π: $C_a(2p_x)$-$C_c(2p_x)$
$C_b{=}C_c$	σ + π	σ: $C_b(sp)$-$C_c(sp^2)$ π: $C_b(2p_y)$-$C_c(2p_y)$

The important point here is that C_b makes two π bonds using two different p orbitals that are perpendicular.

b) The H-C_a-C_b bond angle is 120° because C_a is sp^2-hybridized. The C_a-C_b-C_c bond angle is 180° because C_b is sp-hybridized.

c)



The diagram above shows the unhybridized 2p orbitals involved in forming the π bonds. In order for C_b to make two π bonds, the 2p orbitals of C_a and C_c must be at right angles. This forces the hybrid orbitals of C_a and C_c to lie in different planes and therefore the H's bonded to C_a lie in a different plane than those bonded to C_c.

8. **(12 marks; 1 mark per blank; *no partial credit*)** For the following molecules:

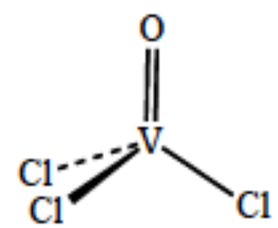
i) Draw the Lewis structure. If more than one non-equivalent resonance structure is possible, only draw the most stable structure.
ii) Indicate any non-zero formal charges in the Lewis structure
iii) Determine the VSEPR geometry and shape of the molecule
iv) Draw the three-dimensional representation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

(a) $VOCl_3$

Lewis Structure:

Lewis: 5 + 6 + (3 × 7) = 32 valence electrons

3D Drawing:



$VOCl_3$ has a distorted tetrahedral shape, with Cl—V—Cl angles of 111°, and Cl—V—O angles of 108°.

Geometry: __**Tetrahedral**__________ **Shape:** __**tetrahedral**______

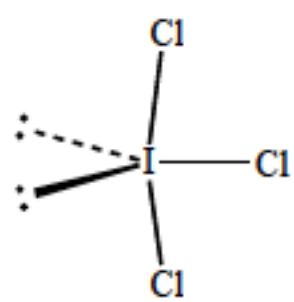
Polarity: __Polar ______________ **Hybridization**:____sp^3______________

(b) ICl_3

Lewis Structure:

Lewis: 7 × 4 = 28 valence electrons

3D Drawing:



Geometry: ____Trigonal Bipyramidal______ **Shape:** _____T-shaped__________

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

9. **(14 marks)** Answer the following questions for A – F.

(a) What is the principle rotation axis for each?

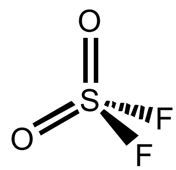
(b) Which has a σ_h?

(c) Which have either a σ_v or a σ_d?

(d) Which if any have a center of inversion?

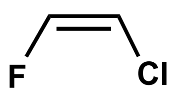
SF_5Br

A

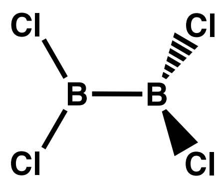


B

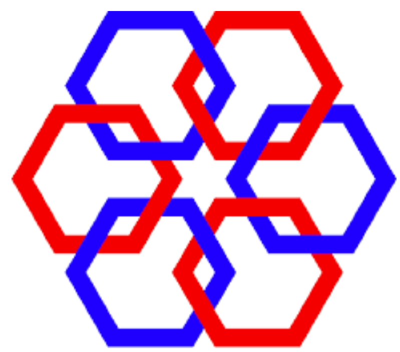
C



D



E



F

Point groups

A: C4v

B: C2v

C: C3v

D: Cs

E: D2d

F: If flat/planar: C3h; If nonplanar: D3; print in black and white: D6h

DATASHEET

Key: 11 – Atomic number; Na – Element symbol; Sodium – Element name; 22.99 – Average atomic mass*

	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)

* 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:

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

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

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

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