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MIDTERM 1: CHM 2311 – Introduction to Structure and Bonding

Professor: Jaclyn Brusso

Date: February 15, 2018

Duration: 75 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 9 questions. You are expected to answer all 9 questions.
- There are 9 pages. Please make sure you have all 9 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	/1
2	/6		7	/7
3	/6		8	/14
4	/4		9	/15
5	/1			
TOTAL				/58

1. (**4 marks**) The energy conservation principle that applies to the photoelectric effect is:

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

where E_{photon} is the energy of the photon, $KE_{electron}$ 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.

(a) If calcium is irradiated with 275 nm light, and the work function for calcium metal is 4.60×10^{-19} J, what is the kinetic energy of the ejected electron?

Answer:
$E_{photon} = hc/\lambda = 7.22 \times 10^{-19}$ J ✔

$KE = E_{photon} - W = 2.62 \times 10^{-19}$ J ✔

(b) What are the speed and de Broglie wavelength of the ejected electron?

Answer:
$KE = \frac{1}{2} m_e v^2 \rightarrow v = (2\ KE/m_e)^{1/2} = 7.59 \times 10^5$ m/s ✔

de Broglie $\lambda = h/m_e v = 9.58 \times 10^{-10}$ m ✔

2. (a) Provide the electron configuration for Ni and Ni^{2+}. (**1 mark; ½ mark each; *no partial credit***)

Answer:
Ni^{2+}: [Ar] $4s^2$ $3d^8$
Ni^{2+}: [Ar] $3d^8$

(b) Using Slater's rules and Z_{eff}, explain the electron configuration obtained in (a). (**5 marks**)

Answer:

Use Slater's rules to calculate the shielding constant and effective nuclear charge of a $3d$ and $4s$ electron.

Rule 1: The electron configuration is written $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^8)(4s^2)$

For a $3d$ electron:

Rule 4a: Each other electron in the $(3d^8)$ group contributes 0.35 to S.
Total contribution $= 7 \times 0.35 = 2.45$

Rule 4b: Each electron in groups to the left of $(3d^8)$ contributes 1.00 to S.
Total contribution $= 18 \times 1.00 = 18.00$
Total $S = 2.45 + 18.00 = 20.45$ ✔
Effective nuclear charge $Z^* = 28 - 20.45 = 7.55$ ✔

For a $4s$ electron:

Rule 3a: The other electron in the $(4s^2)$ group contributes 0.35 to S.

Rule 3b: Each electron in the $(3s^2, 3p^6)(3d^8)$ groups $(n - 1)$ contributes 0.85.
Total contribution $= 16 \times 0.85 = 13.60$

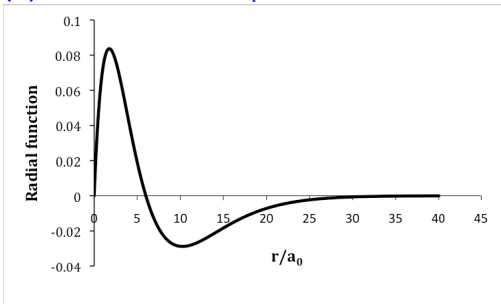
Rule 3c: Each other electron to the left contributes 1.00. Total contribution $=$ $10 \times 1.00 = 10.00$
Total $S = 0.35 + 13.60 + 10.00 = 23.95$ ✔
Effective nuclear charge $Z^* = 28 - 23.95 = 4.05$ ✔

The effective nuclear charge for the $4s$ electron is considerably smaller than the value for the $3d$ ✔ electron, which is equivalent to stating that the $4s$ electron is held less tightly than the $3d$ and should therefore be the first removed upon ionization. This is consistent with experimental observations on nickel compounds that Ni^{2+} has a configuration of [Ar] $3d^8$, rather than [Ar] $4s^2$ $3d^6$, corresponding to loss of the $4s$ electrons from nickel atoms.

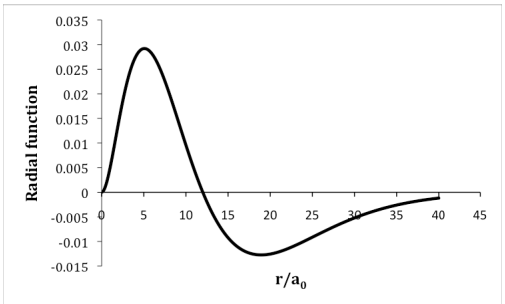
3. (**6 marks; 1 mark each; *no partial credit***) For the $3p_z$ and $4d_{xz}$ hydrogen-like atomic orbitals, sketch the following:
   (a) The radial function R
   (b) The radial probability function $a_o r^2 R^2$
   (c) The boundary surface plots

Answer:

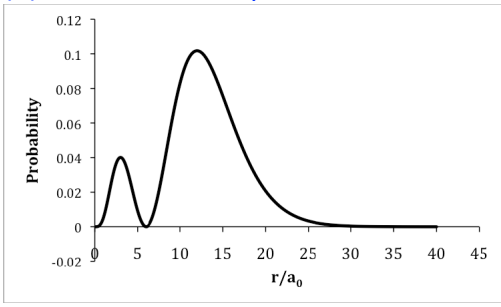
(a) $3p_z$



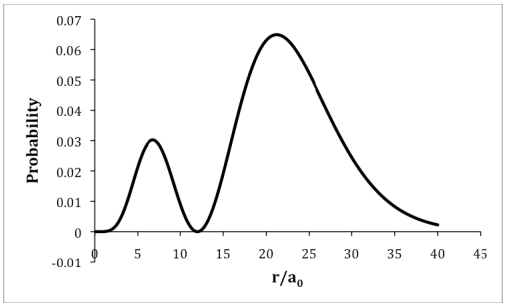
$4d_{xz}$



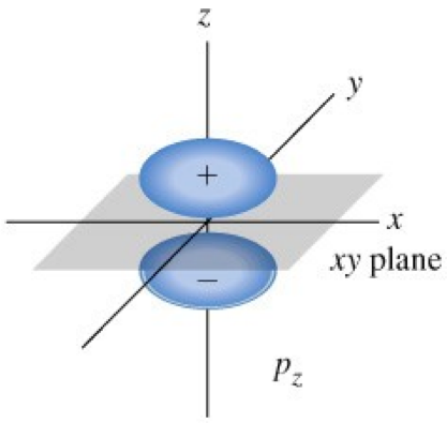
(b) $3p_z$

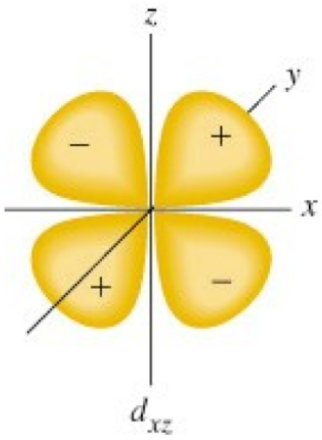


$4d_{xz}$



(c)



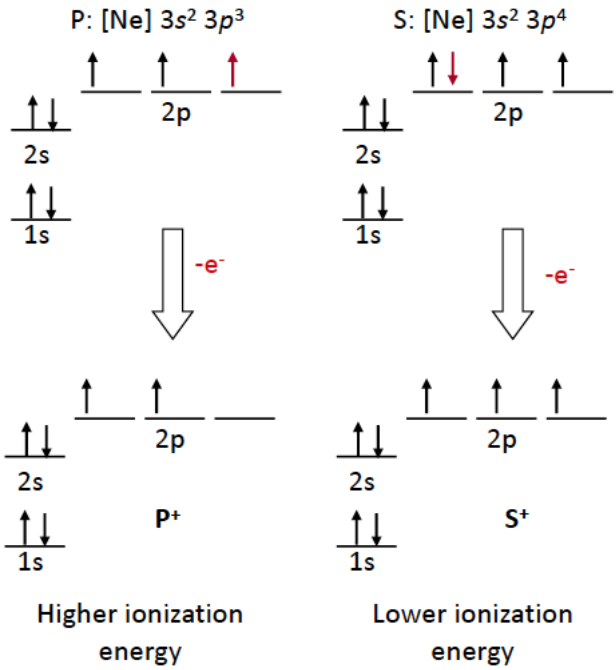


4. (**4 marks; 2 marks each**) Predict and explain:

(a) which of the atoms Mg, P, Si, Al, S has the highest first ionization energy?

Answer:

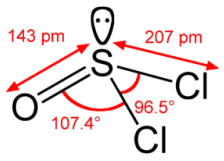
In general, the first ionization potential of an atom increase as Z_{eff} increases. Z_{eff} increases as go from left to right across the periodic table. Based on this argument the answer would be S; however, P has a higher first ionization energy than S due to electron-electron repulsion in S which destabilizes the 2p orbital that contains the electron that would be removed – this makes it easier to remove an electron from S than P.

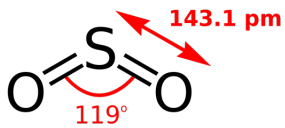


(b) whether the Cl-S-Cl bond angle in thionyl chloride ($SOCl_2$) is larger or smaller than the O-S-O bond angle in the sulfur dioxide (SO_2).

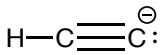
Answer:

Thionyl chloride should have a smaller bond angle because it is tetragonal geometry (trigonal pyramidal shape; sp^3 central atom) whereas sulfur dioxide has trigonal planar geometry (bent shape; sp^2 central atom).





5. **(1 mark)** Provide the hybridization of all the carbon atoms in the acetylene anion (shown below). In what type of orbital do the nonbonding pair of electrons reside?



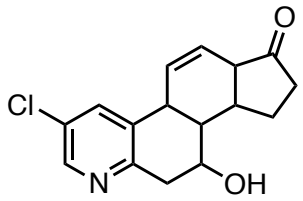
Answer:
The carbon atoms are sp hybridized and the lone pair of electrons reside in an sp orbital.

6. **(1 marks)** What hybridization change does the carbon atom undergo in the combustion of methane?

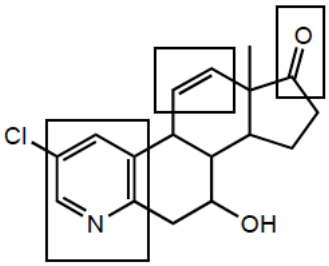
$$CH_{4\,(g)} + 2\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{(g)}$$

Answer: ½ mark each
sp^3: CH_4
sp: CO_2

7. **(7 marks)** In the following molecule, identify all atoms that have a trigonal planar geometry. Can you make any correlations between obvious structural features and the geometries? Explain.



Answer:
½ mark for each atom – 5 marks



All the atoms here that are involved in forming double bonds have trigonal planar geometry and will be best described as sp^2-hybridized. This trend is generally true and the key feature overall is that these regions of the molecule are flat. Interconnected groups of trigonal planar atoms lead to planar regions of a molecule. Considering the orbital pictures, these planar regions can be described as having electron density residing above and below the sigma framework because the p-orbitals used to make the pi bonds lie perpendicular to the plane with the sigma bonds (note allenes as special cases).

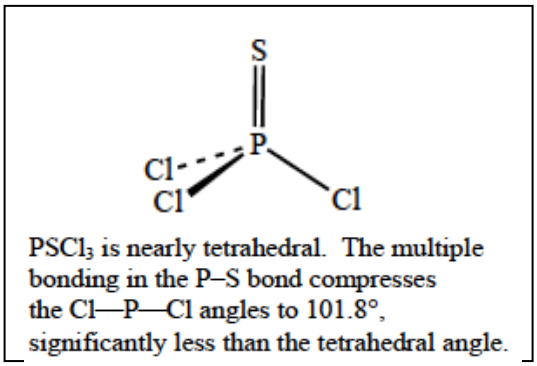
8. **(14 marks; 1 mark per blank; *no partial credit*)** For the following molecules:
   i) Draw the Lewis structure. If more than one non-equivalent resonance structure is possible, only draw the most stable structure.
   ii) Indicate any non-zero formal charges in the Lewis structure
   iii) Determine 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) $PSCl_3$ (P is central)

Lewis Structure:

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

3D Drawing:



$PSCl_3$ is nearly tetrahedral. The multiple bonding in the P–S bond compresses the Cl—P—Cl angles to 101.8°, significantly less than the tetrahedral angle.

Geometry: __Tetrahedral_____ **Shape:** __tetrahedral_____

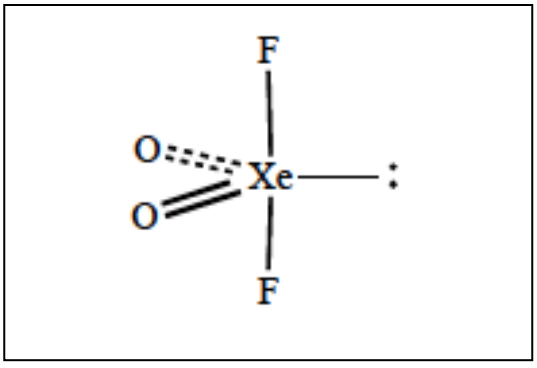
Polarity: __Polar _____ **Hybridization**:____sp^3_____

(b) XeO_2F_2

Lewis Structure:

Lewis: 8 + 6 × 2 + 7 × 2 = 34 valence electrons

3D Drawing:



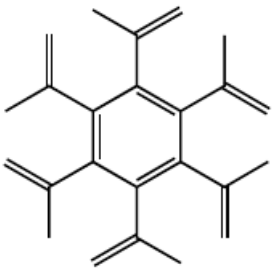
Geometry: ____Trigonal Bipyramidal_____ **Shape:** _____see-saw _____

Polarity: ____Polar _____ **Hybridization**:__sp^3d_____

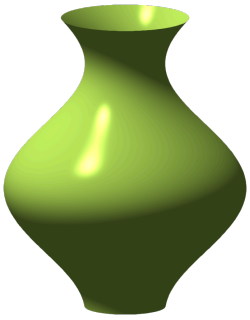
9. **(15 marks)** Answer the following questions for A – F. Consider the molecules as drawn.
   (a) What is the principle rotation axis for each?
   (b) Which if any have a σ_h?
   (c) Which if any have either a σ_v or a σ_d?
   (d) Which if any have a center of inversion?
   (e) Which if any have an improper rotation and what is it?

ClF_3

A

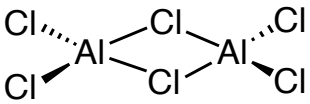


B



C

D



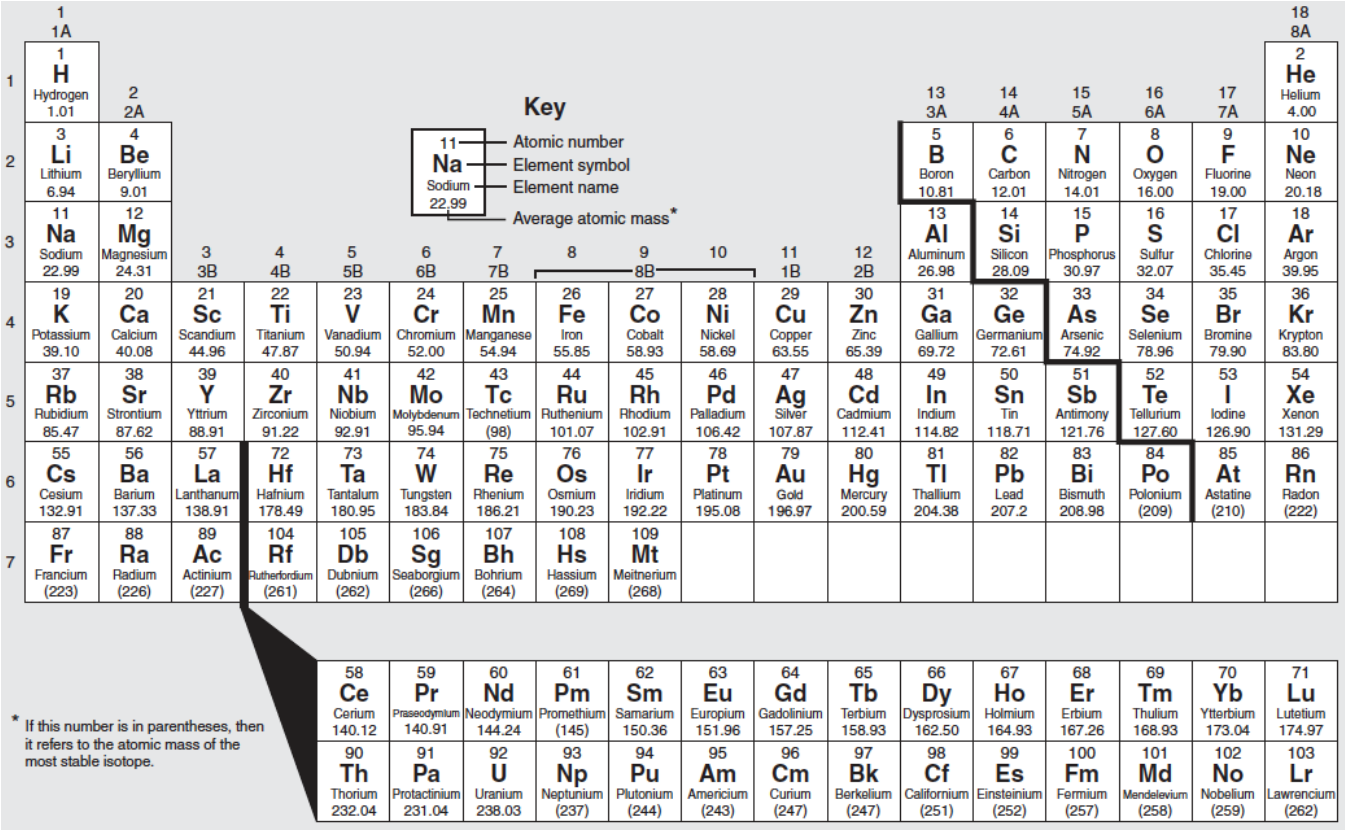
E

F

Answer:
A: C2v
B: C3h
C: C∞v
D: D3d
E: D2h
F: Nonplanar: C3

(a) 6 marks; see point groups above
(b) 1 mark – B
(c) 4 marks – A, C, D, E
(d) 2 marks – D, E
(e) 2 marks – B, D

DATASHEET



1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H Hydrogen 1.01	2 2A																2 He Helium 4.00
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
11 Na Sodium 22.99	12 Mg Magnesium 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	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
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
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
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)
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)

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:

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

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

$\psi(r,\theta,\phi) = R(r)Y(\Theta,\Phi)$

The volume element is $r^2\sin\Theta d\Theta d\Phi dr$

$KE = ½\ mv^2$

$h = mv\lambda$

$h = \lambda p$