CHEMISTRY 362

Descriptive Inorganic Chemistry

M. Y. Daresbourg

Examination I-A

February 12, 2014

<table>
<thead>
<tr>
<th>Question</th>
<th>Points possible</th>
<th>Points received</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>20</td>
<td></td>
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<tr>
<td>III</td>
<td>25</td>
<td></td>
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<tr>
<td>IV</td>
<td>25</td>
<td></td>
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<tr>
<td>V</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Name: ____________________________________________

An Aggie does not lie, cheat or steal or tolerate those who do.

Useful formula: \( \mu_{s.a.} = 2 \sqrt{S(S+1)} \)

Useless Conversion Factors

Ratio of an igloo's circumference to its diameter: Eskimo Pi
2000 pounds of Chinese soup: Won ton
1 millionth of a mouthwash: 1 microscope
Time between slipping on a peel and smacking the pavement: 1 bananosecond
I.

A. Phosphorus exists as $^{31}\text{P}$ in 100% natural abundance. The artificial (man-made) isotope $^{32}\text{P}$ has a half-life of 14.3 days and decays by ejection of a $\beta^-$ (an electron) from its nucleus. What is the resulting element? How long will it take for approximately 90% of the $^{32}\text{P}$ radioisotope to decay?

\[
^{32}\text{P} \rightarrow ^? + \beta^- \quad 100\% \rightarrow 50\% \rightarrow 25\% \rightarrow 12.5\% \\
\text{14.3 days} \rightarrow 28 \text{ days} \rightarrow 43 \text{ days} \quad \sim 3 \text{ half-lives} \quad > 40 \text{ days}
\]

B. Give the electronic configuration of atomic P expressed as $1s^2, 2s, \ldots$. What is the effective nuclear charge on the outermost electron of P? (Note: Slater's rules are provided on the handout. Show your work.)

\[
(1s^2) (2s^2 2p^6) (3s^2 3p^3) \quad 6 = \text{screening constant} ^+ \\
4(0.35) + 8(0.85) + 2 \quad Z_{\text{eff}} = 15 - 10.2 = 4.8 \quad = 10.2
\]

C. Give the ground state term symbol for P. [Hint: First give the electronic configuration of the valence shell electrons in the box diagram approach and show the $m_l$ values on the boxes.] Repeat this exercise for an excited state $P^*$ where one of the 3s electrons has been promoted to a 3p orbital. For full credit, show your work/reasoning.)

\[\begin{align*}
\text{Ground state P:} & \quad \frac{3s^2}{1l} \quad \frac{3p^3}{1l} \\
& \quad m_L = 0 \quad +1 \quad 0 \quad -1 \\
& \quad L = \leq M_L = 0 \\
\text{Excited state P*:} & \quad \frac{3s^2}{1l} \quad \frac{3p^3}{1l} \\
& \quad m_L = 0 \quad +1 \quad 0 \quad -1 \\
& \quad L = \leq M_L = +1 \quad \Rightarrow P \\
& \quad S = \leq M_S = \frac{3}{2}
\end{align*}\]

D. Match the ionization energies and electronegativity values to the element:

<table>
<thead>
<tr>
<th>B, O, N, P, F</th>
<th>Ionization Energy (kJ/mol)</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1314</td>
<td>O</td>
<td>2.04</td>
</tr>
<tr>
<td>1402</td>
<td>N</td>
<td>2.19</td>
</tr>
<tr>
<td>801</td>
<td>B</td>
<td>3.04</td>
</tr>
<tr>
<td>1680</td>
<td>F</td>
<td>3.44</td>
</tr>
<tr>
<td>1012</td>
<td>P</td>
<td>4.00</td>
</tr>
</tbody>
</table>
II. Continuing with phosphorus: A) fill in the blanks, and/or select the correct answer from those provided in brackets, in the following paragraph.

One elemental form of phosphorus is the P₄ molecule shown above. It is a perfect tetrahedron with ____ bond angles. Its symmetry point group is \( T_d \) and it [does or does not] have an inversion center. If [does or does not] contain an improper rotation axis, \( S_4 \).

From its Lewis structure, the P₄ molecule has 6 bonded pairs of electrons and 4 lone pairs.

The bonded pairs of electrons are positioned in ____ hybrid orbitals; the lone pairs are in ____ hybrid orbitals. The s-character in the lone pair orbitals is ____%; the p-character in each bonded pair is ____%. Phosphorus reacts with oxygen in excess to form an oxide of formula P₄O₁₀; in which phosphorus is in its highest oxidation state. That oxidation state is \( \text{V} \) and the formula is \( \text{P}_4 \text{O}_{10} \). * This is a complicated system. Therefore, the blanks that do not contain answers have been awarded credit for any valid attempt.

Molecules of similar structure to P₄ may be isolated from mixtures of arsenic and phosphorus: AsP₃ and As₂P₂ (see drawings). The principal rotation axis of AsP₃ is \( C_3 \) and its point group is \( C_{3v} \).

The principal rotation axis of As₂P₂ is \( C_2 \) and its point group is \( C_{2v} \).

B) The lighter member of the Group VA family, N, exists as the N₂ molecule. Why does not elemental phosphorus exist as P₂? Explain.

- The larger P does not form double or triple (\( \pi \)-bonds) so easily as does N. Hence its bonding capacity is better fulfilled with single bonds.
- 6 single bonds are lower in energy than the use of \( \pi \) bonds.
III. Give the Lewis structures and sketch out the VSEPR predicted molecular structures for the following molecules or molecular ions. For each, give the hybrid orbitals needed by the central atom. Also, give the Principal rotation axis and the key symmetry elements required to make the symmetry point group assignment.

<table>
<thead>
<tr>
<th></th>
<th>Lewis structure</th>
<th>VSEPR Predicted structure</th>
<th>Principal rot’n axis and key symmetry elements</th>
<th>Pt. Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Linear</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) CO₂</td>
<td>Ð = Ð = Ð</td>
<td></td>
<td>C\text{(_\infty)} \cong C\text{(_n)}</td>
<td>D\text{(_{oh})}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sp</td>
<td>E, C\text{(_\infty)}, C\text{(_2)}, \text{i}, \sigma\text{(_v)}, \sigma\text{(_d)}</td>
<td></td>
</tr>
<tr>
<td>b) XeF₄</td>
<td></td>
<td>4\times 4</td>
<td>C\text{(_4)} \cong C\text{(_n)}</td>
<td>D\text{(_{4h})}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sp\text{(_{3d}^2)}</td>
<td>E, C\text{(_4)}, C\text{(_2)}, C\text{(_2)'}, \text{i}, \sigma\text{(_v)}, \sigma\text{(_d)}</td>
<td></td>
</tr>
<tr>
<td>c) PF\text{(_2)}Cl₃</td>
<td></td>
<td>Trigonal Bipyramidal</td>
<td>C\text{(_2)} \cong C\text{(_n)}</td>
<td>D\text{(_{3h})}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sp\text{(_d)}</td>
<td>E, C\text{(_3)}, C\text{(_2)}, \sigma\text{(_h)}, \sigma\text{(_v)}, \sigma\text{(_d)}</td>
<td></td>
</tr>
<tr>
<td>d) PF\text{(_3)}Cl₂</td>
<td></td>
<td>Trigonal Bipyramidal</td>
<td>C\text{(_2)} \cong C\text{(_n)}</td>
<td>C\text{(_2)'_h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sp\text{(_{3d})}</td>
<td>E, C\text{(_2)}, \sigma\text{(_v)}, \sigma\text{(_d)}</td>
<td></td>
</tr>
</tbody>
</table>
IV. The diatomics \( \text{N}_2, \text{CO}, \text{CN}^- \) and \( \text{NO}^+ \) are isoelectronic.

1. Give the Lewis structure for each and determine the formal charges for each atom in each diatomic.

<table>
<thead>
<tr>
<th>( \text{N}_2 )</th>
<th>( \text{CO} )</th>
<th>( \text{CN}^- )</th>
<th>( \text{NO}^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( :\text{N}=\text{N}: )</td>
<td>( :\text{C}=\text{O}: )</td>
<td>( :\text{C}=\text{N}: )</td>
<td>( :\text{N}=\text{O}: )</td>
</tr>
<tr>
<td>Formal</td>
<td>charge</td>
<td>-1</td>
<td>+1</td>
</tr>
</tbody>
</table>

2. The nitrosium ion, \( \text{NO}^+ \), can be reduced to the neutral \( \text{NO} \). Give the molecular orbital electronic configuration of \( \text{NO}^+ \) and \( \text{NO} \) (\( \text{KK} \sigma_{2s}^2 \ldots \)), and compute the bond order of each.

\[
\text{NO}^+ \Rightarrow [\text{KK}] \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2 \pi_{2p}^{*0} ; \quad \text{Bond order} = \frac{8 - 2}{2} = \boxed{3}
\]

\[
\text{NO} \Rightarrow [\text{KK}] \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2 \pi_{2p}^{*2} ; \quad \text{Bond order} = \frac{8 - 3}{2} = \boxed{2.5}
\]

3. \( \text{NO}^+ \) has a N–O bond distance of 1.06 Å. Is the bond distance of \( \text{NO} \) neutral smaller or larger than 1.06 Å? Why?

\( \text{NO} \) neutral will have a longer bond than \( \text{NO}^+ \).

The bond order of \( \text{NO} \) neutral is smaller than that of \( \text{NO}^+ \).

4. Which (\( \text{NO}^+ \) or \( \text{NO} \)) is paramagnetic and what is its spin-only magnetic moment?

\( \text{NO} \) neutral is paramagnetic.

\[
\mathbf{M}_{s.o} = 2\sqrt{s(s+1)} = 2\sqrt{\frac{1}{2}(\frac{1}{2}+1)} = 1.73 \text{ BM}
\]

5. \( \text{NO} \) can be reduced to \( \text{NO}^- \). Give the electronic configuration (\( \text{KK} \sigma_{2s}^2 \ldots \)) of \( \text{NO}^- \), its bond order and ground state term symbol.

\[
\text{NO}^- \Rightarrow [\text{KK}] \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2 \pi_{2p}^{*2}
\]

Bond order = \( \frac{(8 - 4)}{2} = \boxed{2} \)

\[
\begin{array}{c|c|c}
\hline
1 & 1 \\
+1 & -1 \\
\hline
\end{array}
\]

\[
L = 2; \quad m_L = 0 \quad \Rightarrow \boxed{\frac{3}{2}}
\]
V.

A. This question aims to test your understanding of orbitals, symmetry, and character tables. As shown in the example above, a $p_z$ orbital has the same symmetry as an arrow pointing along the $z$-axis. It remains unchanged after each symmetry operation in the $C_{2v}$ point group, $E$, $C_2$, $\sigma_v$, and $\sigma'_{yz}$, and thus "follows" the $A_1$ representation (all 1's). By a similar approach find the representation to which the $p_x$ and $p_y$ orbitals belong. Indicate the position/direction of the $x$ and $y$ vectors after each operation by putting a +1 or -1 in the spaces indicated. Note that $\sigma_v$ is the $xz$ plane and $\sigma'_{yz}$ is the $yz$ plane.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v (xz)$</th>
<th>$\sigma'_{yz}$</th>
<th>No change</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$z$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>$xy$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y$</td>
</tr>
</tbody>
</table>

The $p_x$ orbital:

- $E$  
  $C_2$  
  $\sigma_v (xz)$  
  $\sigma'_{yz}$  

Representation: $\beta_1$

The $p_y$ orbital:

- $E$  
  $C_2$  
  $\sigma_v (xz)$  
  $\sigma'_{yz}$  

Representation: $\beta_2$

B. Sketch a $d_{xy}$ orbital on the Cartesian coordinate axis provided. Place the signs of the lobes of the orbital appropriately. Show or describe the effect of each operation in the $C_{2v}$ point group on that orbital. To what representation does the $d_{xy}$ orbital belong?

\[ \begin{array}{c}
E \rightarrow +1 \\
C_2 \rightarrow +1 \\
\delta_{xz} \rightarrow -1 \\
\delta_{yz} \rightarrow -1 \\
\Rightarrow \quad A_2
\end{array} \]