Chemistry 4000
Introduction to Inorganic Chemistry: The Different Perspectives of Bonding

Problem Set #1 Answer Key

Introduction-

1. An appropriate pentadentate ligand will be accepted. A pentadentate ligand is one that can coordinate a metal at five different atoms/sites.

2. pH influences the M-L interactions. In this particular demonstration, at lower pH one or two of the ligands coordinated with the metal. At higher pH, three of the ligands saturated the coordination sites of the metal. Recall that both of these metal ions "prefer" a coordination number of 6.

Chapter 1-

1.
radial nodes = n-l-1
angular nodes = l

Nodes	3s	4p	3d	5f
Radial	2	2	0	1
Angular	0	1	2	3

2.a. Ti^{3+}: $[Ar]3d^1$, 1 unpaired e^-
2.b. Mn^{2+}: $[Ar]3d^5$, 5 unpaired e^-
2.c. Cu^{2+}: $[Ar]3d^9$, 1 unpaired e^-
2.d. Gd^{3+}: $[Xe]4f^7$, 7 unpaired e^-

3.a
3p: $(1s^2)(2s^2,2p^6)(3s^2,3p^3)$
$S = 0.35(4) + 0.85(8) + 1(2) = 10.2$
$Z^* = Z - S = 15 - 10.2 = $ **4.8**

3.b
4s: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^7)(4s^2)$
$S = 0.35(1) + 0.85(15) + 1(10) = 23.10$
$Z^* = Z - S = 27 - 23.10 = $ **3.9**

3.c
3d: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^5)$
$S = 0.35(4) + 1(18) = 19.40$
$Z^* = Z - S = 25 - 19.40 = $ **5.60**

3.d
3s: $(1s^2)(2s^2,2p^6)(3s^2)$

$S = 0.35(1) + 0.85(8) + 1(2) = 9.15$
$Z^* = Z - S = 12 - 9.15 = \textbf{2.82}$

4. Book problems
1.1

	$_{24}^{50}\text{Cr}$	$_{24}^{52}\text{Cr}$	$_{24}^{53}\text{Cr}$	$_{24}^{54}\text{Cr}$
Proton	24	24	24	24
Electron	24	24	24	24
Neutron	**26**	28	29	30

50 – Z = 50 – 24 = **26**

1.9
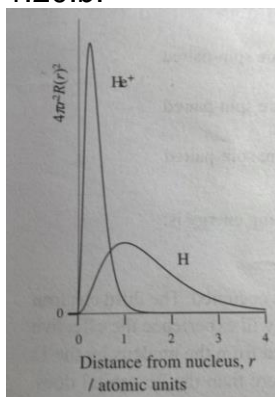
$1m = 10^9 nm$, $\bar{v} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) = \frac{1}{\lambda}$

$$\lambda = \left(R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)10^{-9}\right)^{-1} \Rightarrow n = {}^2\sqrt{\frac{1}{-1\left(\left(\lambda^{-1}(10^9)\frac{1}{R}\right) - \frac{1}{2^2}\right)}}$$

λ (nm)	n
656.28	3
486.13	4
434.05	5
410.17	6

1.20.a. The wave function value for the He^+ will differ of the H due to its Z value, so the plot of R(r) would be shifted to the left.

1.20.b.

The probability of finding an e^- close to the nucleus is higher.

1.34.a. The first ionization state tends to be relatively low and decrease while going down the periodic table due to the shielding effect and the probability of being further away from the nucleus.

1.34.b. Ionization energy for Al and downward is lower than B because the core electrons shield the valence electrons. This trend does not continue because of the poor shielding d and f orbitals.

1.34.c. The trend seems constant until atoms Mn and Zn. In the case of Mn, the electron removal is from the filled 4s orbital. For Zn the 4s3d are fully filled.

1.34.d. The trend is an increase in Z*. It is more difficult to ionize N than O because of the partial stability of the half-filled p orbitals.

1.34.e. Xe being a noble gas would need a high amount of energy to remove an electron from a fully occupied orbital. This energy is higher than that of Cs, which has a half filled s orbital.

1.34.f. Same logic as part e applies, P has a half-filled orbital stability.

1.40.a. See problem 1.34.e

1.40.b. While adding the first electron to O, the atom needs to liberate energy to accept the first electron but while adding the second electron, it feels the negative charge making a repulsion therefore making the negatively charged atom in need of energy to accept the second electron to overcome the repulsion.

1.40.c. The third electron would occupy the 2s instead of the 2p orbital because the 2s is a lower energy system as it is capable of penetrating the 1s orbital more than the 2p.

1.45.a. No other lines fall in the visible region of the electromagnetic radiation spectrum. You also may have weak emission lines. Also maybe some excited states are populated.

1.45.b. $v = \frac{c}{\lambda} = 5.09x10^{14}s^{-1}$

1.45.c. Once electrons are excited a photon emission of a specific energy can be released returning the electrons to the ground state.

Chapter 2-

1. Book problems

2.8. VB theory is better applied when taking in consideration atoms in the ground state. For Ne_2 to be under this theory there would have to be a missing electron per atom and energy would have to be applied for this. This theory does not make this molecule viable. Each Ne already has a filled octet.

2.14 .

	Isoelectronic	Valence electrons
F_2	$[O_2]^{2-}$	Cl_2
NH_3	$[H_3O]^+$	
$[GaBr_4]^-$		$SiBr_4$, $[GaCl_4]^-$
$[SH]^-$		$[OH]^-$
$[BH4]^-$	$[NH_4]^+$	
$[AsF_6]^-$	SeF_6	
$[PBr_4]^+$	$SiBr_4$	$[GaCl_4]^-$
HF	$[OH]^-$	

2.25.
a. Due to the two isotopes of Br (^{79}Br, ^{81}Br) Br_2 coexist as ($^{79}Br)_2$, ($^{81}Br)_2$ and ($^{79}Br^{81}Br$) therefore the MS spectrum peak of Br_2^+ can be m/z= 158, 162 or 160.

b. Br-Br intramolecular distance is 227pm and 331pm is the intermolecular distance.

c. Organizing an MO diagram for Br_2 and Br_2^+, in the Br_2^+, the electron is removed from an antibonding orbital making a higher bond order

2.26.

a. Preference is due to less steric hindrance for the CH_3 in the equatorial position (there being more spare, 120° vs. 90°) and because in VSEPR model the more electronegative ligands occupy axial positions.

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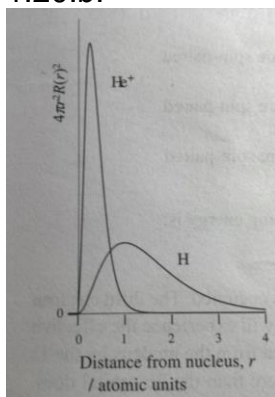|	$^{50}_{24}Cr$	$^{52}_{24}Cr$	$^{53}_{24}Cr$	$^{54}_{24}Cr$
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2.1. a. F_2

14 valence e^-

:$\ddot{F}$-$\ddot{F}$:

Need: 16 valence e^-

Have: $\underline{14 \text{ valence } e^-}$

$\dfrac{2 \text{ valence } e^-}{2}$ = 1 bond

14 - 2 e^- = 12 free e^-

b. BF_3

B: 3 valence e^-

3F: $\underline{3(7) \quad '' \qquad ''}$

24 $\quad '' \qquad ''$

Need: 30 valence e^- (B prefers 6)

$\dfrac{\underline{-24}}{6}$

$\dfrac{6}{2}$ = 3 bonds

24 - 6e^- = 18 e^- free

:$\ddot{F}$-B-$\ddot{F}$:
        |
      :$\ddot{F}$:
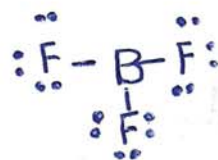
c. NH_3

N: 5 valence e^-

3H: $\underline{3(1)}$

8 $\quad '' \qquad ''$

Need: 14 e^-

$\underline{- 8 e^-}$

$\dfrac{6}{2}$ = 3 bonds

8 - 6 = 2 free e^-

H-$\ddot{N}$-H
     |
     H

d. H_2Se H–S̈e–H

e. H_2O_2
Need: 20 valence e^-
Have: 14 valence e^-
_____

$\frac{6}{2} = 3$

$14 - 6 = 8$ free e^-

H –Ö–Ö– H

f. $BeCl_2$

:C̈l–Be–C̈l:

g. SiH_4

$$\begin{array}{c} H \\ | \\ H–Si–H \\ | \\ H \end{array}$$
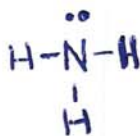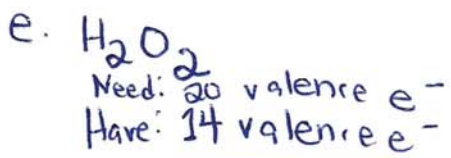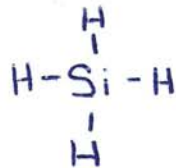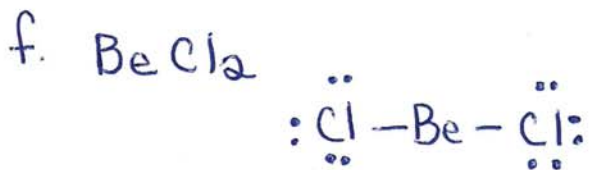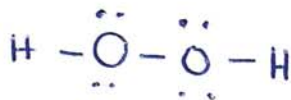
h. PF_5
↓
will expand its valency

40 valence e^- – 5(2e^-) = 30 free e^-

:F̈:
|
:F̈–P<F::
     \F::
|
:F̈:

2.3.

2.18. $\underline{S}OF_4$

↓
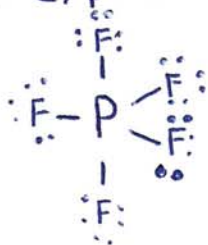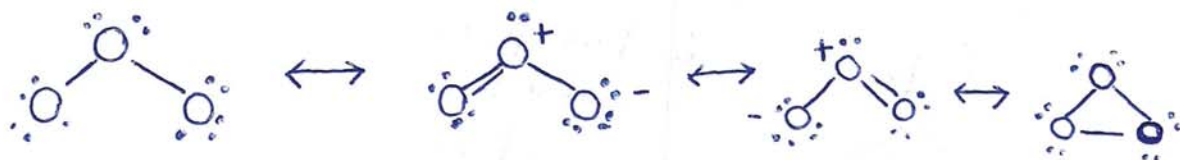
can expand its valency

40 valence e^- — $5(2e^-)$ = 30 free e^-

minimum
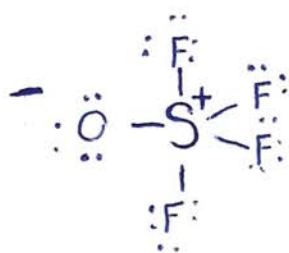
charge separation

∴
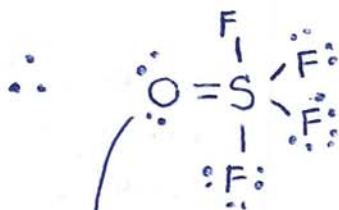
less X atom in equatorial position

a. S−F

b. S=O

19.

a. H_2S

polar
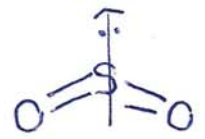
Steric # : 4
2 lone pairs
2 bonded pairs
Geometry: bent

b. CO_2:

$O = C = O$

Nonpolar

Steric # = 2
2 bonded pairs
Geometry: linear

c. SO_2

polar

Steric # = 3
1 lone pair
2 bonded pairs
Geometry: bent

d. BF_3

Steric # 3
3 bonded pairs
Geometry: Trigonal
Net dipole: 0
Nonpolar

Cancel out

e. PF_5

Geometry: Trigonal bipyramidal

Steric #: 5

5 bonded pairs

Nonpolar

$$F-P\overset{F}{\underset{F}{\overset{|}{\rightarrow}}}{}_{F}^{F}$$

f. cis- N_2F_2
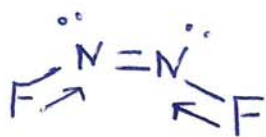
Steric # @ N: 3
2 bonded pairs

Bent geometry @ each N.

$$F\overset{\cdot\cdot}{\nearrow}\overset{\cdot\cdot}{N}=\overset{\cdot\cdot}{N}\underset{F}{\nwarrow}$$

Slightly polar

g. trans- N_2F_2

Bent geometry @ each N.

$$F\overset{\cdot\cdot}{\nearrow}\overset{\cdot\cdot}{N}=N\overset{\nearrow F}{\underset{\cdot\cdot}{}}$$

Non polar

h.

$$H-C\equiv N$$
$$\longleftarrow$$
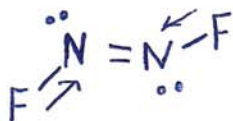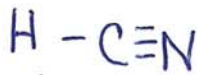
polar

Steric #: 2
2 bonded pairs

Geometry: Linear

2 N_2

N: [He] $2s^2 2p^3$

$\uparrow$ $\uparrow$ $\uparrow$
$2p$

$\uparrow\downarrow$
$\overline{\sigma_g (2p_z)}$

$\uparrow\downarrow$ $\uparrow\downarrow$
$\overline{\pi_u (2p_x)}$ $\overline{\pi_u (2p_y)}$

$\uparrow$ $\uparrow$ $\uparrow$
$2p$

$\uparrow\downarrow$
$2s$
N

$\uparrow\downarrow$
$\overline{\sigma_u * (2s)}$

$\uparrow\downarrow$
$\overline{\sigma_g (2s)}$

$\uparrow\downarrow$
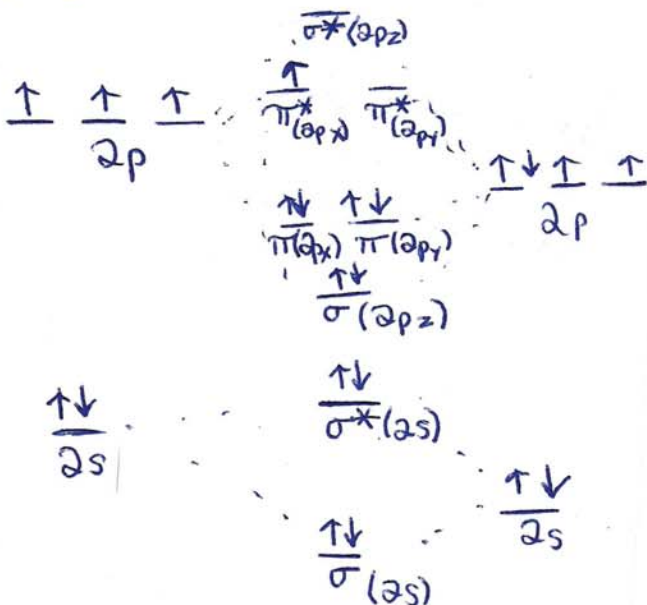$2s$
N
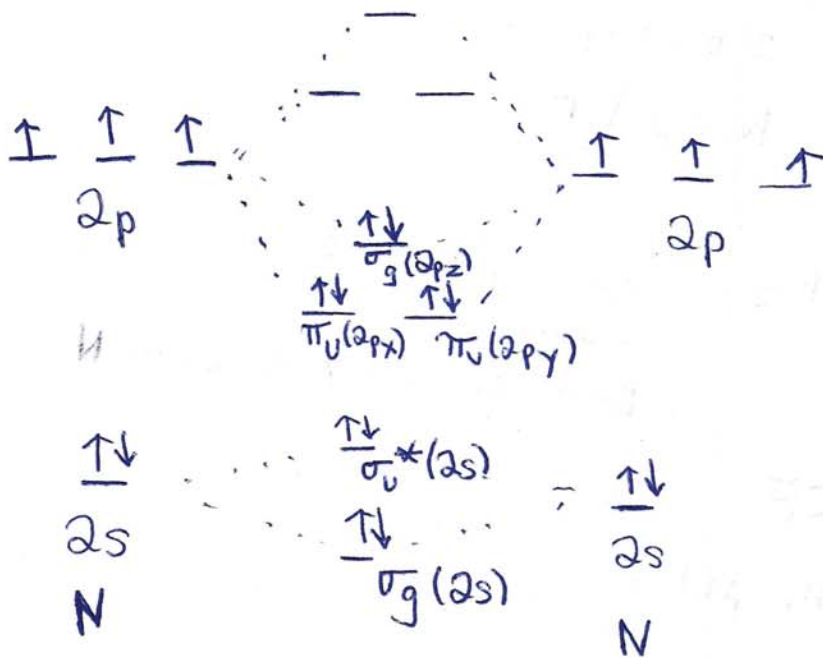
B.O. $= \frac{1}{2}(8-2) = 3$

Very high bond order and therefore should be inert.

NO

N: [He] $2s^2 2p^3$
O: [He] $2s^2 2p^4$

$\chi_O > \chi_N$

B.O $= \frac{1}{2}[8-3] = 2.5$

$\overline{\sigma * (2p_z)}$

$\uparrow$ $\uparrow$ $\uparrow$
$2p$

$\uparrow$
$\overline{\pi^*_{(2p_x)}}$ $\overline{\pi^*_{(2p_y)}}$

$\uparrow\downarrow$ $\uparrow\downarrow$
$\overline{\pi(2p_x)}$ $\overline{\pi(2p_y)}$

$\uparrow\downarrow$ $\uparrow$ $\uparrow$
$2p$

$\uparrow\downarrow$
$\overline{\sigma (2p_z)}$

$\uparrow\downarrow$
$2s$

$\uparrow\downarrow$
$\overline{\sigma * (2s)}$

$\uparrow\downarrow$
$2s$

$\uparrow\downarrow$
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