

Second Hour Exam**5.111**

Write your name below. **Do not open the exam until the start of the exam is announced.** The exam is closed notes and closed book.

1. Read each part of each problem carefully and thoroughly.
 2. Read all parts of each problem. **MANY OF THE LATTER PARTS OF A PROBLEM CAN BE SOLVED WITHOUT HAVING SOLVED EARLIER PARTS.** However, if you need a numerical result that you were not successful in obtaining for the computation of a latter part, make a physically reasonable approximation for that quantity (and indicate it as such) and use it to solve the latter parts.
 3. A problem that requests you to “calculate” implies that several calculational steps may be necessary for the problem’s solution. You must show these steps clearly and indicate all values, including physical constants used to obtain your quantitative result. Significant figure usage must be correct.
 4. If you don’t understand what the problem is requesting, raise your hand and a proctor will come to your desk.
 5. Physical constants, formulas and a periodic table are given on the last page. You may detach this page **once the exam has started.**
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Suggested time

1. 14 minutes (30 points) _____
2. 8 minutes (12 points) _____
3. 8 minutes (20 points) _____
4. 12 minutes (27 points) _____
5. 8 minutes (11 points) _____

Total (100 points) _____

Name _____

1. (30 points) Lewis structures and VSEPR theory

Draw the **most stable** Lewis structure for each of the following molecules, subject to the information given for each. Be sure to **include the lone pairs** and, if applicable, draw any **resonance forms** that are equal in energy. **Indicate any nonzero formal charges.**

(a) (i) (6 points) Draw the Lewis structure of POCl_3 . Include any relevant resonance forms, and indicate any nonzero formal charges.

(ii) (2 points) Name the geometry around the phosphorus atom.

(b) (8 points) Draw the Lewis structure of $(\text{NCNH})^{-1}$ (atom order as indicated). Include any relevant resonance forms, and indicate any nonzero formal charges.

(c) (i) (6 points) Draw the Lewis structure of $(\text{SO}_3)^{-2}$. Include any relevant resonance forms, and indicate any nonzero formal charges.

(ii) (2 points) Name the geometry around the sulfur atom.

(iii) (3 points) Circle the one value that best describes the O-S-O bond angle in $(\text{SO}_3)^{-2}$.

< 90°; 90°; > 90°; < 109.5°; 109.5°; > 109.5°; < 120°; 120°; > 120°; < 180°; 180°; > 180°

(iv) (3 points) Is $(\text{SO}_3)^{-2}$ a **polar** or a **non-polar** molecule?

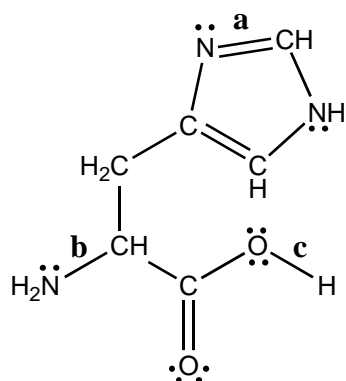
2. (12 points) Ionic bonds

KF has an ionic bond with a bond length of 0.217 nm. Calculate the ΔE , in kJ/mol, for the **formation** of a KF bond from the neutral atoms K and F. For this calculation, assume that the potassium and fluorine ions are point charges. IE and EA information for K and F is provided in the table below.

	Ionization energy (kJ/mol)	Electron affinity (kJ/mol)
potassium (K)	418	48
fluorine (F)	1680	328

3. (20 points) **Hybridization**

(a) (12 points) The structure of the amino acid histidine is provided below. For the indicated bonds, a-c, write the symmetry of each bond, and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form each of the bonds. Where appropriate, include the x, y, or z designations with the orbitals.



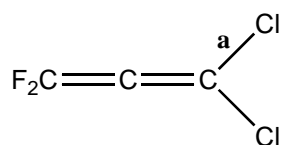
N-C bond a:

N-C bond b:

O-H bond c:

(b) (8 points)

(i) For the molecule below, indicate the symmetry in the C-Cl bond (labeled **a**), and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form the bond. If appropriate, include the x, y, or z designations with the orbitals.



C-Cl bond a:

(ii) Do the chlorine atoms in the F₂C=C=CCl₂ molecule above lie in the **same plane** as the fluorine atoms or in a **perpendicular plane** to the fluorine atoms? Briefly explain your answer (with words or a picture).

4. (27 points) Molecular orbital theory

(a) (21 points)

(i) (9 points) Draw an energy correlation diagram for the molecular orbitals of the **valence electrons** in CN. Label the atomic and molecular orbitals, including the x, y and z designations where appropriate. The relative ordering of the energies of the states must be correct. **Use the full space available** to spread out your energy levels so that the labels for the orbitals fit easily.

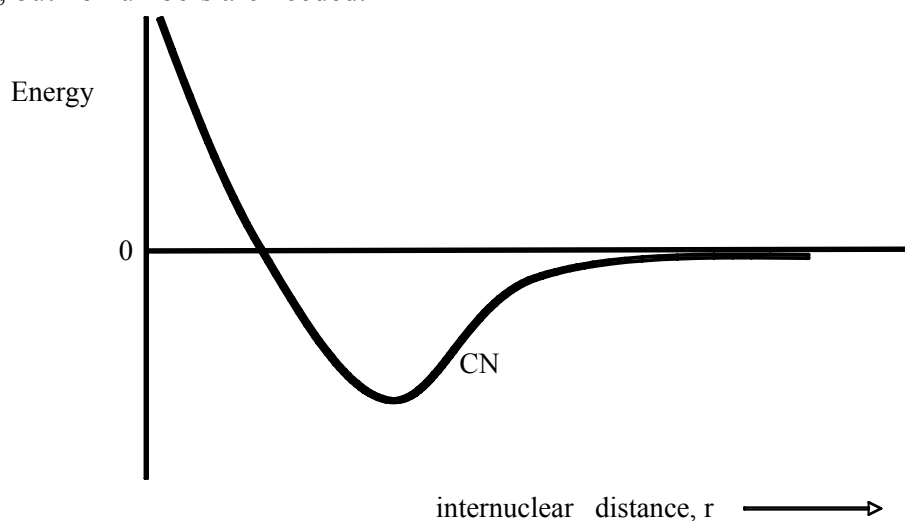
(ii) (2 points) Of the CN molecular orbitals **occupied by valence electrons**, name the orbitals that have a nodal plane along the internuclear (bond) axis.

(ii) (4 points) Determine the bond order of the cyanide molecule, CN, *and* the cyanide **ion**, CN^{-1} .

BO of CN:

BO of CN^{-1} :

(iii) (4 points) Below is an energy diagram of the CN covalent bond in a neutral CN molecule. On the same graph, plot the energy vs. internuclear distance, r , of the CN covalent bond in a CN^{-1} **ion**. Indicate the equilibrium bond distances with arrows. The **relative** values of the bond distances and energies must be correct, but no numbers are needed.



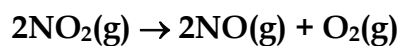
(iv) (2 points) Which of the following are radical species: CN, CN^{-1} , both, or neither?

(b) (6 points)

Write the **valence** electron configuration for O_2 .

5. (11 points) Thermochemistry

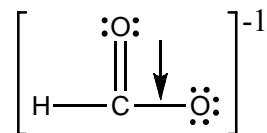
(a) (7 points) Consider the reaction below for the conversion nitrogen dioxide to nitric oxide and O₂.



	ΔH_f° (kJ/mol)
NO ₂ (g)	+33.18
NO(g)	+90.25

Calculate ΔH° (per mol of O₂ formed) for the reaction at 298 K.

(b) (4 points) Using the table of mean bond enthalpies provided, predict the bond enthalpy (in kJ/mol) for the CO bond marked with an arrow in the molecule below.



Bond	Mean Bond Enthalpy (in kJ/mol)
C-H	412
C-C	348
C=C	612
C-O	360
C=O	743

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 ^a
IA	IIA	IIIB	IVB	VB	VIB	VIIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA ^b
<div><div>The Active Metals</div><div><div>1</div><div>H</div><div>1.008</div></div><div><div>3</div><div>Li</div><div>6.941</div></div><div><div>11</div><div>Na</div><div>22.990</div></div><div><div>19</div><div>K</div><div>39.098</div></div><div><div>37</div><div>Rb</div><div>85.468</div></div><div><div>55</div><div>Cs</div><div>132.905</div></div><div><div>87</div><div>Fr</div><div>(223)</div></div></div> <div><div>4</div><div>Be</div><div>9.012</div></div> <div><div>12</div><div>Mg</div><div>24.305</div></div> <div><div>20</div><div>Ca</div><div>40.08</div></div> <div><div>38</div><div>Sr</div><div>87.62</div></div> <div><div>56</div><div>Ba</div><div>137.33</div></div> <div><div>88</div><div>Ra</div><div>226.025</div></div>																	
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2

He

4.003

10

Ne

20.179

18

Ar

39.948

36

Kr

83.80

86

Rn

(222)

The Nonmetals

5

B

10.81

13

Al

26.982

31

Ga

69.72

49

In

114.82

81

Tl

204.38

6

C

12.011

14

Si

28.086

32

Ge

72.59

50

Sn

118.69

82

Pb

207.2

7

N

14.007

15

P

30.974

33

As

74.922

51

Sb

121.75

83

Bi

208.98

8

O

15.999

16

S

32.06

34

Se

78.96

52

Te

127.60

84

Po

(209)

9

F

18.998

17

Cl

35.453

35

Br

79.904

53

I

126.904

85

At

(210)

Transition Elements

25

Mn

54.938

26

Fe

55.847

27

Co

58.933

28

Ni

58.69

29

Cu

63.546

30

Zn

65.38

43

Tc

(98)

44

Ru

101.07

45

Rh

102.906

46

Pd

106.42

47

Ag

107.868

48

Cd

112.41

75

Re

186.21

76

Os

190.2

77

Ir

192.22

78

Pt

195.08

79

Au

196.966

80

Hg

200.59

72

Hf

178.49

73

Ta

180.948

74

W

183.85

104

Unq

(261)

105

Unp

(262)

106

Unh

(263)

Inner Transition Metals

58

Ce

140.12

59

Pr

140.908

60

Nd

144.24

61

Pm

(145)

62

Sm

150.36

63

Eu

151.96

64

Gd

157.25

65

Tb

158.925

66

Dy

162.50

67

Ho

164.930

68

Er

167.26

69

Tm

168.934

70

Yb

173.04

71

Lu

174.967

90

Th

232.038

91

Pa

231.036

92

U

238.029

93

Np

237.048

94

Pu

(244)

95

Am

(243)

96

Cm

(247)

97

Bk

(247)

98

Cf

(251)

99

Es

(252)

100

Fm

(257)

101

Md

(258)

102

No

(259)

103

Lr

(260)

* Lanthanides

† Actinides

$$c = 2.99792 \times 10^8 \text{ m/s}$$

$$h = 6.62608 \times 10^{-34} \text{ J s}$$

$$N_a = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$$

$$m_e = 9.10939 \times 10^{-31} \text{ kg}$$

$$e = 1.60218 \times 10^{-19} \text{ C}$$

$$U(r) = (z_1 z_2 e^2) / (4\pi\epsilon_0 r)$$

$$\epsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2/(\text{Jm})$$

$$\text{Electronegativity} = (IE + EA)/2$$

$$\Delta G = \Delta H - T\Delta S$$

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5.111 Principles of Chemical Science
Fall 2008

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