CHEM-457: Inorganic Chemistry

Midterm II – April 17th, 2014

NAME_____

This exam is comprised of five questions and is 13 pages in length. Please be sure that you have a complete exam and place your name on each page.

Answer each question to the best of your ability. Partial credit will be awarded where appropriate. You are not permitted to use any supplemental materials other than what is included in this test booklet. Calculators are not needed and their use is not permitted for this exam. **PLEASE DO NOT REMOVE ANY PAGES FROM THIS EXAM EXCEPT FOR THE TWO APENDICIES**.

Write all your answers directly in this test booklet and show all work where necessary.

Good Luck!

1. _____ (12 pts)
2. _____ (20 pts)
3. _____ (10 pts)
4. _____ (24 pts)
5. _____ (34 pts)

Total _____

Name: _____

1. **(12 Total Points)** Please give definitions and an example for each of the following (1 point for each definition & 1 point for each example).

   (a) Arrhenius Acid

   (b) Arrhenius Base

   (c) Brønsted-Lowry Acid

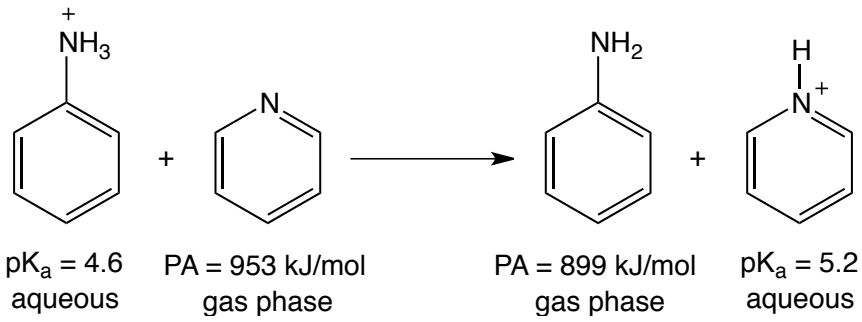
   (d) Brønsted-Lowry Base

   (e) Lewis Acid

   (f) Lewis Base

Name: _____

2. **(20 Total Points)** Consider the following proton transfer reaction and corresponding proton affinities. For this problem, you may assume that entropic factors are negligible such that $\Delta G° \approx \Delta H = \Delta PA$.



(a) (3 Points) Is the above reaction spontaneous in aqueous solution? Please explain you answer.

(b) (3 Points) Is the above reaction complete in aqueous solutions? Please explain you answer.

(c) (8 Points) Determine the free energy change for the proton transfer in the gas phase. Is the above reaction spontaneous in the gas phase? Please explain your answer?

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(d) (3 Points) Which of the four species in the acid-base reaction will be best solvated/stabilized in water? Please explain your answer.

(e) (3 Points) Do you predict the gas phase proton affinity of N,N-dimethylaniline (Ph–NMe_2) to be larger or smaller than that of aniline? Please explain your answer.

Name: _____

3. **(10 Total Points)** The sol-gel synthesis of oxide materials is accomplished using hydrated metal ions such as that of titanium.

$$[Ti(OH_2)_6]^{4+} + H_2O \rightarrow [Ti(OH_2)_5(OH)]^{3+} + H_3O^+$$

(a) (4 Points) Label each of the four species in the above reaction as either an acid or base. Please place your labels directly in the boxes below.

Reactants		**Products**	
$[Ti(OH_2)_6]^{4+}$	H_2O	$[Ti(OH_2)_5(OH)]^{3+}$	H_3O^+

(b) (4 Points) Using hard-soft acid base principles, explain whether H_2O or OH^- will be a better base toward Ti^{4+}.

(c) (2 Points) Do you expect the equilibrium constant (*K*) for the above reaction to be greater than or less than 1.0? Please explain your answer.

Name: _____

4. **(24 total points)** Nitric oxide, which has the chemical formula NO, is a gaseous molecule that functions as a vasodilator in mammals.

   (a) (8 Points) Prepare a molecular orbital energy level diagram for NO. Please be sure to label all atomic orbitals and all molecular orbitals. Please be sure to provide sketches that clearly show how the atomic orbitals interact to form MOs. (Note: you may find the table of *Atomic Orbital Ionization Energies* on page 13 of this exam to be useful in constructing your MO diagram).

Name: _____

(b) (2 points) How does your diagram illustrate the difference in electronegativity between N and O?

(c) (4 points) What are the bond order and multiplicity of NO?

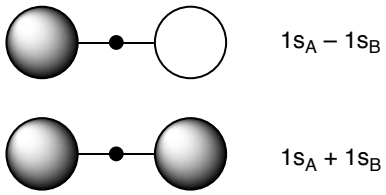
Name: _____

(d) (4 Points) NO^+ and NO^- are also known species. Calculate the bond orders of these species and compare these values with that of NO. Which of these three species would you predict to have shortest bond? Please explain your answer.

(e) (6 points) The ion NO^- can react with H^+ to form a chemical bond. Do you expect this protonation to occur on the oxygen or nitrogen atom of NO^-? Do you expect this acid-base adduct to be linear or bent? Please explain your reasoning.

Name: _____

5. **(34 Total Points)** In this problem, let us consider the bonding for methylene (CH_2) using both the 2s and 2p valence orbitals of C and symmetry adapted linear combinations (SALCs) of H 1s orbitals as the basis set. The two H-atom SALCs are illustrated below.

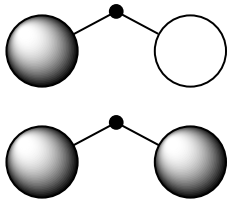


(a) (12 Points) Prepare a molecular orbital energy level diagram for CH_2 in a ***linear*** geometry. Please be sure to label all atomic orbitals, SALCs and molecular orbitals. Please be sure to provide sketches of the group orbitals and clearly show how they interact with the appropriate orbitals on carbon to form MOs. (Note: you may find the table of *Atomic Orbital Ionization Energies* on page 13 of this exam to be useful in constructing your MO diagram).

(b) (2 Points) What is the bond order of linear methylene? Is this species diamagnetic or paramagnetic?

Name: _____

(c) (12 Points) Prepare a molecular orbital energy level diagram for CH_2 in a ***bent*** geometry. The appropriate two H-atom SALCs are illustrated below. Please be sure to label all atomic orbitals, SALCs and molecular orbitals. Please be sure to provide sketches of the group orbitals and clearly show how they interact with the appropriate orbitals on carbon to form MOs. (Note: you may find the table of *Atomic Orbital Ionization Energies* on page 13 of this exam to be useful in constructing your MO diagram).



(d) (2 Points) What is the bond order of bent methylene? Is this species diamagnetic or paramagnetic?

Name: _____

(e) (6 Points) Based on your MO diagrams for linear and bent methylene, which geometry of this species do you expect to be more stable? Please explain your answer.

PERIODIC TABLE OF THE ELEMENTS

1 H 1.0079																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.179
11 Na 22.9898	12 Mg 24.305											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.905	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)									

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)	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)

Name: _____

Name: _____

Atomic Orbital Ionization Energies (eV)

Valence Level	Element	1s	2s	2p	3s	3p	4s	4p
1	H	–13.6						
1	He	–24.5						
2	Li		–5.45					
2	Be		–9.30					
2	B		–14.0	–8.30				
2	C		–19.5	–10.7				
2	N		–25.5	–13.1				
2	O		–32.3	–15.9				
2	F		–46.4	–18.7				
2	Ne		–48.5	–21.5				
3	Na				–5.21			
3	Mg				–7.68			
3	Al				–11.3	–5.95		
3	Si				–15.0	–7.81		
3	P				–18.7	–10.2		
3	S				–20.7	–11.7		
3	Cl				–25.3	–13.8		
3	Ar				–29.2	–15.9		
4	K						–4.34	
4	Ca						–6.07	
4	Zn						–9.42	
4	Ga						–12.6	–5.95
4	Ge						–15.6	–7.56
4	As						–17.6	–9.05
4	Se						–20.8	–10.8
4	Br						–24.0	–12.5
4	Kr						–27.5	–14.3

Valence Level	Element	1s	2s	2p
4	Sc	–4.71	–5.70	–3.22
4	Ti	–5.58	–6.07	–3.35
4	V	–6.32	–6.32	–3.47
4	Cr	–7.19	–6.57	–3.47
4	Mn	–7.93	–6.82	–3.59
4	Fe	–8.68	–7.07	–3.72
4	Co	–9.42	–7.32	–3.84
4	Ni	–10.0	–7.56	–3.84
4	Cu	–10.7	–7.69	–3.97