Name (**in ink**) ANSWER KEY

Student Number (**in ink**) _____

Fall 2014 SC/CHEM 1000 A - Quiz #3

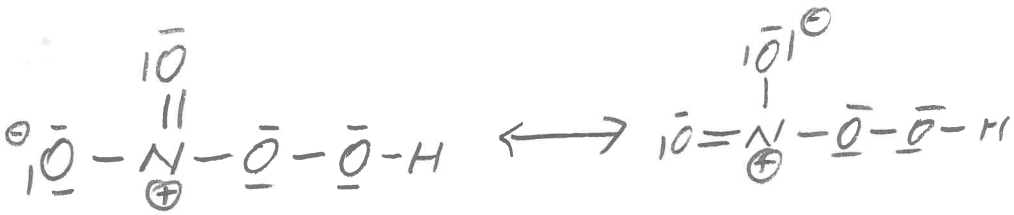
November 20, 2014

Calculators are permitted.
Answer all questions on this paper; **additional paper for rough work is not permitted. You may carry out your work in pencil if you wish, but please write your final answer in ink.**

Assume all gases to be ideal unless otherwise noted

Time Allowed: 50 minutes **Total Marks = 30**

1. **(5 pts)** Peroxynitric acid, HNO_4, is a powerful oxidizing agent formed from the products of air breathing engines, as in automobiles, and is believed to be involved in the production of ozone in the lower atmosphere – a major air pollutant. Draw the most plausible Lewis structure for HNO_4, making sure to indicate all lone pairs and formal charges on each atom. If there are any resonance structures, you must draw them too.

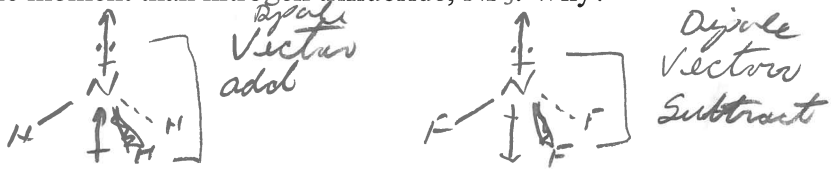


2. **(1 pt each)** BRIEFLY explain each of the following.

(a) Formaldehyde, $H_2C{=}O$, is a common, stable gas, yet the silicon analogue, $H_2Si{=}O$, does not exist and cannot be made. Why?

Si cannot form double Bonds

(b) An N-F bond is much more polar than an N-H bond, yet ammonia, NH_3, has a much greater dipose moment than nitrogen trifluoride, NF_3. Why?



(c) Tetrachlorosilane, $SiCl_4$, has a dipole moment of zero, even though the Si-Cl bond is highly polar. Why?

Td geometry ⇒ all dipole Vectors Cancel

(d) VSEPR theory incorrectly predicts the structure of methyl radical, CH_3. Why is this not surprising?

VSEPR is based on electron PAIR Repulsions.

CH_3 has an unpaired e^-

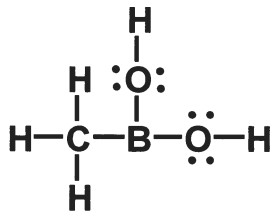
(e) Hypervalence is common in elements having principle quantum number >2, but never found in first-row atoms such as carbon, nitrogen and oxygen. Why not?

First-Row atoms do not have accessible d-orbitals

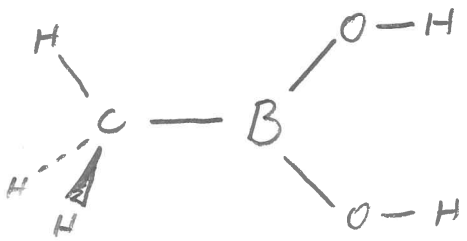
(f) Hypervalence in elements such as sulfur and phosphorus is usually observed when three or more highly electronegative elements are attached (such as oxygen or fluorine). Why are attached electronegative atoms necessary for hypervalence?

To lower the d-orbital energies into the bonding region

3. Methylboronic acid, $CH_3B(OH)_2$, is a reagent used extensively in the pharmaceutical industry. The Lewis structure for $CH_3B(OH)_2$ is shown below.



(a) **(3 pts)** Using VSEPR theory, draw the 3-dimensional shape of the $CH_3B(OH)_2$ molecule, making sure to clearly express the 3-dimensionality using traditional dotted and wedged lines.



(b) **(1/2 pt each)** Referring to your drawing, please indicate (to within ±5 degrees) the following bond angles

O-B-O 120°

H-O-B 109°

H-C-H 109°

(c) **(1/2 pt each)** Referring to the Lewis diagram for $CH_3B(OH)_2$, please indicate the atomic orbital hybridization for

B sp^2

O sp^3

C sp^3

4. (a) **(4 pts)** Using the table of bond energies included in this quiz, estimate the ΔH_f^0 for nitrogen dioxide (NO_2) gas, via the following equation,

$$\tfrac{1}{2}\, N_2(g) + O_2(g) \rightarrow NO_2(g)$$

In estimating the enthalpy you don't need to include the $\Delta(PV)$ term, as it makes only a negligible contribution. The Lewis structures for each species (with any resonance structures omitted) are shown below.

Break

$\frac{1}{2}$ N≡N $+\frac{1}{2}(946)$

1 O=O $+498$

$+971$

Make

1 N–O -222

1 N=O -590

-812

$+159$ kJ

$\Delta H_f^0(EST) = +159\ kJ\ mol^{-1}$

(b) **(2 pts)** If you did part (a) correctly, the experimental enthalpy of formation for $NO_2(g)$ is WAY different from your estimate (by more than 120 kJ mol^{-1}). Without doing any further calculations, explain (briefly) why the estimate based on bond energies is so inaccurate.

Because NO_2 has a resonance structure

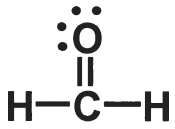
The stabilization due to Resonance is not considered in the estimate.

(c) **(1 pt)** Based on your explanation in part (b), indicate whether you expect the estimated ΔH_f^0 to be greater than, or less than, the experimental ΔH_f^0.

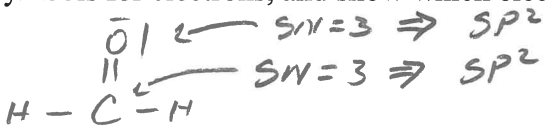
I'd expect $\Delta H_f^0(EST) > \Delta H_f^0(EXP)$

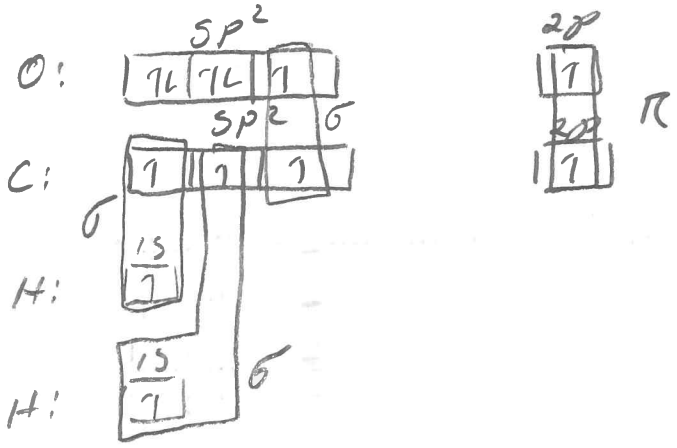
[and it is. $\Delta H_f^0(EXP) = +33\ kJ\ mol^{-1}$]

5. Formaldehyde has the Lewis structure



(a) **(5 pts)** Please draw the valence-bond diagram for formaldehyde below, making sure to label all hybrid orbitals and any unhybridized atomic orbitals. Use the conventional half-arrow symbols for electrons, and show which electrons are shared to form the bonds.





(b) **(1 pt)** Referring to your Lewis structure, what is the bond order between carbon and oxygen?

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