Chem 341
Inorganic Chemistry
Midterm Exam #2, Fall 2000

NAME: _____

- Calculators and model sets are the only aids allowed for this exam. Periodic and character tables are provided at the end of the exam (feel free to separate and keep in front of you).
- Partial marks will be rewarded where applicable, so be sure to show all your work and explain your answers.
- **There are four questions, worth 24, 19, 20 and 17 marks, respectively, for a maximum possible score of 80. Spend an appropriate amount of time on each question.**
- Duration: 60 minutes.

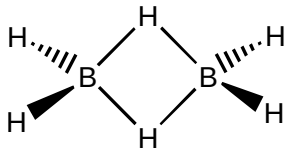
Some potentially useful constants:

$h = 6.626 \times 10^{-34}$ J·s	$c = 3.00 \times 10^{8}$ m·s^{-1}
$N_A = 6.022 \times 10^{23}$ mol^{-1}	$e = 1.602 \times 10^{-19}$ C
$F = e \cdot N_A = 9.649 \times 10^{4}$ C·mol^{-1}	$m_p = 1.673 \times 10^{-27}$ kg
$m_e = 9.109 \times 10^{-31}$ kg	$k = 1.381 \times 10^{-23}$ J K^{-1}
$\pi \simeq 3.1416$	e = the natural number $\simeq 2.718$

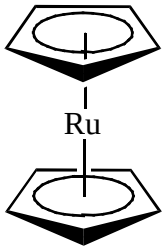
$R = 0.08206$ L·atm·K^{-1}·mol^{-1} $= 8.314$ J·K^{-1}·mol^{-1} $= 8.314$ V·C·K^{-1}·mol^{-1}

1. Give the point groups of the following (you don't need to list the symmetry elements, you can just give the point group). [3 marks each, 24 total]

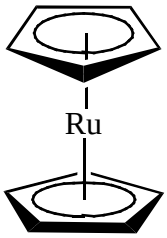
(a) Diborane, Bi_2H_6



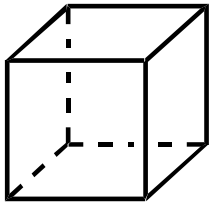
(b) $Ru(C_5H_5)_2$, eclipsed rings



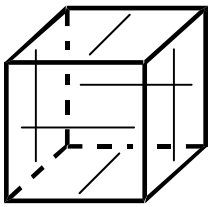
(c) $Ru(C_5H_5)_2$, staggered rings



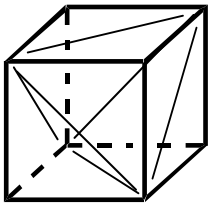
(d) A perfect cube



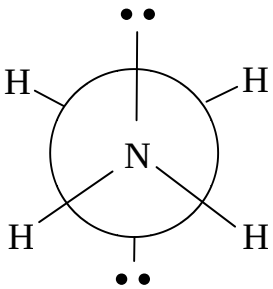
(e) A cube with a line (of equal length) on each face, as shown below:



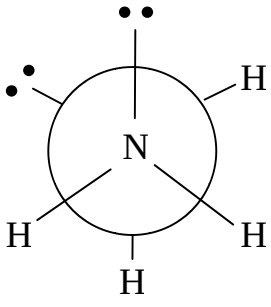
(f) The cube in part e, but with the lines rotated clockwise (wrto the outside of the cube) by 45°:



(g) $H_2N\text{-}NH_2$, where the two lone pairs of the N's are staggered wrto the z-axis. Give the geometry wrto each N.



(h) $H_2N\text{-}NH_2$, gauche conformation



(2) The vibrational symmetries of the inorganic compound phosphoryl chloride, $POCl_3$, are $\Gamma_{Vib} = 3A_1 + 3E$. [19 marks total for this question]

(a) What is the point group, and how many peaks would you expect in the IR spectrum and the Raman spectrum, for this compound? [8 marks]

(b) Which of the above Γ_{Vib} vibrations involve change in bond lengths, $\Gamma_{stretch}$, and change in bond angles, $\Gamma_{deformation}$? [7 marks]

(c) One of the $\Gamma_{stretch}$ vibrations involves only the P-Cl bond. What is the wavenumber of this IR absorption, in cm^{-1}, if the force constant of the bond is 296 $kg \cdot s^{-2}$ and the effective mass is 2.75×10^{-26} kg? [4 marks]

(3) [20 marks total for this question] Given the following two reduction reactions:

$FeCO_{3(s)} + 2e^- \Leftrightarrow Fe_{(s)} + CO_3^{2-}{}_{(aq)}$ $E° = -0.756V$ [1]

$Fe^{2+}{}_{(aq)} + 2e^- \Leftrightarrow Fe_{(s)}$ $E° = +0.400V$ [2]

(a) In which direction is each of the above equilibria, as written, favoured? [2 marks]

(b) Write the two half-reactions for the dissolution of solid ferrous carbonate, and identify the redox couples, oxidizing agent and reducing agent involved in the redox reaction. [6 marks]

(c) What is the solubility product, K_{sp}, for the dissolution of ferrous carbonate? [8 marks]

(d) What is the standard change in free energy, $\Delta G°$, for the dissolution of ferrous carbonate? [4 marks]

(4) Acids and Bases. [17 total marks for this question]

(a) Predict whether the K_{eq} for the following reaction will be greater than or less than unity, and state your reason(s): [3 marks]

$$CdI_{2(s)} + CaF_{2(s)} \Leftrightarrow CdF_{2(s)} + CaI_{2(s)}$$

(b) For aqua acids with a heavy, p-block metal centre, such as Pb^{2+}, what happens to pK_a, as compared to that predicted by the ionic (electrostatic) model, and why? [4 marks]

(c) Give two reasons why phosphoric acid is weaker than sulfuric acid. Using Pauling's Rules, give the acid constants for phosphoric acid. [6 marks]

(d) For a given solvent, what is the pK_a range that is useful for studying a given acid or base? In words, what is the explanation for this phenomenon? [4 marks]

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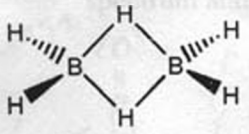

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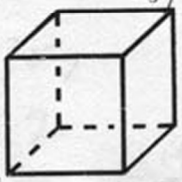

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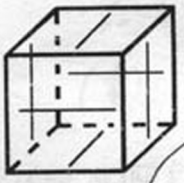

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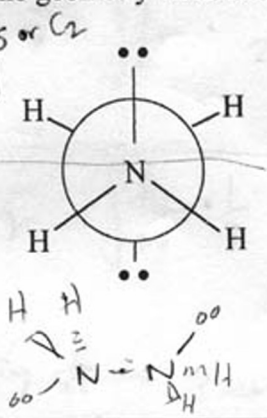

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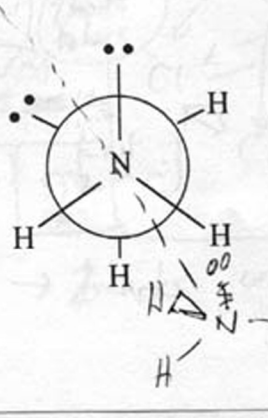
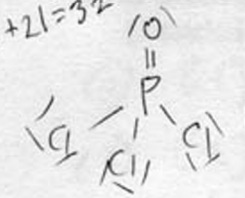


4!

(2) The vibrational symmetries of the inorganic compound phosphoryl chloride, $POCl_3$, are $\Gamma_{Vib} = 3A_1 + 3E$. [19 marks total for this question]

(a) What is the point group, and how many peaks would you expect in the IR spectrum and the Raman spectrum, for this compound? [8 marks]

5+6+21=32

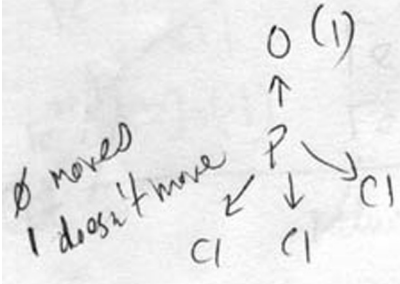


C_{3v} (4), All IR ≠ Raman-active (2) ⇒ 6 bands for each spectrum (2)

9 ≠ 9 (−1)

6 ≠ 9 (12) (−½)

(b) Which of the above Γ_{Vib} vibrations involve change in bond lengths, $\Gamma_{stretch}$, and change in bond angles, $\Gamma_{deformation}$? [7 marks]



C_{3v} | E | $2C_3$ | $3\sigma_v$

4 | 1 | 2 (3)

2 −1 0 (E)

2 2 2 (2A)

4 1 2

∅ moved
1 does if move

⇒ $\Gamma_{str} = 2A_1 + E$ (2)

$\therefore \Gamma_{def} = (3A_1 + 3E) - (E + 2A_1) = A_1 + 2E$ (1)

4 −2 0 (2E)
2 2 2 (2A)
6 0 2

Also, (Takes 6 bonds)

E | $2C_3$ | $3\sigma_v$

6 | 0 | 2 ⇒

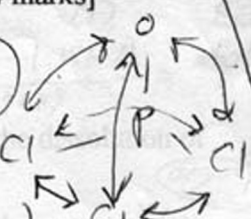
$2E + 2A_1$ ⇓ $\Gamma_{Vib} = 4A_1 + 3E$

(c) One of the $\Gamma_{stretch}$ vibrations involves only the P-Cl bond. What is the wavenumber of this IR absorption, in cm^{-1}, if the force constant of the bond is 296 $kg \cdot s^{-2}$ and the effective mass is 2.75×10^{-26} kg? [4 marks]

P-Cl

$\tilde{\nu} = \sqrt{\frac{k}{m}} \cdot \frac{1}{2\pi c} = \frac{1.04 \times 10^{14}\ s^{-1}}{2\pi \times 3.0 \times 10^{8}\ m/s} = 55,174\ m^{-1} \times \frac{1\ m}{100\ cm}$ (2 marks to here)

$= 5517.4\ cm^{-1}$ (−1 if in m^{-1})



$\tilde{\nu} = \sqrt{\frac{k}{m}} \cdot \frac{1}{2} \pi c$ → 1 mark

$\omega = \sqrt{\frac{k}{m}}$ only → 2 marks $\omega = \sqrt{\frac{296\ kg \cdot s^{-2}}{2.75 \times 10^{-26}\ kg}} = \sqrt{1.08 \times 10^{28}\ s^{-2}} = 1.04 \times 10^{14}\ s^{-1}$

missing $\frac{1}{2\pi}$ → 3 marks

(3) [20 marks total for this question] Given the following two reduction reactions:

$FeCO_{3(s)} + 2e^- \Leftrightarrow Fe_{(s)} + CO_3^{2-}{}_{(aq)}$ $E^\circ = -0.756V$ [1]

$Fe^{2+}{}_{(aq)} + 2e^- \Leftrightarrow Fe_{(s)}$ $E^\circ = +0.400V$ [2]

Harris p. 321 wrong. $E^\circ = -0.400V$

(a) In which direction is each of the above equilibria, as written, favoured? [2 marks]

(1) [1] to the left

(1) [2] to the right

This isn't a redox rxn. +6 to all exams?

(b) Write the two half-reactions for the dissolution of solid ferrous carbonate, and identify the redox couples, oxidizing agent and reducing agent involved in the redox reaction. [6 marks]

(2) Fe^{2+}/Fe^0 [1]

Fe^{2+}/Fe^0 [2] x(-1)

(1) oxidizing agent, or Fe^{2+}

(1) $FeCO_3(s) + 2e^- \rightleftharpoons Fe(s) + CO_3^{2-}{}_{(aq)}$ $E^\circ = -0.756$ V

(1) $Fe(s) \rightleftharpoons Fe^{2+}{}_{(aq)} + 2e^-$ $E^\circ = -0.400$ V

reducing agent (1)

"a number" ... +8 for all exams?

(c) What is the solubility product, K_{sp}, for the dissolution of ferrous carbonate? [8 marks]

$\Delta G^\circ = -RT\ln K$ 1 mark

$K_{sp} = [Fe^{2+}][CO_3^{2-}]$ 1 mark

$E = E^\circ - \frac{RT}{nF}\ln Q$ 2 marks

(2) $FeCO_3(s) \rightleftharpoons Fe^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$, $E^\circ = -1.156$ V

$\Delta G^\circ = -nFE^\circ = -RT\ln K$ $K = \exp\left(\frac{\Delta G^\circ}{RT}\right)$ $E = 0 = E^\circ - \frac{RT}{nF}\ln K$

(3) $K = \exp\left(\frac{nFE^\circ}{RT}\right)$

$= \exp\frac{(2)(9.649\times10^4\ C\cdot mol^{-1})(-1.156V)}{(8.314\ J\cdot K^{-1}\cdot mol^{-1})(298\ K)}$ (1) (1)

$= \exp(-89.575)$

$= 8.31\times10^{-40}$ or 1.265×10^{-40}

(d) What is the standard change in free energy, ΔG°, for the dissolution of ferrous carbonate? [4 marks]

(2 marks)

$\Delta G^\circ = -nFE^\circ = -2(9.649\times10^4\ C\cdot mol^{-1})(-1.156V)$

$= 2.23\times10^5\left(\frac{CV}{mol}\right)$

$\frac{CV}{mol}$: -1

2.1×10^{-11}

$\Delta G = \Delta G^\circ + RT\ln Q$ (1 mark)

$(-2)(9.649\times10^4\ \frac{C}{mol})(-0.756V) = 68{,}701\ J$ $\frac{J}{mol}$

(4) Acids and Bases. [17 total marks for this question]

(a) Predict whether the K_{eq} for the following reaction will be greater than or less than unity, and state your reason(s): [3 marks]

$$CdI_{2(s)} + CaF_{2(s)} \Leftrightarrow CdF_{2(s)} + CaI_{2(s)}$$

(1) less than unity,
(1) since soft Cd^{2+} acid prefers soft I^- base.
(1) & " hard Ca^{2+} " " hard F^- base.
or big en diff for CaF

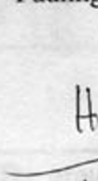
(b) For aqua acids with a heavy, p-block metal centre, such as Pb^{2+}, what happens to pK_a, as compared to that predicted by the ionic (electrostatic) model, and why? [4 marks]

Text (1) ↓r (1) charge ↑(1) Pb^{2+}, softer, more covalent bonding, spreads +ve charge to H_2O ligands, repels H^+, ↑ K_a, (1)

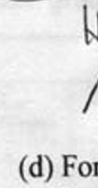
↓ pKa (1)

(c) Give two reasons why phosphoric acid is weaker than sulfuric acid. Using Pauling's Rules, give the acid constants for phosphoric acid [6 marks]

(2)

H_3PO_4  $p=1 \Rightarrow pKa = 8-5(1) = 3$, 8, 13

3 (1)

H_2SO_4  $p=2 \Rightarrow pKa = 8-5(2) = -2$

Also, S smaller, (1) repels H^+ more than P.

(d) For a given solvent, what is the pK_a range that is useful for studying a given acid or base? In words, what is the explanation for this phenomenon? [4 marks]

so acid isn't levelled

$0 \le pKa \le pK_{solth}$ (2) so base isn't levelled

Acids stronger than Solth get levelled (1)

Bases stronger than Sol^- " "

(1)

or S+6, higher ox. # than P5+