UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING
FINAL EXAMINATION, DECEMBER 2001

Third Year
CHE390F – Physical and Inorganic Chemistry
Exam Type : B
Examiner : C.M. Yip

Student First Name: _____

Student Last Name: _____

Student Number: _____

1. Attempt all problems
2. Calculator Type 2 - All non-programmable calculators are allowed. No programmable calculators are permitted.
3. **All work must be done on these sheets. Do not separate the sheets.**
4. Use the back of the sheets if you need more space. Be sure to **clearly** indicate if your answer continues elsewhere. **Draw a box around your answer.**
5. Read each question carefully. The exam lasts 2 hr and 30 minutes.

Question 1	/10
Question 2	/10
Question 3	/15
Question 4	/10
Question 5	/10
Question 6	/15
Question 7	/10
Question 8	/20

Possibly useful information:

R = 8.314 J/mol-K
Avogadro's number: 6.02×10^{23}
Boltzmann's constant: 1.38×10^{-23} J/K
Planck's constant: 6.625×10^{-34} J-s
Mass of a proton: 1.67×10^{-24} g
"LEO the Lion goes GER"
Faraday's constant: 9.648×10^{4} Coulombs / mole

See attached character tables and periodic table

Question 1 (10 points possible)

For each of the following questions, circle your answer or write out the answer as indicated. No marks will be deducted for incorrect answers.

- The bond order of the neutral molecule CN, as predicted by MO (molecular orbital) theory is

  (a) 1 (b) 2 (c) 3 (d) 1.5 (e) 2.5

- Which one of the following orbitals is best used to describe the "hybridization state" for the phosphorus atom, P, in phosphorus pentachloride, PCl_5?

  (a) sp^3d^2 (b) sp (c) sp^3 (d) sp^3d

- What is the systematic name for the following compound?

  - $Cr(NH_3)_3Cl_3$

- For the same type of ligands, explain why the crystal field splitting for an octahedral complex is always greater than that for a tetrahedral complex.

- What are the differences between geometric and optical isomers?

Question 2. (10 points possible)

Draw Lewis structures for the following molecules

- NF_3
- HOBr
- N_2O
- Urea : $(H_2N)_2CO$
- Carbamate (CO_3^{2-})

Question 3. (15 points possible)

(a) The number of nearest neighbours (atoms that make contact) around each atom in a hexagonal close-packed lattice of a metal is

(a) 2 (b) 4 (c) 6 (d) 8 (e) 10

(b) Cesium metal crystallizes in a BCC lattice. If the radius of the Ce atom is 268 pm, calculate the edge length (l) for a unit cell.

(a) 1072 pm (b) 928 pm (c) 804 pm (d) 619 pm (e) 536 pm

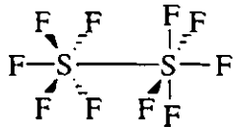
(c) The elastic modulus of diamond is measured by applying a force parallel to the body diagonal of the unit cell and measuring the displacement. A similar measurement is made by applying the force parallel to one of the cube axes. Explain why the two measurements give different values of the elastic modulus.

Question 4. (10 points possible)

(a) If an octahedron is distorted by stretching along the C_3 axis, what is the resulting point group? (It might be very helpful to prepare a sketch here)

(b) If it is stretched along the C_4 axis, what is the resulting point group?

(c) Given the structure for S_2F_{10} shown below, identify the point group and the location of all the symmetry elements



Question 5. (10 points possible)

Assume XeF_4 has D_{4h} symmetry.

(a) Show that the total number of vibrations is indicated by $A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2_{Eu}$

(b) Indicate which modes correspond to (a) infrared; (b) Raman bands. Are there any that are in common?

(c) What are the requirements for an IR active band? What are the corresponding criteria for a Raman active band?

Question 6. (15 points possible)

The *Temkin isotherm* for gas adsorption on solids is

$$v = r \ln sP$$

where r and s are constants

(a) Explain, in detail, how you would analyse your data to prove that it fit the Temkin isotherm.

(b) For N_2 adsorbed to a certain sample of charcoal at -77°C, adsorbed volumes (recalculated to 0°C and 1 atm) per gram of charcoal vs N_2 pressure are

P (atm)	3.5	10.0	16.7	25.7	33.5	39.2
v **(cm^3/g)**	101	136	153	162	165	166

Fit this data to the Temkin isotherm and determine r and s.

Question 7. (10 points possible)

(a) The equilibrium constant for the reaction

$$Sr_{(s)} + Mg^{+2}{}_{(aq)} \Leftrightarrow Sr^{+2}{}_{(aq)} + Mg_{(s)}$$

is 2.69×10^{12} @25°C

Calculate the standard cell potential for a cell made up of the Sr/Sr^{+2} and Mg/Mg^{+2} half cells.

(b) Use standard electrode potentials to find ΔG°_{298} and K°_{298} for the following reaction

$$Cu^{2+}{}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}{}_{(aq)}$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu \quad \varepsilon = 0.339V$$

$$Zn^{2+} + 2e^{-} \rightarrow Zn \quad \varepsilon = -0.792V$$

Question 8. (20 points possible)
One area of particular interest for nanotechnology and specifically materials science is that of molecular magnets whose solid-state structures consist of arrays of molecular units. Unfortunately, a key characteristic is notably lacking in these systems – namely the ability to retain its magnetism well above room temperature.

(a) Define paramagnetism.

(b) In a recent paper by Kou et al., *JACS* , **2001**, *123*, 11809-11810, the following Cu_3Cr_2 ferromagnet solid was discovered. The asymmetric unit and crystallographic view down the *a*-axis are shown below. .

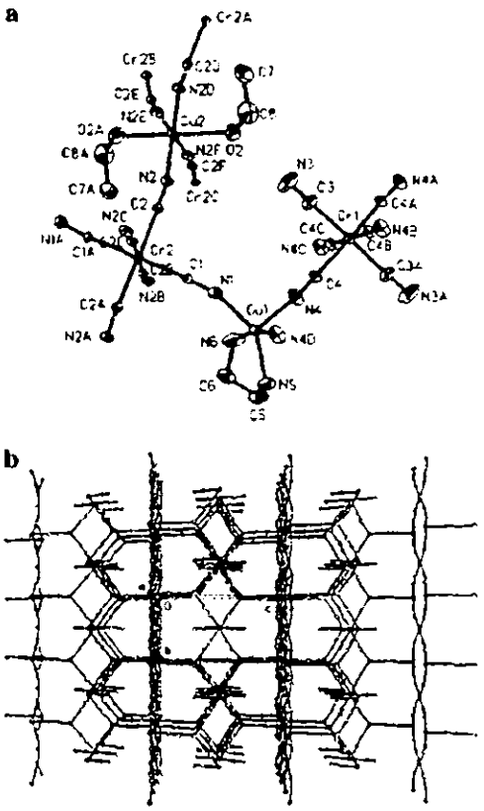


Figure 1. (a) The asymmetric unit of 1. (b) Projection of 1 along the *a*-axis showing the tunneled molecular structure.

The design strategy employed here involves the linkage of two paramagnetic hexacyanometalate(III) and simple transition metal building blocks via a bridging cyano group.

- Comment on the following statement made by the authors:

  These studies have shown that the low-dimensional materials have Tc values generally lower than that of the corresponding 3D analogues, and the few hybrid 3D arrays derived from paramagnetic [M(CN)6]3- and transition metal complexes order at different temperatures..."

  - Your answer should consider the following
    - What is the definition of a low-dimensional material? Does the complex shown above fit your interpretation?
    - Propose why a T_C value would increase upon ordering in 3D.

(c) In Kou's paper, they were working with $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$ Small blue single crystals of this compound were formed by the slow diffusion of $Cu(en)(H_2O)_2SO_4$ in H2O into $K_3[Cr(CN)_6]_5$ in a H_2O-EtOH (2:1) mixture over the course of a few months.

- Write a balanced equation depicting the formation of the polymer.

- Identify the anions used in these coordination complexes.

- How do you think the shape of the anion will influence the T_c value and why?

- What do you think will happen to the compound's magnetic properties if you were to systematically change the cation? What would be your choice and why?