Inorganic Chemistry (Qualification Examination)

5/30/2015

1.

(a) (i) In the cubic unit cell below sketch $\{10\overline{3}\}$. (ii) In the cubic unit cell below sketch $\{10\overline{3}\}$.

![Cubic Unit Cell](image)

(10%)

(b) For each unit cell above, draw the crystallographic feature indicated and label it clearly.

![Cubic Unit Cell](image)

(10%)

(c) Named after Salvatore Dali, dalium (Da) is BCC. Its molar volume is 6.66 cm$^3$/mol. Calculate the density of atoms in (001) of Da. Express your answer in atoms/cm$^2$.

(10%)
2. (a) Draw the energy-level diagram of the target (anode) of an x-ray tube operating at a plate voltage great enough to generate the characteristic lines. Indicate the features associated with the emission (a) $K_{\alpha}$, (b) $K_{\beta}$, (c) $L_{\alpha}$, and (d) $L_{\beta}$ radiation. The drawing need not be to scale but should reflect qualitative distinctions in magnitudes of transition energies.

(10%)

(b) Sketch the emission spectrum (intensity versus wavelength) of an x-ray target that has been bombarded with photons instead of with electrons. Assume that the incident photons have more than enough energy to dislodge K-shell electrons in the target. On your spectrum label the features associated with $K_{\alpha}$ radiation, $K_{\beta}$ radiation, and $L_{\alpha}$ radiation.

(10%)

(c) An x-ray tube fitted with tantalum (Ta) target is emitting radiation at a wavelength of $1.52 \times 10^{-10}$ m. Is this the wavelength of the $K_{\alpha}$ line or the $L_{\alpha}$ line? Support your answer with calculations.

(10%)

3. Here is the (011) plane in a unit cell of magnesium oxide (MgO) which is FCC. Indicate the positions of all atoms lying in the plane. Represent atoms as 2-dimensional slices of space-filling spheres. The values of ionic radii are $\text{Mg}^{2+} = 0.65$ Å and $\text{O}^{2-} = 1.34$ Å. Your sketch need not be drawn to scale; however, you must convey relative values of the ionic dimensions.

(15%)

4. On each of three separate drawings of one face of an FCC unit cell, indicate one of each of the following: (1) substitutional impurity; (2) vacancy; (3) interstitial impurity.

(9%)
5. Give the rotational symmetry of each of the following patterns. Express your answer as n-fold.

(9%)

6. Which one of the following metal oxides is antiferromagnetic in nature
(a) MnO₂, (b) VO₂, (c) TiO₂, (d) CrO₂.
Explain your answers.
(7%)

----------------------------------------------------------The end----------------------------------------------------------
Organic Chemistry

1. Please show how a melamine-formaldehyde resin is prepared and its reaction mechanism. (10 pts)

2. Please provide a mechanism and a representative example of the monomers, initiators, and reaction conditions for each of the following controlled radical polymerizations. (30 pts)
   a) Atom Transfer Radical Polymerization (ATRP)
   b) Nitroxide-Mediated Polymerization (NMP)
   c) Reversible Addition-Fragmentation Chain Transfer (RAFT)

3. Please provide a mechanism and the monomers for the following polymer prepared by the Diels-Alder reaction. (10 pts)

   ![Diels-Alder Reaction](image)

4. Please use examples, equations, schemes, and chemical reactions and structures as necessary to define the following terms. (20 pts)
   a) Trommsdorff effect (autoacceleration in radical polymerization)
   b) Cage effect/initiator efficiency (in radical polymerization)
   c) Step-growth polymerization
   d) Persistent radical effect

5. Please show by chemical equations the polymerization of methyl methacrylate initiated by the thermal decomposition of cumyl hydroperoxide. (15 pts)

6. Bisphenol A is one of the most widely used starting materials for condensation systems. (15 pts)
   a) Show how this compound is prepared and its reaction mechanism.
   b) Show how it is used in the preparation of a commercial epoxide used in epoxy resins.
   c) Show how an aliphatic diamine can be used to cure this epoxide.
1. The pre-exponential factor for the reaction \( \text{H}_2 + \text{I}_2 = 2\text{HI} \) is \( 10^{11} \text{ L mol}^{-1}\text{s}^{-1} \), and the activation energy is 165 kJ mol\(^{-1}\) in the range 300 to 500°C. If the collision diameter is 320 pm, what value of the pre-exponential factor is expected from collision theory at 600 K, and what is the value of the steric factor \( p \)? (At higher temperatures this reaction goes by the unbranched chain mechanism) 20%

2. For the reaction of two different average small radicals at 298 K with a reduced mass of \( 4.98 \times 10^{-26} \text{ kg} \) and a collision diameter of 5 Å,
   a. Evaluate the mean average velocity (cm s\(^{-1}\)).
   b. Calculate the collision cross section (cm\(^2\)) based on hard-sphere collision model.
   c. Calculate the bimolecular rate constant (cm\(^3\)mol\(^{-1}\)s\(^{-1}\)).
      Note: \( k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}\).

3. A second order reaction in solution has rate constants of \( 5.7 \times 10^{-5} \text{ L mol}^{-1}\text{s}^{-1} \) at 25°C and \( 1.64 \times 10^{-4} \text{ L mol}^{-1}\text{s}^{-1} \) at 40°C. Calculate the activation energy and the pre-exponential factor, assuming the Arrhenius equation to apply. 20%

4. For acetic acid in dilute aqueous solution at 25°C, \( K = 1.73 \times 10^{-5} \) and the relaxation time is \( 8.5 \times 10^{-9} \text{ s} \) for a 0.1M solution. Calculate \( k_a \) and \( k_d \) in
   \[
   \text{CH}_3\text{CO}_2\text{H} \xrightleftharpoons[k_d]{k_a} \text{CH}_3\text{CO}_2^- + \text{H}^+
   \]
   20%

5. Hydrogen is dissociatively adsorbed on a metal, and the pressure required to obtain half of the saturation coverage of the surface is 10Pa. (a) What pressure will be required to reach \( \Theta = 0.75 \)? \( \Theta \) is the fraction of coverage on the surface. (b) What pressure would have been required if the adsorption were not dissociative? 20%
1. (a) A 10.0-cm interference wedge is to be built that has a linear dispersion from 400 to 700 nm. Describe the details of its construction. Assume that a dielectric with a refractive index of 1.30 is to be used. (b) Compare the light-gathering power of a lens having a diameter of 5.00 cm and a focal length of 17.5 cm with the lens having a diameter of 34.0 cm and a focal length of 17.0 cm. (c) Consider an infrared grating with 84.0 lines per millimeter and 15.0 mm of illuminated area. Calculate the first-order resolution of this grating. Show your derivation to decide how far apart (in cm\(^{-1}\)) must two lines centered at 1200 cm\(^{-1}\) be if they are to be resolved at the first order.

2. A monochromator with a focal length of 0.78 m was equipped with an echelle grating of 2500 blazes per millimeter. (a) Write down five differences between echelle and echelle gratings. (b) Calculate the reciprocal linear dispersion of the instrument for the first-order spectra. (c) If 2.0 cm of the grating were illuminated, what is the first-order resolving power of the monochromator? (d) At approximately 430 nm, what minimum wavelength difference could in theory be completely resolved by the instrument?

3. Deviation from Beer's Law may arise from chemical and physical causes. (a) Using the UV measurement of the chromate concentration as an example to (i) discuss the chemical cause and (ii) describe the experimental steps to best solve the deviation. (b) Both polychromatic light and stray radiation contribute to the physical cause. (i) Discuss the essential experimental condition to minimize the departure from Beer's Law caused by polychromatic light. Explain, with the aid of properly labeled sketches, the rationale behind. (ii) Assume the stray radiation power in the wavelength of interest is 2.5% of the power level measured in the reference beam. Calculate the percent absorbance error for a transmittance of 25% in a UV measurement.

4. (a) Is spectrophotometry potentially more sensitive than spectrofluorometry? Explain. (b) Explain, with the aid of a properly labeled sketch, why the \(\lambda_e\) of the excitation spectrum of a compound does not overlap with the \(\lambda_e\) of its emission spectrum. (c) How can the synchronous spectra for photoluminescence be taken experimentally? (d) Derive Stern-Volmer equation.

5. (a) Describe the difference between photography and holography. (b) Discuss the important conditions of fabrication and describe, with the aid of a properly labeled sketch, the fabrication process of the volume transmission hologram. (c) List the main functions of use of the volume transmission hologram. (d) Discuss how the volume transmission hologram achieves each of their functions of use. (e) Is the volume transmission hologram of any use in IR spectrometry? Explain in at least 50 words.

6. (a) Use appropriate energy level diagrams (with labels) to discuss if the operating principles of a photodiode detector and an infrared diode laser are the same. (b) What are the performance characteristics of a photodiode detector? (c) Suppose that Mg vapor is used as a lasing medium for a laser. Show your calculation to confirm that heat is not a practical excitation source of laser.

7. (a) Define (i) photoelectric effect and (ii) Bernoulli effect. (b) For each of the effects listed in (a), (i) name a specific instrumental analysis method (which cannot be repeated for different effects) in which the effect is either utilized in its operation or a common phenomenon observed by the method. (Note: using the electrochemical analysis method as an example, the answer expected here would be like "differential pulse voltammetry", not "voltammetry" or "pulse voltammetry". Also, no credit will be given to the rest of the question if an arbitrary method is named here.) (ii) discuss, with the aid of a properly labeled sketch, the operating principle of the analysis method, (iii) explain how the effect influences/depends the operation of the method, (iv) draw a typical spectrum (with proper labels) obtained by the method, (v) use one real example to describe all the analytical information that can be obtained using the method and how the information are derived, (vi) name and sketch a detector used frequently in this method and describe how the signal is transduced in the detector.
A. 19S proteasome subunit
B. 20S proteasome
C. 26S proteasome
D. E1 enzyme
E. E2 enzyme
F. E3 enzyme

X. Substrate ubiquitination
Y. Substrate unfolding
Z. Peptide bond hydrolysis

(1) For X, Y, and Z, please indicate which process is thermodynamically favorable (spontaneous) and which process is not (6 pts). Please explain your answers. (9 pts)

(2) For X, Y, and Z, please describe the enzymes required for each process, choosing from A to F. (9 pts)

(3) The ratio of E1:E2:E3 genes is about 1:50:500 in mammalian genomes. Please explain why this ratio matters in terms of substrate specificity (5 pts).

(4) What is a common structural feature of proteins that undergo ubiquitin-independent degradation by 20S proteasome and why? (6 pts)

(5) There are three kinds of proteasome-associated proteins which can recognize ubiquitin: E3, deubiquitinating enzyme, and poly-ubiquitin receptors. What are their roles in protein degradation at the 26S proteasome? (9 pts)

(6) How do you tell that a protein is polyubiquitinated on Western blots (4 pts)?

(7) What is the function of Rpn13 ubiquitination when the cell is under stress? (5 pts)

(8) Why are there more proteins interacting with alpha subunits of the 20S than beta subunits (5 pts)?
1) What is CRISPR/Cas technique? How do you combine this technique with nanoparticles for gene therapy? (Hints: CRISPRs (clustered regularly interspaced short palindromic repeats) are segments of prokaryotic DNA containing short repetitions of base sequences. Each repetition is followed by short segments of "spacer DNA" from previous exposures to a bacterial virus.

2) In a 2006 nature paper (Nature, 2006, 440, 297) DNA origami was discussed where DNA folding was utilized to create arbitrary nanoscale shapes and patterns. Could you discuss the mechanism of DNA origami? What are the interactions involved in these folding? Please describe an approach using DNA origami to create a drug release system.

3) What is the optical light sheet imaging technique? What are the advantages of the optical light sheet imaging technique? How to achieve sub-micrometer resolution in z direction using optical light sheet imaging technique? (Hint: Science 2014, 346, 1257998)

4) (a) Nanoparticles have been used for ultrasensitive detections, could you design a system to capture protein with aM (10^-18M) sensitivity. Please describe in detail. (b) If you want to make this system portable (the sensitivity can be reduced to fM), could you design a simple device. Please explain your design.

5) For deep tissue imaging there are two major challenges, what are they? How do you solve these problems to obtain better resolution for thick samples?