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Uva Wellassa University, Sri Lanka
End Semester Examination – June /July 2009
SCT 234-2 Advanced Chemistry



Time: Two (02) hours

Total seven (07) Questions

This paper consists of three parts (Part – A, Part – B and Part – C)

Use a separate answer book for each part and return them separately.

Answer two (02) questions from Part - A, one (01) from Part - B and one (01) from Part - C

Universal gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Planck's constant, $h = 6.6262 \times 10^{-34} \text{ J s}$

Avogadro constant, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Velocity of light = $2.99 \times 10^8 \text{ m s}^{-1}$

Mass of electron, $m = 9.1091 \times 10^{-31} \text{ kg}$

Charge on electron, $e = 1.6021 \times 10^{-19} \text{ C}$

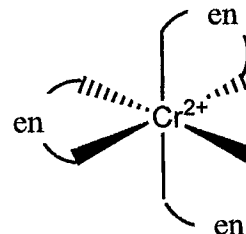
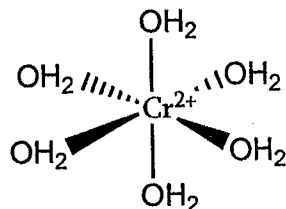
Permittivity of Vacuum, $\epsilon_0 = 8.854185 \times 10^{-12} \text{ kg}^{-1} \text{ m}^{-3} \text{ A}^2$

PART - A

01) i. What assumptions are made in deriving crystal field theory?

(20 marks)

ii.



Suppose you synthesized two octahedral Cr^{2+} complexes, one with three ethylenediamine (en) ligands and the other with six H_2O ligands. As you forgot to label your products, you examine their optical (UV- Visible) absorption spectra and magnetic properties to identify the complexes.

Complex A:

Absorbs (λ_{max}) at 530 nm

$\mu = 4.9 \text{ BM}$

Complex B:

Absorbs (λ_{max}) at 410 nm

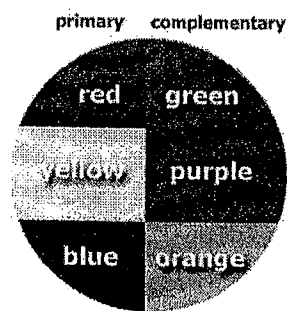
$\mu = 2.9 \text{ BM}$

- a. Decide which ligands form complex A and complex B.
- b. Decide what colour each complex appears to the eye.

Hint:

Use d molecular orbital diagram to justify your answer.

Absorbed light	Wavelength Range / nm
Red	620-700
Yellow	580-620
Orange	560-580
Green	490-560
Blue	430-490
Violet	380-430



(30 marks)

- 02) i. Define the following
- Atomic number
 - Mass number
 - Isotope
 - α decay
 - β decay

(15 marks)

- ii. Draw a diagram to illustrate how binding energy per nucleon varies with the mass number.

(10 marks)

- iii. A radioactive ${}^{40}_{19}\text{K}$ isotope decays to ${}^{40}_{18}\text{Ar}$. Half life of the decay is 1.2×10^9 years. A sample of moon rock is found to contain 18% ${}^{40}_{19}\text{K}$ and 82% ${}^{40}_{18}\text{Ar}$ by mass. Calculate the age of the rock in years.

Hint:

If N_0 atoms were present at the beginning, remaining atoms after time t (N_t) is given by the following equation;

$$N_t = N_0 e^{-\lambda t}$$

(25 marks)

- 03) i. For the ion $[\text{Co}(\text{en})_2\text{NH}_3\text{CN}]^{2+}$ answer the following questions;
- Write the IUPAC name.
 - What is the oxidation state of the central atom?
 - What is the coordination number of the central atom?

(14 marks)

- ii. The compound $\text{Co}(\text{NH}_3)_5\text{SO}_4\text{Br}$, exists in two forms: red and violet. Each form dissociates in water forming two ions. A solution of the red compound forms a precipitate of AgBr on the addition of AgNO_3 solution, but, no precipitate of BaSO_4 upon the addition of BaCl_2 solution. For the violet compound, just the reverse occurs. From this evidence, write the formula of complex ions in each case (label them as "red" or "violet"). Write the IUPAC name of each compound.

(20 marks)

- iii. Using molecular orbital diagrams briefly explain the following
 "[$\text{Ru}(\text{H}_2\text{O})_6$] $^{2+}$ is found to be paramagnetic whereas [$\text{Ru}(\text{CN})_6$] $^{4-}$ is diamagnetic."

(16 marks)

PART - B

- 04) i. Briefly explain the following spectroscopic data.
 $^1\text{H-NMR}$ (CDCl_3) δ_{ppm} of following compounds are varied as follows:

Compound	CH_3Cl	CH_2Cl_2	CHCl_3
δ_{ppm}	3.05	5.30	7.27

(25 marks)

- ii. Sketch the $^1\text{H-NMR}$ spectrum of the *compound A*- $(\text{CH}_3)_3\text{CCHBr-CH}(\text{CH}_3)\text{CHO}$ (IR ν_{max} 1710 cm^{-1}) showing the distance from TMS signal, relative areas (integration) and multiplicity of the signals.

Draw the $^{13}\text{C-NMR}$ spectrum of the *compound A*

(75 marks)

- 05) i. Briefly explain the following spectroscopic data.
 IR ν_{max} of C-C bonds are as follow,

Bond	C-C	C=C	C≡C
$\nu_{\text{max}}/\text{cm}^{-1}$	1000	1600	2200

(25 marks)

- ii. Deduce the structure of *compound B* ($\text{C}_6\text{H}_{12}\text{O}$) having the following spectral data. IR ν_{max} 1715 cm^{-1} ; $^1\text{H-NMR}$ δ_{ppm} 2.35 (t,2H), 2.02 (s,3H), 1.54 (m,2H), 1.24 (m,2H), 0.75 (t,3H); MS m/z 85 and 43

(75 marks)

PART - C

- 06) i. State the Gibb's phase rule. (10 marks)
- ii. a. State Raoult's law for an ideal two component system. (10 marks)
- b. Derive an expression for total pressure in terms of partial pressures and molar fractions. (25 marks)
- c. Sketch the phase diagram (vapour pressure vs composition) for ideal two component solution. (25 marks)
- d. What type of deviation do you expect from a system containing ethanol and heptane components. (15 marks)
- iii. What is meant by congruent melting point and incongruent melting point? (15 marks)

07)

i. State the lever rule.

(20 marks)

ii. A mixture of 50 g of hexane (0.59 mol C_6H_{14}) and 50 g of nitrobenzene (0.41 mol $C_6H_5NO_2$) was prepared at 290 K.

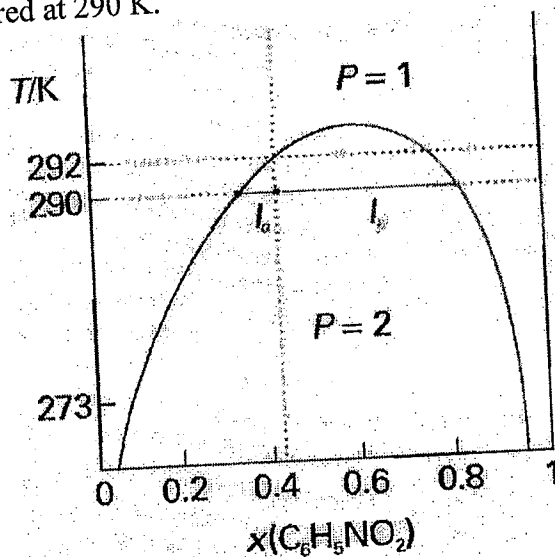
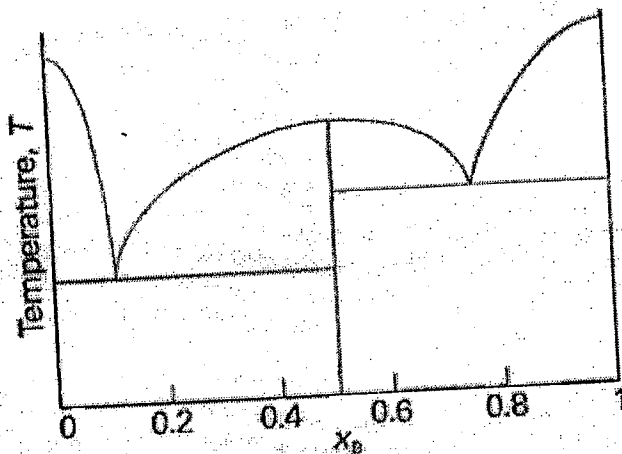


Fig 1: The temperature-composition diagram for hexane and nitrobenzene at 1 atm.

- What are the composition of the phases?
- In what proportions do they occur?
- To what temperature must the sample be heated in order to obtain a single phase?

(40 marks)

iii. Phase diagram of a binary mixture of component A and component B is given below. Label the regions of the following phase diagram. State what substances (if compounds give their formulas) exist in each region. Label each substance in each region as solid, liquid or gas.



(40 marks)