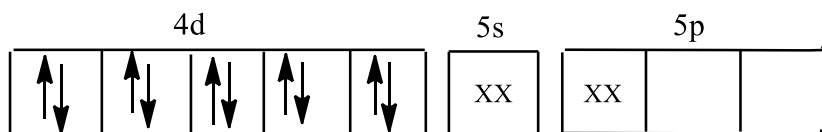


- Q1.** (i) For  $^3\text{H}^{35}\text{Cl}$ ,  $\mu = \frac{3.016 \times 35.45}{(3.016 + 35.45)} \times 1.66 \times 10^{-27} = 4.61 \times 10^{-27} \text{ kg}$
- (a) Energy difference between ground rotational level and first excited state
- (i)  $= \frac{h^2}{I} = h\nu$ , where  $\nu = 218.5 \text{ GHz}$  1 M
- $r = 1.29 \times 10^{-10} \text{ m}$
- For  $^2\text{H}^{35}\text{Cl}$ ,  $\mu = \frac{2.015 \times 35.45}{(2.015 + 35.45)} \times 1.66 \times 10^{-27} = 3.165 \times 10^{-27} \text{ kg}$
- Energy of first excited rotational level  $= \frac{h^2}{I} = 2.114 \times 10^{-22} \text{ J}$  2 M
- Alternate solution:**
- Frequency required for rotational excitation in  $^3\text{H}^{35}\text{Cl}$  is 218.5 GHz, so frequency required for rotational excitation in  $^2\text{H}^{35}\text{Cl}$  is  $\frac{218.5 \times 3}{2} = 327.75 \text{ GHz}$
- Energy of the first excited state in  $^2\text{H}^{35}\text{Cl} = h\nu = 2.17 \times 10^{-22} \text{ J}$
- (ii) No. The energy difference between the ground rotational level and first excited level in  $^2\text{H}^{35}\text{Cl}$  is more than  $^3\text{H}^{35}\text{Cl}$ . So the photon of frequency 218.5 GHz will not result in rotational excitation in  $^2\text{H}^{35}\text{Cl}$ . 1 M + 1 M
- (b) (i)  $\left(6 - \frac{r}{a_0}\right) = 0$
- (r =  $6a_0$ ) 1 M
- (ii) Radial distribution function  $= R^2(r) r^2$
- Radial part of the wavefunction  $R(r) = \frac{2\sqrt{2}}{81\sqrt{3}} \left(\frac{1}{a_0}\right)^{5/2} r \left(6 - \frac{r}{a_0}\right) e^{-\frac{r}{3a_0}}$  1 M
- Radial distribution function  $= \left( \frac{2\sqrt{2}}{81\sqrt{3}} \left(\frac{1}{a_0}\right)^{5/2} r \left(6 - \frac{r}{a_0}\right) e^{-\frac{r}{3a_0}} \right)^2 r^2$
- $= \frac{8}{19683} \left(\frac{1}{a_0}\right)^5 \left(6 - \frac{r}{a_0}\right)^2 e^{-\frac{2r}{3a_0}} r^4$  1 M
- (iii)  $P = \frac{8}{19683} \left(\frac{1}{a_0}\right)^5 \left(6 - \frac{r}{a_0}\right)^2 e^{-\frac{2r}{3a_0}} r^4$
- $\frac{dP}{dr} = \frac{8}{19683} \left(\frac{1}{a_0}\right)^5 \left[ \frac{-2}{a_0} \left(6 - \frac{r}{a_0}\right) e^{-\frac{2r}{3a_0}} r^4 + 4 \left(6 - \frac{r}{a_0}\right)^2 e^{-\frac{2r}{3a_0}} r^3 - \frac{2}{3a_0} \left(6 - \frac{r}{a_0}\right)^2 e^{-\frac{2r}{3a_0}} r^4 \right]$
- $\frac{dP}{dr} = \frac{8}{19683} \left(\frac{1}{a_0}\right)^5 \left(6 - \frac{r}{a_0}\right) r^3 e^{-\frac{2r}{3a_0}} \left[ \frac{-2}{a_0} r + 4 \left(6 - \frac{r}{a_0}\right) - \frac{2}{3a_0} \left(6 - \frac{r}{a_0}\right) r \right]$
- $\frac{dP}{dr} = \frac{8}{19683} \left(\frac{1}{a_0}\right)^5 \left(6 - \frac{r}{a_0}\right) r^3 e^{-\frac{2r}{3a_0}} \left[ \frac{2}{3} \left(\frac{r}{a_0}\right)^2 - 10 \left(\frac{r}{a_0}\right) + 24 \right] = 0$  1 M
- $\left[ \frac{2}{3} \left(\frac{r}{a_0}\right)^2 - 10 \left(\frac{r}{a_0}\right) + 24 \right] = 0$  1 M
- $r = 12a_0 \text{ and } 3a_0$  1 M
- Most probable radius  $= 12a_0$  1 M
- (iv) Probability  $= \int_{1\text{\AA}}^{1.01\text{\AA}} \frac{8}{19683} \left(\frac{1}{a_0}\right)^5 \left(6 - \frac{r}{a_0}\right)^2 e^{-\frac{2r}{3a_0}} r^4 dr$  1 M

<b>GENERAL CHEMISTRY</b>	<b>CHEM F111</b>	<b>Compre Exam. Model Solution</b>
<b>Max. Marks: 87</b>	<b>Duration: 120 minutes</b>	<b>Date: May 14, 2018</b>

- Q2.**  $6B = 364.99 \text{ cm}^{-1}$ . Therefore,  $B = 60.83 \text{ cm}^{-1}$  **1 M**
- (a)** We have,  $B = h/(8\pi^2\mu r^2)c$   
 $\mu = m_H/2 = 1.0079 \times 10^{-3} \text{ kg} / 6.023 \times 10^{23} \times 2 = 8.367 \times 10^{-28} \text{ kg}$   
Therefore,  $B = 60.83 \text{ cm}^{-1} = 6083 \text{ m}^{-1} = 6.626 \times 10^{-34} \text{ Js} / 8 \times (3.14)^2 \times (8.367 \times 10^{-28} \text{ kg}) \times r^2 \times 3 \times 10^8 \text{ ms}^{-1}$   
So,  $r^2 = 5.50165 \times 10^{-21} \text{ m}^2$ .  
Therefore  $r = 7.417 \times 10^{-11} \text{ m} = 74.17 \text{ pm}$  **2 M**
- (b)**  $\epsilon_v = [v + (1/2)]\omega_e - [v + (1/2)]^2\omega_e x_e$   
For fundamental transition,  $\Delta v = +1$  and transition is from  $v = 0$  to  $v = 1$   
Therefore,  $\Delta \epsilon_1 = [1 + (1/2)]\omega_e - [1 + (1/2)]^2\omega_e x_e - (1/2)\omega_e + (1/2)^2\omega_e x_e$   
 $= \omega_e(1 - 2x_e) = 2886 \text{ cm}^{-1}$  ..... (1) **2 M**
- For first overtone,  $\Delta v = +2$  and transition is from  $v = 0$  to  $v = 2$   
Therefore,  $\Delta \epsilon_2 = [2 + (1/2)]\omega_e - [2 + (1/2)]^2\omega_e x_e - (1/2)\omega_e + (1/2)^2\omega_e x_e$   
 $= 2\omega_e(1 - 3x_e) = 5668 \text{ cm}^{-1}$  ..... (2) **2 M**
- Solving Eqs. 1 and 2, we have,  $\omega_e = 2990 \text{ cm}^{-1}$  and  $x_e = 0.0174$  **1 M + 1 M**
- (c)** The exact chemical shift position of uncoupled nucleus A,  $\delta_A = (5.80 + 5.70)/2 = 5.75$  **1 M**  
The exact chemical shift position of uncoupled nucleus X,  $\delta_A = (1.10 + 1.00)/2 = 1.05$  **1 M**  
For first line,  $\nu - \nu_0 = (5.80 \times 100 \times 10^6 \text{ Hz}) / 10^6 = 580 \text{ Hz}$   
For second line,  $\nu - \nu_0 = (5.70 \times 100 \times 10^6 \text{ Hz}) / 10^6 = 570 \text{ Hz}$   
Therefore,  $J_{AX} = (580 - 570) \text{ Hz} = 10 \text{ Hz}$  **2 M**
- Q3.** **(i) CFSE** **0.5 M**
- (a)** In case of octahedral geometry,  $\text{NH}_3$  being a strong field ligand ( $\Delta_o = \text{high}$ ), the electronic configuration is  $t_{2g}^6, e_g^1$ . So CFSE =  $-1.8 \Delta_o$ . **1 M**  
For tetrahedral geometry, electronic configuration is  $e^4 t_2^3$  CFSE =  $-1.2 \Delta_t = -0.53 \Delta_o$  **1 M**  
So, octahedral geometry is favoured. **0.5 M**
- (ii)** As the  $\text{NH}_3$  ligand is very strong ligand, the single electron at the  $e_g$  orbital lies very high in energy. Therefore it can be easily lost making the oxidation state of cobalt as +3. So the complex A behaves like a strong reducing agent. **2 M**
- (b)** CFT. **0.5 M**  
VBT deals with exactly equivalent orbitals who are energetically equivalent. Therefore, it does not leave a scope for the explanation for electronic transition. **1.5 M**  
 $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  complex has only one structural isomer  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ . As a ligand,  $-\text{NO}_2^-$  is stronger than  $-\text{ONO}$ . Therefore the crystal field splitting  $\Delta_o$  of  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  is more than that of  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ . As a consequence,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  is yellow in colour as it absorbs the wavelength of complementary dark blue colour and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$  is red in colour as it absorbs the green region.  
 $\lambda$  (dark blue range)  $< \lambda$  (green range)  
So, in terms of crystal field splitting  $\Delta_o$ ,  $\Delta_o$  of  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+} > \Delta_o$  of  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$  which is justified with observed colours of the complexes. **3 M**

(c) (i)



sp hybridization

So the complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$  is sp hybridized.

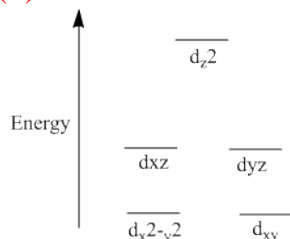
1.5 M

The geometry of the complex is linear.

0.5 M

(without hybridization, if only structure is written correctly, only 0.5 M will be awarded)

(ii)



2 M

Q4. Tetragonal elongation is expected in  $[\text{Fe}(\text{phen})_3]^{3+}$  complex.

(a) Based on CFSE value we can identify elongation or compression.

Here, "phen" is a strong ligand field. It is a  $d^5$  low-spin system. The configuration is  $t_{2g}^5 e_g^0$  system.

The CFSE for elongation is  $\{(-4 \times 1/3) + (1 \times 2/3)\} \delta_2 = -2/3 \delta_2$

1 M

The CFSE for compression is  $\{(-2 \times 2/3) + (3 \times 1/3)\} \delta_2 = -1/3 \delta_2$

1 M

Therefore, tetragonal elongation is possible for  $[\text{Fe}(\text{phen})_3]^{3+}$  complex.

1 M

(without CFSE calculation 0 M will be awarded)

$[\text{Fe}(\text{phen})_3]^{3+}$  complex is more stable than  $[\text{Cu}(\text{phen})_3]^{2+}$  complex.

In  $[\text{Fe}(\text{phen})_3]^{3+}$  complex,  $t_{2g}^5 e_g^0$  configuration is possible and  $t_{2g}$  is unsymmetrical. So, mild distortion is possible.

1 M

Whereas, in  $[\text{Cu}(\text{phen})_3]^{2+}$  complex,  $t_{2g}^6 e_g^3$  configuration is possible and  $e_g$  is unsymmetrical. So, strong distortion is possible. Ligands which are approaching through z direction will be repelled more, which leads instability in  $[\text{Cu}(\text{phen})_3]^{2+}$  complex.

1 M

(answer without mentioning distortion 0 M will be awarded)

(b) The equation is  $-2.303 RT \log_{10} \beta = \Delta H^\circ - T \Delta S^\circ$

or,  $\Delta H^\circ = -2.303 RT \log_{10} \beta + T \Delta S^\circ = (-2.303 \times 8.314 \times 300 \times 14.6) + (300 \times 90)$

1 M

$= -83864.48 + 27000 = -56864.48 \text{ J/mol} = -56.86 \text{ kJ/mol}$

1 M

(no marks will be awarded for the formula only)

The difference in  $\Delta H^\circ$  values is due to chelate effect of "phen" ligand. With the increase in chelation the change in  $\Delta H^\circ$  is more negative.

1 M

(c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  complex is pale color as its electronic configuration is  $t_{eg}^3 e_g^2$ . According to spin selection rule for electronic transition, during transitions between energy levels, an electron does not change its spin, i.e.,  $\Delta S = 0$ . There should not be any change in the spin of the states and their multiplicities should be the same

during the transition of electrons. But, in case of  $t_{eg}^3 e_g^2$  (high-spin),  $\Delta S \neq 0$ , so, spin forbidden. Therefore, the pale color and lower absorptivity are observed. **2 M**

(d) To calculate  $E^0$  the formula is  $E = (nE + n'E' + n''E'') / (n + n' + n'')$ .

Therefore,  $E^0 = [3 \times 2.2 + 1 \times 0.77 + 2 \times (-0.47)] / 6 = [7.37 - 0.94] / 6 = 1.07 \text{ V}$

**2 M**

The species liable to undergo oxidation is Fe.

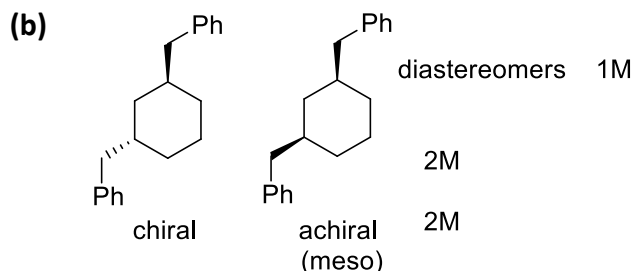
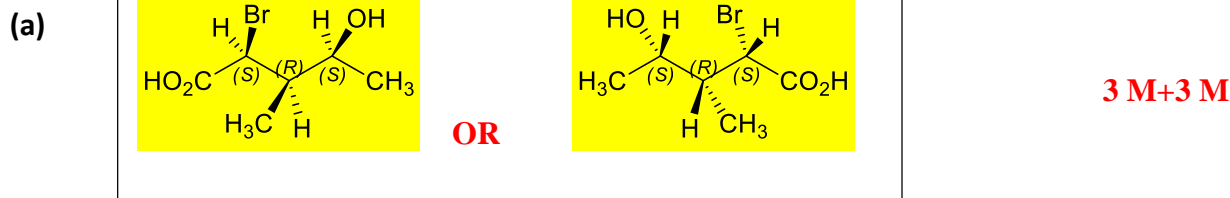
**1 M**

(e) Only one band is expected based on the ground state term. **1 M**

$[\text{CuCl}_4]^{2-}$  is a tetrahedral complex.  $\text{Cu}^{2+}$  is a  $d^9$  system and the ground state term is  $^2D$ . Therefore, the Mulliken symbols for splitting in a tetrahedral environment for D term is E and  $T_2$ . So, the electronic transition is  $^2T_2$  to  $^2E$ . (1M)

(If the notations are in small letters,  $e_g$  and  $t_{2g}$  are used then 0 M will be awarded)

Q5.

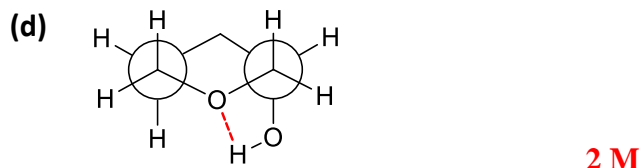


(c) enantiomeric excess (ee) =  $97.5 - 2.5 = 95\%$  **1M**

$$\text{enantiomeric excess (ee)} = \frac{\text{observed rotation}}{\text{rotation of pure enantiomer}} \times 100$$

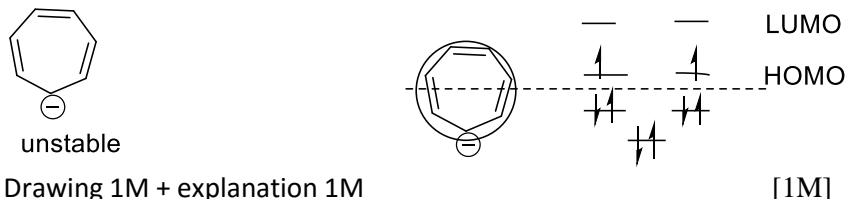
$$\text{rotation of pure enantiomer} = \frac{\text{observed rotation}}{\text{enantiomeric excess (ee)}} \times 100$$

$$\text{rotation of pure enantiomer} = \frac{90.5 \times 100}{95} = -95.26^\circ \quad \mathbf{2M}$$



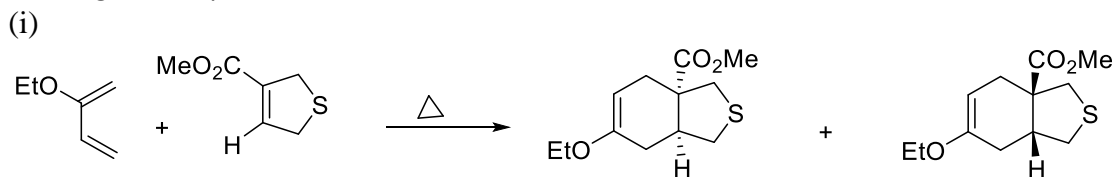
Q6. cycloheptatrienyl anion is more unstable as it has  $8\pi$  electrons and is not aromatic. [1M]

(a)

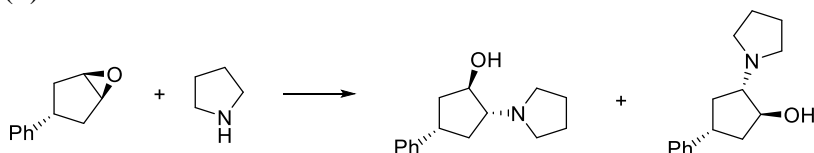


(b)

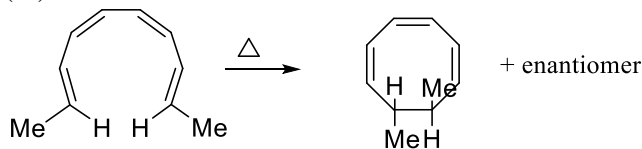
Drawing 1M + explanation 1M



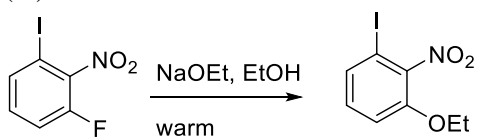
(ii)



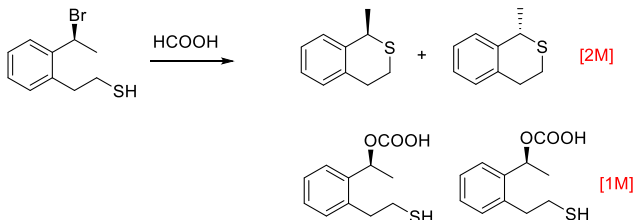
(iii)



(iv)

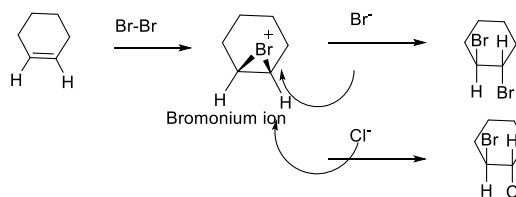


(c)



The material obtained after the reaction is optically inactive 1 M

(d)



1 M for each product shown