BITS PILANI, DUBAI CAMPUS

I YEAR SECOND SEMESTER, 2012-2013

COMPREHENSIVE EXAMINATION-CLOSED BOOK

Course Title: General Chemistry | **Course No: CHEM F111**

Date: 02.06.2013 | **Total Marks: 80**

Time: 3Hrs | **Weightage: 40%**

1. **Answer all questions sequentially. Part-A, B and C separately**
2. **Show stepwise calculation indicating the units wherever it is required**
3. **Useful data: 1 eV=1.602x10^{-19}J, h = 6.626 x 10^{-34} J.s, c = 3 x 10^{10} cm/s, R_H = 109677 cm^{-1}, R=8.314 J/K/mol, Mass of electron = 9.1x 10^{-31} kg, Mass of hydrogen = 1.67x10^{-27} kg, 1 atomic mass unit = 1.66x10^{-27}kg. Atomic Number of H=1, He=2, C=6, N=7, O=8, P=15, S=16, Cl =17, Cr=24, Mn=25, Fe=26, Co=27, Cu=29, Br = 35, I=53. Atomic masses: I=127, Cl=35**

PART-A

1. (i) Estimate the wavelength of an electron accelerated from the rest through a potential difference of 20.00 kV.

   (ii) Calculate the wavelength of the line with n = 4 in the Balmer series of the hydrogen spectrum.

   (iii) Why the electron affinity of Cl is higher than that of S? **[3+3+2 M]**

2. (i) Calculate the zero point energy for an electron that is confined to a one dimensional box of length 2 A°.

   (ii) How many orbitals are there in a shell with n = 3 and what is there designation?

   (iii) Describe the bonding in a PCl_5 molecule in VB terms. **[3+2+2 M]**

3. (i) How many modes of vibration are there in

   (a) Xylene (C_8H_{10}). (b) Fluorine.

   (ii) Vibrational frequency of $^{127}I\,^{35}Cl$ is 384 cm^{-1}. Calculate the force constant.

   (iii) Write the gross and specific selection rule for vibrational transitions. **[2+3+2 M]**

   (i) Give an account of source and detectors used in IR spectrophotometer.

   (ii) Calculate the bond order of O_2^- ion

   (iii) Explain the differences between the bonding and anti-bonding molecular orbitals. **[2+1+2 M]**

PART-B

1. (i) Give the wedge representation of (R)-2-butanol.

   (ii) Draw the structure of (i) trans-1,2-dimethylcyclohexane and (ii) cis-1,3-dimethylcyclohexane and state which one is more stable? **[2+4 M]**

2. (i) Illustrate how the structure of the substrate and the nature of the leaving group affect the rate of S_N1 and S_N2 Reactions?

(ii) Write a note on conformational analysis of Butane. **[4+4 M]**

3. (i) How much heat is required to vaporize liquid butane from its boiling point (-1^{O} C)

(ii) Calculate the standard enthalpy of formation of ethane (C_2H_6) at 298 K from the following data. Enthalpy of combustion of ethane is -1560 kJ/mol.

$\Delta H_f^{o}{}_{298}$ (H_2O) = -286 kJ/mol, $\Delta H_f^{o}{}_{298}$ (CO_2) = -393.5 kJ/mol.

(iii) Formulate the rate law for the reaction, $2\ NO_{(g)} + O_{2(g)} \longrightarrow 2\ NO_{2(g)}$, using steady state approximation. **[2+5+6 M]**

PART-C

1. (i) Suggest a reaction mechanism for the formation of 2–methyl propene from t- butyl chloride

(ii) Give addition reaction of hydrochloric acid to propene and justify the product formed.

[4+4 M]

2. (i) Identify from the following compounds which is aromatic /anti aromatic? Justify your answer.

(a) Cyclopenta dienyl anion (b) Cyclo octatetraene.

(ii) Write the state of hybridization of the central metal atom, magnetic behavior and geometry of the given complexes using VB theory (a) $[Cu(NH_3)_4]^{2+}$ (b) $[Mn(CN)_6]^{4-}$ **[4+6 M]**

3. (i) Draw the structure of oxalate ion and ethylene diamine tetra acetate anion ligands and indicate the coordination sites in the ligands.

(ii) Predict on the basis of CFT whether the following complex is planar, tetrahedral or octahedral. Show the distribution of d-electron of the central metal atom in the splitted d-orbitals. $[Co(NH_3)_6]^{3+}$ **[4+4 M]**

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I YEAR SECOND SEMESTER, 2012-2013

COMPREHENSIVE EXAMINATION-CLOSED BOOK

Course Title: General Chemistry | **Course No: CHEM F111**

Date: 02.06.2013 | **Total Marks: 80**

ANSWERING SCHEME

Time: 3Hrs | **Weightage: 40%**

PART-A.

1. i) $E_K = eV = \frac{1}{2} m_e v^2$

$\therefore p = mv$ (1M)

$= (2 m_e E_K)^{1/2}$

$= (2 m_e eV)^{1/2}$

$\lambda = \frac{h}{(2 m_e eV)^{1/2}}$ (1M)

$\lambda = \frac{6.626 \times 10^{-34} \, Js}{[2 \times (9.11 \times 10^{-31} \, kg) \times (1.602 \times 10^{-19} \, C) \times (20 \times 10^{3} \, V)]^{1/2}}$

$\therefore \lambda = 0.8673 \times 10^{-11} \, m.$ (1M)

1. ii) $\bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$. —— (1)

$n_1 = 2$ — Balmer series.

$n_2 = 4$.

$\therefore \bar{\nu} = 109677 \left[\frac{1}{(2)^2} - \frac{1}{(4)^2}\right] cm^{-1}$.

$= 20,564.44\ cm^{-1}$. —— (1)

$\therefore \lambda = \frac{1}{\bar{\nu}} = 4.86 \times 10^{-5}\ cm = 486\ nm$. —— (1).

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iii) In CH_4, the incoming electron enters the valence shell and experiences a strong attraction from the nucleus. (2).

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2. i) $E = \frac{n^2 h^2}{8 m L^2}$. (1)

$L = 2\ \mathring{A}$; $m_e = 9.11 \times 10^{-31}\ kg$; $n = 1$. (1)

$\therefore E = \frac{(6.626 \times 10^{-34})^2}{8 \times (9.11 \times 10^{-31}) \times 1.602 \times 10^{-19} \times (2 \times 10^{-10})^2}\ J/eV$

$= 9.4\ eV$. (1)

2.ii) $n^2 = (3)^2 = 9$. (1)

one s, three p, five d (1).

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iii) Five σ bonds formed (1)

from sp^3d hybrids on the central P atom. (1)

3.(i) <u>xylene:</u> <u>(C_8H_{10})</u>.

$3N - 6 = 3 \times 18 - 6 = 48$ (1)

<u>F_2</u> $= 3N - 5 = 3 \times 2 - 5 = 1$. (1).

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ii) $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$. $^{127}I^{35}Cl = 384\ cm^{-1}$. (1)

$\mu = \frac{m_A m_B}{m_A + m_B} = \left(\frac{127 \times 35}{127 + 35}\right) . 1.66 \times 10^{-27}$.

$\therefore \mu = 4.5548 \times 10^{-26}\ kg$. (1)

$\therefore \sqrt{k} = 384 \times 2 \times 3.14 \times 3 \times 10^{10} \times 2.1342 \times 10^{-13}$.

$\therefore$ <u>$k = 238\ Nm^{-1}$.</u> (1)

3. ii) Gross selection Rule:

The electric dipole moment of the molecule must change during the vibration. (1)

Specific selection Rule:

$$\Delta v = \pm 1 \quad (1).$$

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4. i) Source of IR:

Mercury arc inside a quartz envelop (or) Nernst filament (or) globar. (1)

Detector: Mercury cadmium telluride (MCT). (1)

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ii) O_2^- : Bond order $= \frac{1}{2}(N_b - N_a)$

$= \frac{1}{2}(8-5).$

$= 1.5.$ (1).

4. iii) <u>Bonding molecular orbitals:</u>

They contribute to the strength of the bond, $\psi = \psi_A + \psi_B$, Energy is decreased and accumulation of electron density in the inter-nuclear region. (1M)

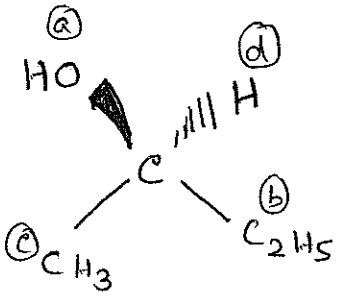
<u>Anti-bonding molecular orbitals:</u>

They decrease the strength of the bond, $\psi = \psi_A - \psi_B$, Energy is raised, and exclusion of electron density from the inter-nuclear region. (1M)

R. Rajan

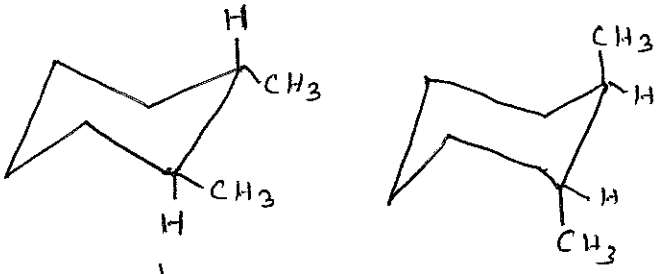
Part - B

1(i)



(2 M)

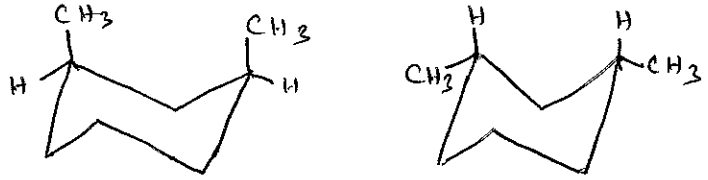
(ii)



trans-1,2-dimethyl cyclohexane

↓ (more stable)

(4 M)



Cis-1,3-dimethyl Cyclohexane

↓ more stable

2(i) $SN2$ reaction rates, (4 M)

methyl > primary > secondary > tertiary. (unreactive by SN2)

Neopentyl halide, though primary, very low rate, SN2.

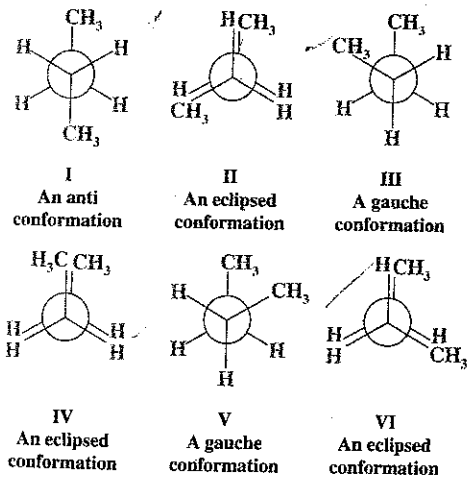
Tertiary halides reacts by SN1, because of the stabilized carbocation.

If the leaving group behaves as weak base after departing then it will be a good leaving group.

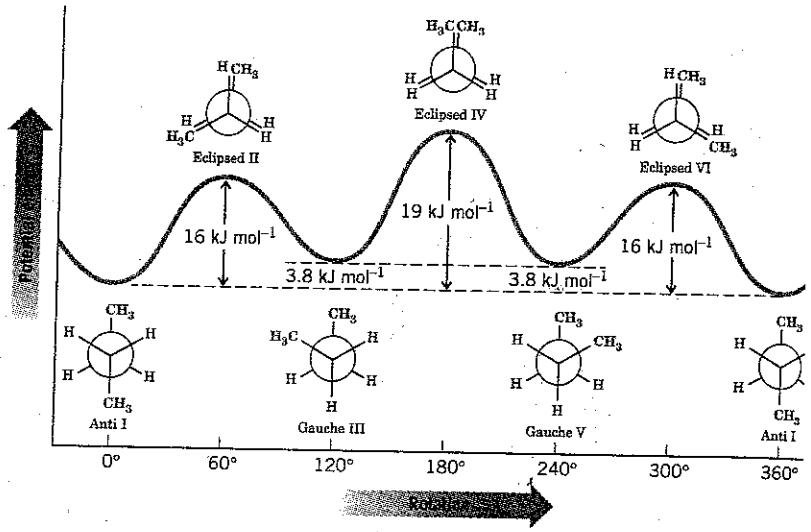
$I^- > Br > Cl^- \gg F^-$.

(ii)

(4 M)



Anti Conformation doesn't have any strain, highly stable.



Potential Energy diagram.

3(i)

$$\frac{\Delta H_v}{T_b} = 85 \text{ J/K/mol} \quad ; \quad T_b = -1^\circ C = 272.15 K$$

(2 M)

$$\Delta H_v = (272.15) \times 85$$

$$= 23.13 \text{ kJ/mol}$$

(ii) $C_2H_6 + 7/2\ O_2 \longrightarrow 2CO_2 + 3H_2O$ (5M)

$$\Delta H_c^\circ = 2\Delta H_f^\circ(CO_2) + 3\Delta H_f^\circ(H_2O) - \Delta H_f^\circ C_2H_6$$

$$\Delta H_f^\circ C_2H_6 = -\Delta H_c^\circ + 2\Delta H_f^\circ(O_2) + 3\Delta H_f^\circ(H_2O)$$

$$= -85 \text{ KJ}$$

(iii) $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$

rate $= k_r [NO]^2 [O_2]$ (6 M)

Step-① $NO + NO \longrightarrow N_2O_2$; Rate of form. $N_2O_2 = k_a [NO]^2$

Step-② $N_2O_2 \longrightarrow NO + NO$; Rate of decomp. of $N_2O_2 = k_a' [N_2O_2]$

Step-③ $N_2O_2 + O_2 \longrightarrow NO_2 + NO_2$; Rate of Consump. of $N_2O_2 = k_b [N_2O_2][O_2]$

Rate of formation of $NO_2 = 2k_b [N_2O_2][O_2]$

Net form. of $N_2O_2 = k_a [NO]^2 - k_a' [N_2O_2] - k_b [N_2O_2][O_2]$

Steady State Approximation:- Net form. of $N_2O_2 = 0$

$\therefore k_a [NO]^2 - k_a' [N_2O_2] - k_b [N_2O_2][O_2] = 0$

ie $[N_2O_2] = \dfrac{k_a [NO]^2}{k_a' + k_b [O_2]}$

$\therefore$ Rate of form. NO_2 is, $2k_b [N_2O_2][O_2]$

$$\Rightarrow \frac{2k_a k_b [NO]^2 [O_2]}{k_a' + k_b [O_2]}$$

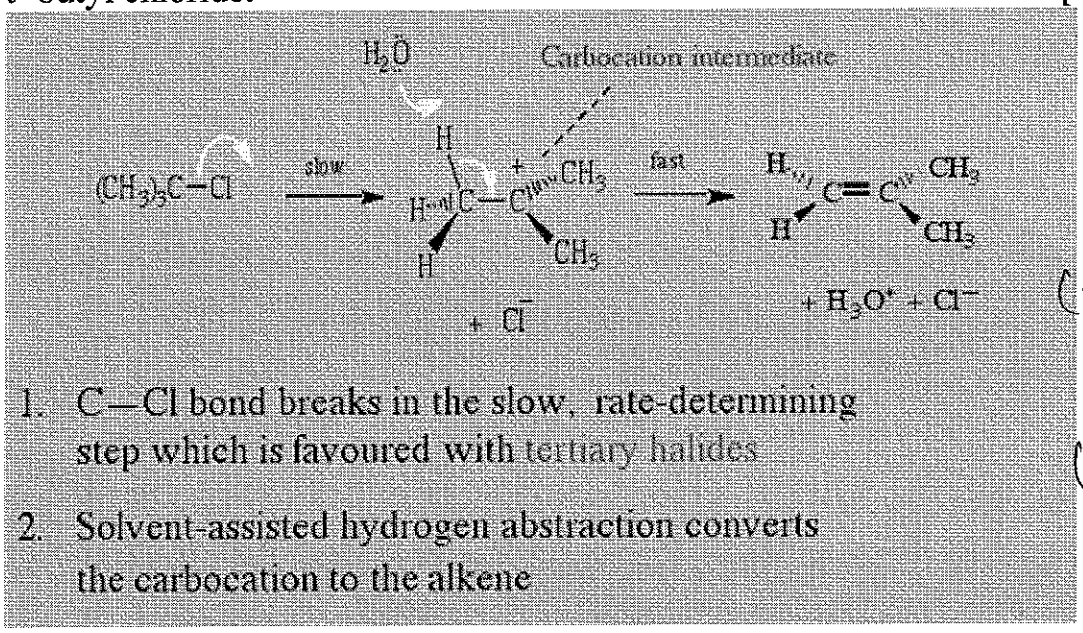
when $k_a' \gg k_b$

$$\Rightarrow \frac{2k_a k_b}{k_a'} [NO]^2 [O_2] = k_r [NO]^2 [O_2]$$

$$k_r = \frac{2k_a k_b}{k_a'}$$

PART-C

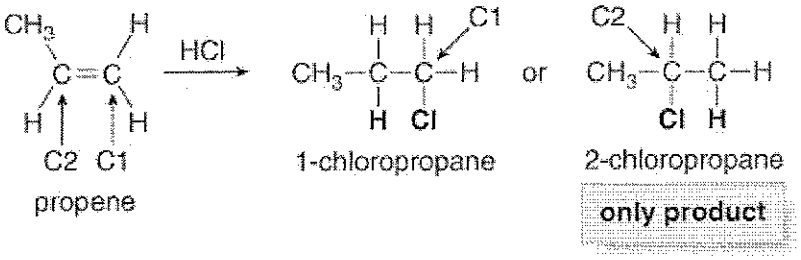
1.(i) a reaction mechanism for the formation of 2 –methyl propene from t- butyl chloride. **[4M]**



(3M)

(1M)

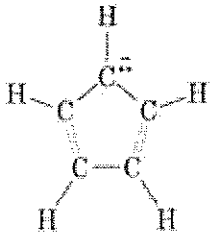
(ii) Addition of hydrochloric acid to propene and justify the product formed **[4M]**



(2M)

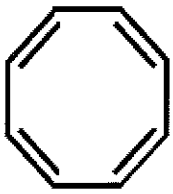
justification (2M)

2.(i)(a) Cyclopenta dienyl anion - **aromatic** It obeys Huckel's rule-contains 6Π electrons –planar-stable **[2M]**



Cyclopentadienyl anion

b)



cyclooctatetraene

anti aromatic

Compounds With 4n π Electrons are **Not Aromatic or Antiaromatic**

- If the ring is larger, it will distort out of planar and behave like an ordinary alkene .It has 8-π electron (four double bonds)and are not delocalized (single and double bonds)
- Cyclooctatetraene has four double bonds, reacting with Br_2, $KMnO_4$, and HCl as if it were four alkenes

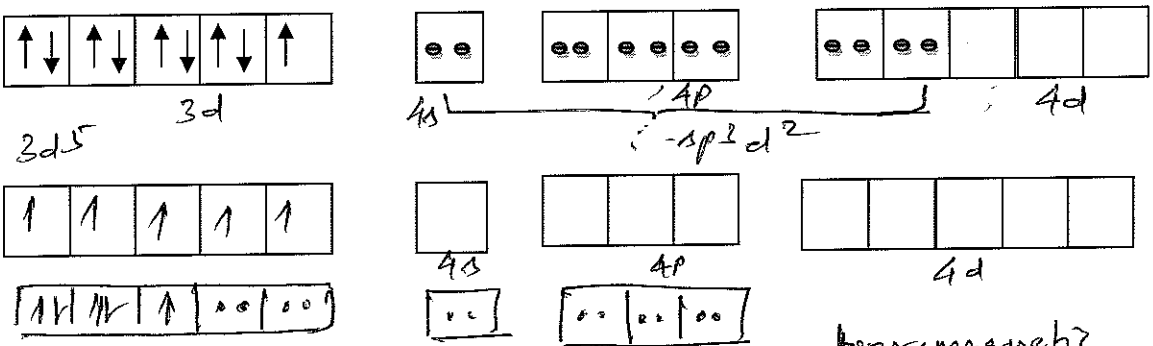
(ii) Write the state of hybridization of the central metal atom, magnetic behavior and geometry of the given complexes using VB theory **(6M)**

$[Cu(NH_3)_4]^{2+}$ $[Mn(CN)_6]^{4-}$

Electronic configuration of Cu^{2+}

Paramagnetic (1)

Cu^{2+} $3d^9$ ion, sp^3d^2 hybridization - octahedral geometry (1)



(1)

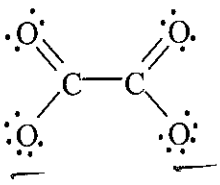
(1)

(1)

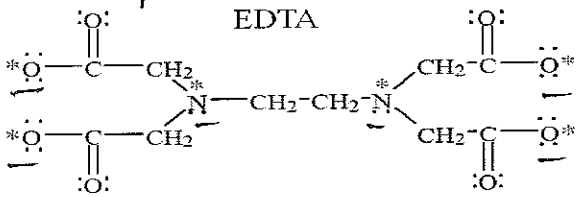
3.(i)

paramagnetic (1)

Octahedral (1)



EDTA

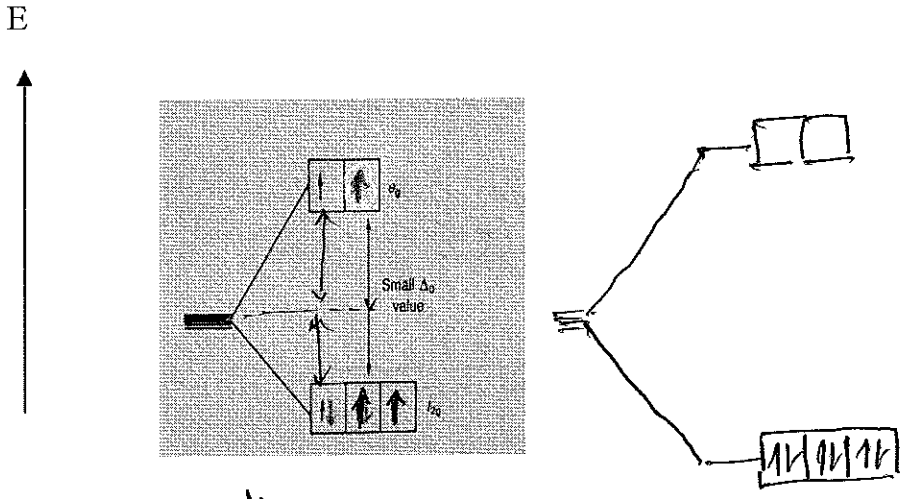


[2 + 2M]

(ii) Predict on the basis of CFT whether the following complex is

planar, tetrahedral or octahedral. Show the distribution of d-electron of the central metal atom in the splitted d-orbitals. **(4M)**

$[Co(NH_3)^6]^{3+}$ Co^{3+} is having 3 d^6 configurations - geometryoctahedral (2M)



$t_{2g}^4 e_g^2$ $t_{2g}^6 e_g^0$

(NH_3) weak field ligand strong field ligand

(2M)

BITS PILANI, DUBAI CAMPUS

I YEAR- SECOND SEMESTER 2012-2013

TEST-II-OPEN BOOK

Course Title: General Chemistry | **Course No: CHEM F111**

Date: 22.04.2013 | **Total Marks: 40**

Time: 50 Min | **Weightage: 20%**

1. Answer all questions sequentially.
2. Show stepwise calculation indicating the units wherever it is required.
3. Only prescribed text book and original hand written class notes are allowed.

1. (a) Find the theoretically possible number of vibrational absorption bands in the IR spectra of (i) Aniline (ii) OCS
   (b) What do you mean by the term charge transfer complexes? Give suitable examples.
   (c) Write the different types of electronic transitions in the order of increasing energy
   (d) How will you arrive at the rate law implied by the mechanism of the following reaction?

$$2\,NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

[4+2+2+5 M]

2. (a) The entropy of vaporization of methanol is 35.27 $kJmol^{-1}$ at its boiling point of 64.1°C. Calculate
   i) The entropy of vaporization of methanol at this temperature and
   ii) The entropy change of surroundings. **[3+1 M]**

   (b) Calculate the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5L to a volume of 50 L at 303 K. **[3 M]**

   c) Calculate the standard reaction Gibbs energy and the equilibrium constant at 25°C for the reaction,

$$CH_{4(g)} + 3Cl_2(g) \rightleftharpoons CHCl_3(l) + 3HCl(g)$$

   (Standard Gibbs energy of formation of $CHCl_3$, HCl and CH_4 are -73.66, -95.30, -50.72 $kJmol^{-1}$ respectively). **[3+3 M]**

3. (a) In a class room of dimensions 10m x 8m x 6m, there are twenty students attending the class of a thermodynamics lecturer. On the average, each individual in the room occupies 0.5 m^3 and produces 100 W heat. Initially the room was at standard temperature and pressure, then sealed and insulated. Calculate the rise in temperature of the air after 15 minutes.
   ($Cv_{(air)}$= 0.717 kJ/kg/K; $R_{(air)}$ = 0.287 kJ/kg/K).
   (b) One mole of an ideal gas is at 0 °C during an expansion process from 3 L to 10 L. Calculate
   i) Work done during expansion ii) heat transfer with surrounding iii) the work required to return the original volume through an isobaric process. **[7+7 M]**

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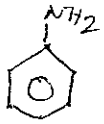
I YEAR SECOND SEMESTER, 2012-2013

TEST-II-OPEN BOOK

Course Title: General Chemistry | Course No: CHEM F111

Date: 22.04.2013 | Total Marks: 40

Time: 50 Min | **Answering Scheme** | Weightage: 20%

1. a, Aniline  $C_6H_5NH_2$ No. of atoms 14

Non linear molecule – No. of vibrational degrees of freedom $= 3N-6$

$= 3(14)-6$ (2M)

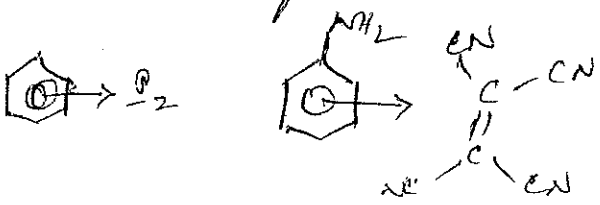
No. of vibrational absorption bands $= 36$

for OCS – linear triatomic molecule

No. of vibr. bands $= 3N-5$; $9-5 = 4$ (2M)

b, Charge transfer Complex – term (1M)

Any two examples (1M)



c, $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n - \pi^*$ (2M)

c) $\Delta_r G^\ominus = \Delta_f G^\ominus(CHCl_3, l) + 3\Delta_f G^\ominus(HCl, g)$

$- \Delta_f G^\ominus(CH_4, g)$

(1M)

$\nu(CHCl_3) = 1, \quad \nu(HCl) = 3,$

$\nu(CH_4) = -1, \quad \nu(Cl_2) = -3.$

$\therefore \Delta_r G^\ominus = (-73.66) + 3 \times (-95.30)$

$- (-50.72)$

$\Delta_r G^\ominus = \underline{-308.84 \text{ kJ mol}^{-1}}.$ (2M)

$\ln K = -\dfrac{\Delta_r G^\ominus}{RT}$ (1M)

$= \dfrac{-(-308.84 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{mol}^{-1}) \times (298.15 \text{ K})}$

$= 124.58$

$\therefore K = \underline{1.3 \times 10^{54}}.$ (2M)

Fast Initial Step

$$2\,NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

- The rate law for this reaction is found (experimentally) to be

$$rate = k\,[NO]^2\,[Br_2]$$ (1M)

- Because termolecular (= trimolecular) processes are rare, this rate law suggests a two-step mechanism.

Fast Initial Step

- A proposed mechanism is

$$Step\ 1:\ NO + Br_2 \rightleftharpoons NOBr_2\quad (fast)$$
$$Step\ 2:\ NOBr_2 + NO \rightarrow 2NOBr\quad (slow)$$

Step 1 is an *equilibrium*-
it includes the forward *and* reverse reactions.

Fast Initial Step

$$Step\ 1:\ NO + Br_2 \rightleftharpoons NOBr_2\quad (fast)$$
$$Step\ 2:\ NOBr_2 + NO \rightarrow 2NOBr\quad (slow)$$

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

$$rate_2 = k_2\,[NOBr_2]\,[NO]$$ (1M)

- But how can we find $[NOBr_2]$?

Fast Initial Step

$$Step\ 1:\ NO + Br_2 \rightleftharpoons NOBr_2\quad (fast)$$
$$Step\ 2:\ NOBr_2 + NO \rightarrow 2NOBr\quad (slow)$$

- $NOBr_2$ can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

$$Rate_f = Rate_r$$ (1M)

2. a) i) $\Delta_{vap}S = \dfrac{\Delta_{vap}H}{T_b}$ (1

$$= \frac{35.27 \times 10^3 \text{ J mol}^{-1}}{(64.1 + 273.15)\text{ K}}$$

$$\begin{array}{r} 64.1 \\ 273 \\ \hline 337.1 \end{array}$$

$0.1046 \text{ kJ K}^{-1} = \underline{\underline{104.6 \text{ J K}^{-1}}}$ (2M)

ii) $\Delta S_{sys} + \Delta S_{sur} = 0$. $\Delta S_{sur} = -\dfrac{\Delta H}{T}$

$\therefore \Delta S_{sur} = \underline{\underline{-104.6 \text{ J K}^{-1}}}$. (1M)

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b) $\Delta S = 2.303 \times n \times R \times \log \dfrac{V_2}{V_1}$. $\left(nR \ln \dfrac{V_2}{V_1}\right)$ (2M)

$$= 2.303 \times 2 \times 8.3145 \times \log \frac{50}{5}$$

$= \underline{\underline{38.29 \text{ J K}^{-1}}}$. (1M)

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3 (a) Total volume of room $= 10 \times 8 \times 6 = 480\ m^3$

Vol. of air = Tot. Vol − Vol. of 21 individual (students + Lecturer)

$= 480 - (21 \times 0.5) = 469.5\ m^3$ (1M)

$m_{air} = \frac{PV}{RT} = \frac{(101 \times 1000) \times 469.5}{(0.287 \times 1000) \times 298} = 554.4\ kg.$ (1M)

$\Delta U = 21 \times (100\ J/s) \times \underbrace{15 \times 60}_{15\ mts} = 1890000\ J.$ (1M)

$\Delta T = \frac{\Delta U}{m C_v} = \frac{1890000}{554.4 \times (0.717 \times 1000)}$

$\Delta T = 4.75^\circ C$ (or) K (4 M)

(b) (i) $W = -nRT \ln\left(\frac{V_2}{V_1}\right)$

$= -1 \times 8.314 \times 273 \times \ln(10/3)$

$= -2.7 \times 10^3\ J$ (2 M)

(ii) $\Delta E = Q + W$ isothermal process: $\Delta E = 0$

$Q = -W$

$Q = 2.7 \times 10^3\ J$ (2M)

(iii) Const. 'P'

$W = -P(V_2 - V_1) \Rightarrow -P\Delta V$

$= -\frac{nRT_1}{V_1} \times (V_2 - V_1)$

$= -\frac{1 \times 8.314 \times 273}{10 \times 10^{-3}} \times (3 - 10) \times 10^{-3}$

$W = 1.6 \times 10^3\ J$ (3 M)

BITS PILANI, DUBAI CAMPUS
I YEAR SECOND SEMESTER, 2012-2013
TEST-I-CLOSED BOOK

Course Title: General Chemistry | **Course No: CHEM F111**
Date: 04.03.2013 | **Total Marks: 50**
Time: 50 Min | **Weightage: 25%**

1. Answer all questions sequentially.
2. Show stepwise calculation indicating the units wherever it is required.
3. Useful Data: h= 6.626 x 10^{-34} J.s, c = 3 x 10^{10} cm/s, m_e= 9.110 x 10^{-31} Kg; R_H=109677 cm^{-1}, R= 8.314 J/K/mol, R=0.0821 litre atm $K^{-1}mol^{-1}$, Atomic number: N = 7, C = 6, P =15, O = 8, Na = 11, Ne = 10, Li = 3, Be =4

1. (i) Light of wavelength 200nm strikes a certain metal which has a photoelectric work function of 2.13eV. Find out the maximum kinetic energy and the velocity of the ejected photoelectron.

   (ii) A moving electron has $5x10^{-25}$ joules of kinetic energy. What is the de-Broglie wavelength of the electron? **[6+5M]**

2. (i) Write the salient features of Born interpretation that helps to understand the physical significance of wave function.
   (ii) Write the boundary conditions for an acceptable wave function. **[2+4M]**

3. (i) How much it is more probable for an electron of wave function $e^{-r/2a0}$, to be found in the nucleus and at a distance of $r = 2a_0$, confined in a small volume dV?

   (ii) Describe (with a diagram) the experiment by which the existence of electron spin was confirmed. **[4+4M]**

4. (i) Calculate the energy of an electron confined in a box of length of 10 pm at n = 4. Show that $9/4^{th}$ of this energy is for the same system at n=6.

   (ii) List the various series of lines obtained in a hydrogen spectrum and present the respective expressions for the wave numbers. **[4+4M]**

5. (i) The atomic radius of nitrogen is lesser than that of carbon while phosphorous has higher value of atomic radius. Justify.

   (ii) Using Hund's rule, predict the ground state electronic configuration of
   a) Oxygen
   b) Phosphorous **[4+4M]**

6. (i) Why the ionization energy of sodium is substantially lower than that of neon?

   (ii) Why the shielding effect of lithium is greater than beryllium?

   (iii) Discuss the effect of atomic number over spin-orbit coupling. Justify your answer. **[3+3+3M]**

BITS PILANI, DUBAI CAMPUS
I YEAR SECOND SEMESTER, 2012-2013
TEST-I-CLOSED BOOK

Course Title: General Chemistry | **Course No: CHEM F111**
Date: 04.03.2013 | **Total Marks: 50**
Time: 50 Min | **Weightage: 25%**

ANSWERING SCHEME

1) i) Energy required to eject electron $E^0 = 2.13\,eV$

$$= 2.13 \times 1.6\times10^{-19}\,J = 3.41\times10^{-19}\,J.$$

$$\text{Energy of photon} = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\times3\times10^{8}\,m/s}{200\times10^{-9}\,m} = 9.943\times10^{-19}\,J$$

Maximum kinetic energy $= E - E^0$

$$= 9.945\times10^{-19}\,J - 3.41\times10^{-19}\,J = 6.535\times10^{-19}\,J$$

$$K.E = \tfrac{1}{2}mv^2 \quad \therefore v = \sqrt{\frac{2K.E}{m}} = \frac{2\times6.535\times10^{-19}\,J}{9.1\times10^{-31}\,kg}$$

$$v = 1.198\times10^{+6}\,m/s$$

ii)

Mass of electron $m = 9.1\times10^{-31}\,kg$

$$K.E = \tfrac{1}{2}mv^2 = 5\times10^{-25}\,J$$

$$\tfrac{1}{2}\times9.1\times10^{-31}\,kg\times v^2 = 5\times10^{-25}\,J$$

$$v = \sqrt{\frac{2\times5\times10^{-25}}{9.1\times10^{-31}}} = 1.048\times10^{3}\,m\,s^{-1}$$

$$h = 6.62\times10^{-34}\,Js = 6.62\times10^{-34}\,kg\,m\,s^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.62\times10^{-34}\,kg\,m^2\,s^{-1}}{9.1\times10^{-31}\,kg\times1.048\times10^{3}\,m\,s^{-1}}$$

$$= 6.94\times10^{-7}\,m$$

2) i) The probability of finding the particle in a small region of space of volume dv is proportional to Ψ^2 dv, where Ψ is the wave function in the region. In other words Ψ^2 is the probability density

ii)

1. It must be single valued (that is, have only a single value at each point): there cannot be more than one probability density at each point.
2. It cannot become infinite over a finite region of space: the total probability of finding a particle in a region cannot exceed 1.
3. The wavefunction is continuous everywhere.
4. It has a continuous slope everywhere.

3(i) At the nucleus, $r = 0$; $\psi = e^{-r/2a_0}$

probability $\propto \psi^2 dV \propto e^0 \, dV$

$\propto 1.0 \, dV$ (2M)

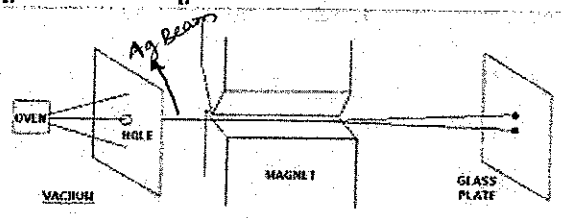
at a distance $r = 2a_0$, $\psi^2 dV \propto (e^{-1})^2 dV$

$\propto 0.135 \, dV$

ratio of probabilities, $1/0.135 = 7.4$. It is more probable by a factor of 7.4, to find the e^- at the nucleus. (2M)

(ii) <u>Stern-Gerlach Experiment:</u>

Beam of Ag atoms shot through strong inhomogeneous magnetic field - splitted in to two beams - 47 e^-s - 46 paired. Remaining one e^- have either ↓ spin or ↑ spin. (2 + 2M)



The experiment of Stern and Gerlach

4(i) $$E_4 = \frac{16 \times (6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31} \times (10 \times 10^{-12})^2}$$

$$= 9.64 \times 10^{-13} \text{ J}$$ (2M)

$$E_6 = 2.17 \times 10^{-12} \text{ J} = \frac{9}{4} E_4$$ (2M)

(ii) $$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right); \; n_1 = 1, 2, 3, \ldots\ldots$$ (2M)

$$n_2 = n_1 + 1, n_1 + 2, \ldots\ldots$$

$n_1 = 1 \Rightarrow$ Lyman Series

$n_1 = 2 \Rightarrow$ Balmer Series

$n_1 = 3 \Rightarrow$ Paschen Series

$n_1 = 4 \Rightarrow$ Bracket Series

$n_1 = 5 \Rightarrow$ Pfund Series. (2M)

5. i) Nitrogen has lesser atomic radius than carbon because of the increased nuclear charge, which draws the electrons in closer to the nucleus;
Atomic radii decrease from left to right across a period. (2M)

The atomic radius of phosphorus is higher. The need to occupy a more distant shell leads to a larger atom;
The atomic radii increase down each group. (2M)

ii) a) <u>Oxygen:</u> <u>At. no: 8.</u>

<u>Hund's rule:</u> [He] $2s^2 2p_x^2 2p_y^1 2p_z^1$.
(2M)

b) <u>Phosphorus:</u> <u>At. no: 15.</u>

[Ne] $3s^2 3p_x^1 3p_y^1 3p_z^1$
(2M)

6. i) <u>Sodium:</u> [Ne] $3s^1$. At. no. : 11.

<u>Neon:</u> At. no. : 10.

The outermost electron in sodium is 3s. It is far from the nucleus, and the latter's charge is shielded by the complete, compact neon-like core. Hence, ionization energy of sodium is substantially lower than that of neon. (3M).

ii) <u>Li:</u> $1s^2\ 2s^1$.

<u>Be:</u> $1s^2\ 2s^2$.

In lithium, the inner two electrons effectively shield the outer one electron of 2s; But, in beryllium, the $1s^2$ electrons shield the two electrons of 2s, which has a relatively lower shielding effect; The extra electron is beryllium is added to the same shell. (3M)

iii) The strength of the spin-orbit coupling increases sharply with atomic number. The increase is due to the orbital magnetic field (2M).

If the nucleus has a high atomic number it will have a high charge, and strong magnetic field. (1M)

—

R. Rajan

BITS, PILANI – DUBAI CAMPUS

A

SECOND SEMESTER 2012 – 2013

First Year Sections 1, 2 & 3

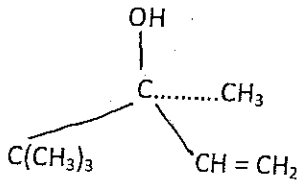
Quiz 2 (Closed Book)

Course Code: CHEM F111	Date: 16-05-2013	Name:----------
Course Title: General Chemistry	Max Marks: 14	ID.No:----------
Duration: 20minutes	Weightage : 7%	Sec.: ----------

Instructions: 1. Attempt all questions

1. Calculate the specific rotation, if 0.90g of an optically active compound dissolved in 20 ml of water in a 200 mm cell gave a rotation of +4.50°. (1M)

2. Assign R/S designation for the following compound indicating the priorities of groups.(2M)



3. Classify the following molecules as chiral or achiral. (2M)
   (i) 2,3 – pentadiene (ii) 2-methylbutane.

4. Draw the potential energy diagram for various conformational isomers of 1-choloropropane (no need to give actual values of potential energy -trend should be shown properly) (3 M)

5. Of the two conformers of Cyclohexane (viz., chair and boat)- which is more stable - What is the reason? (2 M)

6. The hydrolysis of (S)-3-Bromo-3-methylhexane produces both (R) and (S) 3-methyl-3-hexanol Why? (2 M)

7. What is meant by "Concerted Reaction" and this follows which mechanism? (2M)

BITS, PILANI – DUBAI CAMPUS

SECOND SEMESTER 2012 – 2013

First Year Sections 1, 2 & 3

Quiz 2 (Closed Book)

Course Code: CHEM F111 | Date: 16-05-2013 | Course Title: General Chemistry

Max Marks: 14 | Duration: 20minutes | Weightage : 7%

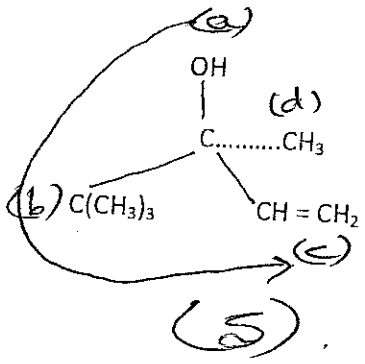
ANSWERING SCHEME

1. Calculate the specific rotation, if 0.90g of an optically active compound dissolved in 20 ml of water in a 200 mm cell gave a rotation of +4.50°. (1M)

$$[\alpha] = \frac{\alpha_{obs.}}{c.l}$$

$$\therefore [\alpha] = \frac{+4.50}{(0.9/20) \times 200 \times 10^{-2}} = 50^\circ$$

2. Assign R/S designation for the following compound indicating the priorities of groups.(2M)

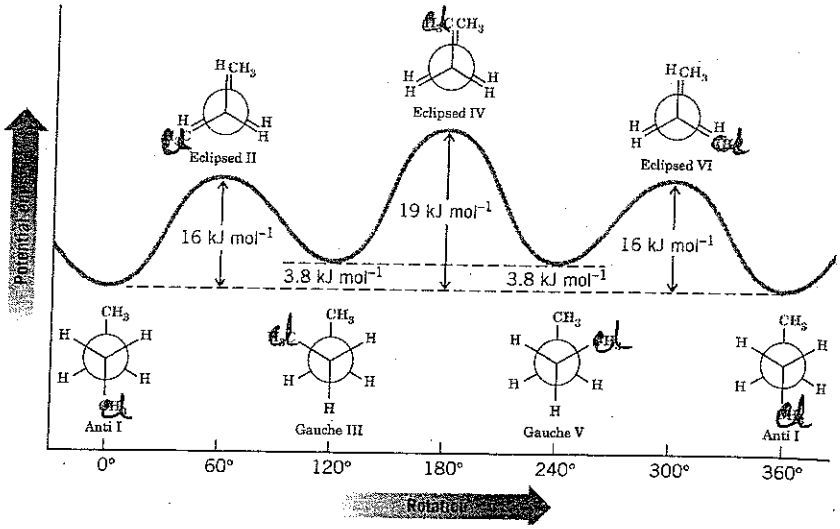


3. Classify the following molecules as chiral or achiral. (2M)
   (i) 2,3 – pentadiene (ii) 2-methylbutane.

i) chiral.

ii) Achiral.

4. Draw the potential energy diagram for various conformational isomers of 1-choloropropane (no need to give actual values of potential energy -trend should be shown properly) (3 M)



5. Of the two conformers of Cyclohexane (viz., chair and boat)- which is more stable - What is the reason? (2 M)

- Chair conformation is more stable
- In boat conformation flagpole - flagpole repulsion increases energy and hence less stable

6. The hydrolysis of (S)-3-Bromo-3-methylhexane produces both (R) and (S) 3-methyl-3-hexanol Why? (2 M)

Because the intermediate Carbo cation is planar, the attack of nucleophile from either side is possible. So Racemization occurs.

7. What is meant by "Concerted Reaction" and this follows which mechanism? (2M)

Simultaneous bond breaking and bond forming.

SN2 -Mechanism.

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BITS PILANI, DUBAI CAMPUS
I YEAR SECOND SEMESTER, 2012-2013
QUIZ-I-CLOSED BOOK

Course Title: General Chemistry | Course No: CHEM F111
Date: 28.03.2013 | Total Marks: 16
Time: 20 Min | Weightage : 8%

Name: | ID. No. 2012A | Sec:

Useful Data: At. No: H =1, P =15.C=6,N=7, F=9

1. Write the valence bond wave function for HI molecule. (2M)

2. Schematically represent the potential energy curve for a hydrogen molecule. (2M)

3. Give the VB description of PH_3. (2M)

4. Give the orbital model of ethyne molecule showing scheme of overlaps and bonds. (3M)

5. With a suitable example depict sp hybridization of carbon showing scheme of overlap and bonds **(2M)**

6. Write the electronic configuration of oxygen molecule and deduce its bond order. **(3M)**

7. Which one of the following has higher bond dissociation energy N_2 or F_2? Why? **(2M)**

A

BITS PILANI, DUBAI CAMPUS
I YEAR SECOND SEMESTER, 2012-2013
QUIZ-I-CLOSED BOOK

Course Title: General Chemistry | **Course No: CHEM F111**
Date: 28.03.2013 | **Total Marks: 16**
Time: 20 Min | **Weightage : 8%**

ANSWERING SCHEME

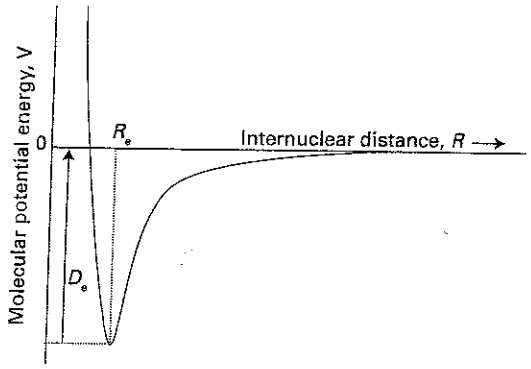
Name: **ID. No. 2012A** **Sec:**

Useful Data: At. No: H =1, P =15.C=6,N=7, F=9

1. Write the valence bond wave function for HI molecule. **(2M)**

$$\psi_{H-I}(1,2) = \psi_H(1)\,\psi_I(2) + \psi_H(2)\,\psi_I(1).$$

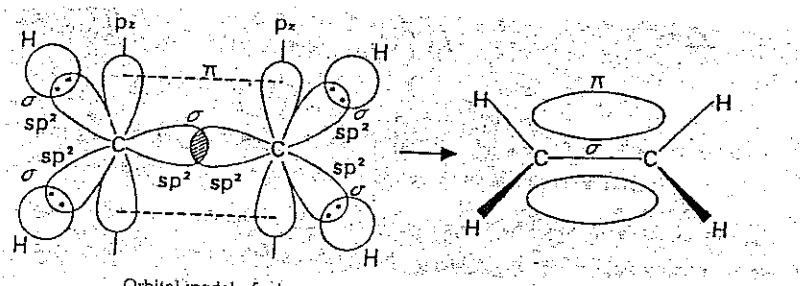
2. Schematically represent the potential energy curve for a hydrogen molecule. **(2M)**



3. Give the VB description of PH_3. **(2M)**

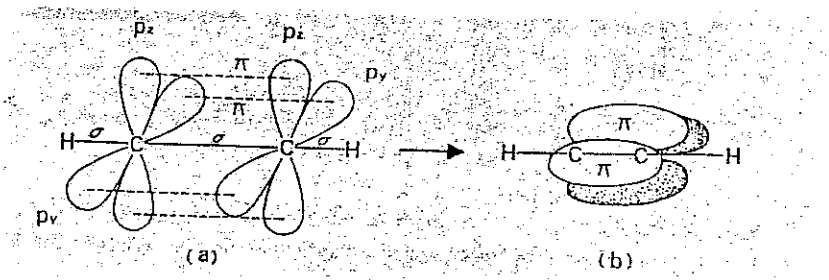
Three σ (P 3p, H 1s) bonds.

4. Give the orbital model of ethyne molecule showing scheme of overlaps and bonds. **(3M)**



Orbital model of ethene molecule. (*a*) shows scheme of overlaps; and (*b*) shows bonds, sigma bonds indicated by straight lines.

5. With a suitable example depict sp hybridization of carbon showing scheme of overlap and bonds **(2M)**



Formation of ethyne molecule. (*a*) shows scheme of overlaps; and (*b*) shows the bonds, σ bonds being indicated by straight lines.

6. Write the electronic configuration of oxygen molecule and deduce its bond order. **(3M)**

O_2 : At. No: 8 :

$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_z}^2, \pi_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_x}^{*1}, \pi_{2p_y}^{*1}$.

$B.O. = \frac{1}{2}(N_b - N_a) = \underline{\underline{2}}$

7. Which one of the following has higher bond dissociation energy N_2 or F_2? Why? **(2M)**

N_2 has higher bond dissociation energy.

B.O. for N_2 is $\underline{\underline{3}}$ & F_2 is $\underline{\underline{1}}$