PAPER : IIT-JAM 2012

CHEMISTRY-CY

NOTE: Attempt ALL the **44 questions.** Questions 1-30 **(Objective questions)** carry ***three*** marks each and questions 31-44 **(Subjective questions)** carry ***fifteen*** marks each.

1. Molecular shape of $SOCl_2$ is:
(a) Square planar (b) Trigonal pyramidal (c) Triangular planar (d) T-shape

2. Number of three-centre two-electron(3c-2e) bonds present in diborane is:
(a) 2 (b) 4 (c) 6 (d) 8

3. The lattice energy of LiF calculated from Born-Lande equation –1000 kJ mol^{-1}. Assume that for both LiF and MgO the Madelung constants, interionic distances and Born exponents have the same value. The lattice energy of MgO in kJ mol^{-1} is:
(a) –4000 (b) –2000 (c) 2000 (d) 4000

4. The compound formed by dissolving elemental gold in *aqua regia* is:
(a) AuCl (b) $AuNO_3$ (c) $H[AuCl_4]$ (d) $H[Au(NO_3)_4]$

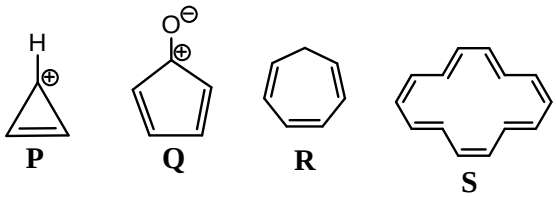
5. Number of moles of ions produced by complete dissociation of one mole of Mohr's salt in water is:
(a) 3 (b) 4 (c) 5 (d) 6

6. The tetrachloro complexes of Ni(II) and Pd(II) respectively, are (atomic numbers of Ni and Pd are 28 and 46 respectively)
(a) diamagnetic and diamagnetic (b) paramagnetic and paramagnetic
(c) diamagnetic and paramagnetic (d) paramagnetic and diamagnetic

7. The total number of steps involved and number of beta particles emitted in the spontaneous decay of $^{238}_{92}U \rightarrow {}^{208}_{82}Pb$ respectively, are
(a) 8 and 6 (b) 14 and 6 (c) 6 and 8 (d) 14 and 8

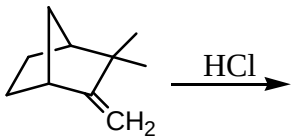
8. A filter paper moistioned with ammonical sodium nitroprusside solution turns violet on contact with a drop of alkaline Na_2S solution. The violet color is due to the formation of
(a) $\left[Fe(SCN)_5(NO)\right]^{1-}$ (b) $\left[Fe(SCN)_5(NO)\right]^{2-}$
(c) $\left[Fe(CN)_5(NOS)\right]^{3-}$ (d) $\left[Fe(CN)_5(NOS)\right]^{4-}$

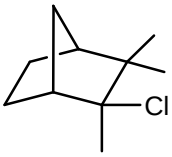
9. The species/compounds that are aromatic among the following are

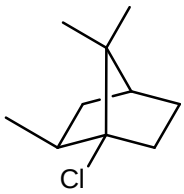


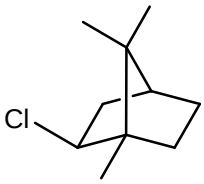
(a) R and S (b) P and Q (c) Q and S (d) P and S

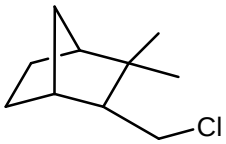
10. The major product obtained in the reaction below is



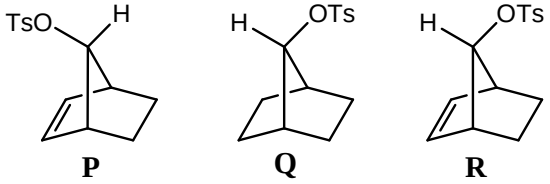
(a) 

(b) 

(c) 

(d) 

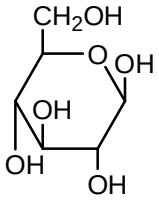
11. The rates of acetolysis for the following norbornyl derivatives are in the order

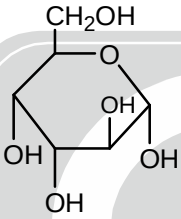


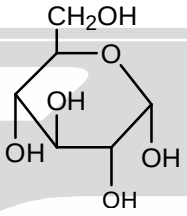
P **Q** **R**

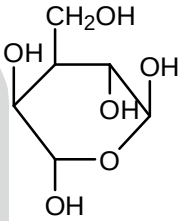
(a) R > Q > P (b) Q > R > P (c) P > R > Q (d) R > P > Q

12. The Haworth projection for α – anomer of D-glucose is:

(a) 

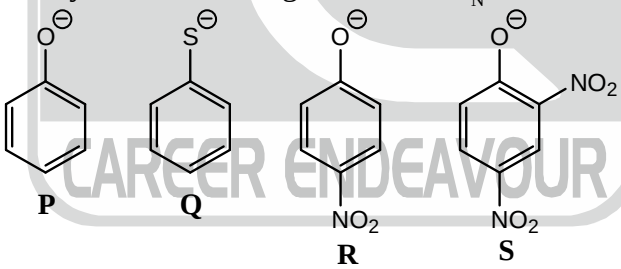
(b) 

(c) 

(d) 

13. The complementary DNA sequence of the given DNA 5'-G-A-A-T-T-C-3' is:
(a) 5'-C-T-T-A-A-G-3' (b) 5'-C-U-U-A-A-G-3'
(c) 3'-C-T-T-A-A-G-5' (d) 3'-G-A-A-T-T-C-5'

14. The order of nucleophilicity of the following anions in a S_N2 reaction is:



P **Q** **R** **S**

(a) Q > R > S > P (b) Q > P > R > S (c) Q > R > P > S (d) P > S > R > Q

15. The pair of conformation that has maximum energy difference is:

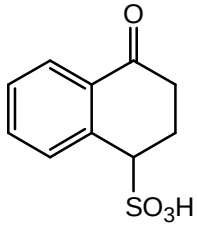
(a)  and

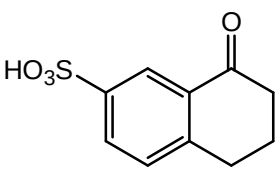
(b)  and

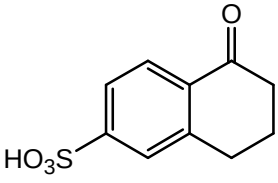
(c)  and

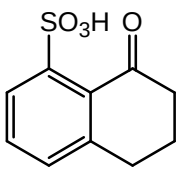
(d)  and

16. The major mono-sulfonation product of α – tetralone is :

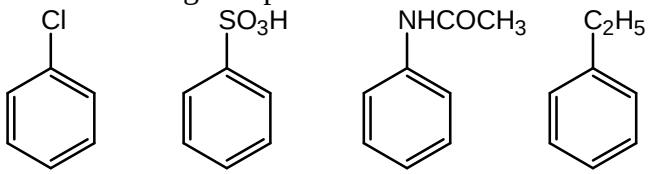
(a) 

(b) 

(c) 

(d) 

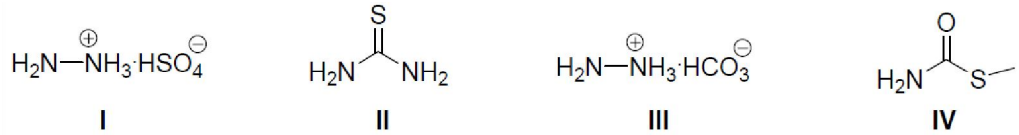
17. Electrophilic nitrations of the following compounds follow the trend



P **Q** **R** **S**

(a) S > R > P > Q (b) R > S > P > Q (c) R > P > S > Q (d) P > S > R > Q

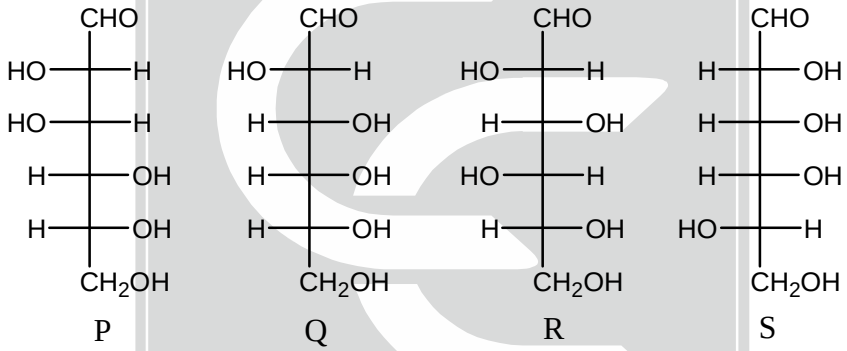
18. The compounds those would not respond to tests of both nitrogen and sulfur with sodium fusion extracts are



I II III IV

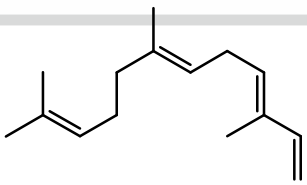
(a) I and III (b) III and IV (c) I and IV (d) II and IV

19. The correct epimeric pair of the following is:



(a) P and Q (b) R and Q (c) Q and S (d) R and S

20. α – Farnesene shown below is a



(a) diterpene having two isoprene units (b) triterpene having three isoprene units
(c) triterpene having four isoprene units (d) sesquiterpene having three isoprene units.

21. For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium constant, K_p is expressed as

(a) $3^3 K_p = \frac{p_{NH_3}}{p_{N_2}^2}$ (b) $3^3 K_p = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3}$ (c) $3^3 K_p = \frac{p_{NH_3}^2}{p_{N_2}^4}$ (d) $3^{3/2} K_p^{1/2} = \frac{p_{NH_3}^2}{p_{N_2}^4}$

22. The average speed of H_2, N_2 and O_2 gas molecules is in the order

(a) $H_2 > N_2 > O_2$ (b) $O_2 > N_2 > H_2$ (c) $H_2 > O_2 > N_2$ (d) $N_2 > O_2 > H_2$

23. The enthalpy of vaporization $\left(\Delta_{vap}H\right)$ is zero at

(a) Boyle temperature (b) critical temperature
(c) inversion temperature (d) boiling temperature.

24. The half-life of any zero-order reaction is:

(a) independent of concentration (b) proportional to inverse of concentration
(c) proportional to concentration (d) proportional to square of the concentration.

25. The molality of $\left(NH_4\right)_2 SO_4$ solution that has the same ionic strength as 1 mol kg^{-1} solution of KCl is:

(a) $\frac{1}{3}$ mol kg^{-1} (b) $\frac{1}{2}$ mol kg^{-1} (c) $\frac{2}{5}$ mol kg^{-1} (d) $\frac{3}{5}$ mol kg^{-1}

26. The standard enthalpy of formation $\left(\Delta_f H^0_{300}\right)$ at 1 bar and 300 K for the formation of $CF_2ClCF_2Cl(g)$ from its constituent elements in the standard state is –900 kJ mol^{-1}. Given R = 8.3 J K^{-1} mol^{-1}, the standard internal energy of formation $\left(\Delta_f U^0_{300}\right)$ at the same pressure and temperature is:

(a) –905 kJ mol^{-1} (b) –895 kJmol^{-1} (c) 895 kJ mol^{-1} (d) 905 kJ mol^{-1}.

27. The percent transmittance of a solution having absorbance (optical density) 1.0 is:

(a) 1 (b) 10 (c) 50 (d) 99

28. The matrix which transforms $\begin{pmatrix} x \\ y \end{pmatrix}$ to $\begin{pmatrix} -y \\ -x \end{pmatrix}$ is:

(a) $\begin{pmatrix} -1 & -1 \end{pmatrix}$ (b) $\begin{pmatrix} -1 \\ -1 \end{pmatrix}$ (c) $\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$ (d) $\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

29. A concentration cell with two hydrogen electrodes at two different pressures is depicted as

$$\begin{matrix} H_2(g)(Pt) \\ p_{H_2} = p_1 \end{matrix} \Big| HCl(aq) \Big| \begin{matrix} H_2(g)(Pt) \\ p_{H_2} = p_2 \end{matrix}$$

The potential (E_{cell}) of the cell is:

(a) $\frac{RT}{F}\ell n\frac{p_2}{p_1}$ (b) $\frac{RT}{F}\ell n\frac{p_1}{p_2}$ (c) $\frac{RT}{2F}\ell n\frac{p_2}{p_1}$ (d) $\frac{RT}{2F}\ell n\frac{p_1}{p_2}$

30. An aqueous solution containing 1 g L^{-1} of a polymer exerts osmotic pressure of 4 torr at 300K. Given R = 0.082 L atm, the molar mass (g mol^{-1}) of the polymer is:

(a) 4500 (b) 4564 (c) 4674 (d) 4800

31. (a) Identify the most acidic compound from the following: CH_3-CH_3, $CH_2=CH_2$ and $CH\equiv CH$, and justify your answer. Draw overlap of the orbitals to show bonding in the most acidic compound using the concept of hybridization. **[Marks: 09]**

(b) Write a balanced chemical equation to represent acid-base reaction of orthoboric acid in water. Addition of ethylene glycol to aqueous orthoboric acid enhances its acidity. Explain the above statement using appropriate chemical equation. **[Marks: 06]**

32. (a) Draw the unit cell structure of NaCl. Calculate the limiting radius ratio of any ionic solid having NaCl like structure. **[Marks: 09]**

(b) Give molecular formula and structure of the compound formed by reaction of $Be(OH)_2$ with acetic acid. **[Marks: 06]**

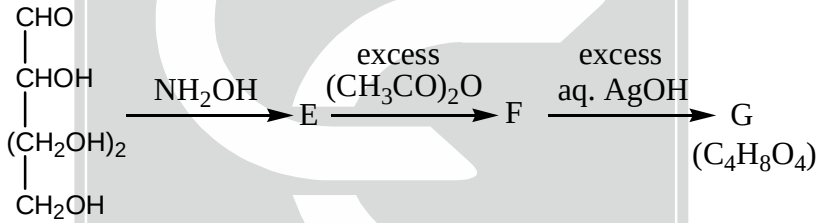
33. (a) The spin-only magnetic moments of $K_3[Fe(oxalate)_3]$ and $K_3[Ru(oxalate)_3]$ are $5.91\,\mu_B$ and $1.73\,\mu_B$, respectively. Write down their ligand field electronic configuration. Justify your answer. Atomic numbers of Fe and Ru are 26 and 44 respectively. **[Marks: 09]**

(b) Draw the structures of NO_2^+, NO_2 and NO_2^-. Arrange them in the increasing order of O–N–O bond angles **[Marks: 09]**

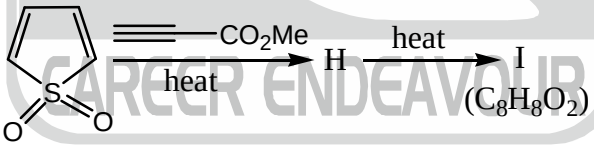
34. (a) Show with labels the splitting of d-orbitals in an octahedral ligand field. Calculate the CFSE of (i) high spin d^6 and (ii) low spin d^6 metal ions in octahedral field. **[Marks: 09]**
(b) Schematically represent orbital overlaps in metal carbonyls. Show the correct signs of the lobes. **[Marks: 06]**

35. (a) A coordination compound is composed of one Co(III), one chloride, one sulfate and four molecules of ammonia. The aqueous solution of the compound gives no precipitate when combined with aqueous $BaCl_2$, while a white precipitate is formed with aqueous $AgNO_3$ solution. Draw its structure and explain the observations with chemical equations. **[Marks: 09]**
(b) Draw the structures of dimethylglyoxime ($DMGH_2$) and its Ni(II) complex formed in aqueous ammonia.
[Marks: 06]

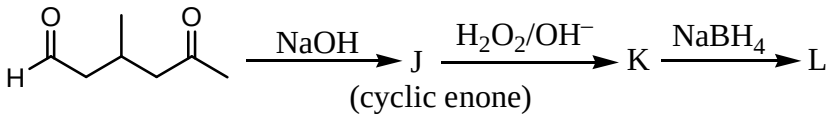
36. (a) Write the structures of **E, F** and **G** in the following scheme of reactions. **[Marks: 09]**



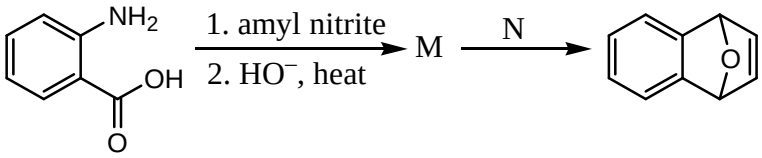
(b) Identify the structues of H and I in the following synthetic transformation **[Marks: 06]**



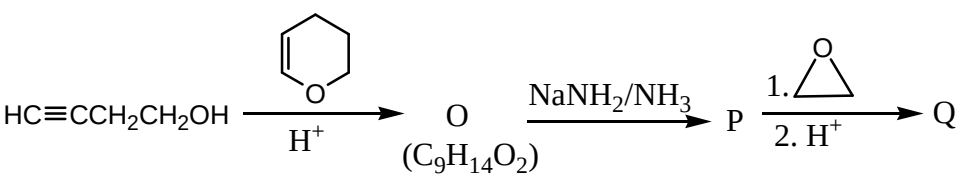
37. (a)Complete the following reaction sequence with appropriate structures of **J**, **K** and **L**.
[Marks: 09]



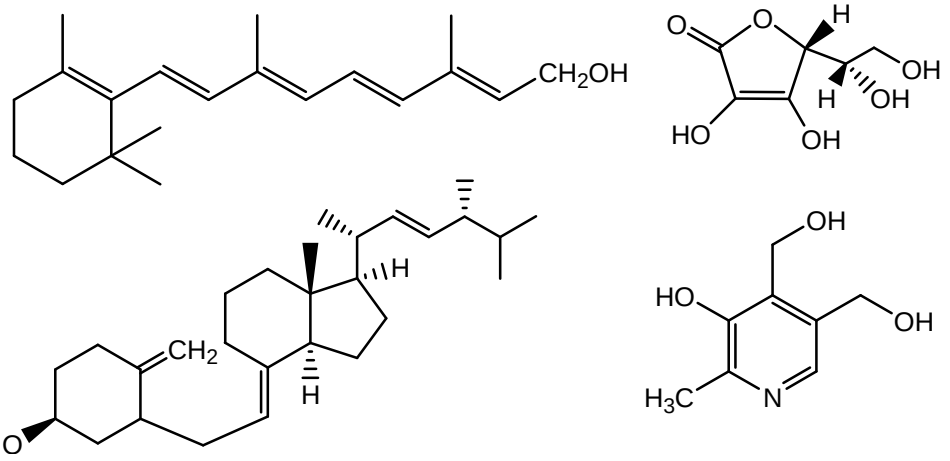
(b) Identify the structures of **M** and **N** in the following synthetic transformation **[Marks: 06]**



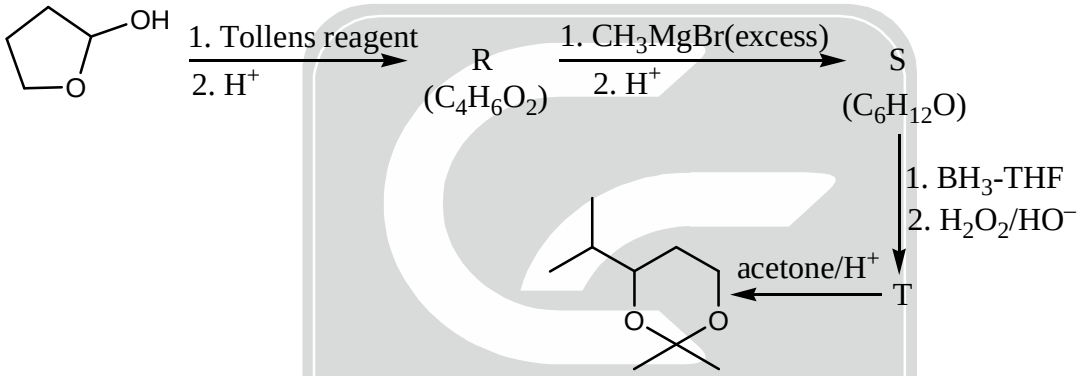
38. (a) In the following reaction scheme, write the structure of **O**, **P** and **Q** **[Marks: 09]**



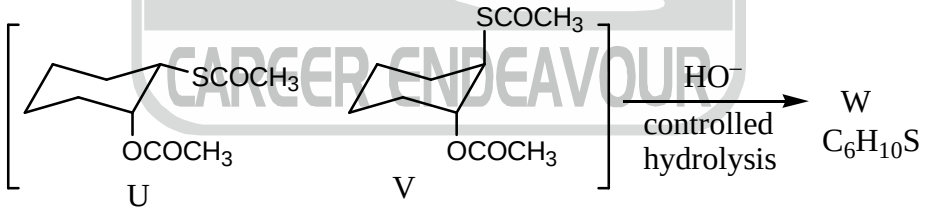
(b) Given below are structures of some natural products. Identify them as vitamin A, B_6, C and D and classify them according to their classes (isoprenoid, alkaloid, carbohydrate and steroid) **[Marks: 06]**



39. **(a)** Write the appropriate structures for **R**, **S** and **T** in the following scheme. **[Marks: 09]**



(b) Choose the correct stereoisomer between U and V that would furnish W on controlled hydrolysis. Write the stable conformation of W. **[Marks: 06]**



40. The mechanism of isomerization of cyclobutene (CB) to 1, 3-butadiene (BD) is as follows.

$$CB + CB \xrightarrow{k_1} CB^* + CB$$

$$CB^* + CB \xrightarrow{k_{-1}} CB + CB$$

$$CB^* \xrightarrow{k_2} BD$$

(a) Show that the rate law is $\frac{d[BD]}{dt} = \frac{k_2.k_1.[CB]^2}{k_{-1}.[CB] + k_2}$ **[Marks: 06]**

(b) The apparent first-order rate constant, $k_{app} = \frac{k_2.k_1.[CB]}{k_{-1}.[CB] + k_2}$. At the CB concentration of 1×10^{-5} mol dm^{-3}, the value of k_{app} reaches 50% of its limiting value obtained at very high concentrations of CB. Evaluate the ratio $\frac{k_2}{k_{-1}}$. **[Marks: 09]**

41. (a) The molar conductance of 0.012 mol dm^{-3} aqueous solution of chloroacetic acid is $100\,\Omega^{-1}\,cm^2\,mol^{-1}$. The ion conductance of chloroacetate and H^+ ions are $50\,\Omega^{-1}\,cm^2\,mol^{-1}$ and $350\,\Omega^{-1}\,cm^2\,mol^{-1}$, respectively. Calculate (i) degree of dissociation and pK_a of chloroacetic acid, and (ii) H^+ ion concentration in the solution. **[Marks: 09]**

(b) Sketch the conductivity versus concentration of base curves for the titration of aqueous solutions of acetic acid (i) with NaOH, and (ii) with NH_4OH. **[Marks: 06]**

42. A solution of a free particle Schrodinger equation $\frac{-h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$ is

$\psi(x) = e^{ikx} = \cos kx + i\sin kx$

(a) Derive expressions for energy 'E' and momentum 'p' of the particle. **[Marks: 09]**

(b) Using the above relations, show that the wavelength (λ) is $\frac{h}{p}$. **[Marks: 06]**

43. (a) Sketch the temperature composition phase diagram at 1 atm pressure for the ethanol-water system. **[Marks: 09]**

(i) Label all the areas in the diagram.

(ii) Indicate the temperaure at which the composition of the vapour is same as that of the liquid. What is this mixture known as?

(iii) What is the degree of freedom at the corresponding composition?

(b) Estimate the pressure necessary to melt ice at –10ºC if the molar volume of liquid water is 18.01 mL and molar volume of ice is 19.64 mL. The entropy change for the melting process is 16.3 $J\,K^{-1}$. Assume that the molar volumes and entropy change remain constant in this temperature range. [100 J = 1 L bar]. **[Marks: 06]**

44. (a) (i) Show that for 'n' moles of a Vander waals gas, $\left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2 a}{V^2}$. **[Marks: 09]**

(ii) Can a gas that obeys the equation of state $p(V - nb) = nRT$ be liquefied? Explain.

(b) Consider ideal mixing of 2 moles of toluene and 2 moles of benzene at 1 atm and 300K. Calculate the values of $\Delta_{mix}V$, $\Delta_{mix}U$, $\Delta_{mix}H$, $\Delta_{mix}G$ and $\Delta_{mix}S$ for the process. ($ln\,2 = 0.69$) **[Marks: 06]**