A

2008-CY

Test Paper Code: CY

Time: 3 Hours Maximum Marks: 300

INSTRUCTIONS

1. The question-cum-answer booklet has **40** pages and has **44** questions. Please ensure that the copy of the question-cum-answer booklet you have received contains all the questions.
2. Write your **Roll Number, Name and the name of the Test Centre** in the appropriate space provided on the right side.
3. Write the answers to the objective questions against each Question No. in the **Answer Table for Objective Questions**, provided on Page No. **9**. Do not write anything else on this page.
4. Each objective question has **4 choices** for its answer: (A), (B), (C) and (D). Only **ONE** of them is the correct answer. There will be **negative marking** for wrong answers to objective questions. The following marking scheme for objective questions shall be used:
   (a) For each correct answer, you will be awarded **3 (Three)** marks.
   (b) For each wrong answer, you will be awarded **-1 (Negative one)** mark.
   (c) Multiple answers to a question will be treated as a wrong answer.
   (d) For each un-attempted question, you will be awarded **0 (Zero)** mark.
   (e) Negative marks for objective part will be carried over to total marks.
5. Answer subjective questions only in the space provided after each question.
6. Do not write more than one answer for the same question. In case you attempt a subjective question more than once, please cancel the answer(s) you consider wrong. Otherwise, the answer appearing last only will be evaluated.
7. All answers must be written in blue/black/blue-black ink only. Sketch pen, pencil or ink of any other colour should not be used.
8. All rough work should be done in the space provided and scored out finally.
9. No supplementary sheets will be provided to the candidates.
10. **Clip board, log tables, slide rule, calculator, cellular phone, pager and electronic gadgets in any form are NOT allowed.**
11. The question-cum-answer booklet must be returned in its entirety to the Invigilator before leaving the examination hall. Do not remove any page from this booklet.
12. Refer to useful data on the reverse.

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2008-CY

READ INSTRUCTIONS ON THE LEFT SIDE OF THIS PAGE CAREFULLY

ROLL NUMBER						

Name:

Test Centre:

Do not write your Roll Number or Name anywhere else in this question-cum-answer booklet.

I have read all the instructions and shall abide by them.

.....

Signature of the Candidate

I have verified the information filled by the Candidate above.

.....

Signature of the Invigilator

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Useful Data

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.08 \times 10^{-3}\ \text{m}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$

$N_A = 6.02 \times 10^{23}$

$k_B = 1.38 \times 10^{-23}\ \text{J K}^{-1}$

$h = 6.6 \times 10^{-34}\ \text{J s}$

$c = 3 \times 10^8\ \text{m s}^{-1}$

$F = 96500\ \text{C mol}^{-1}$

$C_p = 4.2\ \text{J K}^{-1}\ \text{g}^{-1}$ for water

$(2.303RT)/F = 0.059$ V at 298 K

Density of ice and water at 0°C and 1 atm are 0.9 g/cc and 1.0 g/cc, respectively.

$\ln(1/3) = -1.1$; $\ln(1/2) = -0.69$; $\ln(2/3) = -0.41$; $\ln 2 = 0.69$

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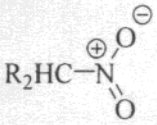
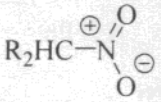
IMPORTANT NOTE FOR CANDIDATES

- **Questions 1-30 (objective questions) carry *three* marks each and questions 31-44 (subjective questions) carry *fifteen* marks each.**
- **Write the answers to the objective questions in the *Answer Table for Objective Questions* provided on page 9 only.**

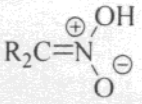
Q.1 The correct statement describing the relationship between



X



Y



Z

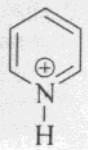
is

(A) **X** and **Y** are resonance structures and **Z** is a tautomer
(B) **X** and **Y** are tautomers and **Z** is a resonance structure
(C) **X**, **Y**, and **Z** are all resonance structures
(D) **X**, **Y** and **Z** are all tautomers

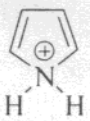
Q.2 Among the following, the correct statement concerning the optical activity is

(A) a molecule containing two or more chiral centres is always optically active
(B) a molecule containing just one chiral centre is always optically active
(C) a molecule possessing alternating axis of symmetry is optically active
(D) an optically active molecule should have at least one chiral centre

Q.3 The correct order of acidity among



(i)



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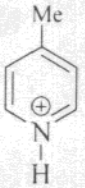

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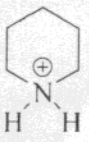
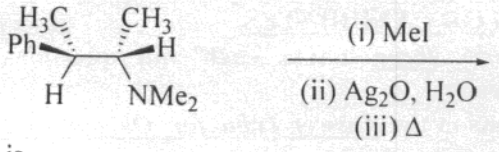


(iv)

is

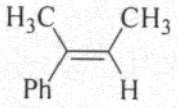
(A) (i) < (ii) < (iii) < (iv)
(B) (iv) < (iii) < (i) < (ii)
(C) (ii) < (i) < (iii) < (iv)
(D) (ii) < (iv) < (i) < (iii)

Q.4 The major product obtained in the following reaction

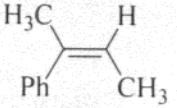


is

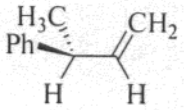
(A)



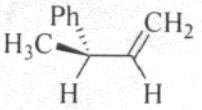
(B)



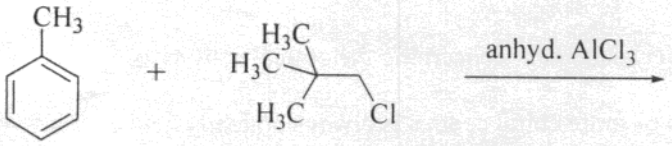
(C)



(D)

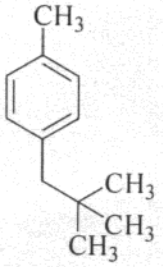


Q.5 The major product of the following reaction



is

(A)



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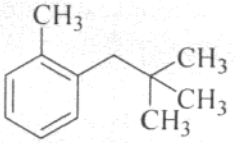

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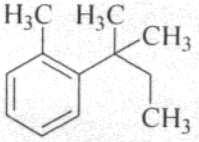

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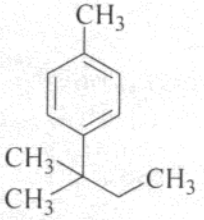
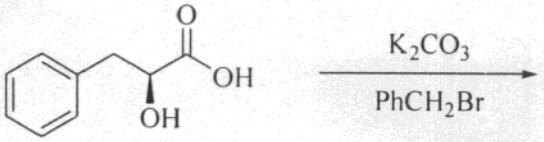


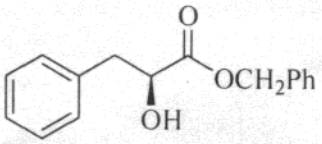
A

Q.6 The major product obtained in the following reaction

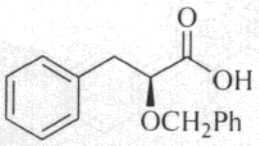


is

(A)



(B)



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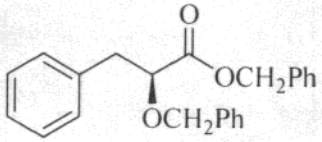
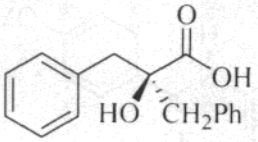


(D)

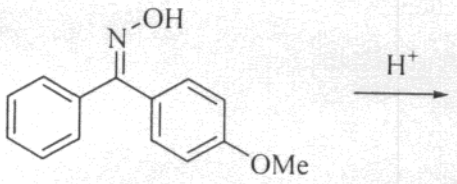


Q.7 *R*-(−)-2-Bromooctane on treatment with aqueous KOH mainly gives 2-octanol that is

(A) optically active with '*R*' configuration
(B) optically active with '*S*' configuration
(C) a racemic mixture
(D) a meso compound

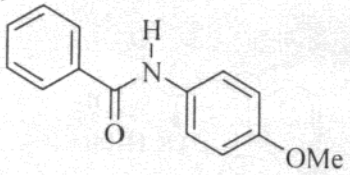
A

Q.8 The major product obtained in the following reaction

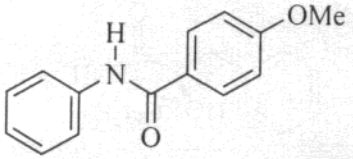


is

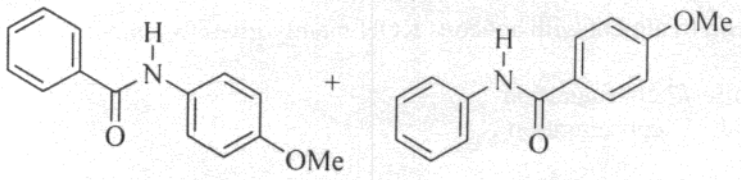
(A)



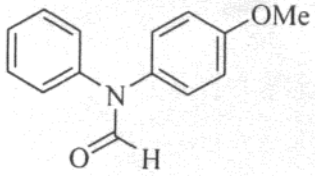
(B)



(C) an equimolar mixture of

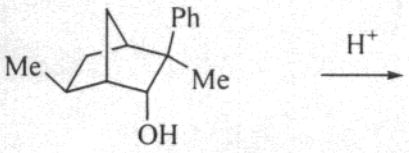


(D)



A

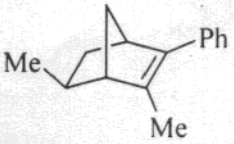
Q.9 The major product obtained in the following reaction



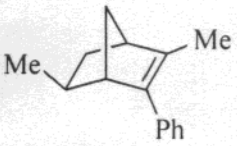
is

(A)

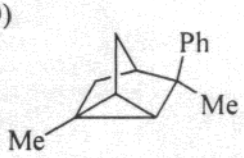
(B)



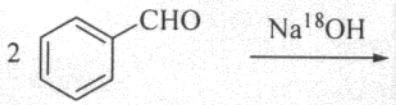
(C)



(D)

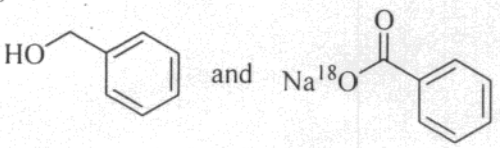


Q.10 The products of the following reaction

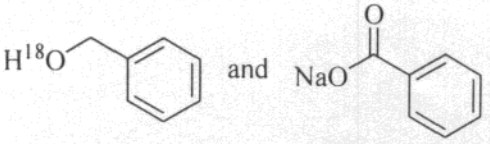


are

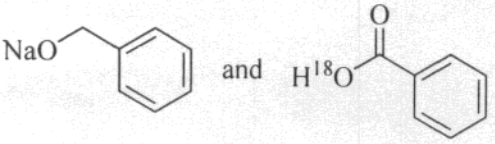
(A)



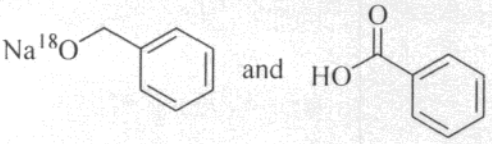
(B)



(C)



(D)



Q.11 When one mole of ice is converted to water at 0°C and 1 atm, the work done (L atm) is

(A) 1.1×10^{-4} (B) 2.0×10^{-3} (C) 2.0×10^{-4} (D) 1.1×10^{-5}

Q.12 When 100 g of water is reversibly heated from 50°C to 75°C at 1 atm, the change in entropy ($J\ K^{-1}$) of the universe is

(A) –0.31 (B) 0.31 (C) 0 (D) 3.1

Q.13 For a zero order reaction, units of the rate constant is expressed as

(A) $M^1 s^{-1}$ (B) $M^0 s^{-1}$ (C) $M^{-1} s^{-1}$ (D) $M^0 s^0$

Q.14 1×10^{-6} moles of the enzyme carbonic anhydrase dehydrates H_2CO_3 to produce 0.6 mol of CO_2 per second. The turnover number of the enzyme is

(A) $N_A \times 6 \times 10^{-5}$
(B) $(1/6) \times 10^{-5}$
(C) $(6 \times 10^5)/N_A$
(D) 6×10^5

Q.15 Given that the most probable speed of oxygen gas is 1000 m s^{-1}, the mean/average speed (m s^{-1}) under the same conditions is

(A) 1224 (B) 1128 (C) 886 (D) 816

Q.16 If the electrons were spin 3/2 particles, instead of spin 1/2, then the number of electrons that can be accommodated in a level are

(A) 2 (B) 3 (C) 4 (D) 5

Q.17 For a particle in a cubic box, the total number of quantum numbers needed to specify its state are

(A) 1 (B) 2 (C) 3 (D) 9

Q.18 The maximum number of phases that can co-exist in equilibrium for a one component system is

(A) 1 (B) 2 (C) 3 (D) 4

Q.19 With increasing pressure, the temperature range over which the liquid state is stable,

(A) decreases
(B) increases
(C) remains constant
(D) decreases till the critical pressure and then increases

Q.20 The conductance at infinite dilution follows the order

(A) $Li^+ > Na^+ > K^+$
(B) $Na^+ > Li^+ > K^+$
(C) $K^+ > Li^+ > Na^+$
(D) $K^+ > Na^+ > Li^+$

Q.21 The V-shape of SO_2 is due to the presence of

(A) two σ- and one π-bonds
(B) two σ- and two π-bonds
(C) two σ-bonds and one lone pair of electrons
(D) two σ- and two π-bonds, and one lone pair of electrons

Q.22 The correct order of the mean bond energies in the binary hydrides is

(A) $CH_4 > NH_3 > H_2O > HF$
(B) $NH_3 > CH_4 > H_2O > HF$
(C) $HF > H_2O > CH_4 > NH_3$
(D) $HF > H_2O > NH_3 > CH_4$

Q.23 In CsCl structure, the number of Cs^+ ions that occupy second nearest neighbour locations of a Cs^+ ion is

(A) 6 (B) 8 (C) 10 (D) 12

Q.24 In the process

$$^{234}_{92}U \longrightarrow {}^{230}_{90}Th + X$$

X is

(A) α particle
(B) β particle
(C) β^+ emission
(D) γ emission

Q.25 For tetrahedral complexes, which always exhibit high spin states, the maximum CFSE (crystal field stabilization energy) is

(A) –8 Dq (B) –12 Dq (C) –16 Dq (D) –20 Dq

Q.26 The most abundant element in earth's crust is

(A) aluminium (B) iron (C) silicon (D) oxygen

Q.27 Metal-carbon multiple bonds in metal carbonyls are preferably identified from the stretching frequency of

(A) carbon–oxygen bond
(B) metal–carbon bond
(C) metal–oxygen bond
(D) carbon–carbon bond

Q.28 In general, magnetic moment of paramagnetic complexes varies with temperature as

(A) T^2 (B) T (C) T^{-2} (D) T^{-1}

Q.29 The compound having an S–S single bond is

(A) $H_2S_2O_3$ (B) $H_2S_2O_4$ (C) $H_2S_2O_7$ (D) $H_2S_2O_8$

Q.30 In a reaction, $Na_2S_2O_3$ is converted to $Na_2S_4O_6$. The equivalent weight of $Na_2S_2O_3$ for this reaction is (mol. wt. of $Na_2S_2O_3$ = M).

(A) M (B) M/4 (C) M/2 (D) M/3

A

Answer Table for Objective Questions

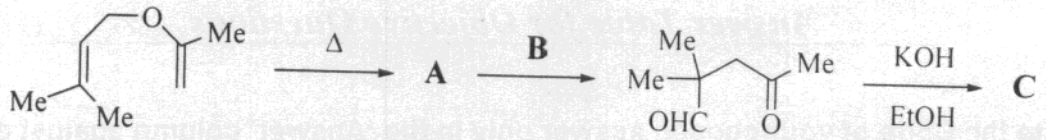
Write the Code of your chosen answer only in the 'Answer' column against each Question No. Do not write anything else on this page.

Question No.	Answer	Do not write in this column	Question No.	Answer	Do not write in this column
01			16		
02			17		
03			18		
04			19		
05			20		
06			21		
07			22		
08			23		
09			24		
10			25		
11			26		
12			27		
13			28		
14			29		
15			30		

FOR EVALUATION ONLY

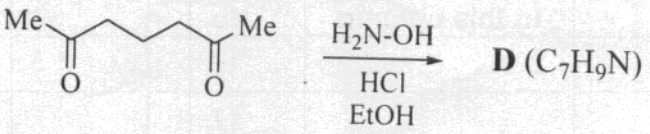
No. of Correct Answers		Marks	(+)
No. of Incorrect Answers		Marks	(–)
Total Marks in Question Nos. 1-30			( )

Q.31 (a) Identify **A**, **B** and **C** in the following reaction sequence.



(9)

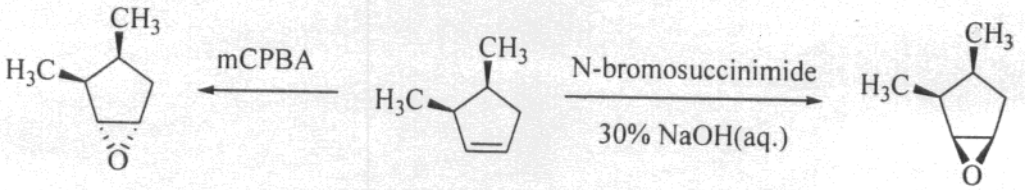
(b) Identify **D** in the following reaction and suggest a suitable mechanism for its formation.



(6)

A

Q.32 (a) Explain with the help of mechanisms, the observed stereoselectivity in the following epoxide formation reactions.

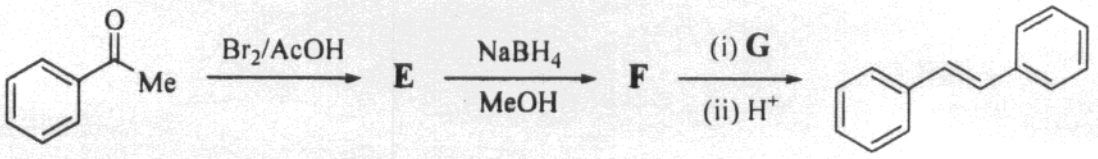


(9)

(b) Explain on the basis of conformational analysis why (1*R*,2*S*)-1,2-dimethyl-cyclohexane is optically inactive at room temperature. (6)

A

Q.33 (a) Identify **E**, **F** and **G** in the following synthetic transformation.



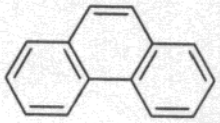
(9)

(b) An optically active compound **H** (C_5H_6O) on treatment with H_2 in the presence of Lindlar's catalyst gave a compound **I** (C_5H_8O). Upon hydrogenation with H_2 and Pd/C, compound **H** gave **J** ($C_5H_{12}O$). Both **I** and **J** were found to be optically inactive. Identify **H**, **I** and **J**. (6)

A

Q.34 (a) A disaccharide **K** gives a silver mirror with Tollen's reagent. Treatment of **K** with MeOH/HCl gives a monomethyl derivative **L**, which does not react with Tollen's reagent. Methylation of **K** with Me_2SO_4 and NaOH affords an octamethyl derivative of **K**, which upon acidic hydrolysis gives a 1:1 mixture of 2,3,4,6-tetra-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-D-glucose. Disaccharide **K** is also hydrolysed by the enzyme maltase. Identify **K** and **L** with proper stereochemistry. (9)

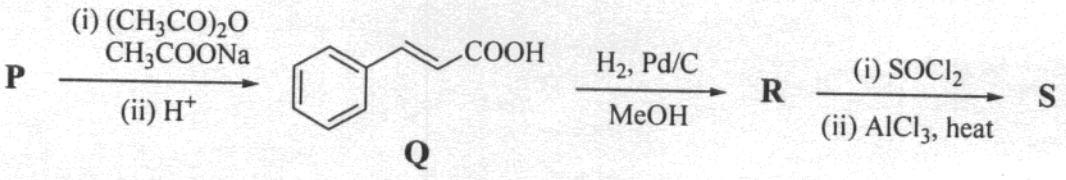
(b) Identify **M** and **N** in the following reaction sequence.



$\xrightarrow[\text{(ii) Zn/AcOH}]{\text{(i) } O_3}$ **M** $\xrightarrow{\text{cat. KCN}}$ **N**

(6)

Q.35 In the following reaction sequence, identify **P**, **R** and **S**. Suggest suitable mechanisms for the conversion of **P** → **Q** and **R** → **S**.



(15)

Q.36 (a) Consider the reactions

(I) $Cr_2O_7^{2-} + H_2O_2 \xrightarrow{A} \underset{\text{unstable}}{CrO(O_2)_2} \xrightarrow{\text{room temp.}} Cr^{3+}$

(II) $Cr^{3+} + H_2O_2 \xrightarrow{B} CrO_4^{2-}$

(i) Identify **A** and **B**.
(ii) What is the role of H_2O_2 in (I) and how does **A** favour the formation of Cr^{3+}?
(iii) What is the role of H_2O_2 in (II) and how does **B** favour the formation CrO_4^{2-}? (9)

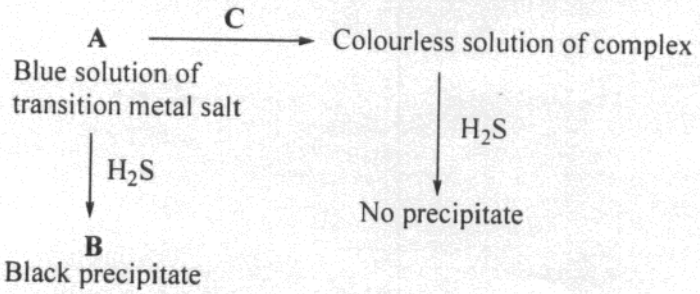
(b) With the help of equations, illustrate the role of a *cis*-1,2-diol in the titration of boric acid with sodium hydroxide. (6)

A

Q.37 (a) Draw the structure of anionic Ca(II)-EDTA chelate. How many rings are formed in the chelate and specify the number of atoms in each ring? (9)

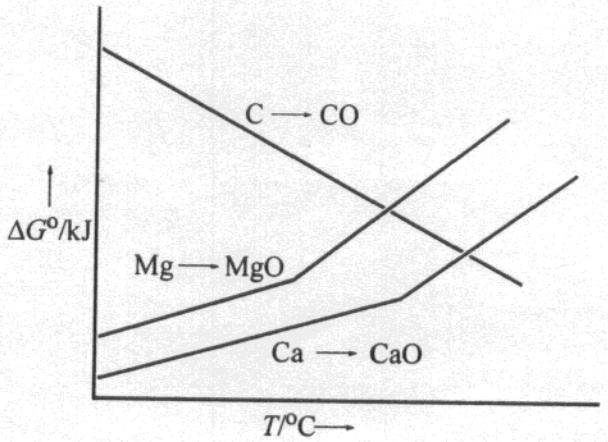
(b) Based on VSEPR theory draw the most stable structure of ClF_3 and XeF_4. (6)

Q.38 (a) Identify **A**, **B** and **C** in the following reaction scheme



(9)

(b) From the Ellingham diagram given below, identify the metal oxide that can be reduced at a lower temperature by carbon. Justify.



(6)

A

Q.39 (a) For the complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$.
(i) show the hybridization using VB (valence bond) theory
(ii) calculate the CFSE (crystal field stabilization energy) (9)

(b) Identify the dark blue complex formed when $[Fe(CN)_6]^{3-}$ is treated with $FeSO_4$ and account for the origin of its colour. (6)

Q.40 (a) Consider the equilibrium

$$\mathbf{A}\,(g) \rightleftharpoons \mathbf{B}\,(g) + \mathbf{C}\,(g)$$

At a constant pressure of 1 atm, **A** dissociates to the extent of 50% at 500 K. Calculate ΔG° (kJ mol^{-1}) for the reaction. (9)

(b) Consider the following redox system

$$Q + 2H^{+} + 2e^{-} \rightleftharpoons QH_2 \qquad E^{\circ} = 0.699\ V$$

Calculate the pH of the solution at 298 K, if the redox potential of the system is 0.817 V. (6)

A

Q.41 (a) A stream of oxygen molecules at 500 K exits from a pin-hole in an oven and strikes a slit that selects the molecules travelling in a specific direction. Given that the pressure outside the oven is 2.5×10^{-7} atm, estimate the maximum distance at which the slit must be placed from the pin-hole, in order to produce a collimated beam of oxygen. (Radius of $O_2 = 1.8 \times 10^{-10}$ m) (9)

(b) Liquid water is to be circulated to transfer heat from a source to a sink at 1 atm. Considering this arrangement as a Carnot engine, calculate the maximum theoretical efficiency that can be expected from the system. (6)

A

A

Q.42 (a) Using Heisenberg's uncertainty principle, derive an expression for the approximate ground state energy of a particle of mass m in a one dimensional box of length L. (9)

(b) The rate of a chemical reaction doubles when the temperature is changed from 300 K to 310 K. Calculate the activation energy (kJ mol^{-1}) for the reaction. (6)

A

Q.43 (a) Consider the reaction

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \qquad \Delta H^\circ = -606.9\ kJ\ mol^{-1}$

Assuming ideal behaviour, calculate ΔU° when 1 mol of CH_4 is completely oxidized at STP. (9)

(b) A photochemical reaction was carried out using a monochromatic radiation (490 nm) of intensity 100 W. When the sample was irradiated for 30 min, 0.3 mol of the reactant was decomposed. Estimate the quantum efficiency assuming 50% absorption. (6)

Q.44 (a) Given that

$$C_p - C_v = \frac{\alpha^2 TV}{\kappa_T} \quad \text{where} \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad \text{and} \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

for a pure substance, show that $C_p - C_v = R$ for 1 mol of an ideal gas. (9)

(b) Find the eigenvalues of the following 3 × 3 matrix given that 2 is one of the eigenvalues. Compute the determinant of the matrix **using the eigenvalues**.

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -2 \\ 1 & -1 & 1 \end{pmatrix}$$

(6)