Q.P. Code :29463

[Time: 2:30 Hours] **[Marks: 60]**

Please check whether you have got the right question paper.

N.B: 1. All questions are compulsory.
2. Figures to the right indicate full marks.
3. Use of non-programmable scientific calculator is allowed.

Useful constants

$c = 2.998 \times 10^{8}$ m.s^{-1}	$e = 1.602 \times 10^{-19}$ C
$R = 8.314$ J.K^{-1} mol^{-1}	$k = 1.3811 \times 10^{-23}$ J.K^{-1}
$= 2.0$ cal. K^{-1} mol^{-1}	
$h = 6.626 \times 10^{-34}$ Js	$1J = 6.24 \times 10^{18}$eV
$m_e = 9.110 \times 10^{-31}$ kg	$1eV = 8.06 \times 10^{3}$ cm^{-1}
$N_A = 6.022 \times 10^{23}$ mol^{-1}	$1amu = 1.66 \times 10^{-27}$ kg

1. A) Attempt **any two** of the following:

i) What are exact differentials? Using thermodynamic relations, show that **4**

$$\left(\frac{\delta Cv}{\delta V}\right) = T\left(\frac{\delta^2 S}{\delta V.\,\delta T}\right) = T\left(\frac{\delta^2 P}{\delta T^2}\right)_V$$

ii) State third law of thermodynamics. How will you determine the absolute entropies of liquid using 3rd law? **4**

iii) What is Joule-Thomson effect? Describe it with an experiment and write the expression for Joule-Thomson coefficient in terms of van der waal's constant. **4**

iv) Define entropy. Write only the expression for entropy change involved in the process of melting, vaporization and sublimation. **4**

1. B) Attempt **any one** of the following:

i) Calculate the change in entropy when 1 g of water at 0°C is heated to 100°C and converted into steam at that temperature. Specific heat of water = 1.0 cal/g°C. Latent heat of vaporization of water at 100°C is 539 cal/g. **4**

ii) Calculate the Joule – Thomson coefficient $(\mu_{J.T})$ for $CO_{2(a)}$ at 273K. The van der waal's constants **a** and **b** are 0.36 Nm^4mol^{-2} and 4.3 x 10^{-6} m^3mol^{-1} respectively. **4**

$C_p = 38.50$ JK^{-1} mol^{-1}

2. A) Attempt **any two** of the following:

i) What are eigen functions and eigen values? Show that the eigen function of a Hermitian operator corresponding to different eigen values are orthogonal. **4**

ii) Write the characteristics of a well behaved function. Indicate which of the following wave functions are acceptable? **4**

a) $\psi = \sin x$ b) $\psi = e^{-x}$

iii) Explain degenerate and non-degenerate energy levels. Find the degree of degeneracy of energy level $19h^2 / 8ma^2$. **4**

iv) For the Hermite differential equation **4**

$$\frac{d^2F}{dy^2} - 2y\frac{dF}{dy} + \left(\frac{\alpha}{\beta} - 1\right)F = 0$$

Obtain the recursion formula.

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2. B) Attempt **any one** of the following:

i) If $\widehat{A} = \frac{d}{dx}$, $\widehat{B} = \frac{d^2}{dx^2}$ and $f(x) = \cos 3x$ **4**
then show that $\widehat{A}$ and $\widehat{B}$ are commutative or non-commutative.

ii) The Hermite polynomials are derived from the generating function. **4**
$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2}$
Calculate the value of the polynomial for n = 1 and n = 2.

3. A) Attempt **any two** of the following:

i) Discuss the gas phase combustion reaction between H_2 and O_2. Explain the term explosion limit and factors affecting it. **4**

ii) Explain the formation and decomposition of phosgene. **4**

iii) Obtain rate law expression for the thermal reaction **4**
$H_2 + Br_2 \rightarrow 2HBr$

iv) Explain in brief the Rice-Ramsperger Kassel Marcus (RRKM) theory. **4**

3. B) Attempt **any one** of the following:

i) The following process follows the first order kinetics **4**
$X \xrightarrow{\mathbf{20d}} Y \xrightarrow{\mathbf{30d}} Z$ where **20d** and **30d** are the half life time of the reaction from X to Y and Y to Z respectively in days. At what stage of time will the concentration of Y become maximum?

ii) On the top of a certain mountain the atmospheric pressure is 530 mm Hg and pure water boils at 360 K. A climber finds that it takes 300 minutes to boil an egg as against 3 minutes at 370 K. **4**
i) What is the relation between rate of boiling the egg and time ?
ii) What is the activation energy for the reaction that occurs when egg is boiled, given that the pre-exponential factor, A remains constant ?

4. A) Attempt **any two** of the following:

i) State the Debye-Huckel's limiting law and explain the terms involved. State any three merits of the law. **4**

ii) Explain the effect showing the dispersion of conductance at high frequencies. **4**

iii) Explain the construction and working of the molten carbonate fuel cell. **4**

iv) Explain the use of enzymes as electrodes. **4**

4. B) Attempt **any one** of the following:

i) Using Debye-Huckel limiting law, calculate the activity coefficient of sodium and sulphate ions and mean activity coefficient of 0.1m sodium sulphate solution at 298k (A = 0.509 at 298K) **4**

ii) Calculate the resting membrane potential for the following: **4**

Ion Species	Intra Cellular Conc in mM	Extra Cellular Conc in mM
Na^+	15	145
K^+	140	4.0

Given that 2.303RT/F = 61 at 298K.

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5. Attempt **any five** of the following: **15**

a) Give the significance of Maxwell thermodynamic relations.
b) Explain the term 'residual entropy' with a suitable example.
c) Write a note on magnetic quantum number.
d) What are the limitations of classical mechanics?
e) Explain the term consecutive reaction with suitable example.
f) Explain the principle of microscopic reversibility and detailed balance mechanism.
g) Explain the time of relaxation for the ionic atmosphere and state the expression for the same.
h) State the functions of the cell membrane.

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