

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

$$c = 2.998 \times 10^8 \text{ m.s}^{-1}$$

$$R = 8.314 \text{ J.K}^{-1} \text{ mol}^{-1}$$

$$= 2.0 \text{ cal. K}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$m_e = 9.110 \times 10^{-31} \text{ kg}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$k = 1.3811 \times 10^{-23} \text{ J.K}^{-1}$$

$$1\text{J} = 6.24 \times 10^{18} \text{ eV}$$

$$1\text{eV} = 8.06 \times 10^3 \text{ cm}^{-1}$$

$$1\text{amu} = 1.66 \times 10^{-27} \text{ kg}$$

1. A) Attempt any two of the following:

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

$$\left(\frac{\delta C_v}{\delta V}\right) = T \left(\frac{\delta^2 S}{\delta V \cdot \delta T}\right) = T \left(\frac{\delta^2 P}{\delta T^2}\right)_V$$

- 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 Nm⁴mol⁻² and 4.3 x 10⁻⁶ m³mol⁻¹ respectively. 4

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

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

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

Obtain the recursion formula.

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

i) If $\hat{A} = \frac{d}{dx}$, $\hat{B} = \frac{d^2}{dx^2}$ and $f(x) = \cos 3x$

then show that \hat{A} and \hat{B} are commutative or non-commutative. 4

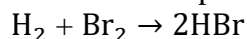
ii) The Hermite polynomials are derived from the generating function. 4

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2}$$

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



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

 $X \xrightarrow{20d} Y \xrightarrow{30d} Z$ 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.

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

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