

Name:

Enrolment No:



UNIVERSITY OF PETROLEUM AND ENERGY STUDIES

End Semester Examination, Dec 2021

Course: M.Sc. Chemistry

Program: Advanced Physical Chemistry

Course Code: CHEM7016

No. of pages: 2

Instructions: Read the instructions given below carefully:

Semester: I

Time 03 hrs.

Max. Marks: 100

SECTION A

All questions are compulsory

S. No.		Marks	CO
Q 1	What are the possible term symbol of the excited states of Na atom with electronic configuration $1s^2 2s^2 2p^6 3d^1$?	4	CO3
Q 2	The transmittance of an alcoholic solution of an organic dye at 500 nm is 20 percent in a 1 cm cell. What is the absorbance of the dye solution?	4	CO3
Q 3	What are gross and specific selection rule for vibrational and rotational spectroscopy?	4	CO1
Q 4	Define micro-canonical, canonical and grand canonical ensembles.	4	CO1
Q 5	Which hydrogenic orbital is represented by radial wave function $\Psi = r^2(\alpha-r)e^{-\beta r}$ where α and β are constants?	4	CO1

SECTION B

Internal choice is given in question No. 4

Q 1	(a) What are the expression of first order and second order perturbation energy corrections? Mention all the terms involved in the expressions. (b) Calculate the first order perturbation correction to the energy for the ground state of a particle in one dimensional box ($0 \rightarrow a$) due to the perturbed part λx .	10	CO2
Q 2	(a) What are the causes of spectral line broadening? (b) Explain the origin of splitting of lines of Cs atomic spectra using spin orbit coupling. Use a diagram with proper labelling and term symbol to explain the spin orbit coupling of Cs (Electronic configuration: $[\text{Xe}]6s^1$).	10	CO2
Q 3	(a) The energy in cm^{-1} of the photon absorbed when a heteronuclear diatomic molecule goes from $v = 0, J = 0$ to $v = 1, J = 1$. Assume the $v = 0$ and $v = 1$ states have the same B values. Given that $\omega_e = 300 \text{ cm}^{-1}$, $B = 2 \text{ cm}^{-1}$, anharmonicity constant (χ_e) = 0.005.	10	CO1

	(b) What are the selection rule of rovibrational transitions of P, Q and R branch? Using a diagram show the origin of P, Q, R branch.		
Q 4	Write down all the Maxwell's relation and criteria of spontaneity (in terms of G and A) using thermodynamic square. OR Distinguish Maxwell Boltzmann, Fermi-Dirac and Bose-Einstein statistics.	10	CO3
SECTION-C Internal choice is given in question No. 2			
Q 1	(a) The vibration of $^{35}\text{Cl}^{35}\text{Cl}$ molecule can be considered as simple harmonic oscillation. The force constant is 400 Nm^{-1} . Calculate the fundamental vibration frequency and the zero point vibrational energy of this molecule in joule. (Given: Plank constant = $6.626 \times 10^{-34} \text{ Js}$). (b) Discuss the relation between canonical and molecular partition function.	10+10	CO2
Q 2	(i) Using variation theorem calculate the ground state energy of a particle of mass "m" in one dimensional box of length "a" described by a trial wave function $\varphi = x(a-x)$. where $0 \leq x \leq a$. (Given: $\int_0^a \varphi^* \varphi dx = \frac{a^5}{30}$) (ii) Find the value of commutator $[x, p_x^2]$, where x is the position and p_x is momentum in the x direction. OR (i) Discuss the principles of Debye-Huckel Theory. (ii) Describe the collision theory of a bimolecular gas phase reaction.	10 +10	CO4