Roll NO. _____

M.Sc. PROGRAM (CHEMISTRY)
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SEMESTER-II EXAMINATION-2019
PAPER CODE-MCHCC-201
PAPER TITLE: PHYSICAL CHEMISTRY-II

Time: Three Hours **Max Marks: 75**

(Write your Roll No. on the top immediately on receipt of question paper)

Attempt all questions. Use of Scientific Calculator is permitted.

Q1. Explain very briefly of the following (ANY FIFTEEN): **[1x15=15]**

A Micellization
B Mass action model
C Reverse micelle
D Solubilization in micelle formation
E Theories of reaction rates.
F Collision theory of Bimolecular Gaseous Reactions.
G Activated complex theory of biomlecular reaction
H Lindemann and Hinshelwood theory of unimolecular reactions and its limitations.
I Rice - Remsperger- Kassel [RRK] and Rice - Remsperger- Kassel- Marcus [RRKM] theory of unimolecular reactions and its limitations.
J Kinetics of complex reaction
K Molecular Partition Function for an Ideal Gas.
L Different type of statistics and effect of temperature on it.
M Various partition function for diatomic molecule.
N Thermodynamic properties in terms of partition function.
O Different types of ensemble and ensemble average
P Methods for determining the order of a reaction
Q Mechanisms of complex reactions: Equilibrium & steady state approximation.
R Effect of temperature on Reaction Rate.
S Arrhenius equation
T Can the activation energy of a reaction be zero or negative?

Q2. Attempt ANY THREE of the following: **[3x5=15]**

A Describe the various factors affecting CMC in aqueous media?
B Derive thermodynamics approach to critical micellar concentration (CMC)?
C The critical micelle concentration (CMC) in pure water at 25 °C is 8.2 mM. Calculate the change in free energy of micellization?
D Derive and describe the Thermodynamics of Micellization?
E Describe the surfactant & its classification (examples of each type)?

Q3. Attempt ANY THREE of the following: **[3x5=15]**

A Calculate the translation partition function for the hydrogen atom at 3000 K confined to move in a box of volume of 2.494×10^5 cm^3. Also, determine the thermal de Broglie wave length?

B Calculate the characteristic rotational temperature and the rotational temperature and the rotational partition function for the H_2 gas at 2727 ^0C given that the moment of inertia of hydrogen gas molecule at this temperature is 4.6033×10^{-48} Kg m^2.

C For H_2 gas at 3,000 K, calculate the characteristics vibrational temperature Θ_{Vib} and the vibrational partition function q'_{vib}? Given that the fundamental vibrational frequency of H_2 molecule, obtained from its Raman spectrum, is 4 405.3 cm^{-1}.

D The energies of the first three energy levels of fluorine atom, determined from spectroscopy, are as follows:

S. No.	Energy level	Energy, cm^{-1}
1	$^2P_{3/2}$	0.0
2	$^2P_{1/2}$	404.0
3	$^2D_{5/2}$	102406.5

Calculate (i) the electronic partition function and (ii) the fractions of fluorine atoms in the three energy level at 1,000 K.

E A system of N particles has, among others, two energy levels with $g_1=2$, $g_2=3$, $U_1=41.84$ kJ mol^{-1} and $U_2=58.55$ KJ mol^{-1}. Calculate the ratio of the number of particles in the two energy states at 1000 K.

Q4. Attempt ANY THREE of the following: **[3x5=15]**

A Consider the following data on the hypothetical reaction $2A + 2B \rightarrow C + 3D$ between reactants A and B to give products:

	[A]	[B]	Rate, r
(1)	6.0×10^{-3}	1.0×10^{-3}	0.012
(2)	6.0×10^{-3}	2.0×10^{-3}	0.024
(3)	2.0×10^{-3}	1.5×10^{-3}	0.002
(4)	4.0×10^{-3}	1.5×10^{-3}	0.008

If the reaction rate is given by $r = [A]^a[B]^b$, then (i) what is the order of the reaction with respect to A? (ii) What is the order of the reaction with respect to B? (iii) What is the overall order? (iv) write the rate law equation (v) calculate the rate constant.

B 5ml of ethyl acetate was added to a flask containing 100 ml of 0.1 M HCl placed in a thermostat maintained at 30 ^0C, 5 ml of the reaction mixture was withdrawn at different intervals of time and after chilling, titration against a standard alkali. The following data were obtained:

Time (minutes):	0	75	119	183	infinite
ml of alkali used :	9.62	12.10	13.10	14.75	21.05

From the above data show that the hydrolysis of ethyl acetate is a first order reaction.

C The following data are obtained for the hydrolysis of benzene diazonium chloride:

$C_6H_5N = N\text{--}Cl + H_2O \rightarrow C_6H_5OH + HCl + N_2(g)$:

Time (min)	0.0	2.0	8.5	16.0	24.0	50.0	infinite.
Pressure (p) of N_2	0.0	1.6	6.2	11.2	15.5	24.4	34.0

at constant volume (arbitrary units)

Assuming first- order kinetics, calculate the rate constant.

D The radioactive decay of elements such as thorium and radon emitting alpha particle follows first - order kinetics. Calculate the number of alpha particles emitted per second by one gram of pure ThO_2 if the half-life of Th_2^{32} is 1.39×10^{10} years. The molar mass of ThO_2 is 264 g mol^{-1}.The $t_{1/2}$ of a reaction is doubled as the initial concentration of the reactant is doubled. What is the order of the reaction?

E The gaseous decomposition of ozone, $2O_3 \rightarrow 3O_2$, obeys the rate law,

$$r = -d[O_3]/dt = k[O_3]^2[O_2].$$

Show that the following mechanism is consistent with the above rate law:

$$O_3 \overset{K}{\rightleftharpoons} O_2 + O \quad \text{(Fast equilibrium)}$$

$$O + O_3 \xrightarrow{k_1} 2O_2 \text{ (Slow)}$$

Q5. Attempt ANY THREE of the following: **[3x5=15]**

A For the thermal decomposition of ozone to oxygen, the following mechanism has been suggested:

Step 1. $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ (Fast equilibrium)

Step 2. $O + O_3 \xrightarrow{k_2} 2O_2$ (Slow)

Use steady state approximation (s.s.a) and other suitable approximation to account for the observed rate law, *viz*, $r = k[O_3]^2[O_2]^{-1}$

B The rate law for the decomposition of gaseous N_2O_5, $N_2O_5 \rightarrow 2NO_2 + 1/2\ O_2$ is observed to be

$$r = -d[N_2O_5]/dt = k[N_2O_5].$$

A reaction mechanism which has been suggested to be consistent with this rate law is:

$$N_2O_5 \overset{K}{\rightleftharpoons} NO_2 + NO_3 \quad \text{(Fast equilibrium)}$$

$$NO_2 + NO_3 \xrightarrow{k_1} NO_2 + NO + O_2 \text{ (Slow)}$$

$$NO + NO_3 \xrightarrow{k_2} 2NO_2 \text{ (Fast)}$$

(a) Show that the mechanism is consistent with the observed rate law.

(b) If $k = 5 \times 10^{-4}\ s^{-1}$, calculate the time required for the N_2O_5 concentration to be reduced to 10% of its original value.

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C Calculate the activation energy of a reaction whose rate constant is tripled by a 10 ^{0}C rise in temperature in the vicinity of 27 ^{0}C.

D The activation energy of a non catalysed reaction at 37 ^{0}C is 83.68 kJ mol^{-1} and the activation energy of the same reaction catalysed by an enzyme is 25.10 kJ mol $^{-1}$. Calculate the ratio of the rate constants of the enzyme-catalysed and the non-catalysed reactions.

E Explain the term *Steric factor*? Consider a bimolecular gaseous reaction between like molecules with collision diameter = 200 pm, molar mass = 100 g mol^{-1} and the steric factor = 1.00. Calculate the Arrhenius pre-exponential factor at (a) 100 ^{0}C and (b) 200 ^{0}C. Also calculate the exponential factor at the two temperatures and comment on your results. E_a= 150 kJ mol^{-1}.

Terms have their usual meaning
Avogadro number: N_A=6 x10^{23}/mol;
Universal gas constant: R=8.31x10^7 erg/mol/K;
Boltzmann Constant: k_B=1.38x10^{-16} erg/K