Semester-I Model Question

Model Questions For Semester-II B.Sc Chemistry Honours

(Physical Chemistry)

1) For a reaction: A→ Products, the rate = k C^n, where n is the order of the raction. For what values of n the reaction will go to completion?
2) Discuss the differential method for the determination of the 'order' of a reaction. Can you distinguish 'order with respect to concentration and order with respect to time ina reaction? Explain.
3)A certain reaction is 20% complete in 12.6 min at 300K and 3.2 min at 340K. Estimate its activation energy E_a.
4) 'Unimolecular reaction are not always first order' —— Discuss using Lindemann mechanism of unimolecular reaction.
5) Write the general expression for the specific rate constant of a with n^{th} order reaction with approximation unit.
6) The half lifetime of a reaction is doubled when the initial concentration is doubled. Find the order of the reaction.
8) The rate of a gaseous reaction is increased by about 100 or 200% whereas the number of collisions
is increased by and 10% for a 10^0C rise in temperature in both cases —— Explain.
9) Define with examples: opposite, consecutive and chain reactions.
10) Reactions of third and higher orders are usually not very common ——Explain the statement. 11) The rate constant for the acid hydrolysis of methyl acetate is dependent on the concentrations of the ester and the acid used but it is a first order reaction. Explain.
12) Examine the statement and indicate which are true or false:
13) Order and molecularity are not always identical
14)What do you mean by order of a reaction with respect to concentration (n_c) and with respect ot time (n_t) ? Find a method of determining both n_c and n_t of a reaction. State the significance of n_c and n_t.
15) 'Unimolecular reaction are not always first order' —— Discuss using Lindemann mechanism of unimolecular reaction.
16) Answer any four:

i) Distinguish between order and molecuarity of a reaction.
ii) The rate constant for the inversion of cane sugar has been found to be directly proportional to the concentration of H^+ ions in the solution. But it is regarded to be a first order reaction. Why?
iii) The order of a reaction is not always an integer.—— Explain.
iv) A reaction of the type A → B → C is called a parallel reaction. Justify or rectify with reasons.
v) Choose the correct answer:
A catalyst increases the speed of a reaction because.

a) It provides the necessary energy to the colliding molecules to cross the energy barrier.
b) It decreases the heat of the reaction.
c) It decreases the order of the reaction.
d) It provides a different reaction path of lower activation energy.

17) A and B react between themselves in the presence of a catalyst C and the catalyzed reaction obey the kinetic equation

$-d[A]/dt = k' [A][B][C]/(1+k''[A])$

where k' and k'' are constants. The mechanisms proposed for the reaction are:

i) $A+C = AC^*$,
$AC^* + B \rightarrow C + \text{products}$

ii) $A + B + C = ABC^*$
$ABC^* \rightarrow C + \text{products}$

Test which mechanism is correct.

18) For two reactions, the frequency factor A for the 1st reaction is 100 times that of the 2nd and the activation energy of the 1st is greater than that of the 2nd by 19.25 kJ/mol. Compare the rate constants of the two reactions at 500 K.

19) Define rate, rate constant and order of a chemical change. What are their conventional units for gas phase reactions?

20) The reaction: $N_2O_2(g) \rightarrow 2NO(g)$, is first order in $[N_2O_2]$. Derive the expressions for the time dependent behaviour of $[N_2O_2]$ & [NO]. At zero time, the concentration of N_2O_2 & NO are $[N_2O_2]$ & zero respectively.

21) The Arrhenius parameter for the reaction, $HO_2(g) + OH(g) \rightarrow H_2O(g) + O_2(g)$, are $A = 5.01 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ and $E_a = 4.18$ kj/mol. Determine the value of the rate constant for this reaction at 298K and at temperature at which the rate constant value is twice that at 298K.

22) What are the special characteristics of enzyme catalyzed reaction? What is the unit of Mechaelis constant?

23) What is meant by a zero order reaction? How does the half life period of a zero order reaction depend on the initial concentration of the reactant?

24) What are the differences between i) Order and molecularity of a reaction and ii) rate and rate constant of a reaction?

25) Discuss briefly the salient features of the collision theory and transition state theory.

26) For the reaction $F_2 + 2ClO_2 = 2FClO_2$ the following data have been obtained at 260K.

$-d[F_2]/dt \times 10^3$ (mole $dm^{-3} s^{-1}$)	Reactant conc. (mole/dm^{-3})	
	$[F_2]$	$[ClO_2]$
1.2	0.10	0.01
4.8	0.10	0.04
2.4	0.20	0.01

Determine the overall order of the reaction. Calculate the rate constant of the reaction when $[F_2] = 0.01$ mole/dm^3 and $[ClO_2] = 0.02$ mole/dm^3 at 260K.

27. (a) Derive the general expression for initial rate of an enzyme catalysed reaction.

(b) Using Lindemann's mechanism show that order of unimolecular decomposition reaction of a gas depends on pressure.

(c) The reaction $2NO + O_2 \rightarrow 2NO_2$ proceeds through the following steps. 2 NO = N_2O (fast) $N_2O_2 + O_2 \rightarrow NO_2$ (slow). Based on this mechanism find the order of the reaction. State the necessary approximations considered.

(d) A first-order reaction is 24.0% complete in 19.7 minutes. How long will the reaction take to be 85.5% complete? Calculate the rate constant for the reaction.

28. (a) Define a zero order reaction. Show that half life period of a zero order reaction depends on the initial concentration of the reactant.
(1+2)

(b) The rate constant for the reaction
SO_2Cl_2 ——> $SO_2 + Cl_2$ is $2.2 \times 10^{-5} S^{-1}$ at 675 K. What fraction of $SO_2C!_2$ will decompose in 90 mins at the same temperature.
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(c) Write down the Arrhenius equation for the effect of temperature on the rate of a reaction and hence show how the activation energy of the reaction can be determin,

(d) Explain with the help of energy profile diagram the action of & catalyst on a reaction.

29) What are condensation polymers and addition polymers ? Give an example of each.

Old 3. (a) Obtain a thermodynamic derivation for the difference *(Cp - Cy)* in terms of the quantities $(\partial U/\partial V)_T$ and $(\partial V/\partial T)_P$

30.An ideal gas $C_v = 5R/2$ is expanded adiabatically aganst a constant pressure of 1 atm until it doubles in volume. If the initial temp, is 25°C, and the initial 5 atm, calculate final temperature; then calculate *q, w,* ΔU and ΔH per mole of gas for the transformation.

31. Derive the relation showing variation of heat of reaction with temperature.

Calculate the enthalpy of fusion *of ice* at -10°C. Given ΔH_f at 0^0 = 6.02kj/mole. C_p , ice = 37.66kj/ mol , C_p , water = 75.31kj/mole.

32) One mole of a monoatomic ideal gas at 77^0C and 5atm. pressure is expanded adiabatically against a constant external pressure of 1 atm in such a way that the final pressure of the gas becomes 1 atm. Calculate the final temperature, ΔU, ΔH and ΔS for the process. Will the values of the changes in these thermodynamics quantities be same or not if the process is operated reversibly and adiabatically? Justify your answer.

33) State the results of Joule-Thomson experiment and explain them. At 300^0C and at pressure 0 to 60 atm, the Joule –Thomson coefficient of nitrogen can be represented by the equation $\mu = 0.014 - 2.50 \times 10^{-4} P$ Assuming the equation to be temperature independent near 300^0C , find the change in temperature on Joule-Thomson expression of the gas from 60atm to 20atm.

34)Explain, 'Standard free energy change'. Will ΔG_P^0 and ΔG_C^0 values be always same for a reaction involving gaseous reactants and products? Give reason.