

Note:

- The examination consists of two parts. Part I (Closed book QUIZ): There are four pages, with 20 questions on the first three pages (each question is of 2 marks), and the fourth page is the answer sheet.
- Match the Code A or B of your question paper with the code on your answer sheet.
- Four options are given in each question. Indicate your choice by entering A, B, C or D as the case may be, in the box provided for each question in the answer sheet given to you. Do not overwrite.
- Choose the most appropriate option. In the case of questions with numerical answers indicate the one which is closest to your result.
- Use last few pages of the OPEN BOOK Answer sheet (will be supplied at the beginning) for rough work.
- Each correct answer will be awarded two marks. One mark will be deducted for every two wrong answers.
- The maximum time allowed for Part I is 120 minutes. Part II may be collected as soon as Part I is submitted. Detach and submit your answer sheet only.

PART I (CLOSED BOOK)

Useful data: USEFUL DATA: $R = 8.3145 JK^{-1} mol^{-1}$; $\mu_B = 9.274 \times 10^{-24} JT^{-1}$; Boltzmann constant $k = 1.381 \times 10^{-23} JK^{-1}$; $cP(\text{centipoise}) = 1.0 \times 10^{-3} Pa s$; $N_A = 6.023 \times 10^{23} mol^{-1}$; $h = 6.626 \times 10^{-34} J s$; $c = 2.9979 \times 10^{10} cm s^{-1}$; $1 W = 1 J s^{-1}$; $1 Pa = 1 Kg m^{-1} s^{-2}$, $1 J = 1 Kg m^2 s^{-2}$; $\epsilon_0 = 8.854 \times 10^{-12} J^{-1} C^2 m^{-1}$; $e = 2.71828$

1. Tick mark (✓) the wrong statement:

- (A) Colloids are thermodynamically unstable with respect to the bulk.
 (B) Colloids are kinetically non-labile.
 (C) The sum of pairwise interaction between colloid particles varies with their separation (R) as $1/R^6$.
 (D) Hydrophobic colloids are flocculated most efficiently by ions of opposite charge type and high charge number.
2. There is mixture of two polymers, one having $M=62 \text{ kgmol}^{-1}$ and the other $M=78 \text{ kgmol}^{-1}$ and their amounts (number in moles) are in the ratio 2:3. Then the number average molar mass (\bar{M}_n) and weight average molar mass (\bar{M}_w), respectively, are

- (A) 72.5 and 71.6 (B) 71.6 and 72.5 (C) 358 and 5188 (D) 5188 and 358

(3) A certain atom has doubly degenerate ground level pair and an upper level of four degenerate states at 450 cm^{-1} above the ground level. In an atomic beam study of the atoms it was observed that 25 per cent of the atoms were in the upper level, and the translational temperature of the beam was 300 K. If the upper and ground level populations are, respectively, denoted by N_{ue} and N_{ge} (for electronic state) and N_{uT} and N_{gT} (for translational state) then,

- (A) $\frac{N_{ue}}{N_{ge}} > \frac{N_{uT}}{N_{gT}}$ (B) $\frac{N_{ue}}{N_{ge}} < \frac{N_{uT}}{N_{gT}}$ (C) $\frac{N_{ue}}{N_{ge}} = \frac{N_{uT}}{N_{gT}}$ (D) $\frac{N_{ue}}{N_{ge}} = \frac{N_{uT}}{N_{gT}} + 0.1$

4. A certain molecule can exist in either a non-degenerate singlet state or a triplet state (with degeneracy 3). The energy of the triplet exceeds that of the singlet by ϵ . Assuming that the molecules are distinguishable (localized) and independent the expression for molar energy at temperature $T = \epsilon/k$ (where 'k' is Boltzmann's constant) is,

- (A) 1.4258RT (B) 1.1036RT (C) 0.5245RT (D) 0.1748RT

5. The standard molar entropy values of C(graphite) at 298 K and 498 K are 5.69 JK^{-1} and 11.63 JK^{-1} , respectively. If 1.00 mol C(graphite) at 298 K is surrounded by thermal insulation and placed next to 1.00 mol C(graphite) at 498 K, also insulated, the number of configurations altogether for the combined but independent systems would be,
- (A) $e^{1.254 \times 10^{25}}$ (B) $e^{5.44 \times 10^{23}}$ (C) $10^{1.254 \times 10^{24}}$ (D) $10^{5.44 \times 10^{23}}$
6. For a vibration with vibrational temperature 1000 K the wave number should be
- (A) 635.2 cm^{-1} (B) 705.2 cm^{-1} (C) 695.2 cm^{-1} (D) 685.2 cm^{-1}
7. For gas phase equilibrium of the type $R \rightleftharpoons P$, the $\Delta_r E_0$ (i.e., zero point energy of the product – zero point energy of the reactant) is positive. Then which of the following statement is wrong,
- (A) When $\Delta_r E_0$ is very large the equilibrium constant, $K \ll 1$.
 (B) When $\Delta_r E_0$ is small but still positive K can never exceed 1.
 (C) At low temperature the system consists of mainly R.
 (D) At high temperature the product P dominates.
8. At 380 K, the rate of decomposition of a gaseous compound initially at a pressure of 12.6 kPa, was 9.71 Pa s^{-1} when 10 per cent had reacted and 7.67 Pa s^{-1} when 20.0 per cent had reacted. The order of the reaction is,
- (A) 1.00 (B) 2.00 (C) 3 (D) 1.7
9. A reaction $2A \rightarrow P$ has a third order rate law with $k = 3.50 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. Time required for the concentration of A to change from 0.06 mol dm^{-3} to $0.015 \text{ mol dm}^{-3}$ is,
- (A) $2.976 \times 10^6 \text{ s}$ (B) $5.952 \times 10^6 \text{ s}$ (C) $1.19 \times 10^7 \text{ s}$ (D) $4.167 \times 10^3 \text{ s}$
10. In a reaction that gives both thermodynamic and kinetic controlled products which of the following statements is true?
- (A) Before the equilibrium the product is thermodynamic controlled
 (B) After the equilibrium the product kinetic controlled
 (C) Relative proportion of the product requiring more activation energy will be decreased if the temperature is increased before the equilibrium.
 (D) Before the equilibrium the product is kinetic controlled
11. The enzyme-catalysed conversion of a substrate at 25°C has a Michaelis constant of $0.042 \text{ mol dm}^{-3}$. The rate of the reaction is $2.45 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the substrate concentration is $0.890 \text{ mol dm}^{-3}$. What is the maximum velocity of this enzymolysis?
- (A) $3.45 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ (B) $2.57 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
 (C) $3.57 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ (D) $4.20 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
12. A photochemical reaction $A \rightarrow B + C$, the quantum efficiency with 550 nm light is $1.2 \times 10^2 \text{ mol einstein}^{-1}$. After exposure of 180 mmol A to the light, 1.5 mmol B is formed. The number of moles of photons absorbed by A is,
- (A) 1.5×10^{-5} (B) 1.25×10^{-5} (C) 1.5 (D) 80000
13. Suppose the reaction $A \rightarrow B$ is driven by light absorption and that its rate is I_a , but the reverse reaction $B \rightarrow A$ is bimolecular and second-order with a rate $k[B]^2$. So, for the 'photostationary state' find which of the following statement is correct?
- (A) $[B] = \left(\frac{k}{I_a}\right)^{1/2}$ (B) $[B] = \left(\frac{k}{I_a}\right)^2$ (C) $[B] \propto A^{1/2}$ (D) $[B] \propto A^{-1/2}$
14. Which one of the following statements is correct regarding the kinetic chain length (λ) in chain polymerization?
- (A) $\lambda = \frac{\text{number of activated centres produced}}{\text{number of monomer units consumed}}$ (B) $\lambda = \frac{\text{rate of propagation of chains}}{\text{number of monomer units consumed}}$
 (C) $\lambda = \frac{\text{rate of production of radicals}}{\text{number of activated centres produced}}$ (D) $\lambda = \frac{\text{rate of propagation of chains}}{\text{rate of production of radicals}}$

15. Let the typical diffusion coefficient for a reactant in aqueous solution at 30°C is $5.4 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. If the critical reaction distance is 0.40 nm, the second-order rate constant for the diffusion-controlled reaction is,
- (A) $1.6355 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (B) $3.271 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
 (C) $1.0408 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (D) $3.271 \times 10^{10} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
16. The fraction of molecular collision having kinetic energy 200 kJ mol^{-1} along the line of flight at temperature 350 K is,
- (A) 0.0146 (B) 1.75×10^{-3} (C) 1.420×10^{-27} (D) 1.420×10^{-30}
17. Tick mark (\surd) the wrong one from the following statements,
- (A) In a colloid flocculation occurs at secondary minimum of the potential energy surface
 (B) In a colloid coagulation occurs at the primary minimum of the potential energy surface
 (C) In a colloid flocculation occurs when the separation between the particles is very small.
 (D) In a colloid flocculation occurs when the ionic strength is very high.
18. The 'hydrophobicity constant' (π) is defined as (here, R- is the non-polar tail and A- is the polar head group),
- (A) $\pi = \log \left(\frac{\text{molar solubility of } R-A \text{ in water}}{\text{molar solubility of } R-A \text{ in octanol}} \times \frac{\text{molar solubility of } H-A \text{ in water}}{\text{molar solubility of } H-A \text{ in octanol}} \right)$
 (B) $\pi = \log \left(\frac{\text{molar solubility of } R-A \text{ in octanol}}{\text{molar solubility of } R-A \text{ in water}} \times \frac{\text{molar solubility of } H-A \text{ in water}}{\text{molar solubility of } H-A \text{ in octanol}} \right)$
 (C) $\pi = \log \left(\frac{\text{molar solubility of } R-A \text{ in water}}{\text{molar solubility of } R-A \text{ in octanol}} \times \frac{\text{molar solubility of } H-A \text{ in octanol}}{\text{molar solubility of } H-A \text{ in water}} \right)$
 (D) $\pi = \log \left(\frac{\text{molar solubility of } R-A \text{ in octanol}}{\text{molar solubility of } R-A \text{ in water}} \times \frac{\text{molar solubility of } H-A \text{ in octanol}}{\text{molar solubility of } H-A \text{ in water}} \right)$
19. The relation between Gibbs energy of activation ($\Delta^\ddagger G$), standard reaction Gibbs energy ($\Delta_r G^\theta$) and reorganization energy (ΔE_R) is,
- (A) $\Delta^\ddagger G = \frac{(2\Delta_r G^\theta + \Delta E_R)}{4\Delta E_R}$ (B) $\Delta_r G^\theta = \frac{(\Delta^\ddagger G + \Delta E_R)^2}{4\Delta E_R}$
 (C) $\Delta_r G^\theta = \frac{(2\Delta^\ddagger G + \Delta E_R)}{4\Delta E_R}$ (D) $\Delta^\ddagger G = \frac{(\Delta_r G^\theta + \Delta E_R)^2}{4\Delta E_R}$
20. Which one of the following statements is true in case of gas phase molecular collision (assume the colliding species are hard spheres)?
- (A) Equilibration of vibrational states is faster than translational states.
 (B) When 'impact parameter' is zero the scattering angle is 'zero'.
 (C) When 'impact parameter' is in between 'zero' and 'sum of the radii of two colliding species' scattering occurs in cones in the forward direction.
 (D) When 'impact parameter' is in between 'zero' and 'sum of the radii of two colliding species' scattering occurs in cones in the backward direction.

END

Birla Institute of Technology & Science, Pilani, Rajasthan 333031
MID-SEMESTER TEST, CHEM F312, Physical Chemistry IV,
1st Semester, 2017-2018, 13-12-2017, Time: 60 min.
(OPEN BOOK) Maximum Marks 20

1. Answer all questions and in sequence.
2. Answer should be brief and to the point and up to the final expected form. Answer left in between will not be credited.
3. Unnecessary and irrelevant lengthy answer will be considered as disqualification.
4. As the test is OPEN BOOK no marks will be awarded just for writing the formula or substituting the values of the parameters.
5. Solution manuals are not allowed. Exchange of study materials and calculators are not allowed.

USEFUL DATA: $R = 8.3145 JK^{-1} mol^{-1}$; $\mu_B = 9.274 \times 10^{-24} JT^{-1}$; Boltzmann constant $k = 1.381 \times 10^{-23} JK^{-1}$;
 $cP(\text{centipoise}) = 1.0 \times 10^{-3} Pa s$; $N_A = 6.023 \times 10^{23} mol^{-1}$; $h = 6.626 \times 10^{-34} J s$; $c = 2.9979 \times 10^{10} cm s^{-1}$; $1 W = 1 J s^{-1}$; $1 Pa = 1 Kg m^{-1} s^{-2}$, $1 J = 1 Kg m^2 s^{-2}$; $\epsilon_0 = 8.854 \times 10^{-12} J^{-1} C^2 m^{-1}$

- Q.1.** A solution consists of 40% by mass of a trimer with $M=25 \text{ kgmol}^{-1}$ and its monomer. What average molar mass would be obtained from measurement of (a) osmotic pressure (b) light scattering?
[2+2=4]
- Q.2.** The densities of two spherical particles are 1.12 g cm^{-3} and 1.2 g cm^{-3} and they differ in radius by a factor of 8, the former being the larger. If the density of the solution is 0.994 g cm^{-3} then what will be relative rate of sedimentation for the two particles?
[4]
- Q.3.** The refractive index of a compound is 1.8 for 645 nm light. Its density at $25^\circ C$ is 2.8 g cm^{-3} . Calculate the polarizability of the molecule at this wavelength. Consider $M = 60 \text{ g mol}^{-1}$. [4]
- Q.4.** Calculate the rotational partition function of SO_2 at 320 K from its rotational constants 2.02736 cm^{-1} , 0.34417 cm^{-1} and 0.293535 cm^{-1} . Also, calculate the rotational contribution to the molar entropy of SO_2 at the same temperature assuming all rotational modes are active.
[2+2=4]
- Q.5.** The equilibrium $A \rightleftharpoons B + C$ at $30^\circ C$ is subjected to a temperature jump that slightly increases the concentrations of B and C. The measured relaxation time is $3.5 \mu s$. The equilibrium constant for the system is $3.0 \times 10^{-14} \text{ mol dm}^{-3}$ at $30^\circ C$, and the equilibrium concentrations of B and C at $30^\circ C$ are both $6.0 \times 10^{-3} \text{ mol dm}^{-3}$. Calculate the rate constants for forward (k_f) and reverse (k_r) steps.
[2+2=4]

END