

**GS-2018 (Chemistry)****TATA INSTITUTE OF FUNDAMENTAL RESEARCH**Written Test in **CHEMISTRY - December 10, 2017**

Duration : Three hours (3 hours)

Name : \_\_\_\_\_ Ref. Code : \_\_\_\_\_

**Please read all instructions carefully before you attempt the questions.**

1. Please fill-in details about name, reference code etc. on the answer sheet. The Answer Sheet is machine-readable. Use only Blue/Black ball point pen to fill-in the answer sheet.
2. Indicate your ANSWER ON THE ANSWER SHEET by blackening the appropriate circle for each question. Do not mark more than one circle for any question : this will be treated as a wrong answer.
3. This is a multiple choice question paper with **ONE** section having a total of 40 questions. Each correct answer will get you 3 marks. Every wrong answer will get you -1 mark. Marks are not awarded or deducted when a question is not attempted. It is better not to answer a question if you are not sure.
4. We advise you to first mark the correct answers on the QUESTION PAPER and then to TRANSFER these to the ANSWER SHEET only when you are sure of your choice.
5. Rough work may be done on blank pages of the question paper. If needed, you may ask for extra rough sheets from an invigilator.
6. **Use of calculators is permitted. Calculator which plots graphs is NOT allowed. Multiple-use devices such as cell phones, smart phones etc., CANNOT be used for this purpose.**
7. In answering the questions, please choose the option that best describes the solution to the problem.
8. Do NOT ask for clarifications from the invigilators regarding the questions. They have been instructed not to respond to any such inquiries from candidates. In case a correction/clarification is deemed necessary, the invigilator(s) will announce it publicly.



## SOME USEFUL DATA

Avogadro number =  $6.02 \times 10^{23} \text{ mol}^{-1}$

$RT/F = 0.0257 \text{ V}$  at  $25^\circ\text{C}$

Faraday constant =  $96500 \text{ C/mol}$

Boltzmann constant  $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$

Mass of an electron =  $9.109 \times 10^{-31} \text{ kg}$

$e = 1.6 \times 10^{-19} \text{ C}$

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

$c = 3 \times 10^8 \text{ m s}^{-1}$

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

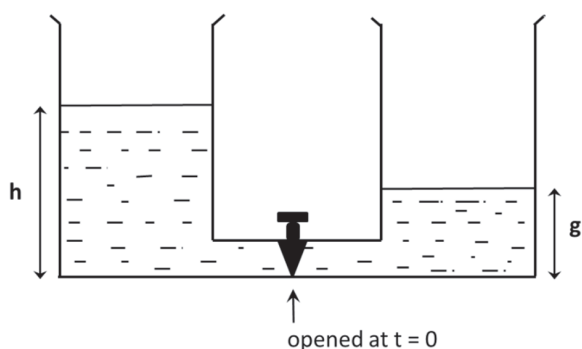
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- 1) For an one-dimensional quantum-mechanical harmonic oscillator
- A) Average linear momentum is nonzero but average displacement is zero.
  - ✓ B) Average linear momentum is zero and average displacement is zero.
  - C) Average linear momentum is zero but average displacement is nonzero
  - D) Average linear momentum and average displacement both are non-zero.
- 2) For electronic transitions in organic molecules, the expected energy ordering of the transitions is:
- A)  $\pi$  to  $\pi^*$  < n to  $\sigma^*$  <  $\sigma$  to  $\sigma^*$  < n to  $\pi^*$
  - B)  $\pi$  to  $\pi^*$  < n to  $\pi^*$  < n to  $\sigma^*$  <  $\sigma$  to  $\sigma^*$
  - ✓ C) n to  $\pi^*$  <  $\pi$  to  $\pi^*$  < n to  $\sigma^*$  <  $\sigma$  to  $\sigma^*$
  - D) n to  $\sigma^*$  <  $\sigma$  to  $\sigma^*$  < n to  $\pi^*$  <  $\pi$  to  $\pi^*$
- 3) The restriction enzyme EcoRI recognizes and cuts a six basepair long DNA sequence (GAATTC). You are given a bacterial genome which is  $5 \times 10^6$  basepairs long of unknown sequence. Estimate the number of EcoRI cut sites that you would expect:
- ✓ A) 1220
  - B) 10037
  - C) 124
  - D) 102874

4) The rotational constant for a diatomic molecule is  $1.9225 \text{ cm}^{-1}$ . In general (within the rigid rotor approximation), at  $T = 600 \text{ K}$ , for rotation state with maximum population ( $J_{\text{max}}$ ) and the position of maximum intensity of pure rotational absorption spectrum ( $I_{\text{max}}$ ), which of the following holds true ?

- A)  $J_{\text{max}} = 7$ , while  $I_{\text{max}}$  position is near transitions originating from  $J = 7$
- B)  $J_{\text{max}} = 10$ , while  $I_{\text{max}}$  position is near transitions originating from  $J = 7$
- C)  $J_{\text{max}} = 7$ , while  $I_{\text{max}}$  position cannot be determined from this information alone
- ✓ D)  $J_{\text{max}} = 10$ , while  $I_{\text{max}}$  position cannot be determined from this information alone

5) If two identical vessels (placed at the same horizontal level) containing water at two different levels are connected by a pipe at time zero by opening the valve slightly, how would the water levels equalize with time ( $t$ )?



- A) Linearly with  $t$
  - ✓ B) Exponentially with  $t$
  - C) As  $t^n$ , where  $t$  is time and  $n$  is an integer,
  - D) Proportional to  $t \cdot \sin(t)$
- 6) Which of the following belong to the same symmetry group as  $\text{NH}_3$ ?

- A)  $\text{BF}_3$
- B)  $\text{CH}_4$
- C)  $\text{CH}_3\text{OH}$
- ✓ D)  $\text{CHCl}_3$

7) The volume of a parallelepiped formed by three polar vectors:  $\mathbf{A} = 1\mathbf{i} + 2\mathbf{j}$ ,  $\mathbf{B} = 4\mathbf{k}$ , and  $\mathbf{C} = 2\mathbf{i} + 4\mathbf{j}$  is

A) 20 cubic units

B) 40 cubic units

C) 12 cubic units

✓ D) 0 cubic units

8) X-ray diffraction (XRD) is a widely used technique to analyse the structure of solids. In an XRD experiment, a solid crystal is irradiated with monochromatic X-rays and the resulting data consists of diffraction spots. These bright spots occur due to the explanation given by which ONE of the following statements?

A) X-rays are being absorbed by the crystal and the structure in turn emits radiation at specific wavelengths

B) X-rays are being refracted through the crystal and the rays bend at specific angles

✓ C) X-rays are being scattered by individual atoms in the solid

D) None of the above

9) Suppose you are carrying out an experiment measuring the Raman spectrum of  $\text{N}_2$  gas in the outdoor air. Where would you find a higher strength of the anti-Stokes line:

✓ A) In Kanyakumari

B) On top of Mt. Everest

C) The strength will be the same in both the places

D) Nitrogen would not have an anti-Stokes Raman line

10) Using the data given below, find out the strongest reducing agent:

$$E^\circ (\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.33 \text{ V}$$

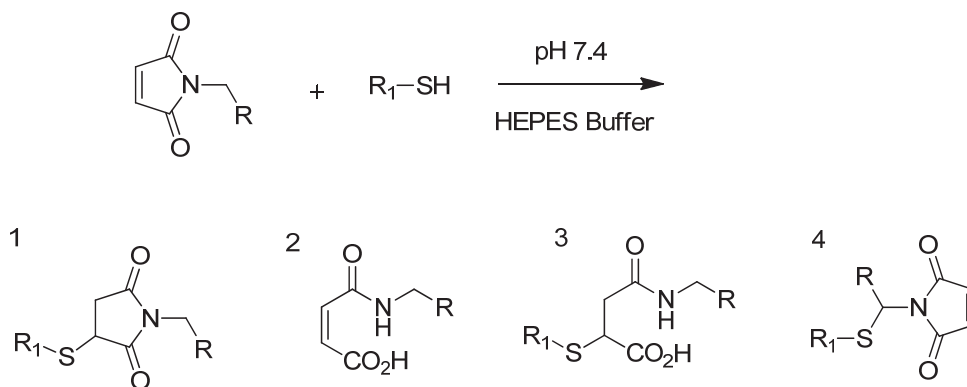
$$E^\circ (\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$$

$$E^\circ (\text{MnO}_4^-/\text{Mn}^{2+}) = 1.51 \text{ V}$$

$$E^\circ (\text{Cr}^{3+}/\text{Cr}) = -0.74 \text{ V}$$

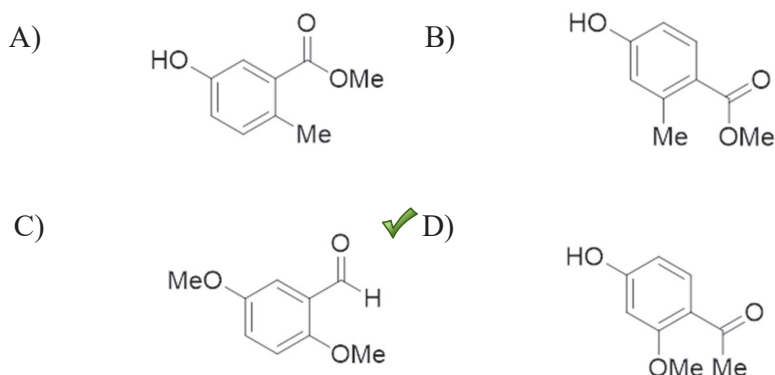
- A)  $\text{Cl}^-$
- B)  $\text{MnO}_4^-$
- ✓ C) Cr
- D)  $\text{Mn}^{2+}$

11) Predict the feasible product/products of the following bio-conjugation reaction.



- ✓ A) 1, 2, and, 3
- B) 1 only
- C) 2, 3 and 4
- D) 1 and 2

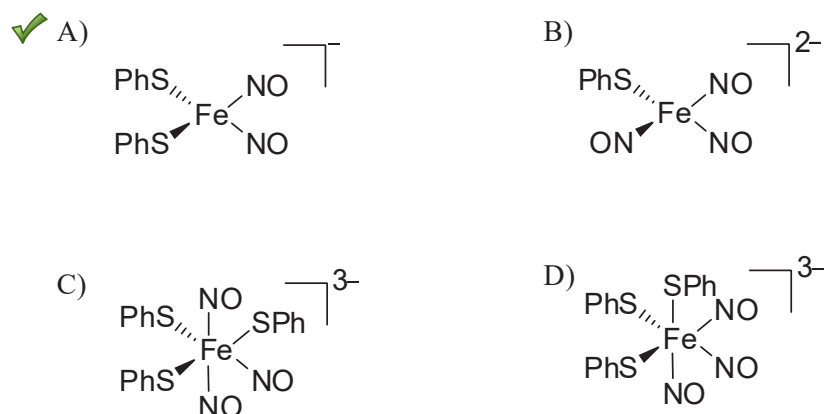
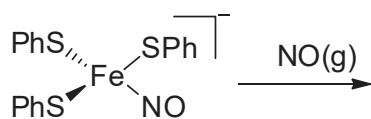
12) An organic compound ( $C_9H_{10}O_3$ ) exhibited the following spectral data: IR: 3400, 1680  $cm^{-1}$ ;  $^1H$ -NMR:  $\delta$ 7.8 (1 H, *doublet*,  $J = 8$  Hz), 7.0 (1 H, *doublet*,  $J = 8$  Hz), 6.5 (1 H, *singlet*), 5.8 (1 H, *singlet*,  $D_2O$  exchangeable), 3.9 (3 H, *singlet*), 2.3 (3 H, *singlet*). The compound is,



13) Which of the following is not correct with regard to the uncertainty principle?

- A) An electron in an atom cannot be defined by a well-defined orbit
- B) The momentum of an electron cannot be measured exactly
- C) A harmonic oscillator possesses a zero-point energy
- D) Measurement of one variable in an atomic system can affect subsequent measurements of certain other variables

14) What is the product of the following reaction?



- 15) Thermal desorption rate of adsorbates from a surface can be estimated by using the Arrhenius equation of the following form:

$$k = A \times \exp(-E_{des}/k_B T_s)$$

Where,  $k$  is the rate constant,  $A$  is the usual pre-exponential factor,  $E_{des}$  is the desorption energy,  $k_B$  is the Boltzmann constant,  $T_s$  is the surface temperature. If none of the adsorbates stick permanently to the surface, which of the following best represents a typical value of  $A$ ?

- A)  $10^3$  sec
- B)  $10^{10}$  sec
- C)  $10^{-7}$  sec<sup>-1</sup>
- ✓ D)  $10^{13}$  sec<sup>-1</sup>
- 16) A unimolecular reaction of chemical species  $A$  interconverting with  $B$  is studied over a small temperature range (15 to 25 °C). It is found that reaction proceeds rapidly and that the  $k_{AB}$  reaction rate has a strong temperature dependence, increasing rapidly (by a factor 5 over the range studied) with increasing temperature. However, the activation free energy  $\Delta G^*$  is known to be quite small  $\sim 5RT$ . What can you conclude about the reaction:
- ✓ A)  $\Delta H^*$  and  $\Delta S^*$  are positive and  $\Delta H^*$  is large compared to  $RT$ .
- B)  $\Delta H^*$  and  $\Delta S^*$  are positive and  $\Delta H^*$  is small compared to  $RT$ .
- C)  $\Delta H^*$  is positive and  $\Delta S^*$  is negative and  $\Delta H^*$  is large compared to  $RT$ .
- D)  $\Delta H^*$  is positive and  $\Delta S^*$  is negative and  $\Delta H^*$  is small compared to  $RT$ .
- 17) Which of the following equations meaningfully represents the change of concentration of a non-ribosomal protein ( $P$ ) inside a cell. Here  $\alpha$  is rate at which proteins are synthesized by the ribosomes from constituent amino acids, and  $\beta$  is the rate of degradation+dilution of the protein due to proteases and cell growth.

A)  $\frac{dP}{dt} = \alpha P - \beta P$

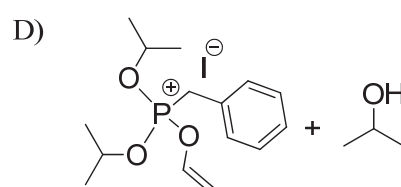
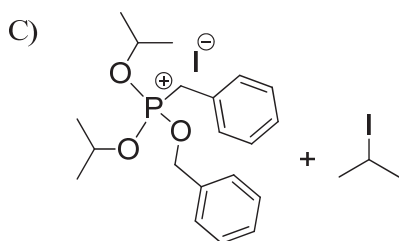
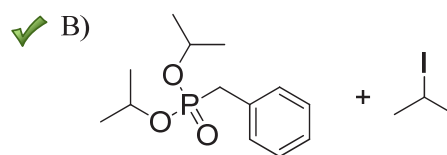
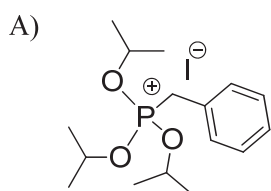
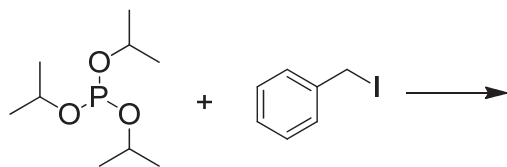
✓ B)  $\frac{dP}{dt} = \alpha - \beta P$

C)  $\frac{dP}{dt} = \alpha P - \beta$

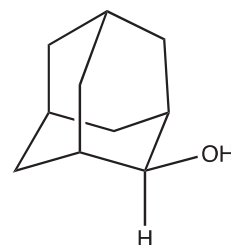
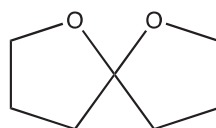
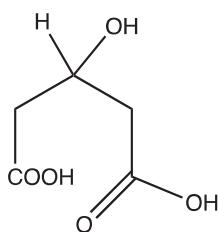
D)  $\frac{dP}{dt} = \alpha + \beta P$



18) Phosphite esters undergo nucleophilic substitution with alkyl halides. Predict the final stable product of the following reaction.



19) Which amongst the following molecules is chiral?



- A) I  
 ✓ B) II  
 C) III  
 D) None of the above

20) Based on the behaviour of the metalloenzymes, consider the following statements

- (i) In the enzymes, Zinc activates  $O_2$  to form peroxide species
- (ii) In the enzymes, Zinc activates  $H_2O$  and provides a Zinc-bound hydroxide
- (iii) In the oxidases, Iron activates  $O_2$  to break the bonding between the two oxygen atoms
- (iv) Zinc ion acts as a nucleophile and attacks at the peptide carbonyl

Which combination of statements is the correct one:

- A) i and ii
- ✓ B) ii and iii
- C) iii and iv
- D) None of the above

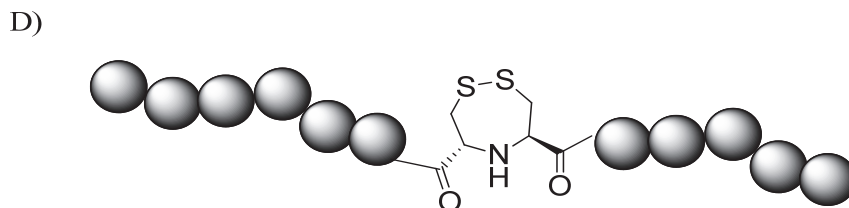
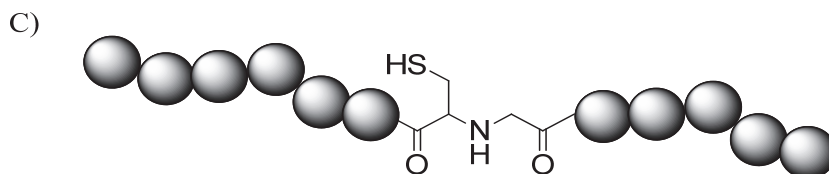
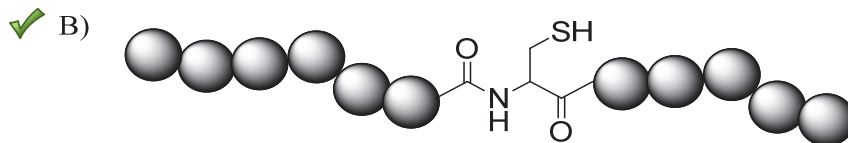
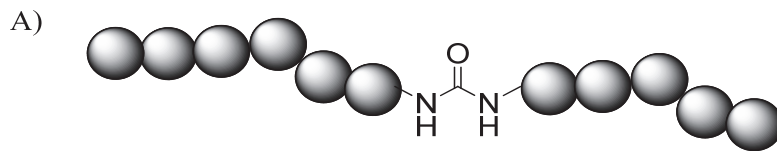
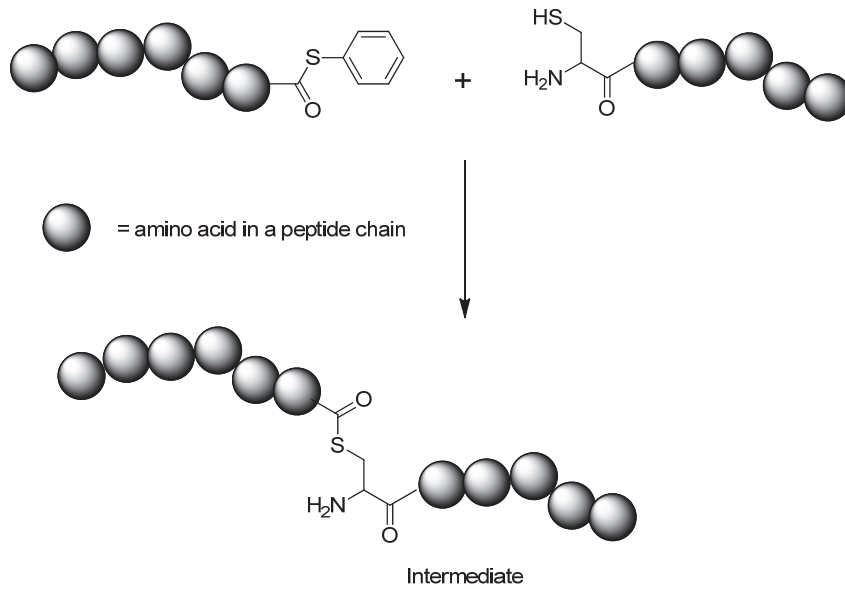
21) For a gas that obeys following equation of state  $P(V-b)= RT$  , where b is a constant and R is an universal gas constant, which of the following is right:

- A)  $\left(\frac{\partial U}{\partial V}\right)_T = b$
- B)  $\left(\frac{\partial U}{\partial V}\right)_T = R$
- C)  $\left(\frac{\partial U}{\partial V}\right)_T = P$
- ✓ D)  $\left(\frac{\partial U}{\partial V}\right)_T = 0$

22) If a cylindrical box with a lid of cross-sectional area  $0.01m^2$  containing air at 1 atmosphere is transferred into a vacuum chamber, how much of a weight would we have to put on the lid of the box in order to maintain the internal pressure? Assume that the lid is loosely put on the box and it is massless.

- A) ~1 kg
- B) ~10 kg
- ✓ C) ~100 kg
- D) insufficient data

23) The following bio-conjugation reaction is known as native chemical ligation (NCL) and is used to stitch peptides together. The intermediate for this reaction has been shown. Predict the product of the following NCL reaction.

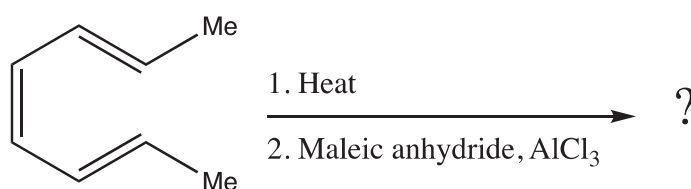


- 24) The fully symmetric C-H stretching mode ( $\nu_1$ ) of  $\text{CH}_4$  was detected to be at  $3025\text{ cm}^{-1}$ . The C-H bending mode ( $\nu_2$ ) on the other hand was detected to be at  $1380\text{ cm}^{-1}$ . If complete H/D exchange labeling was done to produce the molecule  $\text{CD}_4$ , and the frequency ratio  $R_D$  is defined as  $= [\nu_{\text{bend}}/\nu_{\text{stretch}}]$  for  $\text{CD}_4$  while  $R_H = [\nu_{\text{bend}}/\nu_{\text{stretch}}]$  for methane; which of the following statement is TRUE about  $R_H/R_D$  and the vibrational technique used for detection:
- A)  $R_H/R_D = 1.4$  while IR spectroscopy can be used to detect both the symmetric stretch and the bending mode.
  - ✓ B)  $R_H/R_D = 1.0$  while Raman spectroscopy can be used to detect both the symmetric stretch and the bending mode.
  - C)  $R_H/R_D = 1.0$  while IR can detect the symmetric stretch and Raman the bending mode.
  - D)  $R_H/R_D = 1.4$  while Raman can detect the symmetric stretch and IR the bending mode.
- 25) You want to purify a DNA binding protein ( $pI \sim 9.0$ ) from other cellular proteins ( $pI \sim 5.5$ ) by ion exchange chromatography. You have the choice of choosing high pH (9.0) or low pH (5.5) buffers and anion and cation exchange columns. Anion exchange columns are positively charged and cation exchange columns are negatively charged. To purify the protein you will use:
- A) Anion exchange column with a low pH (5.5) buffer.
  - B) Anion exchange column with a high pH (9.0) buffer.
  - C) Cation exchange column with a low pH (5.5) buffer.
  - ✓ D) Cation exchange column with a high pH (9.0) buffer.
- 26) The position of a particle in space has a Gaussian probability distribution function. This implies that the underlying potential energy surface for the particle
- A) Is flat in space
  - B) Has a linear dependence on spatial coordinates
  - ✓ C) Has a quadratic dependence on spatial coordinates
  - D) Has a cubic dependence on spatial coordinates

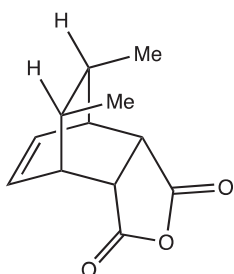
27) The Haber process is commonly known as the reaction of Hydrogen gas with Nitrogen gas to produce ammonia in the presence of a catalyst such as iron. Which of the following statements is true regarding the Haber process:

- A) Iron serves as a homogenous catalyst for this reaction
- B) Increasing the temperature increases the amount of ammonia formed
- ✓ C) Increasing the pressure increases the amount of ammonia formed
- D) All of the above

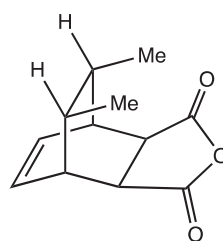
28) Predict the final product of the following reaction:



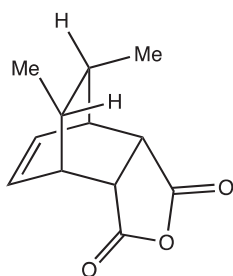
✓ A)



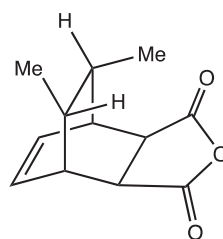
B)



C)



D)



29) Mr. Bhatt has two children; the older child is a boy. Mrs. Ghose also has two children; at least one of them is a girl. Let  $P_B$  be the probability that both children of Mr. Bhatt are boys, and  $P_G$  be the probability that both children of Mrs. Ghose are girls. Assume the following: (1) Birth of boys and girls are independent; (2) no identical twins are born; (3) neither parent followed sex-selective birth of their offsprings, and (4) none of the children was transgender. What would be values of  $P_B$  and  $P_G$ ?

A)  $P_B = P_G$

B)  $P_B < P_G$

✓ C)  $P_B > P_G$

D)  $P_B = P_G = 1/2$

30) The lattice energy of solid NaCl is 180 kcal/mole. The dissolution of the solid in water in the form of ions is endothermic to the extent of 1 kcal/mole. If the hydration energies of  $\text{Na}^+$  and  $\text{Cl}^-$  ions are in the ratio 6:5, what is the enthalpy of hydration of sodium ion?

A) -85.6 kcal/mole

✓ B) -97.6 kcal/mole

C) 82.6 kcal/mole

D) none of the above

31) A particle can occupy either of two energy levels: The ground state with energy zero and an excited state with energy  $\varepsilon > 0$ . At a finite temperature T, the probability of occupying the excited level will be if  $k_B$  is the Boltzmann constant:

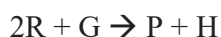
A) 0

B)  $1 + \exp(-\varepsilon/k_B T)$

✓ C)  $\exp(-\varepsilon/k_B T) / (1 + \exp(-\varepsilon/k_B T))$

D)  $1 / (1 + \exp(-\varepsilon/k_B T))$

32) A reaction involving chemical species “R”, “G”, “P” and “H” has the observed stoichiometry:



The experimentally observed rate equation for this reaction is  $\text{rate} = k[R]^2$ .

Which of the following is a possible mechanism for the above reaction?

- A)  $R + G \rightarrow I$  (fast);  $I + R \rightarrow P + H$  (slow)
- B)  $R + R \rightarrow I$  (fast);  $I + G \rightarrow P + H$  (slow)
- ✓ C)  $R + R \rightarrow I$  (slow);  $I + G \rightarrow P + H$  (fast)
- D)  $R + G \rightarrow I$  (slow);  $I + R \rightarrow P + H$  (fast)

33) A bottle contains hydrogen molecule in gaseous state. The nuclear wavefunction of this hydrogen gas is given by:

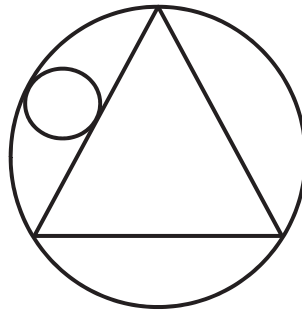
$$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

What would be the NMR spectrum of this hydrogen gas, assuming that the wavefunction does not change during recording of the NMR spectrum?

- A) A single NMR peak
- B) Two NMR peaks, each is a doublet
- C) Three NMR peaks, with relative intensities 1:2:1
- ✓ D) No NMR lines

34) If  $R$  and  $r$  are the radii of outer and inner circles, respectively, then what is  $R/r$ ?

[Hint: the triangle is equilateral]



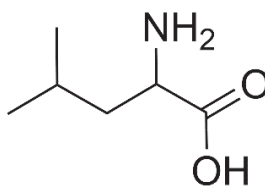
A) 0.5

B) 2

C)  $2\sqrt{3}$

✓ D) 4

35) Where on a given protein are you more likely to find a Leucine residue whose structure is given below:



A) In the interior part of the protein

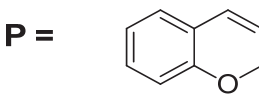
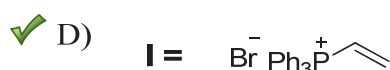
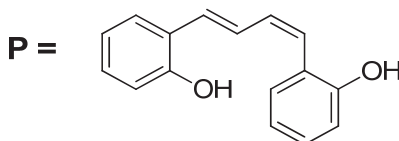
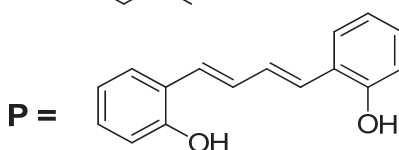
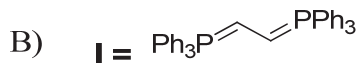
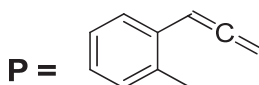
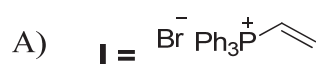
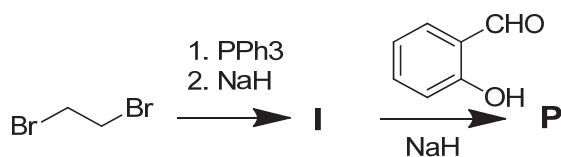
B) In the exterior part

C) Equally likely in the exterior or the interior parts

✓ D) Depends on whether the protein is water-soluble or is a membrane protein



36) Identify the products A and B in the following reaction scheme



37) Consider a polar diatomic molecule (with bond along the x-axis) whose internuclear potential, near the equilibrium geometry is well described by a harmonic oscillator. Suppose a weak electric field ( $\vec{E}$ ) is turned on such that the system is perturbed by an amount  $\mathbf{H}' = -k \times |\vec{E}| \times \mathbf{x}$  ( $k$  is a proportionality constant). Using first order perturbation theory, the shift in the ground state energy level is equal to:

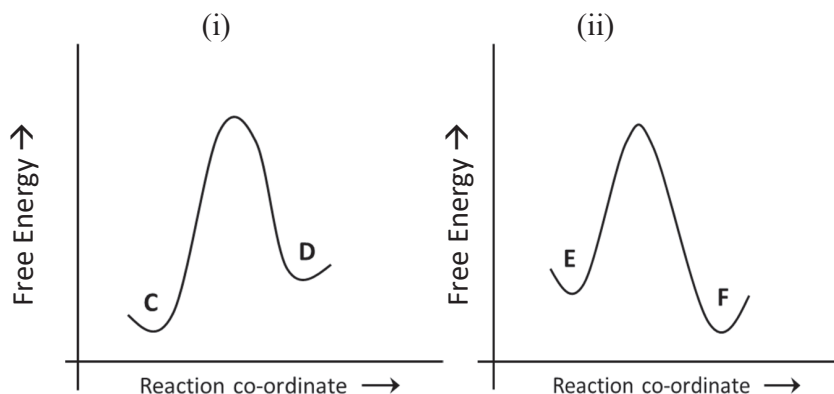
A)  $(1/\sqrt{2}) \times q \times |\vec{E}| \times \mathbf{x}$

✓ B) 0

C)  $-(1/2) \times q \times |\vec{E}| \times \mathbf{x}$

D) None of the above

38) Suppose a reaction  $A \rightarrow B$  is slowly progressing in a closed vessel (no energy or material is supplied from the outside). To speed it up, you have the option of simultaneously carrying out a separate reaction in the same vessel, which can be either be i)  $C \rightarrow D$ , or ii)  $E \rightarrow F$ . The free energy diagram of the reactions i) and ii) are given below in the Figure below respectively. Which reaction would you choose to carry out to speed up  $A \rightarrow B$ ? Assume that the individual reactants C and E as well as products D and F do not interact in any way with A or B.

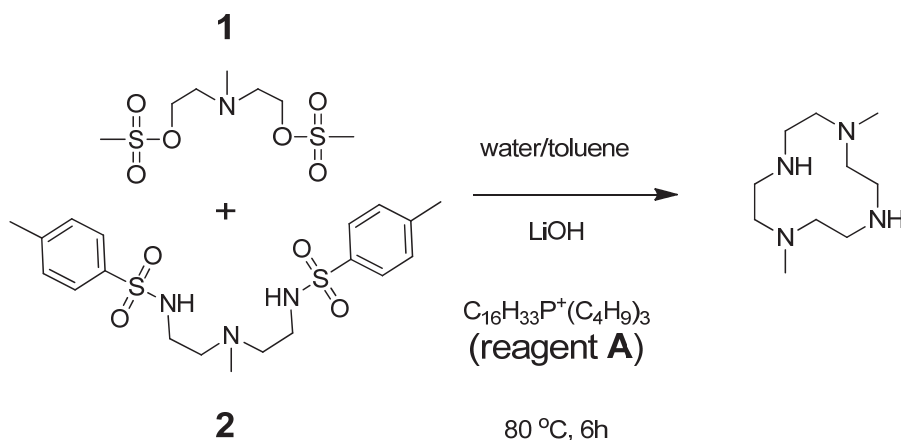


- ✓ A)  $E \rightarrow F$
- B)  $C \rightarrow D$
- C) Neither will affect the rate
- D) Both can help equally

39) Identify the high-spin complex amongst the choices given below:

- A)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- B)  $[\text{Co}(\text{CN})_6]^{3-}$
- ✓ C)  $[\text{CoF}_6]^{3-}$
- D) None of the above

40) What is the role of reagent **A** in the macrocyclization reaction based on the nucleophilic attack of **2** on **1**?



- ✓ A) Reagent **A** is transferred to the toluene layer and pulls hydroxyl ions to toluene to deprotonate **2**.
- B) Reagent **A** acts as a catalyst for the macrocyclization reaction by forming coordinate covalent bonds with **1** and **2**.
- C) Reagent **A** is transferred to water and hydroxyl ions are transferred to toluene to deprotonate **2**.
- D) Reagent **A** reacts with LiOH to form a lithiated intermediate that catalyzes the reaction.

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**The following question does NOT carry any marks and is given to collect information only:**

41) How much time did you take to complete this chemistry exam?

- A) Less than 1 hour
- B) Between 1 to 2 hours
- C) Between 2 to 3 hours
- D) Insufficient time was given

