TIFR M.Sc. CHEMISTRY ENTRANCE - 2018

1. 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

2. 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

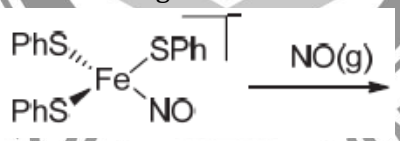
(c) A harmonic oscillator possesses a zero-point energy

(d) Measurement of one variable in an atomic system can affect subsequent measurements of certain other variables

3. Which of the following belong to the same symmetry group as NH_3 ?

(a) BF_3 (b) CH_4 (c) CH_3O (d) $CHCl_3$

4. What is the product of the following reaction?



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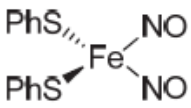

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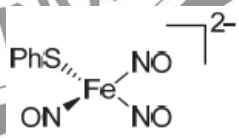

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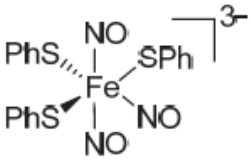

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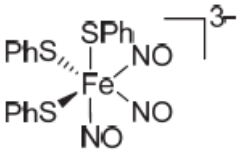


5. Using the data given below, find out the strongest reducing agent:

$E^0\left(CrO_7^{2-}/Cr^{3+}\right)=1.33\ V$ $E^0\left(Cl_2/Cl^-\right)=1.36\ V$

$E^0\left(MnO_4/Mn^{2+}\right)=1.51\ V$ $E^0\left(Cr^{3+}/Cr\right)=-0.74\ V$

(a) Cl^- (b) MnO_4^- (c) Cr (d) Mn^{2+}

6. For electronic transitions in organic molecules, the expected energy ordering of the transitions is:

(a) π to $\pi^* < n$ to $\sigma^* < \sigma$ to $\sigma^* < n$ to π^* (b) π to $\pi^* < n$ to $\pi^* < n$ to $\sigma^* < \sigma$ to σ^*

(c) n to $\pi^* < \pi$ to $\pi^* < n$ to $\sigma^* < \sigma$ to σ^* (d) n to $\sigma^* < \sigma$ to $\sigma^* < n$ to $\pi^* < \pi$ to π^*

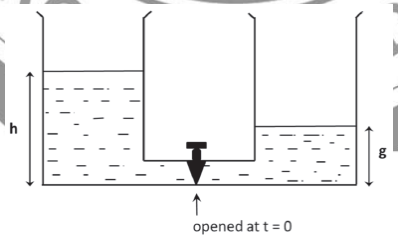
7. The volume of a parallelepiped formed by three polar vectors:
$A = 1i + 2j, B = 4k,$ and $C = 2i + 4j$ is

(a) 20 cubic units (b) 40 cubic units (c) 12 cubic units (d) 0 cubic units

8. 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.

9. Suppose you are carrying out an experiment measuring the Raman spectrum of 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. If two identical vessels placed at the same horizontal level) containing water at two different levels are connected by a pipe at time zero the value slightly, how would the water levels equalize with time (t)?



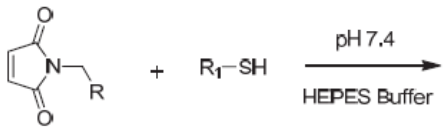
(a) Linearly with t

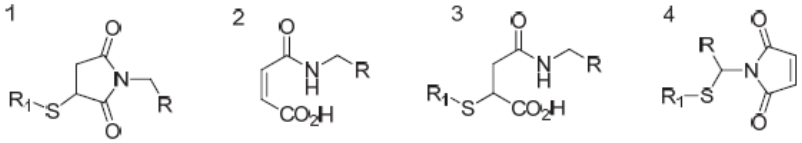
(b) Exponentially with t

(c) As t^n, where t is time and n is an integer

(d) Proportional to t*sin(t)

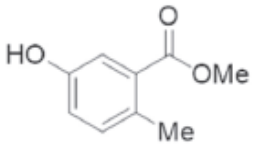
11. Predict the feasible product/products of the following bio-conjugation reaction.

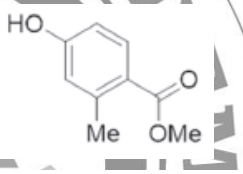


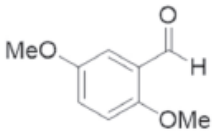


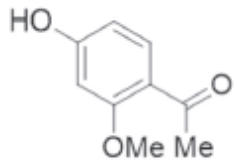
(a) 1, 2, and, 3 (b) 1 only (c) 2, 3 and 4 (d) 1 and 2

12. An organic compound $(C_6H_{10}O_3)$ exhibited the following spectral data: IR: 3400, 1680 cm^{-1}; $^1H\,NMR: \delta 7.8\,(1H, doublet, J = 8\,Hz)$, $7.0\,(1H, doublet, J = 8\,Hz)$, 6.5 $(1H, singlet)$, $5.8\,(1H, singlet, D_2O\ exchangeable)$, $3.9\,(3H, singlet)$, 2.3 $(3H, singlet)$. The compound is,

(a) 

(b) 

(c) 

(d) 

13. The restriction enzyme EcoRI recognizes and cuts a six basepair long DNA sequence (GAATTC). You are given a bacterial genome which is 5×10^6 basepairs long of unknown sequence. Estimate the number of EcoRI cut sites that you would expect:
(a) 1220 (b) 10037 (c) 124 (d) 102874

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

(a) $J_{max} = 7$, while I_{max} position is near transitions originating from $J = 7$

(b) $J_{max} = 10$, while I_{max} position is near transitions originating from $J = 7$

(c) $J_{max} = 7$, while I_{max} position cannot be determined from this information alone

(d) $J_{max} = 10$, while I_{max} position cannot be determined from this information alone

15. Based on the behavior 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

(a) i and ii (b) ii and iii (c) iii and iv (d) None of these

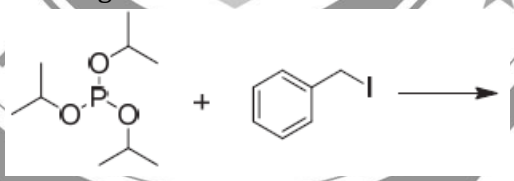
16. For a gas that obeys following equation of state P(V-b) = RT, where b is a constant and R is an universal gas constant, which of the following is right:

(a) $\left(\frac{\delta U}{\delta V}\right)_T = b$ (b) $\left(\frac{\delta U}{\delta V}\right)_T = R$ (c) $\left(\frac{\delta U}{\delta V}\right)_T = P$ (d) $\left(\frac{\delta U}{\delta V}\right)_T = 0$

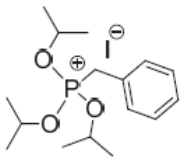
17. If a cylindrical box with a lid of cross-sectional area $0.01\ m^2$ containing air at 1 atmosphere is transferred into a vacuum chamber, how much of a weight would we have to put on the lid of the box in order to maintain the internal pressure? Assume that the lid is loosely put on the box and it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

(a) ~ 1 kg (b) ~ 10 kg (c) ~ 100 kg (d) insufficient data

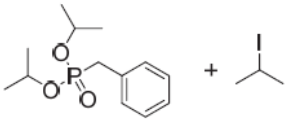
18. Phosphite esters undergo nucleophilic substitution with alkyl halides. Predict the final stable product of the following reaction.



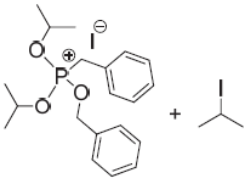
(a)



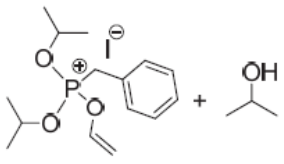
(b)



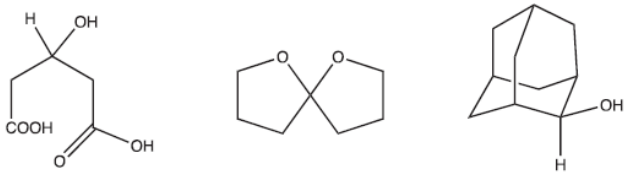
(c)



(d)



19. Which amongst the following molecules is chiral?



I II III

(a) I (b) II (c) III (d) None of these

20. Thermal desorption rate of adsorbates from a surface cane be estimated by using the Arrhenius equation of the following form:

$$k = A \times \exp\left(-E_{des}/kBTs\right)$$

Where, k is the rate constant, A is the usual pre-exponential factor, Edes is the desorption energy, k_B is the Boltzmann constant, Ts 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^{-1} (d) 10^{13} sec^{-1}

21. A unimolecular reaction of chemical species A interconverting with B is studies over a small temperature range $(15 \text{ to } 25°C)$. It is found that reaction proceeds rapidly and that the kAB 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 AG* is known to be quite small ~ 5RT. What can you conclude about the reaction:

(a) ΔH^* and ΔS^* are positive and ΔH^* is large compared to RT.

(b) ΔH^* and ΔS^* are positive and ΔH^* is small compared to RT.

(c) ΔH^* is positive and ΔS^* is negative and ΔH^* is large compared to RT.

(d) ΔH^* is positive and ΔS^* is negative and ΔH^* is small compared to RT.

22. Which of the following equations meaningfully represents the change of concentration of a non-ribosomal protein (P) inside a cell. Here α is rate at which proteins are synthesized by the ribosomes from constituent amino acids, and β 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) $\frac{dP}{dt} = \alpha + \beta P$

23. Mr. Bhatt has two children; the older child is boy. Mrs. Ghose also has two children; at least one of them is a girl. Let Pa be the probability that both children of Mr. Bhatt are boys, and Pa 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) $P_B = P_G = \frac{1}{2}$

24. 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 kacl/mole. If the hydration energies of Na^+ and CC^- ions are in the ratio 6:5, what is the enthalpy of sodium ion?

(a) $-85.6\,\text{kcal/mole}$ (b) $-97.6\,\text{kcal/mole}$

(c) $82.6\,\text{kcal/mole}$ (d) none of the above

25. 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 provability of occupying the excited level will be if k_B is the Boltzmann constant:

(a) 0 (b) $1+\exp(-\varepsilon/k_BT)$

(c) $\exp(-\varepsilon/k_BT)/(1+\exp(-\varepsilon/k_BT))$ (d) $1/(1+\exp(-\varepsilon/k_BT))$

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

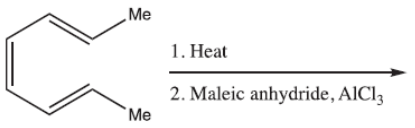
(a) Iron serves as homogenous catalyst for this reaction

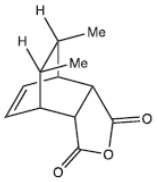
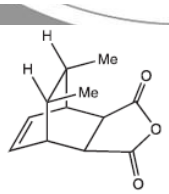
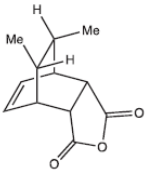
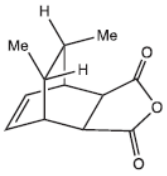
(b) Increasing the temperature increases the amount of ammonia formed

(c) Increasing the pressure increases the amount of ammonia formed

(d) All of the above

27. Predict the final product of the following reaction:



(a)  (b)  (c)  (d) 

28. The fully symmetric C-H stretching mode (a_1) of CH_4 was detected to be at $3025\,\text{cm}^{-1}$. The $C-H$ bending mode (t_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 CD_4, and the frequency ratio R_D is defined as $=\left[V_{bend}/V_{strength}\right]$ for CD_4, while $R_H = \left[V_{bend}/V_{strength}\right]$

for methane; which of the following statements 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 detected the symmetric stretch and Raman the bending mode.

(d) $R_H/R_D = 1.4$ while Raman can detected the symmetric stretch and IR the bending mode.

29. You want to purify a DNA binding protein $(\text{pI} \sim 9.0)$ from other cellular proteins $(\text{pI} \sim 5.5)$ 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 exchanges 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.

30. 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

31. A reaction involving chemical species "R", "G", "P" and "H" has the observed stoichiometry:

$2R + G \rightarrow P + H$

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) $R + G \rightarrow I\,(\text{fast}); \quad I + R \rightarrow P + H\,(\text{slow})$

(b) $R + R \rightarrow I\,(\text{fast}); \quad I + G \rightarrow P + H\,(\text{slow})$

(c) $R + R \rightarrow I\,(\text{slow}); \quad I + G \rightarrow P + H\,(\text{fast})$

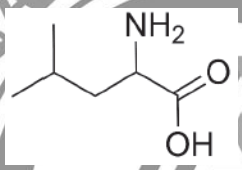
(d) $R + G \rightarrow I\,(\text{slow}); \quad I + R \rightarrow P + H\,(\text{fast})$

32. If R and r are the radii of outer and inner circles, respectively, the hat is R/r?

[Hint: the triangle is equilateral]

(a) 0.5 (b) 2 (c) $2\sqrt{3}$ (d) 4

33. Where on a given protein are you more likely to find a Leucine residue whose is given below:



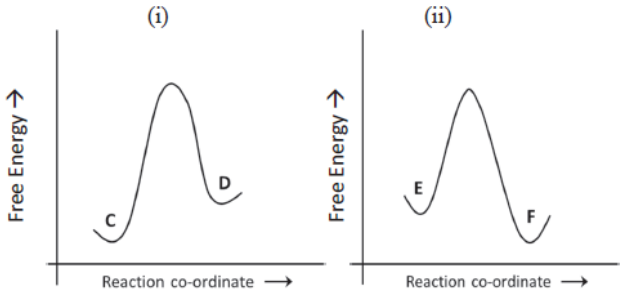
(a) In the interior part of the protein
(b) In the exterior part
(c) Equally likely in the exterior or the interior parts
(d) Depends on whether the protein is water-soluble or is a membrane protein

34. A bottle contains hydrogen molecule is gaseous state. The molecular 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 double
(c) Three NMR peaks, with relative intensities 1:2:1
(d) No NMR lines

35. Suppose a reaction $A \rightarrow B$ is slowly progressing in a closed vessel (no energy or material in 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 chose 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.



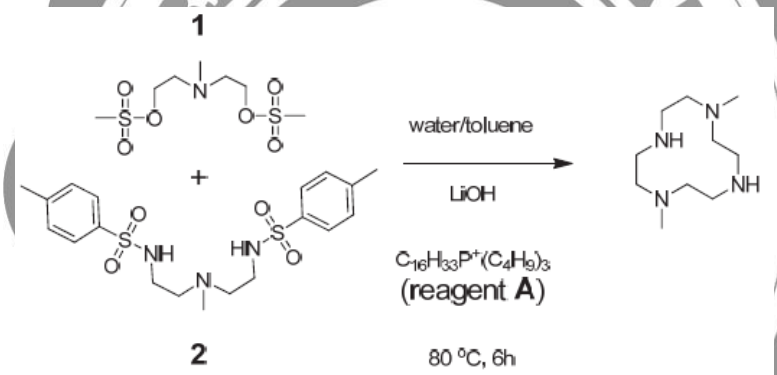
(a) $E \rightarrow F$ (b) $C \rightarrow D$

(c) Neither will affect the rate (d) Both can help equally

36. Identify the high-spin complex amongst the choices given below:

(a) $\left[Co(NH_3)_6\right]^{3+}$ (b) $\left[Co(CN_3)_6\right]^{3-}$ (c) $\left[CoF_6\right]^{3-}$ (d) None of these

37. What is the role of reagent A in the macrocyclization 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 act as a catalyst for the macrocyclization reaction by forming coordinate covalent bonds with 1 and 2.

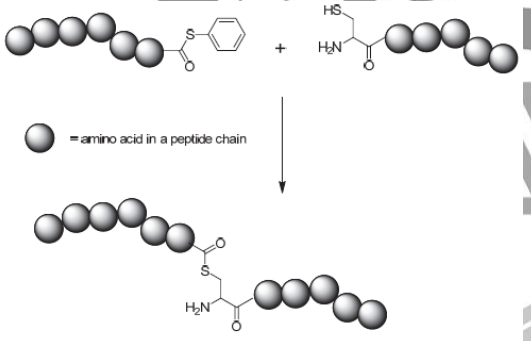
(c) Reagent A is transferred to water and hydroxyl ions are transferred to toluene to deprotonate 2.

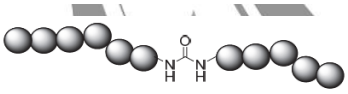
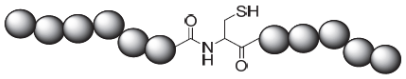
(d) Reagent A reacts with LiOH to form a lithiated intermediate that catalyzes the reaction.

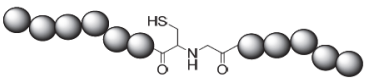
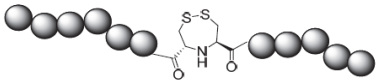
38. Consider a polar diatomic molecule (with bond along the x-axis) whose internuclear potential, near the equilibrium geometry is well described by a harmonic oscillator. Suppose a weak electric field $\left(\vec{E}\right)$ is turned on such that the system is perturbed by a amount $H' = -k\,x\left|\vec{E}\right|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

(a) $\left(1\sqrt{2}\right)\times q\times\left|\vec{E}\right|\times x$ (b) 0 (c) $-\left(1\sqrt{2}\right)\times q\times\left|\vec{E}\right|\times x$ (d) None of these

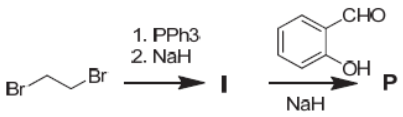
39. The following bio-conjugation reaction is known as native chemical ligation (NCL) and is used to stich to peptides together. The intermediate for this reaction has been shown. Predict the product of the following NCL reaction.

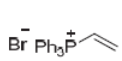
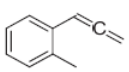


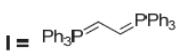
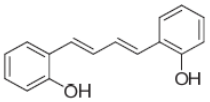
(a)  (b) 

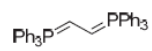
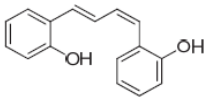
(c)  (d) 

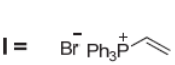
40. Identify the products A and B in the following reaction scheme



(a) I =  P = 

(b) I =  P = 

(c) I =  P = 

(d) I =  P =