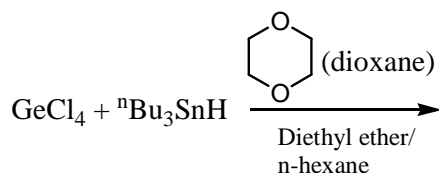


TIFR 2016 CHEMISTRY

1. In a 1g diamond crystal, a scientist wants to replace a few of the carbon atoms with nitrogen atoms. Which of the following statements best describes the resulting material?
- (a) This is not possible as nitrogen has a coordination number of 3 and carbon has a coordination number of 4
 (b) The resulting material will NOT have a cubic diamond structure
 (c) The resulting material will be a defective diamond as it will be p-doped
 (d) The resulting material can be characterized as n-doped diamond.
2. What is the product of the following reaction?



- (a) HGeCl_3 (b) $\text{Cl}_2\text{Ge} : \text{Dioxane}$ (c) $\text{Cl}_3\text{Ge}-\text{Sn}^n\text{Bu}_3$ (d) none of the above.
3. A long column of water in any transparent bottle appears slightly blue. However, if we replace water with heavy water (D_2O) it will look more transparent. This effect is due to
- (a) Rayleigh scattering
 (b) Kinetic isotope effects
 (c) Absorption spectra of H_2O and D_2O are different
 (d) None of the above.
4. The integral $\int_{-a}^a \cos(x) \sin(x) dx$
- (a) Equals to zero for any value of a , and $\cos(x)$ is symmetric in the range of the integral.
 (b) Is not equal to zero except for certain values of a , and $\sin(x)$ is antisymmetric in the range of the integral.
 (c) Is not equal to zero except for certain values of a , and $\cos(x)$ is symmetric in the range of the integral.
 (d) Has a non-zero value depending on a .
5. Which of the following statements is the best definition of the base peak in a mass spectrum?
- (a) The molecular ion peak (b) The lowest m/z peak
 (c) The highest mass rearrangement ion (d) The ion peak of greatest intensity
6. Shown below are the front and side views of the structure of a molybdenum-based metal organic polyon. What is the symmetry of the molecule?



Front view



Side view

- (a) D_{4h} (b) C_{4h} (c) C_{2v} (d) C_4

7. Which of the following is/are implied by the second law of thermodynamics?

(a) $\Delta S > \int_A^B dq(\text{irreversible})/T$ for an irreversible process $A \rightarrow B$ at temperature T .

(b) $\Delta S > 0$ for an isolated system in the course of a spontaneous change

(c) Entropy of the universe always tends to maximum

(d) All of the above.

8. A protein has three folded states F_1, F_2, F_3 and three unfolded states U_1, U_2 and U_3 . Consider transitions between configurations $T_{i \rightarrow f}$ where the initial (i) and (f) configurations each comprise of simple additive combinations of purely folded (e.g. $F_1, F_1 + F_2, F_1 + F_2 + F_3$) or unfolded states (e.g. $U_1, U_1 + U_2, U_1 + U_2 + U_3$). Transitions between folded (or unfolded) configurations are also allowed unless a state is part of both the initial and final configurations. Assuming $T_{i \rightarrow f} = T_{f \rightarrow i}$ the total number of distinct transitions are

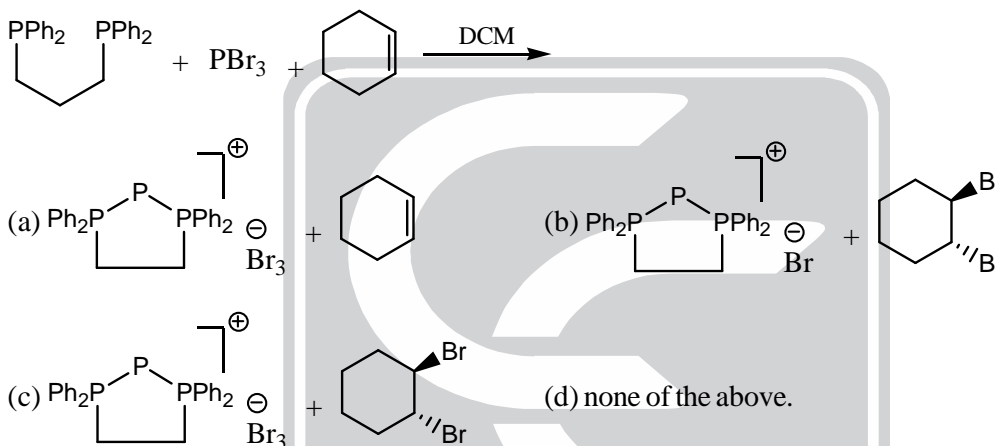
(a) 61

(b) 49

(c) 73

(d) 9

9. What is the product of the following reaction?



10. The specific heat of a certain material monotonically increases with temperature. Two identical blocks of this material are kept at 50°C and 100°C , respectively. The two blocks are now brought in contact with each other. Assume that no heat is lost to the surrounding. When thermal equilibrium is reached after the two blocks are kept in contact, what would be the final temperature of the two blocks?

(a) 75°C

(b) $> 75^\circ\text{C}$

(c) $< 75^\circ\text{C}$

(d) T_f can be either more than or less than 75°C , depending upon the precise variation of the specific heat with temperature.

11. A carpenter claims to have made a rectangular parallelepiped (cuboid), the length of whose three face diagonals are 33, 56 and 65 meters. You are required to determine the length the main diagonal joining a pair of opposite corners of this parallelepiped

(a) $65\sqrt{2}$ meters

(b) $65/\sqrt{2}$ meters

(c) 65 meters

(d) It is not possible to make a rectangular parallelepiped with the claimed dimensions of the three faces.

12. For a canonical ensemble where each system has N, V, T fixed, which of the following statements regarding energy hold(s) true:

(a) Energy of the system does not fluctuate

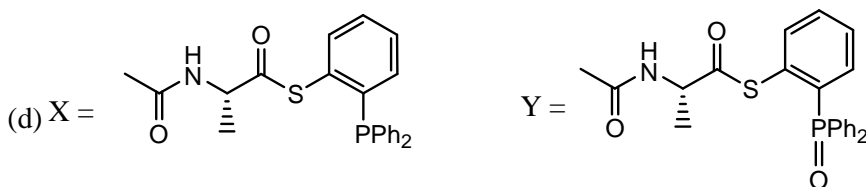
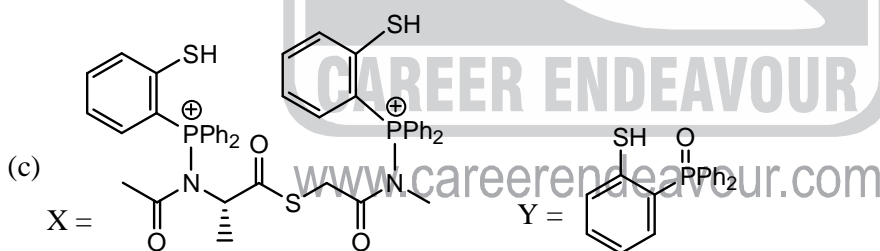
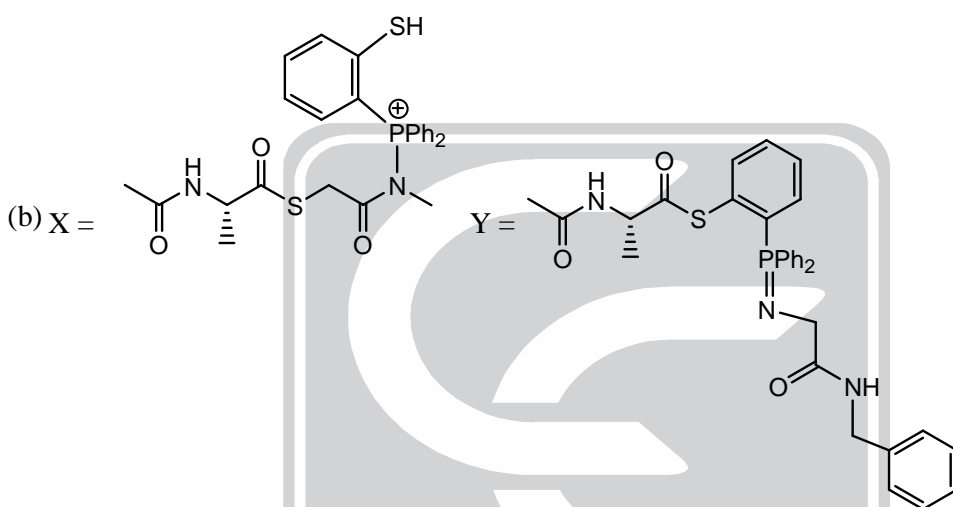
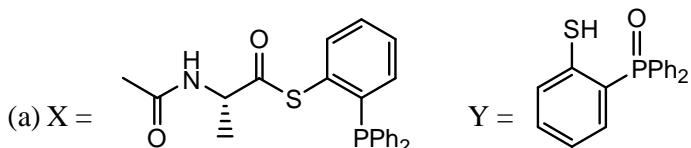
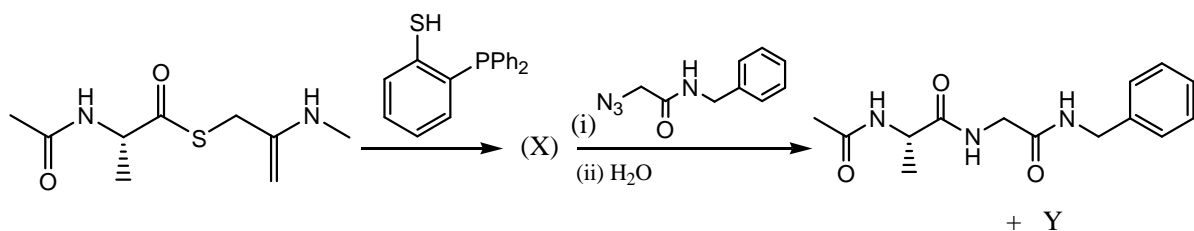
(b) At thermodynamics limit (large N) the fluctuation in energy is extremely narrow

(c) At thermodynamics limit (large N), the fluctuation in energy is extremely broad

(d) All of the above.



13. Predict the products X and Y of the following peptide ligation reaction.

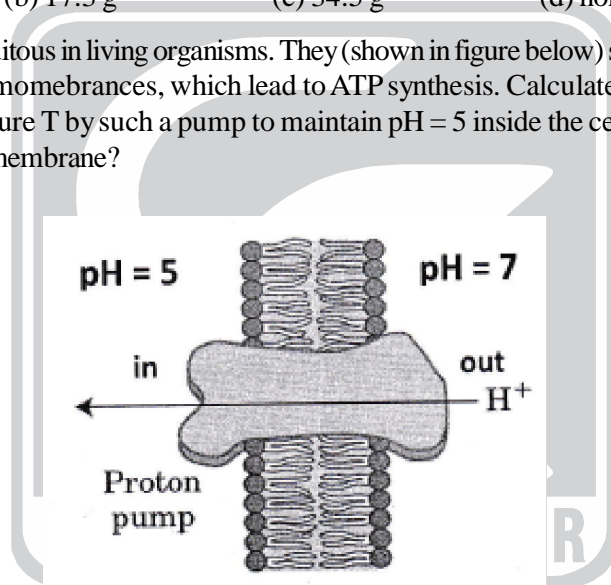


14. Neopentyl chloride, $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$, reacts with a strong base (sodium amide) to produce a new compound. This compound has two $^1\text{H NMR}$ singlets at δ 0.20 ppm and δ 1.05 ppm (intensity ratio = 2 : 3). What is the most probable structure of this compound?

- (a) 2-methyl-2-butene (b) 1,1-dimethylcyclopropane
(c) methylcyclobutane (d) cyclopentane

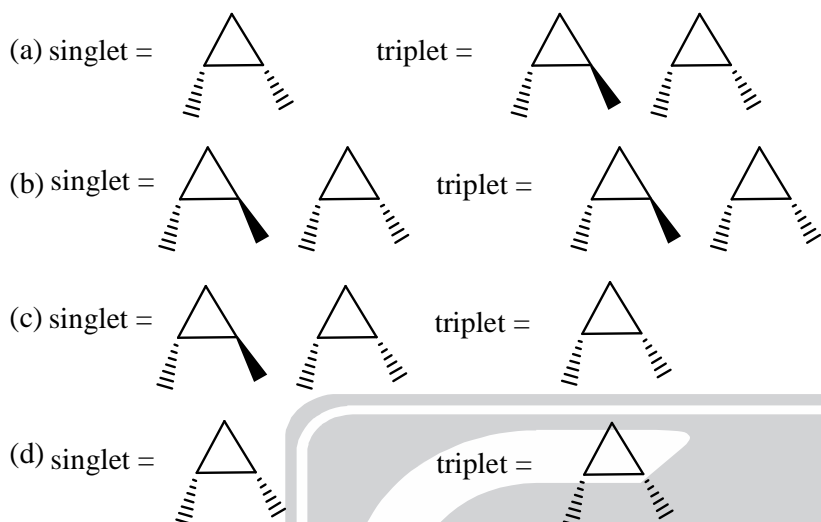
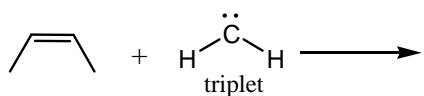
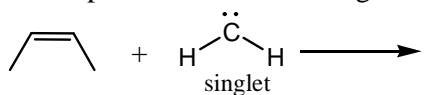


15. The $^1\text{H NMR}$ of 1, 1-dibromoethane consists of two well-separated signals, one large and another one small. Which one of the following statements is correct?
 (a) the large signal is a quartet and the small signal is a doublet
 (b) the large signal is a triplet and the small signal is a singlet
 (c) the large signal is a singlet and the small signal is a triplet
 (d) the large signal is a doublet and the small signal is a quartet
16. For an ideal gas in a closed system at constant temperature T , what are the values of $\frac{\partial U}{\partial V}$ and $\frac{\partial H}{\partial p}$?
 (a) $\frac{\partial U}{\partial V} = 0$ and $\frac{\partial H}{\partial p} = 0$
 (b) $\frac{\partial U}{\partial V} > 0$ and $\frac{\partial H}{\partial p} < 0$
 (c) $\frac{\partial U}{\partial V} < 0$ and $\frac{\partial H}{\partial p} > 0$
 (d) $\frac{\partial U}{\partial V} > 0$ and $\frac{\partial H}{\partial p} > 0$
17. The reaction of nitric oxide with oxygen gas is given by $\text{NO} + \text{O}_2 \longrightarrow \text{NO}_2$. When 25 g of NO is allowed to react with 12g of oxygen gas, the maximum amount of NO_2 formed will be
 (a) 38.3 g (b) 17.3 g (c) 34.5 g (d) none of these
18. Proton pumps are ubiquitous in living organisms. They (shown in figure below) serve as an important regulator of pH gradient across membranes, which lead to ATP synthesis. Calculate the amount of CHEMICAL work done at temperature T by such a pump to maintain $\text{pH} = 5$ inside the cellular compartment against a neutral pH outside the membrane?



- (a) $2 RT$ (b) $2.303 RT$ (c) $4.606 RT$ (d) $23.3 RT$
19. Which of the following observations reflect colligative properties?
 (I) A 0.5 M NaCl solution has a higher vapour pressure than a 0.5M BaCl_2 solution.
 (II) A 0.5M NaOH solution freezes at a lower temperature than pure water
 (III) Pure water freezes at a higher temperature than pure methanol.
 (a) I and II only (b) I and III only (c) II and III only (d) I, II and III
20. ABCD is a rectangle of area 50 m^2 . The mid-points AB, BC and AD are E, F and G, respectively. When EF is extended, DC at H. Similarly, when EG is extended, it meets extended CD at J. What is the area of the triangle EHJ?
 (a) 50 m^2 (b) 100 m^2 (c) 200 m^2
 (d) the area cannot be determined without knowing the length and breadth of the rectangle.

21. Predict the products of the following reactions between cis-2-butene and singlet and triplet methylenes.



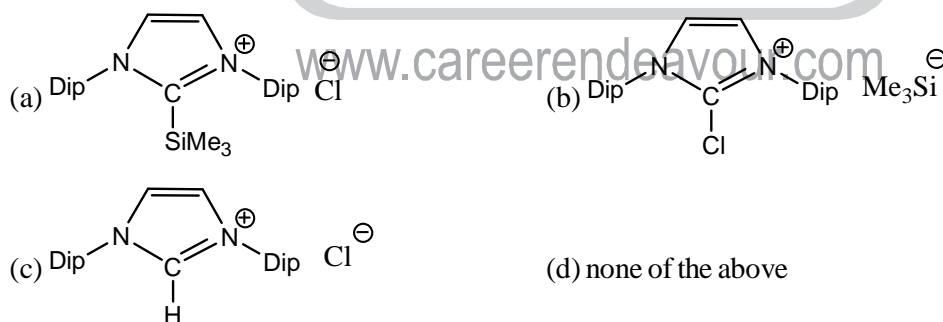
22. Consider an electron with energy E and mass M tunneling through a barrier of height $V > E$ and width W . The total time of the electron spends inside the barrier is

(a) $\frac{\hbar}{V-E}$ (b) $W \times \sqrt{\frac{2M}{E}}$ (c) $\sqrt{\frac{2M(V-E)}{\hbar}}$ (d) $\sqrt{\frac{4M^2(V-E)}{\hbar E}}$

23. What is the product of the following reaction?



Dip = 2, 6-diisopropylphenyl



24. A doubly ionized lithium atom in an excited state ($n = 6$) emits a photon of energy 4.25 eV. What are the quantum number (n) and the energy (E) of the final state?

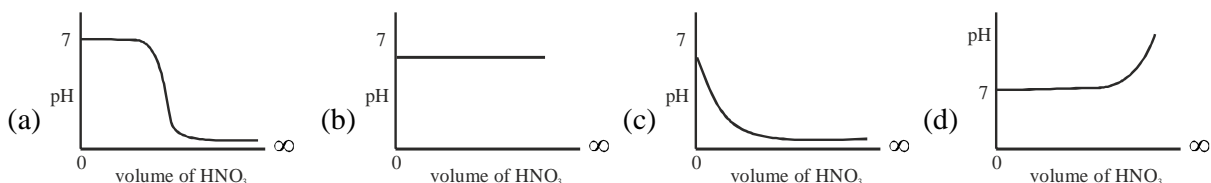
(a) $n = 2, E = -30.6 \text{ eV}$ (b) $n = 3, E = -13.6 \text{ eV}$
 (c) $n = 4, E = -7.65 \text{ eV}$ (d) $n = 5, E = -4.90 \text{ eV}$

25. Which of the following can be labelled as a colloid?

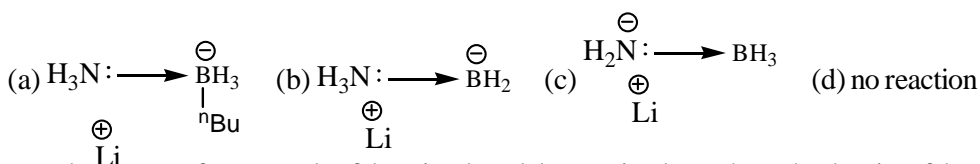
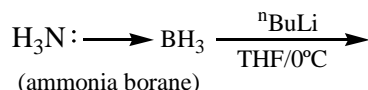
(I) a mixture of water and ethanol (II) milk
 (III) clouds (IV) gemstones
 (a) I, II and III (b) II and III (c) II, III and IV (d) all of the above.



26. A beaker contains 10 mL of dilute buffer solution of pH 7. To this, dilute solution of HNO_3 is added continuously and the pH is measured. Which of the following graphs will be representative to show how the pH varies on addition of HNO_3 ?



27. What is the product of the following reaction?



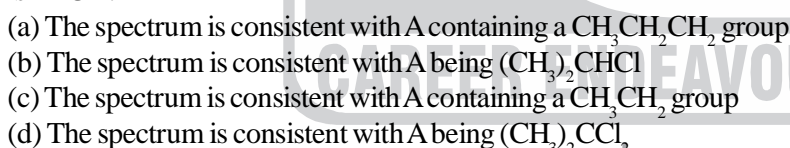
28. Equal volumes of two metals of densities d_1 and d_2 are mixed together. The density of the resulting alloy is given by



29. A $\text{C}_5\text{H}_{12}\text{O}_2$ compound has strong infrared absorption at 3300 to 3400 cm^{-1} . The ^1H NMR spectrum has three singlets at δ 0.9, δ 3.45 and δ 3.2 ppm with relative areas 3 : 2 : 1. Addition of D_2O to the sample eliminates the lower field signal. The ^{13}C NMR spectrum shows three signals all at higher field than δ 100 ppm. Which of the following compounds best fits this data?



30. The ^1H NMR spectrum of a compound A shows a doublet and a septet. Which one of the following statements is TRUE?



31. What is the molecular mass (M) of a compound that has a concentration $w = 1.2\text{ g/L}$ and an osmotic pressure of $\Pi = 0.20\text{ atm}$ at $T = 300\text{ K}$?



32. In a face centered arrangement of A and B atoms. Where A atoms are at the corners of the unit cell and B atoms are at the face centres. For each unit cell, one A atom is missing from a corner position and one B atom is missing from one face position. The simplest formula of the resulting compound will be

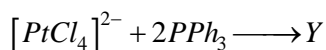
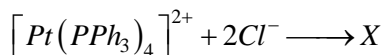


33. For a binary mixture of ideal gas, free energy of mixing is given by $\Delta G_{\text{mix}} = nRT(x \ln x + (1-x) \ln(1-x))$, where x is the mole fraction of one of the components. what are the enthalpy and entropy of mixing of this system?



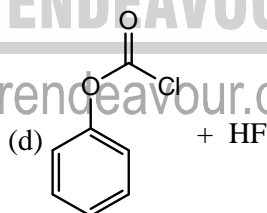
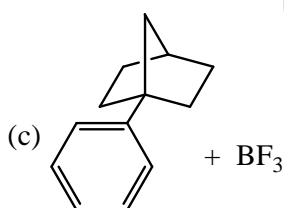
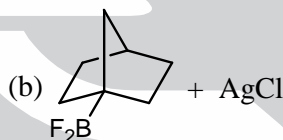
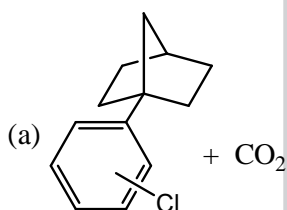
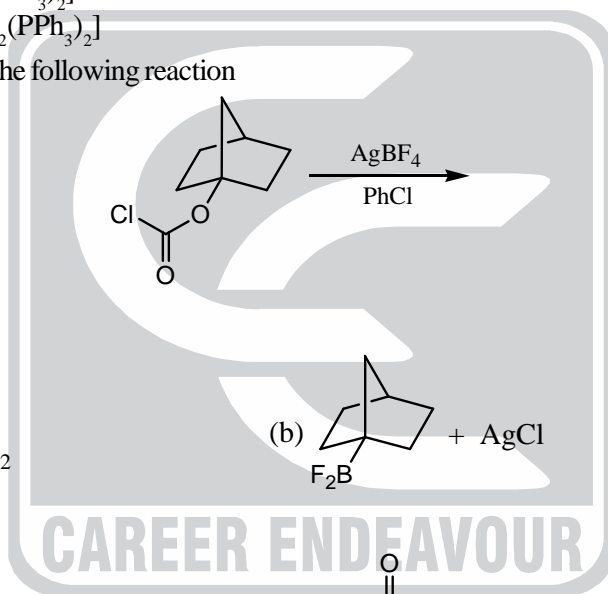
34. Far infrared and microwave radiation is useful in studying the following process
 (a) Transition of inner electrons of atoms
 (b) Transitions of outer (or valence) electrons in atoms or molecules
 (c) Changes in vibrational-rotational states of molecules
 (d) Changes in molecular rotational states only
35. A compound of formula C_5H_{12} gives one signal in the 1H NMR and two signals in the ^{13}C NMR spectra. The compound is
 (a) pentane
 (b) 2-methylbutane
 (c) 2, 2-dimethylpropane
 (d) cannot tell without more information

36. Predict the products of the following reactions:



- (a) $X = \text{trans-}[PtCl_2(PPh_3)_2]$ and $Y = \text{cis-}[PtCl_2(PPh_3)_2]$
 (b) $X = \text{cis-}[PtCl_2(PPh_3)_2]$ and $Y = \text{trans-}[PtCl_2(PPh_3)_2]$
 (c) $X = Y = \text{cis-}[PtCl_2(PPh_3)_2]$
 (d) $X = Y = \text{trans-}[PtCl_2(PPh_3)_2]$

37. Predict the products of the following reaction



38. A set of N vectors, $\vec{X}_1, \vec{X}_2, \dots, \vec{X}_N$ satisfy the eigenvalue equation for an operator A with scalar eigenvalues

$\lambda_1, \lambda_2, \dots, \lambda_N$ (i.e., $A\vec{X}_k = \lambda_k \vec{X}_k$). The linear combination vector $X = \sum_{k=1}^N \vec{C}_k \vec{X}_k$, where \vec{C}_k 's are non-zero

scalar coefficients.

- (a) is not an eigenvector of A
 (b) is an eigenvector of A only if the λ_k 's are all distinct (no two eigenvalue are equal)
 (c) is an eigenvector of A only if the λ_k 's are all equal
 (d) is an eigenvector of only if C_k 's are equal

39. What is the value of $i^{(i+2)}$, where $i = \sqrt{-1}$
- (a) real number (b) complex number
(c) cannot be calculated (d) none of the above.
40. Chemical oxidation of water to produce O_2 gas is an energy demanding reaction, done routinely by plants using the process called photosynthesis. By how many eV will it be uphill if the water oxidation reaction be carried out at pH = 0 versus at pH = 7.0?
- (a) 0.41 eV (b) -1.6 eV
(c) -0.41 eV (d) cannot be calculated based on the data given.

