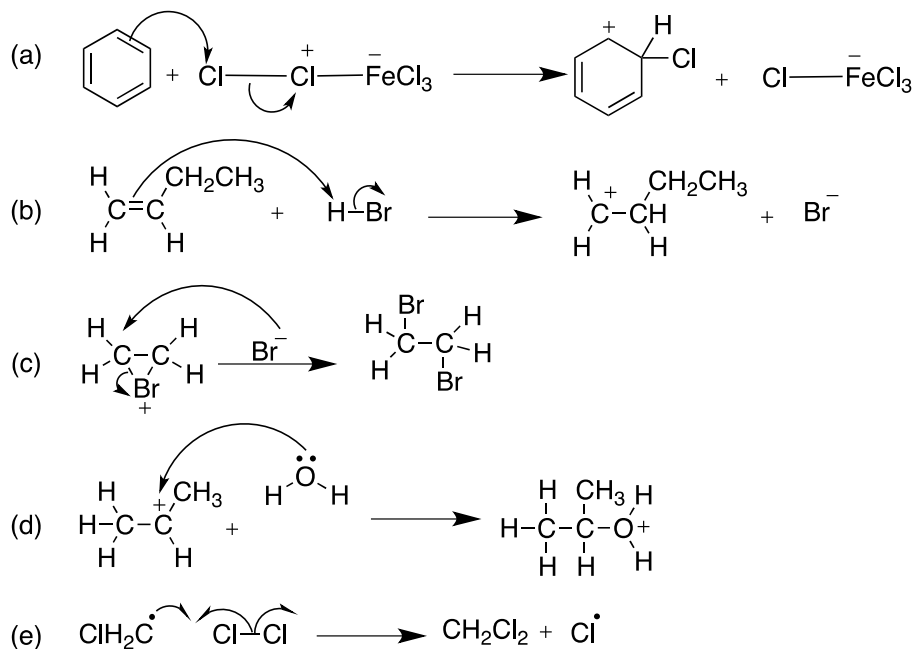


- (1) Place the following ions in order of increasing size: Al^{3+} , P^{3-} , and S^{2-}
 (a) $\text{P}^{3-} < \text{S}^{2-} < \text{Al}^{3+}$ (b) $\text{Al}^{3+} < \text{P}^{3-} < \text{S}^{2-}$ (c) $\text{Al}^{3+} < \text{S}^{2-} < \text{P}^{3-}$
 (d) $\text{P}^{3-} < \text{Al}^{3+} < \text{S}^{2-}$ (e) $\text{S}^{2-} < \text{Al}^{3+} < \text{P}^{3-}$
- (2) Homolysis of a C-C bond forms
 (a) two Carbocations (b) two Carbanions (c) Carbocation and a Carbanion
 (d) two radicals (e) radical and a carbocation
- (3) A fuel/oxidant system consisting of *N,N*-dimethylhydrazine, $(\text{CH}_3)_2\text{NNH}_2$, and dinitrogen tetraoxide, N_2O_4 , (both liquids) is commonly used in space vehicle propulsion. The components react stoichiometrically to form only N_2 (g), CO_2 (g) and H_2O (g). How many moles of gas are produced from 1 mol of $(\text{CH}_3)_2\text{NNH}_2$ with excess N_2O_4 ?
 (a) 8 (b) 9 (c) 10 (d) 11 (e) 12
- (4) Which of the following statements is **best** explained by **resonance**?
 (a) The electron pair geometry of XeOF_4 is octahedral.
 (b) The bonds of NF_3 are less polar than the bonds in CF_4 .
 (c) CH_3Cl contains three single bonds between carbon and hydrogen.
 (d) All the bonds in BH_3 have the same bond order.
 (e) The NO_3^- exhibits only one type of N-O bond.
- (5) The hybridization of phosphorous in PCl_3 is the same as in
 (a) S in SF_4 (b) C in C_2H_2 (c) P in POCl_3 (d) Cl in ClF_3 (e) B in BCl_3
- (6) A solution is prepared by mixing 4.0 mg of sodium ions (in the form of NaCl), 4.00 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), and 96 g of water. How many ppm of Na^+ does this solution contain?
 (a) 29.99 ppm (b) 33.44 ppm (c) 39.99 ppm (d) 78.98 ppm (e) 42.31 ppm
- (7) How many structural isomeric alcohols can be drawn for the molecular formula $\text{C}_5\text{H}_{12}\text{O}$?
 (a) 4 (b) 5 (c) 6 (d) 7 (e) 8
- (8) The hybridization of how many atomic orbitals is involved in sp^3 hybridization?
 (a) 1 (b) 2 (c) 3 (d) 4 (e) 5
- (9) To observe the adsorption capability of activated charcoal, 0.5 g of activated charcoal was shaken with 50 mL of 1.0 mol dm^{-3} oxalic acid. The final oxalic acid concentration after adsorption was found as 0.25 mol dm^{-3} . Thus, how much oxalic acid has adsorbed per gram of activated charcoal? (Oxalic acid molecular weight = 126 g/mol)
 (a) 6.35 g (b) 4.72 g (c) 9.45 g (d) 5.25 g (e) 1.26 g

(10) Which of the following represent the incorrect step/s of reaction mechanisms.



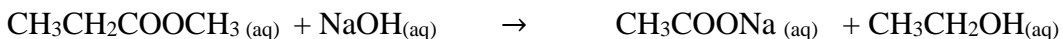
(11) What type of orbital is designated by the quantum numbers, $n = 5$, $\ell = 2$, $m_\ell = +1$?

- (a) 5d (b) 2f (c) 5p (d) 2s (e) 5s

(12) Which of the following molecules is polar: H_2S , CO_2 , NH_3 , BH_3 , and CCl_4 ?

- (a) BH_3 (b) H_2S and NH_3 (c) H_2S , CO_2 , and CCl_4
 (d) CO_2 , NH_3 , and CCl_4 (e) NH_3 , BH_3 , and CCl_4

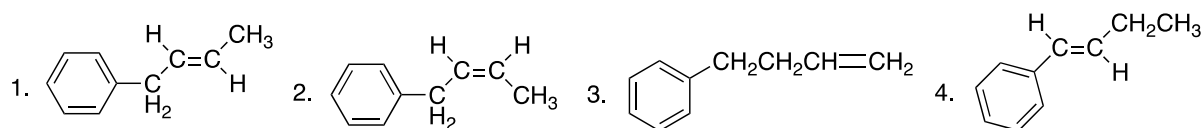
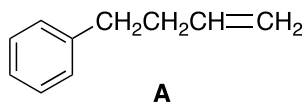
(13) In the presence of NaOH methyl acetate hydrolyzes into acetic acid and methanol according to the equation given below. Reaction occurs slowly at low temperatures.



150 mL of 0.06 M NaOH solution and 0.06 M methyl acetate solution were mixed in a conical flask at 5°C . After 5 minutes 10.00 mL of the mixture was pipetted out and added to a titration flask containing 10.00 mL of 0.05 M HCl . This mixture was titrated against 0.02 M NaOH after adding a couple of drops of phenolphthalein indicator. End point volume of NaOH was 15.40 mL. Determine the OH^- concentration of the reaction mixture in the conical flask at 5 minute. (Assume the reaction has not reached the equilibrium)

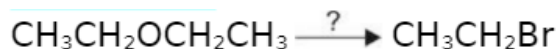
- (a) 0.021 M (b) 0.0192 M (c) 0.210 M (d) 0.187 M (e) 0.40 M

- (14) Which of the following is **not** a suitable method to prepare benzaldehyde?
- (a). Oxidation of toluene (b). Oxidation of benzyl alcohol
(c). Oxidation of methyl benzoate (d). Etard reaction (e). Reduction of benzoic acid
- (15) Which pair from the below list shows an increasing order of the property given?
- (a) Boiling point: $I_2 < Br_2$
(b) Electronegativity: $F < O$
(c) Third ionisation energy: $Ar < Mg$
(d) Radius: $Na < Na^+$
(e) Covalent character: $HI < HBr$
- (16) C_2H_6 , CH_3OH and CH_3F have similar molar masses. Which of the following inequality represents the correct trend in the boiling point of these molecules?
- (a) $CH_3F = CH_3OH = C_2H_6$
(b) $CH_3OH < CH_3F < C_2H_6$
(c) $CH_3F < C_2H_6 < CH_3OH$
(d) $C_2H_6 < CH_3F < CH_3OH$
(e) $C_2H_6 < CH_3OH < CH_3F$
- (17) Acetic acid concentration when 5.00 mL of glacial acetic acid is mixed with 170.0 mL of distilled water is (the density, molecular weight and purity of glacial acetic acid are 1.05 g/mL, 60 g/mol and 97%, respectively.)
- (a) 0.04 M (b) 0.17 M (c) 0.50 M (d) 0.019 M (e) 0.40 M
- (18) Which of the following product/s is/are formed when the below compound (**A**) is reacted with HBr followed by the reaction with alcoholic KOH?

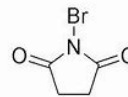


- (a) Only (1) and (2) correct (b) Only (2) and (3) correct
(c) Only (3) and (4) correct (d) Only (1) and (3) correct
(e) Any other number or combination of responses correct

(19) Which of the given is the best reagent to accomplish the following conversion?



- (a) Br_2 in CCl_4 (b) NaBr (c) Br_2 in H_2O (d) Conc HBr (e)



(20) Consider the process of cooling a glass of water under standard atmospheric pressure. At 0°C , the water starts to solidify, forming ice. How do the following thermodynamic functions change during the solidification of water at 0°C ?

- (a) $\Delta H = 0, \Delta S = 0, \Delta G = 0$
 (b) $\Delta H > 0, \Delta S > 0, \Delta G = 0$
 (c) $\Delta H < 0, \Delta S < 0, \Delta G > 0$
 (d) $\Delta H < 0, \Delta S > 0, \Delta G < 0$
 (e) $\Delta H < 0, \Delta S < 0, \Delta G = 0$

(21) Consider the process of heating water under atmospheric pressure higher than the standard atmospheric pressure. By doing so, we can raise the boiling point of water. Suppose we have liquid water at a temperature above 100°C this way. Now the pressure dropped to the standard atmospheric pressure. How do the following thermodynamic functions change immediately after the standard atmospheric pressure is reached?

- (a) $\Delta H > 0, \Delta S > 0, \Delta G < 0$
 (b) $\Delta H > 0, \Delta S > 0, \Delta G = 0$
 (c) $\Delta H < 0, \Delta S < 0, \Delta G > 0$
 (d) $\Delta H < 0, \Delta S > 0, \Delta G < 0$
 (e) $\Delta H < 0, \Delta S < 0, \Delta G = 0$

(22) Which one of the following species does **not** have eight valence electrons surrounding the central atom?

- (a) CCl_4 (b) NH_3 (c) NH_4^+ (d) OF_2 (e) BCl_3

(23) Which of the following alkyl halides would undergo $\text{S}_\text{N}1$ reaction most rapidly?

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-Br}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{-Br}$
 (c) $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{-Br}$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (e) $\text{BrCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$

(24) The second ionization energies for four consecutive elements of the Periodic Table W, X, Y and Z, (they have atomic numbers n, n+1, n+2 and n+3) are $2297.3 \text{ kJ mol}^{-1}$, $2665.8 \text{ kJ mol}^{-1}$, $3051.3 \text{ kJ mol}^{-1}$ and $1145.4 \text{ kJ mol}^{-1}$, respectively. Which of the following pairs of oxides would be the most stable?

- (a) WO, X₂O (b) X₂O, YO₂ (c) W₂O, YO₂ (d) XO₃, Z₂O (e) Y₂O, ZO

(25) $\text{HgO} + 4\text{I}^- + \text{H}_2\text{O} \rightarrow \text{HgI}_4^{2-} + 2\text{OH}^-$

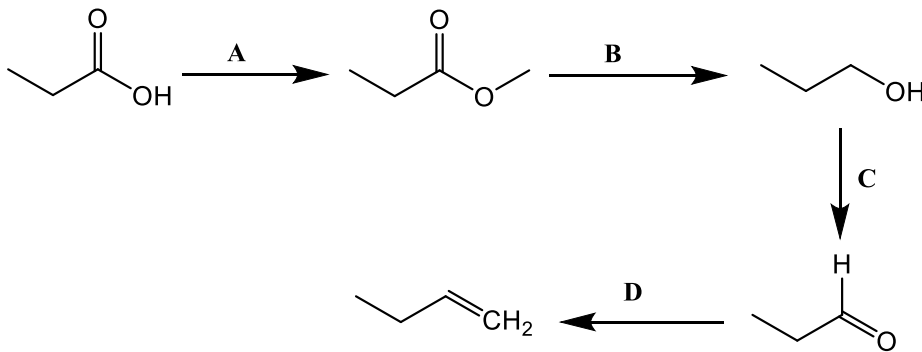
In accordance with the above reaction 0.217 g sample of HgO (MW: 217 g) reacts with excess iodide ions. After some time it was found that only 50% of HgO had reacted. If 0.05 M HCl was used to titrate the resulting solution, the volume of acid needed to reach the end point would be,

- (a) 1.0 mL (b) 10.0 mL (c) 20.0 mL (d) 50.0 mL (e) 100.0 mL

(26) What is the general method of preparation of benzene diazonium chloride below 5°C?

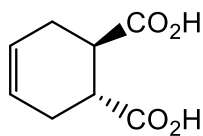
- (a) Decarboxylation of benzoic acid
 (b) Treating aniline with 20% NaNO₂ in aqueous HCl
 (c) Treating aniline with 20% NaNO₃ in aqueous HCl
 (d) Treating aniline with 20% NaNO₂ in aqueous NaOH
 (e) Treating aniline with 20% NaNO₃ in aqueous NaOH

(27) Which of the following answers shows the reagents **A-D** in the correct order for the below reaction scheme?



- | | | | |
|---|---|--|---|
| (a) A: CH ₃ OH, H ⁺ | B: (i) NaBH ₄ , CH ₃ OH | C: CH ₂ =P(Ph) ₃ | D: PCC |
| (b) A: CH ₃ OH, H ⁺ | B: (i) LiAlH ₄ , (ii) H ₃ O ⁺ | C: PCC | D: CH ₂ =P(Ph) ₃ |
| (c) A: CH ₃ OCH ₃ , H ⁺ | B: (i) LiAlH ₄ , (ii) H ₃ O ⁺ | C: KMnO ₄ /H ⁺ | D: CH ₂ =P(Ph) ₃ |
| (d) A: CH ₃ OH, H ⁺ | B: PCC | C: (i) NaBH ₄ , CH ₃ OH | D: CH ₂ =P(Ph) ₃ |
| (e) A: CH ₃ Br | B: (i) NaBH ₄ , CH ₃ OH | C: CH ₂ =P(Ph) ₃ | D: KMnO ₄ /H ⁺ |

(28) Which pair of diene and dienophile would lead to the product shown below?

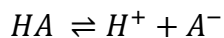


- (a)
- (b)
- (c)
- (d)
- (e)

(29) Elements W and X react to form an ionic compound. W and X have 2 and 6 valence electrons, respectively. What is the formula of this compound formed from the reaction between W and X?

- (a) W_2X_6 (b) WX_3 (c) WX (d) W_3X (e) W_6X_2

(30) Consider the dissociation of a weak acid HA , defined by



$$K_A = \frac{[H^+][A^-]}{[HA]}$$

The ionic product of water is given by $K_w = [H^+][OH^-]$. Which of the following general expressions is/are correct?

(X) $[A^-] = [H^+]$

(Y) $[A^-] = \sqrt{K_A[HA]}$

(Z) $\frac{1}{[A^-]} = \frac{[H^+]}{[H^+]^2 - K_w}$

- (a) Only X (b) Only Z (c) Only Y & Z (d) X, Y, & Z (e) Non of the expressions

- (31) The distribution coefficient of a compound A in a mixture of water and an organic solvent is given by K_D , i.e.,

$$A(\text{aq}) \rightleftharpoons A(\text{org}); K_D = \frac{[A]_{\text{aq}}}{[A]_{\text{org}}}$$

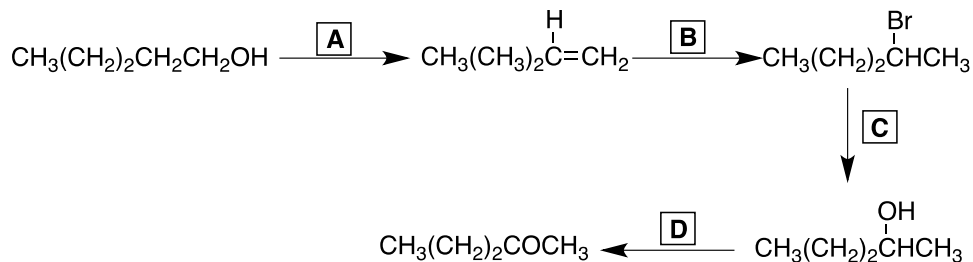
The compound A is dissolved in a volume V of water and is extracted 5 times using a volume nV of the organic solvent. After the extraction, it was found that the aqueous layer retained $1/32$ of the original A content. Which of the following relationships is correct?

- (a) $n = K_D$ (b) $n = \frac{1}{K_D}$ (c) $n + K_D = 1$ (d) $n = \frac{1}{2K_D}$ (e) $n = 2/K_D$

- (32) Which of the following molecules XY_n has the largest Y–X–Y bond angle?

- (a) H_2O (b) NH_3 (c) CO_2 (d) CF_4 (e) BF_3

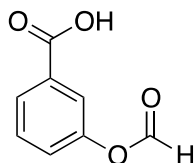
- (33)



In the reaction scheme above, the reagents and conditions of **A** to **D**, respectively are,

- (a) Conc. H_2SO_4 /heat, PBr_3 , dil. NaOH , $\text{K}_2\text{Cr}_2\text{O}_7$ /heat
 (b) dil. H_2SO_4 /heat, HBr , dil. NaOH , $\text{K}_2\text{Cr}_2\text{O}_7$ /heat
 (c) Conc. H_2SO_4 /heat, HBr , dil. H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ /heat
 (d) Conc. H_2SO_4 /heat, HBr , dil. NaOH , $\text{K}_2\text{Cr}_2\text{O}_7$ /heat
 (e) Conc. H_2SO_4 /heat, HBr , dil. NaOH , K_2CO_3 /heat

(34)



What are the products obtained when the above compound is reacted with LiAlH_4 followed by neutralization of the reaction mixture?

- (a) and
- (b) and CH_3OH
- (c) and
- (d)
- (e)

Question 35 and 36 are related.

According to the Maxwell-Boltzmann distribution of the speed of gas molecules, the probability of finding a molecule with speed v is given by

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kT}}.$$

The root mean squared speed, v_{rms} is given by

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \left(\int_0^\infty dv \, v^2 f(v) \right)^{1/2} = \sqrt{\frac{3RT}{M}}$$

We can define two other characteristic velocities. The most probable speed v_p is the speed most likely to be possessed by a molecule. This is found by finding the derivative of $f(v)$ with respect to v and setting it to 0, i.e.,

$$\left(\frac{df(v)}{dv}\right)_{v=v_p} = 0.$$

The mean speed is the average speed of the distribution, given by

These three characteristic speeds are related by

$$v_p = \frac{\sqrt{\pi}}{2} \langle v \rangle = \left(\sqrt{\frac{2}{3}}\right) v_{rms}$$

(35) The expressions for $\langle v \rangle$ and v_p are

$$(a) \langle v \rangle = \frac{8RT}{\pi M}, v_p = \sqrt{\frac{2RT}{M}}$$

$$(b) \langle v \rangle = 2\sqrt{\frac{RT}{\pi M}}, v_p = \sqrt{\frac{2RT}{M}}$$

$$(c) \langle v \rangle = \sqrt{\frac{8RT}{\pi M}}, v_p = \sqrt{\frac{2RT}{M}}$$

$$(d) \langle v \rangle = 2\sqrt{\frac{RT}{\pi M}}, v_p = \sqrt{\frac{3RT}{2M}}$$

$$(e) \langle v \rangle = \sqrt{\frac{8RT}{M}}, v_p = \sqrt{\frac{3RT}{\pi M}}$$

(36) As the temperature increases

(a) $\langle v \rangle : v_p$ increases, $v_{rms} : \langle v \rangle$ increases.

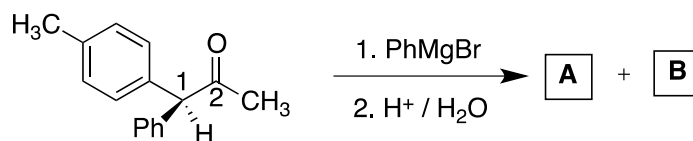
(b) $\langle v \rangle : v_p$ increases, $v_{rms} : \langle v \rangle$ decreases.

(c) $\langle v \rangle : v_p$ decreases, $v_{rms} : \langle v \rangle$ increases.

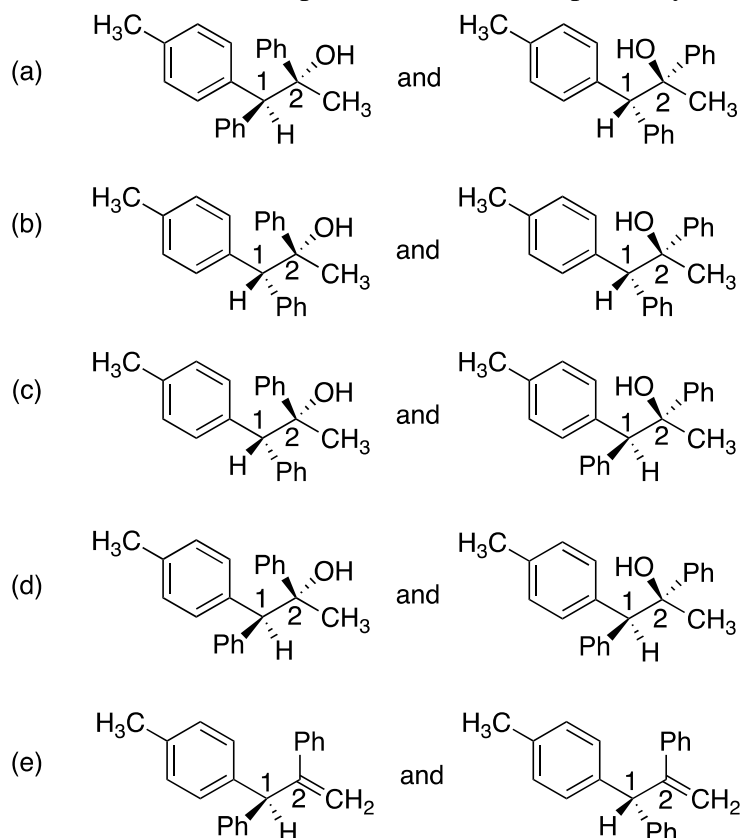
(d) $\langle v \rangle : v_p$ decreases, $v_{rms} : \langle v \rangle$ decreases.

(e) $v_{rms} : \langle v \rangle : v_p$ does not change.

- Answer to the questions 39 to 40 based on the reaction given below.



(37) The correct structures of the products **A** and **B** respectively are,



(38) The absolute configuration of the C-1 and C-2 in the compounds **A** and **B** respectively are,

	A		B	
	C-1	C-2	C-1	C-2
(a)	R	R	R	S
(b)	S	R	R	S
(c)	S	S	S	R
(d)	R	R	S	S
(e)	S	R	S	S

(39) For the stereochemical relationship between **A** and **B**, which of the following is/are true?

- (1) Diastereomers
- (2) Stereoisomers
- (3) Identical
- (4) Enantiomers

- (a) Only (1) and (2) correct
- (b) Only (2) and (3) correct
- (c) Only (3) and (4) correct
- (d) Only (1) and (3) correct
- (e) Any other number or combination of responses correct

Question 40-41 are related

The electrons in conjugated linear polyenes can be studied using the particle in a one-dimensional box model. Energy of the level n of a particle in a 1-Dimensional box model is given by

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where h is Planck constant's, m is mass of electron, and L is the box length.

(40) According to 1-Dimensional box model, which of the following would be the correct expression for the absorption wavelength of a conjugated linear polyene of length L ?

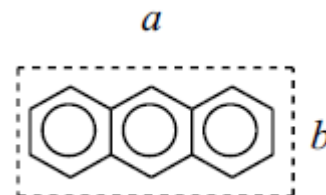
- a. $\frac{(sn)h^2}{8mL^2}$ (b) $\frac{4mL^2}{2(n+1)h}$ (c) $\frac{8mL^2}{(2n+1)h}$ (d) $\frac{24mL^2}{(2n+1)h}$ (e) $\frac{4mL^2}{(2n+1)h}$

(41) If $L = (k+1)d$ where k is the number of C atoms in the conjugated linear polyene and the average length of all C-C single and C=C double bonds is d , the correct expression for the absorption wavelength of 1,3,5-hexatriene based on 1-Dimensional box model is

- (a) $\frac{56mcd^2}{h}$ (b) $\frac{16mcd^2}{h}$ (c) $\frac{8mcd^2}{h}$ (d) $\frac{32mcd^2}{h}$ (e) *non of the above*

(42) The electrons in anthracene can be considered as particles moving in a two-dimensional box whose length is a and width is b . The energies of the π electrons in the box are defined by:

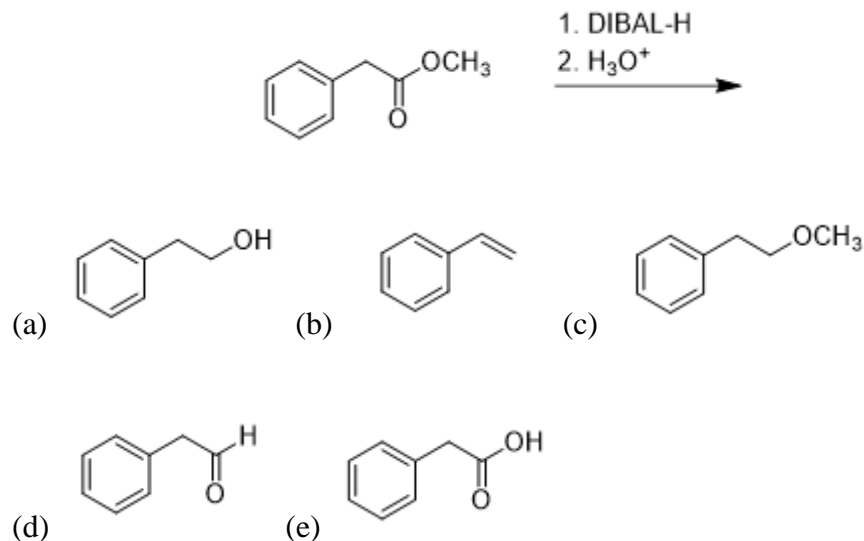
$$E_n = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right) \quad \text{where } (n_x = 1, 2, 3, \dots) \text{ \& } (n_y = 1, 2, 3, \dots)$$



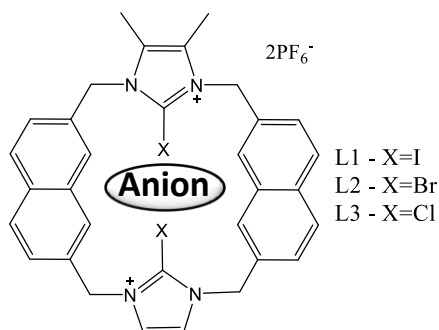
Assuming $a = 3b$, find the HOMO level

- (a) $n_x = 1$ $n_y = 1$ (b) $n_x = 1$ $n_y = 2$ (c) $n_x = 2$ $n_y = 2$ (d) $n_x = 2$ $n_y = 3$
- (e) none of the above

(43) Which of the following is the major organic product obtained from the following reaction?



(44) Binding constants (K_a) of receptor L1 and L3 in a methanol: water mixture are given below ($T=293\text{ K}$).



Anion	L1 (X=I) ($K_a\text{ (M}^{-1}\text{)}$)	L3 (X=Cl) ($K_a\text{ (M}^{-1}\text{)}$)
Cl^-	<10	<10
Br^-	631 000	28 800
I^-	37 100	955 000

Due to the solvation of the anion by water and methanol, the effective charge of anions has the order of $\text{I}^- > \text{Br}^- > \text{Cl}^-$. However, note that for L1, Br^- binds stronger than I^- . Which of the following would be the most accurate statement for receptor L3 ($\text{X}=\text{Cl}$)? (Assume $\text{X} \cdots \text{anion}$ interactions are the same for $\text{X}=\text{Cl}$, Br and I). (Hint: receptor binds anions well when the anion is complementary to the macrocycle binding cavity)

- (a) I^- binding constant of (L2) > (L1) ; is always true
- (b) I^- binding constant of (L2) = (L3) ; is always true
- (c) I^- binding constant of (L2) = (L1) ; is always true
- (d) I^- binding constant of (L2) < (L3) ; is always true
- (e) Cannot predict binding constant trend from the given information

- (45) The counteranion of the series of receptors above is PF_6^- . Considering receptor L3, if the counteranion was exchanged to Br^- , which of the following is most accurate? (Assume the binding of PF_6^- to receptors are negligible).
- (a) Binding constant of I^- would increase
 - (b) Binding constant of I^- would decrease
 - (c) Binding constant of I^- would not change
 - (d) Both a and b are possible
 - (e) Need more information to predict the binding constants

.....END.....