GS-2019 (Chemistry)

Full Name :

_____

Roll No. :

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TATA INSTITUTE OF FUNDAMENTAL RESEARCH

Written Test in **CHEMISTRY**

December 9th, 2018

Duration: Three hours (3 hours)

Please read all instructions carefully before you attempt the questions.

1. Write your FULL NAME and ROLL NUMBER (see hall ticket) in block letters, both on this page and on your answer sheet (at the end of this booklet).
2. 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.
3. Indicate your answers on the ANSWER SHEET by filling completely in the appropriate boxes. Do not mark more than one box for any question; this will be treated as an incorrect answer.
4. We advise you to first mark the correct answers in the QUESTION SHEET, and later transfer them to the ANSWER SHEET only when you are sure of your choice.
5. Rough work may be done on the back of the QUESTION SHEET. If needed, you may ask for extra rough sheets from an invigilator.
6. In answering the questions, please choose the option that best describes the solution to the problem.
7. **Use of calculators is permitted in this subject test.**

SOME USEFUL DATA

Avogadro number = 6.02×10^{23} mol^{-1}
RT/F = 0.0257 V at 25°C
Faraday constant = 96500 C/mol
Boltzmann constant $k_B = 1.38\times10^{-23}$ J K^{-1}
Mass of an electron = 9.109×10^{-31} kg

e = 1.6×10^{-19} C
h = 6.626×10^{-34} J s
c = 3×10^{8} m s^{-1}
R = 8.314 J K^{-1} mol^{-1}

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1. Water boils at a temperature of 373 K and atmospheric pressure of 1 atm. Assuming a constant enthalpy of vaporization of 40.66 kJ/mol, what is the boiling temperature at a high altitude, where the pressure is 0.5 atm?

   A) 270 K

   B) 354 K

   C) 373 K

   D) 403 K

2. What is the molar mass of a compound that has a concentration w = 1.2 g/L in solution and an osmotic pressure of π= 0.20 atm at T= 300 K

   A) 147 g/mol

   B) 3031 g/mol

   C) 17 g/mol

   D) 1432 g/mol

3. Which of the following natural amino acids is not hydrophobic?

   A) Valine

   B) Leucine

   C) Isoleucine

   D) Arginine

4. According to the laws of thermodynamics for which of the following processes is the entropy of a system equal to zero

   a. Exothermic process (heat is released during the process)

   b. Endothermic process (heat is absorbed during the process)

   c. Reversible process

   d. Irreversible process

5. Below is a picture of on Origami pinwheel. What elements of symmetry are present in the pinwheel?



A) Only one 4-fold rotation axis perpendicular to the plane of the pinwheel.

B) A mirror plane perpendicular to the plane of the paper and a 2-fold axis of rotation perpendicular to the plane of the pinwheel.

C) 4 fold rotation axis perpendicular to the plane of the pinwheel and an inversion centre.

D) 2 mirror planes perpendicular to the plane of the paper.

6. Consider the following reactions:

   Reaction 1: 2 cm^3 of hydrogen gas and 1 cm^3 oxygen gas combine to form H_2O (gas)

   Reaction 2: 1 cm^3 of hydrogen gas and 1 cm^3 chlorine gas combine to form HCl (gas)

Assuming ideal gas behaviour, the volumes of the H_2O (gas) and HCl (gas) are:

A) 1 cm^3 H_2O (gas) and 1 cm^3 HCl (gas)

B) 2 cm^3 H_2O (gas) and 2 cm^3 HCl (gas)

C) 3 cm^3 H_2O (gas) and 1 cm^3 HCl (gas)

D) 3 cm^3 H_2O (gas) and 2 cm^3 HCl (gas)

7. The equation y = exp (i*k*x) where i = sqrt (-1) has a purely oscillatory solution if an only if

   A) When *k* is complex

   B) When *k* is imaginary

   C) When *k* is real and negative

   D) When *k* is real and non-zero

8. ψ(r) is the wavefunction for the 1s orbital and r is the distance of the electron form the nucleus. Then the average distance of the 1s electron form the nucleus is given by:

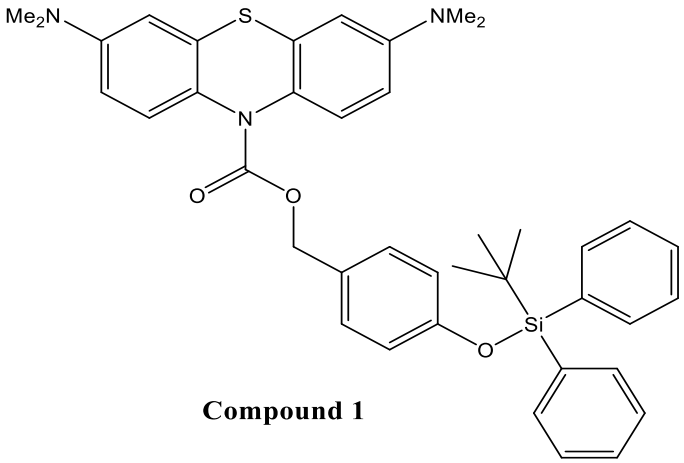
   A) $4\pi \int_{-\infty}^{\infty} \psi(r) r \psi^*(r) r^2 \, dr$

   B) $\int_0^{\infty} \psi(r) \psi^*(r) \, dr$

   C) $4\pi \int_0^{r} \psi(r) r \psi^*(r) r^2 \, dr$

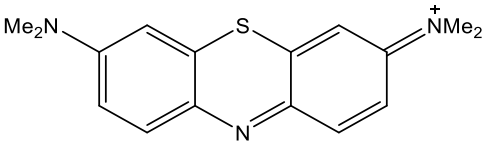
   D) $4\pi \int_0^{\infty} \psi(r) r \psi^*(r) r^2 \, dr$

9. Compound 1 (1 mg) was added to an anti-cavity fluoride toothpaste (25 mg). The toothpaste turned blue. What did compound 1 get converted to?

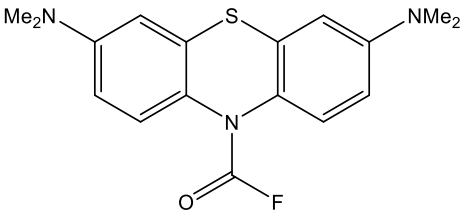


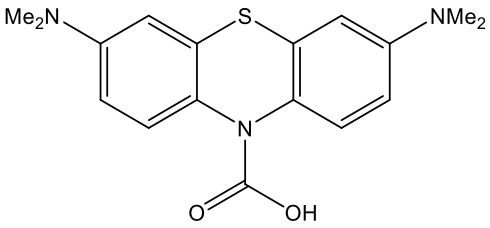
Compound 1

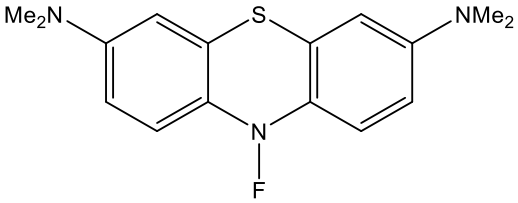
A



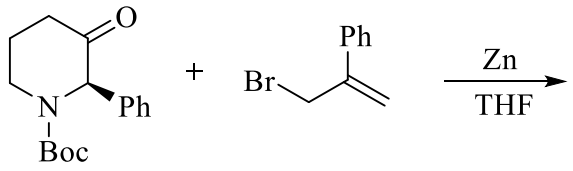
B

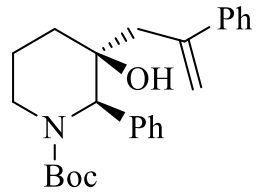


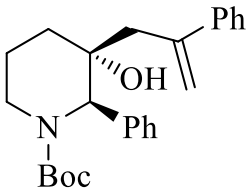


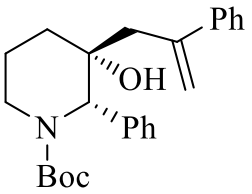


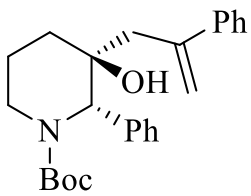
10. Product of the following reaction is



a)


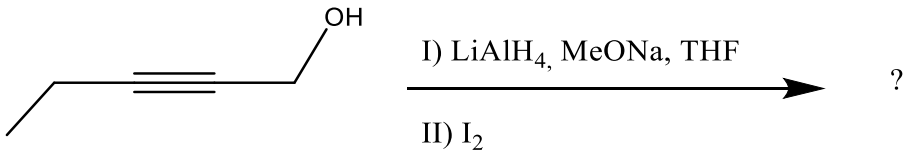
b)


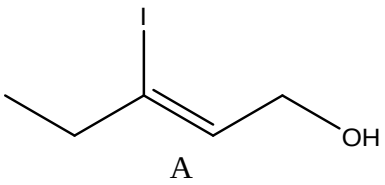
c)


d)


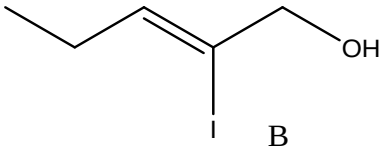
a.

11. What is the main product of below reaction?

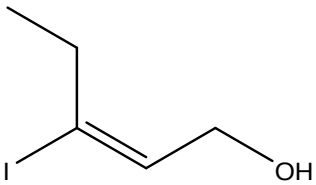




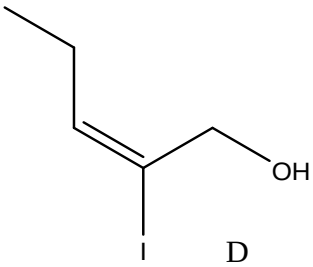
A



B



C



D

A

12. Identify the organic molecule which contains 66.6% carbon, 11.1% hydrogen. In infra-red spectrum of the molecule, bands are observed at 2941-2857, 1715 and 1640 cm^{-1}. In proton NMR, three signals appeared at: i) 7.52 (q, 2H); ii) 7.88 (s, 3H); iii) 8.93 (t, 3H) in ppm scale.

A) Ethyl methyl ketone

B) 2-Butanol

C) 1-Butanaldehyde

D) None of them

13. Which of the following is true for the closest distance D that two solvated ions with like charges (q) can achieve at temperature T:

a) $D \propto \frac{q^2}{T}$

b) $D \propto q^2 T$

c) $D \propto q^2 T^2$

d) $D \propto \frac{q^2}{T^2}$

14. Identify the compound whose molecular ion appears as a pair of equal intensity peaks at m/z = 122 & m/z = 124. Large fragment ions are seen at m/z = 43 (base peak).

A) 1-bromopropane

B) 2-bromopropane

C) Both A and B

D) None of them

15) The total volume of an ethanol solution at 25 °C containing 1.000 kg of water is experimentally found to obey the following expression

V/ml = 1002.9 + 54.67b – 0.3639b^2 + 0.02825b^3,

where b is the numerical value of the molality of ethanol in the solution. At what molality would the partial molar volume of ethanol be the minimum?

(A) Cannot be answered, as not enough information is given.

(B) b = 0 mol/kg

(C) b = 21.74 mol/kg (approx.)

(D) b = 4.29 mol/kg (approx.)

16. The Gibbs free energy of a chemical reaction is given by $\Delta G = \Delta H - T\Delta S$, where ΔH is the enthalpy change, ΔS is the entropy change and T is the temperature. The chemical reaction is said to occur spontaneously and unidirectionally if

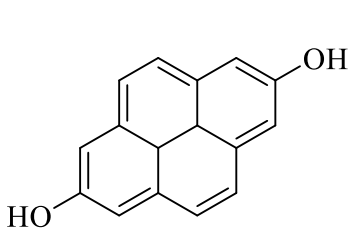
A) $\Delta G = 0$

B) $\Delta S = 0$

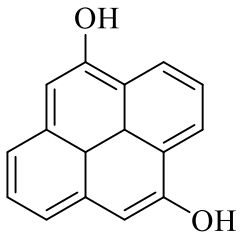
C) $\Delta H = 0$

D) $\Delta G < 0$

17. In the broadband decoupled ^{13}C NMR spectrum, the number of signals appearing for the two pyrenediols A and B.



A



B

a) eight and eight

b) eight and sixteen

c) five and ten

d) five and eight.

18. Consider the following equations in quantum mechanics involving operators and ket vectors:

(i) $\hat{J}^2 \left| j, m_j \right\rangle = j(j+1) \left| j, m_j \right\rangle$ (ii) $\hat{J}_z \left| j, m_j \right\rangle = m_j \left| j, m_j \right\rangle$

(iii) $\hat{J}^{\pm} \left| j, m_j \right\rangle = \sqrt{j(j+1) - m_j(m_j \pm 1)} \left| j, m_j \right\rangle$

Which of them are eigenvalue equations and what would be the eigenvalue of the operator $\hat{J}_x^2 + \hat{J}_y^2$ with respect to the vector $\left| j, m_j \right\rangle$?

(A) (i) and (ii), and $j(j + 1) - 2m_j^2$
(B) (i) ,(ii) and (iii), and $2m_j^2$
(C) (iii), and $j(j + 1) - m_j^2$
(D) (i) and (ii), and $j(j + 1) - m_j^2$

19. In isoelectronic series, VO_4^{3-}, CrO_4^{2-} and MnO_4^-, all members have intense charge transfer transition. The **INCORRECT** statement is

A) Charge transfer transitions are attributed to excitations of electrons from ligand to metal.

B) MnO_4^- exhibits charge transfer at shortest wavelength amongst the three.

C) The wavelengths of transitions increase in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$.

D) The charge on the metal nucleus increases in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$.

20) Suppose one is recording a Raman spectrum of a solution with yellow color light as an excitation source. The detected photons have both green and red color resulting in two peaks. If one starts heating the solution, which of the following is likely to happen?

A) The green peak becomes blue

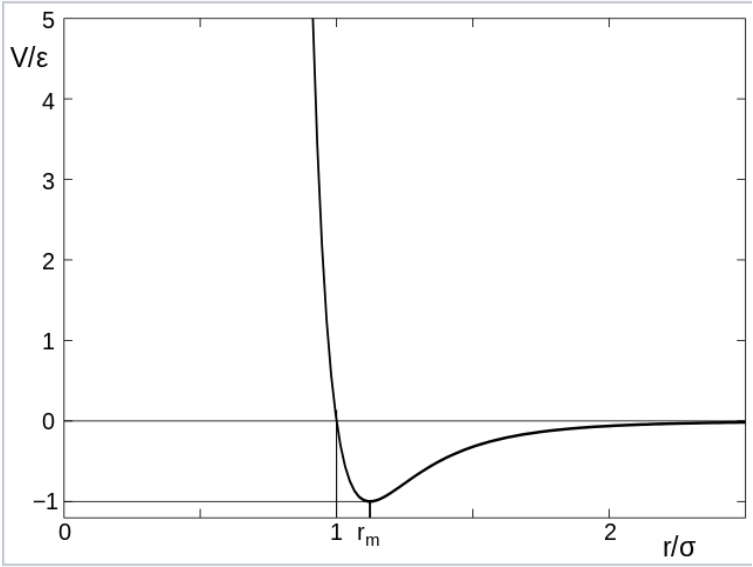
B) The green peak becomes red

C) The photon counts of green peak increases

D) Temperature has no effect on the spectrum

21. The short-ranged intermolecular interactions are often described by the Lennard-Jones potential $V(r)= 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$, which gives the internal energy of interaction between two molecules as a function of intermolecular separation. Here ε is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, r is the distance between the particles, and r_m is the distance at which the potential reaches its minimum. At r_m, the potential function has the value $-\varepsilon$.

If you would like to express the same potential energy function in terms of r_m and ε, the function should be:



a) $V(r)= \varepsilon[(r_m/r)^{12}-2(r_m/r)^{6}]$

b) $V(r)=4\ \varepsilon[(r_m/r)^{12}-(\ r_m\ /r)^{6}]$

c) $V(r)= \varepsilon[(r_m/r)^{12}]$

d) $V(r)= \varepsilon[2(r_m/r)^{12}-(r_m/r)^{6}]$

22. The first order reaction is 90% complete in 30 min. How long will it take to be 99.9% completed?

A) 33.3 min

B) 1.5 hr

C) 55 hr

D) None of the above

23. A bag contains 20 coins each labeled with one-letter code for amino acids. A coin is drawn at random, the letter on the coin is noted down and the coin it kept back in the bag before the next draw. If the process is continued for five times, then what is the probability that the letters on the drawn coins make the word 'DRAWN', in that sequence?

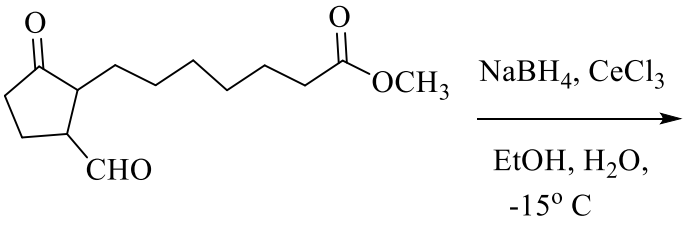
a) 3.125×10^{-7}

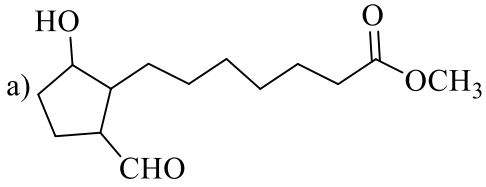
b) .05

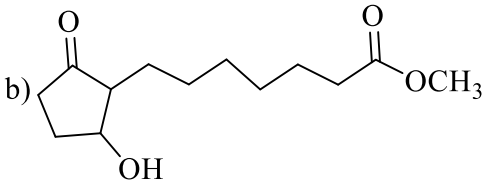
c) 1.0×10^{-10}

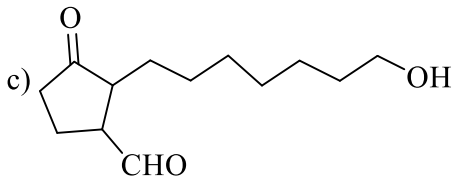
d) Not possible as the word 'DRAWN' has letters which are not codes for amino acids.

24. Predict the product obtained in the following reaction



a)


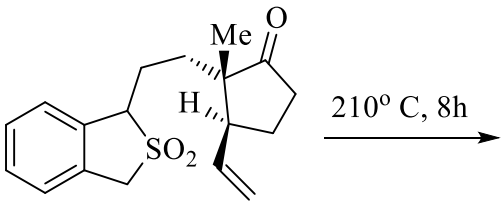
b)


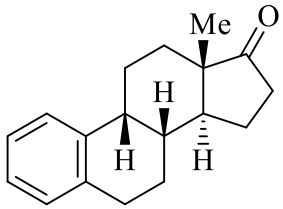
c)


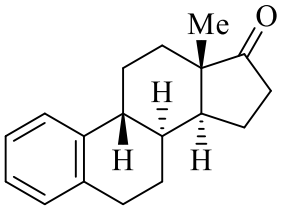
d) all of these.

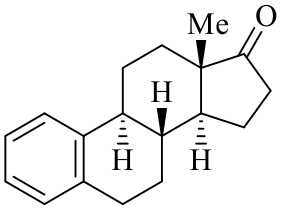
a.

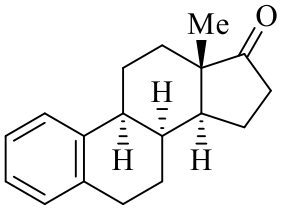
25. Predict the product of the following reaction



a)


b)


c)


d)


c)

26) The Arrhenius rate expression $k = Aexp(-E_a/RT)$ is only an approximation as one finds that the pre-exponential factor **A** is not completely temperature independent. Assume that it weakly depends on temperature as $A = BT^m$. Then the rate expression becomes $k = BT^m exp(-E_b/RT)$. Under these circumstances the relation between E_a and E_b is given by

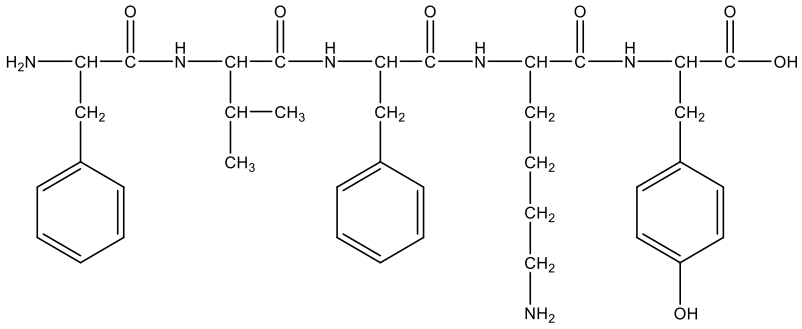
a) $E_a - E_b = mRT$

b) $E_b - E_a = mRT$

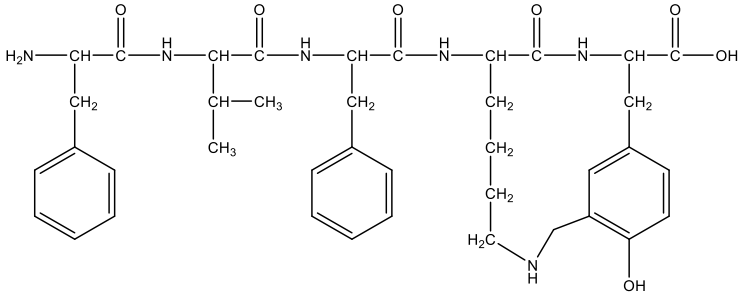
c) $E_a = E_b + (RT^m)$

d) $E_b = E_a + (RT^m)$

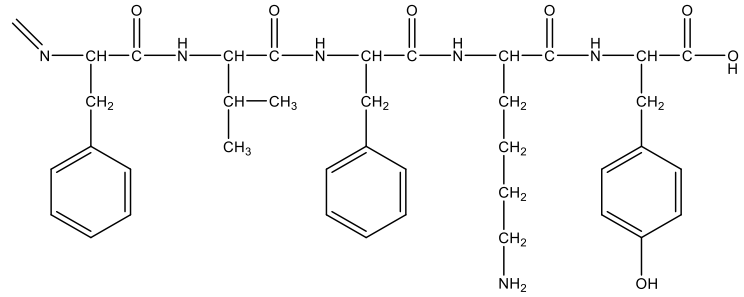
27) A dilute solution of the peptide shown below is treated with excess 10 % formaldehyde in methanol. Predict the product formed.



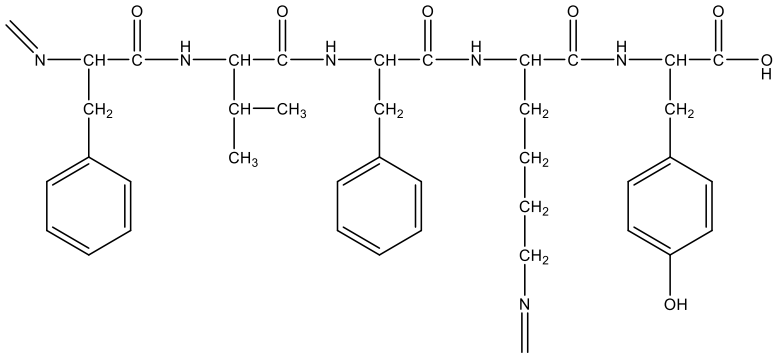
A.



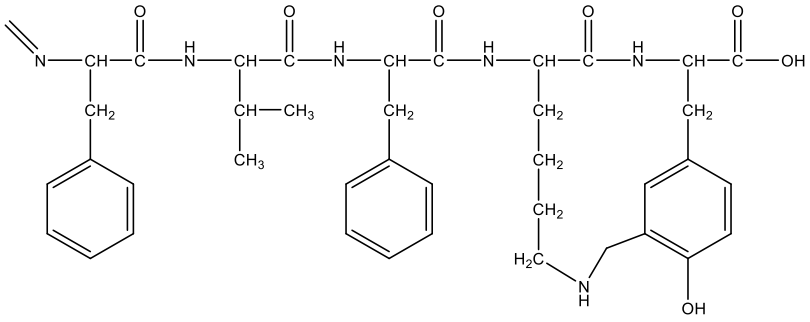
B.



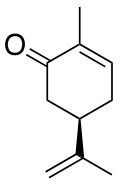
C.



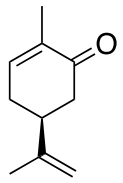
D.



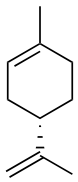
28. Many times enantiomers give rise to different odors. For example, (−)-Carvone (**I**) has sweetish minty smell and (+)-Carvone (**II**) has a spicy aroma, like Persian cumin seeds. Similarly, (+)-Limonene (**III**) is found in oranges and (−)-Limonene (**III**) is found in lemons. What would be the stereochemical descriptors of their absolute configurations?



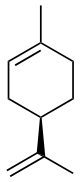
(−)-Carvone
(found in garden mint)
I



(+)-Carvone
(found in Persian cumin)
II



(−)-Limonene
(found in lemons)
III



(+)-Limonene
(found in oranges)
IV

a) **I**) *R*, **II**) *S*, **III**) *R*, **IV**) *S*

b) **I**) *S*, **II**) *R*, **III**) *S*, **IV**) *R*

c) **I**) *R*, **II**) *S*, **III**) *S*, **IV**) *R*

d) **I**) *S*, **II**) *R*, **III**) *R*, **IV**) *S*

29) The clusters Sn_5^{2-}, Ge_9^{4-}, and $Rh_6(CO)_{16}$ have structure respectively:

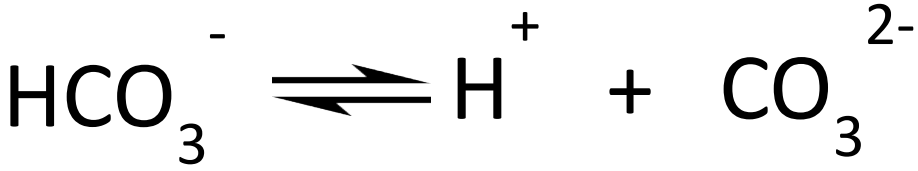
a) closo, nido and arachno

b) closo, nido, and closo

c) arachno, closo, and nido

d) nido, closo, and closo

30) The pK_{a1} of carbonic acid (H_2CO_3) is 6.3 while that of bicarbonate/carbonate equilibrium (pK_{a2}) shown below is 10.3.



Given the above data and pK_w = 14, can one predict the pH of 0.01 M sodium bicarbonate solution in water?

a) 7.5

b) 10.5

c) 8.3

d) 2

31) While the vibrational energy of an oscillator in v = 0 state (ground state) is nonzero, the rotational energy of a rigid rotor in J = 0 state (ground state) can be zero. Pick the correct reason.

A) Vibrational energy of an oscillator consists of both potential as well as kinetic energy whereas the rotational energy of the rotor has only the kinetic energy.

B) It is a rigid rotor.

C) Vibrational and rotational degrees of freedom are decoupled from each other.

D) None of the above.

32) In the photoelectric effect, if the intensity of light falling on the sample is increased, what would be the outcome on the (i) kinetic energy (K.E.) of the ejected electrons and the (ii) total number of electrons that are being ejected.

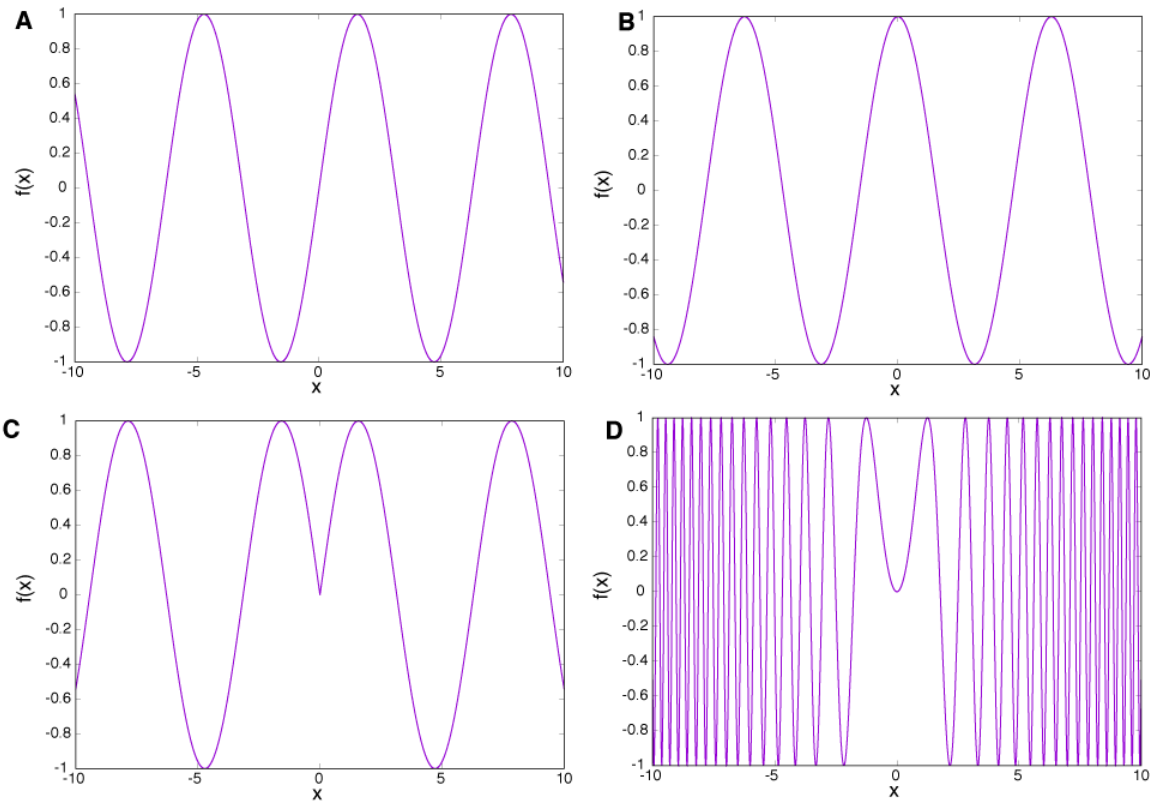
A) (i) The K.E will increase and (ii) number of electrons will also increase

B) (i) The K.E will increase and (ii) number of electrons will remain the same

C) (i) The K.E will remain the same and (ii) number of electrons will increase

D) (i) The KE will remain the same and (ii) number of electrons will also remain the same

33) Which of these represents f(x) = sin|x| where x-axis is in radians?



Answer: c,

34) You are measuring the weight of a sample using a balance. After 7 measurements, the measured weight is 10 ± 1 gm. To get the standard error to ± 0.5 gm, approximately how many measurements will you have to do?

A) 14

B) 49

C) 28

D) 100

35) If the peak in the mass spectrum of C2F6 at mass number 138 is 100 units tall, what will be the heights of the peaks at mass numbers 139 and 140. Isotopic abundances: ^{12}C, 98.89%; ^{13}C, 1.11%; ^{19}F, 100%

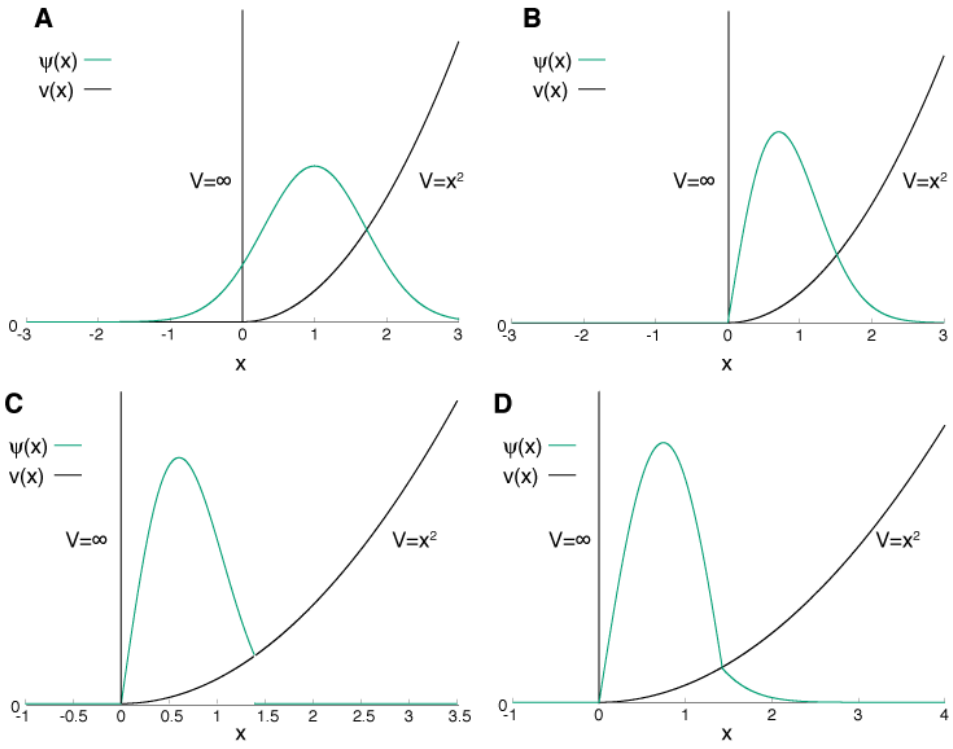
A) 2.24 and 0.0126

B) 1.12 and 0.0126

C) 50 and 25

D) 2.24 and 0.025

36) Which of the wavefunctions sketched below (in green) are valid for the half parabolic potential (in black). Note that the $V(x) = x^2$ for $x > 0$ while ∞ elsewhere.



B)

37) An electron is confined to a 2-D square potential well with dimension of 10 nm and – well depth of 1 eV. For a bound state, what is the maximum possible value of n_x?
(n_x denotes the usual quantum number)

(a) Can not be determined from the information provided

(b) 266

(c) 16

(d) 0

38) The rotation constant for $^{14}N^{15}N$ is measured to be 1.92 cm^{-1}. Which of the statement holds true for the bond length (r_0) for $^{14}N^{15}N$ and its comparison with r_0 for $^{14}N^{14}N$?

(a) $r_0(^{14}N^{15}N)$ = 1.1 Angstrom and $r_0(^{14}N^{15}N) > r_0(^{14}N^{14}N)$

(b) $r_0(^{14}N^{15}N)$ = 1.5 Angstrom and $r_0(^{14}N^{15}N) < r_0(^{14}N^{14}N)$

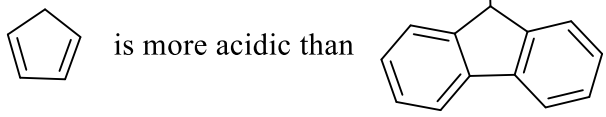
(c) $r_0(^{14}N^{15}N)$ = 1.3 Angstrom and $r_0(^{14}N^{15}N) > r_0(^{14}N^{14}N)$

(d) $r_0(^{14}N^{15}N)$ = 1.1 Angstrom and $r_0(^{14}N^{15}N) < r_0(^{14}N^{14}N)$

39) Which of the following is **INCORRECT**

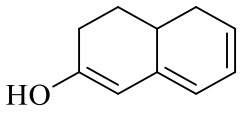
a) $[Fe(H_2O)_6]^{3+}$ is less acidic than $[Fe(H_2O)_6]^{2+}$ in water.

b)

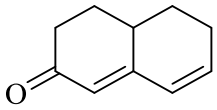


is more acidic than

c)



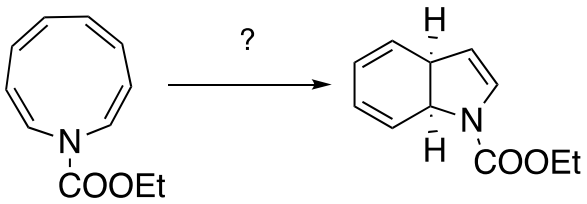
and



are tautomers.

d) Acidity of following oxy-acids in water: $HIO < HIO_2 < HIO_3 < HIO_4$.

40) Predict the reaction condition for the following synthetic transformation?



A) Light

B) Base

C) Heat

D) Acid

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