

Correct Answers are ticked in green.

CHM-X

GS-2012 (Chemistry)

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

Written Test in **CHEMISTRY - December 11, 2011**

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. Read the instructions given on the reverse of the answer sheet before you start filling it up. Use only HB pencils 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. Use of calculator on mobile phone will not be permitted.**
7. 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°C

Faraday = 96500 C/eq. wt.

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

$E_n = -\frac{Z^2}{2n^2}$ a.u. for hydrogen like atom

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

Average velocity = $\sqrt{\frac{8kT}{\pi \cdot m}}$

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

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

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

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

-
1. A quantum mechanical state Q is a superposition of two normalized energy eigenstates A and B in an amplitude ratio 2:1. If the two states are degenerate with a common eigenvalue E, what is the energy of the state Q?
 - A) 0,
 - B) 3E
 - C) 5E
 - D) E ✓
 2. For the above, if the states were non-degenerate and with energy eigenvalues E and $-E$ respectively, then what would be the expectation value of the energy?
 - A) 3E
 - B) 5E
 - C) E
 - D) None of the above ✓
 3. Suppose we inscribe a circle inside an equilateral triangle, and then inscribe a square inside this circle. What is the ratio of the side of the square to the side of the triangle?
 - A) $1: \sqrt{3}$
 - B) 2:5
 - C) $1: \sqrt{6}$ ✓
 - D) 1:2

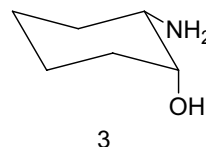
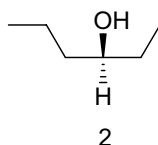
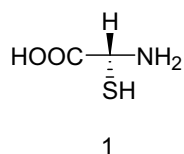
4. The reversible reaction $S \leftrightarrow P$ is catalyzed by a catalyst. The equilibrium constant $K_{eq} = [P]/[S]$ is 2×10^3 . The forward rate constant was found to be $5 \times 10^4 \text{ sec}^{-1}$ and $4 \times 10^{-6} \text{ sec}^{-1}$ in the presence and in the absence of the catalyst respectively. What is the expected rate constant for the reverse reaction in the absence of the catalyst?

- A) $5 \times 10^8 \text{ sec}^{-1}$
- B) $2 \times 10^{-9} \text{ sec}^{-1}$ ✓
- C) $0.8 \times 10^{-10} \text{ sec}^{-1}$
- D) $5 \times 10^{-9} \text{ sec}^{-1}$

5. The molar extinction coefficient (at 550 nm) of compounds A and B are $1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. Solutions of A and B are made at concentrations of $1 \times 10^{-4} \text{ M}$ and $2 \times 10^{-5} \text{ M}$ respectively. In a spectrophotometer set at 550 nm, the percentage of light transmitted by solutions A and B (in two separate experiments) will be:

- A) the same
- B) B will transmit 10 times less light compared to A ✓
- C) B will transmit 5 times less light compared to A
- D) B will transmit 2 times less light compared to A.

6. What are the configurations (R or S) of the chiral centers in the following molecules:



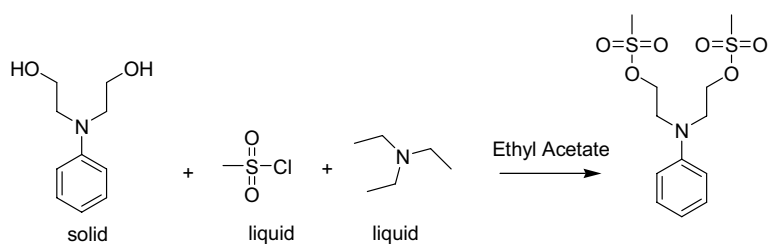
- A) Compound 1 = R; Compound 2 = R; Compound 3 = 1S, 2S
- B) Compound 1 = R; Compound 2 = S; Compound 3 = 1R, 2S ✓
- C) Compound 1 = S; Compound 2 = S; Compound 3 = 1S, 2R
- D) Compound 1 = R; Compound 2 = S; Compound 3 = 1S, 2R

7. What are the oxidation states of the metal ion in the following compounds

1. PdCl₂
2. Pd(PPh₃)₄
3. Pd(OAc)₂
4. ArPdBr where Ar is Aryl

- A) 2, 4, 2, 2
 B) 2, 0, 2, 1
 C) 2, 0, 2, 2 ✓
 D) 0, 0, 0, 2

8. Methanesulfonyl chloride is used commonly to form methanesulfonates upon reaction with alcohols. Methanesulfonates are good leaving groups in nucleophilic substitution reaction. In the following reaction calculate the volumes of methanesulfonyl chloride and triethylamine required in μL . The amount of starting material and the number of equivalents of each reagent is given.



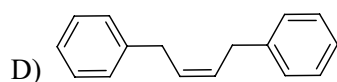
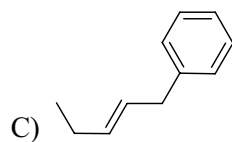
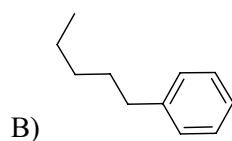
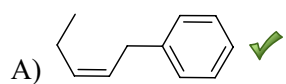
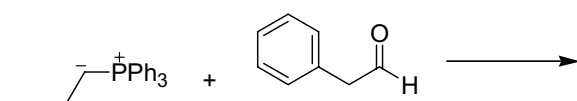
Amount (mg)	100		
equivalents	1	2	3
Density (g/mL)		1.48	0.73
μL		D	E

- A) D = 126, E = 167 ✓
 B) D = 0.085, E = 0.229
 C) D = 85, E = 229
 D) D = 1.1, E = 1.65

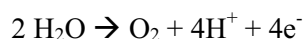
9. The vibrational Raman effect, a considerably weak scattering phenomena, was first reported by Late Sir CV Raman in 1928. The intensity of the individual vibrational resonances observed in a Raman spectrum is proportional to

- A) Number of molecules
- B) Polarizability of the bond
- C) Wavelength of radiation used
- D) All of the above ✓

10. The Wittig reaction is a reaction with an aldehyde or ketone with a phosphonium ylide. Predict the product of the following reaction:



11. The standard redox potential of water oxidation to dioxygen is -1.23 V.



The redox potential of the same reaction at $\text{pH} = 7$ would be:

- A) -0.41 V
- B) -1 V
- C) -0.82 V ✓
- D) -1.64 V

12. Amino acid side-chains in proteins have hydrogen bonds for structural and catalytic reasons. One such combination of H-bonding partners is Histidine associated with a partnering residue such as Tyrosine ($\text{X-H} \cdots \text{N-His}$, where X is the partnering amino acid). If the pK_a of Histidine is 6.1 , estimate the pK_a of the partnering residue (X-H) such that protonation of His at $\text{pH} 6.5$ is a favourable process.

- A) $\text{pK}_a > 10$
- B) $\text{pK}_a < 1$
- C) $\text{pK}_a < 6$ ✓
- D) $\text{pK}_a > 6.5$

13. The total energy expended to charge (total charge = $+q$) a sphere of radius ' r ' in a dielectric medium (ϵ) is given by (in SI units):

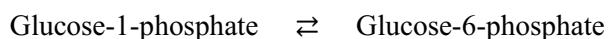
- A) $q^2/4\pi\epsilon r$
- B) $q^2/16\pi\epsilon r$
- C) $q^2/4\pi\epsilon r^2$
- D) $q^2/8\pi\epsilon r$ ✓

14. A substance A is consumed by a reaction of unknown order. The initial concentration is 1mM, and concentrations at later times are as shown:

Time (min)	[A] (mM)
1	0.83
2	0.72
4	0.56
8	0.38
16	0.24

What is the order of the reaction?

- A) zero
 - B) first-order
 - C) second-order ✓
 - D) pseudo-first order
15. ΔG^0 values for the hydrolysis of glucose-1-phosphate and glucose-6-phosphate are -21 kJ/mol and -14 kJ/mol, respectively. What is the equilibrium constant for the following equilibrium at 25^0C ?



- A) 0.06
 - B) 16.9 ✓
 - C) 4798
 - D) 284
16. In a double stranded DNA, if the sequence 5'AGATCC3' appears on one strand of DNA, what sequence in the complementary strand?
- A) 5'AGATCC3'
 - B) 5'CCTAGA3'
 - C) 5'GGATCT3' ✓
 - D) 5'TCTAGG3'

17. One sequence of amino acids repeats for long distances in silk protein. Complete hydrolysis of one mole of a fragment with this sequence gives 2 mol alanine, 3 mol glycine, and 1 mol serine. Partial hydrolysis yields Ala-Gly-Ala, Gly-Ala-Gly, Gly-Ser-Gly, and Ser-Gly-Ala peptides. What is the amino acid repeat?

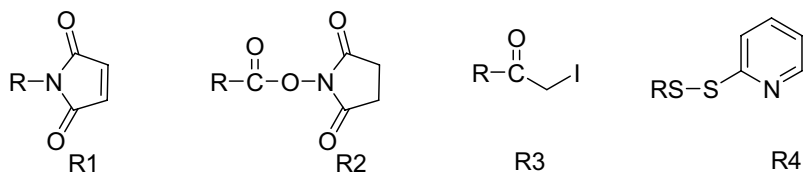
- A) Gly-Gly-Ser-Ala-Gly-Ala
- B) Gly-Gly-Gly-Ala-Ala-Ser
- C) Ser-Ala-Ala-Gly-Gly-Gly
- D) Gly-Ser-Gly-Ala-Gly-Ala ✓

18. Which of the following compounds would give the ^1H NMR spectrum shown below



- A) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{X}$ ✓
- B) $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{X}$
- C) $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CH}_2\text{X}$
- D) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{X}$

19. Which of the following compounds will react with R-SH in aqueous solutions between pH 6.5 and 8.5?



- A) R1, R2 and R3
- B) R2, R3 and R4
- C) R4, R2 and R1
- D) R1, R3 and R4 ✓

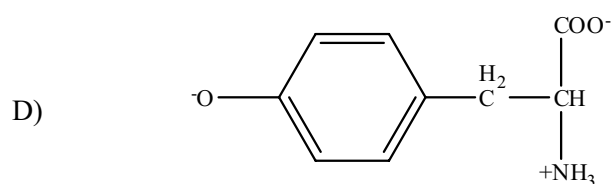
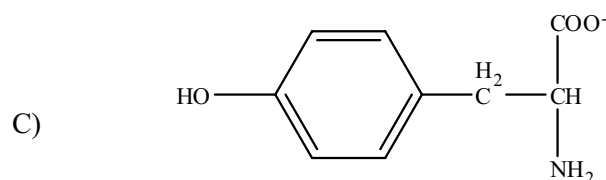
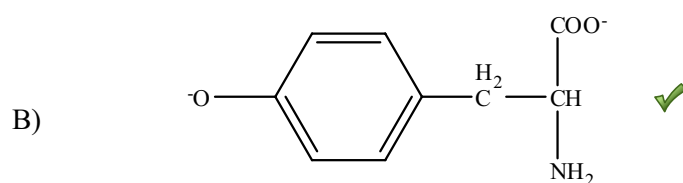
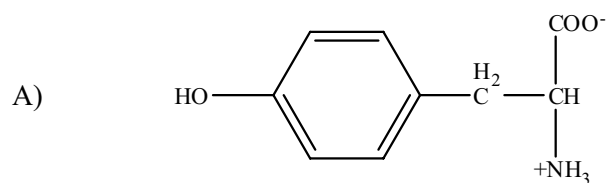
20. In a spherical polar coordinate system, a point A at (x, y, z) in the Cartesian coordinate system can be described by (r, θ , ϕ) where r, θ , and ϕ have their usual meaning. Expression for the volume of an infinitesimally small cube confined by dx, dy, and dz in terms of the spherical coordinate system is given by

- A) $drd\theta d\phi$
- B) $r\sin\theta drd\theta d\phi$
- C) $r^2\sin^2\theta drd\theta d\phi$
- D) $r^2\sin\theta drd\theta d\phi$ ✓

21. Rotational energy of a diatomic molecule is given by $E_{rot} = J(J + 1)hB_e$, where E_{rot} is in Joules. If the rotational constant for H_2 molecule is given as $B_e = 1.8324 \times 10^{12}$ Hz, the rotational period of the H_2 molecule in $J = 10$ level will be

- A) 1.33×10^{-19} sec
- B) 5.0×10^{-15} sec ✓
- C) 5.46×10^{-13} sec
- D) 7.39×10^{-7} sec

22. Tyrosine, at pH 12, has the following structure



23. Quartz crystal watches lose or gain about a second a week. What is the accuracy of these watches in *ppm*?

- A) 1
- B) 1000
- C) 0.605
- D) 1.653 ✓

24. The reaction of sodium ethoxide with ethyl iodide to form diethyl ether is termed

- A) electrophilic substitution
- B) nucleophilic substitution ✓
- C) electrophilic addition
- D) radical substitution

25. Of the following metal ions, which has the largest magnetic moment in its low-spin octahedral complexes?

- A) Fe^{3+}
- B) Co^{3+}
- C) Co^{2+}
- D) Cr^{2+} ✓

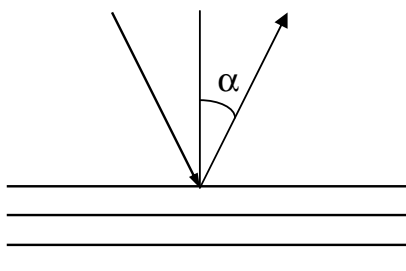
26. In a certain axis of quantization, the z-component of the spin angular momentum, S_z , has the following matrix representation.

$$S_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

What would be the trace of the matrix of S_x^2 (square of the x-component) in the same representation?

- A) $0\hbar^2$
- B) $1\hbar^2$
- C) $2\hbar^2$ ✓
- D) None of the above

27. X-rays of CuK_α (wavelength 154 pm) are diffracted by a set of atomic planes in a crystal in the following manner. The separation of the layers in the crystal is 404 pm. Find the angle α along which the first-order reflection will occur.



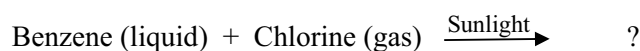
- A) 79° ✓
 B) 45°
 C) 11°
 D) None of the above
28. How many molecules of cetanol (of cross-sectional area $2.58 \times 10^{-19} \text{ m}^2$) can be adsorbed on the surface of a spherical drop of dodecane of radius 17.8 nm?
- A) 3.90×10^3
 B) 1.54×10^4 ✓
 C) 1.54×10^2
 D) 6.5×10^{-5}
29. The velocity of Li^+ ion in water is $2 \times 10^{-2} \text{ cm/sec}$ when 100 V is applied between two electrodes separated by 2 cm. The mobility of Li^+ ion in water is,
- A) $4 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ ✓
 B) $1 \times 10^{-4} \text{ s}^{-1} \text{ V}^{-1}$
 C) $4 \text{ V cm}^2 \text{ s}^{-1}$
 D) $2.5 \times 10^5 \text{ V s cm}^{-2}$

30. The melting point of lithium metal is 454 K, and that of sodium is 371 K. Which of the following statements can explain this difference in their melting points?

- i. Metallic bonding in lithium is stronger than metallic bonding in sodium.
- ii. The delocalised electrons are more strongly attracted to the metal cation of lithium.
- iii. The lithium cations have a greater charge density than sodium cation.
- iv. Li^+ cations are smaller than Na^+ cations.

- A) Only (i) and (ii)
- B) Only (ii) and (iii)
- C) Only (iv)
- D) (i), (ii), (iii), and (iv) ✓

31. What is the final product after the following reaction has gone to completion?



- A) Benzene
- B) Benzenhexachloride ✓
- C) Chlorobenzene
- D) Dichlorobenzene

32. The transition probability for spontaneous emission from state m to state n is given by an expression

$$A_{m \rightarrow n} = \left(\frac{64 \pi^4 \nu_{mn}^3}{3hc^3} \right) \cdot \left(\left| \langle m | \hat{d} | n \rangle \right|^2 \right)$$

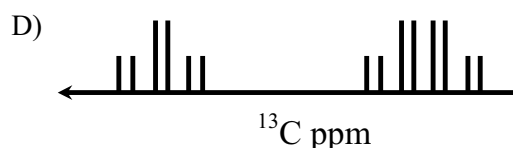
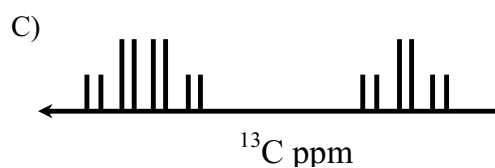
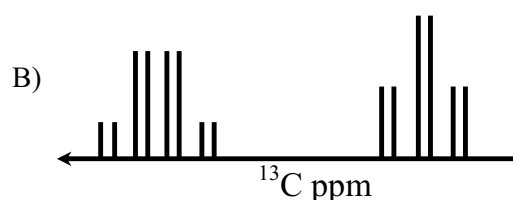
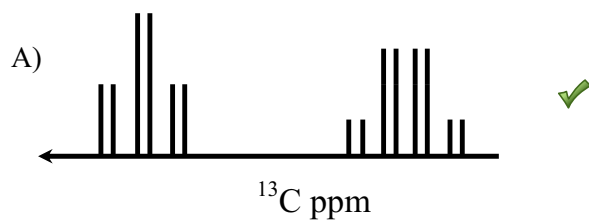
Where, ν_{mn} is the frequency of transition, and the term in the parenthesis is the transition dipole. Assuming that the magnitude of the transition dipole is same for all types of transitions, arrange the average lifetimes for the electronic, vibrational, and rotational transitions in the proper order.

- A) electronic < vibrational < rotational ✓
- B) vibrational < rotational < electronic
- C) rotational < vibrational < electronic
- D) electronic < rotational \approx vibrational

33. At 20 °C, the standard EMF of a certain cell is +0.2699V, and at 30 °C it is +0.2669V. What can you say about the standard entropy of this reaction? Assume that the standard ΔH° and ΔS° are independent of temperature.

- A) $\Delta S^\circ = 0$
- B) $\Delta S^\circ = +ve$
- C) $\Delta S^\circ = -ve$ ✓
- D) Not enough information is given.

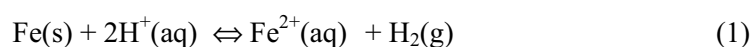
34. Which of the following most closely resembles the ^{13}C NMR spectrum of ethanol? Assume a scalar coupling of 150 Hz among the ^1H and the ^{13}C nuclei within a functional group, a scalar coupling of 50 Hz between the ^{13}C nuclei, a static magnetic field of 11.7 T, and a temperature of 300 K.



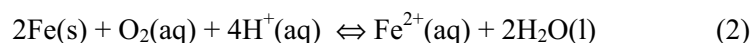
35. The roots of the equation $x^3 + ax^2 - bx + c = 0$ are three consecutive integers. What is the maximum value of b ?

- A) -2
- B) 0
- C) 1 ✓
- D) 2

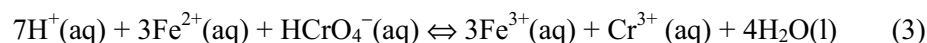
36. The corrosion of iron in contact with an acidic aqueous solution undergoes the following reaction



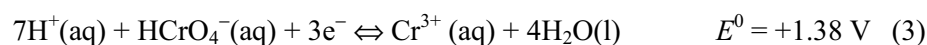
in the **anaerobic** condition, and the following reaction



in the **aerobic** condition. During the corrosion, Fe(II) ions are formed in both conditions. If the water is polluted with Cr(IV), the following reaction may take place.



Reaction (3) be broken down to the following redox half-reactions:



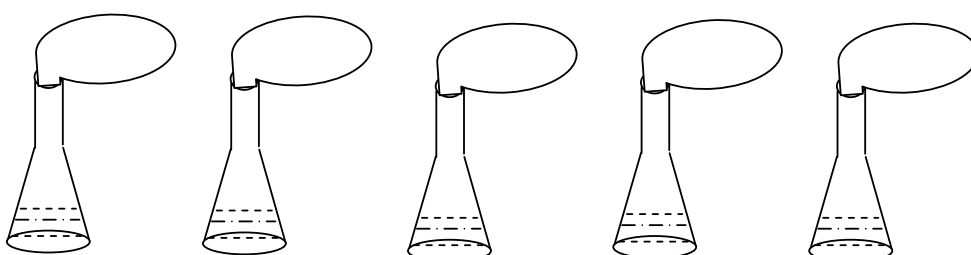
The standard potentials of these reactions are with respect to the normal hydrogen electrode. What would be the approximate value of the equilibrium constant of reaction 3 at 298 K?

- A) 10^{11}
- B) 10^{31} ✓
- C) 10^{-31}
- D) 10^{-11}

37. Consider a container of volume 5.0 L that is divided into two compartments of equal size. In the left compartment there is nitrogen at 1.0 atm and 25 °C; in the right compartment there is hydrogen at the same temperature and pressure. What will happen when the partition is removed?

- A) The entropy increases, and the free energy decreases. ✓
- B) The entropy decreases, and the free energy decreases.
- C) The entropy increases, and the free energy increases.
- D) The entropy decreases, and the free energy increases.

38. Each of the following flasks contains 25 ml of 1M HCl solution in water. To them a certain amount of solid sodium bicarbonate is added and, as shown the picture, then the mouths of the flasks are quickly closed by rubber balloons of identical size. The masses of NaHCO₃ added to the flask 1 through the flask 5 are 0.70 g, 1.00 g, 2.10 g, 4.20 g and 6.30 g, respectively. After waiting for a sufficiently long time, predict the relative size of the 5 balloons.



	Flask 1	Flask 2	Flask 3	Flask 4	Flask 5
1 M HCl	25 ml	25 ml	25 ml	25 ml	25 ml
NaHCO ₃	0.70 g	1.00 g	2.10 g	4.20 g	6.30 g

- A) The size of Balloon 1 = Balloon 2 = Balloon 3 = Balloon 4 = Balloon 5.
- B) The size of Balloon 1 < Balloon 2 < Balloon 3 < Balloon 4 < Balloon 5.
- C) The size of Balloon 1 < Balloon 2 < Balloon 3 = Balloon 4 = Balloon 5. ✓
- D) The size of Balloon 1 < Balloon 2 < Balloon 3 < Balloon 4 = Balloon 5.

39. The degeneracy of the energy level $12h^2/8ma^2$ of a particle in a three dimensional cube of length “a” is

- A) 1 ✓
- B) 3
- C) 6
- D) 12

40. Compound A is more soluble in solvent X when compared to solvent Y. X and Y are immiscible. The partition coefficient of A between the two solvents is 10. 10 mL of a 2×10^{-5} M solution of A in solvent Y is mixed vigorously with 100 mL of solvent X and the two phases are allowed to separate out. The concentration of A in phase Y after the separation would be:

- A) 2×10^{-9} M ✓
 - B) 1.98×10^{-7} M
 - C) 2×10^{-6} M
 - D) 1.8×10^{-7} M
-

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.

GS-2012 (CHEMISTRY)**CHM-X****ANSWER SHEET***Please see reverse for instructions on filling of answer sheet.*

Question Paper Set : X ● Y ○

Name		Reference Code :					
Ref Code		1	○	○	○	○	○
Address		2	○	○	○	○	○
		3	○	○	○	○	○
		4	○	○	○	○	○
		5	○	○	○	○	○
Phone		6	○	○	○	○	○
Email		7	○	○	○	○	○
		8	○	○	○	○	○
		9	○	○	○	○	○
		0	○	○	○	○	○

Would you like to be considered for Biology also :
YES ○ NO ○

SECTION A				
	(A)	(B)	(C)	(D)
1	○	○	○	○
2	○	○	○	○
3	○	○	○	○
4	○	○	○	○
5	○	○	○	○
6	○	○	○	○
7	○	○	○	○
8	○	○	○	○
9	○	○	○	○
10	○	○	○	○
11	○	○	○	○
12	○	○	○	○
13	○	○	○	○
14	○	○	○	○
15	○	○	○	○
16	○	○	○	○
17	○	○	○	○
18	○	○	○	○
19	○	○	○	○
20	○	○	○	○

SECTION A				
	(A)	(B)	(C)	(D)
21	○	○	○	○
22	○	○	○	○
23	○	○	○	○
24	○	○	○	○
25	○	○	○	○
26	○	○	○	○
27	○	○	○	○
28	○	○	○	○
29	○	○	○	○
30	○	○	○	○
31	○	○	○	○
32	○	○	○	○
33	○	○	○	○
34	○	○	○	○
35	○	○	○	○
36	○	○	○	○
37	○	○	○	○
38	○	○	○	○
39	○	○	○	○
40	○	○	○	○
41	○	○	○	○

Signature of the Student

INSTRUCTIONS

The Answer Sheet is machine-readable. Apart from filling in the details asked for on the answer sheet, please make sure that the Reference Code is filled by blackening the appropriate circles in the box provided on the right-top corner. Only use HB pencils to fill-in the answer sheet.

e.g. if your reference code is 15207:

Reference Code :					
1	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
2	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
3	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
4	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
5	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
6	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
7	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
8	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
9	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
0	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>

Also, the multiple choice questions are to be answered by blackening the appropriate circles as described below

e.g. if your answer to question 1 is (b)
and your answer to question 2 is (d)
then

SECTION A				
	(A)	(B)	(C)	(D)
1	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
3	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
4	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>