Correct answers are ticked in green.

CHM-X

GS-2014 (Chemistry)

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

Written Test in **CHEMISTRY - December 8, 2013**
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. Multiple-use devices such as cell phones, smart phones etc., CANNOT be used for this purpose.**

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 = 6.02×10^{23} mol^{-1}
RT/F = 0.0257 V at 25°C
Faraday constant = 96500 C/mol
Boltzmann constant $k = 1.38\times10^{-23}$ J K^{-1}

$e = 1.6\times10^{-19}$ C
$h = 6.626\times10^{-34}$ J s
$c = 3\times10^{8}$ m s^{-1}
R = 8.314 J K^{-1} mol^{-1}

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

Mass of an electron = 9.109×10^{-31} kg

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

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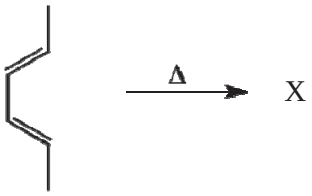
1. For the following reaction,

$$CO_2 + H_2O \rightarrow H_2CO_3$$

the entropy change (ΔS_{system}) was calculated to be –96 J K^{-1} mol^{-1}. The enthalpy change (ΔH) was measured to be –45 kJ K^{-1} mol^{-1}. This reaction is expected to be a spontaneous process. The total change in entropy ($\Delta S_{system+surroundings}$) is

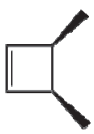
A) +54 J K^{-1} mol^{-1} ✔
B) –96 J K^{-1} mol^{-1}
C) –45096 J K^{-1} mol^{-1}
D) –44004 J K^{-1} mol^{-1}

2. What is the product of the following electrocyclic ring-closing reaction?



X

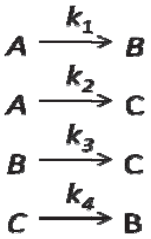
A)  ✔

B) 

C) both A and B

D) none of the above

3. For the following chemical reactions



The rate constants k_1 and k_2 are at least 1000 times slower than either k_3 or k_4. During the course of the above reactions the ratio of the products *B* and *C* will be

A) $[B]/[C] = k_3/k_4$
B) $[B]/[C] = k_4/k_3$ ✔
C) $[B]/[C] = k_2k_3/\ k_1k_4$
D) $[B]/[C] = k_1/k_2$

4. Transition states in chemical reactions are generally not directly observed in experiments because

A) their structures are different from reactants and products
B) they have the highest kinetic energy and hence difficult to capture
C) they have the highest potential energy and their lifetimes are short ✔
D) all of the above

5. A single-stranded RNA has 1200 bases. The total base content of this RNA was found to have the following ratio *A:U:G:C* = 0.2:0.3:0.3:0.2. The probability of a randomly chosen 5 nucleotide long sequence as *GAUGA* is

A) 0.00098
B) 0.00243
C) 0.00032
D) 0.00108 ✔

6. Phosphorescence is a slower process than fluorescence because

A) phosphorescence occurs at longer wavelengths than fluorescence
B) spin angular momentum is not conserved in phosphorescence process ✔
C) both A and B
D) none of the above

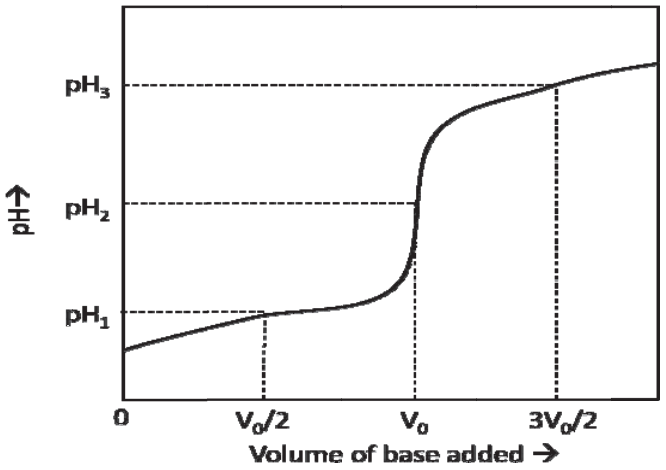
7. The partition constant of a compound between two immiscible solvents *A* and *B* is 10. Solvent *A* is preferred over solvent *B*. You are given 10ml of 0.1M solution of the compound in solvent *B*. This solution is vigorously shaken and equilibrated with 10ml of solvent *A*. After phase separation, the concentration of the compound in solvent *B* is

A) 0.09 M
B) 0.099 M
C) 0.009 M ✔
D) 0.05 M

8. A molecule has a ground state and two excited electronic energy levels, all of which are nondegenerate with the energies: $E_0=0$, $E_1=1\times10^{-20}$ J, and $E_2 = 3\times10^{-20}$ J. If P_0, P_1 and P_3 are fractions of molecules occupied in ground, first and second excited states, respectively, at 298K, then, $P_0 : P_1 : P_2 = ?$

A) 0.919 : 0.081 : 0.001 ✔
B) 0.900 : 0.098 : 0.002
C) 0.666 : 0.333 : 0.111
D) 0.880 : 0.088 : 0.022

9. While carrying out the titration of a weak acid with a strong base, the pH of the solution is measured as a function of the added titrant. The result is shown below.



Three pH values have been marked, corresponding to 3 different volumes of the added base. V_0 corresponds to the 'end point' or the 'stoichiometric point' of neutralization. What is the pk_a of the acid?

A) pH_1 ✔
B) pH_2
A) pH_3
D) cannot be answered because of insufficient information

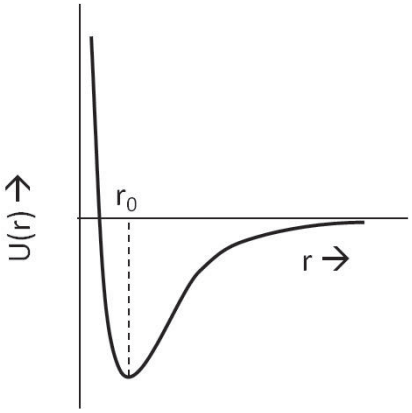
10. Although both NF_3 and NCl_3 are covalent, NCl_3 undergoes hydrolysis whereas NF_3 does not because

A) NF_3 is more stable than NCl_3
B) dipole moment of NF_3 is more than NCl_3
C) electronegativity of F > Cl
D) Cl can expand its octet by using d-orbitals ✔

11. The potential energy of a diatomic molecule, as a function of the internuclear separation *r*, is approximated as

$$U(r) = \frac{A}{r^a} - \frac{B}{r^b}$$

where *A* and *B* are positive constants and $a > b$.



As shown in the above figure, r_0 is the equilibrium bond length. What is the energy necessary to break the bond from its equilibrium position?

A) $\frac{A}{r_0^a} - \frac{B}{r_0^b}$

B) $\frac{B}{r_0^b} - \frac{A}{r_0^a}$

C) $\frac{A}{r_0^a}\left(\frac{a}{b} - 1\right)$

D) both B and C ✔

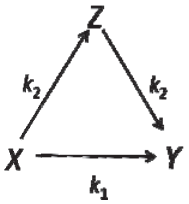
12. The heme is present at the active site of many proteins and enzymes including hemoglobin, cytochromes etc. It is an iron complex of a cyclic aromatic ligand named porphyrin. Several metal complexes of porphyrin synthesized in the laboratory have similar absorption spectra, except that the most intense absorption band position is either red shifted or blue shifted around 400 nm depending on the nature of the metal ion. The origin of this most intense absorption band in these porphyrin complexes is:

A) MLCT transitions
B) LMCT transitions
C) d-d transitions
D) π- π* transitions ✔

13. Which of the following statements is true about ferromagnets?

A) In the presence of a magnetic field, the unpaired spins of a ferromagnet all align with the external field. In the absence of the external magnetic field, spins then revert back immediately to their original state.
B) The origin of magnetism in a ferromagnet arises from randomly arranged paired spins in a lattice.
C) A ferromagnetic material is weaker (in its attraction to an external magnetic field) than a paramagnetic material.
D) none of the above ✔

14. An electron can be transferred between two molecules *X* and *Y* either directly with a rate $k_{XY} = k_1$ or through an intermediate molecule *Z* with rates $k_{XZ} = k_{ZY} = k_2$. If at time $t = 0$ the electron is situated at *X* then average time *t* it will take to reach *Y* is given by:



A) $t = 1/(k_1 + k_2/2)$ ✔
B) $t = 1/k_1 + 1/k_2$
C) $t = 1/(k_1 + 2k_2)$
D) $t = (k_1 + k_2)/(k_1 k_2)$

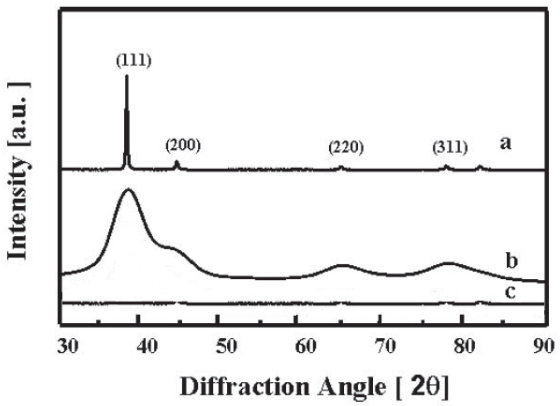
15. For a conservative force field (e.g., gravity): *F*, work done in moving a particle by distance *dr* is $W=F.dr$. which of the following is true

A) *W* around a closed path is zero and *W* is path independent ✔
B) *W* around a closed path is zero and *W* is path dependent
C) *W* around a closed path is non-zero and *W* is path independent
D) *W* around a closed path is non-zero and *W* is path dependent

16. 0.050 mol of acetic acid and 0.20 mol of sodium acetate are mixed and total volume is adjusted to 500 ml in water. The p*K*a for acetic acid (CH_3COOH) is 4.75. If now 0.010 mol of NaOH is added to the above mixture, what will the final pH of the solution be?

A) > pH 7
B) pH will stay at 4.75 because it is a buffered solution
C) > pH 4.75 ✔
D) not sufficient information has been given

17. Given below is a figure showing three X-ray diffraction patterns for (a) bulk metallic gold (commercially available) deposited on a flat polymeric substrate



(along with lattice planes) and (b) nanoparticles of gold that were synthesized in a research lab. These were deposited on the same flat polymeric substrate and (c) is a blank polymeric substrate.

Which of the following statements is true regarding structural quality of the gold nanoparticles that have been synthesized?

A) the gold nanoparticles that have been synthesized are amorphous in nature and not crystalline. As such they do not belong to the FCC lattice
B) there are many impurities present in the sample containing gold nanoparticles
C) insufficient information is given to make a conclusive statement
D) none of the above ✔

18. An artificial soft drink contains 11.0 g/L of tartaric acid $C_4H_6O_6$, and 20 g/L of its potassium salt $C_4H_5O_6K$. What is the pH of the drink?
(Given: K_a tartaric acid = 1.0×10^{-3})

A) 4.24
B) 5.21
C) 3.82
D) 3.16 ✔

19. Which of the catalytic protocols listed below demonstrate a homogeneous catalysis?

I. Pt(s) catalyzing the reaction of O_2(g) with CO(g)
II. Cl(g) catalyzing the decomposition of O_3(g)
III. H_2O_2(aq) decomposition catalyzed by Br^- (aq)

A) *I* only
B) *II* only
C) *I* and *III* only
D) *II* and *III* only ✔

20. FAD is a redox-active molecule which takes part in many important biological reactions. The redox potential of FAD at pH 7.0 is given below.

$$FAD + 2H^{+} + 2e^{-} \rightleftharpoons FADH_2$$

$$E^{\circ}_{FADH_2/FAD} = -0.180V$$

Calculate the redox potential when the media is acidified to pH 0.

A) 0 V
B) 0.24 V ✔
C) 0.12 V
D) none of the above

21. What is $\boldsymbol{i^i}$**?** (Given, $i^2 = -1$)

A) a real number ✔
B) a complex number
C) an imaginary number
D) none of the above

22. The two fine-structure components of a nuclear magnetic resonance transition are observed at chemical shifts of 2.142 and 2.208 ppm in a 300 MHz NMR spectrometer. Calculate the coupling constant.

A) 19.8 Hz ✔
B) 0.066 Hz
C) 6.6 Hz
D) data is insufficient

23. The concentration of a molecule in aqueous solution is (C/1000) L^{-1}, where C is the number of molecules. Assuming the molecule is a sphere of radius r_0 Angstrom, one can estimate the intermolecular (centre-to-centre) separation by:

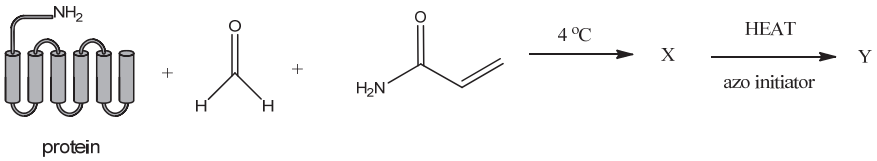
A) $\frac{1}{\sqrt[3]{C}} - 2\times r_0$ metre

B) $\frac{1}{\sqrt[3]{C}}$ metre ✔

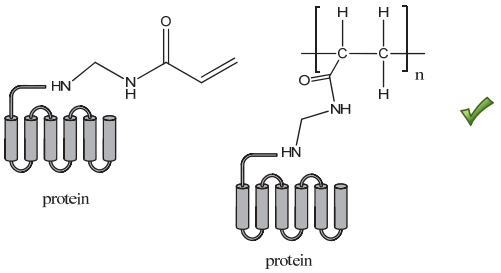
C) $\frac{1}{\sqrt[3]{C}} - 2\times 10^{-10} \times r_0$ metre

D) cannot be estimated based on the information above

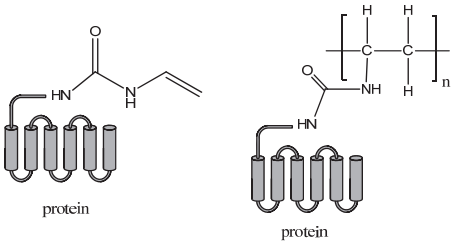
24. Paraformaldehyde (4% by wt), acrylamide (4% wt/vol), and an azo initiator (0.25% wt/vol) were added to a protein. What are the expected products *X* and *Y*?



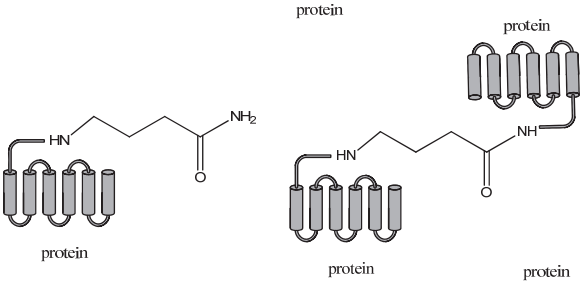
A)



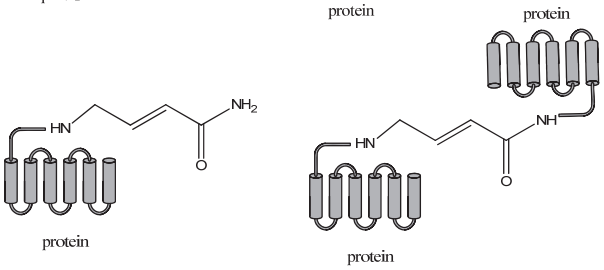
B)



C)



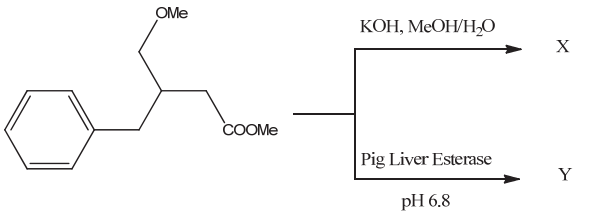
D)



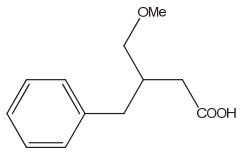
25. Raman scattering is often seen overlapping with fluorescence emanating from the sample. However, fundamentally Raman process is different from fluorescence. This is because

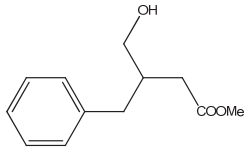
A) Raman scattering is a two-photon process and fluorescence is not
B) Raman process is a scattering process while fluorescence is not
C) Raman process need not be Stokes shifted
D) all of above ✔

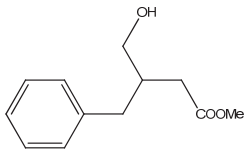
26. Predict the products *X* and *Y* for the following de-protection reactions:

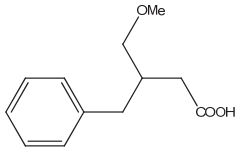


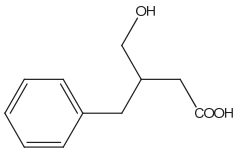
X Y

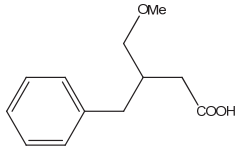
A) 

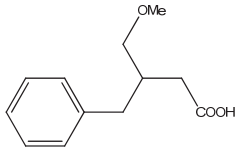


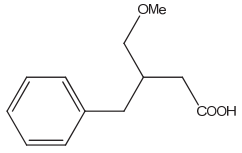
B) 



C) 



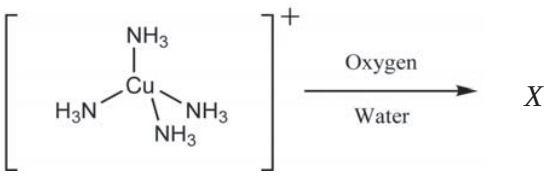
D) 

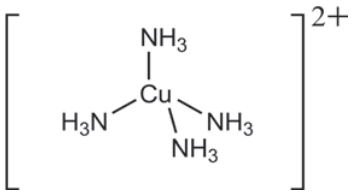


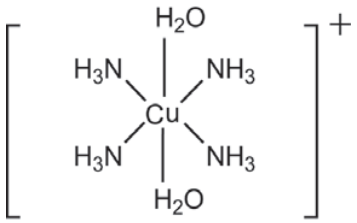
27. Calculate the change in entropy when 1 mol of solid iodine, I_2, at a temperature of 360 K is heated at constant pressure to produce liquid iodine at a temperature of 410 K. The constant pressure molar heat capacity of solid iodine is 54.44 J $K^{-1}mol^{-1}$ and of liquid iodine is 80.67 J K^{-1} mol^{-1}. The melting temperature of iodine is 387 K, and the molar enthalpy of fusion of iodine is 7.87 kJ mol^{-1}.

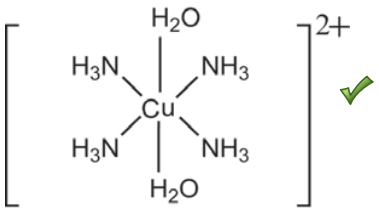
A) 8.6 J K^{-1} mol^{-1}
B) 28.9 J K^{-1} mol^{-1} ✓
C) 20.3 J K^{-1} mol^{-1}
D) 11.7 J K^{-1} mol^{-1}

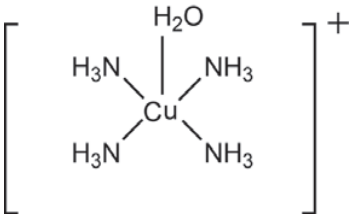
28. What is the product *X* in the following reaction?



A) tetrahedral 

B) octahedral 

C) distorted octahedral 

D) square pyramid 

29. How many molecular orbitals may be constructed from the valence shell orbitals of the constituent atoms in CH_4?

A) 2
B) 4
C) 6
D) 8 ✔

30. Write down the matrix representing a two-step transformation of a general point (x, y, z): rotation through 180^0 (about the z-axis) followed by reflection in an yz mirror plane

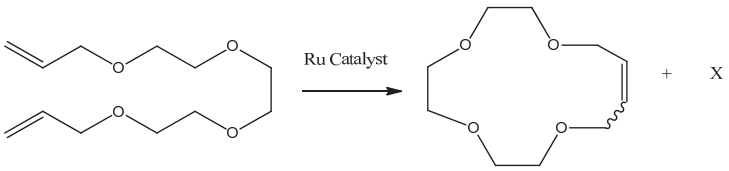
A) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ ✔

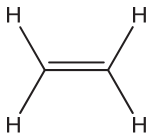
B) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

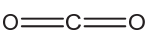
C) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

D) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

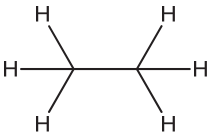
31. What is the side product (X) of the following ring closing metathesis reaction?



A)  ✔

B) 

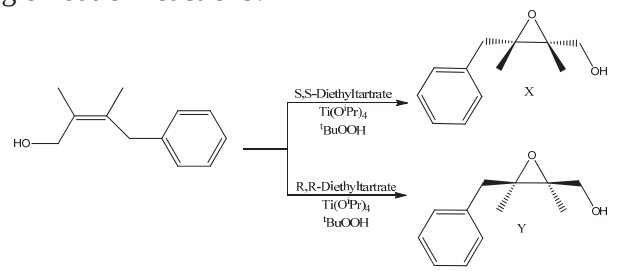
C) 

D) 

32. What is the nature of silicon-oxygen bonds in silica (SiO_2)?

A) polar covalent ✔
B) ionic
C) nonpolar covalent
D) coordinate covalent

33. The Sharpless epoxidation catalyst $Ti(O^iPr)_4$ converts allylic alcohols to epoxides steroselectively. What is the stereochemistry of the products obtained in the following oxidation reactions?



A) *X*: ((2R,3S)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol ✔
Y: ((2S,3R)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol

B) *X*: ((2S,3R)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol
Y: ((2R,3S)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol

C) *X*: ((2R,3R)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol
Y: ((2S,3S)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol

D) *X*: ((2R,3S)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol
Y: ((2S,3S)-3-benzyl-2,3-dimethyloxiran-2-yl)methanol

34. When 10 mL of each liquid of liquid pairs listed below are mixed and then allowed to stand, which pair is most likely to separate into two layers?

A) carbon tetrachloride and hexane
B) ethanol and methanol
C) carbon tetrachloride and methanol ✔
D) hexane and pentane

35. The mathematical expression $e^{i(kx-wt)}$ represents

A) a wave stationary in space but oscillating in time
B) a travelling wave moving in the positive *x* direction ✔
C) a wave stationary in time but periodically varying in space
D) a travelling wave moving in the negative *x* direction

36. Blue copper proteins consist of mono-nuclear copper center bound to 2 imidazole groups (histidine), one thiol group (cysteine) and one thioether group (methionine). The coordination geometry around the metal ion is distorted tetrahedral. What will be the relative value of the redox potential of the metal center (Cu^{2+}/Cu^{+}) in the protein compared to that of $CuSO_4$ in water?

A) more positive ✔
B) more negative
C) equal
D) redox potential of the metal center in the protein will be zero.

37. Vapor pressure of a liquid in a closed container depends upon

A) the volume of the container
B) the volume of the liquid
C) the temperature ✔
D) both B and C

38. Which of the following statements is/are true?

(i) HCl absorbs IR radiation
(ii) CO_2 absorbs IR radiation
(iii) H atom absorbs IR radiation
(iv) H atom absorbs UV-vis and microwave radiation

A) (i) only
B) (i) and (ii) only
C) (i), (ii) and (iii) only
D) (i), (ii), (iii) and (iv) ✔

39. N_2 does not show pure vibrational spectra because

A) triple bond in N_2 is very strong
B) the dipole moment of is N_2 zero ✔
C) both A and B
D) none of the above

40. What is the de Broglie wavelength of an electron that has been accelerated through a potential difference of 100 V?

A) 0.123 nm ✔
B) 0.123 Angstrom
C) 1.23×10^{-11} cm
D) none of the above

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.