

**GS-2013 (Chemistry)**

**TATA INSTITUTE OF FUNDAMENTAL RESEARCH**

Written Test in **CHEMISTRY - December 9, 2012**

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 =  $6.02 \times 10^{23} \text{ mol}^{-1}$

$RT/F = 0.0257 \text{ V}$  at  $25^\circ\text{C}$

Faraday constant =  $96500 \text{ C/mol}$

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

Standard reduction potential of  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$  is  $-1.66 \text{ V}$  at  $25^\circ\text{C}$

Standard reduction potential of  $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$  is  $-0.44 \text{ V}$  at  $25^\circ\text{C}$

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

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

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

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

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1. Which of the following will be strongest acid in pure liquid HF:

- A)  $\text{H}_2\text{O}$
- B)  $\text{SbF}_5$  ✓
- C)  $\text{CH}_3\text{COOH}$
- D)  $\text{NaF}$

2. Which of the following experimental observations best demonstrates the wavelike character of electrons?

- A) The photoelectric effect
- B) The flow of electrons in a metal wire
- C) The diffraction pattern of electrons scattered from a crystalline solid ✓
- D) The deflection of an electron beam by electrical plates

3. What terms can arise from the configuration  $2p^1 3p^1$ ?

- A)  $^3\text{D}, ^1\text{D}, ^3\text{P}, ^1\text{P}, ^3\text{S}, ^1\text{S}$  ✓
- B)  $^3\text{D}, ^3\text{P}, ^3\text{S}$
- C)  $^1\text{D}, ^1\text{P}, ^1\text{S}$
- D)  $^1\text{D}, ^3\text{P}, ^3\text{S}$

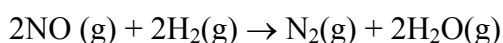
4. What is the degeneracy of the energy level with  $n=6$  ( $n$  being the principal quantum number) in a hydrogenic atom or ion?

- A) 16
- B) 9
- C) 36 ✓
- D) 25

5. Compare the equilibrium bond lengths of AB-type of diatomic molecules  $N_2$ ,  $NO$ ,  $O_2$ ,  $Cl_2$  and  $CN$  with their cations ( $AB^+$ ) and anions ( $AB^-$ ). Which of the following statements is correct in general?

- A) The equilibrium bond lengths of all  $AB^+$  species will be shorter, and that of all  $AB^-$  species will be longer than that of the corresponding AB species.
- B) The equilibrium bond lengths of all  $AB^-$  species will be shorter, and that of all  $AB^+$  species will be longer than that of the corresponding AB species.
- C) The equilibrium bond lengths of  $O_2^+$ ,  $Cl_2^+$  and  $CN^-$  ions will be shorter than the corresponding neutral species. The equilibrium bond lengths of  $N_2^+$ ,  $NO^+$  and  $Cl_2^-$  ions will be longer than the corresponding neutral species. ✓
- D) The equilibrium bond lengths of  $O_2^+$ ,  $Cl_2^+$  and  $CN^-$  ions will be longer than the corresponding neutral species. The equilibrium bond lengths of  $N_2^+$ ,  $NO^+$  and  $Cl_2^-$  ions will be shorter than the corresponding neutral species.

6. The method of initial rates is used to determine the rate law for the reaction given below.



The following initial rates were determined at the given partial pressures ( $p$ ) of reactants.

$p_{NO}(\text{mmHg})$	$p_{H_2}(\text{mmHg})$	Initial rate (M/min)
200	400	0.46
400	200	0.92
400	400	1.85

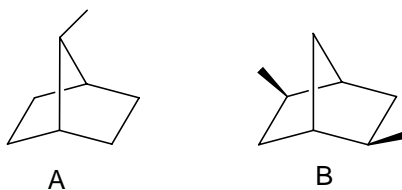
These data imply which of the following rate laws?

- A) rate =  $k p_{NO} p_{H_2}$
- B) rate =  $k p_{NO} p_{H_2}^2$
- C) rate =  $k p_{NO}^2 p_{H_2}$  ✓
- D) rate =  $k p_{NO}^2 p_{H_2}^2$

7. Which of the following molecular species are expected to be paramagnetic?  $O_2^+$ ,  $O_2^-$  and  $O_2^{2-}$  ?

- A) All of them
- B) Only  $O_2^+$  and  $O_2^-$  ✓
- C) Only  $O_2^+$  and  $O_2^{2-}$
- D) Only  $O_2^-$  and  $O_2^{2-}$

8. What are the elements of symmetry present in the following molecules and which of them is chiral?

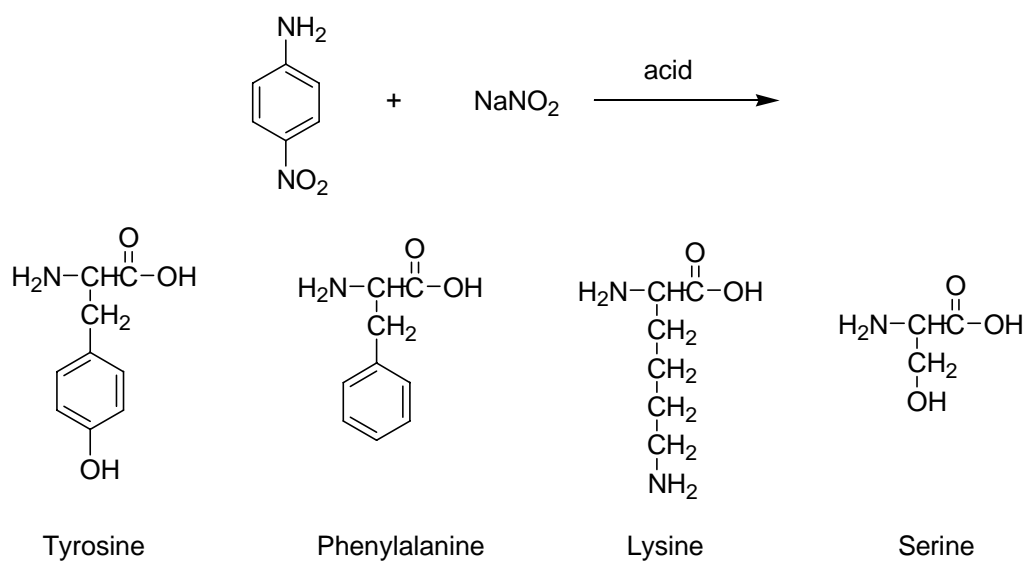


- A) A has a 2-fold rotation axis and B has a plane of symmetry; A is chiral  
 B) A has a plane of symmetry and B has a centre of inversion; B is chiral  
 C) A has a plane of symmetry and B has a 2-fold rotation axis; A is chiral  
 D) A has a plane of symmetry and B has a 2-fold rotation axis; B is chiral ✓

9. The speed of a reaction that involves an enzyme increases as

- A) Temperature decreases  
 B) pH becomes less than optimal  
 C) Substrate concentration increases ✓  
 D) All of the above

10. The product of the following reaction will be able to couple with which amino acids?

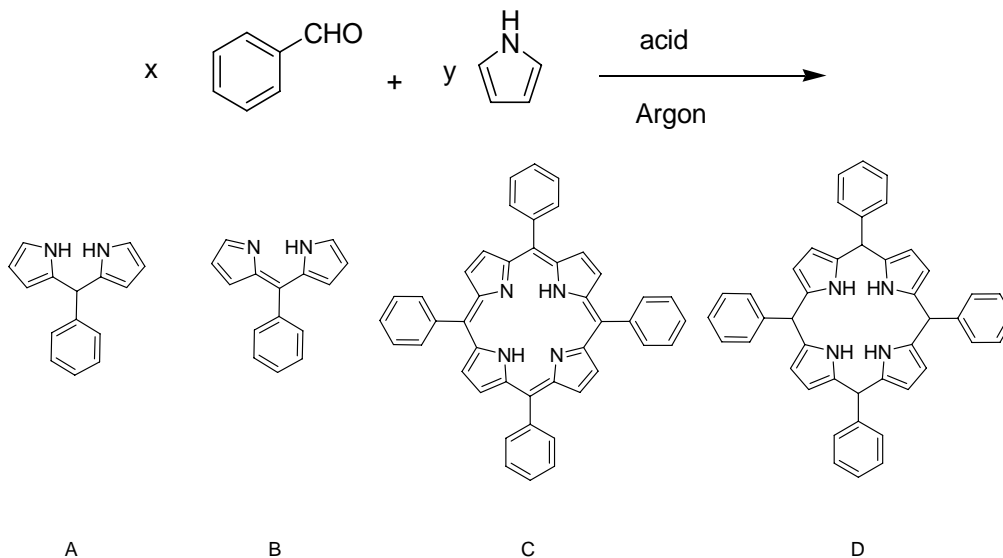


- A) Tyrosine and Phenylalanine ✓  
 B) Tyrosine and Serine  
 C) Lysine and Serine  
 D) Phenylalanine and Lysine

11. If the CO stretching frequency of  $\text{Ni}(\text{CO})_3(\text{P}(\text{OMe})_3)$  is  $A$ , and that of  $\text{Ni}(\text{CO})_2(\text{PMe}_3)_2$  is  $B$ , then

- A)  $A > B$  ✓
- B)  $A = B$
- C)  $A < B$
- D) None

12. Predict the products of the following condensation reaction where  $y : x$  could be either 1 or 2:



- A) A and D
- B) A and B ✓
- C) C and D
- D) C and B

13. The Friedel-Crafts reactions are common in organic chemistry. Which of the following is expected to be a better catalyst?

- A)  $\text{AlBr}_3$
- B)  $\text{AlI}_3$
- C)  $\text{AlCl}_3$  ✓
- D)  $\text{MgCl}_2$

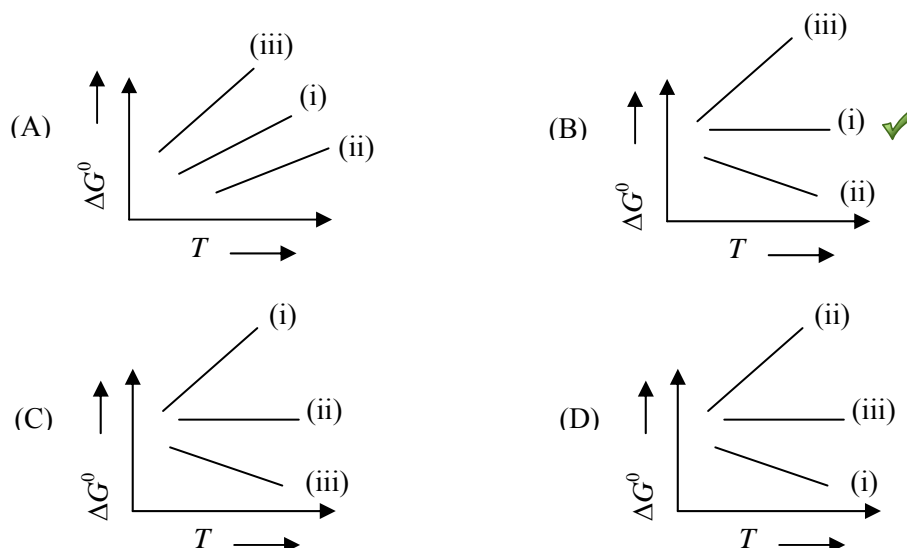
14. Which of the following statements is always true regarding conductors and semi-conductors?

- A) Semi-conductors are half as good as conductors when comparing their electron mobility.
- B) Conductors have large band gaps and semi-conductors have small band gaps.
- C) Conductors and semi-conductors do not conduct electricity at high temperatures.
- D) None of the above statements are true. ✓

15. The standard Gibbs free energies of the following reactions,  $\Delta G^0$ , have been determined at various temperatures.

- (i)  $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$
- (ii)  $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$
- (iii)  $\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$

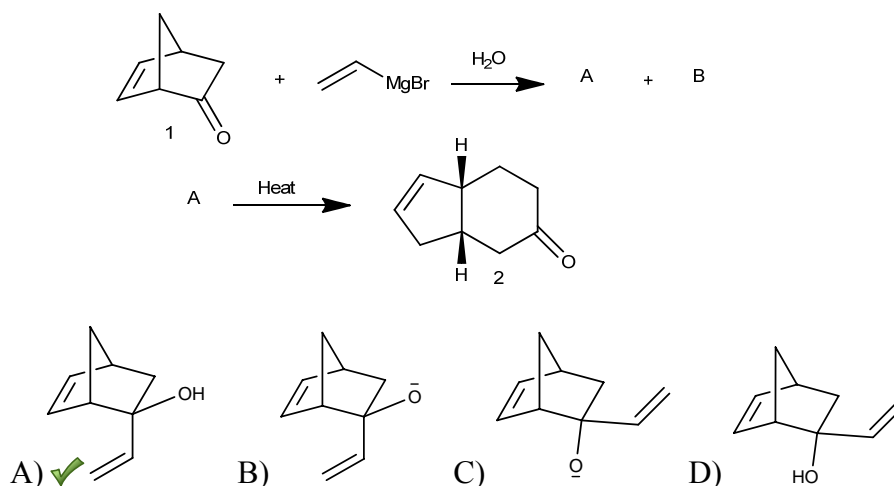
Which of the following plots would represent most likely the temperature dependence of  $\Delta G^0$ ?



16. 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

17. Compound 1 reacts with vinyl Grignard reagent to give two compounds A and B after hydrolysis. A gives compound 2 upon heating. Predict the structure of A.



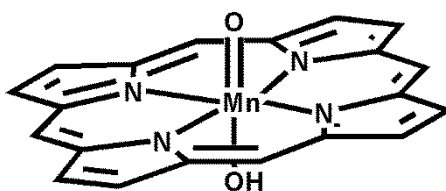
18. Point of group of 1,2-propadiene is

- A)  $C_{2h}$
- B)  $C_{2v}$
- C)  $D_{2h}$
- D)  $D_{2d}$  ✓

19. Which of the following statements is true regarding amphiphilic molecules?

- A) An amphiphilic molecule consists of both a positive charge and a negative charge.
- B) Amphiphilic molecules show spontaneous aggregation behaviour in any solvent and at all concentrations.
- C) Amphiphilic molecules are insoluble in water.
- D) Amphiphilic molecules are known to form liquid crystals. ✓

20. Using crystal field theory, determine the type of d-orbital(s) which will have the lowest energy in the complex shown below. Based on the above, determine the comparative rates of reduction of the Mn(V) to Mn(IV) *versus* Mn(IV) to Mn(III) states.



- A) ( $d_{xy}$ ); Mn(V) to Mn(IV) is slower than Mn(IV) to Mn(III) ✓
- B) ( $d_{xy}, d_{yz}, d_{zx}$ ); Mn(V) to Mn(IV) is slower than Mn(IV) to Mn(III)
- C) ( $d_{z^2}, d_{x^2-y^2}$ ); Mn(V) to Mn(IV) is faster than Mn(IV) to Mn(III)
- D) ( $d_{xy}$ ); Mn(V) to Mn(IV) is faster than Mn(IV) to Mn(III)

21. Which statement is true of the ground state of the  $Co^{2+}$  ion?

- A) The number of unpaired electrons is 0 and the  $Co^{2+}$  ion is paramagnetic.
- B) The number of unpaired electrons is 0 and the  $Co^{2+}$  ion is *not* paramagnetic.
- C) The number of unpaired electrons is 3 and the  $Co^{2+}$  ion is paramagnetic. ✓
- D) The number of unpaired electrons is 3 and the  $Co^{2+}$  ion is *not* paramagnetic.

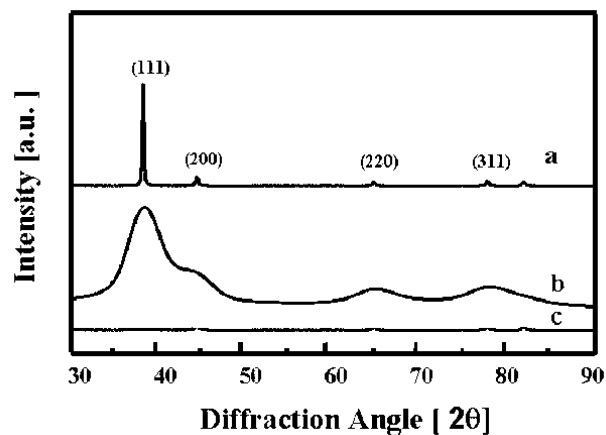
22. How many molecules of cetanol (of cross-sectional area  $2.58 \times 10^{-19} \text{ m}^2$ ) can be adsorbed on the surface of a spherical drop of dodecane of diameter 35.6 nm?

- A)  $6.16 \times 10^4$
- B)  $1.23 \times 10^3$
- C)  $1.54 \times 10^4$  ✓
- D)  $4.90 \times 10^3$

23. In a chemistry lab, the aim of an experiment was to generate well structured, 5nm sized gold nanoparticles. A student experimented with the following synthesis:

*1-nonanethiol ( $C_9H_{19}SH$ ) and  $HAuCl_4$  were first mixed (in a molar ratio of 10:1), and then gold ions were reduced by slowly adding  $NaBH_4$ . In this synthesis, after 2 hours no precipitate was observed and only a very faint pink colloidal solution was obtained. This solution was then evaporated onto a glass slide and the sample characterized by X-ray diffraction.*

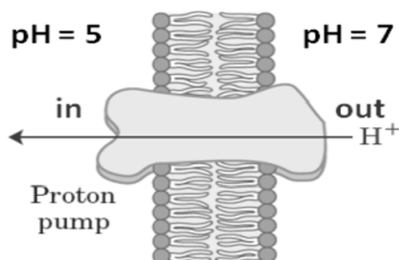
Given below are three XRD patterns. One out of these three patterns was obtained by the student when he/she characterized the sample on the glass slides. Which statement below is true?



- A) The synthesis did not yield gold nanoparticles as there was no precipitate. Therefore, the XRD pattern that will be obtained is that shown as curve (c) – It is almost a flat baseline indicating no product.
- B) 5 nm gold nanoparticles were formed and XRD pattern shown as (a) represents the product. It signifies that the nanoparticles are crystalline and the face-centered cubic (fcc) crystal structure can be clearly used to index the peaks.
- C) 5 nm gold nanoparticles will show size-dependent line broadening and therefore if the product consisted of such particles, then curve (b) will be obtained. ✓
- D) None of the above statements are true.
24. Consider a classical harmonic oscillator with a mass  $m$  and a force constant  $k$  oscillating with a frequency  $\nu$ . Which of the following statements is NOT true for this system?
- A)  $\nu$  increases if  $m$  decreases.
- B) The oscillator is most likely to be found at its equilibrium position. ✓
- C) The acceleration is maximum at its turning points.
- D)  $\nu$  does not depend on how large the amplitude of the oscillation is.

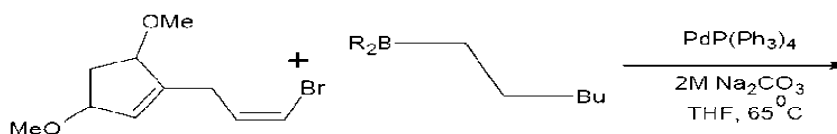


25. Photosynthesis is a process by which light energy gets funnelled into creating chemical potential for generation of proton gradients across membranes. Suppose photosynthesis is only 0.5% efficient in creating such gradients, calculate how many 530 nm photons will be required to create a pH gradient (per mole) as shown below across a cellular membrane under ambient temperature of 300 K?



- A) 1000 photons
- B)  $10^{10}$  photons
- C) 10 photons ✓
- D)  $6 \times 10^{23}$  photons

26. What is the result of the following reaction?

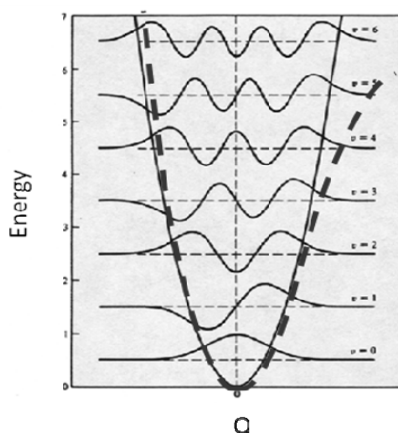


- A)
- B)
- C) Reaction is unfavourable under given reagents
- D) A and B both are plausible ✓

27. What are the limits of detection of the following common analytical methods used with capillary separations: fluorescence, mass spectrometry, UV-vis absorbance, and NMR, respectively, in mol?

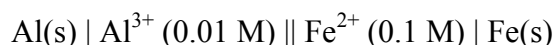
- A)  $10^{-18}$ - $10^{-23}$ ,  $10^{-13}$ - $10^{-21}$ ,  $10^{-13}$ - $10^{-16}$ ,  $10^{-9}$ - $10^{-11}$  ✓
- B)  $10^{-13}$ - $10^{-21}$ ,  $10^{-18}$ - $10^{-23}$ ,  $10^{-13}$ - $10^{-16}$ ,  $10^{-9}$ - $10^{-11}$
- C)  $10^{-18}$ - $10^{-23}$ ,  $10^{-13}$ - $10^{-21}$ ,  $10^{-9}$ - $10^{-11}$ ,  $10^{-13}$ - $10^{-16}$
- D)  $10^{-13}$ - $10^{-21}$ ,  $10^{-13}$ - $10^{-16}$ ,  $10^{-18}$ - $10^{-23}$ ,  $10^{-9}$ - $10^{-11}$

28. Shown below in solid-line is the harmonic potential of a quantum oscillator for a diatomic molecule. If the harmonic potential is suddenly transformed into Morse potential shown in dashed-line how would the zero point energy and shape of wavefunctions change?



- A) Zero-point energy remains the same and wavefunctions do not change.
- B) Zero-point energy remains the same but wavefunction reflects a change on the high Q side.
- C) Zero-point energy changes and wavefunction reflects a change on the high Q side.
- D) Potentials never reflect any change in the shape of the wavefunction ✓

29. The cell potential for the following electrochemical system at 25 °C is:



- A) 1.23 V ✓
- B) 1.21 V
- C) 1.22 V
- D) -2.10 V

30. Given three systems, A, B, and C, what could be they if the spacing between the neighbouring energy levels in A decreases with increasing energy, while that for B is constant, and that for C increases with increasing energy?

- A) A= particle in a one-dimensional box, B= harmonic oscillator, C=electron in hydrogen atom
- B) A= electron in hydrogen atom, B= harmonic oscillator, C= particle in a one-dimensional box ✓
- C) A= particle in a one-dimensional box, B= electron in hydrogen atom, C= harmonic oscillator
- D) A= electron in hydrogen atom, B= particle in a one-dimensional box, C= harmonic oscillator

31. Sodium metal crystallizes in a cubic unit cell. From X-ray diffraction, the unit cell parameter was determined to be  $4.29 \text{ \AA}$ . If the density of the element is known to be  $0.968 \text{ g/cm}^3$ , how many atoms are present in each unit cell?

- A) Not enough information is given to calculate the value.
- B) 1
- C) 2 ✓
- D) 3

32. Electrospray ionization mass spectroscopy produces multiply charged ions of proteins. On application of this technique to hemeprotein it gave a large number of peaks corresponding to different charge-states of the protein. The three consecutive peaks are observed at the  $m/z$  values:

2061, 1767, 1546

The approximate  $m/z$  value of the consecutive fourth peak in the series would be:

- A) 1252
- B) 1374 ✓
- C) 1498
- D) 1325

33.  $A$  is a  $5 \times 5$  matrix with elements  $a_{ij} = a_{ji}$ . Its eigenvalues are  $0, \pm 1$  and  $\pm 2$ . Which of the following statements best describes the properties of the matrix  $A$ ?

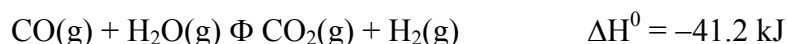
- A)  $A$  can be diagonalized by a unitary transformation.
- B)  $A$  can be diagonalized by an orthogonal transformation.
- C)  $A$  cannot be inverted.
- D) All of the above. ✓

34. Real gases behave differently from ideal gases because:

- (i) the molecules of real gases are in constant motion.
- (ii) molecules of real gases collide with the walls of the container.
- (iii) molecules of real gases have volume.
- (iv) molecules of real gases attract each other.

- A) i and ii
- B) iii only
- C) iii and iv ✓
- D) all of the above

35. The following reaction, conducted in a vessel of capacity 10 litre, has reached equilibrium at 330 K.



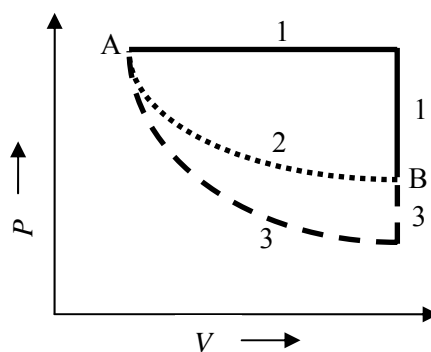
The temperature of the vessel is then increased to 350 K. Which of the following statement is correct before the reaction reaches a new equilibrium at this elevated temperature?

- A) The rate constant of the forward reaction will decrease, and the rate constant of the reverse reaction will increase.
- B) Concentrations of all the species will increase, but increase will be more for the reactants than that for the products.
- C) Both A and B.
- D) None of the above. ✓

36. Global warming is due to increase of

- A) Methane in atmosphere
- B) CO<sub>2</sub> in atmosphere
- C) Water vapour
- D) Methane and CO<sub>2</sub> ✓

37. The state of 2 moles of an ideal gas is changed from the point A to the point B along three different paths, as shown in the following *P-V* diagram. If the change of entropy of the gas in changing its state from state A to B along the path *i* is denoted  $\Delta S_i$ , then which of the following statements is correct?

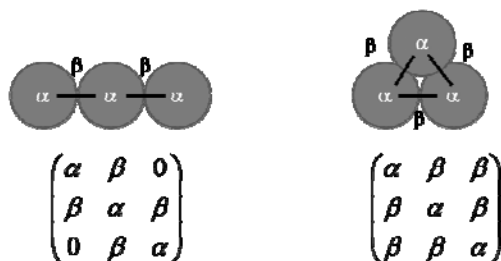


- A)  $\Delta S_1 > \Delta S_2 > \Delta S_3$
- B)  $\Delta S_1 < \Delta S_2 < \Delta S_3$
- C)  $\Delta S_1 \neq \Delta S_2 \neq \Delta S_3$
- D)  $\Delta S_1 = \Delta S_2 = \Delta S_3$  ✓

38. A reaction has a negative (and approximately temperature independent) enthalpy change. It does not proceed spontaneously at room temperature (25 °C). At which of the following temperatures is the reaction more likely to become spontaneous?

- A) -50 °C ✓
- B) 50 °C
- C) 100 °C
- D) 1000 °C

39. In a Hückel tight binding representation with a single orbital per site and nearest neighbour interactions between sites, the Hamiltonian for a cluster of three Na atoms in linear and triangular forms is written as:



Assuming the nearest neighbour coupling  $\beta < 0$ , which form (linear or triangular) of the cluster is more probable for neutral  $\text{Na}_3$  and for the anion  $\text{Na}_3^-$ ?

- A) Linear for  $\text{Na}_3$  and triangular for  $\text{Na}_3^-$
- B) Linear for both
- C) Triangular for  $\text{Na}_3$  and linear for  $\text{Na}_3^-$  ✓
- D) Triangular for both

40. The  $^1\text{H}$  NMR spectrum of a compound with molecular formula  $\text{C}_3\text{H}_7\text{NO}$  shows the following features:

Chemical shift (ppm)	6.50	2.25	1.10
Shape	broad singlet	quartet	triplet

Which of the following is in agreement with this information?

- A)  $(\text{CH}_3)_2\text{C}=\text{NOH}$
- B)  $\text{CH}_3\text{COCH}_2\text{NH}_2$
- C)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  ✓
- D)  $\text{HCON}(\text{CH}_3)_2$

**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.