

IIT-JEE-Chemistry–1999

Time : 3 hours

Max. Marks : 200

GENERAL INSTRUCTIONS

1. Do not break the seal of the question paper before you are instructed to do so by the invigilator.
2. This question paper is in two sections. Section I has 35 objective type question. Section II has 12 regular questions.
3. Answer Section I only on the special machine-gradable OBJECTIVE RESPONSE SHEET (ORS) that is inserted in this booklet. Questions of Section I will not be graded if answered anywhere else.
4. Answer problems of Section II in the answer book.
5. Without breaking the seal of this booklet, take out the Response Sheet (ORS) for section I. Make sure that the ORS has the SAME QUESTION PAPER CODE printed on it as on the top of this page.
6. Write your name, registration number and name of the Centre at the specified locations on the right half of the ORS for Section I.
7. Using a soft HB pencil, darken the appropriate bubble under each digit of your registration number.
8. The Objective Response Sheet will be collected back after 75 minutes have expired from the start of the examination. In case you finish Section I before the expiry of 75 minutes, you may start answering Section II.

INSTRUCTIONS FOR SECTION I

1. Question are to be answered by darkening with a soft HB pencil the appropriate bubble (marked A, B, C or D) against the question number on the left hand side of the Objective Response Sheet.
2. In case you wish to change an answer, erase the of answer completely using a good soft eraser.
3. The answer sheet will be collected back after 75 minutes from the start of the examination.
4. There is no negative marking.
5. Question numbers 1-25 carry 2 marks each and have only one correct answer.
6. Question numbers 26-35 carry 3 marks each, and may have more than one correct answers. All the correct answers must be marked in these questions to any credit.

IMPORTANT INFORMATION

Logarithmic tables can be used.

Use of calculator is not allowed.

Useful data :

Gas constant, $R = 0.082 \text{ L atm K}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$

1 Faraday constant = $96.500 \text{ C mol}^{-1}$

Avagadro number, $N_A = 6.02 \times 10^{23}$

Atomic number : Ni = 28

Relative atomic mass : H = 1;

Cl = 35.5; Cr = 52; Cu = 63.5; Xe = 131

SECTION I

DIRECTIONS: Select the most appropriate alternative A, B, C or D in questions 1-25.

1. The electrons, identified by quantum numbers n and l , (i) $n = 4, l = 1$, (ii) $n = 4, l = 0$, (iii) $n = 3, l = 2$, and (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest, as:

(A) (iv) < (ii) < (iii) < (i)

(B) (ii) < (iv) < (i) < (iii)

(C) (i) < (iii) < (ii) < (iv)

(D) (iii) < (i) < (iv) < (ii)

2. The number of neutrons accompanying the formation of $^{139}\text{Xe}_{54}$ and $^{94}\text{Sr}_{38}$ from the absorption of a slow neutron by $^{235}\text{U}_{92}$, followed by nuclear fission is :

(A) 0

(B) 2

(C) 1

(D) 3

3. The correct order of increasing C–O bond length of CO, CO_2 , CO_3^{2-} is :

(A) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$

(B) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$

(C) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$

(D) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$

4. A gas will approach ideal behaviour at :

(A) low temperature and low pressure

(B) low temperature and high pressure

(C) high temperature and low pressure

(D) high temperature and high pressure

5. The normality of 0.3 M phosphorus acid (H_3PO_3) is

(A) 0.1

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- (C) 0.3
- (D) 0.6

6. The coordination number of a metal crystallizing in a hexagonal close-packed structure is :

- (A) 12
- (B) 4
- (C) 8
- (D) 6

7. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of $Z < Y > X$, then :

- (A) Y will oxidize X and not Z
- (B) Y will oxidize Z and not X
- (C) Y will oxidize both X and Z
- (D) Y will reduce both X and Z

8. The pH of 0.1 M solution of the following salts increases in the order :

- (A) $NaCl < NH_4Cl < NaCN < HCl$
- (B) $HCl < NH_4Cl < NaCl < NaCN$
- (C) $NaCN < NH_4Cl < NaCl < HCl$
- (D) $HCl < NaCl < NaCN < NH_4Cl$

9. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X , Y at equilibrium is affected by :

- (A) temperature and pressure
- (B) temperature only
- (C) pressure only
- (D) temperature, pressure and catalyst

10. In the dichromate dianion :

- (A) 4 Cr—O bonds are equivalent
- (B) 6 Cr—O bonds are equivalent
- (C) all Cr—O bonds are equivalent
- (D) all Cr—O bonds are nonequivalent

11. One mole of calcium phosphide on reaction with excess water gives :

- (A) one mole of phosphine
- (B) two moles of phosphoric acid
- (C) two moles of phosphine
- (D) one mole of phosphorus pentoxide

12. The oxidation number of sulphur in S_8 , S_2F_2 , H_2S respectively, are :

- (A) 0, +1 and -2
- (B) +2, +1 and -2
- (C) 0, +1 and +2

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13. On heating ammonium dichromate, the gas evolved is:

- (A) oxygen
- (B) ammonia
- (C) nitrous oxide
- (D) nitrogen

14. In the commercial electrochemical process for aluminium extraction, the electrolyte used is :

- (A) $\text{Al}(\text{OH})_3$ in NaOH solution
- (B) an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$
- (C) a molten mixture of Al_2O_3 and Na_3AlF_6
- (D) a molten mixture of $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$

15. The geometry of H_2S and its dipole moment are :

- (A) angular and non-zero
- (B) angular and zero
- (C) linear and non-zero
- (D) linear and zero

16. The geometry of $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ are:

- (A) both square planar
- (B) both tetrahedral and square planar, respectively
- (C) both tetrahedral
- (D) square planar and tetrahedral, respectively

17. In compounds of type ECl_3 , where E = B, P, As or Bi, the angles Cl-E-Cl

- (A) $\text{B} > \text{P} = \text{As} = \text{Bi}$
- (B) $\text{B} > \text{P} > \text{As} > \text{Bi}$
- (C) $\text{B} < \text{P} = \text{As} = \text{Bi}$
- (D) $\text{B} < \text{P} < \text{As} < \text{Bi}$

18. In the compound $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH}_2-\text{C} \equiv \text{CH}$, the $\text{C}_2 = \text{C}_3$ bonds is of

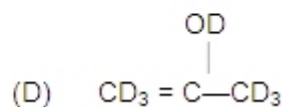
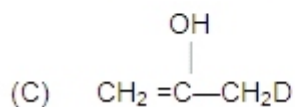
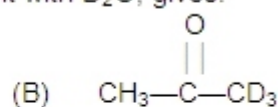
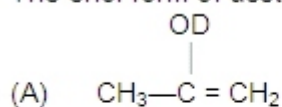
- (A) $\text{sp} - \text{sp}^2$
- (B) $\text{sp}^2 - \text{sp}^3$
- (C) $\text{sp} - \text{sp}^3$
- (D) $\text{sp}^2 - \text{sp}^3$

19. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated the 'C' of CO_2 comes from :

- (A) methyl group
- (B) carboxylic acid group
- (C) methylene group
- (D) bicarbonate

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20. The enol form of acetone, after treatment with D_2O , gives:



21. A positive carbylamines test is given by :

- (A) N, N-dimethylaniline
- (B) 2, 4-dimethylaniline
- (C) N-methyl-o-methylaniline
- (D) p-methylbenzylamine

22. The optically active tartaric acid is named as D – (+) – tartaric acid because it has a positive :

- (A) optical rotation and is derived from D-glucose
- (B) pH in organic solvent
- (C) optical rotation and is derived from D – (+) – glyceraldehyde
- (D) optical rotation only when substituted by deuterium

23. A solution of (+) –2–chloro–2–phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of:

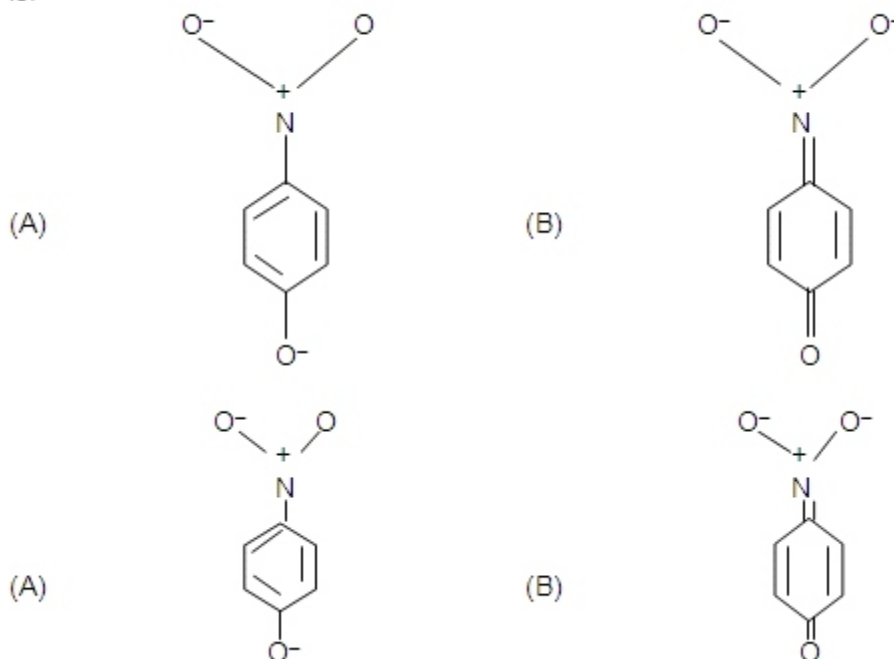
- (A) carbanion
- (B) carbene
- (C) free-radical
- (D) carbocation

24. The product(s) obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be :

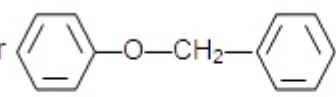
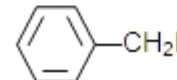
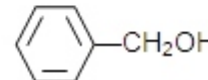
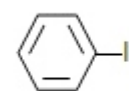
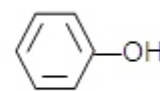
- (A) $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_3 \end{array}$
- (B) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$
- (C) $\text{CH}_3-\text{CH}_2-\text{CHO} + \text{HCHO}$
- (D) $\text{CH}_3-\text{CH}_2-\text{COOH} + \text{HCOOH}$

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25. the most unlikely representation of resonance structures of p-nitrophenoxide ion is:



DIRECTIONS: Question numbers 26-35 carry 3 marks each and may have more than one correct answer. All correct answers must be marked to get any credit in these questions.

26. The ether  when treated with HI produces:
- (A)  (B) 
- (C)  (D) 

27. Toluene, when treated with Br_2/Fe , gives p-bromotoluene as the major product because the CH_3 group :

- (A) is para directing
 (B) is meta directing
 (C) activates the ring by hyperconjugation
 (D) deactivates the ring

28. The following statement(s) is(are) correct :

- (A) A plot of $\log K_p$ versus $1/T$ is linear
 (B) A plot of $\log [X]$ versus time is linear for a first order reaction, $X \rightarrow P$





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(D) A plot of p versus $1/V$ is linear at constant temperature

29. The following is(are) endothermic reaction(s) :

- (A) Combustion of methane
- (B) Decomposition of water
- (C) Dehydrogenation of ethane to ethylene
- (D) Conversion of graphite to diamond.

30. Ground state electronic configuration of nitrogen atom can be represented by:

- (A)  (B) 
- (C)  (D) 

31. In the depression of freezing point experiment, it is found that the:

- (A) vapour pressure of the solution is less than that of pure solvent
- (B) vapour pressure of the solution is more than that of pure solvent
- (C) only solute molecules solidify at the freezing point
- (D) only solvent molecules solidify at the freezing point

32. Ionic radii of :

- (A) $Ti^{3+} < Mn^{2+}$
- (B) $^{35}Cl^- < ^{37}Cl^-$
- (C) $K^+ > Cl^-$
- (D) $P^{3+} > P^{5+}$

33. Ammonia, on reaction with hypochlorite anion, can form:

- (A) NO
- (B) NH_4Cl
- (C) N_2H_4
- (D) HNO_2

34. A buffer solution can be prepared from a mixture of :

- (A) sodium acetate and acetic acid in water
- (B) sodium acetate and hydrochloric acid in water
- (C) ammonia and ammonium chloride in water
- (D) ammonia and sodium hydroxide in water

35. Αν αρωματιχη μολεχυλε ωιλλ :

- (A) ηαπε $4n$ π electrons
- (B) have $(4n + 2)$ π electrons
- (C) be planar
- (D) be cyclic

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SECTION II

INSTRUCTIONS

- (i) There are 12 questions in this section.
- (ii) At the end of the answer to a question, leave about 3 cm blank space, draw a horizontal line and start answer to the next question. The corresponding question number must be written in the left margin. Answer all parts of a question at one place only.
- (iii) The use of Arabic numerals (0, 1, 2,9) only is allowed in answering the question at one place only.

1. (a) A white solid is either Na_2O or Na_2O_2 . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.

(i) Identify the substance and explain with balanced equation.

(ii) Explain what would happen to the red litmus if the white solid were the other compound.

(b) A, B and C are three complexes of chromium (III) with the empirical formula $\text{H}_2\text{O}_6\text{Cl}_3\text{Cr}$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H_2SO_4 , whereas complexed B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4 . Identify A, B and C.

2. (a) An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl . Explain with equations.

(b) How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate?

(c) Give reasons for the following in one or two sentences only.

(i) BeCl_2 can be easily hydrolysed.

(ii) CrO_3 is an acid anhydride.

3. (a) In the following equation,

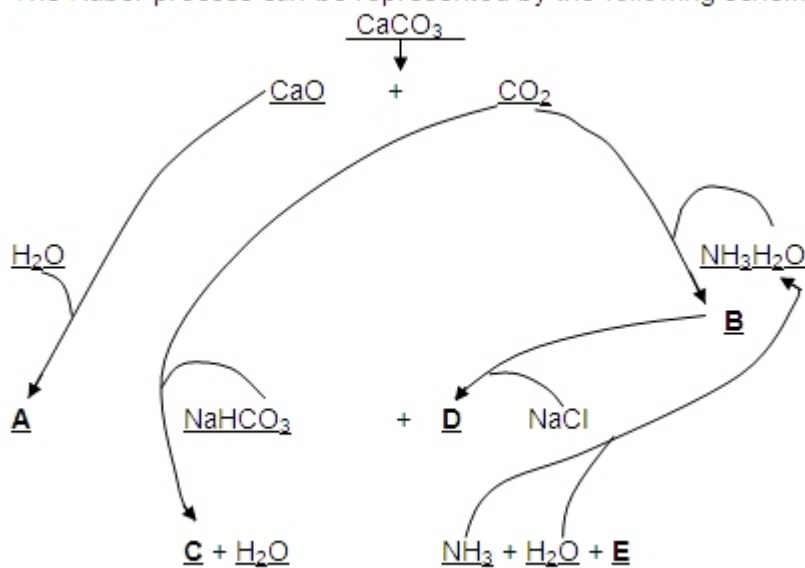


(A = HNO_2 , B = H_2SO_3 , C = NH_2OH). Identify D. Draw the structures of A, B, C and D.

(b) In the Contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2 ?

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4. (a) The Haber process can be represented by the following scheme :



Identify A, B, C, D and E.

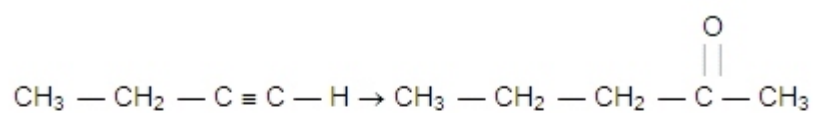
(b) Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the π -orbital overlaps.

(c) Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

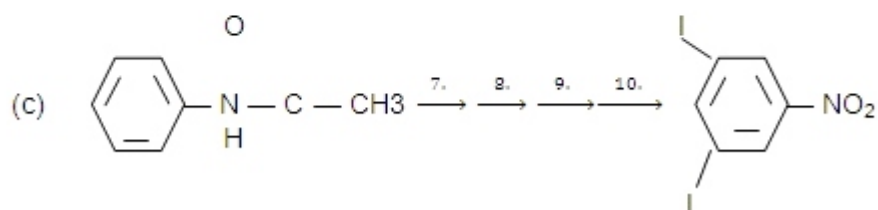
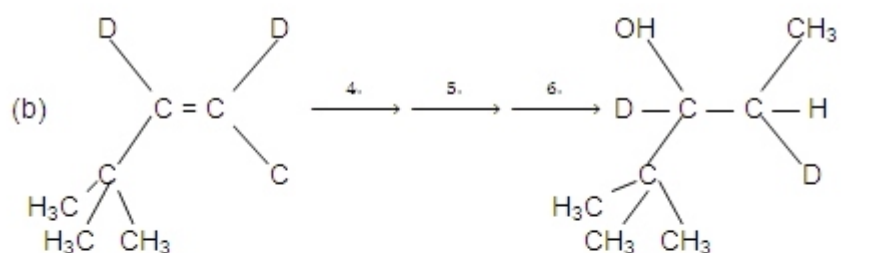
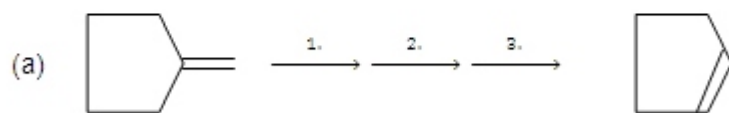
5. (a) Compound A ($\text{C}_8\text{H}_8\text{O}$) on treatment with NH_2OH , HCl gives B and C. B and C rearrange to give D and E, respectively, on treatment with acid. B, C, D and E are all isomers of molecular formula ($\text{C}_8\text{H}_9\text{NO}$). When D is boiled with alcoholic KOH, an oil F ($\text{C}_6\text{H}_7\text{N}$) separates out. F reacts rapidly with CH_3COCl to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid G ($\text{C}_7\text{H}_6\text{O}_2$). Identify A-G.

(b) Carry out the following transformation in not more than three steps.

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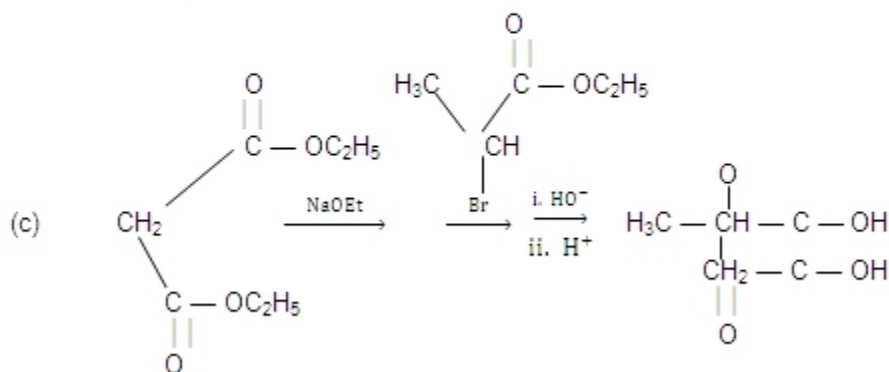
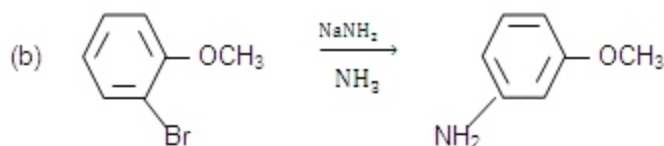
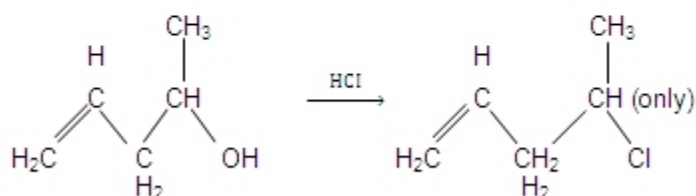
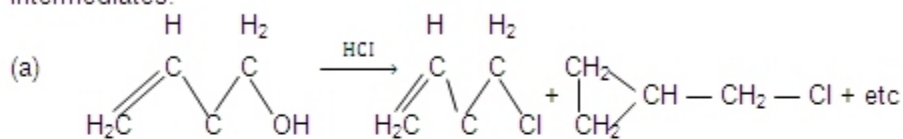
6. Complete the following reactions with appropriate reagents.



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7. Explain briefly the formation of the products giving the structures of the intermediates.



8. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67%, and oxygen : 38.07%,
 (i) Calculate the empirical formula of the minor product.

- (ii) When 5.5 g of the minor product is dissolved in 45g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product is dissolved in 45g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product the determine its molecular and structural formula.
 (Molal boiling point elevation constant of benzene is 2.53 K kg mol⁻¹.)

9. (a) A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm³/g. If the virus is considered to be a single particle, find its molar mass.

- (b) When 3.06 g of solid NH₄HS is introduced into a two-litre evacuated flask at 27°C,

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30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate K_c and K_p for the reaction at 27°C .

(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

10.(a) One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57s to diffuse through the same hole. Calculate the molecular formula of the compound.

(b) The pressure exerted by 12 g of an ideal gas at temperature $t^\circ\text{C}$ in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V . (Molecular weight of the gas = 120)

11.(a) A cell, $\text{Ag} | \text{Ag}^+ || \text{Cu}^{2+} | \text{Cu}$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions.

Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h.

(b) The solubility of $\text{Pb}(\text{OH})_2$ in water is 6.7×10^{-6} M. Calculate the solubility of Pb

$(\text{OH})_2$ in a buffer solution of pH = 8.

12.(a) Estimate the average S–F bond energy in SF_6 . The values of standard enthalpy of formation of $\text{SF}_6(\text{g})$, $\text{S}(\text{g})$ and $\text{F}(\text{g})$ are : 1100, 275 and 80 kJ mol^{-1} respectively.

(b) The rate constant for an isomerisation reaction, $\text{A} \rightarrow \text{B}$ is $4.5 \times 10^{-3} \text{ min}^{-1}$. If the

initial concentration of A is 1 M, calculate the rate of the reaction after 1 h.

(c) A metal crystallizes into two cubic phases, face centered cubic (FCC) and body centered cubic (BCC), whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of FCC and BCC.