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[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 6483

HC

Unique Paper Code : 32171301

Name of the Paper : Inorganic Chemistry – II

Name of the Course : B.Sc. (Hons.) Chemistry

Semester : III

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **any five** questions.
3. **All** questions carry equal marks.

1. (a) Carbon is a better reducing agent below 710°C while carbon monoxide is better reducing agent above 710°C . Explain using Ellingham diagram.

(b) What is inert pair effect? How does it vary down the group? Give reason with suitable example.

(c) Why peroxyacids of sulphur are powerful oxidizing agents? What is the oxidation state of sulphur in Caro's and Marshall's acid?

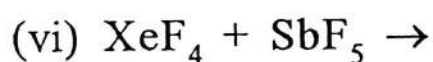
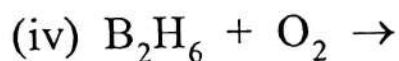
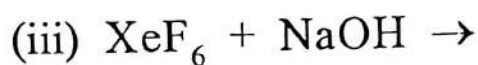
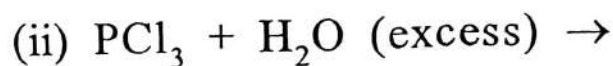
P.T.O.

- (d) Arrange the following in increasing order of solubility. Give reason for the same.

LiF, KF, NaF, CsF, RbF (5,4,3,3)

2. (a) What is vapour phase refining? Give details of Mond's process and van Arkel de Boer process.
- (b) Give the product formed when borazene reacts with water. Justify your answer.
- (c) Give the geometry and shapes of the following on the basis of valence bond theory :
ICl₃, XeF₆, PCl₅
- (d) Why do salts of Mg and Be not impart flame coloration?
(5,3,4½,2½)
3. (a) Discuss the structure of basic beryllium acetate.
- (b) How does the thermal stability of alkaline earth metal carbonates vary down the group? Give reason.
- (c) CO₂ is a gas whereas SiO₂ is a high melting solid. Explain.
- (d) Dilute solution of alkali metals in liquid ammonia behave as strong reducing agent. Explain.
- (e) Arrange the alkali metals in increasing order of electrical conductivity in aqueous solution. Give reason for the same. (3×5)

4. (a) What happens when SO₂ reacts with acidified K₂Cr₂O₇ solution? Give chemical reactions involved.
- (b) Graphite is a good conductor of electricity while diamond is not. Give reason.
- (c) Which is more reactive: White phosphorous or red phosphorous. Why?
- (d) Out of the two which will behave as a reducing agent: Phosphorous acid or phosphoric acid. Why?
- (e) SnCl₂ behaves as a strong reducing agent. (3×5)
5. (a) Arrange the following in increasing order of acidic strength. Give reason.
HOCl, HClO₃, HClO₄, HClO₂
- (b) Silver and mercury can be obtained from their oxides simply by heating at low temperature. Explain with the help of Ellingham diagram.
- (c) AgCN is insoluble in water but soluble in ammonia. Give reason.
- (d) Complete and balance **any five** of the following equations :
- (i) H₃PO₂ + HgCl₂ + H₂O →



6. Give reason(s) for the following :

(a) Phosphoric acid is syrupy and viscous.

(b) ICl_7 does not exist but IF_7 exist.

(c) Which has greater bond angle: NH_3 or NF_3 ? Why?

(d) On reaction with air, Li predominantly forms monoxide, Na forms peroxide and other alkali metal forms superoxides.

(e) Thallium hydroxide is as powerful base as NaOH.

(3×5)

7. Write short notes on the following : (Any three)

(a) Structure and bonding of diborane

(b) Clathrate compounds

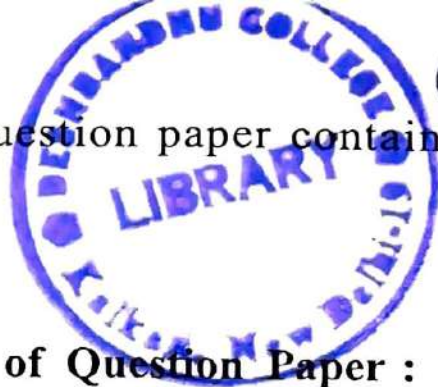
(c) Classification of silicates

(d) Hydrazine

(5×3)

(1800)

[This question paper contains 6 printed pages.]



5

13/17/17
Your Roll No.....

Sr. No. of Question Paper : 6484

HC

Unique Paper Code : 32171302

Name of the Paper : Organic Chemistry – II (Oxygen
Containing Functional Groups)

Name of the Course : B.Sc. (Hons.) Chemistry

Semester : III

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any six questions.
3. Question No. 1 carries 15 marks.

1. (a) An organic compound 'A' (C_4H_9Cl) on hydrolysis with aq. alkali forms compound 'B' ($C_4H_{10}O$). 'B' on oxidation forms another compound 'C' which does not reduce Fehling's solution. On treatment with iodine and NaOH both 'B' and 'C' form iodoform. 'B' on dehydration with cone. H_2SO_4 forms mainly 'D' which

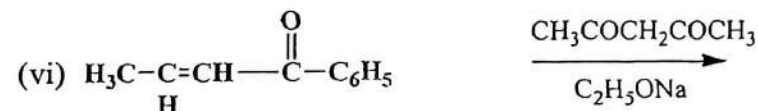
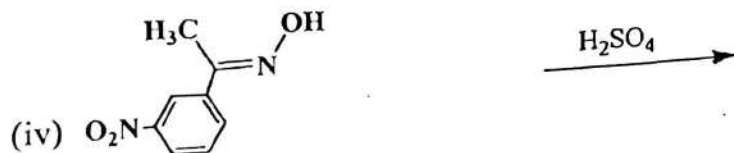
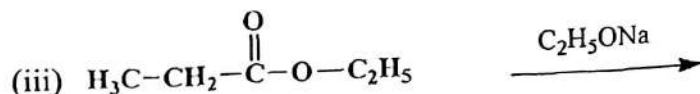
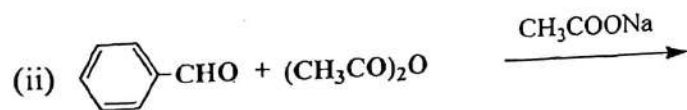
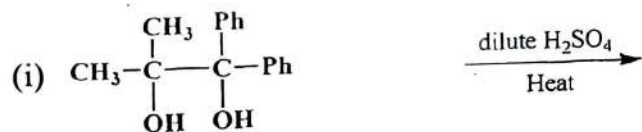
P.T.O.

on ozonolysis forms two molecules of acetaldehyde. Identify A, B, C and D, write the reactions involved and give mechanism of formation of iodoform from compound C.

(b) Write one test with reaction involved to distinguish the following pairs of compounds.

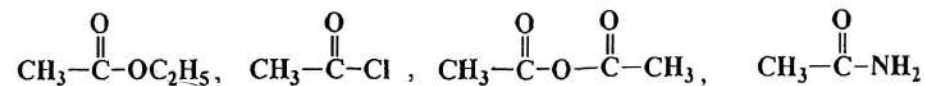
- (i) Ethyl alcohol and methyl alcohol
 (ii) Acetaldehyde and acetophenone. (11,4)

2. (a) Complete the following and give the name of the reaction in each case.



(b) Write the structure of alcohol formed from $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$ on oxymercuration-demercuration and give the mechanism involved. (9,3)

3. (a) Give and explain the relative reactivity order of the following derivatives of carboxylic acid towards nucleophilic substitution reaction



(b) Give the products formed on heating the dicarboxylic acids with the formula $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$ where $n = 0, 1, 3, 5$.

(c) (i) Hydrolysis of $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ proceeds at a much faster rate than that in case of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$.

- (ii) How do you explain the formation of 1-methylcyclopentan-1-ol on hydrolysis of



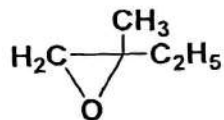
(4×3)

4. (a) Write the sequence of reactions for the preparation of

(i) Isopropyl iodide from n-propyl bromide

(ii) by Wittig reaction

- (b) Write the reaction sequence involved in the ring opening reaction of



with methanol in acidic medium. Also explain the formation of a different product on reaction with sodium methoxide. (6×2)

5. Explain why

(i) Aryl halides undergo nucleophilic displacement reaction easily if a strong electron withdrawing group is present at ortho or para position.

(ii) Vinyl chloride is less reactive than ethyl chloride towards nucleophilic substitution reactions.

(iii) Ketones cannot be prepared from RCOCl and RMgX although they can be prepared from RCOCl and R_2Cd .

(iv) o-Hydroxy benzaldehyde has lower boiling point and decreased water solubility as compared to that of its meta or para isomers. (3×4)

6. (a) Write the synthesis of the following compounds using either ethylacetoacetate or diethylmalonate

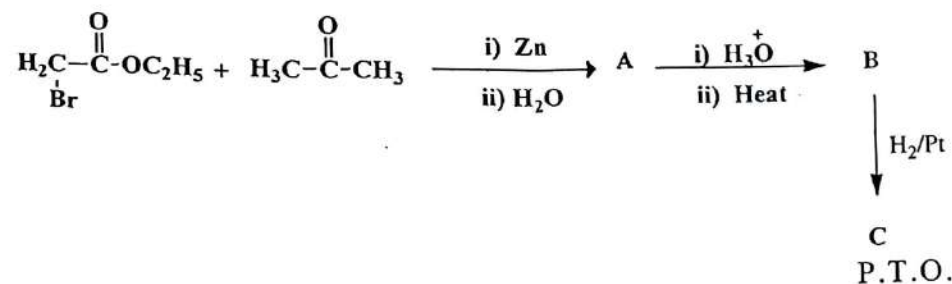
(i) 3-Oxobutanoic acid

(ii) Cyclohexyl methyl ketone

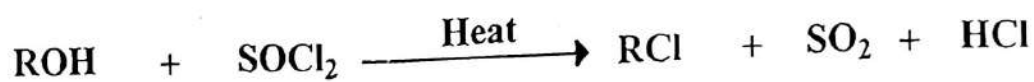
(iii) Hexane-2,5-dione

(b) o-Bromoanisole and m-bromoanisole both give the same product on reaction with NaNH_2 in liquid ammonia. Explain with mechanism. (9,3)

7. (a) Write the structure of the compounds A, B and C. Give mechanism of formation of compound A.



(b) Write down the mechanism for the following reaction



(c) Explain why

(i) Enol form of ethylacetoacetate is more stable than that of ethyl acetate

(ii) Racemization is observed in reactions following SN^1 pathway. (4×3)

8. Write short notes on any **THREE** of the following :

(i) Claisen-Schmidt reaction

(ii) Base catalysed amide hydrolysis

(iii) Michael addition

(iv) Curtius reaction

(4×3)



(6)

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Your Roll No.....

16/12/17

Sr. No. of Question Paper : 6485

HC

Unique Paper Code : 32171303

Name of the Paper : C - 7 Physical Chemistry - III :
Phase Equilibria and Electrochemical
Cells

Name of the Course : B.Sc. (H) Chemistry

Semester : III

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Question number 1 is compulsory.
3. Attempt **six** questions in all, selecting at least **two** questions from each section.
4. **Use of Scientific calculator is permitted.**

Values of constants : $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $F = 96500 \text{ C mol}^{-1}$;
 $(2.303RT/F)$ at $298 \text{ K} = 0.0591$

P.T.O.

1. Attempt any five of the following :

- The slope of the sublimation curve of any substance is greater than that of its vapourisation curve. Explain.
- During thermal analysis the cooling curve of a eutectic mixture has no break point. Explain.
- The tie lines within a binodal curve of a chloroform-acetic acid-water system are parallel neither to the sides of the triangle nor to each other. Why?
- What is the role of salt bridge in electrochemical cells?
- What is an azeotrope? If pure ethanol has a boiling point of 76.6°C and its azeotrope has a boiling point of 76.2°C , what would its graph look like?
- Why can't we use a voltmeter for determining the voltage of a Galvanic cell?
- The effect of temperature and pressure on adsorption process is in accordance with Le Chatelier's principle. Explain.
- Would you use silver spoon to stir a solution of cupric nitrate $\text{Cu}(\text{NO}_3)_2$? Give reason using the following standard potentials :

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.337 \text{ V} \quad \text{and} \quad E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.799 \text{ V}$$

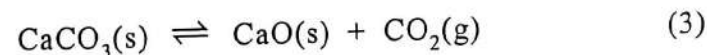
- Triethylamine - water system exhibits a lower consolute temperature and above the CST, the two liquids become partially miscible. Give reason. (3×5)

Section A

- When a liquid that is immiscible with water was steam distilled at 95°C at a total pressure of 99.6 kPa the distillate contained 1.1 g of the liquid per gram of water. Calculate the molar mass of the liquid. The vapour pressure of water is 85.13 kPa at 95°C . (3)
 - Derive Gibbs-Duhem-Margules equation starting from the Gibbs-Duhem equation for a system of two components. (4)
 - Describe the process of fractional distillation of an ideal binary solution with the help of suitable diagrams, alongwith the principle underlying it. (5)
- What is lever rule? Deduce it from pressure versus composition diagram for a binary liquid mixture. (3)
 - Draw and explain the phase diagram of phenol-water system. (4)

- (c) A substance X exists in two allotropic forms A and B in the solid state. At lower temperatures, the substance predominantly exists in A form. The density of both A and B are less than that of the liquid and the density of A form is also less than that of B form. Draw a well labelled one component phase diagram showing the two solid phases, liquid and vapour phases. (5)
4. (a) Derive the expression for Nernst distribution law when the solute undergoes association in one of the phases. (3)
- (b) An aqueous solution contains 0.3 g aspirin in a 50 cm³ solution. 20 cm³ of ether are added to this solution, the mixture is shaken and allowed to attain equilibrium at 298 K. At this temperature, the distribution coefficient between ether and water is 5.0.
- How much aspirin remains in the aqueous phase?
 - If the extraction is carried out using two successive 10 cm³ portions of ether, how much aspirin remains unextracted? (4)
- (c) Draw and discuss the phase diagram of a two component system exhibiting incongruent melting compound formation. (5)

5. (a) Find the number of components in the following system when the reaction is started with 2 moles of CaCO₃; justify your answer.



- (b) Derive the following relation starting from Duhem – Margules equation and show that the vapour phase is richer in the more volatile component when it is in equilibrium with the liquid phase.

$$\frac{dp}{d\chi_A} = \frac{dp_B}{d\chi_A} \left[1 - \frac{\chi_B p_A}{p_B \chi_A} \right] \quad (4)$$

- (c) Draw a well labelled phase diagram of chloroform-acetic acid-water indicating the number of phases and degrees of freedom in various regions. Locate the point inside the equilateral triangle for a ternary mixture with 50% CHCl₃, 20% H₂O and 30% CH₃COOH. (5)

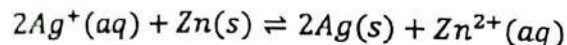
Section B

6. (a) Write the anodic, cathodic half-cell reactions, overall reaction and Nernst equation for the cell:



- (b) How is standard electrode potential of an electrode determined? Derive an expression to determine the accurate value of the standard half cell potential by graphical method. (4)

(c) For the following cell reaction



when $Zn^{2+} = 0.1M$ and $Ag^+ = 10 M$, the cell potential was found to be 1.62 V. Calculate the equilibrium constant of the reaction. (5)

7. (a) Answer whether the following reactions are possible or not, under standard conditions, through appropriate calculations.

(i) $2Fe^{3+} + Fe \rightleftharpoons 3Fe^{2+}$ given that

$$E_{Fe^{3+}, Fe^{2+}/Pt}^0 = +0.771 V \text{ and } E_{Fe^{2+}/Fe}^0 = -0.44 V$$

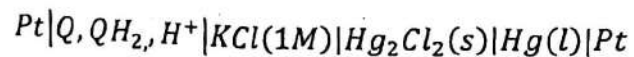
(ii) $Zn^{2+} + Mg \rightleftharpoons Zn + Mg^{2+}$ given that

$$E_{Mg^{2+}/Mg}^0 = +0.337 V \text{ and } E_{Zn^{2+}/Zn}^0 = 0.0763 V$$

($1\frac{1}{2} \times 2$)

(b) What are reference electrodes? Describe the construction of calomel electrode alongwith the necessary diagram and chemical equations. (4)

(c) Determine at 298 K for the cell



(i) its potential when $pH = 5$

(ii) the pH when $E_{cell} = 0$

(iii) the negative electrode when $pH = 8.0$

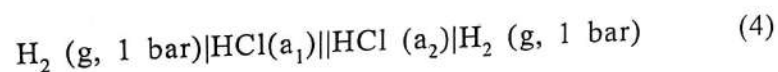
Given

$$E_{Quinhydrone}^0 = +0.6996 V \text{ and } E_{Calomel}^0 = 0.280 V$$

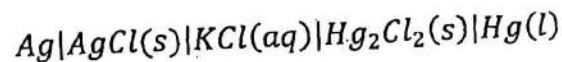
(5)

8. (a) Discuss electrolytic and galvanic cells highlighting the similarities and differences. (3)

(b) What are concentration cells? Derive the expression for potential of the following concentration cell without transference, separated by salt bridge.



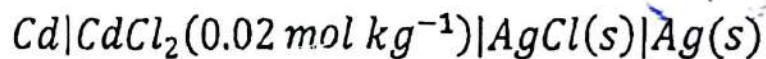
(c) The potential of the following cell is 0.057 V at 298 K.



The temperature coefficient of cell potential is $2.5 \times 10^{-4} \text{ VK}^{-1}$. Write the reaction taking place in the cell. Calculate the Gibbs energy, enthalpy and entropy changes for the reaction at 298 K. (5)

9. (a) How does chemisorption differ from physisorption? (3)

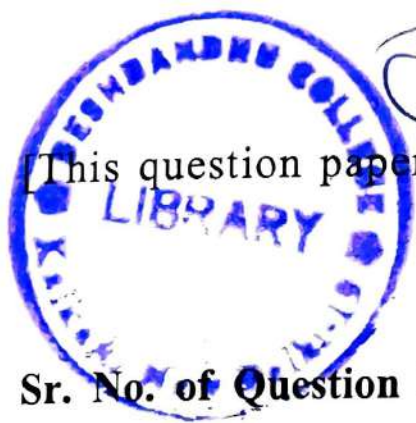
(b) The potential of the cell



is found to be 0.780 V at 25°C. Calculate the mean ionic activity of ions in the solution, at this temperature, given the following standard potentials.

$$E_{\text{Cd}^{2+}/\text{Cd}}^0 = -0.403 \text{ V} \text{ and } E_{\text{AgCl}/\text{Ag}}^0 = 0.222 \text{ V} \quad (4)$$

(c) Discuss qualitatively the BET theory of adsorption alongwith relevant plots. (5)



7 Extra Copy

[This question paper contains 6 printed pages.]

2017

Your Roll No.....

Sr. No. of Question Paper : 8296

HC

Unique Paper Code : 32177902

Name of the Paper : Inorganic Materials of Industrial Importance

Name of the Course : Chemistry : DSE

Semester : III / V

Duration : 3 hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **five** questions in all.
3. Question **1** is compulsory.
4. Attempt any **four other** questions. **All** questions carry equal marks.

1. (a) Fill in the blanks or mark **True/False** as required :

- (i) A battery cannot be recharged and has to be discarded after single use.
- (ii) catalysts are substances that retard a reaction.

P.T.O.

- (iii) are low refractive index materials, generally white in colour, which are added to a paint formulation to increase its volume.
- (iv) In chemical laboratories, glassware is preferred for apparatus which is graduated or needs to be strongly heated.
- (v) Optical fibres function on the principle of,
- (vi) Ammonium nitrate is an example of a Fertilizer.
- (vii) Synthetic zeolites are preferred over natural zeolites for commercial catalytic processes. T/F
- (viii) Vitrification is the process of crystallisation of glass. T/F
- (b) Give one word/phrase for the following (any **five**):
- (i) The special oven in which annealing of glass articles is carried out.
- (ii) Small hard balls produced by the sintering together of limestone and aluminosilicate materials in a cement kiln.

- (iii) Additives in an emulsion paint formulation which prevent excessive foam formation during manufacturing.
- (iv) Common impurity in urea fertiliser which is toxic to plants.
- (v) The process of applying a protective zinc coating to iron or steel.
- (vi) Failure of a paint film by peeling off from the surface.
- (vii) The special name given to the oxide $\text{YBa}_2\text{Cu}_3\text{O}_7$.
(10,5)
2. (a) Distinguish between the following (any **two**):
- (i) Physical Vapour Deposition and Chemical Vapour Deposition.
- (ii) Wet and dry process for the manufacture of cement
- (iii) Soda lime glass and borosilicate glass
- (b) Explain with a diagram the working of Wilkinson's catalyst for the hydrogenation of alkenes. How can the process be made enantioselective in case only one enantiomer of the resulting chiral alkane is desired?

- (c) Write the discharging and charging reactions of a lead storage battery and explain how the battery works. Why is this battery still popular despite its bulk and weight? (2½×2,5,5)
3. (a) Classify the following as direct or indirect fertilizers :
- Calcium superphosphate
 - Calcium carbonate
 - Ammonium nitrate
 - Gypsum
- (b) How does urea function as an effective fertiliser for plants? Give one method for the manufacture of urea.
- (c) How does a flame-retardant paint work? Mention the functions of the following additives in a paint formulation.
- Emulsifying agent
 - Anti-skinning agent
 - Plasticiser
- (d) Why is it necessary to add a retardant to cement? Give an example of a retardant and explain with chemical reactions how it functions in retarding the setting of cement. (2,3,5,5)

4. (a) The trend in the rate of hydrogenation of some alkenes by Wilkinson's catalyst follows the order cyclohexene > *cis*-4-methyl-2-pentene > 1-methylcyclohexene. Explain this trend and identify the step in the catalytic cycle that is most affected.
- (b) Explain the terms chemisorption and desorption with reference to heterogeneous catalysis.
- (c) What are the various steps involved in the manufacture of Portland cement by rotary kiln technology? Explain the reactions taking place in different parts of the kiln.
- (d) What is 'annealing'? What special type of oven is used for the annealing of glass articles? Do you agree that the longer the annealing duration the more durable the glass article? Justify. (3,2,5,5)
5. (a) What do you understand by 'glazing' of ceramic ware? What is the importance of glazing? Explain liquid glazing of ceramics.
- (b) Discuss the characteristics and applications of (i) safety glass (ii) photochromic glass.
- (c) What is a battery? What are the different types of batteries? Give examples. (5,2½×2,5)

6. (a) Briefly describe the formation, characteristics and applications of the following forms of carbon (any **two**) :
- (i) fullerenes
 - (ii) nanotubes
 - (iii) carbon fibre
- (b) What is the purpose of applying surface coatings to objects? Discuss the following methods of surface coating (any **two**) :
- (i) Anodisation
 - (ii) Galvanisation
 - (iii) Electroplating
- (c) What is the composition of Ziegler-Natta catalyst? Is it an example of homogeneous catalysis or heterogeneous catalysis? Illustrate its working cycle diagrammatically.
- (2½×2, 2½×2, 5)

21-10-07 9-10 5.06 8

Unique Paper Code : 217301
Name of the Paper : CHEM- 305: INORGANIC CHEMISTRY
Name of the Course : B. Sc. (H) CHEMISTRY, Part-II
Semester : III
Duration : 3 Hours
Maximum Marks : 75



Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any five questions.
3. All questions carry equal marks.

1. (a) Using hybridization predict the geometry and shape of the following: (8)
SF₄, XeF₂, PCl₅, BrF₅
(b) Molecular oxygen (O₂) is paramagnetic. Explain on the basis of M. O. Theory. (4)
(c) Arrange the following molecules in their decreasing bond angle order and explain the reason. NH₃, CH₄, H₂O (3)
2. (a) Calculate the limiting value of radius ratio for an ionic crystalline solid when the coordination number is four. (8)
(b) NaCl conduct electricity when dissolved in water. Explain. (3)
(c) Calculate Lattice energy in kJ/mole for NaCl using Born-Lande equation. (4)
 $r = 281.0 \text{ pm}$, $N = 6.023 \times 10^{23}$, $\epsilon_0 = 8.85 \times 10^{-12}$, $e = 1.6 \times 10^{-19}$, $A = 1.747$, $n = 8$
3. (a) Calculate the limiting radius ratio of cation to that of anion and predict the geometry and coordination number. Given $r_{Be^{2+}} = 59 \text{ pm}$ and $r_{S^{2-}} = 170 \text{ pm}$. (3)
(b) Which one will have higher bond angle, H₂O or F₂O and why? (3)
(c) Write Born-Lande equation for the Lattice energy of an ionic compound and define the terms in it. (5)
(d) Calculate the % ionic character in HF using electronegativities of Fluorine and Hydrogen as 4.0 and 2.1, respectively. (4)
4. (a) Arrange the following alkaline earth metal carbonates in their decreasing order of thermal stability and explain the reason. (4)
BeCO₃, MgCO₃, CaCO₃, SrCO₃, BaCO₃
(b) Predict the position of Fluorine atoms in PCl₃F₂ molecule on the basis of Bent's rule. Explain the reason. (4)
(c) Which bond is stronger: (3)
(i) σ -bond or π -bond
(ii) single bond or double bond
(d) Which compound in each of the following pairs would have higher Lattice energy and why? (i) MgO and MgS (ii) NaCl and MgCl₂ (4)
5. (a) Write short notes on any two. (8)
(i) dipole-dipole interaction
(ii) hydrogen bonding
(iii) Non equivalent hybrid orbitals

(9)



200

2017

Roll No.....

Sr. No. of Question Paper : 5608
Unique Paper Code : 217305
Name of the Paper : Physical Chemistry-II (CHHT-307)
Name of the Course : B.Sc. (H) Chemistry
Semester : III
Duration : 3 Hours

H

Maximum Marks:75

Instructions for candidates

1. Write your Roll No. on the top immediately on receipt of this question paper
2. Attempt six questions in all
3. Q.No.1 is compulsory
4. Draw the graphs (wherever required) on your answer sheets. Graph paper is not required.
5. Use of scientific calculator is permitted.
6. $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$; $N_A=6.022 \times 10^{23}$

1. Explain briefly any *five* of the following :

- (a) Differentiate between isolated and open system
- (b) Explain with examples spontaneous and non spontaneous processes
- (c) What are extensive and intensive variables? Classify the following as extensive or intensive- energy, molar entropy, heat capacity and chemical potential.
- (d) Explain why Helmholtz free energy is sometimes referred as work function
- (e) Give the significance of chemical potential
- (f) What is Hess's law of constant heat summation? Explain with the help of an example.

(3×5)

2. Derive any *three* of the following relations:

(a) $C_p - C_v = [P + (\partial U / \partial V)_T](\partial V / \partial T)_P$

(b) $TV^{\gamma-1} = \text{constant}$

(c) $(\partial H / \partial P)_T = V - T(\partial V / \partial T)_P$

(d) $\left(\frac{\partial(\frac{\Delta G}{T})}{\partial(\frac{1}{T})} \right)_P = \Delta H$

(4×3)

3.

(a) 1 mole of an ideal gas at 27°C undergoes the volume change from 2 litres to 20 litres under isothermal reversible condition. Calculate w, q, ΔU, ΔS, ΔA and ΔG.

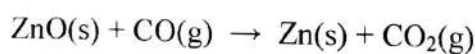
(b) Describe the Joule-Thompson experiment. Show that the expansion in this experiment is an isenthalpic process.

(6,6)

4.

(a) State and explain the third law of thermodynamics. How is it useful in calculating the absolute entropy of a substance.

(b) Calculate the standard enthalpy of reaction



Given: $\Delta H_f^\circ(\text{ZnO,s}) = -348.28 \text{ kJmol}^{-1}$;

$$\Delta H_f^\circ(\text{CO}_2\text{,g}) = -393.51 \text{ kJmol}^{-1}$$
;

$$\Delta H_f^\circ(\text{CO,g}) = -110.53 \text{ kJmol}^{-1}$$

(c) Deduce the free energy function for isothermal conditions. What is the physical significance of G?

(4,4,4)

5.

(a) Deduce the Entropy change for an ideal gas in terms of:

(i) T and V as variables

(ii) P and T as variables

(b) Derive the Maxwell's Thermodynamic Relations

$$(i) (\partial T / \partial V)_S = -(\partial P / \partial S)_V$$

$$(ii) (\partial S / \partial V)_T = (\partial P / \partial T)_V$$

(c) 4 moles of an ideal gas are compressed isothermally at 300 K from $2.02 \times 10^5 \text{ N m}^{-2}$ to $4.04 \times 10^5 \text{ N m}^{-2}$ pressure. Calculate the free energy change for the process. (4,4,4)

6.

(a) Derive the Gibbs-Duhem equation.

(b) Starting from the expression of ΔG_{mix} , show that the entropy of mixing of ideal gases:

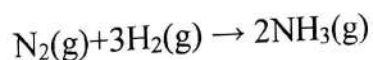
$$\Delta S_{\text{mix}} = -nR \sum x_i \ln x_i$$

(c) 100 g each of ethanol and methanol are mixed at 20°C to prepare an ideal mixture. The vapour pressure of the pure methanol is 88.7 mm and that of ethanol is 44.5 mm at 20°C . Calculate (i) the vapour pressure of solution, (ii) the partial vapour pressure of ethanol and methanol in solution, and (iii) the vapour phase composition. (4,4,4)

7.

(a) Explain the terms osmosis and osmotic pressure. Using the concept of chemical potential, derive an expression for the osmotic pressure of the solution in terms of its concentration.

(b) For the synthesis of ammonia, $K_p = 1.64 \times 10^{-4}$ at 673 K when the reaction is represented by



Calculate ΔG° for the reaction at the given temperature.

(c) Write a short note on abnormal colligative properties of solutions and van't Hoff factor? (4,4,4)

8. Write short notes on any **three** of the following:

(i) Kirchhoff's Law

(ii) Residual Entropy

(iii) Le-Chatelier's Principle

(iv) Differential and Integral enthalpy of solution

(3×4)



(10)

16/12/17

[This question paper contains 5 printed pages]

Your Roll No. :

Sl. No. of Q. Paper : **5609** **H**

Unique Paper Code : 235365

Name of the Course : **B.Sc.(Honours) (Chemistry)**

Name of the Paper : Mathematics-II
(MACT-302)

Semester : III

Time : 3 Hours **Maximum Marks : 75**

Instructions for Candidates :

- Write your Roll No. on the top immediately on receipt of this question paper.
- This question paper has **six** question in **all**.
- Attempt **two** parts from each question.
- All** questions are compulsory.
- Use of scientific calculator is allowed.

1. (a) Solve the boundary value problem :

$$y''(t) - 2y'(t) + 2y(t) = 0, \quad y(0) = 1, \quad y\left(\frac{\pi}{2}\right) = 2$$

$6\frac{1}{2}$

P.T.O.

- (b) Solve the boundary value problem :

$$y''(x) + y'(x) - 6y(x) = 0, \quad y(0) = 1,$$

$$y(x) \rightarrow 0 \text{ as } x \rightarrow \infty \quad 6\frac{1}{2}$$

- (c) Find the solution of the partial differential equation :

$$y^2 \frac{\partial f}{\partial x} + x^2 \frac{\partial f}{\partial y} = 0 \quad 6\frac{1}{2}$$

2. (a) By using double integration, prove that :

$$\int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\pi} \quad 6\frac{1}{2}$$

- (b) Find the value of the integral

$$\iint_D e^{-(x^2+y^2)} dx dy \text{ where } D \text{ is the disk } x^2+y^2 \leq a^2$$

$$6\frac{1}{2}$$

- (c) Find the volume of the sphere $x^2+y^2+z^2 = a^2$ by using spherical polar co-ordinates.

$$6\frac{1}{2}$$

3. (a) Determine the nature of the stationary points of the function $4x^3 - 3x^2y + y^3 - 9y$. 5

- (b) Show that the function $\text{Cos}(ax)\text{Cos}(by)\text{Cos}(cz)$ is an Eigen function of the operator :

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \text{What is the Eigen value?} \quad 5$$

- (c) Determine whether the operators

$$\hat{A} = \frac{d}{dx} \text{ and } \hat{B} = \frac{d^2}{dx^2} + 2\frac{d}{dx}$$

commute or not? 5

4. (a) Show that

$$\frac{d}{dt}(\vec{u} \cdot \vec{v}) = \frac{d\vec{u}}{dt} \cdot \vec{v} + \vec{u} \cdot \frac{d\vec{v}}{dt}$$

$$\frac{d}{dt}(\vec{u} \times \vec{v}) = \frac{d\vec{u}}{dt} \times \vec{v} + \vec{u} \times \frac{d\vec{v}}{dt}$$

Where \vec{u} and \vec{v} are vectors in 3-dimensional space.

$$6\frac{1}{2}$$

- (b) Prove that area of a parallelogram whose sides are the vectors \vec{u} and \vec{v} is $|\vec{u}||\vec{v}|\sin\theta$

where θ is the angle between \vec{u} and \vec{v} .

$6\frac{1}{2}$

- (c) A body of mass m moves along the curve $\vec{r}(t) = (e^t \sin t)\hat{i} + (\sin^{-1}t)\hat{j}$. Find velocity, acceleration and the force acting on the body.

$6\frac{1}{2}$

5. (a) Solve the following set of equations :

$$4x - 3y = 11$$

$$6x + 5y = 7$$

by using Cramer's rule.

$6\frac{1}{2}$

- (b) Find the eigenvalues and eigenvectors of

$$A = \begin{bmatrix} 1 & 2 \\ 2 & 4 \end{bmatrix}$$

$6\frac{1}{2}$

- (c) State the condition under which a square matrix is invertible. Find the characteristic

equation of the matrix $A = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}$ and hence

compute its inverse if it exists. $6\frac{1}{2}$

6. (a) Solve the equation $z^3 = 1$ Find the sum and

product of roots. $6\frac{1}{2}$

- (b) Determine the region in the complex plane

described by $|z+i| < 1$. $6\frac{1}{2}$

- (c) Evaluate the following :

(i) $(1+i)^{20}$

(ii) $(1-i)^{12}$

$6\frac{1}{2}$



(11)

Sl. No. of R.T. 5964

Roll No.

31/1/17

Unique Paper Code : 2171302
Name of the Paper : Paper-6, Organic Chemistry
Name of the Course : B.Sc. (~~Erstwhile~~ ~~FYUP~~) (Hon) Chemistry
Semester : III
Duration : 3 hours
Maximum Marks : 75

F-9

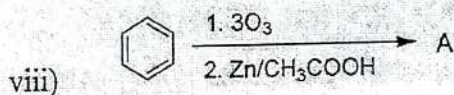
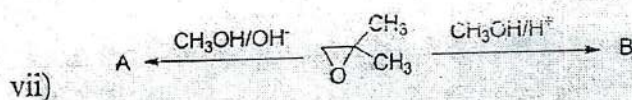
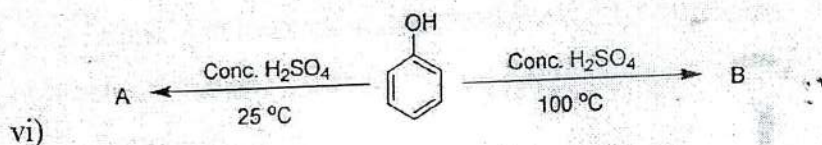
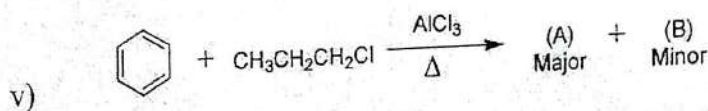
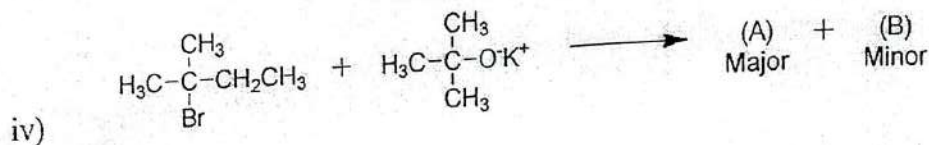
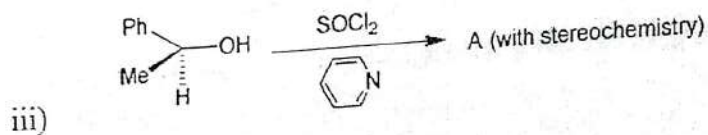
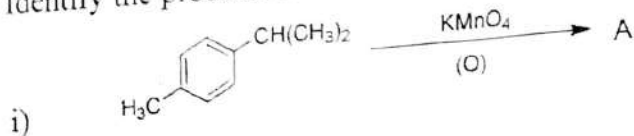
Instructions for Candidates:

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **SIX** questions in all. Question no. 1 is compulsory.
3. Question no. 1 carries 15 marks. Rest of the questions (Ques. no. 2 to 8) is of 12 marks each.

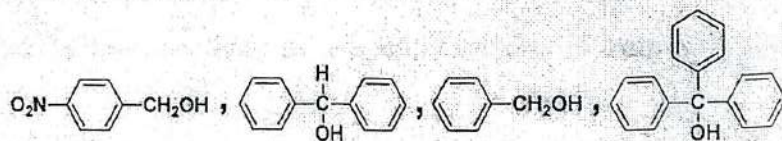
1. a) An organic compound A (C_3H_8O) gives positive iodoform test and on reaction with PBr_3 gives B. B when treated with benzene in presence of $AlCl_3$ gives compound C (C_9H_{12}). Compound C on oxidation by oxygen in alkaline medium at $130^\circ C$ followed by acid treatment gives D (C_6H_6O) and E (C_3H_6O). D is insoluble in $NaHCO_3$ and soluble in $NaOH$. E also gives positive iodoform test. Deduce the structures from A to E. Give the equations involved and explain the mechanism of conversion of C to D and E. (10)
b) Write down key differences between S_N1 and S_N2 reactions. Draw energy profile diagrams for S_N1 and S_N2 reactions. (5)
2. Explain the following. (Any Three) (3 × 4)
 - a) In electrophilic substitution reactions, nitrobenzene reacts very slowly while phenol reacts faster than benzene.
 - b) When $ArOR$ ethers are cleaved with HI , it gives RI and $ArOH$ rather than ArI and ROH .
 - c) The formation of *m*-toluidine along with *p*-toluidine takes place on reaction of *p*-chlorotoluene with potassium amide in liquid ammonia.
 - d) The nucleophilic substitution occurs readily in haloalkanes whereas nucleophilic substitution in alcohols occurs in presence of strong acids as catalyst.

3. a) Identify the products in the following reactions. (Any Six)

(1.5 × 6)



b) Arrange the following compounds in the increasing order of their reactivity with HBr. Give suitable justification. (3)

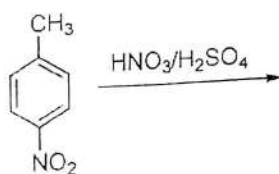


4. a) Carry out the following conversions using suitable reagents. (Any Three) (3 × 3)

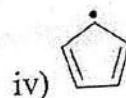
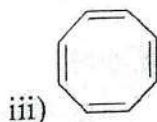
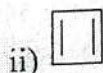
- Benzene to benzyl chloride
- Benzene to *m*-chloronitrobenzene
- Ethyl acetate to *tert.*-butyl alcohol
- Aniline to bromobenzene

b) What happens when *p*-cresol is treated with $\text{CHCl}_3/\text{NaOH}$ and the product is acidified? Name the reaction and gives its mechanism. (3)

5. a) Write the product(s) formed and mechanism of the following reaction. (4)



- b) In case of halogens, reactivity is determined by stronger inductive effect while orientation is largely controlled by resonance. Comment on it. (4)
- c) Why reactivity of aryl halides increases towards nucleophilic substitution reaction with the substitution of $-\text{NO}_2$ group at *o*- and *p*- positions. (4)
6. a) Giving reasons, classify the following compounds as aromatic/non-aromatic/anti-aromatic (**Any Three**). (3)



- b) Write a test with relevant reactions to distinguish between: (3)
- i) *n*-butanol and *tert*-butanol
- ii) methanol and ethanol
- c) Rank the following species in order of their expected $\text{S}_{\text{N}}1$ reactivity giving suitable explanation. (3)
- $(\text{CH}_3)_2\text{CHBr}$, $(\text{CH}_3)_3\text{CBr}$, $\text{CH}_2=\text{CHBr}$.
- d) Methyl group attached to benzene ring has no lone pair of electrons but is still *o/p* directing in nature. Explain. (3)
7. a) Why $\text{S}_{\text{N}}1$ type of reactions normally proceed with retention in configuration. (3)
- b) Comment on the low reactivity of neopentyl halides in both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions. (3)
- c) Give the application of Grignard reagent in the synthesis of 1° , 2° and 3° alcohols. (3)
- d) In synthetic organic chemistry, Friedal-Crafts acylation is often preferred over Friedal-Crafts alkylation. Why? (3)
8. Write short notes giving emphasis on i) reaction involved, ii) mechanism with explanation and iii) limitations (if any). (**Any Three**) (3 × 4)
- a) Pinacol-Pinacolone rearrangement
- b) Birch reduction
- c) Fries rearrangement.
- d) Schotten-Baumann reaction

Sl. No. of Q.P.: 5965

(12)

15/12/17



Unique Paper Code : 2171303
Name of the paper : Paper VII : (Organic + Physical Chemistry)
Name of the Course : B.Sc. (H) Chemistry
Semester : III (~~FYUP~~)
Duration : 3 Hours
Maximum Marks : 75

F-9

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. This paper has **two** Sections.
3. Attempt **any three** questions from each Section.

Section A

(Q.No. 1 is compulsory. Attempt any TWO from rest)

1. (a) An organic compound A (C_3H_6O) forms precipitate with 2,4-dinitrophenylhydrazine and gives positive iodoform test but negative Tollen's test. Compound A reacts with dilute NaOH to form compound B ($C_6H_{12}O_2$) which upon dehydration forms compound C ($C_6H_{10}O$). Compound C forms cyanohydrin D with HCN and also reacts with bromine. Identify A, B, C and D and write all the reactions involved.

(b) How will you convert acetaldehyde to lactic acid?

(c) How will you distinguish between the following pairs of compounds? Write any one method with the reaction(s) involved. (Do *any two*)

(i) Acetone and Benzaldehyde

(ii) Maleic acid and Fumaric acid

(iii) Acetic acid and Phenol

(8+2.5+3)

2. Do *any four* from the following:

(a) What is the role of pH during the reaction of carbonyl compounds with ammonia and its derivatives?

(b) Arrange the following compounds according to their increasing acidity. Justify your answer.

CH_3COOH , $ClCH_2COOH$, $Cl_2CHCOOH$, Cl_3CCOOH

(c) What is the role of CN^- ion during Benzoin condensation?

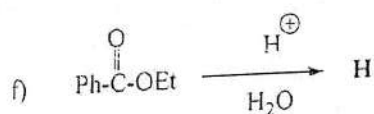
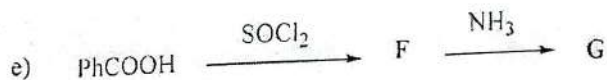
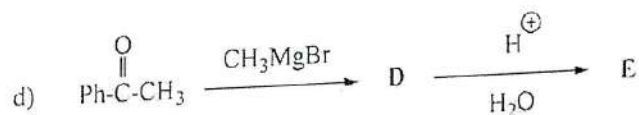
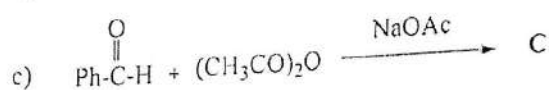
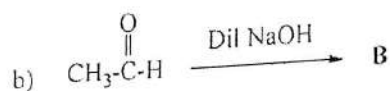
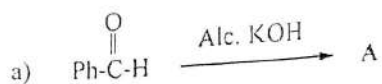
(d) What happens when propionic chloride is treated with ammonia.

(c) What is trans-esterification? Give an example.

(f) Why are organo-Mg or Cd compounds not preferred during Reformatsky reaction?

(3+3-3+3)

3. Complete the following reactions. Give the name of the reaction (wherever applicable) with the mechanism: (Do *any four*)



(3+3+3+3)

4. Write short notes on *any three* of the following:

(a) Keto-enol tautomerism

(b) Claisen condensation

(c) Beckmann rearrangement

(d) Hofmann bromamide degradation

(4+4+4)

Section B

(Attempt any *THREE* questions)

Use of scientific calculator is allowed

5. (a) State whether True or False and justify your answer with suitable reasoning:

i) The energy of activation of a reaction is the difference in energy between the reactants and the products.

ii) During a reaction a catalyst gets used up and has to be replaced each time.

iii) Enzymes are catalysts; they increase the rate of chemical reactions by stabilizing the transition state.

(1.5+1.5+1.5)

(b) Distinguish between (*any three*):

- i) Reaction rate and reaction rate constant
- ii) Order and molecularity
- iii) Differential rate law and integrated rate law
- iv) Stationary and non-stationary chain reactions

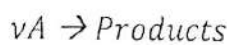
(2+2+2)

(c) Comment on the following statements (*any two*):

- i) Elementary processes with molecularity greater than three are not known
- ii) Order of a reaction may be positive, negative or a fractional value
- iii) Slowest step determines the rate of a reaction

(1+1)

6. (a) The reaction,



is first order reaction with respect to A.

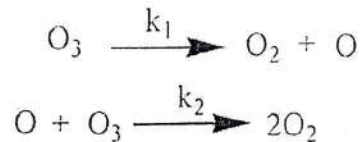
- i) Write down its differential rate law and deduce from it the integrated rate law.
- ii) Show that half-life of such a reaction is independent of the initial concentration of the reactant A.

(b) Find the second order reaction's activation energy with the given information:

$$K_1 = 4.0 \text{ L/mol.s at } 37^\circ\text{C}$$

$$K_2 = 8.0 \text{ L/mol.s at } 87^\circ\text{C}; R = 8.3145 \text{ J/K} \cdot \text{mol}$$

(c) Derive the differential rate law for the decomposition of ozone



(5+4+3.5)

7. (a) Derive an expression for the rate constant on the basis of collision theory for the bimolecular gaseous reactions

$$k_2 = pN_A\pi\sigma_{AB}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} \exp\left(\frac{-E_0}{RT}\right)$$

Compare it with Arrhenius equation and show that

$$E_a = E_0 + \frac{RT}{2}$$

OR

Describe the activated complex theory for rate of a chemical reaction.

(b) For the decomposition of ammonium nitrate in aqueous solution the following data was obtained:

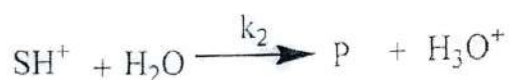
Time (min)	10	15	20	15	∞
Volume of N ₂ (c.c.)	6.25	9.00	11.40	13.65	35.05

(6.5+6)

Show that the reaction is first order.

8. (a) Derive the rate law for the enzyme catalyzed reactions using Michaelis-Menten kinetics. Show that the rate of reaction changes from first order to zero order as the concentration of substrate increases.

(b) An acid HA catalyses the substrate S to products as follows:



Derive the rate law for the reaction. State when it becomes an example of 'general acid catalysis' and it is 'specific hydrogen ion catalysis'

(c) The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of the reaction?

(6+5.5+1)