

2016

CHEMISTRY

(Major)

Paper : 1.1

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. (a) Calculate the change in the internal energy of a system that releases 2300 J of heat and that does 7043 J of work on the surroundings. 1
- (b) The value of ΔH° for the reaction below is -504 kJ :
- $$2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$$
- Calculate the heat (in kJ) released to the surroundings when 12 g of CO(g) reacts completely. 1
- (c) What do you mean by inversion temperature? 2
2. (a) How do you define the criterion for the spontaneity of any process in terms of free energy? 1

- (b) Explain what you understand by the term 'standard Gibbs free energy change'. 1
- (c) Discuss the physical interpretation of any one of the Maxwell relations. 2
3. (a) Sketch the plot of rate versus concentration of a zero-order reaction. 1
- (b) Write down the differential rate law and integrated rate law for a reaction of order $\frac{1}{2}$. 1
- (c) Explain the term 'shape selective catalysis' with examples. 2
4. Answer any two of the following: 3×2=6
- (a) A piece of magnesium of mass 15 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature is 23 °C.
- (b) What is the physical significance of ΔH ? What are the factors that affect the enthalpy of a reaction (ΔH)?
- (c) Explain the principle of liquefaction of gases by Joule-Thomson effect.

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5. Answer any two of the following:
- (a) How is the entropy affected by (i) temperature, (ii) a gas changing from a liquid to a gas, (iii) changing from a solid to a liquid, (iv) dissociating into atoms?
- (b) Calculate ΔG_T° value for the following reaction:
- $$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$$
- Given that for—
- $$\text{N}_2\text{O}_4(\text{g}); \Delta H_f^\circ = +9.16 \text{ kcal mol}^{-1}$$
- $$\text{NO}_2(\text{g}); \Delta H_f^\circ = +33.18 \text{ kcal mol}^{-1}$$
- (c) Show how the thermodynamics was affected from the Nernst theorem.
6. Answer any two of the following:
- (a) Write the rate equation for a zero-order reaction and calculate the half-life of this type of reaction affected by the concentration.

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- (b) A patient is given a certain amount of iodine-131 as a part of a diagnostic procedure for a thyroid disorder. Given that the half-life of radioactive iodine-131 is 8 days. What fraction of the initial iodine-131 would be present in the patient after 24 h, if none of it was eliminated through natural body processes?
- (c) In what way is the rate law for a reaction related to the rate-determining step? Explain with an example.

7. Answer any *two* of the following : $5 \times 2 = 10$

- (a) What do you mean by heat capacity and an adiabatic process? For the reversible adiabatic expansion of an ideal gas, show that $PV^\gamma = \text{constant}$, where

$$\gamma = \frac{C_{p,m}}{C_{v,m}}$$

What is the physical significance of γ ?

$2+3=5$

- (b) A sample of 4.50 g of methane occupies 12.7 dm^3 at 310 K.
- (i) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 torr until its volume has increased by 3.3 dm^3 .

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- (ii) Calculate the work done if the process occurred reversibly.
- (c) Deduce Kirchhoff's equation for the variation of enthalpy of reaction with temperature.

8. Answer any *two* of the following :

- (a) Derive Gibbs-Duhem equation and show that intensive properties of a closed system are not independent.

(b) Starting from the definition of Gibbs free energy (G), deduce the Maxwell relations to show the variations of G with T and P for a closed system. Based on these expressions, draw the necessary graphs to show the variation of G with T and P for a closed system in gaseous phases of a substance.

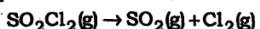
- (c) Find an expression for the change in entropy during the expansion of n mol of an ideal gas from a volume V_1 to a volume V_2 . Calculate the entropy change for 1 mol of an ideal gas expanding reversibly isothermally at 298 K. Calculate ΔS for the same expansion when the same expansion is carried out irreversibly?

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9. Answer any two of the following : $5 \times 2 = 10$

(a) What is a homogeneous catalyst? How does it function in general terms? What do you understand by the catalytic efficiency of an enzyme? $1+2+5=8$

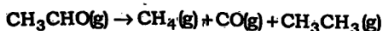
(b) Sulfuryl chloride SO_2Cl_2 is used to manufacture the antiseptic chlorophenol. The following data were collected on the decomposition of SO_2Cl_2 at a certain temperature :



Initial concentration of SO_2Cl_2 (mol L^{-1})	Initial rate of formation of SO_2 ($\text{mol L}^{-1} \text{s}^{-1}$)
0.100	2.2×10^{-6}
0.200	4.4×10^{-6}
0.300	6.6×10^{-6}

What are the rate laws for the reaction? Give the reasons to justify your answer. Calculate the rate constant of the reaction from above data.

(c) Derive the rate law for the thermal decomposition of ethanal (CH_3CHO) in absence of air (shown below) considering the Rice-Herzfeld mechanism :



2016

CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

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for the questions

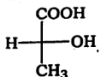
1. Answer the following questions (any seven) :

1×7=7

- (a) Write the IUPAC name of the following compound :



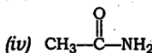
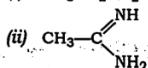
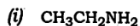
- (b) Convert the following Fischer formula into flying-wedge formula :



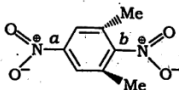
- (c) Arrange the following molecules in order of decreasing dipole moment :



- (d) Acetyl acetone is highly stable in enol form. Explain.
- (e) Arrange the following compounds in order of their correct basicities :



- (f) The molecule does not exist. Explain.
- (g) Between salicylic acid and *p*-hydroxy benzoic acid which is stronger? Explain in terms of H-bonding.
- (h) The C—N bond *a* is shorter than *b* in the following compound. Explain :



2. Answer the following questions (any four) :

2×4=8

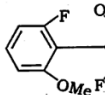
- (a) Calculate the formal charge on each of the constituent atoms of



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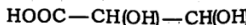
- (b) Between toluene and *t*-butylbenzene which one is more reactive towards electrophilic substitution? Explain.
- (c) Explain whether [1,3] cyclohexadiene is aromatic or not.
- (d) State and explain whether the following molecule will be optically active.



- (e) What product do you expect from the oxidation of butenedioic acid is t-butylbenzene? Write equation as well.

3. Answer the following questions (any four) :

- (a) Draw the number of stereoisomers of the following compound.

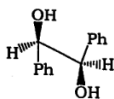


Also find the number of *enantiomeric* and *meso* forms.

- (b) Account for the fact that *t*-butylamine is a stronger base. Which is more basic, guanidine or urea? Explain. Alternant and non-alternant carbons? Give examples.

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- (c) What is resolution of a racemic mixture? What are different methods of resolution of racemic mixture? How will you separate a racemic mixture of an alcohol? $1+1+3=5$
- (d) Explain the cause of optical activity of biphenyls giving suitable substituents. Are there any compounds to show atropisomerism? Give example. $4+1=5$
- (e) Designate the following flying-wedge formula with *R,S*-notations and convert into Fischer projection. What do you understand by stereomutation? $3+2=5$



4. Answer the following questions [either (i) and (ii) or (iii) and (iv) from (a), (b) and (c)] : $10 \times 3 = 30$

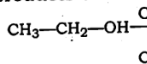
- (a) (i) Draw the orbital picture of different states of nitrene. How can nitrenes be trapped for detection? Give one important reaction of nitrene as intermediate. $2+2+1=5$
- (ii) Explain with example, what you mean by kinetically controlled and thermodynamically controlled reactions. Draw the energy profile diagram. $3+2=5$

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(Continued)

(iii) The *cis*-isomer of cyclohexyl bromide reacts with PhSNa in aqueous solution much faster than the *trans*-isomer. Explain.

(iv) Write the mechanism of the following reaction and name the products :



Also name the products.

(b) (i) The rate of bromination of styrene is greater than that of propene. Place an explanation along with the intermediate formed.

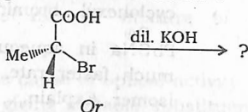
(ii) (1) Which of the following undergo solvolysis more readily?



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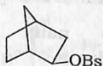
- (2) Find the stereochemistry of the product for the following reaction along with the mechanism :

2



- (iii) What are classical and non-classical carbocations? Give example. The rate of acetolysis of exo-norbornyl brosylate is many times faster than endoisomer. Explain :

3+2=5



exo-norbornyl brosylate

- (iv) Define carbon-free radicals. How are these detected? How can carbon-free radical be generated?

1+2+2=5

- (c) (i) How are the nucleophilic substitution reactions affected by the nature of leaving group and nucleophiles? Explain with examples.

2½+2½=5

- (ii) Explain the criteria for showing optical activity. Draw an allene which displays chirality.

4+1=5

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- Or
- (iii) Define syn- and anti-reactions. Why is syn preferred over anti? Give an example.
- (iv) Draw the chair-cis- and chair-trans-cyclohexane and their optical activities.

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