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# Chapterwise Previous Years' Solved Papers

2015-2000

# GATE Chemistry

Containing 3 Practice Sets

Dr. Sanjay Saxena
Preeti Gupta

# Chapterwise
## Previous Years'

# SOLVED PAPERS
## (2015-2000)

# GATE
# Chemistry

Dr. Sanjay Saxena
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# Take a Ride of **SUCCESS** in **GATE 2016**

Graduate Aptitude Test in Engineering (GATE) is an all India examination that primarily tests the comprehensive understanding of various undergraduate subjects in Engineering and Technology. The GATE score of a candidate reflects a relative performance of that candidate. The score is used for admissions to post-graduate engineering programmes (e.g., M.E., M.Tech, direct Ph.D.) in Indian higher education institutes with financial assistance provided by MHRD and other Government agencies. The score may also used by Public sector units for employment screening purposes.

Most of the PSUs release their recruitment notifications right after the GATE notification, indicating that candidates have to take GATE to be considered for a job in their organisations.

So making a great score in GATE is very considerable for availing all these opportunities. Keeping the above point of view and after exhaustive research, we have come up with the Solved Papers of **GATE Chemistry** for the aspirants who are preparing for GATE Exam. This book contains previous years' (2015-2000) GATE Solved Papers with their authentic solutions to help you getting a good score. The chapterwise solved papers in this book will help the students to find the solutions to their problems and to get through the exam without any difficulty. This integrated package of solved papers has been designed to know about the GATE Exam pattern and to put yourself into the real practice.

After going through this solved paper, aspirants can climb the ladder of success and fulfill their dreams.

We are thankful to Arihant Publications (India) Limited for giving us this opportunity to make such book which will help you to get 100% success in GATE exam.

*Valuable suggestions are always welcome for further improvement.*

**Authors**

# Exploring the **PAGES...**

# GATE

## Graduate Aptitude Test in Engineering

“ Graduate Aptitude Test in Engineering is an all India level examination, conducted and controlled by the Indian Institute of Science in cooperation with seven Indian Institutes of Technology on behalf of the National Coordination Board – GATE, Department of Higher Education, Ministry of Human Resource Development (MHRD), and Government of India. The GATE committee which consists of representatives from the governing institutes is the sole authority for conducting the examination and declaring the results. ”

## GATE Eligibility Criteria

*The following categories of candidates are eligible to appear in GATE*

- Candidates with Bachelor Degree in Engineering/Technology/Architecture (4 years after 10+2) and those who are in the final of such programme.
- Candidates with Master Degree in any branch of Science/Mathematics/Statistics/ Computer Applications or its equivalent and those who are in the final year of such programme.
- Candidates in the second/third/higher year of the Four-year Integrated Master Degree Programme (Post B.Sc.) in Engineering/Technology, or 4th/5th year of Five-year Integrated Master Degree Programme and Dual Degree Programme in Engineering/ Technology
- Candidates with qualifications obtained through examinations conducted by professional societies recognized by UPSC/AICTE (e.g., AMIE by IE (I), AMICE (I) by the Institute of Civil Engineers (India) - ICE (I)) as equivalent to B.E. / B. Tech. The students who have completed his/ her Bachelor Degree in Engineering (4 years after 10+2) or equivalent of such professional courses are also eligible.

## Examination Pattern

The GATE consists of a single paper of 3 hours duration, which contains 65 questions carrying maximum of 100 marks. The question paper is divided into three sections.
First section consists of 25 questions (1 to 25) of ONE MARK each.
Second section consists of 30 questions (26 to 55) of TWO MARKS each.
Third section consists of 10 questions (56 to 65) of ONE MARK (56 to 60) and of TWO MARKS (61 to 65) each.

### Multiple Choice and Numerical Answer Type Questions

The question paper consist of multiple choice and numerical answer type questions. In multiple choice type question, each question has four choices for the answer. In numerical answer type questions, there will be no responses to mark at all. To enter a number as your answer, use the virtual numerical keyboard displayed on the monitor.

## Zones and Institutes for GATE

The GATE is conducted and controlled through eight zones which are as follow

**Zone 1** IISC, Bangalore
**Zone 2** IIT, Bombay
**Zone 3** IIT, Delhi
**Zone 4** IIT, Guwahati
**Zone 5** IIT, Kanpur
**Zone 6** IIT, Kharagpur
**Zone 7** IIT, Madras
**Zone 8** IIT, Roorkee

GATE 2015 exam was conducted by IIT, Kanpur

## Negative Marking in GATE Exam

Incorrect answer carry negative marks i.e., 0.33 for one mark questions and 0.66 for two marks questions. Also there is no negative marking for questions of numerical answer type.

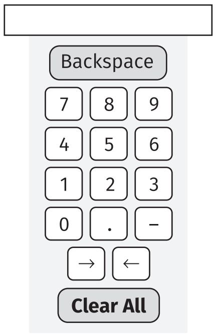
# Answering a Question in Online Test

*Procedure for answering a multiple choice type questions are as follows*

- To select your answer, click on the button of one of the options.
- To deselect your chosen answer, click on the button of the chosen option again or click on the Clear Response button.
- To change your chosen answer, click on the button of another option, and to save your answer, you must click on the Save and Next button.
- To mark the question for review, click on the Mark for Review and Next button.

*Procedure for answering a numerical answer type questions are as follows*

- To enter a number as your answer, use the virtual numerical keypad displayed on the monitor.
- A fraction (e.g.,-0.3 or -.3) can be entered as an answer with or without '0' before the decimal point.
- To clear your answer, click on the Clear Response button and to save your answer, you MUST click on the Save and Next button.
- To mark the question for review, click on the Mark for Review and Next button.



Virtual Numerical Keypad

*If an answer is entered for a question that is Marked for Review, that answer will be considered in the evaluation.*

## Formula for GATE Score of CE, CS, EC, EE and ME Papers

*After the evaluation of the answer normalised marks based on the formula given below was calculated corresponding to the raw marks obtained by a candidate for CE, CS, EC, EE and ME papers. Normalised mark of $j^{th}$ candidate in $i^{th}$session $\overline{M}_{ij}$ in given by*

$$\hat{M}_{ij} = \frac{\overline{M}_t^g - M_q^g}{\overline{M}_{ti} - M_{iq}} (M_{ij} - M_{iq}) + M_q^g$$

*where,*

$M_{ij}$ = the actual marks obtained by the $j^{th}$ candidate in $i^{th}$ session

$\overline{M}_t^g$ = the average marks of the top 0.1% of the candidates considering all sessions

$M_q^g$ = the sum of mean and standard deviation marks of the candidates in the paper considering all sessions

$\overline{M}_{ti}$ = the average marks of the top 0.1% of the candidates in the $i^{th}$ session

$M_{iq}$ = the sum of mean marks and standard deviation $i^{th}$ session

## Formula for GATE Score of all Papers

The formula for GATE score of all papers is given below

$$S = S_q + (S_t - S_q) \frac{M - M_q}{\overline{M}_t - M_q}$$

where,

$S$ = the GATE Score of the candidate,

$M$ = the marks obtained by the candidate in the paper appeared by the candidate in GATE 2013,

$M_q$ = the qualifying mark for general category candidates in the paper,

$\overline{M}_t$ = the mean of marks of top 0.1% or top 10 (whichever is larger) of the candidates who appeared in the paper,

$S_t$ = 900 is the Score assigned to $\overline{M}_t$,

$S_q$ = 350 is the Score assigned to $M_q$.

$M_q$ is usually 25 marks (out of 100) or $\mu+s$, whichever is larger. Here $\mu$ is the mean and $s$ is the standard deviation of marks of all the candidates who appeared in the paper.

## GATE 2015 Cut-off Marks for Some Branches & Categorywise

| BRANCH | GENERAL | SC/ST/PD | OBC (Non-Creamy) |
|---|---|---|---|
| Electronics & Communication Engineering | 25.0 | 16.67 | 22.50 |
| Electrical Engineering | 25.0 | 16.67 | 22.50 |
| Mechanical Engineering | 32.73 | 21.82 | 29.46 |
| Computer Science & IT | 25.0 | 16.67 | 22.50 |
| Civil Engineering | 25.0 | 16.67 | 22.50 |

## Paper Codes for GATE

- Aeronautical/Aerospace Engineering (AE)
- Agricultural Engineering (AG)
- Architecture and Planning (AR)
- Biotechnology (BT)
- Civil Engineering (CE)
- Chemical Engineering (CH)
- Computer Science and Information Technology (CS)
- Chemistry (CY)
- Electronics and Communication Engineering (EC)
- Electrical Engineering (EE)
- Geology and Geophysics (GG)
- Instrumentation Engineering (IN)
- Mathematics (MA)
- Mechanical Engineering (ME)
- Mining Engineering (MN)
- Metallurgical Engineering (MT)
- Physics (PH)
- Production and Industrial Engineering (PI)
- Textile Engineering and Fibre Science (TF)
- Engineering Science (XE)
- Life Science (XL)
- Ecology and Evolution (EY)

## Recent Changes in GATE

### 2014

A new paper **Ecology and Evolution** is introduced in GATE 2014.

Examinations for all the 22 papers will be conducted by an ONLINE Computer Based Test (CBT).

GATE 2014 examination was held during forenoon and afternoon session on alternate weekends (Saturday and Sunday) between 1st February 2014 and 2nd March 2014. Examination for some of the papers in GATE 2014 was held in multiple sessions.

Application Fee has been revised again. It is ₹1500 for Male Candidates (General/OBC), ₹ 750 for Women Candidates of any category, ₹1500 for Other Candidates (General/OBC) and ₹750 SC / ST / PwD* Category Candidates

In terms of pattern, only multiple choice questions and numerical answer type questions are asked, there was no coverage of common date and linked answer type questions.

### 2013

Female candidates are exempted from paying the application fee.

Candidates are required to upload scanned copy of Photograph and Signature.

The Application fee was increased from ₹1000 to ₹1200.

### 2012

Only final year students and passout students were eligible to write GATE exam.

The application process was made completely online, candidates could view their responses of the ORS and also GATE Office released official solutions for GATE papers.

# **PLAN** Your Study to **KNOCK OUT** the Exam

1. **Planning your study after analysing previous years' papers**

   You must plan your study after taking the analysis of previous years' GATE papers. This will give you the idea that which subject usually has the highest weightage in GATE exam and about the topics asked from the particular subject most. After the analysis of previous years' papers of GATE Chemistry, you will be able to make the list of topics to be studied on the priority basis. You also will be able to prepare time schedule to study individual topics.

2. **Prefer standard books for GATE**

   Make an extensive search for standard books in the library and go for the best ones. Try to cover complete syllabus within the time you have (5 or 6 months). If it isn't possible, get expertise in the topics you have studied.

3. **Group study is a great comrade**

   Group study is one of the best ways for preparation of GATE. Assign a few sections/topics to your friend and you focus on the remaining. Then have a brief session and discussion and exchange what both of you have studied/gained. This not only saves your time and efforts but also enhances understanding on the topics/concepts.

4. **Solve the previous years' GATE papers**

   Solve previous years' GATE papers to understand what the actual paper would be like. It also brushes up your mind and tells you the weaknesses in the subject knowledge. So try to solve as many test papers as you can. This is the best way to prepare and get through the GATE.

5. **Practice Sets is a great platform to check yourself**

   Attempt all the 65 questions given in a practice set and then check yourself step by step by considering the answer with solutions given along with each practice set. Because, the practice sets are designed based exactly on the latest exam pattern, hence you will find your strongest and weakest points related to all sections i.e., Aptitude, Mathematics and Engineering disciplines in a particular topic. So, keep practicing and secure your success in GATE.

6. **Analyse your results**

   Analysing the results from your solved questions from the practice sets and solved papers is very significant. If you do not analyse, it does not add value to your performance. You should check and find out where you have mistaken and could have scored more. Know your accuracy rates in various topics and prepare a topicwise datasheet to make record of your performance in different solved papers and practice sets.

7. **Keep the time for Revision**

   As time management is an important factor to crack the exam. Hence, give the appropriate time to each subject and complete that subject within your time schedule. After completion of the whole syllabus, you must have time for the quick revision.

# **TIPS and TACTICS** for a **Successful** Attempt

1. **Read Carefully**
   Make it a habit of always reading the instructions on the front page carefully. Also, before attempting the questions, always read and understand the directions given to attempt a question so that scope for blunders is reduced.

2. **Solve The Easy Questions First**
   Try to bifurcate the questions according to the difficulty level. Always try and attempt the easy questions first as this saves a lot of time. Time management plays a vital part in achieving success.

3. **Strike Off The Wrong Options**
   Try to strike off the wrong options. The options which cannot be the answer even a slightest bit and for which you are cent percent sure, should be separated from the probable answer so that you are able to concentrate on the remaining options and hence you find out the answer easily.

4. **Don't Waste Excessive Time On One Question**
   If you are not able to strike off the wrong options and are unsure of the correct answer then don't waste excessive time as doing so, will lead to a decrease in remaining time and hence other question will suffer.

5. **Use Scribble Pad**
   You can use the scribble pad provided for rough work. You can jot down the points, ideas etc so that least number of mistakes are made while framing the final answer.

6. **Try To Attempt The Leftover Questions Once More**
   After completing all the question go back to the leftover questions and try to give it a shot and solve it once more.

7. **Keep A Time Check**
   During the examination do keep an eye on the time. Try to save time so that you are left with some time to attempt the leftover questions. Try to finish the exam early so that you are left with some amount of time to revise the whole paper once.

8. **Use The Option Of Mark For Review**
   The answer will be considered in the evaluation if an answer is entered for a question that is marked for review.

9. **Use Virtual Numerical Keypad**
   Although, there is no negative marking for numerical answer type questions, but entered a number as your answer if you are sure about that because, these type of questions containing a particular numerical value.

# **GATE Syllabus** for
# Chemistry

## Physical Chemistry

### Structure

Quantum theory: principles and techniques; applications to a particle in a box, harmonic oscillator, rigid rotor and hydrogen atom; valence bond and molecular orbital theories, Hückel approximation; approximate techniques: variation and perturbation; symmetry, point groups; rotational, vibrational, electronic, NMR, and ESR spectroscopy

### Equilibrium

Kinetic theory of gases; First law of thermodynamics, heat, energy, and work; second law of thermodynamics and entropy; third law and absolute entropy; free energy; partial molar quantities; ideal and non-ideal solutions; phase transformation: phase rule and phase diagrams – one, two, and three component systems; activity, activity coefficient, fugacity, and fugacity coefficient; chemical equilibrium, response of chemical equilibrium to temperature and pressure; colligative properties; Debye-Hückel theory; thermodynamics of electrochemical cells; standard electrode potentials: applications – corrosion and energy conversion; molecular partition function (translational, rotational, vibrational, and electronic).

### Kinetics

Rates of chemical reactions, temperature dependence of chemical reactions; elementary, consecutive, and parallel reactions; steady state approximation; theories of reaction rates – collision and transition state theory, relaxation kinetics, kinetics of photochemical reactions and free radical polymerization, homogeneous catalysis, adsorption isotherms and heterogeneous catalysis.

## Inorganic Chemistry

### Main group elements

General characteristics, allotropes, structure and reactions of simple and industrially important compounds: boranes, carboranes, silicones, silicates, boron nitride, borazines and phosphazenes. Hydrides, oxides and oxoacids of pnictogens (N, P), chalcogens (S, Se & Te) and halogens, xenon compounds, pseudo halogens and interhalogen compounds. Shapes of molecules and hard- soft acid base concept. Structure and Bonding (VBT) of B, Al, Si, N, P, S, Cl compounds. Allotropes of carbon: graphite, diamond, C60. Synthesis and reactivity of inorganic polymers of Si and P.

### Fluid Mechanics and Mechanical Operations

Fluid statics, Newtonian and non-Newtonian fluids, Bernoulli equation, Macroscopic friction factors, energy balance, dimensional analysis, shell balances, flow through pipeline systems, flow meters, pumps and compressors, packed and fluidized beds, elementary boundary layer theory, size reduction and size separation, free and hindered settling, centrifuge and cyclones, thickening and classification, filtration, mixing and agitation, conveying of solids.

### Transition Elements

General characteristics of d and f block elements; coordination chemistry: structure and isomerism, stability, theories of metal- ligand bonding (CFT and LFT), mechanisms of substitution and electron transfer reactions of coordination complexes. Electronic spectra and magnetic properties of transition metal complexes, lanthanides and actinides. Metal carbonyls, metal- metal bonds and metal atom clusters, metallocenes; transition metal complexes with bonds to hydrogen, alkyls, alkenes and arenes; metal carbenes; use of organometallic compounds as catalysts in organic synthesis. Bioinorganic chemistry of Na, K. Mg, Ca, Fe, Co, Zn, Cu and Mo.

### Solids

Crystal systems and lattices, miller planes, crystal packing, crystal defects; Bragg's Law, ionic crystals, band theory, metals and semiconductors, Different structures of AX, AX2, ABX3 compounds, spinels.

### Instrumental methods of analysis

Atomic absorption and emission spectroscopy including ICP-AES, UV- visible spectrophotometry, NMR, mass, Mossbauer spectroscopy (Fe and Sn), ESR spectroscopy, chromatography including GC and HPLC and electro-analytical methods (Coulometry, cyclic voltammetry, polarography – amperometry, and ion selective electrodes).

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## Organic Chemistry

### Stereochemistry

Chirality of organic molecules with or without chiral centres. Specification of configuration in compounds having one or more stereogeniccentres. Enantiotopic and diastereotopic atoms, groups and faces. Stereoselective and stereospecific synthesis. Conformational analysis of acyclic and cyclic compounds. Geometrical isomerism. Configurational and conformational effects on reactivity and selectivity/specificity.

### Reaction mechanism

Methods of determining reaction mechanisms. Nucleophilic and electrophilic substitutions and additions to multiple bonds. Elimination reactions. Reactive intermediates- carbocations, carbanions, carbenes, nitrenes, arynes, free radicals. Molecular rearrangements involving electron deficient atoms.

### Organic synthesis

Synthesis, reactions, mechanisms and selectivity involving the following- alkenes, alkynes, arenes, alcohols, phenols, aldehydes, ketones, carboxylic acids and their derivatives, halides, nitro compounds and amines. Use of compounds of Mg, Li, Cu, B and Si in organic synthesis. Concepts in multistep synthesis- retrosynthetic analysis, disconnections, synthons, synthetic equivalents, reactivity umpolung, selectivity, protection and deprotection of functional groups.

### Pericyclic reactions

Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlation, FMO and PMO treatments.

### Photochemistry

Basic principles. Photochemistry of alkenes, carbonyl compounds, and arenes. Photooxidation and photoreduction. Di-π- methane rearrangement, Barton reaction.

### Heterocyclic compounds

Structure, preparation, properties and reactions of furan, pyrrole, thiophene, pyridine, indole and their derivatives.

### Biomolecules

Structure, properties and reactions of mono- and di-saccharides, physicochemical properties of amino acids, chemical synthesis of peptides, structural features of proteins, nucleic acids, steroids, terpenoids, carotenoids, and alkaloids.

### Spectroscopy

Principles and applications of UV-visible, IR, NMR and Mass spectrometry in the determination of structures of organic molecules.

# Solved Paper 2015

# GATE Chemistry

**Time :** 3 hrs **MM :** 100

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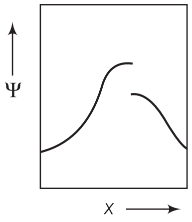
***Read the following instructions carefully***

1. There are 65 questions carrying 100 marks of 3 hrs duration in this paper.
2. Questions 1 to 25 carry 1 mark each and questions 26 to 55 carry 2 marks each.
3. Questions 56 to 65 belong to General Aptitude (GA) Type. Questions 56 to 60 carry 1 mark each and questions 61 to 65 carry 2 marks each.
4. Unattempted questions will carry zero marks.
5. For questions 1 to 25 and 56 to 60, 1/3 mark will be deducted for each wrong answer. For questions 26 to 55 and 61 to 65, 2/3 mark will be deducted for each wrong answer.
6. There is no negative marking for numerical answer type questions.
7. Non-programmable type calculator is allowed. Charts, graph sheets and mathematical tables are not allowed in the examination hall.

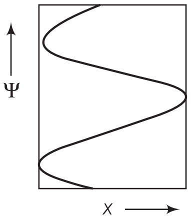
## (1 *Mark Questions*)

**1.** Which one of the following plots represents an acceptable wave function?

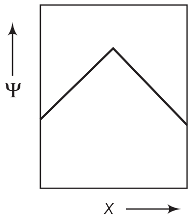
(a)



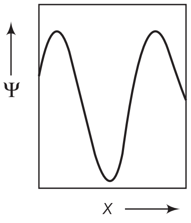
(b)



(c)



(d)



***Sol.*** (d) An acceptable wave function is that

(i) which has single value and is continuous. It means that the probability of finding the particle at time $t$ in an interval $\Delta x$ must be some number between 0 and 1.

(ii) which must be able to normalise.

(iii) in which, the total probability of finding the particle anywhere must be 1.

All these conditions are satisfied with plot given in option (d), so it represents an acceptable wave function.

**2.** When the operator, $-\hbar^2 d^2/dx^2$, operates on the function $e^{-ikx}$, the result is

(a) $k^2\hbar^2 e^{-ikx}$ (b) $ik^2\hbar^2 e^{-ikx}$

(c) $i\hbar^2 e^{-ikx}$ (d) $\hbar^2 e^{-ikx}$

***Sol.*** (a) Function × operator = result

$$e^{-ikx} - \hbar^2 \frac{d^2}{dx^2} = ?$$

$$e^{-ikx} - \hbar \frac{d}{dx} = (-\hbar)(-ik)e^{-ikx}$$

On further differentiation, we get

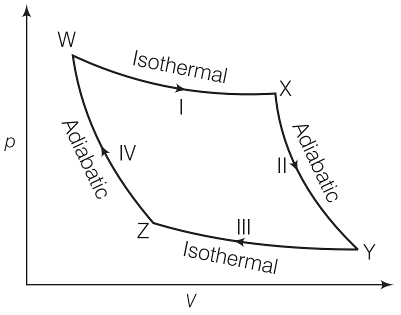
$$(-\hbar)(-ik)e^{-ikx}\frac{d^2}{dx^2} = -\hbar^2(+i^2k^2)e^{-ikx}$$

$$= -1(-1)\hbar^2k^2e^{-ikx} \qquad [\because i^2 = -1]$$

$$= +1 \times \hbar^2k^2e^{-ikx}$$

$$= \hbar^2k^2e^{-ikx}$$

**3.**



From the above Carnot cycle undergone by an ideal gas, identify the processes in which the change in internal energy is non-zero.

(a) I and II
(b) II and IV
(c) II and III
(d) I and IV

**Sol.** (b) Internal energy ($\Delta E$) is a function of temperature ($\Delta T$) since, the temperature remains constant during an isothermal process, so change in internal energy is zero for isothermal process.

For adiabatic process (expansion as well as compression), $q$ is zero but $\Delta T$ is not.

So, $\Delta E$ is also non-zero.

**4.** For an ideal gas with molar mass $M$, the molar translational entropy at a given temperature is proportional to

(a) $M^{3/2}$
(b) $M^{1/2}$
(c) $e^M$
(d) $\ln(M)$

**Sol.** (d) For an ideal gas, the molar translational entropy is calculated by using Sacker-Tetrode equation which is as follows:

$$S_{m,\,t} = R\left\{\frac{3}{2}\ln\,(M/\text{kg mol}^{-1}) + \frac{5}{2}\ln\,(T/\text{K}) - \ln\,(p/\text{pa}) + 20.72\right\}$$

At constant temperature,

$$S_{m,\,t} \propto \ln(M)$$

**5.** Which one of the following defines the absolute temperature of a system?

(a) $\left(\frac{\partial U}{\partial S}\right)_V$
(b) $\left(\frac{\partial A}{\partial S}\right)_V$
(c) $\left(\frac{\partial H}{\partial S}\right)_V$
(d) $\left(\frac{\partial G}{\partial S}\right)_V$

**Sol.** (a) For a thermodynamic process, change in entropy of a system,

$$\Delta S = \frac{dQ_{\text{rev}}}{T} \qquad \ldots\text{(i)}$$

we know that first law of thermodynamics is

$$\Delta U = q + W$$

At constant volume,

$$W = p\Delta V = p \times 0 = 0$$

So, $$\Delta U = q = Q_{\text{rev}} \qquad \ldots\text{(ii)}$$

From Eqs. (i) and (ii)

$$\Delta S = \frac{\Delta U}{T}$$

or $$T = \left(\frac{\Delta U}{\Delta S}\right)_V$$

**6.** Which of the following properties are characteristic of an ideal solution?

I. $(\Delta_{\text{mix}} G)_{T,p}$ is negative
II. $(\Delta_{\text{mix}} S)_{T,p}$ is positive
III. $(\Delta_{\text{mix}} V)_{T,p}$ is positive
IV. $(\Delta_{\text{mix}} H)_{T,p}$ is negative

(a) I and IV
(b) I and II
(c) I and III
(d) III and IV

**Sol.** (b) For ideal solutions, $A$-$B$ forces of interactions are equal to $A$-$A$ and $B$-$B$ forces of interactions. Thus, $(\Delta_{\text{mix}}H)_{T,\,p}$ and $(\Delta_{\text{mix}}V)_{T,\,p}$ are zero for such solution.

However, $(\Delta_{\text{mix}}S)_{T,\,p}$ is positive while $(\Delta_{\text{mix}}G)_{T,\,p}$ is negative (spontaneous process) for such solutions.

**7.** The expression for the equilibrium constant ($K_{\text{eq}}$) for the enzyme catalyzed reaction given below, is

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_4}{\overset{k_3}{\rightleftharpoons}} P + E$$

(a) $\frac{k_1k_3}{k_2k_4}$
(b) $\frac{k_1k_2}{k_3k_4}$
(c) $\frac{k_2k_3}{k_1k_4}$
(d) $\frac{k_1k_4}{k_2k_3}$

**Sol.** (a) For the formation of $ES$

$$k' = \frac{[ES]}{[E][S]} = \frac{k_1}{k_2}$$

For the formation of $P$ and $E$ from $ES$,

$$k'' = \frac{[P][E]}{[ES]} = \frac{k_3}{k_4}$$

Thus, for the conversion of $E$ and $S$ to $P$ and $E$,

$$k = k' \times k'' = \frac{[P][E]}{[E][S]} = \frac{k_1k_3}{k_2k_4}$$

**8.** Given the $E°$ values for the following reaction sequence,

$$\text{Mn}^{6+} \xrightarrow{1.28\text{ V}} \text{Mn}^{5+} \xrightarrow{2.9\text{ V}} \text{Mn}^{4+} \xrightarrow{0.96\text{ V}} \text{Mn}^{3+} \xrightarrow{1.5\text{ V}} \text{Mn}^{2+}$$

the computed value of $E°$ for $\text{Mn}^{6+} \longrightarrow \text{Mn}^{2+}$ (in volts) is _______ .

**Sol.** Electrode potentials are not the thermodynamic functions so they could not be added. They can be calculated from the equation of free energy change,

i.e. $$\Delta G = -\,nFE$$

I. $Mn^{6+} \xrightarrow{1.28\text{ V}} Mn^{5+}, \quad \Delta G_1 = 1.28\text{ F}$

II. $Mn^{5+} \xrightarrow{2.9\text{ V}} Mn^{4+}, \quad \Delta G_2 = -2.9\text{ F}$

III. $Mn^{4+} \xrightarrow{0.96\text{ V}} Mn^{3+}, \quad \Delta G_3 = -0.96\text{ F}$

IV. $Mn^{3+} \xrightarrow{1.5\text{ V}} Mn^{2+}, \quad \Delta G_4 = -1.5\text{ F}$

$\therefore \quad Mn^{6+} \longrightarrow Mn^{2+}$

$$\begin{aligned}\Delta G &= \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 \\ &= -1.28\text{ F} - 2.9\text{ F} - 0.96\text{ F} - 1.5\text{ F} \\ &= -6.64\text{ F}\end{aligned}$$

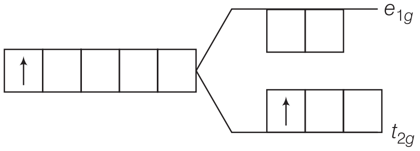
$$\therefore \quad \Delta G = -6.64\text{F} = -nFE = -4 \times F \times E$$

$$E = \frac{6.64}{4} = 1.66$$

**9.** The absorption spectrum of $[Ti(H_2O_6)]^{3+}$ in solution comprises of a maximum with a shoulder. The reason for the shoulder is

(a) ligand-to-metal charge transfer (LMCT)
(b) metal-to-ligand charge transfer (MLCT)
(c) Jahn-Teller distortion
(d) nephelauxetic effect

***Sol.*** (c) Electronic configuration of $[Ti\ (H_2O)_6]^{2+}$ =



Above diagram shows that this complex contains a single electron in one of the three lower energy $t_{2g}$ orbitals. Presence of which leads to distortion in its geometry from octahedral to tetrahedral in which the Ti—OH$_2$ bond along two axes are shorter than those along $x$ and $y$ axes (Jahn-Teller distortion). This electron may go to $d_z^2$ or $d_{x^2-y^2}$ orbitals.

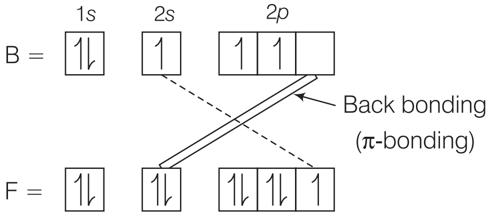
Thus, there should be two absorption bands. The energy gap $\Delta E\ (Ed_z^2 - Ed_{xy})$ is not very much different from the energy gap $\Delta E\ (Ed_{x^2\text{-}y^2} - Ed_{xy})$. Therefore, the two transitions are of close energy givinig rise to two bands at close frequencies which overlap to give a (single) composite absorption band.

**10.** The ease of formation of the adduct, $NH_3 \cdot BX_3$ (where, $X$ = F, Cl, Br) follows the order

(a) $BBr_3 < BCl_3 < BF_3$
(b) $BCl_3 < BF_3 < BBr_3$
(c) $BF_3 < BCl_3 < BBr_3$
(d) $BBr_3 < BF_3 < BCl_3$

***Sol.*** (c) $NH_3 \cdot BX_3$ adduct is formed by the donation of lone pair of N to empty $p$-orbital of B. Thus, more the availability of empty $p$-orbital on B for acceptance of lone pair of N (of $NH_3$), more will be the ease of formation of adduct.

In case of $BF_3$, $p\pi$-$p\pi$ back donation occurs due to the similar energy of $p$-orbitals of B and F. Hence, it has least tendency to form adduct, (i.e. to accept lone pair of N).



The tendency of back bonding (π-bonding) decreases from F to Br (due to increase in energy difference of $p$-orbitals of B and $X$). Hence, ease of formation of adduct increases in the same fashion, i.e. the order is

$$BF_3 < BCl_3 < BBr_3$$

**11.** An efficient catalyst for hydrogenation of alkenes is $[Rh(PPh_3)_3Cl]$. However, $[Ir(PPh_3)_3Cl]$ does not catalyze this reaction, because

(a) $PPh_3$ binds stronger to Ir than to Rh
(b) Cl binds stronger to Ir than to Rh
(c) $PPh_3$ binds stronger to Rh than to Ir
(d) Cl binds stronger to Rh than to Ir

***Sol.*** (a) During hydrogenation process, $[Rh\ (PPh_3)_3Cl]$ is first converted to an active form by losing triphenyl phosphine ligand before entering in the catalytic cycle which is generally occupied by solvent molecules.

Since, the bond formed between $PPh_3$ and Ir is much stronger than that between Rh and $PPh_3$, so lose of $PPh_3$ is not possible. Hence, it cannot be used as a catalyst for this process.

**12.** Among the given pH values, the $O_2$ binding efficiency of haemoglobin is maximum at

(a) 6.8 (b) 7.0 (c) 7.2 (d) 7.4

***Sol.*** (d) The oxygen binding capacity of haemoglobin is maximum at 7.4. This is because at this pH, side chain of histidine β 146 is not protonated and the salt bridge does not form.

However, at low pH, protonation and formation of salt bridge occurs, due to which quarternary structure characteristic of deoxyhaemoglobin is stabilised.

**13.** The intense red colour of $[Fe(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) is due to

(a) metal-to-ligand charge transfer (MLCT)
(b) ligand-to-metal charge transfer (LMCT)
(c) $d$-$d$ transition
(d) inter-valence charge transfer (IVCT)

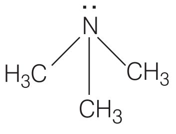
***Sol.*** (a) Electronic configuration of $Fe^{2+}$ = [Ar 40 ]$3d^6$ and $b_{py}$ (2, 2′-bipyridine) is an aromatic ligand with low lying $\pi^*$ orbital, so metal ($Fe^{2+}$) transfers its electron to $\pi^*$ system of the ligand due to which, its colour is intense red. (MLCT)

**14.** The compound with planar geometry is

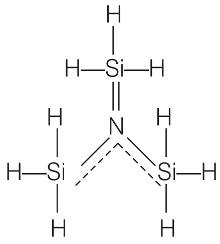
(a) $N(t\text{-Bu})_3$ (b) $NPh_3$

(c) $NF_3$ (d) $N(SiH_3)_3$

***Sol.*** (d) $(CH_3)_3N$ is $sp^3$-hybridised on N with pyramidal shape due to $p\pi$-$p\pi$ bonding whereas in $(SiH_3)_3N$, Si has vacant $d$-orbitals which form $p\pi$-$d\pi$ bonding due to which N becomes $sp^2$-hybridised and has trigonal planar shape.



Pyramidal



Planar

**15.** The electrical conductivity of a metal

(a) increases with increasing temperature

(b) decreases with increasing temperature

(c) is independent of temperature

(d) shows oscillatory behaviour with temperature

***Sol.*** (b) In case of metals, the current (charge) carrying particles are electrons, i.e. a systematic flow of electrons in one direction will be responsible for the conduction of electricity. When temperature increases, some of the electrons get excited and this causes them to move in a not so orderely manner.

Hence, the electrons become less efficient as the charge carries and result in decreased conductivity.

**16.** Which one of the following statements is incorrect?

(a) Frenkel defect is a cation vacancy and a cation interstitial

(b) Frenkel defect is an anion vacancy and a cation interstitial

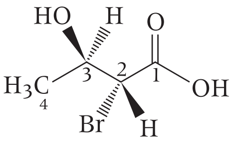
(c) Density of a solid remains unchanged in case of Frenkel defects

(d) Density of a solid decreases in case of Schottky defects

***Sol.*** (b) Frenkel defect is an interstitial defect in which the smaller ion (generally the cation) left its position and occupy some interstitial space (cation vacancy). Since, no ion (species) is lost from the crystal in this defect, so density of the crystal remains unchanged. It is shown by compounds in which cation is much smaller in size as compared to anion, e.g. AgBr, AgI etc.

Schottky defect, on the other hand, is due to missing of equal number of cations and anions from the crystal lattice so, it results in decreased density.

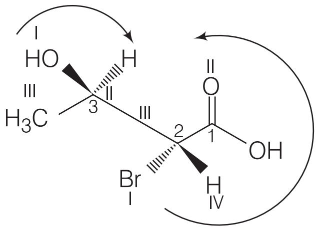
**17.** The absolute configuration of $C_2$ and $C_3$ in the following compound is



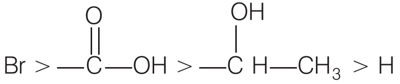
(a) $2R, 3S$ (b) $2S, 3R$

(c) $2S, 3S$ (d) $2R, 3R$

***Sol.*** (d)



For $C_2$, priority order is

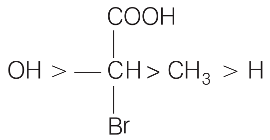


$$Br > —\overset{\overset{\displaystyle O}{\|}}{C}—OH > —\overset{\overset{\displaystyle OH}{|}}{C}H—CH_3 > H$$

H is at the nearest position,

so anticlockwise rotation means $R$ configuration.

For $C_3$, priority order is



$$OH > —\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle COOH}{|}}{C}}H > CH_3 > H$$

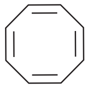
H is at the farthest position.

So, clockwise rotation means $R$ configuration.

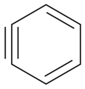
Thus, absolute configuration of $C_2$ and $C_3$ is $2R$ and $3R$.

**18.** Among the following compounds, the one that is non-aromatic, is

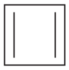
(a)



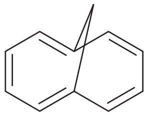
(b)



(c)



(d)

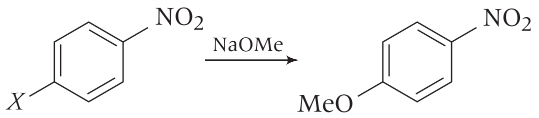


***Sol.*** (a) For being aromatic, a compound should be planar and must has $(4n+2)\,\pi$ electrons. But, if it contains $4n\pi$ electrons, it is antiaromatic.

Cyclooctatetraene is a conjugated eight carbon ring system.

This molecule is not planar but is tub-shaped. A regular octagon has angles of 135° while $sp^2$ angles are most stable at 120°. In order to avoid this angle strain, the molecule assumes as non-planar conformation that avoids most of the overlap between adjacent $\pi$-bond, i.e. non-planarity uncouples the $p$-orbitals and interrupts orbital connectivity. Hence, it is a non-aromatic compound.

**19.** The correct order of reactivity of $p$-halonitrobenzenes in the following reaction is



($X$=F, Cl, Br, I)

(a) $p$-chloronitrobenzene > $p$-iodonitrobenzene > $p$-fluoronitrobenzene > $p$-bromonitrobenzene

(b) $p$-fluoronitrobenzene > $p$-chloronitrobenzene > $p$-bromonitrobenzene > $p$-iodonitrobenzene

(c) $p$-iodonitrobenzene > $p$-bromonitrobenzene > $p$-chloronitrobenzene > $p$-fluoronitrobenzene

(d) $p$-bromonitrobenzene > $p$-fluoronitrobenzene > $p$-iodonitrobenzene > $p$-chloronitrobenzene

***Sol.*** (b) Presence of electron withdrawing —$NO_2$ group makes the $X$ group attached with benzene ring more reactive towards nucleophilic substitution reaction.

Further, more the electronegativity, more is the ease to undergo nucleophilic substitution reaction.

Hence, the correct order of reactivity is

$p$-fluoronitrobenzene > $p$-chloronitrobenzene > $p$-bromonitrobenzene > $p$-iodonitrobenzene

**20.** Tollen's test is negative for

(a) mannose

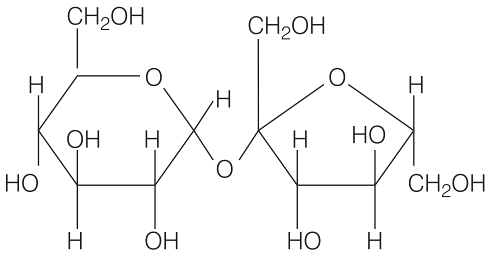
(b) maltose

(c) glucose

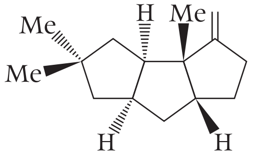
(d) sucrose

***Sol.*** (d) In sucrose, the components glucose and fructose are linked via an ether bond between $C_1$ on the glucosyl subunit and $C_2$ on the fructosyl unit. This bond is called glycosidic linkage.

Since, it does not contain free hemiacetal (anomeric —OH group), so it does not give silver mirror with Tollen's reagent. (i.e. it gives negative Tollen's test.)

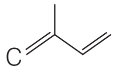


**21.** The compound given below is a



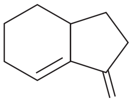
(Hirsutene)

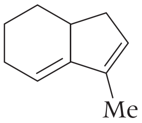
(a) sesterterpene
(b) monoterpene
(c) sesquiterpene
(d) triterpene

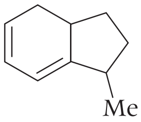
***Sol.*** (c) Since, the given compound (hirsutene) is a 15 carbon compound with 3 isoprene units  so it is a sesquiterpene

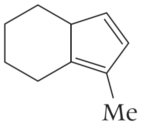
**Note** : Sesterterpene contains 5 isoprene units, monoterpene contains 2 isoprene units and triterpenes have 6 isoprene units.

**22.** Amongst the following, the compound that does not act as a diene in Diels-Alder reaction is

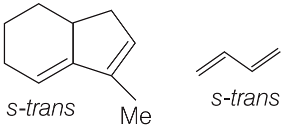
(a) 

(b) 

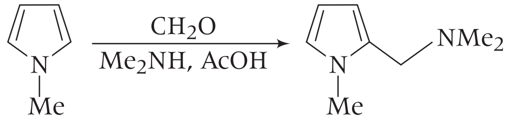
(c) 

(d) 

***Sol.*** (b) Dienes having *s-trans* configuration do not undergo Diels-Alder reaction.



**23.** The following conversion is an example of



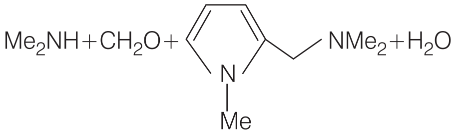
(a) Arndt-Eistert homologation

(b) Mannich reaction

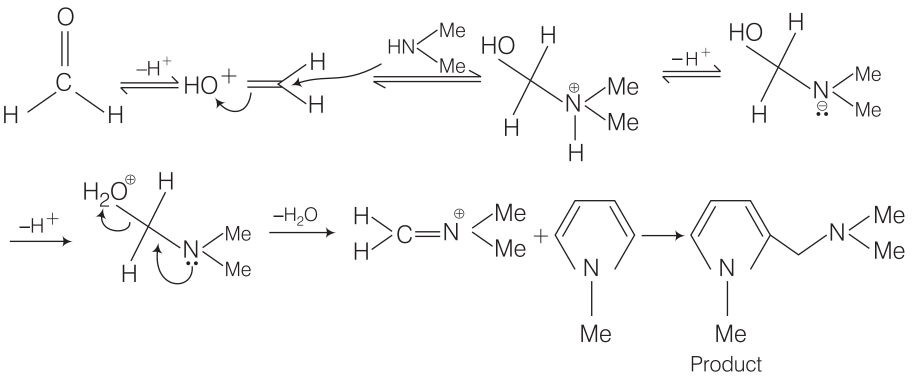
(c) Michael addition

(d) Chichibabin amination reaction

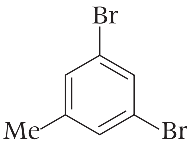
***Sol.*** (b) Mannich reaction involves the combination of an aldehyde usually formaldehyde ($CH_2O$ or HCHO) with ammonia or 1° or 2° amine and a compound containing activated hydrogen.

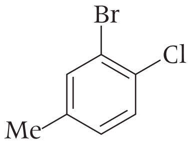


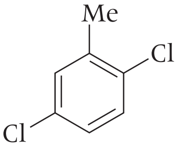
**Mechanism**

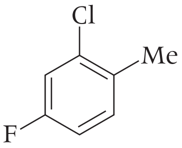


**24.** The mass spectrum of a dihalo compound shows peaks with relative intensities of 1 : 2 : 1 corresponding to $M$, $M+2$ and $M+4$ ($M$ is the mass of the molecular ion), respectively. The compound is

(a)


(b)


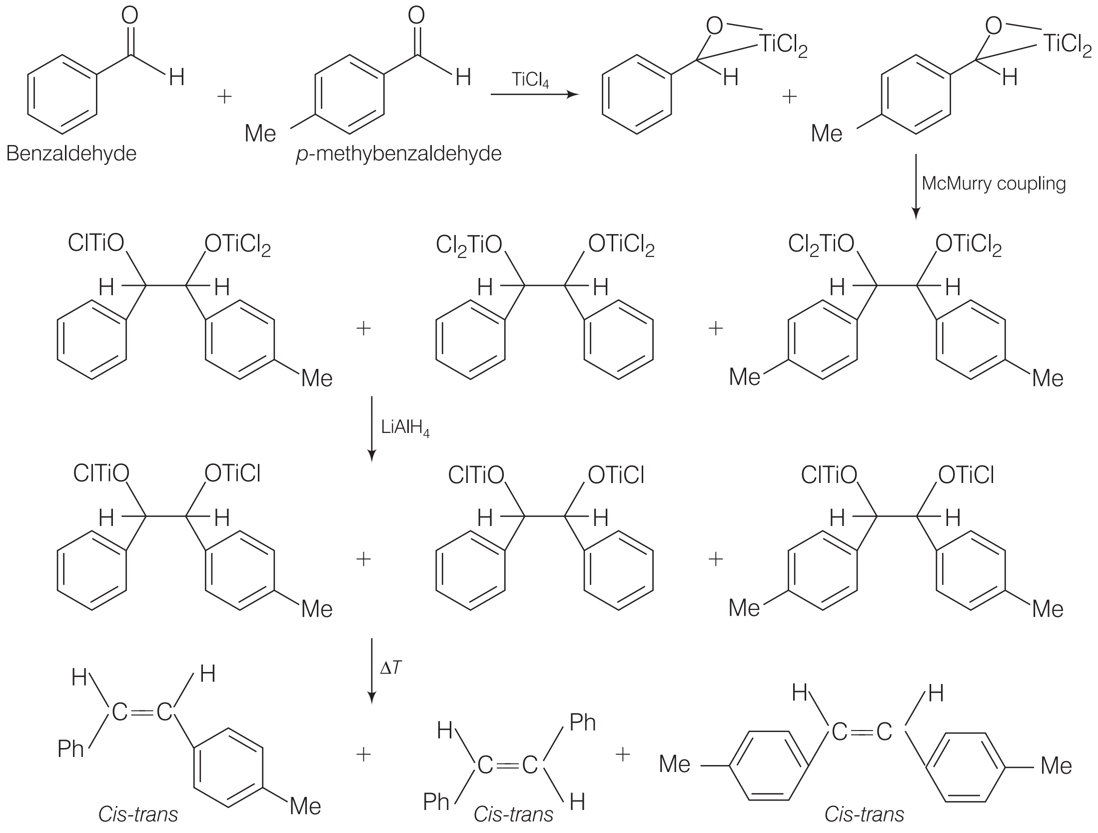
(c)


(d)


***Sol.*** (a) Formation of peaks in 1 : 1 suggests that both the halogen atoms are of Br.
Here, sum of carbon and hydrogen is 90. Thus, the $M+2$ peaks appear at $90 + 79 = 169$ and $90 + 81 = 171$
The $M + 4$ peak is due to the presence of two halo atoms as $90 + 79 + 79 = 248$, $90 + 81 + 81 = 252$ and $90 + 79 + 81 = 250$

**25.** Reaction of benzaldehyde and *p*-methylbenzaldehyde under McMurry coupling conditions ($TiCl_3$ and $LiAlH_4$) gives a mixture of alkenes. The number of alkenes formed is _______ .

***Sol.***



## (2 Marks Questions)

**26.** The difference in the ground state energies (kJ/mol) of an electron in one-dimensional boxes of lengths 0.2 nm and 2 nm is _______ .

***Sol.*** Energy associated with particle in a one-dimensional box,

$$E = \frac{n^2h^2}{8mL^2}$$

When $L = 0.2$ nm

$$E_1 = \frac{n^2h^2}{8\,m\,(0.2)^2}$$

When $L = 2$ nm

$$E_2 = \frac{n^2h^2}{8m\,(2)^2}$$

$$\Delta E = E_1 - E_2 = \frac{n^2h^2}{8m}\left[\frac{1}{(0.2)^2} - \frac{1}{(2)^2}\right]$$

For ground state, $n = 1$ mass of electron $= 9.1\times 10^{-31}$ kg

$$h = 6.6\times 10^{-34}\ \text{Js}$$

On substituting the values,

$$\Delta E = \frac{(1)^2\times(6.6\times10^{-34})^2}{8\times 9.1\times 10^{-31}}\left[\frac{10^{18}\times 100}{4} - \frac{10^{18}}{4}\right]\text{J}$$

$$= 5.98\times 10^{-38}\left[\frac{10^{18}\times 99}{4}\right]$$

$$= 148\times 10^{-38}\times 10^{18} = 1.48\times 10^{-18}\ \text{J}$$

$$= 1.48\times 10^{-18}\times 6.02\times 10^{23}\times 10^{-3}\ \text{kJ/mol}$$

$$= 890.96 \approx 891$$

**27.** The mean ionic activity coefficient of 0.001 molal $ZnSO_4$ (*aq*) at 298 K according to the Debye-Huckel limiting law is (Debye-Huckel constant is 0.509 molal $^{-1/2}$) _______ .

***Sol.*** Mean ionic activity $= \frac{1}{2}[m_1z_1^2 + m_2z_2^2]$

$$= \frac{1}{2}[0.001\,(2)^2 + (0.001)\,(-2)^2]$$

$$= \frac{1}{2}[0.004 + 0.004] = 0.004$$

$$\log\gamma\pm = -0.509\ |z_1z_2|\ \sqrt{I}$$

$$= -0.509|+2, -2|\ \sqrt{0.004}$$

$$= -0.509\times 4\times 0.0632$$

$$= -0.128$$

$$\therefore\quad \gamma\pm = \text{antilog}\,(-0.128) = 0.743$$

**28.** The process given below follows the Langmuir adsorption isotherm.

$$A_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A_{\text{ads}}$$

If θ denotes the surface coverage and *p* denotes the pressure, the slope of the plot of $1/\theta$ *versus* $1/\sqrt{p}$ is

(a) $1/(K_{\text{eq}})^2$ (b) $1/K_{\text{eq}}$

(c) $-1/K_{\text{eq}}$ (d) $1/(K_{\text{eq}})^{1/2}$

***Sol.*** (d) $A_2\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,A_{\text{ads}}$

Here, $k_1$ rate constant for adsorption (for forward reaction) and $k_{-1}$ rate constant for desorption (for backward reaction)

Thus, $$K_{\text{eq}} = \frac{k_1}{k_{-1}} \qquad \text{...(i)}$$

$A_2\,(g) + \text{surface} \rightleftharpoons 2\,A_{\text{ads}}$

At initially $p$ $N$ $0$

(Here $N$ = total number of sites)

At equilibrium $p$ $N\,(1-\theta)$ $N\theta$

$$\therefore\quad \frac{d\theta}{dt} = k_1\,pA_2\,[M]_{\text{surface}} = k_1\,p\times[N\,(1-\theta)]^2$$

For backward reaction, i.e. for desorption,

$$\frac{d\theta}{dt} = k_{-1}\,(N\theta)^2$$

At equilibrium,

$$k_1\,p\,[N\,(1-\theta)]^2 = k_{-1}\,[N\theta]^2$$

$$\frac{k_1p}{k_{-1}} = \frac{[N\theta]^2}{[N\,(1-\theta)]^2} \Rightarrow \frac{k_{-1}}{k_1p} = \frac{[N-N\theta]^2}{[N\theta]^2}$$

$$\sqrt{\frac{k_{-1}}{k_1p}} = \frac{1}{\theta} - 1$$

$$\sqrt{\frac{k_{-1}}{k_1p}} + 1 = \frac{1}{\theta} \quad \text{or} \quad \frac{-1}{\sqrt{K_{\text{eq}}p}} + 1 = \frac{1}{\theta}$$

Thus, if $\frac{1}{\theta}$ is plotted with $\frac{1}{\sqrt{p}}$, slope of the plot is $1/\sqrt{K_{\text{eq}}}$ or $\frac{1}{(K_{\text{eq}})^{1/2}}$.

**29.** For a gas phase unimolecular reaction at temperature 298 K, with a pre-exponential factor of $2.17\times 10^{13}\,\text{s}^{-1}$, the entropy of activation $(\text{JK}^{-1}\text{mol}^{-1})$ is _______ .

***Sol.*** Pre-exponential factor, $A = \frac{k_bT}{h}\exp^{\Delta S^\#/R}$

Here $K_b$ = Boltzmann constant

$= 1.38\times 10^{-23}\ \text{m}^2\text{kg s}^{-2}\text{K}^{-1}$

$T = 298$ K

$h = 6.62\times 10^{-34}\ \text{m}^2\ \text{kg s}^{-1}$

$A = 2.17\times 10^{13}\ \text{s}^{-1}$

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

On substituting values,

$$2.17\times 10^{13} = \frac{1.38\times 10^{-23}\times 298}{6.62\times 10^{-34}}\,e^{\Delta S^\#/8.314}$$

$$2.17\times 10^{13} = 6.212\times 10^{12}\,e^{\Delta S^\#/8.314}$$

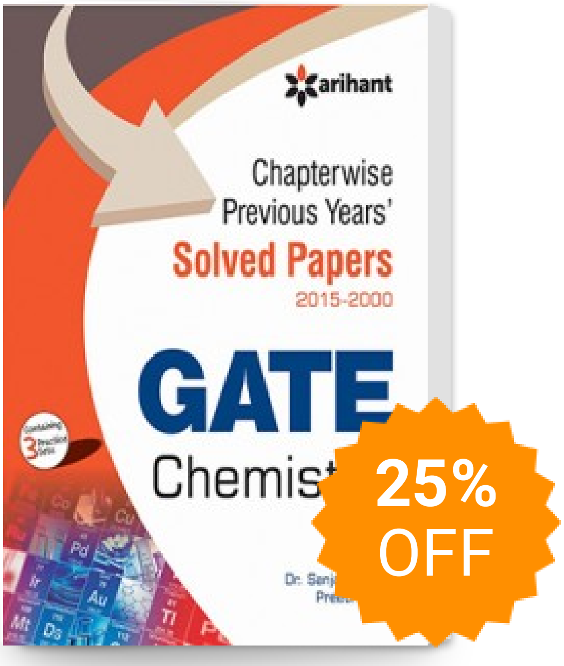
$$e^{\Delta S^\#/8.314} = 3.49$$

$$\frac{\Delta S^\#}{8.314} = \ln 3.49 = 1.25$$

$\therefore$ $\Delta S^\#$ (entropy of activation) $= 1.25\times 8.314$

$= 10.39\ \text{J K}^{-1}\ \text{mol}^{-1}$

# Chapterwise GATE Chemistry Solved Papers(2014-2000)



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