GATE 2017

Graduate Aptitude Test in Engineering

Chemistry

Previous Papers

(2000-2016)

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GATE Papers
Chemistry

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GATE 2017

Graduate Aptitude Test in Engineering

Indian Institute of Technology, Mumbai

Indian Institute of Technology, Kharagpur

Indian Institute of Technology, Delhi

Indian Institute of Technology, Chennai

Indian Institute of Technology, Guwahati

Indian Institute of Technology, Roorkee

Indian Institute of Technology, Kanpur

Preface

The Graduate Aptitude Test in Engineering (GATE) in an online exam conducted by the IITs for admissions to PG courses in IITs, IISc Bangalore, NITs and many state run universities as well as private universities. Also there are more than 37 PSUs that use GATE score for recruitments. A large number of corporates are also using GATE score as a tool to screen students for placements.

GK Publications is well known as the "publisher of choice" to students preparing for GATE and other technical examinations in the country. We published the first set of books in 1994 when GATE exam, both objective and conventional, was conducted in the paper and pencil environment, and used as a check point for entry to post graduate courses in IITs and IISCs. At that time, students had little access to technology and relied mainly on instructor led learning followed by practice with books available for these examinations.

A lot has changed since then!

Today, GATE is conducted in an online only mode with multiple choice and numerical based questions. The score is valid for three years and is used not only for post graduate courses but is also used by major PSUs for recruitment. Today's students have easy access to technology and the concept of a monologue within the classroom has changed to dialogue where students come prepared with concepts and then discuss topics. They learn a lot of things on the go with their mobile devices and practice for mock tests online.

We, as a leading publisher of GATE books, have also embraced change. Today, our books are no more guides and papers only but come with a fully supported mobile app and a web portal. The mobile app provides access to video lectures, short tests and regular updates about the exam. The web portal in additional to what is available on the app provides full length mock tests to mimic the actual exam and help you gauge your level of preparedness. The combination of practice content in print, video lectures, and short and full length tests on mobile and web makes this product a complete courseware for GATE preparation.

This book includes previous years GATE questions along with Answer Keys. It will help the GATE aspirants to know an idea about the pattern of questions asked in GATE examination.

We also know that improvement is a never ending process and hence we welcome your suggestions and feedback or spelling technical errors if any. Please write to us at gkp@gkpublications.com

We hope that our small effort will help you prepare well for the examination.

We wish you all the best!

GK Publications Pvt. Ltd.

About GATE

The Graduate Aptitude Test in Engineering (GATE) conducted by IISc and IITs has emerged as one of the bench mark tests for engineering and science aptitude in facilitating admissions for higher education (M.Tech./Ph.D.) in IITs, IISc and various other Institutes/Universities/Laboratories in India. With the standard and high quality of the GATE examination in 23 disciplines of engineering and science subjects, it identifies the candidate's understanding of a subject and aptitude and eligibility for higher studies. During the last few years, GATE score is also being used as one of the criteria for recruitment in Government Organizations such as Cabinet Secretariat, and National/State Public Sector Undertakings in India. Because of the importance of the GATE examination, the number of candidates taking up GATE exams has increased tremendously and in GATE 2016 more than 9.5 Lac candidates applied for the examination. GATE exams are conducted by the IITs and IISc as a computer based test having multiple choice questions and numerical answer type questions. The questions are mostly fundamental, concept based and thought provoking. This year GATE 2017 shall hold examinations for candidates in Bangladesh, Ethiopia, Nepal, Singapore, Sri Lanka and United Arab Emirates. An Institute with various nationalities in its campus widens the horizons of an academic environment. A foreign student brings with him/her a great diversity, culture and wisdom to share. Many GATE qualified candidates are paid scholarships/assistantship, especially funded by Ministry of Human Resources Development, Government of India and by other Ministries. Indian Institute of Technology Roorkee is the Organizing Institute for GATE 2017.

New in GATE 2017

- GATE examinations shall be conducted in Bangladesh, Ethiopia, Nepal, Singapore, Sri Lanka and United Arab Emirates. The pattern of examination remains same, exam timing/Center shall be notified in admit cards. The International candidates should have completed Bachelor's degree in Engineering or Master's degree in Science in relevant subject or are in the final year of the program.
- February 4th, 5th 11th and 12th 2017 (tentative) in two sessions (Forenoon session: 9.00 AM-12.00 Noon; Afternoon session: 2.00 PM-5.00 PM). Any change in timings or sessions/dates shall be displayed on GATE website (www.gate.iitr.ernet.in). The session timings at GATE International Centers according to their local time shall be notified well in advance.
- The XE (Engineering Sciences) paper now has a new section on Atmospheric and Oceanic Sciences (section H). With this the number of sections in the XE paper has increased to eight (A-H).

- No restriction on second choice examination city to be in the same zone as first choice city. It can be anywhere in India. Thumb impression of candidates needs to be uploaded during the application procedure. Candidates who have completed the qualifying degree, need to upload scanned image of degree completion certificate or final year/semester mark sheet. However, candidates studying in the final year of their qualifying degree need to upload scanned image of pre-final year (or fifth/sixth semester) mark sheet, or provisional certificate letter from his/her Institute as proof of eligibility criterion. Similarly this applies to candidates of AMIE, AMICE and other similar programs.

Why GATE?

Admission to Post Graduate and Doctoral Programmes

Admission to postgraduate programmes with MHRD and some other government scholarships/assistantships in engineering colleges/institutes is open to those who qualify through GATE. GATE qualified candidates with Bachelor's degree in Engineering/Technology/Architecture or Master's degree in any branch of Science/ Mathematics/Statistics/Computer Applications are eligible for admission to Master/Doctoral programmes in Engineering/Technology/Architecture as well as for Doctoral programmes in relevant branches of Science with MHRD or other government scholarships/assistantships. Candidates with Master's degree in Engineering/Technology/Architecture may seek admission to relevant PhD programmes with scholarship/assistantship without appearing in the GATE examination.

Financial Assistance

A valid GATE score is essential for obtaining financial assistance during Master's programs and direct Doctoral programs in Engineering/Technology/Architecture, and Doctoral programs in relevant branches of Science in Institutes supported by the MHRD or other Government agencies. As per the directives of the MHRD, the following procedure is to be adopted for admission to the post-graduate programs (Master's and Doctoral) with MHRD scholarship/ assistantship. Depending upon the norms adopted by a specific institute or department of the Institute, a candidate may be admitted directly into a course based on his/her performance in GATE only **or** based on his/her performance in GATE **and** an admission test/interview conducted by the department to which he/she has applied **and/or** the candidate's academic record. If the candidate is to be selected through test/interview for post-graduate programs, a minimum of 70% weightage will be given to the performance in GATE and the remaining 30% weightage will be given to the candidate's performance in test/interview and/or academic record, as per MHRD guidelines. The admitting institutes could however prescribe a minimum passing percentage of marks in the test/interview. Some colleges/institutes specify GATE qualification as the mandatory requirement even for admission without MHRD scholarship/assistantship.

To avail of the financial assistance (scholarship), the candidate must first secure admission to a program in these Institutes, by a procedure that could vary from

institute to institute. Qualification in GATE is also a minimum requirement to apply for various fellowships awarded by many Government organizations. Candidates are advised to seek complete details of admission procedures and availability of MHRD scholarship/assistantship from the concerned admitting institution. The criteria for postgraduate admission with scholarship/ assistantship could be different for different institutions. The management of the post-graduate scholarship/assistantship is also the responsibility of the admitting institution. Similarly, reservation of seats under different categories is as per the policies and norms prevailing at the admitting institution and Government of India rules. *GATE offices will usually not entertain any enquiry about admission, reservation of seats and / or award of scholarship / assistantship.*

PSU Recruitments

As many as 37 PSUs are using GATE 2016 score for recruitment. It is likely that more number of PSUs may start doing so by next year. Below is the list of PSUs:

MDL, BPCL, GAIL, NLC LTD, CEL, Indian Oil, HPCL, NBPC, NECC, BHEL, WBSEDCL, NTPC, ONGC, Oil India, Power Grid, Cabinet Secretariat, Govt. of India, BAARC, NFL, IPR, PSPCL, PSTCL, DRDO, OPGC Ltd., THDC India Ltd., BBNL, RITES, IRCON, GHECL, NHAI, KRIBHCO, Mumbai Railway Vikas Corporation Ltd. (MRVC Ltd.), National Textile Corporation, Coal India Ltd., BNPM, AAI, NALCO, EdCIL India.

Important :

1. Admissions in IITs/IISc or other Institutes for M.Tech./Ph.D. through GATE 2017 scores shall be advertised separately by the Institutes and GATE 2017 does not take the responsibility of admissions.
2. Cabinet Secretariat has decided to recruit officers for the post of Senior Field Officer (Tele) (From GATE papers of EC, CS, PH), Senior Research Officer (Crypto) (From GATE papers of EC, CS, MA), Senior Research Officer (S&T) (From GATE papers EC, CS, CY, PH, AE, BT) in the Telecommunication Cadre, Cryptographic Cadre and Science & Technology Unit respectively of Cabinet Secretariat. The details of the scheme of recruitment shall be published in National Newspaper/Employment News by the concerned authority.
3. Some PSUs in India have expressed their interest to utilize GATE 2017 scores for their recruitment purpose. The Organizations who intend to utilize GATE 2017 scores shall make separate advertisement for this purpose in Newspapers etc.

Who Can Appear for GATE?

Eligibility for GATE 2017

Before starting the application process, the candidate must ensure that he/she meets the eligibility criteria of GATE 2017 given in Table.

Eligibility Criteria for GATE 2017

Qualifying Degree	Qualifying Degree/Examination (Descriptive)	Description of Eligible Candidates	Year of qualification cannot be later than
B.E./B.Tech./ B.Pharm.	Bachelor's degree holders in Engineering/ Technology (4 years after 10+2 or 3 years after B.Sc./Diploma in Engineering/ Technology)	Currently in the final year or already completed	2017
B. Arch.	Bachelor's degree holders of Architecture (Five years course)	Currently in the final year or already completed	2017
B.Sc. (Research)/ B.S.	Bachelor's degree in Science (Post-Diploma/4 years after 10+2)	Currently in the 4th year or already completed	2017
M. Sc./ M.A./MCA or equivalent	Master's degree in any branch of Science/Mathematics / Statistics / Computer Applications or equivalent	Currently in the final year or already completed	2017
Int. M.E. / M.Tech. (Post-B.Sc.)	Integrated Master's degree programs in Engineering / Technology (Four year program)	Currently in the 2nd/3rd/4th year or already completed	2019
Int. M.E./ M.Tech. or Dual Degree(after Diploma or 10+2)	Integrated Master's degree program or Dual Degree program in Engineering / Technology (Five year program)	Currently in the 4th/5th year or already completed	2018
Int. M.Sc./ Int. B.S.-M.S.	Integrated M.Sc. or Five year integrated B.S.-M.S. program	Currently in the final year or already completed	2017
Professional Society Examinations (equivalent to B.E./B.Tech./B.Arch.)	B.E./B.Tech./B.Arch. equivalent examinations, of Professional Societies, recognized by MHRD/UPSC/AICTE (e.g., AMIE by Institution of Engineers-India, AMICE by the Institute of Civil Engineers-India)	Completed section A or equivalent of such professional courses	NA

In case a candidate has passed one of the qualifying examinations as mentioned above in 2016 or earlier, the candidate has to submit the degree certificate / provisional certificate / course completion certificate / professional certificate / membership certificate issued by the society or institute. In case, the candidate is expected to complete one of the qualifying criteria in 2017 or later as mentioned above, he/she has to submit a certificate from Principal or a copy of marks card for section A of AMIE.

Certificate From Principal

Candidates who have to submit a certificate from their college Principal have to obtain one from his/her institution beforehand and upload the same during the online submission of the application form.

Candidates With Backlogs

Candidates, who have appeared in the final semester/year exam in 2016, but with a backlog (arrears/failed subjects) in any of the papers in their qualifying degree should upload a copy of any one of the mark sheets of the final year,

OR

obtain a declaration from their Principal along with the signature and seal beforehand and upload the same during the online submission of the application form.

Structure of GATE 2017

For the GATE 2017 examination, a candidate can apply for only one of the 23 papers listed in Tables below. The syllabus for each of the papers is given separately. Making a choice of the appropriate paper during GATE application is the responsibility of the candidate. Some guidelines in this respect are suggested below.

The candidate is expected to appear in a paper appropriate to the discipline of his/her qualifying degree. However, the candidate can choose any paper according to his/her admission plan, keeping in mind the eligibility criteria of the institutions in which he/she wishes to seek admission. For more details regarding the admission criteria in any particular institute, the candidate is advised to refer to the website of that institute.

List of GATE Papers and Corresponding Codes

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

*XE Paper Sections	Code	**XL Paper Sections	Code
Engineering Mathematics (Compulsory)	A	Chemistry (Compulsory)	P
Fluid Mechanics	B	Biochemistry	Q
Materials Science	C	Botany	R
Solid Mechanics	D	Microbiology	S
Thermodynamics	E	Zoology	T
Polymer Science and Engineering	F	Food Technology	U
Food Technology	G		
Atmospheric and Oceanic Sciences	H		

*XE (Engineering Sciences) and **XL (Life Sciences) papers are of general nature and will comprise of Sections listed in the above table. More detailed explanation is given as following pages.

General Aptitude Questions

All the papers will have a few questions that test the General Aptitude (Language and Analytical Skills), apart from the core subject of the paper.

XE Paper

A candidate appearing in the XE paper has to answer the following

1. Section A – Engineering Mathematics

2. GA – General Aptitude

3. Any two of XE sections B to H

The choice of two sections from B to H can be made during the examination after viewing the questions. Only two optional sections can be answered at a time. A candidate wishing to change midway of the examination to another optional section must first choose to deselect one of the previously chosen optional sections (B to H).

XL Paper

A candidate appearing in the XL paper has to answer the following

1. Section P – Chemistry

2. GA – General Aptitude

3. Any two of XL sections Q to U

The choice of two sections from Q to U can be made during the examination after viewing the questions. Only two optional sections can be answered at a time. A candidate wishing to change midway of the examination to another optional section must first choose to deselect one of the previously chosen optional sections (Q to U).

Duration and Examination Type

The GATE examination consists of a single paper of **3-hour** duration that contains **65** questions carrying a maximum of **100 marks**. The question paper will consist of both multiple choice questions (MCQ) and numerical answer type (NAT) questions. The pattern of question papers is discussed in following paragraphs.

The examination for all the papers will be carried out in an ONLINE Computer Based Test (CBT) mode where the candidates will be shown the questions in a random sequence on a computer screen. The candidates are required to either select the answer (for MCQ type) or enter the answer for numerical answer type question using a mouse on a virtual keyboard (keyboard of the computer will be disabled). Each candidate will be provided with a scribble pad for rough work. The scribble pad has to be returned after the examination. At the end of the 3-hour window, the computer will automatically close the screen from further actions.

Pattern of Question Papers

In all the papers, there will be a total of 65 questions carrying 100 marks, out of which 10 questions carrying a total of 15 marks will be on General Aptitude (GA).

In the papers bearing the codes AE, AG, BT, CE, CH, CS, EC, EE, IN, ME, MN, MT, PE, PI, TF and XE, the Engineering Mathematics will carry around **15% of the total marks**, the General Aptitude section will carry **15% of the total marks** and the **remaining 70% of the total marks** is devoted to the subject of the paper.

In the papers bearing the codes AR, CY, EY, GG, MA, PH and XL, the General Aptitude section will carry **15% of the total marks** and the **remaining 85% of the total marks** is devoted to the subject of the paper.

GATE 2017 would contain questions of two different types in various papers:

(*i*) **Multiple Choice Questions (MCQ)** carrying 1 or 2 marks each in all papers and sections. These questions are objective in nature, and each will have a choice of four answers, out of which the candidate has to mark the correct answer(s).

(*ii*) **Numerical Answer Questions** of 1 or 2 marks each in all papers and sections. For these questions the answer is a real number, to be entered by the candidate using the virtual keypad. No choices will be shown for this type of questions.

Marking Scheme

For **1-mark** multiple-choice questions, **1/3** mark will be deducted for a wrong answer. Likewise, for **2-mark** multiple-choice questions, **2/3** mark will be deducted for a wrong answer. **There is NO negative marking for numerical answer type questions.**

Consult syllabus before proceeding

General Aptitude (GA) Questions

In all papers, GA questions carry a total of **15 marks**. The GA section includes 5 questions carrying **1-mark** each (sub-total **5 marks**) and 5 questions carrying **2-marks** each (sub-total **10 marks**).

Question Papers other than GG, XE and XL

These papers would contain **25** questions carrying **1-mark** each (sub-total **25 marks**) and **30** questions carrying **2-marks** each (sub-total **60 marks**). The question paper will consist of questions of multiple choice and numerical answer type. For numerical answer questions, choices will not be given. Candidates have to enter the answer (which will be a real number, signed or unsigned, e.g., 25.06, – 25.06, 25, – 25 etc.) using a virtual keypad. An appropriate range will be considered while evaluating the numerical answer type questions so that the candidate is not penalized due to the usual round-off errors.

GG (Geology and Geophysics) Paper

Apart from the General Aptitude (GA) section, the GG question paper consists of two parts: Part A and Part B. Part A is common for all candidates. Part B contains two sections: Section 1 (Geology) and Section 2 (Geo-physics). Candidates will have to attempt questions in Part A and either Section 1 or Section 2 in Part B.

Part A consists of **25** multiple-choice questions carrying **1-mark** each (sub-total **25 marks** and some of these may be numerical answer type questions). Each section in Part B (Section 1 and Section 2) consists of **30** multiple choice questions carrying **2-marks** each (sub-total **60 marks** and some of these may be numerical answer type questions).

XE Paper (Engineering Sciences)

In XE paper, Engineering Mathematics section (Section A) is **compulsory**. This section contains **11** questions carrying a total of **15 marks**: 7 questions carrying **1-mark** each (sub-total **7 marks**), and 4 questions carrying **2-marks** each (sub-total **8 marks**). Some questions may be of numerical answer type questions.

Each of the other sections of the XE paper (Sections B through H) contains 22 questions carrying a total of **35 marks**: 9 questions carrying **1-mark** each (sub-total **9 marks**) and 13 questions carrying **2-marks** each (sub-total **26 marks**). Some questions may be of numerical answer type.

XL Paper (Life Sciences)

In XL paper, Chemistry section (Section P) is **compulsory**. This section contains **15** questions carrying a total of **25 marks**: 5 questions carrying **1-mark** each (sub-total **5 marks**) and 10 questions carrying **2-marks** each (sub-total **20 marks**). Some questions may be of numerical answer type.

Each of the other sections of the XL paper (Sections Q through U) contains 20 questions carrying a total of **30 marks**: 10 questions carrying **1-mark** each (sub-total **10 marks**) and 10 questions carrying **2-marks** each (sub-total **20 marks**). Some questions may be of numerical answer type.

Note on Negative Marking for Wrong Answers

For a wrong answer chosen for the **multiple choice questions** (MCQs), there would be negative marking. For **1-mark** multiple choice questions, **1/3** mark will be deducted for a wrong answer. Likewise, for **2-mark** multiple choice questions, **2/3** mark will be deducted for a wrong answer. However, there is **NO negative marking for a wrong answer in numerical answer type questions**.

GATE Score

After the evaluation of the answers, the raw marks obtained by a candidate will be converted to a normalized GATE Score.

The GATE score will be computed using the formula given below.

Calculation of Normalized Marks for CE, CS, EC, EE and ME papers (multi-session papers)

In GATE 2017, examination for some papers may be conducted in multi-sessions. Hence, for these papers, a suitable normalization is applied to take into account any variation in the difficulty levels of the question papers across different sessions. The normalization is done based on the fundamental assumption that "in all multi-session GATE papers, the distribution of abilities of candidates is the same across all the sessions". This assumption is justified since the number of candidates appearing in multi-session papers in GATE 2017 is large and the procedure of allocation of session to candidates is random. Further it is also ensured that for the same multi-session paper, the number of candidates allotted in each session is of the same order of magnitude.

Based on the above, and considering various normalization methods, the committee arrived at the following formula for calculating the normalized marks for the multi-session papers.

Normalization mark of jth candidate in the ith session $\widehat{M_{ij}}$ is given by

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

where

M_{ij} : is the actual marks obtained by the jth candidate in i^{th} session

$\bar{M}_t^g$: is the average marks of the top 0.1% of the candidates considering all sessions

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

$\bar{M}_{ti}$: is the average marks of the top 0.1% of the candidates in the ith session

M_{iq} : is the sum of the mean marks and standard deviation of the ith session

After evaluation of the answers, normalized marks based on the above formula will be calculated corresponding to the raw marks obtained by a candidate and the GATE 2017 Score will be calculated based on the normalized marks.

For all papers for which there is only one session, actual marks obtained will be used for calculating the GATE 2017 Score.

Calculation of GATE Score For All Papers

GATE 2017 score will be calculated using the formula

$$\text{GATE Score} = S_q + (S_t - S_q)\frac{(M - M_q)}{(\bar{M}_t - M_q)}$$

In the above formulae

M : marks obtained by the candidate (actual marks for single session papers and normalized marks for multi-session papers)

M_q : is the qualifying marks for general category candidate in the paper

$\bar{M}_t$: is the mean of marks of top 0.1% or top 10 (whichever is larger) of the candidates who appeared in the paper (in case of multi-session papers including all sessions)

S_q : 350, is the score assigned to M_q

S_t : 900, is the score assigned to $\bar{M}_t$

In the GATE 2016 score formula, M_q is usually 25 marks (out of 100) or + s, whichever is larger. Here μ is the mean and s is the standard deviation of marks of all the candidates who appeared in the paper.

After the declaration of results, GATE Scorecards can be downloaded by

(a) All SC/ST/PwD candidates whose marks are greater than or equal to the qualifying mark of SC/ST/PwD candidates in their respective papers, and

(b) All other candidates whose marks are greater than or equal to the qualifying mark of OBC (NCL) candidates in their respective papers.

There is no provision for the issue of hard copies of the GATE Scorecards

The GATE 2017 Committee has the authority to decide the qualifying mark/ score for each GATE paper. In case any claim or dispute arises in respect of GATE 2017, the Courts and Tribunals in Bangalore alone shall have the exclusive jurisdiction to entertain and settle any such dispute or claim.

GATE Syllabus 2017

Section 1: Physical Chemistry

Structure: Postulates of quantum mechanics. Time dependent and time independent Schrodinger equations. Born interpretation. Particle in a box. Harmonic oscillator. Rigid rotor. Hydrogen atom: atomic orbitals. Multi-electron atoms: orbital approximation. Variation and first order perturbation techniques. Chemical bonding: Valence bond theory and LCAO-MO theory. Hybrid orbitals. Applications of LCAO-MOT to H_2^+, H_2 and other homonuclear diatomic molecules, heteronuclear diatomic molecules like HF, CO, NO, and to simple delocalized π^- electron systems. Huckel approximation and its application to annular π^- electron systems. Symmetry elements and operations. Point groups and character tables. Origin of selection rules for rotational, vibrational, electronic and Raman spectroscopy of diatomic and polyatomic molecules. Einstein coefficients. Relationship of transition moment integral with molar extinction coefficient and oscillator strength. Basic principles of nuclear magnetic resonance: nuclear g factor, chemical shift, nuclear coupling.

Equilibrium: Laws of thermodynamics. Standard states. Thermochemistry. Thermodynamic functions and their relationships: Gibbs-Helmholtz and Maxwell relations, van't Hoff equation. Criteria of spontaneity and equilibrium. Absolute entropy. Partial molar quantities. Thermodynamics of mixing. Chemical potential. Fugacity, activity and activity coefficients. Chemical equilibria. Dependence of equilibrium constant on temperature and pressure. Non-ideal solutions. Ionic mobility and conductivity. Debye-Huckel limiting law. Debye-Huckel-Onsager equation. Standard electrode potentials and electrochemical cells. Potentiometric and conductometric titrations. Phase rule. Clausius-Clapeyron equation. Phase diagram of one component systems: CO_2, H_2O, S; two component systems: liquid-vapour, liquid-liquid and solid-liquid systems. Fractional distillation. Azeotropes and eutectics. Statistical thermodynamics: microcanonical and canonical ensembles, Boltzmann distribution, partition functions and thermodynamic properties.

Kinetics: Transition State Theory: Eyring equation, thermodynamic aspects. Potential energy surfaces and classical trajectories. Elementary, parallel, opposing and consecutive reactions. Steady state approximation. Mechanisms of complex reactions. Unimolecular reactions. Kinetics of polymerization and enzyme catalysis. Fast reaction kinetics: relaxation and flow methods. Kinetics of photochemical and photophysical processes.

Surfaces and Interfaces: Physisorption and chemisorption. Langmuir, Freundlich and BET isotherms. Surface catalysis: Langmuir-Hinshelwood mechanism. Surface tension, viscosity. Self-assembly. Physical chemistry of colloids, micelles and macromolecules.

Section 2: Inorganic Chemistry

Main Group Elements: Hydrides, halides, oxides, oxoacids, nitrides, sulfides-shapes and reactivity. Structure and bonding of boranes, carboranes, silicones, silicates, boron nitride, borazines and phosphazenes. Allotropes of carbon. Chemistry of noble gases, pseudohalogens, and interhalogen compounds. Acid-base concepts.

Transition Elements: Coordination chemistry structure and isomerism, theories of bonding (VBT, CFT, and MOT). Energy level diagrams in various crystal fields, CFSE, applications of CFT, Jahn-Teller distortion. Electronic spectra of transition metal complexes: spectroscopic term symbols, selection rules, Orgel diagrams, charge-transfer spectra. Magnetic properties of transition metal complexes. Reaction mechanisms: kinetic and thermodynamic stability, substitution and redox reactions.

Lanthanides and Actinides: Recovery. Periodic properties, spectra and magnetic properties.

Organometallics: 18-Electron rule; metal-alkyl, metal-carbonyl, metal-olefin and metal-carbene complexes and metallocenes. Fluxionality in organometallic complexes. Types of organometallic reactions. Homogeneous catalysis - Hydrogenation, hydroformylation, acetic acid synthesis, metathesis and olefin oxidation. Heterogeneous catalysis - Fischer-Tropsch reaction, Ziegler-Natta polymerization.

Radioactivity: Decay processes, half-life of radioactive elements, fission and fusion processes.

Bioinorganic Chemistry: Ion (Na^+ and K^+) transport, oxygen binding, transport and utilization, electron transfer reactions, nitrogen fixation, metalloenzymes containing magnesium, molybdenum, iron, cobalt, copper and zinc.

Solids: Crystal systems and lattices, Miller planes, crystal packing, crystal defects, Bragg's law, ionic crystals, structures of AX, AX_2, ABX_3 type compounds, spinels, band theory, metals and semiconductors.

Instrumental Methods of Analysis: UV-visible spectrophotometry, NMR and ESR spectroscopy, mass spectrometry. Chromatography including GC and HPLC. Electroanalytical methods-polarography, cyclic voltammetry, ion-selective electrodes. Thermoanalytical methods.

Section 3: Organic Chemistry

Stereochemistry: Chirality of organic molecules with or without chiral centres and determination of their absolute configurations. Relative stereochemistry in compounds having more than one stereogenic centre. Homotopic, enantiotopic and diastereotopic atoms, groups and faces. Stereoselective and stereospecific synthesis. Conformational analysis of acyclic and cyclic compounds. Geometrical isomerism. Configurational and conformational effects, and neighbouring group participation on reactivity and selectivity/specificity.

Reaction Mechanisms: Basic mechanistic concepts–kinetic versus thermodynamic control, Hammond's postulate and Curtin-Hammett principle. Methods of determining reaction mechanisms through identification of products, intermediates and isotopic labeling. Nucleophilic and electrophilic substitution reactions (both aromatic and aliphatic). Addition reactions to carbon-carbon and carbon-heteroatom (N,O) multiple bonds. Elimination reactions. Reactive intermediates – carbocations, carbanions, carbenes, nitrenes, arynes and free radicals. Molecular rearrangements involving electron deficient atoms.

Organic Synthesis: Synthesis, reactions, mechanisms and selectivity involving the following classes of compounds – alkenes, alkynes, arenes, alcohols, phenols, aldehydes, ketones, carboxylic acids, esters, nitriles, halides, nitro compounds, amines and amides. Uses of Mg, Li, Cu, B, Zn and Si based reagents in organic synthesis. Carbon-carbon bond formation through coupling reactions - Heck, Suzuki, Stille and Sonogoshira. Concepts of multistep synthesis - retrosynthetic analysis, strategic disconnections, synthons and synthetic equivalents. Umpolung reactivity–formyl and acyl anion equivalents. Selectivity in organic synthesis chem-, regio- and stereoselectivity. Protection and deprotection of functional groups. Concepts of asymmetric synthesis resolution (including enzymatic), desymmetrization and use of chiral auxilliaries. Carbon-carbon bond forming reactions through enolates (including boron enolates), enamines and silyl enol ethers. Michael addition reaction. Stereoselective addition to C=O groups (Cram and Felkin-Anh models).

Pericyclic Reactions and Photochemistry: Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlations - FMO and PMO treatments. Photochemistry of alkenes, arenes and carbonyl compounds. Photooxidation and photoreduction. Di-π methane rearrangement, Barton reaction.

Heterocyclic Compounds: Structure, preparation, properties and reactions of furan, pyrrole, thiophene, pyridine, indole, quinoline and isoquinoline.

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: Applications of UV-visible, IR, NMR and Mass spectrometry in the structural determination of organic molecules.

GATE 1991

CY : CHEMISTRY

Time : 3 Hours | *Maximum marks : 200*

Read the following Instructions carefully :

1. Answers must be written in ENGLISH.
2. The question paper contains two parts 'A' and 'B'.
3. Answer ALL questions from part 'A' first, in the same sequential order as the question paper. These answers should be in the first five pages of the answer book.
4. Answer any TWELVE questions from part 'B'. Begin each answer of part 'B' on a fresh page and in the same sequential order as the question paper.
5. Use of log tables/non-programmable calculators permitted.
6. There will be no negative marking.

General Data :

Gas constant $R = 8.205 \times 10^{-2}$ dm utm *******

$= 8.31\ JK^{-1}\ mol$

$= 1.98\ cal\ K^{-1}\ mol$

Avogadro Number $= 8.02 \times 10^{23}\ mol^{-1}$

Boltzmann constant $= 1.38 \times 10^{-23}\ JK^{-1}$

Faraday $= 96500\ C\ mol^{-1}$

for electron $= 2.007$

$\mu_\beta = 9.274 \times 10^{-24}$ J/Tesla

Atomic weight of Rh = 103

Atomic number of some elements :

O — 23, Cr — 24, Mn — 25, Fe — 26, Co — 27, Ni — 28, Cu — 29, Mo — 42, Te — 52.

PART A

(80 Marks)

Answer ALL the questions.

1. *For each sub-question below, four answers A, B, C and D are provided of which ONE or MORE are correct. Write all the letters corresponding to the correct answers.* (20 × 1 = 20)

1. The shape of BrF_3 is :
   (A) Trigonal pyramidal (B) Trigonal planar
   (C) Trigonal bipyramidal (D) T-shaped

2. The strongest acid (in the gas phase) is :
   (A) H_2O (B) HCl
   (C) HI (D) CH_4

3. The formula of ethylene diamine tetraacetochromate (III) is :
   (A) $[Cr(EDTA)]^{\circ}$ (B) $[Cr(EDTA)]^{-}$
   (C) $[Cr(EDTA)]^{2-}$ (D) $[Cr(EDTA)]^{3-}$

4. The magnetic moment of an octahedral Co (II) complex is 4.0 μ_β. The electron configuration of the complex is :
   (A) $t_{2g}^5\ e_g^2$ (B) $t_{2g}^6\ e_g^1$
   (C) $t_{2g}^3\ e_g^4$ (D) $t_{2g}^4\ e_g^3$

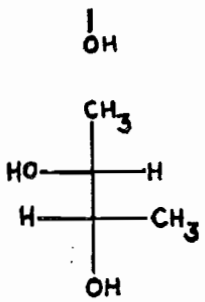
5. An IR band corresponding to the Co-H stretch is observed at 1840 cm^{-1} for $[Co(CN)_5H]^{3-}$. The expected wave number of the corresponding band in $[Co(CN)_5D]^{3-}$ is :
   (A) 1650 cm^{-1} (B) 1301 cm^{-1}
   (C) 1580 cm^{-1} (D) 1857 cm^{-1}

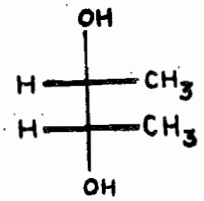
6. NO_2^+ is :
   (A) oxidising agent (B) Lewis acid
   (C) non-linear (D) nitrating agent

7. Which of the following statements about the reactivity of 1-chloroapocamphane (1) towards alcoholic $AgNO_3$ is true ?
   (A) Reacts by SN1 mechanism
   (B) Reacts by SN2 mechanism
   (C) Reacts by SN*i* mechanism
   (D) Does not react

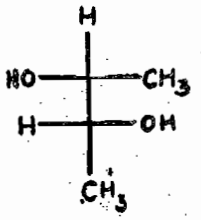
(1)

8. Which of the following structures is (are) not meso–2–, 3– butanediol ?

(A)


(B)


(C)

(D)


9. The reduction of but-2-yne to trans-but-2-ene can be brought about by :
(A) H_2/PtO_2
(B) Li/Liquid NH_3
(C) Li Al H_4
(D) Lindlars catalyst

10. The IUPAC name of

$$CH_3 - CH = \underset{\underset{CHO}{|}}{C} - CH_2 - CH_3 \text{ is :}$$

(A) 3-Formyl-2-pentene
(B) 2-Ethylbut-2-enal
(C) 3-Ethylbut-3-enal
(D) 2-Ethyl crotonaldehyde

11. The reaction of potassium phthalimide with ethyl chloroacetate followed by hydrolysis results in :
(A) glycine
(B) alanine
(C) leucine
(D) valine

12. Natural rubber is an example of :
(A) copolymer
(B) condensation polymer
(C) addition polymer
(D) thermosetting polymer

13. The point group of BF_2^+ is :
(A) $D_{\infty h}$
(B) $D_{\infty v}$
(C) $C_{\infty h}$
(D) $C_{\infty v}$

14. The hybridization in SF_6 molecule is :
(A) $sp^3 d^2$
(B) $sp^2 d^3$
(C) $sp\, d^4$
(D) $sp^3 s'p'$

15. The unit of the wavefunction ψ of a hydrogen atom is :
(A) L^3
(B) L^{-3}
(C) $L^{-3,2}$
(D) dimensionless
Here, L represents length.

16. The Nernst heat theorem is :
(A) $\lim_{T=0} \frac{d(\Delta F)}{dT} = 0$
(B) $\lim_{T=0} \Delta S = 0$
(C) $\lim_{T=0} \Delta C_p = 0$
(D) $\lim_{T=0} \frac{d(\Delta H)}{dT} = 0$

17. For a FCC lattice, which of the following statements is correct ?
(A) h, k, l values are all odd or all even
(B) h, k, l values are all even
(C) h, k, l values are all odd
(D) $h + k + l$ are all even

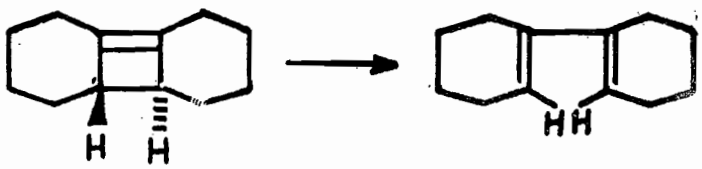
18. Which of the following are the correct criteria for naturally occuring (spontaneous) processes ?
(E = internal energy, S = entropy, G = Gibb's free energy, A = Helmholtz free energy)
(A) $(\Delta G)_{T,V} \leq 0$
(B) $(\Delta A)_{T,P} \leq 0$
(C) $(\Delta S)_{E,P} \geq 0$
(D) $(\Delta E)_{S,V} \leq 0$

19. For Maxwell-Boltzmann distribution of velocities V, which of the following relations are valid ?
Here, average quantities are denoted by $(\ )_{av}$.
(A) $(V^2)_{av} = (V)^2_{av}$
(B) $(V^2)_{av} < (V)^2_{av}$
(C) $(V) - (V)_{av} = ****\ (V^2)_{av} - (V)^2_{av}$
(D) $(V^2)_{av} > (V)^2_{av}$

20. In selection rules, $\Delta E = h\upsilon$ refers to energy conservation. Which other quantities are conserved during a transition ?
(A) linear momentum of the system (B) angular momentum
(C) mass of the system (D) spin of the system.
which refers to a nuclear atom or a molecule.

2. ***Fill in the blank spaces in the following sentennces appropriately :*** **(30 × 1 = 30)**

1. The ligand field stabilization energy in $Ni(CO)_4$ is ..... .
2. BrO_3 is isostructural with a noble gas species ..... .
3. XeF_2 (s) reacts with SbF_5 (*l*) to give ..... .
4. A single resonance line in ^{13}C-NMR spectrum indicates that $Fe(CO)_5$ is a ..... molecule.
5. BF_3 reacts with $LiAlH_4$ in ether to give ..... and $LiAlF_4$.
6. The efficiency of a catalyst is expressed in terms of ..... .
7. The shape of $TeCl_4$ is ..... .
8. Ferrocene reacts with $(CH_3CO)_2O$ and concentrated H_2SO_4 to give ..... .
9. $K_2Ni(CN)_4 + 2K \xrightarrow[\text{Ammonia}]{\text{liquid}}$ ..... .
10. The formula of hexachlorophosphazene is written as ..... .
11. The product of the reaction between cyclohexane carbylic acid chloride and lithium dimethylcuprate is ..... .
12. Hydroboration followed by H_2O_2/HO^- oxidation of 1-methylcyclohexene gives ..... .
13. Stereoregulated polymerisation of propene can be brought about by the use of ..... catalyst.
14. ..... carbenes add to alkenes in a stereospecific cis manner.
15. Oxetanes can be prepared by photochemical reaction between aldehydes or ketones and .....
16. Edman degradation is used to determine the ..... terminal amino acid of a polyepeptide.
17. Nitration ($HNO_3 - H_2SO_4$) of benzene and hexadeutero-benzene proceeds at ..... rate(s).
18. The reaction of sodamide with pyridine in liquid ammonia to give 2-aminopyridine is called ..... .
19. The following pericyclic reaction takes place under ..... conditions.



20. Pyrrole is virtually non-basic because the lone pair of electrons on the nitrogen forms a part of the ..... .

21. The frequency factor for a reaction $A + B \rightarrow [AB]^{\neq} \rightarrow$ products in the absolute rate theory is ..... .

22. The expression used to determine the equilibrium constant from the measured quantity in a cell reaction at temperature T is ..... .

23. The difference between the potential of the electrode when gas evolution is actually observed and the theoretical reversible value for the same solution is called ..... .

24. A catalyst may be defined as a substance which lowers the ..... of activation of a reaction.

25. A non-linear molecule with 7 atoms has 5 single bonds and one double bond. The number of vibrational modes of the molecule is ..... .

26. Hyperfine interaction in ESR is, due to the interaction of nuclear spins with ..... .

27. For a one component system, the number of degrees of freedom above the critical temperature is ..... .

28. A molecule with a S_n axis has also a C_n' axis ($n' < n$) only when n is ..... .

29. Given the absolute entropy of a substance at T = 0, the additional data needed to estimate its absolute entropy at temperature T is ..... .

30. Freezing point depressions are measured for identical weights of two non-associating and non-dissociating substances A and B. The depression in A is three times the depression in B. The molecular weight of B is ..... molecular weight of A.

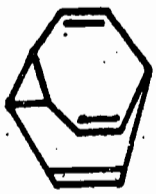
i. ***Account for the following in ONE or TWO sentences.*** *(30 × 1 = 30)*

1. $Cr(CO)_6$ is stabler than $V(CO)_6$.
2. The N-O stretching frequency in linear transition metal nitrosyls is greater than that in non-linear nitrosyls.
3. Tetrahedral complexes are generally high spin.
4. Liquid ammonia solutions of alkali metals are highly conducting.

PAGE 91-8 MS—NO READ

16. Azulene is a relatively strong base forming a protonated species in aqueous sulfuric acid.

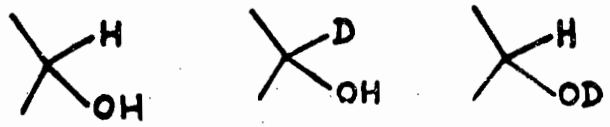
17. The NMR spectrum of bullvalene (A) at 248 K shows two signals in the ratio 4 : 6, whereas at 373 K only one signal is observed.



(A).

18. Liquid acetone at room temperature is stable to UV irradiation while gaseous acetone gives products arising out of α cleavage.

19. The relative rates of oxidation by chromic acid of some isotopically substituted isopropyl alcohols are as shown below.



Relative rate	1.0	0.16	1.0

20. The position of equilibrium of the following reaction shifts to the right when DMSO is used instead of methanol as a solvent.

$$C_6H_5CH_2NO_2 + CH_3O^- \rightleftharpoons (C_6H_5CHNO_2)^- + CH_3OH$$

21. Bohr's theory fails to explain molecular structure.
22. Debye Huckel theory fails at high ionic strengths
23. For a particular vibrational transition from V = 0 (in the ground state) to V' = 4 (in the excited electronic state) the intenisty of transition is found to be greater than the intensity for other values of V'.
24. The Valenece-Bond theory does not predict the formation of the molecule H_2^+.
25. The free electron theory fails to predict the semi-conducting properties of materials.
26. In the crystalline state, Fe, CO and Ni are ferromagnetic whereas Mn is not.
27. Proteins coagulate most readily at their isoelectric point.
28. H_2 reacts photochemically with Cl_2 Br_2 and I_2. But only with Cl_2 a chain reaction results.
29. At $T \rightarrow O$, H_2 occurs only as para-H_2.
30. The mean translational kinetic eaergies of H_2 and I_2 at 300 K happen to be the same.

PART B

(12 × 10 = 120 Marks)

Answer any TWELVE questions.

4. *(a)* Arrange the oxides Al_2O_3, B_2O_3, BaO, CO_2, Cl_2O_7, SO_3 in order from the most acidic through amphoteric to the most basic. Give explanation also. **(3)**
   (b) $(CH_3)_2N-PF_2$ has two basic atoms, P and N. One is bound to B in a complex with BH_3 and the other to B in a complex with BF_3. Decide which is which and state your reason. **(3)**
   (c) What is the trend in hydridic character of $[BH_4]^-$, $[AlH_4]^-$ and $[GaH_4]^-$? Which is the strongest reducing agent ? Give the equation for the reaction of $\{[GaH_4]^-$ with excess IMHCl (aq). Pauling electronegativities of H, B, Al, Ga are 2.20, 2.04, 1.61 and 1.81 respectively. **(4)**

5. *(a)* Derive the ground state term for Ni^{2+}. **(2)**
   (b) $[Ni\ (en)_3]^{2+}$ absorbs at 11,000, 18,500, 30,000 cm^{-1}. Give the assignments of the bonds. **(3)**
   (c) In $[Cu\ (hfacac)_2\ (bipy)]$, there are two short Cu – O bonds and two long Cu – O bonds. Explain, (hfacac = hexafluoroacetylacetone anion; bipy = bipyridine). **(5)**

6. *(a)* How do you prepare $Co_2\ (CO)_8$? Give equation only. **(2)**
   (b) $(C_5H_5)_3\ Ni_3\ (CO)_2$ has a single CO stretching absorption at 1761 cm^{-1}. The IR data indicate that all the C_5H_5 are pentahapto and probably in identical environments. Propose a structure for the compound based on the above information. **(4)**

(c) Provide a plausible reason for the difference in IR wave-numbers :
$Mo(PF_3)_3(CO)_3$ – 2040, 1991 cm^{-1}, versus $Mo(PMe_3)_3(CO)_3$ 1945, 1851 cm^{-1}. (4)

7. (a) Why are J metals such as Mn, Fe, Co and Cu used in redox enzymes in preference to Zn, Ga and Ca ? (3)

(b) Identify one significant role in biological processes for the elements Fe, Mn, Mo and Cu. (4)

(c) What prevents simple iron porphyrins from functioning as O_2 carriers ? (3)

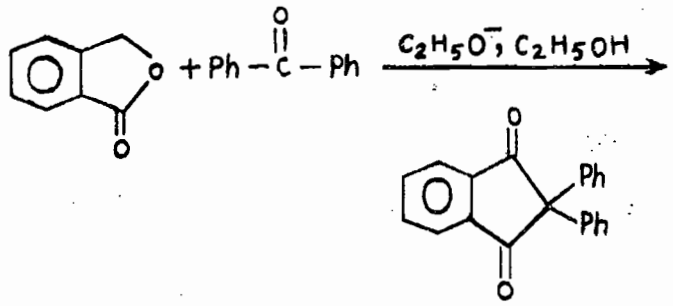
8. (a) Given the reactants PPh_3, NH_3 and $[PtCl_4]^{2-}$, propose efficient routes to cis- and trans- $[PtCl_2(NH_3)(PPh_3)]$. (4)

(b) The mass spectrum of a transition metal carbonyl complex includes peaks at 748, 720 and decreasing every 28 a.m.u. down to 412 and then 309, 206 and 103 a.m.u. Identify the complex. (3)

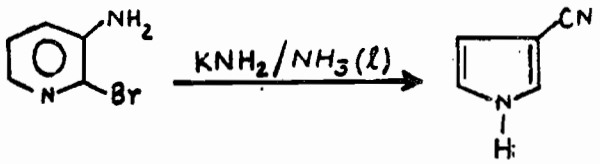
(c) Write a short note on activation analysis. (3)

9. Suggest a suitable mechanism for each of the following reactions :

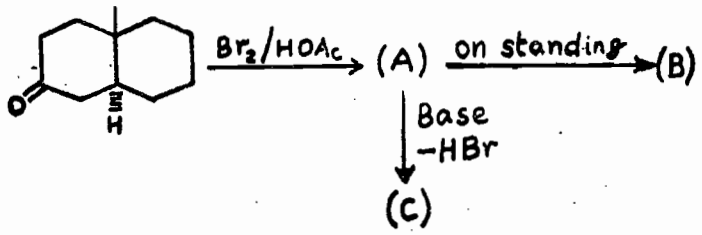
(a)



(b)



10. (a) (5 + 5)



(A) and (B) are stereoisomers.

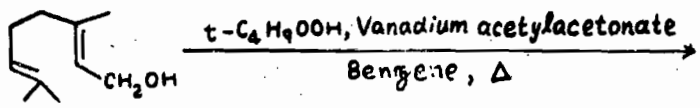
UV data (C_2H_5OH) — (A) : λ_{max} 320 nm ; ϵ 50
(B) : λ_{max} 290 nm ; ϵ 50
(C) : λ_{max} 230 nm ; ϵ 7000

Identify the lettered compounds, (A), (B) and (C). (5)

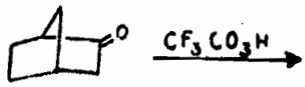
(b) In an experiment performed to oxidize 1,4-butanediol to prepare succindialdehyde, the product obtained had no aldehyde properties. It had a strong IR band at 1.780 cm^{-1} and NMR signals at δ 1.2 (m, 2H), 2.5 (m, 2H), 4.0 (m, 2H). Mass spectrum showed M^+ at m/z 86. Identify the product and account for its formation. (5)

11. Predict the major product of each of the following reactions. Specify stereochemistry wherever relevant. (5 × 2 = 10)

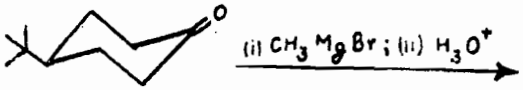
(a)



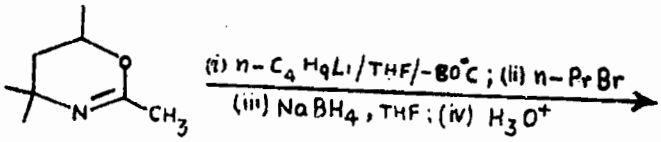
(b)



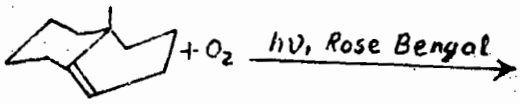
(c)



(d)

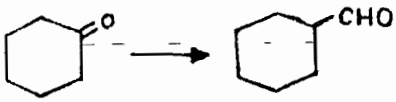


(e)

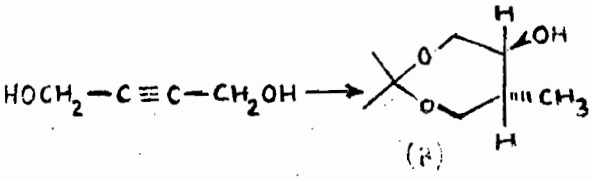


12. Show how the following compounds, (A), (B) and (C) can be synthesized using the starting materials and any other suitable reagents.

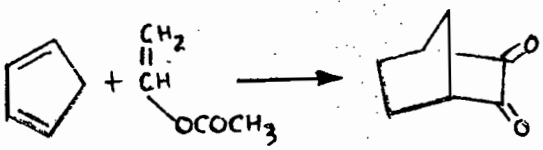
(a)



(b)

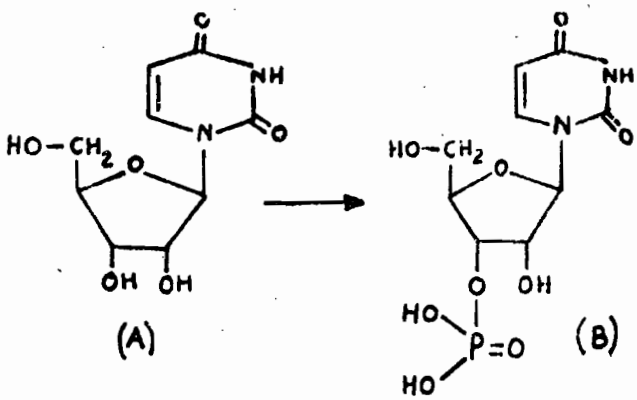


(c)



13. (a) Show how L-alanyl-L-phenylalanine can be synthesized from the respective L-aminoacids with minimum racemization, but without resorting to solid-phase technique (4)

(b) Show how uridine (A) can be converted to uridine-3′-phosphate (B). (3)



(c) Represent schematically the mechanism of acyl transfer by chymotrypsin. (3)

14. *(a)* What are the essential differences between classical statistical mechanics and quantum statistical mechanics ? **(1)**

(b) Obtain a relation for C_v starting from the definition of the partition function and relate C_v to the fluctuations in the value of internal energy. Estimate the molal heat capacity of CO. **(4)**

(c) Show that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$ **(2)**

(d) Show that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

and indicate the physical significance of the result. **(3)**

15. *(a)* Write down either the electronic hamiltonian or a wave function (but not both) for lithium atom. **(2)**

(b) What are the wavefunctions of Be^{3+} ? **(1)**

(c) In a H atom the various quantum numbers are related according to $n > l \geq |ml|$, whereas for the quantum numbers for a particle in a box, there is no such restriction. Explain why ? **(3)**

(d) In Li_2, σ_{2p}, MO lies below π_{2p} while in F_2, σ_{2p} lies above. Account for this. **(2)**

(e) In an MO for H_2^+, $\Psi = \phi_A(1) + \phi_B(2)$. What do ϕ, A, B, 1 and 2 specify ? **(2)**

16. *(a)* In a mole of free radicals of a species at 300 K and a magnetic field of 1.38 Tesla, how many will be the excited spin state ? If these free radicals interact individually with three equivalent protons, how may lines will be seen in the ESR spectrum and what will be their relative line intensities ? **(3)**

(b) Why is $\Delta J = \pm 1$ in rotational (microwave) spectroscopy and $\Delta J = \pm 2$ in rotational Raman spectroscopy ? **(2)**

(c) Under what circumstances is $\Delta S = -nR\sum_i x_i \ln x_i$ valid ? What is ΔS for isothermal mixing at 300 K of 33.6 litres of O_2 and 22.4 litres of N_2 when the final volume of the system is 44.8 litres? **(3)**

(d) Why is it more desirable to study the crystal structure of PbO by neutral diffraction than by X-ray diffraction ? **(2)**

17. *(a)* When can the reaction between ethyl alcohol and acetic anhydride be a pseudounimolecular reaction ? **(2)**

(b) For two reactions, say A and B, the rate constants are measured at two temperatures $T_1 = 300$ K and $T_2 = 310$ K. For reaction A, the rate constant is doubled (by this 10 K rise in temperature) and for reaction B it increases by a factor of 3. What is the relation between the activation energies of the two reactions ? **(2)**

(c) Explain why a large number of unimolecular reactions occurring at surfaces, e.g., the decomposition of HI on gold surface or decomposition of NH_3 on tungsten surface, are kinetically of zero order. **(4)**

(d) A gas is known to obey an equation of state $PV = RT + BP$ with $B = 8.205 \times 10^{-6}$ m^3/mol. What is the fugacity of the gas at 300 atm (and 300 K) ? **(2)**

18. *(a)* At 290 K, the free energy of formation of liquid water is –237.2 kJ/mol and the free energy of ionisation of water into H and OH^- ions is 79.7 kJ/mol. What is the emf of the following cell ?

H_2 (1 atm) | H^+ || OH^- | O_2 (1 atm) **(2)**

(b) If the concentration of Ag Cl in a saturated solution at 298 K is 10^{-5} mol kg^{-1} and the standard potential of Ag^+/Ag is 0.7991 V, determine the standard oxidation potential of the Ag, Ag Cl/Cl^- electrode. **(4)**

(c) The viscosities of solutions of polyisobutylene in benzene at 297 K are

Conc (g/m^3)	0	2000	4000	6000	8000	10^4
$\eta/10^{-3}$ kg m^{-1} s^{-1}	0.647	0.690	0.733	0.777	0.821	0.865

The values of the constants for polyisobutylene in benzene are, $K = 0.083 \times 10^{-6}$ m^3/g and $a = 0.5$. What is the relative molar mass of the polymer ? **(4)**

19. (a) The reduction of triphenylmethanol to triphenylmethane by conc. formic acid is considered to involve the following steps :

$$(C_6H_5)_3\,COH + HCOOH \rightleftharpoons (C_6H_5)_3C^+ + H_2O + HCOO^- \quad \text{... (1)}$$

$$(C_6H_5)_3C^+ + HCOO^- \longrightarrow (C_6H_5)_3\,CH + CO_2 \quad \text{... (2)}$$

(i) If DCOOH is used as the reducing agent, what would be the fate of deuterium ? **(1)**

(ii) What effect, if any, would a nitro group in one of the rings of triphenylmethanol have on the position of equilibrium of step (1) and on the rate of step (2) ? **(2)**

(b) $Cr_2\,(O_2CCH_3)_4\,(H_2O)_2$ is diamagnetic whereas the mononuclear Cr^{II} compounds are strongly paramagnetic. Justify. **(3)**

(c) Can operators operate on the right or on the left or on both sides ? Justify. **(2)**

(d) In a Lennard Jones potential

$$U(r) = 4 \in \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right];$$

at what distance does the minimum in the potential occur ? **(2)**

GATE - 1991

ANSWERS WITH EXPLANATIONS

1.

1.1. (D)

1.2. (C)

Explanation : Easiest dissociation of HI

1.3. (B)

1.4. (A)

1.5. (D)

Explanation : Slight lesser due to difference in the H and Deutron atom.

1.6. (A)

Explanation : It can have electron from others.

1.7. (B)

1.8. (C)

1.9. (A)

Explanation : They provides proton.

1.10. (B)

1.11. (A)

Explanation : Because all others formed from compound having atleast one chiral centre.

1.12. (C)

Explanation : Addition of monomer unit isoprene.

1.13. (D)

Explanation : Due to planar molecule

1.14. (A)

1.15. (D)

1.16. (D)

1.17. (A)

Explanation : They may be either odd or even.

1.18. (D)

Explanation : Because spontaneity needs extra energy

1.19. (B)

1.20. (B)

2.

2.1. 6 D_q, due to d^8 system.

2.2. XeO_2F_2, Trigonal bipyramidal.

2.3. $[XeF]^+ [Sb_2F_{11}]^-$ but in solid gives $[XeF_2 . 2SbF_5]$.

2.4. Singlet.

2.5. B_2H_6,

$$BF_3 + LiAlMn_4 \xrightarrow{\text{Ether}} B_2H_6 + LiAlF_4$$

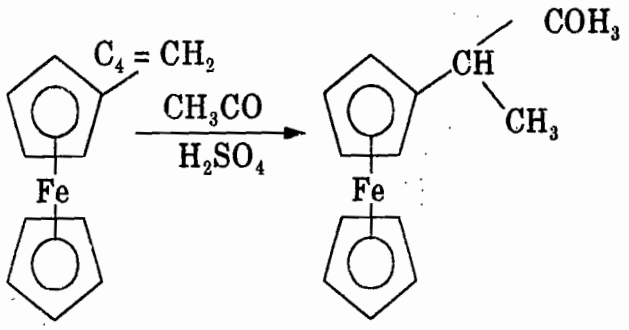
2.6. Volcano curve, (Substrate - adsorbate bond energy).

2.7. Irregular tetrahedral, (sp^3d)

Bond pair — 4

Lone pair — 1

2.8. stable α-carboniun ion,



2.9. $K_4 [Ni_2 (CN)_6]$

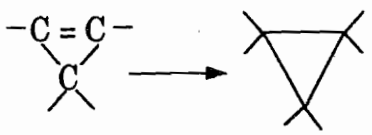
2.10. $(NPCl_2)_x$ where X = 2, 3.....

2.11. Aromatic compound.

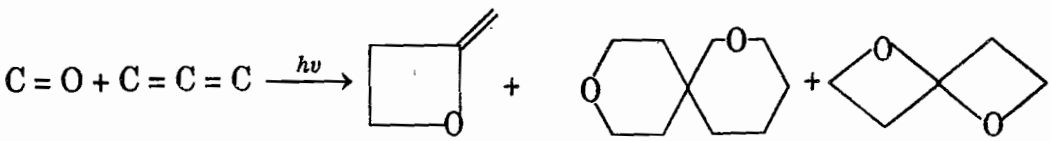
2.12. Chiral alcohol.

2.13. Zieglar Natta catalyst

2.14. Singlet,



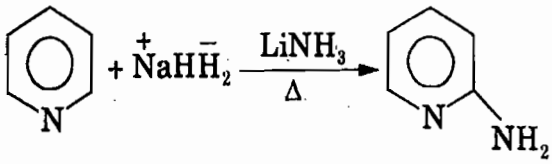
2.15. Allenes,



2.16. Identification

2.17. Same.

2.18. Chichi babin reaction



2.19. Basic

2.20. Aromatic sextet.

2.21. $r = \frac{R_{T'}}{N_A h} = \frac{K_{BT}}{h}$

2.22. $-\Delta G. = RT \ln k = nkE°$.

2.23. Electromotive force

2.24. Energy

2.25. 15,

vibrational modes = 3N – 6

where N = Number of atom for N on linear molecule.

2.26. External mangetic field.

2.27. Three

2.28. odd

2.29. Heat of transformation

2.30. Three times.

R

1.

2.

3.

4.

5.

6.

G

1.

GATE 1994

CY : CHEMISTRY

Time : 3 Hours | *Maximum marks : 200*

Read the following instructions carefully :

1. The question paper contains two sections : 'A' and 'B'.
2. Section A has NINE questions. Answer all questions in this section.
3. Section B has TWENTY questions. Answer any TEN questions in this section.
4. Begin answer for this section on a fresh page.
5. Answers to questions in each section should appear together in the same sequence in which they appear in the question paper.
6. There will be no negative marking.

General Data :

Gas constant $R = 8.314\ JK^{-1}\ mol^{-1}$

Avogadro's Number $= 6.02 \times 10^{23}\ mol^{-1}$

Planck's constant $= 6.626 \times 10^{-34}$ Js

$= 6.626 \times 10^{-27}$ ergs

Velocity of light $= 3.0 \times 10^{8}\ ms^{-1}$

Atomic number of some elements :

Fe – 26, Co – 27, Ni – 28, Cu – 29, Rh – 45

SECTION A

(100 Marks)

1. ***For each sub-question below, four answers A, B, C and D are provided of which ONE is correct. Write the letter corresponding to the correct answer.***
(20 × 1 = 20)

1.1. The compressibility factor for an ideal gas is
(A) 1 (B) 1.5
(C) 2 (D) ∞

1.2. An example of extensive property is
(A) Temperature (B) Internal Energy
(C) Viscosity (D) Molar Heat capacity

1.3. The selection rule for observing rotational Raman spectra is

(A) $\Delta J = \pm 1$ (B) $\Delta J = \pm 2$

(C) $\Delta J = 0$ (D) $\Delta J = \pm 3$

1.4. The point group symmetry of p-dichlorobenzene is

(A) C_{2v} (B) D_{2h}

(C) D_3 (D) C_{2h}

1.5. Pauling's electronegativity scale is based on

(A) Spectroscopic data (B) Ionization Potentials and electron affinity

(C) Thermochemical data (D) Crystallographic data

1.6. For which of the following cases $\Delta S = \Delta H/T$:

(A) A process for which $\Delta C_p = 0$ (B) An adiabatic process

(C) A constant pressure process (D) An isothermal, reversible phase transition

1.7. A certain buffer solution contains equal concentrations of A^- and HA. The K_b for A^- is 10^{-10}. The pH of the buffer is

(A) 7 (B) 10

(C) 4 (D) 14

1.8. For a second order reaction A + B → products, where the initial concentration of the reactants are the same (x mol/lit) and k is the rate constant, the half life of the reaction is

(A) 1/kx (B) 0.693/k

(C) 0.5/k (D) 0.5 kx

1.9. Dipole moment of p-nitroaniline, when compared to nitrobenzene (X) and aniline (Y) will be

(A) Greater than (X) and (Y) (B) Smaller than (X) and (Y)

(C) Greater than (X) but smaller than (Y) (D) Equal to zero

1.10. Most stable carbocation formed from $(CH_3)_3C-Br$, $(C_6H_5)_3C-Br$, $(C_6H_5)_2CHBr$ and $C_6H_5CH_2Br$ would be

(A) $C_6H_5\overset{+}{C}H_2$ (B) $(CH_3)_3\overset{+}{C}$

(C) $(C_6H_5)_3\overset{+}{C}$ (D) $(C_6H_5)_2\overset{+}{C}H$

1.11. Among the following anions *(a)* $\overline{C}H_3$ *(b)* $\overline{N}H_2$ *(c)* OH^- *(d)* F^-, the order of basicity is

(A) $a > b > c > d$ (B) $b > a > c > d$

(C) $c > b > a > d$ (D) $c > a > b > d$

1.12. The most stable conformation of ethylene-glycol is

(A) Anti (B) Gauche

(C) Partially eclipsed (D) Fully eclipsed

1.13. Treatment of furfural with NaOH yields

(A) Furoin

(B) Furoic acid

(C) Furfuryl alcohol and sodium salt of furane – 2 – carboxylic acid

(D) No reaction

1.14. For osazone formation the effective structural unit necessary is

(A) CH_2OCH_3 — CO — CH_2OH — $CHOCH_3$

(B) CH_2OH — CO — CHO — $CH\,OCH_3$

(C) CH_2OH — CO — $CHOCH_3$

(D) CHO — CO — CH_2OH — $CH\,OCH_3$

1.15. In the CsCl structure, the number of ions in a unit cell is

(A) 2 (B) 4

(C) 6 (D) 8

1.16. The Crystal Field Stabilization Energy (CFSE), in units of Δ_0, for $[CoF_3(H_2O)_3]$ is

(A) 0 (B) 0.4

(C) 0.8 (D) 1.8

1.17. The chemical formula for hypophosphoric acid

(A) H_3PO_4 (B) H_3PO_3

(C) $H_4P_2O_5$ (D) $H_4P_2O_6$

1.18. Nitrous acid can behave

(A) only as an oxidant (B) only as a reductant

(C) both as oxidant and reductant (D) as a drying agent

1.19. Wilkinson's catalyst is

(A) $[Rh(CO)_2I_2]^-$ (B) $(Ph_3P)_3RhCl$

(C) $Co_2(CO)_8$ (D) $(Ph_3P)_2Rh(CO)Cl$

1.20. The structure of XeF_4 is

(A) Tetrahedral (B) Square Pyramid

(C) Square Planar (D) Octahedral

2. ***Fill in the blank spaces in the following sentences appropriately.*** (20 × 1 = 20)

2.1. The decomposition of H_2O_2 to H_2O and O_2 is called ..... reaction.

2.2. Reduction of $[CoCl(NH_3)_5]^{2+}$ by $[Cr(H_2O)_6]^{2+}$ is via ..... mechanism.

2.3. The number of unpaired electrons present in $[CoCl_4]^{2-}$ is ..... .

2.4. Bis (glycine) complexes of platinum (II) are examples of ..... isomerism.

2.5. The B—F bond distance in $H_3N \rightarrow BF_3$ is much ..... than that in BF_3^-

2.6. Ferrocinium cation is a ..... electron system.

2.7. Nitrogen and Phosphorus bond together to form a large number of compounds which are call ..... .

2.8. The most stable conformation of the lactone formed from *cis*–4–hydroxycyclohexane carboxylic acid is the ..... .

2.9. In an equilibrium mixture of anomers, α- and β-methyl-D-glucosides, the ..... predominates.

2.10. $(CH_3)_3$ B and $(CH_3)_3C^+$ are ..... .

2.11. Nitromethane having a low molecular weight (61) has high boiling point (101°C) due to ..... .

2.12. ********** ophenone and anisole, iodoform test is given by .....

2.13. Separation of chlorobenzene from benzenediazonium chloride with cuprous chloride and aq. HCO is known as ..... reaction.

2.14. S-configuration of alanine [MeCH(NH_2) COOH] is .....

2.15. The ionization potential of hydrogen atom is 13.6 eV. The ionization potential of Li^{2+} would be ..... eV.

2.16. When Fe (s) is dissolved in aq. HCl in a closed vessel, the work done is .....

2.17. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal .....

2.18. The most probable radius at which the electron will be found is ..... -

2.19. Free energy change (ΔG) is related to the electrochemical cell potential by .....

2.20. A molecule is said to be spherical top if .....

3. ***Indicate whether the following statements are TRUE or FALSE. Give reasons in one or two sentences.*** **(10 × 2 = 20)**

3.1. Complexes of Cu^{2+} usually depart considerably from octahedral geometry.

3.2. The ion $[Fe F_6]^{3-}$ is colourless whereas $[CoF_6]^{3-}$ is coloured.

3.3. Trisilylamine has a planar triangular structure.

3.4. Pyrrole gives potassium salt with KOH whereas aniline does not.

3.5. Cyclooctatetraene is tub-shaped instead of planar.

3.6. 1-butanol on dehydration with Conc. H_2SO_4 gives 2-butene.

3.7. Fructose reduces Tollen's reagent.

3.8. Maximum number of hydrogen bonds in water is two.

3.9. The heat energy (q) absorbed by a gas is ΔH.

3.10. The $n \rightarrow \pi^*$ electronic transition in acetone disappears in strong acid medium.

4. *Match the following choosing one item from column L and the item that is most significantly related to i from column R.* (15 × 1 = 15)

L	*R*
4.1. Fluxional behaviour of molecules	(A) Bond length
4.2. Microwave spectroscopy	(B) Isotopes
4.3. Acidity Function	(C) I.R. spectroscopy
4.4. Mass spectra	(D) Polarizability
4.5. Biological currency of energy	(E) RDX
4.6. Photoelectron spectra	(F) F.A. Cotton
4.7. Woodhard Hoffmann	(G) Ionization Potential
4.8. Benzoin condensation	(H) Fe^{II}, Co^{II}
4.9. Raman spectra	(I) H_o
4.10. Molecular structure	(J) KCN
4.11. Bonding Modes of CO	(K) Electron Diffraction
4.12. Explosive	(L) Free radical
4.13. Octanedral spin equilibrium systems	(M) NMR spectroscopy
4.14. Metal-metal bonding	(N) ATP
4.15. ESR	(O) Orbital symmetry

5. Distinguish between σ- and *x*-bonding interactions (metal-carbon bond formation) in $[PtCl_3(C_2H_4)]^-$ using orbital interaction diagrams. (5)

6. *(a)* Draw the potential energy diagram for a two step reaction going through a stable intermediate in which the first step is rate determining. Indicate the position of intermediate in the diagram. (2)

(b) Suggest a simple chemical test to distinguish between ortho-chlorotoluene and benzyl chloride. (1)

(c) Write the structure of the intermediate formed in the Reimer-Tieman reaction of phenol with chloroform in alkaline medium. (1)

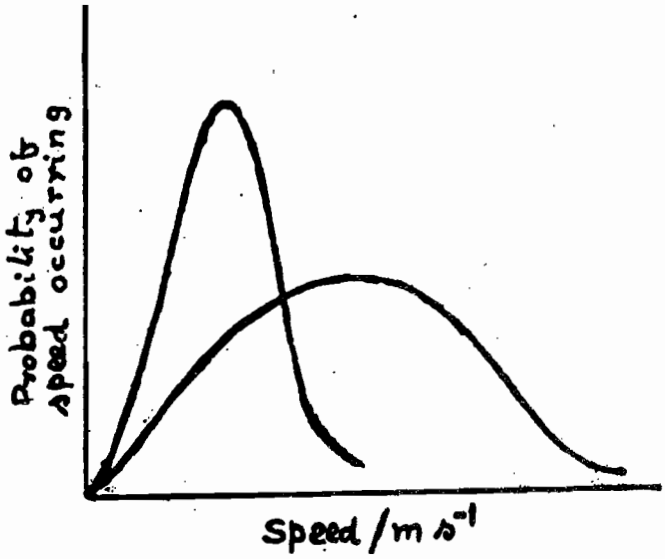
(d) Suggest a chemical method to separate benzaldehyde from benzyl alcohol. (1)

7. *(a)* You are given solid benzoic acid and liquid ethyl benzoate. How do you distinguish them in the $>C=O$ stretching region of the I.R. spectra. (3)

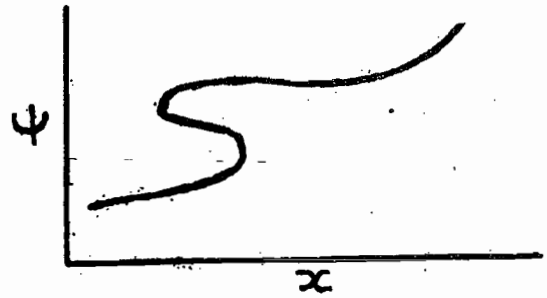
(b) How do you distinguish between chemical shift and coupling constant in NMR spectroscopy? (2)

8. *(a)* What volumes of $\frac{N}{2}$ and $\frac{N}{10}$ HCl must be mixed to give 2 litres of $\frac{N}{5}$ HCl. (2)

(b) In the diagram, indicate the most probable speeds at lower and higher temperatures. (2)



(c) A wave function is represented in the diagram given below



Is ψ an acceptable wave function or not ? Explain. (1)

9. *(a)* Using $E^o = -0.440$ V for Fe^{2+}/Fe couple and 0.771 for Fe^{3+}/Fe^{2+} couple, determine ********* Fe^{3+}/Fe couple.

(b) The decomposition of a substance in presence of an inert gas follows the second order kinetics with $k = (6 \times 10^{10}\ L\ mol^{-1}\ s^{-1})\, e^{-29{,}000\frac{K}{T}}$

What is the activation energy of the reaction ?

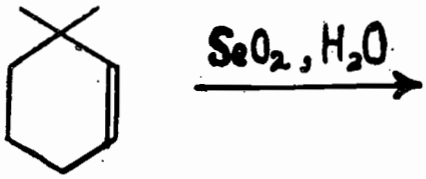
SECTION B

(50 Marks)

Answer any TEN questions in this section

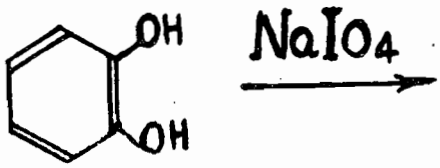
10. Write the products and the intermediates (if any) of the following reactions.

(a) (2)



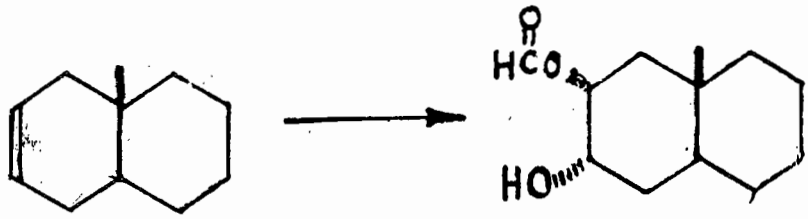
(b) $Me_2C = CH\ CH_2Cl \xrightarrow{aq.\ CaCO_3}$ (3)

(c) (2)

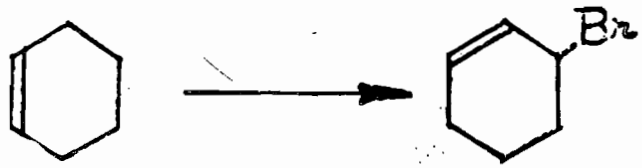


11. What are the specific reagents that could be used to effect the following conversions.

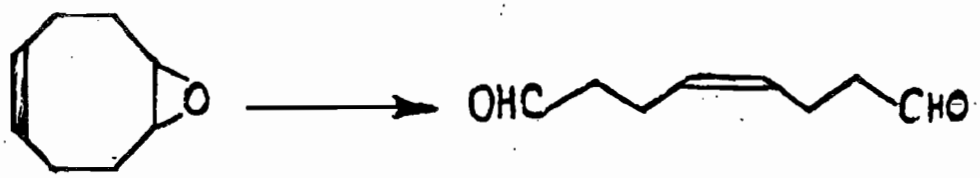
(a) (2)



(b) (1)

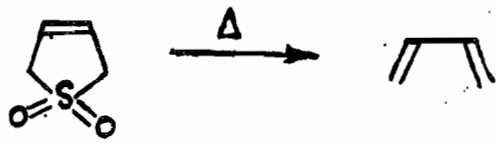


(c) (2)

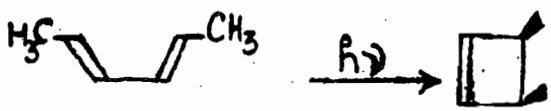


12. Classify the following as electrocyclic, sigmatropic, chelotropic and cycloaddition reactions.

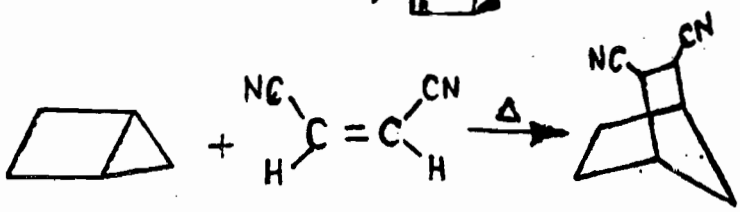
(a)



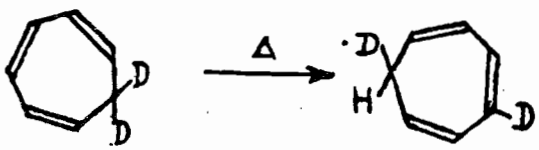
(b)



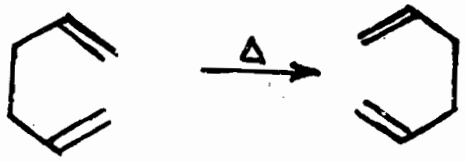
(c)



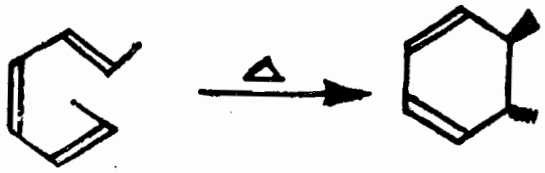
(d)



13. *(a)* Classify the given reaction as sigmatropic of order (i, j)



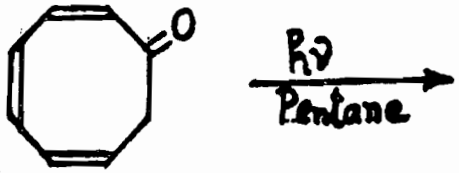
(b) Classify the given reaction as con-or disrotatory.



(c) Predict the products for the following photochemical reactions.

(i) $CH_3\,COCH_2\,CH_2\,CHMe_2 \xrightarrow{h\nu}$

(ii)

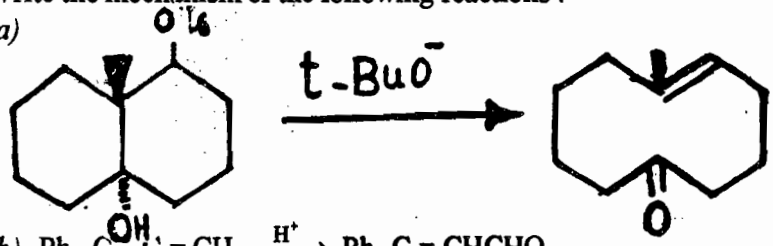


(iii) Benzophenone $\xrightarrow[\text{isopropanol}]{h\nu}$

14. Compound 'A' having a molecular formula C_8H_5O on treatment with Zn and ethylbromoacetate compound 'B' $(C_{12}H_{16}O_3)$. Compound 'B' on dehydration followed by hydrogenation over $SrCo_3$ gave $(C_{12}H_{16}O_2)$. Hydrolysis of 'C' produced 'D' $(C_{20}\,H_{12}O_2)$ as one of the products. Decarboxylation D gave isopropylbenzene. Identify A, B, C and D.

15. Write the mechanism of the following reactions : **(2)**

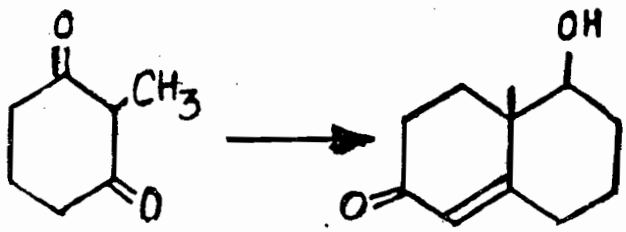
(a)



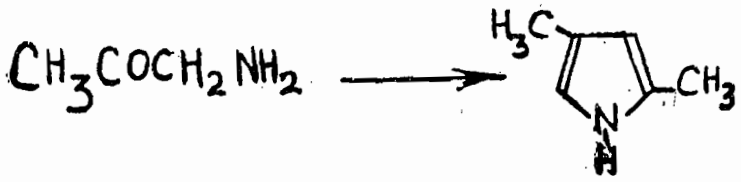
(b) $Ph_2\,C(OH)-C\equiv CH \xrightarrow{H^+} Ph_2\,C = CHCHO$ **(3)**

16. Suggest routes for each of the following transformations. More than one step may be required. Use other necessary reagents.

(a) **(2)**



(b) (1)



(c) $Ph-\overset{\overset{O}{\|}}{C}-\underset{\underset{Ph}{|}}{C}=CHPR \longrightarrow Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CHPh_2$ (2)

17. Complete and balance the following reactions : (5 × 1 = 5)

(a) $HF + SbF_5 \longrightarrow$

(b) $P_4O_{10} + C_2H_5OH \xrightarrow[H_2PtCl_6]{}$

(c) $CH_2 = CH_2 + SiH_4 \xrightarrow[i-PrOH]{}$

(d) $Fe^{3+}(aq) + NH_3OH^+(aq) \longrightarrow$

(e) $Al_2(CH_3)_6 + C_2H_5OH \longrightarrow$

18. Explain, using a frontier orbital energy diagram the change in energy levels of a Ni^{II} complex as it distorts from octahedral to tetragonal to square planar. (5)

19. (a) Borazine forms π complexes such as $B_3N_3H_6 — Cr(CO)_3$. Comment on its bonding aspects. Count the number of valence electrons of chromium in this complex. (3)

(b) Comment on the relative π acidities of the ligands CO and CN^-. (2)

20. Describe a convenient method for the preparation of diborane. Explain its molecular structure from the point of view of orbital interactions. (5)

21. Identify the product (draw structure) of the following reaction :

$$(Rh_3P)_2Rh(H)(CO) \xrightarrow{CH_3CH=CH_2}$$

Also identify the formal oxidation numbers and calculate the number of valence electrons of the metal atom both in the reactant and in the product. (5)

22. Illustrate, using a diagram the principal

23. Identify the specific role of the following (in one or two words) in biological processes.

(A) Ferredoxins

(B) Cytochromes

(C) Haemoglobin

(D) Ferritin

(E) Transferrin

24. (a) Evaluate the commutator $\left(x, \frac{d}{dx}\right)$ operating on an arbitrary function ψ (x).

(b) Calculate the width of one dimensional box for which the difference between lowest energy levels a particle becomes comparable to the average kinetic energy of the particle temperature T.

25. (a) Assume that 1.02×10^{-17} Joules of light energy is needed to see an object. How many photons yellow light ($\lambda = 590$ nm) are needed to generate this energy ?

(b) A certain substance in a solution has a absorption maximum at 550 nm with a molar absorptivity. 1600 $m^2 mol^{-1}$. The width of the absorption curve at half height is 100 nm. Estimate the value of integrated absorption coefficient.

26. The bond length of HI molecule is 1.627 A°. Calculate the rotational spectral frequencies (cm^{-1}) for following transitions :

$$J = 0 \rightarrow J = 1$$
$$J = 1 \rightarrow J = 2$$
$$J = 2 \rightarrow j = 3$$

27. Given the following :

	PCl_3 (l)	PCl_3 (g)
ΔG^o_f (kJ mol^{-1})	– 272.4	– 267.8
ΔH^o_f (kJ mol^{-1})	– 319.7	– 287.0
S^o (JK^{-1} mol^{-1})	217.1	311.7

Estimate the boiling point of PCl_3 (l)

28. Calculate the freezing point of a solution containing 6 gms. of phenol in 100 gms. of benzene if 80% of phenol associates into $(C_6H_5OH)_2$ in benzene at this concentration. The freezing point of benzene is 5 and K_f for benzene is 5.12 k mol^{-1} kg.

29. For the chemical reaction :

$$A + C \rightarrow D$$

Consider the following mechanism :

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$$B + C \xrightarrow{k_3} D$$

Assume that B is an intermediate. Use the steady state approximation and write the rate expression for

GATE - 1994

ANSWERS WITH EXPLANATIONS

1.

1.1 (A)

Explanation : Compressibility factor, $Z = \frac{kT}{PV} = 1$ for ideal gas.

1.2 (B)

1.3 (A)

1.4 (B)

Explanation : Para position of halogen atom make it D_{2h}.

1.5 (A)

1.6 (D)

1.7 (C)

Explanation : $pH + pOH = 14.$

$\therefore$ $pH = 14 - 10 = 4$

1.8 (B)

1.9 (B)

1.10 (C)

Explanation : Depends on no of alkyl group attached.

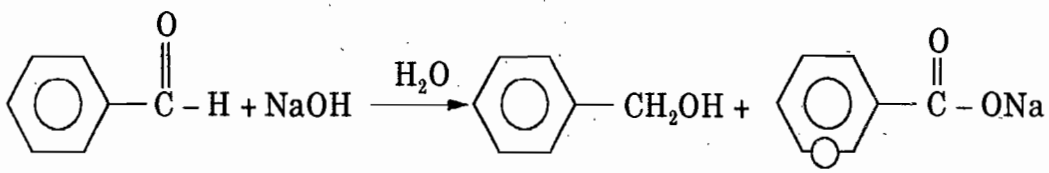
1.11 (A)

Explanation : Basicity will be decided by non-metallic strength

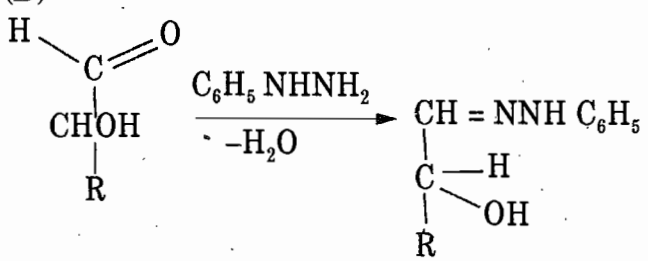
1.12 (A)

Explanation : Anti is always most stable

1.13 (C)



1.14 (D)



1.15 (D)

Explanation : It is obtained by part shared by each atom.

1.16 (B)

1.17 (D)

1.18 (C)

Explanation : It can donate oxygen for hypontious, but gain oxygen for nitric acid.

1.19 (B)

1.20 (D)

Explanation : Fluorine is at four corner of square planar.

2.

2.1 Disproportionation

2.2 Inner sphere mechanism

2.3 3 (Three)

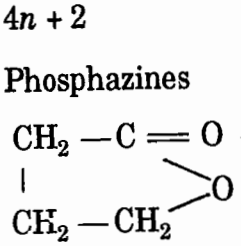
2.4 Coordination position isomerism

2.5 Longer than

2.6 $4n + 2$

2.7 Phosphazines

2.8



(γ- Butyrolactose)

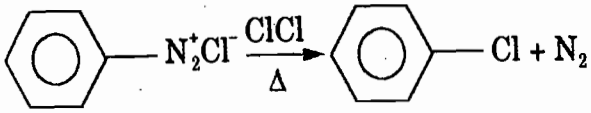
2.9 α-methyl D glucose

2.10 Isoelctronic

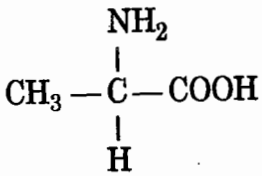
2.11 H-bonding

2.12 ophenone

2.13 Sandmeyer reaction



2.14



2.15 9×13.6 eV (I.E. $= n \times 13.6$ eV)

2.16 Negative

2.17 Moles

2.18 Bohr radius

$$P \propto r^2 e^{-2r/q_0}$$

2.19 $\Delta G = -nFE$

2.20 $I_{xy} = I_{yy} = I_{22} = I = \frac{8}{3} m_1 R^2$

3.

3.1 T

3.2 T

3.3 T

3.4 T

3.5 T

3.6 F

3.7 F

3.8 F

Explanation : Because of two electronegative H-atom and one O-atom.

3.9 T

Explanation : Endothermic reaction.

3.10 F

4.

4.1 (O)

4.2 (N)

4.3 (I)

4.4 (B)

4.5 (A)

Explanation : ADP is transferred into ATP.

4.6 (L)

4.7 (M)

4.8 (J)

4.9 (D)

4.10 (G)

4.11 (C)

4.12 (E)

4.13 (F)

4.14 (H)

4.15 (K)

GATE 1995

CY : CHEMISTRY

Time : 3 Hours | *Maximum marks : 200*

Read the following instructions carefully :

1. Write all the answers in the answerbook.
2. This paper contains two consists of two sections : 'A' and 'B'.
3. Section **A** has **TEN** questions. Answer **ALL** questions in this section.
4. Section **B** has **TWENTY** questions. Answer any **TEN** questions from this section. Strike off the answers which are not to be evaluated; else only the **FIRST TEN** answers will be considered.

   Answer to this section should start on a fresh page and should **NOT** be mixed with answers to Section **A**.
5. Answers to questions and answers to the parts of a question should appear together in the same sequence in which they appear in the question paper.
6. In all questions of 5 marks, write clearly the important steps in your answer. These steps carry partial credit.
7. There will be no negative marking.

General Data :

Gas constant $R = 8.205 \times 10^{-2}\ dm^3\ atm\ K^{-1}\ mol^{-1}$

$= 8.31\ JK^{-1}\ mol^{-1}$

$= 1.98\ cal\ K^{-1}\ mol^{-1}$

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

Boltzmann constant $= 1.38 \times 10^{-23}\ JK^{-1} = 0.695\ cm^{-1}\ K^{-1}$

Faraday $= 96500\ C\ mol^{-1}$

$1\ eV = 96.485\ kJ\ mol^{-1}$

SECTION A

(100 Marks)

1. ***For each sub-question below, four answers A, B, C and D are provided of which ONE is correct. Write the letters corresponding to the correct answer in your answer book.*** **(35 × 1 = 35)**

   1.1. XeF_2 on hydrolysis yields

   (A) $XeOF_4$ (B) XeO_3

   (C) XeO_2F_2 (D) Xe

1.2. Which of the following molecules will have a permanent dipole moment ?
(A) SiF_4 (B) XeF_4
(C) SF_4 (D) BF_3

1.3. Which of the following compounds is optically active ?
(A) Pt $(NH_3)_2$ Cl_2 (B) Ni $(CO)_2$ $(PPh_3)_2$
(C) trans-Co $(en)_2Cl_2$ (D) cis-Co$(en)_2$ Cl_2

1.4. Among the following isostructural compounds, identify the compound which has the highest lattice energy
(A) LiF (B) LiCl
(C) NaCl (D) MgO

1.5. A transition metal complex shows a magnetic moment of 5.20 B.M. at room temperature. The number of unpaired electrons on the metal is
(A) 3 (B) 4
(C) 5 (D) 2

1.6. For a valence electron in a ^2D state, the possible J values are
(A) 5/2, 1/2 (B) 5/2, 3/2
(C) 3/2, 1/2 (D) 3/2, 0

1.7. ********** from present in carbonic anhydrase is
(A) cobalt (B) nickel
(C) zinc (D) magnesium

1.8. Phosphorus pentoxide, P_4O_{10} on hydrolysis gives
(A) H_3PO_3 (B) H_3PO_4
(C) HPO_3 (D) H_3PO_2

1.9. The complexes [Co (1, 2-diaminopropane)$_2$ Cl_2]$^+$ and [Co(1,3-diaminopropane)$_2$$Cl_2$]$^+$ represent an example of
(A) ligand isomerism (B) linkage isomerism
(C) ionization isomerism (D) coordination isomerism

1.10. For $Ti(H_2O)_5{}^{3+}$, the absorption maximum due to *d-d* transition is found at 20,000 cm^{-1}. Therefore the crystal field stabilization energy is
(A) –20,000 cm^{-1} (B) $\frac{4}{9} \times 20{,}000$ cm^{-1}
(C) 8000 cm^{-1} (D) –8000 cm^{-1}

1.11. The formula of the pyrosilicate ion is
(A) $SiO_4{}^{4-}$ (B) $Si_2O_7{}^{6-}$
(C) $Si_3O_9{}^{6-}$ (D) $Si_6O_{18}{}^{12-}$

1.12. In a polarogram, the wave height is a measure of
(A) migration current (B) diffusion current
(C) residual current (D) decomposition potential

1.13. Aqueous titanium (IV) solution develops intense orange colour on addition of H_2O_2. The colour is due to
(A) *d-d* transition (B) $n \rightarrow$ II transition of the peroxo group
(C) reduction of the Ti(IV) to Ti(III) (D) charge transfer transition.

1.14. The average speed of CO_2, benzene, deuterium and methane increases in the order
(A) CO_2 < benzene < deuterium < methane
(B) benzene < CO_2 < methane < deuterium
(C) deuterium < methane < CO_2 < benzene
(D) deuterium < CO_2 < benzene < methane

1.15. If the two CH_2 planes in ethylene are perpendicular to each other, what is the point group of the molecule ?
(A) C_{2v} (B) C_{2h}
(C) D_{2d} (D) D_{2h}

1.16. The number of peaks in the ESR spectrum of CH_3 radical is
(A) 1 (B) 2
(C) 3 (D) 4

1.17. For mixing of two ideal gases at 25°C and 1 atm, which one of the following is incorrect ?
(A) $\Delta G_{mix} = 0$ (B) $\Delta H_{mix} = 0$
(C) $\Delta V_{mix} = 0$ (D) $\Delta S_{mix} = 0$

1.18. The criterion for irreversibility for a process involving no work or pressure-volume work is
(A) $(dS)_{V,u} < 0$ (B) $(dS)_{V,u} > 0$
(C) $(dS)_{T,P} < 0$ (D) $(dS)_{T,V} > 0$

1.19. The mean ionic molality of 2-1 electrolyte is
(A) $4^{1/3}$ m (B) $m^{2/3}$
(C) $27^{1/4}$ m (D) 108 m

1.20. If the rate laws are expressed in concentration unit mol dm^{-3}, the unit of the third order reaction rate constant is
(A) dm^3 mol^1 sec^1 (B) dm^3 mol^{-1} sec^{-1}
(C) dm^6 mol^{-2} sec^{-1} (D) dm^{-3} mol^1 sec^{-1}

1.21. For a pure substance, the slope of the plot of Gibbs free energy (G) against T at constant pressure is
(A) S (B) –S
(C) –H (D) $-C_P$

1.22. The enthalpy of vaporization of water is zero
(A) at 0°C (B) at the critical temperature
(C) at the boiling point (D) under no conditions

1.23. The isobaric thermal coefficient of an ideal gas is
(A) 1/T (B) 1/P
(C) R (D) Zero

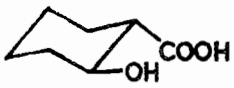
1.24. The reaction of 4-bromobenzyl chloride with sodium cyanide in ethanol leads to
(A) 4-bromobenzyl cyanide (B) 4-cyanobenzyl chloride
(C) 4-cyanobenzyl cyanide (D) 4-bromo-2-cyanobenzyl chloride

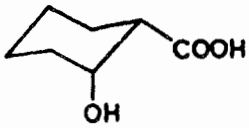
1.25. Which one of the following reactions will not result in the formation of anisole ?
(A) Phenol + dimethyl sulphate in the presence of base
(B) Sodium phenoxide treated with methyl iodide
(C) Reaction of diazomethane with phenol
(D) Reaction of methylmagnesium iodide with phenol

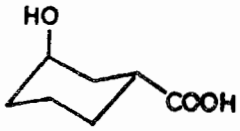
1.26. Reaction of R-2-butanol with p-toluenesulphonyl chloride and pyridine by LiBr gives
(A) R-2-butyl tosylate
(B) S-2-butyl tosylate
(C) R-2-butyl bromide
(D) S-2-butyl bromide

1.27. Rearrange the following in the increasing order of acidity
(i) benzoic acid
(ii) *p*-methoxybenzoic acid
(iii) *o*-methoxybenzoic acid
(A) *(i)* < *(ii)* < *(iii)*
(B) *(iii)* < *(i)* < *(ii)*
(C) *(ii)* < *(i)* < *(iii)*
(D) *(iii)* < *(ii)* < *(i)*

1.28. Identify the hydroxycyclohexanecarboxylyic acid which, upon heating, readily gives a bicyclic lactone

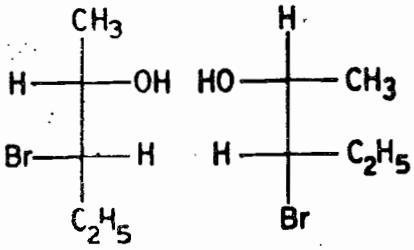
(A) 

(B) 

(C) 

(D)

1.29.



The molecules represented by the above two structures are
(A) identical
(B) enantiomers
(C) diastereomers
(D) epimers

1.30. *o*-Methylbenzophenone does not readily undergo photoreduction when irradiated in isopropyl alcohol because
(A) it does not undergo photoexcitation
(B) of photoenolization
(C) the reduction potential is higher than that of acetone
(D) of stereic hindrance of the ortho methyl group

1.31. Sucrose is
(A) α-glucopyranosyl-β-fructofuranoside
(B) α-glucopyranosyl-α-fructofuranoside
(C) β-glucopyranosyl-α-fructofuranoside
(D) β-glucopyranosyl-β-fructofuranoside

1.32. When methyl glucopyranoside reacts with periodic acid, how many moles of the oxidising agent are consumed per mole of the sugar ?
(A) 1
(B) 2
(C) 3
(D) 4

1.33. A solution of optically active 1-phenylethanol in acidified aqueous medium racemizes due to
(A) enolization
(B) carbonium ion formation
(C) alkene formation
(D) reversible oxidation-reduction

1.34. Methylcyclohexene can be converted to trans-2-methylcyclohexanol by
(A) acid catalyzed hydration
(B) oxymercuration followed by reduction
(C) hydroboration followed by oxidation
(D) epoxidation followed by LAH reduction.

1.35. Read the following assertion and its likely reason and choose the correct conclusion from the list given
Assertion A : Pyridine is less basic than piperidine
Reason R : The lone pair of electrons on the nitrogen in pyridine is delocalized
(A) Both A and R are true and R is the right explanation of A
(B) Both A and R are true but R is not the right explanation of A
(C) A is true, R is false
(D) A is false, R is true

2. ***Fill in the blank space in the following sentences appropriately :*** **(25 × 1 = 25)**

2.1. If A is the absorbance and T is the transmittance, A is related to T by the relation .....

2.2. XeO_2F_2 can be prepared by treating $XeOF_4$ with .....

2.3. B_2H_6 reacts with CO to give .....

2.4. The reaction :
$Co(H_2O)_5\ Cl^{2+} + Cr\ (H_2O)_6^{2+} \rightarrow Co\ (H_2O)_6^{2+} + Cr\ (H_2O)_5\ Cl^{2+}$
occurs through ..... mechanism.

2.5. In Tanabe-Sugano diagrams, the values for various electronic states of the metal ion are plotted against ..... values.

2.6. The two geometrical isomers possible for $[Ru\ (H_2O)_3\ Cl_3]$ are called ..... and ..... isomers.

2.7. According to Curie-Weiss law, the magnetic susceptibility corrected for diamagnetism, χ_M = ... where the symbols have their usual meanings.

2.8. When an atom is missing from its normal lattice site creating a vacancy, it is known as .....

2.9. The coordination number of cation in face centred and body centred cubic lattices are ..... and ..... respectively.

2.10. For the decay of ClO radicals, the plot of log $t_{1/2}$ versus log $[ClO]_0$ yields a straight line of slope = – 0.88. The order of the reaction is .....

2.11. The point group to which the molecule PCl_5 belongs is .....

2.12. Because of weak hydrogen bond formation, a mixture of acetone and chloroform will show ..... deviation from Raoult's law.

2.13. The cathodic reaction in the hydrogen-oxygen fuel cell with acid electrolyte is .....

2.14. The conductivity ($\Omega^{-1}\ m^{-1}$) of 0.1 mol L^{-1} NaCl solution at 25° C is . ..... given that the ionic mobilities for Na^+ and Cl^- at this concentration are 4.26×10^{-8} and $6.80 \times 10^{-8}\ m^2\ V^{-1}\ s^{-1}$ respectively.

2.15. For the reaction, $CO(g) + H_2\ O(g) \rightarrow CO_2\ (g) + H_2\ (g)$, ΔH^o, ΔS^o and ΔG^o at 298 K are –41.19 kJ, –42.4 J $mol^{-1}\ deg^{-1}$ and –28.55 kJ respectively. The minimum temperature at which the reaction will go to the opposite direction is .....

2.16. Vant Hoff isochore may be written as $\frac{d \text{ in K}}{d(1/T)}$ = ...

2.17. The acidity of the hydrogen in acetylene is due to ..... of the carbon.

2.18. Pyrrole is unstable in acid solution because protonation of the nitrogen results in .....

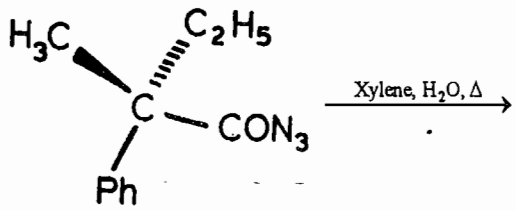
2.19. An aldohexose of the L-series which gives the same saccharic acid upon HNO_3 oxidation, as D-glucose is ..... (Draw the open chain structure in Fischer projection).

2.20. A 1, 3– suprafacial sigmatropic rearrangement with inversion of configuration is allowed under ..... condition.

2.21. The greater stability of α-methylglucoside over the β-isomer is due to .....

2.22. Irradiation of cyclohexene in methanol gives cyclohexyl methyl ether. The reactive intermediate which undergoes addition of methanol is .....

2.23. The structure of the product of the reaction shown below is .....



2.24. The enamine route for the alkylation of 2-methylcyclohexanone results in alkylation at the ..... position.

2.25. In the reaction between an alkyl halide in benzene and aqueous NaCN, tetrabutylammonium bromide is used as a .....

3. *(a)* Match the reagents in List-I with the descriptions in List-II. (2)

List - I	*List - II*
1. $CH_2 = C(CN)(Cl)$	A. Protection of amino group
2. $H - C \equiv C^- Na^+$	B. Ketene equivalent
3. $CH_3 - O - CH_2 Cl$	C. Protection of Hydroxyl group
4.	D. Formaldehyde equivalent
	E. $CH_3 CO^-$ equivalent

(b) Match each of the reactions given in List-I with the appropriate reagent from List-II and application from List-III. (3)

List-I	*List-II*	*List-III*
1. Vilsmeir-Haack reaction	A. aminoalcohol + HNO_2	W. Formylation
2. Wolff Fearrangement	B. $POCl_3$ + dialkylformamide	X. Indirect method of dehydration of alcohols
3. Demjanov rearrangement	C. Pyrolysis of xanthate	Y. Ring expansion of cycloalkanone
	D. Diazoketone + Ag_2O	Z. Homologation of carboxylic acids

4. *(a)* Match the compounds/species given in List-I with the structures in List-II. (2)

List-I	*List -II*
1. XeF_4	A. Angular
2. $Ni(CN)_5^{3-}$	B. Linear
3. NO_2^+	C. Square pyramid
4. $Zn(CN)_4^{2-}$	D. Trigonal bipyramid
	E. Tetrahedral
	F. Square planar

(b) Match each of the compounds in List-I with the appropriate oxidation state from List-II and the coordination number from List-III. (3)

List-I	*List-II*	*List-III*
1. Zeiss salt	0	3
2. $Ni(CO)_4$	1	4
3. $[Co(NH_3)_5 Cl] Cl_2$	2	5
	3	6

5. *(a)* Match the molecules given with the ground state electronic configurations and the dissociation energies (eV) (2)

Molecule	*Electronic Configuration*	*Dissociation Energy (eV)*
N_2^+	$[Be_2]\ (\pi_u\ 2p)^4\ (\sigma_g\ 2p)^2$	9.6
N_2	$[Be_2]\ (\pi_u\ 2p)^4\ (\sigma_g\ 2p)^1$	8.73

(b) Match the ions with the first ionization potential (eV) (1)

Ion	*First ionization potential (eV)*
He^+	216.6
Li^{++}	54.16
Be^{+++}	121.8

(c) Match the molecules with the rotor types (1)

Molecules	*Rotor types*
C_6H_6	Asymmetric top
CCl_4	Spherical top
CH_2Cl_2	Symmetric top

(d) Match the thickness (Å) of the ionic atmosphere ($1/\kappa$) in water at 25°C with the valence type of the electrolyte (0.01 M) (1)

Valence type	*Thickness (Å) of $1/\kappa$*
uni-uni	3.94
uni-bi	5.58
uni-ter	9.64

6. (a) Define isothermal Joule-Thomson coefficient and isoenthalpic Joule-Thomson coefficient and find a relation between the two. (3)

(b) Explain why, for the compounds $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ the carbonyl stretching frequency decreases in that order (2060, 1890, and 1790 cm^{-1} respectively). (2)

7. (a) Calculate the value of the most probable radius of the ground state of the H – – atom described by $\psi = \frac{1}{\sqrt{\pi}} e^{-r}$ (r in atomic units). (3)

(b) The spacing between the successive lines in the rotational spectrum of $^1H^{35}Cl$ is 10.4 cm^{-1}. What should be the spacing in $^2D^{35}Cl$? (2)

8. (a) For the reaction

$$\left[CO(NH_3)_6\right]^{3+} + 6H_3O^+ \longrightarrow \left[CO(H_2O)_6\right]^{3+} + 6NH_4^+$$

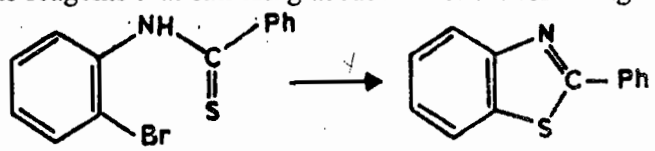
the equilibrium constant is 10^{25}. However, the complex can be boiled in strong HCl solution without appreciable decomposition. Explain. (2)

(b) $Ni(en)_3^{2+}$, where en = enthylenediamine, is nearly 10^{10} times more stable than $Ni(NH_3)_6^{2+}$. Explain qualitatively the enhanced stability of the former from thermodynamic considerations. (2)

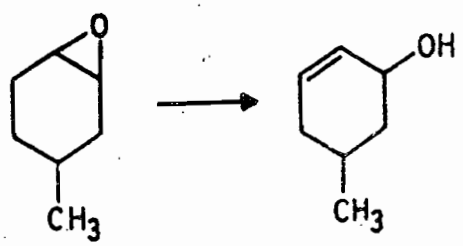
(c) Give the d orbital splitting for $VO(H_2O)_5^{2+}$, given that V = 0 distance is very short. (1)

9. Give the reagents that can bring about each of the following conversions. (5 × 1 = 5)

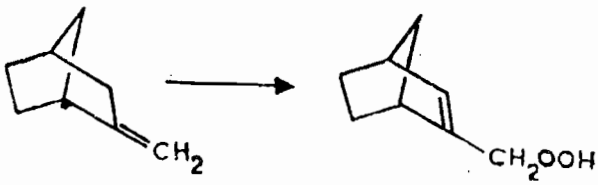
(a)

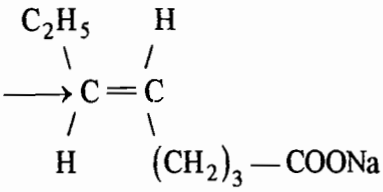


(b)

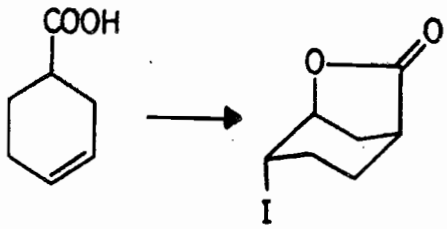


(c)

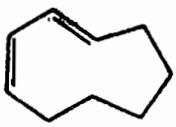


(d) $C_2H_5-C\equiv C-(CH_2)_3-COONa \longrightarrow$ 

(e)

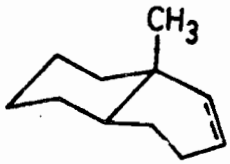


10. Give the structures (conformations or stereochemical representation wherever relevant) of the products A to E in the following reactions. Mechanisms or explanations are not required.

(a)  $\xrightarrow{h\nu}$ A (electrocyclic reaction) **(1)**

(b) Furan + dimethyl acetylenedicarboxylate → B **(2)**

B $\xrightarrow{\text{heat}}$ acetylene + C

(c) 

+ m-chloroperbenzoic acid → D

D + $LiAlH_4$ → E **(2)**

SECTION B

(50 Marks)

Answer any TEN questions in this section. (10 × 5 = 50)

11. (a) Account for the fact that in $KCuF_3$ two Cu-F distances are at 1.96 Å and four Cu-F distances are at 2.07 Å **(2)**

(b) Explain the observation that the effective magnetic moment of copper acetate monohydrate is 1.4 B.M. per copper atom at room temperature and it decreases with temperature. **(2)**

(c) Why is $CuSO_4 . 5H_2O$ coloured blue while anhydrous $CuSO_4$ is nearly colourless ? **(1)**

12. (a) Three bands at about 9000, 11000 and 16000 cm^{-1} assignable to *d-d* transitions are found for $Cu(NH_3)_4^{2+}$ species. Assign the bands giving *d*-orbital splittings. **(2)**

(b) Give the structure of $(C_5H_5)_4$ Ti. At –30° C, two ^{1}HNMR signals are observed and above 60°C, only one NMR signal is observed. Interpret these findings. (3)

13. (a) Consider a molecule AB_5 with trigonal bipyramid structure, and replace one of the B atoms in *(i)* axial position and *(ii)* in the equatorial position by a lone pair. Explain which of the two resulting structures will be more stable giving reasons and also point out any distortions that may occur. (3)

(b) How do you explain qualitatively the position of I^- and CO at the opposite ends of the spectrochemical series from crystal field/ligand field theories ? (2)

14. (a) How do you synthesise the cis and trans-isomers of $[Pt(NH_3)_2 Cl_2]$ using trans-effect ? (3)

(b) Why, unlike NO_3^-, PO_3^- exists only as oligomer species, $(PO_3)_n^{n-}$? (2)

15. (a) Giving equations, indicate how XeO_4 is prepared ? What is its structure ? (2)

(b) Compare the structure and conductivity of hexagonal boron nitride with graphite. (3)

16. (a) Give the structure of the active sites in Rubredoxin and mention its role. (2)

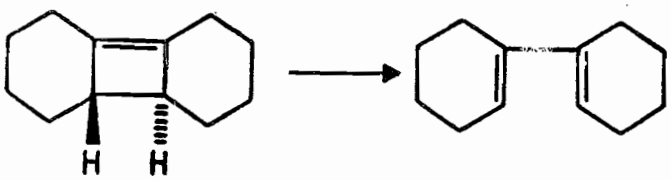
(b) Distinguish between *n* and *p* type semiconductors diagrammatically. Give an example of each. (3)

17. (a) Explain why *(i)* an excess of supporting electrolyte and *(ii)* a small amount of freshly prepared gelatin are added to the electroactive species in polarographic analysis. (3)

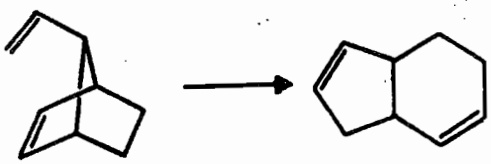
(b) Give two limitations of Beer's law. (2)

18. (a) Classify the following pericyclic reactions as *i*, *j*-sigmatropic rearrangement, con- or dis-rotatory electrocyclic reaction etc. and indicate whether they are thermally or photochemically allowed

(i) (2)



(ii) (2)



(b) Ketene adds on to alkenes to form cyclobutanones. What is the correct nomenclature, with faciality included, for this cycloaddition ? (e.g. the thermal Diels-Alder reaction is described as $_{\pi}4_s + {}_{\pi}2_s$ cycloaddition) (1)

19. Reduction of 4-*t*-butylcyclohexanone by lithium aluminium hydride gives a mixture of 2 stereoisomeric alcohols.

(a) Draw their conformations. (1)

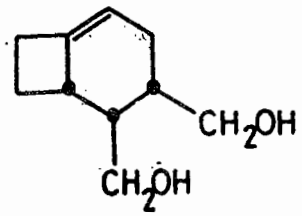
(b) Which one is the major product ? (1)

(c) Which isomer will undergo dehydration to the cyclohexene faster ? (1)

(d) Which will undergo oxidation by Cr(VI) reagents faster? (1)

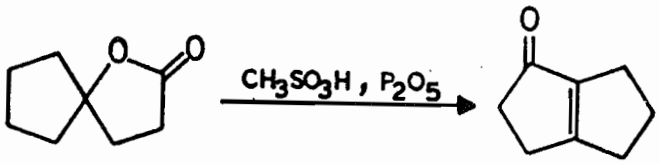
(e) How can the two be differentiated by ^{1}H NMR spectroscopy ? (1)

20. Methylmagnesium bromide, acetylene, cyclobutanone and maleic anhydride are made available to you. Using these and other common reagents and solvents, design a synthesis of (5)

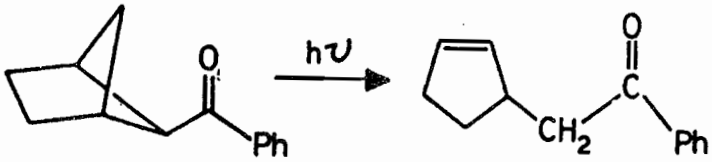


21. Suggest reasonable mechanisms for the following reactions

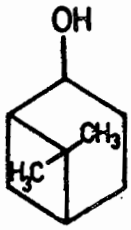
(a) (3)



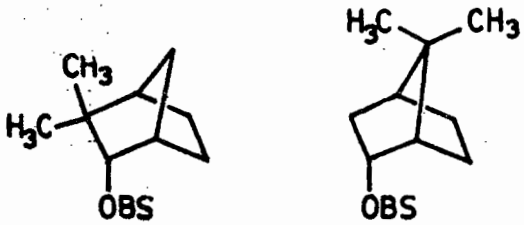
(b) (2)



22. *(a)* Draw the conformations of the two stereoisomers of : (1)

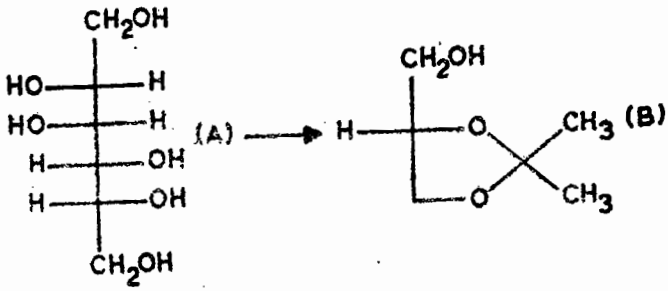


(b) Upon treatment with *p*-bromobenzenesulphonyl chloride (BSCl) in pyridine, one of the isomers of the above alcohol gives A and the other gives B. Identify which gives A and which gives B and show how the rearrangements proceed. (4)

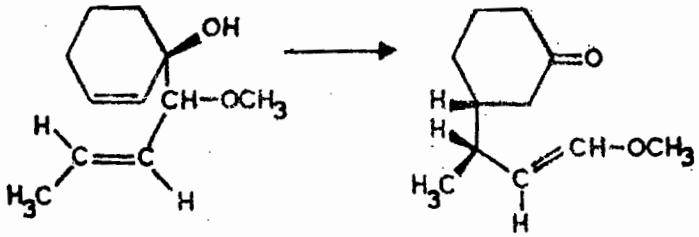


(A) (B)

23. *(a)* may be converted to the chiral ketal, B. (3)



(b) Show how the following transformation may be brought about and indicate its mechanism. **(2)**



24. A carboxylic acid of molecular formula $C_{11}H_{14}O_2$ upon treatment with $SOCl_2$ followed by treatment of the product with anhydrous $AlCl_3$ in CS_2 gives A, $C_{11}H_{12}O$. The IR spectrum of A has a strong band at 1690 cm^{-1} and its proton NMR spectrum has three signals in the intensity ratio (low to high field) 2:1:3. On heating A with hydrazine and KOH in ethylene glycol, a hydrocarbon, B is obtained, with the following PMR spectrum.

δ 1.22, singlet, 6 H
δ 1.85, triplet, 2H, J = 7 Hz
δ 2.83, triplet, 2H, J = 7 Hz
δ 7.02, singlet, 4H

write down the reactions giving the structure of all the intermediates and final product and interpret the spectra. **(5)**

25. Use the following cell, deriving necessary relations, to determine the ionic product, K_w of water at 25°C.

Pt, H_2 (1 atm) | NaOH (m_1) NaCl (m_2) AgCl (s) | Ag
$m_1 = m_{NaOH} = 0.0100$ mol kg^{-1}
$m_2 = m_{NaCl} = 0.01125$ mol kg^{-1}
E_{cell} at 25°C = 1.04864 volts

Standard oxidation potential of Ag, AgCl, Cl^- = – 0.2224 volts at 25°C. Assume activity coefficients to be unity in all calculations. **(5)**

26. *(a)* Given $E^0_{Cu^{2+}|Cu(s)} = 0.337$ V and $E^0_{Cd^{2+}|Cd(s)} = -0.403$ V at 25°C, will Cd(s) precipitate Cu(s) from a solution (assume reactants and products to be at unit activity) ? Write down the feasible cell reaction and obtain the equilibrium constant (K) for the reaction. **(3)**

(b) For the reaction, in a certain temperature range,

$$N_2(g) + O_2(g) = 2NO(g)$$

the plot of ln K_p against 1/T gives a slope of -2.2×10^4 K. What is the enthalpy change for the reaction ? **(2)**

27. The reaction,

$$H_2O_2 + 2S_2O_3^{2-} + 2H^+ \rightarrow 2H_2O + S_4O_6^{2-}$$

is independent of hydrogen ion concentration in the pH range 4–6. If the reaction is second order, derive an expression for the rate constant and compute its value from the data supplied : **(5)**

$[H_2O_2]_{initial} = 0.0368$ mol L^{-1}
$[S_2O_3^{2-}]_{initial} = 0.0204$ mol L^{-1}
pH = 5.0, temp = 25°C

time (min) :	36	43
$[S_2O_3^{2-}]$ (mol L^{-1}) :	5.18×10^{-3}	4.16×10^{-3}

28. The fundamental and the first overtone of $^1H^{35}Cl$ occur at 2885.9 and 5668.0 cm^{-1} respectively. Calculate the harmonic vibrational frequency (ν_e) and force constant of $^1H^{35}Cl$. (5)

29. For the mechanism

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

$$C \xrightarrow{k_3} D$$

derive an expression for the rate of formation of D with the steady state approximation for C. Also, relate the pre-exponential factor A, and activation energy E for the apparent second order rate constant in terms of A_1, A_2, A_3 and E_1, E_2, E_3 for the composite steps under the condition $k_3 << k_2$. (5)

30. *(a)* A binary solution contains n_1 moles of solvent of molecular weight M_1 and 1 moles of solute of molecular weight M_2 in V litres. If ρ is the density of the solution and C is the concentration in mols per litre, prove that the partial molar volume of the solvent $\left(\overline{V}_1\right)$ is given by the expression:

$$\overline{V}_1 = \frac{M_1}{1000\left(\rho - c\dfrac{d\rho}{dc}\right)}$$ (3)

(b) Find $\hat{A}^2$ if $\hat{A} = x + \dfrac{d}{dx}$ operating on an arbitrary function $f(x)$. (2)

GATE - 1995

ANSWERS WITH EXPLANATIONS

1.

1.1 (C)

Explanation : $XeF_2 + H_2O \rightarrow XeO_2F_2$.

1.2 (A)

1.3 (C)

Explanation : Optically active isomers shows mirror image and this compound shows.

1.4 (C)

Explanation : Due to their parking.

1.5 (C)

Explanation : Magnetic moment = $n\sqrt{n+2}$

1.6 (B)

1.7 (B)

1.8 (B)

1.9 (B)

Explanation : In linkage isomerism, the point of contact with metal atom is different.

1.10 (A)

Explanation : Because only one term for orgel diagram.

1.11 (B)

1.12 (B)

1.13 (C)

Explanation : $\underset{\text{(Colourless)}}{Ti\,(IV)} \xrightarrow{H_2O_2} \underset{\text{(coloured)}}{Ti\,(III)}$

1.14 (B)

Explanation : Inversly proportional to molecular weight.

1.15 (D)

1.16 (D)

1.17 (D)

Explanation : For ideal solution,

$$\Delta G_{mix} = 0$$
$$\Delta Vi_{mix} = 0$$
$$\Delta H_{mix} = 0$$

1.18 (D)

1.19 (C)

1.20 (C)

1.21 (B)

Explanation : $\left(\frac{\partial G}{\partial T}\right)_P = -S$

1.22 (D)

Explanation : Vapourisation of water always needs certain amount of energy.

1.23 (C)

1.24 (B)

Explanation : 4-bromobenzyl chloride + NaCN $\xrightarrow{\text{Ethanol}}$ 4-cyanobenzyl chloride

1.25 (B)

1.26 (B)

Explanation : 2-Butanol (R) + p-tolulensulphonyl chloride + pyridine $\xrightarrow{\text{LiBr}}$ S-2-butyl tosylate.

1.27 (C)

1.28 (B)

1.29 (D)

1.30 (D)

Explanation : Ortho methyl group first resist the internal molecule to interact.

1.31 (A)

1.32 (D)

Explanation : Methyl glucopyranoside + 4 HIO_4 $\longrightarrow$ product.

1.33 (A)

1.34 (B)

1.35 (D)

Explanation : Pyridine is more basic than peperidine.

2.

2.1. $A \propto \frac{1}{T}$

2.2. $XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$

2.3. $2H_3BCO$

2.4. Inner sphere mechanism

2.5. Partition function values.

2.6. Ionisation, hydrate isomers.

2.7. $\chi_M = g\sqrt{J(J+1)}$

2.8. Schottky defect.

2.9. 12, 8

2.10. First order

11. D_3h

12. Large deviation

13. $H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

14. 11.06×10^{-8}, $\wedge_0 = \lambda^+ + \lambda^-$ (Kohlr asasch's law).

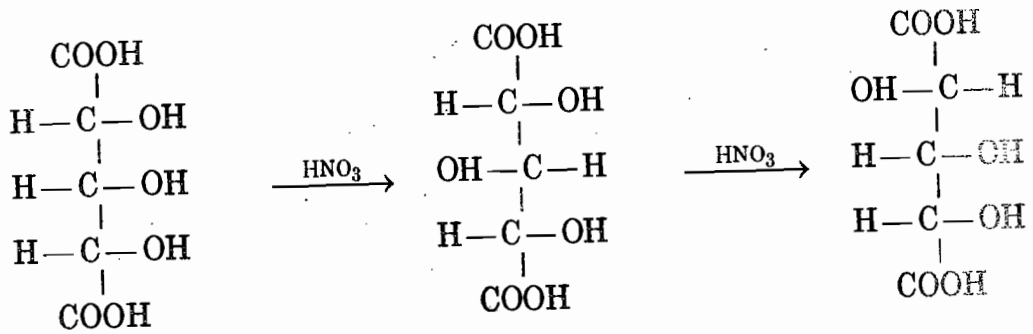
15. 32°

16. $\dfrac{d\ln K}{d(1/T)} = -\Delta_r p\theta$

17. Higher electronegativity

18. Aromatic acid.

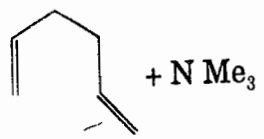
19.



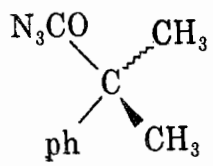
20. Cyclic

21. Symmatry

22.



23.



24. Beta position

25. Reagent.

3.

(A) 1 ⟶ C
2 ⟶ D
3 ⟶ E
4 ⟶ B

(B) 1 ⟶ B ⟶ W
2 ⟶ D ⟶ X
3 ⟶ A ⟶ Y

4.

(A) 1 ⟶ F
2 ⟶ D
3 ⟶ A
4 ⟶ E

(B)

List I		List II		List III
1	⟶	2	⟶	3
2	⟶	0	⟶	4
3	⟶	1	⟶	6

5.

(A)

Antecule		Electronic configuration		Dissociation energy
N_2^+	⟶	$(Be_2)\ (\pi_u\ 2p)^4\ (\sigma_g\ 2p)^1$	⟶	8.73 eV
N_2	⟶	$(Be_2)\ (\pi_u\ 2p)^4\ (\sigma_g\ 2p)^2$	⟶	9.6 eV

(B)

Ion		First ionisation Potential
He^+	⟶	216.6 eV
Li^{++}	⟶	121.8 eV
Be^{+++}	⟶	54.16 eV

(C)

Molecules		Rotator types
C_6H_6	⟶	spherical top
CCl_4	⟶	symmetric top
CH_2Cl_2	⟶	Asymmetric top

(D)

Valence Type		Thickness
Uni-uni	⟶	9.64 A°
Uni-bi	⟶	5.58 A°
Uni-ter	⟶	3.94 A°

GATE 1996

CY : CHEMISTRY

Time : 3 Hours *Maximum marks : 200*

Read the following instructions carefully :

1. Write all the answers in the answerbook.
2. This paper contains TWO SECTIONS : 'A' and 'B'.
3. **Section A** has **EIGHT** questions. Answer ALL questions in this section.
4. **Section B** has **TWENTY** questions. Answer any TEN questions from this section if more number of questions are attempted, strike off the answers which are not to be evaluated; else only the **FIRST TEN** unscored answers will be considered.
5. Answers to **Section B** should start on a fresh page and should not be mixed with answers to Section **A**.
6. Answers to questions and answers to parts of question should appear together and should not be separated.
7. In all questions of 5 marks, write clearly the important steps in your answer. These steps carry partial credit.
8. There will be no negative marking.

General Data :

Gas constant $R = 8.205 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}

$= 8.314$ JK^{-1} mol^{-1}

$= 1.987$ Cal K^{-1} mol^{-1}

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

Boltzmann Constant $= 1.38 \times 10^{-23}$ JK^{-1}

$= 0.695$ cm^{-1} K^{-1}

Planck Constant $h = 6.626 \times 10^{-34}$ JS

Rydberg Constant $R_H = 109737$ cm^{-1}

Faraday $= 96500$ C mol^{-1}

1 eV $= 96.485$ K J mol^{-1}

Atomic mass unit $= 1.66 \times 10^{-27}$ kg

Speed of light $= 3 \times 10^8$ ms^{-1}

Atomic numbers : V 23, Cr 24, Mn 25, Fe 26, Co 27, Ni 28, W 74

SECTION A

(100 Marks)

1. ***For each of the sub-questions (1.1 to 1.35) four answers A, B, C and D are provided of which ONE is correct. Write in your answer book the alphabet corresponding to the correct answer against the sub-question.*** (35 × 1 = 35)

1.1. For which one of the following ions, the colour is NOT due to a *d-d* transition ?

(A) CrO_4^{2-} (B) $Cu(NH_3)_4^{2+}$

(C) $Ti(H_2O)_6^{3+}$ (D) CoF_6^{3-}

1.2. Which one of the following statements is correct for XeO_2F_2 ?

(A) It has a square planar structure
(B) It has a trigonal bipyramid based structure
(C) It is isostructural with XeF_4
(D) It has a tetrahedral structure

1.3. Which one of the following octahedral complexes will be distorted ?

(A) $[Cr(H_2O)_6]^{2+}$ (B) $[Cr(H_2O)_6]^{3+}$

(C) $[Mn(H_2O)_6]^{2+}$ (D) $[Fe(H_2O)_6]^{3+}$

1.4. The crystal field splitting energy (Δ) for $CoCl_6^{4-}$ is 18000 cm^{-1}. The Δ for $CoCl_4^{2-}$ would be

(A) 18000 cm^{-1} (B) 16000 cm^{-1}
(C) 8000 cm^{-1} (D) 2000 cm^{-1}

1.5. Molar absorptivity of a compound expressed in the unit $l\ mol^{-1}\ cm^{-1}$ does NOT depend on

(A) the nature of the compound (B) the concentration of the solution
(C) the width of the sample cell (D) the resolution of the spectrophotometer

1.6. $B_{10}C_2H_{12}$ is isoelectronic with

(A) $B_{12}H_{12}^{2-}$ (B) $B_{12}H_{12}$

(C) $B_{12}H_{12}^{+}$ (D) $B_{12}H_{12}^{2+}$

1.7. Which one of the following free ions has the lowest magnetic moment ?

(A) Ce^{3+} (B) Nd^{3+}
(C) Sm^{3+} (D) Gd^{3+}

1.8. Which one of the following has the largest band gap energy ?

(A) Germanium (B) Silicon
(C) Tellurium (D) Diamond

1.9. Which one of the following IR frequencies is the closest to that of a triply bridged CO group ?

(A) 1700 cm^{-1} (B) 1810 cm^{-1}
(C) 1920 cm^{-1} (D) 2140 cm^{-1}

1.10. Which one of the following is a monobasic acid ?

(A) $H_4P_2O_7$ (B) H_3PO_4
(C) H_3PO_3 (D) H_3PO_2

1.11. Which one of the following is most easily reduced ?
(A) $V(CO)_6$
(B) $Cr(CO)_6$
(C) $Fe(CO)_5$
(D) $Ni(CO)_4$

1.12. The number of possible isomers for the octahedral complex ion $[Co(en)Cl_2Br_2]^-$ is
(A) 2
(B) 4
(C) 6
(D) 8

1.13. Which one of the following molecules exists as a monomer under ambient conditions ?
(A) Trimethyl aluminium
(B) Triethyl aluminium
(C) Triphenyl aluminium
(D) Trimesityl aluminium

1.14. Which one of the following complex ions shows the minimum intensity of absorption in the uv-visible region ?
(A) $\left[Cr(H_2O)_6\right]^{2+}$
(B) $\left[V(H_2O)_6\right]^{2+}$
(C) $\left[Mn(H_2O)_6\right]^{2+}$
(D) $\left[Co(H_2O)_6\right]^{2+}$

1.15. Fisher projection indicates
(A) Horizontal substituents above the plane
(B) Vertical substituents above the plane
(C) Both horizontal and vertical substituents below the plane
(D) Both horizontal and vertical substituents above the plane

1.16. Diels-Alder reaction normally yields endo-adduct as a major product. This is due to
(A) Higher stability of the product
(B) Faster rate of formation of the endo-adduct
(C) Steric hindrance
(D) Secondary orbital interactions between a diene and a dienophile

1.17. How many stereoisomers are there for tartaric acid ?
(A) 2
(B) 3
(C) 4
(D) 5

1.18. Bromination of toluene gives
(A) only meta-substituted product
(B) only para-substituted product
(C) mixture of ortho- and para-substituted products
(D) mixture of ortho- and meta-substituted products

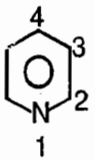
1.19. Table sugar is
(A) a disaccharide consisting of D-glucose and D-fructose
(B) a monosaccharide
(C) a disaccharide consisting of two D-glucose units
(D) D-glucose

1.20. In the reaction of cyclopentadiene with acrylate ester giving Diels-Alder reaction products, the interacting frontier orbitals are
(A) HOMO of a diene and LUMO of a dienophile
(B) HOMO of a dienophile and LUMO of a diene
(C) HOMO of a diene and HOMO of a dienophile
(D) LUMO of a diene and LUMO of a dienophile

1.21. When methyl group is in the axial position in methyl cyclohexane, the molecule has
(A) One *n*-butane Gauche interaction
(B) Two *n*-butane Gauche interaction
(C) No *n*-butane Gauche interaction
(D) Three *n*-butane Gauche interaction

1.22. The cleavage $R' - \underset{\underset{O}{\|}}{C} - R \xrightarrow{h\nu} R' - \underset{\underset{O}{\|}}{C^{\bullet}} + R^{\bullet}$ is called
(A) Norrish type I
(B) Norrish type II
(C) Beta-cleavage
(D) Grob fragmentation

1.23. SN^1 reaction on optically active substrates mainly gives
(A) Retention in configuration
(B) Inversion in configuration
(C) Racemic product
(D) No product

1.24. 

undergoes electrophilic substitution reaction preferentially
(A) at position 2
(B) at position 3
(C) at position 4
(D) at positions 2 and 4

1.25. In E_2 elimination, some compounds follow Hoffmann's rule which means
(A) the double bond goes to the most substituted position
(B) the compound is resistant to elimination
(C) no double bond is formed
(D) the double bond goes mainly toward the least substituted carbon

1.26. Lithium dialkyl amide base, on reaction with cyclohexanone, abstracts
(A) axial hydrogen preferentially
(B) equatorial hydrogen preferentially
(C) axial and equatorial in non-preferential manner
(D) neither axial nor equatorial hydrogen

1.27. The internal pressure of one mole of a Van der Waal gas is equal to
(A) zero
(B) b^2
(C) $\frac{a}{v^2}$
(D) $b - \frac{a}{RT}$

1.28. Solid CO_2 is called 'dry ice' because
(A) at 25° C and 1 atm, only solid and vapour phases of CO_2 are in equilibrium
(B) the critical temperature of CO_2 is above 25°C
(C) the boiling point of liquid CO_2 is above 100°C
(D) the melting point of solid CO_2 is 0°C

1.29. The absorption isotherm is defined as the dependence of
(A) surface coverage on the temperature at a fixed pressure
(B) surface coverage on the pressure at a fixed temperature
(C) surface coverage on the oxidation state of the surface material
(D) rate of a surface reaction on the pressure at a fixed temperature

1.30. The minimum energy for an endothermic reaction will be
(A) not less than ΔH for the reaction
(B) less than ΔH for the reaction
(C) zero
(D) equal to the solvation energy

1.31. Ethanol and methanol form nearly ideal solutions. The mole fraction of methanol in a solution obtained by mixing 100 g of each is approximately
(A) 0.8
(B) 0.2
(C) 0.4
(D) 0.6

1.32. The triple point of water is at
(A) 273.16 K
(B) 273.16 K and 760 Torr
(C) 273.16 K and 4.58 Torr
(D) 760 Torr

1.33. How many states (distinguished by the quantum number m_J) belong to the ground state of the chlorine (Atomic number : 17) atom ?
(A) 4
(B) 1
(C) 3
(D) 2

1.34. The symmetry operations other than identity E in the point group C_{3v} are
(A) $C_3(z)$, σ_v
(B) $2C_3(z)$, $3\sigma_v$
(C) $2C_3(z)$, $3C_2(x, y, z)$, $3\sigma_v$
(D) $3C_2(x, y, z)$, $3\sigma_v$, $3\sigma_h$

1.35. The diffusion current in a polarogram is proportional to
(A) the residual current
(B) the migration current
(C) the wave height
(D) the concentration of the supporting electrolyte

2. ***For each of the sub-questions (2.1 to 2.10) four answers A, B, C and D are provided of which ONE is correct. Write in the answerbook the alphabet corresponding to the correct answer against the sub-question.***
(10 × 2 = 20)

2.1. Which one of the following statements for hemoglobin is NOT correct ?
(A) The binding with O_2 is weaker in comparison with myoglobin
(B) Iron is 5-coordinated
(C) Iron is coplanar with the porphyrin ring in the absence of oxygen
(D) The oxidation state of iron is + 2

2.2. The organometallic compound $W(C_5H_5)_2(CO)_2$ follows the 18 - electron rule. The hapticities of the two cyclopentadienyl groups are
(A) 5 and 5
(B) 3 and 5
(C) 3 and 3
(D) 1 and 5

2.3. For $H_3[PMo_{12}O_{40}]$ which one of the following statements is NOT true ?
(A) The nearest neighbours of P are 4 oxygen atoms
(B) The nearest neighbours of Mo are 6 oxygen atoms
(C) It is called a 12-hetero-poly acid
(D) It is synthesized by heating phosphate solution with ammonium molybdate and NaOH

2.4. Which one of the following statements for borazine is NOT correct ?
(A) It has six B-H bounds
(B) It has three B=N bonds
(C) It has three N-H bonds
(D) It has a cyclic structure

2.5. One mole of an ideal gas ($C_p = 29.234\ JK^{-1}\ mol^{-1}$) is expanded reversibly and adiabatically from 1 dm^3 to 10 dm^3. If the initial temperature is 750 K, the final temperature will be

(A) 1000 K (B) 750 K
(C) 300 K (D) 100 K

2.6. The dissociation constant of a weak acid HA is 2.5×10^{-5} at 25°C. The degree of hydrolysis of 0.01 M of its sodium salt NaA will be approximately

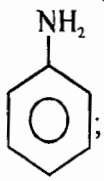
(A) 2×10^{-10} (B) 1×10^{-14}
(C) 0.02 (D) 2×10^{-4}

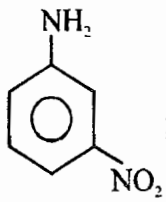
2.7. The overall rate $\frac{d[P]}{dt}$, for the reaction $2A \overset{K}{\rightleftharpoons} B;\ B + C \xrightarrow{k_f} P$ is given by

(A) $K\,k_f[A]^2\,[C]$ (B) $K\,[A]\,[B]$
(C) $k_f[B]\,[C]$ (D) $K\,k_f[A]^2\,[B]\,[C]$

2.8. The wavelength of light emitted when electron falls from the $n = 50$ orbit to the $n = 49$ orbit of H - atom, is

(A) 55 nm (B) 0.55 cm
(C) 0.55 Å (D) 55 m

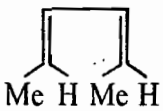
2.9. Among the compounds *(a)* 

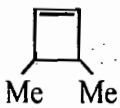
; *(b)* Et_3N; *(c)* 

; *(d)*

the order of basicity is

(A) $d > c > b > a$ (B) $b > a > c > d$
(C) $c > d > b > a$ (D) $a > c > d > b$

2.10. Transformation 

to 

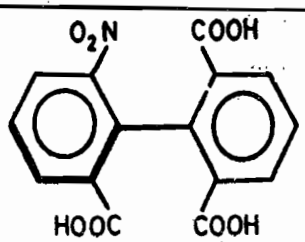
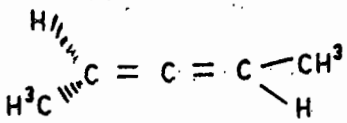
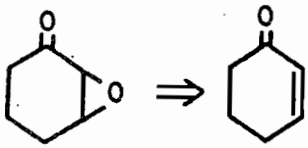
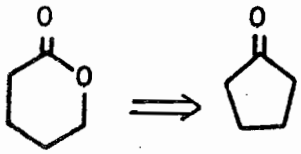
is feasible by a

(A) Thermal disrotatory process (B) Photochemical disrotatory process
(C) Thermal conrotatory process (D) Photochemical conrotatory process

3. *(a)* Match the items in List-I with the information in List-II. **(4 × 1 = 4)**

List-I	*List-II*
(1) Carboxypeptidases	(A) Iron
(2) Ilkovic Equation	(B) Zinc
(3) $[Rh(PPh_3)_2Cl]$	(C) Molecular sieves
(4) Zeolites	(D) Polarography
	(E) Ziegler-Natta catalyst
	(F) Hydrogenation catalyst

(b) Match the structures in List-I with the information in List-II. **(4 × 1 = 4)**

List-I	*List-II*
(1) 	(A) Erythro
	(B) Planar
(2) 	(C) Optically active
	(D) Optically inactive
(3) 	(E) H_2O_2/OH^-
	(F) CO_2
(4) 	(G) *m*-chloroper-benzoic acid

(c) Match the molecules in List-I with the number of vibrations in List-II. **(2 × 1 = 2)**

List-I	*List-II*
(1) NO_2 (2) CH_4	(A) 3 (B) 4 (C) 8 (D) 9

(d) Match the items in List-I with the information in List-II. **(2 × 1 = 2)**

List-I	*List-II*
(1) Purification of nitrobenzene. (2) Ideal solution of two liquids	(A) Molecular distillation (B) Vacuum distillation (C) Fractional-distillation (D) Steam distillation

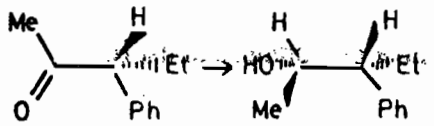
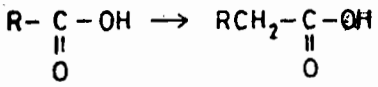
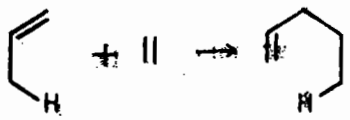
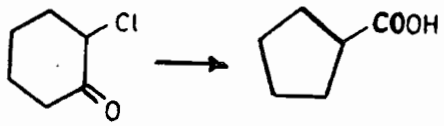
(e) Match the items in List-I with the information in List-II. **(2 × 1 = 2)**

List-I	*List-II*
(1) Third law of thermodynamics (2) Adiabatic flame temperature	(A) Carnot cycle (B) $S = k \ln W$ (C) Kirchoff's equation (D) $dG = Vdp - SdT$

(f) Match the items in List-I with the information in List-II. **(2 × 1 = 2)**

List-I	*List-II*
(1) Product of $\left[CH_3COO^-\right]\left[CH_3COOH_2^+\right]$	(A) Hydrolysis constant
(2) Product of $\left[Ag^+\right]^2\left[SO_4^{2-}\right]$	(B) Stability constant
	(C) Solubility product
	(D) Self-ionization constant

(g) Match the transformations in List-I with the information in List-II. **(4 × 1 = 4)**

List-I	*List-II*
(1) 	(A) Ene reaction
(2) 	(B) Diels-Alder reaction
(3) 	(C) Cram's product
(4) 	(D) Anti-Cram product
	(E) Arndt-Eistert synthesis
	(F) Beckmann rearrangement
	(G) Favorskii rearrangement

4. *(a)* When 229 J of energy is supplied to 3 moles of a gas at constant pressure, the temperatur of the gas increases by 2.55 K. Calculate C_p and C_v for the gas, assuming ideal behaviour **(2)**

(b) For a cell in which the overall reaction is

$$2\,Cu^+ = Cu^{2+} + Cu$$

E° at 298 K is +0.184 V. Calculate ΔG° for the reaction. (

5. *(a)* Insulin $(C_6H_{10}O_5)_x$ is dissolved in a suitable solvent and the osmotic pressure (π) of solution of various concentrations (c) is measured at 20°C. The intercept of a plot of π/c against c is found to be 4.65×10^{-3}. What is the molecular weight of insulin ? **(2)**

(b) In a one litre container, 10^{23} gas molecules each of mass 10^{-25} Kg, are present. The root mean square velocity of the molecules is 1000 ms^{-1}.

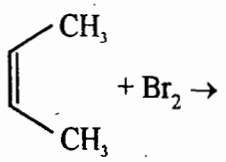
(i) What is the total kinetic energy of the molecules ?

(ii) What is the temperature of the gas ? **(3)**

6. *(a)* Why are the absorption bands of complexes of the lanthanides much sharper than those of the transition metals ? **(2)**

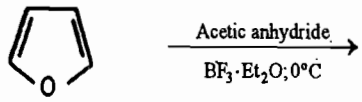
(b) The enthalpy of hydration of Fe^{2+} ion is 12 Kcal mol^{-1} higher than what would be expected if there were no crystal field stabilisation energy. Estimate the magnitude of Δ for $\left[Fe\left(H_2O\right)_6\right]^{2+}$. ($\Delta$ is crystal field splitting) **(3)**

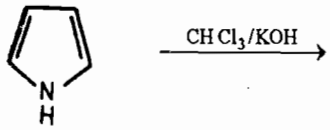
7. *(a)* A metal ion, Cr^{3+} forms an octahedral complex $\left[Cr\left(NH_3(OH)_2Cl_3\right)\right]^{2-}$. Sketch all its isomers. (3)

(b) 

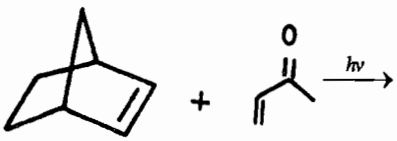
(i) Write all the stereoisomeric products from the above reaction.
(ii) What is the relationship between the products ? (2)

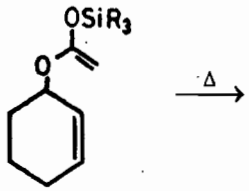
8. Write down the major products in the following reactions : (5 × 1 = 5)

(a) 

(b) 

(c)

(d) 

(e) 

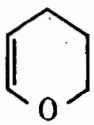
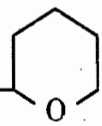
SECTION B

(50 Marks)

Answer any TEN questions in this section. All questions carry equal marks.

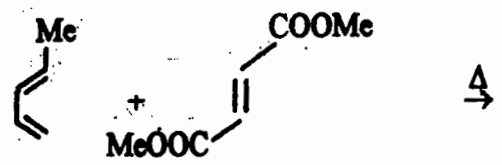
9. Suggest a suitable mechanism for the following reactions :

(a) $Ph_2C(OH)-CMe_2(OH) \xrightarrow{H^+} Ph-C(=O)-CMe_2(Ph)$ (3)

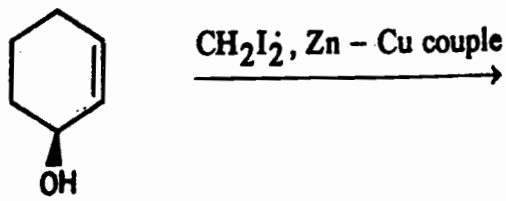
(b) CH_3-CH_2-OH +  $\xrightarrow{H^+}$ CH_3-CH_2-O-  (2)

10. *(a)* Write the major product with correct relative stereochemistry in the following reactions.

(i) (2)



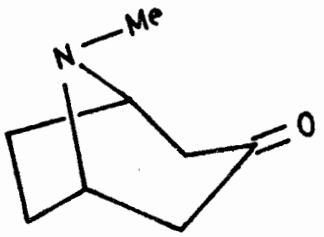
(ii) (1)



(b) Write the reagents for reduction of alkyne to cis-alkene and trans-alkene separately. (2)

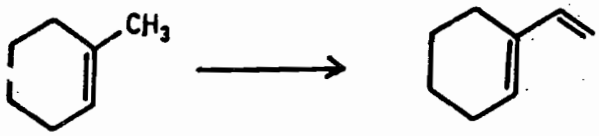
11. *(a)* Reaction of an alkene with N-bromosuccinimide gives allylic bromide. Write a suitable mechanism for the reaction by taking an example of cyclohexene. (2)

(b) Retrosynthetic analysis of the compound shown indicates that the Mannich transform can be used to synthesize it. Identify all the precursors used in this transform. (3)

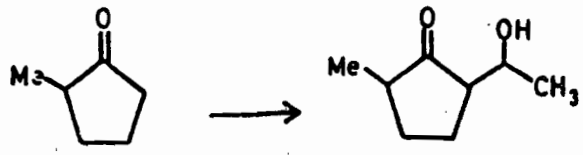


12. How will you carry out the following transformations (these may involve multiple steps) ?

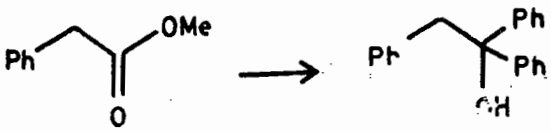
(A) (2)



(B) (2)

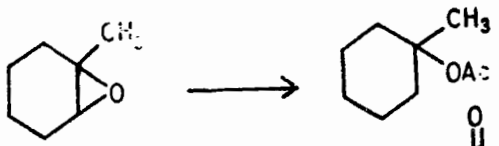


(C) (1)

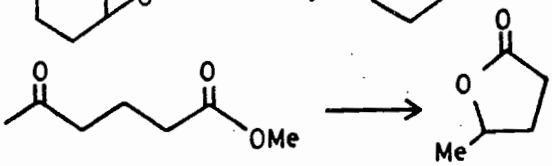


13. *(a)* Write appropriate reagent(s) for the following reactions (may involve more than one step).

(i) (2)



(ii) (2)



(b) In which way is resonance different from hyperconjugation ? (1)

14. A ketone of molecular formula C_8H_8O, upon treatment with $NaBH_4$ gives (A) of molecular formula $C_8H_{10}O$. The IR spectrum of (A) has a strong band at 3600 cm^{-1}. Reaction of (A) with methanesulfonyl chloride in the presence of a base gave (B). (B) was then treated with NaI in acetone and the resulting product on reaction with $NaCNBH_3$ gave a hydrocarbon with the following ^1H NMR data.

δ	0.9	triplet, 3H
δ	2.6	quartet, 2H
δ	7.1	broad singlet

Write all the reactions giving the structures of all the intermediates. Identify the ketone and the hydrocarbon. **(5)**

15. *(a)* Explain how a quaternary ammonium salt acts as a phase transfer catalyst. Take the example of alkyl halide to alkyl cyanide conversion. **(3)**
(b) Write the structure of 18 - crown - 6. **(1)**
(c) Cite two examples of ambident nucleophiles. **(1)**

16. *(a)* When $\left[Ni(NH_3)_4\right]^{2+}$ is treated with concentrated HCl, two compounds A and B having the same formula $Ni(NH_3)_2Cl_2$ are formed. A reacts readily with $Ag_2C_2O_4$ to give a white precipitate whereas B does not. Identify A and B and explain the difference in reactivity toward $Ag_2C_2O_4$. **(3)**
(b) How is $Mn_2(CO)_{10}$ converted to $CH_3Mn(CO)_5$? **(2)**

17. *(a)* Ethylene cannot be hydrogenated catalytically using Wilkinson catalyst. Draw the structures of catalytic reaction intermediates and explain. **(3)**
(b) Identify A and B in the following reaction scheme

$$XeF_6 \xrightarrow{H_2O\,(excess)} A \xrightarrow{XeOF_4} B$$ **(2)**

18. *(a)* For the following conversion suggest suitable reagents

$$Mg_3B_2 \xrightarrow{X?} B_2H_6 \xrightarrow{Y?} B_3H_6N_3 \xrightarrow{Z?} B_3H_9N_3Cl_3$$ **(3)**

(b) The complex $\left[Co\,(en)_3\right]^{3+}$ exists in the form of two optical isomers. Using this information show that this complex cannot have a trigonal prismatic geometry. **(2)**

19. The IR spectrum of compound $(C_5H_5)_2Fe_2(CO)_4$ exhibits two bands at 1800 cm^{-1} and 1930 cm^{-1}. The ^1H NMR spectrum of this organometallic complex shows only one line and the compound is diamagnetic. Derive the structure of the complex. **(5)**

20. *(a)* How is ferrocene converted to $(\eta^5 - C_5H_5)\,Fe\left(\eta^5 - C_5H_4COOH\right)$? **(2)**
(b) Which type of semiconductor is obtained by doping pure silicon with arsenic ? What is its charge carrier ? **(2)**

21. *(a)* $Co(\eta^5 - C_5H_5)_2$ is more readily oxidised than ferrocene. Explain. **(2)**
(b) For the octahedral complex $[CoL_6]^{3+}$ the crystal field splitting, $\Delta \approx 473$ nm. The pairing energy for the cobalt (III) ion is 15000 cm^{-1}. Calculate the magnetic moment of the complex. **(3)**

22. *(a)* The vapour pressure of two liquids A and B are 44.5 Torr and 88.7 Torr, respectively, at 300 K. Calculate the mole fraction of B in the vapour above a solution obtained by mixing 50 gms of each. The molecular weights of A and B are 46 and 32, respectively. **(3)**

(b) An aqueous sucrose solution freezes at –0.31°C. Given that $k_f = 1.86$ and $k_b = 0.51$ for water, calculate the molality of the solution and also its boiling point. (2)

23. A Carnot cycle operates on a temperature difference of 200 K. One-third of the heat absorbed from the source at T_2 is discharged as waste heat to the sink at T_1. The cycle does 400 J of work. Calculate q_1, q_2, T_1 and T_2. (5)

24. (a) Derive an expression to evaluate the most probable distance from the proton to 1s electron in a hydrogen - like atom. The radial wavefunction $\psi_{1s} = 2\left(\frac{z}{a_o}\right)^{3/2} \exp^{-\frac{zr}{a_o}}$, where z is the atomic number and a_o is the Bohr radius. (3)

(b) The chemical shift of CH_3 protons in acetaldehyde is $\delta = 2.2$ and that of CHO proton is 9.8. In an applied field of 10 T, what is the difference in local magnetic field between the two types of protons in the molecule ? (2)

25. Calculate the frequency in wavenumbers for the first rotational transition ($J = 0 \rightarrow 1$) in $D^{35}Cl$. The D – Cl bond length is 120 pm. (5)

26. Calculate the ionic strength and the mean activity coefficient for 1.0×10^{-4} M $Al_2(SO_4)_3$ solution in water at 25°C. (5)

27. (a) The elements E (identity), C_2, σ_h, i belong to the C_{2h} point group. Construct the group multiplication table. (3)

(b) Calculate the entropy change for the transformation
H_2O (liq, 1 atm) $\rightarrow$ H_2O (g, 0.1 atm) at 100°C.
ΔH_{vap} for H_2O is 40670 J. (2)

28. (a) The ground state of chlorine atom is fourfold degenerate. The first excited state is 881 cm^{-1} higher in energy and is twofold degenerate. What is the value of the electronic partition function at 27°C ? (3)

(b) Determine how many degrees of freedom are there in a system composed of a saturated solution of sodium chloride, water vapour and sodium chloride crystals. (2)

GATE - 1996

ANSWERS WITH EXPLANATIONS

1.

1.1 (A)

Explanation : In CrO_4^{2-}, Cr (VI) has d^0 configuration. There is d-d transistion. The colour is due to charge transfer.

1.2 (B)

1.3 (A)

Explanation : In $[Cr(H_2O)_6]^{2+}$, Cr (II) has d^4 configuration with unsymmetrical arrangement of electrons, in the d (e.g) orbital. (John-Teller distortion).

1.4 (C)

Explanation : The splitting of tetrahedral complex is 4/9 of octahedral.

1.5 (B) or (C) or (D)

1.6 (A)

1.7 (C)

Explanation : Due to spin orbit coupling.

1.8 (D)

1.9 (B)

1.10 (D)

1.11 (A)

Explanation : In $V(CO)_6$, the E.A.N. of V is $23 + 2 \times 6 = 35$, which is one less than stable E.A.N. value of 36. So it tends to gain an electron.

1.12 (B)

1.13 (D)

Explanation : Due to steric hinderence, trimesityl aluminium does not dimerize.

1.14 (C)

Explanation : $[Mn(H_2O)_6]^{2+}$ is practically colourless, since spin selection rule ($\Delta s = 0$) is not obeyed.

1.15 (A)

1.16 (D)

Explanation : The secondary interaction of orbitals in the transiter state is not sterically possible for the exo product.

1.17 (B)

Explanation : The dI form is not a stereoisomer. It is a mixture of two stereoisomers.

1.18 (C)

1.19 (A)

1.20 (A)

1.21 (B)

1.22. (A)

1.23 (C)

1.24 (B)

1.25 (D)

1.26 (A)

Explanation : The hydrogen is abstracted from the axial position due to steroelectronic factors.

1.27. (C)

1.28 (A)

1.29 (B)

1.30 (A)

1.31 (D)

Explanation : Mole fraction of methanol $= \dfrac{\frac{100}{32}}{\frac{100}{32}+\frac{100}{46}} = \dfrac{3.125}{3.125+2.174}$

$$= \frac{3.125}{5.299} = \mathbf{0.59}$$

1.32 (C)

1.33 (D)

Explanation : Ground state of cl atom, K.L.l. $3s^2, 3p^5$

$$s = +\frac{1}{2}\ ;\ J = 2s + 1 = 2$$

134. (B)

1.35 (C)

2

2.1 (C)

Explanation : In the absence of oxygen, Fe^{2+} is coplanar with the porphyrin ring.

2.2 (A)

2.3 (D)

Explanation : Conc. HNO_3 should be used in the place of NaoH.

2.4 (A)

Explanation : Borazine has three B-H bonds and not sixe.

2.5 (C)

Explanation :

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{y-1}$$

$$= \left(\frac{1}{10}\right)^{0.397}$$

Because,

$$\left(\frac{C_P}{C_V}\right) = \frac{29.234}{29.234 - 8.314} = 1.397$$

$$\therefore \quad \frac{T_2}{T_1} = 0.4009$$

$$T_2 = 750 \times 0.4009$$

$$= 300.7\ k.$$

2.6 (D)

Explanation :

$$K_h = \frac{10^{-14}}{2.5 \times 10^{-5}} = 0.4 \times 10^{-9} = 4 \times 10^{-10}$$

$$A^- + H_2O \rightarrow HA + OH^-$$

$$K_h \approx \alpha^2 c$$

$$\therefore \quad \alpha^2 = \frac{4 \times 10^{-10}}{0.01} = 4 \times 10^{-8}$$

$$\therefore \quad \alpha = 2 \times 10^{-4}$$

2.7 (A)

Explanation :

$$\frac{d(p)}{dt} = K_f(B)(C)$$

$$K = \frac{(B)}{(A)^2}$$

$$\Rightarrow \quad B = K \times (A)^2$$

$$\therefore \quad \frac{d(p)}{dt} = K_f K (A)^2 (C).$$

2.8 (B)

Explanation :

$$\bar{v} = 1.097 \times 10^5 \text{ cm}^{-1} \left(\frac{1}{49^2} - \frac{1}{50^2} \right)$$

$$= 1.097 \times 10^5 \times 4.165 \times 10^{-4} - 4.0 \times 10^{-4} \text{ cm}^{-1}$$

$$= 1.097 \times 10^5 \times 1.65 \times 10^{-5} \text{ cm}^{-1}$$

$$= 1.51 \text{ cm}^{-1}$$

$\therefore$ Corresponding wavelength $= \frac{1}{(8)} cm = 0.5525 \text{ cm}^{-1}$

2.9 (B)

2.10 (C)

Explanation : in trans 2, 4 – bexdiene $\xrightarrow[\text{conrotation}]{\text{Thermal}}$ cis 3, 4 – dimethyl cyclobutene.

3.

(A) 1. (D)
2. (C)
3. (G)
4. (E)

(B) 1. (D)
2. (C)
3. (G)
4. (E)

(C) 1. (A)
2. (D)

(D) 1. (D)
2. (C)

(E) 1. (B)
2. (C)

(F) 1. (D)
2. (C)

(g) 1. (C)
2. (E)
3. (A)
4. (G)

GATE 1997

CY : CHEMISTRY

Time : 3 Hours | *Maximum marks : 200*

Read the following instructions carefully :

1. Write all the answers in the answerbook.
2. This paper contains TWO SECTIONS :'A' and 'B'.
3. **Section A** has **EIGHT** questions. Answer **ALL** questions in this section.
4. **Section B** has **TWENTY** questions. Answer any **TEN** questions from this section. If more number of questions are attempted, strike off the answers which are not to be evaluated; else only the **FIRST TEN** unscored answers will be considered.
5. Answers to **Section B** should start on a fresh page and should not be mixed with answers to **Section A.**
6. Answers to questions and answers to parts of a question should appear together and should not be separated.
7. In all questions of 5 marks, write clearly the important steps in your answer. These steps carry partial credit.
8. There will be no negative marking.

General Data :

Gas constant $R = 8.205 \times 10^{-2}\ dm^3\ atm\ K^{-1}\ mol^{-1}$

$= 8.314\ JK^{-1}\ mol^{-1}$

$= 1.987\ Cal\ K^{-1}\ mol^{-1}$

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

Boltzmann constant $= 1.38 \times 10^{-23}\ JK^{-1} = 0.695\ cm^{-1}\ K^{-1}$

Planck Constant, $h = 6.626 \times 10^{-34}\ Js$

Faraday $= 96500\ C\ mol^{-1}$

$1\ eV = 96.485\ kJ\ mol^{-1}$

1 Joule = 1 Volt Coulomb

Atomic mass unit $= 1.66 \times 10^{-27}\ kg$

Mass of electron, $m_e = 9.1 \times 10^{-31}\ kg$

Speed of light, $c = 3 \times 10^8\ ms^{-1}$

SECTION A

(100 Marks)

1. ***For each of the sub-questions (1.1 to 1.45) four answers A, B, C and D are provided of which ONE is correct. Write in your answer book, the alphabet corresponding to the correct answer against the sub-question.*** **(45 × 1 = 45)**

1.1. The zero point energy of a harmonic oscillator is
(A) $\hbar\omega$ (B) zero
(C) $\frac{1}{2}\hbar\omega$ (D) $\frac{2}{3}\hbar\omega$

1.2. Which of the following diatomic molecules would be stabilized by the removal of an electron ?
(A) C_2 (B) CN
(C) N_2 (D) O_2

1.3. Which of the following molecules has the lowest vibrational stretching frequency ?
(A) $^4H\,^{35}Cl$ (B) $^2H\,^{35}Cl$
(C) $^4H\,^{36}Cl$ (D) $^4H\,^{37}Cl$

1.4. The point group symmetry of the staggered form of ethane molecule is
(A) C_{3v} (B) D_{3d}
(C) D_{3h} (D) D_3

1.5. The fine structure and intensity ratios expected in the proton NMR spectrum of $^{14}NH_4^+$ ion (for ^{14}N, I = 1) are
(A) singlet (B) doublet, 1 : 1
(C) triplet, 1 : 1 : 1 (D) triplet, 1 : 2 : 1

1.6. An ideal liquid solution has equal mole fractions of two volatile components A and B of different vapour pressures. In the vapour above the solution, the mole fractions of A and B are
(A) equal (0.5) for both (B) 1.0 for A and 0.0 for B
(C) 0.0 for B, and 1.0 for A (D) not equal

1.7. If ΔG^0 is zero for a reaction, then
(A) $\Delta H = 0$ (B) $\Delta S = 0$
(C) K (equilibrium constant) = 0 (D) K = 1

1.8. A method of removing excess solute from a colloidal solution is by
(A) distillation (B) recrystallization
(C) dialysis (D) gas chromatography

1.9. The heat of formation (ΔH_f^0) of CO_2 (*g*) is equal to
(A) zero
(B) molar heat of combustion of graphite
(C) sum of heat of formation of CO (*g*) and O_2 (*g*)
(D) molal heat of combustion of CO (*g*)

1.10. Of the following mixtures, the most likely mixture nearer to ideal solution is
(A) sodium chloride – water (B) ethanol – benzene
(C) heptane – water (D) heptane – octane

1.11. For the reaction, A → products the plot of | A | versus time is a straight line. The order of the reaction is
(A) zero
(B) first
(C) second
(D) pseudo-first

1.12. For a first order reaction, the half-life is 50s. Identify the correct statement from the following.
(A) The reaction is complete in 100s
(B) The reaction begins after 50s
(C) The same quantity of A is consumed for every 50s of the reaction
(D) Quantity of A remaining after 100s is half of what remains after 50s

1.13. For the reaction, 2A + B → C + 2D which is first order in A and also first order in B, the rate is given by
(A) $k\,[A]^2\,[B]$
(B) $k\,[A]\,[B]^2$
(C) $k\,[A]^2$
(D) $k\,[A]\,[B]$

1.14. The absorption of a gas is described by the Langmuir absorption isotherm with K = 0.3 kPa^4. At a pressure of 0.2 kPa, the fractional coverage is
(A) 0.14
(B) 0.28
(C) 0.43
(D) 0.70

1.15. According to the Kinetic theory of gases, the root mean square velocity is
(A) proportional to the temperature
(B) proportional to the square of the temperature
(C) proportional to the square root of the temperature
(D) inversely proportional to the square root of the temperature

1.16. The lowest energy term symbol for the Si atom is
(A) ^3P
(B) ^3S
(C) ^3D
(D) ^3P

1.17. If the ionization energy of hydrogen atom is 13.6 eV, the expected third ionization energy of the lithium atom is
(A) 13.6 × 3eV
(B) 13.6 × 2 eV
(C) 13.6 × 6 eV
(D) 13.6 × 9 eV

1.18. Calcium fluoride crystallizes in fluorite structure. The coordination number for the cation and anion is respectively
(A) 6, 6
(B) 6, 4
(C) 4, 6
(D) 8, 4

1.19. The electrical resistivity of a semiconductor
(A) increases with temperature
(B) decreases with temperature
(C) increases at low temperature and then decreases at high temperature
(D) does not change with temperature

1.20. The expected spin-only magnetic moments for $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$ respectively are
(A) 1.73 and 1.73 B.M.
(B) 1.73 and 5.92 B.M.
(C) 0.0 and 1.73 B.M.
(D) 0.0 and 5.92 B.M.

1.21. Which one of the following molecules does not obey the 18–electron rule ?

(A) $[Mn(CO)_6]^+$ (B) $Fe(CO)_5$

(C) $[Cr(CO)_5]^{2-}$ (D) $[Mn(CO)_4 Cl_2]^{2-}$

1.22. Which of the following species/molecules has a planar geometry ?

(A) $Ni(CO)_4$ (B) SF_4

(C) $Co\ Cl_4^{2-}$ (D) XeF_4

1.23. The molecule that does not possess a permanent dipole moment is

(A) NF_3 (B) BF_3

(C) CH_2Cl_2 (D) NO_2

1.24. An example of the species having a quadrupole bond is

(A) $Mn_2(CO)_{10}$ (B) $Cr_2\ O_7^{2-}$

(C) $Re_2\ Cl_8^{2-}$ (D) $Hg_2(CH_3\ COO)_2$

1.25. The metal ion which is **most likely** to show the low spin-high spin equilibria in its complexes has the electronic configuration

(A) d^3 (B) d^4

(C) d^6 (D) d^8

1.26. The crystal field stabilization energy (CFSE) will be the highest for

(A) $Co\ F_6^{3-}$ (B) $Co\ (CNS)_4^{2-}$

(C) $Mn\ (H_2O)_6^{2+}$ (D) $Co\ (NH_3)_6^{3+}$

1.27. Which of the following molecules is the strongest protonic acid ?

(A) $H_6\ Te\ O_6$ (B) $Sb\ H_3$

(C) PH_3 (D) $B_2\ H_6$

1.28. Which of the following ligands will form a stable complex with Ln^{3+} ion ?

(A) H_2O (B) CO

(C) C_2H_4 (D) $P\ Pph_3$

1.29. A radiation which has an energy of N 50 kJ mol^{-1} falls in the following region of the electromagnetic spectrum

(A) infrared (B) visible

(C) ultraviolet (D) microwave

1.30. The function of the reference electrode in coulometric analysis is to

(A) control the potential of the cathode

(B) control the potential of the anode

(C) enable the measurement of the potential of the auxiliary electrode

(D) enable the measurement of the potential of the working electrode

1.31. In the ^1H–NMR spectrum of toluene, the resonance due to CH_3 group is expected at

(A) δ 0.5 (B) δ 1.25

(C) δ 2.5 (D) δ 3.5

1.32. The reactive intermediate in a typical Simmons-Smith reaction is a

(A) carbonium ion (B) carbene

(C) carbanion (D) free radical

1.33. The one among the compounds given below, with highest dipole moment is
(A) naphthalene (B) phenanthrene
(C) anthracene (D) azulene

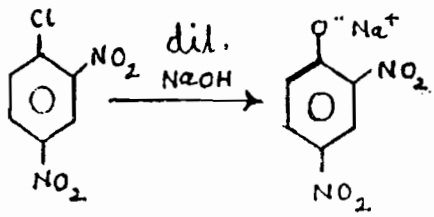
1.34. The most appropriate reagent to convert $RCOOEt \rightarrow RCH_2OH$ is
(A) $LiAlH_4$ (B) $Na\ BH_4$
(C) $H_2/Pd–C$ (D) Li/NH_3 (liq)

1.35. The electrophilic aromatic substitution proceeds through a
(A) free radical (B) sigma complex
(C) benzyne (D) carbene

1.36. The conversion, $PhCN \rightarrow PhCOCH_3$, can be achieved most conveniently by reaction with
(A) CH_3MgBr followed by hydrolysis
(B) I_2 – NaOH; $CH_3\ I$
(C) dil. H_2SO_4 followed by reaction with CH_2N_2
(D) LAH followed by reaction with $CH_3\ I$

1.37. For the complete conversion of D-glucose into the corresponding ozazone, the minimum number of equivalents of phenyl hydrazine required are
(A) two (B) three
(C) four (D) five

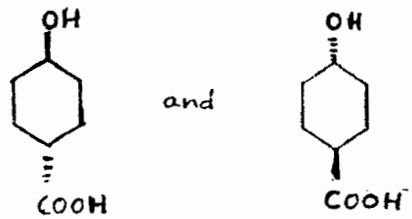
1.38.



The above transformation proceeds through
(A) electrophilic addition (B) benzyne intermediate
(C) activated nucleophilic substitution (D) oxirane

1.39. In the UV spectrum of cyclohexenone, the absorption at $\lambda_{max} \sim 215$ nm is due to the transition
(A) $\sigma \rightarrow \sigma^*$ (B) $\sigma \rightarrow n$
(C) $\pi \rightarrow n$ (D) $\pi \rightarrow \pi^*$

1.40. The compounds given below are



(A) enantiomers (B) identical
(C) regioisomers (D) diastereomers

1.41. Conversion of cyclohexene to cyclohexanol can be conveniently achieved by
(A) $NaOH–H_2O$ (B) $Br_2–H_2O$
(C) hydroboration, oxidation (D) hydroboration, hydrolysis

1.42. The most convenient spectroscopic technique to establish the presence of inter-molecular hydrogen bonding in hydroxy compounds is

(A) UV (B) IR
(C) EPR (D) Mass

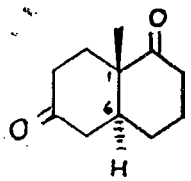
1.43. The most suitable catalyst for the hydrogenation of 2–hexyne → Cis–2–hexene is

(A) Pd–$BaSO_4$ (B) $(Ph_3P)_3RbCl$
(C) 10% Pd–C (D) Raney Ni

1.44. In the boat conformation of cyclohexane, the most destabilizing interaction is

(A) eclipsing (B) 1, 3–diaxial
(C) 1, 3–diequatorial (D) flagpole–flagpole

1.45. The configurations (R, S–notation) at C–1 and C–6 of the compound given below are



(A) 1S, 6S (B) 1S, 6R
(C) 1R, 6R (D) 1R, 6S

2. ***Fill in the blank spaces in the following sentences appropriately*** **(15 × 1 = 15)**

2.1. Sodium atom is paramagnetic because it has ..... electrons.

2.2. The total degeneracy of a *p*-orbital in the absence of magnetic field is .....

2.3. A real gas behaves like an ideal gas when the temperature is high and the pressure is .....

2.4. If for a reaction both ΔH and ΔS are negative, the reaction proceeds in the forward direction at ..... temperatures.

2.5. The reaction, A + B → 2C, proceeds by a single step bimolecular mechanism, the rate of the reaction is given by .....

2.6. The molecule ClF_3 has ..... non-bonded electron pairs.

2.7. Octahedral Copper (II) complexes undergo tetragonal distortion due to ..... effect.

2.8. The hydrolysis products in the reaction between PCl_3 and H_2O are HCl and .....

2.9. The transition metal present in Vitamin B–12 is .....

2.10. The planar structure of $N(SiH_3)_3$ is due to ..... bonding.

2.11. The hybridization of the central carbon atom in an Alkene is .....

2.12. The Claisen rearrangement is an example of ..... sigmatropic shift.

2.13. Conversion of cyclohexanone oxime to caprolactam can be effected by ..... rearrangement.

2.14. The haloform reaction of acetophenone produces .....

2.15. Formation of the endo product in a Diels–Alder rection is due to ..... interactions between the diene and dienophile.

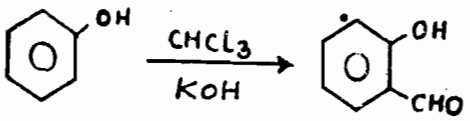
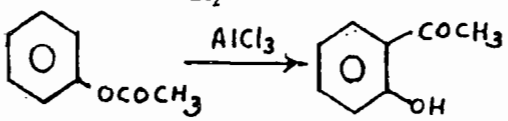
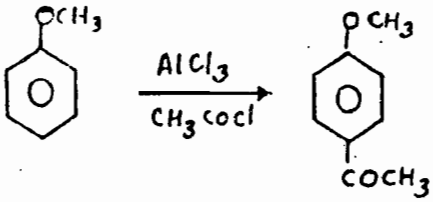
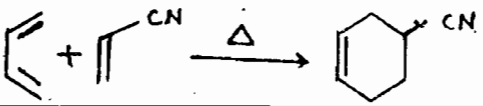
3. *(a)* Match the techniques given in List-I with the regions given in the List-II **(5 × 1 = 5)**

List-I	*List-II*
(1) Vibrational spectroscopy	(A) Microwave
(2) Electronic spectroscopy	(B) Gamma rays
(3) Rotational spectroscopy	(C) Radio freqency
(4) Mossbauer spectroscopy	(D) Infrared
(5) Nuclear magnetic resonance spectroscopy	(E) Ultraviolet-visible

(b) Match the compounds given in List-I with the information given in List-II **(5 × 1 = 5)**

List-I	*List-II*
(1) $Ti\ Cl_4\ At\ Et_3$	(A) Geometrical isomerism
(2) $Pt\ Cl_2\ (NH_3)_2$	(B) Hydrogenation
(3) $[Co\ (en)_3]^{3+}$	(C) Fluxional molecule
(4) $Rh\ Cl\ (Pph_3)_3$	(D) Polymerisation
(5) $Fe\ (Cp)_2\ (CO)_2$	(E) Optical isomerism

(c) Match the transformations in List-I with the name reactions in List-II : **(5 × 1 = 5)**

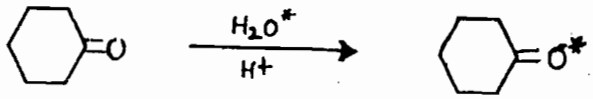
List-I	*List-II*
(1) 	(A) Diels-Alder Reaction
(2) $RCONH_2 \xrightarrow[Br_2]{NaOH} RNH_2$	(B) Friedel Craft's Reaction
(3) 	(C) Hoffman's Rearrangement
(4) 	(D) Reimer Tiemann Reaction
(5) 	(E) Fries Rearrangement

4. *(a)* Chromium (II) acetate is diamagnetic. Write the structure of the molecule and account for its magnetic behaviour. **(3)**

(b) Write down the product and mechanism of the reaction between HCl (gas) and trans–$[Ir\ Cl\ (CO)\ (Pph_3)_2]$. **(2)**

5. *(a)* Using the crystal field model, explain the structure and magnetic properties of $Ni\ (CO)_4$ and $Ni\ (CN)_4^{2-}$. **(3)**

(b) Write the plausible mechanism for the following : **(2)**



(O^* indicates ^{18}O labelled oxygen)

6. *(a)* The E^0_{cell} of an aluminium-air battery is 2.73 volts and it involves a 12 electron process. Calculate the free energy change (ΔG^o) of the battery in kJ. **(3)**

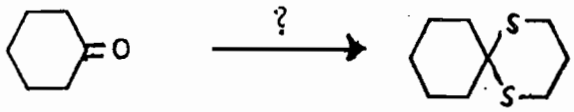
(b) For the following reaction

$$H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,HCl\,(aq.)$$

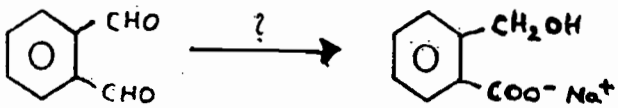
ΔG^o is –262 kJ. Calculate the equilibrium constant (K) for the reaction at 298 K. **(2)**

7. *(a)* Suggest suitable reagents to bring about the following transformations. **(2)**

(i)

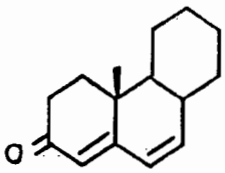


(ii)

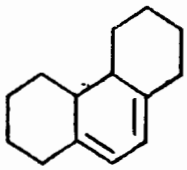


(b) Using the Vander Waal's equation, calculate the pressure exerted by one mole of chlorine gas confined to a volume of 1.0 L at 273 K. The value of the Vander Waal's constants for chlorine gas are $a = 6.5\ L^2.\ atm\ mol^{-1}$ and $b = 0.06\ L\ mol^{-1}$. **(3)**

8. *(a)* Following the Woodward rules, calculate the expected λ_{max} values for the two compounds given below : **(4)**



(I)



(II)

(b) Explain why in the mass spectrum of bromobenzene, there will be two peaks at m/z 156 and 158 of approximately equal intensity. **(1)**

SECTION B

(50 Marks)

Answer any TEN questions. All questions carry equal marks.

9. *(a)* Derive the rate law for the following reaction. Assume that the rate of formation and disappearance of $NOCl_2$ are equal in the first step

$$NO + Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO\,Cl\ (fast)$$

$$NO + NO\,Cl_2 \xrightarrow{k_3} 2NOCl\ (slow)$$ **(3)**

(b) A zero order reaction is 50% complete in 30 min. How long, after the start of the reaction, will the reaction be 80% complete ? **(2)**

10. *(a)* Calculate the osmotic pressure of 0.005 M solution of cinnamaldehyde at 25°C. (2)
(b) 20.5 g of naphthalene is dissolved in 1.0 kg of cyclohexane. It lowers the freezing point by 32°C. Calculate the freezing point depression constant (Kf). (3)

11. *(a)* The first order reaction (A → products) has a half-life of 46.2 min at 25°C, 5.8 min at 77°C, and 2.6 min at 102°C. Calculate the activation energy (in kJ) of the reaction graphically. (4)
(b) At what temperature would the half-life be 10.0 min ? (1)

12. An electron is confined to a two-dimensional square box of side 1.0 nm. What is
(a) its minimum energy and
(b) the minimum excitation energy ? (5)

13. The internuclear distance of $H^{35}Cl$ is 0.13 nm, and the force constant is 500 Nm^{-1}. Calculate
(a) The moment of inertia of the $H^{35}Cl$ molecule and
(b) The first excitation energy in cm^{-1} of $H^{35}Cl$ molecule in the harmonic approximation. (2 + 3)

14. The dissociative adorption of oxygen on tungsten is described by the Langmuir isotherm with K = 0.35 kPa^{-1}. Calculate the fractional surface coverage at a pressure of 1 kPa. (5)

15. *(a)* Calculate the ratio of the rate of effusion of deuterium and hydrogen. (2)
(b) Calculate the root mean square velocity of hydrogen at 298 K. (3)

16. Give the products of the following reactions and the **********
(a) Cis–Pt $Cl_2(NH_3)_2$ + pyridine → ?
(b) Na [R Fe $(CO)_4$] + CO → ?
(R = alkyl)
(c) NO + O_3 → ?
(d) $[Pt\,Cl_4]^{2-} + Cl_2$ → ?
(e) $(\eta^6 - C_6H_6)Cr(CO)_3 + CH_3COCl + AlBr_3$ → ?

17. *(a)* Draw an Orgel diagram and explain the electronic spectrum of $Co\,F_6^{3-}$, which occurs as a broad and split band in the visible region. (3)
(b) The electronic spectrum of $KMnO_4$ shows a broad band at 18000 cm^{-1}. While in K_2CrO_4, the band is observed at a higher frequency 26000 cm^{-1}. Assign the bands and explain the trend. (2)

18. *(a)* Using the VSEPR theory, predict the number of lone pairs and draw the structures of PCl_5, IF_5 and XeF_2. (3)
(b) Using the 18–electron rule, find out the $M_0 - M_0$ bond order in $[(\eta^5 - C_p)\,M_0\,(CO)_3]_2$. Draw the possible isomers for the molecule (C_p = Cyclopentadienyl anion). (2)

19. *(a)* Write down the detailed mechanism of the reaction between $[Co(NH_3)_5Cl]^{+2}$ and $[Cr(H_2O)_6]^{+2}$ to form $[Co(H_2O)_6]^{+2}$ and $[Cr(H_2O)_5Cl]^{+2}$ (3)
(b) Using crystal field model, explain why Fe_3O_4 has an inverse spinel structure while Mn_3O_4 has a normal spinel structure. (2)

20. *(a)* Predict whether the reactants or products are favoured in the following equilibria

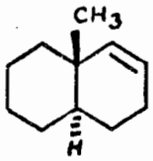
$$CuI_2 + Cu_2O \rightleftharpoons 2\,CuI + CuO$$ (2)

(b) Explain why $AlBr_3$ dimerises to Al_2Br_6, while BCl_3 is monomeric. (2)
(c) Explain why the magnetic moment of trivalent gadolinium (Z = 64) complexes can be obtained by the spin-only formula but not for trivalent terbium complexes. (1)

21. *(a)* On passing monochromatic light through a solution of 0.004 M in a cell of 20 mm thick, the intensity of the transmitted light was reduced by 50 per cent. Calculate the molar extinction coefficient and give its unit. (3)

(b) Why ampérometric titration is a better method than polarographic method for quantitative analysis? **(2)**

22. Provide the structures of the products A–E with appropriate stereochemical notation (wherever relevant) in the following schemes.

(a) 

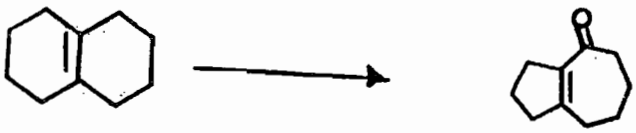
+ *m*–chloroperbenzoic acid $\longrightarrow$ A $\xrightarrow{LiAlH_4}$ B **(2)**

(b)

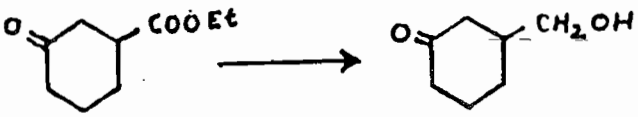
+ diethyl acetylene dicarboxylate $\longrightarrow$ C $\xrightarrow{\Delta}$ D + Acetylene **(2)**

(c)
+ Ph CHO $\xrightarrow{h\nu}$ E **(1)**

23. Suggest how to bring about the following transformations (may require more than one step)

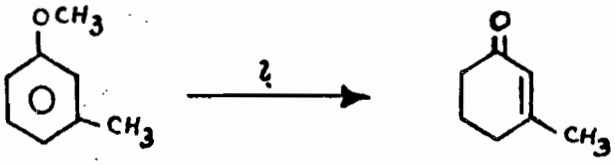
(a) 

(2)

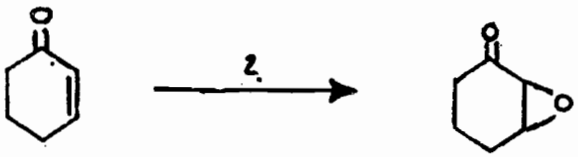
(b) 

(3)

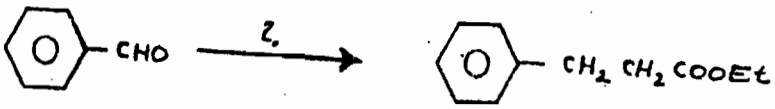
24. How would you carry out the following multi-step transformations ?

(a) 

(2)

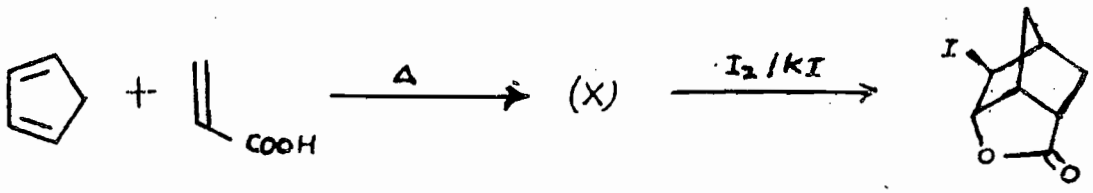
(b) 

(1)

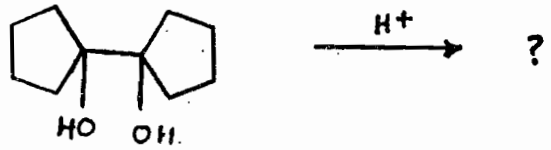
(c) 

(2)

25. (a) Explain the following reaction sequence with plausible mechanisms. **(3)**

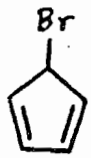


(b) Give the expected product or products and the mechanism for the following *****



26. *(a)* Suggest a method of preparation of *p*-aminobenzoic acid starting from toluene. **(3)**

(b) Which one of the following bromides will undergo facile solvolysis ? Justify. **(2)**



(I)

(II)

27. Reaction of an organic compound, A, with a mixture of conc. H_2SO_4 and conc. HNO_3 gave two isomeric compounds, B (major) and C (minor). The compound B exhibited the following spectral characteristics:

Molecular formula : $C_7H_7NO_3$

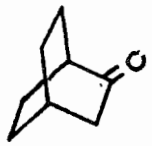
IR : 3040, 1610, 1510, 1350 and 1030 cm^{-1}

^1H – NMR : δ 8.1 (2 H, d, J = 8 Hz), 6.8 (2 H, d, J = 8 Hz) and 3.9 (3H, s).

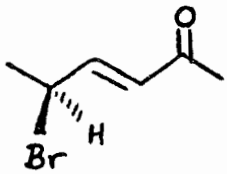
Deduce the structures of A, B and C and explain the reaction. **(5)**

28. *(a)* Write the IUPAC names (including the stereochemical notations wherever applicable) for the following compounds.

(i) **(1)**



(ii) **(2)**



(b) Between pyrrole and pyridine which one is more basic ? Explain why ? **(2)**

ANSWERS WITH EXPLANATIONS

1.

1.1. (C)

1.2. (D)

Explanation : Due to their distribution in various molecular orbital.

1.3. (D)

1.4. (B)

1.5. (C)

Explanation : Fine structure = Triplet

Intensity Ratio = 1 : 1 : 1

1.6. (D)

Explanation : Because their vapour pressures are different.

1.7. (D)

Explanation : $\Delta G = 2.303\ RTmk$

$\Delta G = 0$

$\Rightarrow \quad m\,k = 0$

$\therefore \quad K = 1$

1.8. (C)

1.9. (B)

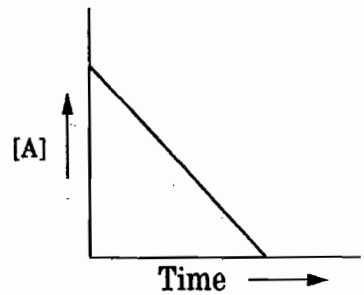
Explanation : $C + \frac{1}{2}\,0_2 \rightarrow CO_2$

Formation of CO_2 is the same reaction as combustion of graphite.

1.10. (D)

1.11. (A)

Explanation :



1.12. (D)

Explanation : Quantity of A initially = M

$$\text{Quantity of A after 50 sec} = \frac{M}{2} \text{ (One Half Life)}$$

$$\text{Quantity of A after 100 sec} = \frac{M}{4} \text{ (Two Half Life)}$$

1.13. (D)

Explanation : Rate, $R = K(A)^a (B)^b$

$a = 1$

$b = 1$

$\therefore$ $R = R(A)(B)$

1.14. (D)

Explanation : $K = \frac{K_a}{K_d}$

1.15. (C)

Explanation : $V_{R.M.S.} = \sqrt{\frac{3RT}{M}}$

1.16. (A)

1.17. (D)

1.18. (D)

Explanation : $Ca^{2+} \rightarrow$ F.O.C. int all

$F^- \rightarrow$ occupy all tetrahedral voids

$\therefore$ Coordination no of ca $\rightarrow 8$

Coordination no of F $\rightarrow 4$

1.19. (B)

1.20. (D)

Explanation : $\mu_M = \sqrt{s(s+1)}$

1.21. (D)

Explanation : E.A.N. $= 25 + 2 \times 4 + 2 \times 1 + 2 = 37$

1.22. (D)

1.23. (B)

1.24. (B)

1.25. (A)

1.26. (D)

Explanation : Low spin – High spin oxidation state

1.27. (A)

1.28. (D)

1.29. (A)

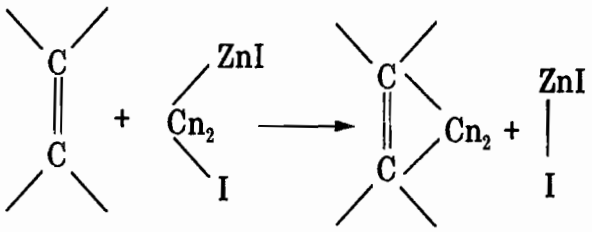
Explanation : Energy decreases with increasing wavelength.

1.30. (D)

1.31. (B)

1.32. (B)

Explanation :



1.33. (D)

1.34. (A)

Explanation : Rcoo ft + Liain$_4$ $\longrightarrow$ RCH$_2$on

1.35. (B)

1.36. (A)

1.37. (B)

1.38. (C)

1.39. (D)

1.40. (B)

Explanation : Because they have exchanged their position.

1.41. (C)

1.42. (D)

1.43. ***Explanation :*** z-hexyne $\xrightarrow{10\%\ p_d - c}$ cis – 2 – hexene.

1.44. (C)

Explanation : Chair and boat axial to that compound.

1.45. (B)

2.

2.1. Unpaired electrons

2.2. Three

2.3. Low

2.4. All

2.5. R = K (A) (B)

2.6. 18 + 4

2.7. John Teller effect

2.8. $Pocl_3$

2.9. CO

2.10. $d\pi - p\pi$ bounding

2.11. sp^2

2.12. 2, 6 ortho sigmatropic shift

2.13. Beckman Rearrangement

2.14. Sodium Benzoate

2.15. Stereospecific and *c* is interaction.

Solution [3]

(A)

1	$\longrightarrow$	A
2	$\longrightarrow$	E
3	$\longrightarrow$	D
4	$\longrightarrow$	B
5	$\longrightarrow$	C

(B)

List I		**List II**
1	$\longrightarrow$	D
2	$\longrightarrow$	A
3	$\longrightarrow$	E
4	$\longrightarrow$	B
5	$\longrightarrow$	C

(C)

List I		**List II**
1	$\longrightarrow$	D
2	$\longrightarrow$	C
3	$\longrightarrow$	E
4	$\longrightarrow$	B
5	$\longrightarrow$	A

GATE 1998

CY : CHEMISTRY

Time : 3 Hours | *Maximum marks : 200*

Read the following instructions carefully :

1. Write all the answers in the answer book only.
2. This paper contains TWO SECTIONS : 'A' and 'B'.
3. **Section A** has **SEVEN** questions. Answer **ALL** questions in this section.
4. **Section B** has **TWENTY** questions. Answer any **TEN** questions from this section. If more number of questions are attempted, score off the answers not to be evaluated, else only the **FIRST TEN** unscored answers will be considered.
5. Answers to **Section B** should start on a fresh page and should not be mixed with answers to **Section A.**
6. Answers to questions and answers to parts of a question should appear together and should not be separated.
7. In all questions of 5 marks each, write clearly the important steps in your answer. These steps carry partial credit.
8. There will be no negative marking.

General Data :

Speed of light,	$c = 3 \times 10^8$ ms^{-1}
Charge of electron,	$e = 4.8 \times 10^{-10}$ e.s.u.
	$= 1.60 \times 10^{-19}$ C
	1 eV = 96.485 kJ mol^{-1}
	$= 1.602 \times 10^{-12}$ ergs.
	Faraday = 96500 C mol^{-1}
Planck constant,	$h = 6.626 \times 10^{-34}$ Js
Gas constant,	R = 8.314 JK^{-1} mol^{-1}
	= 1.987 Cal K^{-1} mol^{-1}
	$= 8.205 \times 10^{-2}$ dm^{-1} atm K^{-1} mol^{-1}

SECTION A

(100 Marks)

1. ***For each of the sub-question (1.1 to 1.40) four answers A, B, C and D are provided of which ONE is correct. Write in your answer book, the alphabet corresponding to the correct answer against the sub-question number.*** (40 × 1 = 40)

1.1. If water kept in an insulated vessel at –10°C suddenly freezes, the entropy change of the system
(A) increases
(B) is equal to that of the surroundings
(C) decreases
(D) is zero

1.2. ********** gas expands isothermally and reversibly at 300 K from 10 to 100 litres then
(A) $\Delta G = -1{,}382$ Cal
(B) $\Delta H = \Delta G = -2{,}764$ Cal
(C) $\Delta E = \Delta G = 691$ Cal
(D) $\Delta S = \Delta G = 0$

1.3. The ionic strength of a solution containing 0.1 molal each of copper sulphate and aluminium sulphate is
(A) 0.2 m
(B) 0.7 m
(C) 1.9 m
(D) 1.0 m

1.4. If the slope and intercept values for a Langmuir absorption process are 0.55 Pa cm^{-3} and 0.525×10^{-3} cm^{-1}, respectively, the value of adsorption coefficient (Pa^{-1}) is
(A) 1,904
(B) 1.818
(C) 1×10^{-3}
(D) 1.047×10^{3}

1.5. The ratio of the temperatures at which the average velocity of ethane (T_1) is equal to the root mean square velocity of benzene (T_2) is
(A) 0.151
(B) 0.048
(C) 1.209
(D) 0.389

1.6. The relationship between volume change in an isothermal process (Δ Vi) and an adiabatic process (Δ Va) for a pressure change from P_1 to P_2 is
(A) $\Delta Vi > \Delta Va$
(B) $\Delta Vi < \Delta Va$
(C) $\Delta Vi = \Delta Va$
(D) $\Delta Vi = \Delta Va = 0$

1.7. If the value of K_0 of the reaction $A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$ is 6×10^{-4} mol m^{-3} at 530 K, the value of K_p (in Nm^{-2}) is
(A) 2.64
(B) 0.64
(C) 2.60×10^{-4}
(D) 1.38×10^{-5}

1.8. For the E.M.F. of a hydrogen electrode to be zero, the pressure of hydrogen required in neutral pH is
(A) 1×10^{-7} atm
(B) 1×10^{-14} atm
(C) 1.0 atm
(D) 0.0 atm

1.9. Given K_b for NH_3 as 1.85×10^{-5}, the pH of 0.2 N NH_4Cl solution is
(A) 4.98
(B) 5.02
(C) 5.13
(D) 6.87

1.10. The vapour pressure at 300 K of water and that of a 5 molar solution of a non-volatile solute in water are 25 and 20 mm Hg, respectively. The activity coefficient of water in the solution is
(A) 0.87
(B) 0.92
(C) 0.80
(D) 1.00

1.11. A Carnot engine operates between 600 and 800 K and absorbs 2,000 calories from the source per cycle. The work done (in Cal) per cycle is

(A) 1,000 (B) 500
(C) 666 (D) 2,000

1.12. The reduction potential values of Cu^{2+}/Cu and Cu^{2+}/Cu^{+} are +0.34 and +0.15 V, respectively. The equilibrium constant for the reaction, $Cu + Cu^{2+} \rightleftharpoons 2\,Cu^{+}$ is

(A) 3.60×10^{-7} (B) 4.95×10^{-8}
(C) 8.32×10^{-6} (D) 3.01×10^{-12}

1.13. For the reaction scheme

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C; \qquad B + C \xrightarrow{k_3} D$$

the rate equation for the formation of D is given as

(A) $\dfrac{d[D]}{dt} = \dfrac{k_1 k_3 C_A C_B}{k_2 + k_3 C_B}$ (B) $\dfrac{d[D]}{dt} = \dfrac{k_1 k_2 k_3 C_A C_B}{k_2 + k_3 C_B}$

(C) $\dfrac{d[D]}{dt} = \dfrac{k_1 k_3 C_A C_B^2}{k_2 + k_3 C_B}$ (D) $\dfrac{d[D]}{dt} = \dfrac{k_1 k_3 C_A C_B}{k_2 k_3 + k_3 C_B}$

1.14. In a first order reaction, if the time taken for completion of 50 per cent of the reaction is t seconds, the time required for completion of 99.9 per cent of the reaction is

(A) 10 t (B) 5t
(C) 100 t (D) 2t

1.15. In a certain reaction, ten per cent of the reactant is consumed in 15 minutes at 310 K but only in 5 minutes at 330 K. The activation energy of the reaction (in kCal mol^{-1}) is

(A) 30.2 (B) 5.6
(C) 11.2 (D) 50.5

1.16. For the reaction, $2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$ the rate expression can be written in the following ways :

$$\frac{d[N_2]}{dt} = k_1\,[NO]\,[H_2]$$

$$\frac{d[H_2O]}{dt} = k\,[NO]\,[H_2]$$

$$-\frac{d[NO]}{dt} = k_1'\,[NO]\,[H_2]$$

$$-\frac{d[H_2]}{dt} = k_1''\,[NO]\,[H_2]$$

The relationship between k, k_1, k_1' and k_1'' is

(A) $k = k_1 = k_1' = k_1''$ (B) $k = 2k_1 = k_1' = k_1''$
(C) $k = 2k_1' = k_1 = k_1''$ (D) $k = k_1 = k_1' = 2k_1''$

1.17. Water gas in an equimolar mixture of
(A) CO and N_2
(B) CO and H_2O
(C) CO_2 and N_2
(D) CO and H_2

1.18. The number of electrons involved in the reduction of nitrate ion to hydrazine is
(A) 8
(B) 7
(C) 5
(D) 3

1.19. In a molecule of phosphorus (V) oxide there are
(A) 4 P–P, 10 P–O and 4P = O bonds
(B) 12 P–O and 4P = O bonds
(C) 2P–O and 4P = O bonds
(D) 6 P–P, 12 P–O and 4P = O bonds

1.20. The number of 3-centre 2-electron bonds in tetraborane (10) is
(A) 4
(B) 3
(C) 5
(D) 2

1.21. The basic reaction involved in the synthesis of silicones is
(A) the hydrolysis of trimethyl chlorosilane
(B) the hydrolysis of dimethyl dichlorosilane
(C) the hydrolysis of ethyl chlorosilane
(D) the acid hydrolysis of dimethyl silane

1.22. In the reaction : $Cl_2 + ClF + SbF_5 \rightarrow [Cl_3]\,[SbF_6]$ the role of chlorine is to
(A) stabilize Cl^+
(B) function as Lewis base
(C) function as Lewis acid
(D) form the cation

1.23. The gaseous product of the reaction of boron trifluoride with tetrahydroborate ion is
(A) F_2
(B) HF
(C) H_2
(D) B_2H_6

1.24. The square pyramidal molecular shape is adopted by
(A) SOF_4
(B) $XeOF_4$
(C) $ScOCl_4$
(D) PF_5

1.25. The molecular orbital configuration of the Re-Re bond is $[Re_2Cl_8]^{2-}$ is
(A) $\sigma^2\,\pi^4\,\delta^1\,\delta^{*1}$
(B) $\sigma^2\,\pi^2\,\delta^2\,\delta^{*2}$
(C) $\sigma^2\,\pi^2\,\delta^2\,\pi^{*2}$
(D) $\sigma^2\,\pi^4\,\delta^2$

1.26. Among the following, the unstable carbonyl species is
(A) $Mn(CO)_5Cl$
(B) $[Mn(CO)_5]^-$
(C) $[Mn(CO)_5]^+$
(D) $Mn(CO)_5$

1.27. The magnetic susceptibility of a paramagnetic substance
(A) is independent of temperature
(B) attains the maximum value at Neel temperature
(C) increases gradually with decrease in temperature followed by a steep rise after Curie temperature
(D) increases with decrease of temperature

1.28. The effective magnetic moment is maximum for
(A) $K_4Mn(CN)_6$
(B) K_2MnO_4
(C) K_2MnCl_4
(D) $KMnO_4$

1.29. Among the statements given, one that does not describe the actinide elements correctly is
(A) all the actinide elements exhibit radioactivity
(B) the trans-curium actinides are all man-made
(C) uranium and plutonium readily form oxo-cations
(D) actinides are all used as nuclear fuels

1.30. The correct statement among the following that describes the property of lanthanides is
(A) Lanthanides exhibit variable oxidation states either +2 and +3 or +3 and +4
(B) Lathanide elements are all coloured
(C) the coordination number of aquated Lanthanide ion is usually nine
(D) the magnetic moment values of Lanthanides depend only on their unpaired electrons

1.31. Among the species given, the one possessing charge-transfer transition in the visible region is
(A) $Th(C_2O_4)_2$ (B) $[Cr(NCS)_6]^{3-}$
(C) ZnS (D) HgI_2

1.32. For a complex, MX_3Y_3 possessing triagonal prismatic geometry, the number of possible isomers is
(A) 2 (B) 4
(C) 3 (D) 6

1.33. Among $(CH_3)_3P$, NO^+, CN^- and I_3^- ligands, the one which is not a π - acceptor Ligand is
(A) I_3^- (B) CN^-
(C) NO^+ (D) $(CH_3)_3P$

1.34. In a close packed (*hcp, ccp*) arrangement of a lattice comprising of *n* atoms of a kind, the number of tetrahedral and octahedral holes present respectively are
(A) 2*n* and 2*n* (B) *n* and *n*
(C) *n* and 2*n* (D) 2*n* and *n*

1.35. An element crystallizes both in FCC and BCC lattices. If the density of the element in the two forms is the same, the ratio of unit cell length of FCC to that of BCC lattice is
(A) $(2)^{\frac{1}{3}}$ (B) $\left(\frac{1}{2}\right)^{\frac{1}{3}}$
(C) $(4)^{\frac{1}{3}}$ (D) $\left(\frac{1}{4}\right)^{\frac{1}{3}}$

1.36. Among the following, the incorrect statement is
(A) the electrical conductivity of solid sodium chloride is less than its melt
(B) the electrical conductivity of pure silicon increases with the increase of temperature
(C) the electrical conductivity of sodium in liquid ammonia decreases with decrease of temperature
(D) the electrical conductivity of aluminium decreases with increase of temperature.

1.37. The formula of the basic structural unit in **********
(A) SiO_3^{2-} (B) SiO_2
(C) $Si_2O_5^{2-}$ (D) $Si_4O_{11}^{6-}$

1.38. The incorrect statement among the following is
(A) in constant potential coulometry, the amount of substance deposited during electrolysis depends only on the applied current

(B) in potentiometric titrations, the resultant potential is a function of the amount of titrant added
(C) in amperometry, the voltage applied between the indicator electrode and reference electrode is constant
(D) in colorimetry, the absorption is measured at a fixed wave length characteristic of the coloured species

1.39. The reduction potentials of $Cr_2O_7^{2-}/Cr^{3+}$ and Cl^{3+}/Cr are + 1.33 and –0.74 V, respectively. The reduction potential of $Cr_2O_7^{2-}/Cr$ is
(A) + 0.295 V (B) + 0.590 V
(C) + 0.195 V (D) + 1.770 V

1.40. In polarography, if '*m*' is the mass of the mercury drop and '*t*' is the drop time, the diffusion current is proportional to
(A) $(m)^{\frac{1}{3}}\ (t)^{\frac{1}{6}}$ (B) $(m)^{\frac{2}{3}}\ (t)^{\frac{1}{3}}$
(C) $(m)^{\frac{2}{3}}\ (t)^{\frac{1}{6}}$ (D) $(m)^{\frac{3}{2}}\ (t)^{\frac{1}{6}}$

2. ***For each of the sub-questions (2.1 to 2.35) given below four answers—A, B, C and D—are provided, of which ONE is the correct answer. Write in your answer book, the alphabet corresponding to the correct answer against the sub-question number.*** (35 × 1 = 35)

2.1. A ball of mass 200 g is moving with a velocity of 10 m sec^{-1}. If the error in the measurement of velocity is 0.1%, the uncertainty in its position is
(A) 3.3×10^{-31} m (B) 3.3×10^{-27} m
(C) 5.3×10^{-25} m (D) 5.3×10^{-32} m

2.2. The HOMO in CO is
(A) π-bondng (B) σ-bonding
(C) π-antibonding (D) σ-antibonding

2.3. The point group symmetry of BrF_5 is
(A) D_{3n} (B) D_{4v}
(C) C_{4v} (D) C_{3v}

2.4. The point group symmetry, T_d of $[PO_4]^{3-}$ is lowered to C_{2v} when
(A) one of its oxygen is linked to another atom
(B) two of its oxygen are linked to another atom
(C) three of its oxygen are linked to three other atoms
(D) all the four oxygen are linked to four other atoms

2.5. The nature of π-bond present in perchlorate ion is
(A) O ($d\pi$) → Cl ($p\pi$) (B) O ($p\pi$) → Cl ($d\pi$)
(C) ****** (D) O($d\pi$) → Cl ($p\pi$)

2.6. In the Infrared spectrum of Cl_2 ion the number of experimentally observed ****
(A) 4 (B) 3
(C) 2 (D) 6

2.7. Spectrum of a gaseous containing H_2, D_2, O_2 and N_2 Shous
(A) 4150, 1560, 2200 and 2950 (B) 1560, 2200, 4150 and 2950
(C) 4150, 2950, 1560 and 2200 (D) 2950, 2200, 1560 and 4150

2.8. The source of ultra-violet radiation used in UV-visible spectro Spectrophotometer is
(A) mercury vapour lamp
(B) sodium vapour lamp
(C) halogen vapour lamp
(D) hydrogen vapour lamp

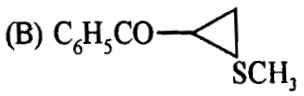
2.9. For any NMR active nucleus, the magnitude of radiofrequency required for observing nuclear magnetic resonance phenomenon depends on
(A) strength of the magnetic field
(B) choice of the nucleus
(C) both on magnetic field strength and choice of the nucleus
(D) the nuclear energy levels

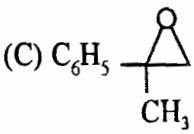
2.10. Among the following complex species, the one which is EPR active is
(A) $Ni(CO)_4$
(B) $[Co(NH_3)_5Cl]^{2+}$
(C) $[Cu(C_2O_4)_2]^{2-}$
(D) $Mo(CO)_6$

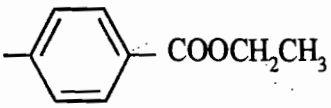
2.11. The aromaticity of the following heterocycles is in the order
(A) thiophene > pyrrole > furan > pyridine
(B) furan > pyrrole > thiophene > pyridine
(C) pyridine > thiophene > pyrrole > furan
(D) pyridine > furan > pyrrole > thiophene

2.12. The product of the reaction between acetophenone and $(H_3C)_2\overset{\oplus}{S}\overset{\ominus}{C}H_2$ is

(A) $C_6H_5COCH_2CH_2\overset{\oplus}{S}(CH_3)_2\overset{\ominus}{X}$

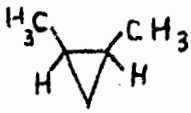
(B) 

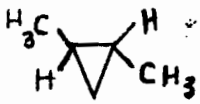
(C) 

(D) 

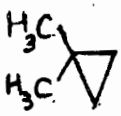
2.13. The reaction of $C_6H_5CH = CHCHO$ with $NaBH_4$ gives
(A) $C_6H_5CH_2CH_2CH_2OH$
(B) $C_6H_5CH = CHCH_2OH$
(C) $C_6H_5CH_2CH_2CHO$
(D) $C_6H_5CH_2CHOHCH_3$

2.14. The reaction of E-2-butene with CH_2I_2 and zinc-copper couple in ether medium leads to the formation of

(A) 

(B) 

(C)

(D) 

2.15. During the photolysis of ketones in Norrish type II cleavage
(A) a homolytic scisson leads to the formation of a radical intermediate
(B) CO is produced
(C) Photoexcited carbonyl group abstracts a gamma hydrogen in the primary step
(D) radicals formed dimerize

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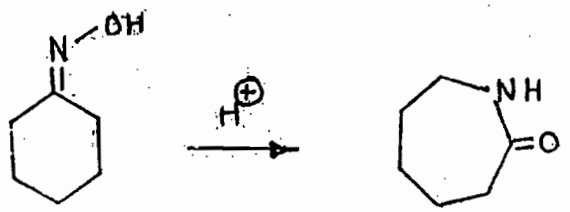
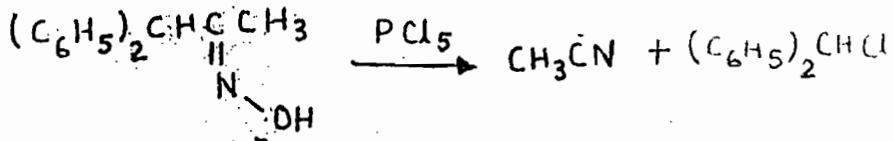
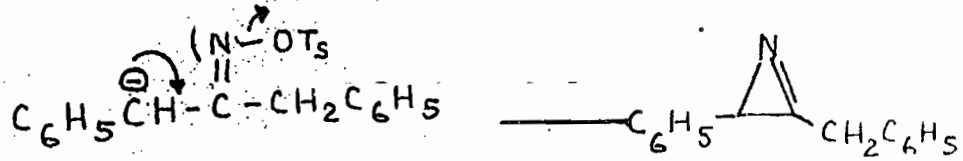
2.16. Rapid interconversion of α–D–glucose and β–D–glucose in solution is known as
(A) racemization
(B) asymmetric induction
(C) fluxional isomerization
(D) mutarotation

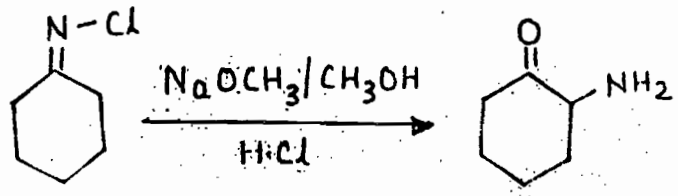
2.17. Lindlar catalyst is
(A) Na in alcohol
(B) Raney nickel
(C) Pd | $CaCO_3$
(D) Na | liq. NH_3

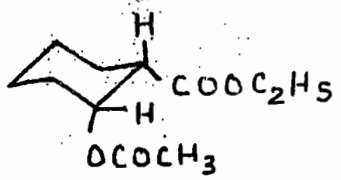
2.18. An example of fragmentation reaction is

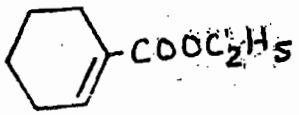
(A) 

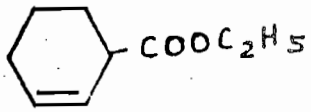
(B) 

(C) 

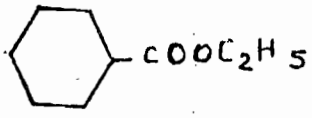
(D) 

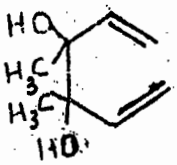
2.19. The major product of pyrolysis of  is

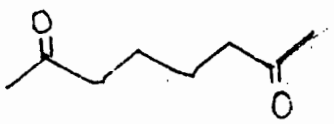
(A) 

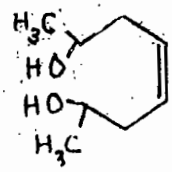
(B) 

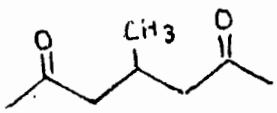
(C)

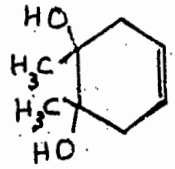
(D) 

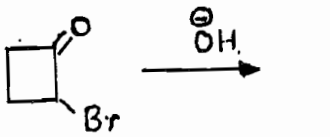
2.20. On heating  undergoes oxy-Cope rearrangement to give

(A) 

(B) 

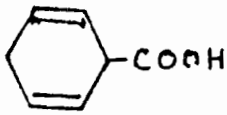
(C) 

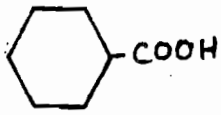
(D) 

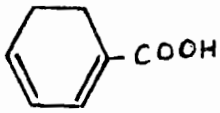
2.21. The reaction,  is an example of

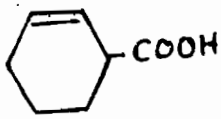
(A) Wolff rearrangement
(B) semi-benzilic mechanism
(C) Steven's rearrangement
(D) Wagner-Meerwin rearrangement

2.22. The Birch reduction of benzoic acid gives

(A) 

(B) 

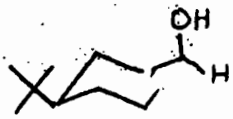
(C) 

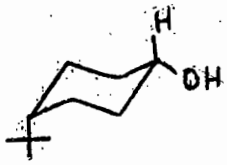
(D) 

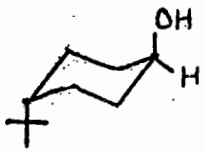
2.23. Among the following, the correct statement is
(A) absorption of radiation shifts to longer wavelength region with increase in conjugation
(B) absorption of radiation shifts to higher energy region with increase in conjugation
(C) intensity of $n \rightarrow \pi^*$ transition decreases upon conjugation
(D) intensity of $\sigma \rightarrow \sigma^*$ transition decreases upon conjugation

2.24. **********

(A)

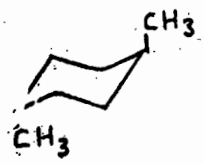
(B) 

(C) 

(D) 

2.25. The stable form of trans-1, 4-dimethylcyclohexane is represented as

(A)

(B) 

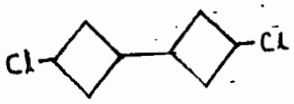
(C)

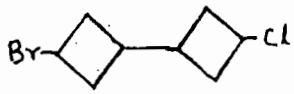
(D)

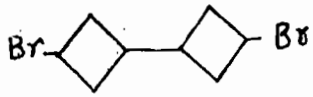
2.26. The reaction of elemental sulphur with Grignard reagent followed by acidification leads to the formation of
(A) mercaptan
(B) sulphoxide
(C) thioether
(D) sulphonic acid

2.27. The Baeyer's angle strain is expected to be maximum in
(A) cyclodecane
(B) cyclopentane
(C) cyclohexane
(D) cyclooctane

2.28. The reaction of 1-bromo-3-chlorocyclobutane with metallic sodium in dioxane under reflux conditions gives

(A) 

(B) 

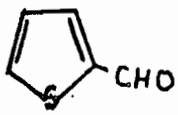
(C) 

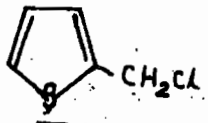
(D)

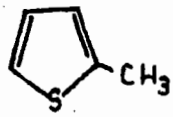
2.29. The carboxylic acid which has maximum solubility in water is
(A) phthalic acid
(B) succinic acid
(C) malonic acid
(D) salicylic acid

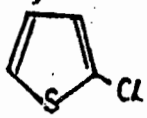
2.30. The most suitable reagent for producing dichlorocarbene from chloroform is
(A) sodium acetate
(B) potassium-*t*-butoxide
(C) triethylamine
(D) pyridine

2.31. Thiophene reacts with HCHO in presence of aqueous HCl to give

(A) 

(B) 

(C) 

(D) 

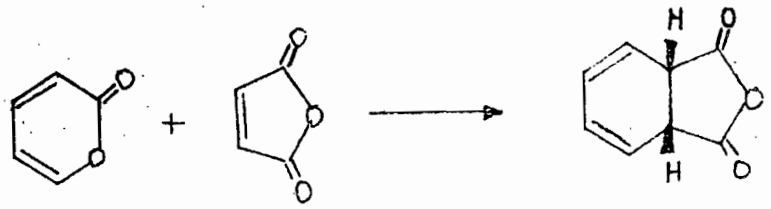
2.32. Osmium tetroxide is a reagent used for
(A) hydroxylation of acetylenes
(B) hydroxylation of olefins to give *cis* diols
(C) hydroxylation of olefins to give *trans* diols
(D) hydroxylation of carbonyl compounds

2.33. The correct order of priority of groups $-SCH_3$ (I), $-NO_2$ (II), $-C \equiv CH$ (III), and $-CH_2C_6H_7$ (IV), on the basis of CIP classification, respectively, is
(A) I, III, II, IV
(B) IV, III, II, I
(C) II, IV, I, III
(D) III, IV, II, I

2.34. Lactose on hydrolysis with dil. HCl gives
(A) glucose and fructose
(B) glucose and mannose
(C) fructose and mannose
(D) glucose and galactose

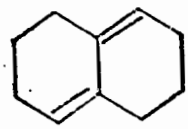
2.35. In thermal decomposition of acetaldehyde, the overall order of the reaction is 3/2 with respect to acetaldehyde. The chain terminating step for this reaction kinetics is
(A) combination of two CH_3CO radicals to give $CH_3COCOCH_3$
(B) combination of two CH_3 radicals to give C_2H_6
(C) combination of CH_3CO and CH_3 radicals to give CH_3COCH_3
(D) reaction of CH_3 radical with acetaldehyde to give methane

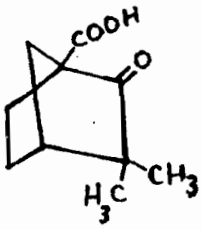
3. *(a)* Propose a mechanism for the reaction, **(2)**



(b) *cis*-2-Aminocyclohexanol on reaction with aqueous sodium nitrite in presence of dil. HCl at 0°C gives a ring contracted aldehyde and cyclohexanone. Suggest a suitable mechanism for the formation of the products. **(3)**

4. *(a)* Account for the following :
(i) *cis*-4-Hydroxycyclohexane carboxylic acid lactonizes whereas the *trans*-isomer does not.

(ii) The diene,  does not undergo Diels-Alder reaction.

(iii) The keto-acid, 

does not undergo decarboxylation on heating. **(3)**

(b) Give the reaction steps for the conversion of benzaldehyde into acetophenone. **(2)**

5. *(a)* For a particle in a one dimensional box with its potential energy zero, deduce the deBroglie relation from its energy expression. **(3)**

(b) The reduction potentials of Ag^+/Ag and Fe^{3+}/Fe^{2+} are 0.799 and 0.771 V, respectively. Calculate the equilibrium constant of the reaction, **(2)**

$$Ag + Fe^{3+} \rightleftharpoons Fe^{2+} + Ag^+$$

6. *(a)* Give the balanced reactions for the following :
(i) Reaction of potassium superoxide with carbon dioxide
(ii) Hydrolysis of phosphorus sulphide
(iii) Reaction of sodium chlorite with nitrogen trichloride. **(3)**

(b) Calculate the percent ionic character of hydrogen chloride if its observed dipole moment is 1.02 D. The covalent radii of hydrogen and chlorine are 0.30 and 0.975 Å, respectively. **(2)**

7. *(a)* Give the order of bond angle in nitronium ion, nitrite ion and nitrogen dioxide. Justify the answer. (2)

(b) Give the structure of

(i) $[S_2O_7]^{2-}$ and *(ii)* $[Si_3O_9]^{6-}$ (2)

(c) An intrinsic semiconductor has a band gap of 1.5 eV. Calculate the wavelength of the electromagnetic radiation required to cause the material photoconducting. (1)

SECTION B

(50 Marks)

Answer any TEN questions. All questions carry equal marks.

8. *(a)* Recovery of elemental silver from silver residues from photographic processing (AgCl) is achieved by converting it into A, using a common ionic compound B. The compound A upon heating decomposes to give an intermediate compound C before giving metallic silver as the end product. Identify A, B and C by giving equations for the reactions involved. (3)

(b) Give the structure of IF_7 and different angles subtended at iodine centre. (2)

9. *(a)* Consider a stepwise ligand displacement reaction of hexaaquonickel (II) ion with ammonia, and give the composition and structure of all the possible geometrical isomers of this system. (3)

(b) Give the geometry of phosphorus and iron in the ionic compound formed by mixing equimolar ratio of PCl_5 and $FeCl_3$. (1)

(c) Experimentally found value of Si-F distance in SiF_4 is less than that of the theoretical value. Give reason. (1)

10. *(a)* On the basis of Orgel diagram, give the expected electronic transitions of the species, $[V(H_2O)_6]^{3+}$. (3)

(b) Give *(i)* the products of the reaction between trimethylphosphine oxide and sulphur tetrafluoride and *(ii)* their structures. (2)

11. Reaction of sodium borohydride with compound, A which is formed by the reaction of NH_4Cl and BCl_3 at 140°C gives compound, B. Both B and diborane give the same hydrolysis product C. A molecule of B consumes three molecules of HCl to give D. Identify A, B, C and D. Give the structure of D. (5)

12. *(a)* The crystal structure of zinc blende. ZnS is related to the diamond structure with zinc and sulphur atoms occupying carbon sites. If the coordinates of one of the zinc sites are (000), give the fractional coordinates of the remaining Zn and S sites in the unit cell. (2)

(b) If in the above, the covalent radii of Zn and S are 1.32 and 1.04 Å respectively, calculate the unit cell length of zinc blende. (2)

(c) Give the effect of addition of Co^{2+}_{aq} to the equilibrium reaction, $\underset{\text{(Plae Pink)}}{Co^{2+}_{aq}} + \underset{\text{(Colourless)}}{4NC\overline{S}}$ $\underset{\text{(blue)}}{[Co(NCS)_4]^{2+}}$ on the % transmittance of the solution. (1)

13. *(a)* Indicate the reaction steps and conditions for the following conversions :

(i) PCl_5 to poly-dichlorophosphazene

(ii) CO to urea. (4)

(b) Give with equation solvolysis product of chlorine in ammonia. (1)

14. *(a)* Account for the following :

(i) $HClO_4$ is an acid and an oxidising agent whereas $H_2C_2O_4$ is an acid and a reducing agent.

(ii) HCl is not a suitable acid medium for permanganimetric estimations.
(iii) Among the complexes, $[Ni(OH_2)_6]^{2+}$, $[Ni(en)_3]^{2+}$ and $[Ni(NH_3)_6]^{2+}$, $[Ni(en)_3]^{2+}$ is most stable. (3)

(b) Give the products for the following reactions :
(i) the reaction of ammonia with disulphur dichloride.
(ii) the reaction of bromate and chloride in acid medium. (2)

15. (a) The average bond energies of S_8, H_2 and H_2S are 264, 436 and 338 kJ mol^{-1}, respectively. Estimate the enthalpy of the reaction, $S_8 + 8H_2 = 8H_2S$. (2)
(b) In the determination of manganese by atomic absorption method, a solution containing a liquor of unknown strength gives a meter reading of 23. Another sample containing this solution with added 50 ppm of manganese solution gives a meter reading of 92.5. Each reading was corrected by the background. Calculate the concentration of managanese in the original solution. (2)
(c) Addition of an acid to a buffer solution of sodium acetate and acetic acid does not alter the pH of the solution significantly. Give reason. (1)

16. (a) Given that the carbon-carbon bond distance in cyclobutadiene as 1.4 Å show that it is paramagnetic molecule by considering its π-electrons as freely moving particles in a two-dimensional box. (3)
(b) Consider ^{31}P–NMR spectra of the scrambled products of the reaction between PCl_3 and PF_3, and mention the NMR parameter that helps in their unambiguous characterization. (2)

17. (a) Draw the overlap scheme of the bonding orbitals in Al_2Br_6, and specify the nature of the orbitals. (2)
(b) Give the wave functions of the molecular orbitals of diborane in terms of its orbitals ϕ_{B1}, ϕ_{B2} and ϕ_H. (2)
(c) The rate of decomposition of N_2O is maximum with π-type semiconducting oxide catalyst. Give reason. (1)

18. The isomerization of cyclopropane follows the Linde mann mechanism and is found to be unimolecular. The rate constant at high pressure is 1.5×10^{-4} s^{-1} and that at low pressure is 6×10^{-6} $torr^{-1}$ s^{-1}. Find out the pressure of cyclopropane at which the reaction changes its order. (5)

19. (a) If the vapour pressure of two pure liquids are 400 and 910 mm Hg at 80°C, find out
(i) the composition of the mixture that boils at 80°C. (3)
(ii) the composition of the vapour.
(b) The E.M.F. of the cell, $Pb|PbCl_2||AgCl|$ Ag at 300 K is 0.50 V. If the temperature coefficient of E.M.F. is -2×10^{-4} volt deg^{-1}, calculate ΔH and ΔS for the cell reaction, $Pb + 2AgCl \rightarrow PbCl_2 + 2Ag$. (2)

20. (a) Ten moles of a gas is allowed to expand from a state, A, at 10 atm and 300 K, to a state, B, at 100 atm and 600 K. If the value of C_p is 6.955 Cal deg^{-1}, calculate the entropy change of this process. (3)
(b) The acid dissociation constant of butyric acid at 300 K is 1.48×10^{-5} and its molar conductance at infinite dilution is 0.04 mho m^2 mol^{-1}. Calculate the equivalent conductance of the acid of 0.01 M solution. (2)

21. (a) In a photohalogenation reaction of an organic compound, the radiation of wave length 340 nm is absorbed at the rate of 1.5×10^{-3} J sec^{-1} for 30 min. If only 80 per cent of the energy absorbed is effective for photohalogenation and only 45×10^{16} molecules are consumed, calculate the quantum yield. (3)

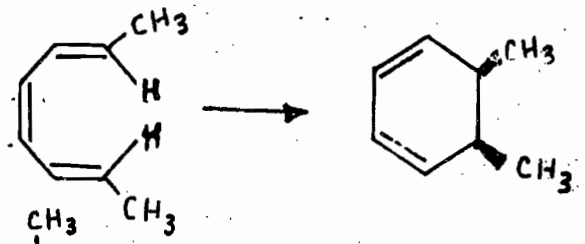
(b) Indicate the role of copper (II) in the oxidation of ethylene to acetaldehyde by Wacker process giving reactions. (4)

22. (a) An organic compound of molecular formula, $C_9H_{10}O_2$ showed three peaks in the PMR spectrum as given below :
δ 1.96, singlet, 3H;
δ 5.0, singlet, 2H and
δ 7.2, singlet, 5H
One of the intense IR bands of this compound appears at 1740 cm^{-1}. Deduce the structure of the compound. (3)

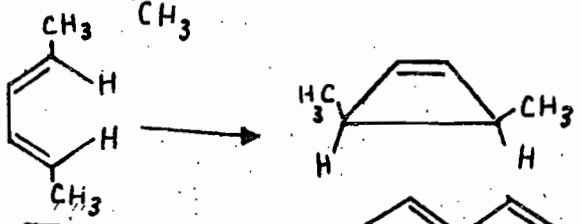
(b) In the E.I. mass spectrum of 2-hexanone an intense peak at m/z 58 is observed. Identify the structure and justify. (2)

23. (a) For each of the following concerted reactions, specify the ********** mode of rotation :

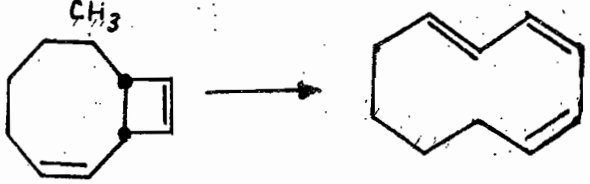
(i)



(ii)

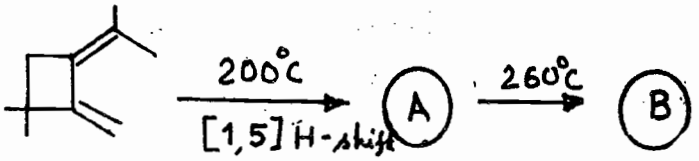


(iii)



(3)

(b) The following transformation proceeds by th nce indicated. Give the structures of A and B: (2)



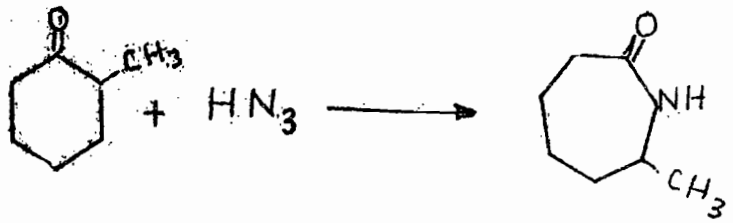
24. (a) Methyl α-D-Glycoside A reacts in 1 : 2 mole ratio with HIO_4 to give a mole of HCOOH and B. The compound B is also obtained when methyl glucoside, C reacts in equimolar ratio with HIO_4 and with no formic acid formation. Identify the structures of A, B and C. (3)

(b) Give the streochemical structure of the alcohol formed in the reaction. (1)

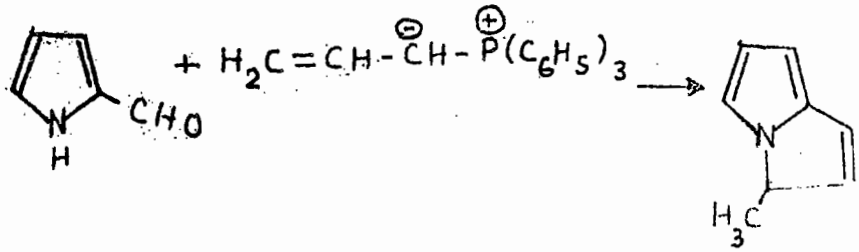
$$C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO + CH_3Mg\,Br \longrightarrow \text{Alcohol}$$

(c) On heating, maleic acid gives its anhydride at a much lower temperature compared to fumaric acid. Explain. (1)

25. ********** mechanism for the following reactions.

(a) 

(3)

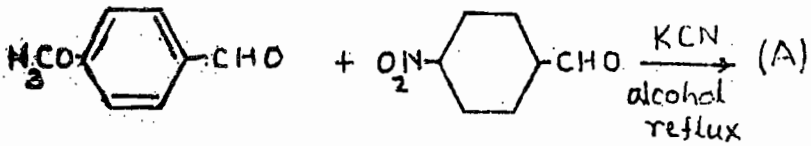
(b) 

(2)

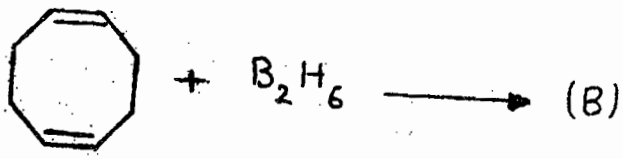
26. (a) Give the steps for the transformation : (3)

(b) Predict the structure of the olefin formed by dehalogenation of meso 2, 3- dibromobutane with Newmann projections. (2)

27. Give the structure of the products in the following reactions.

(a) 

(1)

(b) 

(1)

(c) $CH_3\,CH\,Br\,CHOHCH_2Br \xrightarrow{\ominus OH} (C)$ (1)

(d) INDOLE + CH_2O + $(C_2H_5)_2\,NH \longrightarrow (D)$ (1)

(e) $C_6H_5COC_6H_5 + (C_6H_5)_2\,CH_2 \xrightarrow{KNH_2} (E)$ (1)

ANSWERS WITH EXPLANATIONS

1.

1.1 (D)

Explanation : Because no contact with surrounding.

1.2 (D)

1.3 (A)

Explanation :

$$I = \frac{1}{2}\sum (z)^2 m$$

$$= \frac{1}{2} \times (2)^2 \times 0.1 \text{ m}$$

$$= 0.2 \text{ m.}$$

1.4 (D)

1.5 (B)

Explanation :

$$\text{av. velocity} = \sqrt{\frac{8RT_1}{\pi M_{m_1}}}$$

$$\text{R.M.S.} = \sqrt{\frac{3RT_2}{M_{m_2}}}$$

$$\therefore \quad \frac{T_1}{T_2} = \frac{3R \times 22 \times 30}{8R \times 78 \times 7} = \frac{495}{1092} = 0.48$$

1.6 (B)

1.7 (B)

1.8 (A)

Explanation :

$$E = E^\circ - 2.303\ RT \log \frac{P_{H_2}}{P^{H+}}$$

1.9 (B)

Explanation :

$$P^H = P^{Kb} \pm \log \frac{(\text{salt})}{(\text{base})}$$

$$= -\log 1.85 \times 10^{-5} + \log \frac{(NH_4^+cl^-)}{(NH_3)}$$

1.10 (C)

1.11 (D)

Explanation : Net heat absorbed = work done by the system

1.12 (C)

1.13 (B)

Explanation :

$$K_3 = \frac{(D)}{(B)(C)}$$

$$K_2 = \frac{(A)\,(B)}{(C)}$$

$$K_1 = \frac{(C)}{(A)\,(B)}$$

1.14 (D)

Explanation :

$$t_1 = \frac{2.303}{0.693}t$$

1.15 (C)

1.16 (B)

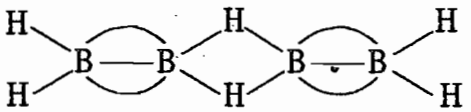
1.17 (D)

1.18 (B)

1.19 (A)

1.20 (A)

Explanation :



1.21 (B)

1.22 (B)

1.23 (D)

Explanation : $BF_3 + (HBO_3)_4 \longrightarrow B_2H_6$.

124 (B)

1.25 (B)

1.26 (D)

Explanation : Because V.A.N $= 25 + 2 \times 5$

$= 35$, which is not obeying 18 electron rule.

1.27 (A)

1.28 (A)

1.29 (D)

1.30 (D)

Explanation : Unpaired electrons only devides magnetic moment.

1.31 (B)

1.32 (A)

1.33 (C)

1.34 (C)

1.35 (A)

1.36 (B)

Explanation : electrical conductivity of pure silicon decreases with temperature.

1.37 (A)

Explanation : Silicate coins unit.

1.38 (B)

1.39 (B)

Explanation : Reduction potential = 1.33 + (– 0.74) = + 0.590 v.

1.40 (C)

Explanation : $i_d = 607_H D^{1/2} m^{2/3} t^{1/6}$ c.

2.

2.1 (D)

Explanation : $\Delta.x. \Delta p = \frac{h}{4\pi}$

2.2 (A)

2.3 (A)

2.4 (D)

Explanation : Involvement of oxygen atoms reduces the no of elements of symmetry.

2.5 (C)

Explanation : O (Pπ) ⟶ Cl (Dπ)

2.6 (A)

2.7 (B)

Explanation : Depends on electronic arrangement.

2.8 (D)

2.9 (C)

2.10 (C)

2.11 (C)

Explanation : Aromaticity will depend on ring and hetero atom.

2.12 (A)

2.13 (A)

Explanation : $NaBH_4$ reduces double bond when it is conjugated with phenyl group.

$$C_6H_5CH = CH\ CHO \xrightarrow{NaBH_4} C_6\ H_5\ CH_2\ CH_2\ CH_2\ OH$$

2.14 (C)

2.15 (C)

2.16 (D)

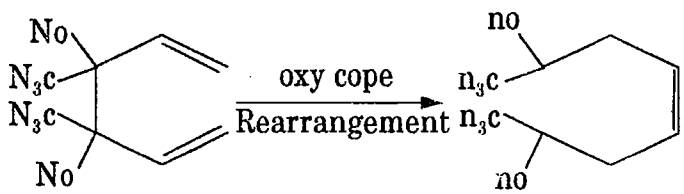
2.17 (B)

2.18 (B)

12.9 (A)

2.20 (D)

Explanation :



2.21 (D)

2.22 (A)

Explanation : Terminal double bond is reduced by Na in liq NH_3 in presence of alcohol.

2.23 (B)

2.24 (D)

2.25 (B)

2.26 (A)

Explanation : $S + R - Mgx \xrightarrow{n+}$ inercaptans.

2.27 (B)

Explanation : Due to odd c-atom.

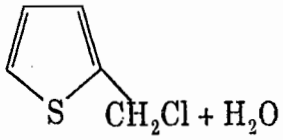
2.28 (A)

2.29 (C)

Explanation : Solubility in water decreases in increasing molecular weight.

2.30 (D)

2.31 (B)

Explanation : Thiophene + HCHO $\xrightarrow{aq^{HCl}}$ 

32. (A)

33. (C)

34. (D)

Explanation : D – glactose + D – glucose

35. (D)

GATE 1999

CY : CHEMISTRY

Time : 3 Hours *Maximum marks : 200*

Read the following instructions carefully :

1. All answers must be written **only in the answer book** provided.
2. This paper contains **TWO SECTIONS :'A' and 'B'.**
3. **Section A** consists of two questions of the multiple choice type. Question 1 consists of **TWENTY FIVE** sub-questions each of **TWO** marks and Question 2 consists of **TWENTY FIVE** sub-questions each of **ONE** mark.
4. The answers to the multiple choice questions must be written only in the boxes provided in the first sheet of the answer book.
5. Answers to **Section B** should be started on a fresh page and should not be mixed with the answers to **Section A.** Question numbers must be written legibly and correctly in the answer book.
6. Section B consists of **TWENTY** questions each of **FIVE** marks. **ANY FIFTEEN** out of them have to be answered. *If more number of questions are attempted, score of the answers not to be evaluated, else only the first fifteen unscored answers will be considered strictly.*
7. In all 5 mark questions, clearly show the important steps in your answers, these steps will carry partial credit.
8. There will be NO NEGATIVE marking.

Useful Data :

Gas constant	R = 0.08205 litre atm K^{-1} mol^{-1}
	= 8.314 JK^{-1} mol^{-1}
	= 1.987 Cal K^{-1} mol^{-1}
Boltzmann constant	= 1.38×10^{-23} JK^{-1}
Planck Constant, h	= 6.626×10^{-34} Js
Avogadro Number	= 6.02×10^{23} mol^{-1}
Charge of electron, e	= 4.8×10^{-10} esu
	= 1.60×10^{-19} C
1 eV	= 1.602×10^{-12} ergs
	= 96,485 kJ mol^{-1}
Faraday	= 96500 C mol^{-1}
Mass of electron, m_e	= 9.1×10^{-31} kg
Atomic mass unit	= 1.66×10^{-27} kg
Speed of light, c	= 3.0×10^{8} ms^{-1}
1 bar	= 750 torr

SECTION A

(75 Marks)

1. *There are 25 sub-questions in Question 1. Each sub-question carries 2 marks. Four answers – A, B, C and D – are provided, of which one is correct. Write in your answer book, the alphabet corresponding to the correct answer against the sub-question number.* (25 × 2 = 50)

1.1. The ground state of V^{3+} ion is
(A) $^3F_2$ (B) $^5D_0$
(C) $^3F_4$ (D) $^2D_{5/2}$

1.2. The final product containing chromium in the reaction between $[Co(NH_3)_5Cl]^{2+}$, $[Cr(H_2O)_6]^{2+}$ and H_3O^+ is
(A) $[Cr(NH_3)(H_2O)_4Cl]^{2+}$ (B) $[Cr(H_2O)_6]^{3+}$
(C) $[Cr(NH_3)_5Cl]^{2+}$ (D) $[Cr(H_2O)_5Cl]^{2+}$

1.3. The correct order of increasing thermal stability among the following compounds is
(A) $SrSO_4 < CaSO_4 < MgSO_4 < BeSO_4$ (B) $BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4$
(C) $CaSO_4 < BeSO_4 < MgSO_4 < SrSO_4$ (D) $MgSO_4 < BeSO_4 < CaSO_4 < SrSO_4$

1.4. A solution of a compound shows a transmittance of 0.800 in a 1.0 cm cell at 525 nm. The transmittance is a 5.0 cm cell at the same wave length would be
(A) 0.160 (B) 0.654
(C) 0.240 (D) 0.327

1.5. The value of $E_{3/4} - E_{1/4}$ (in millivolts) from a polarogram, for a two electron reversible reduction reaction is
(A) –56.4 (B) +56.4
(C) –28.2 (D) +28.2

1.6. Borax is used in preparing
(A) soda glass (B) pyrex glass
(C) opal glass (D) portland cement

1.7. According to band theory of bonding, conduction occurs in *very good conductors* because
(A) valence band is full (B) valence band and conduction band overlap
(C) band gap is appreciable (D) band gap is small

1.8. Uranium exhibits several oxidation states because
(A) it is an inner transition cement (B) its atomic number is high
(C) 5 *f* orbitals participate in bonding (D) it forms strong bond with oxygen

1.9. The ionic strength of 0.01 M K_2SO_4 is
(A) 0.01 (B) 0.02
(B) 0.03 (D) 0.04

1.10. The following mechanism was proposed for the photolysis of HI into H_2 and I_2.

$$HI + h\upsilon \rightarrow H + I$$
$$H + HI \rightarrow H_2 + I$$
$$2I\upsilon \rightarrow I_2$$

The overall quantum yield of the reaction is
(A) 0.5 (B) 1
(C) 2 (D) 4

1.11. The standard enthalpy of hydrogenation of ethene is –32.7 kcal/mol and that of benzene is –49.0 kcal/mol. The stabilization energy (in kcal/mol) of benzene due to electron delocalization from the given data is

(A) 81.7 (B) 49.1
(C) 36.0 (D) 16.3

1.12. The orbital angular momentum (in units of $h/2\pi$; where h is the Planck's constant) of an electron in the $3d$ orbital is

(A) 2 (B) 3
(C) $2^{1/2}$ (D) $6^{1/2}$

1.13. The radioactive decay of

$$^{239}_{92}U \rightarrow ^{239}_{94}Pu$$

is an example of

(A) zero order reaction (B) photochemical reaction
(C) chain reaction (D) consecutive reaction

1.14. Accounting to Maxwell distribution, as temperature increases, the fraction of the molecules moving about with root mean square speed

(A) decreases (B) increases
(C) remains unaffected (D) tends to infinity

1.15. The entropy change associated with the freezing of 1 mole of water at 0°C and 1 atm (heat of fusion under these conditions is 6.0 kJ/ml) is

(A) –6 J/K (B) –22 J/K
(C) + 22 J/K (D) +6 J/K

1.16. The phase diagrams of CO_2 and H_2O differ in that

(A) the slope of the solid-liquid equilibrium curve is positive for the former and negative for the latter
(B) the slope of the solid-liquid equilibrium curve is negative for the former and positive for the latter
(C) the slope of the solid-vapour equilibrium curve is negative for the former and positive for the latter
(D) the slope of the solid-vapour equilibrium curve is positive for the former and negative for the latter

1.17. The decomposition of a gas on a surface follows the rate law : Rate $\propto$ {KP/(1 + KP)} where P is pressure and K is a constant. The order of the reaction at high pressures is

(A) zero (B) 1/2
(C) 1 (D) 2

1.18. Which of the following compounds contains diastereotopic protons ?

(A) ethyl chloride (B) 1, 2-dichloropropane
(C) 2-methylpropene (D) 1, 2-dichloroethane

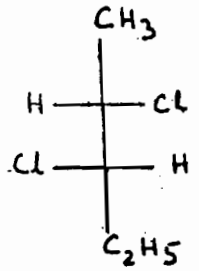
1.19. Which of the following is true for the electrophilic aromatic substitution reaction ?

(A) involves a single step (B) involves a free radical intermediate
(C) $k^H / k^D > 5$ (D) $k^H / k^D = 1$

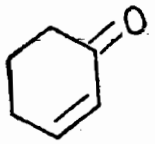
1.20. The reaction of *erythro* 1-bromo-1, 2-diphenylpropane with alcoholic KOH gives
(A) (Z) – 1, 2–diphenyl-1-propene
(B) (E) – 1, 2–diphenyl-1-propene
(C) both (Z) and (E)–1, 2-diphenyl-1-propene
(D) 1, 2-diphenyl-1-propanol

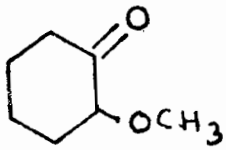
1.21. The conversion of vinylcyclopropane to cyclopentene upon heating is an example of which of the following sigmatropic rearrangements ?
(A) [3, 3] (B) [1, 3]
(C) [1, 5] (D) [1, 2]

1.22. The configuration at C-2 and C-3 of the compound given below is



(A) 2R, 3S (B) 2S, 3R
(C) 2S, 3S (D) 2R, 3R

1.23. The major product in the reaction of 2-chlorocyclohexanone with sodium methoxide is
(A)


(B)


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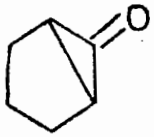
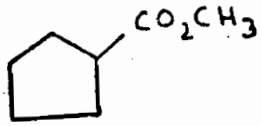
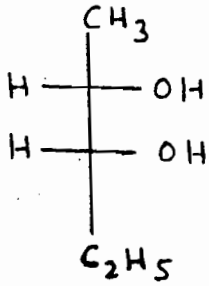
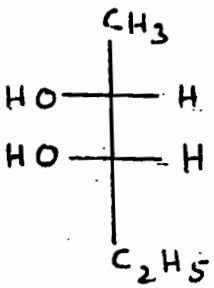


(D)


1.24. The following two compounds are

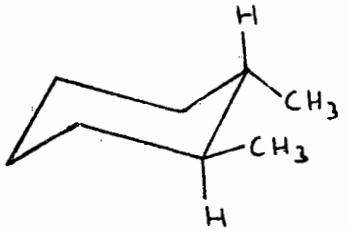




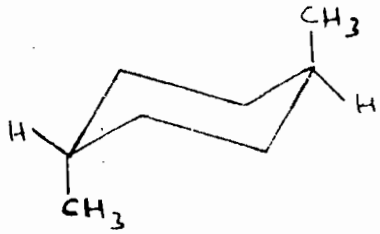
(A) enantiomers (B) diastereomers
(C) identical (D) epimers

1.25. Which of the following is a *cis*-isomer ?

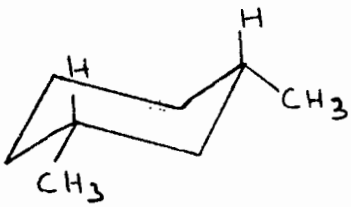
(A)



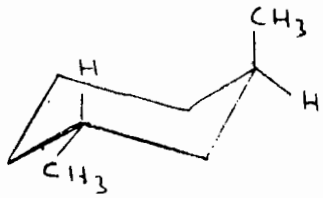
(B)



(C)



(D)



2. ***There are 25 sub-questions in Question 2. Each sub-question carries 1 mark. Four answers – A, B, C and D – are provided, of which one is correct. Write in your answer book, the alphabet corresponding to the correct answer against the sub-question number.*** **(25 × 1 = 25)**

2.1. Which of the following electronic transitions corresponds to the lowest energy band in the absorption spectrum of Ni(ethylenediamine)$_3^{2+}$?

(A) $^3T_{2g} \leftarrow {}^3A_{2g}$
(B) $^3T_{1g}$ (F) $\leftarrow {}^3A_{2g}$
(C) $^3T_{1g}$ (P) $\leftarrow {}^3A_{2g}$
(D) $^4A_{2g} \leftarrow {}^4T_{2g}$

2.2. Which of the following products is obtained on heating, B_2H_6 with NH_3 in the ratio (1 : 2) at higher temperatures ?

(A) $B_3N_3H_3$
(B) $B_2H_6 2NH_3$
(C) Boron nitride
(D) $B_3N_3H_6$

2.3. Which of the following does not obey 18 electron rule ?

(A) $Cr(CO)_6$
(B) $Fe(CO)_5$
(C) $V(CO)_6$
(D) $Mn_2(CO)_{10}$

2.4. Which of the following represents a set of hard acid and soft base respectively ?

(A) Fe^{3+} and F
(B) Fe^{3+} and S^{2-}
(C) Ag^+ and S^{2-}
(D) Ag^+ and F^-

2.5. Which of the following will have the molecular shape of a trigonal bipyramid ?

(A) PF_3Cl_2
(B) IF_5
(C) BrF_5
(D) SbF_5^{2+}

2.6. Which of the following, when doped into a crystal of ultra purified Germanium, will convert it into a *p*-type semiconductor ?

(A) C
(B) As
(C) In
(D) Na

2.7. The $E_{1/2}$ in the case of polarographic reversible reduction is dependent on the

(A) concentration of the metal ion
(B) diffusion current
(C) limiting current
(D) nature of the metal ion

2.8. Which of the following compounds is expected to exhibit fluoresence ?
(A) pyridine
(B) quinoline
(C) pyrrole
(D) furan

2.9. Which of the following electrolytes is used in highly developed hydrogen-air fuel cells ?
(A) phosphoric acid
(B) 1 M KOH
(C) H_2SO_4
(D) $[Na_2CO_3]_{aq}$

2.10. If 'n' denotes a quantum number and 'c' the velocity of light, the energy of a particle of mass 'm', in a box of length 'l' is proportional to
(A) l^2
(B) m^2
(C) n^2
(D) $c^{1/2}$

2.11. Wave function in quantum mechanics represents
(A) a state of the system
(B) shape of the system
(C) probability of the system
(D) energy of the system

2.12. A 1s orbital refers to
(A) a circular track in an atom in which an electron travels
(B) a one electron wave function
(C) an observable property of the system
(D) a Hermitian operator

2.13. Work done in the free expansion of an ideal gas is zero because
(A) the intermolecular forces are zero
(B) there is no friction
(C) external pressure acting on the system is zero
(D) perfect vacuum cannot be created

2.14. Consider the system of a sealed copper vessel containing one litre of water placed in the ventillated room. According to the second law of thermodynamics the
(A) entropy of the system tends to a maximum
(B) free energy of the system tends to a minimum
(C) potential energy of the system and surroundings tends to a minimum
(D) enthalpy of the surroundings tends to a maximum

2.15. The standard free energy of formation of $H_2O(l)$ at 25°C is given as –237.1 kJ/mol. The standard free energy of formation of H_2O (g) at 25°C is
(A) greater (less negative) than –237.1 kJ/mol
(B) less (more negative) than –237.1 kJ/mol
(C) equal to –237.1 kJ/mol because an equilibrium exists between the liquid and the vapour
(D) not defined because H_2O (g) at 25°C is unstable

2.16. Which of the following will have the lowest frequency ?
(A) $\nu_{C\text{-}H}$
(B) $\nu_{C\text{-}C}$
(C) $\nu_{C\text{-}O}$
(D) $\nu_{C\text{-}Br}$

2.17. In collision theory, the preexponential factor is
(A) independent of temperature
(B) proportional to temperature
(C) proportional to square of temperature
(D) proportional to square root of temperature

2.18. Aldoses and ketoses are differentiated by
(A) Tollen's reagent
(B) Fehling's solution
(C) Br_2 water
(D) HIO_4

2.19. Which of the following dicarboxylic acids contains the most acidic hydrogen ?

(A) maleic acid (B) fumaric acid

(D) succinic acid (D) malonic acid

2.20. Which of the following compounds on reaction with CH_3MgBr will give a tertiary alcohol ?

(A) C_2H_5CHO (B) $C_2H_5CO_2CH_3$

(C) C_2H_5COOH (D) $CH_3CH—CHCH$ (O)

2.21. *Trans*-cyclohexane - 1, 2 - diol can be obtained by the reaction of cyclohexene with

(A) $KMnO_4$ (B) O_sO_4

(C) peroxy formic acid (D) SeO_2

2.22. The most stable diene among the following is

(A) 1, 4-pentadiene (B) 1, 2-butadiene

(C) 1, 3-butadiene (D) 1, 4-cyclohexadiene

2.23. Among the following compounds, the most basic compound is

(A)

(B)

(C)

(D)

2.24. Which of the following is not an aromatic compound ?

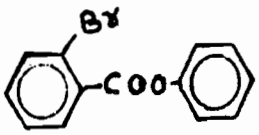
(A)

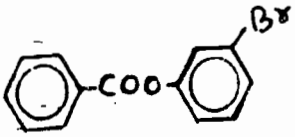
(B)

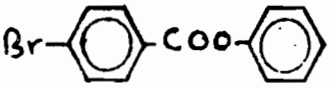
(C)

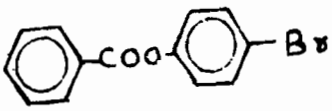
(D)

2.25. The major product expected from the mono-bromination of phenyl benzoate is

(A) 

(B) 

(C) 

(D) 

SECTION B

This section contains 20 questions. Answer any 15. Each question carries 5 marks.

3.1. Draw the structure of $(NPCl_2)_3$ and complete the reaction.
$[NPCl_2]_3 + 6\ C_6H_5Li \rightarrow$ (3)

3.2. Draw the structure of Perovskite, $CaTiO_3$ (2)

4.1. Complete the following action
$XeF + 6H_2O \rightarrow$ (1)

4.2. Predict the structure of $XeOF_4$ on the basis of VSEPR theory. (2)

4.3. What are AMPHIBOLES ? What are their special structural features? (2)

5.1. Complete the reaction
$3\ [Ca_3(PO_4)_2 . CaF_2] + 7\ H_2SO_4 \rightarrow$ (2)

5.2. PF_3 can act as donor molecule while NF_3 shows little tendency to act as donor. Account for this observation. (2)

5.3. Draw the structure of N_2O_5 in the gas phase. (1)

6.1. Draw the structure of Ruthenocene (1)

6.2. Complete the following reaction
$2C_5H_6 + FeCl_2 + 2Et_2NH \rightarrow$ (2)

6.3. Draw the structure of $Fe_2\ (CO)_9$. (2)

7.1. The proton NMR spectrum of $(C_5H_5)_4T_1$ showed two peaks at –30°C and one peak at 62°C. Explain this observation. (2)

7.2. Tris (trifluoroacetylacetonato) cobalt (III) is formed from a bidentate ligand trifluoroacetylacetone $\{CF_3C(OH) = CHCOCH_3\}$. Draw the structure of the complex. Predict the isomerism and draw structures of isomers if isomerism is possible. (3)

8.1. Match the following metal in I with the appropriate biomolecule in II. (3)

I	*II*
(A) Zn	*(i)* phosphotransferase
(B) Cu	*(ii)* peroxidase
(C) Fe	*(iii)* carboxypeptidase
	(iv) haemocyanine
	(v) nitrogenase

8.2. The reaction $[Co(NH_3)_5Cl]^{2+} + OH^- = [Co(NH_3)_5OH]^{2+} + Cl^-$ obeys a rate law which is compatible with S_NICB mechanism. Give the steps in the mechanism. (2)

9.1. 10 ml solution of a 0.001 M metal solution and 10 ml of a 0.003 M ligand solution were mixed. The final concentration of the metal complex ML_3 was 0.000499 M. Calculate the stability constant of the complex. (2)

9.2. Substances A and B were found to have retention times of 17.30 and 19.92 minutes respectively on a 25.0 cm column. The widths (at the base) for A and B were 1.10 and 1.22 minutes respectively. Calculate resolution, the average number of plates in the column and the plate neight. (3)

10.1. Indicate the splitting pattern in the proton NMR of acetaldehyde. **(2)**

10.2. Which among the following electronic transitions will have the lowest energy. (1)

(A) $n \rightarrow \sigma^*$ (B) $n \rightarrow \pi^*$

(C) $\sigma \rightarrow \sigma^*$ (D) $\pi \rightarrow \pi^*$

10.3. Which of the following molecules shows rotational absorption spectrum ? (1)

(A) CO_2 (B) OCS

(C) CH_4 (D) C_6H_6

10.4. How many lines are expected in the ESR spectrum of benzene radical anion in solution ? **(1)**

11. The rate of the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ doubled when the temperature initially at 298 K, was increased by 5°. Determine the activation energy for this reaction. **(5)**

12. For the bromide catalyzed decomposition **********

$2H_2O_2(aq) \rightarrow 2H_2O\ (aq) + O2$ **(8)**

a mechanism proposed involves three steps : *(i)* a preequilibrium step; *(ii)* a reaction between Br^- and $HOOH_2^+$ to give HOBr and H_2O which is considered to be the slowest step and *(iii)* a fast step involving the release of O_2 (*g*). It is further observed experimentally that the rate of this reaction depends on pH and Br^- concentration. Give the complete mechanism and obtain the rate law. **(5)**

13. A mixture of H_2S and CH_4 was placed in an empty container along with a catalyst and the equilibrium $2H_2S(g) + CH_4\ (g) = 4H_2\ (g) + CS_2\ (g)$ was established at 700°C and 760 torr. The equilibrium concentrations (in mole fractions) of H_2S, CH_4, H_2 and CS_2 were determined to be 0.54, 0.26, 0.16 and 0.04 respectively. Calculate K_P^o (standard pressure equilibrium constant) for the reaction at 700°C. **(5)**

14. Sketch the π molecular orbital energy level diagram for the allyl system under Huckel approximation, and compute the delocalization energy of allyl cation. **(5)**

15. Let $<V>$, $<T>$ and $<E>$ denote the average potential energy, the average kinetic energy and the average total energy of a particle. If '*x*' represents the positional coordinate and potential energy V is proportional to x^b, '*b*' being constant, then assume that $2<T> = b<V>$. Calculate the ratios $<T>/<V>$ and $<E>/<V>$ for *(i)* a harmonic oscillator and *(ii)* the hydrogen atom. **(5)**

16. Calculate the potential of pentane/oxygen fuel cell given that the standard free energies of formation (in kJ/mol) at 298 K are –8.2, –237.2 and –394.4 for pentane. $H_2O(l)$ and $CO_2(g)$ respectively. **(5)**

17. A cyclic ketone A (C_5H_8O) on reaction with $NaOCH_3$ gives a product B which has the following spectral properties :

IR: 1740 cm^{-1} (s), 1160 cm^{-1} (s)

UV: transparent above 200 nm

^{1}H-NMR: δ 3.6 (3H, singlet); δ 1.2 (9H, singlet);

Mass : m/e/ : 116, 85, 59, 31

Deduce the structures of A and B. (5)

18.1. Suggest a mechanism for the acid catalyzed mutarotation of D - (+) - glucose. **(3)**

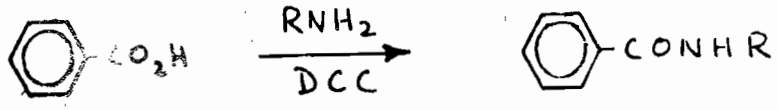
18.2. Pyrrole undergoes electrophilic substitution preferably at 2-position. Explain. **(2)**

19.1. How could the carbobenzoxy method be used to prepare alanyl-glycine (ala-gly) ? **(3)**

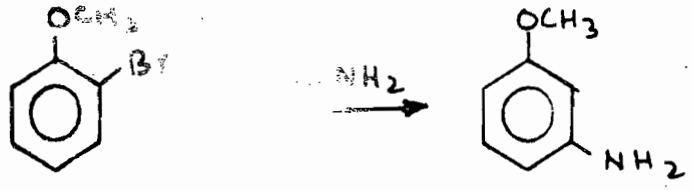
19.2. The pK_1 and pK_2 values for alanine are 2.34 and 9.60 respectively. What is its isoelectric point? **(2)**

20. Suggest a suitable mechanism for each of the following reactions. **(3 + 2)**

(i)

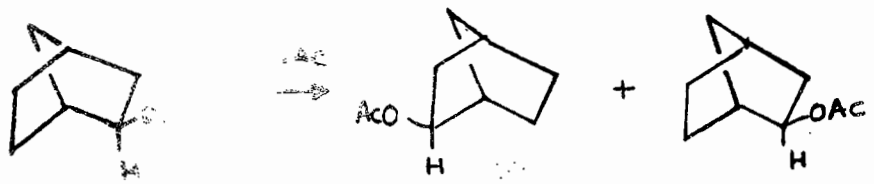


(ii)

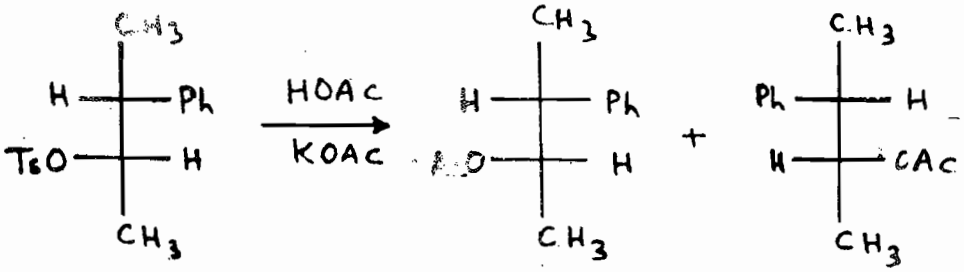


21. Account for the formation of the following products. **(3 + 2)**

(i)

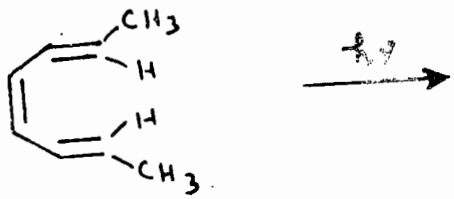


(ii)

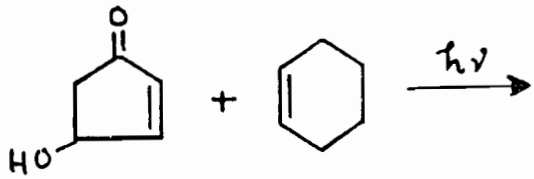


22. Give the structures of the products in each of the following reactions.

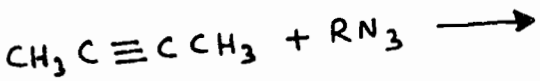
(i)



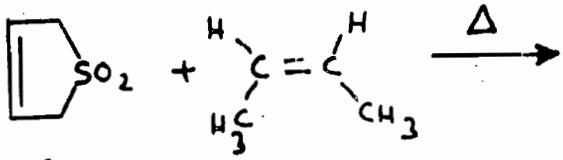
(ii)



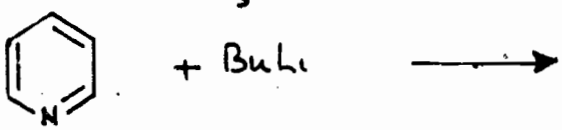
(iii)



(iv)



(v)

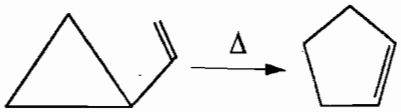


1.19. (B)

1.20. (C)

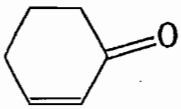
1.21. (B)

Explanation :



1.22. (B)

1.23. (B)

Explanation : 2-chlorocyclo Hexanone + Sodium Methoyixe → 

1.24. (C)

1.25. (C)

2.

2.1. (D)

2.2. (D)

Explanation : $3B_2H_6 + 6NH_3 \xrightarrow{200°C} 2B_3N_3H_6 + 12H_2$

2.3. (C)

Explanation : Because, E.A.N. = 23 + 2 × 6 = 35

2.4. (B)

2.5. (A)

2.6. (B)

Explanation : Only Arsenic have less electron.

2.7. (C)

2.8. (C)

2.9. (B)

2.10. (A)

2.11. (A)

Explanation : Because electron behave as wave particle.

2.12. (B)

2.13. (A)

Explanation : Because molecules of gases are free to move in container for ideal gas.

2.14. (B)

2.15. (A)

Explanation : Increases with change of state from solid to gas.

2.16. (D)

2.17. (D)

Explanation : $A = 3.893 \times 10^{29}\, p\, (w)^2 \left(\frac{I}{M}\right)^{1/2}$

2.18. (D)

Explanation : They give different test.

2.19. (D)

2.20. (D)

Explanation : CH_2 CH—CHCH + CH_3 Mg Br ⟶ 3° Alcohol.

O

2.21. (D)

2.22. (C)

2.23. (A)

Explanation : Because of Hetro atom is most basic their other compound.

2.24. (C)

2.25. (D)

GATE - 2000

CY : CHEMISTRY

Duration: Three Hours | *Maximum Marks*: 100

Useful Data:

Atomic Numbers : vanadium, 23; chromium, 24; manganese, 25; iron, 26; cobalt, 27; nickel, 28; ruthenium, 44; rhenium, 75; platinum, 78.

Atomic mass : H, 1 amu; D, 2 amu.

1 amu $= 1.66 \times 10^{-27}$ kg

R $= 0.0821$ atm k^{-1} $mol^{-1} = 8.314$ JK^{-1} mol^{-1}

SECTION–A (75 Marks)

1. *There are 25 sub-questions in Question 1. Each sub-question carries 2 marks. Four answers – a, b, c and d – are provided, of which one is correct. Write in your answer book, the alphabet corresponding to the correct answer against the sub-question number.* **(25 × 2 = 50)**

1.1. Which among the following molecules belong to point group C_{4v} ?

(*a*) $[BF_4]Na^+$ (*b*) $XeOF_4$

(*c*) XeF_4 (*d*) $[PtCl_4]^{2-}$

1.2. The ^{19}F NMR spectrum of PCl_2F_3 (I for $^{31}P = 1/2$, I for $^{19}F = 1/2$) shows

(*a*) two triplets and two doublets

(*b*) two triplets and one doublet

(*c*) two doublets and one triplet

(*d*) three triplets and one doublet

1.3. The compound $(SiH_3)_3N$ is expected to be

(*a*) pyramidal and more basic than $(CH_3)_3N$

(*b*) planar and less basic than $(CH_3)_3N$

(*c*) pyramidal and less basic than $(CH_3)_3N$

(*d*) planar and more basic than $(CH_3)_3N$

1.4. The infrared and Raman spectrum of BF_3 are expected to show

(*a*) the same number of peaks

(*b*) more absorption peaks in IR in comparison to Raman

(*c*) more absorption peaks in Raman in comparison with IR

(*d*) absorption peaks present in Raman are absent in R

1.5. The complex with maximum CFSE is

(*a*) $[CoCl_4]^{2-}$ (*b*) $[Co(H_2O)_6]^{3+}$

(*c*) $CoF_3(H_2O)_3$ (*d*) $[CoF_6]^{3+}$

1.6. The compound which has four metal-metal bonds is

(*a*) $Fe_2(CO)_9$ (*b*) $Co_2(CO)_8$

(*c*) $[Re_2Cl_8]^{2-}$ (*d*) $[Ru_3(CO)]_{12}$

1.7. The complex with spin-only magnetic moment of ~ 4.9 B.M. is

(*a*) $[F_e(H_2O)_6^{2+}$ (*b*) $[Fe(CN)_6]^{3-}$

(*c*) $[Fe(CN)_6]^{4-}$ (*d*) $[Fe(H_2O)_6]^{3+}$

1.8. The complex which exhibits lowest energy electronic absorption band is

(*a*) $[NiCl_4]^{2-}$ (*b*) $[Ni(H_2O)_6]^{3+}$

(*c*) $[Ni(CN)_4]^{2-}$ (*d*) $Ni(CO)_4$

1.9. The system for which energy (E) increases quadratically with the quantum number (n) is

(*a*) particle-in-a-one dimensional box

(*b*) hydrogen atom

(*c*) one dimensional harmonic oscillator

(*d*) rigid rotor

1.10. Among the following orbitals of a diatomic molecule, the bonding one is

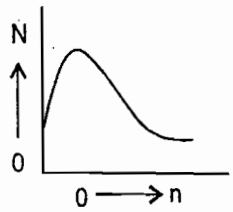
(*a*) $1\sigma_u$

(*b*) $2\sigma_u$

(*c*) $1\pi_u$

(*d*) $1\pi_g$

1.11. The population (N)distribution over states (n) of a diatomic molecule corresponds to



(*a*) translation

(*b*) vibration

(*c*) rotation

(*d*) electronic

1.12. $^2P_{3/2}$ is the ground state of

(*a*) H (*b*) Li

(*c*) B (*d*) F

1.13. The vapour pressure of components 'A' and 'B' are 200 torr and 100 torr respectively. Assuming a solution of these components obeys Raoult's law, the mole fraction of component 'A' in vapour phase in equilibrium with a solution containing equimoles of 'A' and 'B' is

(*a*) 0.33 (*b*) 0.66

(*c*) 0.80 (*d*) 0.50

1.14. The half-life time for a reaction at initial concentrations of 0.1 and 0.4 mol^{-1} are 200 s and 50s respectively. The order of the reaction is

(*a*) 0 (*b*) 1

(*c*) 2 (*d*) 3

1.15. The pH of a buffer solution containing 4×10^{-3} and 0.4 moles of acetic acid ($pk_a = 4.76$) and sodium acetate respectively will be

(*a*) 6.76 (*b*) 4.76

(*c*) 2.76 (*d*) 0.76

1.16. Under the equilibrium conditions for the reaction $C(s) + CO_2(g) \leftrightarrows 2\ CO(g)$, the total pressure is 12 atm. The value of K_p is

(*a*) 16 (*b*) 0.5

(*c*) 2 (*d*) 32

1.17. An aqueous solution containing m moles of non-volatile solute freezes at –0.186°C. The elevation in the boiling point of the same squeous solution (K_f = 1.86° K_b = 0.512°) would be

(*a*) 0.186 (*b*) 0.512

(*c*) 0.0512 (*d*) 0.512/1.86

1.18. The two H's at C-2 and C-3 in (2R, 3S) tartaric acid

(*a*) enantiotopic

(*b*) diastereotopic

(*c*) homotopic

(*d*) constitutionally heterotopic

1.19. Oxymercuration-demercuration reaction of 1-methylcyclohexene gives

(*a*) *cis*-2-methylcyclohexanol

(*b*) *trans*-2-methylcyclohexanol

(*c*) 1-methylcyclohexanol

(*d*) mixture of *cis* and *trans*-2-methylcyclohexanol

1.20. Bromination of (E)-2 butenedioic acid gives

(*a*) (2R, 3S)-2, 3-dibromosuccinic acid

(*b*) (2R, 3R)-2 3-dibromosuccinic acid

(*c*) a mixture of (2R, 3R)-and (2S, 3S)-2, 3-dibromosuccinic acid

(*d*) (2S, 3S)-2, 3-dibromosuccinic acid

1.21. 4-Pentenoic acid when treated with I_2 and $NaHCO_3$ gives

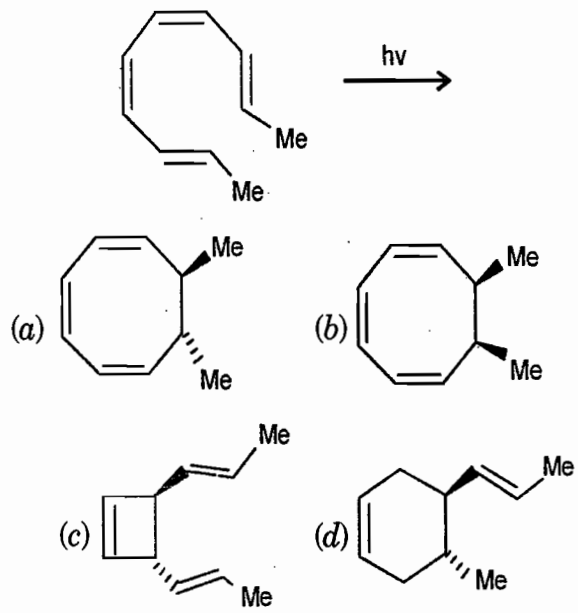
(*a*) 4, 5-diiodopentanoic acid

(*b*) 5-iodomethyl-dihydrofuran-2-one

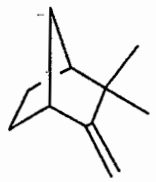
(*c*) 5-iodo-tetrahydropyran-2-one

(*d*) 4-pentenoyliodide

1.22. The following tetraene upon photolysis gives

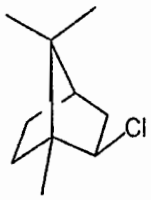


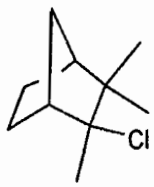
1.23. The product formed upon heating camphene with HCl is

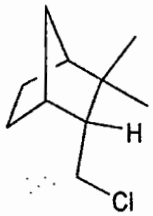


(Camphene)

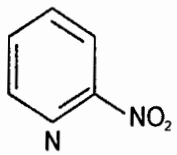
(a)

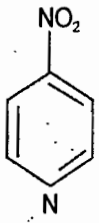
(b) 

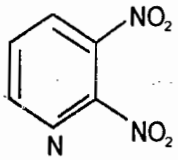
(c) 

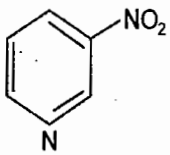
(d) 

1.24. Pyridine undergoes electrophilic nitration at elevated temperatures to give the following as a major product :

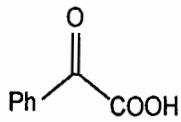
(a) 

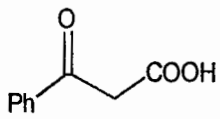
(b) 

(c) 

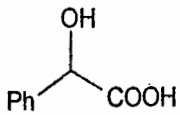
(d) 

1.25. Among the following, the acid which undergoes fastest decarboxylation is:

(a) 

(b) 

(c) PhCOOH

(d) 

2. *There are 25 sub-questions in Question 2. Each sub-question carries 1 marks. Four answers – a, b, c and d – are provided, of which ONE is correct. Write in your answer book, the alphabet corresponding to the correct answer against the sub-question number.* **(25 × 1 = 25)**

2.1. Which of the following statements about the molecule NOCl is correct?

(a) It has a linear structure

(b) It belongs to the point group C_s

(c) It does not have dipole moment

(d) It is a chiral molecule

2.2. Which of the following is an *orachno* borane?

(a) $[B_6H_6]^{2-}$ (b) $[B_5H_9]$

(c) $[B_2H_6]$ (d) $[B_6H_{12}]$

2.3. C_{60} has

(a) 14 pentagons and 18 hexagons

(b) 12 pentagons and 20 hexagons

(c) 10 pentagons and 20 hexagons

(d) 12 pentagons and 18 hexagons

2.4. The order of acidity in boron trihalides is

(a) $BF_3 > BCl_3 > BBr_3$

(b) $BBr_3 > BCl_3 > BF_3$

(c) $BF_3 > BBr_3 > BCl_3$

(d) $BBr_3 > BF_3 > BCl_3$

2.5. The compound which obeys 18-electron rule is

(a) $Mn(CO)_3$ (b) $Fe(CO)_4$

(c) $V(CO)_6$ (d) $Cr(CO)_6$

2.6. The Si-O-Si bond angle in $Me_3SiOSiMe_3$ is

(a) ~ 120° (b) ~ 180°

(c) ~ 90° (d) ~ 109°

2.7. The compound which exhibits Jahn-Teller distortion is

(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{3+}$

(c) $[Cr(H_2O)_6]^{3+}$ (d) $[Fe(CN)_6]^{4-}$

2.8. The orange colour of $Cr_2O_7^{2-}$ is due to

(a) metal to ligand charge transfer transition

(b) ligand to metal charge transfer transition

(c) crystal-field transition

(d) charge-transfer complex formation

2.9. Among the following molecules, the shortest bond length is to be found in

(*a*) C_2 (*b*) N_2

(*c*) O_2 (*d*) F_2

2.10. Among the following diatomic molecules, the one that shows EPR signal is

(*a*) Li_2 (*b*) B_2

(*c*) C_2 (*d*) N_2

2.11. Among the following elements, the one that acts as the major component in a semiconductor is

(*a*) C (*b*) Si

(*c*) Ga (*d*) As

2.12. Among the singlet (S), doublet (D) and triplet (T) electronic states, phosphorescence involves transition between

(*a*) S and S (*b*) D and D

(*c*) T and T (*d*) S and T

2.13. In a system, when the chemical potential of each component is the same for all the phases, the equilibrium is said to be

(*a*) metastable equilibrium

(*b*) thermal equilibrium

(*c*) composition equilibrium

(*d*) mechanical equilibrium

2.14. The number of molecules of an ideal gas in a 8.21 container at 380 torr and 27°C will be

(*a*) 1.0×10^{23} (*b*) 1.0×10^{22}

(*c*) 6.02×10^{23} (*d*) 12.04×10^{23}

2.15. The criterion for the spontaneity of a process is

(*a*) $\Delta S_{sys} > 0$

(*b*) $\Delta S_{surr} > 0$

(*c*) $\Delta S_{sys} + \Delta S_{surr} > 0$

(*d*) $\Delta S_{sys} - \Delta S_{surr} > 0$

2.16. ΔH and ΔE for the reaction $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$ at constant temperature are related as

(*a*) $\Delta H = \Delta E$ (*b*) $\Delta H = \Delta E + RT$

(*c*) $\Delta H = \Delta E + 3RT$ (*d*) $\Delta H = \Delta E - 3RT$

2.17. For an ideal gas following adiabatic reversibel expansion, plot of log *p* versus log V is linear with a slope equal to ($\gamma = C_p/C_v$)

(*a*) $1/\gamma$ (*b*) $-1/\gamma$

(*c*) γ (*d*) $-\gamma$

2.18. Toluene when refluxed with Br_2 in the presence of light mainly gives

(*a*) *o*-bromotoluene

(*b*) *p*-bromotoluene

(*c*) Mixture of *o*-and *p*-bromotoluene

(*d*) benzylbromide

2.19. Optically active 2-octanol rapidly loses its optical activity when exposed to

(*a*) dilute acid (*b*) dilute base

(*c*) light (*d*) humidity

2.20. 1-Hexyne upon treatment with disiamylborane followed by oxidation with H_2O_2 gives

(*a*) hexanoic acid (*b*) hexenol

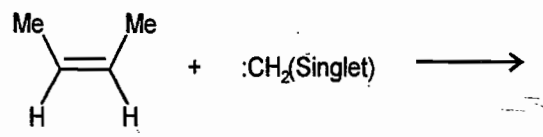
(*c*) hexanal (*d*) hexanol

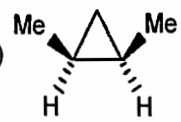
2.21. (E)-3-bromo-3 hexene when treated with $CH3O^-$ in CH_3 OH gives

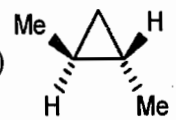
(*a*) 3-hexyne (*b*) 2-hexyne

(*c*) 2, 3-hexadiene (*d*) 2, 4-hexadiene

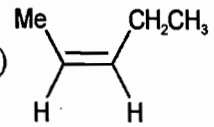
2.22. The major product formed in the following reaction is



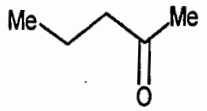
(*a*)


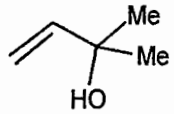
(*b*)


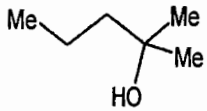
(*c*) 50 : 50 mixture of above two compounds

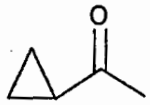
(*d*)


2.23. Methyl vinyl ketone upon reaction with $LiCuMe_2$ gives a major product whose structure is

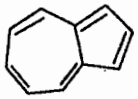
(*a*) 

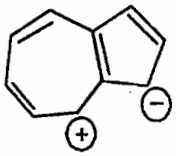
(*b*) 

(*c*) 

(*d*) 

2.24. The following hydrocarbon has a dipole moment of 0.8D because



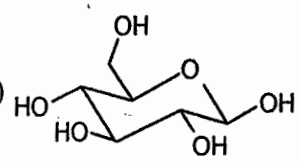
(*a*) it exists as  in which both the rings exhibit aromaticity

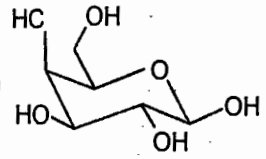
(*b*) charge separation permits conformational stability

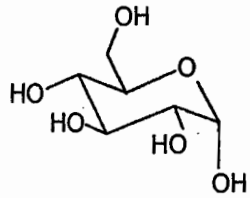
(*c*) the two rings are of different size

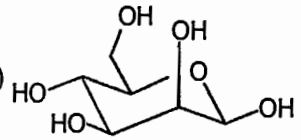
(*d*) the molecule obeys $4n + 2$ Huckel rule

2.25. β-D-Glucose is represented as:

(*a*) 

(*b*) 

(*c*) 

(*d*) 

SECTION–B

This section contains 20 questions. Answer any 15. Each question carries 5 marks.

3.1. Write the structures of the following compounds

(*a*) S_4N_4 (*b*) $1, 2 = B_4C_2H_6$

(*c*) SF_4CH_2 **(3)**

3.2. Account in about 10 lines the fact that the IR stretching frequency of the P-O bond increases in the order

$(CH_3)_3PO < Cl_3PO < F_3PO$ **(2)**

4. Complete the following reactions supplying the missing reactant or product **(5)**

(*a*) $n[(CH_3)_2\ SiO_4] + (CH_3)_3SiOSi(CH_3)_3 \xrightarrow{H_2SO_4} A$

(*b*) $Al_2(CH_3)_6 + 6H_2O \longrightarrow B + C$

(*c*) $3BCl_3 + 3NH_4Cl \longrightarrow D$

(*d*) $E \xrightarrow[\text{haptane, 77 K}]{h\nu, 270\,\text{nm}} (Mes)_2\,Si = Si(Mes)_2$

(Mes = 2, 4, 6-trimethylphenyl)

(*e*) $SbF_5 + BrF_3 \longrightarrow F + G$

5.1. State whether the following is true or false and explain your choice in about 3 lines. "The Ni-C bond length in nickelocene is longer than the Fe-C bond length in ferrocene." **(2)**

5.2. Write the structure of $CO_4(CO)_{12}$. Using the isolobal analogy show which of the following fragments you would use to replace one of the cobalt fragments in the above cluster? Write the structure of the cluster so formed. **(3)**

(*a*) CH_2 (*b*) CH

(*c*) NH_2 (*d*) CH_3

6.1. From among the following reactions identify the type of reaction involved viz., oxidative-addition, reductive elimination, insertion or addition. Justify your choice. **(3)**

(*a*) $[RhI_3(CO)_2CH_3]^- \rightarrow [RhI_3\,CO(\text{solvent})(COCH_3)]^-$

(*b*) $[Co_2(CO)_8] + H_2 \rightleftarrows 2[CoH(CO)_4]$

(*c*) $Mn_2(CO)_{10} + Br_2 \rightarrow 2MnBr(CO)_5$

6.2. Write the structures of the products formed in the following reactions, keeping in view the 18-electron rule. **(2)**

(*a*) $\eta^4C_4H_6Fe(CO)_3 + HCl \rightarrow$

(*b*) $(\eta^5Cp)_2\ Fe + HBF_4 \rightarrow$

7.1. Lower the symmetry of a complex, closer is its magnetic moment, to the spin-only value. Explain in 2-3 sentences. **(2)**

7.2. Write and *d*-orbital splitting diagrams for a square pyramidal and a trigonal bipyramidal complex. **(3)**

8.1. Draw the active site structure of rubredoxin and two common forms of ferredoxins. **(3)**

8.2. Cytochrome C is a redox protein but myoglobin is an oxygen storage protein. Justify in 2-3 sentences. **(2)**

9.1. The complex $[Fe(H_2O)_6]^{2+}$ displays two overlaping absorption bands at ~ 1000 nm. Provide an explanation in 2-3 sentences. **(2)**

9.2. Comment in 5-6 lines on the metal-olefin bonding in $K[PtCl_3(C_2H_4]$ **(3)**

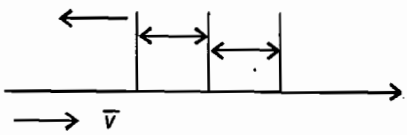
10. O_3 molecule has a bent geometry in its ground electronic state. Using Huckel approximation, derive the eigen values of the π molecular orbitals of O_3 and write down the electronic configuration. Also how schematically all the three π molecular orbitals and label them bonding, nonbonding and antibonding. **(5)**

11.1. Show how would you distinguish between propanal and acetone using NMR spectroscopy. Label the axes properly and schematically show all the important features in the spectrum. **(3)**

11.2. Using Raman spectrum and IR spectrum, show how you will determine whether a substance is *trans*-or *cis*-1, 2-dichloroethylene (without knowing the frequencies at which different vibrational modes occur). **(2)**

12.1. H_2 has one of the largest rotational constants ($B_e = h/8\pi^2 Ic \sim 60\ cm^{-1}$) for a diatomic molecule. predict the spacing between the lines in the rotational Raman spectrum indicated. **(2)**

Rayleigh line



12.2. Predict the spacing between the same set of lines in the rotational Raman spectrum of HD. **(3)**

13. Two half cells of hydrogen-oxygen fuel cell under basic conditions can be depicted as $OH^-/O_2(g)/Pt$ and $OH^-/H_2(g)/Pt$ and their standard electrode potentials at 25°C are 0.4009 and –0.8279 V respectively. Write the half cell reactions and the complete cell reaction. Depict the complete cell and calculate the emf of the cell. **(5)**

14. The solubility of Ag_2CrO_4 in water is 8×10^{-5} mol kg^{-1} at 25°C and its solubility in 0.04 mol kg^{-1} $NaNO_3$ solution is 8.84×10^{-5} mol kg^{-1}. What is the mean ionic activity coefficient of Ag_2CrO_4 in 0.04 mol kg^{-1} $NaNO_3$? **(5)**

15. The formation of phosgene by the reaction $CO + Cl_2 \rightarrow COCl_2$ appears to follow the mechanism:

$$Cl_2 \xrightarrow{k_1} 2Cl$$

$$Cl + CO \xrightarrow{k_2} COCl$$

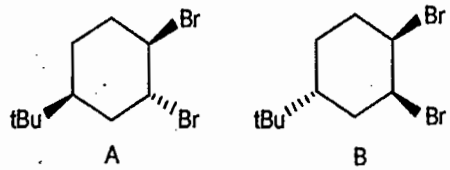
$$COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$$

$$COCl \xrightarrow{k_4} CO + Cl$$

$$2Cl \xrightarrow{k_5} Cl_2$$

Assuming that the intermediates COCl and Cl are in a steady state, find the rate law for the formation of $COCl_2$. **(5)**

16.1. Account for the fact that only one of the following compounds A and B give the expected elimination product with KI in acetone. **(3)**



16.2. Account for the fact that aniline is not a suitable substrate in the Friedel-Crafts alkylation reaction. **(2)**

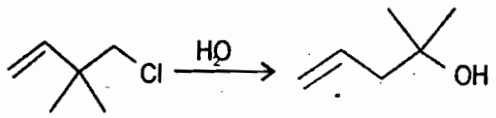
17. Suggest a suitable method and write all the steps for the following transformations:

(*i*) anisole to 2-cyclohexenone **(2)**

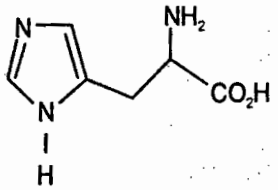
(*ii*) malonic ester to cyclobutanecraboxylic acid **(3)**

18.1. An industrial preparation of phenol and acetone makes use of cumene and atmospheric oxygen as starting materials to produce cumene hydroperoxide which is then converted to products. Suggest what steps are involved in the process. **(3)**

18.2. Suggest a plausible mechanism for the following hydrolysis reaction. **(2)**

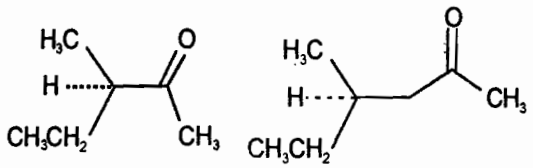


19.1. Explain briefly which nitrogen of the side chain ring of histidine is protonated in the monocationic form? **(2)**



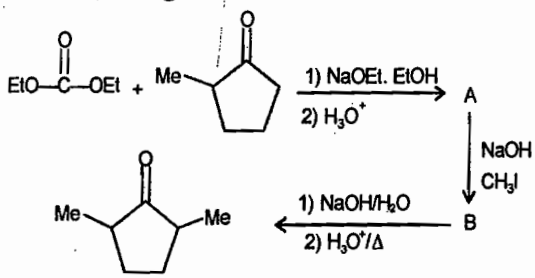
(Histidine)

19.2 Optically active ketone A undergoes racemization in basic solution. Suggest a mechanism for this process. Explain whether ketone B would also recemize in basic solution? **(3)**

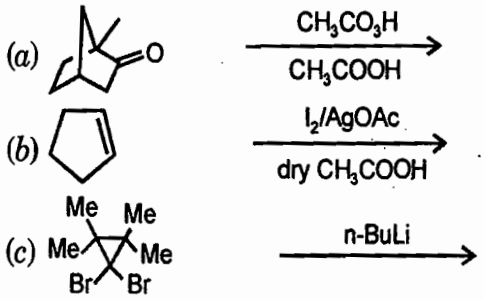


A B

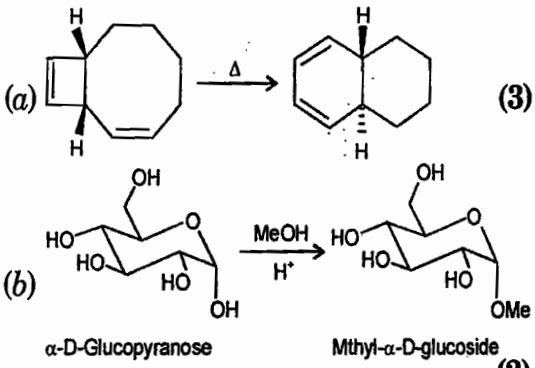
20.1. Write the missing products, A and B in the following reaction scheme. **(2)**



20.2. Write the structure of the major product in the following reactions. **(1 × 3 = 3)**



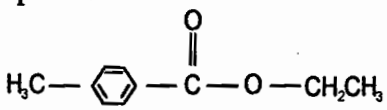
21. Suggest a suitable mechanism for each of the following reactions.



(3)

(2)

22.1. Predict the approximate chemical shifts and multiplicities for the absorptions in the ^1H NMR spectrum of the following compound. **(2)**



22.2 Explain how the peaks at m/z 115, 101 and 73 arise in the mass spectrum of 3-methyl-3-heptanol. **(3)**

ANSWERS

1.1. (*b*)	**1.2.** (*b*)	**1.3.** (*a*)	**1.4.** (*b*)	**1.5.** (*b*)	**1.6.** (*b*)	**1.7.** (*c*)	**1.8.** (*b*)
1.9. (*c*)	**1.10.** (*d*)	**1.11.** (*c*)	**1.12.** (*c*)	**1.13.** (*a*)	**1.14.** (*a*)	**1.15.** (*b*)	**1.16.** (*b*)
1.17. (*c*)	**1.18.** (*a*)	**1.19.** (*b*)	**1.20.** (*c*)	**1.21.** (*d*)	**1.22.** (*b*)	**1.23.** (*b*)	**1.24.** (*c*)
1.25. (*b*)	**2.1.** (*a*)	**2.2.** (*a*)	**2.3.** (*d*)	**2.4.** (*a*)	**2.5.** (*d*)	**2.6.** (*d*)	**2.7.** (*d*)
2.8. (*d*)	**2.9.** (*b*)	**2.10.** (*b*)	**2.11.** (*b*)	**2.12.** (*d*)	**2.13.** (*c*)	**2.14.** (*c*)	**2.15.** (*c*)
2.16. (*c*)	**2.17.** (*d*)	**2.18.** (*d*)	**2.19.** (*b*)	**2.20.** (*b*)	**2.21.** (*c*)	**2.22.** (*a*)	**2.23.** (*d*)

EXPLANATIONS

1.3. More basic due to more basicity of C than silicon.

1.5. Because the electrons count is different for all the compound.

1.6. $CO_2\ (CO)_8$ has two different CO atom belonging to 4 metal – metal bond.

1.10. Because others are migercede having non bonding orbitals.

1.13. Mole Fraction of component is inversly proportional to vapour pressure.

1.14. Because graph is straight line.

1.16.
$$K_p = \frac{P_B \times P_C}{P_A}$$

$$\therefore \left\{\left(\frac{a-x}{a+x}\right)p\right\}^2 = \left(\frac{x}{a+x}\right)p$$

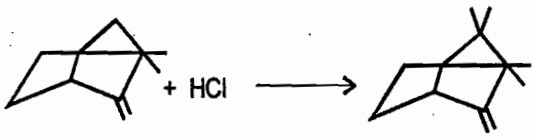
1.17.
$$K_b = \frac{RT_0^2}{L_v 1000}$$

$$K_f = \frac{RT_0^2}{L_f 1000}$$

1.18. Exhibiting optical isomerism link dextro, levo, mero and vacunic mixture.

1.22. Because canrotation takes place.

1.23.



1.25. B-Ketoacids undergo further decarboxylation.

2.4. Acidity of Boron halides decreases with electronegativity of halogen atoms.

2.5. E.A.No = 24 + 2 × 6 = 36

2.8. Orange colour arise due to charge transfer.

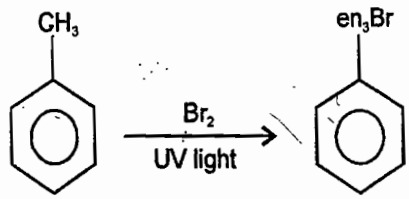
2.9. Bond length decreases with increasing bond order.

2.13. Because chemical potential is of different compounds.

2.15. Spontancity will occur only when energy will be greater than zero.

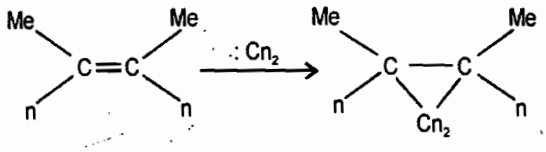
2.17. For adiabatic reversible expansion by P versus – y is linear.

2.18.



2.20. Hexyne + Disiamylborane $\xrightarrow[H_2O_2]{\text{Oxidatron}}$ Hexanol

2.21.



GATE - 2001

CY : CHEMISTRY

Duration: Three Hours | *Maximum Marks*: 100

Useful Data:

Atomic Numbers :

B = 5, C = 6, F = 9, Mg = 12, Al = 13, P = 15, S = 16, Ti = 22, V = 23, Cr = 24, Mn = 25, Fe = 26, Co = 27, Ni = 28, Cu = 29, Ir = 77, U = 92, Am = 95, Cm = 96, Cf = 98.

Atomic mass : H, 1 amu; D, 2 amu. 1 amu = 1.66×10^{-27} kg

Gas Constant, R =0.083143 L bar k^{-1} mol^{-1} = 8.3143 K^{-1} mol^{-1}

Faraday Constant F =96,484.6 C mol^{-1}

Debye Hiickel coefficient for aqueous solutions,

A =0.509 $kg^{1/2}$ $mol^{-1/2}$ at 25°C

SECTION–A (75 Marks)

1. *This question consists of TWENTY FIVE sub-questions (1.1-1.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which onlly one is correct. Answer each sub-question by darkening the appropriate bubble on the OBJECTIVE RESPONSE SHEET (ORS) using a soft HB pencil. Do not use the ORS for any rough work. You may like to use the Answer Book for any rough work, if needed.*

1.1. Icosahedral structure is generally exhibited by

(*a*) C (*b*) Si

(*c*) Ge (*d*) B

1.2. The hybrid orbitals used by bromine atom in BrF_3 are

(*a*) sp^2 (*b*) sp^3

(*c*) sp^3d (*d*) sp^3d^2

1.3. The metal ion present in carbonic anhydrase is

(*a*) Mn (*b*) Zn

(*c*) Cu (*d*) Fe

1.4. The most acidic aqua ion is

(*a*) $Fe(H_2O)_6^{3+}$ (*b*) $Co(H_2O)_6^{3+}$

(*c*) $Ti(H_2O)_6^{3+}$ (*d*) $Cr(H_2O)_6^{3+}$

1.5. Which one of the following metal fragments, $d^n - ML_m$, is isolobal with CH?

(*a*) $d^7 - ML_5$ (*b*) $d^8 - ML_4$

(*c*) $d^9 - ML_3$ (*d*) $d^5 - ML_6$

1.6. The softest acid amongst the following is

(*a*) Al^{3+} (*b*) Li^+

(*c*) Ca^{2+} (*d*) Ag^+

1.7. The chromium (III) species formed soon after electron transfer between $IrCl_6^{2-}$ and $Cr(H_2O)_6^{2+}$ is

(*a*) $Cr(H_2O)_6^{3+}$ (*b*) $Cr(H_2O)_5Cl^{2+}$

(*c*) $CrCl_6^{3-}$ (*d*) $Cr(H_2O)_3Cl_3$

1.8. The strongest reducing ion of the following is

(*a*) U^{3+} (*b*) Am^{3+}

(*c*) Cm^{3+} (*d*) Cf^{3+}

1.9. The first ionization potential of Mg, Al, P and S follows the order

(*a*) Mg < Al < P < S (*b*) Al < Mg < P < S

(*c*) Al < Mg < S < P (*d*) Mg < Al < S < P

1.10. As per the uncertainty principle, $\Delta x \cdot \Delta p_y =$

(*a*) h (*b*) $h/2\pi$

(*c*) λ (*d*) zero

1.11. The second lower state of particle in a cubic box is

(*a*) non degenerate

(*b*) doubly degenerate

(*c*) triply degenerate

(*d*) six-fold degenerate

1.12. In comparision to the frequency of the EPR transition, the NMR transition frequency is

(*a*) much higher (*b*) much lower

(*c*) almost same (*d*) none of these

1.13. The symmetry point group of the BF_3 molecule is

(*a*) C_{3v} (*b*) D_{3h}

(*c*) C_{2v} (*d*) D_{2h}

1.14. For an irreversible adiabatic expansion of a perfect gas from volume V_i to V_f, the change in entropy of the gas is

(*a*) $nR\ln(V_f/V_i)$ (*b*) zero

(*c*) less than zero (*d*) greater than zero

1.15. For the cell Ag(s) |AgCl (satd), NaCl(aq, m_1)| NaCl(aq, m_2), AgCl(satd)|Ag(*s*) where m_1 and m_2 are different molalities ($m_1 > m_2$), the standard cell potential is

(*a*) $-RT\ln(m_1/m_2)$ (*b*) zero

(*c*) $-RT\ln(a_1/a_2)$ (*d*) $-FRT\ln(a_1)$

1.16. For an ideal dilute solution, which one of the following statements is correct? (γ and x are activity coefficient and mole fraction respectively)

(*a*) γ (solvent) $\rightarrow 0$ as x (solvent) $\rightarrow 1$

(*b*) γ (solute) $\rightarrow 1$ as x (solute) $\rightarrow 1$

(*c*) γ (solvent) $\rightarrow 1$ as x (solvent) $\rightarrow 1$

(*d*) γ (solvent) $\rightarrow 0$ as x (solvent) $\rightarrow 1$

1.17. For the reaction :

$Br_2(g) + BF_2(g) \rightarrow 2BrF_3(g)$, the equilibrium constant at 2000 K and 1.0 bar is 5.25. When the pressure is increased by 8-fold, the equilibrium constant

(*a*) increases by a factor of 1.86

(*b*) decreases by a factor of 1.86

(*c*) remains same

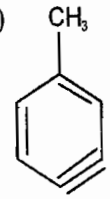
(*d*) increases by a factor of 8

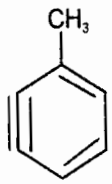
1.18. 2-Phenyl ethanol may be prepared by the reaction of phenyl magnesium bromide with

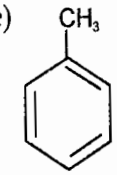
(*a*) HCHO (*b*) CH_3CHO

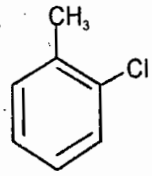
(*c*) CH_3COCH_3 (*d*)

1.19. *o*-Chlorotoluene reacts with sodamide in liquid ammonia to give *o*-toluidine, and *m*-toluidine. This reaction proceeds through an intermediate.

(*a*) 

(*b*) 

(*c*) 

(*d*) 

1.20. The number of signals observed in ^1H NMR spectrum of 3, 5-dibromotoluene is

(*a*) 3 (*b*) 4

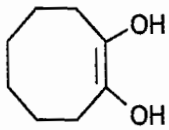
(*c*) 2 (*d*) 6

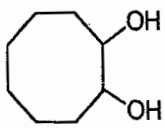
1.21. Which one of the following molecules will have $n \rightarrow \pi^*$ transition at the longest wavelength?

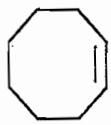
(*a*) HCHO (*b*) $CH_3COC_2H_5$

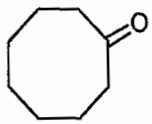
(*c*) $C_6H_5COC_6H_5$ (*d*) $CH_3COC_6H_5$

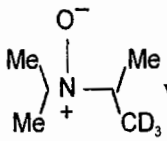
1.22. The reaction of cyclooctyne with $HgSO_4$ in the presence of aqueous H_2SO_4 gives

(*a*) 

(*b*) 

(*c*) 

(*d*) 

1.23. Pyrolysis of 

would be

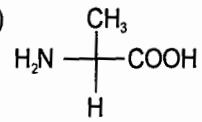
(*a*) A mixture of $CH_2 = CH - CD_3$ and $CH_3 - CH = CD_2$

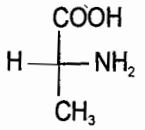
(*b*) $CH_3 - CH = CD_2$

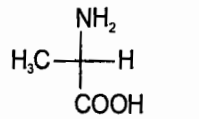
(*c*) $Me_2N^+ = C(CD)_3(CH_3)$

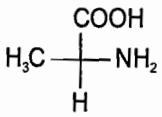
(*d*) $CH_2 = CH - CD_3$

1.24. Amongst the following amino acids, the (R)– enantiomer is represented by

(*a*) 

(*b*) 

(*c*) 

(*d*) 

1.25. Arrange the following halides in the decreasing order of SN^1 reactivity

$CH_3CH_2CH_2Cl$, $CH_2 = CHCH(Cl)CH_3$, $CH_3CH_2CH(Cl)CH$

(I) (II) (III)

(*a*) I > II > III (*b*) II > I > III

(*c*) II > III > I (*d*) III > II > I

2. *This question consists of TWENTY FIVE sub-questions (2.1 – 2.25) of TWO marks each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct. Answer each sub-question by darkening the appropriate bubble on the OBJECTIVE RESPONSE SHEET (ORS) using a soft HB pencil. Do not use the ORS for any rough work. You may like to use the Answer Book for any rough work, if needed.*

2.1. The volume of 1 N $KMnO_4$ required to reach equivalence point in the titration with 0.01 mole of ferrous oxalate dissolved in dilute H_2SO_4 is

(*a*) 3 cm^3 (*b*) 30 cm^3

(*c*) 10 cm^3 (*d*) 20 cm^3

2.2. The number of possible geometrical isomers for octahedral $Co(ox)(PMe_3)_2NH_3Cl$ complex is

(*a*) 2 (*b*) 3

(*c*) 4 (*d*) 5

2.3. Among the following, the paramagnetic species is

(*a*) B_2 (*b*) C_2

(*c*) O_2^{2-} (*d*) CO

2.4. The purple colour of iodine vapours is due to

(*a*) *d-d* transition

(*b*) $\pi - \sigma^*$ transition

(*c*) charge-transfer transition

(*d*) $\pi^* - \sigma^*$ transition

2.5. Amongst the following, the strongest oxidizing anion is

(*a*) CrO_4^{2-} (*b*) VO_4^{3-}

(*c*) FeO_4^{2-} (*d*) MnO_4^{2-}

2.6. ^{19}F NMR spectrum of meridional isomer of octahedral $RhCl_3F_3$ complex, [^{103}Rh (I = ½); ^{19}F (I = ½)] assuming $J_{Rh-F} > J_{F-F}$, will show

(*a*) one doublet

(*b*) two doublets and one triplet

(*c*) two doublets and two triplets

(*d*) one singlet and two triplets

2.7. Which one of the following will show *closo* structure?

(*a*) B_5H_9 (*b*) $B_{12}H_{12}^{2-}$

(*c*) B_4H_{10} (*d*) B_5H_{11}

2.8. The correct order of energy level of *d*-orbitals in ferrocene is

(*a*) $dx^2 - y^2, dxy < dz^2 < dxz, dyz$

(*b*) $dz^2 < dxz, dyz < dx^2 - y^2, dxy$

(*c*) $dx^2 - y^2, dxy < dxz, dyz < dz^2$

(*d*) $dyz, dxz < dx^2 - y^2, dxy < dz^2$

2.9. Two moles of a monoatomic perfect gas initially at 4.0 bar and 47°C undergoes reversible expansion in an insulated container. The temperature at which the pressure reduces to 3.0 bar is

(*a*) 200 K (*b*) 285 K

(*c*) 310 K (*d*) 320 K

2.10. The mean ionic activity coefficient of 0.0005 mol kg^{-1} $CaCl_2$ in water at 25°C is

(*a*) 0.98 (*b*) 0.67

(*c*) 0.81 (*d*) 0.91

2.11. For the cell : $Cd(Hg) \mid CdSO_4\,(8/3)\,H_2O(s) \mid CdSO_4(aq, \text{satd.}) \mid Hg_2SO_4(s) \mid Hg$

The temperature dependence of emf in Volts is given by

$B = 1.0185 - 4.05 \times 10^{-5}(T - 293) - 9.5 \times 10^{-7}(T - 293)^2$

The change in entropy at 25°C for the cell reaction is

(*a*) $-253\ K^{-1}\ mol^{-1}$

(*b*) $9.65\ J\ K^{-1}\ mol^{-1}$

(*c*) $8.3 \times 10^{-4}\ J\ K^{-1}\ mol^{-1}$

(*d*) zero

2.12. Two separate bulbs contain ideal gases A and B respectively. The density of gas A is twice that of gas B and molecular weight of gas A is half of that of gas B. The ratio of pressure of gas A to that of gas B is

(*a*) 3 (*b*) 6

(*c*) 4 (*d*) 1

2.13. Choose the correct criterion of spontaneity in terms of the properties of the system alone.

(*a*) $(dS)_{U,V} > 0$ (*b*) $(dS)_{T,P} > 0$

(*c*) $(dS)_{H,P} < 0$ (*d*) $(dG)_{T,V} < 0$

2.14. Compared to C_2H_6, the value of van der Wall's constant "*a*" and "*b*" for He will be

(*a*) both will be smaller

(*b*) "*a*" will be larger but "*b*" will be smaller

(*c*) "*b*" will be larger but "*a*" will be smaller

(*d*) both will be larger

2.15. When 1.0 mol of a perfect gas expands from 5.0 dm^3 to 25.0 dm^3 isothermally at 25°C, it yields 3.99 kJ of work. The process of expansion was

(*a*) reversible

(*b*) irreversible

(*c*) without change in entropy

(*d*) against $p_{ex} = 0$

2.16. Given than $\Psi_{n,l,m}(r, \theta, \phi) = R_{nl}(r)\,Y_{lm}(\theta, \phi)$; $R_{20}(r) \propto (2 - r/a_o)\,e^{-r/ao}$; $Y_{0,0}(\theta, \phi) = 1/\sqrt{4\pi}$

The position of radial node in the 2*s* orbital is at

(*a*) $r = a_o$ (*b*) $r = 2a_o$

(*c*) $r = a_o/2$ (*d*) $r = a_o/4$

2.17. Consider the following reaction and use the data given below

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$\Delta H^0(25°C) = -92.2$ kJ

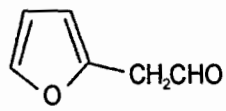
Substance	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$C_p/(J\ K^{-1}\ mol^{-1})$	29.1	28.8	35.1

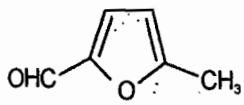
Assuming C_p to be independent of temperature, the reaction at 100°C compared to that at 25°C will be

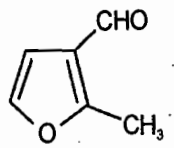
(*a*) endothermic (*b*) less exothermic

(*c*) more exothermic (*d*) having $\Delta H° = 0$

2.18. The reaction of 2-methylfuran with DMF-$POCl_3$ would give

(*a*)


(*b*)


(*c*)


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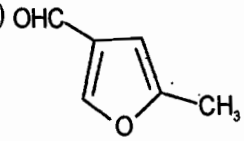
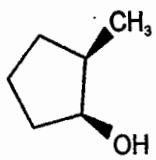
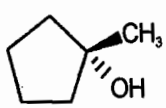


2.19. The major product formed duirng the **hydroboration-oxidation** of 1-methyl cyclopentene is

(*a*)


(*b*)


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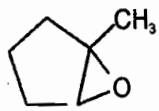
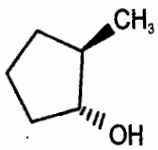


(*d*)


2.20. Which one of the following carbonyl compounds will give a gragment ion at $m/z = 58$ in their mass spectra?

(*a*) $C_2H_5CH(CH_3)CHO$

(*b*) $CH_3CH_2CH_2CH_2CHO$

(*c*) $CH_3CH_2CH_2COCD_3$

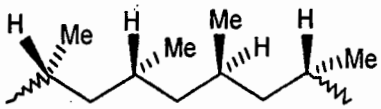
(*d*) $(CH_3)_2CHCH_2CHO$

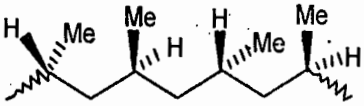
2.21. The decreasing order of reactivity of *meta*-nitrobromobenzene (I); 2, 4, 6-trinitrobromobenzene (II); *para*-nitrobromobenzene (III); and 2, 4-dinitrobromobenzene (IV) towards OH^- ions is

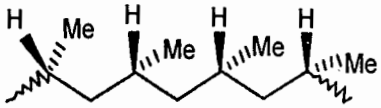
(*a*) I > II > III > IV (*b*) II > IV > III > I

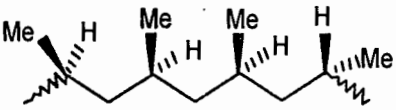
(*c*) IV > II > III > I (*d*) II > IV > I > III

2.22. Identify the isotactic polypropylene from the following

(*a*) 

(*b*) 

(*c*) 

(*d*) 

2.23. Which one of the following compounds will form an **osazone** derivative?

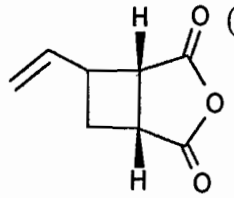
(*a*) $CH_3CH_2COCH_2OH$

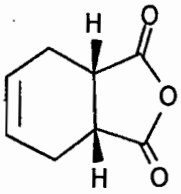
(*b*) $CH_3COCH_2CH_2OH$

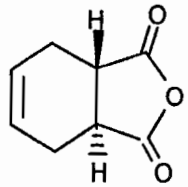
(*c*) $CH_3CH_2CHOHCH_2OH$

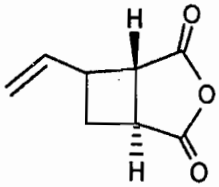
(*d*) $CH_3CH_2COCH_2OCH_3$

2.24. Buta-1, 3-diene on heating with maleic anhydride would give

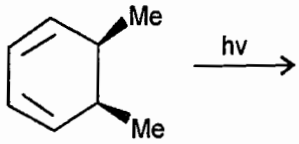
(*a*) 

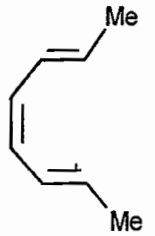
(*b*) 

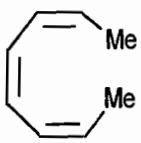
(*c*) 

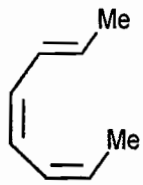
(*d*) 

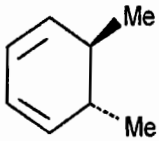
2.25. The product obtained during the following photochemical reaction is



(*a*) 

(*b*) 

(*c*) 

(*d*) 

SECTION–B (75 Marks)

This section contains TWENTY questions of FIVE marks each. ANY FIFTEEN out of these questions have to be answered on the Answer Book provided.

3.1. There are two isomers of $Pi(NH_3)_2Cl_2$. X and Y. When X is reacted with thiurea (tu). $Pt(tu)_4^{2+}$ is formed while Y on reaction with thiourea yields $Pt(NH_3)_2(tu)_2$. Identify X and Y and explain the reaction. **(3)**

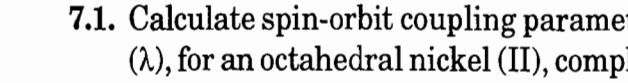
3.2. Ligand substitution reaction on metal clusters are often found to occur by associative mechanism by breaking of a M-M bond and thereby providing an open coordination site for the incoming ligand. Which one of the two clusters, $Co_4(CO)_{12}$ of $Ir_4(CO)_{12}$ is expected to undergo faster exchange with ^{13}CO? Suggest an explanation. **(2)**

4.1. Using crystal-field theory, account for the fast that in square-pyramidal $[Ni(CN)_5]^{3-}$ ion, the axial Ni – C bond (217 pm) is longer than Ni – C basal bonds (187 pm), while in trigonal bipyramidal $[CuCl_5]^{3-}$ ion, the axial Cu – Cl bonds (229 pm) are shorter than the Cu – Cl equatorial ones (239 pm). **(3)**

4.2. Between complexes $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5Br]^{2+}$ which one should have a lower energy charge-transfer band and why? **(2)**

5. Write the Russell-Saunders terms of the configuration p^1d^1 and identify the ground term. Indicate population of electrons in different *d*-orbitals corresponding to $^3T_{1g}(F)$, $^3T_{2g}(F)$ and $^3A_{2g}(F)$ states for d^2 configuration in octahedral symmetry. **(5)**

6.1. Propose the structure of compounds **A**, **B** and **C** satisfying EAN rule in the following reactions: **(3)**



6.2. Explain why 16-or 14-electron configurations are favoured over 18-electron configurations for the elements at the end of the transition series? **(2)**

7.1. Calculate spin-orbit coupling parameter (λ), for an octahedral nickel (II), complex exhibiting spin allowed *d-d* bands at 10,750 cm^{-1}, 17,500 cm^{-1} and 28,200 cm^{-1} respectively. The experimentally determined magnetic moment is 3.2 BM. **(3)**

7.2. Explain why pKa of $(CH_3)_3$ SiOH (pKa $\approx$ 11) is lower than that of $(CH_3)_3$ COH (pKa $\approx$ 16). **(2)**

8.1. Define capacity factor. What is the effect of large capacity factor on the separation of analytes? How can capacity factors be optimized in gas chromatography? **(3)**

8.2. What prevents simple iron porphyrins from functioning as O_2 carriers like haemoglobin? **(2)**

9. Identify all the symmetry operations for HCHO with rotation axis as the *z*-axis and plane of the molecule being the *yz* plane. Will the transition from an a_1 to b_1 orbital be allowed in HCHO? What will be the polarization of the corresponding $b_1 \rightarrow a_1$ emission? **(5)**

10.1. Using quantization condition for de Broglie wavelength on a ring, derive the expression for rotational energy levels of a rigid homonuclear diatomic rotor of bond length $2r$. **(2)**

10.2. Given $\psi_n(x) = (2)^{1/2} \sin(n\pi x)$, show that eigen functions $\psi_1(x)$ and $\psi_2(x)$ of a particle in a one dimensional box of length 1 are orthogonal. **(3)**

11. The emf of the cell Ag(*s*)|AgCl (satd), KCl (0.05 mol dm^{-3})| $AgNO_3$(0.1 mol dm^{-3}) |Ag(*s*) is 0.431 V at 298.15 K. The mean avtivity coefficient of KCl is 0.817 and that of $AgNO_3$ is 0.723. Calculate the solubility product of AgCl at 25°C. **(5)**

12.1. A paramagnetic substance ($A_2B_3 \cdot 5H_2O$) initially at T = 0.30 K was magnetized by application of strong magnetic field while the sample was surrounded by helium gas in contact with a cold reservoir. Subsequently, helium gas was pumped away and the magnetic field was slowly reduced to zero. Calculate the change in temperature of the sample using the data given below: **(3)**

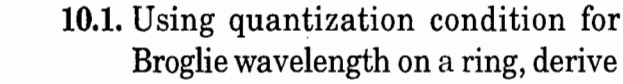
Unmagnetized sample		*Magnetized sample*	
T/K	*S/(JK^{-1} mol^{-1})*	*T/K*	*S/(JK^{-1} mol^{-1})*
0.30	0.40	0.30	0.19
0.25	0.32	0.25	0.15
0.18	0.19	0.20	0.12
0. 15	0.14	0.15	0.10

12.2. When 2 moles of liquid **A** and 4 moles of liquid **B** are mixed, experimental measurements give entropy of mixing as 42 J K^{-1}. Show whether the solution **AB** thus formed is ideal or not. **(2)**

13.1. The LCAOs : $\phi_1 = (1_{sA} + 1_{sB})$ and $\phi_2 = (1_{sA} - 1_{sB})$ approximate the lowest σ and σ^* orbitals of H_2^+ respectively. Show that the σLCAO is of *g*-type and σ^* *u* type. [1_{s_A} and 1_{s_B} are the 1's orbitals centered on H_A and H_B of $(H_A - H_B)^+$]. **(2)**

13.2. The fundamental vibrational frequency of HCl is 2885 cm^{-1}. Assuming that HCl and DCl may be treated as Simple Harmonic Oscillator, calculate the fundamental frequency of DCl. **(3)**

14.1. The conversion of A to B and C goes through the following mechanism



Show that the equilibrium constant (K) of the overall reaction is

$$K = \frac{k_1 k_3}{k_2 k_4}$$ **(3)**

14.2. The rate of the acid catalyzed hydrolysis of ethylaccetate in HCl solution obeys the following rate law

Rate $= -d[\text{ester}]/dt = k[\text{ester}][\text{HCl}]$

where $k = 0.1$ mol^{-1} dm^{-3} h^{-1}. Neglecting any back reactioon, calculate the time required for half the ester to be hydrolyzed if the initial concentration of ester and HCl are 0.02 mol dm^{-3} and 0.01 mol dm^{-3} respectively **(2)**

15.1. Using the data given below, calculate the equilibrium constant and enthalpy of the following reaction at 25°C. **(3)**

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Substance	$\Delta G_f^\circ/(kJ\ mol^{-1})$	$S^\circ/(JK^{-1}\ mol^{-1})$
$NO_2(g)$	51.31	240.06
$N_2O_4(g)$	97.89	304.29

15.2. When 1.0 mol of $CH_4(g)$ is oxidized to carbon dioxide and water according to the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

the corresponding thermodynamic parameters are: $\Delta H^\circ = -890$ kJ mol^{-1}, and $\Delta S^\circ = -140.3$ JK^{-1} mol^{-1}. Assuming ideal gas behaviour, calculate the amount of energy that can be extracted as work at 25°C. **(2)**

16. Acid catalyzed dehydration of a tertiary alcohol A($C_6H_{14}O$) gives one major compound B, and one minor compound C both having molecular formula C_6H_{12}. Spectroscopic data of these compounds are as follows:

Compound B:

IR: 1660 cm^{-1}, 3080 cm^{-1}

^{1}H NMR δ: 0.91 (*t*, J = 7 Hz, 3H), 1.60 (*s*, 3H). 1.70 (*s*, 3H), 1.98 (quin, J = 7 Hz, 2H), 5.08 (*t*, J = 7 Hz, 1 H)

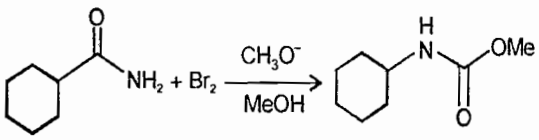
Compound C:

IR: 1640 cm^{-1}, 3090 cm^{-1}

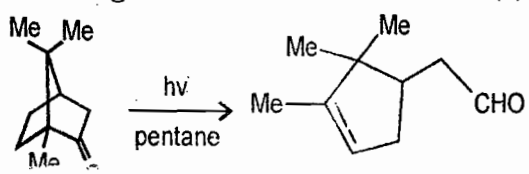
^{1}H NMR δ: 0.92 (*t*, J = 7 Hz, 3H), 1.40 (sextet, J = 7Hz, 2H), 1.74 (*s*, 3H), 2.02 (*t*, J = 7 Hz, 2H), 4.78(*s*, 2H)

Deduce the structure of A, B and C. **(5)**

17.1. Suggest a plausible mechanism for the following reaction **(3)**

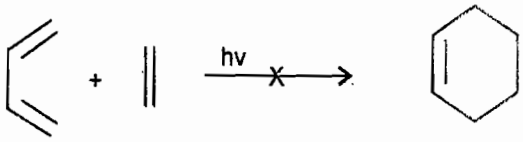


17.2. Propose a mechanism for the photochemical reaction given below. **(2)**

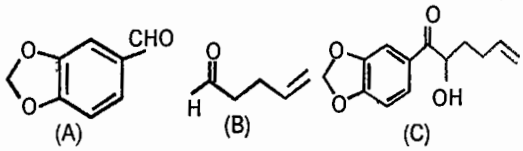


18.1. Draw π orbitals of buta-1, 3-diene and ethylene, and identify their HOMO and LUMO. **(3)**

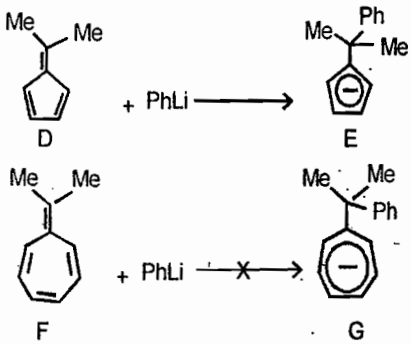
18.2. Using "frontier orbital concept", explain why the $\pi^{4s} + \pi^{2s}$ cycloaddition given below is **photochemically not allowed**? **(2)**



19.1. Suggest a synthetic route to the hydroxy-ketone C using A and B starting materials. **(3)**

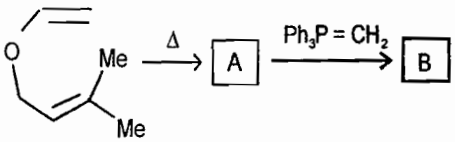


19.2 The reaction of dimethyl fulvene D with PhLi readily gives the anion E. However, the analogous compound F does not react with PhLi to give the corresponding anion G. Explain. **(2)**

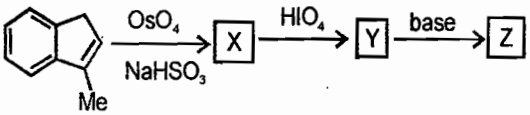


20.1. Outline a synthesis of *para*-nitropropyl-benzene from benzene **(3)**

20.2. Predict the products in the following reactions **(2)**

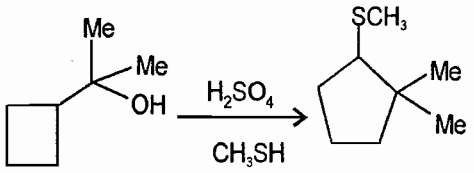


21.1. Write the structure of the products X, Y and Z in the following sequence of reactions. **(3)**

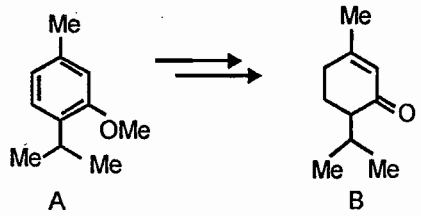


21.2. D-Glucose and D-fructose interconvert into each other in aqueous alkaline solution. Suggest a mechanism for the interconversion. **(2)**

22.1. Propose a mechanism of the following reaction. **(3)**



22.2 Suggest a route for synthesis of the enone B from A. **(2)**



ANSWERS

1.1. (*c*)	**1.2.** (*c*)	**1.3.** (*b*)	**1.4.** (*c*)	**1.5.** (*d*)	**1.6.** (*d*)	**1.7.** (*d*)	**1.8.** (*d*)	**1.9.** (*d*)
1.10. (*b*)	**1.11.** (*d*)	**1.12.** (*a*)	**1.13.** (*b*)	**1.14.** (*c*)	**1.15.** (*c*)	**1.16.** (*d*)	**1.17.** (*b*)	**1.18.** (*b*)
1.19. (*b*)	**1.20.** (*b*)	**1.21.** (*c*)	**1.22.** (*d*)	**1.23.** (*c*)	**1.24.** (*a*)	**1.25.** (*c*)	**2.1.** (*c*)	**2.2.** (*c*)
2.3. (*a*)	**2.4.** (*d*)	**2.5.** (*a*)	**2.6.** (*b*)	**2.7.** (*b*)	**2.8.** (*b*)	**2.9.** (*d*)	**2.10.** (*a*)	**2.11.** (*c*)
2.12. (*c*)	**2.13.** (*a*)	**2.14.** (*b*)	**2.15.** (*b*)	**2.16.** (*c*)	**2.17.** (*c*)	**2.18.** (*a*)	**2.19.** (*a*)	**2.20.** (*d*)
2.21. (*b*)	**2.22.** (*d*)	**2.23.** (*c*)	**2.24.** (*a*)	**2.25.** (*b*)				

EXPLANATIONS

1.2. It will use hybrid orbital obtained after mixing of orbitals.

1.4. Because T_i can donate its d-electron very easily.

1.7. $IrCl_6^{2-} + Cr(H_2O)_6^{2+} \rightarrow Cr(H_2O)_3Cl_3$

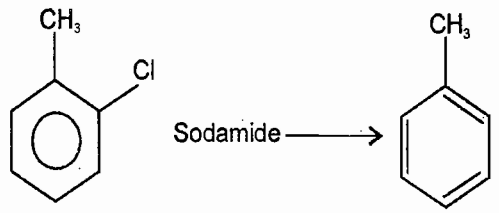
1.9. Because phosphorous have half filled orbital.

1.12. Because two types of magnetic interaction taxes place.

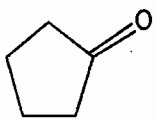
1.16. Because activity coefficient is zero initially.

1.18. Phenyl magnesium bromid + $CH_3CH_0 \rightarrow$ 2-phenylethanl.

1.19.



1.22. Cycloctyne + $HgSO_4$ $\xrightarrow[\text{aq.}]{H_2SO_4}$



1.25. SN^1 reactivity depends on halide connected with α-carbon.

2.3. Paramagnetic species are those which have unpaired electron in their molecular orbital configuration.

2.5. Because they do not obey E.A.N. rule.

2.7. Since cage like structure is called closo structure.

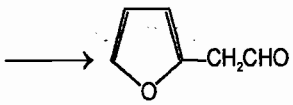
2.8. It will depend on molecular orbital configuration.

2.12. Because pressure is directly proportional to density pressure is inversely proportional to mole wt.

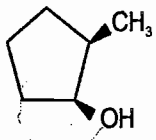
2.13. Since energy should be greater than zero.

2.14. For spontaniety

2.18. 2-methyl furan + $POCl_3$(DMF)

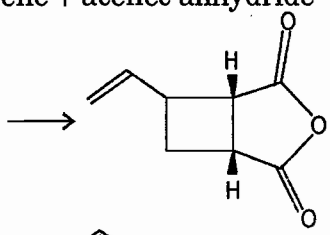


2.19. methyl cyclopentane $\xrightarrow[\text{Oxidation}]{\text{Hydroboration}}$

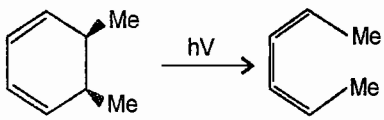


2.21. Because necleoperile is para oriented.

2.24. Buta – 1, 3 – diene + aceliec anhydride



2.25.



GATE - 2002

CY : CHEMISTRY

Duration: Three Hours | *Maximum Marks*: 100

Useful Data:

Atomic Numbers:

Ti = 22, V = 23, Cr = 24, Mn = 25, Fe = 26, Co = 27, Ni = 28, Cu = 29

Atomic mass : H, 1 amu; D, 2 amu; Cu, 63.6 amu. 1 amu = 1.66×10^{-27} kg.

Gas constant	$R = 8.314\ JK^{-1}\ mol^{-1}$
Faraday Constant	$F = 96{,}500\ C\ mol^{-1}$, 1 cal = 4.184 J
Avogadro number	$N = 6.023 \times 10^{23}\ mole^{-1}$
Planck's constant	$h = 6.626 \times 10^{-34}$ Js
Velocity of light	$c = 3 \times 10^{8}\ m\ s^{-1}$

Nuclear spin 1 ^{1}H $^{1}/_{2}$, ^{13}C $^{1}/_{2}$, ^{19}F $^{1}/_{2}$, ^{35}Cl 3/2

SECTION–A (75 Marks)

1. *This question consists of TWENTY FIVE sub-questions (1.1 – 1.25) of ONE mark each. Four each of these sub-questions, four possible answers (A, B, C and D) are given, out of which only one is correct. Answer each sub-question by darkening the appropriate bubble on the OBJECTIVE RESPONSE SHEET (ORS) using a soft HB pencil. Do not use the ORS for any rough work. You may like to use the Answer Book for any rough work, if needed.*

1.1. The ground state of aluminium atom is

(*a*) $^{2}P_{1/2}$ (*b*) $^{2}P_{3/2}$

(*c*) $^{4}D_{5/2}$ (*d*) $^{4}D_{1/2}$

1.2. The point group symmetry of the free nitrate ion is

(*a*) D_{3h} (*b*) C_{3v}

(*c*) C_{3h} (*d*) D_3

1.3. The total number of vibrational degrees of freedom of H_2O_2 is

(*a*) 7 (*b*) 6

(*c*) 4 (*d*) 9

1.4. The velocity of the electron in the hydrogen atom

(*a*) increases with increasing principal quantum number

(*b*) decreases with increasing principal quantum number

(*c*) is uniform for any value of the principal quantum number

(*d*) first increases and then decreases with principal quantum number

1.5. The enthalpy of formation of AgCl is obtained from the enthalpy change from which one of the following processes?

(*a*) $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$

(*b*) $Ag(s) + {}^{1}/_{2}\ Cl_2(g) \rightarrow AgCl(s)$

(*c*) $AgCl \rightarrow Ag(s) + {}^{1}/_{2}\ Cl_2(g)$

(*d*) $Ag(s) + AuCl \rightarrow Au(s) + AgCl(s)$

1.6. The nernst equation for the reaction. $A^{2+} + 2e \rightarrow B$, in terms of the free energy change is

(*a*) $\Delta G = \Delta G^{\circ} + 2.303\ RT \ln \frac{[B]}{[A]}$

(*b*) $\Delta G = \Delta G^{\circ} = -2.303\ RT \ln \frac{[B]}{[A]}$

(*c*) $-\Delta G = -\Delta G^{\circ} + 2.303\ RT \ln \frac{[B]}{[A]}$

(*d*) $\Delta G = -\Delta G^{\circ} + 2.303\ RT \ln \frac{[B]}{[A]}$

1.7. 0.1 M aqueous solution of which of the following compounds will exhibit the largest depression of freezing point?

(*a*) KCl (*b*) $C_6H_{12}O_6$

(*c*) K_2SO_4 (*d*) $Al_2(SO_4)_3$

1.8. The vapour pressure of a pure solvent is 0.8 atm. A non-volatile substance B is added to the solvent and its vapour pressure drops to 0.6 atm. The mole fraction of the component B in the solution is

(*a*) 0.75 (*b*) 0.50

(*c*) 0.25 (*d*) 0.20

1.9. The existence of two different coloured complexes of $Co(NH_3)4\ Cl_2$ is due to

(*a*) optical isomerism

(*b*) linkage isomerism

(*c*) geometrical isomerism

(*d*) coordination isomerism

1.10. Which of the following species has two nonbonded electron pairs on the central atom?

(*a*) $TeCl_4$ (*b*) ClF_3

(*c*) ICl_2 (*d*) PCl_3

1.11. The complex which obeys the 18 electron rule is

(*a*) $Fe(CO)_4$ (*b*) $Ni(CO)_3(PPh_3)$

(*c*) $Cr(CO)_5$ (*d*) $Cr(C_5H_5)_2$

1.12. When sodium carbonate is added to an aqueous solution of copper sulfate, which one of the following compounds is precipitated?

(*a*) $Cu(CO_3)_2$ (*b*) $Cu(OH)(CO_3)$

(*c*) $Cu(HCO_3)_2$ (*d*) $Cu(OH)_2$

1.13. The complex formed in the brown ring test for nitrates is

(*a*) $[Fe(H_2O)_5NO]^{3+}$

(*b*) $[Fe(H_2O)_5NO]^{2+}$

(*c*) $[Fe(H_2O)_4(NO)_2]^{2+}$

(*d*) $[Fe(H_2O)_4(NO)_2]^{3+}$

1.14. The transmittance of an alcoholic solution of a certain compound at 500 nm is 1 per cent in a 1 cm cell. Its absorbance is

(*a*) 1.0 (*b*) 2.0

(*c*) 2.5 (*d*) 4.0

1.15. The species which has a square planar structure is

(*a*) BF_4^- (*b*) $FeCl_4^-$

(*c*) SF_4 (*d*) XeF_4

1.16. Electron transfer from $Fe(H_2O)_6^{2+}$ to $Fe(H_2O)_6^{3+}$ is likely to occur via

(*a*) *d-d* transition

(*b*) inner sphere electron transfer

(*c*) SN_1 mechanism

(*d*) outer sphere electron transfer

1.17. In allene, hybridization of the central and terminal carbons, respectively, are

(*a*) sp^2 and sp^2 (*b*) sp^2 and sp^3

(*c*) sp and sp^2 (*d*) sp and sp^3

1.18. Among the isomers of C_4H_6 given below, the compound which exhibits an absorption band at 3300 cm^{-1} in the IR spectrum, is

(*a*) 1, 3-butadiene (*b*) 1-butyne

(*c*) 2-butyne (*d*) cyclobutene

1.19. Among formaledhyde, acetaldehyde and benzaldehyde, the aldehydes which undergo Cannizaro's reaction are

(*a*) all the three

(*b*) formaldehyde and acetaldehyde

(*c*) acetaldehyde and benzaldehyde

(*d*) formaldehyde and benzaldehyde

1.20. Reaction of benzyl benzoate with an excess of methylmagnesium bromide generates a mixture of

(*a*) benzyl alcohol and benzoic acid

(*b*) benzyl methyl ether and 2-phenyl-propan-2 ol

(*c*) benzyl alcohol and 2-phenylpropan-2-ol

(*d*) ethyl benzene and benzoic acid

1.21. Benzaladehyde can be prepared by reacting phenylmagnesium bromide with

(*a*) N, N-dimethylformamide

(*b*) carbon dioxide

(*c*) formaldehyde

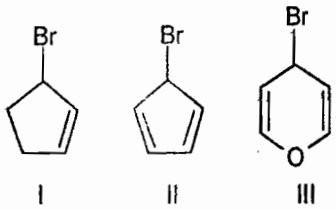
(*d*) ethyl chloroformate

1.22. Proteins are biopolymers. The monomer units present in them are

(*a*) carbohydrates (*b*) amino acids

(*c*) fatty acids (*d*) alkenes

1.23. Among the bromides I-III given below, the order of their reactivity in the SN_1 reaction is



(*a*) III > II > I

(*b*) II > III > I

(*c*) III > I > II

(*d*) II > I > III

1.24. Reaction of phenyl acetate with anhydrous aluminium chloride generates a mixture of

(*a*) ortho-, meta- and para-hydroxyacetophenones

(*b*) meta-and para-hydroxyacetophenones

(*c*) ortho-and meta-hydroxyacetophenones

(*d*) ortho-and para-hydroxyacetophenones

1.25. The major product formed in the reaction of anisole with lithium, liquid ammonia and *t*-butanol is

(*a*) 1-methoxycyclohexa-1, 4-diene

(*b*) 2-methoxycyclohexa-1, 3-diene

(*c*) 1-methoxycyclohexa-1, 3-diene

(*d*) 3-methoxycyclohexa-1, 4-diene

2. *This question consists of TWENTY FIVE sub-questions (2.1 – 2.25) of TWO marks each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct. Answer each sub-question by darkening the appropriate bubble on the OBJECTIVE RESPONSE SHEET (ORS) using a soft HB pencil. Do not use the ORS for any rough work. You could use the Answer Book for any rough work, if needed.*

2.1. Consider an orthorhombic unit cell of dimensions a = 450 pm, b = 650 pm, and c = 400 pm. The perpendicular distance between the (110) planes is

(*a*) 650 pm (*b*) 450 pm

(*c*) 370 pm (*d*) 500 pm

2.2. The spacing between the rotational lines of HF is 40 cm^{-1}. The corresponding spacing between the rotational lines in DF is approximately

(*a*) 20 cm^{-1} (*b*) 30 cm^{-1}

(*c*) 60 cm^{-1} (*d*) 7.5 cm^{-1}

2.3. The activation energy for the decomposition of H_2O_2 is 76 kJ/mol at room temperature and the decomposition is very slow. When a little iodide is added, the activation energy decreases to 57 kJ mol^{-1}. The rate coefficient increases approximately by a factor of

(*a*) 500 (*b*) 1000

(*c*) 2000 (*d*) 50

2.4. The probability of finding a free particle inside the left half of a 1-dimensional box of length L is

(*a*) L/2 (*b*) √(2/L)

(*c*) 2/L (*d*) 1/2

2.5. The force between two electrons separated by 0.1 nm in vacuum ($\varepsilon_0 = 8.854 \times 10^{-12}\ J^{-2}\ C^{-2}\ m^{-1}$) is

(*a*) 2.31×10^{-8} N (*b*) -2.31×10^{-8} N

(*c*) -1.15×10^{-8} N (*d*) 1.155×10^{-8} N

2.6. Assuming that there is no chemical reaction, the change in entropy when 2 mols of N_2, 3 mols of H_2 and 2 mols of HN_3 are mixed at constant temperature is

(*a*) $-62.79\ JK^{-1}$ (*b*) $62.79\ JK^{-1}$

(*c*) $125.58\ JK^{-1}$ (*d*) $-125.58\ JK^{-1}$

2.7. The half-life of a first order reaction varies with temperature according to

(*a*) $\ln t_{1/2} \propto 1/T$ (*b*) $\ln t_{1/2} \propto T$

(*c*) $t_{1/2} \propto 1/T^2$ (*d*) $t_{1/2} \propto T^2$

2.8. The ionization constant of formic acid, which ionizes to an extent of 4.2%, in 0.1 M aqueous solution is

(*a*) 0.92×10^{-2} (*b*) 1.84×10^{-2}

(*c*) 1.84×10^{-4} (*d*) 0.920×10^{-4}

2.9. Radiatioin of 10^{14} Hz falls in the region of

(*a*) radiofrequency (*b*) microwave

(*c*) visible (*d*) X-rays

2.10. The bond order for N2, O2, N_2^-, O_2^- varies as

(*a*) $N_2 > N_2^- > O_2 > O_2^-$

(*b*) $N_2 > O_2 > N_2^- > O_2^-$

(*c*) $O_2 > N_2 > O_2^- > N_2^-$

(*d*) $N_2^- > N_2 > O_2^- > O_2$

2.11. Sodium metal crystallizes in the body centered cubic lattice with cell edge a. The radius of the sodium atom is

(a) $a/\sqrt{2}$ (b) $a\sqrt{3}/2$

(c) $a\sqrt{3}/4$ (d) $a/2\sqrt{2}$

2.12. The metal involved in nitrogenase are

(a) Fe and Mg (b) Mo and K

(c) Mo and Fe (d) Fe and K

2.13. The compolexes $V(C_6H_6)_2$ and $Cr(C_6H_6)_2$ are both readily oxidized in air to their respective cations. The number of unpaired electrons, respectively, in each are

(a) 0, 0 (b) 1, 0

(c) 0, 1 (d) 1, 1

2.14. The lowest energy d-d transition in the Cr(III)complexes varies in the order

(a) $CrCl_6^{3-} < Cr(H_2O)_6^{3+} < Cr(en)_3^{3+} < Cr(CN)_6^{3-}$

(b) $CrCl_6^{3-} < Cr(en)_3^{3+} < Cr(H_2O)_6^{3+} < Cr(CN)_6^{3-}$

(c) $Cr(CN)_6^{3-} < CrCl_6^{30} < Cr(H_2O)_6^{3+} < Cr(en)_3^{3+}$

(d) $Cr(H_2O)_6^{3+} < Cr(en)_3^{3+} < CrCl_6^{3-} < Cr(CN)_6^{3-}$

2.15. The bonding of cyclopentadienyl in $Ti(Cp)_4$ is such that

(a) all Cp rings are pentahapto

(b) one Cp ring is pentahapto and the other three rings are monohapto

(c) two Cp rings are monohapto and the other two rings are pentahapto

(d) all Cp rings are monohapto

2.16. The structures of O_3 and N_3^- are

(a) linear and bent, respectively

(b) both linear

(c) both bent

(d) bent and linear, respectively

2.17. Lability of the ions Cr^{2+}, Mn^{2+} and V^{2+} should follow the order

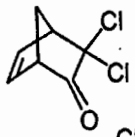
(a) $Cr^{2+} > Mn^{2+} > V^{2+}$

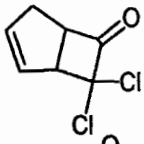
(b) $Mn^{2+} > Cr^{2+} > V^{2+}$

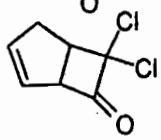
(c) $Mn^{2+} > V^{2+} > Cr^{2+}$

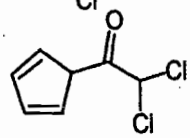
(d) $V^{2+} > Cr^{2+} > Mn^{2+}$

2.18. The major product formed in the reaction of cyclopentadiene with mixture of dichloroacetyl chloride and triethylamine is

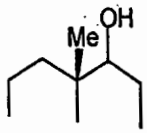
(a) 

(b) 

(c) 

(d) 

2.19. The configurations at the three chiral centres in the bicyclodecanol given below, are



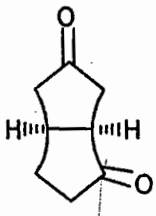
(a) 1S, 2S, 6R

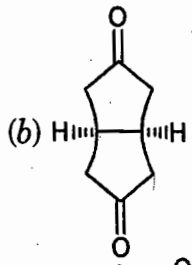
(b) 1S, 2S, 6S

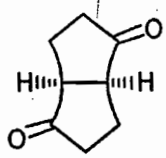
(c) IR, 2S, 6R

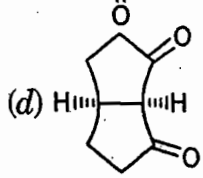
(d) 1R, 2S, 6R

2.20. Among the bicyclo [3.3.0] octanediones given below, which one will exhibit FIVE signals in the broad band decoupled ^{13}C NMR spectrum?

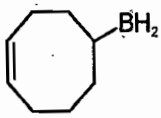
(a) 

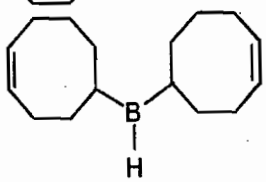
(b) 

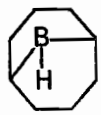
(c) 

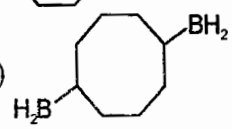
(d) 

2.21. The major product formed in the reaction of 1, 5-cyclooctadiene with 0.5 equivalent of diborane is

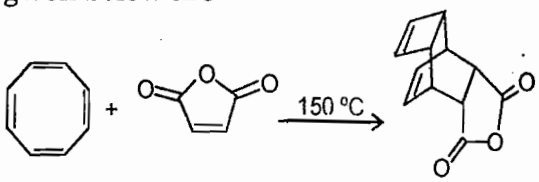
(a) 

(b) 

(c) 

(d) 

2.22. The two pericyclic reactions successively involved in the thermal transformation given below are



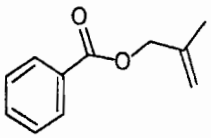
(*a*) 6π-electrocyclization followed by [4 + 2] π-cycloaddition

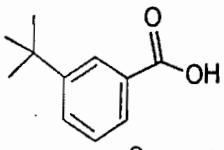
(*b*) 8π-cycloaddition followed by [2 + 2] π-electrocyclization

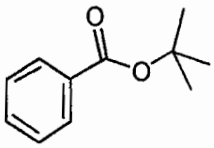
(*c*) 6π-cycloaddition followed by [2 + 2] π-electrocyclization

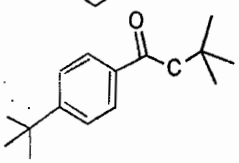
(*d*) 4π-electrocyclization followed by [4 + 2] p-cycloaddition

2.23. The major product formed in the reaction of benzoic acid with isobutylene in the presence of a catalytic amount of sulfuric acid is

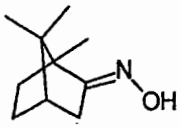
(*a*) 

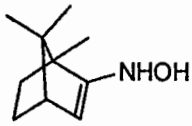
(*b*) 

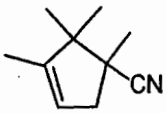
(*c*) 

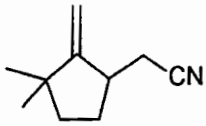
(*d*) 

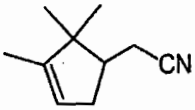
2.24. The major product formed in the reaction of the oxime given below with sulfuric acid is



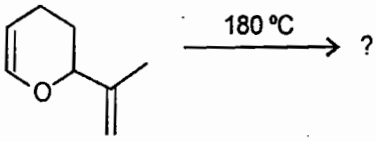
(*a*) 

(*b*) 

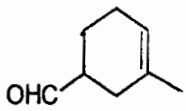
(*c*) 

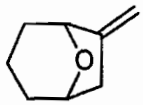
(*d*) 

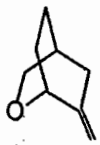
2.25. The major product formed in the thermal reaction given below, is



(*a*) 4(H)-pyran

(*b*) 

(*c*) 

(*d*) 

SECTION–B (75 Marks)

This section consists of TWENTY questions of FIVE marks each. ANY FIFTEEN out of these questions have to be answered on the Answer Book provided.

3. For the reaction, trans-PtL_2Cl_2 + Y → trans - PtL_2ClY + Cl^- the rate constant K varies as follows:

	Y	L	K(10^{-3} M^{-1} S^{-1})
(*i*)	PPh_3	Py	249,000
(*ii*)	SCN	Py	180
(*iii*)	I-	Py	107
(*v*)	SCN	PEt_3	371

(*a*) What is mechanism of the reaction? **(2)**

(*b*) Explain the variations observed. **(3)**

4.1. Calculate the number of theoretical plates for a column where the retention time for a compound is two minutes and the width of the peak at the base is 10 s. **(2)**

4.2. Why is the thermal conductivity detector unsuitable for the gas chromatographic detection of hexachlorobenzene? **(1)**

4.3. What types of HPLC columns are suitable for the analysis of organic compounds such as

(*a*) cyclohexene, cyclohexane, methylcyclohexane

(c) glycerol, 1, 2-dihydroxy propane, 1, 3 dihydroxy propane **(2)**

5. Write down the products formed in each of the following reactions.

5.1. $P_2S_5 + PCl_5 \longrightarrow$

5.2. $S + NH_3$ (liquid) $\rightleftharpoons$

5.3. $NaBH_4 + I_2 \longrightarrow$

5.4. $XeO_3 + OH^- \rightleftharpoons$

5.5. SiO2 + HF(*aq*) $\longrightarrow$ **(5)**

6.1. Draw the structures of the Wilkinson's catalyst and the product formed on its reaction with hydrogen. **(2)**

6.2. What is the product formed in the reaction of $RCo(CO)_4$ with CO in the presence of hydrogen? Indicate clearly the intermediates involved. **(3)**

7.1. Distinguish between limiting current and residual current in a polargogram. **(2)**

7.2. What is the separation between the anodic and cathodic waves in cyclic voltammetry experiment for the reversible one-electron and two-electron processes? (2)

7.3. How does the separation vary with the scan rate for a quasi-reversible process? (1)

8.1. Give the structures of

(*a*) H_3CPF_4 and (*b*) XeO_2F_2 (2)

8.2. MgO and NaF are isoelectronic and crystallize in NaCl structure. Why MgO is twice as hard as NaF and has a much higher melting point than NaF? (2)

8.3. Why does the lowest energy transfer band shifts from 18,000 cm^{-1} in $KMnO_4$ to 26,000 cm^{-1} in K_2CrO_4? (1)

9.1. Aqueous solution of $MnCl_2$ exhibits a number of very weak intensity absorption bands ($\varepsilon \sim 0.01$) between 18,000 to 42,000 cm^{-1} while solution of $TiCl_3$ in dilute sulfuric acid exhibits a relatively strong band at 20,000 cm^{-1} with a shoulder at 17,400 cm^{-1} ($\varepsilon \sim 10$). Account for these observations. **(3)**

9.2. Explain the variation of hydration energies of divalent metal ions from calcium to zine. (2)

10.1. Calculate the vapour pressure of toluene at 100°C assuming that Trouton's rule is obeyed. The boiling point of toluene is 110°C. (3)

10.2. The vapour pressure of ethanol at 20°C is 44.5 mm. When 15g of a non-volatile compound A is dissolved in 500g of ethanol, the vapur pressure decreases to 43.5 mm. Calculate the molecular weight of A. (2)

11.1. 0.1 M $CuSO_4$ solutioin is electrolyzed employing Cu electrodes using a current of 10 A for 1 h. Calculate the weight of Cu deposited. (2)

11.2. A Solution contains 0.1 mol/dm³ of Cl^-, 0.1 mol/dm³ of Br^- and 0.1 mol/dm³ of I^-. Solid $AgNO_3$ is gradually added to this solution. Assuming that the volume does not change, answer the following questions.

K_{sp} (AgCl) = 1.7×10^{-10} $(mol/dm^3)^2$;
K_{sp} (AsBr) = 5.0×10^{-13} $(mol/dm^3)^2$
K_{sp}(AgI) = 8.5×10^{-17} $(mol/dm^3)^2$

(*a*) Which salt will precipitate first?

(*b*) What is the concentration of Ag^+ ions required to start precipitation?

(*c*) What will be the concentatioin of the first ion when the second salt begins to precipitate? (3)

12.1 For BCl_3 molecule, the Cl atoms are numbered as 1, 2, 3. Examine whether the operations $\sigma_v(1)$ $\sigma_v(2)$ commute. Indicate the symmetry operatioin equivalent to the binary operations in each case.

12.2. Give the symmetry operation equivalent to **(2)**

(i) C_4^6 (*ii*) S_4^2

13. Upon absorption of light of 266 nm, ozone dissociates in the following way

$$O_3(g) \rightarrow O_2(g) + O(g)$$

The power of the incident radiation is 20 mW and the sample of ozone is exposed for a period of 3 hrs. The amount of ozone that is photolysed in 10 μ mol. Calculate the quantum yield for the ozone photolysis reaction.

14.1. Acetic acid show two signals a and *b* at δ = 8.0 ppm and 3.8 ppm, respectively in a 50 MHz NMR spectrometer. Calculate the separation in frequency between the two signals on a 300 MHz spectrometer. (2)

14.2. The is wavefunction for the hydrogen atom is

$$R_{is}(r) = (1/\sqrt{\pi})\,(1/a_0)^{3/2} \exp(-r/a_0)$$

Calculate the probability that the electron will be found within the first Bohar radius. (3)

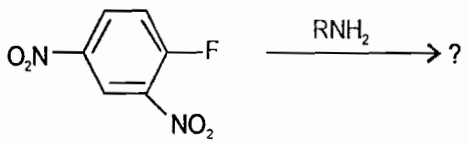
15.1. A substance is four times more soluble in $CHCl_3$ than in H_2O. If 10g of the substance is dissolved in 500 ml of water, how much of it will be removed by extraction with 500 ml of $CHCl_3$? (3)

15.2. The root mean square velocity of O_2 molecules is 575 ms^{-1}. Find out the temperature of O_2 gas. (2)

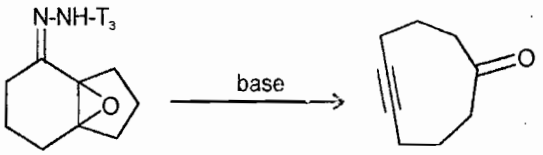
16.1. Set up the Huckel determinant for methyleneimine ($H_2C = NH$) taking $\beta_{C\text{-}N}$ as 1.0 β and α_N as α + 0.5 β, where α and β represent the usual Coulomb and resonance integrals respectively, and obtain the Huckel molecular orbital energy levels. (3)

16.2. Explain, why the ^1H NMR spectrum of *p*-dichlorobenzene shows a singlet, whereas *p*-difluorobenzene shows a multiplet.

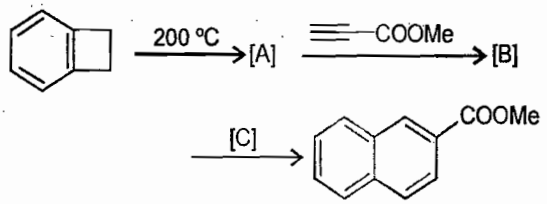
17.1. Identify the structure of the major product formed in the following reaction, and give a mechanism of its formation (2)



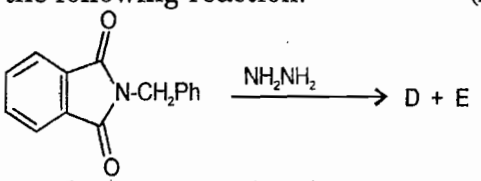
17.2. Give a suitable mechanism for the following transformation. (3)



18.1. Identify the products/reagents (A-C) in the following sequence. (3)

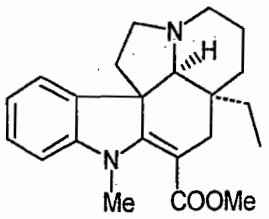


18.2. Write structures of the products formed in the following reaction. (2)



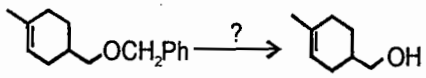
19.1. Write the conformational structures of the two cyclic isomers of glucose which are responsible for the phenomenon of mutarotation. (2)

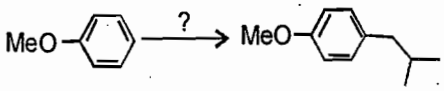
19.2. The optically active compound given below was found to racemise on heating in a microwave oven. Given a suitable explanation. (3)

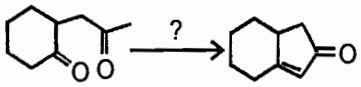


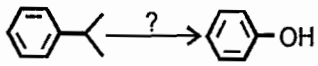
20. Suggest suitable reagents to bring about the following transformations (may require more than one step). (5)

(*i*) PhBr $\xrightarrow{?}$ PhD

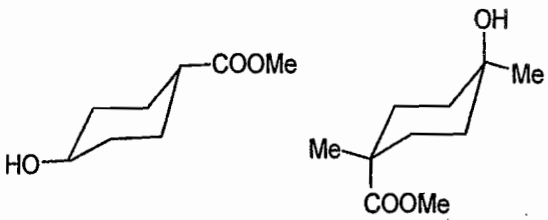
(*ii*) 

(*iii*) 

(*iv*) 

(*v*) 

21.1. Among the two hydroxyesters given below, which one will readily lactonise on treatment with a mild base. Write the structure of the product and justify your answer briefly. (2)



21.2. Identify the reactive intermediate involved in the reaction of furan with a mixture of HNO_3 and H_2SO_4. Write the mechanism and the structure of the final product. (3)

22. A sweet smelling organic compound **A** (mol. formula $C_8H_{16}O_2$) on reaction with lithium aluminium hydride furnishes a single primary alcohol **B.** Whereas reaction of **A** with an excess of methylmagnesium bromide furnishes two alcohols **B** and **C.** In the ^1H NMR spectrum, compound **B** exhibits signals at δ 3.8 (2 H, *d* J = 7 Hz), 1.8 (1 H, *m*), 1.6(1 H, brs, exchangeable with D_2O) and 0.9(6H, *d*, J = 7.2 Hz). Identify the structures of the compounds A, B and C, and explain the reactions. (5)

ANSWERS

1.1. (*a*)	**1.2.** (*a*)	**1.3.** (*b*)	**1.4.** (*a*)	**1.5.** (*b*)	**1.6.** (*b*)	**1.7.** (*d*)	**1.8.** (*c*)	**1.9.** (*d*)
1.10. (*b*)	**1.11.** (*d*)	**1.12.** (*c*)	**1.13.** (*b*)	**1.14.** (*a*)	**1.15.** (*d*)	**1.16.** (*b*)	**1.17.** (*b*)	**1.18.** (*c*)
1.19. (*d*)	**1.20.** (*a*)	**1.21.** (*d*)	**1.22.** (*b*)	**1.23.** (*a*)	**1.24.** (*d*)	**1.25.** (*c*)	**2.1.** (*b*)	**2.2.** (*c*)
2.3. (*c*)	**2.4.** (*a*)	**2.5.** (*a*)	**2.6.** (*d*)	**2.7.** (*b*)	**2.8.** (*a*)	**2.9.** (*a*)	**2.10.** (*a*)	**2.11.** (*c*)
2.12. (*c*)	**2.13.** (*b*)	**2.14.** (*c*)	**2.15.** (*c*)	**2.16.** (*d*)	**2.17.** (*d*)	**2.18.** (*b*)	**2.19.** (*c*)	**2.20.** (*c*)
2.21. (*c*)	**2.22.** (*d*)	**2.23.** (*d*)	**2.24.** (*d*)	**2.25.** (*d*)				

EXPLANATIONS

1.3. For non planar molecule,

Vibrational degrees of freedom

$= 3N - 6$ (where N = no of atoms)

$= 3 \times 4 - 6 = 6$

1.4. Energy for detachment of electron decreases with increasing no of shells.

1.6. Because, $\Delta G^{o} = \Delta G - 2.303\ RTh_1 \dfrac{(B)}{(A)}$

1.7. Depression in freezing point increases on increase in molecular weight.

1.8. Mole fraction of B

$$= \frac{0.8 - 0.6}{0.8} = \frac{0.2}{0.8} \times 100 = 25\%$$

1.10. Because chlorine atom has seven electrons in valence shell.

1.11. E.A.N. $= 24 + 6 \times 2 = 36$

1.14. Absurbance =by $\left(\dfrac{I_0}{I}\right)$

Where π_0 = Intensity of incident radiation

I = Intensity of emerging radiation

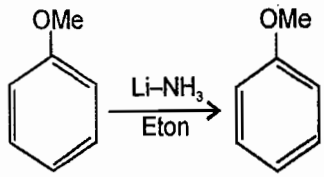
1.17. Because one carbon atom is double bounded while terminal is single bonded.

1.19. Because No. of carbon α Hydrogen atom in this case.

1.21. Phenyl (magnesium bromide + Ethyl chloroformite → Benzol dehyde.

1.24. Phenyl acetate + Anhydrous $AlCl_3$ → ortho and para–hydroxantophehons.

1.25.



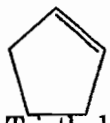
2.4. It will be only dependent on length of the size of one dimensional box.

2.6. For 1 units it is 62.74 JK = 1.

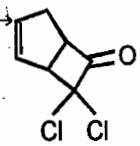
2.10. It will depend on the arrangement of electron in mlecular orbitals.

2.17. Liability of cations will be maximum for lowest atomic no.

2.18.



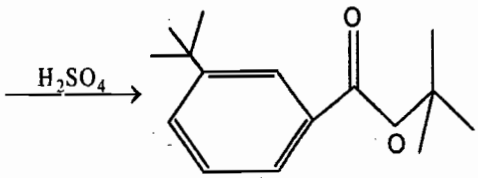
+Dichloroacetyl Chloride + Triethyl amine →



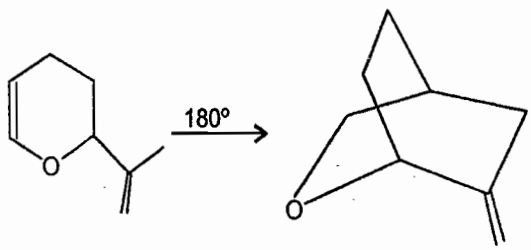
2.21. 1.5 – cycloctadiene + Diborane

→

2.23. Benzoic acid + Isobutylene



2.25.



GATE - 2003

CY : CHEMISTRY

Duration: Three Hours | *Maximum Marks*: 100

Atomic Numbers	: B = 5, C = 6, Ti = 22, Cr = 24, Mn = 25, Fe = 26, Co = 27, Ni = 28, Br = 35, Ru = 44, Rh = 45, I = 53, Xe = 54, Re = 75
Gas Constant R	: 8.314 $JK^{-1} mol^{-1}$
Faraday Constant F	: 96,500 C mol^{-1}
Planck Constant h	: 6.626×10^{-34} J s
Boltzmann Constant k	: 1.3807×10^{-23} J K^{-1}
Avogadro number N	: 6.023×10^{23} mol^{-1}

Q. 1-30 Carry One Mark Each

1. A diabatic reversible expansion of a monatomic gas (M) and a diatomic gas (D) at an initial temperature T_i, has been carried out independently from initial volume V_1 to final volume V_2. The final temperature (T_M for monatomic and T_D for diatomic) attained will be

(*a*) $T_M = T_D > T_i$ (*b*) $T_M < T_D < T_i$

(*c*) $T_M > T_D > T_i$ (*d*) $T_M = T_D = T_i$

2. The rate of evaporation of a liquid is always faster at a higher temperature because

(*a*) the enthalpy of vapourisation is always endothermic

(*b*) the enthalpy of vapourisation is always exothermic

(*c*) the enthalpy of vapourisation is zero

(*d*) the internal pressure of the liquid is less than that of the gas

3. The internal pressure of a van der waals gas is

(*a*) independent of the molar volume

(*b*) inversely proportional to the molar volume

(*c*) inversely proportional to square of the molar volume

(*d*) directly proportional to the molar volume

4. In a consecutive first order reaction,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(where k_1 and k_2 are the respective rate constants)species B has transient existence. Therefore.

(*a*) $k_1 \approx k_2$

(*b*) $k_1 = 2k_2$

(*c*) $k_1 >> k_2$

(*d*) $k_1 << k_2$

5. For a free radical polymerisation reaction, the kinetic chain length 'γ', is defined as the ratio

(*a*) $\dfrac{\text{propagation rate}}{\text{initiation rate}}$

(*b*) $\dfrac{\text{initiation rate}}{\text{propagation rate}}$

(*c*) $\dfrac{\text{initiation rate}}{\text{termination rate}}$

(*d*) $\dfrac{\text{propagation rate}}{\text{termination rate}}$

6. The reaction that proceeds autocatalytically is

(*a*) as oscillatory reaction

(*b*) hydrolysis of an ester by a mineral acid

(*c*) the synthesis of ammonia (Harber's process)

(*d*) Ziegler-Natta polymerisation

7. An example for an ion-selective electrode is
   (a) quinhydrone electrode
   (b) hydrogen electrode
   (c) glass electrode
   (d) dropping mercury electrode

8. The following equilibrium is established for an aqueous acetic acid solution

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^{\oplus}$$

Upon addition of 1.0 g of solid sodium chloride to 20 ml of 1N solution of acetic acid,
   (a) the pH of the solution does not change
   (b) the pH of the solution decreases
   (c) the pH of the solution increases
   (d) the pH of the solution is 7

9. According to MO theory, for the atomic species 'C_2'
   (a) bond order is zero and it is paramagnetic
   (b) bond order is zero and it is diamagnetic
   (c) bond order is two and it is paramagnetic
   (d) bond order is two and it is diamagnetic

10. The sensitivity of a 600 MHz NMR spectrometer is more than that of a 60 MHz spectrometer because
   (a) population of spin states is directly proportional to the applied magnetic field
   (b) population of spin states is inversely proportional to the applied magnetic field
   (c) according to the Boltzmann distribution law, the excess population in the lower spin state increases with increasing applied magnetic field
   (d) the spectral scan width is more for a 600 MHz spectrum compared to a 60 MHz spectrum.

11. The magnetic moment of an octahedral Co(II) complex is 4.0 μ_B. The d-electron configuration of Co(II) is
   (a) $t_{2g}^4 e_g^3$ (b) $t_{2g}^5 e_g^2$
   (c) $t_{2g}^6 e_g^1$ (d) $t_{2g}^3 e_g^4$

12. The square planar complex, $[IrCl(PPh_3)_3]$ undergoes oxidative addition of Cl_2 to give two products, which are
   (a) *fac*–and *mer*–isomers
   (b) *cis*–and *trans*–isomers
   (c) linkage isomers
   (d) enatiomers

13. The ligand field bands of lanthanide complexes are generally sharper than those of transition metal complexes because
   (a) transitions are allowed for lanthanide complexes
   (b) intensity of the bands are higher for lanthanide complexes
   (c) *f*-orbitals have higher energy than *d*-orbitals
   (d) *f*-orbitals, compared to *d*-orbitals, interact less effectively with ligands

14. Nature has chosen Zn(II) ion at the active site of many hydrolytic enzymes because
   (a) Zn(II) is a poor Lewis acid
   (b) Zn(II) does not have chemically accessible redox states
   (c) Zn(II) forms both four and higher coordination complexes
   (d) Zn(II) forms weak complexes with oxygen donor ligands

15. $BH_3.CO$ is more stable than $BF_3.CO$ because
   (a) CO is a soft base and BH_3 and BF_3 are soft and hard acids respectively
   (b) CO is a hard base and BH_3 and BF_3 are hard and soft acids respectively
   (c) CO is a soft base and BH_3 and BF_3 and hard and soft acids respectively
   (d) CO is a soft acid and BH_3 and BF_3 are soft and hard bases respectively

16. Using chlorobenzene as solvent, the reagents needed for an efficient synthesis of borazine are
   (a) NH_4Cl and BCl_3
   (b) NH_4Cl, BCl_3 and $NaBH_4$
   (c) NH_4Cl and $NaBH_4$
   (d) NH_3 and BCl_3

17. The crystal systems having the highest and the lowest symmetries respectively, are

(*a*) cubic and rhombohedral

(*b*) cubic and triclinic

(*c*) rhombohedral and monoclinic

(*d*) cubic and monoclinic

18. The dark purple colour of $KMnO_4$ is due to

(*a*) *d-d* transition

(*b*) ligand field transition

(*c*) charge transfer transition

(*d*) $\sigma - \pi^*$ transition

19. The metallic character of beryllium is due to

(*a*) partially filled 2*s* band

(*b*) completely filled 2*s* band

(*c*) overlap of 2*s* and 2*p* bands

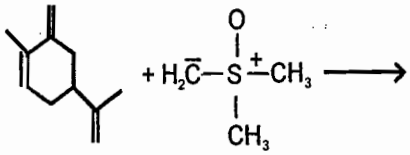
(*d*) empty 2*p* band

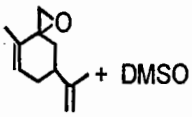
20. The values of CO stretching frequencies of (1) $Ni(CO)_7$ (2) $Ni(CO)_3(PMe_3)$ and (3) $Ni(CO)_2(PMe_3)_2$ follow the trend

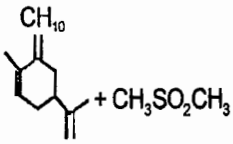
(*a*) (1) > (2) > (3) (*b*) (3) > (2) > (1)

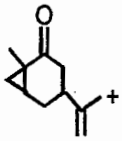
(*c*) (1) > (3) > (2) (*d*) (2) > (3) > (1)

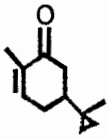
21. The products formed in the following reaction are



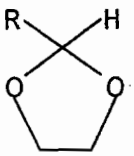
(*a*)  + DMSO

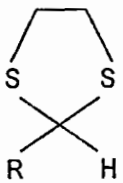
(*b*)  + $CH_3SO_2CH_3$

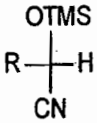
(*c*)  + DMSO

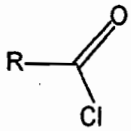
(*d*)  + DMSO

22. The acyl anion equivalents, among the following compounds (P–S), are

(P) 

(Q) 

(R) 

(S) 

(*a*) P and Q (*b*) Q and R

(*c*) P and S (*d*) Q and S

23. ^{1}H-NMR spectrum of a compound with molecular formula $C_4H_9NO_2$ shows δ 5.30 (broad, 1H), 4.10 (q, 2H), 2.80(d, 3H), 1.20 (*t*, 3H) ppm. The structure of the compound that is consistent with the above data is

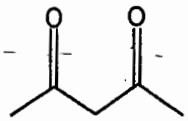
(*a*) $CH_3NHCOOCH_2CH_3$

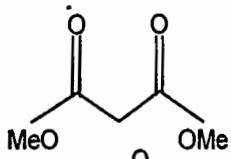
(*b*) $CH_3CH_2NHCOOCH_3$

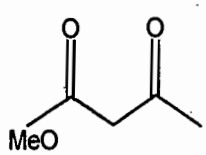
(*c*) $CH_3OCH_2CONHCH_3$

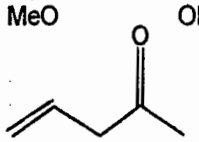
(*d*) $CH_3CH_2OCH_2CONH_2$

24. Among the following compounds, the one that undergoes deprotonation most readily in the presence of a base, to form a carbanion is

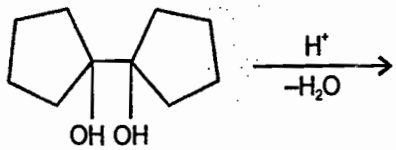
(*a*) 

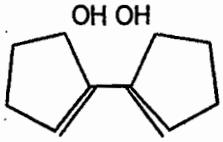
(*b*) 

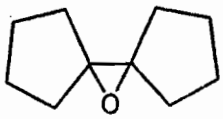
(*c*) 

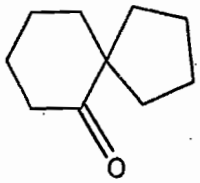
(*d*) 

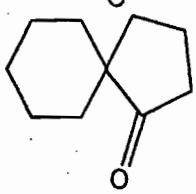
25. The structure of the product formed in the reaction given below is



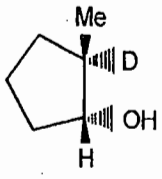
(*a*) 

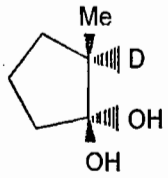
(*b*) 

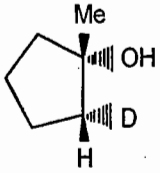
(*c*) 

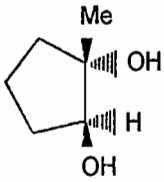
(*d*) 

26. Hydroboration of 1-methylcyclopentene using B_2D_6, followed by treatment with alkaline hydrogen peroxide, gives

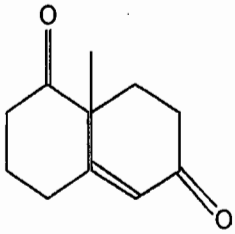
(*a*) 

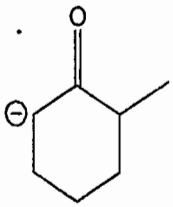
(*b*) 

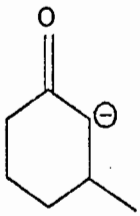
(*c*) 

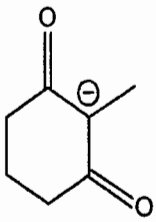
(*d*) 

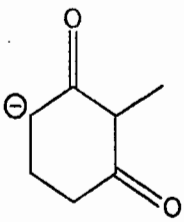
27. The enolate ion that reacts with 3-buten-2-one to form (Y) is



(*a*) 

(*b*) 

(*c*) 

(*d*) 

28. Electrocyclization of E, Z, E-octa-2, 4, 6-triene under photochemical condition, gives

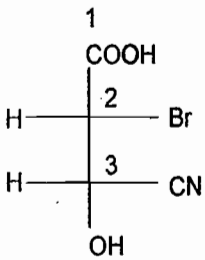
(*a*) trans-5, 6-dimethylcyclohexa = 1, 3-diene

(*b*) cis-5, 6-dimethylcyclohexa-1, 3-diene

(*c*) a mixture of trans-and cis-5, 6-dimethylcyclohexa-1, 3-diene

(*d*) 1, 2-dimethylcyclohexa-1, 3-diene

29. The absolute configurations of the two chiral centers in the following molecule are



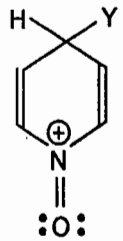
(*a*) 2(R), 3(S)

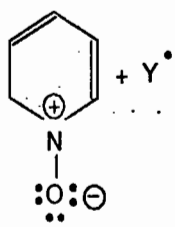
(*b*) 2(R), 3(R)

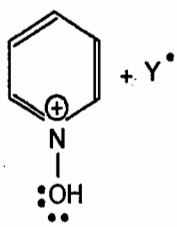
(*c*) 2(S), 3(S)

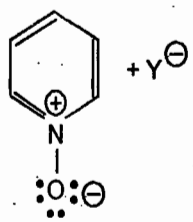
(*d*) 2(S), 3(R)

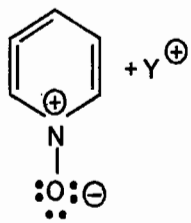
30. A pyridine derivative (P) reacts with (Y).(Y) can be a free radical, cation or anion. The structure of intermediate (Q) formed in the reaction is given below. (P) and (Y) respectively, are



(*a*) 

(*b*) 

(*c*) 

(*d*) 

Q. 31-90 Carry Two Marks Each

Q. 31-36 are "Matching" exercises. Choose the correct one from the alternatives A, B, C and D.

31. **I**

P. $ZnSO_4(aq) + K_4[Fe(CN_6)](aq) \rightarrow$ Products

Q. $Zn(s) + CuSO_4(aq) \rightarrow$ Products

R. $H_2 + Cl_2 \xrightarrow{\Delta}$ Products

S. Fischer-Tropsch synthesis of hydrocarbons

II

1. Enzymatic reaction
2. Chain reaction
3. Redox reaction
4. Precipitation reaction
5. Surface reaction
6. Hydrolysis reaction

(*a*) P – 2, Q – 4, R – 5, S – 6

(*b*) P – 1, Q – 3, R – 2, S – 4

(*c*) P – 4, Q – 3, R – 2, S – 5

(*d*) P – 1, Q – 6, R – 2, S – 5

32.

I	II
P. Supporting electrolyte	1. Overpotential
Q. $Zn(Hg)_{a=1} \mid ZnCl_2(aq) \mid Zn(Hg)_{Q=2}$	2. Residual current
R. Inversion temperature	3. Electrolyte concentration cell
S. Entropy of vapourisation	4. Electrode concentration cell
	5. Trouton's rule
	6. Joule-Thomson expansion

(*a*) P – 2, Q – 4, R – 6, S – 5
(*b*) P – 2, Q – 4, R – 3, S – 6
(*c*) P – 1, Q – 4, P – 6, S – 3
(*d*) P – 1, Q – 3, R – 6, S – 5

33.

I	II
P. Kroenecker delta	1. Electronic transition
Q. Franck-Condon principle	2. Isothermal process
R. Kirchoff's equation	3. Orthonormal set
S. Glass transition temperature	4. Reaction enthalpy
	5. Turnover number
	6. Polymer

(*a*) P – 1, Q – 3, R – 5, S – 6
(*b*) P – 3, Q – 1, R – 4, S – 6
(*c*) P – 1, Q – 3, R – 5, S – 2
(*d*) P – 3, Q – 1, R – 6, S – 2

34.

I	II
P. Liver alcohol dehydrogenase	1. Cu at the active site
Q. Cytochrome C oxidase	2. Fe and Cu at the active site
R. Hemocyanin	3. Zn at the active site
S. Myoglobin	4. Fe at the active site
	5. Mo at the active site
	6. Cu and Zn at the active site

(*a*) P – 6, Q – 2, R – 1, S – 4
(*b*) P – 3, Q – 2, R – 1, S – 4
(*c*) P – 3, Q – 2, R – 4, S – 5
(*d*) P – 5, Q – 6, R – 1, S – 2

35.

I	II
P. $(PPh_3)_3RhCl$	1. Friedel-crafts catalyst
Q. $[Rh(CO)_2I_2]$	2. Hydroformylation of alkenes
R. $[PdCl_4]^2$	3. Hydrogenation catalyst
S. $[HCo(CO)_4]$	4. The Wacker process
	5. Monsanto catalyst for acetic acid
	6. Reppe catalyst

(*a*) P – 3, Q – 5, R – 4, S – 2
(*b*) P – 4, Q – 1, R – 6, S – 2
(*c*) P – 5, Q – 4, R – 2, S – 1
(*d*) P – 3, Q – 2, R – 1, S – 5

36.

I	II
P. $[Cr(H_2O)_6]^{3+}$	1. C_{3v}
Q. $Fe_2(CO)_9$	2. D_{3h}
R. Eclipsed ferrocene	3. O_h
	4. D_{3d}
	5. D_{5h}
	6. D_{4h}

(*a*) P–3, Q–2, R–5 (*b*) P–2, Q–4, R–1
(*c*) P–6, Q–2, R–5 (*d*) P–3, Q–6, R–4

37. For the reaction, $Hg_2Cl_2(s) + H_2(g) \rightarrow 2Hg(l) + 2\,HCl(aq)$, the correct representation of the cell and the thermodynamic properties ΔG, ΔH and ΔS at 298 K respectively, are (given: $E_{298} = 0.2684$ V and temperature coefficient $= 3 \times 10^{-4}$ VK^{-1})

(*a*) $Pt|H_2(g, 1\,atm)|HCl\,(aq)|Hg_2Cl_2(s)|Hg(l)$
$\Delta G = -51.8\ kJmol^{-1}$, $\Delta H = -69\ kJ\,mol^{-1}$, $\Delta S = -58\ JK^{-1}\,mol^{-1}$

(*b*) $Pt|H_2(g, 1\,atm)|HCl(aq)|Hg_2Cl_2(s)|Hg(l)$
$\Delta G = -25.9\ kJmol^{-1}$, $\Delta H = -34.5\ kJ\,mol^{-1}$, $\Delta S = -29\ JK^{-1}\,mol^{-1}$

(*c*) $Hg(l)|Hg_2Cl_2(s)|HCl(aq)|H_2(g, 1\,atm)|Pt$
$\Delta G = -51.8\ kJmol^{-1}$, $\Delta H = -69\ kJ\,mol^{-1}$, $\Delta S = -58\ JK^{-1}\,mol^{-1}$

(*d*) $|Hg(l)|\,Hg_2Cl_2(s)|HCl\,(aq)|H_2(g, 1\,atm)|Pt$
$\Delta G = 51.8\ kJmol^{-1}$, $\Delta H = 69\ kJ\,mol^{-1}$, $\Delta S = 69\ JK^{-1}\,mol^{-1}$

38. Among CH_3Cl, CH_2Cl_2 $CHCl_3$, CH_3Br and CH_3I in the gaseous state, the one having highest molar entropy value at room temperature is

(*a*) $CHCl_3$ (*b*) CH_3Cl

(*c*) CH_3Br (*d*) CH_3I

39. Two solid components form a congruent melting solid in situ. The phase diagram of the system has

(*a*) five invariant points, two equilibria involving three phases and two equilibria involving two phases

(*b*) three invariant points, two equilibria involving three phases and three equilibria involving two phases

(*c*) five invariant points, two equilibria involving three phases and three equilibria involving two phases.

(*d*) three invariant points, three equilibria involving three phases and two equilibria involving two phases

40. H_2 and Br_2 react to give HBr by the following steps

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br + M(\text{fast}), (K = k_1/k_{-1})$$

$$Br + H_2 \xrightarrow{k_2} HBr + H\ (\text{slow})$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br\ (\text{fast})$$

The probable rate law for the above sequence is

(*a*) rate $= k_2(K)^{1/2}[H_2][Br_2]^{1/2}$

(*b*) rate $= k_2[H_2][Br_2]$

(*c*) rate $= k_2(k_1)^{1/2}[H_2][Br_2]^{1/2}$

(*d*) rate $= k_2(K)^{1/2}[H_2][Br]^{1/2}$

Q. 41-42 is given below solve the problem and choose the correct answers

For the opposing reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

The forward reaction has values $E_a = 100$ kJ mol^{-1} and $A = 1.0 \times 10^{10}$ M^{-1} s^{-1}. The equilibrium concentration of A, B, C and D are 1.0 M, 2.0 M, 5.0 M and 4.0 M respectively, at 700 K.

41. The values of k_1 and k_{-1}, respectively, at this temperature are

(*a*) 20 M^{-1} s^{-1} and 2.0 M^{-1}s^{-1}

(*b*) 345 M^{-1}s^{-1} and 34.5 M^{-1} s^{-1}

(*c*) 34.5 M^{-1}s^{-1} and 3.45 M^{-1}s^{-1}

(*d*) 200 M^{-1}s^{-1} and 20 M^{-1}s^{-1}

42. The rate constant (k_1) for the forward reaction at 1000 K is

(*a*) 5.98×10^4 M^{-1} min^{-1}

(*b*) 5.98×10^2 M^{-1} s^{-1}

(*c*) 1.00×10^3 M^{-1} s^{-1}

(*d*) 5.98×10^4 M^{-1} s^{-1}

43. For the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Compute the entropy change (in J/K/mol) for the process and comment on the sign of the property.

Data:

Species	$NH_3(g)$	$N_2(g)$	$H_2(g)$
S°(J/K/mol)	192.3	191.5	130.6

(*a*) $\Delta S° = -37.65$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction

(*b*) $\Delta S° = -198.7$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction

(*c*) $\Delta S° = -31.25$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction

(*d*) $\Delta S° = +31.25$ J/K/mol; the positive sign indicates that the reaction is spontaneous.

44. The translational partition function of a hydrogen molecule confined in a 100 ml flask at 298 K (Molecular weight of hydrogen = 2.016) is

(*a*) 2.8×10^{20} (*b*) 2.8×10^{25}

(*c*) 2.8×10^{26} (*d*) 2.8×10^{27}

45. $\Delta H°_{298}$ for the reaction

$$C_2H_4(g) \rightarrow CH_4(g) + CO(g)$$

is – 16.0 kJ. From the given data, evaluate the temperature at which ΔH will be zero.

Substance	$C_2H_4O(g)$	$CH_4(g)$	$CO(g)$
C_p(J/K/mol)	50	36	30

(*a*) 1298 K (*b*) 1000 K

46. At 273 K, N_2 is adsorbed on a mica surface. A plot of 1/V vs 1/P (V in m^3 and P in torr) gives a straight line with a slope equal to 2.0×10^{-5} torr m^{-3} and an intercept equivalent V_m equal to 4.0×10^{-8} m^3. The adsorption coefficient and the number of molecules of N_2 forming the mono layer, respectively, are

(*a*) 1.25×10^{12} $torr^{-1}$ and 1.075×10^{18}

(*b*) 2.5×10^{12} $torr^{-1}$ and 1.075×10^{18}

(*c*) 2.5×10^{12} $torr^{-1}$ and 1.75×10^{18}

(*d*) 1.25×10^{10} $torr^{-1}$ and 1.075×10^{18}

47. For the reaction, $2Cl(g) \rightarrow Cl_2(g)$ the thermodynamic properties

(*a*) ΔG, ΔH and ΔS are positive

(*b*) ΔG, ΔH and ΔS are negative

(*c*) ΔG and ΔH are negative and ΔS is positive

(*d*) ΔG is negative and ΔH and ΔS are positive

48. The standard free energies of formation of $H_2S(g)$ and CdS(s) at 1000 °C are – 49.0 kJ/mol and –127.2 kJ/mol, respectively. Use these data to predict whether $H_2(g)$ will reduce CdS (s) to metallic Cd at this temperature

(*a*) $\Delta G = -78.2$ kJ/mol and H_2 reduces CdS

(*b*) $\Delta G = -39.1$ kJ/mol and H_2 reduces CdS

(*c*) $\Delta G = 0$ kJ/mol and the reaction is at equilibrium

(*d*) $\Delta G = +78.2$ kJ/mol and the reaction is not feasible

49. From the data of two half-cell reactions:

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ $E° = +0.22$ V

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = +0.80$ V

the solubility product of AgCl at 298 K, is calculated to be

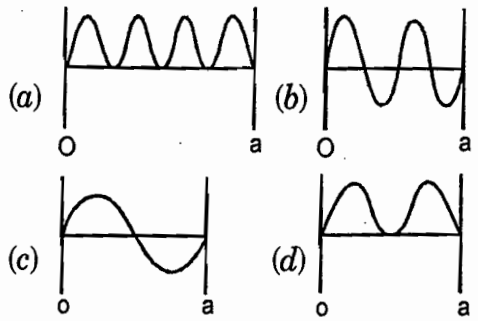
(*a*) 1.5×10^{-10}

(*b*) 2.1×10^{-7}

(*c*) 3.0×10^{-3}

(*d*) 1.2×10^{-5}

50. For the energy level $(2h^2/ma^2)$ the probability for a particle of mass 'm' over the length 'a' of a one-dimensional box is depicted by



51. Among the complexes (*i*) $(C_6H_6)_2$ Cr, (*ii*) $[HMn(CO)_5]$, (*iii*) $[(CH_3CO)Rh(CO)I_3]^-$ and (*iv*) $CpFe(CO)_2(CH_3)$, the 18-electron rule is not followed in

(*a*) (*iii*) only (*b*) (*ii*) and (*iii*)

(*c*) (*i*) and (*iv*) (*d*) (*i*) only

52. the incorrect statement regarding the Fischer-type metal carbene complexes is that

(*a*) carbene acts as a σ-donor and π-acceptor

(*b*) all atoms directly connected to carbene C atom are coplanar

(*c*) the bond between the metal and the carbene C atom has partial double bond character

(*d*) the carbene C atom is nucleophilic

53. The xenon compounds that are isotructural with IBr_2^- and BrO_3^- respectively are

(*a*) linear XeF_2 and pyramidal XeO_3

(*b*) bent XeF_2 and pyramidal XeO_3

(*c*) bent XeF_2 and planar XeO_3

(*d*) linear XeF_2 and tetrahedral XeO_3

54. Using the Wade rules, the structure of $B_{10}C_2H_{12}$ can be predicted. Teh structure and the number of isomers of $B_{10}C_2H_{12}$ respectively, are

(*a*) *nido* and two

(*b*) *closo* and three

(*c*) *nido* and one

(*d*) *closo* and two

55. The number of manganese ions in tetrahedral and octahedral sites, respectively in Mn_3O_4 are

(*a*) one Mn^{2+} and two Mn^{3+}

(*b*) one Mn^{3+} and two Mn^{2+}

(*c*) two Mn^{3+} and one Mn^{2+}

(*d*) two Mn^{2+} and one Mn^{3+}

56. Gold crystallizes in face-centered-cubic lattice. The atomic weight and density of gold are 196.97 and 19.4 g/cm^3 respectively. The length of the unit cell is

(*a*) 2.563 Å (*b*) 3.230 Å

(*c*) 4.070 Å (*d*) 8.140 Å

57. Solid $CO_2(CO)_8$ shows infrared CO stretching bands at 1857, 1886, 2001, 2031, 2044, 2059, 2071 and 2112 cm^{-1}. When $CO_2(CO)_8$ is dissovled in hexane, the carbonyl bands at 1857 and 1886 cm^{-1} disappear. These changes in the infrared spectrum in hexane are due to

(*a*) loss of terminal CO

(*b*) structural change of $CO_2(CO)_8$ involving conversion of terminal CO to bridging CO

(*c*) dissociation of $CO_2(CO)_8$ to $CO(CO)_4$

(*d*) structural changes of $CO_2(CO)_8$, involving conversion of bridging CO to terminal CO

58. Match the silicate minerals (column I) with their compositions (column II) and order of hardness (column III)

I	II	III
P. talc	U. $KAl_3Si_3O_{10}(OH)_2$	X. high
Q. muscovite	V. $Mg_3Si_4O_{10}(OH)_2$	Y. low
R. margarite	W. $CaAl_4Si_2O_{10}(OH)_2$	Z. intermediate

(*a*) P, V, Y – Q, U, Z – R, W, X

(*b*) P, U, X – Q, V, Z – R, W, Y

(*c*) P, W, X – Q, V, Y – R, U, Z

(*d*) P, V, Z – Q, U, Y – R, W, X

59. The structure of $P_4N_4Cl_8$ is $P_4N_4F_8$ is planar because

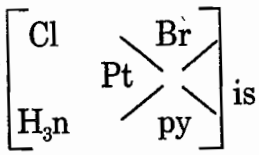
(*a*) F is more electronegative than Cl

(*b*) F is smaller in size than that of Cl

(*c*) F is more polarizable than Cl

(*d*) Extent of π-electron delocalization is more in $P_4N_4Cl_8$ than in $P_4N_4F_8$

60. The correct order of addition of NH_3, pyridine (*py*) and Br^- to $[PtCl_4]^{2-}$ to obtain



is

(*a*) *py*, Br^- and NH_3

(*b*) Br^-, *py* and NH_3

(*c*) NH_3 *py* and Br^-

(*d*) NH_3, Br^- and *py*

61. $[Ru(C_2H_5)Cl(PPh_3)_3]$ is stable only under a pressure of ethene because

(*a*) it is a 16-electron complex

(*b*) it forms an 18-electron adduct with ethene

(*c*) one of the decomposition products is ethene

(*d*) it prevents α-elimination of ethene

62. The ground state Term Symbols for p^3 and d^3 electronic configurations respectively, are

(*a*) ^4S and ^4F (*b*) ^4D and ^4F

(*c*) ^1D and ^4F (*d*) ^4S and ^2G

63. The "styx" code for diborane is

(*a*) 2020 (*b*) 2200

(*c*) 2002 (*d*) 0220

64. $[CoCl(NH_3)_5]^{3+} + [Cr(H_2O)_6]^{2+}$

$\rightarrow [Co(H_2O)(NH_3)_5]^{2-} + [CrCl(H_2O)_5]^{3+}$

The correct statement regarding the above reaction is that

(*a*) it follows outer-sphere mechanism

(*b*) it follows inner-sphere mechanism with NH_3 acting as the bridging ligand

(*c*) it follows inner-sphere mechanism with Cl^- acting as the briding ligand

(*d*) it is not an electron-transfer reaction

65. The percentage transmittance of a transition metal complex at 360 nm and at 25°C is 25% for a 6×10^{-4} mol L^{-1} solution ina 1 cm cell. The molar absorption coefficient in the unit of L mol^{-1} cm^{-1} is

(*a*) ~ 1.0×10^{-3} (*b*) ~ 1.0×10^{3}

(*c*) ~ 2.0×10^{3} (*d*) ~ 1.0×10^{4}

66. The bond order of the metal-metal bonds in $[Re_2Cl_8]^{2-}$, $[Re_2Cl_6(P(C_2H_5)_3)_2]$ and $[Re_2Cl_4(P(C_2H_5)Ph_2)_4]$ respectively are

(*a*) 4, 4 and 3 (*b*) 3, 4 and 4

(*c*) 4, 2 and 3 (*d*) 2, 3 and 4

Q. 67–73 Contains a statement (S) with a reason (R) and an assertion (A). for each question, choose the correct answer from the following four choices.

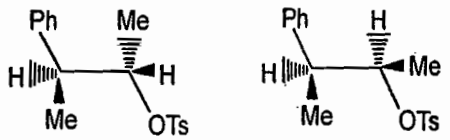
(*a*) Both R and A are correct

(*b*) Both R and A are wrong

(*c*) R is correct but A is wrong

(*d*) R is wrong but A is correct

67.



Statement: Solvolysis of tosylates (I) and (II) shown above, in acetic acid yield the corresponding acetates.

Reason: Due to neighbouring group participation of the bridged phenonium ion, achiral intermediates are formed in both cases of (I) and (II).

Assertion: Tosylate (I) gives an acetate with retention of configuration and tosylate (II) gives a recemic mixture of acetates.

68. Statement: Cyclopentadiene can potentially undergo Diels-Alder reaction ($4\pi + 2\pi$) and $2\pi + 2\pi$ cycloaddition reactions with ketenes. However, it reacts to give stereospecifically only one product.

Reason: Due to *sp* hybridisation of the ketene carbon $2\pi_s + 2\pi_a$ cycloaddition is feasible and thermally this reaction is symmetry allowed.

Assertion: Ketenes undergo only $2\pi + 2\pi$ cycloaddition reaction with 1, 3-dienes.

69. Statement: 1.3-Dichlorallene is optically active and the enantiomers are resolvable.

Reason: Optical activity is due to the presence of chiral center in the molecule.

Assertion: The enantiomers are resolvable because interconversion of enantiomers is possible only if there is a free rotation about C = C bonds, which is absent.

70. Statement: At 273 K, the fugacities (in atm) of N_2 are 97.03 and 1839 at the experimental pressures (atm) of 100 and 1000, respectively.

Reason: At 1000 atm, the system is above the critical temperature and pressure.

Assertion: The contribution of the repulsive forces is more dominant at 1000 atm.

71. Statement: For the equilibrium,

$$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

A plot of ln K_p vs 1/T gives a linear relationship with a positive slope.

Reason: The reaction is exothermic.

Assertion: The free energy change for the reaction is more negative at higher temperatures.

72. Statement: The potential for the cell,

$Pt|H_2(g, latm)|HCl\,(m)|\,AgCl(s)|Ag(s)$

decreases as the concentration of HCl is increased.

Reason: The mean ionic activity coefficient decreases with increase in HCl concentration.

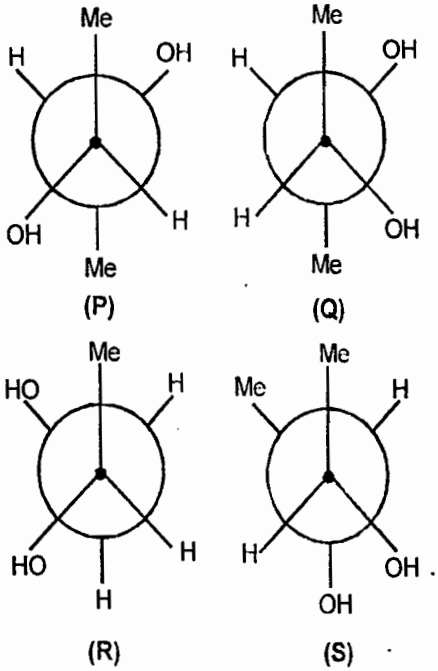
Assertion: In a plot of E vs [HCl], the intercept at the potential axis is equal to the standard reduction potential of the hydrogen electrode.

73. Statement: Oxygen is preferred to air for welding metals using acetylene gas.

Reason: With air, metal nitrides are formed resulting in poor welding.

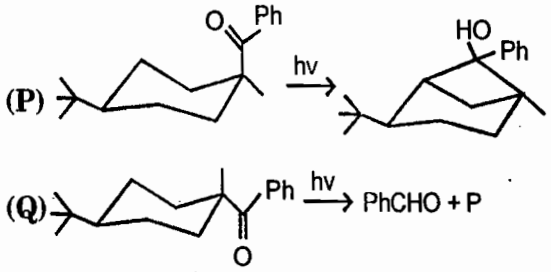
Assertion: With air, inert nitrogen dissipates the heat of combustion and hence, the maximum temperature attained is less than that with oxygen.

74. Among the following, the Newman projections of meso-2, 3-butanediol are



(*a*) P, Q (*b*) P, R
(*c*) R, S (*d*) Q, S

75. The correct description of the following two reactions is that

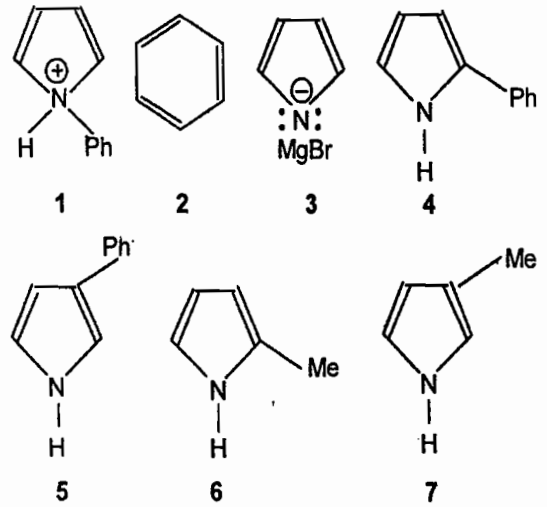


(*a*) both P and Q undergo α-cleavage reaction
(*b*) P undergoes only Norrish type II reaction whereas Q undergoes only Norrish type I reaction
(*c*) Q gives P by photochemical chair to chair interconversion of the cyclohexane Ring
(*d*) both P and Q undergo Norrish type I reaction, but only Q gives S through this mechanism

76. A 10.0 g mixture of n-butane and 2-butene was treated with bromine in CCl_4 and it consumed 8.0 g of bromine (Atomic wt. = 80). Another 10.0 g of the same mixture was hydrogenated to get n-butane only. The weight of 2-butene in the original mixture and the gain in the weight of the mixture after hydrogenation, respectively are

(*a*) 2.8 g and 0.1 g (*b*) 5.6 g and 0.4 g
(*c*) 7.2 g and 0.8 g (*d*) 8.6 g and 1.0 g

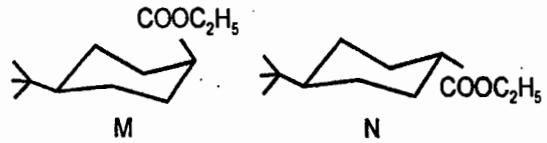
77. Pyrrole + PhMgBr → E + F
F + MeCl → G + H
F + MeCl → no reaction without a catalyst



The structure of products E-H, respectively are

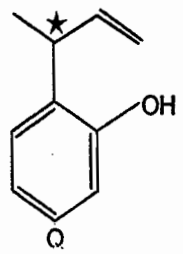
(*a*) 3, 2, 6, 7 (*b*) 4, 5, 6, 1
(*c*) 3, 4, 5, 2 (*d*) 3, 2, 4, 5

78. Regarding the saponification of M and N shown below, the correct statement is that



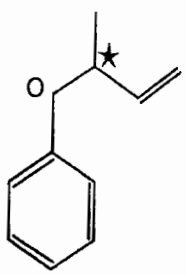
(*a*) M reacts faster than N because the transition state is less crowded for M than for N
(*b*) M reacts slower than N because the transition state if more crowded for M than for N
(*c*) N and M react at the same rate because of formation of tetrahedral intermediate in both cases
(*d*) N reacts slower than M because of its greater thermodynamic stability

79. Reactant P labelled with ^{14}C (labelled carbon marked with a star)rearranged to product Q on heating

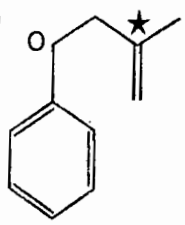


The structure of reactant P is

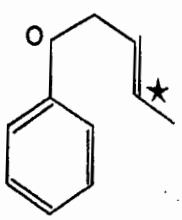
(a)



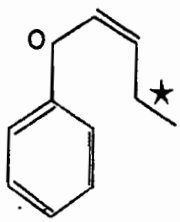
(b)



(c)



(d)



80. $RCH_2COR + R'X \xrightarrow{[(CH_3)_2CH]_2NLi} P + Q$

In the above reaction, X is a halogen and the products P and Q are

(I) $R'N[CH(CH_3)_2]_2$

(II) $RCH(R')COR$

(III) $RCH=C(OR')-R$

(IV) $RCH_2C(R)(OH)-N[CH(CH_3)_2]_2$

(a) I and II (b) II and III

(c) III and IV (d) I and IV

81. Among the halobenzenes, the one that undergoes electrophilic aromatic substitution most readily and the reason for its higher reactivity are

(a) fluorobenzene; the benzenonium ion intermediate is stablished by 2p (F), 2p(C)overlap which is most efficient

(b) chlorobenzene; very high electron affinity of chlorine considerably lowers the energy of activation of the reaction

(c) bromobenzene; high polarising power of the halogen atom helps in effective stablisation of the benzenonium ion intermediate

(d) iodobenzene; iodine atom has the lowest electronegativity and hence electron density of the phenyl ring is least disturbed.

82. Among the carboxylic acids shown below, the ones that exhibit stereoisomerism and also form, on heating, cyclic anhydrides are

(I) $HOOCCH(CH_3)CH_2CH_2COOH$

(II) $HOOCCH(i\text{-}C_3H_7)COOH$

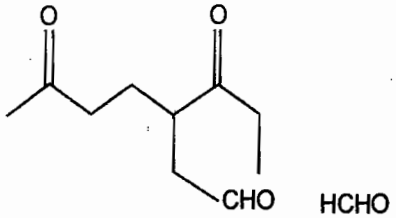
(III) $HOOCCH(C_2H_5)CH_2COOH$

(IV) $HOOCC(CH_3)(C_2H_5)COOH$

(a) (I) and (II) (b) (I) and (III)

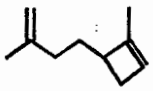
(c) (II) and (III) (d) (II) and (IV)

83. The reactants that lead to products (X) and (Y) on ozonolysis are

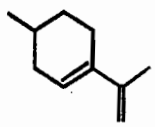


(X) (Y)

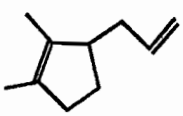
(I)



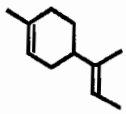
(II)



(III)



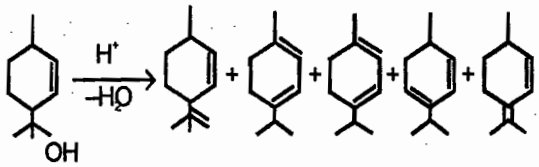
(IV)



(a) (I) and (IV) (b) (I) and (III)

(c) (II) and (III) (d) (II) and (IV)

84.



On the basis of Woodward-Fieser rules, the dienes that have λ_{max} values in the range 268-273 nm are

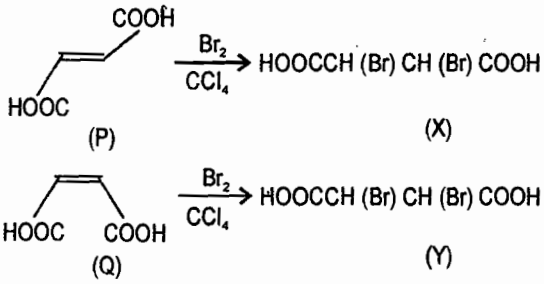
(a) P and Q

(b) P and R

(c) Q and R

(d) Q and S

85.



The correct statements with respect to the above pair of pair of reactions are that

(I) the reactions are stereospecific

(II) (X) is erythro and (Y) is threo isomer

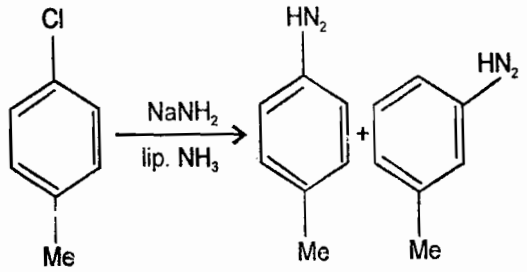
(III) (X) is threo and (Y) is erythro isomer

(IV) each of (P) and (Q) gives a mixture of (X) and (Y)

(*a*) (I) and (II) (*b*) (I) and (III)

(*c*) (I) and (IV) (*d*) (II) and (IV)

86.



The above reaction is an example of

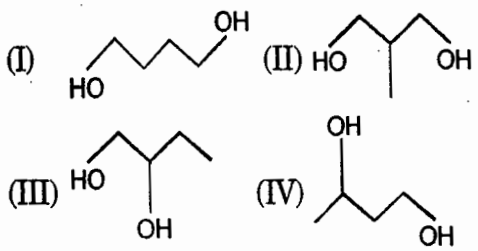
(*a*) nucleophilic substitution of addition-elimination mechnism

(*b*) electrophilic substitution by addition-elimination mechanism

(*c*) radical substitution reaction

(*d*) nucleophilic substitution involving benzyne intermediate

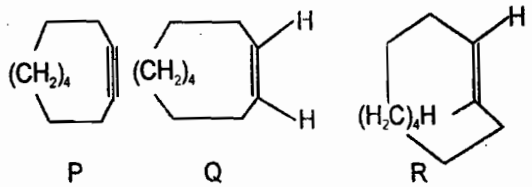
87. Diols (I–IV) which react with CrO_3 in aqueous H_2SO_4 and yield products that readily undergo decarboxylation on heating, are



(*a*) (I) and (II) (*b*) (II) and (III)

(*c*) (II) and (IV) (*d*) (I) and (IV)

88. Reactant P gives products Q and/or R.



The possible reagents are:

(I) 2Na/liq.NH_3 (II) H_2/Pd $CaCO_3$(quinoline)

(III) $2H_3$/Pd/C

The correct statement with respect to the conversion is

(*a*) Q is obtained on treatment with reagent (I)

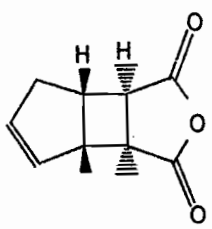
(*b*) R and Q are obtained on treatement with reagent (III)

(*c*) R is obtained on treatment with reagent (I)

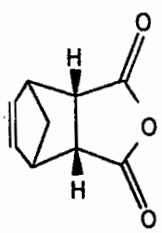
(*d*) R is obtained on treatment with reagent (II)

89. The product obtained in the thermal reaction of cyclopentadiene with maleic anhydride is

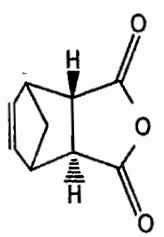
(*a*)



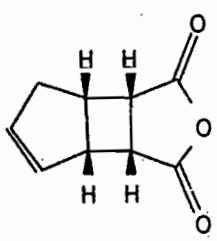
(*b*)



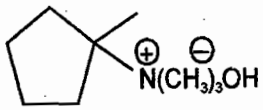
(*c*)



(*d*)

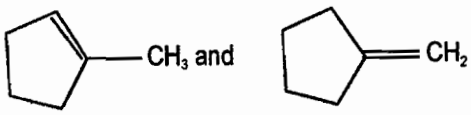


90. Two alkenes, X(91%, yield) and Y(9% yield) are formed when the following is heated.

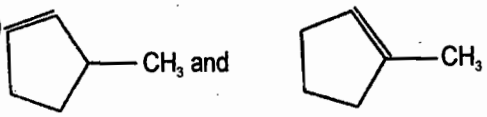


The structures of X and Y, respectively are

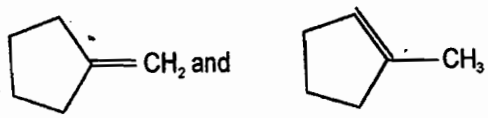
(*a*)



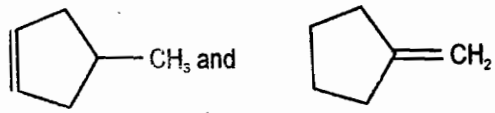
(*b*)



(*c*)



(*d*)



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GATE - 2004

CY : CHEMISTRY

Duration: Three Hours | *Maximum Marks*: 100

SOME USEFUL DATA

Gas constant	$R = 8.314\ JK^{-1}\ mol^{-1} = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$
Faraday Constant	$h = 96{,}500\ C\ mol^{-1}$
Planck constant	$h = 6.626 \times 10^{-34}\ Js$
Boltzmann constant	$k = 1.3807 \times 10^{-23}\ JK^{-1}$
Avogadro number	$N = 6.023 \times 10^{23}\ mol^{-1}$

Atomic numbers

B	=	5	C	=	6	N	=	7
O	=	8	F	=	9	Si	=	14
Cl	=	17	Mn	=	25	Co	=	27
Ni	=	28	Cu	=	29	Ir	=	77

Q. 1 – 30 Carry One Mark Each

1. In units of $\frac{h^2}{8ml^2}$, the energy difference between levels corresponding to 3 and 2 node eigenfunctions for a particle of mass m in a one dimensional box of length l is

(*a*) 1 (*b*) 3

(*c*) 5 (*d*) 7

2. On the basis of LCAO-MO theory, the magnetic characteristics of N and N_2^+ are

(*a*) both diamagnetic

(*b*) both paramagnetic

(*c*) N_2 diamagnetic and N_2^+ paramagnetic

(*d*) N_2 paramagnetic and N_2^+ diamagnetic

3. The v_{rms} of a gas at 300 K is 30 $R^{1/2}$. The molar mass of the gas, in kg mol^{-1}, is

(*a*) 1.0 (*b*) 1.0×10^{-1}

(*c*) 1.0×10^{-2} (*d*) 1.0×10^{-3}

4. The coefficient of performance of a perfect refrigerator working reversibly between the temperatures T_c and T_h is given by

(*a*) $\frac{T_c - T_h}{T_c}$ (*b*) $\frac{T_h - T_c}{T_c}$

(*c*) $\frac{T_c}{T_h - T_c}$ (*d*) $\frac{T_h}{T_h - T_c}$

5. At a given temperature and pressure, the phase diagram of a three component system shows a binodal curve. If the two components are chloroform and water; the third component, among the choices given below, is

(*a*) benzene

(*b*) acetic acid

(*c*) toluene

(*d*) carbon tetrachloride

6. A certain reaction proceeds in a sequence of three elementary steps with the rate constants k_1, k_2 and k_3. If the observed rate constant (k_{obs}) of the reaction is expressed as $K_{obs} = (k_1/k_2)^{1/2}$, the observed activation energy (E_{obs}) of the reaction is

(*a*) $\frac{1}{2}\left[\frac{E_1}{E_2}\right] + E_3$ (*b*) $\frac{E_3 + E_1}{E_2}$

(*c*) $E_3\left[\frac{E_1}{E_2}\right]^{1/2}$ (*d*) $E_3 + \frac{1}{2}(E_1 - E_2)$

7. Which one of the following is an example of a maximum boiling azeotrope?

(*a*) $H_2O - HCl$

(*b*) $H_2O - C_2H_5OH$

(*c*) $CHCl_3 - CH_3OH$

(*d*) $CCl_4 - CH_3OH$

8. For the reaction $A + B \rightleftharpoons X^{\ddagger} \rightarrow P$, Ea = 20.0 $kJ\ mol^{-1}$ at 300 K. The enthalpy change for the formation of the activated complex from the reactants in $kJ\ mol^{-1}$.

(a) 12 (b) 15

(c) 23 (d) 25

9. In an osmotic pressure measurement, a plot of height of solution (h) of density (ρ) versus concentration (gL^{-1}) was made at a temperature T. The slope of the plot will be equal to (where g, given in the choices below, is the acceleration of free fall)

(a) $\frac{\rho RT}{gM}$ (b) $\frac{gRT}{\rho M}$

(c) $\frac{RT}{\rho gM}$ (d) $\frac{gRM}{\rho T}$

10. If 0.001 M of a substance quenches the efficiency of fluorescence by 20%, the value of Stem-Volmer constant in M^{-1} is

(a) 100 (b) 150

(c) 200 (d) 250

11. Which one of the following is NOT a photodetector?

(a) Bolometer

(b) Charge-transfer device

(c) Photomultiplier tube

(d) Silicon diode

12. The nature of excitation signal used for cyclic voltammetry is

(a) linear scan (b) differential pulse

(c) triangular (d) square wave

13. The structure of SF_4 is

(a) octahedral

(b) tetrahedral

(c) trigonal bipyramidal

(d) square planar

14. The number of metal-metal bonds present in $Ir_4(CO)_{12}$ are

(a) 4 (b) 5

(c) 6 (d) 8

15. The zero magnetic moment of octachedral K_2NiF_6 is due to

(a) low spin d^6 Ni(IV)complex

(b) low spin d^8 Ni(II)complex

(c) high spin d^8 Ni(II)complex

(d) high spin d^6 Ni(IV) complex

16. The number of hyperfine split lines observed in ESR spectrum of methly radical is

(a) 1

(b) 4

(c) 6

(d) 8

17. The absorption of $Co(NH_3)_6^{2+}$ is

(a) stronger than that of $[Co(NH_3)_5Cl]^{2+}$

(b) stronger than that of $[MnCl_4]^{2-}$

(c) weaker than that of $[MnCl_4]^{2-}$ but stronger than that of $[CO(NH_3)_5Cl]^{2+}$

(d) weaker than those of both $[MnCl_4]^{2-}$ and $[Co(NH_3)_5Cl]^{2+}$

18. Which one of the following statements about ferrocence is FALSE?

(a) It obeys the 18-electron rule

(b) It is diamagnetic

(c) It is an orange solid

(d) It resists electrophilic substitution

19. The bond angle of Cl_2O is

(a) smaller than that of F_2O

(b) greater than that of H_2O

(c) smaller than that of H_2O

(d) same as that of F_2O

20. The half-wave potential for a reversible reduction of a metal ion in polarography is independent of

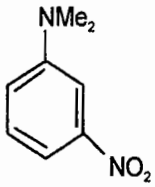
(a) concentration of the supporting electrolyte

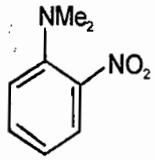
(b) concentration of the electroactive species

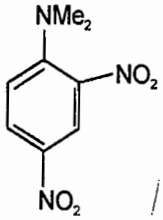
(c) concentration of the complexing agent

(d) temperature of the solution

21. The major product formed on nitration of N, N-dimethylaniline with conc. $H_2SO_4^-$ HNO_3 mixture is

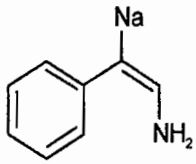
(*a*) 

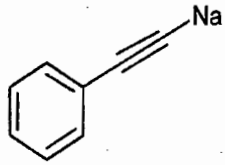
(*b*) 

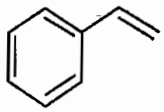
(*c*) 

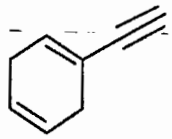
(*d*)

22. Reaction of phenylacetylene with sodamide in liquid ammonia generates

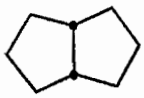
(*a*) 

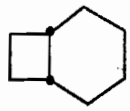
(*b*) 

(*c*) 

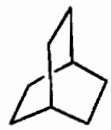
(*d*) 

23. Proton decoupled ^{13}C NMR spectrum of a bicyclooctane (N_8H_{14})exhibits only two signals. The structure of the compound is

(*a*) 

(*b*) 

(*c*)

(*d*) 

24. Cyclohexyl benzyl ether when reacted with hydrogen in the presence of 10% palladium on charcoal generates a mixture of

(*a*) cyclohexanol and benzyl alcohol

(*b*) cyclohexane and benzyl alcohol

(*c*) cyclohexanol and toluene

(*d*) cyclohexane and toluene

25. In electrophilic aromatic substitution reactions, nitro group is meta-directing, because the nitro group

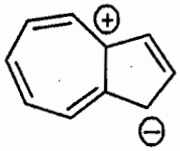
(*a*) increases electron density at *meta*-position

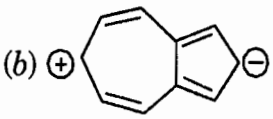
(*b*) increases electron density at *ortho*- and *para*-positions

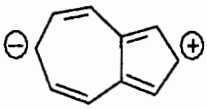
(*c*) decreases electron density at *meta*-position

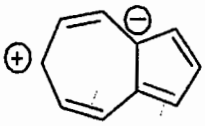
(*d*) decreases electron density at *ortho*-and *para*-positions

26. Among the resonance forms given below, the one which contributes most to the stability of azulene is

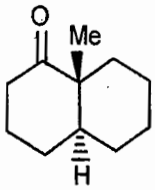
(*a*) 

(*b*) 

(*c*) 

(*d*) 

27. The configurations at the two asymmetric centres (C-1 and C-6) in the bicyclo [4.4.0] decane, given below, are



(*a*) 1R, 6R

(*b*) 1R, 6 S

(*c*) 1S, 6S

(*d*) 1S, 6 R

28. The reactive intermediate involved in the conversion of phenol to salicyldehyde using chloroform and sodium hydroxide is

(*a*) Cl_2C: (*b*) Cl_2CH^+

(*c*) Cl_2CH^- (*d*) Cl_2CH^+

29. Conversion of Ph-NH_2 into Ph-CN can be accomplished by

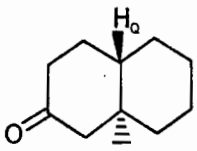
(*a*) reaction with sodium cyanide in the presence of nickel catalyst

(*b*) reaction with chloroform and sodium hydroxide

(*c*) diazotisation followed by reaction with CuCN

(*d*) reaction with ethyl formate followed by thermolysis

30. The vicinal coupling constant J expected for the protons H_P and H_Q in the compound given below will be in the range



(*a*) 0-2 Hz

(*b*) 4-6 Hz

(*c*) 8-10Hz

Q. 31-90 Carry Two Marks Each

31. For one mole of an ideal gas

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T =$$

(*a*) -1 (*b*) $-\frac{R^2}{P^2}$

(*c*) $+1$ (*d*) $\frac{R^2}{P^2}$

32. Neglecting the mass of hydrogen (1.0 amu) and deuterium (2.0 amu) with respect to that of iodine (127 amu), the ratio between fundamental vibrational frequencies of HI and DI is

(*a*) $\frac{1}{2}$ (*b*) 2

(*c*) $\frac{1}{\sqrt{2}}$ (*d*) $\sqrt{2}$

33. The population of Jth rotational level N_j is given by $N_j = N_o(2J + 1)e^{-[j(j+1)B]/kT}$. The J value of rotational level with maximum population (J_{max}) is given by

(*a*) $\frac{(2kT/B)-1}{\sqrt{2}}$ (*b*) $\frac{\sqrt{2kT/B}-1}{2}$

(*c*) $\frac{kT}{B}$ (*d*) $\frac{B}{kT}$

34. The fugacity coefficient ϕ is given by ln $\phi = \int_0^p \left(\frac{z-1}{P}\right) dp$ where z is the compressibility factor, and p the pressure. The fugacity of a gas governed by the gas law $p(V_m - b) = RT$ is

(*a*) $p \ln(V_m/RT)$ (*b*) $pe^{b/RT}$

(*c*) $pe^{-bp/RT}$ (*d*) $pe^{bp/RT}$

35. The number and symmetry type of normal modes of vibration of H_2O are

(*a*) 3 and $2A_1 + B_2$ (*b*) 3 and $2A_1 + A_2$

(*c*) 3 and $2A_1 + B_1$ (*d*) 4 and $3A_1 + B_2$

36. The gaseous reaction $2A + B \rightarrow C$, with partial pressures of $p_A = 0.1$ atm; $p_B = 0.001$ atm and $p_C = 1.0$ atm, proceeds to the left at 298 K. The equilibrium constant, K_p for the above reaction is

(*a*) 1.0×10^4 (*b*) 1.0×10^5

(*c*) 1.0×10^6 (*d*) 1.0×10^7

37. The change in entropy when one mole of an ideal gas is compressed to one-fourth of its initial volume and simultaneously heated to twice its initial temperature is

(*a*) $(C_V - R)\ln 4$ (*b*) $(C_V - 2R)\ln 2$

(*c*) $(C_V - 2R)\ln 4$ (*d*) $(C_V + 2R)\ln 2$

38. For the reaction $A(s) \rightleftharpoons B(l) + 2\,C(g)$, $\Delta G°$(in Joules) = 90800 – 100T. The partial pressure of C(g) at 600 K in Torr is

(*a*) 15 (*b*) 22

(*c*) 35 (*d*) 46

39. Match the following:

P. $\left(\frac{\partial U}{\partial S}\right)_V$	I. A
Q. $\left(\frac{\partial U}{\partial V}\right)_S$	II. – S
R. $\left(\frac{\partial G}{\partial P}\right)_T$	III. T
S. $\left(\frac{\partial G}{\partial T}\right)_P$	IV. – P
	V. H
	VI. V

(*a*) P – III	Q - IV	R - VI	S - II
(*b*) P - III	Q - I	R - II	S - V
(*c*) P - I	Q - III	R - V	S - II
(*d*) P - IV	Q - III	R - VI	S - V

40. Match the following:

P. 4n + 2 rule	I. Woodward-Hoffmann rule
Q. single valued	II. Bound system
R. $\langle p_x \rangle = 0$	III. Hartree-Fock Theory
S. photochemically allowed	IV. Huckel theory
	V. Wave function
	VI. unbound system

(*a*) P – I	Q - III	R - IV	S - VI
(*b*) P - IV	Q - V	R - II	S - VI
(*c*) P - II	Q - VI	R - III	S - I
(*d*) P - IV	Q - V	R - II	S - I

41. The solubility product of silver sulphate at 298 K is 1.0×10^{-5}. If the standard reduction potential of the half-cell $Ag^+ + e \rightarrow Ag$ is 0.80 V, the standard reduction potential of the half-cell $Ag_2SO_4 + 2e \rightarrow 2Ag + SO_4^{2-}$ is

(*a*) 0.15 V (*b*) 0.22 V
(*c*) 0.65 V (*d*) 0.95 V

42. The criterion for spontaneous change in terms of the state functions is

(*a*) $dU_{s,V} \geq 0$ (*b*) $dA_{T,V} \geq 0$
(*c*) $dS_{U,V} \geq 0$ (*d*) $dG_{T,V} \leq 0$

43. One mole of an ideal gas ($C_V = 1.5$ R) at a temperature 500 K is compressed from 1.0 atm to 2.0 atm by a reversible isothermal path. Subsequently, it is expanded back to 1.0 atm by a reversible adiabatic path. The volume of the final state in litre is

(*a*) 15.6 (*b*) 20.5
(*c*) 31.1 (*d*) 41.0

44. The vapour pressures of the pure components P and Q are 700 Torr and 500 Torr, respectively. When the two phases are in equilibrium at 1.0 atm, the mole fraction of P in the liquid phase is 0.6 and in the vapour phase 0.4. The activity co-efficient of component P in the solution on the basis of Raoult's law is

(*a*) 0.60 (*b*) 0.72
(*c*) 0.92 (*d*) 1.01

45. The concentration of oxygen in water in mg L^{-1}. If the Henry's law constant for oxygen at 298 K is 2.80×10^7 Torr, the partial pressure of oxygen in the atmosphere in Torr is,

(*a*) 2 (*b*) 32
(*c*) 50 (*d*) 70

46. Decomposition of ammonia on tungsten at 850°C has a rate constant value of 0.10 Torr s^{-1}. If the initial pressure of ammonia is 100 Toor, the pressure of ammonia (in Torr) at $t = 200$ s is

(*a*) 10 (*b*) 20
(*c*) 50 (*d*) 80

47. For the reaction of the type $P \xrightarrow{k_1} Q \xrightarrow{k_2} R$, given that $[P]_0 = 1.0$ M; $k_1 = 1 \times 10^{-3}$ s^{-1} and $k_2 = 1 \times 10^{-4}$ s^{-1}, the time at which the concentrations of Q and R are 0.5966 M and 0.0355 M, respectively, is

(*a*) 500 s (*b*) 750 s
(*c*) 1000 s (*d*) 1500 s

48. The spinels $CoFe_2O_4$ and $FeFe_2O_4$ respectively, are

(*a*) inverse and inverse
(*b*) inverse and normal
(*c*) normal and normal
(*d*) normal and inverse

49. According to Wade's rule, the structures of $B_{10}C_2H_{12}$ and $[B_2C_2H_{11}]^{2-}$, respectively, are

(*a*) closo and arachno
(*b*) nido and closo
(*c*) closo and nido
(*d*) nido and arachno

50. The overall charge present on the cyclic silicate anion $[Si_6O_{18}]^{n-}$ is

(*a*) 6 (*b*) 12
(*c*) 18 (*d*) 24

51. The ground state term symbols for high spin d^5s^1 and d^5 configurations, respectively, are

(*a*) ^3S and ^6S (*b*) ^6P and ^3S
(*c*) ^7S and ^6S (*d*) ^7P and ^6S

52. The reagents required for the synthesis of cyclic phosphazene $N_4P_4Cl_8$ are

(*a*) PCl_5 and NH_3 (*b*) $POCl_3$ and NH_4Cl
(*c*) $POCl_3$ and HN_3 (*d*) PCl_5 and NH_4Cl

53. The isomerisms that are possible in the Co(III)complexes $(Co(NH_3)_3(NO_2)_3]$ and $[Co(NH_3)_5NO_2]Cl_2$, respectively, are

(*a*) co-ordination and position
(*b*) optical and linkage
(*c*) geometrical and linkage
(*d*) optical and optical

54. The perxenate ion XeO_4^{4-} can be prepared by

(*a*) direct reaction of Xe with oxygen

(*b*) reaction of XeF_6 with oxygen

(*c*) hydrolysis of XeF_6 in acidic medium

(*d*) hydrolysis of XeF_6 in basic medium

55. In tetrahedral geometry, which one of the following sets of electronic configurations will have orbital contribution to the magnetic moment?

(*a*) d^3, d^4, d^8 and d^9 (*b*) d^1, d^6, d^7 and d^9

(*c*) d^3, d^4, d^7 and d^9 (*d*) d^1, d^3, d^4 and d^9

56. The most suitable route to prepare the trans isomer of $[PtCl_2(NH_3)(PPh_3)]$ is

(*a*) $[PtCl_4]^{2-}$ with PPh_3 followed by reaction with NH_3

(*b*) $[PtCl_4]^{2-}$ with NH_3 followed by reaction with PPh_3

(*c*) $[Pt(NH_3)_4]^{2+}$ with HCl followed by reaction with PPh_3

(*d*) $[Pt(NH_3)_4]^{2+}$ with PPh_3 followed by reaction with HCl

57. A solution containing 5 ppm of $KMnO_4$ (F.W. = 159) has a transmittance of 0.360 measured in a 1 cm cell at 500 nm. The molar absorptivity of $KMnO_4$ in L mol^{-1} cm^{-1} is

(*a*) 1.1×10^4 (*b*) 1.4×10^4

(*c*) 1.9×10^4 (*d*) 2.7×10^4

58. Match the following:

P. coulometry	I. dropping mercury electrode
Q. ion selective electrode	II. current efficiency
R. polarography	III. dead stop end point
S. amperometry	IV. membrane potential
	V. conductometer
	VI. actinometer

(*a*) P – II	Q - IV	R - I	S - III
(*b*) P - I	Q - II	R - III	S - V
(*c*) P - VI	Q - V	R - III	S - IV
(*d*) P - III	Q - IV	R - I	S - VI

59. Match the following:

P. ferritin	I. electron transport
Q. vitamin B_{12}	II. ionophore
R. cytochromes	III. oxygen transport
S. valinomycin	IV. nitrogen fixation
	V. organometallic enzyme
	VI. iron storage

(*a*) P – VI	Q - IV	R - II	S - I
(*b*) P - I	Q - III	R - VI	S - IV
(*c*) P - III	Q - V	R - IV	S - VI
(*d*) P - VI	Q - V	R - I	S - II

60. The number of absorption bands observed $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$, respectively, are

(*a*) 1 and 3 (*b*) 0 and 1

(*c*) 0 and 3 (*d*) 3 and 1

61. Regarding the catalytic cycle of hydrogenation of alkenes involving $RhCl(PPh_3)_3$ as the catalyst, the correct statement is

(*a*) only 18-electron Rh complex is involved

(*b*) 14-, 16-and 18-electron Rh complexes are involved

(*c*) 14-and 16-electron Rh complexes are involved

(*d*) 16-and 18-electron Rh complexes are involved

62. The infra-red stretching frequency V_{CO} of P-S follows the order

(P) $Mn(CO)_6^+$

(Q) CO

(R) $H_3B \leftarrow CO$

(S) $[V(CO)_6]^-$

(*a*) P > R > S > Q (*b*) S > P > R > Q

(*c*) Q > S > P > R (*d*) R > Q > P > S

63. The structures of $N(CH_3)_3$ and $N(SiH_3)_3$, respectively are

(*a*) trigonal planar and pyramidal

(*b*) pyramidal and trigonal planar

(*c*) pyramidal and pyramidal

(*d*) trigonal planar and trigonal planar

64. Which one of the following is NOT correct in chromatography?

t_M = Retention time for a species that is not retained by the stationery phase.

T_R = Retention time for the analyte

$(t_R)_n$ = Retention time for the component n

W_n = Width of the peak at its base for the component n

(*a*) Resolution = $\dfrac{(t_R)_2 - (t_R)_1}{2(W_1 + W_2)}$

(*b*) Capacity factor = $\dfrac{t_R - t_M}{t_M}$

(*c*) Separation factor = $\dfrac{(t_R)_2 - t_M}{(t_R)_1 - t_M}$

(*d*) No. of theoretical plates = $16\left(\dfrac{t_R}{W}\right)^2$

65. Thermal reaction of allyl phenyl ether generates a mixture of *ortho*-and *para*-*allyl* phenols. The *para*-allyl phenol is formed via

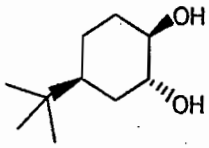
(*a*) a[3, 5]-sigmatropic shift

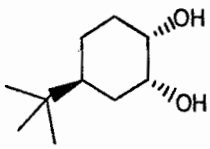
(*b*) firt *ortho-allyl* phenol is formed, which then undergoes a [3, 3]-sigmatropic shift

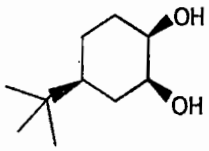
(*c*) two consecutive [3, 3]-sigmatropic shifts

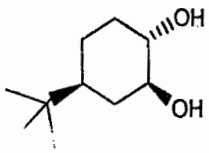
(*d*) dissociation to generate allyl cation, which then adds at *para*-position

66. Of the favour vicinal diols shown below, only three are cleaved by HIO_4, the diol which is NOT cleaved HIO_4 is

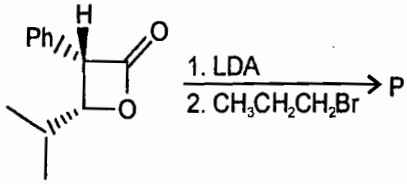
(*a*) 

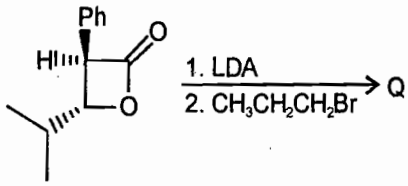
(*b*) 

(*c*) 

(*d*) 

67. With respect to the two reactions shown below, the correct statements about their stereochemical nature is [LDA = LiN($^iPr_2$]

(*i*) 

(*ii*) 

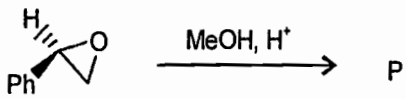
(*a*) the reactions are stereoselective, because P and Q are the same

(*b*) the reactions are non-stereoselective, beacause P and Q are the same

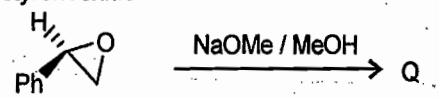
(*c*) the reactions are stereoselective, because P and Q are diastereomers

(*d*) the reactions are enantioselective, because P and Q are enantiomers

68. For the reactions shown below, identify the correct statement with regard to the products formed.

(*i*) 

(S)-styreneoxide

(*ii*) 

(S)-styreneoxide

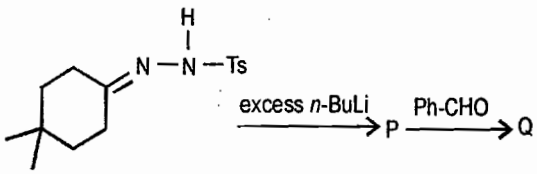
(*a*) P and Q are identical, both are optically active

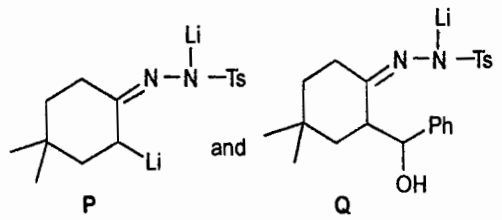
(*b*) P and Q are positional isomers, P is racemic and Q is optically active

(*c*) P and Q are positional isomers, P is optically active and Q is racemic

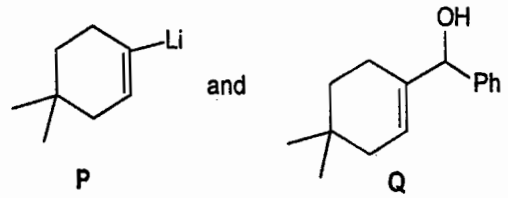
(*d*) P and Q are positional isomers, both are optically active

69. In the reaction shown below, identify the correct combination of the intermediate P and the product Q.

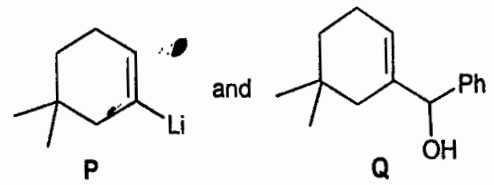


(a)


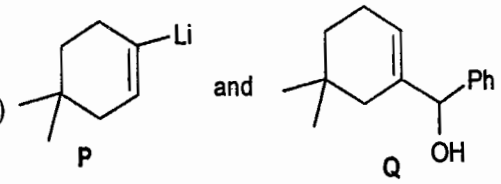
P Q

(b)


P Q

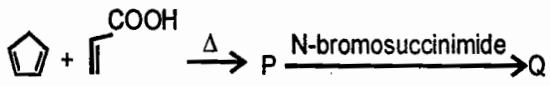
(c)


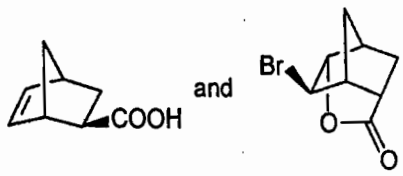
P Q

(d)


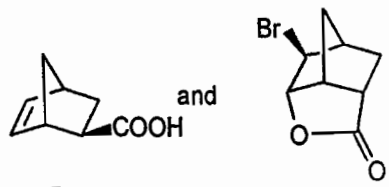
P Q

70. In the two step reaction shown below, identify the correct combination of products P and Q.

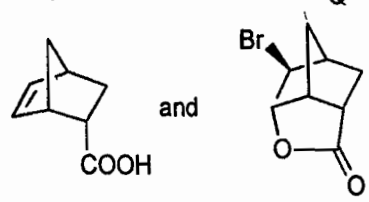


(a)


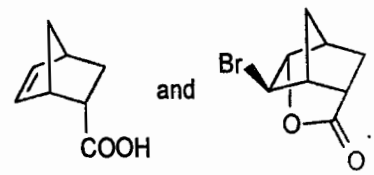
P Q

(b)


P Q

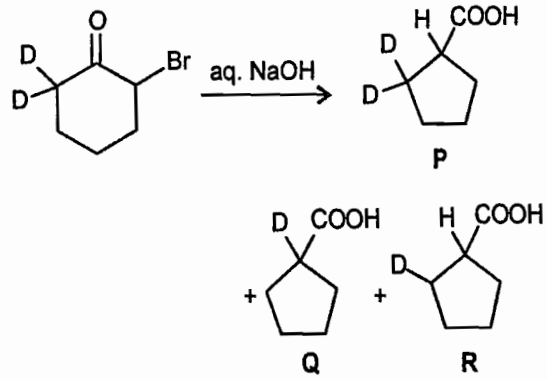
(c)


P Q

(d)


P Q

71. On the basis of Favorskii rearrangement mechanism, the ratio of the products P, Q and R given below, will be, respectively,



(a) 2:1:1 (b) 1:1:1

(c) 1:0:1 (d) 0:1:1

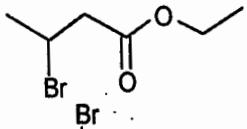
72. An organic compound having molecular formula $C_6H_{11}BrO_2$ exhibits the following peaks in ^1H NMR spectrum.

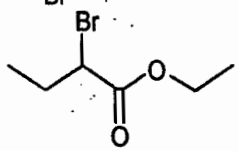
δ 4.1 (2H, q, J = 7.5Hz),

4.0 (2H, t, J = 7.5 Hz), 1.5-2.2 (4H, m),

1.25 (3H, t, J = 7.5 Hz)

The structure of the compound is

(a)


(b)


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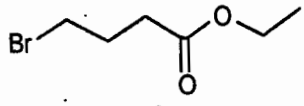
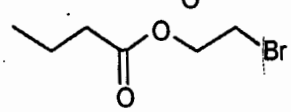
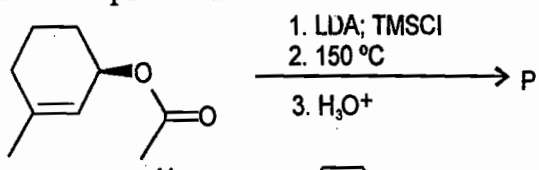
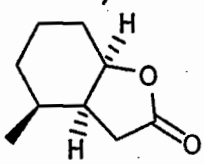


(d)


73. The product P formed in the following three steps reaction is



(a)


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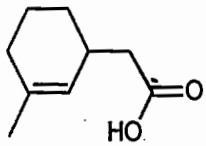

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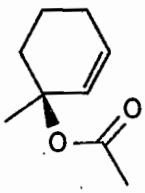

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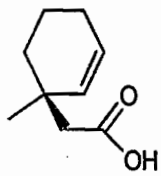
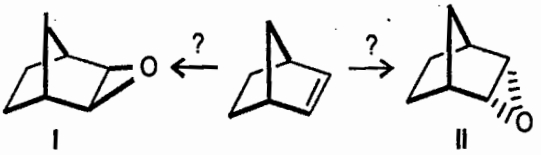


74. Identify the correct choice of reagents, among P, Q and R, for the transformation of norbornene into the epoxides I and II

P = H_2O_2-AcOH Q = H_2O_2-NaOH

R = HOBr followed by aq. NaOH



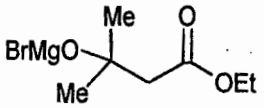
(*a*) P gives I and Q gives II

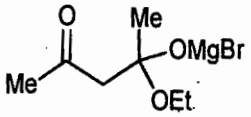
(*b*) R gives I and P gives II

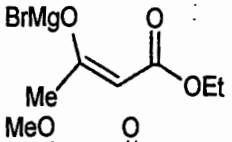
(*c*) Q gives I and R gives II

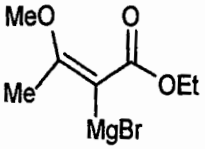
(*d*) P gives I and R gives II

75. Reaction of ethyl acetoacetate with one equivalent of methylmagnesium bromide gives

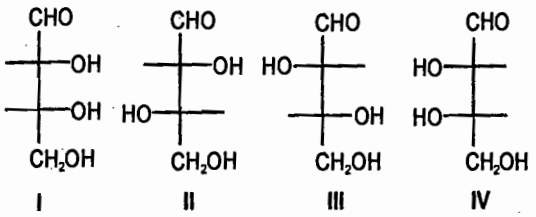
(*a*) 

(*b*) 

(*c*) 

(*d*) 

76. For the aldotetroses I-IV, the combination of TRUE statements, among P-T, is



P = I and II are diastereomers and II and III are enantiomers

Q = I and IV are mesomers and are optically inactive

R = I and III can be interconverted by a base catalysed isomerisation

S = only I and IV are HIO_4 cleavable

T = I and III are D-sugars and II and IV are L-sugars

(*a*) Q, R, T (*b*) P, R, T

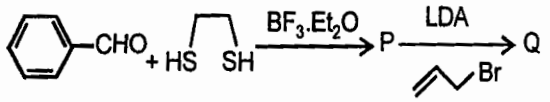
(*c*) Q, S, T (*d*) P, Q, S

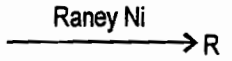
77. Match the compounds P-S with their carbonyl stretching frequencies (cm^{-1}) I-VI in IR spectroscopy.

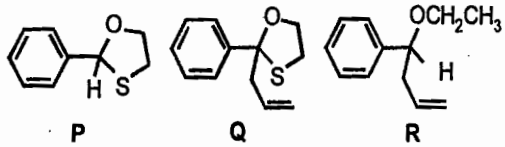
P. acetone	I. 1870
Q. ethyl acetate	II. 1800
R. acetamide	III. 1740
S. acetyl chloride	IV. 1700
	V. 1660
	VI. 1600

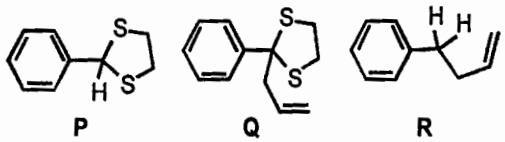
(*a*) P – IV	Q - III	R - I	S - VI
(*b*) P - III	Q - VI	R - V	S - II
(*c*) P - IV	Q - III	R - V	S - II
(*d*) P - II	Q - V	R - III	S - VI

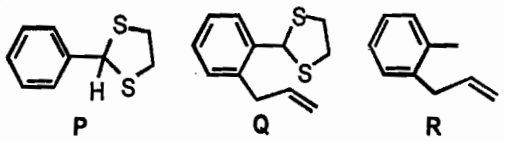
78. In the following three step transformation, identify the correct combination of product P, Q and R. [LDA = LiN(^{i}Pr)$_2$]

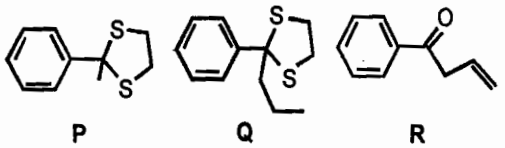




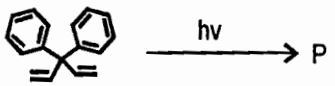
(*a*) 

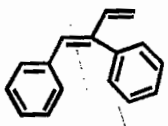
(*b*) 

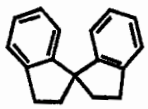
(*c*) 

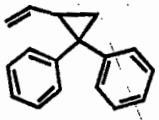
(*d*) 

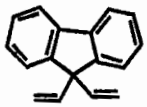
79. The major product P formed in the following photochemical reaction is



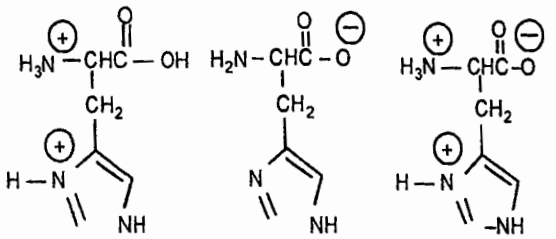
(*a*) 

(*b*) 

(*c*) 

(*d*) 

80. Three molecular ionic states, P-R, are possible for the amino acid histidine. Identify the correct choice of pH values, respectively, for the observation of the ionic states P-R.



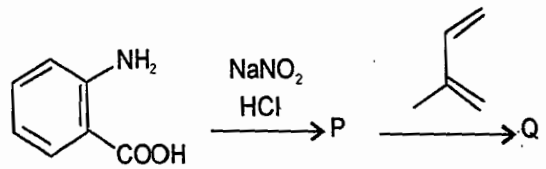
(*a*) P at pH 1 ; Q at pH 12 ; R at pH 7

(*b*) P at pH 7 ; Q at pH 1 ; R at pH 12

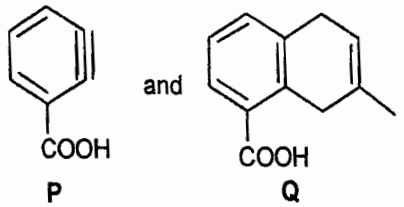
(*c*) P at pH 12 ; Q at pH 7 ; R at pH 1

(*d*) P at pH 12 ; Q at pH 1 ; R at pH 7

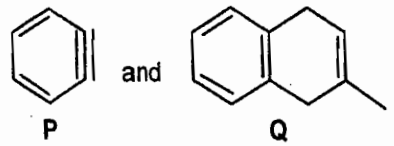
81. In the reaction shown below, identify the correct combination of the intermediate P and the product Q.



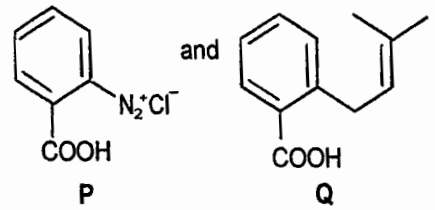
(*a*)



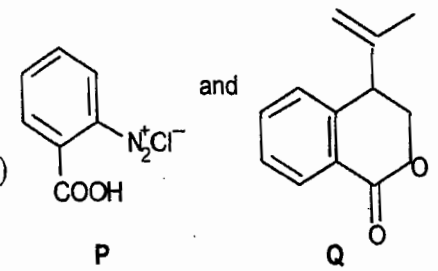
(*b*)



(*c*)



(*d*)



Direction (Q. 82-90) : *Following questions contain a Statement with a Reason and an Assertion. For each question, choose the correct answer from the following four choices.*

(*a*) Both Reason and Assertion are correct

(*b*) Both reason and Assertion are wrong

(*c*) Reason is correct and Assertion is wrong

(*d*) Reason is wrong but Assertion is correct

82. Statement : Solid carbon dioxide is called as dry ice.

Reason : CO_2 sublimes when kept in open atmosphere.

Assertion : Triple point of CO_2 lies above one atmosphere.

83. Statement : Entropy of pure, perfectly crystalline substance is zero at absolute zero of temperature.

Reasn : At absolute zero, molecules can have only one orientation.

Assertion : Statistical definition of entropy is given by the equation, $S = k \ln W$, where W is the probability of orientation

84. Statement : Catalytic decomposition of ammonia on platinum takes place at 1000°C.

Reason : Ammonia is more strongly adsorbed than hydrogen on platinum.

Assertion : The rate law for the decomposition of ammonia on platinum is given as, Rate $= k \dfrac{P_{NH_3}}{P_{H_2}}$ s

85. Statement : $CoCl_4^{2-}$ is a regular tetrahedron but $CuCl_4^{2-}$ is a distorted tetrahedron.

Reason : Unsymmetrical distribution of electrons in e_g orbital leads to distortion in $CuCl_4^{2-}$.

Assertion : Cl^- ligands interact differently with orbitals of unequal electron population. This leads to distortion in tetrahedral geometry.

86. Statement : Schottky and Frenkel defects are stoichiometric defect occuring in crystal lattices.

Reason : Schottky defects are due to the absence of one positive and one negative ion and Frenkel defects are due to the presence of one hole and one ion in an interstitial position.

Assertion : The ratio of number of atoms of one kind to the number of atoms of the other kind does not correspond exactly to the ideal whole number ratio implied by the formula which leads to stoichiometric defects.

87. Statement : Ga is below Al in Group IIIA, yet the atomic size of Ga is almost the same as that of Al.

Reason : Lanthanide contraction

Assertion : Poor shielding of nuclear charge results in outer electrons being more firmly held by the nucleus.

88. Statement : 5-Bromopyrimidine ($C_4H_3BrN_2$) exhibits two prominent peaks in the mass spectrum at m/z 158 and 160 in the ratio of 1 : 1.

Reason : There are two basic centers in the molecule, which are protonated.

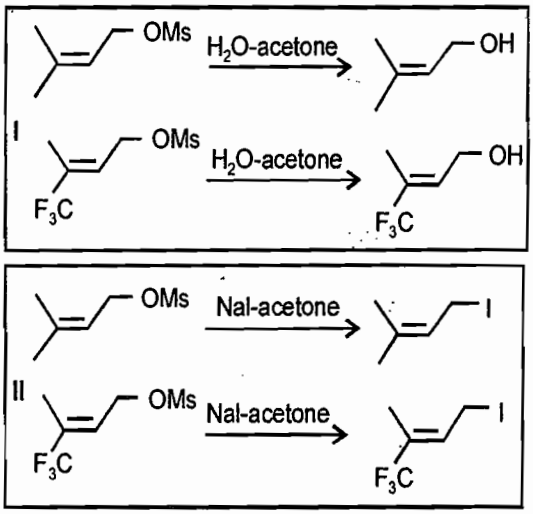
Assertion : There are two isotopes of bromine, ^{79}Br and ^{81}Br, that occur in the ratio of 1 : 1.

89. Statement : Pyridine is more basic than pyrrole.

Reason : The nitrogen in pyrrole carries a proton while the nitrogen in pyridine does not.

Assertion : Nitrogens in trigonal geometry are generally more basic than the nitrogens in tetrahedral geometry.

90. Statement : Replacement of CH_3 with CF_3 decreases the rate of reaction I, but increases the rate of reaction II.



Reason : Reaction I proceeds through SN_1 mechanism and reaction II proceeds through SN_2 mechanism.

Assertion : Being an electron withdrawing group, CF_3 destabilizes the transition state in SN_1 reaction, but stabilizes the transition state in SN_2 reaction.

ANSWER

1. (*c*)	**2.** (*c*)	**3.** (*a*)	**4.** (*b*)	**5.** (*b*)	**6.** (*d*)	**7.** (*a*)	**8.** (*b*)
9. (*c*)	**10.** (*c*)	**11.** (*b*)	**12.** (*)	**13.** (*c*)	**14.** (*c*)	**15.** (*c*)	**16.** (*d*)
17. (*c*)	**18.** (*d*)	**19.** (*b*)	**20.** (*a*)	**21.** (*d*)	**22.** (*b*)	**23.** (*d*)	**24.** (*d*)
25. (*d*)	**26.** (*b*)	**27.** (*d*)	**28.** (*b*)	**29.** (*c*)	**30.** (*a*)	**31.** (*c*)	**32.** (*d*)
33. (*)	**34.** (*c*)	**35.** (*)	**36.** (*a*)	**37.** (*)	**38.** (*)	**39.** (*c*)	**40.** (*d*)
41. (*d*)	**42.** (*d*)	**43.** (*)	**44.** (*)	**45.** (*)	**46.** (*)	**47.** (*)	**48.** (*b*)
49. (*b*)	**50.** (*a*)	**51.** (*c*)	**52.** (*c*)	**53.** (*a*)	**54.** (*d*)	**55.** (*c*)	**56.** (*)
57. (*)	**58.** (*a*)	**59.** (*d*)	**60.** (*a*)	**61.** (*)	**62.** (*)	**63.** (*c*)	**64.** (*)
65. (*a*)	**66.** (*c*)	**67.** (*)	**68.** (*)	**69.** (*)	**70.** (*)	**71.** (*)	**72.** (*)
73. (*)	**74.** (*b*)	**75.** (*b*)	**76.** (*d*)	**77.** (*c*)	**78.** (*)	**79.** (*)	**80.** (*)
81. (*a*)	**82.** (*a*)	**83.** (*d*)	**84.** (*b*)	**85.** (*c*)	**86.** (*a*)	**87.** (*a*)	**88.** (*c*)
89. (*c*)	**90.** (*a*)						

EXPLANATION

1. $$\Delta E = \frac{(2n+1)h^2}{8mL^2}$$

Here, $n = 2$

$$\therefore \quad \Delta E = \frac{5L^2}{8mL^2}$$

2. N_2 has no unpaired electron – dia

N_2^+ has no unpaired electron – para.

3. $$V_{rms} = \sqrt{\frac{3RT}{M}}$$

$$30R^{1/2} = R^{1/2}\sqrt{\frac{3\times 300}{M}}$$

$$\Rightarrow \quad M = 1.$$

5. Third component should have partial mutual solubility with each other.

8. $$\Delta H^{0\#} = E_a + (\Delta V^{\#}_{g=1})\,RT$$

$$= 20 - \left(\frac{2\times 8.314\times 300}{1000}\right) kJ.$$

9. $$PV = nRT$$

$$\Rightarrow \quad h\rho gV = \frac{W}{M}RT.$$

$$\Rightarrow \quad \frac{hV}{W} = \frac{RT}{\rho gM}$$

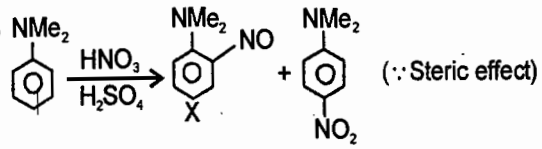
10. Stern-Volmer constant, $(M^{-1}) = \dfrac{20\%}{0.001}$

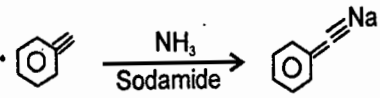
$= 200.$

15. d^8 unpaired.

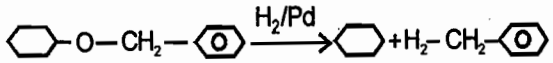
16. $2(I + 1) = 8$

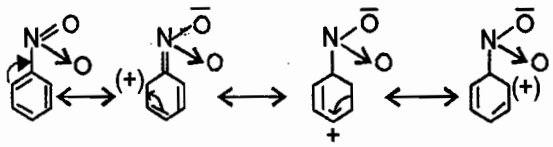
19. 111°

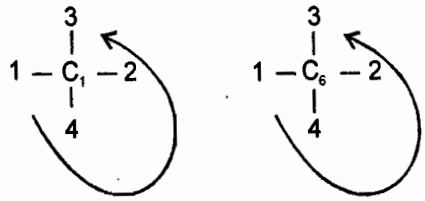
21. 

22. 

23. Only 2 different types of carbon.

24. 

25. 

27. 

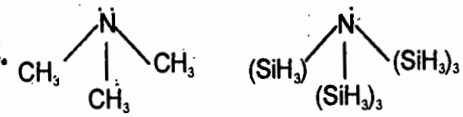
29. $Ph\,NH_2 \xrightarrow[HCl]{NaNO_2} Ph - \overset{+}{N}_2\,Cl \xrightarrow{CuCN} Ph - CN.$

32. $v \propto \sqrt{\dfrac{1}{\mu}}$ and $\dfrac{1}{\mu} = \dfrac{1}{m_1} + \dfrac{1}{m_2}$

$$\frac{\mu_{HI}}{\mu_{DI}} = \frac{1}{2}$$

36. $K_p = \dfrac{p}{p_A^2\, p_B}$

41. $E_{cell} = E^0_{cell} - nRT + \ln S.$

63. 

GATE - 2005

CY : CHEMISTRY

Duration: Three Hours | *Maximum Marks*: 100

SOME USEFUL DATA

Gas constant	R	= 8.314 J K^{-1} mol^{-1}
		= 0.082 L atm K^{-1} mol^{-1}
Faraday constant	F	= 96,500 C mol^{-1}
Planck constant	h	= 6.626×10^{-34} J s
Boltzman constant	k_B	= 1.381×10^{-23} J K^{-1}
Avogadro number	N	= 6.023×10^{23} mol^{-1}

Atomic numbers

B	=	5	C	=	6	N	=	7
O	=	8	F	=	9	Si	=	14
Cl	=	17	Cr	=	24	Mn	=	25
Fe	=	26	Co	=	27	Ni	=	28
Cu	=	29	Mo	=	42	La	=	57
Ce	=	58	Re	=	75			

Q. 1 – Q. 30 Carry One Mark Each

1. The complexes $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl.H_2O$ are examples of

(*a*) ionization isomerism
(*b*) linkage isomerism
(*c*) geometric isomerism
(*d*) optical isomerism

2. In the trigonal bipyramidal crystal field, the d orbital with the highest energy is

(*a*) d_{xy} (*b*) $d_{x^2-y^2}$
(*c*) d_{yz} (*c*) d_{z^2}

3. The magnetic moment of the complex $K_3[CoF_6]$ is 5.0 μ_B. The total stabilization energy will be

(*a*) $-0.4\,\Delta_0$ (*b*) $-0.4\,\Delta_0 + P$
(*c*) $-2.4\,\Delta_0 + 3P$ (*d*) $-1.8\,\Delta_0 + 3\,P$

4. The metal present at the active site of the protein carboxypeptidase A is

(*a*) zinc (*b*) molybdenum
(*c*) magnesium (*d*) cobalt

5. The neutral complex which follows the 18-electron rule is

(*a*) $(\eta^5\text{-}C_5H_5)Fe(CO)_2$
(*b*) $(\eta^5\text{-}C_5H_5)Mo(CO)_3$
(*c*) $(\eta^5\text{-}C_5H_5)_2CO$
(*d*) $(\eta^5\text{-}C_5H_5)Re(\eta^6\text{-}C_6H_6)$

6. The shape of the molecule XeO_2F_2 is

(*a*) distorted tetrahedral
(*b*) square planar
(*c*) trigonal bipyramidal
(*d*) tetrahedral

7. Triple superphosphate is made by treating phosphate rock with

(*a*) conc. H_2SO_4 (*b*) conc. HNO_3
(*c*) conc. HCl (*d*) conc. H_3PO_4

8. The number of hydroxy (OH) groups present in phosphorus acid is

(*a*) one (*b*) two
(*c*) three (*d*) four

9. Out of the following, the one which is not an excitation source for IR spectrometer is

(*a*) tungsten filament lamp

(*b*) Nernst glower

(*c*) deuterium lamp

(*d*) mercury arc

10. One of the following is not related to polarography

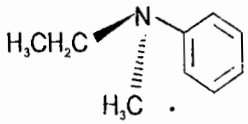
(*a*) limiting current

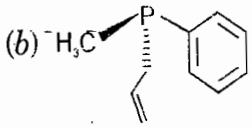
(*b*) diffusion current constant

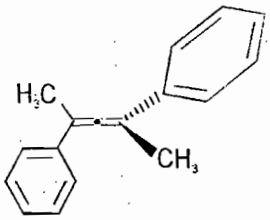
(*c*) Ilkovic equation

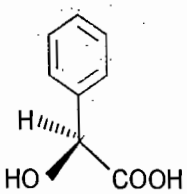
(*d*) current efficiency

11. Among the following, the optically inactive compound is

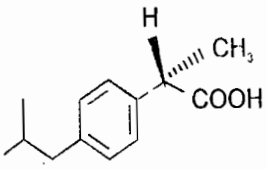
(*a*) 

(*b*) 

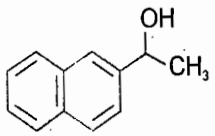
(*c*) 

(*d*) 

12. Esterification of the acid P with the alcohols Q will give



(S)-P



(±)-Q

(*a*) only one enantiomer

(*b*) a mixture of diastereomers

(*c*) a mixture of enantiomers

(*d*) only one diastereomer

13. ^{1}H NMR spectrum of [18]-annulene shows

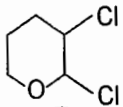
(*a*) only one peak at δ 7.2 (18H)

(*b*) only one peak at δ 5.0 (18H)

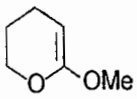
(*c*) two peaks at δ 9.0 (12H) and δ – 3.0 (6H)

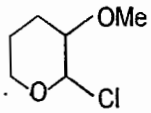
(*d*) two peaks at δ 9.0 (6H) and δ – 3.0 (12H)

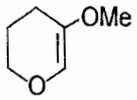
14. The compound formed on methanolysis of P is

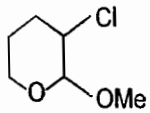


P

(*a*) 

(*b*) 

(*c*) 

(*d*) 

15. The pK_a values for the three ionizable groups X, Y and Z of glutamic acid are 4.3, 9.7 and 2.2 respectively

$$\underset{X}{HO_2C}-CH_2-\underset{\underset{+NH_3}{|}}{\underset{Y}{CH}}-\underset{Z}{CO_2H}$$

The isoelectric point for the amino acid is

(*a*) 7.00 (*b*) 3.25

(*c*) 4.95 (*d*) 5.95

16. Bridge-head hydrogen of the conformer of *cis*-decalin is positioned as

(*a*) *a, a*

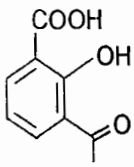
(*b*) *e, e*

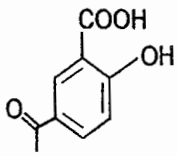
(*c*) *a, e*

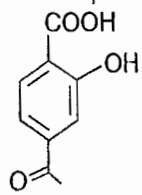
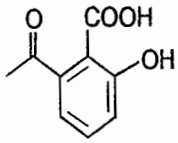
(*d*) *pseudo-a, pseudo-e*

[*a* = axial; *e* = equatorial]

17. The major product of the acetylation of salicylic acid with Ac_2O/H^+ followed by heating with anhydrous $AlCl_3$ is

(*a*) 

(*b*) 

(*c*) 

(*d*)