SYLLABUS FOR GOA UNIVERSITY ADMISSIONS RANKING TEST (GU-ART) IN CHEMISTRY

Inorganic Chemistry

Atomic Structure
Evidence for the electrical nature of matter; discharge tube experiments; Thomson's atomic model; Rutherford model; Bohr's model, probability picture of electron, quantum numbers, Shapes of *s*, *p*, *d* orbitals, Aufbau and Pauli exclusion principles, Hund's rule; Electronic configurations; effective nuclear charge.

Chemical Bonding
Covalent bond, Valence Bond Theory (VBT), limitations, directional characteristics of covalent bond, types of hybridization and shapes of simple inorganic molecules and ions. Valence Shell Electron Pair Repulsion (VSEPR) Theory for determination of molecular shapes; Molecular Orbital Theory, homonuclear and heteronuclear diatomic molecules (CO and NO), multicenter bonding in electron deficient molecules, bond strength and bond energy, percentage ionic character from dipole moment and electronegativity difference.

Periodic Properties
Atomic and ionic radii, ionization energy, electron affinity and electronegativity, definition, methods of determination, trends in periodic table and applications in predicting and explaining the chemical behavior.

Acids, Bases and Non Aqueous Solvents
Arrhenius Concept and Bronsted Theory. The Lux-Flood Solvent Systems. Lewis Concept of Acids and Bases. Physical Properties of solvent. Types of Solvents and their general characteristics. Reactions in non aqueous solvents with respect to liquid NH_3 and liquid SO_2.

s and p block elements
Comparative study including diagonal relationship of groups. Chemical properties of Noble Gases

Chemistry of d-block elements
General characteristics of *d*-block elements (1^{st}, 2^{nd} and 3^{rd} series). Comparative treatment (3*d*, 4*d*, *5d*) in respect of Ionic radii, oxidation states, magnetic behaviour, spectral properties and stereochemistry.

Chemistry of Lanthanides and Actinides
Electronic structure, oxidation states and ionic radii and lanthanide contraction, complex formation, occurrence and isolation, lanthanide compounds. General features and chemistry of actinides, chemistry of separation of Np, Pu and Am from U, similarities between later actinides and later lanthanides.

Ionic Solids
Ionic structures, radius ratio effect and coordination number, limitation of radius ratio rule, lattice defects, semiconductors, lattice energy and Born-Haber cycle, solvation energy and solubility of ionic solids, polarizing power and polarizability, Fajan's rule, metallic bond, free electron, valence bond and band theories.

Coordination compounds
Werner's coordination theory and its experimental verification, effective atomic number concept, chelates, Isomerism in coordination compounds, nomenclature of coordination compounds, valence bond theory of transition metal complexes.

Oxidation and Reduction

Use of redox potential data-analysis of redox cycle, redox stability in water–Frost, Latimer and Pourbaix diagrams. Principles involved in the extraction of the elements.

Organic Chemistry

Structure and Bonding
Hybridization, C-C bond lengths and bond angles, bond energy, localized and delocalized chemical bonds, definition and examples of resonance, hyperconjugation, inductive and field effects, intramolecular and intermolecular hydrogen bonding.

Fundamentals of Organic Chemistry
Types of reagents; electrophiles and nucleophiles with examples. Types of Organic Reactions: Addition, Elimination, Substitution, Oxidation, Reduction and Re-arrangement. Reactive intermediates, carbocations, carbanions, free radicals, carbenes, arynes and nitrenes; examples, shape and ways of formation and reaction.

Alkanes, Alkenes, dienes and alkynes
IUPAC nomenclature of alkanes. General methods of formation (with special reference to Wurtz reaction, Kolbe reaction, Corey-House reaction & decarboxylation of carboxylic acids). IUPAC nomenclature of alkenes, general methods of formation, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides, regioselectivity in alcohol dehydration. The Saytzeff rule, Hoffmann elimination, physical properties and relative stabilities of alkenes. Chemical reactions of alkenes: Epoxidation, ozonolysis, hydration, hydroxylation and oxidation with mechanism. Markownikoff's rule, hydroboration-oxidation, oxymercuration-reduction. Polymerization of alkenes. Substitution at the allylic and vinylic positions of alkenes. Industrial applications of ethene and propene. Nomenclature and classification of dienes; isolated, conjugated and cumulated dienes. Diels-Alder reaction. Nomenclature, structure and bonding in alkynes. General methods of formation. Chemical reactions of alkynes, acidity of alkynes.

*Stereochemistry of organic compounds***:**
Newman and saw horse formulae, Fischer and flying wedge formulae. Concept of isomerism. Types of isomerism. Conformational isomerism-Conformational analysis of ethane and *n*-butane; conformations of cyclohexane, axial and equatorial bonds, conformation of mono-substituted cyclohexane derivatives. Optical isomerism – elements of symmetry, molecular chirality, definition and examples of enantiomers, stereogenic centre, optical activity, properties of enantiomers, chiral and achiral molecules with two stereogenic centers, diastereomers, *-threo* and *-erythro* diastereomers, meso compounds, resolution of enantiomers, inversion, retention and racemization. Specification of configuration at chiral centers: Sequence rules and R:S system of nomenclature. Geometric Isomerism - Determination of configuration of geometric isomers. E and Z system of nomenclature, geometric isomerism in oximes and alicyclic compounds. Difference between configuration and conformation.

Arenes and Aromaticity
Nomenclature of benzene derivatives. Structure of benzene: molecular formula and Kekule structure. Stability and C–C bond lengths of benzene, resonance structure, aromaticity: The Huckel's rule, aromatic ions, anti-aromaticity. Aromatic electrophilic substitution; Mechanism of nitration, halogenation, sulphonation and Friedel-Crafts reaction. Activating and deactivating substituents, orientation and *ortho*/*para* ratio.

Alkyl and aryl halides
Nomenclature and classes of alkyl halides, general methods of formation, chemical reactions. Mechanism and stereochemistry of nucleophilic substitution reactions of alkyl halides, S_N2 and S_N1 reactions with energy profile diagrams, solvent effect. The addition – elimination (bimolecular displacement) and the elimination – addition (benzyne) mechanisms of nucleophilic aromatic substitution reactions. Relative reactivities of alkyl halides vs. allyl, vinyl and aryl halides.

Electromagnetic Spectrum: Absorption Spectra
Ultraviolet (UV) absorption spectroscopy, Beer-Lambert law, Molar absorptivity, presentation and analysis of UV spectra, Types of electronic transitions, effect of conjugation. Concept of chromophore and auxochromes, Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated dienes and enones, Woodward-Fieser rules for calculation of UV maxima of the above two systems. Numerical problems on above. Infrared spectroscopy, molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, measurement of IR spectrum, Finger print region and its use to establish identity, Applications to determine purity, to study progress of chemical reactions and hydrogen bonding. Characteristic absorptions of various functional groups and interpretation of IR spectra of simple organic compounds. Simple problems in structure elucidation using UV and IR spectroscopy.

Alcohols
Classification and nomenclature. Monohydric alcohols–methods of preparations by reduction of carbonyl compounds, carboxylic acids, and esters, using Grignard reaction. Hydrogen bonding, acidic nature. Reactions of alcohols–esterification, oxidation and dehydration with mechanism.
Dihydric alcohols– Nomenclature, methods of preparation by hydroxylation of alkenes and acid catalyzed opening of epoxides. Reactions of vicinal glycols– pinacol-pinacolone rearrangement with mechanism

Ethers and Epoxides
Nomenclature of ethers and methods of preparation by Williamson synthesis, from alcohols by use of diazomethane and by use of H_2SO_4. Physical properties. Chemical reactions: cleavage with HI. Synthesis of epoxides by reaction of alkenes with peracids and by elimination from vicinal halohydrins.

Aldehydes and Ketones
Nomenclature and structure of the carbonyl group. Synthesis of aldehydes by oxidation of alcohols and reduction of acid chlorides, synthesis of ketones by oxidation of alcohols, from nitriles by Grignard reaction and from carboxylic acids. Mechanism of nucleophilic additions to carbonyl group with particular emphasis on benzoin, Aldol, Perkin and Knovenagel condensations, reaction with ammonia and its derivatives. Mechanism and applications Wittig reaction and Mannich reaction.

Phenols
Nomenclature, structure and bonding. Preparation of phenols by alkali fusion of aromatic sulphonic acids, Dow's process from chlorobenzene and from Cumene through hydroperoxide rearrangement. Physical properties and acidic character. Comparative acid strengths of alcohols and phenols, resonance stabilization of the phenoxide ion. Reaction of phenols–Electrophilic aromatic substitution, acylation and carboxylation. Mechanisms of Fries rearrangement, Claisen rearrangement, Gattermann synthesis and Riemer-Tiemann reaction.

Oxidation and Reduction reactions of carbonyl compounds
Oxidation of aldehydes, Mechanism and applications of Baeyer-Villiger oxidation of ketones, Cannizzaro reaction, Meerwein-Pondorf-Verley, Clemmensen, Wolff-Kischner, $LiAlH_4$ and $NaBH_4$ reduction.

Carboxylic Acids
Nomenclature, structure and bonding. Physical properties, acidity and effects of substituents on acid strength. Preparation of carboxylic acids by oxidation of carbonyl compounds, carbonation of Grignard reagent, hydrolysis of cyanides, preparation of aromatic acids by oxidation of alkyl benzenes. Reactions of carboxylic acids. Hell-Volhard-Zelinsky reaction, synthesis of acid chlorides, esters and amides. Reduction of carboxylic acids. Mechanism of decarboxylation. Dicarboxylic acids: Methods of preparation and effect of heat and dehydrating agents with reference to malonic acid only.

Carboxylic Acid Derivatives

Structure and nomenclature of acid chlorides, esters, amides and acid anhydrides. Physical properties. Methods of preparation from carboxylic acids and interconversion of acid derivatives by nucleophilic acyl substitution. Mechanisms of esterification and acidic and basic hydrolysis of esters with evidences.

Organic Compounds of Nitrogen

Preparation of nitroalkanes and nitroarenes. Chemical reactions of nitroalkanes. Mechanisms of nucleophilic substitution in nitroarenes and their reductions in acidic, neutral and alkaline media. Picric acid – preparation and properties.

Structure and nomenclature of amines, physical properties. Stereochemistry of amines. Separation of a mixture of primary, secondary and tertiary amines. Structural features affecting basicity of amine. Amine salts as phase-transfer catalysts. Preparation of alkyl and aryl amines by reduction of nitro compounds and nitriles, reductive amination of carbonyl compounds, Gabriel phthalimide reaction and Hofmann bromamide reaction.

Physical Chemistry

Mathematical Concepts

Logarithmic relations, curve sketching, linear graphs, slopes, differentiation of functions, Critical points, partial differentiation. Integration of some useful functions.

Gaseous State

Postulates of kinetic theory of gases, van der Waals equation of state. Critical phenomena; PV isotherms, continuity of states, isotherms of van der Waals equation, relationship between critical constants and van der Waal's constants, the law of corresponding states, reduced equation of state. Molecular Velocities: Root mean square, average and most probable velocities. Qualitative discussion of the Maxwell's distribution of molecular velocities, collision number, mean free path and collision diameter, liquefaction of gases.

Chemical Kinetics

Rate of reaction, factors influencing the rate of a reaction concentration, temperature, pressure, solvent, light, catalyst Concentration dependence of rates mathematical characteristics of simple chemical reaction. Zero order, first order, second order, pseudo order, half life & mean life. Determination of order of reaction: Differential method Integration method, Method of half life period & Isolation method. Radioactive decay as a first order phenomenon. Theories of Chemical Kinetics.

Thermodynamics

Thermodynamic terms, properties of system. State & path functions & their differentials. Thermodynamic process. Concept of work & heat. First law of thermodynamics. Joule's law, Joule-Thomson coefficient & inversion temperature. Calculation of w, q, dU, dH, for the expansion of ideal gases under isothermal & adiabatic conditions for reversible processes. Thermochemistry, Heat of reaction at constant pressure & at constant volume. Enthalpy of neutralization, bond dissociation energy & its calculation from thermochemical data. Temperature dependence of enthalpy. Kirchoff's equation. Second law of thermodynamics, Carnot cycle and its efficiency, Carnot theorem. Thermodynamic scale of temperature.

Concept of entropy, Entropy change in ideal gases and mixing of gases. Third law of thermodynamics: Nernst heat theorem, statement and concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs and Helmholtz functions; Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities, A & G as criteria for thermodynamic equilibrium and spontaneity, their advantages over entropy change. Variation of G and A with P, V & T.

Phase Equilibrium

Statement and meaning of the terms –phase, component and degree of freedom, derivation of Gibbs phase rule, phase equilibria of i) one component system. ii) two component system– solid –liquid equilibria, simple eutectic, Solid solutions –compound formation with congruent melting point (Mg-Zn) and incongruent melting point (NaCl-H_2O), ($FeCl_3$-H_2O) and ($CuSO_4$-H_2O) system. Freezing mixtures, acetone –dry ice.

Liquids–liquid mixtures– ideal liquid mixtures, Raoult's and Henry's law. Non–ideal system –azeotropes- HCl-H_2O and ethanol – water systems Partially miscible liquids–phenol –water, trimethylamine–water, nicotine –water systems. Lower and upper consolute temperature. Effect of impurity on consolute temperature. Immiscible liquids, steam distillation. Nernst distribution law– thermodynamic derivation, applications.

Solutions
Methods of expressing concentrations of solutions, activity & activity coefficients.

Liquid State
Intermolecular forces, structure of liquids (Qualitative description) Structural differences between solids, liquids and gases. Liquid crystal: Classification, structure of nematic and cholestric phases. Thermography and seven segment cell. Surface between a liquid and vapour. Surface tension by capillary rise method, stalagmometer method. Viscosity of liquids,

Electrochemistry
Electrical transport –conduction in metals and in electrolyte solutions, specific conductance and equivalent conductance measurement of equivalent conductance, variation of equivalent and specific conductance with dilution. Migration of ions and Kohlrausch law, Arrhenius theory of electrolyte dissociation and its limitations, weak and strong electrolytes, Ostwald's dilution law its uses and limitations. Debye–Huckel-Onsager's equation for strong electrolytes. Transport number, Hittorf method and moving boundary method. Applications of conductivity measurements: determination of degree of dissociation, determination of ka of acids, solubility product of a sparingly soluble salt, conductometric titrations.

Solid State
Space lattice, unit cell. Laws of crystallography –(i) law of constancy of interfacial angels
(ii) law of rationality of indices (iii) law of symmetry elements in crystals. X-ray diffraction by crystals derivation of Bragg equation. Determination of crystal structure of NaCl, KCl and CsCl.

Colloidal State
Definition of colloids, classification of colloids. Solids in liquids (sols): properties–kinetic, optical and electrical, stability of colloids, protective action, Hardy-Schulze law gold number. Liquids in liquids (emulsions): types of emulsions, preparation. Emulsifier Liquids in solids: classification, preparation and properties, inhibition, general applications of colloids

Concepts from Experimental Chemistry

(*Students are expected to answer questions based on the following experiments*)

Calibrations of Burette and Pipettes; Preparation of stock solution (viz. 0.1 M $K_2Cr_2O_7$ or 100 ppm $KMnO_4$) and dilution to different concentrations;
Semi-micro qualitative analysis: Analysis of inorganic mixtures containing four ions only. (Two cations from Pb^{2+}, Bi^{3+} ,Cu^{2+}, Cd^{2+}, Sn^{2+}, Sb^{3+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, $(NH_4)^+$, K^+ and two anions from X^- (X= Cl or Br or I), $(NO_2)^-$, $(NO_3)^-$, $(SO_3)^{2-}$, $(CO_3)^{2-}$, $(SO_4)^{2-}$, $(CrO_4)^{2-}$, $(PO_4)^{3-}$.

Gravimetric Experiments for precipitation of manganese as Mn-pyrophosphate; nickel as Ni-DMG; aluminium as Al_2O_3 from aluminium sulphate; barium as $BaSO_4$ and iron as Fe_2O_3
Titrimetric experiments for Standarization of acid (HCl), base (NaOH), oxidizing agent ($KMnO_4$)
Estimation of copper / calcium / nickel /zinc and magnesium by EDTA method; ferrous ion using internal indicator ($K_2Cr_2O_7$ method); Determination of alkali content in antacid tablet using standard HCl solution.

Organic Estimations: Estimations of Acetamide, Aniline and Glucose. Organic Derivatives: Benzoyl derivative of *β*-naphthol and aniline. Bromo derivative of phenol and aniline.

Qualitative Organic Analysis Principles governing identification of organic compounds and the separation of binary mixture of organic compounds.

Partition coefficient of I_2 between $C_2H_4Cl_2$ and H_2O
Conductometric studies for the determination of i) strong acid (HCl) ii) weak acid (CH_3COOH) present in the given solution iii) amount of chloride ion in given solution iv) the solubility and solubility product of sparingly soluble salts ($BaSO_4$, $PbSO_4$, $CaSO_4$, $SrSO_4$)
Solubility of benzoic acid at room temperature (RT) and below RT
Kinetics of inversion of i) cane sugar in the presence of HCl,
ii) the order of the reaction between $K_2S_2O_8$ + KI (a = b)
Reaction between i) H_2O_2 and HI ii) $HBrO_3$ and HI.
Study of surface tension using stalagmometer
Preparation of standard solutions based on normality, molarity, molality, ppm and mole fraction.

Reference Books:

1] P Atkins, J De Paula & J Keeler, *Atkins' Physical Chemistry*, International Edition, Oxford University Press, 2018
2] J D Lee, *Concise Inorganic Chemistry*, Wiley, 5th Edition.
3] F A Cotton, G Wilkinson & P L Gaus, *Basic Inorganic Chemistry*, Wiley Eastern, 3rd Edition, 2001
4] C N R Rao, *University General Chemistry*, McMillan Co., 1993.
5] J March, *Advanced Organic Chemistry*; John Wiley, 6th Edition,
6] P Atkins, T Overton, J Rourke, M Weller & F Armstrong, *Shriver & Atkins' Inorganic Chemistry*, Oxford University Press, 5th Edition, 2010.
7] R T Morrison, R N Boyd & S K Bhattacharjee, *Organic Chemistry*, 7th Edition, Pearson.
8] F Carey, *Organic Chemistry*; 5th Edition, Tata McGraw Hill India, 2007.
9] G Svelha, *Vogel's Qualitative Inorganic Analysis*, Pearson, 2006 7th Edition,
10] J Mendham, R. C. Denney, J. D. Barnes & M. J. K. Thomas, *Vogel's Text Book of Quantitative Chemical Analysis*, 6th Edition, Pearson Education Asia, 2002
11] R M Silverstein, F X Webster & D J Kiemle, *Spectrometric Identification of Organic Compounds*, 7th Edition 2005
12] B S Furniss, A J Hannaford, P W G Smith & A R Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th Edition ELBS.
13] J Clayden, N Greeves & S,Warren *Organic Chemistry* 2nd Edition, Oxford University Press, 2012
14] M Weller, T Overton, J Rourke & F Armstrong *Inorganic Chemistry* International Edition, Oxford University Press, 2018