GOA UNIVERSITY
Taleigao Plateau

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

Note: This syllabus is based on core papers (theory & practicals) of Semesters I to IV of B Sc with Chemistry programme as approved by UG BoS in Chemistry and Academic Council of Goa University.

Inorganic Chemistry

1. **Atomic Structure**
   Review of: Bohr's theory and its limitations, dual behaviour of matter and radiation, de Broglie's relation, Heisenberg Uncertainty principle. Hydrogen atom spectra. Need of a new approach to Atomic structure. What is Quantum mechanics? Time independent Schrodinger equation and meaning of various terms in it. Significance of ψ and ψ2, Schrödinger equation for hydrogen atom. Radial and angular parts of the hydrogenic wave functions (atomic orbitals) and their variations for 1s, 2s, 2p, 3s, 3p and 3d orbitals (Only graphical representation). Radial and angular nodes and their significance. Radial distribution functions and the concept of the most probable distance with special reference to 1s and 2s atomic orbitals. Quantum numbers and their significance, Discovery of spin, spin quantum number (s) and magnetic spin quantum number (ms). Shapes of s, p and d atomic orbitals, nodal planes. Rules for filling electrons in various orbitals, Electronic configurations of the atoms. Stability of half-filled and completely filled orbitals, concept of exchange energy. Relative energies of atomic orbitals, Anomalous electronic configurations.
2. **Transition Elements**
   General characteristic properties of 3d series with special reference to electronic configuration, variable valency, colour, magnetic and catalytic properties. Ability to form complexes and stability of various oxidation states (Latimer diagrams) for Mn, Fe and Cu. Lanthanides: Electronic configurations, oxidation states, colour, magnetic properties, lanthanide contraction, separation of lanthanides (ion exchange method only). Actinides : Electronic configuration and General characteristics.
3. **Chemical Bonding and Molecular Structure** Ionic Bonding: General characteristics of ionic bonding. Energy considerations in ionic bonding, lattice energy and solvation energy and their importance in the context of stability and solubility of ionic compounds. Statement of Born-Landé equation for calculation of lattice energy, Born-Haber cycle and its applications, polarizing power and polarizability. Fajan's rules, ionic character in covalent compounds, bond moment, dipole moment and percentage ionic character.
4. **Coordination Chemistry**
   IUPAC system of nomenclature. Bonding in complexes based on Valence Bond Theory (VBT), Inner and outer orbital complexes of Cr, Fe, Co, Ni and Cu (coordination numbers 4 and 6). Different types of structural and stereo-isomerism including optical isomerism in complexes with coordination numbers 4 and 6. Drawbacks of VBT.
5. **Crystal Field Theory**
   Crystal field splitting in octahedral complexes. Crystal field stabilization energy (CFSE), Crystal field effects for weak and strong fields. Spectrochemical series. Crystal Field Splitting in Tetrahedral complexes. Calculation of CFSE. Comparison of CFSE for Oh and Td complexes. Factors affecting the magnitude of 10Dq. Merits and Demerits of Crystal Field Theory.

Organic Chemistry:

1. **Fundamentals of Organic Chemistry**

   Curved arrow notation, drawing electron movement with arrows, half and double headed arrows, in organic reaction mechanisms. Physical Effects, Electronic Displacements: Inductive Effect, Electromeric Effect, Resonance and Hyperconjugation. Cleavage of Bonds: Homolysis and Heterolysis.Structure, shape and reactivity of organic molecules: Nucleophiles and electrophiles. Reactive Intermediates: Carbocations, Carbanions and free radicals. Strength of organic acids and bases: Comparative study with emphasis on factors affecting pK values. Aromaticity: Benzenoids and Hückel's rule.

2. **Aliphatic Hydrocarbons**

   Functional group approach for the following reactions (preparations & reactions) to be studied in context to their structure. Alkanes: (Upto 5 Carbons). Preparation: Catalytic hydrogenation, Wurtz reaction, Kolbe's synthesis, from Grignard reagent. Reactions: Free radical Substitution: Halogenation. Alkenes: (Upto 5 Carbons) Preparation: Elimination reactions: Dehydration of alkenes and dehydrohalogenation of alkyl halides (Saytzeff's rule); cis alkenes (Partial catalytic hydrogenation) and trans alkenes (Birch reduction). Reactions: cis-addition (alk. KMnO4) and trans-addition (bromine), Addition of HX (Markownikoff's and anti-Markownikoff's addition), Hydration, Ozonolysis, oxymecuration-demercuration, Hydroboration-oxidation. Alkynes: (Upto 5 Carbons) Preparation: Acetylene from CaC2 and conversion into higher alkynes; by dehalogenation of tetra halides and dehydrohalogenation of vicinal-dihalides.Reactions: formation of metal acetylides, addition of bromine and alkaline KMnO4, ozonolysis and oxidation with hot alk. KMnO4.

3. **Stereochemistry**

   Concept of isomerism. Types of isomerism. Stereoisomerism, conformational isomerism. Conformations with respect to ethane, butane and cyclohexane. Interconversion of Wedge Formula, Newmann, Sawhorse and Fischer representations. Concept of chirality (upto two carbon atoms). Configuration: Geometrical and Optical isomerism; Enantiomerism, Diastereomerism and Meso compounds). Threo and erythro; D and L; cis – trans nomenclature; CIP Rules: R/ S (for upto 2 chiral carbon atoms) and E / Z Nomenclature (for upto two C=C systems).

4. **Aromatic hydrocarbons**

   Preparation (Case benzene): from phenol, by decarboxylation, from acetylene, from benzene sulphonic acid. Reactions: (Case benzene): Electrophilic substitution: nitration, halogenation and sulphonation. Friedel-Craft's reaction (alkylation and acylation) (upto 4 carbons on benzene). Side chain oxidation of alkyl benzenes (upto 4 carbons on benzene).

5. **Alkyl and Aryl Halides**

   Alkyl Halides (Upto 5 Carbons) Types of Nucleophilic Substitution (SN1, SN2 and SNi) reactions. Preparation: from alkenes and alcohols. Reactions: hydrolysis, nitrite & nitro formation, nitrile & isonitrile formation.Elimination vs substitution. Aryl Halides Preparation: (Chloro, bromo and iodo-benzene case): from phenol, Sandmeyer & Gattermann reactions. Reactions (Chlorobenzene): Aromatic nucleophilic substitution (replacement by –OH group) and effect of nitro substituent. Benzyne Mechanism: KNH2/NH3 (or NaNH2/NH3). Reactivity and Relative strength of C-Halogen bond in alkyl, allyl, benzyl, vinyl and aryl halides.

6. **UV –Visible Spectroscopy in Organic Chemistry**

   Introduction to spectroscopy : 3 UV Spectroscopy: Beer-Lambert's law, Types of electronic transitions, λmax, Chromophores and Auxochromes, Bathochromic and Hypsochromic shifts, Intensity of absorption. Visible Spectroscopy: Effect of conjugation on colour. Application of Woodward - Fieser rules for calculation of λmax for the following systems: α, β unsaturated aldehydes, ketones. Conjugated dienes: alicyclic, homoannular and heteroannular, extended conjugated systems (aldehydes, ketones and dienes). Distinction between cis and trans isomers.

7. **Alcohols, Phenols, Ethers and Carbonyl Compounds**

   Alcohols: Preparation: Preparation of 1o, 2o and 3o alcohols: using Grignard reagent, Ester hydrolysis, Reduction of aldehydes, ketones, carboxylic acid and esters. Reactions: With sodium, HX (Lucas test), esterification, oxidation (with PCC, alk. $KMnO_4$, acidic dichromate, conc. HNO_3). Oppeneauer oxidation Diols: oxidation of diols using HIO_4. Pinacol-Pinacolone rearrangement with mechanism. Ethers (aliphatic and aromatic): Williamson's synthesis of ethers. Cleavage of ethers with HI. Aldehydes and ketones (aliphatic and aromatic): (Formaldehye, acetaldehyde, acetone and benzaldehyde) Preparation: from acid chlorides and from nitriles. Reactions – Reaction with HCN, ROH, $NaHSO_3$, NH_2-G derivatives. Iodoform test. AldolCondensation, Cannizzaro's reaction, Wittig reaction, Benzoin condensation. Clemmensen reduction and Wolff Kishner reduction. Meerwein-Pondorff Verley reduction. Phenols: (Phenol case) Preparation: Cumene hydroperoxide method, from diazonium salts. Reactions: Electrophilic substitution: Nitration, halogenation and sulphonation. Reimer-Tiemann Reaction, Gattermann-Koch Reaction, Houben–Hoesch Condensation, Schotten –Baumann Reaction.

8. **Carboxylic acids and their derivatives**

   Carboxylic acids (aliphatic and aromatic) Preparation: Acidic and Alkaline hydrolysis of esters. Reactions: Hell - Volhard - Zelinsky Reaction. Carboxylic acid derivatives (aliphatic): (upto 5 carbons) Preparation: Acid chlorides, Anhydrides, Esters and Amides from acids and their interconversions. Reactions: Comparative study of nucleophilicity of acyl derivatives. Reformatsky reaction, Perkin condensation (mechanism).

9. **Amines and Diazonium Salts**

   Amines (aliphatic and aromatic): (upto 5 carbons) Preparation: from alkyl halides, Gabriel's phthalimide synthesis, Hofmann bromamide reaction (Hofmann rearrangement). Reactions: Hofmann vs. Saytzeff elimination, Carbylamine test, Hinsberg test, with HNO_2, Schotten – Baumann reaction. Electrophilic substitution (case aniline): nitration, bromination, sulphonation. Diazonium salts: Preparation from aromatic amines, conversion to benzene, phenol, dyes.

10. **Amino Acids and Peptides**

    Preparation of Amino Acids: Strecker synthesis, Gabriel's phthalimide synthesis. Terms: Zwitterion, Isoelectric point and Electrophoresis. Reactions of Amino acids: Ester of – COOH group, acetylation of $–NH_2$ group, complexation with Cu^{2+} ions, ninhydrin test. Synthesis of simple peptides (upto dipeptides) by N-protection (tbutyloxycarbonyl and phthaloyl) & C-activating groups and Merrifield solid-phase synthesis.

11. **Carbohydrates:**

    Classification and General Properties, Glucose and Fructose (open chain and cyclic structure), Determination of configuration of monosaccharides, absolute configuration of Glucose and Fructose, Mutarotation, Osazone formation, Killiani Fischer synthesis.

Physical Chemistry

1. **Kinetic Theory of Gases**

   Postulates of Kinetic Theory of Gases, deviation of real gases from ideal behaviour, compressibility factor, causes of deviation. van der Waals equation of state for real gases. Boyle temperature (derivation not required). Critical phenomena, critical constants and their calculation from van der Waals equation. Andrews isotherms for CO_2. Maxwell Boltzmann distribution laws of molecular velocities and molecular energies (graphic representation – derivation not required) and their importance. Temperature dependence of these distributions. Most probable, average and root mean square velocities (no derivation), collision number, collision frequency, collision diameter and mean free path of molecules.

2. **Chemical Kinetics**

The concept of reaction rates. Effect of temperature, pressure and catalyst on reaction rates. Order and molecularity of a reaction. Derivation of integrated rate equations for zero, first and second order reactions (both for equal and unequal concentrations of reactants). Half–life of a reaction. General methods for determination of order of a reaction. Concept of activation energy and its calculation from Arrhenius equation. Theories of Reaction Rates: Collision theory and Activated Complex theory of bimolecular reactions.

3. **Chemical Energetics**

Need of thermodynamics and the Laws of Thermodynamics. Important principles and definitions of thermochemistry. Concept of standard state and standard enthalpies of formations, integral and differential enthalpies of solution and dilution. Calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data. Variation of enthalpy of a reaction with temperature – Kirchhoff's equation. Statement of Third Law of thermodynamics and calculation of absolute entropies of substances.

4. Chemical Equilibrium:

Free energy change in a chemical reaction. Thermodynamic derivation of the law of chemical equilibrium. Definition of ΔG and ΔGo, Le Chatelier's principle. Relationships between Kp, Kc and Kx for reactions involving ideal gases.

5. Phase Equilibrium

Phases, components and degrees of freedom of a system, criteria of phase equilibrium, Phase diagrams of one-component systems (water, sulphur and CO2) and two component systems involving eutectics, congruent and incongruent melting points (Zn-Mg, NaCl-H2O).

6. Solutions

Thermodynamics of ideal solutions: Ideal solutions and Raoult's law, deviations from Raoult's law – non-ideal solutions. Vapour pressure-composition and temperature composition curves of ideal and non-ideal solutions. Azeotropes. Partial miscibility of liquids: Critical solution temperature, distillation and fractional distillation.

7. Liquids

Surface tension and its determination using stalagmometer. Effect of temperature on surface tension. Viscosity of a liquid and determination of coefficient of viscosity using Ostwald viscometer and factors affecting viscosity.

8. Ionic Equilibria

Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect. Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions. Solubility and solubility product of sparingly soluble salts.

9. Conductance

Conductivity, equivalent and molar conductivity and their variation with dilution for weak and strong electrolytes. Kohlrausch's law of independent migration of ions. Ionic mobility and factors affecting ionic mobility. Transference number and its experimental determination using moving boundary methods. Applications of conductance measurements: solubility and solubility products of sparingly soluble salts, ionic product of water, conductometric titrations (only acid-base).

10. Electrochemistry

Reversible and irreversible cells. Concept of EMF of a cell. Measurement of EMF of a cell. Nernst equation and its importance. Types of electrodes. Standard electrode potential. Electrochemical series. Thermodynamics of a reversible cell, Concentration cells with transference and without transference.

Liquid junction potential and salt bridge. pH determination using hydrogen electrode and quinhydrone electrode.

11. Solids

Forms of solids, symmetry elements, unit cells, crystal systems, Bravais lattice. Laws of crystallography - Law of constancy of interfacial angles, Law of rational indices. Miller indices, X–Ray diffraction by crystals, Bragg's law. Particle size determination using powder method. Structures of NaCl, KCl and CsCl (qualitative treatment only).

No direct topics found in CBCS syllabus Sem I to IV. However, many of these topics get introduced/ covered considerably in Class-XI/ XII Chemistry of Goa Board. Are equally important as part of basic chemistry. Should we retain this in the syllabus or not?

Concepts from Experimental Chemistry

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

Volumetric Analysis:

1. Estimation of sodium carbonate and sodium hydrogen carbonate present in a mixture.
2. Estimation of oxalic acid by titrating with KMnO4.
3. Estimation of water of crystallization in Mohr's salt by titrating with standardised KMnO4.
4. Estimation of Fe (II) ions by titrating it with K2Cr2O7 using internal indicator.
5. Estimation of Cu (II) ions iodometrically using Na2S2O3.

Semi-micro qualitative analysis: not more than four ionic species (two anions and two cations): (4 Mixtures) Cations : NH4+, Pb2+, Ag+, Bi3+, Cu2+, Cd2+, Sn2+, Fe3+, Al3+, Co2+, Cr3+, Ni2+, Mn2+, Zn2+, Ba2+, Sr2+, Ca2+, K+. Anions : CO32-, S2–, SO2–, SO42-, NO3–, Cl–, Br–, I–, NO2–, PO43-, F- (Spot tests should be carried out wherever feasible)

GRAVIMETRIC/VOLUMETRIC

1. Estimate the amount of Nickel present in a given solution as bis(dimethylglyoximato) Nickel(II) in a given solution gravimetrically by counterpoise filter paper.
2. Estimation of (i) Mg2+ or (ii) Zn2+ by complexometric titrations using EDTA.
3. To estimate the amount of Bismuth present in the given solution of Bi(NO3)2.3H2O by complexometric titration.
4. To estimate the amount of Nitrite present in the given NaNO2 solution by titrating v/s Ceric ammmonium sulphate / Ceric sulphate.

Organic Preparations: Mechanisms involved in the following reactions to be discussed.

(a) Bromination of Phenol/Aniline
(b) Benzoylation of amines/phenols
(c) 2,4-dinitrophenylhydrazone of benzaldehyde/acetophenone
(d) Nitration of acetanilide to p-nitroacetanilide.
(e) Oxime of Cyclohexanone
(f) Chalcone from benzaldehyde and acetophenone
(g) Iodoform from acetone
(h) Hippuric acid from glycine (Benzoylation-Schotten Baumann reaction)
(i) Osazone from Glucose (Nucleophilic addition)
(j) Phthalic acid to Phthalic Anhydride to Phthalimide
(k) Preparation of Azo dye

Organic Estimations:

(i) Estimation of glycine by formylation method

(ii) Estimation of Glucose by oxidation

(iii)(iii) Estimation of Acetamide by hydrolysis

Systematic Qualitative Organic Analysis

Analysis of Organic Compounds possessing monofunctional groups (carboxylic, aldehyde, ketone, amide, nitro, amines) and preparation of one derivative of each group. (Analysis of single compound and its derivative preparation)

1. Purification of organic compounds:

2. Thin layer chromatographic techniques:

Thermochemistry

1. Determination of heat capacity of calorimeter.

2. Determination of enthalpy of neutralization of hydrochloric acid with sodium hydroxide.

3. Determination of enthalpy of ionization of acetic acid.

4. Study of the solubility of benzoic acid in water and determination of ΔH.

Chemical Kinetics:

1. To study the effect of nature of reactants on the rate of reactions

2. Determination of relative strength between HCl and Urea hydrochloride for hydrolysis of methyl acetate

3. To determine the rate constant and order of reaction between KI and $K_2S_2O_8$.

4. Study of saponification of ethyl acetate with sodium hydroxide at equal concentration of ester and alkali.

5. Compare the strengths of HCl and H_2SO_4 by studying kinetics of hydrolysis of methyl acetate.

Ionic equilibria : pH measurements- Measurement of pH of different solutions like aerated drinks, fruit juices, shampoos and soaps (use dilute solutions of soaps and shampoos to prevent damage to the glass electrode) using pH meter.

Phase Equilibria

a) To draw the phase diagram of the binary system - diphenyl amine and α – Naphthol and find the eutectic temperature.

b) Study the mutual solubility of phenol and water at various temperatures and hence determine the critical solution temperature.

c) Study the effect of addition of NaCl on critical solution temperature of phenol water system and study of the effect of impurities on it.

Conductance and Conductometric titrations:

a) Determination of cell constant.

b) Determination of equivalent conductance, degree of dissociation and dissociation constant of a weak acid.

i. Strong acid vs. strong base

ii. Weak acid vs. strong base

Potentiometry and Potentiometric titrations

i. Strong acid vs. strong base (Quinhydrone method)

ii. Potassium dichromate vs. Ferrous Ammonium sulphate

Surface tension measurement

Determination of the surface tension of a liquid or a dilute solution using a stalagmometer.

Solutions of Solids in Liquids

Determine solubility curve for KCl from 250C to 500C.

Viscosity measurement

a) Determination of the viscosity of a liquid or dilute solution using an Ostwald's viscometer.

b) Study of the variation of viscosity of an aqueous solution with concentration of solute.

COLORIMETRIC EXPERIMENTS

1. Draw calibration curve (absorbance at λmax vs. concentration) for various concentrations of a given coloured compound ($KMnO_4$/ $CuSO_4$) and estimate the concentration of the same in a given solution.

2. Determine the composition of the Fe^{3+}-salicylic acid complex solution by Job's method.

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