11.1) CORE CHEMISTRY IN EUROPEAN UNIVERSITIES

List of Topics

GENERAL CHEMISTRY

Units, measurement and equations

Conservation of matter, chemical reaction, chemical equations. Relative atomic and molecular mass. Formulae (formulas), stoichiometry, stoichiometric coefficients and their meaning. The mole concept.

States of matter

Properties of solids, liquids and gases.

Atomic structure

Composition of matter, protons, neutrons and electrons, isotopes. Electronic configuration of atoms, Hund's rules and the Aufbau principle. Atomic orbitals, hybridisation: sp3, sp2 and sp orbitals and their influence on structure.

The Periodic Table. Periodicity of properties, including radii, ionisation enthalpies, electron affinities, electronegativities.

Bonding

The ionic and covalent concepts, metallic bonding, Lewis structures, orbital overlap. Sigma and pi bonds - valence bond and molecular orbital approaches. MO energy level diagrams for bond formation. Localised and delocalised bonds; valence-bond, resonance and molecular orbital representation of delocalisation; electronegativity and bond polarity; homolysis and heterolysis.

Intermolecular interactions - hydrogen bonding, van der Waals (London) forces.

Acids and bases

BRØNSTED acid-base theory, Lewis concept of acids and bases.

Symmetry

Symmetry operations and elements: planes, centres and axes of symmetry.

ANALYTICAL CHEMISTRY

General

Elements of data analysis and presentation relevant to analytical chemistry. An overview of titrimetric and gravimetric methods. Analytical aspects of equilibria [acid/base, oxidation/reduction, complexation, precipitation, ion-exchange, liquid/liquid, partition, and their various interactions]

Theory and practice of titrimetric analysis.

Specific technique

Electrochemical analytical methods, in particular: potentiometry, electrogravimetry, Coulommetry, voltammetry (classical, Tast, pulse polarography, cyclic, stripping), and conductimetric methods.

Chromatography, in particular: gas-liquid chromatography (GLC), high performance liquid chromatography (HPLC), gas chromatography (GC), ion-exchange chromatography.

Thermal analysis, in particular: differential thermal analysis (DTA), thermogravimetry (TG), differential scanning calorimetry (DSC).

Electrophoresis.

Coupled techniques, in particular: gas chromatography - mass spectrometry (GCMS), gas chromatography - infrared spectroscopy (GCIR), inductively coupled plasma mass spectrometry (ICPMS).

X-ray diffraction.

Electron microscopy

Spectroscopy for quantitative analysis

Quantitative use of nmr, ir and uv-visible spectroscopy.

Kinetic methods in spectroscopy

Atomic absorption and emission; fluorescence.

X-ray absorption and fluorescence.

INORGANIC CHEMISTRY

Nomenclature

IUPAC nomenclature for binary inorganic compounds. Use of oxidation numbers in nomenclature.

Stereochemistry

Three-dimensional structures of small molecules. The valence-shell electron pair repulsion model. Geometry of co-ordination compounds.

The concepts of inorganic chemistry

Physical properties of inorganic compounds, oxidation states, and chemical reactivity.

Co-ordination number and ligand concept [including chelation], oxidation states. Frost and Latimer diagrams, hard and soft acids and bases.

Magnetic and electrical properties.

Colour in inorganic compounds. [Spectrochemical series].

Basic ideas of crystal field leading to ligand field and the molecular orbital treatment of complexes.

Methods of structure determination in inorganic chemistry.

Systematic description of the elements

The reasons for the separation of s, p, d, and f elements in describing their properties.

The basic chemical properties of the most important elements. In particular the following should be covered:

Hydrogen compounds, oxo compounds, halides and a brief mention of the noble gases, nitrides, the concept of metal complexes [but not detailed treatment of large molecules], existence of organometallic compounds.

Special Topics

Nuclear and radiochemistry, catalysis, co-ordination chemistry [to include ideas of hard and soft acids and bases, and Lewis acids and bases], organometallic compounds, metal ions in solution, solvolysis, and catenation. Molecules which form rings, chains, or cages [including mention of silicates and polyphosphates], metal ions in biology, an introduction to the solid state [defects, nonstoichiometric compounds (including an idea of the existence of mixed-valence species), close packing, optical and electronic properties.]

ORGANIC CHEMISTRY

Nomenclature

IUPAC nomenclature for straight and branched chain hydrocarbons, monocyclic cycloalkanes, benzene and naphthalene, simple aromatic heterocyclic compounds, and their derivatives having any of the functional groups included in the organic chemistry core.
Sequence rules for specification of ligand priority, the E/Z designation, R/S to specify absolute configuration (Cahn, Ingold, Prelog).

Stereochemistry

Tetrahedral carbon, stereogenic (chiral) centres, chirality in molecules, geometrical and optical isomerism, optical activity, specific rotation, enantiomers, diastereomers, meso compounds, racemic mixtures and their separation. Conventions for representing three-dimensional chemical structures, conformations of ethane and butane, steric hindrance and preferred conformation. Conformation and *cis-trans* isomerism in cycloalkanes, axial and equatorial bonds in cyclohexane, conformational mobility of cyclohexane. The stereochemical requirements of substitution, addition, and elimination reactions.

Reactions and Mechanism

Types of organic reaction, reaction mechanisms, rates and equilibria, reaction co-ordinate energy diagrams, intermediates and transition states. Basic ideas of mechanism - electronegativity, polarisation, curly arrows, electrophiles and nucleophiles, reactive intermediates - carbocations, carbanions, free radicals. Acid-base catalysis.

Substitution, addition and elimination reactions.

General mechanisms for SN1, SN2, SNAr, E1, E2 and electrophilic aromatic substitution reactions, the influence of reagents and reaction conditions, the competition between nucleophilic substitution and elimination. Addition to carbon-carbon multiple bonds. Addition and addition-elimination reactions at carbonyl, imino and nitrile groups; esterification, hydrolysis and analogues.

Alkylation and acylation of enols and enolates

Acidity of hydrogen atoms alpha to carbonyl, nitrile and nitro groups, keto-enol tautomerism, reactivity of enols, alpha halogenation of carbonyl compounds. Enolate ion formation and reactivity, alkylation of enolate ions, decarboxylation, the use of ethyl acetoacetate and malonic esters in synthesis. Enolate acylation, carbonyl condensation reactions, aldol reaction and analogues, the Claisen condensation and related reactions. The Cannizzaro reaction.

Rearrangement reactions

Carbocation rearrangements (Wagner-Meerwein, pinacol), Beckmann, Baeyer-Villiger, Hofmann and Curtius rearrangements.

Functional group chemistry and classes of organic compounds

Alkanes: Sources, preparation, oxidation, free radical halogenation, combustion. Cycloalkanes - small, medium and large rings, ring strain.

Alkenes: Electronic structure, *cis-trans* isomers, preparation via elimination reactions. Addition reactions - hydrogenation (including the Lindlar catalyst), electrophilic addition of HX, H2O, halogens, orientation of alkene addition reactions, Markovnikov's rule, carbocation structure and stability, addition in the presence of peroxides - anti-Markovnikov. Hydroboration. Oxidation of alkenes by manganate(VII), peroxo-acids, and ozone. Conjugated dienes, resonance, stability of allylic carbocations, 1,2- and 1,4- addition to dienes. Cycloaddition reactions (Diels-Alder).

Alkynes: Structure and preparation. Electrophilic addition of H2, water, HX and X2, acidity, formation of alkyne anions, coupling reactions.

Aromatic Compounds: Structure and stability of benzene, resonance, Hückel's rule, simple non-benzenoid aromatics (cyclopentadienyl, tropylium). Electrophilic aromatic substitution - halogenation, nitration, sulfonation, the Friedel- Crafts alkylation and acylation reactions. Isomerism of benzene derivatives, reactivity and orientation of reactions on substituted aromatic rings, oxidation and reduction of aromatic compounds. Side-chain halogenation, benzyl as a free radical, cation and anion. Naphthalene. Kinetic *vs.* thermodynamic control.

Alkyl halides (haloalkanes and haloaromatic compounds): Preparation from alcohols, nucleophilic substitution reactions, elimination reactions, Grignard reagents. Haloaromatics and haloalkenes, their resistance to nucleophilic attack. Allylic bromination.

Alcohols and phenols, ethers and epoxides: Primary, secondary and tertiary alcohols. Acidity of alcohols and phenols, hydrogen bonding. Synthesis of alcohols from alkenes and from carbonyl compounds. Reactions of alcohols - with hydrogen halides, phosphorus halides, dehydration, reaction with metals, acylation, oxidation. Synthesis and reactions of phenols - oxidation, acylation. Williamson ether synthesis, acidic cleavage, cyclic ethers and crown ethers. Synthesis and ring-opening reactions of epoxides.

Amines and other nitrogen functions: Primary, secondary and tertiary amines, amine basicity, synthesis of amines by substitution and reduction reactions, reactions of amines - alkylation, Hofmann exhaustive methylation, acylation, preparation of diazonium compounds - and their use in synthesis; nitro compounds, ureas.

Aldehydes and ketones: Structure and properties of the carbonyl group, synthesis of aldehydes and ketones, oxidation and reduction of aldehydes and ketones, nucleophilic addition of water, alcohols, amino compounds, and Grignard reagents. Conjugate addition to unsaturated carbonyl systems (Michael addition).

Carboxylic acids and derivatives: Structure, and properties of carboxylic acids, acidity, pK values, the effect of substituents on acidity. Synthesis of carboxylic acids, nucleophilic acyl substitution reactions - esterification, acid halide and amide formation. Reactions of acid halides, acid anhydrides, esters, and amides - solvolysis, hydrogenolysis, reduction, reactions with Grignard reagents. Preparation and reactions of nitriles.

Sulfur, phosphorus and silicon chemistry

Thiols and sulfides, sulfoxides and sulfones. Structure, nomenclature, preparation and reactions of simple organophosphorous and organosilicon compounds. The Wittig and

Wadsworth-Emmons reactions, Peterson olefin

Heterocyclic compounds

Pyrrole, furan, thiophen, pyridine, aromaticity in monocyclic heterocyclic compounds, electrophilic and nucleophilic attack, oxidation and reduction, acid/base properties.

Polymers

Free radical and ionic polymerisation of alkenes (addition or chain growth). Step-growth (condensation) polymerisation.

Biomolecules

Aminoacids and peptides: structures of common amino acids, dipolar (zwitterionic) nature, isoelectric points, the peptide bond. A brief introduction to the major classes of biomolecules: i.e. Carbohydrates, proteins, lipids and nucleic acids, steroids, terpenoids, alkaloids, vitamins. Where suitable they can be used to exemplify aspects of organic chemistry covered elsewhere.

Spectroscopy in Organic Chemistry

Spectroscopy and mass spectrometry for structure determination
Infrared (ir) spectroscopy, characteristic group frequencies.
Ultraviolet (uv) and visible spectra, colour and conjugation.
Nuclear magnetic resonance (nmr) spectroscopy, chemical equivalence, the delta scal chemical shift.
1H nmr spectra, integration, proton counting, spin-spin coupling, the n+1 rule.
13C nmr spectroscopy, multiplicity in off-resonance spectra.
Mass spectra, molecular ions, accurate mass, isotope signals, and simple fragmentations.

Synthetic methodology

Systematic approaches to the design of syntheses, utilisation of reactions of functional groups for synthesis, functional group interconversions and the formation of carbon-carbon and carbon-heteroatom bonds, application and removal of protecting groups, analysis and modification of synthetic sequences. Use of retrosynthetic analysis and the disconnection approach, synthons and corresponding reagents.

PHYSICAL CHEMISTRY

Nomenclature

Use of SI units and IUPAC names and symbols for the elements.

States of matter (Gases)

The kinetic theory of gases, the Maxwell-Boltzmann distribution. The van der Waals equation, the virial equation, molecular size and interactions, intermolecular potential, the Clapeyron equation.

Solids

Types of solid - ionic, covalent, molecular, metallic - and their properties.

Lattices and lattice energy. Common packing arrangements, unit cell, cubic, body and face centred cells, percentage of occupied space, rock salt and other simple structures. Bragg equation.

Solution

Solution contrasted with heterogeneous mixture; solubility, saturated solutions and equilibrium; dissociation in solution, strong and weak electrolytes; precipitation and solubility product; solute/solute and solute/solvent interactions, concept of ideal solution and deviations from ideal behaviour. Ion-solvent interaction and qualitative interpretation. Energetics of solvation and its comparison and interpretation. Henry's law, Raoult's law, colligative properties (boiling point elevation, freezing point depression, osmotic pressure).

Chemical thermodynamics

Definition, measurement and practical scales of temperature, zero principles (the zeroth law). First law and its relationship with thermochemistry, enthalpy, comparison and correlation of thermochemical data.

Reaction profile diagrams, exothermic and endothermic reactions, rate-determining step. Heats of reaction and their application to deduce heats of formation; bond energies, bond dissociation energies, Hess's law. Concept of Gibbs energy and Gibbs energy change.

Variation of heat of reaction with temperature, Kirchhoff's law. Second law, concept of entropy and its physical and statistical significance, population of quantised energy levels. Delta S for phase changes and temperature changes. Delta S for chemical reactions, and their comparison and interpretation. Comparison of influence of delta H and T delta S on magnitude of delta G and interpretation in molecular terms, the Clausius-Clapeyron equation and its uses. The Gibbs-Helmholtz equation. The variation of delta G with temperature, pressure and concentration in chemical equilibria, the reaction isotherm. Variation in ln(Kp) with temperature. Concept of chemical potential and its variation with temperature, pressure and composition.

Calculations of equilibrium constants from thermodynamic data and their uses. The van't Hoff equation. Activity. The Third law and its significance, zero-point energy, calculation of absolute entropies.

Chemical equilibrium

Mass action, equilibrium calculations, Le Chatelier's principle, the effect of temperature, pressure and catalysts on equilibrium; acid/base equilibria, H-ion and pH equilibria, buffer solutions.

Phase equilibria

Application of Gibbs' Phase rule in various multi-component systems, distillation diagrams, theoretical plate concept, non-ideal mixtures, azeotropes, partition of a solute between two immiscible solvents. Binary condensed systems, phase-diagrams and their interpretation, eutectics, solid compounds, solid solutions.

Electrochemistry

Electrolytes, electrolysis, Faraday's laws, the galvanic cell, electrical work. Standard electrodes, concentration cells, Nernst equation. Electrolytic conduction, ionic diffusion and transport. Chemical potential and activities in solution. The limiting Debye-Hückel equation and its uses. Electrode equilibria. Reversible electrodes and their Nernstian behaviour, reversible galvanic cells, emf and its relationship with electrolyte equilibria and thermodynamic quantities for cell reactions. The electrochemical measurement of pH and associated problems. Selective-ion electrodes, their Nernstian behaviour and performance characteristics.

Aspects of non-equilibrium electrochemistry - electrochemical kinetics, electroanalytical chemistry, electrochemical synthesis, industrial electrochemistry, batteries and fuel cells, corrosion. Relation between reaction rate and electric current density ($j = zFv$), basic principles of electrode kinetics, the electric double layer, the Tafel equation, Butler-Volmer law, Fick's laws.

Chemical kinetics and catalysis

Rate of reaction and factors that affect it, rate constant, rate equation, control of rates, concept of mechanism, the distinction between homogeneous and heterogeneous reactions and catalyses. Order of reaction, molecularity. Arrhenius equation, activation energy. Chain reactions. Experimental methods of studying rate of reaction. Evaluation of rate constant for zero-, first- and second-order reactions. Variation of rate constant with temperature, evaluation of activation energy and pre-exponential factor. Simple collision theory. Unimolecular reactions and the Lindemann theory. Parallel and consecutive reactions. Rate determining step and steady state approximation. Thermodynamic formulation of activation parameters, enthalpy and entropy of activation, and their interpretation, nature of transition state. Kinetics and mechanism of homogeneous catalysed reactions.

Principles of spectroscopy and mass spectrometry

The electromagnetic spectrum. The Boltzmann distribution and quantised energy levels, energy level occupancy for nuclear, rotational, vibrational and electronic energy levels and their associated energy transitions. Harmonic oscillator and rigid rotor models. Vibration of a diatomic molecule, force constant. Principles of infrared and Raman spectra of molecules, calculation and comparison of bond lengths and force constants, concepts of fundamental bands, overtone and combination bands. Electronic spectral transitions. The Franck-Condon principle. Absorption in the visible and ultraviolet, atomic absorption spectroscopy. The Beer-Lambert law. The physico-chemical principles of nuclear magnetic resonance and electron spin resonance spectroscopy, and mass spectrometry.

Quantum chemistry

Principles of quantum mechanics, the Schroedinger equation and its application to simple systems - particle in a box, harmonic oscillator, and rigid rotor, the de Broglie principle, Heisenberg's uncertainty principle.

PRACTICAL WORK

A range of laboratory exercises at a suitable level to be carried out by every student, relating to the chemistry detailed in the Core. Instruction and practice to be given in basic manipulative skills, and in the use of appropriate apparatus and instrumentation. Techniques developing safety and good practice must be adopted. Organic chemistry to include exercises in synthetic chemistry, problem solving, qualitative organic analysis and structure determination. Physical chemistry must include the use of error analysis in the treatment of experimental data. Inorganic chemistry to include synthetic chemistry, problem solving, and compound characterisation by appropriate means, including spectroscopy.

Analytical chemistry to include exercises in volumetric, gravimetric, and instrumental analysis.

11.2) LIST OF LEARNING OBJECTIVES OF CORECHEM European Chemistry Thematic Network

Learning objectives for Core Chemistry

GENERAL CHEMISTRY

Units, measurement and equations

Distinguish matter and energy, mass and weight. Conservation of mass. Understand the significance of units, interconvert measurements in different units. Distinguish elements, compounds, mixtures, and the nature of chemical contrasted with physical reactions. Understand the basis of relative atomic and molecular mass, and the basis for the standard.

Understand the ideas of constant composition and multiple proportions. Calculate a percentage composition from formula. Use relative atomic masses to calculate relative molecular mass, and accurate mass measurement to obtain a molecular formula. Obtain empirical and molecular formulae from elemental compositions and relative molecular masses. Balance chemical equations.

Understand the idea and basis of the mole. Interconvert mass and molar quantities. Use molar ratios to solve problems on reacting quantities from equations, and to calculate percentage yields. Understand the concept of molarity and its manipulation. Use Avogadro's number to convert from molecular to molar scale.

States of matter

Describe the characteristic properties of solids, liquids and gases, and provide an explanation of their behaviour, including melting, freezing, boiling and condensing, based on particle theory.

Atomic structure

Describe the structure of the nuclear atom and outline the experimental basis that established it (including the Rutherford experiment). Explain the existence of isotopes.

Describe atomic structure in terms of electronic shells and subshells, and orbitals. Draw an energy level diagram for the hydrogen atom, and relate it to the spectrum of atomic hydrogen. Describe the four quantum numbers for the hydrogen atom, and show how they may be extended to other elements. Interpret orbitals in terms of probability. Know boundary surfaces for s, p, and d electrons. Interpret quantum numbers in terms of properties for atoms other than hydrogen. Know the restrictions on quantum numbers and hence derive the limiting numbers of electrons in shells. Use the Aufbau principle, and Hund's rules to build up electron configurations, and relate them to the construction of the Periodic Table. Understand periodicity from configuration across and down the Table, and explain trends in radii, ionisation enthalpies, electron affinities, and electronegativities.

Bonding

Understand and explain ideas of ionic and covalent bonding. Describe metallic bonding and relate to metallic properties. Identify the state of hybridisation of an atom in a given molecule, and indicate how this will influence the structure and reactivity of that molecule. Write Lewis structures for simple molecules. Distinguish sigma and pi bonds. Describe their formation in terms of orbital overlap of s, p, and d electrons and hence determine bond orders; and in terms of molecular orbital energies using a molecular orbital energy-level diagram. Sketch bonding, non-bonding and antibonding orbitals from s, p, and d combinations. Describe conditions for delocalisation to occur, explain its occurrence using the theories of resonance and p-orbital overlap, and outline the characteristics of delocalised bonds.

Relate covalence and ionicity to electron configuration. Predict the direction of dipoles in polar molecules. Explain the reasons for the formation of covalent or ionic bonds

Give reasons for the occurrence of intermolecular interactions (van der Waals forces, and hydrogen-bonding). Recognise possibilities for inter- and intra-molecular hydrogen bonding and van der Waals (London) forces in a molecule, and use these intermolecular interactions to explain such phenomena as the physical properties and solubility of molecules, the structure of large biomolecules, and molecular recognition.

Acids and bases

State the BRØNSTED acid-base theory and its applications to salt hydrolysis, buffers and solubility. State the Lewis concept of acids and bases, and identify Lewis acids and bases.

Symmetry

Identify symmetry elements in objects of known structure.

ANALYTICAL CHEMISTRY

General

Distinguish accuracy and precision, systematic and random errors, and develop the concepts of confidence interval, control charts and tests for significance. Use simple linear calibration (regression) to evaluating an unknown quantity for a measured datum, with the proper uncertainty. Recognise the utility of multivariate analysis, and use multivariate techniques. Apply numerical and experimental optimisation procedures. Be familiar with software packages, which implement these techniques.

Extend an understanding of simple equilibria in solution, based on the donor/acceptor principle to the more complex simultaneous equilibria encountered in real analytical situations. Reliably carry out a range of titrimetric procedures within acceptable limits; calculate and present results

Be aware of the experimental limitations, and estimate the degree of uncertainty in the results obtained, using different analytical instruments and methods. Select the most appropriate titrimetric procedure - classical, potentiometric, conductimetric, gravimetric, or spectrophotometric - for a given task.

Specific techniques

Have experience of using each of the listed techniques in the laboratory.

Understand the basic physico-chemical principles of the listed techniques, and apply it to the interpretation of the results obtained. Understand the basic construction and mode of operation of each of the instrumental components required for the analytical techniques listed. Be aware of the potential and limitations of each technique, and the possible sources of error. Make comparisons between the performance of different techniques and select the one(s) most suitable for a given task.

Know the basic thermodynamics involved in electrochemical analytical. Compare the qualitative and quantitative performances of the various electroanalytical techniques. Use the

underlying thermodynamics of ion selective electrodes (including pH glass electrodes) to explain sensitivity and selectivity. Discuss the use of microelectrodes (for *in vivo* measurements), modified electrodes, and electrochemical and biosensors.
Explain the basis of chromatographic separation, from the principles of simple extraction and counter-current separation. Describe the factors that lead to deviation from ideal chromatographic behaviour, and explain the efficiency of the separation procedure by height equivalent to a theoretical plate (HETP) theory. Classify the different chromatographic procedures according to the nature of stationary and mobile phases involved, and choose an appropriate chromatographic or electrophoretic technique and system to separate a particular mixture.
Apply differential scanning calorimetry (DSC), in both inert and air/oxygen atmospheres to determine such values as the glass transition temperature and the melting point of polymers. Apply the theoretical principles of the thermal analysis techniques to an interpretation of the experimental results.
Understand the physical principles, and the instrumentation, required in the technique of powder diffraction, and its application to qualitative and quantitative phase analysis.
Be familiar with the technique of scanning electron microscopy (SEM) and its connections with other modern surface analytical techniques.

Spectroscopy for quantitative analysis

Apply spectroscopy to the monitoring of kinetic experiments and interpret the results obtained.
Understand the nature and application of analogue and digital signals, and procedures for A/D and D/A conversion. Explain the basics of digital treatment (filtering) of signals by transform methods, by convolution and deconvolution operations; and the principles on which FT-based spectroscopic techniques work.
Demonstrate the capability of X-ray fluorescence (XRF) in both qualitative and quantitative analyses, especially in industry.

INORGANIC CHEMISTRY

Nomenclature

Recognise symbols for all s, p and d block elements.
Given an ionic representation of a simple binary inorganic compound assign to it a correct name. Draw the ions, with correct charges, given the name of a simple binary inorganic compound. Use oxidation numbers correctly in nomenclature.

Stereochemistry

Derive shapes of simple molecules from VSEPR, and rationalise variations in bond angles. Sketch molecules with simple, standard geometries, showing structural relationships of isomers. Describe geometries of simple structures in terms of hybridisation. Use known stereochemistry of reaction to predict the outcome of reactions at co-ordinated metal ions.

The concepts of inorganic Chemistry

Recognise when ionic or covalent structures are to be expected. Identify giant molecule structures and polymers. Explain polarisability trends in the Periodic Table, and ionic/covalent interactions. Predict whether compounds will be gases, liquids or solids.
Define oxidation state and assign oxidation states from molecular formulae. Use oxidation states to identify electron configurations.

Define ligand, co-ordination number, and the geometry of compounds with common co-ordination numbers. Understand chelation, and qualitatively explain the chelate effect. Relate geometries to simple symmetry concepts. Use data to construct Latimer [E0] and Frost [nE0/OS] diagrams, and interpret them. Identify and explain the mode of action of hard and soft acids and bases.

Understand the ideas of diamagnetism and paramagnetism, and their relation to electronic structure for molecules and ions. Evaluate a spin-only moment. Understand ideas of electrical conductivity, and ionic mobility. Understand the basic reasons for conduction, semi-conduction and non-conduction. Relate properties to electronic levels.

Predict how d-orbitals split in simple geometries. Know the spectrochemical series and use it to interpret spectra. Understand the idea of charge-transfer and relate it to oxidation state, interpret colours of do complexes. Interpret the splittings of orbital levels geometrically.

Understand when the methods of crystallography and spectroscopy are applicable. Explain qualitatively the principles of X-ray crystallography. Familiarity with accuracy of X-ray data. Use such data to derive ionic radii from simple ionic solids, and evaluate the atoms in a unit cell.

Systematic description of the elements

For hydrogen - know the isotopes and their structures, types of compound formed, types of bonding, which occur, origin of isotope effects.

Know the structures and bonding types of simple oxide compounds. Predict basic or acidic behaviour. Understand the acid anhydride concept.

Know the formulae and basic bonding concepts of halides of representative metals and non-metals. Rationalise hydrolytic behaviour, and products of hydrolysis.

Rationalise and interpret the general trends in the chemistry of main group compounds.

Explain the reasons for the existence of noble-gas derivatives, and their basic properties.

Classify organic compounds of the metals, their stabilities and reactivities.

Special Topics

(AN EXAMPLE IS GIVEN HERE)

Radio and nuclear chemistry: Define and exemplify isotope, nuclide, nuclear fission, nuclear fusion, half-life. Write equations for fission reactions, alpha and beta decay, neutron induced (reactor) processes, and (stellar) fusion reactions. Calculate ages using radio-dating procedures. Outline the production of nuclear energy.

ORGANIC CHEMISTRY

Nomenclature

Know the correct names (both prefix and suffix forms) of common functional groups. Given a structure or abbreviated formula use IUPAC nomenclature to name correctly straight and branched chain hydrocarbons, monocyclic cycloalkanes, benzene and naphthalene, simple aromatic heterocyclic compounds, and their simple substituted derivatives. Given an IUPAC name for any of the above correctly draw its structure.

Use the sequence rules for specification of configuration to identify and name correctly isomers of doubly-bonded or cyclic compounds having either E or Z configurations, or isomers (or individual stereogenic (chiral) centres) having R or S absolute configurations.

Stereochemistry
Recognise a stereogenic (chiral) centre in a molecular structure. Identify and distinguish between identical molecules, enantiomers and diastereomers from structural representations. Recognise a meso compound from its structure. With or without the aid of molecular models, represent the three-dimensional nature of a molecule using "flying wedge" or Newman projection conventions. Describe methods for separating a racemic mixture. Account for steric hindrance between neighbouring groups on bonds and across rings. Relate potential energy to dihedral angle during bond rotation, and justify the selection of a preferred conformation. Calculate a specific rotation and an enantiomeric excess from appropriate data. Correlate *cis* and *trans* substituents on cyclohexane rings with axial and equatorial disposition. Use known stereochemistry of reaction to predict the outcome of reactions at saturated centres, double bonds, cyclohexane rings, and co-ordinated metal ions. Use the products of reaction to identify stereospecific reaction paths.

Reactions and mechanism
Classify a given chemical transformation as addition, elimination, substitution, condensation, rearrangement, solvolysis, oxidation, reduction, and as subject to acid or base catalysis. Use the functional group principle to predict the chemical behaviour of a given molecule. Indicate *sigma* and *pi* bond polarisation caused by the electronegativity of atoms in a given molecule, and use it to predict direction of heterolysis, acid or base properties, and electrophilic or nucleophilic behaviour or sites of electrophilic or nucleophilic attack.
Distinguish between a transition state (activated complex) and a reactive intermediate. Under specified reaction conditions, recognise reagents as electrophiles or nucleophiles. Given starting materials (substrates), reagents, and reaction conditions, propose the outcome of a reaction; and whether given products or not, propose a possible mechanism for the course of the reaction, using "curly arrows" to indicate electron movements. Explain the differing stability of related reactive intermediates, and the influence of this stability on the course of a reaction.
Illustrate acid-base catalysed reactions; and show how acids (H+) and bases may be incorporated into the mechanism of a reaction.

Nucleophilic substitution: Given the reactants (a) identify nucleophile, electrophilic centre and leaving group; (b) decide (if possible) whether an SN1, SN2 or other mechanism will operate; (c) predict the structure of the products; (d) indicate how changes in reaction conditions, or the reactants could influence the outcome to the reaction; (e) decide whether or not a reaction will go; and (f) comment on the relative rates of the SN reactions. Suggest the best reagents and reaction conditions for carrying out a given transformation. Use curly arrows and reaction co-ordinate diagrams to show the mechanism of SN1, SN2 and SNAr reactions.

Elimination: Given the substrate, reagent and reaction conditions (a) predict the structure of the product(s), indicating the stereochemistry where necessary; b) predict which elimination product will predominate where more than one product can be formed; (c) predict whether substitution or elimination will predominate; and (d) explain how the conformation and configuration of a substrate can affect the outcome of an elimination reaction. Use curly arrows and reaction co-ordinate diagrams to show the mechanisms of El and E2 reactions.

Addition: Given the reactants (a) predict the structure of the product, indicating its stereochemistry; and (b) predict which addition product will predominate, where more than one product can be formed. Explain how the selection of the reagent can determine the orientation of addition. Specify the reagents and conditions needed to form a given product by an addition reaction.

Electrophilic aromatic substitution: Use curly arrows and reaction co-ordinate diagrams to show the mechanisms of electrophilic aromatic substitution. Predict and explain the position of entry of a second substituent, and the rate of substitution, into a monosubstituted benzene. Explain the different reactivity, and the positions of substitution, of aromatic heterocycles.

Carbonyl compounds: Illustrate with curly arrows the mechanisms by which nucleophiles and electrophiles react with carbonyl compounds. Recognise the common tetrahedral intermediate in mechanistic explanations of the reactions of both aldehydes and ketones and carboxylic acids and their derivatives with nucleophiles. Use curly arrows to show the mechanisms of these reactions. Explain the mechanism of Grignard reactions.
Alkylation and acylation of enols and enolates: Explain the acidity of C-H bonds adjacent to a carbonyl or other electron-withdrawing group, and show how this leads to valuable intermediates for the formation of carbon-carbon bonds through alkylation and acylation. Utilise ethyl acetoacetate and malonic ester in the synthesis of ketones and carboxylic acid derivatives. Differentiate between tautomers and resonance forms. Explain the ease of decarboxylation of beta-ketocarboxylic acids. Describe the role of acid and base catalysis in carbonyl condensation reactions. Recognise limitations in the use of condensation reactions in synthesis.

Rearrangement reactions: Using curly arrows outline the general mechanism for carbocation rearrangements (carbon to carbon migration), and rearrangements involving electron deficient nitrogen or oxygen (carbon to nitrogen, carbon to oxygen migration). Predict the products and give a mechanism for a rearrangement reaction given substrate and reaction conditions, or provide a mechanism for a reaction where substrate and product are given.

Polymers: Suggest mechanisms for chain-growth and step growth polymerisation, using "fish-hook" or curly arrows as appropriate.

Functional group chemistry
Be familiar with the general chemistry of the following classes of organic compounds: alkanes, alkenes, alkynes, alkyl halides (halo alkanes), alcohols, phenols, ethers. epoxides, amines and other nitrogen functions, aldehydes, ketones, carboxylic acids and their derivatives (acid halides, acid anhydrides, esters, and amides), nitriles, benzene and its monosubstituted derivatives, and the simple monocyclic heterocycles.
In addition, for the following classes of organic compounds:

Alkanes: Account for "strain" in small rings. Relate the difficulty of forming cyclic systems to the size of ring required.

Alkenes: Use simple orbital overlap theory to account for non-rotation about *pi* bonds, conjugation, the stability of allyl carbocations, and the features of the Diels-Alder reaction. Utilise the chemo- and stereo-selective nature of the Lindlar catalyst.

Aromatic compounds: Explain the structure, stability and reactivity of benzene using the concept of resonance. Identify simple non-benzenoid aromatic molecules by using Hückel's rule. Distinguish between Friedel-Crafts alkylation and acylation reactions for use in synthesis. Explain the stability of the benzyl free radical, cation and anion, and show how this determines the chemistry of toluene and its side-chain derivatives.
Explain how reaction conditions determine the position of substitution in naphthalene.

Alkyl halides (haloalkanes and haloaromatic compounds): Exploit the usefulness of alkyl halides in synthesis, especially through substitution and organometallic reagents. Account for the reduced reactivity of "non activated" halo aromatics and halo alkenes.

Alcohols and phenols, ethers and epoxides: Exploit the usefulness of alcohols and epoxides in synthesis. Account for the acidity of phenols. Explain the behaviour of crown ethers.

Amines and other nitrogen functions: Distinguish between the behaviour of amines as nucleophiles and bases, and between nitrogen in sp3, sp2 and sp hybridisation. Account for the basicity of amines, and the reduced basicity of amides. Exploit the usefulness of diazonium compounds in the synthesis of substituted benzene derivatives.

Aldehydes and ketones: Explain how the typical reactions of carbonyl compounds (protonation, addition, addition-elimination and substitution) can be understood from a knowledge of their structure. Predict the expected product of the reaction of a specified carbonyl compound with a given reagent under stated conditions. Predict the product for the reaction of a Grignard reagent with a carbonyl compound. Explain why 1,4- as well as 1,2-nucleophilic addition takes place with conjugated carbonyl systems.

Carboxylic acids and derivatives: Show how the group adjacent to a carbonyl group modifies the chemical behaviour of that carbonyl, and how its own chemistry is affected. Predict the product and explain the mechanism for reaction of a Grignard reagent with carboxylic acid derivatives, carbon dioxide and nitriles.

Sulfur, phosphorus and silicon chemistry
Relate the organic chemistry of silicon, sulfur and phosphorus to that of carbon, oxygen, and nitrogen, showing similarities and differences Outline a mechanism for the Wittig and Peterson reactions, and show how the Wittig and Wadsworth-Emmons reactions can be used in synthesis.

Heterocyclic compounds
Compare the aromaticity of pyrrole, furan, thiophen and pyridine with that of benzene, showing similarities and differences. Explain the different effect that nitrogen has on the chemistry of pyrrole and pyridine in rationalising their contrasting chemical behaviour. Relate the differing chemistry of pyrrole, furan and thiophen to the influence of the heteroatom.

Polymers
Recognise a given molecular structure as (a) an initiator, (b) an addition polymer, (c) a condensation polymer, (d) a monomer for addition polymerisation, or (e) a monomer for condensation polymerisation. Name polymers according to their monomer(s). Outline the

sequence of reactions involved in (a) radical-initiated addition polymerisation and (b) condensation polymerisation. Predict the polymer that would result from a given monomer(s) or deduce the monomer(s) that would give rise to a given polymer. Relate the physical properties of an addition or condensation polymer to its molecular structure.

Biomolecules

Recognise features of general organic chemistry in given examples of the chemistry of biomolecules. Predict the behaviour of biomolecules under given reaction conditions based on a knowledge of general organic chemistry. Recognise the importance of hydrogen bonding, and other molecular interactions, in the chemistry of biomolecules.

Spectroscopy and mass spectrometry for structure determination

Use infrared (ir), and 13C and proton nuclear magnetic resonance (nmr) spectroscopy, separately or in combination with each other, or with additional information from ultraviolet/visible (uv/vis) spectroscopy, mass spectrometry (ms), analytical data or descriptive chemistry, to identify structural features or complete structures of "unknown" molecules. Determine a molecular formula from the accurate mass of a molecular ion. Calculate a "double bond equivalent" from a molecular formula.

Synthetic methodology

Devise a synthetic sequence by working back from a target molecule using reactions and reagents encountered previously, or by proposing analogous reactions and reagents. In devising a synthetic sequence recognise the need for (a) functional group interconversions (especially oxidations and reductions); (b) carbon-carbon bond formation reactions; and (c) skeletal carbon-heteroatom bond formation; and identify these three features within a synthetic sequence. Modify a given synthetic sequence to give a route to a similar target molecule. Utilise the chemistry of different classes of compound studied to introduce and modify (interconvert) functional groups. Use where appropriate the application and removal of a suitable protecting group in a synthetic sequence. Utilise the reactions of Grignard reagents, alkynides, the nitrile anion, enols and enolates in carbon-carbon bond formation en route to a target molecule.

Depict the four possible synthons generated by a bond disconnection, and select the more suitable pair by relating each synthon to a viable reagent. Identify sites where a functional group interconversion is necessary before a useful disconnection can be made.

PHYSICAL CHEMISTRY

Nomenclature

State, and correctly identify the abbreviations for the base, and the derived, SI physical quantities and units, in particular force, pressure, and energy. Express all units in terms of base units (and dimensions).

States of matter (Gases)

Outline the main features of the kinetic theory of gases, and use it to derive the expression for the pressure of an ideal gas. Recognise how the Maxwell distribution of molecular speeds varies with temperature and molar mass, and distinguish between the mean speed and the root mean square speed of the molecules. Sketch the general form of the intermolecular potential energy curve for two molecules, and discuss its form in terms of attractive and repulsive interactions. Discuss the deviations from ideal gas behaviour shown by real gases in terms of p-V isotherms, the compression factor, the virial equation of state, and the van der Waals equation of state. Discuss the physical significance of the critical constant of a gas.

Solids

Give examples of types of solid, and describe bonding. Distinguish amorphous and crystalline solids. Calculate co-ordination numbers, molecules or atoms per unit cell for simple lattices, and derive empirical formulae. Relate lattice type, dimensions, density, molar mass, and Avogadro's number. Calculate empty space in structures. Use the Bragg equation to find spacings from angle of diffraction.

Solution

Perform calculations based on solubility products. State Henry's law and carry out calculations based on it. State Raoult's Law for the partial pressure of a gas above a mixture. Define colligative properties. Derive an expression for the depression of freezing point and calculate the molar mass of the solute. Derive an expression for the elevation of boiling point and use it to determine the molar mass of an involatile solute. Define osmotic pressure, derive van't Hoff equation and use it to determine the molar mass of a solute.

Chemical thermodynamics

Define and use practical scales of temperature. State the zeroth Law. Define the terms: thermodynamic system, surroundings, closed system and isolated system, internal energy, heat and work, thermodynamic reversibility, and the heat capacity of a system. State the First Law of thermodynamics.

Define the terms endothermic and exothermic reaction, and enthalpy of reaction. Use a table of bond dissociation energies to determine whether a given reaction will be exothermic or endothermic. Define the Gibbs function of a system and use it as a criterion for the direction of spontaneous change. Relate Gibbs energy to the position of equilibrium for a reaction. Express the equilibrium constant of a reaction in terms of the standard Gibbs functions of the reactants and products. State and use Hess's Law.

Define enthalpy, and relate changes of enthalpy in a system to the heat transferred at constant pressure. Define extensive and intensive properties, state functions, and exact differentials. Define standard state of a substance. Derive and use Kirchoff's Law for the temperature dependence of the reaction enthalpy. Relate the reaction enthalpy to the change in internal energy.

Define and use the enthalpy of combustion, bond enthalpy, and enthalpy of atomisation.

Define thermodynamic entropy. State the Clausius inequality and use it to show that spontaneous processes are accompanied by an increase of entropy. State the Second Law of thermodynamics. Calculate the change of entropy during a phase transition, during irreversible processes, and for chemical reactions; and also the change in entropy in the surroundings of a system. Relate the macroscopic definition of entropy to molecular structure. Indicate mathematically how the Gibbs function depends on the pressure and the temperature. State how the Gibbs function changes when the composition of a system changes. Derive and use the Gibbs-Helmholtz equation. Indicate mathematically how the equilibrium constant depends on the temperature and derive and use the van't Hoff equation. State the activity concept. State the Third Law of thermodynamics. Define the zero-point energy. Calculate the absolute entropy of a substance.

Chemical equilibrium

Write and expression for an equilibrium constant and manipulate this expression to calculate the quantities of reactants or products present at equilibrium. Write reaction quotients for reversible reactions. Use Le Chatelier's Principle to explain how a system in equilibrium responds to changes in quantity, pressure and temperature. Use Kc and Kp and interconvert. Discuss equilibria involving [H+], calculate pH, explain the action of a buffer solution.

Phase equilibria

State the Gibbs phase rule and apply it to single and multi-component systems. Derive the virial equation and use it to determine the molar mass of a polymer or an enzyme. Interpret a temperature-composition diagram and use it to determine the course of distillation of a mixture. Interpret phase diagrams.

Electrochemistry

Identify anode, cathode in cells. Calculate the maximum work from V for given charge. Manipulate standard potentials, e.g. for E0. and delta G0 for cells. Obtain V of concentration cells at non-standard conditions.

Explain equilibria in electrolytes. Define the activity, the activity coefficient and the mean activity coefficients of ions in solution. Describe the ionic atmosphere and state its role in determining the value of the mean activity coefficients of ions. Define ionic strength and the electrochemical potential of an electrolyte solution. Derive and use the Debye-Hückel Limiting Law for the mean activity coefficient and indicate how it deviates from ideal behaviour. Define electrode potential and describe the sign convention. Derive and use the Nernst equation for the potential of a reversible electrode. Describe the operation of a galvanic cell. Explain the thermodynamic reversibility of an electrochemical cell. Define the electromotive force (emf) of a cell and relate it to the spontaneous direction of change of the cell reaction. Derive and use the Nernst equation for the concentration dependence of emf of a cell, and to define the standard emf. Relate the standard emf to the equilibrium constant of the cell reaction, and to the thermodynamics quantities for cell reactions. Use emf measurements to determine pH, pK, and analytical determinations.

Describe how a potential difference arises at an interface and describe the electric double layer model. Outline how the rate coefficient for an electrochemical reaction changes with the potential difference across a metal-solution interface. Write an expression for the Tafel equation, construct Tafel plots from experimental data, and indicate the physical significance of the Tafel coefficients. Outline assumptions made in deriving the Butler-Volmer equation, and deduce the Tafel equation from the Butler-Volmer equation at both positive and negative values of overpotential. Describe the operation of a battery or a fuel cell. Predict or rationalise the power output of a given storage battery or fuel cell in terms of the cell emf, the overpotential at each electrode, the current efficiency and the internal cell resistance. Indicate how factors that determine the resistance of a solution at the limiting current density at an electrode are minimised in industrial cells, for example in the chlor-alkali industry. Describe various types of corrosion and the methods that can be used to reduce them. Indicate factors that determine the type and site of corrosion under a given set of circumstances.

Chemical kinetics and catalysis

Given an equation, define the rate of reaction in terms of concentrations, and derive the rate constant for the reaction. Define the order and the molecularity of a reaction. Find order from rate law, and give rate law for any step. Identify first and second order reactions. Define the half life of a reaction and relate it to reaction order. Find half-lives for first and second order reactions. Identify initiation, propagation and termination steps of a chain reaction. Use activation energy to find the effect of a change in temperature on rate. Obtain activation energy from the changes of rate constant with temperature.

Describe how the concentrations of reacting and/or forming species are monitored. Use the method of initial slopes to determine reaction order. Integrate zero-, first-, and second order rate laws for concentration as a function of time. Determine order from the time-dependence of concentrations. Describe Ostwald's isolation method and define pseudo-first-order rate law. Describe Arrhenius-type behaviour of simple reactions, and determine their activation energy and pre-exponential factor. Illustrate the simple collision theory. Describe Lindemann's theory of unimolecular reactions. Solve the rate laws for parallel reactions, and for simple consecutive reactions. Describe and justify the steady-state approximation and define the rate-determining step of a reaction. Derive the rate laws for reactions involving a pre-equilibrium. Illustrate the simple activation-state theory. Define Gibbs function of activation, entropy of activation and enthalpy of activation. State the kinetics and the simpler mechanisms of homogeneous catalysis.

Principles of spectroscopy and mass spectrometry

Describe the electromagnetic spectrum, and the working of a spectrometer. State the formula for the Boltzmann distribution, and indicate the relative populations of translational, rotational, vibrational, and electronic energy levels at different temperatures. State the associated energy transitions. Derive the formulas for the energy levels of the harmonic oscillator and the rigid rotor. Quote the vibrational energy levels of a diatomic molecule. State the meaning of the force constant. List the basic features of Raman Spectroscopy. Calculate and compare bond lengths and force constants. State the concepts of fundamental bands, overtone and combination bands. Describe the electronic spectral transitions. State the Franck-Condon principle. Classify absorptions in the visible and ultraviolet regions. Understand and apply the principles of atomic absorption spectroscopy. Understand the derivation of, recognise, and apply, the Beer-Lambert law; identify the limits of its validity and factors causing deviation from it. State the physico-chemical principles of nmr, esr, and mass spectrometry. Describe the generation of the nuclear magnetic resonance and electron spin resonance signals, and the factors that lead to their modification. Explain the basic principles of mass spectrometry, including the methods of ionisation.

Quantum chemistry

Describe the experimental observations on the photoelectric effect and show that they imply the existence of photons. Describe the observations on the Compton effect and show that they are evidence for the quantum theory. Write and interpret the Schroedinger equation. Apply the Schroedinger equation to simple systems: e.g. particle in a box, rigid rotor and harmonic oscillator, and interpret the experimental data.