CEM 333 Review and Study Guide

Introductory Material (Chapter 1)

- Know differences between classical and instrumental methods
- Recognize and give examples for data domains (electrical and non-electrical, digital, time, analog), interdomain conversions
- Understand differences between a detector, transducer and sensor
- What are analog and digital signals (parallel and serial)?
- What is a figure of merit (definitions for precision, bias, sensitivity, detection limit, dynamic range, limit of quantitation, limit of linearity, selectivity)
- Know equations for standard deviation, variance, relative standard deviation, standard deviation of mean, bias, selectivity
- Understand how to construct calibration curves, calculation of slopes and intercepts

Introduction to Spectroscopy (Chapter 6)

- Define wave properties (definitions and equations for amplitude, phase, frequency, wavelength, wavenumber, velocity, refractive index. dispersion)
- Convert between photon energy, wavelength, frequency, wavenumber
- Know approximate wavelengths for IR, visible and UV radiation and describe absorption, emission and relaxation in terms of energy levels
- Understand electronic, vibrational and rotational transitions and differences between line and continuum spectra. Blackbody radiation
- What are the origins of radiative and non-radiative emission, resonant and non-resonant transitions, fluorescence and phosphorescence (time scales and electronic structure)?

Optical Spectrophotometry (Chapter 7)

- Use of Beer's Law and definition of absorbance, transmittance, %T, molar absorptivity and interconversions
- Describe (and sketch where applicable) basic instrument components - sources (lamps and lasers), wavelength selectors (filters, prisms and Eschelette gratings including multiple order effects), sample container materials, detectors (photocell, phototube, photomultiplier tube, photodiode arrays, thermal detectors)
- What is the difference between single and multichannel detection?
- How do we measure of monochromator performance - definitions and equations of spectral purity, dispersion, bandwidth, light gathering?
- Understand the effect of slit width on resolution

UV-Vis Spectrophotometry (Chapters 13&14)

- Know how to apply Beer's Law to mixtures (use of simultaneous equations)
- What causes deviations from Beer's Law - chemical, physical, instrumental?
- Differences between single beam, double beam, double beam in time and double beam in space. Basic components and light path in each
- Understand significance of molar absorptivity (strong, weak and forbidden transitions)
- Qualitatively describe excitation in organic and inorganic molecules - absorption spectra and bonding, charge transfer, ligand field splitting, "the spectrochemical series", solvent absorption and shifts

Luminescence Spectrometry (Chapter 15)

- Understand electronic structure of atoms (n, m, l, s quantum numbers) and electronic term symbols
- Be able to calculate and sketch diagrams for spin multiplicity and singlet, doublet and triplet states
- Define emission and spin changing, lifetimes of states, fluorescence and phosphorescence, internal conversion, external conversion, intersystem crossing, dissociation and predissociation
- How likely is fluorescence - quantum yields and factors affecting quantum yields?
- Quantitative fluorescence measurements, differences between fluorometers and spectrofluorometers, emission fluorescence spectra and excitation-emission fluorescence spectra
- Describe and sketch experimental arrangement and components
- Briefly describe chemiluminescent reactions and give an example

Infrared Spectrometry (Chapter 16)

- Definition of near, mid and far IR
- Understand difference between permanent and dynamic dipoles and the IR activity of a molecule
- Describe and sketch types of vibrations - stretches (symmetric, asymmetric) and bends (scissor, rock, wag, torsion). The IR active modes of CO_2
- The success of classical (spring) methods for calculation of vibrational frequencies and sketch the parabolic E vs. displacement curve of the harmonic oscillator
- Give equation for energy of classical vibrational levels
- Understand the influence of quantum mechanics on vibrational frequencies - zero point energies and single absorption frequencies, anharmonicity and dissociation, electron repulsion
- Know the vibrational selection rule, breakdown of selection rule and overtones
- Be able to calculate the number of normal modes for a linear and non-linear molecule and vibrational coupling
- Describe and sketch where appropriate typical instrumentation (common sources and transducers)
- Understand the Fourier transform process, throughput and multiplex advantages, signal-to-noise ratios
- Basic operating principles of the FTIR spectrometer, retardation, beats, increasing resolution
- Applications of IR, group frequencies and fingerprint regions, quantitative vs. qualitative and sample preparation (gases, liquids and solids)

Flow Injection Analysis (Chapter 33)

- Know the advantages and disadvantages of automatic and automated instruments, batch and continuous analysis
- Be able to draw air segmented continuous flow instrumentation and flow profiles
- Know typical flow injection instrumentation (injection, pumps, reactors, detectors)
- Where does laminar flow profile in FIA come from? Transport mechanisms in flowing tube (longitudinal, radial diffusion and hydrodynamic flow)
- Definition, significance and equations of dispersion
- Stopped flow techniques and usefulness for kinetic measurements

Introduction to Electroanalytical Techniques (Chapter 22)

- Electrochemical cells (understand differences between single cells, divided cells, electrolytic cells and Galvanic cells, reversible, irreversible cells)
- Define anode and cathode - oxidation (anode) and reduction (cathode) reactions
- What about charge transport in cells (wires, ions and redox reactions), electrical double layers, mechanisms of transfer of reactant and products to electrode surfaces (migration, diffusion, convection)?
- Know which is a Faradaic (redox) current and non-Faradaic (charging) current
- Be able to write cell diagram and conventions (anode=left)
- Briefly review the thermodynamics of cells (activity vs. molarity, activity coefficients and derivation of the Nernst equation)
- Be able to define of cell potential E(cathode)-E(anode) when half-reactions written as reductions
- What is a standard electrode (standard only at 1 M activity)? Construction and redox chemistry of the saturated hydrogen electrode, the silver/silver chloride electrode and the calomel electrode
- Can you predict spontaneous reaction from E^{0}'s (more positive, more likely to go as reduction so forms cathode, electrons flow toward this electrode so it is +ve)?
- Can you calculate of E from Nernst equation (effect of activity), understand limitations of Nernst equation (activity vs. molarity, reaction and formal potentials)?
- Understand current flow in electrochemical cell, phenomena causing reduction in E, ohmic drop, polarization effects (charge-transfer, reaction, diffusion, crystallization overvoltages) and their sources

Potentiometry (Chapter 23)	• What are potentiometric measurements? (measurement of potential/voltage) • Which standard electrode (calomel and Ag/AgCl) to use? Indicator electrodes (metallic and membrane) • Understand operation of metallic electrode of the first kind (direct response to activity), second kind (through complex formation) • Describe membrane (ion selective) electrodes, crystalline vs. non-crystalline, operation of glass electrode for pH measurements (porous glass composition, equilibria at surfaces, membrane potentials - junction and boundary), alkaline error in glass electrodes, extension to other ions than H^+ • What is a liquid membrane electrode (immobilized liquid) such as CaDAP and when would we need one? • How does a gas sensing electrode such as PTFE/polymer membrane for CO_2 work? • Understand operation of biosensors (based on enzymatic reactions and production of small molecules)
Voltammetry (Chapter 25)	• What are voltammetric measurements? (measurement of current) • Why three versus two electrode systems, what do the working, counter and reference electrodes do, and where does the current flow? What is a potentiostat? • Advantages of using microelectrodes? • Describe voltammograms and voltammetric waves, oxidation and reduction of water at high potentials, reduction waves of analyte • Know that the half wave potential is fixed for species, limiting current is proportional to concentration • Understand hydrodynamic (stirred) voltammetry, influence of dissolved oxygen, transport mechanisms (mostly diffusion and convection), formation of Nernst layer • Describe polarography (unstirred - diffusion dominates), creation of new electrode surface, dropping electrodes, variation in current with drop lifetime, Ilkovic equation relating maximum or average current to diffusion coefficient, residual currents, advantages/disadvantages of dropping Hg electrode • What is the difference between current sampled (at one time in drop life) and differential pulse (sample before and after voltage spike) polarography?
Atomic Absorption Spectrometry (Chapters 8&9)	• Energy level diagrams, spin-orbit coupling, electronic term symbols (revisited) • Definition of an electronvolt and conversion to joules • Comment on complexity of atomic and ionic spectra (increases with # electrons), approximate magnitude of line widths and line broadening phenomena (Uncertainty Principle, Doppler, pressure broadening) • What is the effect of temperature on populations? Be able to give the Boltzmann equation • Describe and sketch where appropriate instrumentation: nebulization (pneumatic, ultrasonic) atomization (electrothermal direct insertion, ablation) and excitation (arc, spark, plasma, flame, electrothermal) of solids and solutions, flame structure and characteristic temperatures, graphite furnace (drying, ashing and firing) • Describe atomic absorption (AAS) instrumentation, intrinsic difficulties associated with narrow lines for absorption, the hollow cathode lamp
Atomic Emission Spectrometry (Chapter 10)	• Advantages and disadvantages of AAS and AES? • Understand plasma sources (ICP, DC), advantages of plasma vs. flame, arc or spark, plasma structure • What about spectrometers: slew-scan monochromators, multichannel monochromators, Eschelle monochromators, arc and spark sources? • Examples of applications

Introduction to Separations (Chapter 26)	• Differences between planar and column chromatography? • Understand and define stationary phase, mobile phase, and basic principle of operation of chromatography (equilibrium or partitioning between stationary phase and mobile phase), partition ratio ($K=c_s/c_m$), retention time (t_R), dead time t_M, migration rate (L/t_R) • What does capacity factor, partition ratio and selectivity factor physically mean? What is the relationship between migration rate, partition ratio and capacity factor (k')? What values of k' give good peak separations? • Define of selectivity factor (α) and how it relates to k', K and t_R and t_M • Give measures of column efficiency - theoretical equivalent plate height (H), number of plates (N) and equations, zone broadening and resolution. Which factors affect resolution (H, k', α, u) • Understand factors affecting H: the van Deemter equation $H=A+B/u+Cu$. Know and understand terms, and how each varies with flow rate (u) • Define the general elution problem (time vs resolution)
Gas Chromatography (Chapter 27)	• What are the equations for retention volume • Understand origin of pressure drop for flow resisting column (inlet pressure high, flow low, outlet pressure low, flow high), and need for average flow rate • Instrumentation (mobile phase (carrier gas), ovens, columns, detectors) • How about injection: on column injection, injection ports, rotary valves with sample loops? • Split, splitless columns? • Understand operating principles of common detectors: FID, TCD, ECD, MS • Know the differences between packed, open tubular (capillary) columns (SCOT and WCOT), bonded and cross-linked columns • What are typical GC stationary phase materials (immobilized liquids) and their properties (in particular polarity)? • What is temperature programming and how does it work?
Liquid Chromatography (Chapter 28)	• Be able to identify key features of liquid-liquid (partition), adsorption (liquid-solid), ion-exchange and size exclusion chromatography • Advantages of gradient elution (solvent programming) over isocratic techniques? • Describe and sketch, where appropriate, instrumentation: injection, high pressure pumps, mixing valves for solvent programming, typical columns and stationary phase materials, use of guard columns, detectors • Know the terms normal (non-polar solvent) and reversed-phase (polar solvent) partition chromatography, stationary phase choice and mobile phase choice (polarity indices), elution order • Describe adsorption liquid chromatography, stationary phase (silica or alumina), eluent strengths • Describe ion-exchange liquid chromatography, anionic and cationic exchange groups, ion equilibria, elution order • Understand principles of size exclusion liquid chromatography, exclusion and permeation limits, total, internal and external volumes of pores, applications
Electrophoresis (Chapter 30)	• Understand migration rate is affected by (i) mass (ii) charge (influence of pH, ionic strength) (iii) electric field. Write fundamental equation linking migration rate with electric field strength ($v=\mu_e \cdot E$) • Understand differences between slab and capillary EP. Advantages and disadvantages of each. • What differences are there between transport mechanisms leading to zone broadening that are present in chromatography and not EP? • What is electromigration, electroosmosis and how does the latter work (influence of capillary wall material)? How do these phenomena influence elution order for ions? • Know the differences between electrokinetic and pressure injection in capillary electrophoresis • Understand the use of "indirect detection" techniques for capillary EP

Mass Spectrometry (Chapter 20)	• Understand differences between gas phase and desorption sources, hard and soft ion sources • Fundamental principles of electron impact (EI) ionization sources, origin of fragmentation in EI spectra, isotope and collision product peaks, chemical ionization (CI) sources and techniques, field ionization (FI) sources and spectra • Fundamental principles of matrix-assisted laser desorption ionization (MALDI) technique, electrospray ionization (ESI), fast atom bombardment (FAB) • Know how to calculate resolution ($R=m/\Delta m$) for mass analyzers, know fundamental equation ($m/z=B^2r^2r/2V$) for magnetic sector analyzer • Describe and sketch, where appropriate, instrumentation: inlet systems, direct probe and GC inlet, magnetic (single) focusing and magnetic-electrostatic (double) focusing mass analyzers, quadrupole mass analyzers • Applications of MS and clues for identification: exact molecular weight calculations, isotopic distribution and calculations, comparison and library searches, interfacing of MS with other techniques