Chemistry 2301

Introduction:

Review of terminology used in thermodynamics

Review of differential and integral calculus and introduction to multivariate differential calculus.

The properties of real gases:

Equations of state for real gases, van der Waals, the virial equation of state for volume and pressure, The Redlich-Kwong equation of state, The Berthelot equation of state, the truncated virial equation of state.

The compressibility factor Z. Effect on Z due to pressure and temperature changes

The co-existence of phases and the critical point

The properties of supercritical fluids

Isotherms of real gases, the critical isotherm

The relationship between the critical constant values of a real gas and the van der Waals constants.

The law of corresponding states

The Boyle temperature of a real gas.

The first law of thermodynamics

Review: State and path functions. Sign conventions

The reversible pathway

PV work for a reversible expansion/contraction of ideal and real gases

PV work for an irreversible expansion/contraction of an ideal gas

PV work in chemical reactions at constant pressure.
Comparing PV work for reversible and irreversible isothermal expansions

Heat and heat capacity

Standard molar heat capacity, isobaric and isochoric.

Temperature dependence of heat capacities. Calculate heat lost or gained using temperature dependent molar heat capacities.

$C_p$ vs $C_v$ for solids, liquids and gases.

Internal energy $U$

Kinetic and potential energy contributions to $U$.

The first law of thermodynamics.

Internal energy of an ideal gas.

Applications of the first law: isochoric change, expansion into a vacuum

Meaning of $\Delta U$: $\Delta U$ and heat

Application of the first law to an isobaric change, Enthalpy $H$ and the meaning of $\Delta H$, $q_p$ and $w$.

Application of the first law to a cyclic change

Application of the first law to adiabatic processes, adiabatic expansion into a vacuum.

Heat capacity for an ideal gas

Adiabatic expansion, reversible and irreversible application to an ideal gas, real gases behaving ideally:

Calculation of final $T$, $\Delta U$, $\Delta H$, $q$ and $w$

Calorimetry: Bunsen ice calorimeter, Bomb calorimeter

Calculation of $\Delta H$ for a process involving both temperature and phase changes.
Enthalpy of reaction as a function of temperature. Calculation of new $\Delta H$ using constant heat capacities and also using temperature dependent heat capacities including Shomate equation heat capacities.

The Joule-Thompson experiment.

**Entropy and The second and Third Laws of Thermodynamics:**

The Carnot cycle:

An example: Calculations of pressures, volumes at each stage, heat, work, $\Delta U$, efficiency for the 4 steps and the cycle. Introduction to thermodynamic entropy.

Statements of the second law:

Calculations of $\Delta S$ for simple reversible systems, isothermal expansion/contraction, isochoric, isobaric heating and cooling, phase changes, adiabatic expansion/contraction.

Problems including temperature, pressure and phase changes and adiabatic expansion/contraction of a gas. Calculation of $\Delta S_{\text{system}}$, $\Delta S_{\text{surr}}$, $\Delta S$ universe.

Entropy of mixing for ideal gases.

The third law of thermodynamics, absolute entropies, calculation of low temperature absolute entropies.

Calculation of $\Delta S$ at temperatures other than 25°C using temperature dependent heat capacities.

Statistical entropy, $n$-particle microstates, Boltzmann’s equation for entropy, residual entropy

The Clausius Inequality and spontaneity. Indicators of equilibrium

Gibbs energy and Helmholtz energy: spontaneity and equilibrium

Thermodynamic functions and natural variables.

**The Maxwell relations:** derivation and applications to real gases:
Internal pressure of gases, solids, and liquids and the thermodynamic equation of state.

Finding $\Delta H$ and $\Delta U$ for real gases using Maxwell-like relations.

Gibbs energy and work

Helmholtz energy and total work.

Molar Gibbs energy of a real gas and fugacity

Conversion of chemical energy to work

**Chemical Potential and Phase Equilibria:**

Partial molar quantities

The Gibbs phase rule and single component phase diagrams

Derivation of the Claperon equation:

The Pressure-Temperature phase diagram of water and Carbon dioxide.

Movement in a phase diagram: connecting two points on the Fusion curve and solid-solid phase transition curves.

Derivation of the Clausius-Claperon equation and its application to the liquid vapor and solid vapor coexistence curves.

Calculation of triple point temperature and pressure using a point each on the liquid vapor and solid vapor coexistence curves.

Horizontal and vertical movement in a phase diagram using chemical potential (molar Gibbs energy) anf $dG_m = V_m \, dP - S_m \, dT$

Vapor pressure as a function of applied pressure.

$\Delta G_m$ for solid-solid phase changes (graphite –diamond) as a function of applied pressure. Converting graphite to diamonds.

**The Thermodynamics of ideal and real solutions.**
The concept of chemical potential.

Raoult’s law as a limiting law.

Ideal solutions. Pressure composition diagram for an ideal solution.

Thermodynamic variable for ideal solutions.

Liquid-vapor pressure composition diagram for an ideal solution: concept of a tie-line

Application of Gibbs phase rule to a Liquid-vapor pressure composition diagram for an ideal solution

Temperature-composition phase diagram for an ideal solution and its application to fractional distillation.

Real solutions: Liquid-vapor pressure composition diagrams, positive and negative deviation from Raoult’s law;

The ideal dilute solution

Henry’s law and the Henry’s law standard state

Raoult’s law and Henry’s law activities and activity co-efficients

Henry’s law and the molality standard state.

Gibbs energy of mixing for non-ideal solutions

Extreme Non-ideal behaviour in binary solutions, extreme positive and negative deviation from Raoult’s law and azeotropes and the corresponding temperature-composition phase diagrams. Distillation of extreme non-ideal solutions.

Colligative properties:

Raoult’s law, freezing point depression, boiling point elevation and osmotic pressure: effect of association and dissociation on colligative properties.
Accounting for non-ideal behaviour using freezing point depression and osmotic pressure measurements to determine molar masses of dissolved solutes.

Using chemical potentials to explain freezing point depression and boiling point elevation.

Solutions of electrolytes:

Ion concentrations, activities, and activity coefficients. Ion pair formation.

Mean ionic molality, activity and activity coefficients

Debye huckel Theory, permittivity, dielectric constants, Debye-Huckel limiting law

Ionic strength.

The Davies equation:

Calculation of mean ionic activity coefficients using the Debye-Huckel limiting law and the Davies equation.

**Chemical equilibrium and thermodynamics:**

The true K, activity and activity coefficients:

Application to finding solubility of an ionic compound using the Davies equation and an iterative method.

Review:

\[ \Delta G \text{ and } \Delta G^0, \text{ the reaction quotient the relationship between } \Delta G^0 \text{ and } K. \]

Problems using \[ \Delta H^0 = T \Delta S^0 \text{ and } \Delta G^0 = -RT\ln K \]

The temperature dependence of the equilibrium constant and the van’t Hoff equation:

Graphical determination of \( \Delta H^0 \) and \( \Delta S^0 \) from K and T data:

Reactions involving gases: \( K_p \) and \( K_x \):
Challenging equilibrium problems:

The Biochemists standard state, $\Delta G^o$ and $\Delta G^0$/: Calculating $\Delta G^0$/ etc.

**Chemical Kinetics:**

First year review:

Defining rates normalized rate, calculating instantaneous rates from the slope of a concentration versus time graph, the differential rate law, integrated rate laws for single reactant reactions and the half life concept, zero order, first order, second order, nth order, units of $k$ as an indicator of reaction order.

Reactions with two different reactants: Derivation of the integrated rate law. Calculations involving the integrated rate law.

Reversible reactions: Derivation of the integrated rate law: half life and relaxation time for reversible reactions: Calculations involving the integrated rate law.

Sequential reactions: The integrated rate law for the reactant, intermediate and product, determining the time at which the intermediate concentration is at a maximum. Calculations associated with the integrated rate laws.

Competing or parallel reactions. The integrated rate law for the reactant and product s, branching ratio and yield.

The experimental study of fast reactions:

Perturbation-relaxation techniques (shock tube, flash photolysis, T-jump experiments)

Derivation of integrated rate law for $A + B \rightarrow C$ and relaxation time.

Application to the ionization of water.

**Reaction mechanisms and rate theories:**

Review: Elementary processes and molecularity
Collision theory, postulate of Arrhenius, graphical determination of Arrhenius parameters.

Hard Sphere Collision Theory:
Collision frequency, reduced mass, collision diameter, collision cross section, effective speed, calculation of total collision frequency

Reaction mechanisms and rate laws: some basics:
The rate limiting approximation + example
The pre-equilibrium approximation + example
The Steady State approximation + example
The Lindemann-Hinshelwood Mechanism for "unimolecular" gas phase reactions. Derivation of integrated rate law.
3-step mechanisms with third step rare limiting + example
Deducing a mechanism from a rate law: useful guidelines + example
Chain reactions + example for derivation of integrated rate law using steady state approximation
Chain initiation, propagation and termination steps
Branching chain reactions and branching steps + example
Enzyme catalysis
Specificity
The Michaelis-Menton mechanism for Enzyme catalysis: Derivation of integrated rate law
The Lineweaver-Burk plot to find the Michaelis-Menton constant and the maximum rate.
Transition State Theory
Thermodynamics of the Activated Complex for gas phase reactions, Eyring equation and Eyring parameters. Calculation of Eyring parameters from Arrhenius parameters.