Physical Chemistry: Review Topics

Basic differentiation and integration
Functions of many variables
Partial differentiation; total derivative; basic relations involving partial derivatives

I. THERMODYNAMICS

- Ideal gas laws
  - $pV = nRT$
  - $U = cNRT$

- Van der Waals equation
  - Molecular forces
  - Molecular size
  - Critical point

- First Law of Thermodynamics

  Conservation of energy: $dU = dQ + dW$

  Work = (force) x (distance)
  $dW = -pdV$; p-V diagram and work
  $dU = dQ + dW = dQ - pdV$
  Work by an ideal gas in an isothermal expansion

  Specific heats: C_p and C_v
  $C_p - C_v = R$
  Adiabatic process: $dQ=0$
  for an ideal gas $pV^{\gamma} = \text{constant}$. $\gamma = (C_p/C_v)$

  Thermochemistry:
  - Enthalpy $H = U+pV$
    - $H=H(p,T,N)$
    - Derivatives of enthalpy: $(\partial H/\partial p)_{T,N} = V$, ... etc.
  - Enthalpy or heat vaporization
  - Enthalpy or heat of fusion
  - Enthalpy of formation
  - Enthalpy or heat of reaction; change with T and p.
  - Bond enthalpies

- Second Law of Thermodynamics

  Carnot's theorem for a reversible heat engine

Efficiency of a reversible heat engine

Definition of entropy in a reversible process: $dS=dQ/T$
The Second Law
Entropy is a state function: $S=S(U,V,N)$ or $S=S(T,V,N)$
Entropy changes in phase changes: $\Delta S=\Delta H/T$

- Helmholtz free energy: $A = U-TS$
  $A=A(T,V,N)$
  At constant V and T, $A \dashrightarrow A_{min}$ as the system approaches equilibrium
  Derivatives of A: $(\partial A/\partial T)_{v,N} = -S$ .... etc.
  At constant T: $\Delta A=\Delta U - T\Delta S$ ...etc.

- Gibbs Free energy: $G = U -TS + pV=H-TS$
  $G=G(T,p,N)$
  At constant T and p, $G \dashrightarrow G_{min}$ as the system approaches equilibrium
  Derivatives of G: $(\partial G/\partial T)_{p,N} = -S$ .... etc.

  At constant T: $\Delta G = \Delta H - T\Delta S$ ...etc.

  Concept of chemical potential: μ

  $$dU=TdS-pdV+Nd\mu$$

  Relation between chemical potentials at equilibrium
  Expression for chemical potential: $\mu(p,T)=\mu(p_0,T_0) +RT \ln a$
  a= activity
- General Thermodynamic Relations
  $U=U(S,V,N)$
  $U=TS-pV+\Sigma \mu_k N_k$
  $G=\Sigma \mu_k N_k$; $(\partial G/\partial N)_{p,T} = \mu$
  Gibbs-Duhem equation: $SdT-Vdp+\Sigma N_k d\mu_k=0$
  Helmholtz equation
  Gibbs-Helmholtz equation
  Maxwell relations

- Phase Equilibrium
  Phase diagram; critical point; triple point
  At equilibrium, p,T and μ of the phases are equal
  Clapeyron equation
  Clausius-Clapeyron equation

Gibbs phase rule

- Solutions
  - Raoult's law
  - Henry's law
  - Boiling point elevation
  - Freezing point depression
  - Osmosis

- Chemical equilibrium
  - Relation between chemical potentials at equilibrium.
  - The law of mass action.
  - Equilibrium constants K_p and K_c.
  - ΔG of formation. Calculating ΔG of reactions from ΔG's of formation
  - Relation between ΔG and equilibrium constant
  - Variation of K with temperature (Van't Hoff equation)

- Electrochemical equilibrium
  - Electrical potential
  - Electrochemical cells
  - Electrochemical potential
  - Nernst equation
  - Activities of electrolytes; activity coefficients
    - Ionic strength; Debey-Huckel equation for activity
  - Standard Electrode potentials

- Boltzmann principle: $N(E) = \text{Const. } \exp(-E/kT)$
  - Relative occupation numbers

II. KINETICS AND DYNAMICS

- Reaction rates
  - Rate laws: First order, second order etc.
  - Experimental determination of rate equation
  - Principle of detailed balance and equilibrium
  - Variation of rates with temperature; Arrhenius law; activation energy

- Kinetic theory
  - Boltzmann principle
  - Maxwell distribution of velocities
  - Average speed; most probable speed
  - Number of collisions per second
  - Transition-state theory of reactions
  - Thermodynamics of transition-state theory

III QUANTUM THEORY

- Basic Quantum Theory
  - Wave nature of particles
  - Particle nature of light

- Schrodinger equation:
  - Operators and wave functions
  - Eigenvalues and eigenfunctions
  - Probability ditribution

- Particle in a box
  - Eigenvalues
  - Eigenfunctions

- Simple harmonic oscillator
  - Eigenvalues
  - Eigenfunctions

- Hydrogen atom
  - Eigenvalues
  - Eigenfunctions (s,p, d .. orbitals)
  - Lyman, Balmer and Paschen series
  - Electron spin
  - Pauli exclusion principle

- Quantization of angular momentum
  - Angular momentum operator
  - Rigid rotor:

Eigenvalue. Eigenfunctions.

- Molecular Orbitals and symmetry
- Rotational and vibrational spectroscopy
- Magnetic resonance spectroscopy
  EPR
  NMR