Physical Chemistry II (Chem 252/442)

Topics Midterm Exam 2 (Materials covered in L6-L15)

1. **Basic Thermodynamics Laws and Ensembles**

   Thermodynamic Laws 0-3, internal energy *U* , path independence, heat energy vs. work→ state functions, mechanical heat equivalent, Equipartition theorem
   Concept of statistical ensembles, isolated/closed, canonical, grand canonical
   Relative numbers of particles vs. number of particle states, number of measurements
   Microstates of multi-particle systems, ergodicity-Ergodic Theorem
   Heat exchange and transfer, phenomenological meaning of temperature, heat energy, E/T

2. **Spontaneous Transformation vs. Equilibrium**

   Stationary state vs. equilibrium state, time dependence,
   Relation of entropy with number of available vs. occupied states,
   Boltzmann and statistical entropy, reason for logarithmic term $\boldsymbol{Ln}\,\Omega.$, extensivity of entropy,
   Entropy growth with and without heat transfer, dependence on macroscopic properties of ensembles, 2nd Law of thermodynamics, "arrow of time"
   Reversible vs. irreversible processes, isothermal and adiabatic expansion & compression of gases, heat capacities, thermodynamic entropy,
   Cyclic thermodynamic engines, Carnot processes, entropy as energy carrier,
   Helmholtz and Gibbs free energy functions as driving forces for spontaneous processes, free energy minimum.
   Application to chemical reactions, chemical potential → dependence on T,p

3. **Kinetics and Transport in Dilute Multiparticle Systems**

   Role of particle interactions, properties of conservative potential (example: Lennard-Jones potential, binding=bonding energy)
   Scattering in dilute gases, scattering cross section, mean free path, and random kinetic energy spectrum,
   Universal shape of Maxwell-Boltzmann distributions, mean and most probable energies and velocities/speeds, how to obtain temperature information from the spectrum,

Master Equation for spontaneous transformations of multiparticle configurations, transition rates, mass transfer flux, asymptotic configuration state, relation to microscopic entropy,
Random walk displacement processes, binary partitions of integer numbers means=expectation values and variances
Brownian motion of macroscopic bodies in random media, effects of random particle collisions on macroscopic bodies,
Dissipation and relaxation of macroscopic energy deposits in multiparticle systems,
Fick's diffusion laws, Fokker-Planck advective diffusion, diffusion equation,
Diffusion in continuous and structured multiparticle media, basis and structure of mass/particle transport coefficients, related energy/heat transport.

4. Mathematical Tools

Taylor/Maclaurin expansion series,
Probability distributions, parameters defining Gaussian (normal) distributions,
Binary partitions of integer numbers (binomial coefficients, Binomial Theorem)
Total and partial differentials for multi-variate functions, e.g., thermodynamic equilibrium state functions, dU=.., dS=…,.
Partial derivatives with variables held constant.
Binomial coefficients, Binomial Theorem, Error function

5. Sample Numerical Calculations