

## PHYSICAL CHEMISTRY

The Physical chemistry placement examination will cover topics selected broadly from those normally encountered in the undergraduate physical chemistry curriculum for chemistry majors. Since some of the concepts of physical chemistry are not easily captured on first contact with them, we suggest that you review your previous work in this area, with special emphasis upon basic chemical thermodynamics. The following outline describes in some detail a set of topics upon which your review might be constructed. It may be helpful to read again selected area from the text you used in your physical chemistry course; it is presumed that you will have used a text such as: Atkins, Castellan, Levine, Mortimer, or some other text of comparable depth. The solution of problems in physical chemistry is encouraged as a productive method of testing your comprehension during the review.

### A. Introduction to Quantitative Description of Physicochemical Systems: The Gaseous State.

#### A. Macroscopic Approach

State determinacy

Classic gas studies; temperature scales

The ideal gas law

Density as a gas variable

PVT relationships for ideal and real gases

Equations of state including virial expansions

Properties calculable from equations of state:  $\alpha, \beta$

Critical constants and reduced equations of state; the law of corresponding states

#### B. Microscopic Approach - Kinetic Molecular Theory of Gases

Postulates for Ideal gas and derivation of  $PV = 1/3 Nmu^2$

Averages of functions of discretely and continuously distributed variables

Maxwell - Boltzmann Statistics

Distribution functions: 3 dim. velocity; 1 dim.

velocity; speed; energy; reduced speed; reduced energy

Evaluation of  $\bar{u}, \bar{u}^2$ , as functions of T., ideal gas law derived

Further evidence supporting K.M.T.: effusion, direct experimental determination of speed distribution, Brownian motion: the isothermal atmosphere  $\bar{X}^2$ , and Perrin's experiments

Non-ideal gases: hard sphere, soft sphere (Lennard-Jones) and real

Non-ideal volume effects: mean free path, particle

Volume corrections, viscosity

Attractive Forces

**Miscellaneous Topics:** Graham's Law; Dalton's Law;

Mechanical degrees of freedom and Equipartition

Principle - energies and heat capacities

## II. Thermodynamics

- B. Preliminary Physics and Math: mechanical work, potential energy, partial derivative transformations
- B. Definition of fundamental terms: systems, surroundings, wall, state, etc.
- C. The 0th Law; temperature scales
- D. The 1st Law definition of work, heat, and additional fundamental terms; interconversion of work and heat; exact and inexact differentials and the Euler condition; PV work; reversible and irreversible processes; work other than PV work; analysis of simple processes in terms of 1st law; introduction of additional fundamental terms; heat capacities, enthalpy: Joule and Joule-Thompson experiments; adiabatic processes
- E. Thermochemistry;  $\Delta H, \Delta E$  and heat evolution; Hess's Law; heats of formation; standard states; standard heats of formation: temperature dependence of  $\Delta H$ : the relative enthalpy function  $H_T - H_0$ .
- F. The 2nd Law: S, a property demonstrated via Carnot cycle analysis; evaluation of  $\Delta S$  for various reversible and irreversible processes; the absolute temperature scale; thermal efficiency of engines
- G. Criteria of Equilibrium: the fundamental criterion of spontaneity; introduction of G and A functions as useful in obtaining criteria of equilibrium under various conditions; analysis of criteria of equilibrium for various conditions
- H. Thermodynamic relationships involving E, H, S, A, G including pressure and temperature derivatives; Maxwell relations; Gibbs-Helmholtz relation; evaluation of state functions from thermal data alone - motivation for 3rd Law
- I. Open system thermodynamics; composition as a variable; the chemical potential; homogeneous functions and the Euler theorem; the Gibbs-Duhem relation
- J. Phase equilibrium; Gibbs phase rule derived; 1 component phase equilibrium; the Clausius-Clapeyron relation
- K. Binary solution thermodynamics; fugacity and activity introduced; ideal binary solution; dilute non-ideal solutions and colligative properties (vapor pressure lowering; boiling point elevation; freezing point lowering; distribution coefficient; osmotic pressure)
- L. Remainder of 2 component phase equilibrium: liquid-vapor, azeotropes; partially miscible systems; liquid-solid; eutectics; peritectics; solid-solid; cooling curves
- M. Chemical equilibrium: homogeneous case; derivation for ideal gases of connection between  $\Delta G^\circ$  and  $K_p, K_c, K_x$ ; temperature dependence,  $K_a$ ; heterogeneous equilibria
- N. 3rd Law: evaluation of thermodynamic state functions using thermal data only; Debye Law
- O. Electrochemistry-equilibrium aspects: examples of cell reactions including particularly those corresponding to

physical changes such as gas expansion or solution dilution; half-cell potentials; combination of half-cell potentials to obtain cell and other half-cell potentials; electrical work and thermodynamics of cells; temperature and concentration dependence of emf

- III. **Reaction Kinetics:** simple rate laws with chemical examples; physical methods of obtaining concentration vs. time; order; integrations of rate laws of various orders; determination of order; elementary reactions; simple combinations of elementary reactions; simple combinations of elementary reactions opposing reactions, parallel reactions, consecutive reactions; temperature dependence of rates; aspects of collision theory; Lindemann scheme for 1st order process following collision activation; the steady state approximation; chain reactions; reaction mechanisms including energetic considerations in choice of elementary steps; catalysis (biochemical): transition state theory and thermodynamics of rates

### C. Quantum Chemistry

Transition from classical to quantum mechanics:

radiation laws, wave-particle duality

- B. Old quantum theory of hydrogen atom: derivation of results for circular orbits; degeneracy; selection rules-qualitative discuss
- C. New quantum theory; deBroglie relation; Heisenberg principle and physical consequences
- D. Operator approach to QM: fundamental postulates; properties of operators
- E. Solution of time-independent problems for various potentials
  - 1.) free particle
  - 2.) particle in 1 dim., 2 dim., 3 dim., infinite wells with brief discussion of finite well, barrier penetration and tunnelling
  - 3.) particle in harmonic potential; vibrational spectroscopy; derivation of selection rules
  - 4.) particle in Central field
  - 5.) nuclear part of diatomic problem; rotational levels; rotational spectroscopy
- F. Analytical and descriptive treatment of more complex problems:
  - 1.) spin, symmetry requirements of wave functions
  - 2.) He atom, the variation principle
  - 3.) polyelectronic atoms, Aufbau prinzip, Hund's rules and S.O.S.-A.O.'s
  - 4.) ionic bonding
  - 5.) covalent bonding:  $H_2^+$  and  $H_2^-$  valence bond and M.O. methods, second approximations in VB and M.O. descriptions
  - 6.) covalent bonding: homonuclear diatomics, S.O.S.-.O.'s
  - 7.) further extension of covalent bonding; heteronuclear diatomics, polyatomics via localized

bonding M.O.'s, atomic orbital hybridization and  
L.C.A.O.- M.O.'s

**V. Statistical Thermodynamics**

- A. Mathematics of statistics, microstates and macrostates
- B. Fundamental postulate of physical statistics
- C. Derivation of Maxwell-Boltzmann Law