Study Guide

Chapter 1

1) Definition of pressure
2) Pressure due to Hg column $\mathbf{P} = \rho g h$
3) Ideal gas law PV=nRT
4) Kinetic theory of gas

$E_k = \frac{3}{2} nRT$ or $\varepsilon_k = \frac{3}{2} k_B$T for monoatomic gas

5) Rate of effusion

$\bar{\upsilon} \approx \frac{1}{\sqrt{\rho}}$ or $\bar{\upsilon} \approx \frac{1}{\sqrt{M}}$

6) Molecular collision

$\lambda = \frac{\bar{\upsilon}_A}{Z_A}$ Mean free path; Given collision diameter, find λ

What is $\bar{\upsilon}_A$, Z_A given above eqn.?

7) $P = P_0 e^{\frac{-mg}{RT} z} = P_0 e^{\frac{-E_p}{RT}}$
8) Maxwell distribution : Distribution shape for different T/ Gases
9) Real gas $Z = \frac{PV_m}{RT} \neq 1$
10) What is T_c? Shape of isotherms above/below T_c?
11) vdW eqn. $(P + \frac{a}{V_m^2})(v_m - b) = RT$
12) Law of corresponding states, reduced quantities

$(P_r + \frac{3}{V_r^2})(V_r - \frac{1}{3}) = \frac{8}{3} T_r$; what is meaning?

Chapter 2

1) What is first law of thermodynamics?
2) Reversible PV work = $-\int Pdv$
   maximum work?
3) Definition of C_p , C_v
   Relation C_p, C_v for ideal gas, liquid, solid
4) Enthalpy: $H = U+PV$
   P=const: $\Delta Q_P = \Delta H$; V=const: $\Delta Q_V = \Delta U$
5) Hess law
   Example in book: glucose → maltose, ΔH=?
6) Calculate ΔU, ΔH, Q for ideal gas processes,
   Isothermal, adiabatic, constant V,T; constant P,T

Chapter 3

1) Second law of thermodynamics
2) Carnot cycle (engine)

   Q, W, ΔU in each step; which step absorbs/releases heat?

$$\oint \frac{dQ_{rev}}{T} = 0; \oint \frac{dQ_{irr}}{T} < 0$$

3) Entropy: $dS = \frac{dQ_{rev}}{T}$
4) $\int_A^B \frac{dQ_{irr}}{T} = 0$ for **adiabatic** process

   $\Delta S > 0$ for irreversible process

5) Calculate ΔS for phase changes
6) Calculate ΔS for ideal gas T, V changes
7) Calculate $_{\Delta}S$ for mixing gases, solutions

   $\Delta S = -R (x_1 \text{In } x1 + x_2 \text{In } x_2)$
8) Third law of thermodynamics
9) Equilibrium conditions, what thermodynamic quantities characterize (determine) equilibrium under which conditions?
10) Direction of spontaneous process, when do the following conditions apply?

    $\Delta S > 0, \Delta G < 0, \Delta A < 0$

Chapter 4

13) What is the practical equilibrium constant in terms of pressure, concentration, mole fraction or activity?

14) Relationships between K_p and K_c, and between K_p and K_x?

15) Relation between the standard-state ΔG and the thermodynamic equilibrium constants?

16) Do K_p and K_c K_x. and K_a depend on P, V, and T?

17) What is the definition of chemical potential?

18) What is Le Chatelier principle?

19) What is the direction of the shift in equilibrium upon a change in pressure and volume?

20) How does a reaction shift if one adds A or C after the equilibrium is established? Does ΔG change?

21) What does the degree of association mean for the above reaction?

22) Remember the van't Hoff equation in two forms: derivative with respect to dT and d(1/T) .

23) What is the x axis and y axis in a van't Hoff plot? What is the slope? What is the intercept?

24) A way to shift the equilibrium is to couple the reaction of interest with a second one. To make an unfavorable reaction possible, what is the requirement for the second reaction?

Chapter 5+6

1) Definition for phase.

2) What is the number of phases in a) a gas mixture; b) an aqueous solution of NaCl, c) a metal alloy; d) a suspension of oil in water; e) an aqueous solution of NaCl and $MgCl_2$?

3) Number of components c: minimum number of species necessary to specify the composition of the system = number of species in the system minus the number of constraints.

4) Variance of the system (degrees of freedom) is the number of independent intensive variables for describing the system, such as temperature, pressure or concentration.

5) What is the phase rule?

6) Draw a phase diagram for water. Point out the co-existence curves (or phase boundaries) for liquid-solid; liquid-gas; gas-solid equilibriums; triple point and critical point.

7) What is the thermodynamic quantity that drives phase transition at constant pressure?

8) At triple point what is the thermodynamic quantity that is the same for all three phases?

9) What is Raoult's law (Chapter 5, p.196-199)?

10) Given a pressure-composition (P-x/y) diagram for a liquid mixture in equilibrium with vapor, what is the number of number of degree of freedom f in the liquid, vapor phase and the coexistence region?

11) Given a point in the diagram, read out the composition in the liquid and vapor phase.

12) Explain how isothermal distillation works. Which phase is removed during the distillation? Which component is left in the residual liquid?

13) How does the diagram change if the liquid mixture has positive or negative deviation from the ideal behavior?

14) When does one want to use the temperature-composition diagram to describe the liquid-vapor equilibrium? Which curve is the boiling point curve? What are the boiling points for the pure liquids? Which liquid is more volatile?

15) Explain fractional distillation. What kind of liquid mixtures can be separated using fractional distillation?

16) What kind of liquid mixtures can be separated using steam distillation?

17) What is an azeotrope?

Chapter 9

1) Definition of the rate of a reaction, the rate of consumption for a reactant, and the rate of formation for a product.

2) What are elementary reactions? Definitions of the 0th, 1st and 2nd order reactions.

3) What is the rate constant or coefficient?

4) Rate equations for 0^{th}, 1^{st} and 2^{nd} order reactions.

5) What is a half-life? Half-life for 0th and 1st order reactions.

6) How to distinguish 0th and 1st order reactions based on kinetic data, such as the plots of [A] vs time, ln([A]0/[A]) vs time, ln[A] vs time?

7) K_c in terms of rate constants?

8) Relaxation methods to study very fast reactions (temperature jump)

9) Arrhenius equation, determine activation energy from measurements of rate constants, compare with Eyring equation.

Chapter 10

1) Rate equations for consecutive reactions
2) Steady-state treatment
3) Rate constants and equilibrium constants
4) Enzyme catalysis; Michaelis-Menton model (equation)