

Study guide for the final exam

Chemistry 341, Fall 2014

For the following, you should understand the concepts, know (have memorized) the key equations, understand what all the symbols mean, and be able to explain the equations in words and to appreciate their context. Please pay close attention to the *Summary* at the end of each chapter. The final exam is on Wednesday, Dec. 17, 8am to 11am in our usual room. It is a comprehensive exam, but with a little more emphasis on material since the second midterm.

Chapter 2: The first law

- Internal energy change, $\Delta U = q + w$; $q_V = \Delta U$
- Heat capacities: $C_V = dU/dT$; $C_p = dH/dT$
- Enthalpy: $H = U + pV$; $q_p = \Delta H$
- Heats of reaction, heats of formation, enthalpies of phase transitions: $\Delta_r H^\circ$, $\Delta_f H^\circ$, ΔH_ϕ
- *State variables* do not depend on history; U , H , p , V , T and chemical composition are state variables. *Equations of state* are relations among state variables (since they are not all independent); see Eq. 2.31 (solids/liquids) or Eq. 2.34 (gases) for examples; you do not need to memorize these.

Chapter 3: The second law

- Entropy: $\Delta S = q_{rev}/T$; entropy change of surroundings: $\Delta S_{sur} = -\Delta H/T$
- Temp. dependence of entropy, at constant pressure: $dS = (C_p/T)dT$
- phase transitions: $\Delta_{trs}S(T_\phi) = \Delta_\phi H(T_\phi)/T_\phi$; this implies that $\Delta G_\phi(T_\phi) = 0$
- Gibbs (free) energy: $G = H - TS$
- principal differential: treating G as a function of T , p , n_A , n_B, \dots , then $dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B + \dots$
- dependence of G on temp. and pressure: $\left(\frac{\partial G}{\partial p}\right)_T = V$; $\left(\frac{\partial G}{\partial T}\right)_p = -S$; $\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{-H}{T^2}$

Chapter 4: Free energy and chemical equilibria

- The chemical potential is a partial molar Gibbs energy: $G = n_A \mu_A + n_B \mu_B$
- Reaction Gibbs energy: $\Delta_r G = \Delta_r G^\circ + RT \ln Q$; $\Delta_r G = 0$ at equilibrium
- Chemical potential in a gas: $\mu_j = \mu_j^\circ + RT \ln p_j$
- Chemical potential of solute or solvent in dilute solution: $\mu_j = \mu_j^\circ + RT \ln x_j$
- General expression for chemical potentials: $\mu_j = \mu_j^\circ + RT \ln(a_j)$
- van't Hoff equation: $d(\ln K_{eq})/d(1/T) = -\Delta_r H^\circ/R$, or $\ln K_2 = \ln K_1 + (\Delta_r H^\circ/R) \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

Chapter 5: Statistical foundations of biophysical chemistry

- Boltzmann distribution: $p_i = \exp(-\beta E_i)/Q$, where $\beta = 1/k_B T$
- Partition function: $Q = \sum_i g_i \exp(-\beta E_i)$
- Entropy: $S = -k_B \sum_i p_i (\ln p_i)$; note that this is a more general expression than Eq. 5.38 in your text
- Average number of ligands bound: $\nu = (d \ln Q / d \ln S)$, where $S = K[A]$; same formula, with a different interpretation of S, for conformational changes like helix-coil transitions.
- “p” items: $\text{pH} = -\log_{10} a_{H^+}$; $\text{p}K_a = -\log_{10} K_a$; $\text{pH} + \text{pOH} = \text{p}K_w \sim 14$

Chapter 6: Physical equilibria

- Clapeyron equation: $(\partial T / \partial p)_\phi = T_\phi \Delta_\phi V_m / (\Delta_\phi H_m)$
- Raoult’s law: $\mu_A = \mu_A^\circ + RT \ln x_A$; Henry’s law: $\mu_B = \mu_B^\circ + RT \ln(k_B x_B)$
- Concentration scales: mole fraction $x_j = n_j / (n_i + n_j)$, molality $b_j = n_j / m_{\text{solvent}}$, molarity $[J] = n_j / V$.
- Osmotic pressure, $\Pi V = n_B RT$, or $\Pi = cRT$

Chapter 7: Electrochemistry

- transfer across a membrane: $\Delta\mu = \Delta\mu_C + \Delta\mu_V = RT \ln(a_{in}/a_{out}) + zFV$
- Nernst equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/\nu F) \ln Q$
- dependence of cell potential on pH: $E = E' - \frac{\nu_{H^+} RT \ln 10}{\nu_e F} \times \text{pH}$

Chapter 8: Motions of biological molecules

- Fick’s first and second laws: $J = -D(dc/dx)$; $\partial c / \partial t = D(\partial^2 c / \partial x^2)$
- Mean-square displacement (3 dimensions): $\langle d^2 \rangle = 6Dt$
- Stoke’s law for a spherical particle: $f = 6\pi\eta a$; Stokes-Einstein relation: $D = kT/f$

Chapter 9: Rates of chemical reactions

- first-order reaction: $c(t) = c(0) \exp(-k_1 t)$
- half life for a non-reversible first-order reaction: $t_{1/2} = (\ln 2)/k_1$
- Second-order reaction: $\frac{1}{c(t)} = \frac{1}{c(0)} + k_2 t$
- Arrhenius equation: $k_r = \exp(-E_a/RT)$
- relation of equilibrium and rate constants: $K = k_1/k_{-1}$; relaxation times (first-order reactions): $x = x_0 \exp(-t/\tau)$; $\tau^{-1} = k_1 + k_{-1}$
- Transition-state theory: $k = \left(\frac{kT}{h}\right) \exp(-\Delta G^\ddagger/RT)$