Study guide for the final exam

Chemistry 342, (01:160:342), Spring 2012
Physical Chemistry of Biochemical Systems

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 *Checklist of key concepts* and the *Checklist of key equations* at the end of each chapter.

Material you can skip (although it is worth a read!): Molecular orbital theory (pp. 373-387); Section 10.8 (pp. 392-402); Sections 11.2 to 11.4 (pp. 410-424); sections 12.6 to 12.8 (pp. 486-489), and pp. 483-506.

The final exam is on Wednesday, May 9, 8am to 11am. It is a comprehensive exam, but with a little more emphasis on material since the second midterm.

1 Chapter 1: The first law

- Internal energy change, $\Delta U = q + w$; $q_V = \Delta U$
- Heat capacities: $C_V = dU/dT$; $C_p = dH/dT$
- Enthalphy: $H = U + pV$; $q_p = \Delta H$
- Heats of reaction, heats of formation: $\Delta_r H^{\ominus}$, $\Delta_f H^{\ominus}$
- Explain how a differential scanning calorimeter works, and what it measures
- Enthalpies of phase transitions: $\Delta_{trs} H^{\ominus}$

2 Chapter 2: 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: $\Delta_{trs} S(T_{trs}) = \Delta_{trs} H(T_{trs})/T_{trs}$
- Boltzmann entropy and distribution: $S = -k \sum p_i \ln p_i$; $p_i = \exp(-\beta E_i)/Z$, where $Z = \sum \exp(-\beta E_i)$
- Gibbs (free) energy: $G = H - TS$

3 Chapter 3: Phase equilibria

- Dependence of G on temp, pressure, composition: $dG = Vdp - SdT + \mu_A n_A + \mu_B n_B + \ldots$
- The chemical potential is a partial molar Gibbs energy: $G = n_A \mu_A + n_B \mu_B$
- Chemical potential in a gas: $\mu_j = \mu_j^\ominus + RT \ln p_j$
- Chemical potential of solute or solvent in dilute solution: $\mu_j = \mu_j^* + RT \ln x_j$
- Concentration scales: mole fraction $x_j = n_j/(n_i + n_j)$, molality $b_j = n_j/m_{solvent}$, molarity $[J] = n_j/V$.
- Osmotic pressure, $\Pi V = n_B RT$

4 Chapter 4: Chemical equilibria

- Reaction Gibbs energy: $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$
- Equilibrium constant: $\Delta_r G^\ominus = -RT \ln K$
- Biological standard state: $\Delta_r G^\oplus = \Delta_r G^\ominus + 7\nu RT \ln 10$
- "p" items: pH=$-\log_{10} a_{H+}$; p$K_a = -\log_{10} K_a$; pH+pOH=p$K_w \sim 14$
- Henderson-Hasselbalch eq: pH=p$K_a - \log_{10} \frac{[acid]}{[base]}$
- van't Hoff equation: $\ln K_2 = \ln K_1 + (\Delta_r H^\ominus/R) \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

5 Chapter 5: Ion and electron transport

- mean activity coefficients, $\gamma_\pm = (\gamma_+^p \gamma_-^q)^{1/s}$; $s = p + q$
- ionic strength: $I = \frac{1}{2} \sum z_i^2 b_i$
- transfer across a membrane: $\Delta G_m = RT \ln(a_{in}/a_{out}) + zF\Delta\phi$
- Nernst equation: $E_{cell} = E_{cell}^\ominus - (RT/\nu F) \ln Q$
- dependence of cell potential on pH: $E = E' - \frac{\nu_{H+} RT \ln 10}{\nu_e F} \times pH$

6 Chapter 6: Rates of reactions

- differences between differential and integrated rate laws
- half life for a non-reversible first-order reaction: $t_{1/2} = (\ln 2)/k_r$
- Arrhenius equation: $k_r = \exp(-E_a/RT)$

7 Chapter 7: Understanding rate laws

- relation of equiibrium and rate constants: $K = k_r/k_r'$
- relaxation times: $x = x_0 \exp(-t/\tau)$; $\tau^{-1} = k_r + k_r'$
- diffusion controlled reaction: $k_d = (8RT/3\eta)$ [you don't need to memorize this one!]

8 Chapter 8: Biochemical reactions and transport

- Fick's first and second laws: $J = -D(dc/dx)$; $\partial c/\partial t = D(\partial^2 c/\partial x^2)$
- Diffusion constant temperature dependence: $D = D_0 \exp(-E_a/RT)$
- Ion mobility: $u = ez/6\pi\eta a$
- Stokes-Einstein relation: $D = kT/(6\pi\eta a)$
- Form of a Lineweaver-Burke plot

9 Chapter 9: Basics of quantum mechanics

- Bohr frequency relationship: $\Delta E = h\nu$
- de Broglie relation: $\lambda = h/p$
- Schrodinger equation: $-(\hbar^2/2m)(d^2\psi/dx^2) + V(x)\psi = E\psi$

10 Chapter 10: Chemical bonding

- Valence bond wavefunction: $\psi(1,2) = [\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)]\,[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
- Basic bonding terms: promotion, hybridization, resonance
- Combination of orbitals: if $\psi = c_A\psi_A + c_B\psi_B$, then one gets the following simultaneous equations:

$$\begin{aligned} (H_{AA} - ES_{AA})c_A + (H_{AB} - ES_{AB})c_B &= 0 \\ (H_{BA} - ES_{BA})c_A + (H_{BB} - ES_{BB})c_B &= 0 \end{aligned}$$

  The equation for the allowed values of E:

$$\det \begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

  In the Huckel approximation, this becomes:

$$\det \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \Rightarrow E = \alpha \pm \beta$$

11 Chapter 11: Macromolecules

- Coulomb's law: $V = q_1 q_2 / 4\pi\varepsilon_0 r$
- Lennard-Jones potential: $V = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right]$
- induced dipole moments: $\mu* = \alpha E$, where μ is a dipole moment $= \sum_i q_i x_i$ or $\int \rho(x) x dx$
- interaction of a charge and a dipole: $V = \mu_1 q_2 \cos\theta / (4\pi\varepsilon_0 r^2)$

12 Chapter 12: Basics of spectroscopy

- Beer-Lambert law: $I_f = I_0 \exp(-\varepsilon[J]L)$
- wave properties: $\nu\lambda = c$; $\tilde{\nu} = \nu/c = 1/\lambda$
- stimuated absorption and emission: $rate = NBI$; for spontaneous emission, $rate = NB(8\pi h\nu^3/c^3)$
- selection rules for vibrations: $\Delta n = \pm 1$
- explain the nature of fluorescence and phosphorescence