

Study guide for exam #2

Chemistry 341, (01:160:341), Fall 2014 Physical Chemistry of Biochemical Systems

1 Key concepts and equations

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.

1.1 Chapter 4: Free energy and chemical equilibria

- Dependence of G on temp, pressure, composition: $dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$
- The chemical potential is a partial molar Gibbs energy: $G = n_A \mu_A + n_B \mu_B$
- Reaction Gibbs energy: $\Delta_r G = \Delta_r G^\circ + RT \ln Q$
- Equilibrium constant: $\Delta_r G^\circ = -RT \ln K$
- 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 $\ln K_2 = \ln K_1 + (\Delta_r H^\circ/R) \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

1.2 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: $\text{pH} = -\log_{10} a_{H^+}$; $\text{p}K_a = -\log_{10} K_a$; $\text{pH} + \text{pOH} = \text{p}K_w \sim 14$
- Henderson-Hasselbalch eq: $\text{pH} = \text{p}K_a - \log_{10} \frac{[\text{acid}]}{[\text{base}]}$

1.3 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 $\Pi = cRT$

2 Sample exam questions

1. What is meant by the activity of a solute? Give its defining equation, and explain in words the meaning of each mathematical symbol that you use.
2. Compute the pH of an aqueous solution of 0.1 M acetic acid (CH_3COOH). The $\text{p}K_a$ of acetic acid is 4.74.
3. At 37° , K_w is about 2.5×10^{-14} ; what is the pH of neutral water at this temperature?
4. Can the external pressure p_{ex} ever be negative? What would this mean (in words)? Draw a picture of how you might (try to) measure a negative pressure.
5. At constant pressure and composition, does the Gibbs energy always increase with increasing temperature? or always decrease? or sometimes increase and sometimes decrease? Justify your answer.
6. The first excited vibrational energy level of the Cl_2 molecule is 558 cm^{-1} above its lowest energy level, where cm^{-1} is a unit of energy equal to $1.986 \times 10^{-23} \text{ J}$. What is the ratio of the population of the first excited state to the population of the lowest (ground) state?
7. What is plotted on the horizontal and vertical axes of a typical "phase diagram"? Give a rough sketch of the phase diagram of water. Identify the normal freezing and boiling points.