

Study guide for exam #1

Chemistry 488, (01:160:488), Spring 20123
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. For each of the first four chapters, please pay close attention to the *Checklist of key concepts* and the *Checklist of key equations*.

1.1 Chapter 1

- 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: $\Delta_r H^\ominus$, $\Delta_f H^\ominus$
- Explain how a differential scanning calorimeter works, and what it measures
- Enthalpies of phase transitions: $\Delta_{trs} H^\ominus$

1.2 Chapter 2

- 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: $G = H - TS$

1.3 Chapter 3

- 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: $G = n_A \mu_A + n_B \mu_B$
- 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 $b_j = n_j / m_{\text{solvent}}$, molarity $[J] = n_j / V$.
- Osmotic pressure, $\Pi V = n_B RT$

1.4 Chapter 4

- 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: $\text{pH} = -\log_{10} a_{H^+}$; $\text{p}K_a = -\log_{10} K_a$; $\text{pH} + \text{pOH} = \text{p}K_w \sim 14$
- Henderson-Hasselbalch eq: $\text{pH} = \text{p}K_a - \log_{10} \frac{[\text{acid}]}{[\text{base}]}$
- van't Hoff equation: $d(\ln K_{eq})/d(1/T) = -\Delta_r H^\ominus / R$, or $\ln K_2 = \ln K_1 + (\Delta_r H^\ominus / R) \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

2 Sample exam questions

1. Explain (define in words) each of the symbols in the following expressions; explain their limitations (what they assume)
 - (a) $\Delta H = \Delta U + p\Delta V$
 - (b) $\Delta_r H^\ominus(T') = \Delta_r H^\ominus(T) + \Delta_r C_p \times (T' - T)$
2. Starting from $dU = dq + dw$, show that $dU = TdS - pdV$. (Hint: see justification 3.1 in the book).
3. Using the result of problem 2, derive expressions for $(\partial U / \partial S)_V$ and $(\partial U / \partial V)_S$.
4. 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.
5. Draw a sketch of an osmometer, identifying all the parts. What does this measure?
6. Same as question 5, but for a differential scanning calorimeter.
7. Compute the pH of an aqueous solution of 0.1 M acetic acid (CH_3COOH).
8. At 37° , K_w is about 2.5×10^{-14} ; what is the pH of neutral water at this temperature?
9. 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.
10. 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.