Study guide for exam #1

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. For each of the first three chapters, please pay close attention to the *Summary* at the end of the chapter.

1.1 Chapter 2

- 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: $\Delta_r H^{\ominus}$, $\Delta_f H^{\ominus}$
- Enthalpies of phase transitions: $\Delta_\phi H$, where ϕ can refer to fusion (melting) or vaporization (boiling)
- *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.

1.2 Chapter 3

- Entropy: $\Delta S = q_{rev}/T$; entropy change of surroundings: $\Delta S_{sur} = -\Delta H/T$
- Temp. dependence of entropy, at constant pressure: $dS = (C_p/T)dT$
- pressure dependence of entropy, at constant T: $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$
- 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 $T, p, n_A, n_B, \ldots$, then $dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B + \ldots$
- dependence of G on temp. and pressure: $\left(\frac{\partial G}{\partial p}\right)_T = V$; $\left(\frac{\partial G}{\partial T}\right)_p = -S$; $\left(\frac{\partial (G/T}{\partial T}\right)_p = \frac{-H}{T^2}$

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 $dU = TdS - pdV$. (You may assume reversible changes.)

3. Using the result of problem 2, derive expressions for $(\partial U/\partial S)_V$ and $(\partial U/\partial V)_S$.

4. 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.

5. What is the dependence of enthalpy upon temperature? upon pressure? Are the answers different for a gas than for a solid or liquid?