

CHAPTER 7
PRINCIPLES OF CHEMICAL EQUILIBRIUM
CHAPTER OUTLINE

HW: Questions are below. Solutions are in separate file on the course web site.

Sect. Material

1. Introduction to Chemical Equilibria
2. Theoretical Background: Dependence of $\Delta_r G^\circ$ on Activity
3. The Equilibrium Constant
4. Effect of Compression on Chemical Equilibrium
5. Effect of Temperature on Chemical Equilibrium
6. Some Equilibrium Calculations
7. Binding of Ligands to Macromolecules
8. Gibbs Energy and the Biological Standard State
9. Glycolysis

Chapter 7 Homework

- 7.1** One of the most extensively studied reactions in industrial chemistry is the synthesis of ammonia from nitrogen and hydrogen (known as the Haber Process): $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
- The standard Gibbs energy of formation of $\text{NH}_3(\text{g})$ is -16.5 kJ/mol at $25 \text{ }^\circ\text{C}$. What is the reaction Gibbs energy when the partial pressures of N_2 , H_2 and NH_3 are 3.0 bar , 1.0 bar and 4.0 bar , respectively?
- What is the spontaneous direction of the reaction in this case?
- 7.2** The equilibrium constant for the reaction $\text{A} + \text{B} \rightleftharpoons 2 \text{C}$ is reported as 3.4×10^4 . What would it be for the reaction written as:
- (a) $2 \text{A} + 2 \text{B} \rightleftharpoons 4 \text{C}$
(b) $(1/2) \text{A} + (1/2) \text{B} \rightleftharpoons \text{C}$
- 7.3** The standard reaction Gibbs Energy for the isomerization of cis-2-pentene to trans-2-pentene at $127 \text{ }^\circ\text{C}$ is -3.67 kJ/mol . Calculate the equilibrium constant for this isomerization.
- 7.4** The standard reaction enthalpy of the reaction:
 $\text{Zn}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2(\text{g})$, is approximately constant at $+224 \text{ kJ/mol}$ at temperatures between 920 K and 1280 K . The standard reaction Gibbs energy is $+33 \text{ kJ/mol}$ at 1280 K .
- Calculate the temperature (in $^\circ\text{C}$) at which $K = 1$.
- 7.5** Consider the reaction: $2 \text{Al}_2\text{O}_3(\text{s}) + 3 \text{Si}(\text{s}) \rightarrow 3 \text{SiO}_2(\text{s}) + 4 \text{Al}(\text{s})$
Use the data in the table below to determine the Standard reaction Gibbs energy for this reaction at $25 \text{ }^\circ\text{C}$.

Compound	$\Delta_f H^\circ$	S_m°
Al_2O_3	-1675.7 kJ/mol	50.9 J/mol-K
Si		18.8
SiO_2	-910.9	41.8
Al		28.3

- 7.6** Calculate the standard Biological Gibbs Energy for the reaction:
 $\text{Pyruvate}^- + \text{NADH} + \text{H}^+ \rightarrow \text{Lactate}^- + \text{NAD}^+$
at $37 \text{ }^\circ\text{C}$ given that $\Delta_r H^\circ = -66.6 \text{ kJ/mol}$

Informational Notes (FYI, but not required to answer the question):

- (1) NAD^+ is then oxidized form of nicotinamide dinucleotide
- (2) This reaction occurs in muscle cells deprived of oxygen during strenuous exercise and can lead to cramps

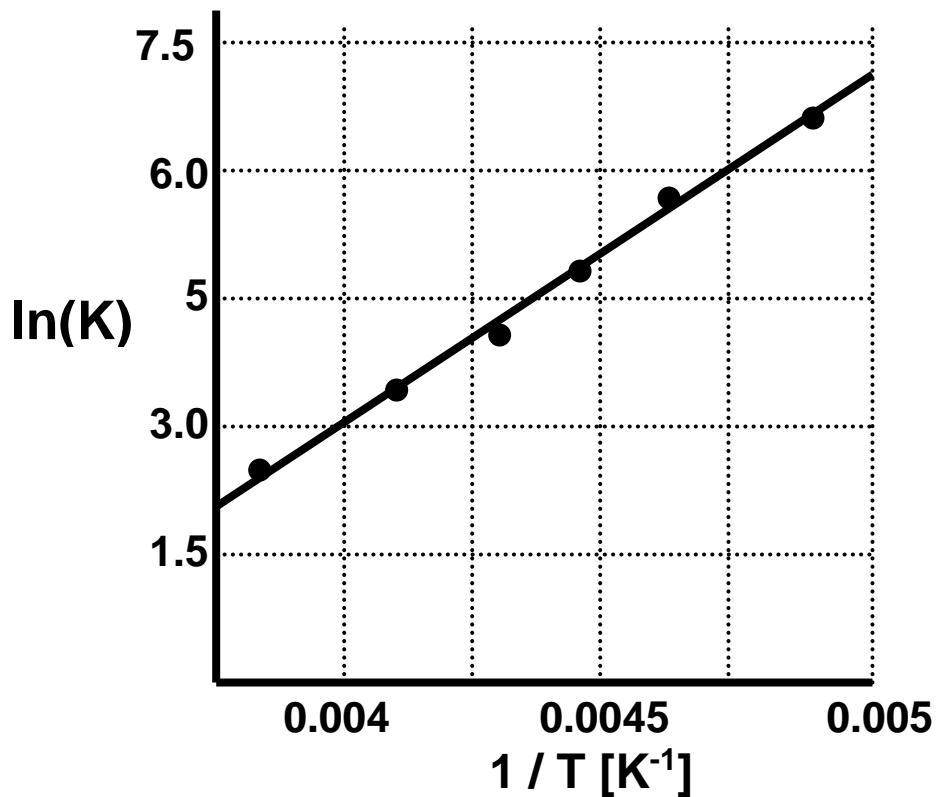
- 7.7** In a gas-phase equilibrium mixture of SbCl_5 , SbCl_3 and Cl_2 at $227\text{ }^\circ\text{C}$, $P_{\text{SbCl}_5} = 0.15\text{ bar}$ and $P_{\text{SbCl}_3} = 0.20\text{ bar}$.
Calculate the equilibrium partial pressure of Cl_2 (in bar), given that $K = 3.5 \times 10^{-4}$ for the reaction $\text{SbCl}_5(\text{g}) \rightleftharpoons \text{SbCl}_3(\text{g}) + \text{Cl}_2(\text{g})$.
- 7.8** In the Haber process for ammonia, $K = 0.036$ for the reaction,
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at $227\text{ }^\circ\text{C}$.
If a reactor has initial partial pressures $P_{\text{N}_2} = P_{\text{H}_2} = 0.02\text{ bar}$, $P_{\text{NH}_3} = 0\text{ bar}$, calculate the partial pressure of $\text{NH}_3(\text{g})$ at equilibrium.
Note: Because $K \ll 1$, you can assume that the concentrations of N_2 and H_2 remain basically at their initial concentrations.
- 7.9** Consider the equilibrium, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$. The value of the equilibrium constant is $K = 337$ at $100\text{ }^\circ\text{C}$ and $K = 7.1 \times 10^{-5}$ at $500\text{ }^\circ\text{C}$
(a) Determine the enthalpy (ΔH°) and entropy (ΔS°) changes for this reaction.
(b) Determine the value of the equilibrium constant at $300\text{ }^\circ\text{C}$.
(c) At $500\text{ }^\circ\text{C}$, the initial pressures (before reaction to form NH_3) of N_2 and H_2 are 1.0 bar and 3.0 bar , respectively. Calculate the pressures of all 3 gases at equilibrium [Note: You can make the assumption that very little NH_3 is formed relative to the initial pressures of N_2 and H_2 to simplify your calculation].
(d) Determine the Gibbs energy change for the reaction at $500\text{ }^\circ\text{C}$ for $P_{\text{N}_2} = P_{\text{H}_2} = 0.2\text{ bar}$ and $P_{\text{NH}_3} = 2.5\text{ bar}$
- 7.10** At $25\text{ }^\circ\text{C}$, the equilibrium constant is 8.9×10^{-5} for the decomposition of fructose-1,6-diphosphate [FDP] to form glyceraldehyde-3-phosphate [GAP] and dihydroxyacetone phosphate [DHAP], $\text{FDP} = \text{GAP} + \text{DHAP}$.
(a) Starting at an initial concentration of 0.1 M FDP (before decomposition), calculate the concentrations of FDP, GAP and DHAP at equilibrium. Perform the calculation (i) with no simplifying assumptions, (ii) with the simplifying assumption that relatively little FDP decomposes.
(b) Repeat the above calculations for an initial concentration of $1 \times 10^{-5}\text{ M}$ FDP.
(c) Determine the Gibbs energy change for the reaction for $[\text{GAP}] = [\text{DHAP}] = 2 \times 10^{-5}\text{ M}$ and $[\text{FDP}] = 0.5\text{ M}$.

7.11 For the equilibrium reaction, $A = B$, the van't Hoff plot [$\ln(K)$ vs. $1/T$] below was obtained.

Analysis of the graph shows that the Slope = 4000 K and Intercept = -13.0

Note: Determination of the slope and intercept is given in the solution. However, you will not be asked to perform the graphical analysis on a test.

Calculate $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for this reaction.



- 7.12** As we learned in class, the average number of ligands bound to a protein, R , is related to the ligand concentration, $[L]$, by the relation:

$$R = \frac{n[L]}{K + [L]}$$

where n is the maximum number of bound ligands and K is the average dissociation constant.

A protein binds a ligand (e.g. Ca^{2+}) via the overall equilibrium $\text{P} + n\text{L} = \text{PL}_n$, with the average dissociation constant, K . A pair of equilibrium dialysis experiments were performed with a total protein concentration, $[\text{P}]_{\text{tot}} = 0.004 \text{ M}$. (1) When $[\text{L}]_{\text{outside}} = 0.110 \text{ M}$, $[\text{L}]_{\text{inside}} = 0.211 \text{ M}$. (2) When $[\text{L}]_{\text{outside}} = 0.620 \text{ M}$, $[\text{L}]_{\text{inside}} = 0.785 \text{ M}$.

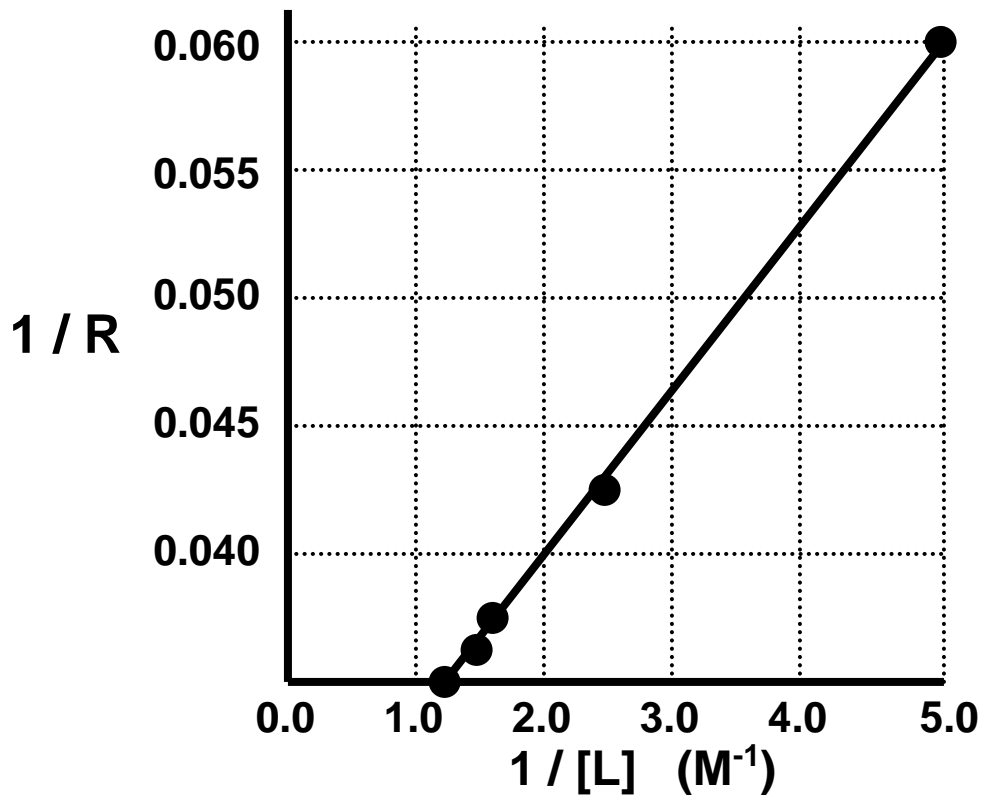
Calculate the total maximum number of attached ligands, n , and the average dissociation constant, K .

- 7.13** For a typical ligand binding experiment, a plot of $1/R$ vs. $1/[L]$ (Hughes-Klotz plot) yielded the graph below.

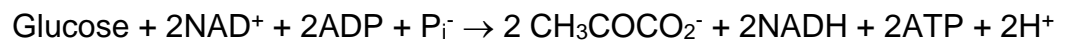
Analysis of the graph shows that the Slope = $6.67 \times 10^{-3} \text{ M}$ and Intercept = 2.67×10^{-2}

Note: Determination of the slope and intercept is given in the solution. However, you will not be asked to perform the graphical analysis on a test.

Calculate n and K for this protein-ligand system.



7,14 The reaction for the overall Glycolysis reaction is:



The Biological Chemistry Standard State Reaction Gibbs Energy change is: $\Delta G^{\circ'} = -80.7 \text{ kJ}$. Calculate the Physical Chemistry Standard State Reaction Gibbs Energy change, ΔG° .