Practice Test Questions 7
Free Energy and Equilibrium

1.

(a) What is the difference between ΔG and $\Delta G°$? Be specific.

(b) For which of the following reactions would you expect the values for ΔG and $\Delta G°$ to be the same at 25 ℃?

i. $2\ Na_{(s)} + Cl_{2(g)} \rightarrow\ 2\ NaCl_{(s)}$

ii. $Ba(OH)_2 \cdot 8H_2O_{(s)}\ +\ 2\ KSCN_{(s)}\ \rightarrow\ Ba(SCN)_{2(s)}\ +\ 2\ KOH_{(aq)}\ +\ 8\ H_2O_{(l)}$

iii. $2\ O_{3(g)} \rightarrow\ 3\ O_{2(g)}$

iv. $C_{(s,diamond)} \rightarrow\ C_{(s,graphite)}$

2. Consider the following reaction:

$$H_{2(g)} + Cl_{2(g)} \rightarrow\ 2\ HCl_{(g)}$$

What is ΔG for this reaction when the partial pressures of $H_{2(g)}$ and $Cl_{2(g)}$ are both 3.5 bar, the partial pressure of $HCl_{(g)}$ is 0.5 bar and the temperature is 25 ℃?

3. The reaction below comes to equilibrium at 400 ℃ in a 2 L flask.

$$4\ HCl_{(g)} + O_{2(g)} \rightarrow\ 2\ Cl_{2(g)} + 2\ H_2O_{(g)}$$

Analysis of the equilibrium mixture shows that it contains 60g of Cl_2, 12g of H_2O, 20g of HCl and 8g of O_2. Calculate the equilibrium constant.

4. Calculate the equilibrium constant for the reaction below at 25 ℃:

$$CO_{(g)} + Cl_{2(g)} \rightarrow\ COCl_{2(g)}$$

5. The equilibrium constant for the reaction below is 0.352 at 25 ℃:

$$H_{2(g)} + I_{2(s)} \rightarrow\ 2\ HI_{(g)}$$

Suppose that an excess of solid iodine is placed in a rigid flask with 0.400 bar of hydrogen gas and 0.300 bar of hydrogen iodide. In what direction will the reaction proceed?

6. Industrially, liquid methanol is made by reaction of carbon monoxide with hydrogen, a mixture sometimes known as syngas (or synthesis gas). The reaction is carried out at high temperatures in the presence of a catalyst.

Suppose that you have developed a new catalyst for this reaction. You have a cylinder of syngas which is regulated to deliver 0.4 bar of CO and 1.5 bar of H_2. Is there any point in trying your catalyst at 25 ℃?

In other words, is the reaction producing liquid methanol from syngas spontaneous at 25 ℃ *given the pressures of* CO *and* H_2 *delivered by your cylinder?*

7. One of the steps in the industrial production of sulfuric acid is the oxidation of sulfur dioxide to sulfur trioxide using oxygen. In industry, a catalyst and elevated temperatures are also used to speed up the reaction.

Is the forward reaction for this step (production of SO_3) at 25.00 ℃ still thermodynamically allowed if atmospheric pressures of O_2 are used (0.21 bar), and the SO_2 and SO_3 pressures in your reactor are 0.45 bar and 5.00 bar, respectively?

8. When heated, potassium chlorate decomposes into solid potassium chloride and oxygen gas:

$$2\ KClO_{3(s)} \rightarrow\ 2\ KCl_{(s)}\ + 3\ O_{2(g)}$$

(a) Write the reaction quotient expression for this reaction in terms of the activities of **all** substances?

(b) Simplify your answer to part (a) by substituting concentrations, partial pressures and activities equal to 1 where appropriate.

(c) If solid potassium chlorate is placed in a sealed reaction vessel at 25 ℃, what would be the partial pressure of oxygen at equilibrium?

(d) Is this reaction likely to reach equilibrium? Comment.

9. Consider the following formula.

$$\Delta_r G = \Delta_r G° + RTlnQ$$

(a) What must the value for Q be if all reactants/products are in the standard state? Briefly explain how you arrived at this value.

(b) Explain the origin of each of the following applications of Le Chatelier's Principle:

i. Increasing the concentration of a reactant will shift an equilibrium to the product side.

ii. Decreasing the volume of an equilibrium reaction involving gases will shift it to the side of the fewest gas molecules.

10. $P_{4(s)}$ can react with $O_{2(g)}$ to give $P_4O_{10(s)}$.

(a) Write a balanced chemical equation for this reaction.

(b) Write the reaction quotient expression for this reaction in terms of activities.

(c) Calculate ΔG for this reaction if $P_{4(s)}$ is exposed to air which contains 0.21 bar $O_{2(g)}$ at 25 ℃. Based on this value, in which direction is this reaction favoured under these conditions?

11. In the process for manufacturing bleach, chlorine gas reacts when it is stirred into an aqueous solution of sodium hydroxide, yielding aqueous sodium hypochlorite (bleach) and aqueous sodium chloride. The balanced net ionic equation for this reaction is:

$$Cl_{2(g)} + 2\,OH^-_{(aq)} \rightarrow Cl^-_{(aq)} + ClO^-_{(aq)} + H_2O_{(l)}$$

Calculate the equilibrium constant for this reaction at 25℃.

12. Consider the following reaction:

$$B_2O_{3(s)} + 6\,HF_{(g)} \rightarrow 2\,BF_{3(g)} + 3\,H_2O_{(l)}$$

(a) Write the reaction quotient expression for this reaction in terms of activities.

(b) A flask contains 12 g B_2O_3, 0.25 bar HF, 0.36 bar BF_3 and 100 mL H_2O at 25.00 ℃. Calculate the free energy change for the reaction under these conditions, and determine whether it is favoured in the forward or reverse direction.

13. Calculate the acid ionization constant (K_a) of the ammonium ion (NH_4^+) at 25 ℃.

In other words, calculate the equilibrium constant for the reaction below at 25 ℃.

$$NH^+_{4(aq)} \rightarrow NH_{3(aq)} + H^+_{(aq)}$$

14. Magnesium dissolves in aqueous acid according to the equation given below under standard conditions. Will the reaction at 25.00 ℃ still be thermodynamically allowed at a pH of 6.00, an external pressure of 2.00 bar of hydrogen gas and Mg^{2+} concentration of 0.100 $\frac{mol}{L}$?

$$Mg_{(s)} + 2\,H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$

15. The equilibrium constant for the reaction below is $K_{sp} = 1.1 \times 10^{-10}$

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

Calculate the standard free energy of formation of the aqueous Ba^{2+} ion and compare the value obtained to that given in the data table.

16. 15 mL of a solution containing $2.8 \times 10^{-4}\ \frac{mol}{L}$ calcium nitrate is mixed with 25 mL of a solution containing $8.6 \times 10^{-3}\ \frac{mol}{L}$ sodium fluoride at 25 ℃.

Does calcium fluoride precipitate out?

17. Two hydrogen atoms react to form a hydrogen molecule under standard conditions:

$$2\ H_{(g)} \rightarrow\ H_{2(g)}$$

(a) What information does the phrase "standard conditions" give you about the conditions under which this reaction is being studied?

(b) Is $\Delta_r G°$ positive, negative or zero for this reaction? Briefly, justify your answer.

(c) Is $\Delta_r S°°$ positive, negative or zero for this reaction? Briefly, justify your answer.

(d) Is $\Delta_r H°$ positive, negative or zero for this reaction? Briefly, justify your answer.

(e) Will there be any temperature at which this reaction is not favoured in the forward direction? If 'yes', will it be high or low temperatures (and why)? If 'no', why not?

18.

(a) Textbooks of Organic Chemistry usually list the pK_a of water as being 15.7 at 25 ℃. This number is derived from the K_a expression for the generic reaction:

$$HA_{(aq)} \rightarrow\ H^+_{(aq)}\ +\ A^-_{(aq)}$$

in which water acts as the acid HA. For pure water, $[H_2O] = 55.6\ M$ so that in this derivation:

$$pK_a(H_2O) = -log[K_a(H_2O)] = -log\left(\frac{[H^+][OH^-]}{[H_2O]}\right) = -log\left(\frac{K_w}{[H_2O]}\right) = 15.7$$

Based on your understanding of thermodynamic equilibrium constants, comment on this derivation of the pK_a of water.

(b) Calculate K_w from $\Delta G°$ for the appropriate reaction at 25 ℃. *You must include a balanced thermodynamic chemical reaction to get full marks for this question.*

19. The equilibrium constant for the reaction below is 28.5 at 25 ℃.

$$4\ KO_{2(s)}\ +\ 2\ CO_{2(g)}\ \rightarrow\ 2\ K_2CO_{3(s)}\ +\ 3\ O_{2(g)}$$

(a) If the reaction reaches equilibrium when the partial pressure of carbon dioxide is 0.073 bar, what is the partial pressure of oxygen in the apparatus?

(b) This reaction is used to produce oxygen in some self-contained breathing devices. Why do you think this is a good choice of reaction for that purpose? There is more than one valid answer to this question.