Supplemental Questions
for
Equilibrium

1. Let the equilibrium constants for the following reactions be K_1, K_2, and K_3, respectively.

$XeF_6\ (g) + H_2O\ (g) \rightleftharpoons XeOF_4\ (g) + 2\ HF\ (g)$	K_1
$XeO_4\ (g) + XeF_6\ (g) \rightleftharpoons XeO_3F_2\ (g) + XeOF_4\ (g)$	K_2
$XeO_4\ (g) + 2\ HF\ (g) \rightleftharpoons XeO_3F_2\ (g) + H_2O\ (g)$	K_3

Write K_3 in terms of K_1 and K_2.

2. Starting with $\Delta G = -RT\ln K$, prove that reversing a reaction means that the equilibrium constant for the new reaction, K', is $1/K$, where K is the equilibrium constant for the original reaction.

3a. At 25.0 °C the equilibrium constant, written in terms of the pressure, for the reaction shown below is 1.34×10^{-2}.

$$AsF_5\,(g) \rightleftharpoons AsF_3\,(g) + F_2\,(g)$$

What will be the concentration of each species at equilibrium if you start with a 1.000 L flask containing 2.5000×10^{-2} mole AsF_5?

b. This reaction takes place in a single step. Draw the reaction profile for this reaction with the Gibbs energy on the *y*-axis. CAUTION! There is more to this question then there appears! You will need information from parts a and b to do this correctly.

4a. At 900.0 °C, K_p = 1.04 for the reaction: $CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g).
To an empty 50.0-L flask is introduced 715.0 g $CaCO_3$. The flask and its contents are then heated to 900.0 °C, what will the pressure in the flask be when equilibrium is attained at that temperature?

b. What is the minimum amount of $CaCO_3$ that must be added to the flask so that equilibrium can be attained at 900.0 °C?

5a. The reaction of ethylene, C_2H_4, with H_2 to give ethane, C_2H_6 is shown below. K_c for the reaction is 9.42 at 25.0 °C. A constant volume reaction vessel is loaded with gas such that

$$C_2H_4\,(g) + H_2\,(g) \rightleftharpoons C_2H_6(g)$$

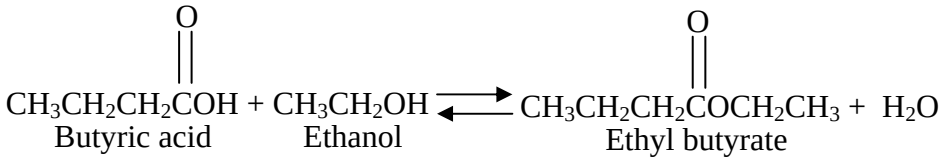
$[C_2H_4] = 0.350$ M, $[H_2] = 0.300$ M and $[C_2H_6] = 0.225$. What is the concentration of each chemical species once this mixture reaches equilibrium?

b. The pressure on the system was increased by decreasing the volume. Will there be more of the reactants or product formed once the system reestablishes equilibrium? Why?

c. Platinum (Pt) is a catalyst for this reaction. If Pt was added to the initial gas mixture given above, will the concentration of C_2H_6 (g) be increased once the equilibrium is reached? Briefly explain.

d. If some of the C_2H_6 initially placed in the vessel was labeled with ^{13}C, would any of the C_2H_4 contain ^{13}C when equilibrium is achieved? Why?

6. Esters are pleasant smelling organic compounds that are the product of the reaction of a carboxylic acid with an alcohol. One of these is ethyl butyrate (smells like pineapple), which is produced by the reaction of butyric acid with ethanol according to the reaction given below.



a. To maximize the amount of ethyl butyrate present at equilibrium, which of the following solvents water, a mixture that is 95% ethanol and 5% water, 100 % ethanol or acetonitrile (a non-reactive solvent, would you choose? Briefly explain your choice.

b. If butyric acid, ethanol, ethyl butyrate and D_2O (water where all the hydrogen is the ^2H isotope) are placed in a reaction vessel such that their concentrations are at their respective equilibrium concentrations, will any of the deuterium ever be found in the butyric acid or the ethanol? Why?

c. This reaction is often run in the presence of a small amount of a strong acid, yet the strong acid does not appear in the overall balanced chemical equation. Explain the role of H^+ in this reaction.

d. In the space below qualitatively sketch how the concentration of butyric acid and ethyl butyrate changes with time over the course of this reaction.

7. An amount of solid ammonium chloride is placed in an evacuated container and heated so that it decomposed to hydrogen chloride gas and ammonia gas. When equilibrium is established the pressure in the container was found to be 4.4 atm.

a. Write the balanced chemical equation for this reaction.

b. What is K_p for this reaction at this temperature?

c. What is K_c for this reaction under these conditions (T = 300.0 °C)?

8a. If 0.250 mole SO_2Cl_2, 0.150 mole SO_2 and 0.0500 mole Cl_2 are placed in a 12.0-L reaction vessel at a temperature where K_c for the reaction shown below is 7.77×10^{-2}, what will be the concentrations of each chemical species when the system reaches equilibrium?

$$SO_2Cl_2\ (g) \rightleftharpoons SO_2\ (g) + Cl_2\ (g)$$

b. What is ΔG for this reaction (T = 100.0 °C)? Predict the signs of ΔS and ΔH and give a brief justification of your predicted signs.

9. Calcium carbonate, $CaCO_3$, can exist in two forms: calcite and aragonite, denoted $CaCO_3$ (s, calcite) and $CaCO_3$(s, aragonite), respectively. Both will dissolve in water according to the balanced chemical equation $CaCO_3$ (s) $\rightleftharpoons$ Ca^{2+} (aq) + CO_3^{2-} (aq). At 25.00 °C, calcite has an equilibrium constant for this reaction of 3.8×10^{-9} while for aragonite the equilibrium constant is 6.0×10^{-9}.

a. Ignoring all other equilibria, which form of $CaCO_3$ is more soluble in water? Why?

b. Derive the equilibrium constant for the reaction that converts calcite to aragonite in terms of the equilibrium constants for calcite and aragonite dissolving in water.

c. What is ΔG^0 for the conversion of calcite to aragonite?

d. Given that CO_3^{2-} undergoes the reaction shown below in aqueous solution, what effect does increasing the $[OH^-]$ have on the solubility of $CaCO_3$?

$$CO_3^{2-}\,(aq) + H_2O\,(aq) \rightleftharpoons HCO_3^-\,(aq) + OH^-\,(aq)$$