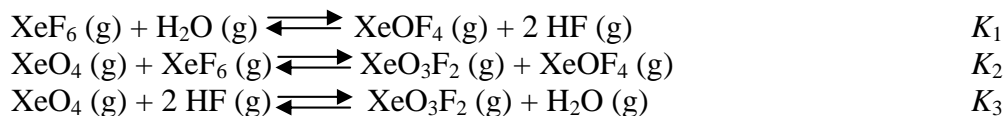


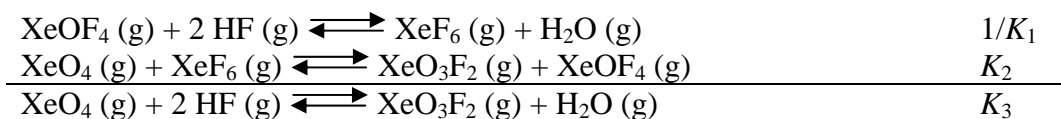
**Supplemental Questions  
for  
Equilibrium**

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



Write  $K_3$  in terms of  $K_1$  and  $K_2$ .

*The third reaction can be obtained by reversing first reaction and adding second one to it.*



**Therefore,  $K_3 = K_2/K_1$**

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.

**Let  $\Delta G$  be the change in the Gibbs energy for the first reaction, and  $\Delta G'$  be the change in the Gibbs energy for the reversed reaction.**

**For the initial reaction**  $\Delta G = -RT \ln K$

**For the new reaction**  $\Delta G' = -RT \ln K'$

**Since  $\Delta G' = -\Delta G$ ,**  $RT \ln K = -RT \ln K'$

**And**  $\ln K' = -\ln K$

**By the properties of logarithms**  $\ln K' = \ln K^{-1}$

**This implies**  $K' = K^{-1}$

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



What will be the concentration of each species at equilibrium if you start with a 1.000 L flask containing  $2.5000 \times 10^{-2}$  mole  $\text{AsF}_5$ ?

*Calculate the initial concentration of  $\text{AsF}_5$ .*

$$[\text{AsF}_5] = \frac{2.5000 \times 10^{-2} \text{ mole}}{1.000 \text{ L}} = 2.500 \times 10^{-2} \text{ M}$$

*Convert  $K_p$  to  $K_c$ , where  $\Delta n = 1$ .*

$$K_p = K_c (RT)^{\Delta n}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.34 \times 10^{-2}}{(0.082057 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mole}^{-1} \cdot 298.15 \text{ K})^1} = 5.48 \times 10^{-4}$$

*Calculate  $Q$*

$$Q = \frac{[\text{AsF}_3][\text{F}_2]}{[\text{AsF}_5]} = \frac{0 \cdot 0}{2.500 \times 10^{-2}} = 0$$

**$Q < K$ , so reaction shifts toward products.**

	$\text{AsF}_5(\text{g})$	$\text{AsF}_3(\text{g})$	$\text{F}_2(\text{g})$
<b>Initial</b>	$2.500 \times 10^{-2}$	<b>0</b>	<b>0</b>
<b>Change</b>	<b>-x</b>	<b>+x</b>	<b>+x</b>
<b>Equilibrium</b>	$2.500 \times 10^{-2} - x$	<b>x</b>	<b>x</b>

*Substitute into the equilibrium expression and solve.*

$$K = \frac{[\text{AsF}_3][\text{F}_2]}{[\text{AsF}_5]} = \frac{x \cdot x}{(2.500 \times 10^{-2} - x)} = 5.48 \times 10^{-4}$$

$$x^2 + 5.48 \times 10^{-4} - 1.37 \times 10^{-5} = 0$$

Use the quadratic formula to solve for  $x$ .

$$x = \frac{-5.48 \times 10^{-4} \pm \sqrt{(5.48 \times 10^{-4})^2 - 4(1)(-1.37 \times 10^{-5})}}{2}$$

$$x = -3.98 \times 10^{-3} \text{ (physically unreasonable) and } x = 3.43 \times 10^{-3}$$

Calculate the final concentrations

$$[\text{AsF}_5] = 2.500 \times 10^{-2} - 3.43 \times 10^{-3} = 2.156 \times 10^{-2} \text{ M}$$

$$[\text{AsF}_3] = 3.44 \times 10^{-3} \text{ M}$$

$$[\text{F}_2] = 3.44 \times 10^{-3} \text{ M}$$

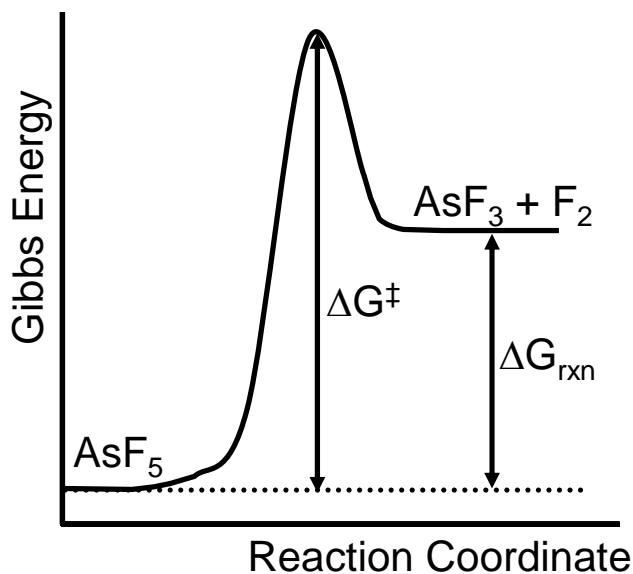
**The concentration of  $\text{AsF}_5$  at equilibrium is  $2.156 \times 10^{-2} \text{ M}$ , while that of  $\text{AsF}_3$  and  $\text{F}_2$  are both  $3.44 \times 10^{-3} \text{ M}$ .**

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 than there appears! You will need information from parts a and b to do this correctly.

Calculate  $\Delta G$  (this way we know where the reactants are relative to the products in energy). We need to use  $K_c$  for this.

$$\Delta G = -RT \ln K = -(8.314510 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K}) \ln(5.48 \times 10^{-4}) = +18.6 \frac{\text{kJ}}{\text{mole}}$$

The reaction is non-spontaneous, so the following reaction profile is appropriate.



4a. At 900.0 °C,  $K_p = 1.04$  for the reaction:  $\text{CaCO}_3 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$ .  
 To an empty 50.0-L flask is introduced 715.0 g  $\text{CaCO}_3$ . 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?

**For this reaction the equilibrium expression is  $K_p = p_{\text{CO}_2}$ .**

**As long as there is sufficient  $\text{CaCO}_3$  to support the equilibrium, the pressure of  $\text{CO}_2$  will equal  $K_p$  (assumed to be in atm), which in this case will also be the total pressure (no other gases are present).**

**The pressure in the flask at equilibrium is 1.04 atm.**

b. What is the minimum amount of  $\text{CaCO}_3$  that must be added to the flask so that equilibrium can be attained at 900.0 °C?

*The minimum amount of  $\text{CaCO}_3$  will be that gives the number of moles of  $\text{CO}_2$  that will give a pressure of 1.04 atm in a 50.0-L flask at 900.0 °C.*

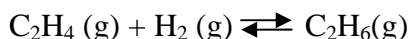
$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(1.04 \text{ atm})(50.0 \text{ L})}{(0.082057 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(900.0 + 273.15 \text{ K})} = 0.540_2 \text{ mole CO}_2$$

$$0.540_2 \text{ mole CO}_2 \left( \frac{1 \text{ mole CaCO}_3}{1 \text{ mole CO}_2} \right) \left( \frac{100.087 \text{ g}}{1 \text{ mole CaCO}_3} \right) = 54.1 \text{ g CaCO}_3$$

**The minimum amount of  $\text{CaCO}_3$  needed is 54.1 g.**

5a. The reaction of ethylene,  $\text{C}_2\text{H}_4$ , with  $\text{H}_2$  to give ethane,  $\text{C}_2\text{H}_6$  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



$[\text{C}_2\text{H}_4] = 0.350 \text{ M}$ ,  $[\text{H}_2] = 0.300 \text{ M}$  and  $[\text{C}_2\text{H}_6] = 0.225$ . What is the concentration of each chemical species once this mixture reaches equilibrium?

	$\text{C}_2\text{H}_4 (\text{g})$	$\text{H}_2 (\text{g})$	$\text{C}_2\text{H}_6 (\text{g})$
<b>Initial</b>	<b>0.350</b>	<b>0.300</b>	<b>0.225</b>
<b>Change</b>	<b>-x</b>	<b>-x</b>	<b>x</b>
<b>Equilibrium</b>	<b>0.350-x</b>	<b>0.300-x</b>	<b>0.225+x</b>

$$Q = \frac{[\text{C}_2\text{H}_6]}{[\text{C}_2\text{H}_4][\text{H}_2]} = \frac{0.225}{(0.350)(0.300)} = 2.14$$

**$Q < K$ , so reaction proceeds to the right.**

$$K = \frac{[C_2H_6]}{[C_2H_4][H_2]} = \frac{0.225 + x}{(0.350 - x)(0.300 - x)} = 9.42$$

$$9.42x^2 - 7.12x + 0.764 = 0$$

$$x = \frac{7.12 \pm \sqrt{(-7.12)^2 - 4(9.42)(0.764)}}{2(9.42)} = \frac{7.12 \pm \sqrt{50.6_{94} - 28.7_{88}}}{18.8_4}$$

$$x = \frac{7.12 \pm \sqrt{21.9_{06}}}{18.8_4} = \frac{7.12 \pm 4.68}{18.8_4}$$

$$x = 0.626 \text{ (physically unreasonable)}$$

$$x = 0.130$$

$$[C_2H_4] = 0.350 - 0.130 \text{ M} = 0.220 \text{ M}$$

$$[H_2] = 0.300 - 0.130 \text{ M} = 0.170 \text{ M}$$

$$[C_2H_6] = 0.225 + 0.130 \text{ M} = 0.355 \text{ M}$$

**At equilibrium the concentration of  $C_2H_4$  is 0.220 M, the concentration of  $H_2$  is 0.170 M and the concentration of  $C_2H_6$  is 0.355 M.**

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?

**Increasing the pressure by decreasing the volume effectively increases the concentrations. Since the product of the concentrations of the denominator in the reaction quotient will be larger than the numerator,  $Q$  will be less than  $K$  and the reaction will go toward products. This means that there will be more product once the system reestablishes equilibrium.**

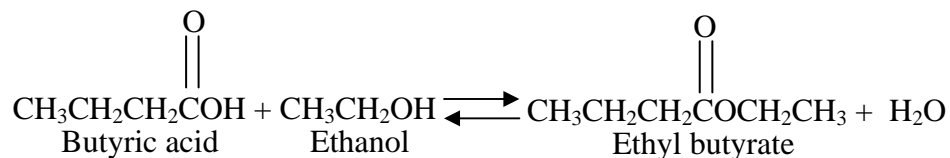
c. Platinum (Pt) is a catalyst for this reaction. If Pt was added to the initial gas mixture given above, will the concentration of  $C_2H_6$  (g) be increased once the equilibrium is reached? Briefly explain.

**Catalysts can only change the time taken to reach equilibrium (they speed up a reaction by lowering its activation energy), not the amount of products and reactants present at equilibrium (this is determined by  $\Delta G$ ).**

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?

**Yes, some of the  $C_2H_4$  would contain  $^{13}C$  because equilibria are dynamic** (*which means that the chemical reactions still occur on the molecular level, even though on the macroscopic level it appears that the reaction has stopped changing*).

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.

**Ethanol is a reactant, so increasing its concentration should, according to LeChâtelier's Principle, shift this equilibrium toward the desired product. Therefore, this reaction should be run in 100% ethanol.**

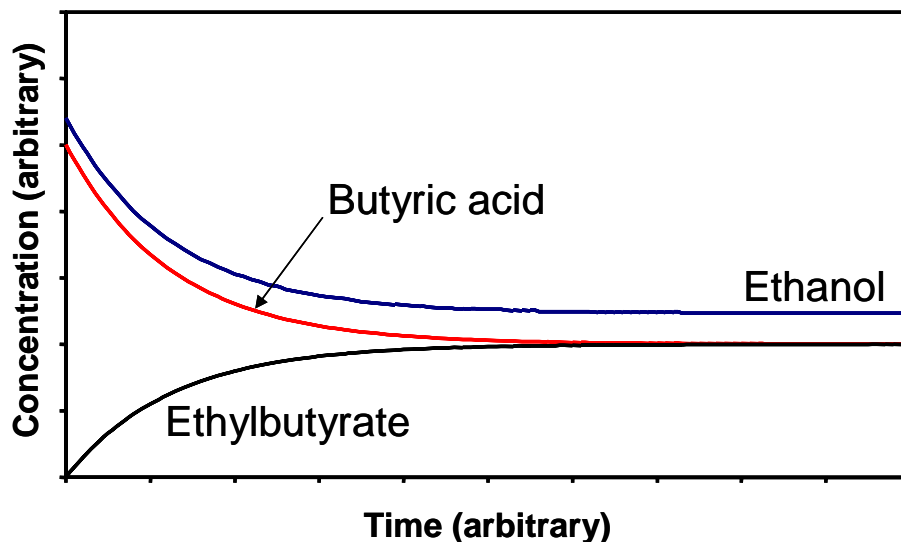
b. If butyric acid, ethanol, ethyl butyrate and  $D_2O$  (water where all the hydrogen is the  $^2H$  isotope) are placed in a reaction vessel such that their concentrations are at their respective equilibrium concentrations, will any of the deuterium ever be found in the butyric acid or the ethanol?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

**Yes, some of the deuterium ( $^2H$  isotope) will be found in the reactants, because equilibria are dynamic (both the forward and reverse reactions are always occurring, even though the overall concentrations of the reactants and products do not change).**

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.

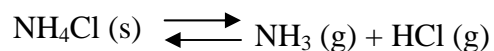
**Since  $H^+$  does not appear in the overall balanced equation, and it must have been added for a reason, it is safe to assume that the  $H^+$  functions as a catalyst (added to speed up the reaction).**

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?

*The expression for  $K_p$  is*

$$K_p = p_{\text{NH}_3} p_{\text{HCl}}$$

*and*

$$p_{\text{NH}_3} + p_{\text{HCl}} = 4.4 \text{ atm}$$

*but*

$$p_{\text{NH}_3} = p_{\text{HCl}} = p$$

$$p + p = 4.4 \text{ atm}$$

$$p = 2.2 \text{ atm}$$

The expression for  $K_p$  becomes

$$K_p = p^2 = (2.2)^2 = 4.8$$

**The value for  $K_p$  is 4.8.**

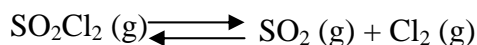
c. What is  $K_c$  for this reaction under these conditions ( $T = 300.0\text{ }^\circ\text{C}$ )?

$$K_p = K_c(RT)^{\Delta n}$$

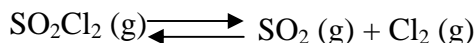
$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{4.8}{(0.082057 \cdot 573.15)^2} = 2.2 \times 10^{-3}$$

**$K_c$  for this reaction is  $2.2 \times 10^{-3}$ .**

8a. If 0.250 mole  $\text{SO}_2\text{Cl}_2$ , 0.150 mole  $\text{SO}_2$  and 0.0500 mole  $\text{Cl}_2$  are placed in a 12.0-L reaction vessel at a temperature where  $K_c$  for the reaction shown below is  $7.77 \times 10^{-2}$ , what will be the concentrations of each chemical species when the system reaches equilibrium?



First calculate the concentrations of all species present from the given number of moles and the given volume.



Initial	0.02083	0.0125	0.00417
Change	-x	+x	+x
Final	0.02083-x	0.0125+x	0.00417+x

Determine the reaction quotient to find the direction that this reaction will shift so as to come to equilibrium.

$$Q = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{(0.0125)(0.00417)}{0.02083} = 2.5 \times 10^{-3}$$

**Since  $Q < K$ , this reaction will shift to the right.**

$$K = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{(0.0125 + x)(0.00417 + x)}{0.02083 - x} = 7.77 \times 10^{-2}$$

No simplifying approximations can be made, so we must solve the quadratic equation.

Solving the quadratic equation (work not shown) gives  $x = -0.109$  (rejected as being physically impossible) and  $x = 0.0148$ .

Substituting this back in for  $x$  in the expressions for the final concentrations gives

$$[\text{SO}_2\text{Cl}_2] = 0.0060 \text{ M}$$

$$[\text{SO}_2] = 0.0273 \text{ M}$$

$$[\text{Cl}_2] = 0.0190 \text{ M}$$

b. What is  $\Delta G$  for this reaction ( $T = 100.0 \text{ }^\circ\text{C}$ )? Predict the signs of  $\Delta S$  and  $\Delta H$  and give a brief justification of your predicted signs.

*For a gas, need to use  $K_p$  in the  $\Delta G$  calculation. So, first convert given  $K_c$  to  $K_p$ .*

$$K_p = K_c(RT)^{\Delta n} = 7.77 \times 10^{-2} (0.082057 \cdot 373.15)^{+1} = 2.37_9$$

*Now calculate  $\Delta G$ .*

$$\Delta G = -RT \ln K = -(8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(373.15 \text{ K}) \ln(2.37_9)$$

$$\Delta G = -2.69 \frac{\text{kJ}}{\text{mole}}$$

**$\Delta G$  for this reaction is  $-2.69 \text{ kJ/mole}$ .**

**In this reaction one particle breaks down to form two particles, so it is likely that  $\Delta S$  is greater than 0. With a small, negative  $\Delta G$  and a positive  $\Delta S$ ,  $\Delta H$  could either be positive (with  $T\Delta S > \Delta H$ , but not much larger) or negative.**

9. Calcium carbonate,  $\text{CaCO}_3$ , can exist in two forms: calcite and aragonite, denoted  $\text{CaCO}_3$  (s, calcite) and  $\text{CaCO}_3$ (s, aragonite), respectively. Both will dissolve in water according to the balanced chemical equation  $\text{CaCO}_3$  (s)  $\rightleftharpoons$   $\text{Ca}^{2+}$  (aq) +  $\text{CO}_3^{2-}$  (aq). At 25.00 °C, calcite has an equilibrium constant for this reaction of  $3.8 \times 10^{-9}$  while for aragonite the equilibrium constant is  $6.0 \times 10^{-9}$ .

a. Ignoring all other equilibria, which form of  $\text{CaCO}_3$  is more soluble in water? Why?

**Aragonite has the higher K, so at equilibrium the concentration of each ion is higher, meaning more aragonite dissolved. So, aragonite is more soluble in water.**

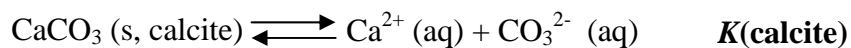
*Note that this comparison can be directly made only because both compounds dissociate to give the same number of ions. If they did not, we would have to actually calculate the amount of each substance that dissolved.*

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.

*The reaction that we need is*



*Can get K for this reaction from the equilibrium constants for aragonite,  $K(\text{aragonite})$ , and calcite,  $K(\text{calcite})$ , dissolving in water as follows.*



$$K = \frac{K(\text{calcite})}{K(\text{aragonite})} = \frac{3.8 \times 10^{-9}}{6.0 \times 10^{-9}} = 0.63$$

**The equilibrium constant for the conversion of calcite to aragonite is 0.63.**

c. What is  $\Delta G^0$  for the conversion of calcite to aragonite?

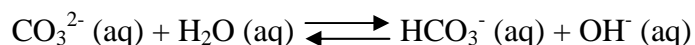
*Since the equilibria were determined at 25.00 °C,  $\Delta G^0$  can be directly calculated from the equilibrium constant found in part b.*

$$\Delta G^0 = -RT \ln K = -\left(8.314510 \frac{J}{K \cdot mole}\right)(298.15K) \ln(0.63)$$

$$\Delta G^0 = +1.1 \frac{kJ}{mole}$$

**For the conversion of calcite to aragonite  $\Delta G^0$  is +1.1 kJ/mole.**

d. Given that  $\text{CO}_3^{2-}$  undergoes the reaction shown below in aqueous solution, what effect does increasing the  $[\text{OH}^-]$  have on the solubility of  $\text{CaCO}_3$ ?



**Increasing the  $[\text{OH}^-]$  shifts this equilibrium to the left and thus increases the  $[\text{CO}_3^{2-}]$ , by Le Châtelier's Principle. The increase in the  $[\text{CO}_3^{2-}]$  shifts the equilibrium that defines the solubility of  $\text{CaCO}_3$  to the left also (toward  $\text{CaCO}_3$ ). This means that less  $\text{CaCO}_3$  dissolves and the solubility of  $\text{CaCO}_3$  falls as the  $[\text{OH}^-]$  increases.**