

*Chemistry 2e*  
**13: Fundamental Equilibrium Concepts**  
**13.1: Chemical Equilibria**

1. What does it mean to describe a reaction as “reversible”?

Solution

The reaction can proceed in both the forward and reverse directions.

3. If a reaction is reversible, when can it be said to have reached equilibrium?

Solution

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the forward and reverse reactions continue to proceed, but at equal rates.

5. If the concentrations of products and reactants are equal, is the system at equilibrium?

Solution

Not necessarily. A system at equilibrium is characterized by *constant* reactant and product concentrations, but the values of the reactant and product concentrations themselves need not be equal.

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*Chemistry 2e*  
**13: Fundamental Equilibrium Concepts**  
**13.2: Equilibrium Constants**

7. Explain why an equilibrium between  $\text{Br}_2(l)$  and  $\text{Br}_2(g)$  would not be established if the container were not a closed vessel shown in Figure 13.4.

**Solution**

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the  $\text{Br}_2$  vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

9. Among the solubility rules previously discussed is the statement: All chlorides are soluble except  $\text{Hg}_2\text{Cl}_2$ ,  $\text{AgCl}$ ,  $\text{PbCl}_2$ , and  $\text{CuCl}$ .

(a) Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{PbCl}_2(s)$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

**Solution**

(a)  $K_c = [\text{Ag}^+][\text{Cl}^-] < 1$ .  $\text{AgCl}$  is insoluble; thus, the concentrations of ions are much less than 1 M;

(b)  $K_c = \frac{1}{[\text{Pb}^{2+}][\text{Cl}^-]^2} > 1$  because  $\text{PbCl}_2$  is insoluble and formation of the solid will reduce the concentration of ions to a low level ( $< 1 M$ ).

11. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene:  $3\text{C}_2\text{H}_2(g) \rightleftharpoons \text{C}_6\text{H}_6(g)$ .

Which value of  $K_c$  would make this reaction most useful commercially?  $K_c \approx 0.01$ ,  $K_c \approx 1$ , or  $K_c \approx 10$ . Explain your answer.

**Solution**

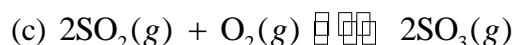
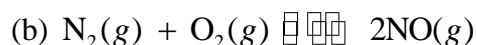
Since  $K_c = \frac{[\text{C}_6\text{H}_6]}{[\text{C}_2\text{H}_2]^3}$ , a value of  $K_c \approx 10$  means that  $\text{C}_6\text{H}_6$  predominates over  $\text{C}_2\text{H}_2$ . In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

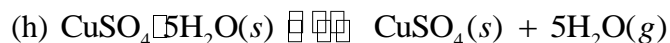
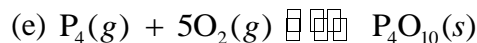
13. For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$  for a titration reaction?

**Solution**

$K_c > 1$ ; the product must be formed in overwhelmingly large proportions.

15. Write the mathematical expression for the reaction quotient,  $Q_c$ , for each of the following reactions:



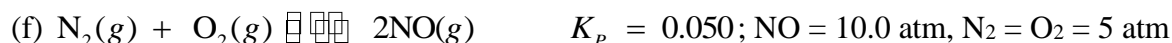
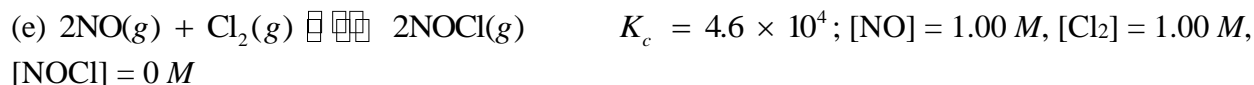
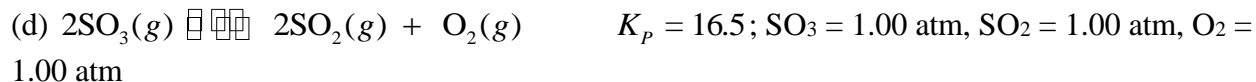
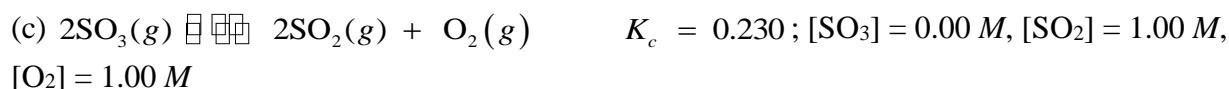
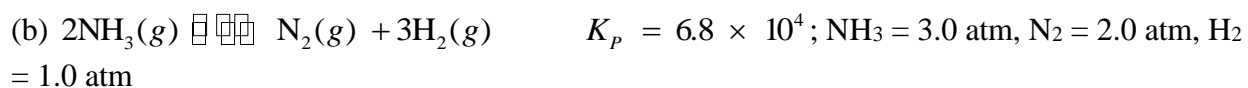
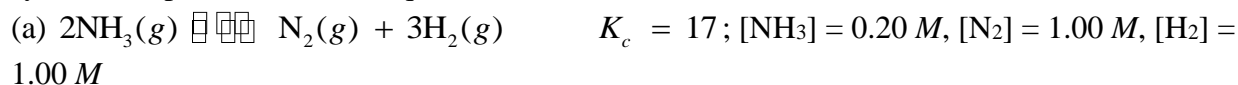


Solution

(a)  $Q_c = \frac{[\text{CH}_3\text{Cl}][\text{HCl}]}{[\text{CH}_4][\text{Cl}_2]}$ ; (b)  $Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$ ; (c)  $Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$ ; (d)  $Q_c = [\text{SO}_2]$ ; (e)

$Q_c = \frac{1}{[\text{P}_4][\text{O}_2]^5}$ ; (f)  $Q_c = \frac{[\text{Br}]^2}{[\text{Br}_2]}$ ; (g)  $Q_c = \frac{[\text{CO}_2]}{[\text{CH}_4][\text{O}_2]^2}$ ; (h)  $Q_c = [\text{H}_2\text{O}]^5$

17. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.



Solution

(a)  $Q_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{(1.00)(1.00)^3}{(0.20)^2} = 25$

 $Q_c > K_c$ , proceeds left;

(b)  $Q_p = \frac{P_{\text{N}_2}(P_{\text{H}_2})^3}{(P_{\text{NH}_3})^2} = \frac{(2.0)(1.0)^3}{(3.0)^2} = 0.22$

 $Q_p < K_p$ , proceeds right;

(c)  $Q_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{(1.00)^2(1.00)}{(0)} = \text{undefined}$

 $Q_c > K_c$ , proceeds left;

(d)  $Q_p = \frac{(P_{\text{SO}_2})^2 P_{\text{O}_2}}{(P_{\text{SO}_3})^2} = \frac{(1.00)^2(1.00)}{(1.00)^2} = 1.00$

 $Q_p < K_p$ , proceeds right;

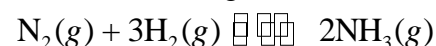
$$(e) Q_p = \frac{(P_{\text{NOCl}})^2}{(P_{\text{NO}})^2 P_{\text{Cl}_2}} = \frac{(0)^2}{(1.00)^2 (1.00)} = 0$$

$Q_p < K_p$ , proceeds right;

$$(f) Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(10.0)^2}{(5.00)(5.00)} = 4$$

$Q_c > K_c$ , proceeds left

19. The following reaction has  $K_p = 4.50 \times 10^{-5}$  at 720 K.



If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium?  $P(\text{NH}_3) = 93 \text{ atm}$ ,  $P(\text{N}_2) = 48 \text{ atm}$ , and  $P(\text{H}_2) = 52 \text{ atm}$

Solution

The reaction quotient expression for this problem is  $Q_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$ . Plugging in the given

values of partial pressures gives  $\frac{(93)^2}{((48) \times (52)^3)}$ , so  $Q_p = 1.3 \times 10^{-3}$ . Since this value is larger

than  $K_p$  ( $4.50 \times 10^{-5}$ ), the system will shift toward the reactants to reach equilibrium.

21. Which of the systems described in Exercise 15 are homogeneous equilibria? Which are heterogeneous equilibria?

Solution

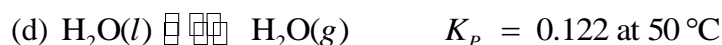
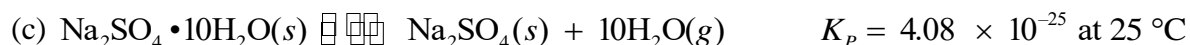
(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

23. For which of the reactions in Exercise 15 does  $K_c$  (calculated using concentrations) equal  $K_p$  (calculated using pressures)?

Solution

When the number of gaseous components are the same on both sides of the equilibrium expression,  $K_c$  will equal  $K_p$ . This situation occurs in (a) and (b).

25. Convert the values of  $K_c$  to values of  $K_p$  or the values of  $K_p$  to values of  $K_c$ .

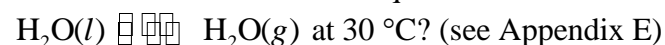


Solution

$K_p = K_c (RT)^{\Delta n}$ , where  $\Delta n$  is the sum of gaseous products minus the sum of gaseous reactants.

(a)  $\Delta n = (2) - (1 + 3) = -2$ ,  $K_p = 0.50[0.08206 \times 673.15]^{-2} = 1.6 \times 10^{-4}$ ; (b)  $\Delta n = (2) - (1 + 1) = 0$ ,  $K_p = K_c(RT)^0 = K_c = 50.2$ ; (c)  $\Delta n = (10) - (0) = 10$ ,  $K_c = K_p(RT)^{-\Delta n}$ ,  $K_c = 4.08 \times 10^{-25}[0.08206 \times 298.15]^{-10} = 5.34 \times 10^{-39}$ ; (d)  $\Delta n = (1) - (0) = 1$ ,  $K_c = 0.122(0.08206 \times 323.15)^{-1} = 4.60 \times 10^{-3}$

27. What is the value of the equilibrium constant expression for the change



Solution

The equilibrium expression for this transformation is  $K_p = P_{\text{H}_2\text{O}}$ . The vapor pressure of  $\text{H}_2\text{O}$  at  $30^\circ\text{C}$  is 31.8 torr. Converting to atmospheres gives  $31.8 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.042 \text{ atm}$ .

Therefore,  $K_p = P_{\text{H}_2\text{O}} = 0.042$ .

29. Write the reaction quotient expression for the ionization of  $\text{NH}_3$  in water.

Solution

$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$ . Because the concentration of water is a constant, the term  $[\text{H}_2\text{O}]$  is normally incorporated into the reaction quotient as well as the final

equilibrium constant.  $Q_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$

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## Chemistry 2e

## 13: Fundamental Equilibrium Concepts

## 13.3: Shifting Equilibria: Le Châtelier's Principle

31. The following equation represents a reversible decomposition:



Under what conditions will decomposition in a closed container proceed to completion so that no  $\text{CaCO}_3$  remains?

**Solution**

The amount of  $\text{CaCO}_3$  must be so small that  $P_{\text{CO}_2}$  is less than  $K_P$  when the  $\text{CaCO}_3$  has completely decomposed. In other words, the starting amount of  $\text{CaCO}_3$  cannot completely generate the full  $P_{\text{CO}_2}$  required for equilibrium.

33. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

**Solution**

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

34. The following reaction occurs when a burner on a gas stove is lit:



Is an equilibrium among  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  established under these conditions? Explain your answer.

**Solution**

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

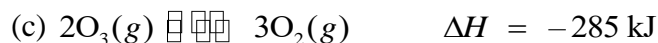
36. Suggest four ways in which the concentration of hydrazine,  $\text{N}_2\text{H}_4$ , could be increased in an equilibrium described by the following equation:



**Solution**

Add  $\text{N}_2$ ; add  $\text{H}_2$ ; decrease the container volume; heat the mixture.

38. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?



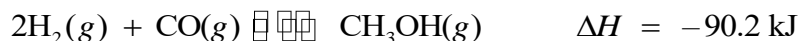
**Solution**

(a)  $T$  increase = shift right,  $V$  decrease = shift left; (b)  $T$  increase = shift right,  $V$  decrease = no effect; (c)  $T$  increase = shift left,  $V$  decrease = shift left; (d)  $T$  increase = shift left,  $V$  decrease = shift right.

## 13.3: Shifting Equilibria: Le Châtelier's Principle

40. Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

(a) Write the expression for the equilibrium constant ( $K_c$ ) for the reversible reaction



(b) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if more  $\text{H}_2$  is added?

(c) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CO}$  is removed?

(d) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CH}_3\text{OH}$  is added?

(e) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if the temperature of the system is increased?

(f) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if more catalyst is added?

Solution

(a)  $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2[\text{CO}]}$ ; (b)  $[\text{H}_2]$  increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  increases; (c)  $[\text{H}_2]$

increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  decreases; (d)  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  increases; (e)  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  decreases; (f) no changes.

42. Water gas, a mixture of  $\text{H}_2$  and  $\text{CO}$ , is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction



(b) What will happen to the concentration of each reactant and product at equilibrium if more  $\text{C}$  is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2\text{O}$  is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if  $\text{CO}$  is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

Solution

(a)  $K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$ ; (b)  $[\text{H}_2\text{O}]$  no change,  $[\text{CO}]$  no change,  $[\text{H}_2]$  no change; (c)  $[\text{H}_2\text{O}]$

decreases,  $[\text{CO}]$  decreases,  $[\text{H}_2]$  decreases; (d)  $[\text{H}_2\text{O}]$  increases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  decreases; (e)  $[\text{H}_2\text{O}]$  decreases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

44. Ammonia is a weak base that reacts with water according to this equation:



Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of  $\text{NaOH}$

(b) Addition of  $\text{HCl}$

(c) Addition of  $\text{NH}_4\text{Cl}$

**Solution**

Only (b). In (a), addition of a strong base forces the equilibrium toward forming more  $\text{NH}_3(aq)$ . In (b), the addition of  $\text{HCl}$  consumes  $\text{OH}^-$ , shifting the equilibrium right and increasing the conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$ . In (c),  $\text{NH}_4^+$  ion causes the equilibrium to shift to the left, forming more  $\text{NH}_3(aq)$ .

46. Suggest two ways in which the equilibrium concentration of  $\text{Ag}^+$  can be reduced in a solution of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ag}^+$ , and  $\text{NO}_3^-$ , in contact with solid  $\text{AgCl}$ .

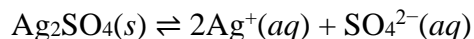


$$\Delta H = -65.9 \text{ kJ}$$

**Solution**

Add  $\text{NaCl}$  or some other salt that produces  $\text{Cl}^-$  to the solution. Cooling the solution forces the equilibrium to the right, precipitating more  $\text{AgCl}(s)$ .

48. A solution is saturated with silver sulfate and contains excess solid silver sulfate:



A small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive  $\text{Ag}^+$  ions. Explain this observation.

**Solution**

Though the solution is saturated, the dynamic nature of the solubility equilibrium means the opposing processes of solid dissolution and precipitation continue to occur (just at equal rates, meaning the dissolved ion concentrations and the amount of undissolved solid remain constant). The radioactive  $\text{Ag}^+$  ions detected in the solution phase come from dissolution of the added solid, and their presence is countered by precipitation of nonradioactive  $\text{Ag}^+$ .

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*Chemistry 2e*  
**13: Fundamental Equilibrium Concepts**  
**13.4: Equilibrium Calculations**

50. A reaction is represented by this equation:



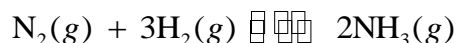
(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations  $\leq 1 M$ , identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

Solution

$K_c = \frac{[C]^2}{[A][B]^2}$ . There are many different sets of equilibrium concentrations; two are  $[A] = 0.1 M$ ,  $[B] = 0.1 M$ ,  $[C] = 1 M$ ; and  $[A] = 0.01$ ,  $[B] = 0.250$ ,  $[C] = 0.791$ .

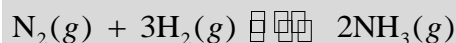
52. What is the value of the equilibrium constant at 500 °C for the formation of  $NH_3$  according to the following equation?



An equilibrium mixture of  $NH_3(g)$ ,  $H_2(g)$ , and  $N_2(g)$  at 500 °C was found to contain 1.35 M  $H_2$ , 1.15 M  $N_2$ , and  $4.12 \times 10^{-1} M NH_3$ .

Solution

The reaction may be written as



The equilibrium constant for the reaction is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(4.12 \times 10^{-1})^2}{(1.15)(1.35)^3} = 0.0600 = 6.00 \times 10^{-2}$$

54. A 0.72-mol sample of  $PCl_5$  is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of  $PCl_3(g)$  and 0.40 mol of  $Cl_2(g)$ . Calculate the value of the equilibrium constant for the decomposition of  $PCl_5$  to  $PCl_3$  and  $Cl_2$  at this temperature.

Solution

The decomposition of  $PCl_5$  to  $PCl_3$  and  $Cl_2$  is given as



$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Let  $x =$  change in  $[PCl_5]$ .

	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
Initial concentration (M)	0.72	0	0
Change (M)	$-x$	$x$	$x$
Equilibrium concentration (M)	$0.72 - x = 0.32$	$0 + x = 0.40$	$0 + x = 0.40$

$$K_c = \frac{(0.40)(0.40)}{(0.32)} = 0.50$$

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13.4: Equilibrium Calculations

56. Calculate the value of the equilibrium constant  $K_P$  for the reaction

$2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$  from these equilibrium pressures: NO, 0.050 atm;  $\text{Cl}_2$ , 0.30 atm; NOCl, 1.2 atm.

Solution

$$K_P = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]} = \frac{(1.2)^2}{(0.050)^2(0.30)} = \frac{1.44}{(2.5 \times 10^{-3})(0.30)} = 1.9 \times 10^3$$

58. A sample of ammonium chloride was heated in a closed container.



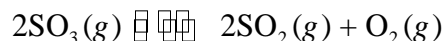
At equilibrium, the pressure of  $\text{NH}_3(g)$  was found to be 1.75 atm. What is the value of the equilibrium constant  $K_P$  for the decomposition at this temperature?

Solution

Because the decomposition must generate the same pressure of HCl as  $\text{NH}_3$ , 1.75 atm of HCl must be present.  $K_P = P_{\text{NH}_3} P_{\text{HCl}} = (1.75 \text{ atm})(1.75 \text{ atm}) = 3.06$

60. Complete the partial ICE tables below.

(a)



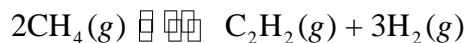
change    \_\_\_                    \_\_\_            +x

(b)



change    \_\_\_            +x                    \_\_\_            \_\_\_

(c)



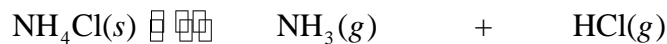
change    \_\_\_                    +x                    \_\_\_

(d)



change    \_\_\_            +x                    \_\_\_            \_\_\_

(e)



change                                    +x                    \_\_\_

(f)



change                    +x                    \_\_\_

Solution

(a)  $-2x, +2x$ ; (b)  $+\frac{4}{3}x, -\frac{2}{3}x, -2x$ ; (c)  $-2x, +3x$ ; (d)  $+x, -x, -3x$ ; (e)  $+x$ ; (f)  $-\frac{1}{4}x$

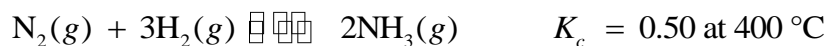
62. Why are there no changes specified for Ni in Exercise 60, part (f)? What property of Ni does change?

Solution

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Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

64. Analysis of the gases in a sealed reaction vessel containing  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  at equilibrium at  $400^\circ\text{C}$  established the concentration of  $\text{N}_2$  to be  $1.2\text{ M}$  and the concentration of  $\text{H}_2$  to be  $0.24\text{ M}$ .



Calculate the equilibrium molar concentration of  $\text{NH}_3$ .

**Solution**

Write the equilibrium constant expression and solve for  $[\text{NH}_3]$ .

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{[\text{NH}_3]^2}{[1.2][0.24]^3} = 0.50$$

$$[\text{NH}_3]^2 = 1.2 \times (0.24)^3 \times 0.50 = 0.0083$$

$$[\text{NH}_3] = 9.1 \times 10^{-2}\text{ M}$$

66. What is the pressure of  $\text{BrCl}$  in an equilibrium mixture of  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{BrCl}$  if the pressure of  $\text{Cl}_2$  in the mixture is  $0.115\text{ atm}$  and the pressure of  $\text{Br}_2$  in the mixture is  $0.450\text{ atm}$ ?



**Solution**

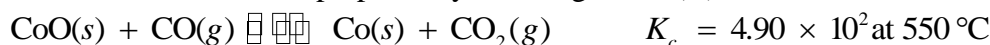
Write the equilibrium constant expression and solve for  $P_{\text{BrCl}}$ .

$$K_p = \frac{(P_{\text{BrCl}})^2}{P_{\text{Cl}_2} P_{\text{Br}_2}} = \frac{(P_{\text{BrCl}})^2}{(0.115)(0.450)} = 4.7 \times 10^{-2}$$

$$(P_{\text{BrCl}})^2 = 0.115 \times 0.450 \times 4.7 \times 10^{-2} = 2.43 \times 10^{-3}\text{ atm}$$

$$P_{\text{BrCl}} = 4.9 \times 10^{-2}\text{ atm}$$

68. Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.



What concentration of  $\text{CO}$  remains in an equilibrium mixture with  $[\text{CO}_2] = 0.100\text{ M}$ ?

**Solution**

Write the equilibrium constant expression and solve for  $[\text{CO}]$ .

$$K_c = \frac{[\text{CO}_2]}{[\text{CO}]} = \frac{0.100}{[\text{CO}]} = 4.90 \times 10^2$$

$$[\text{CO}] = \frac{0.100}{4.90 \times 10^2} = 2.04 \times 10^{-4}\text{ M}$$

70. Sodium sulfate 10-hydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , dehydrates according to the equation



What is the pressure of water vapor at equilibrium with a mixture of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$ ?

**Solution**

Because two of the substances involved in the equilibrium are solids, their activities are 1, and their pressures are constant and do not appear in the equilibrium expression.

$$K_p = 4.08 \times 10^{-25} = (P_{\text{H}_2\text{O}})^{10}$$

$$P_{\text{H}_2\text{O}} = \sqrt[10]{4.08 \times 10^{-25}} = 3.64 \times 10^{-3}\text{ atm}$$

72. A student solved the following problem and found the equilibrium concentrations to be  $[\text{SO}_2] = 0.590\text{ M}$ ,  $[\text{O}_2] = 0.0450\text{ M}$ , and  $[\text{SO}_3] = 0.260\text{ M}$ . How could this student check the work without reworking the problem? The problem was: For the following reaction at  $600^\circ\text{C}$ :

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What are the equilibrium concentrations of all species in a mixture that was prepared with  $[\text{SO}_3] = 0.500 M$ ,  $[\text{SO}_2] = 0 M$ , and  $[\text{O}_2] = 0.350 M$ ?

**Solution**

Calculate  $Q$  based on the calculated concentrations and see if it is equal to  $K_c$ . Because  $Q$  does equal 4.32, the system must be at equilibrium.

74. Assume that the change in concentration of  $\text{N}_2\text{O}_4$  is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of  $\text{N}_2\text{O}_4$  with chloroform as the solvent.



(b) Confirm that the change is small enough to be neglected.

**Solution**

(a) Write the starting conditions, change, and equilibrium constant in tabular form.

	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$
<b>Initial concentration (M)</b>	0	0.129
<b>Change (M)</b>	+2x	-x
<b>Equilibrium concentration (M)</b>	2x	0.129 - x

Since  $K$  is very small, ignore  $x$  in comparison with 0.129 M. The equilibrium expression is

$$K_c = 1.07 \times 10^{-5} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{(0.129 - x)} = \frac{(2x)^2}{0.129}$$

$$x^2 = \frac{0.129 \times 1.07 \times 10^{-5}}{4} = 3.45 \times 10^{-7}$$

$$x = 5.87 \times 10^{-4}$$

The concentrations are:

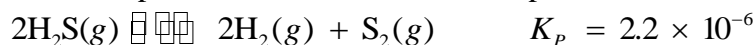
$$[\text{NO}_2] = 2x = (5.87 \times 10^{-4})(2) = 1.17 \times 10^{-3} M$$

$$[\text{N}_2\text{O}_4] = 0.129 - x = 0.129 - 5.87 \times 10^{-4} = 0.128 M$$

(b) The assumption that  $x$  is negligibly small compared to 0.129 is confirmed by comparing the initial concentration of the  $\text{N}_2\text{O}_4$  to its concentration at equilibrium (they differ by just 1 in the least significant digit's place).

76. Assume that the change in pressure of  $\text{H}_2\text{S}$  is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of  $\text{H}_2\text{S}$  with an initial pressure of 0.824 atm.



(b) Confirm that the change is small enough to be neglected.

**Solution**

(a) Write the balanced equation, and then set up a table with initial pressures and the changed pressures using  $x$  as the change in pressure. The simplest way to find the coefficients for the  $x$  values is to use the coefficient in the balanced equation.

	$2\text{H}_2\text{S}(g) \rightleftharpoons 2\text{H}_2(g) + \text{S}_2(g)$		
Initial pressure (atm)	0.824	0	0
Change (atm)	-2x	+2x	+x
Equilibrium pressure (atm)	0.824 - 2x	2x	x

$$K_p = 2.2 \times 10^{-6} = \frac{(P_{\text{S}_2})(P_{\text{H}_2})^2}{(P_{\text{H}_2\text{S}})^2} = \frac{[x][2x]^2}{[0.824 - 2x]^2}$$

Neglecting the change in reactant concentration (2x), as instructed, yields:

$$2.2 \times 10^{-6} = \frac{[x][2x]^2}{[0.824]^2}$$

$$2.2 \times 10^{-6} = \frac{4x^3}{[0.679]}$$

$$1.494 \times 10^{-6} = 4x^3$$

$$3.73 \times 10^{-7} = x^3$$

$$7.20 \times 10^{-3} = x$$

Final equilibrium pressures:

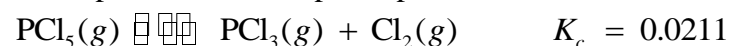
$$[\text{H}_2\text{S}] = 0.824 - 2x = 0.824 - 2(7.20 \times 10^{-3}) = 0.824 - 0.0144 = 0.810 \text{ atm}$$

$$[\text{H}_2] = 2x = 2(7.2 \times 10^{-3}) = 0.014 \text{ atm}$$

$$[\text{S}_2] = [x] = 0.0072 \text{ atm}$$

(b) The assumption that 2x is negligibly small compared to 0.824 is confirmed by comparing the initial concentration of the H<sub>2</sub>S to its concentration at equilibrium (0.824 atm versus 0.810 atm, a difference of less than 2%).

78. What are the concentrations of PCl<sub>5</sub>, PCl<sub>3</sub>, and Cl<sub>2</sub> in an equilibrium mixture produced by the decomposition of a sample of pure PCl<sub>5</sub> with [PCl<sub>5</sub>] = 2.00 M?



Solution

As all species are gases and are in M concentration units, a simple K<sub>c</sub> equilibrium can be solved using the balanced equation:

	$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$		
Initial concentration (M)	2.00	0	0
Change (M)	-x	+x	+x
Equilibrium concentration (M)	2.00 - x	x	x

$$K_c = 0.0211 = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{[x][x]}{[2.00 - x]}$$

$$0.0211 = \frac{x^2}{[2.00 - x]} = 0.0422 - 0.0211x = x^2$$

Begin by arranging the terms in the form of the quadratic equation:

$$ax^2 + bx + c = 0$$

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$$x^2 + 0.0211x - 0.0422 = 0$$

Next, solve for  $x$  using the quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0422)}}{2(1)}$$
$$= \frac{-0.0211 \pm \sqrt{0.0004452 + 0.1688}}{2} = \frac{-0.0211 \pm 0.4114}{2}$$

$$= 0.195 \text{ M or } -0.216 \text{ M}$$

Since concentrations must be positive, only the positive root (0.195) is physically significant. The final equilibrium concentrations are:  $[\text{PCl}_5] = 2.00 - x = 2.00 - 0.195 = 1.80 \text{ M}$ ;  $[\text{PCl}_3] = [\text{Cl}_2] = x = 0.195 \text{ M}$ .

79. Calculate the number of grams of HI that are at equilibrium with 1.25 mol of  $\text{H}_2$  and 63.5 g of iodine at 448 °C.



Solution

The number of moles of  $\text{I}_2$  is

$$\text{mol} = \frac{63.5 \text{ g}}{253.809 \text{ g mol}^{-1}} = 0.250 \text{ mol I}_2$$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

The unit for each concentration term is moles per liter. If the volume were known for this exercise, the number of moles in each term should be divided by this volume. However, there are two terms in the numerator and two terms in the denominator, so these volumes cancel one another. Consequently, for any expression with the same number of numerator terms as denominator terms, the number for moles can be used in place of moles per liter. In this exercise, the volume is not needed even though it is given.

$$(\text{mol HI})^2 = K \times \text{mol H}_2 \times \text{mol I}_2$$
$$= 50.2 \times 1.25 \text{ mol} \times 0.250 \text{ mol}$$
$$= 15.7 \text{ mol}^2$$

$$\text{mol HI} = \sqrt{15.7 \text{ mol}^2} = 3.96 \text{ mol}$$

$$\text{Mass(HI)} = 3.96 \text{ mol} \times 127.9124 \text{ g/mol} = 507 \text{ g}$$

81. What is the minimum mass of  $\text{CaCO}_3$  required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant ( $K_c$ ) is 0.50 for the decomposition reaction of  $\text{CaCO}_3$  at that temperature?



Solution

At equilibrium the concentration of  $\text{CO}_2 = K_c = 0.50 \text{ M}$ . The number of moles  $\text{CO}_2$  in the system is then  $\text{mol CO}_2 = 6.5 \text{ L} \times 0.50 \text{ mol/L} = 3.3 \text{ mol}$ . The minimum amount of  $\text{CaCO}_2$  must then exceed:

$$3.3 \text{ mol CO}_2 \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol CO}_2} = 3.3 \text{ mol CaCO}_3$$

$$3.3 \text{ mol CO}_2 \times \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = 330 \text{ g}$$

84. The equilibrium constant ( $K_c$ ) for this reaction is 5.0 at a given temperature.



- (a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H<sub>2</sub> in a liter. How many moles of CO<sub>2</sub> were there in the equilibrium mixture?
- (b) Maintaining the same temperature, additional H<sub>2</sub> was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H<sub>2</sub> in a liter. How many moles of CO<sub>2</sub> were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

Solution

(a) For this reaction,  $K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 5.0$ . The concentrations at equilibrium are 0.20M

CO, 0.30 M H<sub>2</sub>O, and 0.90 M H<sub>2</sub>. Substitution gives  $K = 5.0 = \frac{[\text{CO}_2][0.90]}{[0.20][0.30]}$ ;

$[\text{CO}_2] = \frac{5.0(0.20)(0.30)}{0.90} = 0.33 \text{ M}$ ; Amount of CO<sub>2</sub> = 0.33 mol × 1 = 0.33 mol.

(b) At the particular temperature of reaction,  $K_c$  remains constant at 5.0. The new concentrations are 0.40 M CO, 0.30 M H<sub>2</sub>O, and 1.2 M H<sub>2</sub>.

$$\frac{[\text{CO}_2](1.2)}{(0.40)(0.30)} = 5.0$$

$$[\text{CO}_2] = 0.50 \text{ M}$$

Amount of CO<sub>2</sub> = 0.50 mol × 1 = 0.50 mol. Added H<sub>2</sub> forms some water as a result of a shift to the left after H<sub>2</sub> is added.

86. Consider the equilibrium



- (a) What is the expression for the equilibrium constant ( $K_c$ ) of the reaction?
- (b) How must the concentration of NH<sub>3</sub> change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
- (c) If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of NO<sub>2</sub>?
- (d) If the change in the pressure of NO<sub>2</sub> is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O<sub>2</sub> change?

Solution

$$(a) K_c = \frac{[\text{NH}_3]^4[\text{O}_2]^7}{[\text{NO}_2]^4[\text{H}_2\text{O}]^6}$$

- (b) Because [NH<sub>3</sub>] is in the numerator of  $K_c$ , [NH<sub>3</sub>] must increase for  $Q_c$  to reach  $K_c$ .
- (c) The increase in system volume would lower the partial pressures of all reactants (including NO<sub>2</sub>).
- (d) The relative changes in pressures are related by the stoichiometry of the reaction.

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$$P_{\text{O}_2} = \frac{7}{4} P_{\text{NO}_2} = \frac{7}{4} (28 \text{ torr}) = 49 \text{ torr}$$

88. Liquid  $\text{N}_2\text{O}_3$  is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to  $\text{NO}$  and  $\text{NO}_2$ . At  $25^\circ\text{C}$ , a value of  $K_P = 1.91$  has been established for this decomposition. If  $0.236$  moles of  $\text{N}_2\text{O}_3$  are placed in a  $1.52\text{-L}$  vessel at  $25^\circ\text{C}$ , calculate the equilibrium partial pressures of  $\text{N}_2\text{O}_3(\text{g})$ ,  $\text{NO}_2(\text{g})$ , and  $\text{NO}(\text{g})$ .

**Solution**

Write the balanced equilibrium expression. With all of the species as gases, it is a straightforward  $K_P$  problem to solve. However, *all* species must be converted to pressures, from other units related to concentration. For  $\text{N}_2\text{O}_3$ , with  $0.236$  mol in  $1.52$  L at  $25^\circ\text{C}$ :

$$PV = nRT$$

$$\begin{aligned} P &= \frac{n}{V} RT \\ &= \frac{0.236 \text{ mol}}{1.52 \text{ L}} \times \frac{(0.08206 \text{ L atm})(298.15 \text{ K})}{\text{mol K}} \\ &= 3.80 \text{ atm} \end{aligned}$$

Write the balanced equation and the equilibrium changes:

	$\text{N}_2\text{O}_3(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \text{NO}_2(\text{g})$		
Initial pressure (atm)	3.80	0	0
Change (atm)	$-x$	$+x$	$+x$
Equilibrium pressure (atm)	$3.80 - x$	$x$	$x$

$$K_P = \frac{(P_{\text{NO}})(P_{\text{NO}_2})}{(P_{\text{N}_2\text{O}_3})}$$

$$1.91 = \frac{x^2}{(3.80 - x)}$$

$$7.258 - 1.91x = x^2$$

$$0 = x^2 + 1.91x - 7.258$$

$$0 = ax^2 + bx + c$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-1.91 \pm \sqrt{(1.91)^2 - 4(1)(-7.258)}}{2(1)}$$

$$= \frac{-1.91 \pm \sqrt{3.648 + 29.032}}{2}$$

$$= \frac{-1.91 \pm \sqrt{32.680}}{2}$$

$$= \frac{-1.91 \pm 5.717}{2}$$

$$= 1.90 \text{ atm or } -3.81 \text{ atm}$$



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As negative pressure is physically relevant and so the positive root is used. The final pressures are:  $P_{\text{N}_2\text{O}_3} = 3.80 - x = 3.80 - 1.90 = 1.90 \text{ atm}$  and  $P_{\text{NO}} = P_{\text{NO}_2} = x = 1.90 \text{ atm}$ .

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