CHAPTER 17 EQUILIBRIUM: THE EXTENT OF CHEMICAL REACTIONS

END–OF–CHAPTER PROBLEMS

17.1 If the rate of the forward reaction exceeds the rate of reverse reaction, products are formed faster than they are consumed. The change in reaction conditions results in more products and less reactants. A change in reaction conditions can result from a change in concentration or a change in temperature. If concentration changes, product concentration increases while reactant concentration decreases, but the *K*^c remains unchanged because the *ratio* of products and reactants remains the same. If the increase in the forward rate is due to a change in temperature, the rate of the reverse reaction also increases. The equilibrium ratio of product concentration to reactant concentration is no longer the same. Since the rate of the forward reaction increases more than the rate of the reverse reaction, K_c increases (numerator, [products], is larger and denominator, [reactants], is smaller).

$$
K_{\rm c} = \frac{\text{[products]}}{\text{[reactants]}}
$$

- 17.2 The faster the rate and greater the yield, the more useful the reaction will be to the manufacturing process.
- 17.3 A system at equilibrium continues to be very dynamic at the molecular level. Reactant molecules continue to form products, but at the same rate that the products decompose to re-form the reactants.
- 17.4 If *K* is very large, the reaction goes nearly to completion. A large value of *K* means that the numerator is much larger than the denominator in the *K* expression. A large numerator, relative to the denominator, indicates that most of the reactants have reacted to become products. $K = \frac{|\text{products}|}{\sqrt{1 - \frac{1}{n}}}$ | reactants | products reactants
- 17.5 One cannot say with certainty whether the value of *K* for the phosphorus plus oxygen reaction is large or small (although it likely is large). However, it is certain that the reaction proceeds very fast.
- 17.6 **No**, the value of *Q* is determined by the mass action expression with arbitrary concentrations for products and reactants. Thus, its value is not constant.
- 17.7 The equilibrium constant expression is $K = [O_2]$ (we do not include solid substances in the equilibrium expression). If the temperature remains constant, *K* remains constant. If the initial amount of Li_2O_2 present was sufficient to reach equilibrium, the amount of O_2 obtained will be constant, regardless of how much $Li_2O_2(s)$ is present.
- 17.8 a) On the graph, the concentration of HI increases at twice the rate that H_2 decreases because the stoichiometric ratio in the balanced equation is 1H2: 2HI. *Q* for a reaction is the ratio of concentrations of products to concentrations of reactants. As the reaction progresses the concentration of reactants H_2 and I_2 decrease and the concentration of product HI increases, which means that *Q* increases as a function of time.

$$
H_2(g) + I_2(g) = 2HI(g)
$$
 $Q = \frac{[HI]^2}{[H_2][I_2]}$

The value of *Q* increases as a function of time until it reaches the value of *K*.

b) No, Q would still increase with time because the $[I_2]$ would decrease in exactly the same way as $[H_2]$ decreases.

17.9 A homogeneous equilibrium reaction exists when **all** the components of the reaction are in the same phase (i.e., gas, liquid, solid, aqueous).

$$
2NO(g) + O_2(g) \leq 2NO_2(g)
$$

A heterogeneous equilibrium reaction exists when the components of the reaction are in different phases. $Ca(HCO_3)_2(aq) = CaCO_3(s) + H_2O(l) + CO_2(g)$

17.10
$$
1/2N_2(g) + 1/2O_2(g) \leq NO(g)
$$

\n
$$
Q_{c(\text{form})} = \frac{[NO]}{[N_2]^{1/2} [O_2]^{1/2}}
$$
\n
$$
NO(g) \leq 1/2N_2(g) + 1/2O_2(g)
$$
\n
$$
Q_{c(\text{decomp})} = \frac{[N_2]^{1/2} [O_2]^{1/2}}{[NO]}
$$

 $Q_{c(decomp)} = 1/Q_{c(form)}$, so the constants do differ (they are the reciprocal of each other).

17.11 Plan: Write the reaction and then the expression for Q. Remember that $Q = \frac{[C]^{\text{c}}[D]}{[D]}$ $|A|$ " $|B|$ $C|^\circ[D]$ A^{μ} [B c r_n d Write the reaction and then the expression for *Q*. Remember that $Q = \frac{1}{\int_{\alpha} \int_{a}^{a} \ln \frac{b}{b}}$ where A and B are

reactants, C and D are products, and *a*, *b*, *c*, and *d* are the stoichiometric coefficients in the balanced equation. Solution:

The balanced equation for the first reaction is

 $3/2H_2(g) + 1/2N_2(g)$ \Rightarrow NH₃(g) (1)

The coefficient in front of NH_3 is fixed at 1 mole according to the description. The reaction quotient for this F_{M} F_{M} T

reaction is
$$
Q_1 = \frac{[NH_3]}{[H_2]^{3/2} [N_2]^{1/2}}
$$
.

In the second reaction, the coefficient in front of N_2 is fixed at 1 mole. $3H_2(g) + N_2(g) \leq 2NH_3(g)$ (2)

The reaction quotient for this reaction is $Q_2 = \frac{L}{|H_2|^3 |N_2|}$ 2 3 3 2 J L¹2 NH H_2 | N $=\frac{\lfloor NH_3\rfloor}{\lfloor .1\rfloor^2}$

 Q_2 is equal to Q_1^2 .

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

17.12 Plan: Remember that $Q_c = \frac{[C]^c [D]}{[C]^c}$ $|A|$ " $|B|$ $C|^c[D]$ A^{μ} [B c Γ n d $=$ $\frac{1}{\int_{A}^{a} \ln \sqrt{a^b}}$ where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are

the stoichiometric coefficients in the balanced equation. Solution:

Solution:

\na)
$$
4NO(g) + O_2(g) \leq 2N_2O_3(g)
$$

\n
$$
Q_c = \frac{[N_2O_3]^2}{[NO]^4 [O_2]}
$$
\nb) $SF_6(g) + 2SO_3(g) \leq 3SO_2F_2(g)$

\n
$$
Q_c = \frac{[SO_2F_2]^3}{[SF_6][SO_3]^2}
$$
\nc) $2SC1F_5(g) + H_2(g) \leq S_2F_{10}(g) + 2HCl(g)$

\n
$$
Q_c = \frac{[S_2F_{10}][HCl]^2}{[SCIF_5]^2 [H_2]}
$$

17.13 a)
$$
2C_2H_6(g) + 7O_2(g) = 4CO_2(g) + 6H_2O(g)
$$

\n
$$
Q_c = \frac{[CO_2]^4 [H_2O]^6}{[C_2H_6]^2 [O_2]^7}
$$
\nb) $CH_4(g) + 4F_2(g) = CF_4(g) + 4HF(g)$
\n
$$
Q_c = \frac{[CF_4][HF]^4}{[CH_4][F_2]^4}
$$
\nc) $2SO_3(g) = 2SO_2(g) + O_2(g)$
\n
$$
Q_c = \frac{[SO_2]^2 [O_2]}{[SO_3]^2}
$$

17.14 Plan: Compare each equation with the reference equation to see how the direction and coefficients have changed. If a reaction has been reversed, the *K* value is the reciprocal of the *K* value for the reference reaction. If the coefficients have been changed by a factor *n*, the *K* value is equal to the original *K* value raised to the *nth* power. Solution:

a) The *K* for the original reaction is *K* c $\left| \mathrm{H}_2 \right|$ $\left| \mathrm{S}_2 \right|$ $| \mathrm{H}_2 \mathrm{S} |$ 2 2 P_2 2 2 H_2 ² [S $_{\rm H_2}$ S =

The given reaction $1/2S_2(g) + H_2(g) \leftrightarrows H_2S(g)$ is the reverse reaction of the original reaction and the coefficients of the original reaction have been multiplied by a factor of 1/2. The equilibrium constant for the reverse reaction is the reciprocal (1/*K*) of the original constant. The *K* value of the original reaction is raised to the 1/2 power.

$$
K_{c (a)} = (1/K_c)^{1/2} = \frac{[H_2S]}{[S_2]^{1/2}[H_2]}
$$

$$
K_{c (a)} = (1/1.6x10^{-2})^{1/2} = 7.90569 = 7.9
$$

b) The given reaction $S = 1.5(0.55 \text{ Hz})$ (c) 1.5/2S (c) in the

b) The given reaction $5H_2S(g) \leftrightarrows 5H_2(g) + 5/2S_2(g)$ is the original reaction multiplied by 5/2. Take the original *K* to the 5/2 power to find *K* of given reaction.

$$
K_{\rm c~(b)} = (K_{\rm c})^{5/2} = \frac{\left[H_2\right]^5 \left[S_2\right]^{5/2}}{\left[H_2 S\right]^5}
$$

$$
K_{\rm c~(b)} = (1.6 \times 10^{-2})^{5/2} = 3.23817 \times 10^{-5} = 3.2 \times 10^{-5}
$$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

17.15
$$
K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}
$$

\na) $K_{c(a)} = [K_c]^{1/2} = \frac{[N_2]^{1/2}[H_2O]}{[NO][H_2]}$
\nThus, $K_{c(a)} = [K_c]^{1/2} = (6.5 \times 10^2)^{1/2} = 25.495 = 25$
\nb) $K_c = [K_c]^{-2} = \frac{[NO]^4 [H_2]^4}{[N_2]^2 [H_2O]^4}$
\n $K_c = [K_c]^{-2} = (6.5 \times 10^2)^{-2} = 2.36686 \times 10^{-6} = 2.4 \times 10^{-6}$

17.16 Plan: The concentration of solids and pure liquids do not change, so their concentration terms are not written in the reaction quotient expression. Remember that stoichiometric coefficients are used as exponents in the expression for the reaction quotient.

Solution:

a)
$$
2Na_2O_2(s) + 2CO_2(g) = 2Na_2CO_3(s) + O_2(g)
$$

\n
$$
Q_c = \frac{[O_2]}{[CO_2]^2}
$$
\nb) $H_2O(l) = H_2O(g)$
\n
$$
Q_c = [H_2O(g)]
$$
 Only the gaseous water is used. The " (g) " is for emphasis.
\nc) $NH_4Cl(s) = NH_3(g) + HCl(g)$
\n
$$
Q_c = [NH_3][HCl]
$$

17.17 a) H₂O(l) + SO₃(g)
$$
\Leftrightarrow
$$
 H₂SO₄(aq)
\n
$$
Q_c = \frac{[H_2SO_4]}{[SO_3]}
$$
\nb) 2KNO₃(s) \Leftrightarrow 2KNO₂(s) + O₂(g)
\n
$$
Q_c = [O_2]
$$
\nc) S₈(s) + 24F₂(g) \Leftrightarrow 8SF₆(g)
\n
$$
Q_c = \frac{[SF_6]^8}{[F_2]^{24}}
$$

17.18 Write balanced chemical equations for each reaction, and then write the appropriate equilibrium expression. a) $4HCI(g) + O_2(g) = 2Cl_2(g) + 2H_2O(g)$

$$
Q_{c} = \frac{[Cl_{2}]^{2} [H_{2}O]^{2}}{[HCl]^{4} [O_{2}]}
$$

b) $2As_{2}O_{3}(s) + 10F_{2}(g) \le 4AsF_{5}(l) + 3O_{2}(g)$

$$
Q_{c} = \frac{[O_{2}]^{3}}{[F_{2}]^{10}}
$$

c) $SF_{4}(g) + 2H_{2}O(l) \le SO_{2}(g) + 4HF(g)$

$$
Q_{c} = \frac{[SO_{2}][HF]^{4}}{[SF_{4}]}
$$

d) $2MoO_{3}(s) + 6XeF_{2}(g) \le 2MoF_{6}(l) + 6Xe(g) + 3O_{2}(g)$

$$
Q_{c} = \frac{[Xe]^{6}[O_{2}]^{3}}{[XeF_{2}]^{6}}
$$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

17.19 Plan: Add the two equations, canceling substances that appear on both sides of the equation. Write the Q_c expression for each of the steps and for the overall equation. Since the individual steps are added, their Q_c 's are multiplied and common terms are canceled to obtain the overall *Q*c. Solution:

a) The balanced equations and corresponding reaction quotients are given below. Note the second equation must be multiplied by 2 to get the appropriate overall equation.

(1)
$$
Cl_2(g) + F_2(g) \qquad \qquad \Rightarrow 2CIF(g)
$$
\n
$$
\frac{(2) \cdot 2CIF(g) + 2F_2(g) \Rightarrow 2CIF_3(g)}{[CIF_2][F_2]}
$$
\n
$$
\frac{(2) \cdot 2CIF(g) + 2F_2(g) \Rightarrow 2CIF_3(g)}{[CIF_2]^2 [F_2]^2}
$$
\n
$$
\text{Overall: } Cl_2(g) + 3F_2(g) \Rightarrow 2CIF_3(g)
$$
\n
$$
Q_2 = \frac{[CIF_3]^2}{[CIF_2]^2 [F_2]^2}
$$
\n
$$
Q_{\text{overall}} = \frac{[CIF_3]^2}{[CI_2][F_2]^3}
$$
\n
$$
Q_2 = \frac{[CIF_3]^2}{[CIF_2][F_2]^3}
$$

b) The reaction quotient for the overall reaction, Q_{overall} , determined from the reaction is:

$$
Q_{\text{overall}} = \frac{[CIF_3]^2}{[CI_2][F_2]^3}
$$

$$
Q_{\text{overall}} = Q_1 Q_2^2 = \frac{[CIF]^2}{[CI_2][F_2]} \times \frac{[CIF_3]^2}{[CIF]^2 [F_2]^2} = \frac{[CIF_3]^2}{[CI_2][F_2]^3}
$$

- 17.20 According to the ideal gas equation, *PV* = *nRT*. Concentration and pressure of gas are directly proportional as long as the temperature is constant: $C = n/V = P/RT$.
- 17.21 *K_c* and K_p are related by the equation $K_p = K_c (RT)^{\Delta n}$, where Δn represents the change in the number of moles of gas in the reaction (moles gaseous products – moles gaseous reactants). When ∆*n* is zero (no change in number of moles of gas), the term $(RT)^{\Delta n}$ equals 1 and $K_c = K_p$. When Δn is not zero, meaning that there is a change in the number of moles of gas in the reaction, then $K_c \neq K_p$.
- 17.22 a) $K_p = K_c (RT)^{\Delta n}$. Since Δn = number of moles gaseous products number of moles gaseous reactants, Δn is a positive integer for this reaction. If ∆*n* is a positive integer, then (*RT*) [∆]*ⁿ* is greater than 1. Thus, *K*^c is multiplied by a number that is greater than 1 to give K_p . K_c is smaller than K_p . b) Assuming that $RT > 1$ (which occurs when $T > 12.2$ K, because 0.0821 (R) x 12.2 = 1), $K_p > K_c$ if the number of moles of gaseous products exceeds the number of moles of gaseous reactants. $K_p < K_c$ when the number of moles of gaseous reactants exceeds the number of moles of gaseous product.

17.23 Plan: Δ*n*_{gas} = moles gaseous products – moles gaseous reactants. a) Number of moles of gaseous reactants = 0; number of moles of gaseous products = 3; $\Delta n_{\rm gas} = 3 - 0 = 3$ Solution: b) Number of moles of gaseous reactants = 1; number of moles of gaseous products = 0; $\Delta n_{\rm gas} = 0 - 1 = -1$ c) Number of moles of gaseous reactants = 0; number of moles of gaseous products = 3; $\Delta n_{\rm gas} = 3 - 0 = 3$

17.24 a)
$$
\Delta n_{\text{gas}} = 1
$$
 b) $\Delta n_{\text{gas}} = -3$ c) $\Delta n_{\text{gas}} = 1$

17.25 Plan: First, determine Δn for the reaction and then calculate K_c using $K_p = K_c (RT)^{\Delta n}$. a) Δn = moles gaseous products – moles gaseous reactants = $1 - 2 = -1$ Solution: $K_{\text{p}} = K_{\text{c}} (RT)^{\Delta n}$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

$$
K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{3.9 \times 10^{-2}}{[(0.0821)(1000.)]^{-1}} = 3.2019 = 3.2
$$

b) Δn = moles gaseous products – moles gaseous reactants = $1 - 1 = 0$

$$
K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{28.5}{\left[(0.0821)(500.) \right]^0} = 28.5
$$

17.26 First, determine Δ*n* for the reaction and then calculate K_c using $K_p = K_c (RT)^{\Delta n}$. a) ∆*n* = moles gaseous products – moles gaseous reactants = 2 – 2 = 0

$$
K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{49}{[(0.0821)(730.)]^0} = 49
$$

b)
$$
\Delta n
$$
 = moles gaseous products – moles gaseous reactants = 2 – 3 = –1

$$
K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.5 \times 10^{10}}{[(0.0821)(500.)]^{-1}} = 1.02625 \times 10^{12} = 1.0x10^{12}
$$

- 17.27 When *Q* < *K*, the reaction proceeds to the **right** to form more products. The reaction quotient and equilibrium constant are determined by [products]/[reactants]. For *Q* to increase and reach the value of *K*, the concentration of products (numerator) must increase in relation to the concentration of reactants (denominator).
- 17.28 a) The reaction is $2D \leftrightarrow E$ and $K_c = \frac{[E]}{[D]^2}$.

Concentration of D = Concentration of E = $(3 \text{ spheres})\left(\frac{0.0100 \text{ mol}}{1 \text{ sphere}}\right)\left(\frac{1}{1.00 \text{ L}}\right) = 0.0300 M$

$$
K_{\rm c} = \frac{\text{[E]}}{\text{[D]}^2} = \frac{\text{[0.0300]}}{\text{[0.0300]}^2} = 33.3333 = 33.3
$$

b) In Scene B the concentrations of D and E are both $0.0300 \text{ mol}/0.500 \text{ L} = 0.0600 \text{ M}$

$$
Q_c = \frac{[E]}{[D]^2} = \frac{[0.0600]}{[0.0600]^2} = 16.66666 = 16.7
$$

B is not at equilibrium. Since $Q_c < K_c$, the reaction will proceed to the right.

In Scene C, the concentration of D is still $0.0600 M$ and the concentration of E is $0.0600 \text{ mol}/0.500 L = 0.120 M$ E E $[0.120]$

$$
Q_c = \frac{[L]}{[D]^2} = \frac{[0.120]}{[0.0600]^2} = 33.3333 = 33.3
$$

Since $Q_c = K_c$ in Scene C, the reaction is at equilibrium.

17.29 Plan: To decide if the reaction is at equilibrium, calculate Q_p and compare it to K_p . If $Q_p = K_p$, then the reaction is at equilibrium. If $Q_p > K_p$, then the reaction proceeds to the left to produce more reactants. If $Q_p < K_p$, then the reaction proceeds to the right to produce more products. Solution:

$$
Q_{\rm p} = \frac{P_{\rm H_2} P_{\rm Br_2}}{P_{\rm HBr}^2} = \frac{(0.010)(0.010)}{(0.20)^2} = 2.5 \times 10^{-3} > K_{\rm p} = 4.18 \times 10^{-9}
$$

 Q_p > K_p , thus, the reaction is **not** at equilibrium and will proceed to the **left** (towards the reactants). Thus, the numerator will decrease in size as products are consumed and the denominator will increase in size as more reactant is produced. Q_p will decrease until $Q_p = K_p$.

17.30
$$
Q_p = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2} = \frac{(0.10)^2 (0.10)}{(0.10)^2} = 0.10 < K_p = 60.6
$$

 Q_p < K_p Thus, the reaction is **not** at equilibrium and will proceed to the **right** (towards the products).

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

17.31 There is insufficient information to calculate the partial pressures of each gas (*T* is not given). There is sufficient information to determine the concentrations and hence Q_c . Convert the K_p given to K_c using $K_p = K_c (RT)^{\Delta n}$. Compare the Q_c to the K_c just calculated and make a prediction.

 Δn = moles gaseous products – moles gaseous reactants = $2 - 2 = 0$ Since $\Delta n = 0$, $K_p = K_c = 2.7$ (Note: If Δn had any other value, we could not finish the calculation without the temperature.)

$$
Q_{\rm c} = \frac{[\rm CO_2][\rm H_2]}{[\rm CO][\rm H_2O]} = \frac{[0.62/2.0][0.43/2.0]}{[0.13/2.0][0.56/2.0]} = 3.662 > K_{\rm c} = 2.7
$$

 $Q_c > K_c$ Thus, the reaction is **not** at equilibrium and will proceed to the **left** (towards the reactants).

- 17.32 When x mol of CH₄ reacts, 2x mol of H₂O also reacts to form x mol of CO₂ and 4x mol of H₂. This is based on the 1:2:1:4 mole ratio in the reaction. The final (equilibrium) concentration of each reactant is the initial concentration minus the amount that reacts. The final (equilibrium) concentration of each product is the initial concentration plus the amount that forms.
- 17.33 a) The approximation applies when the change in concentration from initial to equilibrium is so small that it is insignificant. This occurs when K is small and initial concentration is large. b) This approximation will not work when the change in concentration is greater than 5%. This can occur when [reactant]_{initial} is very small, or when [reactant]_{change} is relatively large due to a large *K*.
- 17.34 Plan: Since all equilibrium concentrations are given in molarities and the reaction is balanced, construct an equilibrium expression and substitute the equilibrium concentrations to find K_c . Solution:

$$
K_{\rm c} = \frac{\text{[H1]}^2}{\text{[H}_2\text{][I}_2]} = \frac{\left[1.87 \times 10^{-3}\right]^2}{\left[6.50 \times 10^{-5}\right] \left[1.06 \times 10^{-3}\right]} = 50.753 = 50.8
$$

17.35
$$
K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{[0.114][0.342]^3}{[0.0225]^2} = 9.0077875 = 9.01
$$

17.36 Plan: Calculate the initial concentration of PCl₅ from the given number of moles and the container volume; the reaction is proceeding to the right, consuming PCl_5 and producing products. There is a 1:1:1 mole ratio between the reactants and products.

Solution:

Initial $[PCl_5] = 0.15 \text{ mol}/2.0 \text{ L} = 0.075 \text{ M}$ Since there is a 1:1:1 mole ratio in this reaction: $x = [PCl₅]$ reacting (-x), and the amount of $PCl₃$ and of $Cl₂$ forming (+x). Concentration (M) PCl₅ (g) $PCl_5(g)$ $\qquad \qquad \Rightarrow \qquad PCl_3(g)$ + 0.075 $Initial$ 0.075 0 0 0 $Cl₂(g)$ Equilibrium $0.075 - x$ Change $-x$ $-x$ $+x$ $+x$

17.37 The reaction table requires that the initial $[H_2]$ and $[F_2]$ be calculated: $[H_2] = 0.10 \text{ mol}/0.50 \text{ L} = 0.20 \text{ M}$; $[F_2] = 0.050$ mol/0.50 L = 0.10 *M*.

17.38 Plan: Two of the three equilibrium pressures are known, as is *K*p. Construct an equilibrium expression and solve for P_{NOC} . Solution:

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

$$
K_{\rm p} = 6.5 \times 10^4 = \frac{P_{\rm NOCl}^2}{P_{\rm NO}^2 P_{\rm Cl_2}}
$$

$$
6.5 \times 10^4 = \frac{P_{\rm NOCl}^2}{(0.35)^2 (0.10)}
$$

$$
P_{\rm NOCl} = \sqrt{(6.5 \times 10^4)(0.35)^2 (0.10)} = 28.2179 = 28 \text{ atm}
$$

A high pressure for NOCl is expected because the large value of K_p indicates that the reaction proceeds largely to the right, i.e., to the formation of products.

17.39
$$
C(s) + 2H_2(g) = CH_4(g)
$$

\n $K_p = \frac{P_{CH_4}}{P_{H_2}^2} = 0.262$
\n $P_{CH_4} = K_p P_{H_2}^2 = (0.262)(1.22)^2 = 0.38996 = 0.390 atm$

17.40 Plan: Use the balanced equation to write an equilibrium expression and to define x. Set up a reaction table, substitute into the K_p expression, and solve for x. Solution:

 $NH_4HS(s) \Leftrightarrow H_2S(g) + NH_3(g)$

 $x = [NH₄H_S]$ reacting (-x), and the amount of $H₂S$ and of NH₃ forming (+x) since there is a 1:1:1 mole ratio between the reactant and products.

(It is not necessary to calculate the molarity of $NH₄HS$ since, as a solid, it is not included in the equilibrium expression.)

17.41
$$
2H_2S(g) = 2H_2(g) + S_2(g)
$$

\n $[H_2S] = 0.45 \text{ mol}/3.0 \text{ L} = 0.15 \text{ M}$
\nConcentration (*M*) $2H_2S(g) = 2H_2(g) + S_2(g)$
\nInitial $0.15 = 0$
\nChange $-2x + 2x + x$
\nEquilibrium $0.15 - 2x = 2x$
\n $K_c = 9.30 \times 10^{-8} = \frac{[H_2]^2 [S_2]}{[H_2S]^2} = \frac{[2 \times 1]^2 [x]}{[0.15 - 2 \times 1]^2}$
\nAssuming $0.15 M - 2 \times 0.15 M$
\n $9.30 \times 10^{-8} = \frac{[2 \times 1]^2 [x]}{[0.15]^2} = \frac{4 \times 3}{0.15^2}$
\n $\times = 8.0575 \times 10^{-4} M$
\n $[H_2] = 2x = 2 (8.0575 \times 10^{-4} M) = 1.6115 \times 10^{-3} = 1.6x10^{-3} M$
\n(Since $(1.6 \times 10^{-3})/(0.15) < 0.05$, the assumption is OK.)

17.42 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of each

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

reactant from the given amounts and container volume, use the balanced equation to define x and set up a reaction table, substitute into the equilibrium expression, and solve for x, from which the concentration of NO is calculated.

Solution:

The initial concentrations of N₂ and O₂ are $(0.20 \text{ mol}/1.0 \text{ L}) = 0.20 M$ and $(0.15 \text{ mol}/1.0 \text{ L}) = 0.15 M$, respectively.

 $N_2(g) + O_2(g)$ \Rightarrow 2NO(*g*) There is a 1:1:2 mole ratio between reactants and products. Concentration (M) $N_2(g)$ + $2(g) + O_2$ **Initial** 0.20 0.15 0 (g) \Rightarrow $2NO(g)$ Change $-x$ $-x$ $+x$ $+2x$ Equilibrium $0.20 - x$ $0.15 - x$ $2x$ (1:1:2 mole ratio) $K_c = 4.10 \times 10^{-4} = \frac{[NO]^2}{[N_2][O_2]}$ 2 2 $\mathbf{I} \mathbf{V}_2$ $= \frac{[NO]^2}{[N_2][O_2]} = \frac{[2x]^2}{[0.20 - x][0.15 - x]}$ $2 x$ ² $\frac{1}{0.20 - x \left| \left[0.15 - x \right] \right|}$ Assume $0.20 M - x \approx 0.20 M$ and $0.15 M - x \approx 0.15 M$ $4.10x10^{-4}$ $[0.20 || 0.15]$ $4x^2$ $=$ $\frac{1}{2}$ $\frac{1}{2$ $x = 1.753568x10^{-3} M$ $x = 1.753568x10^{-3} M$
[NO] = 2x = 2(1.753568x10⁻³ M) = 3.507136x10⁻³ = **3.5x10⁻³** [NO] = 2x = 2(1.753568x10⁻³ *M*) = 3.507136x10⁻³ = **3.5x10⁻³** *M*
(Since $(1.8x10^{-3})/(0.15) < 0.05$, the assumption is OK.)

17.43 $2NO_2(g) = 2NO(g) + O_2(g)$ Pressure (atm) $_2(g)$ $\qquad \qquad \Rightarrow \qquad 2\text{NO}(g) \qquad + \qquad \text{O}_2$ $Initial$ 0.75 0 0 0 $O_2(g)$ Equilibrium $0.75 - 2x$ 2x x Change $-2x$ $+2x$ $+x$ $K_p = 4.48 \times 10^{-13} = \frac{18040_2}{2}$ 2 $R_{\rm NO}^2 P_{\rm O}$ 2 NO $= \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2} = \frac{(2 \text{x})^2 (\text{x})}{(0.75 - 2 \text{x})}$ 2 2 $(2x)^{2}$ (x $0.75 - 2x$ Assume 0.75 atm – $2x \approx 0.75$ atm $4.48x10^{-13} = \frac{(4x^2)(x)}{x^2}$ (0.75) 2 2 $4x^2$)(x 0.75 $=\frac{(4x^2)(x)}{(x^2)^2}=\frac{(4x^3)}{(x^2)^2}$ (0.75) 3 2 4x 0.75 $x = 3.979x10^{-5}$ atm $= 4.0x10^{-5}$ atm O_2 *P* $N_{\text{NO}} = 2x = 2(3.979x10^{-5} \text{ atm}) = 7.958x10^{-5} = 8.0x10^{-5} \text{ atm NO}$

17.44 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of ICl from the given amount and container volume, use the balanced equation to define x and set up a reaction table, substitute into the equilibrium expression, and solve for x, from which the equilibrium concentrations can be calculated. S_{olute}

Solution:			
[ICI]	0.500 mol/5.00 L) = 0.100 M		
Concentration (M)	2ICI(g)	$\frac{1}{2}(g)$	$\frac{1}{2}(g)$
Initial	0.100	0	0
Change	$-2x$	$+x$	$+x$
Equilibrium	0.100 - 2x	x	x
$K_c = 0.110 = \frac{[I_2][CI_2]}{[ICI]^2} = \frac{[x][x]}{[0.100 - 2x]^2}$			

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

$$
0.110 = {\frac{[x]}{[0.100 - 2x]}^2}
$$
 Take the square root of each side:
\n
$$
0.331662 = {\frac{[x]}{[0.100 - 2x]}}
$$

\n
$$
x = 0.0331662 - 0.663324x
$$

\n
$$
1.663324x = 0.0331662
$$

\n
$$
x = 0.0199397
$$

\n
$$
[\text{I}_{2}]_{eq} = [\text{Cl}_{2}]_{eq} = x = 0.0199397 = 0.0199 \text{ M}
$$

\n
$$
[\text{IC}]]_{eq} = 0.100 - 2x = 0.100 - 2(0.0199397) = 0.0601206 = 0.0601 \text{ M}
$$
IC

- 17.45 Concentration (*M*) $SCl_2(g)$ + $2C_2H_4(g)$ \Rightarrow
Initial 0.675 0.973 0 $\frac{\text{SCI}_2(g)}{0.675}$ $SCH_2CH_2Cl)_2(g)$ Equilibrium $0.675 - x$ $0.973 - 2x$ x Change $-x$ $-2x$ $+x$ $[S(CH_2CH_2Cl)_2]_{eq} = x = 0.350 M$ $[SCl₂]$ _{eq} [C $= 0.675 - x = 0.675 - 0.350 = 0.325 M$ $_2$ H₄]_{eq} *K* $= 0.973 - 2x = 0.973 - 2(0.350) = 0.273 M$ c $\left| \text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2 \right|$ $| | |C_2|| | C_2H_4 |$ 2 ^{2 12 2 12} 2 2 $\lfloor 2^{114} \rfloor$ SCH_2CH_2Cl $\rm SCl_2$ $\rm \parallel C_2H$ $=\frac{[S(CH_2CH_2Cl)_2]}{[SCH_2CH_2Cl]_2}=\frac{[0.350]}{[SCH_2CH_2Cl]_2}$ $[0.325][0.273]^2$ 0.350 0.325 [0.273 $= 14.4497$ $K_p = K_c (RT)^{\Delta n}$ $\Delta n = 1 \text{ mol} - 3 \text{ mol} = -2$ $K_{\text{p}} = (14.4497) [(0.0821)(273.2 + 20.0)]^{-2} = 0.0249370 =$ **0.0249**
- 17.46 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of each reactant from the given amounts and container volume, use the balanced equation to define x, and set up a reaction table. The equilibrium concentration of N_2 is known, so x can be calculated and used to find the other equilibrium concentrations. Substitute the equilibrium concentrations into the equilibrium expression to find K_c . Solution:

4NH₃(g) + 3O₂(g)
$$
\frac{1}{2}
$$
 2N₂(g) + 6H₂O(g)
\nInitial [NH₃] = Initial [O₂] = (0.0150 mol)/(1.00 L) = 0.0150 M
\nConcentration (M) 4NH₃(g) + 3O₂(g) $\frac{1}{2}$ 2N₂(g) + 6H₂O(g)
\nInitial 0.0150 0.0150 0
\nChange
\nEquilibrium 0.0150 - 4
\n[N₂] $\epsilon_q = 2x = 1.96x10^{-3} M$
\n $x = (1.96x10^{-3} M)/2 = 9.80x10^{-4} M$
\n[H₂O]_{eq} = 6x = 6(9.80x10⁻⁴)
\n[O₂] $\epsilon_q = 0.0150 - 4x = 0.0150 - 4(9.80x10^{-3})$
\n $[O2]eq = 0.0150 - 3x = 0.0150 - 4(9.80x10^{-4}) = 1.1080x10^{-2} M$
\n $[O2]eq = 0.0150 - 3x = 0.0150 - 3(9.80x10^{-4}) = 1.2060x10^{-2} M$
\n $K_c = \frac{[N2]2 [H2O]6}{[NH3]4 [O2]3 = \frac{[1.96x10^{-3}]2 [5.8800x10^{-3}]6}{[1.1080x10^{-2}]3]} = 6.005859x10^{-6} = 6.01x10^{-6}$
\n17.47 Pressure (atm) FeO(s) + CO(g) \Rightarrow Fe(s) + CO₂(g)
\nInitial
\n $K_p =$

17-10

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

- 17.48 Equilibrium position refers to the specific concentrations or pressures of reactants and products that exist at equilibrium, whereas equilibrium constant refers to the overall ratio of equilibrium concentrations and not to specific concentrations. Changes in reactant concentration cause changes in the specific equilibrium concentrations of reactants and products (equilibrium position), but not in the equilibrium constant.
- 17.49 A positive Δ*H*_{rxn} indicates that the reaction is endothermic, and that heat is consumed in the reaction: $NH_4Cl(s)$ + **heat** $\leftrightarrows NH_3(g)$ + HCl(*g*)

a) The addition of heat (high temperature) causes the reaction to proceed to the right to counterbalance the effect of the added heat. Therefore, more products form at a higher temperature and container **(B)** with the largest number of product molecules best represents the mixture.

b) When heat is removed (low temperature), the reaction shifts to the left to produce heat to offset that disturbance. Therefore, NH_3 and HCl molecules combine to form more reactant and container (A) with the smallest number of product gas molecules best represents the mixture.

- 17.50 Equilibrium component concentration values may change but the mass action expression of these concentrations is a constant as long as temperature remains constant. Changes in component amounts, pressures (volumes), or addition of a catalyst will not change the value of the equilibrium constant.
- 17.51 a) Rate_f = k_f [reactants]^x. An increase in reactant concentration shifts the equilibrium to the right by increasing the initial forward rate. Since $K = k_f / k_r$ and k_f and k_r are not changed by changes in concentration, *K* remains constant.

b) A decrease in volume causes an increase in concentrations of gases. The reaction rate for the formation of fewer moles of gases is increased to a greater extent. Again, the *k* ^f and *k*^r values are unchanged.

17.52 a) An exothermic reaction can be written as: reactants \Rightarrow products + heat. A rise in temperature (increase in heat) favors the reverse direction of the reaction, i.e., the formation of reactants and consumption of products. Since $K =$ [products]/[reactants], the addition of heat increases the denominator and decreases the numerator, making K_2 smaller than K_1 . Since $K = k_f / k_r$ and an increase in temperature increases k_r to a greater extent, the value of K is lower at the increased temperature.

b) An endothermic reaction can be written as: reactants $+$ heat $\frac{1}{2}$ products. A rise in temperature (increase in heat) favors the forward direction of the reaction, i.e., the formation of products and consumption of reactants. Since $K =$ [products]/[reactants], the addition of heat increases the numerator and decreases the denominator, making K_2 larger than K_1 . For an endothermic reaction, k_f increases more than k_r with an increase in temperature and $K_2 = k_f / k_r$ is larger than K_1 .

- 17.53 $XY(s) = X(g) + Y(s)$ Since product Y is a solid substance, addition of solid Y has no effect on the equilibrium position (as long as some Y is present). **Scene A** best represents the system at equilibrium after the addition of two formula units of Y. More Y is present but the amounts of X and XY do not change.
- 17.54 Plan: If the concentration of a substance in the reaction increases, the equilibrium position will shift to consume some of it. If the concentration of a substance in the reaction decreases, the equilibrium position will shift to produce more of it.

Solution:

a) Equilibrium position shifts **towards products**. Adding a reactant (CO) causes production of more products as the system will act to reduce the increase in reactant by proceeding toward the product side, thereby consuming additional CO.

b) Equilibrium position shifts **towards products**. Removing a product (CO₂) causes production of more products as the system acts to replace the removed product.

c) Equilibrium position **does not shift**. The amount of a solid reactant or product does not impact the equilibrium as long as there is some solid present.

d) Equilibrium position shifts **towards reactants**. When product is added, the system will act to reduce the increase in product by proceeding toward the reactant side, thereby consuming additional $CO₂$; dry ice is solid

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

carbon dioxide that sublimes to carbon dioxide gas. At very low temperatures, $CO₂$ solid will not sublime, but since the reaction lists carbon dioxide as a gas, the assumption that sublimation takes place is reasonable.

17.55 a) **no change** b) **no change** c) **shifts towards the products** d) **shifts towards the reactants**

17.56 Plan: An increase in container volume results in a decrease in pressure (Boyle's law). Le Châtelier's principle states that the equilibrium will shift in the direction that forms more moles of gas to offset the decrease in pressure.

Solution:

a) **More F** forms (two moles of gas) and **less F 2** (one mole of gas) is present as the reaction shifts towards the right.

b) **More C 2H2 and H2** form (four moles of gas) and **less CH4** (two moles of gas) is present as the reaction shifts towards the right.

- 17.57 a) **more CO₂ and H₂O; less C₃H₈ and O₂** b) **more NH**₃ **and O**₂; **less N**₂ **and H**₂**O**
- 17.58 Plan: The purpose of adjusting the volume is to cause a shift in equilibrium to the right for increased product yield. Increasing the volume of the container results in a shift in the direction that forms more moles of gas, while decreasing the container volume results in a shift in the direction that forms fewer moles of gas. Solution:

a) Because the number of reactant gaseous moles $(4H₂)$ equals the product gaseous moles $(4H₂O)$, a change in volume will have **no effect** on the yield.

b) The moles of gaseous product (2CO) exceed the moles of gaseous reactant $(1O_2)$. A decrease in pressure favors the reaction direction that forms more moles of gas, so **increase** the reaction vessel volume.

17.59 a) **increase volume** b) **decrease volume**

17.60 Plan: An increase in temperature (addition of heat) causes a shift in the equilibrium away from the side of the reaction with heat. Recall that a negative value of $\Delta H_{\text{rxn}}^{\circ}$ indicates an exothermic reaction, while a positive

value of $\Delta H_{\text{rxn}}^{\circ}$ indicates an endothermic reaction.

Solution:

a) $CO(g) + 2H_2(g)$ ≒ $CH_3OH(g) + heat$ ΔH_{rxn}° $\Delta H_{\text{rxn}}^{\circ}$ = –90.7 kJ

The reaction is exothermic, so heat is written as a product. The equilibrium shifts to the left, away from heat, towards the reactants, so amount of product **decreases**.

b)
$$
C(s)
$$
 + H₂ $O(g)$ + heat $\leq CO(g)$ + H₂ (g) ΔH_{rxn}° = 131 kJ

The reaction is endothermic, so heat is written as a reactant. The equilibrium shifts to the right, away from heat, towards the products, so amounts of products **increase**.

c) $2NO_2(g) + heat \leq 2NO(g) + O_2(g)$

The reaction is endothermic, so heat is written as a reactant. The equilibrium shifts to the right, away from heat, towards the product, so amounts of products **increase**.

d) $2C(s) + O_2(g)$ \leq $2CO(g) +$ heat

The reaction is exothermic, so heat is written as a product. The equilibrium shifts to the left, away from heat, towards the reactants; amount of product **decreases**.

17.61 a) **decrease** b) **decrease** c) **decrease** d) **increase**

17.62
$$
4Fe_3O_4(s) + O_2(g) = 6Fe_2O_3(s)
$$
 $K_p = 2.5x10^{87}$ at 298 K
\na) $K_p = \frac{1}{P_{O_2}} = 2.5x10^{87}$
\n $P_{O_2} = 4.0x10^{-88}$ atm

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

b)
$$
Q_p = \frac{1}{P_{O_2}} = 1/(0.21) = 4.7619
$$

\n $K_p > Q_p$ thus, the reaction will proceed to the **right**.
\nc) $K_p = K_c (RT)^{\Delta n}$
\n $K_c = K_p/(RT)^{\Delta n}$
\n $K_c = (2.5 \times 10^{87}) / [(0.0821)(298)]^{-1} = 6.11645 \times 10^{88} = 6.1 \times 10^{88}$

17.63 Plan: An increase in temperature (addition of heat) causes a shift in the equilibrium away from the side of the reaction with heat, while a decrease in temperature (removal of heat) causes a shift in the equilibrium towards the side with heat. Increasing the volume of the container (pressure decreases) results in a shift in the direction that forms more moles of gas, while decreasing the container volume (pressure increases) results in a shift in the direction that forms fewer moles of gas. Adding a reactant causes a shift in the direction of products. Solution:

a)
$$
SO_2(g) + 1/2O_2(g) \leq SO_3(g) +
$$
 heat

The forward reaction is exothermic ($\Delta H_{\text{rxn}}^{\circ}$ is negative), so it is favored by **lower temperatures**. Lower temperatures will cause a shift to the right, the heat side of the reaction. There are fewer moles of gas as products $(1SO_3)$ than as reactants $(1SO_2(g) + 1/2O_2)$, so products are favored by **higher pressure**. High pressure will cause a shift in equilibrium to the side with the fewer moles of gas.

b) Addition of O₂ would **decrease** Q since $Q = \frac{150Q_{31}}{[SO_{2}][O_{2}]^{1/2}}$ $[SO_3]$ $[SO_2][O_2]$ would **decrease** Q since $Q = \frac{Q}{Q} \frac{Q}{Q} \frac{Q}{Q} \frac{Q}{Q}$, and have **no impact on K**.

c) To enhance yield of SO_3 , a low temperature is used. Reaction rates are slower at lower temperatures, so a catalyst is used **to speed up the reaction**.

17.64 a) $3H_2(g) + N_2(g)$ $\leq 2NH_3(g)$ The mole ratio $H_2:N_2 = 3:1$; at equilibrium, if $N_2 = x$, $H_2 = 3x$; P_{NH_3} = 50. atm

$$
K_{\rm p} = \frac{\left(P_{\rm NH_3}\right)^2}{\left(P_{\rm N_2}\right)\left(P_{\rm H_2}\right)^3} = 1.00 \times 10^{-4}
$$
\n
$$
K = \frac{\left(50\right)^2}{4.00 \times 10^{-4}}
$$

$$
K_{\rm p} = \frac{(3.00 \times 10^{-4})}{(x)(3x)^{3}} = 1.00x10^{-4}
$$

\n
$$
x = 31.02016 = 31 \text{ atm N}_{2}
$$

\n
$$
3x = 3(31.02016) = 93.06049 = 93 \text{ atm H}_{2}
$$

\n
$$
P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (31.02016 \text{ atm}) + (93.06049 \text{ atm}) + (50. \text{ atm})
$$

\n= 174.08065 = 174 atm total

b) The mole ratio H₂:N₂ = 6:1; at equilibrium, if N₂ = x, H₂ = 6x; P_{NH₃} = 50. atm

$$
K_{\rm p} = \frac{(50.)^2}{(x)(6x)^3} = 1.00x10^{-4}
$$

x = 18.445 = **18 atm N₂**
6x = 6(18.445) = 110.67 = **111 atm H₂**
P_{total} = P_{nitrogen} + P_{hydrogen} + P_{ammonia} = (18.445 atm) + (110.67 atm) + (50. atm)
= 179.115 = **179 atm total**

This is not a valid argument. The total pressure in b) is greater than in a) to produce the same amount of $NH₃$.

17.65 a) You are given a value of K_c but the amounts of reactant and product is given in units of pressure. Convert K_c to K_p .

 $K_{\rm p} = K_{\rm c} (RT)^{\Delta n}$ $\Delta n = 1 - 2 = -1$ (1 mol of product, C₂H₅OH and 2 mol of reactants, C₂H₄ +

$$
\mathrm{H}_2\mathrm{O})
$$

 $K_{\rm p} = K_{\rm c}(RT)^{-1} = (9 \times 10^3)[(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) (600. \text{ K})]^{-1} = 1.8270 \times 10^2 \text{ (unrounded)}$ Substitute the given values into the equilibrium expression and solve for $P_{\text{C}_2\text{H}_4}$.

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

$$
K_{\rm p} = \frac{P_{\rm C_2H_2OH}}{P_{\rm C_2H_4}P_{\rm H_2O}} = \frac{200.}{P_{\rm C_2H_4} (400.)} = 1.8270 \times 10^2
$$

$$
P_{\rm C_2H_4} = 2.7367 \times 10^{-3} = 3 \times 10^{-3} \text{ atm}
$$

b) The forward direction, towards the production of ethanol, produces the least number of moles of gas and is favored by **high pressure**. A **low temperature** favors an exothermic reaction.

c) **No**, condensing the C_2H_5OH would not increase the yield. Ethanol has a lower boiling point (78.5°C) than water (100^oC). Decreasing the temperature to condense the ethanol would also condense the water, so moles of gas from each side of the reaction are removed. The direction of equilibrium (yield) is unaffected when there is no net change in the number of moles of gas.

17.66 a)
$$
Q_c = \frac{[XY]^2}{[X_2][Y_2]}
$$

\nb) $\text{Scene A: } Q_c = \frac{[0]^2}{[0.4][0.4]} = 0$
\n $\text{Scene B: } Q_c = \frac{[0.4]^2}{[0.2][0.2]} = 4$
\n $\text{Scenes C-E: } Q_c = \frac{[0.6]^2}{[0.1][0.1]} = 36 = 4 \times 10^1$

c) Time is progressing to the **right**. Frame A must be the earliest time.

d) $K = 4x10^1$

e) **Scene B**. At higher temperatures, the reaction shifts to the left (forming more X_2 and Y_2).

f) **None**. Volume (pressure) has no effect on the position of the equilibrium since there are two moles of gas on each side.

17.67
$$
n/V = M = P/RT = \frac{(2.0 \text{ atm})}{(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})((273.2 + 25.0) \text{ K})} = 0.0816919 \text{ M each gas}
$$

\n $H_2(g) + CO_2(g) \Rightarrow H_2O(g) + CO(g)$
\nInitial 0.0816919 0.0816919 0
\nChange 0.0816919 - x 0.0816919 - 0.03449 = 0.0472019 mol/L
\nM of H₂ at equilibrium = 0.0816919 - x = 0.0816919 - 0.03449 = 0.0472019 mol/L
\nM of H₃ at equilibrium = $(1.00 \text{ N}) \frac{(0.0472019 \text{ mol}) (2.016 \text{ g})}{(0.095150 \text{ m}) (0.095150 \text{ m})} = 0.005150 \text{ m}$

Mass (g) of H₂ = (1.00 L) $\left(\frac{0.0472019 \text{ mol}}{\text{L}} \right) \left(\frac{2.016 \text{ g}}{1 \text{ mol}} \right)$ = 0.095159 = **0.095 g H₂**

17.68 To get the two equations to sum to the desired equation, the first equation must be reversed and doubled. This will result in squaring the reciprocal of its K_c value. The other equation does not need to be changed. Adding the two equations means the new K_c value will be the product of the individual K_c values.

$$
2NO(g) \le N_2(g) + O_2(g)
$$

\n
$$
K_1 = (K_c)^{-2} = 4.340 \times 10^{18} = K_2
$$

\n
$$
2NO_2(g) \le 2NO(g) + O_2(g)
$$

\n
$$
K_2 = K_c = 1.1 \times 10^{-5}
$$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

Overall: $2NO_2(g) = N_2(g) + 2O_2(g)$ K_c (overall) = $K_1K_2 = 4.774 \times 10^{13} = 4.8 \times 10^{13}$ *M*

17.69 Plan: Write the equilibrium expression. You are given a value of K_c but the amounts of reactants and product are given in units of pressure. Convert K_c to K_p and use the equilibrium pressures of SO_3 and O_2 to obtain the equilibrium pressure of SO_2 . For part b), set up a reaction table and solve for x. The equilibrium concentrations can then be used to find the K_c value at the higher temperature. The concentration of SO_2 is converted to pressure using the ideal gas law, $PV = nRT$.

Solution:

a) $K_{\text{p}} = K_{\text{c}} (RT)^{\Delta n}$

 Δn = moles gaseous products – moles gaseous reactants = $2 - 3 = -1$ (two mol of product, SO₃, and three mol of reactants, $2 SO₂ + O₂$)

$$
K_{\rm p} = K_{\rm c}(RT)^{\Delta n} = K_{\rm c}(RT)^{-1} = (1.7 \times 10^8)[(0.0821 \text{ L-atm/mol-K})(600. \text{ K})]^{-1} = 3.451 \times 10^6
$$

\n
$$
K_{\rm p} = \frac{P_{\rm SO_3}^2}{P_{\rm SO_2}^2 P_{\rm O_2}} = \frac{(300.)^2}{P_{\rm SO_2}^2 (100.)} = 3.451 \times 10^6
$$

\n
$$
P_{\rm SO_2} = 0.016149 = \textbf{0.016 atm}
$$

b) Create a reaction table that describes the reaction conditions. Since the volume is 1.0 L, the moles equals the molarity. Note the 2:1:2 mole ratio between $SO_2:O_2:SO_3$.

Substitute equilibrium concentrations into the equilibrium expression and solve for *K* c .

$$
K_{\rm c} = \frac{\left[{\rm SO}_3\right]^2}{\left[{\rm SO}_2\right]^2\left[{\rm O}_2\right]} = \frac{\left[0.0020\right]^2}{\left[0.0020\right]^2\left[0.0018\right]} = 555.5556 = 5.6x10^2
$$

The pressure of SO_2 is estimated using the concentration of SO_2 and the ideal gas law (although the ideal gas law is not well behaved at high pressures and temperatures).

 $PV = nRT$

$$
P_{\text{SO}_2} = \frac{nRT}{V} = \frac{(0.0020 \text{ mol}) \left(0.0821 \frac{\text{L-atm}}{\text{mol-K}} \right) (1000. \text{ K})}{(1.0 \text{ L})} = 0.1642 = 0.16 \text{ atm}
$$

17.70 Plan: Set up a reaction table to find the equilibrium amount of $CaCO₃$ after the first equilibrium is established and then the equilibrium amount after the second equilibrium is established.

Solution:

The equilibrium pressure of $CO_2 = P_{CO_2} = 0.220$ atm.

The amount of calcium carbonate solid in the container at the first equilibrium equals the original amount, 0.100 mol, minus the amount reacted to form 0.220 atm of carbon dioxide. The moles of $CaCO₃$ reacted is equal to the number of moles of carbon dioxide produced. Use the pressure of $CO₂$ and the ideal gas equation to calculate the moles of $CO₂$ produced:

 $PV = nRT$

$$
Moles of CO_2 = n = \frac{PV}{RT}
$$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

$$
n = \frac{(0.220 \text{ atm})(10.0 \text{ L})}{(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(385 \text{ K})} = 0.0696015 \text{ mol CO}_2
$$

Moles of CaCO₃ reacted = moles of CO₂ produced = 0.0696015 mol

Moles of CaCO₃ remaining = initial moles – moles reacted = 0.100 mol CaCO₃ – 0.0696015 mol CaCO₃

 $= 0.0304$ mol CaCO₃ at first equilibrium

As more carbon dioxide gas is added, the system returns to equilibrium by shifting to the left to convert the added carbon dioxide to calcium carbonate to maintain the partial pressure of carbon dioxide at 0.220 atm (*K* p). Convert the added 0.300 atm of CO_2 to moles using the ideal gas equation. The moles of CO_2 reacted equals the moles of $CaCO₃$ formed.

Moles of CO₂ =
$$
n = \frac{PV}{RT}
$$

\n
$$
n = \frac{(0.300 \text{ atm})(10.0 \text{ L})}{(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(385 \text{ K})} = 0.09491 \text{ mol CO}_2
$$

Moles of CaCO₃ produced = moles of CO_2 reacted = 0.09491 mol CaCO₃ Add the moles of $CaCO₃$ formed in the second equilibrium to the moles of $CaCO₃$ at the first equilibrium position.

Moles of $CaCO_3$ = moles at first equilibrium + moles formed in second equilibrium $= 0.0304 \text{ mol} + 0.09491 = 0.12531 \text{ mol CaCO}_3$

Mass (g) of CaCO₃ = (0.12531 mol CaCO₃)
$$
\left(\frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \right)
$$
 = 12.542 = **12.5 g CaCO₃**

- 17.71 a) $C_2H_4(g) + 3O_2(g)$ $\leq 2CO_2(g) + 2H_2O(g)$ b) $4NO_2(g) + 6H_2O(g)$ $\leq 4NH_3(g) + 7O_2(g)$
- 17.72 The first equation is in the correct form, but the second equation must be reversed. Reversing the equation leads to the reciprocal of the *K* value.

$$
\frac{4/2H_2(g) + 1/2O_2(g)}{H(g) \Leftrightarrow 1/2O_2(g) \Leftrightarrow HO(g)}
$$
\n
$$
K_{c1} = 0.58
$$
\n
$$
K_{c2} = (K_{c2})^{-1} = (1.6 \times 10^{-3})^{-1} = 625
$$
\n
$$
K_{c2} = (K_{c2})^{-1} = (1.6 \times 10^{-3})^{-1} = 625
$$
\n
$$
K_{c(overall)} = K_{c1} \times (K_{c2})^{-1}
$$
\n
$$
= 0.58 \times 625 = 362.5 = 3.6 \times 10^2
$$

17.73 Plan: Use the volume fraction of O_2 and CO_2 to find the partial pressure of each gas and substitute these pressures into the equilibrium expression to find the partial pressure of CO. Use *PV* = *nRT* to convert the partial pressure of CO to moles per liter and then convert to pg/L. Solution:

a) Calculate the partial pressures of oxygen and carbon dioxide because volumes are proportional to moles of gas, so volume fraction equals mole fraction. Assume that the amount of carbon monoxide gas is small relative to the other gases, so the total volume of gases equals $V_{\text{CO}_2} + V_{\text{O}_2} + V_{\text{N}_2} = 10.0 + 1.00 + 50.0 = 61.0$.

$$
P_{\text{CO}_2} = \left(\frac{10.0 \text{ mol CO}_2}{61.0 \text{ mol gas}}\right) (4.0 \text{ atm}) = 0.6557377 \text{ atm}
$$

$$
P_{\text{O}_2} = \left(\frac{1.00 \text{ mol O}_2}{61.0 \text{ mol gas}}\right) (4.0 \text{ atm}) = 0.06557377 \text{ atm}
$$

Use the partial pressures and given K_p to find P_{CO} .

 $2CO_2(g) = 2CO(g) + O_2(g)$ $K_{\rm p} = \frac{-\cos^2 2}{\sqrt{2}}$ 2 $R_{\rm CO}^2 P_{\rm O}$ 2 CO $=\frac{P_{\rm CO}^2 P_{\rm O_2}}{P_{\rm CO_2}^2} = \frac{P_{\rm CO}^2 (0.06557377)}{(0.6557377)^2}$ 2 CO 2 0.06557377 0.6557377 $\frac{P_{\text{CO}}^2 (0.06557377)}{P_{\text{CO}}^2} = 1.4 \times 10^{-28}$ *P* $P_{\text{CO}} = 3.0299 \text{x} 10^{-14} = 3.0 \text{x} 10^{-14}$ atm

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

b) $PV = nRT$ $\frac{n_{\text{CO}}}{V} = \frac{P}{RT} = \frac{(3.0299 \times 10^{-14} \text{ atm})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{1 \text{ Hz}} \right) (800 \text{ K})}$ $3.0299x10^{-14}$ atm $0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} (800 \text{ K})$ − $\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)$ $= 4.61312x10^{-16}$ mol/L Concentration (pg/L) of $CO =$ 16 12 4.61312x10⁻¹⁶ mol CO $($ 28.01 g CO $)($ 1 pg L \parallel 1 mol CO \parallel 10⁻¹² g − $\left(\frac{4.61312 \times 10^{-16} \text{ mol CO}}{L}\right) \left(\frac{28.01 \text{ g CO}}{1 \text{ mol CO}}\right) \left(\frac{1 \text{ pg}}{10^{-12} \text{ g}}\right)$ = 0.01292 = **0.013 pg CO/L** 17.74 a) $\text{Fe}^{2+} + 2\text{Fe}^{3+}$ b) $(0.050 \text{ mol H}_2\text{O})/(1.0 \text{ L}) = 0.050 M \text{H}_2\text{O}$ *K* c $| \mathrm{H}_{2} |$ $| H_2 O |$ 4 2 4 2 H $_{\rm H_2O}$ $=\frac{\left[H_2\right]^4}{\left[1-\frac{4}{x}\right]} = 5.1 = \frac{\left[4x\right]}{x}$ $\left[0.050 - 4x \right]$ 4 4 4 $0.050 - 4$ *x* − *x* $1.50277 = \frac{[4x]}{[6.858]}$ $\left| 0.050 - 4x \right|$ 4 $0.050 - 4$ $\frac{x}{-4x}$ $x = (7.50553 \times 10^{-3} \text{ mol/L})(1.0 \text{ L}) = 7.50553 \times 10^{-3} \text{ mol Fe}_3\text{O}_4$ reacting Mass Fe₃O₄ = $(7.50553 \times 10^{-3})(231.55 \text{ g} \text{Fe}_3\text{O}_4/1 \text{ mol} \text{Fe}_3\text{O}_4) = 1.7494 = 1.7 \text{ g} \text{Fe}_3\text{O}_4$ 17.75 $M_2(g) + N_2(g)$ \Rightarrow 2MN(*g*) $|MN|$ $|M_2|$ 2 2 JLIN₂ $=\frac{\text{[MN]}^2}{\text{[M}_2 \text{][N}_2\text{]}}$ Scene A: Concentrations: $[M_2] = [N_2] = 0.20 M$; $[MN] = 0.40 M$ *K* c $| 0.40 |$ $| 0.20 |$ $[0.40]^{2}$ $=\frac{10.20}{[0.20][0.20]} = 4.0$ Scene B: Concentration (*M*) $M_2(g)$
Initial 0.60 Initial 0.60 0.30 0 (g) \Rightarrow $2MN(g)$ Equilibrium $0.60 - x$ $0.30 - x$ $2x$ Change $-x$ – x $-x$ +2x $K_c = 4.0 = \frac{[2x]}{[0.68 - \frac{1}{2}]}$ $| 0.60 - x |$ $2x$ ² $=4.0 = \frac{1}{\left[0.60 - x\right]\left[0.30 - x\right]}$ $4.0 =$ 2 2 4x $0.18 - 0.90 x + x$ $4x^2 = 0.72 - 3.6x$ $3.6x = 0.72$ x = 0.20 *M* $[M_2] = 0.60 - x = 0.60 - 0.20 = 0.40$ *M* $[N_2] = 0.30 - x = 0.30 - 0.20 = 0.10 M$ $[MN] = 2x = 2(0.20 M) = 0.40 M$ 17.76 Calculate K_c . *K* c $| CO_2 || H_2 |$ $| CO|$ H₂O 2 J[11 ₂ 2 $=\frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}=\frac{[0.40][0.10]}{[0.10][0.10]}$ 0.40 || 0.10 $\frac{10!}{0.10}$ = 4.0 Calculate new concentrations. New $H_2 = 0.10 M + (0.60 mol/2.0 L) = 0.40 M$ Concentration (M) CO(*g*) + H₂O(*g*) \leftrightarrows $CO₂(g) + 0.40$
-x Initial 0.10 0.10 0.40 0.40 $H_2(g)$ Change $+x$ 0.10 0.40 0.40

Equilibrium $0.10 + x$ 0.10 + x 0.40 – x – x – x
 $0.40 - x$ 0.40 – x 0.40 – x Change $+x$ $+x$ $-x$ $-x$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

$$
K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.40 - x][0.40 - x]}{[0.10 + x][0.10 + x]} = \frac{[0.40 - x]^2}{[0.10 + x]^2} = 4.0
$$

$$
\frac{[0.40 - x]}{[0.10 + x]} = 2.0
$$

$$
x = 0.066667
$$

$$
[CO] = [H_2O] = 0.10 + x = 0.10 + 0.066667 = 0.166667 = 0.17 M
$$

$$
[CO_2] = [H_2] = 0.40 - x = 0.40 - 0.066667 = 0.333333 = 0.33 M
$$

- 17.77 Although the yield is favored by low temperature, the rate of formation is not. In fact, ammonia forms so slowly at low temperatures that the process becomes uneconomical. In practice, a compromise is achieved that optimizes yield and rate (high pressure, continual removal of NH 3, increasing the temperature).
- 17.78 Plan: Write a reaction table given that P_{CH_4} (init) = P_{CO_2} (init) = 10.0 atm, substitute equilibrium values into the equilibrium expression, and solve for P_{H_2} .

Solution:
\na) Pressure (atm)
$$
CH_4(g) + CO_2(g)
$$
 $\approx 2CO(g) + 2H_2(g)$
\nInitial
\nChange $-x$ $-x$ $+2x$ $+2x$
\nEquilibrium $10.0 - x$ $10.0 - x$ $2x$ $2x$
\n $K_p = \frac{P_{CO}^2 P_{H_2}^2}{P_{CH_4} P_{CO_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 3.548 \times 10^6$ (take square root of each side)
\n $\frac{(2x)^2}{(10.0 - x)} = 1.8836135 \times 10^3$
\n $4x^2 + (1.8836135 \times 10^3 \times) - 1.8836135 \times 10^4 = 0$
\n $a = 4$ $b = 1.8836135 \times 10^3$ $c = -1.8836135 \times 10^4$
\n $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
\n $x = 9.796209$
\n $P_{H_2} = 2x = 2(9.796209) = 19.592419$ atm
\n $P_{H_2} = 2x = 2(9.796209) = 19.592419$ atm

If the reaction proceeded entirely to completion, the partial pressure of H_2 would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H_2 form for each mole of CH_4 or CO_2 that reacts).

The percent yield is
$$
\frac{19.592418 \text{ atm}}{20.0 \text{ atm}}(100\%) = 97.96209 = 98.0\%
$$
.

b) Repeat the calculations for part a) with the new K_p value. The reaction table is the same.

$$
K_{\rm p} = \frac{P_{\rm CO}^2 P_{\rm H_2}^2}{P_{\rm CH_4} P_{\rm CO_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 2.626 \times 10^7
$$

$$
\frac{(2x)^2}{(10.0 - x)} = 5.124451 \times 10^3
$$

A quadratic is needed:

$$
4x^2 + (5.124451 \times 10^3 \text{ x}) - 5.124451 \times 10^4 = 0
$$

a = 4 \t b = 5.124451 \times 10^3 \t c = -5.124451 \times 10^4

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

$$
x = \frac{-5.124451x10^{3} \pm \sqrt{(5.124451x10^{3})^{2} - 4(4)(-5.124451x10^{4})}}{2(4)}
$$

$$
x = 9.923144
$$

 P_{H_2} = 2x = 2(9.923144) = 19.84629 atm

If the reaction proceeded entirely to completion, the partial pressure of H_2 would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H_2 form for each mole of CH_4 or CO_2 that reacts).

The percent yield is
$$
\frac{19.84629 \text{ atm}}{20.0 \text{ atm}}(100\%) = 99.23145 = 99.0\%
$$
.

c) van't Hoff equation:

$$
K_{1} = 3.548 \times 10^{6}
$$

\n
$$
T_{1} = 1200.
$$
 K $\Delta H_{\text{rxn}}^{2} = ?$
\n
$$
K_{2} = 2.626 \times 10^{7}
$$

\n
$$
T_{2} = 1300.
$$
 K $\Delta H_{\text{rxn}}^{2} = ?$
\n
$$
\ln \frac{K_{2}}{K_{1}} = -\frac{\Delta H_{\text{rxn}}^{2}}{R} \left(\frac{1}{T_{2}} - \frac{1}{T_{1}} \right)
$$

\n
$$
\ln \frac{2.626 \times 10^{7}}{3.548 \times 10^{6}} = -\frac{\Delta H_{\text{rxn}}^{2}}{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right)} \left(\frac{1}{1200. \text{ K}} - \frac{1}{1300. \text{ K}} \right)
$$

 $2.0016628 = \Delta H_{\text{rxn}}^{\circ} (7.710195 \text{x} 10^{-6})$

$$
\Delta H_{rxn}^{\circ} = 2.0016628/7.710195 \times 10^{-6} = 2.5961247 \times 10^{5} = 2.60 \times 10^{5}
$$
 J/mol

(The subtraction of the 1/*T* terms limits the answer to three significant figures.)

17.79 Plan: Add the two reactions to obtain the overall reaction. Multiply the second equation by 2 to cancel the moles of CO produced in the first reaction. K_p for the second reaction is then $(K_p)^2$. K_p for the overall reaction is equal to the product of the K_p values for the two individual reactions. Calculate K_c using $K_p = K_c (RT)^{\Delta n}$. Solution:

a)
$$
2CH_4(g) + O_2(g) \Leftrightarrow 2CO_2(g) + 4H_2(g) \qquad K_p = 9.34 \times 10^{28}
$$

$$
2CO_2(g) + 2H_2O(g) \Leftrightarrow 2CO_2(g) + 2H_2(g) \qquad K_p = (1.374)^2 = 1.888
$$

 $2CH_4(g) + O_2(g) + 2H_2O(g)$ \leq $2CO_2(g) + 6H_2$ b) *K* (*g*) $p_p = (9.34 \times 10^{28})(1.888) = 1.76339 \times 10^{29} = 1.76 \times 10^{29}$ c) ∆*n* = moles gaseous products – moles gaseous reactants = 8 – 5 = 3 (8 moles of product gas – 5 moles of reactant gas) $K_{\rm p} = K_{\rm c} (RT)^{\Delta n}$ *K K* 29

$$
K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.76339 \times 10^{29}}{[(0.0821 \text{ atm} \cdot \text{L/mol} \cdot \text{K})(1000)]^3} = 3.18654 \times 10^{23} = 3.19 \times 10^{23}
$$

d) The initial total pressure is given as 30. atm. To find the final pressure use the relationship between pressure and number of moles of gas: $n_{initial}/P_{initial} = n_{final}/P_{final}$

Total mol of gas initial = 2.0 mol $\text{CH}_4 + 1.0$ mol $\text{O}_2 + 2.0$ mol $\text{H}_2\text{O} = 5.0$ mol Total mol of gas final = 2.0 mol CO_2 + 6.0 mol H_2 = 8.0 mol (from mole ratios)

$$
P_{\text{final}} = (30. \text{ atm} \text{ reactants}) \left(\frac{8 \text{ mol products}}{5 \text{ mol reactants}} \right) = 48 \text{ atm}
$$

17.80 Plan: Write an equilibrium expression. Use the balanced equation to define x and set up a reaction table, substitute into the equilibrium expression, and solve for x, from which the pressure of N or H is calculated. Convert log K_p to K_p . Convert pressures to moles using the ideal gas law, $PV = nRT$. Convert moles to atoms using Avogadro's number. Solution:

a) The initial pressure of N₂ is 200. atm.
200. Log
$$
K_p = -43.10
$$
; $K_p = 10^{-43.10} = 7.94328 \times 10^{-44}$
64. $K_p = 10^{-43.10} = 7.94328 \times 10^{-44}$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

Initial
\n
$$
\frac{1 \text{Chain}}{200-x} = \frac{42x}{2x}
$$
\n
$$
K_p = \frac{(P_N)^2}{(P_{N_2})} = 7.94328 \times 10^{-44}
$$
\n
$$
\frac{(2x)^2}{(200-x)} = 7.94328 \times 10^{-44}
$$
\nAssume 200. - x = 200.
\n
$$
\frac{(2x)^2}{(200)} = 7.94328 \times 10^{-41}
$$
\n
$$
4x^2 = 1.588656 \times 10^{-41}
$$
\n
$$
x = 1.992897 \times 10^{-21}
$$
\n
$$
P_x = 2x = 2(1.992897 \times 10^{-21})
$$
\n
$$
P_x = 2.8 = 2(1.992897 \times 10^{-21})
$$
\n
$$
P_x = 2.8 = 2(1.992897 \times 10^{-21})
$$
\n
$$
P_x = 2.8 = 2(1.992897 \times 10^{-21})
$$
\n
$$
P_x = 2.8 = 2(1.992897 \times 10^{-21})
$$
\n
$$
R_y = 2.8 = 2.01187 \times 10^{-18}
$$
\n
$$
R_y = 1600.
$$
\n
$$
R_y = 1600.
$$
\n
$$
R_y = \frac{(R_1)^2}{(R_{1y})} = 5.01187 \times 10^{-18}
$$
\nAssume 600. - x = 600.
\n
$$
\frac{(2x)^2}{(600 - x)} = 5.01187 \times 10^{-18}
$$
\nAssume 600. - x = 600.
\n
$$
\frac{(2x)^2}{(600 - x)} = 5.01187 \times 10^{-15}
$$
\n
$$
x = 2.741862 \times 10^{-8}
$$
\n
$$
R_x = 2.741862 \times 10^{-8}
$$
\n
$$
R_y = 2x = 2(2.741862 \times 10^{-8}) = 5.48372 \
$$

d) The more reasonable step is $N_2(g) + H(g) \rightarrow NH(g) + N(g)$. With only twenty-nine N atoms in 1.0 L, the first reaction would produce virtually no $NH(g)$ molecules. There are orders of magnitude more N_2 molecules than N atoms, so the second reaction is the more reasonable step.

17.81 a) Scenes B and D represent equilibrium.

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

b) C, A, B = D
c) [Y] = (4 spheres)
$$
\left(\frac{0.025 \text{ mol}}{1 \text{ sphere}}\right) \left(\frac{1}{0.40 \text{ L}}\right) = 0.25 \text{ M}
$$

[Z] = (8 spheres) $\left(\frac{0.025 \text{ mol}}{1 \text{ sphere}}\right) \left(\frac{1}{0.40 \text{ L}}\right) = 0.50 \text{ M}$

$$
K_{\rm c} = \frac{[Z]^2}{[Y]} = \frac{[0.50]^2}{[0.25]} = 1.0
$$

17.82 The *K* is very small, thus the reaction will shift to the right to reach equilibrium. To simplify the calculations, assume the equilibrium shifts entirely to the left, and then a little material reacts to reach equilibrium. Shifting entirely to the left gives $[H_2S] = 0.600$, and $[H_2] = [S_2] = 0$.

Clearly, for the gives
$$
\mu_2
$$
 is a 1.421 = 1.021 = 0.002, and μ_2 is a 2H₂(*g*) = 3.2H₂(*g*) = 3.2H₂(*g*) + 3.2(*g*)

\nInitial\n
$$
\begin{array}{rcl}\n\text{Change} & -2x & +2x & +x \\
\hline\n\text{Equilibrium} & 0.600 - 2x & 2x & x\n\end{array}
$$
\n
$$
K_c = \frac{\begin{bmatrix} H_2 \end{bmatrix}^2 \begin{bmatrix} S_2 \end{bmatrix}}{\begin{bmatrix} 2s \end{bmatrix}^2 \begin{bmatrix} x \end{bmatrix}} = 9.0x10^{-8} \quad \text{Assume } 2x \text{ is small compared to } 0.600 \, M. \\
\begin{bmatrix} 0.600 - 2x \end{bmatrix}^2 = 9.0x10^{-8} \quad \text{Assume } 2x \text{ is small compared to } 0.600 \, M. \\
\begin{bmatrix} 2x \end{bmatrix}^2 \begin{bmatrix} x \end{bmatrix} = 9.0x10^{-8} \quad \text{Assume } 2x \text{ is small compared to } 0.600 \, M. \\
x = 2.008x10^{-3} \quad \text{(assumption justified)} \\
\begin{bmatrix} H_2S \end{bmatrix} = 0.600 - 2x = 0.600 - 2(2.008x10^{-3}) = 0.595984 = 0.596 \, M \, H_2S \\
\begin{bmatrix} H_2 \end{bmatrix} = 2x = 2(2.008x10^{-3}) = 4.016x10^{-3} = 4.0 \, x \, 10^{-3} \, M \, H_2\n\end{array}
$$
\n
$$
[S_2] = x = 2.008x10^{-3} = 2.0x10^{-3} \, M \, S_2
$$

17.83 Plan: Write an equilibrium expression. Use the balanced equation to define x and set up a reaction table, $K_{\rm p} = K_{\rm c}(RT)^{\Delta n}$ to find $K_{\rm c}$. substitute into the equilibrium expression, and solve for x, from which the equilibrium pressures of the gases are calculated. Add the equilibrium pressures of the three gases to obtain the total pressure. Use the relationship

a) Pressure (atm) Solution: $2(g) + O_2$ Initial 0.780 0.210 0 (*g*) 2NO(*g*) Equilibrium $0.780 - x$ $0.210 - x$ $2x$ Change $-x$ $-x$ $+x$ $+2x$ $K_{\rm p} = \frac{(P_{\rm NO})}{(P_{\rm Q})}$ $(P_{\rm N_2}) (P_{\rm O_2})$ 2 NO N_2 /(¹O $=\frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} = 4.35 \times 10^{-31}$ $(2x)$ $(0.780 - x)(0.210 - x)$ $(2 x)^2$ $\frac{(2 \times 1)}{(0.780 - x)(0.210 - x)}$ = 4.35x10⁻³¹ Assume x is small because *K* is small. $(2x)$ $(0.780)(0.210)$ $(2 x)^2$ $\frac{(24)}{(0.780)(0.210)} = 4.35 \times 10^{-31}$ $x = 1.33466x10^{-16}$

Based on the small amount of nitrogen monoxide formed, the assumption that the partial pressures of nitrogen and oxygen change to an insignificant degree holds.

*P*_{nitrogen} (equilibrium) = (0.780 – 1.33466x10⁻¹⁶) atm = **0.780 atm N₂**

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

 P_{oxygen} (equilibrium) = (0.210 – 1.33466x10⁻¹⁶) atm = **0.210 atm O**₂ *P* N_{NO} (equilibrium) = 2(1.33466x10⁻¹⁶) atm = 2.66933x10⁻¹⁶ = **2.67x10⁻¹⁶ atm NO** b) The total pressure is the sum of the three partial pressures: $0.780 \text{ atm} + 0.210 \text{ atm} + 2.67 \text{x} 10^{-16} \text{ atm} = 0.990 \text{ atm}$ c) $K_{\rm p} = K_{\rm c} (RT)^{\Delta n}$ Δn = moles gaseous products – moles gaseous reactants = $2 - 2 = 0$ (two moles of product NO and two moles of reactants N_2 and O_2) $K_{\rm p} = K_{\rm c} (RT)^{0}$

 $K_c = K_p = 4.35 \times 10^{-31}$ because there is no net increase or decrease in the number of moles of gas in the course of the reaction.

- 17.84 $C_5H_{11}OH + CH_3COOH \cong CH_3COOC_5H_{11} + H_2O$ Removing water should help to increase the yield of banana oil. Both isopentyl alcohol and acetic acid are more soluble in water than isopentyl acetate. Thus, removing water will increase the concentration of both reactants and cause a shift in equilibrium towards the products.
- 17.85 $Q(g) \Leftrightarrow R(g)$ $K = \frac{[R]}{[Q]}$ For Scene A at equilibrium: $K = \frac{[R]}{[Q]} = \frac{[2]}{[6]} = 0.33$ For Scene B: $Q(g)$ \Rightarrow $R(g)$ Initial 10 2 $\frac{\text{Snaig}}{\text{Equilibrium}}$ Change $-x$ $+x$ $0.33 = \frac{[2 + x]}{[10 - x]}$ $x = 0.977 = 1$ $Q = 10 - x = 10 - 1 = 9$; $R = 2 + x = 2 + 1 = 3$

17.86 a)
$$
K_p = (P_{H_2O})^{10} = 4.08 \times 10^{-25}
$$

 $P_{\text{H}_2\text{O}} = \frac{10}{3}4.08 \times 10^{-25} = 3.6397 \times 10^{-3} = 3.64 \times 10^{-3} \text{ atm}$

b) (1) Adding more Na 2SO4 (*s*) will **decrease** the ratio of hydrated form/anhydrous form merely because you (2) Reducing the container size will **increase** the pressure (concentration) of the water vapor, which will shift the equilibrium to the reactant side. The ratio of hydrated form/anhydrous form will increase. are increasing the value of the denominator, not because the equilibrium shifts. (3) Adding more water vapor will **increase** the concentration of the water vapor, which will shift the equilibrium to the reactant side. The ratio of hydrated form/anhydrous form will increase. (4) Adding N_2 gas will not change the partial pressure of the water vapor, so the ratio of hydrated form/anhydrous form **will not change**.

17.87 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of each reactant from the given amounts and container volume, use the balanced equation to define x, and set up a reaction table. The equilibrium concentration of CO is known, so x can be calculated and used to find the other equilibrium concentrations. Substitute the equilibrium concentrations into the equilibrium expression to find K_c . Add the molarities of all of the gases at equilibrium, use $(M)(V)$ to find the total number of moles, and then use $PV = nRT$ to find the total pressure. To find [CO]_{eq} after the pressure is doubled, set up another reaction table in which the initial concentrations are equal to the final concentrations from part a) and add in the additional CO. Solution:

The reaction is: $CO(g) + H_2O(g) \leq CO_2(g) + H_2(g)$ a) Initial [CO] and initial $[H_2O] = 0.100 \text{ mol}/20.00 \text{ L} = 0.00500 \text{ M}.$

^{© 2013} by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.

Initial 0.00500 *M* 0.00500 *M* 0
\nChange
\n
$$
\frac{1}{2}
$$

\nEquilibrium = 0.00500 - x 0.000500 - x 0.00000 - x 0.00000
\nx = 0.00276 *M* = [CO₂] [H₂]
\n
$$
K_e = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.00276][0.00276]}{[0.00224][0.00224]} = 1.518176 = 1.52
$$
\n(b) *M*_{total} = [CO₁] [CO₁ + [H₂] = (0.00224 *M*) + (0.00224 *M*) + (0.00276 *M*) + (0.00276 *M*)
\n
$$
H_{total} = (M_{total}/V) = (0.01000 \text{ mol/L})(20.00 \text{ L}) = 0.2000 \text{ mol total}
$$
\n*PV* = *nRT*
\n*P*_{total} = *n*_{final} *RT/V* =
$$
\frac{(0.2000 \text{ mol})(0.08206 \frac{\text{L} \cdot \text{at}}{\text{mol} \cdot \text{mol} \cdot \text{K}} = (20.000 \text{ L}) \text{K})}{(20.00 \text{ mol K})} = 0.9625638 = 0.9626 \text{ atm}
$$
\nc) Initially, an equal number of moles must be added = 0.2000 mol CO
\nd) Set up a table with the initial concentrations equal to the final concentrations from part a), and then add 0.2000 mol CO2000 *M* to compare the added CO.
\nd) Set up a table with the initial concentrations equal to the final concentrations from part a), and then add 0.2000 mol CO2000 *M* to 0.00276 *M* 0.00276 *M* 0.00276 <

© 2013 by McGraw-Hill Education. This is proprietary material solely for authorized instructor use. Not authorized for sale or distribution in any manner. This document may not be copied, scanned, duplicated, forwarded, distributed, or posted on a website, in whole or part.