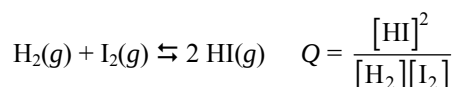


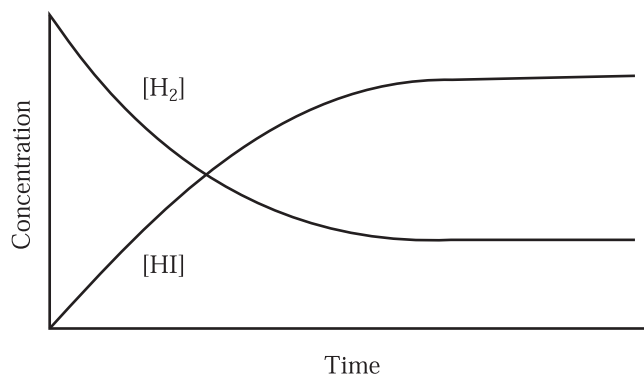
CHAPTER 17 EQUILIBRIUM: THE EXTENT OF CHEMICAL REACTIONS

- 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).

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

- 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. 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.
- 17.5 **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.
- 17.6 The equilibrium constant expression is $K = [\text{O}_2]$. 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 $\text{Li}_2\text{O}_2(\text{s})$ is present.
- 17.7 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 1 H_2 :2 HI .
 Q for a reaction is the ratio of concentrations of products to concentrations of reactants. As the reaction progresses the concentration of reactants decrease and the concentration of products increase, which means that Q increases as a function of time.

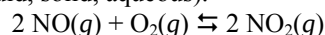




The value of Q increases as a function of time until it reaches the value of K .

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

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

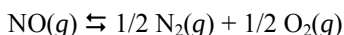


A heterogeneous equilibrium reaction exists when the components of the reaction are in different phases.



- 17.9 $1/2 \text{N}_2(g) + 1/2 \text{O}_2(g) \rightleftharpoons \text{NO}(g)$

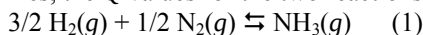
$$Q_{c(\text{form})} = \frac{[\text{NO}]}{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}$$



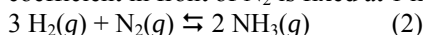
$$Q_{c(\text{decomp})} = \frac{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]}$$

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

- 17.10 Yes, the Q values for the two reactions do differ. The balanced equation for the first reaction is



The coefficient in front of NH_3 is fixed at 1 mole according to the description. In the second reaction, the coefficient in front of N_2 is fixed at 1 mole.

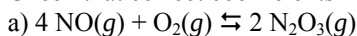


The reaction quotients for the two equations and their relationship are:

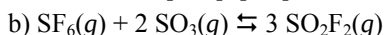
$$Q_1 = \frac{[\text{NH}_3]}{[\text{H}_2]^{3/2}[\text{N}_2]^{1/2}} \quad Q_2 = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

$$Q_2 = Q_1^2$$

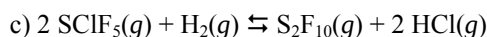
- 17.11 Check that correct coefficients from balanced equation are included as exponents in the mass action expression.



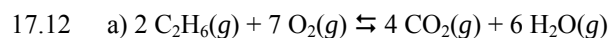
$$Q_c = \frac{[\text{N}_2\text{O}_3]^2}{[\text{NO}]^4[\text{O}_2]}$$



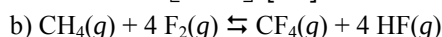
$$Q_c = \frac{[\text{SO}_2\text{F}_2]^3}{[\text{SF}_6][\text{SO}_3]^2}$$



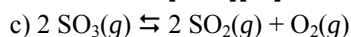
$$Q_c = \frac{[\text{S}_2\text{F}_{10}][\text{HCl}]^2}{[\text{SClF}_5]^2[\text{H}_2]}$$



$$Q_c = \frac{[\text{CO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{C}_2\text{H}_6]^2 [\text{O}_2]^7}$$



$$Q_c = \frac{[\text{CF}_4][\text{HF}]^4}{[\text{CH}_4][\text{F}_2]^4}$$



$$Q_c = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

17.13 The Q for the original reaction is $Q_{\text{ref}} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$

a) The given reaction $\frac{1}{2} \text{S}_2(g) + \text{H}_2(g) \rightleftharpoons \text{H}_2\text{S}(g)$ is the reverse reaction of the original reaction multiplied by a factor of $\frac{1}{2}$. The equilibrium constant for the reverse reaction is the inverse of the original constant. When a reaction is multiplied by a factor, K for the new equation is equal to the K of the original equilibrium raised to a power equal to the factor. For the reaction given in part a), take $(1/K)^{1/2}$.

$$Q_a = (1/Q_{\text{ref}})^{1/2} = \frac{[\text{H}_2\text{S}]}{[\text{S}_2]^{1/2} [\text{H}_2]}$$

$$K = (1/1.6 \times 10^{-2})^{1/2} = 7.90569 = \mathbf{7.9}$$

b) The given reaction $5 \text{H}_2\text{S}(g) \rightleftharpoons 5 \text{H}_2(g) + \frac{5}{2} \text{S}_2(g)$ is the original reaction multiplied by $\frac{5}{2}$. Take the original K to the $\frac{5}{2}$ power to find K of given reaction.

$$Q_a = (Q_{\text{ref}})^{5/2} = \frac{[\text{H}_2]^5 [\text{S}_2]^{5/2}}{[\text{H}_2\text{S}]^5}$$

$$K = (1.6 \times 10^{-2})^{5/2} = 3.23817 \times 10^{-5} = \mathbf{3.2 \times 10^{-5}}$$

17.14 $Q_{c(\text{ref})} = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2 [\text{H}_2]^2}$

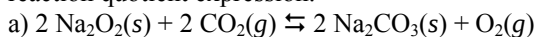
a) $Q_c = [Q_{c(\text{ref})}]^{1/2} = \frac{[\text{N}_2]^{1/2} [\text{H}_2\text{O}]}{[\text{NO}][\text{H}_2]}$

$$\text{Thus, } K_c = [K_{c(\text{ref})}]^{1/2} = (6.5 \times 10^2)^{1/2} = 25.495 = \mathbf{25}$$

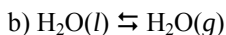
b) $Q_c = [Q_{c(\text{ref})}]^{-2} = \frac{[\text{NO}]^4 [\text{H}_2]^4}{[\text{N}_2]^2 [\text{H}_2\text{O}]^4}$

$$K_c = [K_{c(\text{ref})}]^{-2} = (6.5 \times 10^2)^{-2} = 2.36686 \times 10^{-6} = \mathbf{2.4 \times 10^{-6}}$$

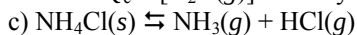
17.15 The concentration of solids and pure liquids do not change, so their concentration terms are not written in the reaction quotient expression.



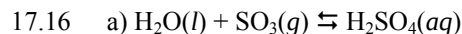
$$Q_c = \frac{[\text{O}_2]}{[\text{CO}_2]^2}$$



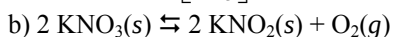
$Q_c = [\text{H}_2\text{O}(\text{g})]$ Only the gaseous water is used. The “(g)” is for emphasis.



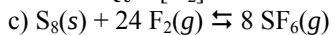
$$Q_c = [\text{NH}_3][\text{HCl}]$$



$$Q_c = \frac{[\text{H}_2\text{SO}_4]}{[\text{SO}_3]}$$

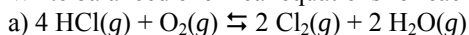


$$Q_c = [\text{O}_2]$$

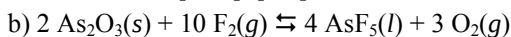


$$Q_c = \frac{[\text{SF}_6]^8}{[\text{F}_2]^{24}}$$

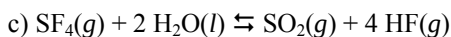
17.17 Write balanced chemical equations for each reaction, and then write the appropriate equilibrium expression.



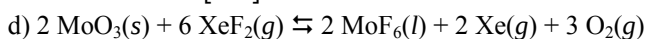
$$Q_c = \frac{[\text{Cl}_2]^2 [\text{H}_2\text{O}]^2}{[\text{HCl}]^4 [\text{O}_2]}$$



$$Q_c = \frac{[\text{O}_2]^3}{[\text{F}_2]^{10}}$$

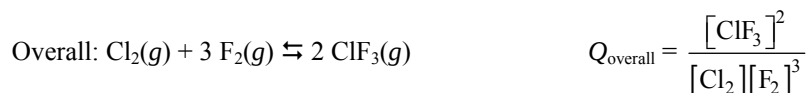
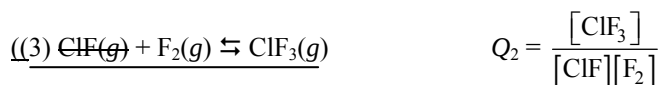
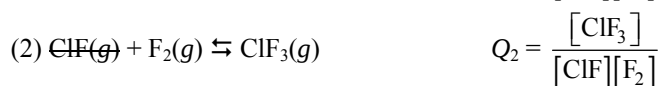
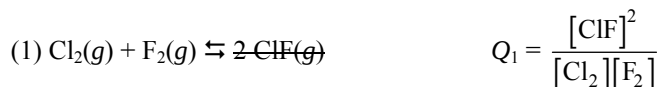


$$Q_c = \frac{[\text{SO}_2][\text{HF}]^4}{[\text{SF}_4]}$$



$$Q_c = \frac{[\text{Xe}]^2 [\text{O}_2]^3}{[\text{XeF}_2]^6}$$

- 17.18 a) The balanced equations and corresponding reaction quotients are given below. Note the second equation must occur twice to get the appropriate overall equation.



- b) The second equation occurs twice, thus it could simply be multiplied by two and its reaction quotient squared. The reaction quotient for the overall reaction, Q_{overall} , determined from the reaction is:

$$Q_{\text{overall}} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

$$Q_{\text{overall}} = Q_1 Q_2^2 = Q_1 Q_2 Q_2 = \frac{[\text{ClF}]^2}{[\text{Cl}_2][\text{F}_2]} \times \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]} \times \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

- 17.19 According to the Ideal Gas Equation, $PV = nRT$. Concentration and pressure of gas are directly proportional as long as the temperature is constant: $C = n/V = P/RT$.

- 17.20 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 Δn 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 $K_c \neq K_p$.

- 17.21 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. If Δn is a positive integer, then $(RT)^{\Delta n}$ 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 $T > 12.2 \text{ K}$, because $0.0821 \text{ (R)} \times 12.2 = 1$), **$K_p > K_c$** 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.

- 17.22 a) Number of moles of gaseous reactants = 0; Number of moles of gaseous products = 3; $\Delta n = 3 - 0 = 3$
 b) Number of moles of gaseous reactants = 1; Number of moles of gaseous products = 0; $\Delta n = 0 - 1 = -1$
 c) Number of moles of gaseous reactants = 0; Number of moles of gaseous products = 3; $\Delta n = 3 - 0 = 3$

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

- 17.24 First, determine Δn for the reaction and then calculate K_c using $K_p = K_c(RT)^{\Delta n}$.

a) Δn = Number of product gas moles – Number of reactant gas moles = $1 - 2 = -1$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{3.9 \times 10^{-2}}{[(0.0821)(1000.)]^{-1}} = 3.2019 = \mathbf{3.2}$$

b) Δn = Number of product gas moles – Number of reactant gas moles = $1 - 1 = 0$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{28.5}{[(0.0821)(500.)]^0} = \mathbf{28.5}$$

- 17.25 First, determine Δn for the reaction and then calculate K_c using $K_p = K_c(RT)^{\Delta n}$.
- a) $\Delta n = \text{Number of product gas moles} - \text{Number of reactant gas moles} = 2 - 2 = 0$
 $K_c = K_p / (RT)^{\Delta n} = (49) / [(0.0821) (730.)]^0 = \mathbf{49}$
- b) $\Delta n = \text{Number of product gas moles} - \text{Number of reactant gas moles} = 2 - 3 = -1$
 $K_c = K_p / (RT)^{\Delta n} = (2.5 \times 10^{10}) / [(0.0821) (500.)]^{-1} = 1.02625 \times 10^{12} = \mathbf{1.0 \times 10^{12}}$
- 17.26 When $Q < K$, the reaction proceeds to the **right** to form more products. The reaction quotient and equilibrium constant are determined by $[\text{products}] / [\text{reactants}]$. 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).
- 17.27 a) The reaction is $2D \leftrightarrow E$ and $K_c = \frac{[E]}{[D]^2}$
- Concentration of D = Concentration of E = $(3 \text{ spheres}) \left(\frac{0.0100 \text{ mol}}{1 \text{ sphere}} \right) \left(\frac{1}{1.00 \text{ L}} \right) = 0.0300 \text{ M}$
- $K_c = \frac{[E]}{[D]^2} = \frac{[0.0300]}{[0.0300]^2} = 33.3333 = \mathbf{33.3}$
- b) In Scene B the concentrations of D and E are both $0.0300 \text{ mol} / 0.500 \text{ L} = 0.0600 \text{ M}$
- $Q_c = \frac{[E]}{[D]^2} = \frac{[0.0600]}{[0.0600]^2} = 16.6666 = 16.7$
- 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 $0.0600 \text{ mol} / 0.500 \text{ L} = 0.120 \text{ M}$
- $Q_c = \frac{[E]}{[D]^2} = \frac{[0.0600]}{[0.120]^2} = 4.1667 = 4.17$
- C is **not at equilibrium**. Since $Q_c < K_c$, the reaction will proceed to the **right**.
- 17.28 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.
- $Q_p = \frac{P_{H_2} P_{Br_2}}{P_{HBr}^2} = \frac{(0.010)(0.010)}{(0.20)^2} = 2.5 \times 10^{-3} > K_p = 4.18 \times 10^{-9}$
- $Q_p > K_p$, thus, the reaction is **not** at equilibrium and will proceed to the **left** (toward 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 $Q_p = K_p$.
- 17.29 $Q_p = \frac{P_{NO}^2 P_{Br_2}}{P_{NOBr}^2} = \frac{(0.10)^2 (0.10)}{(0.10)^2} = 0.10 < K_p = 60.6$
- $Q_p < K_p$ Thus, the reaction is **not** at equilibrium and will proceed to the **right** (toward the products).
- 17.30 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.
- $\Delta n = \text{Number of product gas moles} - \text{Number of reactant gas moles} = 2 - 2 = 0$
- 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).
- $Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.62/2.0][0.43/2.0]}{[0.13/2.0][0.56/2.0]} = 3.662 \text{ (unrounded)} > K_c = 2.7$
- $Q_c > K_c$ Thus, the reaction is **not** at equilibrium and will proceed to the **left** (towards the reactants).

- 17.31 When x mol of CH_4 reacts, $2x$ mol of H_2O also reacts to form x mol of CO_2 and $4x$ mol of H_2 . 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.
- 17.32 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 $[\text{reactant}]_{\text{initial}}$ is very small, or when $[\text{reactant}]_{\text{change}}$ is relatively large due to a large K .
- 17.33 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 .

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[1.87 \times 10^{-3}]^2}{[6.50 \times 10^{-5}][1.06 \times 10^{-3}]} = 50.753 = \mathbf{50.8}$$

17.34 $K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{[0.114][0.342]^3}{[0.0225]^2} = 9.0077875 = \mathbf{9.01}$

- 17.35 The reaction table requires that the initial $[\text{PCl}_5]$ be calculated: $[\text{PCl}_5] = 0.15 \text{ mol}/2.0 \text{ L} = 0.075 \text{ M}$
Since there is a 1:1:1 mole ratio in this reaction:

$$x = [\text{PCl}_5] \text{ reacting } (-x), \text{ and the amount of } \text{PCl}_3 \text{ and of } \text{Cl}_2 \text{ forming } (+x).$$

Concentration (M)	$\text{PCl}_5(g)$	$\rightleftharpoons$	$\text{PCl}_3(g)$	+	$\text{Cl}_2(g)$
Initial	0.075		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.075 - x$		x		x

- 17.36 The reaction table requires that the initial $[\text{H}_2]$ and $[\text{F}_2]$ be calculated: $[\text{H}_2] = 0.10 \text{ mol}/0.50 \text{ L} = 0.20 \text{ M}$;
 $[\text{F}_2] = 0.050 \text{ mol}/0.50 \text{ L} = 0.10 \text{ M}$

$$x = [\text{H}_2] = [\text{F}_2] \text{ reacting } (-x); 2x = [\text{HF}] \text{ forming } (+2x)$$

Concentration (M)	$\text{H}_2(g)$	+	$\text{F}_2(g)$	$\rightleftharpoons$	$2\text{HF}(g)$
Initial	0.20		0.10		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.20 - x$		$0.10 - x$		$2x$

- 17.37 Two of the three equilibrium pressures are known. Construct an equilibrium expression and solve for P_{NOCl} .

$$K_p = 6.5 \times 10^4 = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}P_{\text{Cl}_2}}$$

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

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

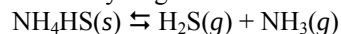
A high pressure for NOCl is expected because the large value of K_p indicates that the reaction proceeds largely to the right, i.e., to the formation of products.

- 17.38 $\text{C}(s) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_4(g)$

$$K_p = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} = 0.262$$

$$P_{\text{CH}_4} = K_p P_{\text{H}_2}^2 = (0.262)(1.22)^2 = 0.38996 = \mathbf{0.390 \text{ atm}}$$

- 17.39 The ammonium hydrogen sulfide will decompose to produce hydrogen sulfide and ammonia gas until $K_p = 0.11$:



$x = [\text{NH}_4\text{HS}]$ reacting ($-x$), and the amount of H_2S and of NH_3 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 NH_4HS since, as a solid, it is not included in the equilibrium expression.)

Concentration (M)	$\text{NH}_4\text{HS}(s)$	$\rightleftharpoons$	$\text{H}_2\text{S}(g)$	+	$\text{NH}_3(g)$
Initial	—		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	—		x		x

$$K_p = 0.11 = (P_{\text{H}_2\text{S}})(P_{\text{NH}_3}) \quad (\text{The solid } \text{NH}_4\text{HS} \text{ is not included.})$$

$$0.11 = (x)(x)$$

$$x = P_{\text{NH}_3} = 0.33166 = \mathbf{0.33 \text{ atm}}$$

- 17.40 $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$

$$[\text{H}_2\text{S}] = 0.45 \text{ mol} / 3.0 \text{ L} = 0.15 \text{ M}$$

Concentration (M)	$2 \text{H}_2\text{S}(g)$	$\rightleftharpoons$	$2 \text{H}_2(g)$	$\text{S}_2(g)$
Initial	0.15		0	0
Change	$-2x$		$+2x$	$+x$
Equilibrium	$0.15 - 2x$		$2x$	x

$$K_c = 9.30 \times 10^{-8} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{[2x]^2 [x]}{[0.15 - 2x]^2}$$

$$\text{Assuming } 0.15 \text{ M} - 2x \approx 0.15 \text{ M}$$

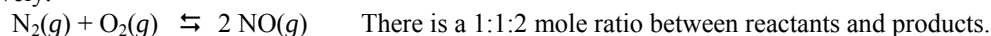
$$9.30 \times 10^{-8} = \frac{[2x]^2 [x]}{[0.15]^2} = \frac{4x^3}{0.15^2}$$

$$x = 8.0575 \times 10^{-4} \text{ M (unrounded)}$$

$$[\text{H}_2] = 2x = 2(8.0575 \times 10^{-4} \text{ M}) = 1.6115 \times 10^{-3} = \mathbf{1.6 \times 10^{-3} \text{ M}}$$

(Since $(1.6 \times 10^{-3})/(0.15) < 0.05$, the assumption is OK.)

- 17.41 The initial concentrations of N_2 and O_2 are $(0.20 \text{ mol}/1.0 \text{ L}) = 0.20 \text{ M}$ and $(0.15 \text{ mol}/1.0 \text{ L}) = 0.15 \text{ M}$, respectively.



Concentration (M)	$\text{N}_2(g)$	$\text{O}_2(g)$	$\rightleftharpoons$	$2 \text{NO}(g)$	
Initial	0.20	0.15		0	
Change	$-x$	$-x$		$+2x$	(1:1:2 mole ratio)
Equilibrium	$0.20 - x$	$0.15 - x$		$2x$	

$$K_c = 4.10 \times 10^{-4} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{[2x]^2}{[0.20 - x][0.15 - x]}$$

$$\text{Assume } 0.20 \text{ M} - x \approx 0.20 \text{ M} \quad \text{and} \quad 0.15 \text{ M} - x \approx 0.15 \text{ M}$$

$$4.10 \times 10^{-4} = \frac{4x^2}{[0.20][0.15]}$$

$$x = 1.753568 \times 10^{-3} \text{ M (unrounded)}$$

$$[\text{NO}] = 2x = 2(1.753568 \times 10^{-3} \text{ M}) = 3.507136 \times 10^{-3} = \mathbf{3.5 \times 10^{-3} \text{ M}}$$

(Since $(1.8 \times 10^{-3})/(0.15) < 0.05$, the assumption is OK.)

17.42

	$2 \text{NO}_2(g) \rightleftharpoons 2 \text{NO}(g) + \text{O}_2(g)$	
Pressure (atm)	$2 \text{NO}_2(g)$	$2 \text{NO}(g) \quad \text{O}_2(g)$
Initial	0.75	0 0
Change	$-2x$	$+2x \quad +x$
Equilibrium	$0.75 - 2x$	$2x \quad x$

$$K_p = 4.48 \times 10^{-13} = \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2} = \frac{(2x)^2 (x)}{(0.75 - 2x)^2}$$

Assume $0.75 \text{ atm} - 2x \approx 0.75 \text{ atm}$

$$4.48 \times 10^{-13} = \frac{(4x^2)(x)}{(0.75)^2} = \frac{(4x^3)}{(0.75)^2}$$

$$x = 3.979 \times 10^{-5} \text{ atm} = \mathbf{4.0 \times 10^{-5} \text{ atm O}_2}$$

$$P_{\text{NO}} = 2x = 2(3.979 \times 10^{-5} \text{ atm}) = 7.958 \times 10^{-5} = \mathbf{8.0 \times 10^{-5} \text{ atm NO}}$$

- 17.43 Construct a reaction table, using $[\text{ICl}]_{\text{init}} = (0.500 \text{ mol}/5.00 \text{ L}) = 0.100 \text{ M}$, and substitute the equilibrium concentrations into the equilibrium expression. There is a 2:1:1 mole ratio between reactant and products:

Concentration (M)	$2 \text{ICl}(g)$	$\rightleftharpoons$	$\text{I}_2(g)$	+	$\text{Cl}_2(g)$	
Initial	0.100		0		0	
Change	$-2x$		$+x$		$+x$	(2:1:1 mole ratio)
Equilibrium	$0.100 - 2x$		x		x	

$$K_c = 0.110 = \frac{[\text{I}_2][\text{Cl}_2]}{[\text{ICl}]^2} = \frac{[x][x]}{[0.100 - 2x]^2}$$

$$0.110 = \frac{[x]^2}{[0.100 - 2x]^2}$$

Take the square root of each side:

$$0.331662 = \frac{[x]}{[0.100 - 2x]}$$

$$x = 0.0331662 - 0.663324x$$

$$1.663324x = 0.0331662$$

$$x = 0.0199397$$

$$[\text{I}_2]_{\text{eq}} = [\text{Cl}_2]_{\text{eq}} = \mathbf{0.0200 \text{ M}}$$

$$[\text{ICl}]_{\text{eq}} = 0.100 - 2x = 0.601206 = \mathbf{0.060 \text{ M ICl}}$$

17.44

Concentration (M)	$\text{SCl}_2(g)$	+	$2 \text{C}_2\text{H}_4(g)$	$\rightleftharpoons$	$\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2(g)$
Initial	0.675		0.973		0
Change	$-x$		$-2x$		$+x$
Equilibrium	$0.675 - x$		$0.973 - 2x$		x

$$[\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2]_{\text{eq}} = x = 0.350 \text{ M}$$

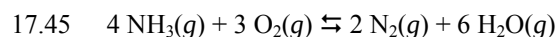
$$[\text{SCl}_2]_{\text{eq}} = 0.675 - x = 0.675 - 0.350 = 0.325 \text{ M}$$

$$[\text{C}_2\text{H}_4]_{\text{eq}} = 0.973 - 2x = 0.973 - 2(0.350) = 0.273 \text{ M}$$

$$K_c = \frac{[\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2]}{[\text{SCl}_2][\text{C}_2\text{H}_4]^2} = \frac{[0.350]}{[0.325][0.273]^2} = 14.4497 \text{ (unrounded)}$$

$$K_p = K_c(\text{RT})^{\Delta n} \quad \Delta n = 1 \text{ mol} - 3 \text{ mol} = -2$$

$$K_p = (14.4497)[(0.0821)(273.2 + 20.0)]^{-2} = 0.0249370 = \mathbf{0.0249}$$



To find the equilibrium constant, determine the equilibrium concentrations of each reactant and product and insert into the equilibrium expression. Since $[\text{N}_2]$ increases from 0 to $1.96 \times 10^{-3} \text{ M}$, the concentration of H_2O gas will increase by 3 times as much (stoichiometric ratio is $6 \text{ H}_2\text{O} : 2 \text{ N}_2$) and the concentration of reactants will decrease by a factor equivalent to the stoichiometric ratio (2 for NH_3 and $3/2$ for O_2). Since the volume is 1.00 L, the concentrations are equal to the number of moles present.

Concentration (M)	$4 \text{ NH}_3(g)$	+	$3 \text{ O}_2(g)$	$\rightleftharpoons$	$2 \text{ N}_2(g)$	+	$6 \text{ H}_2\text{O}(g)$
Initial	0.0150		0.0150		0		0
Change	$-4x$		$-3x$		$+2x$		$+6x$
Equilibrium	$0.0150 - 4x$		$0.0150 - 3x$		$+2x$		$+6x$

All intermediate concentration values are unrounded.

$$[\text{N}_2]_{\text{eq}} = 2x = 1.96 \times 10^{-3} \text{ M}$$

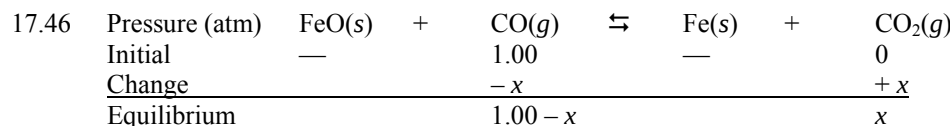
$$[\text{H}_2\text{O}]_{\text{eq}} = (6 \text{ mol H}_2\text{O} / 2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 5.8800 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3]_{\text{eq}} = (0.0150 \text{ mol NH}_3 / 1.00 \text{ L}) - (4 \text{ mol NH}_3 / 2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 1.1080 \times 10^{-2} \text{ M}$$

$$[\text{O}_2]_{\text{eq}} = (0.0150 \text{ mol O}_2 / 1.00 \text{ L}) - (3 \text{ mol O}_2 / 2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 1.2060 \times 10^{-2} \text{ M}$$

$$K_c = \frac{[\text{N}_2]^2 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^3} = \frac{[1.96 \times 10^{-3}]^2 [5.8800 \times 10^{-3}]^6}{[1.1080 \times 10^{-2}]^4 [1.2060 \times 10^{-2}]^3} = 6.005859 \times 10^{-6} = \mathbf{6.01 \times 10^{-6}}$$

If values for concentrations were rounded to calculate K_c , the answer is 5.90×10^{-6} .



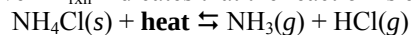
$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = 0.403 = \frac{x}{1.00 - x}$$

$$x = 0.28724 = \mathbf{0.287 \text{ atm CO}_2}$$

$$1.00 - x = 1.00 - 0.28724 = 0.71276 = \mathbf{0.71 \text{ atm CO}}$$

17.47 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. Reactant concentration changes cause changes in the specific equilibrium concentrations of reactants and products (equilibrium position), but not in the equilibrium constant.

17.48 A positive ΔH_{rxn} indicates that the reaction is endothermic, and that heat is consumed in the reaction:



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 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.

17.49 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.

17.50 a) $\text{Rate}_f = k_f [\text{Reactants}]^x$. An increase in reactant concentration shifts the equilibrium to the right by increasing the initial forward rate. Since $K_{\text{eq}} = k_f / k_r$ and k_f and k_r are not changed by changes in concentration, K_{eq} 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.

c) An increase in temperature increases k_r to a greater extent for an exothermic reaction and thus lowers the K_{eq} value.

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

17.61 $4 \text{ Fe}_3\text{O}_4(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 6 \text{ Fe}_2\text{O}_3(\text{s})$ $K_p = 2.5 \times 10^{87}$ at 298 K

a) $K_p = \frac{1}{P_{\text{O}_2}} = 2.5 \times 10^{87}$

$P_{\text{O}_2} = 4.0 \times 10^{-88} \text{ atm}$

b) $Q_p = \frac{1}{P_{\text{O}_2}} = 1/(0.21) = 4.7619$ (unrounded)

$K_p > Q_p$ thus, the reaction will proceed to the **right**.

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

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

$\Delta n = 0 - 1 = -1$

$K_c = (2.5 \times 10^{87}) / [(0.0821)(298)]^{-1} = 6.11645 \times 10^{88} = \mathbf{6.1 \times 10^{88}}$

17.62 a) $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{heat}$

The forward reaction is exothermic (ΔH_{rxn} 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 (1 SO_3) than as reactants (1 $\text{SO}_2 + \frac{1}{2} \text{O}_2$), 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 O_2 would **decrease Q** ($Q = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$) 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**.

17.63 a) $Q_c = \frac{[\text{XY}]^2}{[\text{X}_2][\text{Y}_2]}$

b) Scene A: $Q_c = \frac{[0]^2}{[0.4][0.4]} = \mathbf{0}$

Scene B: $Q_c = \frac{[0.4]^2}{[0.2][0.2]} = \mathbf{4}$

Scenes C-E: $Q_c = \frac{[0.6]^2}{[0.1][0.1]} = 36 = \mathbf{4 \times 10^1}$

c) **left-to-right**. Frame A must be the earliest time.

d) $K = 4 \times 10^1$

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.

17.64 Calculate K_c

$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.40][0.10]}{[0.10][0.10]} = 4.0$

Calculate new concentrations

New $\text{H}_2 = 0.10 \text{ M} + (0.60 \text{ mol} / 2.0 \text{ L}) = 0.40 \text{ M}$

Concentration (M)	$\text{CO}(\text{g})$	+	$\text{H}_2\text{O}(\text{g})$	$\rightleftharpoons$	$\text{CO}_2(\text{g})$	+	$\text{H}_2(\text{g})$
Initial	0.10		0.10		0.40		0.40
Change	+x		+x		-x		-x
Equilibrium	$0.10 + x$		$0.10 + x$		$0.40 - x$		$0.40 - x$

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.40 - x][0.40 - x]}{[0.10 + x][0.10 + x]} = \frac{[0.40 - x]^2}{[0.10 + x]^2} = 4.0$$

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

$$x = 0.066667 \text{ (unrounded)}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.10 + x = 0.10 + 0.066667 = 0.166667 = \mathbf{0.17 \text{ M}}$$

$$[\text{CO}_2] = [\text{H}_2] = 0.40 - x = 0.40 - 0.066667 = 0.333333 = \mathbf{0.33 \text{ M}}$$

- 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 .

$$K_p = K_c(RT)^{\Delta n} \quad \Delta n = 1 - 2 = -1 \text{ (1 mol of product, } \text{C}_2\text{H}_5\text{OH} \text{ and 2 mol of reactants, } \text{C}_2\text{H}_4 + \text{H}_2\text{O})$$

$$K_p = K_c(RT)^{-1} = (9 \times 10^3)[(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(600. \text{ K})]^{-1} = 1.8270 \times 10^2 \text{ (unrounded)}$$

Substitute the given values into the equilibrium expression and solve for $P_{\text{C}_2\text{H}_4}$.

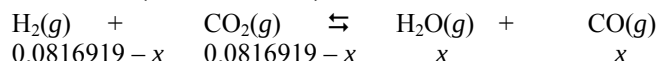
$$K_p = \frac{P_{\text{C}_2\text{H}_5\text{OH}}}{P_{\text{C}_2\text{H}_4} P_{\text{H}_2\text{O}}} = \frac{200.}{P_{\text{C}_2\text{H}_4} (400.)} = 1.8270 \times 10^2$$

$$P_{\text{C}_2\text{H}_4} = 2.7367 \times 10^{-3} = \mathbf{3 \times 10^{-3} \text{ atm}}$$

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 $\text{C}_2\text{H}_5\text{OH}$ would not increase the yield. Ethanol has a lower boiling point (78.5°C) than water (100°C). 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 $n/V = M = P / RT = \frac{(2.0 \text{ atm})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)((273.2 + 25.0) \text{ K})} = 0.0816919 \text{ M each gas (unrounded)}$



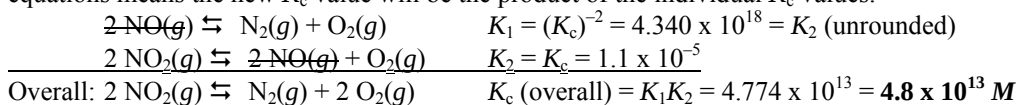
$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = 0.534 = \frac{[x][x]}{[0.0816919 - x][0.0816919 - x]} = \frac{[x]^2}{[0.0816919 - x]^2}$$

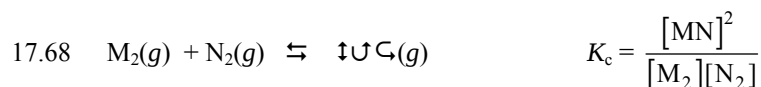
$$(0.534)^{1/2} = 0.730753 = \frac{[x]}{[0.0816919 - x]}$$

$$x = 0.03449 \text{ (unrounded)}$$

$$\text{Mass H}_2 [(0.0816919 - 0.03449) \text{ mol/L}](1.00 \text{ L}) (2.016 \text{ g H}_2/\text{mol}) = 0.095159 = \mathbf{0.095 \text{ g H}_2}$$

- 17.67 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.





Scene A: Concentrations: $[M_2] = [N_2] = 0.20 M$; $[MN] = 0.40 M$

$$K_c = \frac{[0.40]^2}{[0.20][0.20]} = 4.0$$

Scene B:

Concentration (M)	$M_2(g)$	$N_2(g)$	$\rightleftharpoons$	$2MN(g)$
Initial	0.60	0.30		0
Change	$-x$	$-x$		$+2x$
Equilibrium	$0.60 - x$	$0.30 - x$		$2x$

$$K_c = 4.0 = \frac{[2x]^2}{[0.60 - x][0.30 - x]}$$

$$4.0 = \frac{4x^2}{0.18 - 0.90x + x^2}$$

$$4x^2 = 0.72 - 3.6x + 4x^2$$

$$3.6x = 0.72$$

$$x = 0.20 M$$

$$[M_2] = 0.60 - x = 0.60 - 0.20 = \mathbf{0.40 M}$$

$$[N_2] = 0.30 - x = 0.30 - 0.20 = \mathbf{0.10 M}$$

$$[MN] = 2x = 2(0.20 M) = \mathbf{0.40 M}$$

17.69 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 .

$$K_p = K_c(RT)^{\Delta n} \quad \Delta n = 2 - 3 = -1 \quad (2 \text{ mol of product, } SO_3 \text{ and 3 mol of reactants, } 2 SO_2 + O_2)$$

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^{-1} = (1.7 \times 10^8)[(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(600. \text{ K})]^{-1} = 3.451 \times 10^6 \text{ (unrounded)}$$

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

$$P_{SO_2} = 0.016149 = \mathbf{0.016 atm}$$

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 $SO_2:O_2:SO_3$

Concentration (M)	$2 SO_2(g)$	$+$	$O_2(g)$	$\rightleftharpoons$	$2 SO_3(g)$
Initial	0.0040		0.0028		0
Change	$-2x$		$-x$		$+2x$
Equilibrium	$0.0040 - 2x$		$0.0028 - x$		$2x = 0.0020$

$x = 0.0010$, therefore:

$$[SO_2] = 0.0040 - 2(0.0010) = 0.0020 M$$

$$[O_2] = 0.0028 - 0.0010 = 0.0018 M$$

$$[SO_3] = 2(0.0010) = 0.0020 M$$

Substitute equilibrium concentrations into the equilibrium expression and solve for K_c .

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[0.0020]^2}{[0.0020]^2 [0.0018]} = 555.5556 = \mathbf{5.6 \times 10^2}$$

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).

$$P_{SO_2} = \frac{nRT}{V} = \frac{(0.0020 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (1000. \text{ K})}{(1.0 \text{ L})} = 0.1642 = \mathbf{0.16 atm}$$

- 17.70 The equilibrium constant for the reaction is $K_p = P_{\text{CO}_2} = 0.220 \text{ atm}$.

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 CaCO_3 reacted is equal to the number of moles of carbon dioxide produced. Use the pressure of CO_2 and the Ideal Gas Equation to calculate the moles of CaCO_3 reacted:

$$\text{Moles CaCO}_3 = \text{moles CO}_2 = n = PV/RT$$

$$n = \frac{(0.220 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(385 \text{ K})} = 0.06960 \text{ mol CaCO}_3 \text{ lost (unrounded)}$$

$$0.100 \text{ mol CaCO}_3 - 0.06960 \text{ mol CaCO}_3 = 0.0304 \text{ mol CaCO}_3 \text{ at first equilibrium}$$

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 CaCO_3 formed.

$$\text{Moles CaCO}_3 = \text{moles CO}_2 = n = PV/RT$$

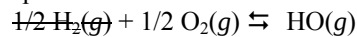
$$n = \frac{(0.300 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(385 \text{ K})} = 0.09491 \text{ mol CaCO}_3 \text{ formed (unrounded)}$$

Add the moles of CaCO_3 formed in the second equilibrium to the moles of CaCO_3 at the first equilibrium position and convert to grams.

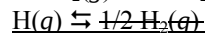
$$\text{Mass CaCO}_3 = \left(\frac{0.0304 \text{ mol} + 0.09491 \text{ mol CaCO}_3}{1 \text{ mol CaCO}_3} \right) \left(\frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \right) = 12.542 = \mathbf{12.5 \text{ g CaCO}_3}$$

- 17.71 a) $\text{C}_2\text{H}_4(g) + 3 \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)$
b) $4 \text{NO}_2(g) + 6 \text{H}_2\text{O}(g) \rightleftharpoons 4 \text{NH}_3(g) + 7 \text{O}_2(g)$

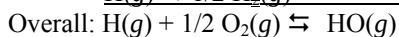
- 17.72 The first equation is in the correct form, but the second equation must be reversed. Reversing the equation leads to the reciprocal of the K value.



$$K_{c1} = 0.58$$



$$K_{c2} = (K_{c1})^{-1} = 6.25 \times 10^2 \text{ (unrounded)}$$



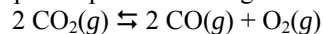
$$K_{c(\text{overall})} = K_{c1} \times (K_{c2})^{-1} = 362.5 = \mathbf{3.6 \times 10^2}$$

- 17.73 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 $V_{\text{CO}_2} + V_{\text{O}_2} + V_{\text{N}_2} = 10.0 + 1.00 + 50.0 = 61.0$.

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

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

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



$$K_p = \frac{P_{\text{CO}}^2 P_{\text{O}_2}}{P_{\text{CO}_2}^2} = \frac{P_{\text{CO}}^2 (0.06557377)}{(0.6557377)^2} = 1.4 \times 10^{-28}$$

$$P_{\text{CO}} = 3.0299 \times 10^{-14} = \mathbf{3.0 \times 10^{-14} \text{ atm}}$$

b) Convert partial pressure to moles per liter using the ideal gas equation, and then convert moles of CO to grams.

$$n_{\text{CO}}/V = P/RT = \frac{(3.0299 \times 10^{-14} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(800 \text{ K})} = 4.6131 \times 10^{-16} \text{ mol/L (unrounded)}$$

$$\left(\frac{4.6131 \times 10^{-16} \text{ mol CO}}{\text{L}}\right)\left(\frac{28.01 \text{ g CO}}{1 \text{ mol CO}}\right)\left(\frac{1 \text{ pg}}{10^{-12} \text{ g}}\right) = 0.01292 = \mathbf{0.013 \text{ pg CO/L}}$$

17.74 a) $\text{Fe}^{2+} + 2 \text{Fe}^{3+}$

b) $(0.050 \text{ mol H}_2\text{O})/(1.0 \text{ L}) = 0.050 \text{ M H}_2\text{O}$

$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} = 5.1 = \frac{[4x]^4}{[0.050 - 4x]^4}$$

$$1.50277 = \frac{[4x]}{[0.050 - 4x]} \text{ (unrounded)}$$

$$x = (7.50553 \times 10^{-3} \text{ mol/L})(1.0 \text{ L}) = 7.50553 \times 10^{-3} \text{ mol Fe}_3\text{O}_4 \text{ reacting (unrounded)}$$

$$\text{Mass Fe}_3\text{O}_4 = (7.50553 \times 10^{-3})(231.55 \text{ g Fe}_3\text{O}_4/1 \text{ mol Fe}_3\text{O}_4) = 1.7494 = \mathbf{1.7 \text{ g Fe}_3\text{O}_4}$$

17.75 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).

17.76 a) Write a reaction table given that $P_{\text{CH}_4}(\text{init}) = P_{\text{CO}_2}(\text{init}) = 10.0 \text{ atm}$, substitute equilibrium values into the equilibrium expression, and solve for P_{H_2} .

Pressure (atm)	$\text{CH}_4(\text{g})$	+	$\text{CO}_2(\text{g})$	$\rightleftharpoons$	$2 \text{ CO}(\text{g})$	+	$2 \text{ H}_2(\text{g})$
Initial	10.0		10.0		0		0
Change	$-x$		$-x$		$+2x$		$+2x$
Equilibrium	$10.0 - x$		$10.0 - x$		$2x$		$2x$

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{H}_2}^2}{P_{\text{CH}_4} P_{\text{CO}_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 3.548 \times 10^6 \text{ (take square root of each side)}$$

$$\frac{(2x)^2}{(10.0 - x)} = 1.8836135 \times 10^3$$

A quadratic is necessary:

$$4x^2 + (1.8836135 \times 10^3 x) - 1.8836135 \times 10^4 = 0 \text{ (unrounded)}$$

$$a = 4 \quad b = 1.8836135 \times 10^3 \quad c = -1.8836135 \times 10^4$$

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

$$x = \frac{-1.8836135 \times 10^3 \pm \sqrt{(1.8836135 \times 10^3)^2 - 4(4)(-1.8836135 \times 10^4)}}{2(4)}$$

$$x = 9.796209 \text{ (unrounded)}$$

$$P(\text{hydrogen}) = 2x = 2(9.796209) = 19.592418 \text{ atm (unrounded)}$$

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).

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

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

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{H}_2}^2}{P_{\text{CH}_4} P_{\text{CO}_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 2.626 \times 10^7$$

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

A quadratic is needed:

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

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

$$x = \frac{-5.124451 \times 10^3 \pm \sqrt{(5.124451 \times 10^3)^2 - 4(4)(-5.124451 \times 10^4)}}{2(4)}$$

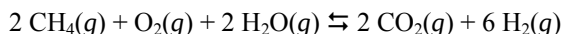
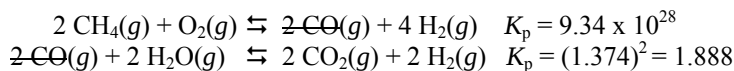
$$x = 9.923138 \text{ (unrounded)}$$

$$P(\text{hydrogen}) = 2x = 2(9.923138) = 19.846276 \text{ atm (unrounded)}$$

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).

$$\text{The percent yield is } \frac{19.846276 \text{ atm}}{20.0 \text{ atm}}(100\%) = 99.23138 = \mathbf{99.0\%}.$$

- 17.77 a) 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 $(K_p)^2$.



$$\text{b) } K_p = (9.34 \times 10^{28})(1.888) = 1.76339 \times 10^{29} = \mathbf{1.76 \times 10^{29}}$$

$$\text{c) } \Delta n = 8 - 5 = 3 \quad (8 \text{ moles of product gas} - 5 \text{ moles of reactant gas})$$

$$K_c = \frac{K_p}{[RT]^{\Delta n}}$$

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

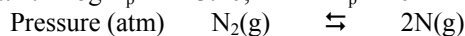
d) The initial total pressure is given as 30. atm. To find the final pressure use relationship between pressure and number of moles of gas: $n_{\text{initial}}/P_{\text{initial}} = n_{\text{final}}/P_{\text{final}}$

$$\text{Total mol of gas initial} = 2.0 \text{ mol CH}_4 + 1.0 \text{ mol O}_2 + 2.0 \text{ mol H}_2\text{O} = 5.0 \text{ mol}$$

$$\text{Total mol of gas final} = 2.0 \text{ mol CO}_2 + 6.0 \text{ mol H}_2 = 8.0 \text{ mol}$$

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

- 17.78 a) Careful reading of the problem indicates that the given K_p occurs at 1000. K and that the initial pressure of N_2 is 200. atm. $\log K_p = -43.10$; $K_p = 10^{-43.10} = 7.94328 \times 10^{-44}$



$$\text{Initial} \quad 200. \quad 0$$

$$\text{Change} \quad -x \quad +2x$$

$$\text{Equilibrium} \quad 200 - x \quad 2x$$

$$K_p = \frac{(P_{\text{N}})^2}{(P_{\text{N}_2})} = 7.94328 \times 10^{-44}$$

$$\frac{(2x)^2}{(200. - x)} = 7.94328 \times 10^{-44} \quad \text{Assume } 200. - x \cong 200.$$

$$P_N = 2x = \sqrt{(200.)(7.94328 \times 10^{-44})} = 3.985795 \times 10^{-21} = \mathbf{4.0 \times 10^{-21}}$$

b) $\text{Log } K_p = -17.30$; $K_p = 10^{-17.30} = 5.01187 \times 10^{-18}$

Pressure (atm)	$\text{H}_2(g) \rightleftharpoons 2\text{H}(g)$	
Initial	600.	0
Change	$-x$	$+2x$
Equilibrium	$600 - x$	$2x$

$$K_p = \frac{(P_H)^2}{(P_{H_2})} = 5.01187 \times 10^{-18}$$

$$\frac{(2x)^2}{(600. - x)} = 5.01187 \times 10^{-18} \quad \text{Assume } 600. - x \cong 600.$$

$$P_H = 2x = \sqrt{(600.)(5.01187 \times 10^{-18})} = 5.48372 \times 10^{-8} = \mathbf{5.5 \times 10^{-8}}$$

c) Convert pressures to moles using the ideal gas law. $PV = nRT$. Convert moles to atoms using Avogadro's number.

$$\begin{aligned} \text{Moles } N/V = P/RT &= \frac{(3.985795 \times 10^{-21} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(1000. \text{K})} \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}}\right) \\ &= 29.2356 = \mathbf{29 \text{ N atoms/L}} \end{aligned}$$

$$\begin{aligned} \text{Moles } H/V = P/RT &= \frac{(5.48372 \times 10^{-8} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(1000. \text{K})} \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}}\right) \\ &= 4.022 \times 10^{14} = \mathbf{4.0 \times 10^{14} \text{ H atoms/L}} \end{aligned}$$

d) The more reasonable step is $\text{N}_2(g) + \text{H}(g) \rightarrow \text{NH}(g) + \text{N}(g)$. With only 29 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.

17.79 a) $3 \text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$ The mole ratio $\text{H}_2/\text{N}_2 = 3/1$; if $\text{N}_2 = x$, $\text{H}_2 = 3x$ $P_{\text{NH}_3} = 50. \text{ atm}$

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = 1.00 \times 10^{-4}$$

$$K_p = \frac{(50.)^2}{(x)(3x)^3} = 1.00 \times 10^{-4}$$

$$x = 31.02016 = \mathbf{31 \text{ atm } N_2}$$

$$3x = 3(31.02016) = 93.06048 = \mathbf{93 \text{ atm } H_2}$$

$$\begin{aligned} P_{\text{total}} &= P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (31.02016 \text{ atm}) + (93.06048 \text{ atm}) + (50. \text{ atm}) \\ &= 174.08064 = \mathbf{174 \text{ atm total}} \end{aligned}$$

b) $K_p = \frac{(50.)^2}{(x)(6x)^3} = 1.00 \times 10^{-4}$ $\text{N}_2 = x$ and $\text{H}_2 = 6x$

$$x = 18.44 = \mathbf{18 \text{ atm } N_2}$$

$$6x = 6(18.44) = 110.64 = \mathbf{111 \text{ atm } H_2}$$

$$\begin{aligned} P_{\text{total}} &= P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (18.44 \text{ atm}) + (110.64 \text{ atm}) + (50. \text{ atm}) \\ &= 179.09 = \mathbf{179 \text{ atm total}} \end{aligned}$$

This is not a valid argument. The total pressure in (b) is greater than in (a) to produce the same amount of NH_3 .

- 17.80 a) Equilibrium partial pressures for the reactants, nitrogen and oxygen, can be assumed to equal their initial partial pressures because the equilibrium constant is so small that very little nitrogen and oxygen will react to form nitrogen monoxide. After calculating the equilibrium partial pressure of nitrogen monoxide, test this assumption by comparing the partial pressure of nitrogen monoxide with that of nitrogen and oxygen.

Pressure (atm)	$\text{N}_2(g)$	+	$\text{O}_2(g)$	$\rightleftharpoons$	$2\text{NO}(g)$
Initial	0.780		0.210		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.780 - x$		$0.210 - x$		$2x$

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} = 4.35 \times 10^{-31}$$

$$\frac{(2x)^2}{(0.780 - x)(0.210 - x)} = 4.35 \times 10^{-31} \text{ Assume } x \text{ is small because } K \text{ is small.}$$

$$\frac{(2x)^2}{(0.780)(0.210)} = 4.35 \times 10^{-31}$$

$$x = 1.33466 \times 10^{-16} \text{ (unrounded)}$$

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.

$$P_{\text{nitrogen}} (\text{equilibrium}) = (0.780 - 1.33466 \times 10^{-16}) \text{ atm} = \mathbf{0.780 \text{ atm N}_2}$$

$$P_{\text{oxygen}} (\text{equilibrium}) = (0.210 - 1.33466 \times 10^{-16}) \text{ atm} = \mathbf{0.210 \text{ atm O}_2}$$

$$P_{\text{NO}} (\text{equilibrium}) = 2 (1.33466 \times 10^{-16}) \text{ atm} = 2.66932 \times 10^{-16} = \mathbf{2.67 \times 10^{-16} \text{ atm NO}}$$

- b) The total pressure is the sum of the three partial pressures:

$$0.780 \text{ atm} + 0.210 \text{ atm} + 2.67 \times 10^{-16} \text{ atm} = \mathbf{0.990 \text{ atm}}$$

- c) $K_p = K_c(RT)^{\Delta n}$ $\Delta n = 2 \text{ mol NO product} - 2 \text{ mol reactant (1 N}_2 + 1 \text{ O}_2) = 0$

$$K_p = K_c(RT)^0$$

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

- 17.81 a) Scenes B and D represent equilibrium.

- b) C, A, B = D

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

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

$$K_c = \frac{[\text{Z}]^2}{[\text{Y}]} = \frac{[0.50]^2}{[0.25]} = \mathbf{1.0}$$

- 17.82 $\text{C}_5\text{H}_{11}\text{OH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOC}_5\text{H}_{11} + \text{H}_2\text{O}$

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 toward the products.

- 17.83 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 $[\text{H}_2\text{S}] = 0.600$, and $[\text{H}_2] = [\text{S}_2] = 0$.

	$\text{H}_2\text{S}(g)$	$\rightleftharpoons$	$2 \text{ H}_2(g)$	+	$\text{S}_2(g)$
Initial	0.600 M		0 M		0 M
Change	$-2x$		$+2x$		$+x$
Equilibrium	$0.600 - 2x$		$+2x$		$+x$

$$K_c = \frac{[H_2]^2 [S_2]}{[H_2S]^2} = 9.0 \times 10^{-8}$$

$$\frac{[2x]^2 [x]}{[0.600 - 2x]^2} = 9.0 \times 10^{-8} \text{ Assume } 2x \text{ is small compared to } 0.600 \text{ M.}$$

$$\frac{[2x]^2 [x]}{[0.600]^2} = 9.0 \times 10^{-8}$$

$$x = 2.008 \times 10^{-3} \text{ (unrounded) assumption justified}$$

$$[H_2S] = 0.600 - 2x = 0.600 - 2(2.008 \times 10^{-3}) = 0.595984 = \mathbf{0.596 \text{ M } H_2S}$$

$$[H_2] = 2x = 2(2.008 \times 10^{-3}) = 4.016 \times 10^{-3} = \mathbf{4.0 \times 10^{-3} \text{ M } H_2}$$

$$[S_2] = x = 2.008 \times 10^{-3} = \mathbf{2.0 \times 10^{-3} \text{ M } S_2}$$

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

$$P_{H_2O} = \sqrt[10]{4.08 \times 10^{-25}} = 3.6397 \times 10^{-3} = \mathbf{3.64 \times 10^{-3} \text{ atm}}$$

b) (1) Adding more $Na_2SO_4(s)$ will decrease the ratio of hydrated form/anhydrous form merely because you are increasing the value of the denominator, not because the equilibrium shifts.

(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.

(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.

17.85 The reaction is: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

a) Set up a table with the initial CO and initial $H_2 = 0.100 \text{ mol}/20.00 \text{ L} = 0.00500 \text{ M}$.

	CO	H_2O	CO_2	H_2
Initial	0.00500 M	0.00500 M	0	0
Change	-x	-x	+x	+x

$$\text{Equilibrium} \quad 0.00500 - x \quad 0.00500 - x \quad x \quad x$$

$$[CO]_{\text{equilibrium}} = 0.00500 - x = 2.24 \times 10^{-3} \text{ M} = [H_2O] \quad (\text{given in problem})$$

$$x = 0.00276 \text{ M} = [CO_2] = [H_2]$$

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.00276][0.00276]}{[0.00224][0.00224]} = 1.518176 = \mathbf{1.52}$$

$$b) M_{\text{total}} = [CO] + [H_2O] + [CO_2] + [H_2] = (0.00224 \text{ M}) + (0.00224 \text{ M}) + (0.00276 \text{ M}) + (0.00276 \text{ M}) = 0.01000 \text{ M}$$

$$n_{\text{total}} = M_{\text{total}} V = (0.01000 \text{ mol/L}) (20.00 \text{ L}) = 0.2000 \text{ mol total}$$

$$P_{\text{total}} = n_{\text{total}} RT/V = \frac{(0.2000 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 900.) \text{ K})}{(20.00 \text{ L})} = 0.9625638 = \mathbf{0.9626 \text{ atm}}$$

c) Initially, an equal number of moles must be added = **0.2000 mol CO**

d) Set up a table with the initial concentrations equal to the final concentrations from part (a), and then add 0.2000 mol CO/20.00 L = 0.01000 M to compensate for the added CO.

	CO	H_2O	CO_2	H_2
Initial	0.00224 M	0.00224 M	0.00276 M	0.00276 M
Added CO	0.01000 M			
Change	-x	-x	+x	+x
Equilibrium	0.01224 - x	0.00224 - x	0.00276 + x	0.00276 + x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.00276 + x][0.00276 + x]}{[0.01224 - x][0.00224 - x]} = 0.9625638$$

$$\frac{[7.6176 \times 10^{-6} + 5.52 \times 10^{-3} x + x^2]}{2.74176 \times 10^{-5} - 1.448 \times 10^{-2} x + x^2} = 0.9625638$$

$$7.6176 \times 10^{-6} + 5.52 \times 10^{-3} x + x^2 = (0.9625638)(2.74176 \times 10^{-5} - 1.448 \times 10^{-2} x + x^2)$$

$$7.6176 \times 10^{-6} + 5.52 \times 10^{-3} x + x^2 = 2.6391189 \times 10^{-5} - 1.3937923 \times 10^{-2} x + 0.9625638 x^2$$

$$0.0374362 x^2 + 1.9457923 \times 10^{-2} x - 1.8773589 \times 10^{-5} = 0$$

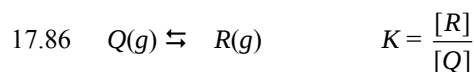
$$a = 0.0374362 \quad b = 1.9457923 \times 10^{-2} \quad c = -1.8773589 \times 10^{-5}$$

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

$$x = \frac{-(1.9457923 \times 10^{-2}) \pm \sqrt{(1.9457923 \times 10^{-2})^2 - 4(0.0374362)(-1.8773589 \times 10^{-5})}}{2(0.0374362)}$$

$$x = 9.6304567 \times 10^{-4} \text{ (unrounded)}$$

$$[\text{CO}] = 0.01224 - x = 0.01224 - (9.6304567 \times 10^{-4}) = 0.011276954 = \mathbf{0.01128 \text{ M}}$$



For Scene A at equilibrium:

$$K = \frac{[R]}{[Q]} = \frac{[2]}{[6]} = 0.33$$

For Scene B:

	$Q(g)$	$\rightleftharpoons$	$R(g)$
Initial	10		2
Change	$-x$		$+x$
Equilibrium	$10 - x$		$2 + x$

$$0.33 = \frac{[2 + x]}{[10 - x]}$$

$$x = 0.977 = 1$$

$$Q = 10 - x = 10 - 1 = \mathbf{9}$$

$$R = 2 + x = 2 + 1 = \mathbf{3}$$