

15 Chemical Equilibrium

Visualizing Concepts

#1, 4, 6, 9 on next page

15.2 Yes. The first box is pure reactant A. As the reaction proceeds, some A changes to B. In the fourth and fifth boxes, the relative amounts (concentrations) of A and B are constant. Although the reaction is ongoing the rates of $A \rightarrow B$ and $B \rightarrow A$ are equal, and the relative amounts of A and B are constant.

15.3 *Analyze.* Given box diagram and reaction type, determine whether $K > 1$ for the equilibrium mixture depicted in the box.

Plan. Assign species in the box to reactants and products. Write an equilibrium expression in terms of concentrations. Find the relationship between numbers of molecules and concentration. Calculate K.

Solve. Let red = A, blue = X, red and blue pairs = AX. (The colors of A and X are arbitrary.) There are 3A, 2B, and 8AX in the box.

$M = \text{mol/L}$. Since moles is a counting unit for particles, mol ratios and particle ratios are equivalent. We can use numbers of particles in place of moles in the molarity formula. $V = 1 \text{ L}$, so in this case, $[A] = \text{number of A particles}$.

$$K = \frac{[AX]}{[A][X]}; \quad [AX] = 8/V = 8; [A] = 3/V = 3; [X] = 2/V = 2. \quad K = \frac{8}{[3][2]} = \frac{8}{6} = 1.33$$

15.5 *Analyze/Plan.* The reaction with the largest equilibrium constant has the largest ratio of products to reactants. Count product and reactant molecules. Calculate ratios and compare. *Solve.*

$$K = \frac{[C_2H_4X_2]}{[C_2H_4][X_2]}. \quad \text{Use numbers of molecules as an adequate measure of concentration.}$$

(While the volume terms don't cancel, they are the same for all parts. For the purpose of comparison, we can ignore volume.) *Solve.*

$$(a) \quad 8 \text{ C}_2\text{H}_4\text{Cl}_2, \quad 2 \text{ Cl}_2, \quad 2 \text{ C}_2\text{H}_4. \quad K = \frac{8}{(2)(2)} = 2$$

$$(b) \quad 6 \text{ C}_2\text{H}_4\text{Br}_2, \quad 4 \text{ Br}_2, \quad 4 \text{ C}_2\text{H}_4. \quad K = \frac{6}{(4)(4)} = 0.375 = 0.4$$

$$(c) \quad 3 \text{ C}_2\text{H}_4\text{I}_2, \quad 7 \text{ I}_2, \quad 7 \text{ C}_2\text{H}_4. \quad K = \frac{3}{(7)(7)} = 0.0612 = 0.06$$

From the smallest to the largest equilibrium constant, $(c) < (b) < (a)$.

Check. By inspection, there are the fewest product molecules and the most reactant molecules in (c); most product and least reactant in (a).

- 15.7 For the reaction $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$, $\Delta n = 0$ and $K_p = K_c$. We can evaluate the equilibrium expression in terms of concentration. Also since $\Delta n = 0$, the volume terms in the expression cancel and we can use number of particles as a measure of moles and molarity. The mixture contains 2A, 4AB and 2A₂.

$$K_c = \frac{[A][AB]}{[A_2][B]} = \frac{(2)(4)}{(2)(2)} = 2; B = 2$$

2 B atoms should be added to the diagram.

- 15.8 *Analyze.* Given the diagram and reaction type, calculate the equilibrium constant K_c .

Plan. Analyze the contents of the cylinder. Express them as concentrations, using number of particles as a measure of moles, and $V = 1$ L. Write the equilibrium expression in terms of concentration and calculate K_c . *Solve.*

- (a) The mixture contains 2A₂, 2B, 4AB. $[A_2] = 2$, $[B] = 2$, $[AB] = 4$.

$$K_c = \frac{[AB]^2}{[A_2][B]^2} = \frac{(4)^2}{(2)(2)^2} = 2$$

- (b) A decrease in volume favors the reaction with fewer particles. This reaction has two particles in products and three in reactants, so a decrease in volume favors products. The number of AB (product) molecules will increase.

Note that a change in volume does not change the value of K_c . If V decreases, the number of AB molecules must increase in order to maintain the equilibrium value of K_c .

- 15.10 (a) Exothermic. In both reaction mixtures (orange and blue), $[AB]$ decreases as T increases.
- (b) In the reaction, there are fewer moles of gas in products than reactants, so greater pressure favors production of products. At any single temperature, $[AB]$ is greater at $P = y$ than at $P = x$. Since the concentration of the product, AB, is greater at $P = y$, $P = y$ is the greater pressure.

Equilibrium; The Equilibrium Constant

- 15.12 (a) $K_c = \frac{[C][D]}{[A][B]}$; if K_c is large, the numerator of the K_c expression is much greater than the denominator and products will predominate at equilibrium.

- (b) $K_c = k_f/k_r$; if K_c is large, k_f is larger than k_r and the forward reaction has the greater rate constant.

15.14 (a) $K_c = \frac{[O_2]^3}{[O_3]^2}$ (b) $K_c = \frac{1}{[Cl_2]^2}$

(c) $K_c = \frac{[C_2H_6]^2[O_2]}{[C_2H_4]^2[H_2O]^2}$ (d) $K_c = \frac{[CH_4]}{[H_2]^2}$

15 Chemical Equilibrium

Visualizing Concepts

- 15.1 (a) $k_f > k_r$. According to the Arrhenius equation [14.19], $k = Ae^{-E_a/RT}$. As the magnitude of E_a increases, k decreases. On the energy profile, E_a is the difference in energy between the starting point and the energy at the top of the barrier. Clearly this difference is smaller for the forward reaction, so $k_f > k_r$.
- (b) From the Equation [15.5], the equilibrium constant = k_f/k_r . Since $k_f > k_r$, the equilibrium constant for the process shown in the energy profile is greater than 1.

15.4 *Analyze/Plan.* Given that element A = red and element B = blue, evaluate the species in the reactant and product boxes, and write the reaction. Answer the remaining questions based on the balanced equation. *Solve.*

- (a) reactants: $4A_2 + 4B$; products: $4A_2B$
balanced equation: $A_2 + B \rightarrow A_2B$

(b)
$$K_c = \frac{[A_2B]}{[A_2][B]}$$

(c) $\Delta n = \Sigma n(\text{prod}) - \Sigma n(\text{react}) = 1 - 2 = -1.$

(d) $K_p = K_c(RT)^{\Delta n}$, Equation [15.14].

If you have a balanced equation, calculate Δn . Use Equation [15.14] to calculate K_p from K_c , or vice versa.

- 15.6 *Analyze.* Given box diagrams, reaction type, and value of K_c , determine whether each reaction mixture is at equilibrium.

Plan. Analyze the contents of each box, express them as concentrations (see Solution 5.3). Write the equilibrium expression, calculate Q for each mixture, and compare it to K_c . If $Q = K$, the mixture is at equilibrium. If $Q < K$, the reaction shifts right (more product). If $Q > K$, the reaction shifts left (more reactant).

Solve.
$$K_c = \frac{[AB]^2}{[A_2][B_2]}$$

For this reaction, $\Delta n = 0$, so the volume terms cancel in the equilibrium expression. In this case, the number of each kind of particle can be used as a representation of moles (see Solution 5.3) and molarity.

(a) Mixture (i): $1A_2, 1B_2, 6AB$; $Q = \frac{6^2}{(1)(1)} = 36$

$Q > K_c$, the mixture is not at equilibrium.

$$\text{Mixture (ii): } 3A_2, 2B_2, 3AB; Q = \frac{3^2}{(3)(2)} = 1.5$$

$Q = K_c$, the mixture is at equilibrium.

$$\text{Mixture (iii): } 3A_2, 3B_2, 2AB; Q = \frac{2^2}{(3)(3)} = 0.44$$

$Q < K_c$, the mixture is not at equilibrium.

(b) Mixture (i) proceeds toward reactants.

Mixture (iii) proceeds toward products.

15.9 If temperature increases, K of an endothermic reaction increases and K of an exothermic reaction decreases. Calculate the value of K for the two temperatures and compare. For this reaction, $\Delta n = 0$ and $K_p = K_c$. We can ignore volume and use number of particles as a measure of moles and molarity. $K_c = [A][AB]/[A_2][B]$

$$(1) \quad 300 \text{ K, } 3A, 5AB, 1A_2, 1B; K_c = (3)(5)/(1)(1) = 15$$

$$(2) \quad 500 \text{ K, } 1A, 3AB, 3A_2, 3B; K_c = (1)(3)/(3)(3) = 0.33$$

K_c decreases as T increases, so the reaction is exothermic.

Equilibrium; The Equilibrium Constant

15.11 *Analyze/Plan.* Given the forward and reverse rate constants, calculate the equilibrium constant using Equation [15.5]. At equilibrium, the rates of the forward and reverse reactions are equal. Write the rate laws for the forward and reverse reactions and use their equality to answer part (b). *Solve.*

$$(a) \quad K_c = \frac{k_f}{k_r}, \text{ Equation [15.5];} \quad K_c = \frac{3.8 \times 10^{-2} \text{ s}^{-1}}{3.1 \times 10^{-1} \text{ s}^{-1}} = 0.12$$

For this reaction, $K_p = K_c = 0.12$.

$$(b) \quad \text{rate}_f = \text{rate}_r; k_f[A] = k_r[B]$$

Since $k_f < k_r$, in order for the two rates to be equal, $[A]$ must be greater than $[B]$.

15.13 *Analyze/Plan.* Follow the logic in Sample Exercises 15.1 and 15.6. *Solve.*

$$(a) \quad K_c = \frac{[N_2O][NO_2]}{[NO]^3}$$

$$(b) \quad K_c = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

$$(c) \quad K_c = \frac{[CO]^4}{[Ni(CO)_4]}$$

$$(d) \quad K_c = \frac{[H^+][F^-]}{[HF]}$$

$$(e) \quad K_c = \frac{[Ag^+]^2}{[Zn^{2+}]}$$

homogeneous: (a), (b), (d); heterogeneous: (c), (e)

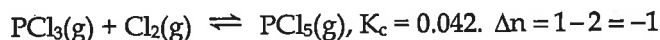
15.15 *Analyze.* Given the value of K_c , predict the contents of the equilibrium mixture.

Plan. If $K_c \gg 1$, products dominate; if $K_c \ll 1$, reactants dominate. *Solve.*

(a) mostly reactants ($K_c \ll 1$)

(b) mostly products ($K_c \gg 1$)

15.17 *Analyze/Plan.* Follow the logic in Sample Exercise 15.2. *Solve.*



$$K_p = K_c(\text{RT})^{\Delta n} = 0.042(\text{RT})^{-1} = 0.042/\text{RT}$$

$$K_p = \frac{0.042}{(0.08206)(500)} = 0.001024 = 1.0 \times 10^{-3}$$

15.19 *Analyze.* Given K_c for a chemical reaction, calculate K_c for the reverse reaction.

Plan. The equilibrium expressions for the reaction and its reverse are the reciprocals of each other, and the values of K_c are also reciprocal. Evaluate which species are favored by examining the magnitude of K_c . *Solve.*

$$(a) \quad K_c(\text{forward}) = \frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]} = 1.3 \times 10^{-2}$$

$$K_c(\text{reverse}) = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} = \frac{1}{1.3 \times 10^{-2}} = 76.92 = 77$$

(b) $K_c < 1$ when NOBr is the product, and $K_c > 1$ when NOBr is the reactant. At this temperature, the equilibrium favors NO and Br₂.

15.21 *Analyze.* Given K_p for a reaction, calculate K_p for a related reaction.

Plan. The algebraic relationship between the K_p values is the same as the algebraic relationship between equilibrium expressions.

$$\text{Solve.} \quad K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}} = 1.85$$

$$(a) \quad K_p = \frac{P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = \frac{1}{1.85} = 0.541$$

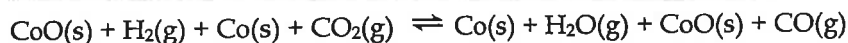
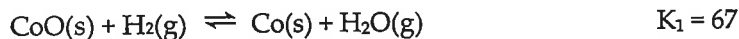
$$(b) \quad K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = (1.85)^2 = 3.4225 = 3.42$$

$$(c) \quad K_p = K_c(\text{RT})^{\Delta n}; \Delta n = 2 - 3 = -1; T = 1000 \text{ K}$$

$$K_p = K_c(\text{RT})^{-1} = K_c/\text{RT}; K_c = K_p(\text{RT})$$

$$K_c = 3.4225(0.08206)(1000) = 280.85 = 281$$

15.23 *Analyze/Plan.* Follow the logic in Sample Exercise 15.5. *Solve.*





$$K_c = K_1 \times K_2 = 67 \times \frac{1}{490} = 0.1367 = 0.14$$

15.25 *Analyze/Plan.* Follow the logic in Sample Exercise 15.6. *Solve.*

(a) $K_p = P_{\text{O}_2}$

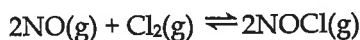
(b) The molar concentration, the ratio of moles of a substance to volume occupied by the substance, is a constant for pure solids and liquids.

Calculating Equilibrium Constants

15.27 *Analyze/Plan.* Follow the logic in Sample Exercise 15.8 using concentrations rather than pressures. *Solve.*

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]_2} = \frac{(4.79 \times 10^{-4})(4.79 \times 10^{-4})}{(3.53 \times 10^{-3})^2} = 0.018413 = 0.0184$$

15.29 *Analyze/Plan.* Follow the logic in Sample Exercise 15.8. *Solve.*



$$K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \times P_{\text{Cl}_2}} = \frac{(0.28)^2}{(0.095)^2 (0.171)} = 50.80 = 51$$

15.31 *Analyze/Plan.* Follow the logic in Sample Exercise 15.9. Since the container volume is 1.0 L, mol = M. *Solve.*

(a) First calculate the change in [NO], $0.10 - 0.062 = 0.038 = 0.04$ M. From the stoichiometry of the reaction, calculate the changes in the other pressures. Finally, calculate the equilibrium pressures.

| | | | | | | | |
|---------|------------------------|---|-------------------------|----------------------|------------------------|---|---------------------------------|
| | $2\text{NO}(\text{g})$ | + | $2\text{H}_2(\text{g})$ | \rightleftharpoons | $\text{N}_2(\text{g})$ | + | $2\text{H}_2\text{O}(\text{g})$ |
| initial | 0.10 M | | 0.050 M | | 0 M | | 0.10 M |
| change | -0.038 M | | -0.038 M | | +0.019 M | | +0.038 M |
| equil. | 0.062 M | | 0.012 M | | 0.019 M | | 0.138 M |

Strictly speaking, the change in [NO] has one decimal place and thus one sig fig. This limits equilibrium pressures to one decimal place for all but H_2O , and K_c to one sig fig. We compute the extra figures and then round.

(b)
$$K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]^2} = \frac{(0.019)(0.138)^2}{(0.062)^2(0.012)^2} = \frac{(0.02)(0.14)^2}{(0.06)^2(0.01)^2} = 653.7 = 7 \times 10^2$$

15.33 *Analyze/Plan.* Follow the logic in Sample Exercise 15.9, using partial pressures, rather than concentrations. *Solve.*

(a)
$$P = nRT/V; P_{\text{CO}_2} = 0.2000 \text{ mol} \times \frac{500 \text{ K}}{2.000 \text{ L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 4.1030 = 4.10 \text{ atm}$$

$$P_{\text{H}_2} = 0.1000 \text{ mol} \times \frac{500 \text{ K}}{2.000 \text{ L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 2.0515 = 2.05 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = 0.1600 \times \frac{500 \text{ K}}{2.000 \text{ L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 3.2824 = 3.28 \text{ atm}$$

- (b) The change in $P_{\text{H}_2\text{O}}$ is $3.51 - 3.28 = 0.2276 = 0.23 \text{ atm}$. From the reaction stoichiometry, calculate the change in the other pressures and the equilibrium pressures.

| | | | | | | | |
|---------|-------------------------|---|------------------------|----------------------|-----------------------|---|--------------------------------|
| | $\text{CO}_2(\text{g})$ | + | $\text{H}_2(\text{g})$ | \rightleftharpoons | $\text{CO}(\text{g})$ | + | $\text{H}_2\text{O}(\text{g})$ |
| initial | 4.10 atm | | 2.05 atm | | 0 atm | | 3.28 atm |
| change | -0.23 atm | | -0.23 atm | | +0.23 | | +0.23 atm |
| equil | 3.87 atm | | 1.82 atm | | 0.23 atm | | 3.51 atm |

(c)
$$K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \times P_{\text{H}_2}} = \frac{(0.23)(3.51)}{(3.87)(1.82)} = 0.1146 = 0.11$$

Without intermediate rounding, equilibrium pressures are $P_{\text{H}_2\text{O}} = 3.51$, $P_{\text{CO}} = 0.2276$, $P_{\text{H}_2} = 1.8239$, $P_{\text{CO}_2} = 3.8754$ and $K_p = 0.1130 = 0.11$, in good agreement with the value above.

Applications of Equilibrium Constants

- 15.35 (a) A reaction quotient is the result of the law of mass action for a general set of concentrations, whereas the equilibrium constant requires equilibrium concentrations.
- (b) In the direction of more products, to the right.
- (c) If $Q_c = K_c$, the system is at equilibrium; the concentrations used to calculate Q must be equilibrium concentrations.
- 15.37 *Analyze/Plan.* Follow the logic in Sample Exercise 15.10. We are given molarities, so we calculate Q directly and decide on the direction to equilibrium. *Solve.*

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = 2.19 \times 10^{-10} \text{ at } 100^\circ\text{C}$$

(a)
$$Q = \frac{(3.3 \times 10^{-6})(6.62 \times 10^{-6})}{(2.00 \times 10^{-3})} = 1.1 \times 10^{-8}; Q > K$$

The reaction will proceed left to attain equilibrium.

(b)
$$Q = \frac{(1.1 \times 10^{-7})(2.25 \times 10^{-6})}{(4.50 \times 10^{-2})} = 5.5 \times 10^{-12}; Q < K$$

The reaction will proceed right to attain equilibrium.

(c)
$$Q = \frac{(1.48 \times 10^{-6})^2}{(0.0100)} = 2.19 \times 10^{-10}; Q = K$$

The reaction is at equilibrium.

- 15.39 *Analyze/Plan.* Follow the logic in Sample Exercise 15.11. We are given concentrations, so write the K_c expression and solve for $[\text{Cl}_2]$. Change molarity to partial pressure using the ideal gas equation and the definition of molarity. *Solve.*

$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}; [\text{Cl}_2] = \frac{K_c[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2]} = \frac{(0.078)(0.108)}{0.052} = 0.16200 = 0.16 \text{ M}$$

$$PV = nRT, P = \frac{n}{V}RT; \frac{n}{V} = M; P = M RT; T = 100^\circ\text{C} + 273 = 373 \text{ K}$$

$$P_{\text{Cl}_2} = \frac{0.16200 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 373 \text{ K} = 4.959 = 5.0 \text{ atm}$$

$$\text{Check. } K_c = \frac{(0.052)(0.162)}{(0.108)} = 0.078. \text{ Our values are self-consistent.}$$

- 15.41 *Analyze/Plan.* Follow the logic in Sample Exercise 15.11. In each case, change given masses to molarities solve for the equilibrium molarity of the desired component, and calculate mass of that substance present at equilibrium. *Solve.*

$$(a) \quad K_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} = 1.04 \times 10^{-3}$$

$$[\text{Br}_2] = \frac{0.245 \text{ g Br}_2}{0.200 \text{ L}} \times \frac{1 \text{ mol Br}_2}{159.8 \text{ g Br}_2} = 0.007666 = 0.00767 \text{ M}$$

$$[\text{Br}] = (K_c[\text{Br}_2])^{1/2} = [(1.04 \times 10^{-3})(0.007666)]^{1/2} = 0.002824 = 0.00282 \text{ M}$$

$$\frac{0.002824 \text{ mol Br}}{\text{L}} \times 0.200 \text{ L} \times \frac{79.90 \text{ g Br}}{\text{mol}} = 0.0451 \text{ g Br(g)}$$

$$\text{Check. } K_c = (0.002824)^2 / (0.007666) = 1.04 \times 10^{-3}$$

$$(b) \quad K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 55.3; [\text{HI}] = (K_c[\text{H}_2][\text{I}_2])^{1/2}$$

$$[\text{H}_2] = \frac{0.056 \text{ g H}_2}{2.00 \text{ L}} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 0.01389 = 0.014 \text{ M}$$

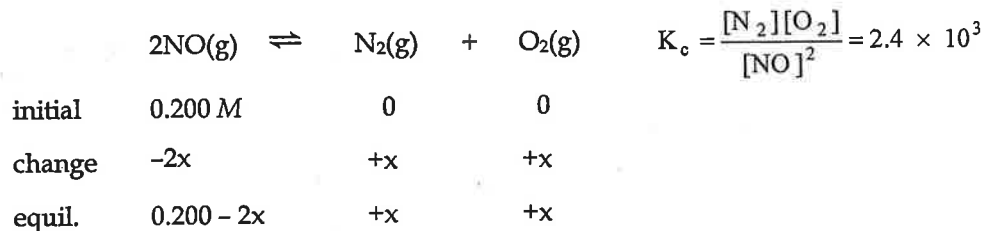
$$[\text{I}_2] = \frac{4.36 \text{ g I}_2}{2.00 \text{ L}} \times \frac{1 \text{ mol I}_2}{253.8 \text{ g I}_2} = 0.008589 = 0.00859 \text{ M}$$

$$[\text{HI}] = [(55.3)(0.01389)(0.008589)]^{1/2} = 0.08122 = 0.081 \text{ M}$$

$$0.08122 \text{ mol HI} \times 2.00 \text{ L} \times \frac{127.9 \text{ g HI}}{\text{mol HI}} = 20.78 = 21 \text{ g HI}$$

$$\text{Check. } K_c = \frac{(0.08122)^2}{(0.01389)(0.008589)} = 55.3$$

- 15.43 *Analyze/Plan.* Follow the logic in Sample Exercise 15.12. Since molarity of NO is given directly, we can construct the equilibrium table straight away. *Solve.*



$$2.4 \times 10^3 = \frac{x^2}{(0.200 - 2x)^2}; (2.4 \times 10^3)^{1/2} = \frac{x}{0.200 - 2x}$$

$$x = (2.4 \times 10^3)^{1/2} (0.200 - 2x); x = 9.798 - 97.98x; 98.98x = 9.798, x = 0.09899 = 0.099 \text{ M}$$

$$[\text{N}_2] = [\text{O}_2] = 0.099 \text{ M}; [\text{NO}] = 0.200 - 2(0.09899) = 0.00202 = 0.002 \text{ M}$$

$$\text{Check. } K_c = (0.09899)^2 / (0.00202)^2 = 2.4 \times 10^3$$

- 15.45 *Analyze/Plan.* Write the K_p expression, substitute the stated pressure relationship, and solve for P_{Br_2} . *Solve.*

$$K_p = \frac{P_{\text{NO}}^2 \times P_{\text{Br}_2}}{P_{\text{NOBr}}^2}$$

When $P_{\text{NOBr}} = P_{\text{NO}}$, these terms cancel and $P_{\text{Br}_2} = K_p = 0.416 \text{ atm}$. This is true for all cases where $P_{\text{NOBr}} = P_{\text{NO}}$.

- 15.47 (a) $\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \quad K_c = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5}$

At equilibrium, $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = x$

$$K_c = 2.4 \times 10^{-5} = x^2; x = 4.9 \times 10^{-3} \text{ M Ca}^{2+} \text{ and SO}_4^{2-}$$

- (b) A saturated solution of $\text{CaSO}_4(\text{aq})$ is $4.9 \times 10^{-3} \text{ M}$.

3.0 L of this solution contain:

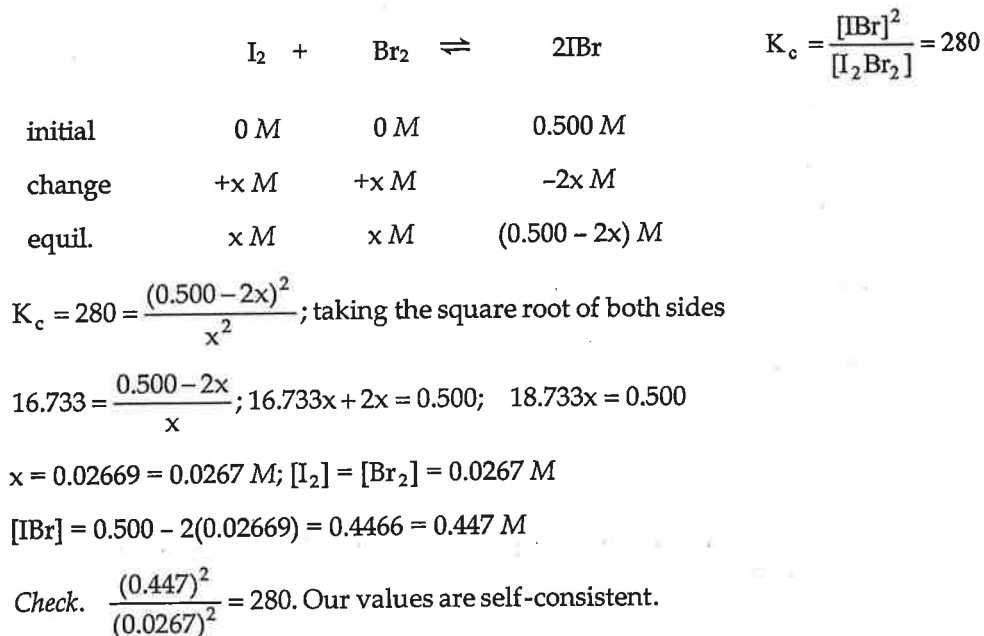
$$\frac{4.9 \times 10^{-3} \text{ mol}}{\text{L}} \times 3.0 \text{ L} \times \frac{136.14 \text{ g CaSO}_4}{\text{mol}} = 2.001 = 2.0 \text{ g CaSO}_4$$

A bit more than 2.0 g CaSO_4 is needed in order to have some undissolved $\text{CaSO}_4(\text{s})$ in equilibrium with 3.0 L of saturated solution.

- 15.49 *Analyze/Plan.* Follow the approach in Solution 15.43. Calculate $[\text{IBr}]$ from mol IBr and construct the equilibrium table.

$$\text{Solve. } [\text{IBr}] = 0.500 \text{ mol} / 1.00 \text{ L} = 0.500 \text{ M}$$

Since no I_2 or Br_2 was present initially, the amounts present at equilibrium are produced by the reverse reaction and stoichiometrically equal. Let these amounts equal x . The amount of HBr that reacts is then $2x$. Substitute the equilibrium molarities (in terms of x) into the equilibrium expression and solve for x .



LeChâtelier's Principle

- 15.51 *Analyze/Plan.* Follow the logic in Sample Exercise 15.13. *Solve.*
- Shift equilibrium to the right; more $\text{SO}_3(\text{g})$ is formed, the amount of $\text{SO}_2(\text{g})$ decreases.
 - Heating an exothermic reaction decreases the value of K . More SO_2 and O_2 will form, the amount of SO_3 will decrease.
 - Since, $\Delta n = -1$, a change in volume will affect the equilibrium position and favor the side with more moles of gas. The amounts of SO_2 and O_2 increase and the amount of SO_3 decreases; equilibrium shifts to the left.
 - No effect. Speeds up the forward and reverse reactions equally.
 - No effect. Does not appear in the equilibrium expression.
 - Shift equilibrium to the right; amounts of SO_2 and O_2 decrease.
- 15.53 *Analyze/Plan.* Given certain changes to a reaction system, determine the effect on K_p , if any. Only changes in temperature cause changes to the value of K_p . *Solve.*
- no effect
 - no effect
 - increase equilibrium constant
 - no effect
- 15.55 *Analyze/Plan.* Use Hess's Law, $\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$, to calculate ΔH° . According to the sign of ΔH° , describe the effect of temperature on the value of K . According to the value of Δn , describe the effect of changes to container volume.
- Solve.*
- $$\Delta H^\circ = \Delta H_f^\circ \text{NO}_2(\text{g}) + \Delta H_f^\circ \text{N}_2\text{O}(\text{g}) - 3\Delta H_f^\circ \text{NO}(\text{g})$$

$$\Delta H^\circ = 33.84 \text{ kJ} + 81.6 \text{ kJ} - 3(90.37 \text{ kJ}) = -155.7 \text{ kJ}$$
 - The reaction is exothermic because it has a negative value of ΔH° . The equilibrium constant will decrease with increasing temperature.

(c) yes $\downarrow V \rightarrow$ product 198 $\uparrow V \leftarrow$ reactant