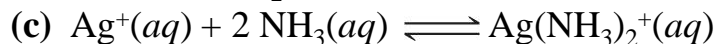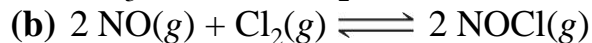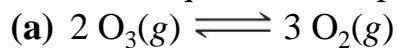# Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:
(a) $2 O_3(g) \rightleftharpoons 3 O_2(g)$
(b) $2 NO(g) + Cl_2(g) \rightleftharpoons 2 NOCl(g)$
(c) $Ag^+(aq) + 2 NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

Solution

Analyze We are given three equations and are asked to write an equilibrium-constant expression for each.

Plan Using the law of mass action, we write each expression as a quotient having the product concentration terms in the numerator and the reactant concentration terms in the denominator. Each concentration term is raised to the power of its coefficient in the balanced chemical equation.

Solve

(a) $K_c = \dfrac{[O_2]^3}{[O_3]^2}$

(b) $K_c = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$

(c) $K_c = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Continued

Practice Exercise 1

For the reaction $2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g)$, which of the following is the correct equilibrium-constant expression?
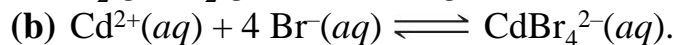
(a) $K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$

(b) $K_c = \dfrac{2[SO_2][O_2]}{2[SO_3]}$

(c) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

(d) $K_c = \dfrac{2[SO_3]}{2[SO_2][O_2]}$

Practice Exercise 2

Write the equilibrium-constant expression K_c for
(a) $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$,
(b) $Cd^{2+}(aq) + 4 Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$.
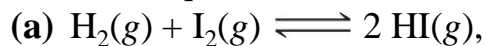
Sample Exercise 15.2 Converting between K_c and K_p

For the Haber process,

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
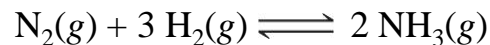
$K_c = 9.60$ at 300 °C. Calculate K_p for this reaction at this temperature.

Solution

Analyze We are given K_c for a reaction and asked to calculate K_p.

Plan The relationship between K_c and K_p is given by Equation 15.15. To apply that equation, we must determine Δn by comparing the number of moles of product with the number of moles of reactants (Equation 15.16).

Solve With 2 mol of gaseous products ($2\,NH_3$) and 4 mol of gaseous reactants ($1\,N_2 + 3\,H_2$), $\Delta n = 2 - 4 = -2$. (Remember that Δ functions are always based on *products minus reactants*.) The temperature is $273 + 300 = 573$ K. The value for the ideal-gas constant, R, is 0.08206 L-atm/mol-K. Using $K_c = 9.60$, we therefore have

$$K_p = K_c\,(RT)^{\Delta n} = (9.60)(0.08206 \times 573)^{-2}$$

$$= \frac{(9.60)}{(0.08206 \times 573)^2} = 4.34 \times 10^{-3}$$

Sample Exercise 15.2 Converting between K_c and K_p

Continued

Practice Exercise 1

For which of the following reactions is the ratio K_p/K_c largest at 300 K?
(a) $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(c) $Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4 CO(g)$
(d) $C(s) + 2 H_2(g) \rightleftharpoons CH_4(g)$

Practice Exercise 2

For the equilibrium $2 SO_3(g) \rightleftharpoons 2 SO_2(g) + O_2(g)$, K_c is 4.08×10^{-3} at 1000 K. Calculate the value for K_p.

Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three systems at equilibrium, all in the same-size containers. **(a)** Without doing any calculations, rank the systems in order of increasing K_c. **(b)** If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate K_c for each system.

(i)   (ii)   (iii)
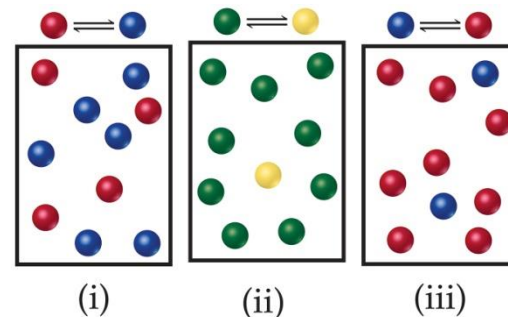
Solution

Analyze We are asked to judge the relative magnitudes of three equilibrium constants and then to calculate them.

Plan (a) The more product present at equilibrium, relative to reactant, the larger the equilibrium constant. **(b)** The equilibrium constant is given by Equation 15.8.

Solve
(a) Each box contains 10 spheres. The amount of product in each varies as follows: (i) 6, (ii) 1, (iii) 8. Therefore, the equilibrium constant varies in the order (ii) < (i) < (iii), from smallest (most reactants) to largest (most products).
(b) In (i), we have 0.60 mol/L product and 0.40 mol/L reactant, giving $K_c = 0.60/0.40 = 1.5$. (You will get the same result by merely dividing the number of spheres of each kind: 6 spheres/4 spheres = 1.5.) In (ii), we have 0.10 mol/L product and 0.90 mol/L reactant, giving $K_c = 0.10/0.90 = 0.11$ (or 1 sphere/9 spheres = 0.11). In (iii), we have 0.80 mol/L product and 0.20 mol/L reactant, giving $K_c = 0.80/0.20 = 4.0$ (or 8 spheres/2 spheres = 4.0). These calculations verify the order in (a).

Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

Continued

Comment Imagine a drawing that represents a reaction with a very small or very large value of K_c. For example, what would the drawing look like if $K_c = 1 \times 10^{-5}$? In that case, there would need to be 100,000 reactant molecules for only 1 product molecule. But then, that would be impractical to draw.

Practice Exercise 1

The equilibrium constant for the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ at 2 °C is $K_c = 2.0$. If each yellow sphere represents 1 mol of N_2O_4 and each brown sphere 1 mol of NO_2 which of the following 1.0 L containers represents the equilibrium mixture at 2 °C?
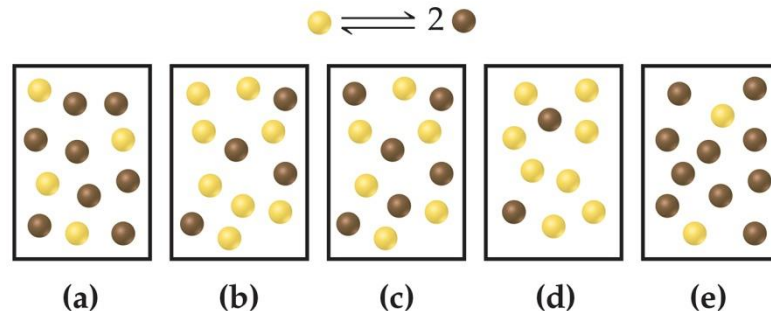
Practice Exercise 2
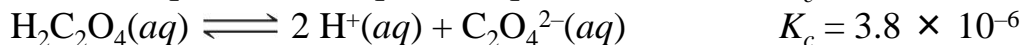
For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$, $K_p = 794$ at 298 K and $K_p = 55$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?

Sample Exercise 15.4 Combining Equilibrium Expressions

Given the reactions

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad\qquad K_c = 6.8 \times 10^{-4}$$
$$H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4{}^{2-}(aq) \qquad\qquad K_c = 3.8 \times 10^{-6}$$

determine the value of K_c for the reaction

$$2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$$

Solution

Analyze We are given two equilibrium equations and the corresponding equilibrium constants and are asked to determine the equilibrium constant for a third equation, which is related to the first two.

Plan We cannot simply add the first two equations to get the third. Instead, we need to determine how to manipulate these equations to come up with equations that we can add to give us the desired equation.

Solve
If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get

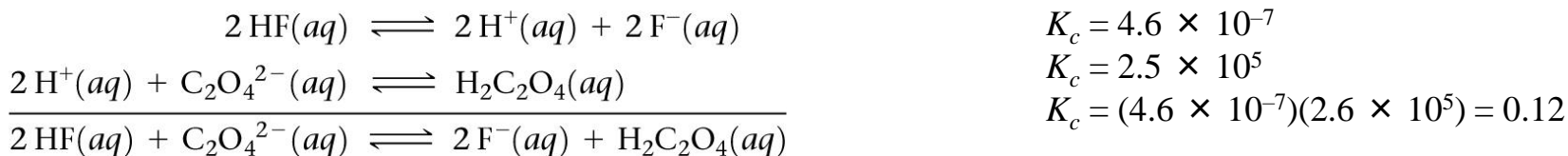$$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) \qquad\qquad K_c = (6.8 \times 10^{-4})^2 = 4.6 \times 10^{-7}$$

Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives

$$2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) \qquad\qquad K_c = \frac{1}{3.8 \times 10^{-6}} = 2.6 \times 10^5$$

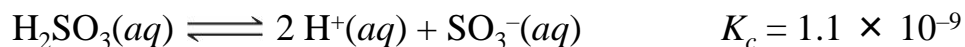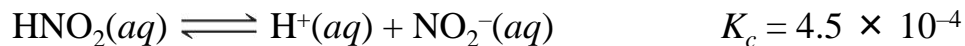# Sample Exercise 15.4 Combining Equilibrium Expressions

Continued

Now, we have two equations that sum to give the net equation, and we can multiply the individual K_c values to get the desired equilibrium constant.

$$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) \qquad K_c = 4.6 \times 10^{-7}$$

$$2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) \qquad K_c = 2.5 \times 10^5$$

$$\overline{2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)}$$

$$K_c = (4.6 \times 10^{-7})(2.6 \times 10^5) = 0.12$$

Practice Exercise 1

Given the equilibrium constants for the following two reactions in aqueous solution at 25 °C,

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2{}^-(aq) \qquad K_c = 4.5 \times 10^{-4}$$

$$H_2SO_3(aq) \rightleftharpoons 2\,H^+(aq) + SO_3{}^-(aq) \qquad K_c = 1.1 \times 10^{-9}$$

what is the value of K_c for the reaction?

$$2\,HNO_2(aq) + SO_3{}^{2-}(aq) \rightleftharpoons H_2SO_3(aq) + 2\,NO_2{}^-(aq)$$

(a) 4.9×10^{-13} **(b)** 4.1×10^5 **(c)** 8.2×10^5 **(d)** 1.8×10^2 **(e)** 5.4×10^{-3}

Practice Exercise 2

Given that, at 700 K, $K_p = 54.0$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, determine the value of K_p for the reaction $2\,NH_3(g) + 3\,I_2(g) \rightleftharpoons 6\,HI(g) + N_2(g)$ at 700 K.

Sample Exercise 15.5 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Write the equilibrium-constant expression K_c for

(a) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$
(b) $SnO_2(s) + 2\ CO(g) \rightleftharpoons Sn(s) + 2\ CO_2(g)$
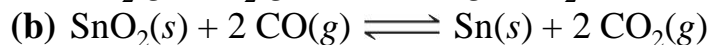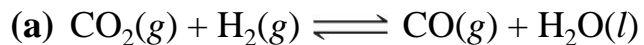
Solution

Analyze We are given two chemical equations, both for heterogeneous equilibria, and asked to write the corresponding equilibrium-constant expressions.

Plan We use the law of mass action, remembering to omit any pure solids and pure liquids from the expressions.

Solve
(a) The equilibrium-constant expression is

$$K_c = \frac{[CO]}{[CO_2][H_2]}$$

Because H_2O appears in the reaction as a liquid, its concentration does not appear in the equilibrium-constant expression.

(b) The equilibrium-constant expression is

$$K_c = \frac{[CO_2]^2}{[CO]^2}$$

Sample Exercise 15.5 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Continued

Because SnO_2 and Sn are pure solids, their concentrations do not appear in the equilibrium-constant expression.

Practice Exercise 1

Consider the equilibrium that is established in a saturated solution of silver chloride, $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$. If solid AgCl is added to this solution, what will happen to the concentration of Ag^+ and Cl^- ions in solution?
(a) $[Ag^+]$ and $[Cl^-]$ will both increase **(b)** $[Ag^+]$ and $[Cl^-]$ will both decrease **(c)** $[Ag^+]$ will increase and $[Cl^-]$ will decrease **(d)** $[Ag^+]$ will decrease and $[Cl^-]$ will increase **(e)** neither $[Ag^+]$ nor $[Cl^-]$ will change

Practice Exercise 2

Write the following equilibrium-constant expressions:
(a) K_c for $Cr(s) + 3\,Ag^+(aq) \rightleftharpoons Cr^{3+}(aq) + 3\,Ag(s)$,
(b) K_p for $3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$.

Sample Exercise 15.6 Analyzing a Heterogeneous Equilibrium

Each of these mixtures was placed in a closed container and allowed to stand:

(a) $CaCO_3(s)$
(b) $CaO(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p
(c) $CaCO_3(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p
(d) $CaCO_3(s)$ and $CaO(s)$

Determine whether or not each mixture can attain the equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Solution

Analyze We are asked which of several combinations of species can establish an equilibrium between calcium carbonate and its decomposition products, calcium oxide and carbon dioxide.

Plan For equilibrium to be achieved, it must be possible for both the forward process and the reverse process to occur. For the forward process to occur, some calcium carbonate must be present. For the reverse process to occur, both calcium oxide and carbon dioxide must be present. In both cases, either the necessary compounds may be present initially or they may be formed by reaction of the other species.

Sample Exercise 15.6 Analyzing a Heterogeneous Equilibrium

Continued

Solve Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present. **(a)** $CaCO_3$ simply decomposes, forming $CaO(s)$ and $CO_2(g)$ until the equilibrium pressure of CO_2 is attained. There must be enough $CaCO_3$, however, to allow the CO_2 pressure to reach equilibrium. **(b)** CO_2 continues to combine with CaO until the partial pressure of the CO_2 decreases to the equilibrium value. **(c)** Because there is no CaO present, equilibrium cannot be attained; there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some CO_2 to react with CaO). **(d)** The situation is essentially the same as in (a): $CaCO_3$ decomposes until equilibrium is attained. The presence of CaO initially makes no difference.

Practice Exercise 1

If 8.0 g of $NH_4HS(s)$ is placed in a sealed vessel with a volume of 1.0 L and heated to 200 °C the reaction $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ will occur. When the system comes to equilibrium, some $NH_4HS(s)$ is still present. Which of the following changes will lead to a reduction in the amount of $NH_4HS(s)$ that is present, assuming in all cases that equilibrium is re-established following the change?
**(a)** Adding more $NH_3(g)$ to the vessel **(b)** Adding more $H_2S(g)$ to the vessel **(c)** Adding more $NH_4HS(s)$ to the vessel **(d)** Increasing the volume of the vessel **(e)** Decreasing the volume of the vessel

Practice Exercise 2

When added to $Fe_3O_4(s)$ in a closed container, which one of the following substances—$H_2(g)$, $H_2O(g)$, $O_2(g)$— allows equilibrium to be established in the reaction $3\ Fe(s) + 4\ H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\ H_2(g)$?

Sample Exercise 15.7 Calculating *K* When All Equilibrium Concentrations Are Known

After a mixture of hydrogen and nitrogen gases in a reaction vessel is allowed to attain equilibrium at 472 °C, it is found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
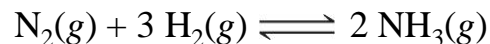
Solution

Analyze We are given a balanced equation and equilibrium partial pressures and are asked to calculate the value of the equilibrium constant.

Plan Using the balanced equation, we write the equilibrium constant expression. We then substitute the equilibrium partial pressures into the expression and solve for K_p.

Solve

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

Continued

Practice Exercise 1

A mixture of gaseous sulfur dioxide and oxygen are added to a reaction vessel and heated to 1000 K where they react to form $SO_3(g)$. If the vessel contains 0.669 atm $SO_2(g)$, 0.395 atm $O_2(g)$, and 0.0851 atm $SO_3(g)$ after the system has reached equilibrium, what is the equilibrium constant K_p for the reaction $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$?
(a) 0.0410 **(b)** 0.322 **(c)** 24.4 **(d)** 3.36 **(e)** 3.11

Practice Exercise 2

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C:
$[CH_3COOH] = 1.65 \times 10^{-2}\ M$; $[H^+] = 5.44 \times 10^{-4}\ M$; and $[CH_3COO^-] = 5.44 \times 10^{-4}$ M. Calculate the equilibrium constant K_c for the ionization of acetic acid at 25 °C. The reaction is

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Sample Exercise 15.8 Calculating *K* from Initial and Equilibrium Concentrations

A reaction vessel containing 1.000×10^{-3} *M* H_2 gas and 2.000×10^{-3} *M* I_2 gas is heated to 448 °C where the following reaction takes place

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$
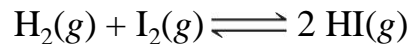
What is the value of the equilibrium constant K_c if once the system comes to equilibrium at 448 °C the concentration of HI is 1.87×10^{-3} *M*?

Solution

Analyze We are given the initial concentrations of H_2 and I_2 and the equilibrium concentration of HI. We are asked to calculate the equilibrium constant K_c for $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$.

Plan We construct a table to find equilibrium concentrations of all species and then use the equilibrium concentrations to calculate the equilibrium constant.

Solve

(1) We tabulate the initial and equilibrium concentrations of as many species as we can. We also provide space in our table for listing the changes in concentrations. As shown, it is convenient to use the chemical equation as the heading for the table.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\ HI(g)$
Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)			
Equilibrium concentration (*M*)			1.87×10^{-3}

Sample Exercise 15.8 Calculating *K* from Initial and Equilibrium Concentrations

Continued

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(2) We calculate the change in HI concentration, which is the difference between the equilibrium and initial values:

$$\text{Change in [HI]} = 1.87 \times 10^{-3} \, M - 0 = 1.87 \times 10^{-3} \, M$$

(3) We use the coefficients in the balanced equation to relate the change in [HI] to the changes in $[H_2]$ and $[I_2]$:

$$\left(1.87 \times 10^{-3} \, \frac{\text{mol HI}}{\text{L}}\right)\left(\frac{1 \, \text{mol H}_2}{2 \, \text{mol HI}}\right) = 0.935 \times 10^{-3} \, \frac{\text{mol H}_2}{\text{L}}$$

$$\left(1.87 \times 10^{-3} \, \frac{\text{mol HI}}{\text{L}}\right)\left(\frac{1 \, \text{mol I}_2}{2 \, \text{mol HI}}\right) = 0.935 \times 10^{-3} \, \frac{\text{mol I}_2}{\text{L}}$$

(4) We calculate the equilibrium concentrations of H_2 and I_2, using initial concentrations and changes in concentration. The equilibrium concentration equals the initial concentration minus that consumed:

$$[H_2] = (1.000 \times 10^{-3} \, M) - (0.935 \times 10^{-3} \, M) = 0.065 \times 10^{-3} \, M$$
$$[I_2] = (2.000 \times 10^{-3} \, M) - (0.935 \times 10^{-3} \, M) = 1.065 \times 10^{-3} \, M$$

Continued

(5) Our table now is complete (with equilibrium concentrations in blue for emphasis):

	$H_2(g)$	$+$	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial concentration (*M*)	1.000×10^{-3}		2.000×10^{-3}		0
Change in concentration (*M*)	-0.935×10^{-3}		-0.935×10^{-3}		$+1.87 \times 10^{-3}$
Equilibrium concentration (*M*)	0.065×10^{-3}		1.065×10^{-3}		1.87×10^{-3}

Notice that the entries for the changes are negative when a reactant is consumed and positive when a product is formed.

Finally, we use the equilibrium-constant expression to calculate the equilibrium constant:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

Comment The same method can be applied to gaseous equilibrium problems to calculate K_p, in which case partial pressures are used as table entries in place of molar concentrations. Your instructor may refer to this kind of table as an ICE chart, where ICE stands for *I*nitial – *C*hange – *E*quilibrium.

Sample Exercise 15.8 Calculating *K* from Initial and Equilibrium Concentrations

Continued

Practice Exercise 1

In Section 15.1, we discussed the equilibrium between $N_2O_4(g)$ and $NO_2(g)$. Let's return to that equation in a quantitative example. When 9.2 g of frozen N_2O_4 is added to a 0.50 L reaction vessel that is heated to 400 K and allowed to come to equilibrium, the concentration of N_2O_4 is determined to be 0.057 M. Given this information, what is the value of K_c for the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ at 400 K? **(a)** 0.23 **(b)** 0.36 **(c)** 0.13 **(d)** 1.4 **(e)** 2.5

Practice Exercise 2

The gaseous compound BrCl decomposes at high temperature in a sealed container: $2 BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$. Initially, the vessel is charged at 500 K with $BrCl(g)$ at a partial pressure of 0.500 atm. At equilibrium, the $BrCl(g)$ partial pressure is 0.040 atm. Calculate the value of K_p at 500 K.

Sample Exercise 15.9 Predicting the Direction of Approach to Equilibrium

At 448 °C, the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$
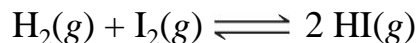
is 50.5. Predict in which direction the reaction proceeds to reach equilibrium if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2, and 3.0×10^{-2} mol of I_2 in a 2.00-L container.

Solution

Analyze We are given a volume and initial molar amounts of the species in a reaction and asked to determine in which direction the reaction must proceed to achieve equilibrium.

Plan We can determine the starting concentration of each species in the reaction mixture. We can then substitute the starting concentrations into the equilibrium-constant expression to calculate the reaction quotient, Q_c. Comparing the magnitudes of the equilibrium constant, which is given, and the reaction quotient will tell us in which direction the reaction will proceed.

Solve
The initial concentrations are

$$[HI] = 2.0 \times 10^{-2}\ mol/2.00\ L = 1.0 \times 10^{-2}\ M$$
$$[H_2] = 1.0 \times 10^{-2}\ mol/2.00\ L = 5.0 \times 10^{-3}\ M$$
$$[I_2] = 3.0 \times 10^{-2}\ mol/2.00\ L = 1.5 \times 10^{-2}\ M$$

Continued

The reaction quotient is therefore

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because $Q_c < K_c$, the concentration of HI must increase and the concentrations of H_2 and I_2 must decrease to reach equilibrium; the reaction as written proceeds left to right to attain equilibrium.

Practice Exercise 1

Which of the following statements accurately describes what would happen to the direction of the reaction described in the sample exercise above, if the size of the container were different from 2.00 L? **(a)** The reaction would proceed in the opposite direction (from right to left) if the container volume were reduced sufficiently. **(b)** The reaction would proceed in the opposite direction if the container volume were expanded sufficiently. **(c)** The direction of this reaction does not depend on the volume of the container.

Practice Exercise 2

At 1000 K, the value of K_p for the reaction $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$ is 0.338. Calculate the value for Q_p, and predict the direction in which the reaction proceeds toward equilibrium if the initial partial pressures are $P_{SO_3} = 0.16$ atm; $P_{SO_2} = 0.41$ atm; $P_{O_2} = 2.5$ atm.

Sample Exercise 15.10 Calculating Equilibrium Concentrations

For the Haber process, $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, $K_p = 1.45 \times 10^{-5}$, at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

Solution

Analyze We are given an equilibrium constant, K_p, and the equilibrium partial pressures of two of the three substances in the equation (N_2 and H_2), and we are asked to calculate the equilibrium partial pressure for the third substance (NH_3).

Plan We can set K_p equal to the equilibrium-constant expression and substitute in the partial pressures that we know. Then we can solve for the only unknown in the equation.

Solve
We tabulate the equilibrium pressures:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$
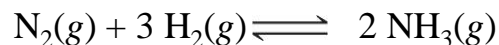
Equilibrium pressure (atm)	0.432 0.928	x

Because we do not know the equilibrium pressure of NH_3, we represent it with x. At equilibrium, the pressures must satisfy the equilibrium-constant expression:

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

We now rearrange the equation to solve for x:

$$x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$$

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3} \, \text{atm} = P_{NH_3}$$

Check We can always check our answer by using it to recalculate the value of the equilibrium constant:

$$K_p = \frac{(2.24 \times 10^{-3})^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

Practice Exercise 1

At 500 K, the reaction $2 \, NO(g) + Cl_2(g) \rightleftharpoons 2 \, NOCl(g)$ has $K_p = 51$. In an equilibrium mixture at 500 K, the partial pressure of NO is 0.125 atm and Cl_2 is 0.165 atm. What is the partial pressure of NOCl in the equilibrium mixture? **(a)** 0.13 atm **(b)** 0.36 atm **(c)** 1.0 atm **(d)** 5.1×10^{-5} atm **(e)** 0.125 atm

Practice Exercise 2

At 500 K, the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ has $K_p = 0.497$. In an equilibrium mixture at 500 K, the partial pressure of PCl_5 is 0.860 atm and that of PCl_3 is 0.350 atm. What is the partial pressure of Cl_2 in the equilibrium mixture?

Sample Exercise 15.11 Calculating Equilibrium Concentrations from Initial Concentrations

A 1.000-L flask is filled with 1.000 mol of $H_2(g)$ and 2.000 mol of $I_2(g)$ at 448 °C. The value of the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$
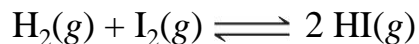
at 448 °C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

Solution

Analyze We are given the volume of a container, an equilibrium constant, and starting amounts of reactants in the container and are asked to calculate the equilibrium concentrations of all species.

Plan In this case, we are not given any of the equilibrium concentrations. We must develop some relationships that relate the initial concentrations to those at equilibrium. The procedure is similar in many regards to that outlined in Sample Exercise 15.8, where we calculated an equilibrium constant using initial concentrations.

Solve

(1) We note the initial concentrations of H_2 and I_2:

$$[H_2] = 1.000\ M \text{ and } [I_2] = 2.000\ M$$

Continued

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(2) We construct a table in which we tabulate the initial concentrations:

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000		2.000		0
Change in concentration (M)					
Equilibrium concentration (M)					

(3) We use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The H_2 and I_2 concentrations will decrease as equilibrium is established and that of HI will increase. Let's represent the change in concentration of H_2 by x. The balanced chemical equation tells us that for each x mol of H_2 that reacts, x mol of I_2 are consumed and $2x$ mol of HI are produced:

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000		2.000		0
Change in concentration (M)	$-x$		$-x$		$+2x$
Equilibrium concentration (M)					

Continued

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(4) We use initial concentrations and changes in concentrations, as dictated by stoichiometry, to express the equilibrium concentrations. With all our entries, our table now looks like this:

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)	$1.000 - x$	$2.000 - x$	$2x$

(5) We substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

If you have an equation-solving calculator, you can solve this equation directly for x. If not, expand this expression to obtain a quadratic equation in x:

$$4x^2 = 50.5(x^2 - 3.000x + 2.000)$$
$$46.5x^2 - 151.5x + 101.0 = 0$$

Solving the quadratic equation (Appendix A.3) leads to two solutions for x:

$$x = \frac{-(-151.5) \pm \sqrt{(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

When we substitute $x = 2.323$ into the expressions for the equilibrium concentrations, we find *negative* concentrations of H_2 and I_2. Because a negative concentration is not chemically meaningful, we reject this solution. We then use $x = 0.935$ to find the equilibrium concentrations:

$$[H_2] = 1.000 - x = 0.065\ M$$

$$[I_2] = 2.000 - x = 1.065\ M$$

$$[HI] = 2x = 1.87\ M$$

Check We can check our solution by putting these numbers into the equilibrium-constant expression to assure that we correctly calculate the equilibrium constant:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 51$$

Comment Whenever you use a quadratic equation to solve an equilibrium problem, one of the solutions to the equation will give you a value that leads to negative concentrations and thus is not chemically meaningful. Reject this solution to the quadratic equation.

Sample Exercise 15.11 Calculating Equilibrium Concentrations from Initial Concentrations

Continued

Practice Exercise 1

For the equilibrium $Br_2(g) + Cl_2(g) \rightleftharpoons 2 BrCl(g)$, the equilibrium constant K_p is 7.0 at 400 K. If a cylinder is charged with $BrCl(g)$ at an initial pressure of 1.00 atm and the system is allowed to come to equilibrium what is the final (equilibrium) pressure of BrCl? **(a)** 0.57 atm **(b)** 0.22 atm **(c)** 0.45 atm **(d)** 0.15 atm **(e)** 0.31 atm

Practice Exercise 2

For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant K_p is 0.497 at 500 K. A gas cylinder at 500 K is charged with $PCl_5(g)$ at an initial pressure of 1.66 atm. What are the equilibrium pressures of PCl_5, PCl_3, and Cl_2 at this temperature?

Sample Exercise 15.12 Using Le Châtelier's Principle to Predict Shifts in Equilibrium

Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad\qquad \Delta H° = 58.0\ kJ$$

In which direction will the equilibrium shift when **(a)** N_2O_4 is added, **(b)** NO_2 is removed, **(c)** the pressure is increased by addition of $N_2(g)$, **(d)** the volume is increased, **(e)** the temperature is decreased?

Solution

Analyze We are given a series of changes to be made to a system at equilibrium and are asked to predict what effect each change will have on the position of the equilibrium.

Plan Le Châtelier's principle can be used to determine the effects of each of these changes.

Solve
(a) The system will adjust to decrease the concentration of the added N_2O_4, so the equilibrium shifts to the right, in the direction of the product.
(b) The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2; thus, the equilibrium shifts to the right.
(c) Adding N_2 will increase the total pressure of the system, but N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 are therefore unchanged, and there is no shift in the position of the equilibrium.
(d) If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right.

Sample Exercise 15.12 Using Le Châtelier's Principle to Predict Shifts in Equilibrium

Continued

(e) The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more N_2O_4. Note that only this last change also affects the value of the equilibrium constant, K.

Practice Exercise 1

For the reaction

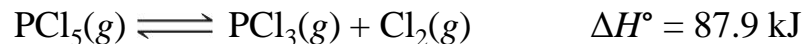$$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g) \qquad \Delta H° = -904\ kJ$$
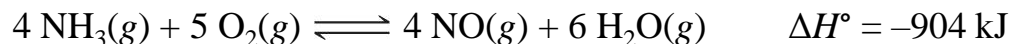
which of the following changes will shift the equilibrium to the right, toward the formation of more products?
(a) Adding more water vapor (b) Increasing the temperature (c) Increasing the volume of the reaction vessel
(d) Removing $O_2(g)$ (e) Adding 1 atm of $Ne(g)$ to the reaction vessel.

Practice Exercise 2

For the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H° = 87.9\ kJ$$

in which direction will the equilibrium shift when (a) $Cl_2(g)$ is removed, (b) the temperature is decreased, (c) the volume of the reaction system is increased, (d) $PCl_3(g)$ is added?

Sample Integrative Exercise Putting Concepts Together

At temperatures near 800 °C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called *water* gas. **(a)** At 800 °C the equilibrium constant for this reaction is $K_p = 14.1$. What are the equilibrium partial pressures of H_2O, CO, and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H_2O in a 1.00-L vessel? **(b)** What is the minimum amount of carbon required to achieve equilibrium under these conditions? **(c)** What is the total pressure in the vessel at equilibrium? **(d)** At 25 °C the value of K_p for this reaction is 1.7×10^{-21}. Is the reaction exothermic or endothermic? **(e)** To produce the maximum amount of CO and H_2 at equilibrium, should the pressure of the system be increased or decreased?

Solution

(a) To determine the equilibrium partial pressures, we use the ideal-gas equation, first determining the starting partial pressure of water.

$$P_{H_2O} = \frac{n_{H_2O}RT}{V} = \frac{(0.100 \text{ mol})(0.08206 \text{ L-atm}/\text{mol-K})(1073 \text{ K})}{1.00 \text{ L}} = 8.81 \text{ atm}$$

We then construct a table of initial partial pressures and their changes as equilibrium is achieved:

	C(s) +	H$_2$O(g) $\rightleftharpoons$	CO(g) +	H$_2$(g)
Initial partial pressure (atm)		8.81	0	0
Change in partial pressure (atm)		$-x$	$+x$	$+x$
Equilibrium partial pressure (atm)		$8.81 - x$	x	x

Sample Integrative Exercise Putting Concepts Together

Continued

There are no entries in the table under $C(s)$ because the reactant, being a solid, does not appear in the equilibrium-constant expression. Substituting the equilibrium partial pressures of the other species into the equilibrium-constant expression for the reaction gives:

$$K_p = \frac{P_{CO}P_{H_2}}{P_{H_2O}} = \frac{(x)(x)}{(8.81 - x)} = 14.1$$

Multiplying through by the denominator gives a quadratic equation in x: $x^2 = (14.1)(8.81 - x)$

Solving this equation for x using the quadratic formula yields $x = 6.14$ atm. $x^2 + 14.1x - 124.22 = 0$
Hence, the equilibrium partial pressures are $P_{CO} = x = 6.14$ atm,
$P_{H_2} = x = 6.14$ atm, and $P_{H_2O} = (8.81 - x) = 2.67$ atm.

(b) Part (a) shows that $x = 6.14$ atm of H_2O must react for the system to achieve equilibrium. We can use the ideal-gas equation to convert this partial pressure into a mole amount.

$$n = \frac{PV}{RT}$$

$$= \frac{(6.14 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L-atm}/mol\text{-}K)(1073 \text{ K})} = 0.0697 \text{ mol}$$

Thus, 0.0697 mol of H_2O and the same amount of C must react to achieve equilibrium. As a result, there must be at least 0.0697 mol of C (0.836 g C) present among the reactants at the start of the reaction.

Sample Integrative Exercise Putting Concepts Together

Continued

(c) The total pressure in the vessel at equilibrium is simply the sum of the equilibrium partial pressures:

$$P_{total} = P_{H_2O} + P_{CO} + P_{H_2}$$
$$= 2.67 \text{ atm} + 6.14 \text{ atm} + 6.14 \text{ atm} = 14.95 \text{ atm}$$

(d) In discussing Le Châtelier's principle, we saw that endothermic reactions exhibit an increase in K_p with increasing temperature. Because the equilibrium constant for this reaction increases as temperature increases, the reaction must be endothermic. From the enthalpies of formation given in Appendix C, we can verify our prediction by calculating the enthalpy change for the reaction:

$$\Delta H° = \Delta H_f°(CO(g)) + \Delta H_f°(H_2(g)) - \Delta H_f°(C(s, \text{graphite}))$$
$$- \Delta H_f°(H_2O(g)) = +131.3 \text{ kJ}$$

The positive sign for $\Delta H°$ indicates that the reaction is endothermic.

(e) According to Le Châtelier's principle, a decrease in the pressure causes a gaseous equilibrium to shift toward the side of the equation with the greater number of moles of gas. In this case, there are 2 mol of gas on the product side and only one on the reactant side. Therefore, the pressure should be decreased to maximize the yield of the CO and H_2.