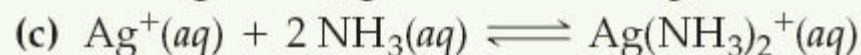
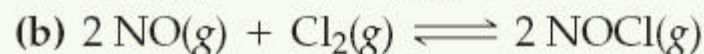
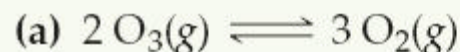


Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:



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.

$$\text{Solve: (a) } K_c = \frac{[\text{O}_2]^3}{[\text{O}_3]^2}, \text{ (b) } K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]}, \text{ (c) } K_c = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

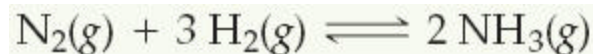
Practice Exercise

Write the equilibrium-constant expression K_c for (a) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$,
(b) $\text{Cd}^{2+}(aq) + 4 \text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$

$$\text{Answers: (a) } K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}, \text{ (b) } K_c = \frac{[\text{CdBr}_4^{2-}]}{[\text{Cd}^{2+}][\text{Br}^-]^4}$$

Sample Exercise 15.2 Converting between K_c and K_p

In the synthesis of ammonia from nitrogen and hydrogen,



$K_c = 9.60$ at $300\text{ }^\circ\text{C}$. 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 15.14. To apply that equation, we must determine Δn by comparing the number of moles of product with the number of moles of reactants (Equation 15.15).

Solve: There are two moles of gaseous products (2NH_3) and four moles of gaseous reactants ($1 \text{N}_2 + 3 \text{H}_2$). Therefore, $\Delta n = 2 - 4 = -2$. (Remember that Δ functions are always based on products minus reactants.) The temperature, T , is $273 + 300 = 573\text{ K}$. The value for the ideal-gas constant, R , is $0.0821\text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$. Using $K_c = 9.60$, we therefore have

$$K_p = K_c(RT)^{\Delta n} = (9.60)(0.0821 \times 573)^{-2} = \frac{(9.60)}{(0.0821 \times 573)^2} = 4.34 \times 10^{-3}$$

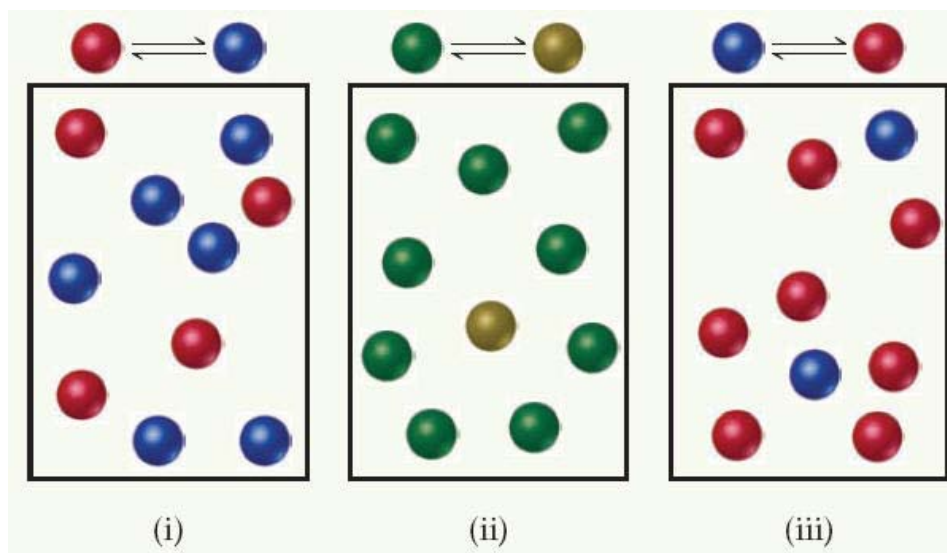
Practice Exercise

For the equilibrium $2 \text{SO}_3(\text{g}) \rightleftharpoons 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$, K_c is 4.08×10^{-3} at 1000 K . Calculate the value for K_p .

Answer: 0.335

Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three different systems at equilibrium, all in the same size containers. **(a)** Without doing any calculations, rank the three systems in order of increasing equilibrium constant, 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.



Solution

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

Plan: **(a)** The more product that is present at equilibrium, relative to the reactant, the greater the equilibrium constant. **(b)** The equilibrium constant is given by the concentrations of products over reactants.

Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

Solution (continued)

Solve:

(a) Each box contains 10 spheres. The amount of product in each varies as follows: (i) 6, (ii) 1, (iii) 8. Thus, the equilibrium constant varies in the order (ii) < (i) < (iii).

(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).

Comment: Imagine that there was a drawing, like those above, 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

For the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, $K_p = 794$ at 298 K and $K_p = 54$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?

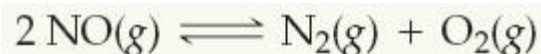
Answer: The formation of product, HI, is favored at the lower temperature because K_p is larger at the lower temperature.

Sample Exercise 15.4 Evaluating an Equilibrium Constant When an Equation is Reversed

The equilibrium constant for the reaction of N_2 with O_2 to form NO equals $K_c = 1 \times 10^{-30}$ at 25°C :



Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction:



Solution

Analyze: We are asked to write the equilibrium-constant expression for a reaction and to determine the value of K_c given the chemical equation and equilibrium constant for the reverse reaction.

Plan: The equilibrium-constant expression is a quotient of products over reactants, each raised to a power equal to its coefficient in the balanced equation. The value of the equilibrium constant is the reciprocal of that for the reverse reaction.

Solve:

Writing products over reactants, we have

$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2}$$

Both the equilibrium-constant expression and the numerical value of the equilibrium constant are the reciprocals of those for the formation of NO from N_2 and O_2 :

$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}$$

Comment: Regardless of the way we express the equilibrium among NO , N_2 , and O_2 , at 25°C it lies on the side that favors N_2 and O_2 . Thus, the equilibrium mixture will contain mostly N_2 and O_2 , with very little NO present.

Sample Exercise 15.4 Evaluating an Equilibrium Constant When an Equation is Reversed

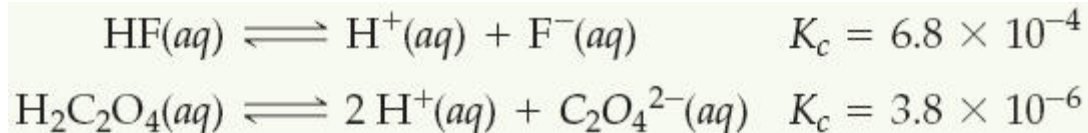
Practice Exercise

For the formation of NH_3 from N_2 and H_2 , $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, $K_p = 4.34 \times 10^{-3}$ at 300°C . What is the value of K_p for the reverse reaction?

Answer: 2.30×10^2

Sample Exercise 15.5 Combining Equilibrium Expressions

Given the following information,



determine the value of K_c for the reaction

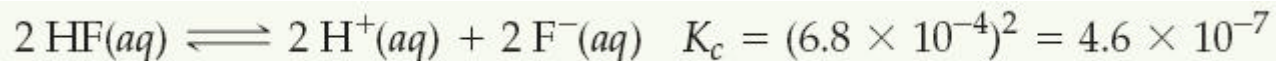


Solution

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 the equations to come up with the steps that will add to give us the desired equation.

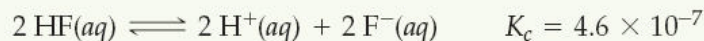
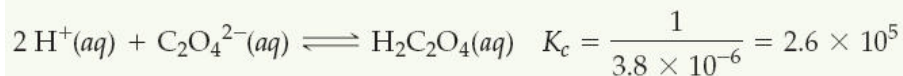
Solve: If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get



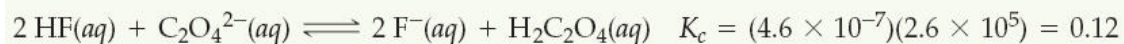
Sample Exercise 15.5 Combining Equilibrium Expressions

Solution (continued)

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



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.



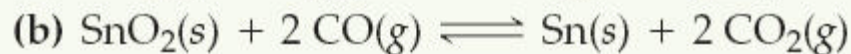
Practice Exercise

Given that, at 700 K, $K_p = 54.0$ for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, determine the value of K_p for the reaction $2 \text{NH}_3(\text{g}) + 3 \text{I}_2(\text{g}) \rightleftharpoons 6 \text{HI}(\text{g}) + \text{N}_2(\text{g})$ at 700 K.

Answer: $\frac{(54.0)^3}{1.04 \times 10^{-4}} = 1.51 \times 10^9$

Sample Exercise 15.6 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Write the equilibrium-constant expression for K_c for each of the following reactions:



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, pure liquids, and solvents from the expressions.

Solve:

(a) The equilibrium-constant expression is

$$K_c = \frac{[\text{CO}]}{[\text{CO}_2][\text{H}_2]}$$

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

(b) The equilibrium-constant expression is

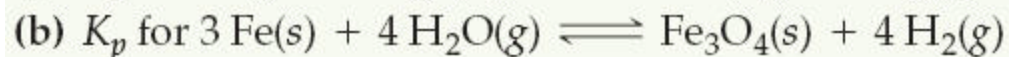
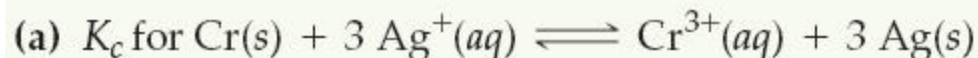
$$K_c = \frac{[\text{CO}_2]^2}{[\text{CO}]^2}$$

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

Sample Exercise 15.6 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Practice Exercise

Write the following equilibrium-constant expressions:



Answers: (a) $K_c = \frac{[\text{Cr}^{3+}]}{[\text{Ag}^+]^3}$, (b) $K_p = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4}$

Sample Exercise 15.7 Analyzing a Heterogeneous Equilibrium

Each of the following mixtures was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$: (a) pure CaCO_3 , (b) CaO and a CO_2 pressure greater than the value of K_p , (c) some CaCO_3 and a CO_2 pressure greater than the value of K_p , (d) CaCO_3 and CaO ?

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

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 $\text{CaO}(s)$ and $\text{CO}_2(g)$ 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) There is no CaO present, so equilibrium cannot be attained because there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some of the 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.

Sample Exercise 15.7 Analyzing a Heterogeneous Equilibrium

Practice Exercise

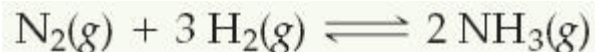
When added to $\text{Fe}_3\text{O}_4(s)$ in a closed container, which one of the following substances— $\text{H}_2(g)$, $\text{H}_2\text{O}(g)$, $\text{O}_2(g)$ —will allow equilibrium to be established in the reaction

$$3 \text{Fe}(s) + 4 \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 4 \text{H}_2(g)?$$

Answer: only $\text{H}_2(g)$

Sample Exercise 15.8 Calculating K When All Equilibrium Concentrations Are Known

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472 °C. The equilibrium mixture of gases was analyzed and 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



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:

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

Practice Exercise

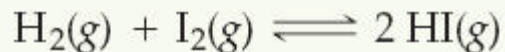
An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C: $[\text{HC}_2\text{H}_3\text{O}_2] = 1.65 \times 10^{-2} \text{ M}$; $[\text{H}^+] = 5.44 \times 10^{-4} \text{ M}$; and $[\text{C}_2\text{H}_3\text{O}_2^-] = 5.44 \times 10^{-4} \text{ M}$. Calculate the equilibrium constant K_c for the ionization of acetic acid at 25 °C. The reaction is



Answer: 1.79×10^{-5}

Sample Exercise 15.9 Calculating K from Initial and Equilibrium Concentrations

A closed system initially containing $1.000 \times 10^{-3} \text{ M H}_2$ and $2.000 \times 10^{-3} \text{ M I}_2$ at 448°C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is $1.87 \times 10^{-3} \text{ M}$. Calculate K_c at 448°C for the reaction taking place, which is



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 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$.

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

Solve: First, 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.

Second, we calculate the change in concentration of HI, which is the difference between the equilibrium values and the initial values:

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
Initial	$1.000 \times 10^{-3} \text{ M}$		$2.000 \times 10^{-3} \text{ M}$		0 M
Change					
Equilibrium					$1.87 \times 10^{-3} \text{ M}$

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

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

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

Sample Exercise 15.9 Calculating K from Initial and Equilibrium Concentrations

Solution (continued)

Third, we use the coefficients in the balanced equation to relate the change in $[\text{HI}]$ to the changes in $[\text{H}_2]$ and $[\text{I}_2]$:

Fourth, we calculate the equilibrium concentrations of H_2 and I_2 , using the initial concentrations and the changes. The equilibrium concentration equals the initial concentration minus that consumed:

The completed table now looks like this (with equilibrium concentrations in blue for emphasis):

$$[\text{H}_2] = 1.000 \times 10^{-3} \text{ M} - 0.935 \times 10^{-3} \text{ M} = 0.065 \times 10^{-3} \text{ M}$$

$$[\text{I}_2] = 2.000 \times 10^{-3} \text{ M} - 0.935 \times 10^{-3} \text{ M} = 1.065 \times 10^{-3} \text{ M}$$

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
Initial	$1.000 \times 10^{-3} \text{ M}$		$2.000 \times 10^{-3} \text{ M}$		0 M
Change	$-0.935 \times 10^{-3} \text{ M}$		$-0.935 \times 10^{-3} \text{ M}$		$+1.87 \times 10^{-3} \text{ M}$
Equilibrium	$0.065 \times 10^{-3} \text{ M}$		$1.065 \times 10^{-3} \text{ M}$		$1.87 \times 10^{-3} \text{ M}$

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

Sample Exercise 15.9 Calculating K from Initial and Equilibrium Concentrations

Solution (continued)

Finally, now that we know the equilibrium concentration of each reactant and product, we can use the equilibrium-constant expression to calculate the equilibrium constant.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

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.

Practice Exercise

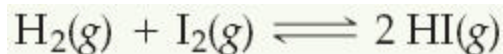
Sulfur trioxide decomposes at high temperature in a sealed container: $2 \text{SO}_3(\text{g}) \rightleftharpoons 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$.

Initially, the vessel is charged at 1000 K with $\text{SO}_3(\text{g})$ at a partial pressure of 0.500 atm. At equilibrium the SO_3 partial pressure is 0.200 atm. Calculate the value of K_p at 1000 K.

Answer: 0.338

Sample Exercise 15.10 Predicting the Direction of Approach to Equilibrium

At 448 °C the equilibrium constant K_c for the reaction



is 50.5. Predict in which direction the reaction will proceed to reach equilibrium at 448 °C 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

$$[\text{HI}] = 2.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{H}_2] = 1.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{I}_2] = 3.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.5 \times 10^{-2} \text{ M}$$

The reaction quotient is therefore

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

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 will proceed from left to right as it moves toward equilibrium.

Sample Exercise 15.10 Predicting the Direction of Approach to Equilibrium

Practice Exercise

At 1000 K the value of K_p for the reaction $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$ is 0.338. Calculate the value for Q_p , and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are $P_{\text{SO}_3} = 0.16 \text{ atm}$; $P_{\text{SO}_2} = 0.41 \text{ atm}$; $P_{\text{O}_2} = 2.5 \text{ atm}$.

Answer: $Q_p = 16$; $Q_p > K_p$, and so the reaction will proceed from right to left, forming more SO_3 .

Sample Exercise 15.11 Calculating Equilibrium Concentrations

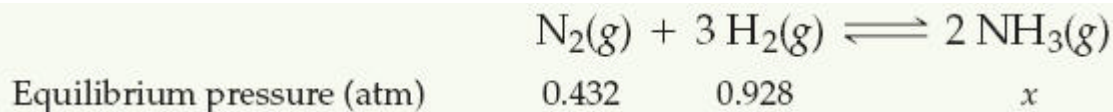
For the Haber process, $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, $K_p = 1.45 \times 10^{-5}$ at 500°C . In an equilibrium mixture of the three gases at 500°C , the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial 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 as follows:



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

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

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

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3} \text{ atm} = P_{\text{NH}_3}$$

We now rearrange the equation to solve for x :

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

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

Sample Exercise 15.11 Calculating Equilibrium Concentrations

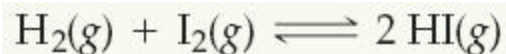
Practice Exercise

At 500 K the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ 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?

Answer: 1.22 atm

Sample Exercise 15.12 Calculating Equilibrium Concentrations from Initial Concentrations

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



at 448 °C is 50.5. What are the equilibrium concentrations of H_2 , I_2 , and HI in moles per liter?

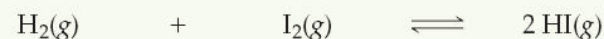
Solution

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 15.9, where we calculated an equilibrium constant using initial concentrations.

Solve: First, we note the initial concentrations of H_2 and I_2 in the 1.000-L flask:

$$[\text{H}_2] = 1.000 \text{ M} \quad \text{and} \quad [\text{I}_2] = 2.000 \text{ M}$$



Initial	1.000 M	2.000 M	0 M
Change			
Equilibrium			

Second, we construct a table in which we tabulate the initial concentrations:

Sample Exercise 15.12 Calculating Equilibrium Concentrations from Initial Concentrations

Solution (continued)

Third, we use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The concentrations of H_2 and I_2 will decrease as equilibrium is established and that of HI will increase. Let's represent the change in concentration of H_2 by the variable x . The balanced chemical equation tells us the relationship between the changes in the concentrations of the three gases:

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

For each x mol of H_2 that reacts, x mol of I_2 are consumed and $2x$ mol of HI are produced:

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$$

Initial	1.000 M	2.000 M	0 M
Change	$-x$	$-x$	$+2x$
Equilibrium			

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$$

Initial	1.000 M	2.000 M	0 M
Change	$-x$	$-x$	$+2x$
Equilibrium	$(1.000 - x) \text{ M}$	$(2.000 - x) \text{ M}$	$2x \text{ M}$

Sample Exercise 15.12 Calculating Equilibrium Concentrations from Initial Concentrations

Solution (continued)

Fifth, we substitute the equilibrium concentrations into the equilibrium-constant expression and solve for the unknown, x :

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

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 :

$$x = \frac{-(-151.5) \pm \sqrt{1(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

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:

$$[\text{H}_2] = 1.000 - x = 0.065 \text{ M} \\ [\text{I}_2] = 2.000 - x = 1.065 \text{ M} \\ [\text{HI}] = 2x = 1.87 \text{ M}$$

Sample Exercise 15.12 Calculating Equilibrium Concentrations from Initial Concentrations

Solution (continued)

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

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 51$$

Comment: Whenever you use a quadratic equation to solve an equilibrium problem, one of the solutions will not be chemically meaningful and should be rejected.

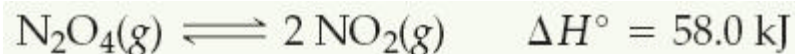
Practice Exercise

For the equilibrium $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the equilibrium constant K_p has the value 0.497 at 500 K. A gas cylinder at 500 K is charged with $\text{PCl}_5(\text{g})$ at an initial pressure of 1.66 atm. What are the equilibrium pressures of PCl_5 , PCl_3 , and Cl_2 at this temperature?

Answer: $P_{\text{PCl}_5} = 0.967 \text{ atm}$; $P_{\text{PCl}_3} = P_{\text{Cl}_2} = 0.693 \text{ atm}$

Sample Exercise 15.13 Using Le Châtelier's Principle to Predict shifts in Equilibrium

Consider the equilibrium



In which direction will the equilibrium shift when (a) N_2O_4 is added, (b) NO_2 is removed, (c) the total pressure is increased by addition of $\text{N}_2(\text{g})$, (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 products.

(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. (This is the opposite of the effect observed in Figure 15.13, where the volume was decreased.)

(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 .

Sample Exercise 15.13 Using Le Châtelier's Principal to Predict shifts in Equilibrium

Practice Exercise

For the reaction

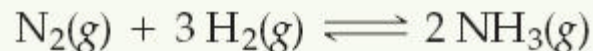


in which direction will the equilibrium shift when **(a)** $\text{Cl}_2(\text{g})$ is removed, **(b)** the temperature is decreased, **(c)** the volume of the reaction system is increased, **(d)** $\text{PCl}_3(\text{g})$ is added?

Answer: **(a)** right, **(b)** left, **(c)** right, **(d)** left

Sample Exercise 15.14 Predicting the Effect of Temperature on K

(a) Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction



(b) Determine how the equilibrium constant for this reaction should change with temperature.

Solution

Analyze: We are asked to determine the standard enthalpy change of a reaction and how the equilibrium constant for the reaction varies with temperature.

Plan: (a) We can use standard enthalpies of formation to calculate ΔH° for the reaction. (b) We can then use Le Châtelier's principle to determine what effect temperature will have on the equilibrium constant.

Solve:

(a) Recall that the standard enthalpy change for a reaction is given by the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient in the balanced chemical equation, less the same quantities for the reactants. At 25 °C, ΔH_f° for $\text{NH}_3(\text{g})$ is -46.19 kJ/mol . The ΔH_f° values for $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ are zero by definition because the enthalpies of formation of the elements in their normal states at 25 °C are defined as zero (Section 5.7). Because 2 mol of NH_3 is formed, the total enthalpy change is

$$(2 \text{ mol})(-46.19 \text{ kJ/mol}) - 0 = -92.38 \text{ kJ}$$

(b) Because the reaction in the forward direction is exothermic, we can consider heat a product of the reaction. An increase in temperature causes the reaction to shift in the direction of less NH_3 and more N_2 and H_2 . This effect is seen in the values for K_p presented in Table 15.2. Notice that K_p changes markedly with changes in temperature and that it is larger at lower temperatures.

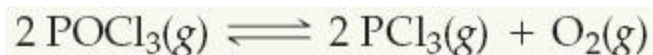
Sample Exercise 15.14 Predicting the Effect of Temperature on K

Solution (continued)

Comment: The fact that K_p for the formation of NH_3 from N_2 and H_2 decreases with increasing temperature is a matter of great practical importance. To form NH_3 at a reasonable rate requires higher temperatures. At higher temperatures, however, the equilibrium constant is smaller, and so the percentage conversion to NH_3 is smaller. To compensate for this, higher pressures are needed because high pressure favors NH_3 formation.

Practice Exercise

Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction



Use this result to determine how the equilibrium constant for the reaction should change with temperature.

Answer: $\Delta H^\circ = 508.3 \text{ kJ}$; the equilibrium constant will increase with increasing temperature

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 H₂:



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 H₂O, CO, and H₂ in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H₂O 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 H₂ 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 hydrogen.

$$P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}RT}{V} = \frac{(0.100 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(1073 \text{ K})}{1.00 \text{ L}} = 8.81 \text{ atm}$$

Sample Integrative Exercise Putting Concepts Together

Solution (continued)

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

	C(s)	+	H ₂ O(g)	⇌	CO(g)	+	H ₂ (g)
Initial			8.81 atm		0 atm		0 atm
Change			-x		+x		+x
Equilibrium			8.81 - x atm		x atm		x atm

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

$$K_p = \frac{P_{\text{CO}}P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = \frac{(x)(x)}{(8.81 - x)} = 14.1$$

Multiplying through by the denominator gives a quadratic equation in x :

$$\begin{aligned}x^2 &= (14.1)(8.81 - x) \\x^2 + 14.1x - 124.22 &= 0\end{aligned}$$

Sample Integrative Exercise Putting Concepts Together

Solution (continued)

Solving this equation for x using the quadratic formula yields $x = 6.14$ atm. Hence, the equilibrium partial pressures are $P_{\text{CO}} = x = 6.14$ atm, $P_{\text{H}_2} = x = 6.14$ atm, and $P_{\text{H}_2\text{O}} = (8.81 - x) = 2.67$ 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.

$$n = \frac{PV}{RT} = \frac{(6.14 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(1073 \text{ K})} = 0.0697 \text{ mol}$$

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.

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

$$P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{CO}} + P_{\text{H}_2} = 2.67 \text{ atm} + 6.14 \text{ atm} + 6.14 \text{ atm} = 14.95 \text{ atm}$$

(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, $\Delta H^\circ = \Delta H^\circ_f(\text{CO}) + \Delta H^\circ_f(\text{H}_2) - \Delta H^\circ_f(\text{C}) - \Delta H^\circ_f(\text{H}_2\text{O}) = +131.3$ kJ. The positive sign for ΔH° 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 two moles of gas on the product side and only one on the reactant side. Therefore, the pressure should be reduced to maximize the yield of the CO and H_2 .