

Chapter 15

Chemical Equilibrium

Concept Check 15.1

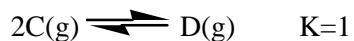
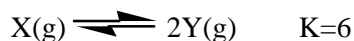
Two substances A and B react to produce substance C. When reactant A decreases by an amount x , product C increases by amount x . When reactant B decreases by an amount x , product C increases by amount $2x$. Write the chemical equation for the reaction.

Solution

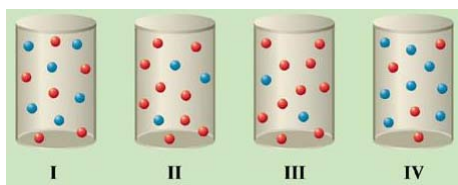
The statement that when reactant A decreases by an amount x , product C increases by amount x implies that A and C have the same coefficients. The statement that when reactant B decreases by an amount x , product C increases by amount $2x$ implies that the coefficient of C is twice that of B. Therefore, the coefficient of A is twice that of B. The simplest equation satisfying these conditions is $2A + B \rightarrow 2C$.

Concept Check 15.2

Consider the following hypothetical reactions. The equilibrium constants K given for each reaction are defined in terms of a concentration unit of molecules per liter.



Assume that the reactions have reached equilibrium. Match each of these reaction with one of the containers I to IV (each of which has a volume of 1L). Identify the "color" of each molecule (that is, is A red or blue?).



Solution

To answer this question, find the relationship between the two species present using the equilibrium constant expression and its value. For the first reaction, $A(g) \rightleftharpoons B(g)$, with $K = 2$, this becomes

$$K = 2 = \frac{[B]}{[A]}$$

This reduces to $[B] = 2[A]$. This corresponds to the container that has twice as many balls of one color than the other color, namely container IV. Here, the blue molecules are B (eight of them), and the red molecules are A (four of them).

For the second reaction, $X(g) \rightleftharpoons 2 Y(g)$, with $K = 6$, this becomes

$$K = 6 = \frac{[Y]^2}{[X]}$$

This reduces to $[Y]^2 = 6[X]$. This corresponds to container I, where there are six of each color molecule. Since there are the same numbers of each molecule, you cannot determine which color corresponds to which molecule.

For the third reaction, $2 C(g) \rightleftharpoons D(g)$, with $K = 1$, this becomes

$$K = 1 = \frac{[D]}{[C]^2}$$

This reduces to $[C]^2 = [D]$. This corresponds to container II. The red balls (nine of them) correspond to molecule D, and the blue balls (three of them) correspond to molecule C.

Concept Check 15.3

Carbon monoxide and hydrogen react in the presence of a catalyst to form methanol, CH_3OH :



An equilibrium mixture of these three substances is suddenly compressed so that the concentrations of all substances initially double. In what direction does the reaction go as a new equilibrium is attained?

Solution

The concentration of each substance initially doubles. This means that each concentration factor in the reaction quotient expression is double that in the initial equilibrium mixture. Because this expression contains $[\text{CO}][\text{H}_2]^2$ in the denominator, the denominator increases by a factor of 2^3 . However, the numerator contains only $[\text{CH}_3\text{OH}]$, which merely doubles. So, the reaction quotient equals 2 divided by 2^3 , or $1/4$, times the equilibrium constant. To approach the equilibrium constant, the numerator of the reaction quotient must increase and the denominator must decrease. This means that more CH_3OH must be produced. The reaction goes from left to right.

Concept Check 15.4

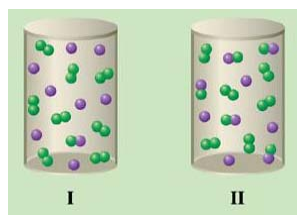
A and B react to produce C according to the chemical equation: $\text{A} + \text{B} \rightarrow \text{C}$. Enough A and B are added to an equilibrium reaction mixture of A, B, and C so that when equilibrium is again attained the amounts of A and B are doubled in the same volume. How is the amount of C changed?

Solution

The equilibrium-constant expression is $[\text{C}]/([\text{A}][\text{B}])$. A new equilibrium is attained in which the equilibrium-constant expression is $[\text{C}']/([\text{A}'][\text{B}']) = [\text{C}']/(2[\text{A}]2[\text{B}])$, where primes indicate new equilibrium concentrations. The value of the equilibrium-constant expression, though, must remain fixed in value, so $[\text{C}']/(2[\text{A}]2[\text{B}])$ equals $[\text{C}]/([\text{A}][\text{B}])$. This means that the new concentration of C, or $[\text{C}]'$, must be 4 times larger than the original equilibrium value. Thus, the concentration of C is quadrupled.

Concept Check 15.5

Given the hypothetical exothermic reaction $\text{A}_2(\text{g}) + 2\text{B}(\text{g}) \rightarrow 2\text{AB}(\text{g})$ at equilibrium, decide which of the following containers represents the reaction mixture at the higher temperature? (The other container represents the reaction at a lower temperature.)

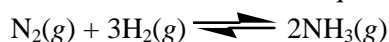


Solution

For an exothermic reaction, as the temperature is increased, the reaction shifts towards the reactant side to absorb the heat and counteract the temperature increase. This corresponds to the case where there are mostly reactant molecules and very few product molecules, namely container I. At lower temperatures, the reaction shifts towards the product side to release heat. This corresponds to the case where there is a larger proportion of product molecules to reactant molecules, namely container II.

Conceptual Problem 15.13

During an experiment with the Haber process, a researcher put 1 mol N_2 and 1 mol H_2 into a reaction vessel to observe the equilibrium formation of ammonia, NH_3 .



When these reactants come to equilibrium, assume that x mol H_2 react. How many moles of ammonia form?

Solution

For each three moles of H_2 that react, two moles of ammonia form. The mole ratio is

$$\frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2}$$

If x mol H_2 react, the amount of ammonia that forms is

$$x \text{ mol H}_2 \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} = \frac{2x}{3} \text{ mol NH}_3.$$

Conceptual Problem 15.14

Suppose liquid water and water vapor exist in equilibrium in a closed container. If you add a small amount of liquid water to the container, how does this affect the amount of water vapor in the container? If, instead, you add a small amount of water vapor to the container, how does this affect the amount of liquid water in the container?

Solution

The addition of a pure liquid does not affect an equilibrium (the pure liquid does not appear in the equilibrium constant; in effect, the concentration of the liquid does not change). Thus, the amount of water vapor does not change appreciably (more precisely, the amount of vapor decreases slightly because the liquid takes up more room in the container). If, instead, you add water vapor to the container, vapor condenses until the original vapor pressure is restored. Thus, the amount of liquid water in the container increases.

Conceptual Problem 15.15

A mixture initially consisting of 2 mol CO and 2 mol H₂ comes to equilibrium with methanol, CH₃OH, as the product:



At equilibrium, the mixture will contain which of the following?

- less than 1 mol CH₃OH
- 1 mol CH₃OH
- more than 1 mol CH₃OH but less than 2 mol
- 2 mol CH₃OH
- more than 2 mol CH₃OH

Solution

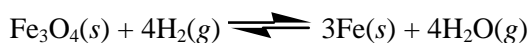
Hydrogen, H₂, is the limiting reactant, so the maximum amount of CH₃OH that could form is 1 mol. However, because the reaction comes to equilibrium before it can go to completion, less than 1 mol of CH₃OH forms. The answer is a.

Conceptual Problem 15.16

When a continuous stream of hydrogen gas, H₂, passes over hot magnetic iron oxide, Fe₃O₄, metallic iron and water vapor form. When a continuous stream of water vapor passes over hot metallic iron, the oxide Fe₃O₄ and H₂ form. Explain why the reaction goes in one direction in one case but in the reverse direction in the other.

Solution

The system must exist as an equilibrium mixture of all four substances. The reaction can be represented as



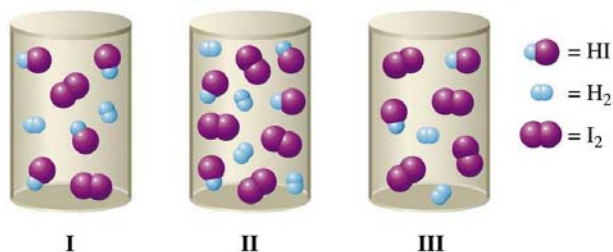
If you pass H₂(g) over iron oxide, the reaction shifts to the right and metallic iron and water vapor form. If, instead, you pass water vapor over metallic iron, the reaction shifts to the left, and iron oxide and H₂ will form. An excess of one reactant pushes the reaction in the opposite direction.

Conceptual Problem 15.17

For the reaction $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$ carried out at some fixed temperature, the equilibrium constant is 2.0.

- Which of the following pictures correctly depicts the reaction mixture at equilibrium?

- b. For the pictures that represent nonequilibrium situations, describe which way the reaction will shift to attain equilibrium.



Solution

- a. The equilibrium constant expression for this reaction is

$$K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 2.0$$

The equilibrium case is where the reaction quotient, Q , is equal to the equilibrium constant, K . This occurs in picture III, where

$$Q = \frac{(2)(4)}{(2)^2} = 2.0 = K$$

- b. For picture I, the reaction quotient is

$$Q = \frac{(2)(2)}{(4)^2} = 0.25 < K$$

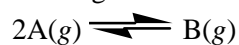
Since $Q < K$, the reaction shifts towards the product ($\text{H}_2 + \text{I}_2$) side.
For picture II, the reaction quotient is

$$Q = \frac{(4)(4)}{(4)^2} = 1.0 < K$$

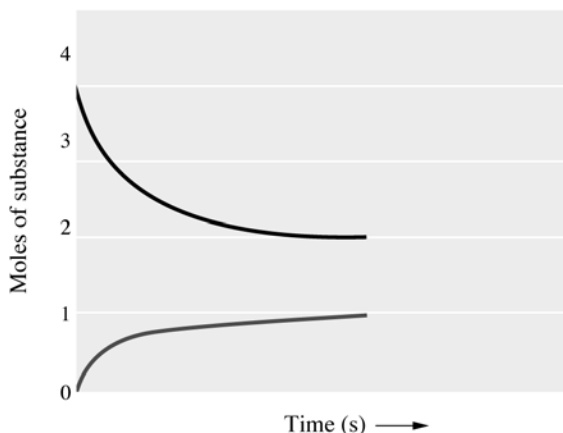
Since $Q < K$, the reaction shifts towards the product ($\text{H}_2 + \text{I}_2$) side.

Conceptual Problem 15.18

An experimenter introduces 4.0 mol of gas A into a 1.0-L container at 200 K to form product B according to the reaction



Using the following data collected during the experiment, calculate the equilibrium constant at 200 K.



Concept Target

- Interpret a graph of experimental data to determine the equilibrium constant for a reaction.

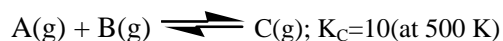
Solution

Equilibrium has been reached when the concentration of reactants and products is constant. The equilibrium region on the graph is where the lines flatten out indicating that the concentrations of reactants and products are not changing. At equilibrium, the concentration of A is approaching 2.0 M, and the concentration of B is approaching 1.0 M. Substituting into the equilibrium constant expression gives

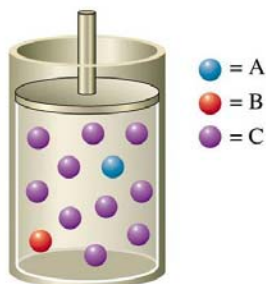
$$K_c = \frac{[B]}{[A]^2} = \frac{1.0}{(2.0)^2} = 0.25$$

Conceptual Problem 15.19

The following reaction is carried out at 500 K in a container equipped with a movable piston.



After the reaction has reached equilibrium, the container has the composition depicted here.



Suppose the container volume is doubled.

- How does the equilibrium composition shift?
- How does the concentration of each of the reactants and the product change? (That is, does the concentration increase, decrease, or stay the same?)

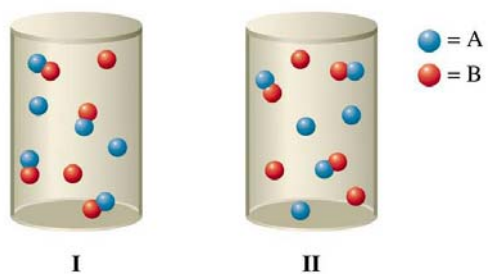
Solution

Equilibrium has been reached when the concentration of reactants and products is constant. The equilibrium region on the graph is where the lines flatten out indicating the concentrations of reactants and products are not changing. At equilibrium, the concentration of A is approaching 2.0 M, and the concentration of B is approaching 1.0 M. Substituting into the equilibrium constant expression gives

$$K_c = \frac{[B]}{[A]^2} = \frac{1.0}{(2.0)^2} = 0.25$$

Conceptual Problem 15.20

For the endothermic reaction $AB(g) \rightleftharpoons A(g) + B(g)$, the following represents a reaction container at two different temperatures. Which one (I or II) is at the lower temperature?



Solution

For an endothermic reaction, as the temperature lowers, the reaction shifts towards the reactant side, producing heat and counteracting the lowering of the temperature. This corresponds to container I, where there is a smaller proportion of product molecules to reactant molecules. In terms of the reaction quotient, Q , the lower temperature corresponds to the container with the smaller value of Q (container I).