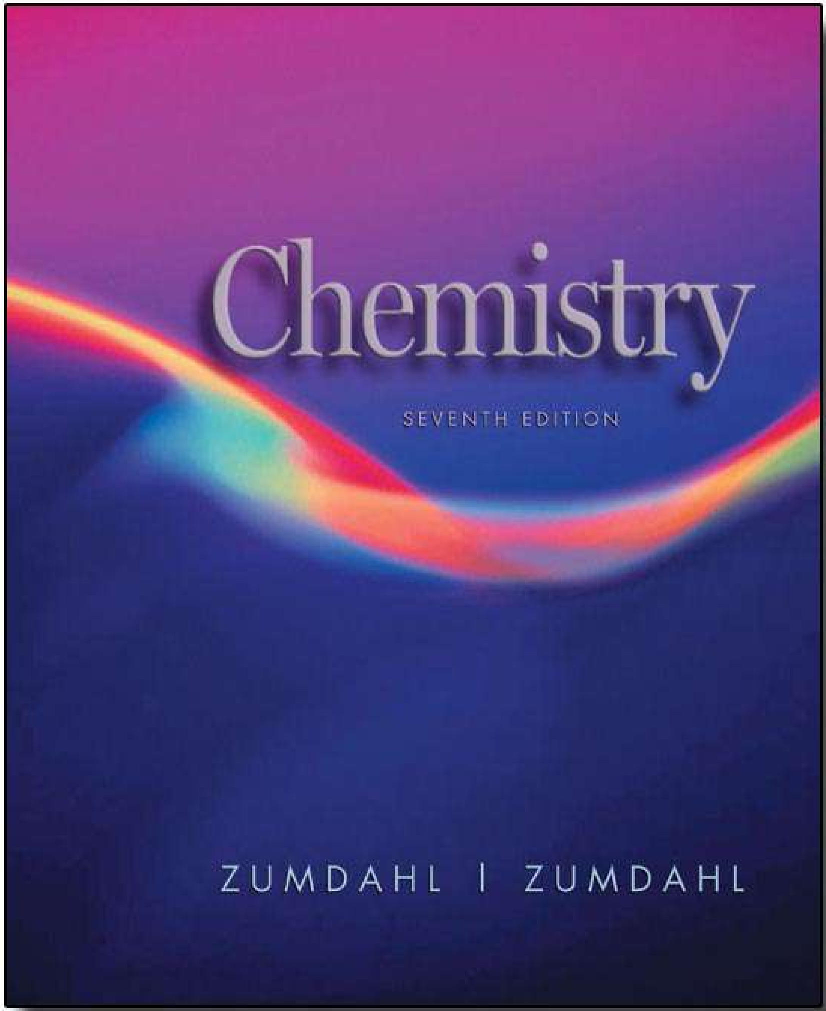
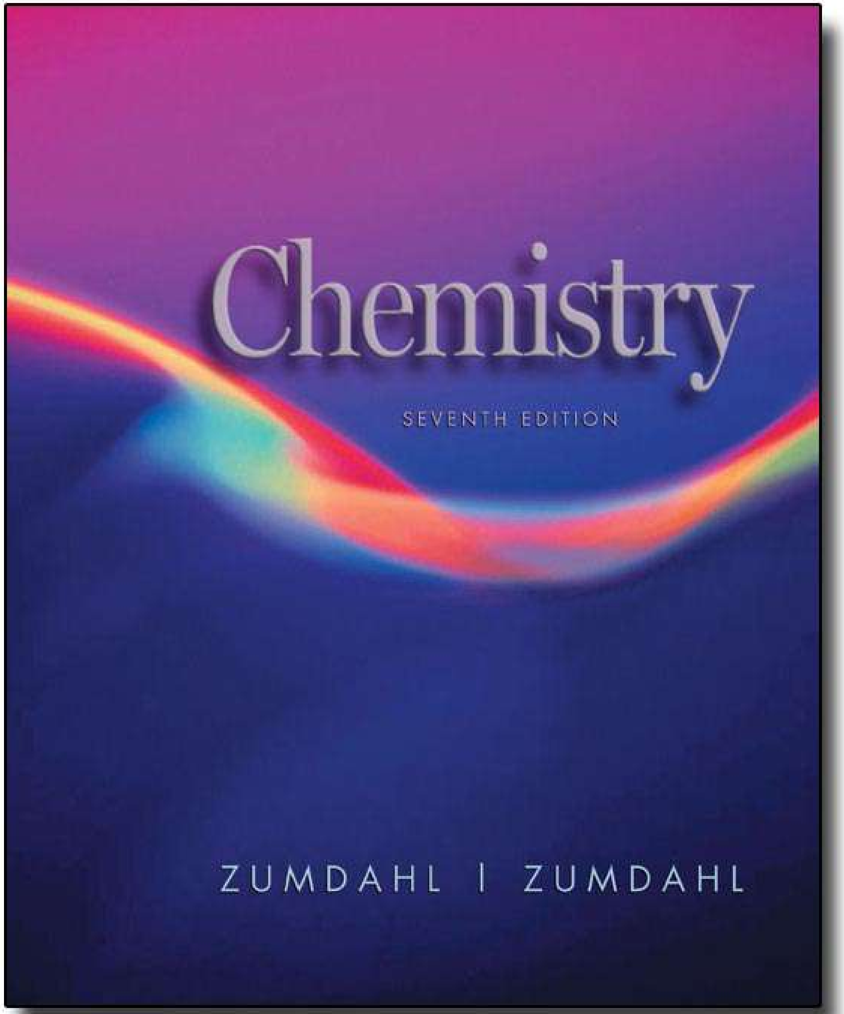


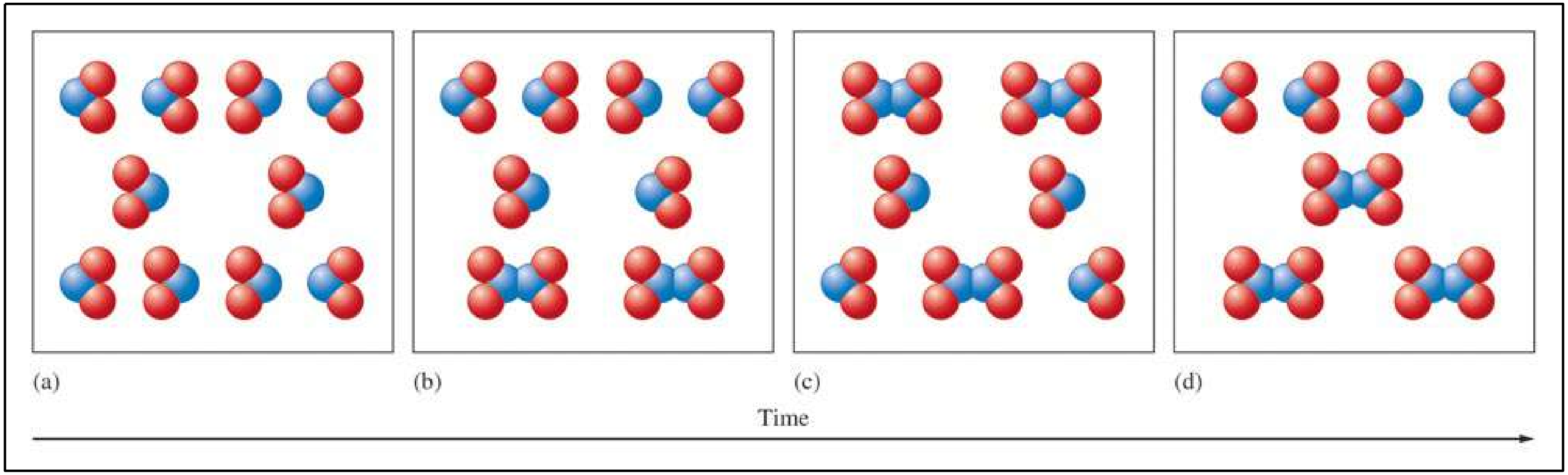
Chapter Thirteen:

CHEMICAL EQUILIBRIUM



The Equilibrium Condition

Figure 13.1 a-d A Molecular Representation of the Reaction $2NO_2(g)$ - $N_2O_4(g)$

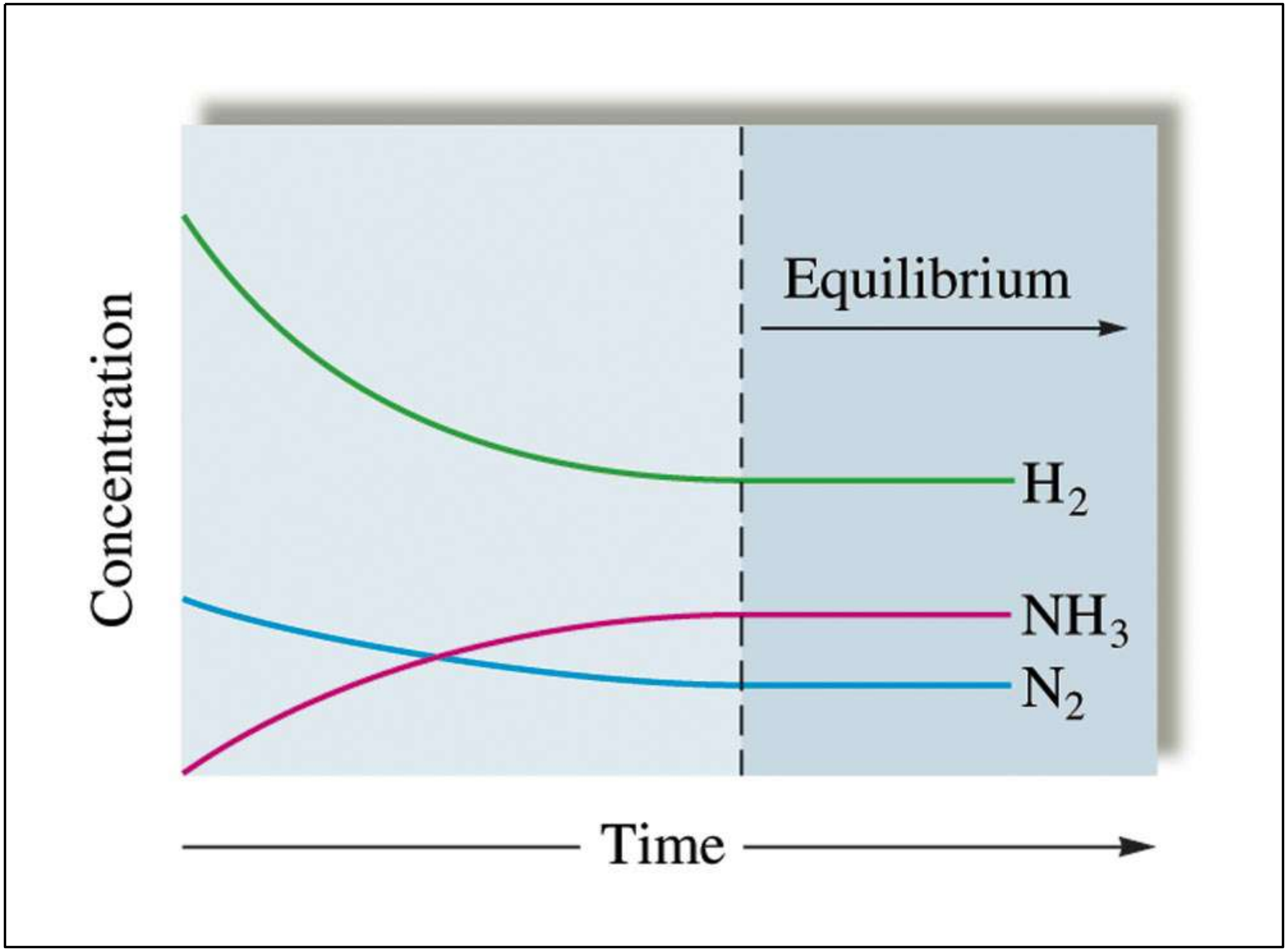


Chemical Equilibrium

- The state where the concentrations of all reactants and products remain constant with time.

- On the molecular level, there is frantic activity. Equilibrium is not static, but is a highly dynamic situation.

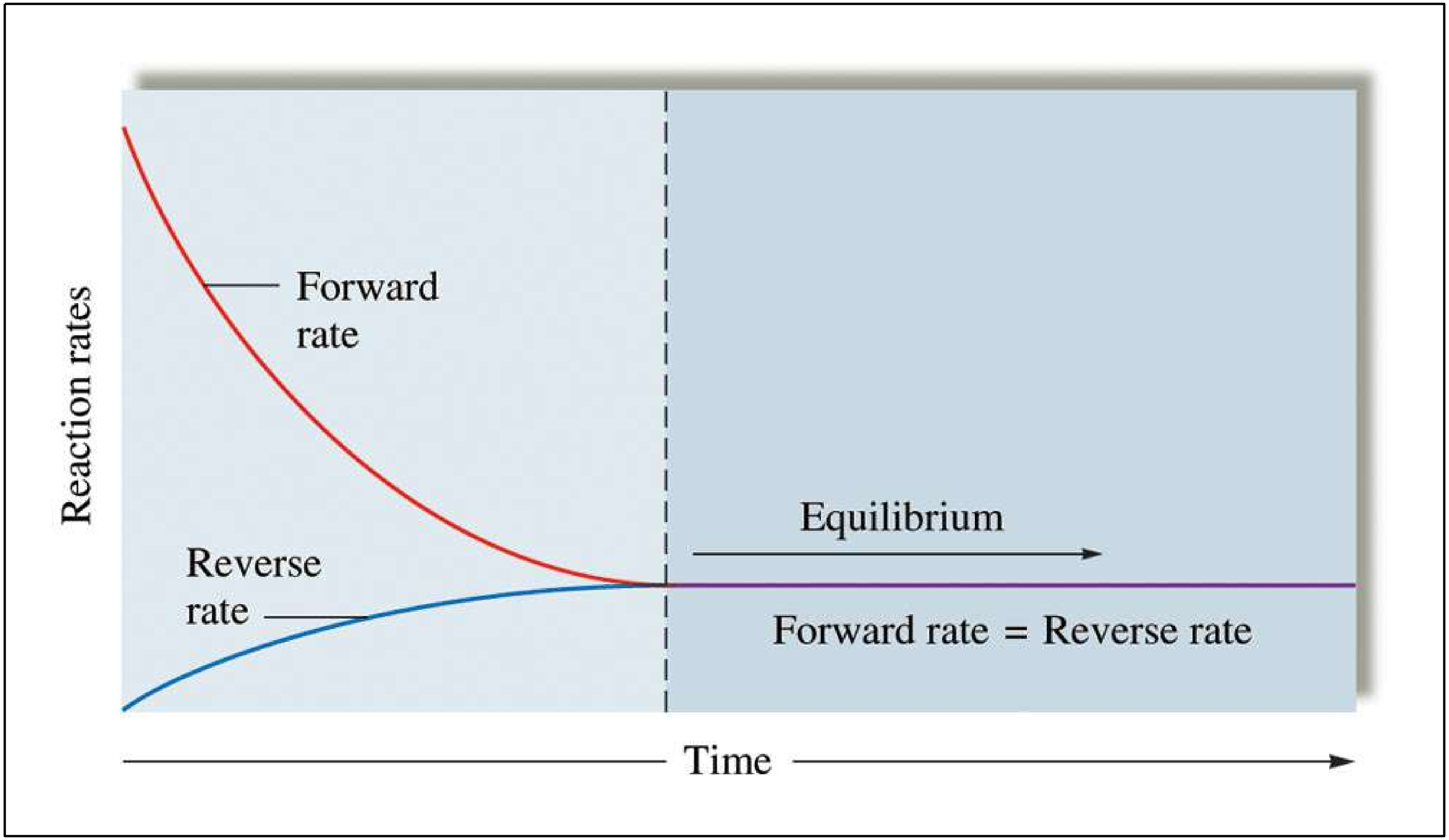
The Ammonia Synthesis Equilibrium



Equilibrium Is:

- Macroscopically static.
- Microscopically dynamic

The Changes with Time in the Rates of Forward and Reverse Reactions



React 1

Consider an equilibrium mixture in a closed vessel reacting according to the equation

$$H_2O(g) + CO(g) \rightleftarrows H_2(g) + CO_2(g)$$

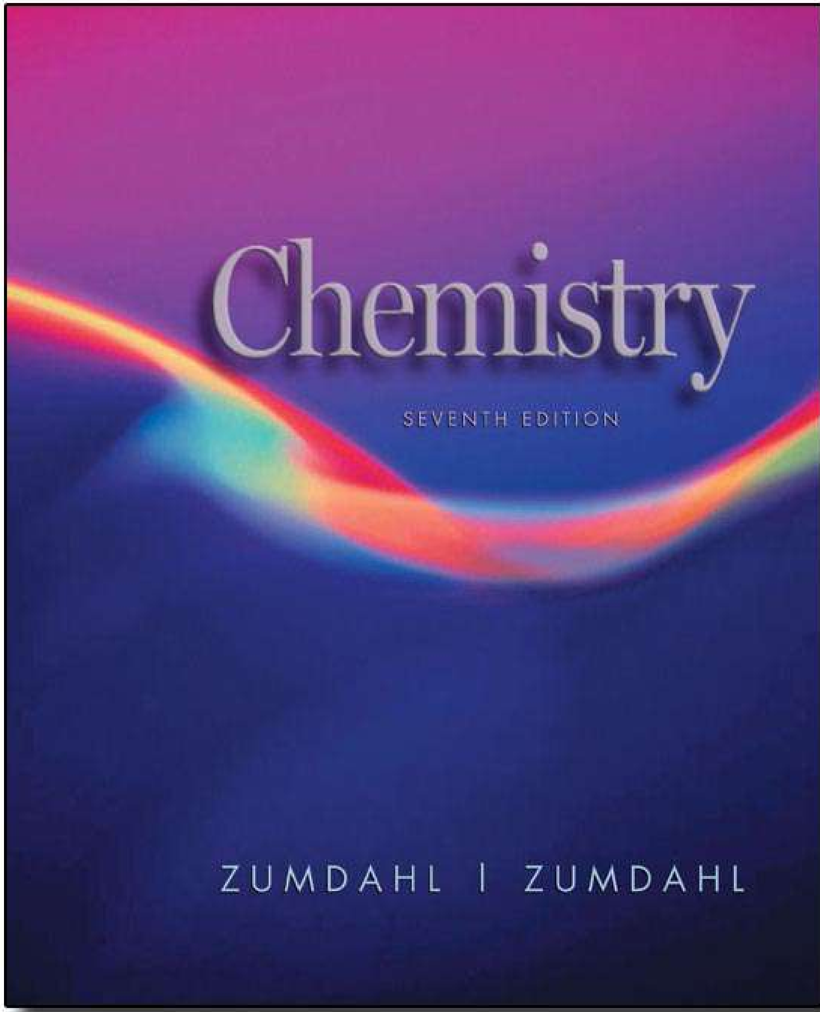
You add more H_2O to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.

React 2

Consider an equilibrium mixture in a closed vessel reacting according to the equation

$$H_2O(g) + CO(g) \rightleftarrows H_2(g) + CO_2(g)$$

- You add more H_2 to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.



The Equilibrium Constant and Applications

The Equilibrium Constant

$$jA + kB \rightleftharpoons lC + mD$$

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

Table 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g)$ -- $2NH_3(g)$

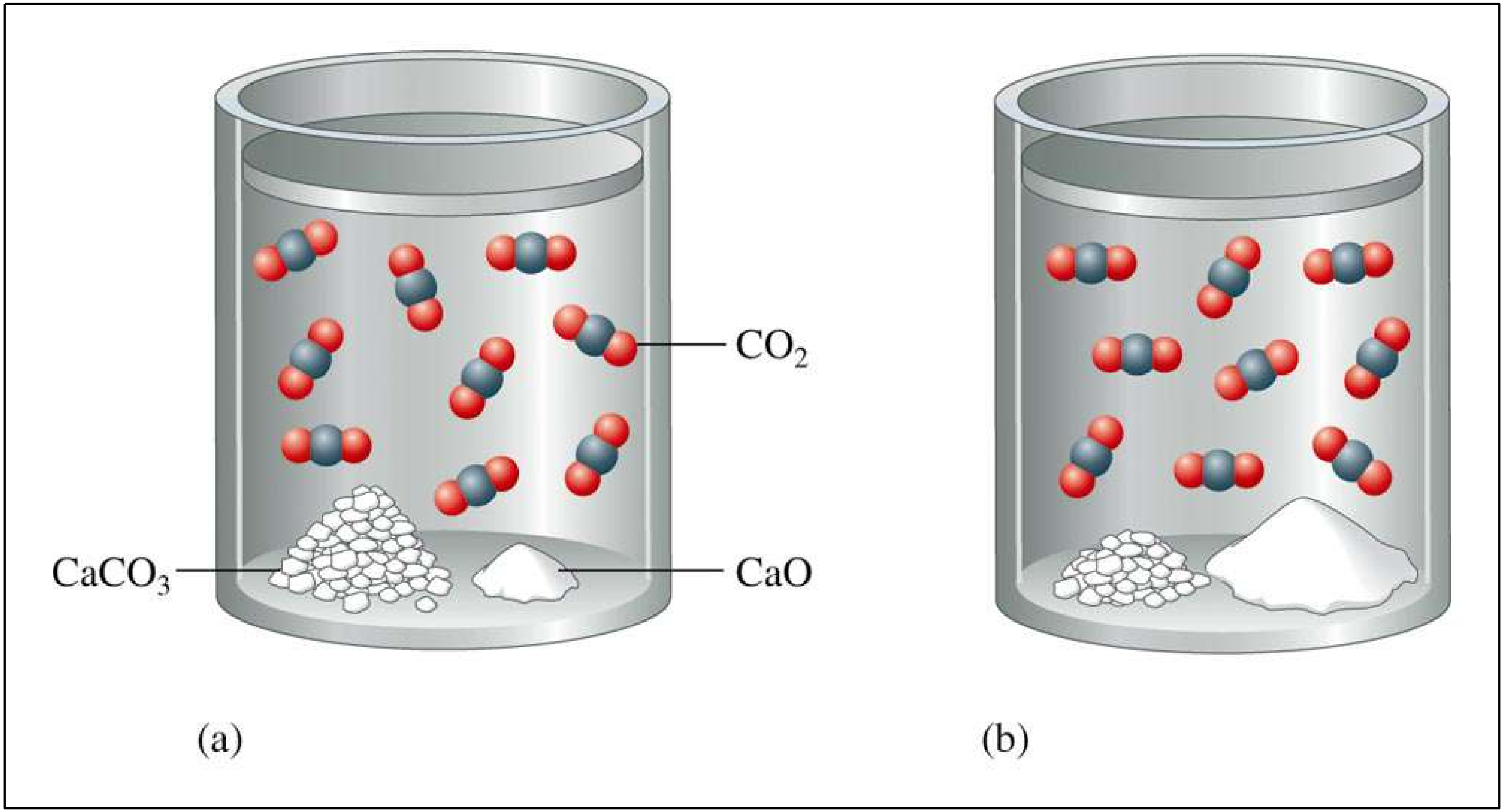
TABLE 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

Anhydrous Ammonia is Injected into the Solid to Act as a Fertilizer

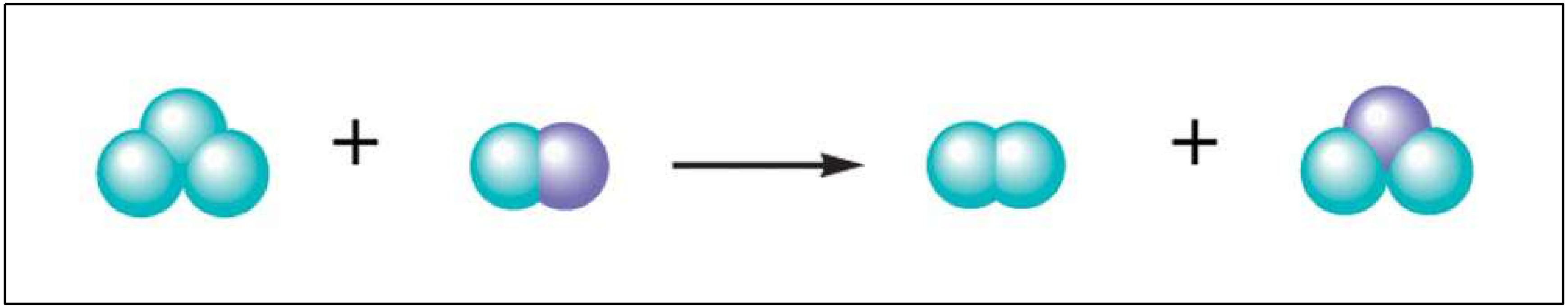
The Seven Sisters Chalk Cliffs in East Sussex, England

Figure 13.6 a-b The Position of the Equilibrium

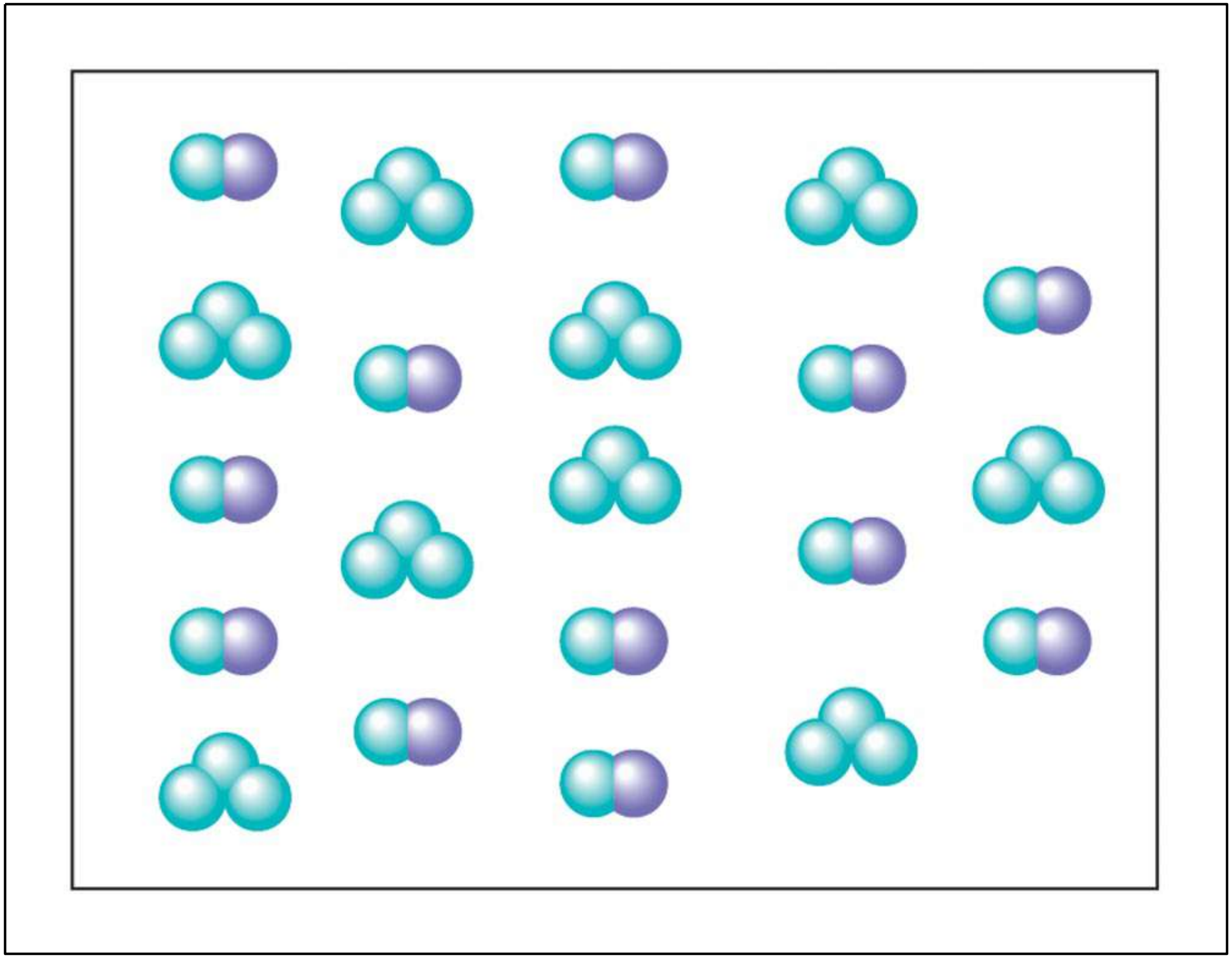


Hydrated Copper (II) Sulfate on the Left. Water Applied to Anhydrous Copper (II) Sulfate, on the Right, Forms the Hydrated Compound

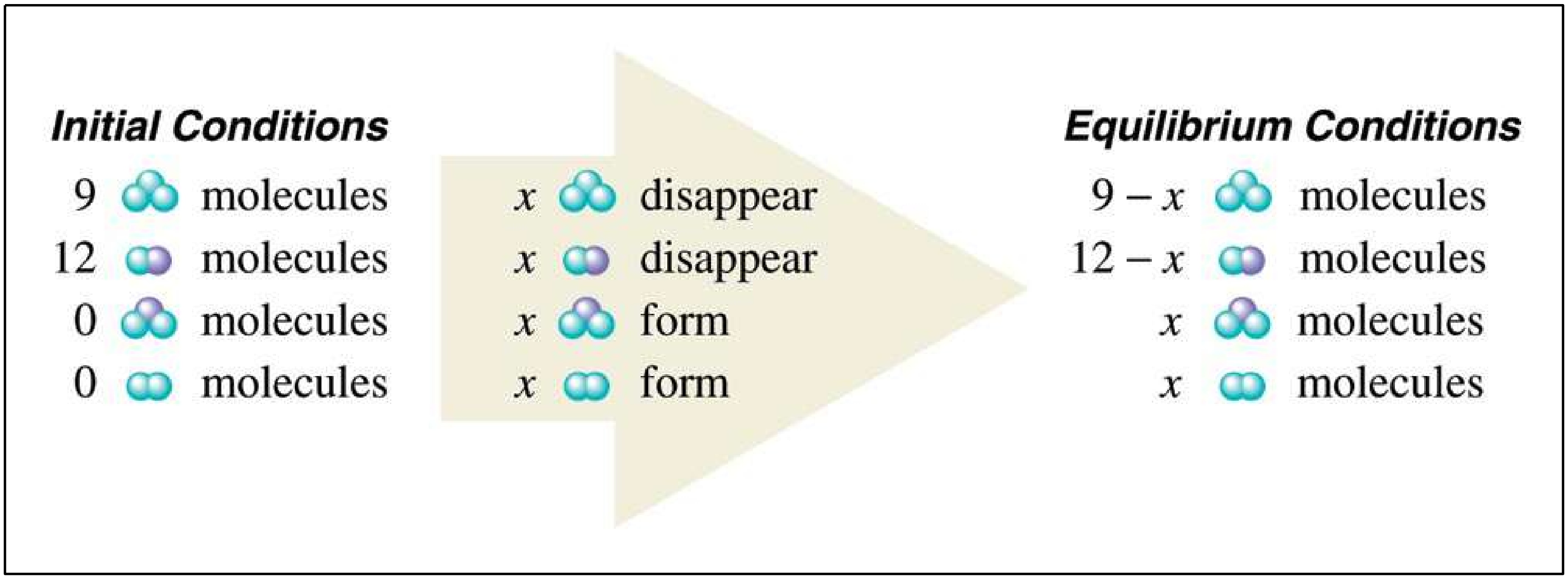
Reaction



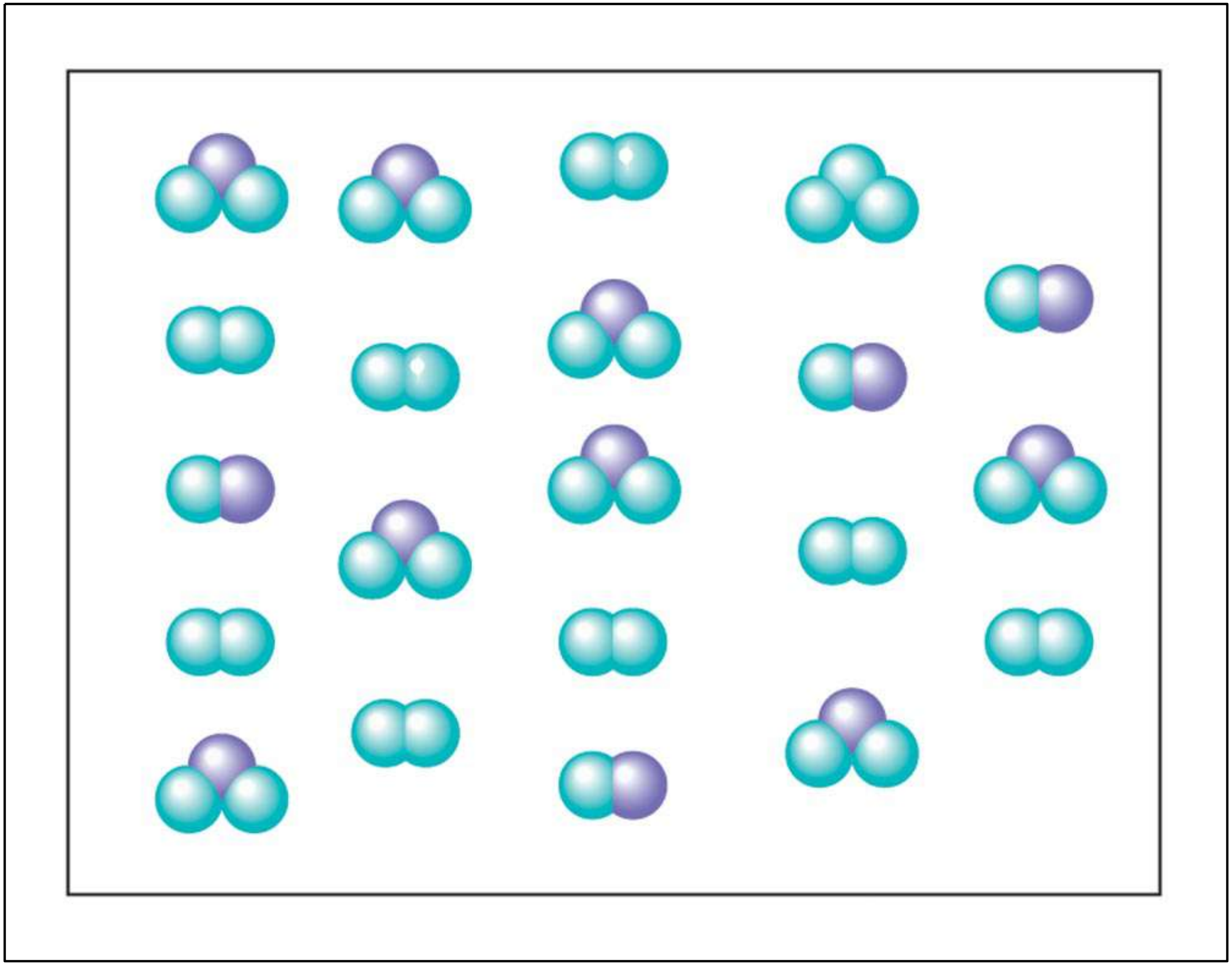
Two Types of Molecules are Mixed Together in the Following Amounts



Conditions of Equilibrium Reactions



Equilibrium Mixture



React 4

Consider the reaction represented by the equation

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

- Trial #1

6.00 *M* $Fe^{3+}(aq)$ and 10.0 *M* $SCN^{-}(aq)$ are mixed and at equilibrium the concentration of $FeSCN^{2+}(aq)$ is 4.00 *M*.

What is the value for the equilibrium constant for this reaction?

React 4

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

Initial	6.00	10.00	0.00
Change	-4.00	-4.00	+4.00
Equilibrium	2.00	6.00	4.00

React 4

Consider the reaction represented by the equation

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

- Trial #2:

  Initial: 10.0 M $Fe^{3+}(aq)$ and 8.00 M $SCN^{-}(aq)$

  Equilibrium: __?__ M $FeSCN^{2+}(aq)$

React 4

Consider the reaction represented by the equation

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

- Trial #3:

  Initial: 6.00 M $Fe^{3+}(aq)$ and 6.00 M $SCN^{-}(aq)$

  Equilibrium: __?__ M $FeSCN^{2+}(aq)$

React 7

A 2.0 mol sample of ammonia is introduced into a 1.00 L container. At a certain temperature, the ammonia partially dissociates according to the equation

$$NH_3(g) \rightleftharpoons N_2(g) + H_2(g)$$

At equilibrium 1.00 mol of ammonia remains.

Calculate the value for *K*.

Photo 13.4 Apollo II Lunar Landing

React 8

A 1.00 mol sample of $N_2O_4(g)$ is placed in a 10.0 L vessel and allowed to reach equilibrium according to the equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K = 4.00 \times 10^{-4}$$

Calculate the equilibrium concentrations of $N_2O_4(g)$ and $NO_2(g)$.

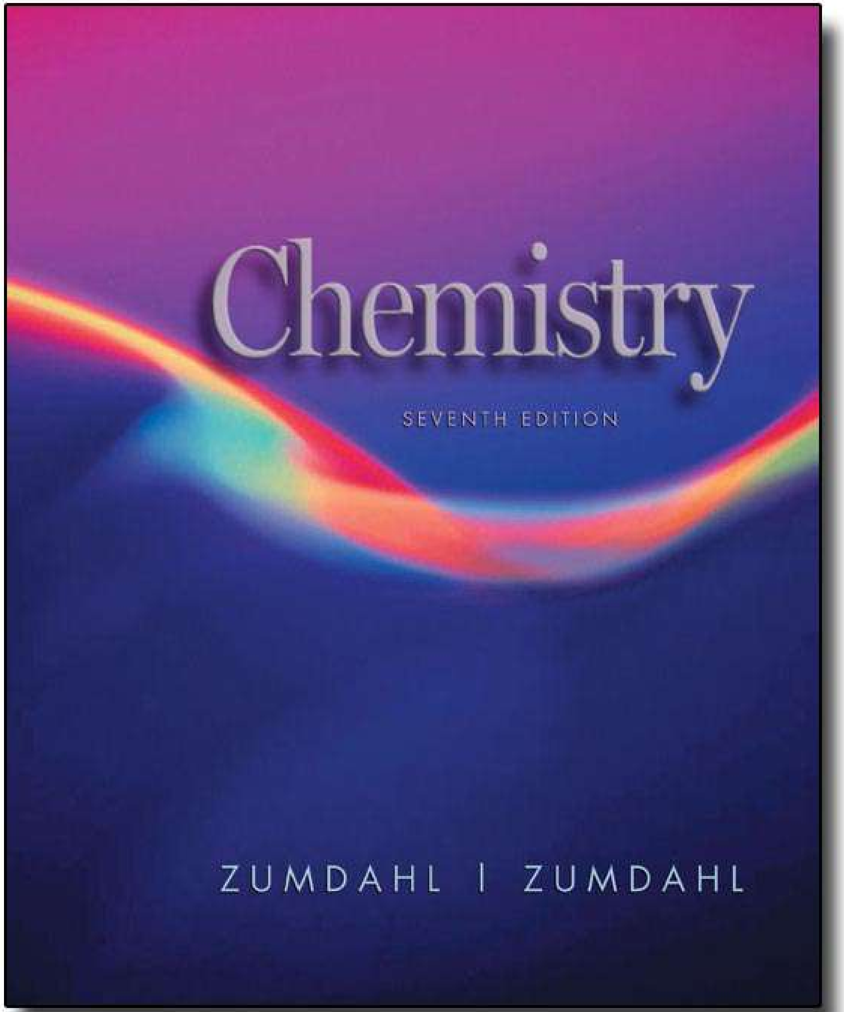
React 6

Consider the reaction represented by the equation

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

	Fe^{3+}	SCN^{-}	$FeSCN^{2+}$
Trial #1	9.00 *M*	5.00 *M*	1.00 *M*
Trial #2	3.00 *M*	2.00 *M*	5.00 *M*
Trial #3	2.00 *M*	9.00 *M*	6.00 *M*

Find the equilibrium concentrations for all species.



LeChâtelier's Principle

Le Châtelier’s Principle

If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

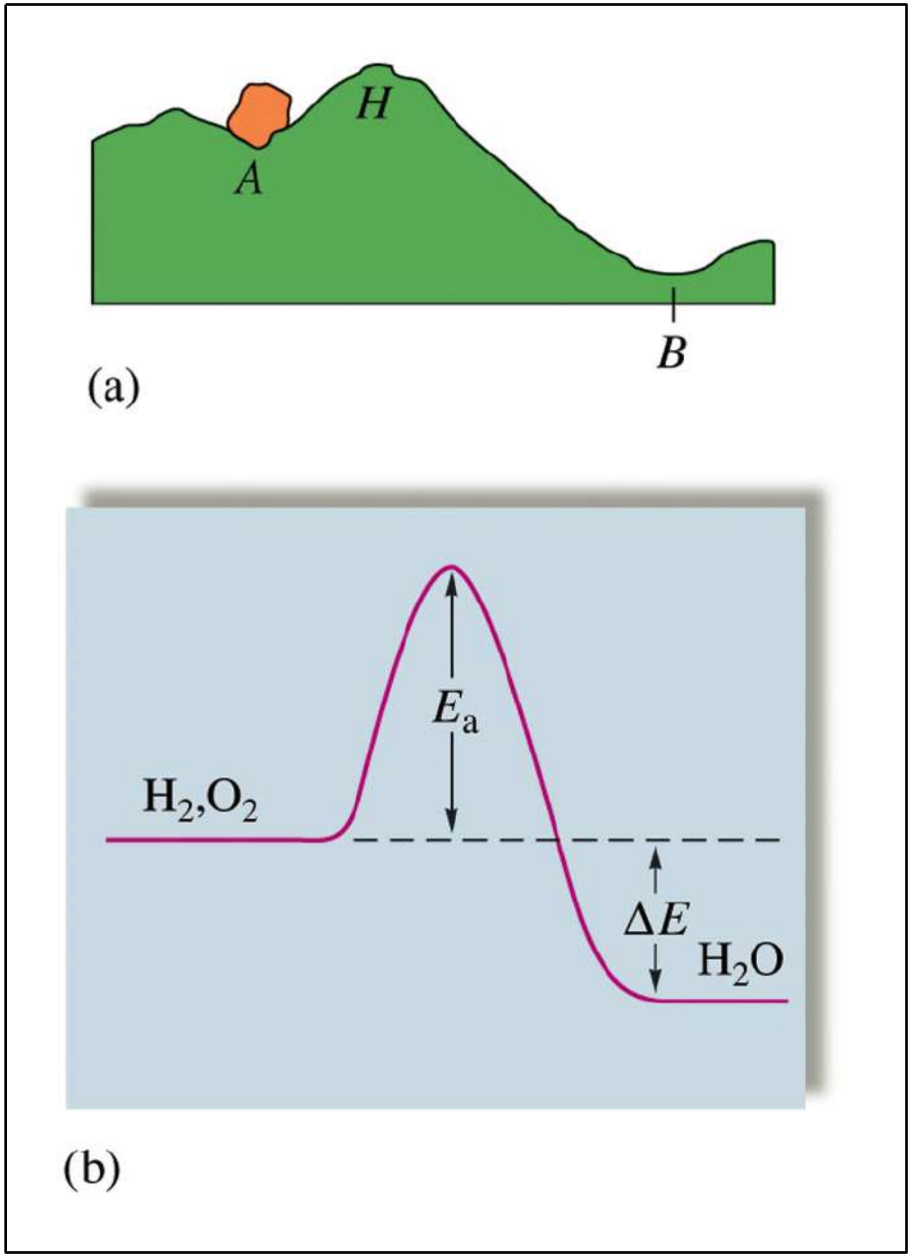
Table 13.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure

TABLE 13.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure*

	Total Pressure		
Temperature (°C)	*300 atm*	*400 atm*	*500 atm*
400	48% NH_3	55% NH_3	61% NH_3
500	26% NH_3	32% NH_3	38% NH_3
600	13% NH_3	17% NH_3	21% NH_3

*Each experiment was begun with a 3:1 mixture of H_2 and N_2.

The magnitude of K for the reaction depends on Thermodynamics, but the reaction rate depends on Ea.



Effects of Changes on the System

1. Concentration: The system will shift away from the added component.

2. Temperature: K will change depending upon the temperature (treat the energy change as a reactant).

Figure 13.8 a-c (a) The Initial Equilibrium Mixture of N_2, H_2, and NH_3 (b) Addition of N2. (c.) The New Equilibrium Position for the System Containing More N_2 (due to Less H_2, and More NH_3 than in (a)

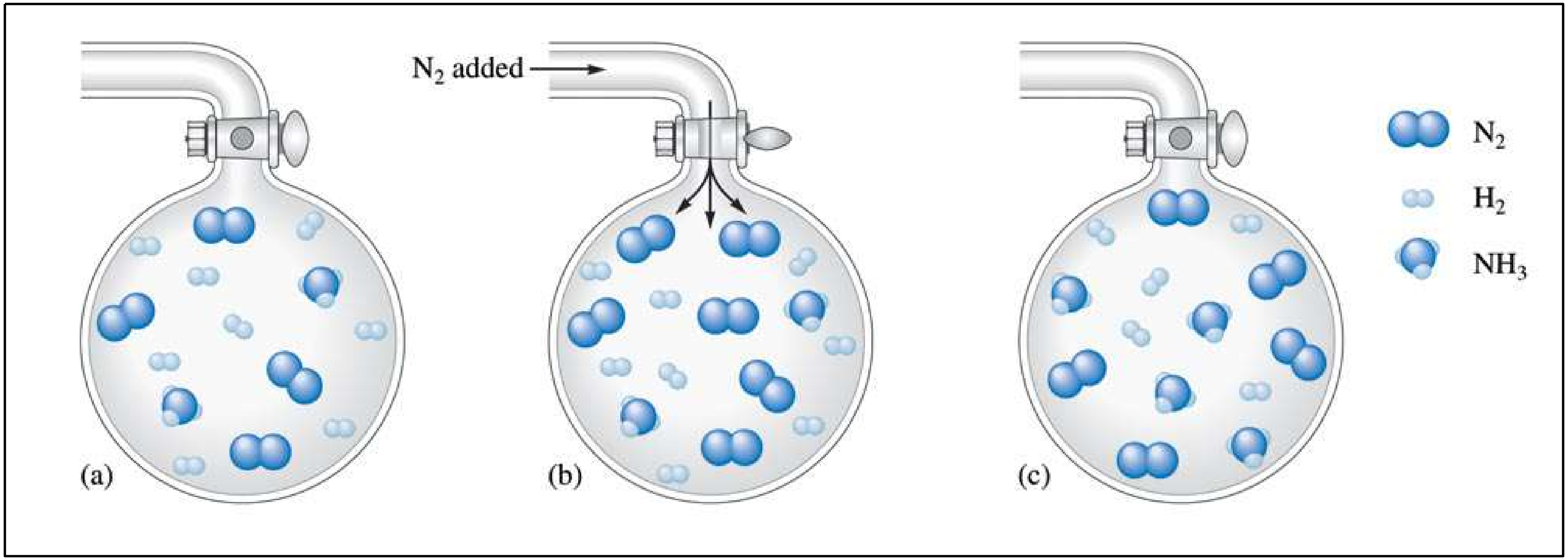


Photo 13.5 a-b LeChatelier's Principle II

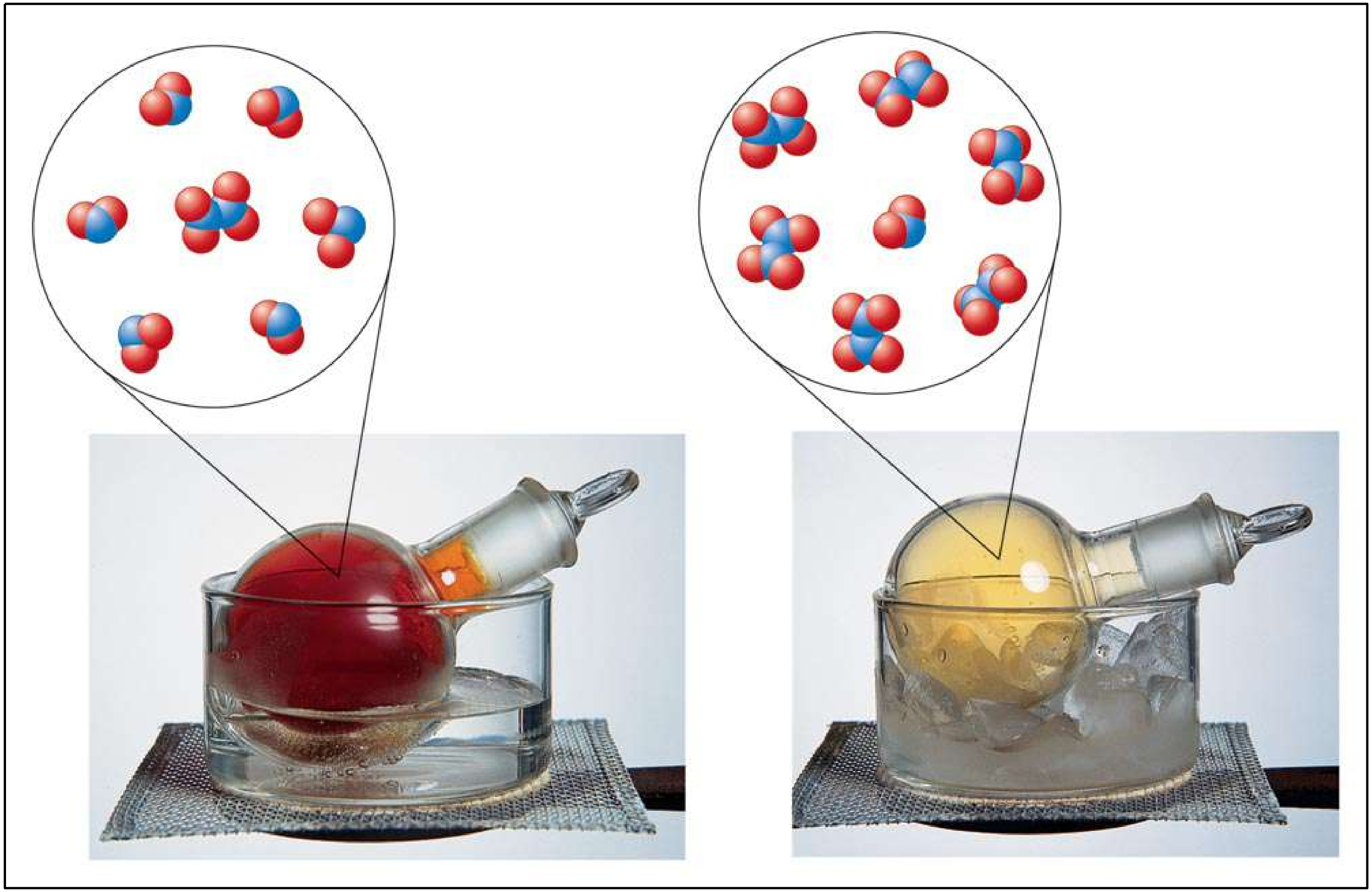


Table 13.3 Observed Value of K for the Ammonia Synthesis Reaction as a Function of Temperature

TABLE 13.3 Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*

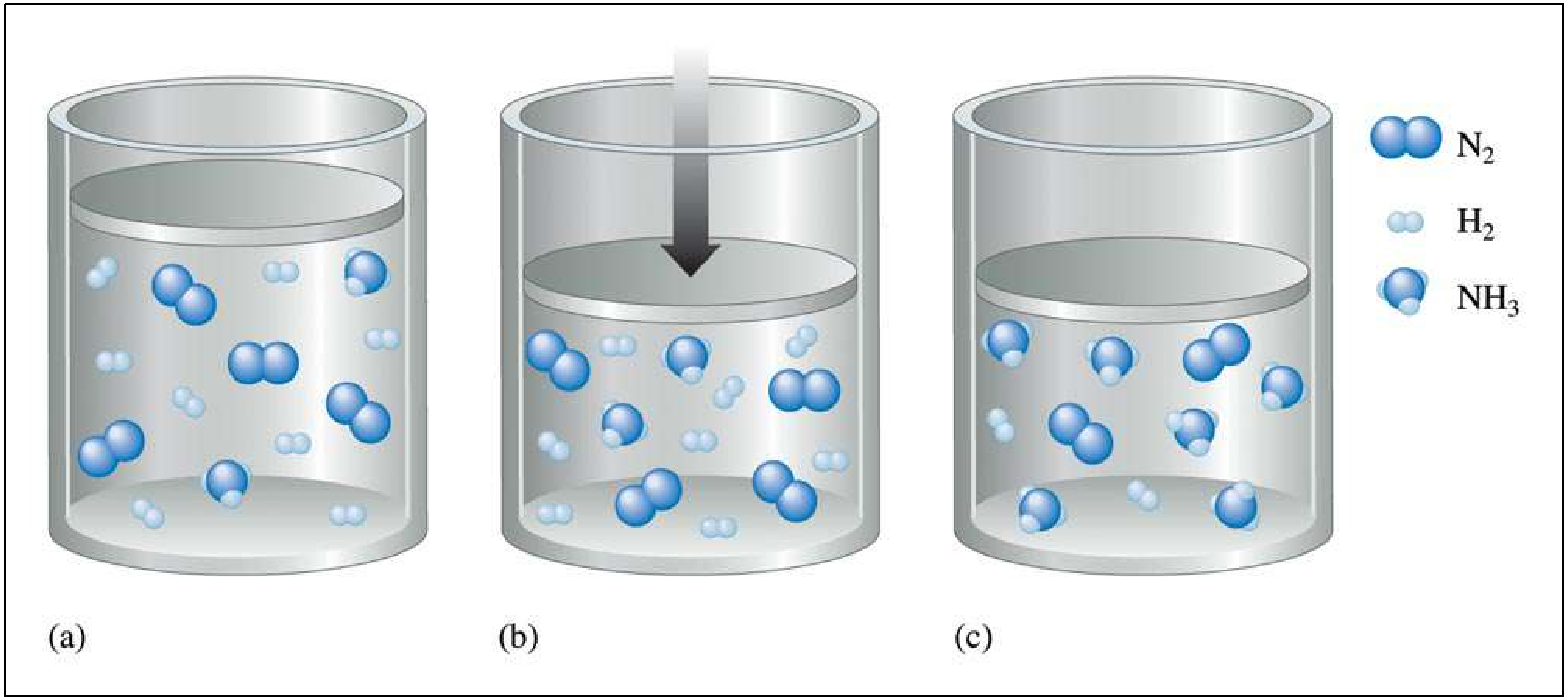
Temperature (K)	*K*
500	90
600	3
700	0.3
800	0.04

*For this exothermic reaction, the value of *K* decreases as the temperature increases, as predicted by Le Châtelier's principle.

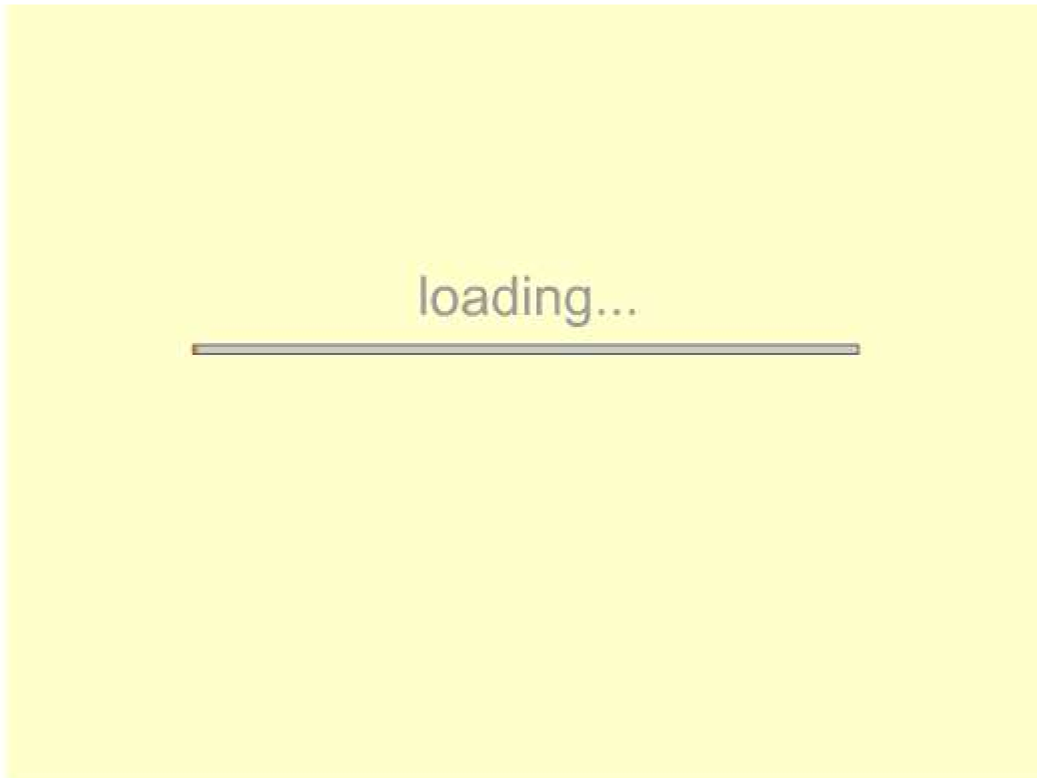
Effects of Changes on the System

3. Pressure:
   a) Addition of inert gas does not affect the equilibrium position.
   b) Decreasing the volume shifts the equilibrium toward the side with fewer moles.

Figure 13.9 a-c (a) A Mixture of $NH_3(g)$, $N_2(g)$, and $H_2(g)$ at Equilibrium (b) The Volume is Suddenly Decreased (c) The New Equilibrium Position for the System Containing More NH_3 and Less N_2 and H_2



LeChâtelier’s Principle



Equilibrium Decomposition of N_2O_4

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Table 13.4 Shifts in the Equilibrium Position for the Reaction 58 kJ + $N_2O_4(g)$ -- $2NO_2(g)$

TABLE 13.4 Shifts in the Equilibrium Position for the Reaction 58 kJ + $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Change	Shift
Addition of $N_2O_4(g)$	Right
Addition of $NO_2(g)$	Left
Removal of $N_2O_4(g)$	Left
Removal of $NO_2(g)$	Right
Addition of $He(g)$	None
Decrease container volume	Left
Increase container volume	Right
Increase temperature	Right
Decrease temperature	Left