Section 16.4

Disturbing a Chemical Equilibrium
Le Chatelier's Principle

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Equilibrium and the Equilibrium Constant

In this section…

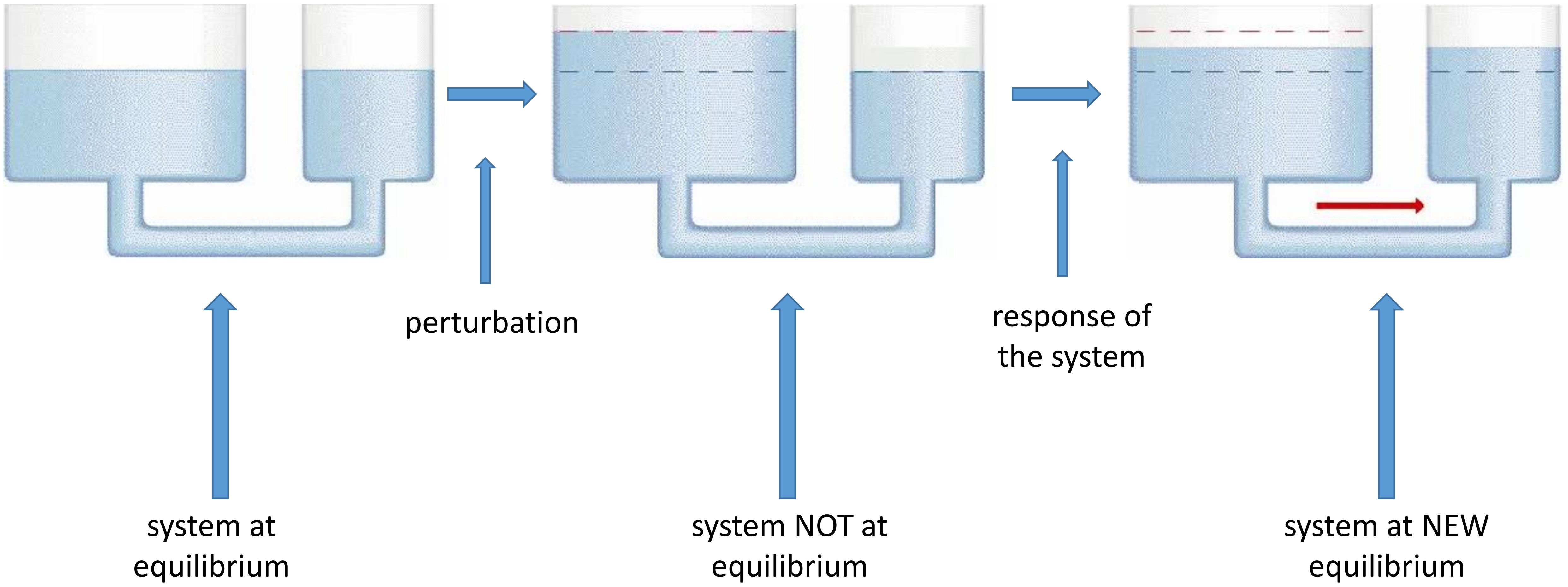
a. Le Chatelier's Principle
b. Adding or removing a reactant or product
c. Changing the volume of the system
d. Changing the temperature

Le Chatelier’s Principle

General Idea:

If a chemical system at equilibrium is disturbed so that it is no longer at equilibrium, the system will respond by reacting in either the forward or reverse direction so as to counteract the disturbance, resulting in a new equilibrium composition.

Le Chatelier’s Principle: Water Tank Analogy



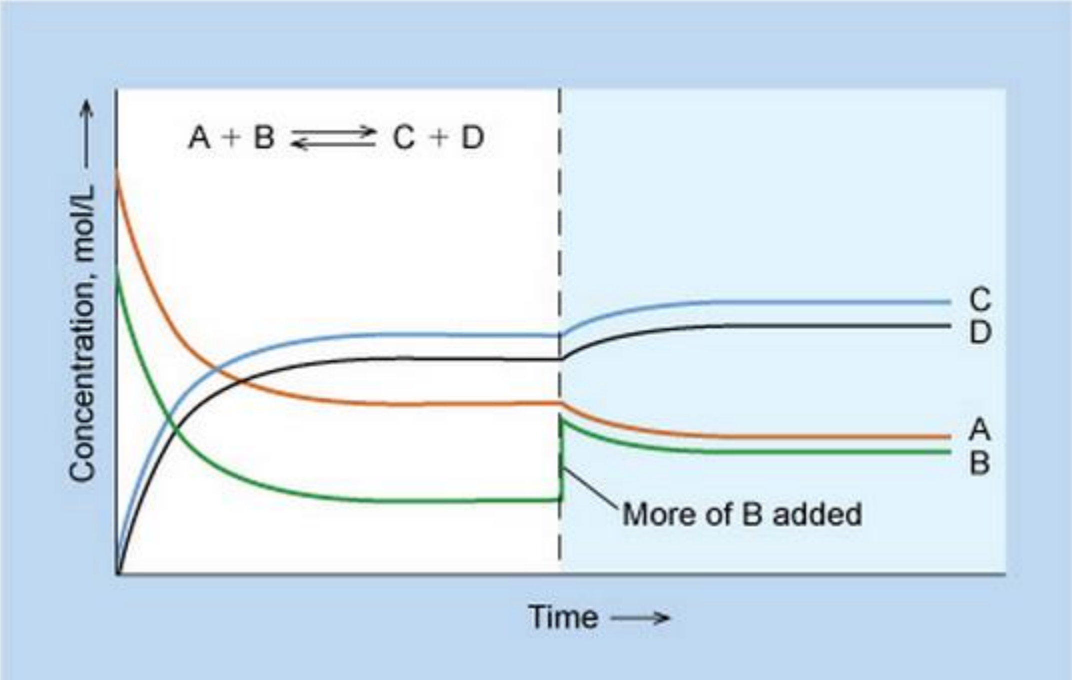
Addition or Removal of a Reactant or Product: Concept

NOTE: K does not change when volume changes.

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

$$K = \frac{[\mathrm{FeSCN^{2+}}]}{[\mathrm{Fe^{3+}}][\mathrm{SCN^{-}}]}$$

Addition or Removal of a Reactant or Product: Graphical



Addition or Removal of a Reactant or Product: Example

Some $FeSCN^{2+}$ is allowed to dissociate into Fe^{3+} and SCN^{-} at 25 °C. At equilibrium,

$[FeSCN^{2+}] = 0.0768$ M
$[Fe^{3+}] = [SCN^{-}] = 0.0232$ M.

Additional Fe^{3+} is added so that $[Fe^{3+}]_{new} = 0.0300$ M and the system is allowed to once again reach equilibrium. What happens?

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq) \qquad K = 142 \text{ at } 25\ ^{\circ}C$$

a. In which direction will the system shift to re-attain equilibrium?

Addition or Removal of a Reactant or Product: Example

Initial concentrations: [$FeSCN^{2+}$] = 0.0768 M, [Fe^{3+}] = [SCN^-] = 0.0232 M.
Additional Fe^{3+} is added so that $[Fe^{3+}]_{new}$ = 0.0300 M

b. What will the concentrations be when equilibrium is reestablished?

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftarrows FeSCN^{2+}(aq) \qquad K = 142 \text{ at } 25\ ^\circ C$$

Pathway:

1. Write equilibrium expression
2. Construct ICE table
3. Express equilibrium concentrations in terms of initial concentrations and "x" (the amount reacting)
4. Insert into equilibrium expression and solve for the numerical value of x
5. Use x and initial concentrations to determine equilibrium concentrations

Initial concentrations: $[FeSCN^{2+}] = 0.0768$ M, $[Fe^{3+}] = [SCN^-] = 0.0232$ M.
Additional Fe^{3+} is added so that $[Fe^{3+}]_{new} = 0.0300$ M

b. What will the concentrations be when equilibrium is reestablished?

	$Fe^{3+}(aq)$ +	$SCN^-(aq)$ $\rightleftarrows$	$FeSCN^{2+}(aq)$	$K = 142$ at 25 °C
initial	0.0300	0.0232	0.0768	
change				
equilibrium				

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{0.0768 + x}{(0.0300 - x)(0.0232 - x)} = 142$$

$0 = 142x^2 - 8.55x + 0.0220$

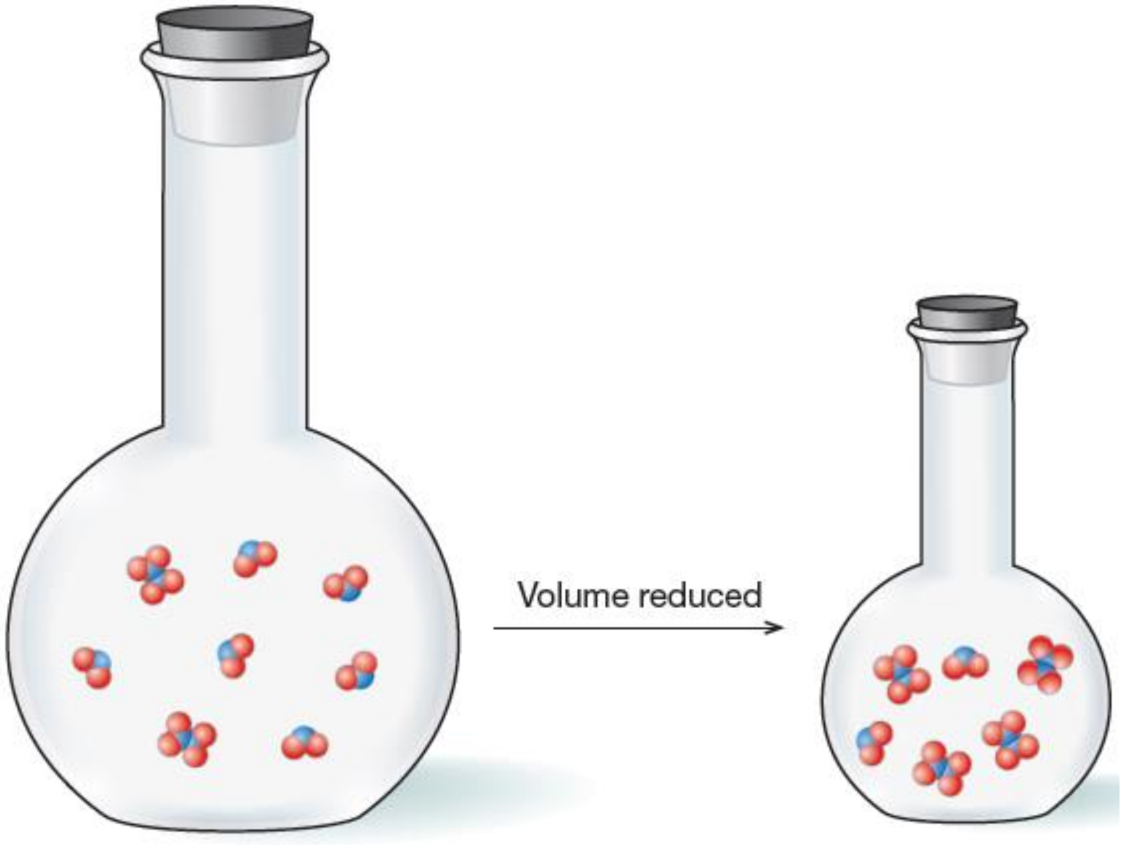
$x = 0.00267$ or 0.0575

$[Fe^{3+}] = 0.0300 - x = 0.0273$ M

$[SCN^-] = 0.0232 - x = 0.0205$ M

$[FeSCN^{2+}] = 0.0768 + x = 0.0795$ M

Changing the Volume: Concept



$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \quad K = 171$

$[N_2O_2]$ increases when volume is reduced because it has fewer moles.

Table 15.4.2 Effect of Volume Change on an Equilibrium System

Change	System Response	Effect on K
Decrease volume	Shifts to form fewer moles of gas	No change
Increase volume	Shifts to form more moles of gas	No change

NOTE: K does not change when volume changes.

Changing the Volume: Example

NO_2 and N_2O_4 are in equilibrium with in a 2-L container with concentrations:

$[NO_2] = 0.314$
$[N_2O_4] = 0.413$

What will the concentrations be if the sample is transferred to a 1-L flask and equilibrium is reestablished?

System shifts:

$$N_2O_4(g) \rightleftarrows 2\ NO_2(g) \qquad K = 0.690 \text{ at } 50\ °C$$

	$N_2O_4(g)$	$\rightleftarrows$	$2\ NO_2(g)$
Initial (M)	0.286		0.628
Change (M)			
Equilibrium (M)			

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.628 - 2x)^2}{0.286 + x} = 0.690$$

$$0 = 4x^2 - 3.20x + 0.197$$

$$x = 0.0672 \text{ and } 0.733$$

$$[NO_2] = 0.628 - 2x = 0.494\ M$$

$$[N_2O_4] = 0.286 + x = 0.353\ M$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.494)^2}{0.353} = 0.691$$

Changing the Temperature: Concept

Exothermic reaction: reactants $\rightleftarrows$ products + *heat*

Endothermic reaction: reactants + *heat* $\rightleftarrows$ products

When Temperature Increases:

Exothermic reaction shifts to the left: reactants $\leftarrow$ products + *heat*

Endothermic reaction shifts to the right: reactants + *heat* $\rightarrow$ products

When Temperature Decreases:

Exothermic reaction shifts to the right: reactants $\rightarrow$ products + *heat*

Endothermic reaction shifts to the left: reactants + *heat* $\leftarrow$ products

Table 15.4.3 Effect of Temperature Change on an Equilibrium System

Change	Reaction Type	System Response	Effect on *K*
Increase temperature	Exothermic	Shifts to the left ($\leftarrow$)	Decreases
Increase temperature	Endothermic	Shifts to the right ($\rightarrow$)	Increases
Decrease temperature	Exothermic	Shifts to the right ($\rightarrow$)	Increases
Decrease temperature	Endothermic	Shifts to the left ($\leftarrow$)	Decreases

Changing the Temperature: Qualitative Example

$$2\ NO_2(g) \rightleftarrows N_2O_4(g) \qquad K = 170 \text{ at } 298K \qquad \Delta H^\circ = -57.1 \text{ kJ/mol}$$

What will happen if Temperature Increases?

Changing the Temperature: Calculating how K Changes with Temperature

van’t Hoff Equation (not related to van’t Hoff factor): $$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Sulfur dioxide reacts with oxygen to form sulfur trioxide. The equilibrium constant, K_p, for this reaction is 0.365 at 1150 K.

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g) \qquad \Delta H^o = -198\ \text{kJ/mol}$$

a. What will happen to O_2 concentration when the temperature of an equilibrium system is increased?

b. Estimate the value of the equilibrium constant at 1260 K.

$$\ln\left(\frac{K_2}{0.365}\right) = -\frac{-198\ \text{kJ/mol}}{8.3145 \times 10^{-3}\ \text{kJ/K}\cdot\text{mol}}\left(\frac{1}{1260\ \text{K}} - \frac{1}{1150\ \text{K}}\right)$$

$$K_2 = 0.0599$$