17.6 Changing Reaction Conditions and the Equilibrium State

• **Le Chatelier’s principle** – when a system at equilibrium is disturbed, the equilibrium “shifts” in a direction that minimizes the effect of the disturbance
  
  – A chemical system can be disturbed by changing the values of $Q$ or $K$ so that temporarily $Q \neq K$

  • Changing concentrations of reactants or products ($Q$ changes)
  • Changing pressure for gas reactions ($Q$ changes)
  • Changing temperature ($K$ changes)

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**Example:** Given $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$. How can the yield of NH$_3$ be increased by manipulating the concentrations of reactants and products?

→ Add more N$_2$ and H$_2$

→ Remove some NH$_3$

**Changing Pressure or Volume**

• Affects the concentrations of gaseous reactants and products ($Q$ changes)

→ **Changing the partial pressure** of a gaseous reactant or product

→ The concentration of the reactant or product changes and the equilibrium shifts accordingly as described before

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**Changing Concentration**

• If the concentration increases, the system reacts to consume some of it; If the concentration decreases, the system reacts to produce some of it

→ **Adding reactants or removing products**

→ The equilibrium shifts toward the products in order to consume the added reactants or generate the removed products

→ $Q$ decreases $\rightarrow Q < K \rightarrow$ reaction shifts forward

→ **Adding products or removing reactants**

→ The equilibrium shifts toward the reactants in order to consume the added products or generate the removed reactants

→ $Q$ increases $\rightarrow Q > K \rightarrow$ reaction shifts in reverse

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→ **Changing the total pressure** of the reaction mixture by changing its volume

→ **Compression** ($\uparrow P$ by $\downarrow V$)

→ The equilibrium shifts in a direction that consumes gases and relieves the pressure

⇒ The equilibrium shifts toward the side with fewer moles of gas

**Example:** $A(g) + B(g) \leftrightarrow C(g)$

2 mol gas $\leftrightarrow$ 1 mol gas

$Q_p = \frac{P_c}{P_A P_B} \frac{(n_A RT / V)}{(n_A RT / V)(n_B RT / V)} = \frac{n_C}{n_A n_B} \times \frac{V}{RT}$

⇒ As $V$ is reduced, $Q$ decreases ($Q<K$) and the reaction shifts forward

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Expansion ($\downarrow P$ by $\uparrow V$)

- The equilibrium shifts in a direction that produces more gases and increases the pressure
  - This shifts toward the side with more moles of gas

Compression and expansion do not affect reactions in which the number of moles of gases is the same on both sides of the equation

Changing the total pressure of the reaction mixture by adding an inert gas

- The equilibrium is not affected because the partial pressures and concentrations of the components do not change

Example: Given $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$. How can the yield of NH$_3$ be increased by changing the pressure (volume) of the reaction mixture?

$\quad 4 \text{ mol gas} \leftrightarrow 2 \text{ mol gas}$

Increasing the pressure (compression) shifts the equilibrium to the right toward less moles of gas (4 mol $\rightarrow$ 2 mol) and improves the yield of NH$_3$

Example: Given $Cl_2(g) + H_2(g) \leftrightarrow 2HCl(g)$. What is the effect of increasing the volume of the reaction container?

$\quad 2 \text{ mol gas} \leftrightarrow 2 \text{ mol gas}$

Increasing the volume (expansion) has no effect on the reaction since the number of moles of gas is the same on both sides of the equation

Changing Temperature

- Affects the value of $K$
  
  Increasing $T$ by adding heat to the reaction mixture favors the endothermic reaction which consumes the added heat
  
  Decreasing $T$ by removing heat from the reaction mixture favors the exothermic reaction which produces heat

Example: $A + B \leftrightarrow C + D + \text{heat} \quad \Delta H < 0$

- The forward reaction is exothermic, while the reverse reaction is endothermic
  
  Increasing $T$ favors the endothermic reaction so the reaction shifts in reverse

Example: Given $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ with $\Delta H^\circ = -92 \text{ kJ/mol}$. How can the yield of NH$_3$ be increased by manipulating the temperature?

- The forward reaction is exothermic
  
  Lowering the temperature facilitates the forward reaction and improves the yield of NH$_3$

Changing $T$ changes the value of $K$

- Increasing $T$ increases $K$ for endothermic reactions
  
  Increasing $T$ decreases $K$ for exothermic reactions
  
  Increasing $T$ increases more the rate constant of the endothermic reaction (which has higher activation energy) $\Rightarrow K = \frac{k_{\text{fwd}}}{k_{\text{rev}}}$$\Rightarrow$ If the forward reaction is endothermic, $K$ increases

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The $T$ dependence of $K$ is given by the van’t Hoff equation:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{\text{rxn}}^o}{R} \left( \frac{T_2}{T_1} - 1 \right)$$

→ The equation allows the calculation of $K$ at one temperature knowing the value of $K$ at another temperature and $\Delta H^o$ of the reaction.

**Example:** Given $\text{N}_2(g) + \text{O}_2(g) \leftrightarrow 2\text{NO}(g)$ with $\Delta H^o = 181 \text{ kJ/mol}$. If $K_p = 4.3 \times 10^{-31}$ at 298 K, what is $K_p$ at 3000 K?

$T_1 = 298 \text{ K}$  
$K_{p1} = 4.3 \times 10^{-31}$

$T_2 = 3000 \text{ K}$  
$K_{p2} = ?$

$$\ln \frac{K_{p2}}{4.3 \times 10^{-31}} = -\frac{181 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{3000 \text{K}} - \frac{1}{298 \text{K}} \right)$$

$$K_{p2} = 4.3 \times 10^{-31} \times \exp \left( -\frac{181 \times 10^3}{8.314} \left( \frac{1}{3000} - \frac{1}{298} \right) \right)$$

$K_{p2} = 1.6 \times 10^{-2}$

→ $K_p$ is much larger at 3000 K because the forward reaction is endothermic and therefore is favored by $\uparrow T$.

### The Effect of Catalysts

- Catalysts **do not affect the equilibrium state** and the value of $K$ because they speed up equally both the forward and reverse reactions.

- Catalysts only shorten the time needed to reach equilibrium.

**Example:** Given $\text{N}_2(g) + 3\text{H}_2(g) \leftrightarrow 2\text{NH}_3(g)$ with $\Delta H^o = -92 \text{ kJ/mol}$. What are the optimum conditions for the synthesis of NH$_3$?

→ Pump in more N$_2$ and H$_2$ and remove NH$_3$ (NH$_3$ can be removed by cooling $\rightarrow$ condensation).

→ Increase $P$ and decrease $T$.

→ At lower $T$, a catalyst is needed to speed up the process.

<table>
<thead>
<tr>
<th>Table 17.4</th>
<th>Effect of Various Disturbances on an Equilibrium System</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Disturbance</strong></td>
<td><strong>Net Direction of Reaction</strong></td>
</tr>
<tr>
<td>Concentration</td>
<td>Increase [reactant]</td>
</tr>
<tr>
<td></td>
<td>Decrease [reactant]</td>
</tr>
<tr>
<td></td>
<td>Increase [product]</td>
</tr>
<tr>
<td></td>
<td>Decrease [product]</td>
</tr>
<tr>
<td>Pressure</td>
<td>Increase $P$ (decrease $V$)</td>
</tr>
<tr>
<td></td>
<td>Decrease $P$ (increase $V$)</td>
</tr>
<tr>
<td></td>
<td>Increase $P$ (add inert gas, no change in $V$)</td>
</tr>
<tr>
<td>Temperature</td>
<td>Increase $T$</td>
</tr>
<tr>
<td></td>
<td>Decrease $T$</td>
</tr>
<tr>
<td>Catalyst added</td>
<td>None; forward and reverse equilibrium attained sooner; rates increase equally</td>
</tr>
</tbody>
</table>