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)

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 → $Q<K$ → 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 → $Q>K$ → reaction **shifts in reverse**

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 (changes Q)

➤**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 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: $\underbrace{A(g) + B(g)}_{\text{2 mol gas}} \leftrightarrow \underbrace{C(g)}_{\text{1 mol gas}}$

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

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

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

→The equilibrium shifts in a direction that produces more gases and increases the pressure

⇒The equilibrium **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

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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 changing the pressure (volume) of the reaction mixture?

4 mol gas ↔ 2 mol gas
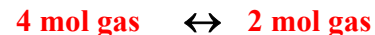
⇒ Increasing the pressure (compression) shifts the equilibrium to the right toward less moles of gas (4 mol → 2 mol) and improves the yield of NH_3

Example: Given $Cl_{2(g)} + H_{2(g)} \leftrightarrow 2HCl_{(g)}$. What is the effect of increasing the volume of the reaction container?

2 mol gas ↔ 2 mol gas
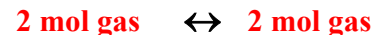
⇒ Increasing the volume (expansion) has no effect on the reaction since the number of moles of gas is the same on both sides of the equation

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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: $A + B \leftrightarrow C + D + heat$ $\Delta H < 0$

→The forward reaction is exothermic, while the reverse reaction is endothermic

⇒ Increasing T favors the endothermic reaction so the reaction shifts in reverse

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➤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) → $K = k_{fwd}/k_{rev}$ ⇒ If the forward reaction is endothermic, K increases

Example: Given $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$ with ΔH^o = -92 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

> The T dependence of K is given by the van't Hoff equation

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

→ The equation allows the calculation of K at one temperature knowing the value of K at another temperature and ΔH^o of the reaction

Example: Given $N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)}$ with $\Delta H^o = 181$ kJ/mol. If $K_p = 4.3 \times 10^{-31}$ at 298 K, what is K_p at 3000 K?

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

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

$$\ln\frac{K_{p2}}{4.3\times10^{-31}} = -\frac{181\times10^3\ \text{J/mol}}{8.314\ \text{J/mol}\cdot\text{K}}\left(\frac{1}{3000\text{K}} - \frac{1}{298\text{K}}\right)$$

$$\frac{K_{p2}}{4.3\times10^{-31}} = \exp\left(-\frac{181\times10^3}{8.314}\left(\frac{1}{3000} - \frac{1}{298}\right)\right)$$

$$K_{p2} = 4.3\times10^{-31} \times \exp\left(-\frac{181\times10^3}{8.314}\left(\frac{1}{3000} - \frac{1}{298}\right)\right)$$

$$K_{p2} = 1.6\times10^{-2}$$

→ 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 $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$ with $\Delta H^o = -92$ 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 → condensation)

→ Increase P and decrease T

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

Table 17.4 Effect of Various Disturbances on an Equilibrium System

Disturbance	Net Direction of Reaction	Effect on Value of K
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase P (decrease V)	Toward formation of fewer moles of gas	None
Decrease P (increase V)	Toward formation of more moles of gas	None
Increase P (add inert gas, no change in V)	None; concentrations unchanged	None
Temperature		
Increase T	Toward absorption of heat	Increases if $\Delta H^0_{rxn} > 0$ Decreases if $\Delta H^0_{rxn} < 0$
Decrease T	Toward release of heat	Increases if $\Delta H^0_{rxn} < 0$ Decreases if $\Delta H^0_{rxn} > 0$
Catalyst added	None; forward and reverse equilibrium attained sooner; rates increase equally	None