

17.6 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)

Example: Given $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$. 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

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

$\rightarrow Q$ 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

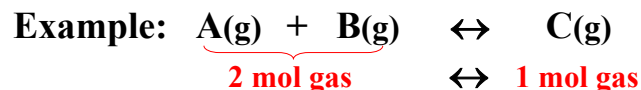
$\rightarrow O$ increases $\rightarrow O > K \rightarrow$ reaction **shifts in reverse**

➤ **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**



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

⇒ 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

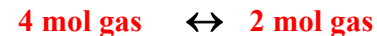
⇒ The equilibrium **shifts toward the side with more moles of gas**

➤ 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**

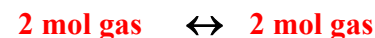
→ The equilibrium **is not affected** because the partial pressures and concentrations of the components do not change

Example: Given $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$. How can the yield of NH_3 be increased by changing the pressure (volume) of the reaction mixture?



⇒ 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 $\text{Cl}_2(\text{g}) + \text{H}_2(\text{g}) \leftrightarrow 2\text{HCl}(\text{g})$. What is the effect of increasing the volume of the reaction container?



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

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

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

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

Example: Given $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$ with $\Delta H = -92 \text{ kJ/mol}$. 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

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

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

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

Example: Given $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$ with $\Delta H = -92 \text{ kJ/mol}$. If $K = 1$ at C , what is K at C ?