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*≠*K***
    - Changing concentrations of reactants or products (***Q*** changes)
    - Changing pressure for gas reactions (***Q*** changes)
    - Changing temperature (***K*** changes)

Example: Given $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$. 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

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**

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

➢**Compression** (↑***P*** by ↓***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: $\mathbf{A_{(g)} + B_{(g)} \leftrightarrow C_{(g)}}$

2 mol gas ↔ 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** (↓***P*** by ↑***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 $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$. 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 $\mathbf{Cl_{2(g)} + H_{2(g)} \leftrightarrow 2HCl_{(g)}}$. 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

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

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

Example: Given $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$ with ΔH = -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 $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$ with ΔH = -92 kJ/mol. If K = 1 at C, what is K at C?