


Chemical equilibrium

15.1 Gibbs energy and equilibrium

- Chemical systems come to equilibrium when they reach a state of minimum Gibbs energy.
- Chemical equilibrium is a dynamic equilibrium.
- The thermodynamic equilibrium constant, K , is defined in terms of activities by

$$K = \frac{\prod (a(\text{products}))_{\text{eqm}}^{v_p}}{\prod (a(\text{reactants}))_{\text{eqm}}^{v_r}}$$

- K is dimensionless, so has no units.
- Equilibrium constants can also be written in terms of partial pressures (K_p) or concentrations (K_c).

 For practice questions on these topics, see questions 1–3 at the end of this chapter (p.721).

15.2 The direction of a reaction: the reaction quotient


- The thermodynamic equilibrium constant, K , is defined in terms of the activities of components in a reaction at equilibrium by

$$K = \frac{\prod (a(\text{products}))_{\text{eqm}}^{v_p}}{\prod (a(\text{reactants}))_{\text{eqm}}^{v_r}}$$

- The reaction quotient, Q , is defined in terms of the activities by

$$Q = \frac{\prod (a(\text{products}))^{v_p}}{\prod (a(\text{reactants}))^{v_r}}$$

- If $Q < K$, the forward reaction proceeds. If $Q > K$, the reverse reaction proceeds. If $Q = K$, the system is at equilibrium.

 For practice questions on these topics, see questions 4, 5, and 10 at the end of this chapter (p.721).

15.3 Gibbs energy and equilibrium constants

- The thermodynamic equilibrium constant, K , for a reaction is linked to the standard Gibbs energy change by

$$\Delta_r G^\ominus = -RT \ln K$$

- If a reaction, $R \rightleftharpoons P$, has a Gibbs energy change more negative than $-22.8 \text{ kJ mol}^{-1}$ at 298 K, then the reaction will effectively go to completion.



For practice questions on these topics, see questions 6–8 and 19–21 at the end of this chapter (pp.722–723).

15.4 Calculating the composition of reactions at equilibrium

- If the equilibrium concentrations of all except one component are known, using the equilibrium constant allows calculation of the unknown concentration.
- The equilibrium composition of a reaction can be found from the equilibrium constant and starting quantities by considering the fraction that reacts, α .



For practice questions on these topics, see questions 9 and 13–16 at the end of this chapter (p.722).

15.5 Effect of conditions on reaction yields and K

- The effect of changing conditions on chemical reactions can be predicted qualitatively using Le Chatelier's principle: when a change is made to a system in dynamic equilibrium, the system responds to minimize the effect of the change.
- The equilibrium constant does not vary with pressure at constant temperature but the position of equilibrium can depend on the total pressure.
- The effect of temperature on the equilibrium constant is described by the van't Hoff equation

$$\ln K = \frac{\Delta_r S^\ominus}{R} - \left(\frac{\Delta_r H^\ominus}{R} \right) \frac{1}{T}$$

- Addition of a catalyst accelerates both forward and reverse reactions and so does not influence the position of equilibrium.



For practice questions on these topics, see questions 11, 12, 17, 18, and 22–25 at the end of this chapter (pp.722–723).



Concept review

By the end of this chapter, you should be able to do the following.

- Define and use the three types of equilibrium constant: K_c , K_p , and the thermodynamic equilibrium constant, K .
- Define and use the reaction quotient, Q .
- Calculate Q given the composition of a reaction mixture.
- Calculate K from $\Delta_r G^\ominus$ and vice versa.
- Calculate the composition of an equilibrium mixture from K , given appropriate data.
- Describe and explain how the equilibrium constant and composition change when experimental conditions such as pressure, concentration, and temperature are varied.
- Use the van't Hoff equation to describe the effect of changing temperature on chemical equilibrium and to obtain values for $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ from a plot of $\ln K$ against $1/T$.
- Apply equilibrium thermodynamics to real chemical situations.



Key equations

Thermodynamic equilibrium constant

$$K = \frac{\prod (a(\text{products}))_{\text{eqm}}^{v_p}}{\prod (a(\text{reactants}))_{\text{eqm}}^{v_r}} \quad (15.1)$$

The reaction quotient

$$Q = \frac{\prod (a(\text{products}))^{v_p}}{\prod (a(\text{reactants}))^{v_r}} \quad (15.2)$$

Relationship between $\Delta_r G^\ominus$ and K

$$\Delta_r G^\ominus = -RT \ln K \quad (15.4)$$

$$K = e^{\left(\frac{-\Delta_r G^\ominus}{RT}\right)} \quad (15.5)$$

van 't Hoff equation showing variation of K with temperature

$$\ln K = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT} \quad (15.10)$$