**Example calculation (1)**

Aluminium production by electrolysis:

Molten cryolite, \( \text{Na}_2\text{AlF}_6 \), is used as a solvent for aluminium ore bauxite (\( \text{Al}_2\text{O}_3 \)). Cryolite undergoes slight decomposition with heat to produce small amounts of \( \text{F}_2 \), a toxic gas which may escape into the air.

\[ \text{Na}_2\text{AlF}_6 (l) \rightarrow 3\text{Na}^+ (l) + \text{Al}^3+ (l) + 3\text{F}_2 (g) \]

\( K_c = 2 \times 10^{-104} \text{ mol L}^3 \) at 1300 K

- What is the concentration of \( \text{F}_2 \) at this temperature?

\( K_c = [\text{F}_2]^3 \),

so \([\text{F}_2] = (2 \times 10^{-104})^{1/3} = 3 \times 10^{-35} \text{ mol L}^{-1}\)

**Example calculation (2)**

1. Initial concentration of \( \text{N}_2\text{O}_4 \):

\[ \frac{0.0240}{0.372} \text{ mol L}^{-1} = 0.0645 \text{ mol L}^{-1} \]

2. \( \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) \)

- Initially: \( 0.0645 \text{ mol L}^{-1} \)
- Let \( x \) = amount of \( \text{N}_2\text{O}_4 \) reacted
- Change: \( +2x \) \text{ mol L}^{-1}
- Equil: \( 0.0645-x \text{ mol L}^{-1} \)

3. \( K_c = 4.61 \times 10^{-3} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{(0.0645-x)} \)

**Example calculation (3)**

1. Find the equilibrium concentrations of \( \text{N}_2 \), \( \text{O}_2 \) & \( \text{NO} \) at 2400 K if we start with 0.20 mol \( \text{N}_2 \) and 0.20 mol \( \text{O}_2 \) in a 5.0 L vessel.

\( K_c = 2.5 \times 10^{-3} \) at 2400 K

\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \]

- Initial: \( 0.20/5.0 \text{ mol L}^{-1} \)
- Change: \( -x \) \text{ mol L}^{-1} \)
- Equil: \( (0.040 - x)(0.040 - x) \text{ mol L}^{-1} \)

\( K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.040-x)(0.040-x)} = 2.5 \times 10^{-3} \)

**Example calculation (4)**

Solid silver is added to a solution with these initial concentrations: \( [\text{Ag}^+] = 0.200 \text{ M} \), \( [\text{Fe}^{2+}] = 0.100 \text{ M} \), and \( [\text{Fe}^{3+}] = 0.300 \text{ M} \). The following reversible reaction occurs:

\( \text{Ag}^+(aq) + 2\text{Fe}^{2+}(aq) \rightleftharpoons \text{Ag}^{2+}(aq) + 2\text{Fe}^{3+}(aq) \)

\( K_c = 2.98 \text{ L mol}^{-1} \)

What are the ion concentrations when equilibrium is established?

\[ \text{Ag}^+(aq) + 2\text{Fe}^{2+}(aq) \rightleftharpoons \text{Ag}^{2+}(aq) + 2\text{Fe}^{3+}(aq) \]

- Initial: \( 0.200 \text{ mol L}^{-1} \)
- \( 0.100 \text{ mol L}^{-1} \)
- \( 0.300 \text{ mol L}^{-1} \)

Which way does the equilibrium shift?

\[ Q = \frac{[\text{Fe}^{3+}]^2}{[\text{Ag}^+][\text{Fe}^{2+}]^2} = \frac{0.000}{0.001} = 1500 \]

Eq’m will shift to the
Example calculation (4)

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$$

Initial: 0.200 0.100 0.300 mol/L
Change: -X -X -X mol/L
Equilibrium 0.200-X 0.100-X 0.300-X mol/L

$$K = \frac{0.300 \cdot x}{(0.200 + x) \cdot (0.200 + x)}$$

The allowable solution of this quadratic equation is x = 0.11. (You should check this.)

Therefore,

$$[Ag^+] = 0.200 + x = 0.31 M$$

$$[Fe^{2+}] = 0.100 + x = 0.21 M$$

$$[Fe^{3+}] = 0.300 - x = 0.19 M$$

Example calculation (5)

Lead iodide is an almost insoluble salt with a dense golden yellow color. It is used in ornamental work requiring a gold-like color. The solubility product equilibrium constant is 7.1x10^{-9} mol^3/L^3. Calculate the solubility of PbI₂ (assume excess solid).

The balanced equation is:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq); \quad K_{sp} = 7.1 \times 10^{-9}$$

Initial: 0 0 0 mol/L
Change: -x 2x 0 mol/L
Equilibrium X 2x 0 mol/L

$$K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 7.1 \times 10^{-9} \text{ mol}^3/L^3$$

Solve for x and work out how many mol/L of PbI₂ will dissolve.

Solution next lecture.

Example calculation (6)

NOCl is an important transient molecule in the ozone cycle of the stratosphere. It exists in equilibrium with NO and Cl₂. At 35°C the eq/m constant, K ≈ 1.6x10^{-6} mol/L. In a laboratory experiment where the decomposition of NOCl was studied, 1.0 mole of NOCl was placed into a 2.0 L flask. What are the equilibrium concentrations of NOCl, NO, and Cl₂?

The balanced equation is:

$$2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g); \quad K = 1.6 \times 10^{-5}$$

Initial: 0.50 0 0 mol/L
Change: -2X -2X -X mol/L
Equilibrium 0.50-2X 2X X mol/L

$$2X^2 + X - 1.6 \times 10^{-5} \Rightarrow X^3 - 0.1 \times 10^{-5}$$

Solution next lecture.

Example calculation (7)

When gases are involved, the equilibrium constant may be written in terms of pressure, rather than concentration. For example, in example (6), the eq/m constant for the decomposition of NOCl used concentrations. It might equally well have referred to the partial pressures of NOCl, NO and Cl₂. For example, at 35°C:

$$2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g); \quad K_p = 4.1 \times 10^{-4} \text{ atm}$$

The solution to problems using $K_p$ are exactly the same as previously, but of course the answer comes out in pressure units, rather than concentration.

If gases are involved, and there is any likelihood of confusion, then the equilibrium constant is usually denoted as either $K_p$ or $K_c$.

Example questions

**CONCEPTS**
- The approach to solving for $K_p$
- When to use small $x$ approximation

**CALCULATIONS**
- Work out $K_p$ from given concentrations
- Work out $K_c$ from given concentrations

Relationship between $K_p$ and $K_c$

Pressure and concentration are linked by the ideal gas law:

$$PV = nRT$$

Using the NOCl example:

$$2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$$

$K_p = 1.6 \times 10^{-6}$ mol/L

$K_c = 4.1 \times 10^{-4}$ atm

$$K_c = \left( \frac{P}{RT} \right)^{n_{prod}} = \left( \frac{P}{RT} \right)^{n_{react}} - K_p \times \frac{1}{RT}$$

Check $K_p = \frac{4.1 \times 10^{-4}}{0.021 \times 23 = 35} = 1 \times 10^{-9} = K_c$

Relationship between $K_p$ and $K_c$

The preceding derivation is just one example of a general relationship

$$K = K_p \left( \frac{RT}{n_{prod}} \right)^{n_{prod}}$$

or

$$K = K_c \left( \frac{RT}{n_{react}} \right)^{n_{react}}$$

Example (4) or (5) or (6) or (7)