

**Chemical Equilibrium III**

**Reaction Quotient**

- Whether equilibrium favours reactants or products

\[
aA + bB \rightleftharpoons cC + dD
\]

**Reaction Quotient:**

\[
Q_r = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

Defined for a system not necessarily at equilibrium

At equilibrium:

\[
Q_r = K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

**Le Châtelier’s Principle**

“*When a chemical system in a state of equilibrium is disturbed, it reattains equilibrium by undergoing a net reaction that reduces the effect of the disturbance*”

- Increase reactant concentrations
  \[ \Rightarrow Q_r \Rightarrow K_c \]
- Increase pressure / decrease volume
  \[ \Rightarrow K_c \text{ changes, then } Q_r \Rightarrow K_c \]
- Increase temperature
  \[ \Rightarrow \]

**Equilibria involving Difference States of Matter**

- Open system - exchanges material with surroundings.
- Closed systems - no exchange: can reach equilibrium;
  
  # molecules/s returning to liquid = # escaping to vapour

**Open And Closed Systems**

- Liquid ↔ vapour

**Equilibria with Pure Liquid or Pure Solid**

\[
2\text{HgO (s)} \rightleftharpoons 2\text{Hg (l)} + \text{O}_2 (g)
\]

\[
K_e = \frac{[\text{Hg}^2]^2[\text{O}_2]}{[\text{HgO}]^2}
\]

**Some Important Equations**

<table>
<thead>
<tr>
<th>Form of Chemical Equation</th>
<th>Form of ( Q )</th>
<th>Value of ( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference reaction: ( A \rightleftharpoons B )</td>
<td>( Q_{net} = \frac{[B]}{[A]} )</td>
<td>( K_{net} = \frac{[B]<em>{eq}}{[A]</em>{eq}} )</td>
</tr>
<tr>
<td>Reverse reaction: ( B \rightleftharpoons A )</td>
<td>( Q = \frac{1}{Q_{net}} = \frac{[A]}{[B]} )</td>
<td>( K = \frac{1}{K_{net}} )</td>
</tr>
<tr>
<td>Reaction as sum of two steps: ( (1) \ A \rightleftharpoons C )</td>
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</tbody>
</table>
\[
Q_{overall} = Q_1 \cdot Q_2 = \frac{[C]}{[A]} \cdot \frac{[B]}{[C]} = \frac{[B]}{[A]}
\] | \( K_{overall} = K_1 \cdot K_2 \) |
| \( (2) \ C \rightleftharpoons B \) | 
\[
Q_{overall} = Q_1 \cdot Q_2 = \frac{[D]}{[E]} \cdot \frac{[E]}{[D]} = 1
\] | \( K_{overall} = K_1 \cdot K_2 \) |

Coefficients multiplied by \( a \)

\[
Q = Q_{net}^a \quad K = K_{net}^a
\]
Activity

BY CONVENTION:
• for solution standard state = 1 M; activity = concentration.
• for gas, standard state = 1 atm, activity = pressure
• for solids & liquids: standard state = pure solid or liquid, whose concentration does not change; activity = 1 always

the concentrations of liquids and solids do not appear in the expressions for \( K_c \) and \( K_p \)

Equilibria with Pure Liquid or Pure Solid

Hence for \( 2\text{HgO} (s) \leftrightarrow 2\text{Hg} (l) + \text{O}_2 (g) \):
\[
K_c = [\text{O}_2 ]; \quad K_p = p_{\text{O}_2}
\]
- independent of amount of solid or liquid present

• Example: evaporation of water

\[
\text{H}_2\text{O} (l) \leftrightarrow \text{H}_2\text{O} (g)
\]
Vapour pressure in sealed vessel in presence of liquid is always the same (at given temperature) irrespective of how much liquid water is present

Temperature Variation of \( K_c \)

\[
K_c \propto e^{-\Delta H^0/RT}
\]

- size of \( K_c \) determined by thermodynamics
- \( \Delta H^0 \) = 0, hence \( e^{-\Delta H^0/RT} \) increases with increasing \( T \)

Temperature Variation of \( K_p \)

\[ K_p = \text{constant} \]

- \( \Delta H^0 \) = 0, hence \( e^{-\Delta H^0/RT} \) increases with increasing \( T \)

Optimising Reaction Conditions

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

• CONCENTRATION
  - remove the product or increase the reactants, i.e. make \( Q_p \) smaller and push the reaction toward products (e.g. liquefy the ammonia and recycle the \( \text{N}_2 \) and \( \text{H}_2 \))

• PRESSURE
  - increasing the total pressure (for this reaction!) makes \( Q_p \) smaller since there are 4 moles of gaseous reactants to 2 moles gaseous product; reaction is shifted toward products

• CATALYSTS
  - no effect on value of \( K_c \) or position of equilibrium but increases rate at which equilibrium is attained.

Example (Aluminium production by electrolysis):

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

\[ \text{Na}_3\text{AlF}_6 (l) \rightarrow 3\text{Na} (l) + \text{Al} (l) + 3\text{F}_2 (g) \]

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

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

Optimising the Conditions for a Reaction

Haber Process for the production of ammonia:

\[ \text{N}_2 (g) + 3\text{H}_2 (g) \rightarrow 2\text{NH}_3 (g) \]
\( \Delta H = -92.22 \text{kJ m}^{-1} \)

\[ K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 4.0 \times 10^4 \text{ at 25 } ^\circ \text{C} \]
- \( K_c \) favours \( \text{NH}_3 \) at low \( T \) (exothermic), but rate too slow
- A large equilibrium constant indicates that the reaction proceeds toward the right almost completely but indicates nothing about how fast the reaction occurs
- Run at high \( T \), high pressure with \( \text{V}_2\text{O}_5 \) catalyst
- Gives compromise between rate and yield (i.e., how fast reaction goes to equilibrium vs optimal concentrations at equilibrium)

See Silberberg

Solving Equilibrium Problems

1. Write balanced equation
2. Write reaction quotient expression, \( Q \)
3. Convert all amounts to M or atm
4. If reaction direction is unknown compare \( Q \) with \( K \)
5. Construct a reaction table
6. Substitute amounts into \( Q \)
7. To simplify the maths assume \( x \) is negligible \( ([\text{A}_{\text{init}}] - x = [\text{A}_{\text{init}}]) \)
8. Solve for \( x \)
9. Solve for the equilibrium amounts

Silberberg, Fig 17.6