Chemical Equilibrium II

Silberberg 2nd Ed, Chapter 17

www.chem.usyd.edu.au/hpage3.htm (login "chem", passwd "chem@usyd")

Any questions or requests - email to c.kepert@chem.usyd.edu.au
Equilibrium Constants

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

- At equilibrium:

\[
K_c = \frac{[C_{eq}]^c [D_{eq}]^d}{[A_{eq}]^a [B_{eq}]^b}
\]

\[
K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}
\]

\[ K_p = K_c (RT)^{\Delta n} \]
Dynamic Equilibrium

Example: \( \text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2 \)

colourless \hspace{1cm} \text{brown}

Equilibrium conc’ns *do not* depend on the starting composition.
Example

Finding Equilibrium Constants

\[ 2\text{SO}_3 (g) \rightleftharpoons 2\text{SO}_2 (g) + \text{O}_2 (g) \]

• Initially we have 0.060 mol SO\(_3\) in a 1.0 L container at 1000 K; at equilibrium we find 36.7\% of the SO\(_3\) has dissociated.

Find \( K_c \).
Example cont’d

Conc’ns (M):

\[ 2\text{SO}_3 (g) \rightleftharpoons 2\text{SO}_2 (g) + \text{O}_2 (g) \]
Another Example

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

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

Data: \( K_c = 2.5 \times 10^{-3} \) at 2400 K
Another Example cont’d

Conc’n (M): \[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \]
Another Example cont’d
See Silberberg!

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>PCl₃(g)</th>
<th>+</th>
<th>Cl₂(g)</th>
<th>⇌</th>
<th>PCl₅(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original equilibrium</td>
<td>0.200</td>
<td></td>
<td>0.125</td>
<td></td>
<td>0.600</td>
</tr>
<tr>
<td>Disturbance</td>
<td></td>
<td></td>
<td>0.075</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New initial</td>
<td>0.200</td>
<td></td>
<td>0.200</td>
<td></td>
<td>0.600</td>
</tr>
<tr>
<td>Change</td>
<td>−x</td>
<td></td>
<td>−x</td>
<td></td>
<td>+x</td>
</tr>
<tr>
<td>New equilibrium</td>
<td>0.200 − x</td>
<td></td>
<td>0.200 − x</td>
<td></td>
<td>0.600 + x</td>
</tr>
</tbody>
</table>

*Experimentally determined value.
Variation of $K_c$ with Form of Balanced Equation

$$2\text{SO}_2 + \text{O}_2 \iff 2\text{SO}_3$$

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = 0.15 \text{ M}^{-1}$$

- Reaction written in reverse: $2\text{SO}_3 \overset{K_{c,r}}{\iff} 2\text{SO}_2 + \text{O}_2$

$$K_{c,r} = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{1}{K_c} = \frac{1}{0.15} = 6.7 \text{ M}$$

- Reaction written as: $\text{SO}_2 + \frac{1}{2}\text{O}_2 \overset{K_{c2}}{\iff} \text{SO}_3$

$$K_{c2} = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = (K_c)^{1/2} = 0.39 \text{ M}^{1/2}$$
A particular $K$ has meaning only in relation to a particular form of the balanced equation.

If an equation is multiplied by a positive or negative integer or fraction $n$, then the new value of $K_c$ is raised to the $n$th power.

- **DEMONSTRATION:**
  - Solution of I$_2$ in I$^-$ (aq) is I$_3^-$ (aq)
  - Solution of I$_2$ in organic solvent is I$_2$ (org. phase)

  \[
  \text{I}_2 \text{ (org. phase)} + \text{I}^- \text{ (aq)} \rightleftharpoons \text{I}_3^- \text{ (aq)}
  \]

  Colour intensities of both layers the same, no matter how they were prepared.
Example: Combining Equilibrium Constants

Find the eq. constant for \( \text{SO}_2 + \text{CO}_2 \rightleftharpoons \text{SO}_3 + \text{CO} \)

\[
K_{c1} = \frac{[\text{SO}_3][\text{CO}]}{[\text{SO}_2][\text{CO}_2]}
\]

If we are given the equilibrium constants for

\[
\begin{align*}
\text{SO}_2 + \frac{1}{2}\text{O}_2 & \rightleftharpoons \text{SO}_3 & K_{c2} \\
\text{CO}_2 & \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2 & K_{c3}
\end{align*}
\]
Example: Combining Equilibrium Constants cont’d

\[
\begin{align*}
\text{SO}_2 + \text{CO}_2 & \rightleftharpoons \text{CO} + \text{SO}_3 & K_{c1} \\
\text{SO}_2 + \frac{1}{2}\text{O}_2 & \rightleftharpoons \text{SO}_3 & K_{c2} \\
\text{CO}_2 & \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2 & K_{c3}
\end{align*}
\]
Reaction Quotient

For a system not necessarily at equilibrium,

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

**Reaction Quotient:**

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

At equilibrium:

\[ Q_c = K_c \]
Reaction Quotient and Equilibrium Constant

- If $Q_c < K_c$
- If $Q_c = K_c$
- If $Q_c > K_c$
At some high temperature,

\[ 2\text{HF (g)} \rightleftharpoons \text{H}_2 (g) + \text{F}_2 (g) \quad K_c = 1 \times 10^{-13} \]

Concentrations when reactants first mixed are found to be
\[ [\text{HF}] = 0.5 \text{ M} ; [\text{H}_2] = 1 \times 10^{-3} \text{ M} ; [\text{F}_2] = 4 \times 10^{-3} \text{ M} \]

– Is this system at equilibrium?
– If not, what must occur for equilibrium to be established?
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”
Equilibria involving Difference States of Matter

e.g., Decomposition of calcium carbonate: \[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO} \text{ (s)} + \text{CO}_2 \text{ (g)} \]