Equilibrium Constants

\[ \text{aA + bB} \rightleftharpoons \text{cC + dD} \]

- At equilibrium:
  \[ K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
  \[ K_c = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b} \]
  \[ K_p = K_c (RT)^{\Delta n} \]

Dynamic Equilibrium

Equilibrium conc's 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 \(\text{SO}_3\) in a 1.0 L container at 1000 K; at equilibrium we find 36.7% of the \(\text{SO}_3\) 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

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

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

Another Example cont'd

Conc'n (M): \[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \]

See Silberberg!

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>(\text{PCL}_3(g))</th>
<th>(\text{Cl}_2(g))</th>
<th>(\approx)</th>
<th>(\text{PCL}_2(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original equilibrium</td>
<td>0.200</td>
<td>0.125</td>
<td>=0.600</td>
<td></td>
</tr>
<tr>
<td>Disturbance</td>
<td>+0.075</td>
<td>0.200</td>
<td>0.600</td>
<td></td>
</tr>
<tr>
<td>New Initial</td>
<td>0.200</td>
<td>0.200</td>
<td>0.600</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>New equilibrium</td>
<td>0.200 - x</td>
<td>0.200 - x</td>
<td>0.600 + x (0.637)*</td>
<td></td>
</tr>
</tbody>
</table>

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

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

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

- Reaction written in reverse: $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$
  $K_{c,r} = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{1}{K_c} = 0.15$ = 6.7 M

- Reaction written as: $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$
  $K_{c,2} = \frac{[\text{SO}_2]}{[\text{SO}_3][\text{O}_2]^{1/2}} = (K_c)^{1/2} = 0.39 \text{ M}^{1/2}$

Summary

A particular $K_c$ 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 $\text{I}_2$ in $\text{I}^–$ (aq) is $\text{I}_3^–$ (aq)
  - Solution of $\text{I}_2$ in organic solvent is $\text{I}_2$ (org. phase)

  $\text{I}_2$ (org. phase) + $\text{I}^–$ (aq) $\rightleftharpoons$ $\text{I}_3^–$ (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

$\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3 \quad K_{c1}$

$\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2 \quad K_{c2}$

Reaction Quotient

For a system not necessarily at equilibrium,

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

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

At equilibrium: $Q_c = K_c$

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”

Example: Combining Equilibrium Constants cont’d

$\text{SO}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{SO}_2 \quad K_{c1}$

$\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3 \quad K_{c2}$

$\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2 \quad K_{c3}$

Example

At some high temperature,

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

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?

Equilibria involving Difference States of Matter

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