**Chemical Equilibrium II**

**Equilibrium Constants**

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

- At equilibrium:
  \[ \frac{[C]_e^c [D]_e^d}{[A]_e^a [B]_e^b} = K_p \]
  \[ K_e = \left( \frac{p_C}{p_A} \right)^c \left( \frac{p_D}{p_B} \right)^d \]
  \[ K_p = K_e (RT)^\Delta_n \]

**Dynamic Equilibrium**

Example:

- \( N_2O_4 \rightleftharpoons 2 \text{NO}_2 \)
  - Colourless \( \rightarrow \) Brown

**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 \( K_e \).

**Example cont’d**

**Another Example**

**Another Example cont’d**

**See Silberberg!**

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>( \text{PCL}_3(g) )</th>
<th>( \text{Cl}_2(g) )</th>
<th>( \text{PCl}_5(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original equilibrium</td>
<td>0.200</td>
<td>0.125</td>
<td>0.600</td>
</tr>
<tr>
<td>Disturbance</td>
<td>+0.075</td>
<td>+0.075</td>
<td>+0.075</td>
</tr>
<tr>
<td>New Initial</td>
<td>0.200</td>
<td>0.200</td>
<td>0.600</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>New equilibrium</td>
<td>0.200 - x</td>
<td>0.200 - x</td>
<td>0.600 + x</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: $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$

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

- Reaction written as: $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$

$$K_{c,2} = \frac{[\text{SO}_2][\text{O}_2]^2}{[\text{SO}_3]^2} = (K_c)^{1/2} = 0.39 \text{ M}^{1/2}$$

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

  $\text{I}_2$ (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 cont’d

<table>
<thead>
<tr>
<th>REACTION</th>
<th>EQUILIBRIUM CONSTANT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{SO}_2$</td>
<td>$K_{c,1}$</td>
</tr>
<tr>
<td>$\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$</td>
<td>$K_{c,2}$</td>
</tr>
<tr>
<td>$\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$</td>
<td>$K_{c,3}$</td>
</tr>
</tbody>
</table>

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: $Q_c = K_c$

Example: Combining Equilibrium Constants

Find the eq. const. for $\text{SO}_3 + \text{CO}_2 \rightleftharpoons \text{SO}_4 + \text{CO}$

$$K_{c,1} = \frac{[\text{SO}_3][\text{CO}]}{[\text{SO}_2][\text{CO}_2]}$$

If we are given the equilibrium constants for $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$, $K_j$

$\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$, $K_r$

Reaction Quotient and Equilibrium Constant

- If $Q_c < K_c$
- If $Q_c = K_c$
- If $Q_c > K_c$

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**”

Equilibria involving Difference States of Matter

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

Example

At some high temperature,

$$2\text{HF} (g) \rightleftharpoons \text{H}_2 (g) + \text{F}_2 (g)$$

$K_c = 1 \times 10^{-13}$

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?