17.5 Solving Equilibrium Problems

- Calculation of $K_c$ (or $K_p$) values from measured equilibrium concentrations (or pressures)
- Calculation of equilibrium concentrations (or pressures) from $K_c$ (or $K_p$) values

**Equilibrium tables** ("ice" tables) – give the initial, $i$, change of, $c$, and equilibrium, $e$, concentrations of reactants and products

- For a general reaction: $A + 2B \leftrightarrow C$

  $\rightarrow [A]_i$, $[B]_i$, $[C]_i$ – initial concentrations
  $\rightarrow [A]_e$, $[B]_e$, $[C]_e$ – equilibrium concentrations

  $\rightarrow \Delta[A]$, $\Delta[B]$, $\Delta[C]$, – change in the concentrations

  $\rightarrow [A]_e = [A]_i + \Delta[A]$ \(\text{same is valid for } B \text{ and } C\)

**Using Equilibrium Quantities to Calculate $K$**

- If all equilibrium concentrations are given, substitute in the mass action expression to find $K$
- If the initial concentrations and one equilibrium concentration are given, use an *ice* table to find $K$

**Example:** 1.00 mol of NH$_3$ is sealed in a 1.00 L container and heated to 500 K. Calculate $K_c$ for 2NH$_3$(g) $\leftrightarrow$ N$_2$(g) + 3H$_2$(g), if at equilibrium the concentration of NH$_3$ is 0.58 M.

  $\rightarrow [NH_3]_i = 1.00 \text{ mol}/1.00 \text{ L} = 1.00 \text{ M}$

  $\rightarrow [N_2]_i = [H_2]_i = 0$

  $\rightarrow [NH_3]_e = 0.58 \text{ M}$

**A + 2B $\leftrightarrow$ C**

$\rightarrow \Delta[C] = +x$

$\rightarrow \Delta[A] = -\Delta[C] \times (1 \text{ mol } A/1 \text{ mol } C) = -\Delta[C] = -x$

$\rightarrow \Delta[B] = -\Delta[C] \times (2 \text{ mol } B/1 \text{ mol } C) = -2\Delta[C] = -2x$

$$
\begin{array}{c|ccc}
& A & 2B & \leftrightarrow C \\
\hline
i & [A]_i & [B]_i & [C]_i \\
\hline
c & -x & -2x & x \\
e & [A]_i - x & [B]_i - 2x & [C]_i + x \\
\end{array}
$$

$\Rightarrow K_c = \frac{[C]}{[A][B]^2} = \frac{([C]_i + x)}{([A]_i - x)([B]_i - 2x)^2}$

$\rightarrow$ The equation can be used to calculate $K_c$ if $x$ is known or to calculate $x$ if $K_c$ is known

**Example:**

$$
\begin{array}{c|ccc}
& 2NH_3(g) & \leftrightarrow & N_2(g) + 3H_2(g) \\
\hline
i & 1.00 & 0 & 0 \\
\hline
c & -2x & +x & +3x \\
e & 1.00 - 2x & x & 3x \\
\end{array}
$$

$\rightarrow [NH_3]_e = 1.00 - 2x = 0.58$

$\Rightarrow x = (1.00 - 0.58)/2 = 0.21$

$\rightarrow [N_2]_e = x = 0.21 \text{ M}$

$\rightarrow [H_2]_e = 3x = 0.63 \text{ M}$

$\Rightarrow K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{[0.21][0.63]^3}{[0.58]^2} = 0.16$
Using $K$ to Calculate Equilibrium Quantities

- If $K$ and all but one equilibrium concentrations are given, substitute in the mass action expression for $K$ to find the unknown concentration.
- If the initial concentrations and $K$ are given, use an ice table to find the equilibrium concentrations.

**Example:** 0.50 mol of HI is sealed in a 2.0 L reactor and heated to 700°C. Calculate the equilibrium concentrations of all species if at 700°C, $K_c = 0.022$ for $2\text{HI(g)} \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$.

1. $[\text{HI}]_i = 0.50 \text{ mol/2.0 L} = 0.25 \text{ M}$
2. $[\text{I}_2]_i = [\text{H}_2]_i = 0$

Using the quadratic formula

**Example:** 0.50 mol HI and 0.30 mol H$_2$ are sealed in a 2.0 L reactor and heated to 700°C. Calculate the equilibrium concentrations of all species if at 700°C, $K_c = 0.022$ for $2\text{HI(g)} \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$.

1. $[\text{HI}]_i = 0.50 \text{ mol/2.0 L} = 0.25 \text{ M}$
2. $[\text{H}_2]_i = 0.30 \text{ mol/2.0 L} = 0.15 \text{ M}$
3. $[\text{I}_2]_i = 0$

Using the quadratic formula for the quadratic equation $ax^2 + bx + c = 0$:

- For $a = 2 + 1 = 3$, $b = -2$, $c = 0$, $K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 0.022$

- $\frac{x \cdot x}{(0.25 - 2x)^2} = 0.022 \Rightarrow \sqrt{\frac{x^2}{(0.25 - 2x)^2}} = \sqrt{0.022}$

- $\frac{x}{0.25 - 2x} = \sqrt{0.022} \Rightarrow x = \frac{0.0371}{1 + 0.297} = 0.029$

- $[\text{H}_2]_e = [\text{I}_2]_e = x = 0.029 \text{ M}$
- $[\text{HI}]_e = 0.25 - 2x = 0.25 - 2 \times 0.029 = 0.19 \text{ M}$
Using simplifying assumptions

Example: A mixture of 0.060 M N₂ and 0.040 M H₂ is heated to a temperature where $K_c = 0.0010$ for $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$. Calculate the equilibrium concentration of NH₃.

→ [N₂]ᵢ = 0.060 M
→ [H₂]ᵢ = 0.040 M
→ [NH₃]ᵢ = 0

\[
K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.0010
\]

<table>
<thead>
<tr>
<th>i</th>
<th>N₂(g) + 3H₂(g) ⇌ 2NH₃(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.060</td>
</tr>
<tr>
<td>2</td>
<td>-x</td>
</tr>
<tr>
<td>3</td>
<td>-3x</td>
</tr>
<tr>
<td>4</td>
<td>0.060 - x</td>
</tr>
<tr>
<td>5</td>
<td>0.040 - 3x</td>
</tr>
</tbody>
</table>

\[
\begin{array}{c|c|c|c}
 i & N_2 & H_2 & NH_3 \\
---&---&---&---
 0 & 0.060 & 0.040 & 0 \\
 c & -x & -3x & +2x \\
 e & 0.060 - x & 0.040 - 3x & 2x \\
\end{array}
\]

Simplifying assumptions are not always justified

Example: A mixture of 0.060 M N₂ and 0.040 M H₂ is heated to a temperature where $K_c = 10$. for $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$. Calculate the equilibrium concentration of NH₃.

→ Using the assumption from the previous problem leads to:

\[
\frac{4x^2}{(0.060)(0.040)^3} = 10. \quad \Rightarrow \quad x = \sqrt[4]{\frac{10 \times 0.060 \times 0.040^3}{4}} = 0.0031
\]

→ The assumption is not justified since x and 3x are more than 5% of 0.060 and 0.040

→ We must solve the equation without assumptions

Successive approximation

→ Using the same formula as in the previous problem without neglecting x and 3x leads to:

\[
x_{n+1} = \sqrt[4]{\frac{10 \times (0.060 - x_n)(0.040 - 3x_n)^3}{4}}
\]

→ This formula allows the calculation of the (n+1)th approximation for x from the nth approximation

→ For n=0, assume $x_0=0$ (x is expected to be small)
→ For n=1 (1st iteration)

\[
x_1 = \sqrt[4]{\frac{10 \times (0.060 - 0)(0.040 - 3 \times 0)^3}{4}} = 0.0031
\]
→ For \( n=2 \) (2\(^{\text{nd}}\) iteration)
\[
x_2 = \sqrt[4]{\frac{10 \times (0.060 - 0.0031)(0.040 - 3 \times 0.0031)^3}{4}} = 0.0020
\]

→ For \( n=3 \) (3\(^{\text{rd}}\) iteration)
\[
x_3 = \sqrt[4]{\frac{10 \times (0.060 - 0.0020)(0.040 - 3 \times 0.0020)^3}{4}} = 0.0024
\]

→ For \( n=4 \) (4\(^{\text{th}}\) iteration)
\[
x_4 = \sqrt[4]{\frac{10 \times (0.060 - 0.0024)(0.040 - 3 \times 0.0024)^3}{4}} = 0.0023
\]

→ For \( n=5 \) (5\(^{\text{th}}\) iteration) → \( x_5 = 0.0023 \)

→ Since \( x_5 \approx x_4 \) (convergence) \( \Rightarrow x = 0.0023 \)

\( \Rightarrow [\text{NH}_3]_e = 2x = 2 \times (0.0023) = 0.0046 \text{ M} \)

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**Equilibrium Calculations for Reactions with Unknown Direction**

**Example:** 0.50 mol \( H_2 \), 0.50 mol \( I_2 \) and 0.50 mol \( HI \) are mixed in a 1.0 L container and heated to a temperature where \( K_c = 0.45 \) for the reaction \( H_2(g) + I_2(g) \leftrightarrow 2HI(g) \). Calculate \([HI]\) at equilibrium.

\( \Rightarrow [H_2]_i = [I_2]_i = [HI]_i = 0.50 \text{ mol/1.0 L} = 0.50 \text{ M} \)

\( \Rightarrow \) Since all reactants and products are present initially, the direction of the reaction must be determined first

\( \Rightarrow Q_c \) must be calculated and compared to \( K_c \)

\[
Q_c = \frac{[\text{HI}]^2}{[H_2][I_2]} = \frac{0.50^2}{0.50 \times 0.50} = 1 > K_c
\]

\( \Rightarrow Q_c > K_c \Rightarrow \) the reaction proceeds to the left

\[
\begin{array}{c|ccc}
\text{ } & H_2(g) & + & I_2(g) & \leftrightarrow 2\text{HI(g)} \\
\text{i} & 0.50 & 0.50 & 0.50 \\
\text{c} & +x & +x & -2x \\
\text{e} & 0.50 + x & 0.50 + x & 0.50 - 2x \\
\end{array}
\]

\[
K_c = \frac{[\text{HI}]^2}{[H_2][I_2]} = 0.45
\]

\[
\frac{(0.50 - 2x)^2}{(0.5 + x)(0.5 + x)} = 0.45 \Rightarrow \frac{(0.50 - 2x)^2}{(0.5 + x)^2} = \sqrt{0.45}
\]

\[
\frac{0.50 - 2x}{0.5 + x} = \sqrt{0.45} \Rightarrow (0.50 - 2x) = \sqrt{0.45} \times (0.5 + x)
\]

\[
0.50 - 0.67 \times 0.50 = 2x + 0.67x \Rightarrow x = \frac{0.165}{2 + 0.67} = 0.062
\]

\( \Rightarrow [\text{HI}]_e = 0.50 - 2x = 0.50 - 2 \times 0.062 = 0.38 \text{ M} \)