14.2 Solving Equilibrium Problems

The iΔe Process

Dr. Fred Omega Garces
Chemistry 201
Miramar College
Solving Equilibrium Problems

There are many types of equilibrium problems which arise in the real world and in chemistry exams. These problems can be broken down into two basic types.

1. The first type is one in which the equilibrium concentrations are given and the equilibrium constant must be solved.

   **Given:** \([\text{Conc}] \text{ at equilb}\)  
   **Solve:** \(K_{eq}\)

2. The second type is one in which both the equilibrium constant and the initial concentration are given and the concentrations at equilibrium are solved for.

   **Given:** \([\text{Conc}]_0\) and \(K_{eq}\)  
   **Solve:** \([\text{Conc}] \text{ at equilb}\)
Type 1: Equilibrium

The first type of problem is the type in which the equilibrium concentrations are given and the equilibrium constant, $K_{eq}$, must be solved.

**Given:** [Conc] at equilb  
**Solve:** $K_{eq}$

**Steps involved in the equilibrium calculations.**

1. Write the balanced equation for the reaction.

2. Write the equilibrium expression using the Mass Action Expression.

3. Plug the equilibrium concentration into the Mass Action and solve for the equilibrium constant, $K_{eq}$. 
1. Calculating $K_{eq}$: $K_c - K_p$ relationship (Type1)

Carbon dioxide is placed in a 5.00-L high-pressure reaction vessel at 1400°C. Given the following reaction, $CO_{(g)} + \frac{1}{2} O_{2\,(g)} \rightleftharpoons CO_{2\,(g)}$, calculate the equilibrium constant $K_c$ and $K_p$ after equilibrium is achieved with 4.95 mol of $CO_2$, 0.0500 mol of CO, and 0.0250 mol of $O_2$ found in the container.

$T = 1400°C$

$V = 5.0 \text{ L}$

<table>
<thead>
<tr>
<th>$CO_{(g)}$</th>
<th>$+ \frac{1}{2} O_{2,(g)}$</th>
<th>$\rightleftharpoons CO_{2,(g)}$</th>
</tr>
</thead>
</table>

Supplemental: Calculate the partial pressure of each gas at equilibrium
## 2. Calculating $K_{eq}$ iCe - method (Type1 & 2)

A mixture of 0.1000 mol of $CO_2$, 0.05000 mol of $H_2$, and 0.1000 mol of $H_2O$ is placed in a 1.000 L vessel. The following equilibrium reaction is established:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

At equilibrium $[CO_2] = 0.0954$ M. (a) Calculate the equilibrium concentrations of $H_2$, $CO$, and $H_2O$. (b) Calculate the $K_c$ for the reaction (c) Calculate $K_p$ for the reaction?

<table>
<thead>
<tr>
<th></th>
<th>$CO_2(g)$</th>
<th>$H_2(g)$</th>
<th>$CO(g)$</th>
<th>$H_2O(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>0.1000M</td>
<td>0.0500</td>
<td>-</td>
<td>0.1000</td>
</tr>
<tr>
<td>$V = 5.0$ L</td>
<td>$\Delta$</td>
<td>$-X$</td>
<td>$-X$</td>
<td>$+X$</td>
</tr>
<tr>
<td>$[e]$</td>
<td>0.0954</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

**Supplemental:** Calculate the partial pressure of each gas at equilibrium.
Type 2: Equilibrium

The second type of problems provides information on both the equilibrium constant and the initial concentration. The concentrations at equilibrium must be solved for.

Given: \([\text{Conc}]_o\) and \(K_{eq}\)  
Solve: \([\text{Conc}]\) at equilb

Steps involve in the equilibrium calculations.

1. Write the balanced equation for the reaction.
2. Write the equilibrium expression using the Mass Action Expression.
3. List the initial conditions.
4. Set up the iΔe table and solve for the equilibrium concentration in terms of a variable (\(x\)).
5. Plug the equations expressing the equilibrium concentration into the mass action expression and solve for \(x\).
6. Assign the value of \(x\) to the equilibrium concentration equation and determine the numerical value for the equilibrium concentration for each specie in the reaction.
3a. **Calculation: Product formed @ Equilibrium (Type2)**

How much SO$_3$ is formed when 0.50 mol of SO$_2$ and 0.50 mol NO$_2$ are in 1.00 L at 821 °C. $K_c = 6.85$ at this temperature.

\[
\begin{array}{c|cccc}
\text{i} & \text{SO}_2(g) & + & \text{NO}_2(g) & \rightleftharpoons \text{SO}_3(g) & + & \text{NO}_2(g) \\
\hline
\text{i} & 0.50 \text{ M} & 0.50 \text{M} & 0.00 & 0.00 \\
\Delta [e] &
\end{array}
\]

Supplemental: If this was a stoichiometry problem, what is the mole of SO$_3$ when reaction is complete?
3a. **Calculation: Product formed @ Equilibrium (Type2)**

How much $SO_3$ is formed when 0.50 mol of $SO_2$ and 0.50 mol $NO_2$ are in 1.00 L at 821 °C. $K_c = 6.85$ at this temperature.

\[
\begin{align*}
SO_2(g) + NO_2(g) & \rightleftharpoons SO_3(g) + NO(g) \\
\text{Initial} & \quad \begin{array}{c}
0.50 \text{ M} \\
0.50 \text{ M}
\end{array} & \quad \begin{array}{c}
0.00 \\
0.00
\end{array} \\
\Delta & \quad \begin{array}{c}
-X \\
-X
\end{array} & \quad \begin{array}{c}
+X \\
+X
\end{array} \\
[e] & \quad \begin{array}{c}
0.50 - X \\
0.50 - X
\end{array} & \quad \begin{array}{c}
+X \\
+X
\end{array}
\end{align*}
\]
3b. Calculation: Product formed @ Equilibrium (Type2)

How much SO$_3$ is formed when 0.50 mol of SO$_2$ and 1.00 mol NO$_2$ are in 1.00 L at 821 °C. $K_c = 6.85$ at this temperature. (Non-perfect square)

\[
\begin{align*}
\text{SO}_2(g) + \text{NO}_2(g) & \rightleftharpoons \text{SO}_3(g) + \text{NO}(g) \\
\hline
i & 0.50 \text{ M} & 1.00 \text{ M} & 0.00 & 0.00 \\
\Delta & \\
\end{align*}
\]
4. Calculating $K_{eq}$: Method of Approximation (Type2)

NOCl decomposes to form the gases NO and Cl$_2$. At 35°C the equilibrium constant is $K_c = 1.6 \cdot 10^{-5}$. If 1.0 mol of NOCl is placed in a 2.0 L flask what are the concentration of all specie at equilibrium?

$$2\text{NOCl}_\text{(g)} \rightleftharpoons 2\text{NO}_\text{(g)} + \text{Cl}_2\text{(g)} \quad K_c = 1.6 \cdot 10^{-5}$$

\begin{array}{c|ccc}
\text{i} & 0.50 \text{ M} & 0 & 0 \\
\text{V} = 2.0 \text{ L} & \Delta & -2X & +2X & +X \\
\text{[e]} & 0.5 - 2X & +2X & +X \\
\end{array}
Assumption Check

When making assumptions, if a reaction has a relatively small $k_{eq}$ and a relatively large initial reactant concentration, then the concentration change ($x$) can often be neglected without introducing significant error. This does not mean $x = 0$, because then this would mean there is no reaction. It means that if a reaction proceeds very little (small $k$) and if you start with a high reactant concentration, very little will be used up, so the following holds.

$$[\text{react}]_o - x \approx [\text{react}]_{eq} \approx [\text{react}]_o$$

When making the assumption that $x$ is negligible, you must check that the error introduced is not significant. If the assumption results in a change (error) in concentration of less than 5%, the error is not significant and the assumption is justified.

To test the assumption, use the following formula:

$$\left(\frac{\Delta \text{conc}}{\text{initial concentration}}\right) \cdot 100 < 5\%$$

In the previous problem, the assumption is check by the following calculations:

$$\left[\frac{2x}{0.5}\right] \cdot 100 = \left[ \frac{2(1 \cdot 10^{-2})}{0.5} \right] \cdot 100 = 4\% < 5\%$$

The assumption is valid in this example.
Assumption Check $\frac{[\text{React}]_{\text{initial}}}{k_{eq}}$

In general, simplifying assumptions works when the initial concentration of the reactant is high but not when it is low. To summarize, we assume that $x (\Delta [\text{React}])$ can be neglected if $K_{eq}$ is small relative to $[\text{React}]_{\text{initial}}$. The benchmark in justifying the assumption is-

Your job is to determine what is the threshold for $\frac{[\text{React}]_{\text{initial}}}{k_{eq}}$ so that the assumption is justified.

**Answer**
5. Calculating $K_{eq}$: Quadratic or iteration?

At 250 °C, the reaction $\text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g)$ has an equilibrium constant $K_c = 1.80$. If 0.100 mol PCl$_5$ is added to a 5.00-L vessel, what are the concentrations of all species at equilibrium? What % of the reactant remains?

<table>
<thead>
<tr>
<th></th>
<th>$\text{PCl}_5 (g)$</th>
<th>$\text{PCl}_3 (g)$</th>
<th>$\text{Cl}_2(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>0.02 M</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$-X$</td>
<td>$+X$</td>
<td>$+X$</td>
</tr>
<tr>
<td>$[e]$</td>
<td>0.02 - $X$</td>
<td>$+X$</td>
<td>$+X$</td>
</tr>
</tbody>
</table>
6. Calculation: Product formed @ Equilibrium (Type2)

Exactly 4 mol of $SO_3$ is sealed in a 5.0 L container @1500K. $K_c$ is $9.34 \cdot 10^3$ for the rxn, what are the conc. of all specie at equilb?
An engineer is studying the oxidation of $SO_2$ to produce the precursor, $SO_3$, in the manufacture of sulfuric acid. The $K_p = 1.7 \cdot 10^8$ at 600. K for the reaction.

\[2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\]

i) At equilibrium $p_{SO_3} = 300.$ atm and $p_{O_2} = 100.$ atm. Calculate $p_{SO_2}$

ii) The engineer places a mixture of 0.0040 mol of $SO_2(g)$ and 0.0028 mol of $O_2(g)$ in a 1.0-L container and raises the temperature to 1000K. The reaction reaches equilibrium and 0.0020 mol of $SO_3(g)$ is present. What would the engineer calculate the $K_c$ and $P_{SO_2}$ for the reaction to be 1000K. Does the engineer expects the reaction to be exothermic or endothermic?
Procedure for Solving Equilibrium Problems

1. Write the balanced equation for the reaction.
2. Write the equilibrium expression using the Mass Action Expression.
3. List the initial conditions.
4. Determine the type of equilibrium problem you have.
   Type 1 - Given the equilibrium concentration, solve for $K_{eq}$.
   Type 2 - Given $K_{eq}$ and initial concentration, solve for conc. @ equilb.

**Type 1**
Plug the equilibrium concentration into the Mass Action and solve for the equilibrium constant, $K_{eq}$.

**Type 2**

a) Set up the iΔe table and solve for the equilibrium concentration in terms of a variable ($x$).
b) Plug the equations expressing the equilibrium concentration into the mass action expression and solve for $x$
c) Assign the value of $x$ to the equilibrium concentration equation and determine the numerical value for the equilibrium concentration for each specie in the reaction.