EQUILIBRIUM

Academic Success Center
Definition

• Equilibrium is a state where the concentrations of the reactants and products no longer change with time.

• *This doesn’t mean there is no movement between the molecules in the reaction.*

• Imagine a leveling off effect: \( \text{rate } \text{fwd} = \text{rate } \text{reverse} \)

• All reactions are reversible
Why It is Important

• Equilibrium can be used to tell which direction a reaction will shift, towards the reactants or towards the products.

• The amounts of products and reactants can also be obtained through equilibrium calculations.
**K\text{eq}**

- \(K_{eq}\) is the equilibrium constant \(K\)
- It is a ratio of concentrations of products over reactants. This is the concentrations at which equilibrium is reached.

**Example:**

\[N_2 + 3H_2 \rightleftharpoons 2NH_3\]

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

Product / Reactant
\[ K_{eq} \]

\[ \text{\textit{N}}_2 + 3\text{\textit{H}}_2 \longrightarrow \text{\textit{2NH}}_3 \]

\[ K = \frac{[\text{\textit{NH}}_3]^2}{[\text{\textit{N}}_2][\text{\textit{H}}_2]^3} \]

Notice the superscript 2 outside the [ ] of \( \text{\textit{NH}}_3 \) and the superscript 3 outside the [ ] of \( \text{\textit{H}}_2 \). This is the coefficient in front of the product in the equilibrium equation above.
The magnitude of $K$ can tell us how far a reaction proceeds to the products at a given temperature. 

- **Small** $K = 2 \times 10^{-28}$ yields little product before reaching equilibrium.
- **Large** $K = 3.2 \times 10^{25}$ has little reactants since the reaction goes to completion.
- **Intermediate** $K = 6$ has amounts of both product and reactants after reaching equilibrium.

This is simply a spectrum of $K$ values. The terms large, small and intermediate are relative, because there is varying amount of products and reactants depending on the given $K$ value.
Reaction Quotient Q

• Similar to K – at equilibrium $K = Q$
• $Q$ represents varying concentrations of reactants and products.

Chemical equation: $aA + bB \leftrightarrow cC + dD$

By rearranging products / reactants with coefficients as exponents we get the rxn quotient:


Example

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$

$Q = [CH_4][H_2O]^2/[H_2]^4[CO_2]$
Comparing Q and K

- Q < K Denominator [reactants] is larger than numerator [products] Therefore reactants $\rightarrow$ products since more product is needed for $Q = K$. *Think: what do I need to do to increase Q to reach K?*

Either decrease the denominator or increase the numerator. $\rightarrow$ Favors Products
Comparing Q and K

• Q > K Large Numerator [products] / Small denominator [reactants] – Therefore, in order for Q = K favors reactants

• Shift towards reactants since Q needs to become smaller. Larger denominator = smaller Q
EXAMPLE

- Gaseous CH₄ and H₂O were mixed in a 0.64L flask at 1800K. At equilibrium, the flask contains 0.36 mol of CO, 0.081 mol of H₂ and 0.051 mol of CH₄. What is the concentration of [H₂O] at equilibrium?

K = 0.28 for

CH₄ + H₂O ⇌ CO + 3H₂
Solution

• First use the balanced equation to write the reaction quotient.

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$$

Rearranging to form products / reactants would give us the Q (rxn quotient) used to solve the problem

$$Q = [\text{CO}][\text{H}_2]^3 / [\text{CH}_4][\text{H}_2\text{O}]$$
Solution continued

- Values given in the problem: Volume of flask = 0.64 L, mol of CH$_4$ = 0.051, mol of CO = 0.36, mol of H$_2$ = 0.081, K = 0.28

- Determine the concentrations with known values.

  \[ [\text{CH}_4] = \frac{0.051 \text{ mol}}{0.64 \text{ L}} = 0.080 \text{ M} \]
  \[ [\text{CO}] = \frac{0.36 \text{ mol}}{0.64 \text{ L}} = 0.56 \text{ M} \]
  \[ [\text{H}_2] = \frac{0.081 \text{ mol}}{0.64 \text{ L}} = 0.13 \text{ M} \]
Solution continued

• Since $Q = K$ at equilibrium we rearrange our reaction quotient to solve for the concentration of $H_2O$

$$[H_2O] = [CO][H_2]^3 / [CH_4]K$$

$$[H_2O] = (0.56M)(0.13M)^3 / (0.051M)(0.28)$$

$$= 0.055 \text{ M}$$
Example 2

- In one experiment, 2.00 mol of CH$_4$, 2.00 mol of CS$_2$, 4.00 mol of H$_2$S, and 4.00 mol of H$_2$ are mixed in a 500 mL vessel at 960K, at this temperature $K = 0.046$ for the equation:

$$\text{CH}_4 + 2\text{H}_2\text{S} \rightleftharpoons \text{CS}_2 + 4\text{H}_2$$

- What direction will the reaction proceed to reach equilibrium?
Solution 2

- Use the balanced chemical equation to find the reaction quotient.

\[ \text{CH}_4 + 2\text{H}_2\text{S} \leftrightarrow \text{CS}_2 + 4\text{H}_2 \]

\[ Q = [\text{CS}_2][\text{H}_2]^4 / [\text{CH}_4][\text{H}_2\text{S}]^2 \]
Solution 2 continued

- With known values, solve for $Q$ and compare it with $K$ to see which direction moves towards equilibrium.

- Known values: 2.00 mol of $\text{CH}_4$, 2.00 mol of $\text{CS}_2$, 4.00 mol of $\text{H}_2\text{S}$, 4.00 mol of $\text{H}_2$, 500 mL volume of flask, $K = 0.046$

  
  
  
  $[\text{CH}_4] = \frac{2.00 \text{ mol}}{0.500 \text{ L}} = 4.00 \text{M}$

  
  
  $[\text{CS}_2] = \frac{2.00 \text{ mol}}{0.500 \text{ L}} = 4.00 \text{M}$

  
  
  $[\text{H}_2\text{S}] = \frac{4.00 \text{ mol}}{0.500 \text{ L}} = 8.00 \text{M}$

  
  
  $[\text{H}_2] = \frac{4.00 \text{ mol}}{0.500 \text{ L}} = 8.00 \text{M}$
Solution 2 continued

• Solve for Q by plugging in values.

\[ Q = [\text{CS}_2][\text{H}_2]^4 / [\text{CH}_4][\text{H}_2\text{S}]^2 \]

\[ Q = (4.00)(8.00)^4 / (4.00)(8.00)^2 \]

=64.0

Compare Q to K

64 > 0.046

Therefore Q is larger and the denominator [reactants] needs to be increased or numerator [products] decreased in order for equilibrium to be reached.

FAVORS REACTANTS \( \xrightarrow{\text{rxn goes to the left}} \)
Example 3

• In one experiment, 2.00 mol of CH\(_4\), 2.00 mol of CS\(_2\), 4.00 mol of H\(_2\)S, and 4.00 mol of H\(_2\) are mixed in a 500 mL vessel at 960K, at this temperature K = 0.046 for the equation:

\[ \text{CH}_4 + 2\text{H}_2\text{S} \rightleftharpoons \text{CS}_2 + 4\text{H}_2 \]

• If [CH\(_4\)] = 4.96M at equilibrium, what are the equilibrium concentrations of the other substances?
A reaction table should be set up in order to see the changes that occur when the reaction proceeds towards equilibrium.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>CH$_4^+$</th>
<th>2H$_2$S$\leftrightarrow$</th>
<th>$\rightarrow$CS$_2^+$</th>
<th>4H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Solution 3

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<thead>
<tr>
<th>Concentration (M)</th>
<th>CH$_4^+$</th>
<th>2H$_2$S$\leftrightarrow$</th>
<th>$\rightarrow$CS$_2^+$</th>
<th>4H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>4.00</td>
<td>4.00</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Equilibrium</td>
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</tbody>
</table>

- *Initial values are plugged in* (values were solved for in Example 2)
The positive change on the reactants side is because we found that in Example 2, that the chemical reaction reaches equilibrium by favoring the reactants.

Note that change (x) is effected by the coefficients in the chemical equation.
Solution 3. continued

• Solve for ‘x.’ Since the concentration of CH₄ at equilibrium is already known we can set up:

\[
[\text{CH}_4] = 4.96 \text{ M} = 4.00\text{M} + x
\]

\[
x = 0.96 \text{ M}
\]
Solution 3 continued

Now that ‘x’ is obtained, plug in the values in order to solve for the equilibrium concentration values of the rest of the components.

\[ [H_2S] = 8.00M + 2x = 8.00 M + 2(0.96M) = 9.92M \]
\[ [CS_2] = 4.00 M - x = 4.00 - 0.96 M = 3.04M \]
\[ [H_2] = 8.00 M - 4x = 8.00 - 4(0.96M) = 4.16M \]
Further Look

• What happens to the chemical reaction if products and reactants are added and removed?

\[ \text{CH}_4 + 2\text{H}_2\text{S} \rightleftharpoons \text{CS}_2 + 4\text{H}_2 \]

What happens if the concentration of CH₄ is increased?
Adding/Removing Products/Reactants

**Shortcut**: Which ever side increases in amount, the reaction will shift away from in order to reach equilibrium.

Similarly, which ever side decreases in amount the reaction will shift towards in order to reach equilibrium.

**Example**: If $H_2S$ is lowered then the reaction shift towards the reactants. If $CS_2$ is increased, the reaction will also shift towards the reactants.

\[
CH_4 + 2H_2S \rightleftharpoons CS_2 + 4 H_2
\]
Adding/Removing continued

- \( \text{H}_2\text{S} + \text{O}_2 \rightleftharpoons 2\text{S} + 2\text{H}_2\text{O} \)

a) What happens if the amount of S is raised?
b) What happens if the amount of \( \text{H}_2\text{O} \) is lowered?

The next step should be analyzing Le Chatelier’s principles.
Problems

• The formation of HI is:
\[
H_2 + I_2 \rightleftharpoons 2HI
\]

H₂ and I₂ were placed in a container and allowed to reach equilibrium at a certain temperature. At equilibrium the concentration of H₂ = 6.50 \times 10^{-5}, I₂ is 1.06 \times 10^{-3}, and HI concentration is 1.87 \times 10^{-3}. What is the K_{eq}?
Problems

• At 2000K, $K_{eq}=4.10 \times 10^{-4}$ for the equation $N_2 + O_2 \leftrightarrow 2NO$

What is the concentration of NO when a mixture of 0.20 mol $N_2$ and 0.15 mol of $O_2$ reach equilibrium in a 1.0 L container?