Chemical Equilibrium Basics

**Reading:** Chapter 16 of Petrucci, Harwood and Herring (8th edition)

**Problem Set:** Chapter 16 questions 25, 27, 31, 33, 35, 43, 71
Chemical Equilibrium

All chemical reactions are reversible; that is, if a reaction can occur in one direction:

$$\text{CO}(g) + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(g)$$

then the reverse reaction can also occur:

$$\text{CH}_3\text{OH}(g) \rightarrow \text{CO}(g) + 2\text{H}_2(g)$$

This applies to both elementary and overall reactions.

As a reaction proceeds, the rate of the forward reaction decreases and the reverse reaction increases until they are equal. This balance is called equilibrium.
Approach to Equilibrium - Example

*Elementary reactions:*

\[
\begin{align*}
(1) \quad & \text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g) \quad \text{(forward)} \\
(2) \quad & 2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \quad \text{(reverse)}
\end{align*}
\]

\[
\begin{align*}
\text{rate}(1) &= k_1[\text{N}_2\text{O}_4] \\
\text{rate}(2) &= k_2[\text{NO}_2]^2
\end{align*}
\]

At \( t=0 \) let \([\text{N}_2\text{O}_4] > 0 \) and \([\text{NO}_2] = 0\), then \( \text{rate}(1) > \text{rate}(2) \).

- As time passes, \([\text{N}_2\text{O}_4]\) decreases and \([\text{NO}_2]\) increases.
- Rate(1) decreases and rate(2) increases until they are equal.
- When \( \text{rate}(1) = \text{rate}(2) \), we have equilibrium.
Approach to Equilibrium - continued

When rate(1) = rate(2), we have equilibrium. Therefore:

\[ k_1[N_2O_4] = k_2[NO_2]^2 \]

\[ \frac{k_1}{k_2} = \frac{[NO_2]^2}{[N_2O_4]} \equiv K_c = \text{equilibrium constant} \]

At equilibrium:

- Concentrations remain constant.
- Both reactions continue to occur.
- This is a dynamic equilibrium.
Constant Conditions

In a **static** system, nothing happens. *Example*: Neon in the Earth's atmosphere is neither produced nor consumed.

At **steady-state**, the rate of production is balanced by the rate of consumption. *Example*: Oxygen in the atmosphere is produced by photosynthesis and consumed by respiration.

Dynamic **equilibrium** is a steady-state in which the consumption process is the exact opposite of the production process. *Example*: \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \).

People sometimes use equilibrium for all three of these. This is **unacceptable** in chemistry.
Examples of Equilibrium

In a closed container, H$_2$O(l) will come into equilibrium with H$_2$O(g). (But H$_2$O(g) and H$_2$O(l) are not in equilibrium in the atmosphere.)

(a) I$_2$ in H$_2$O(l) (yellow).

(b) I$_2$ equilibrium between H$_2$O(l) (top) and CCl$_4$(l) (bottom, purple). Most I$_2$ is in the CCl$_4$. 
Evidence of Dynamic Equilibrium

\[ \text{AgI(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq) \]

Make up a saturated solution with excess solid AgI.

Add a small amount of radioactive $^{131}\text{I}^-(aq)$ to the solution.

The radioactivity will gradually appear in the solid AgI.
The Equilibrium Constant

Elementary reaction: \( aA + bB + ... \rightleftharpoons gG + hH + ... \)

At equilibrium: \( k_f[A]^a[B]^b... = k_b[G]^g[H]^h... \)

so \( K_C = \frac{[G]^g[H]^h...}{[A]^a[B]^b...} = \text{equilibrium constant} \)

This applies to every step in a reaction mechanism.
For the overall reaction, \( K_C \) has the same form:

- products in the numerator, reactants in the denominator
- multiply concentrations raised to powers
- powers are the stoichiometric coefficients
Equilibrium Constant vs. Rate Laws

These are similar, but different.

- Both involve products of concentrations.
- The rate law **may or may not** include reactants, products, and other species.
- The equilibrium constant includes **all** reactants and products, but **only** reactants and products.
- In the equilibrium constant, the powers are the stoichiometric coefficients. Not so for rate laws (except elementary reactions).
Equilibrium Constant - Examples

\[ \text{CO(g)} + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \quad K_C = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2} \]

\[ \frac{1}{2}\text{CO(g)} + \text{H}_2(\text{g}) \rightleftharpoons \frac{1}{2}\text{CH}_3\text{OH}(\text{g}) \quad K_C = \frac{[\text{CH}_3\text{OH}]^{1/2}}{[\text{CO}]^{1/2} [\text{H}_2]} \]

\[ \text{CH}_3\text{OH}(\text{g}) \rightleftharpoons \text{CO(g)} + 2\text{H}_2(\text{g}) \quad K_C = \frac{[\text{CO}] [\text{H}_2]^2}{[\text{CH}_3\text{OH}]} \]

The correct expression for the equilibrium constant depends on how the reaction is written.
Approach to Equilibrium

$$\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$$

- Three different initial conditions.
- Equilibrium reached in each case.
- Different final conditions.
- All satisfy the equilibrium condition.
# Final State - Equilibrium

<table>
<thead>
<tr>
<th>TABLE 16.1</th>
<th>Three Approaches to Equilibrium in the Reaction$^a$</th>
<th>[ \frac{[CH_3OH]}{[CO] [H_2]^2} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(g) + 2 H$_2$(g) $\rightleftharpoons$ CH$_3$OH(g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment 1</td>
<td></td>
<td>=&gt; 14.5</td>
</tr>
<tr>
<td>Initial amounts, mol</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Equilibrium amounts, mol</td>
<td>0.911</td>
<td>0.822</td>
</tr>
<tr>
<td>Equilibrium concentrations, mol/L</td>
<td>0.0911</td>
<td>0.0822</td>
</tr>
<tr>
<td>Experiment 2</td>
<td></td>
<td>=&gt; 14.4</td>
</tr>
<tr>
<td>Initial amounts, mol</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Equilibrium amounts, mol</td>
<td>0.753</td>
<td>1.506</td>
</tr>
<tr>
<td>Equilibrium concentrations, mol/L</td>
<td>0.0753</td>
<td>0.151</td>
</tr>
<tr>
<td>Experiment 3</td>
<td></td>
<td>=&gt; 14.5</td>
</tr>
<tr>
<td>Initial amounts, mol</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Equilibrium amounts, mol</td>
<td>1.380</td>
<td>1.760</td>
</tr>
<tr>
<td>Equilibrium concentrations, mol/L</td>
<td>0.138</td>
<td>0.176</td>
</tr>
</tbody>
</table>

The concentrations printed in blue are used in the calculations in Table 16.2.

$^a$Reaction carried out in a 10.0-L flask at 483 K.
Beyond Concentrations

- In reality, rate laws do not always give the exact dependence of reaction rate on concentration.
- Also, equilibrium constants using concentrations, $K_C$, are not constant (sometimes not nearly so).
- The expressions we use here are approximations.
- The thermodynamic equilibrium constant, $K_{eq}$, is defined using activities instead of concentrations.
- We use concentrations as approximations to activities.
Activities

- Thermodynamic equilibrium constants use activities.
- Activities are usually defined to be dimensionless.
- Thermodynamic equilibrium constants are dimensionless.
- Activities of pure solids and pure liquids are unity (1.0...).
- For dilute solutions:
  - solute activities approximately equal concentrations, the solvent activity is approximately unity.
- For ideal gases, activities equal partial pressures.
- We will treat solutions as dilute and gases as ideal.
Equilibrium Constant - More Examples

\[2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})\]

\[K_{eq} = \frac{a_{\text{H}_2\text{O}}^2}{a_{\text{H}_2}a_{\text{O}_2}} \approx \frac{1}{P_{\text{H}_2}P_{\text{O}_2}}\]

\[\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})\]

\[K_{eq} = \frac{a_{\text{CaO}}a_{\text{CO}_2}}{a_{\text{CaCO}_3}} \approx P_{\text{CO}_2}\]

\[2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})\]

\[K_{eq} \approx [\text{H}_3\text{O}^+][\text{OH}^-]\]

\[\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})\]

\[K_{eq} \approx \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]}\]
Equilibrium Constants Involving Gases

\[ \text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \]

For this reaction at 483 K, we found that:

\[ K_C = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = 14.5 \]

The thermodynamic equilibrium constant is:

\[ K_{eq} \approx \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}}P_{\text{H}_2}^2} = K_P \]

These are not the same.
Converting between $K_C$ and $K_P$

From the ideal gas law: $PV = nRT$

So, for CO: $P_{CO} = \left(\frac{n_{CO}}{V}\right)RT = [CO]RT$

So: $K_P = \frac{P_{CH_3OH}}{P_{CO}P_{H_2}^2} = \frac{[CH_3OH]RT}{[CO]RT[H_2]^2(RT)^2}$

and $K_P = \frac{[CH_3OH]}{[CO][H_2]^2(RT)^2} = \frac{K_C}{(RT)^2}$

$K_C = 14.5$ at $T = 483$ K. $R = 0.08206$ L atm mol$^{-1}$ K$^{-1}$

So $RT = 39.6$ L atm mol$^{-1}$ and $K_P = 9.23 \times 10^{-3}$
Magnitudes of Equilibrium Constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant, $K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$</td>
<td>$1.4 \times 10^{83}$ at 298 K</td>
</tr>
<tr>
<td>$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$</td>
<td>$1.9 \times 10^{-23}$ at 298 K</td>
</tr>
<tr>
<td>$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$</td>
<td>$1.0$ at about 1200 K</td>
</tr>
<tr>
<td>$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$</td>
<td>$3.4$ at 1000 K</td>
</tr>
<tr>
<td></td>
<td>$1.6 \times 10^{-21}$ at 298 K</td>
</tr>
<tr>
<td></td>
<td>$10.0$ at about 1100 K</td>
</tr>
</tbody>
</table>

- Equilibrium constants have a very wide range of values.
- Equilibrium constants can change enormously with changes in temperature.
Significance of Magnitude of $K$

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$$

$$K_P = \frac{1}{P_{H_2}^2 P_{O_2}} = 1.4 \times 10^{83} \text{ at } 298 \text{ K}$$

If $p_{O_2} = 0.21 \text{ bar}$, what is the equilibrium $p_{H_2}$?

$$P_{H_2}^2 = \frac{1}{K_P P_{O_2}} \Rightarrow P_{H_2} = \frac{1}{\sqrt{K_P P_{O_2}}} = \frac{1}{\sqrt{(1.4 \times 10^{83})(0.21)}}$$

$$\Rightarrow P_{H_2} = 5.8 \times 10^{-42} \text{ bar} \Rightarrow < 1 \text{ molecule in the entire atmosphere}$$
Significance of $K$ - continued

- **All** reactions are **reversible**. So there are always some reactants left at equilibrium.

- A small $K$ means that a reaction can **not** proceed in the direction written (to the right). It is **unfavorable**.

- A reasonably large $K$ means that the reaction **may** proceed. It is **favorable**. But it might be very slow.

- If $K$ is so large that the equilibrium concentration of a reactant is negligible, we say that the reaction "**goes to completion**".

- If $K$ is **very** small, the reverse reaction goes to completion.
Significance of $K$ - example

- $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad K_P = 4.7 \times 10^{-31}$ at 298 K

  The reaction can not proceed in the direction written. At 298 K, no significant NO can form from air.

- $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad K_P = 1.3 \times 10^{-4}$ at 1800 K

  At 1800 K, significant NO may form. It turns out that the rate is fast at high temperatures.

- $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \quad K_P = 2.1 \times 10^{30}$ at 298 K

  At 298 K, the NO may convert completely back to N$_2$ and O$_2$. But the rate is very slow.
The Equilibrium Constant - Summary

• All reactions are reversible. When the rates of the forward and reverse reactions are equal, we have equilibrium.

• Equilibrium is a dynamic state, both forward and reverse reactions continue to occur.

• The equilibrium constant, $K$, gives the condition that must obtain at equilibrium.

• $K$ can be used to determine the direction in which a reaction is allowed to proceed. But the reaction might be very slow.

• $K$ is expressed in terms of activities. Using concentrations or partial pressures is an approximation.
Predicting the Direction of Change

\[ \text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \]

- If we start with only \text{CO} and \text{H}_2, the reaction will initially proceed to the \textit{right}.
- If we start with only \text{CH}_3\text{OH}, the reaction will initially proceed to the \textit{left}.
- What if we start with a mixture of reactants and products? In what direction will the reaction proceed?

The answer depends on where the reaction stops - so it depends on the \textit{equilibrium constant}. But how?
The Reaction Quotient

- The reaction quotient, \( Q \), is defined to be the same as the equilibrium constant, but using initial conditions instead of equilibrium conditions.

\( Q \) is used to decide the direction of change from a specific set of initial conditions.

- If \( Q < K \), the reaction will proceed to the right.
- If \( Q > K \), the reaction will proceed to the left.
- If \( Q = K \), the reaction is at equilibrium.

- \( Q_C \) is defined using concentrations; \( Q_P \) is defined using partial pressures. Must be consistent with \( K_C \) or \( K_P \).
Using the Reaction Quotient

\[
CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad K_C = 14.5 \text{ at } 483 \text{ K}
\]

Initial conditions: \([CO] = 1.0 \text{ M}, [H_2] = 0.30 \text{ M}, [CH_3OH] = 2.5 \text{ M}\)

In which direction will the reaction proceed?

\[
Q_C = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{2.5}{(1.0)(0.30)^2} = 28
\]

\(Q_C > K_C \quad \Rightarrow \text{The reaction proceeds to the left.}\)
Using the Reaction Quotient - continued

What happens as the reaction proceeds?

\[ CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \]

We have \( Q_C > K_C \), so the reaction proceeds to the left.

In other words, the rate of the reverse reaction is greater than the rate of the forward reaction.

**Thus:** [CH\(_3\)OH] decreases, [CO] increases, [H\(_2\)] increases

\[ Q_C = \frac{[CH_3OH]}{[CO][H_2]^2} \quad \Rightarrow \quad Q_C \text{ decreases until } Q_C = K_C \]

When \( Q_C = K_C \), equilibrium is reached. The forward and reverse rates are equal.
More on Using the Reaction Quotient

What if conditions change?

\[ \text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \]

At equilibrium, \( Q_C = K_C \). What if we then add more CO?

\[ Q_C = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} \]

- Adding CO makes \( Q_C \) smaller.
- Then \( Q_C < K_C \).
- The reaction proceeds to the right.

As the reaction proceeds \([\text{CH}_3\text{OH}] \uparrow, [\text{CO}] \downarrow, [\text{H}_2] \downarrow, Q_C \uparrow\).

Eventually \( Q_C = K_C \) and we have a new equilibrium.

All concentrations are different from our first equilibrium.
Le Châtelier’s Principle

When an equilibrium system is subjected to a change, it responds by attaining a new equilibrium that partially offsets the impact of the change.

<table>
<thead>
<tr>
<th>Input (Change)</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>increase inside pressure</td>
<td>increase volume</td>
</tr>
<tr>
<td>increase outside pressure</td>
<td>reduce volume</td>
</tr>
<tr>
<td>increase in temperature</td>
<td>absorb heat</td>
</tr>
<tr>
<td>increase in concentration</td>
<td>shift away from that species (as directed by $Q$)</td>
</tr>
</tbody>
</table>
Le Châtelier’s Principle - Example

Closed container with liquid water and water vapor in equilibrium:

\[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \]

- *Increase external pressure*: Volume decreases, some \( \text{H}_2\text{O}(g) \) changes to \( \text{H}_2\text{O}(l) \) (shift to left).

- *Add He(g) to increase internal pressure*: Volume increases, some \( \text{H}_2\text{O}(l) \) changes to \( \text{H}_2\text{O}(g) \) (shift to right).

- *Increase temperature*: Some \( \text{H}_2\text{O}(l) \) changes to \( \text{H}_2\text{O}(g) \) (shift to right absorbs heat).
Adding/Removing Reactants or Products

The equilibrium will shift to partially offset the change.

\[ \text{CO(g) + 2H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)} \]

- **Change**: adding \( \text{CH}_3\text{OH} \)
  
  **Response**: equilibrium shifts to left

- **Change**: adding CO
  
  **Response**: equilibrium shifts to right

- **Change**: removing \( \text{CH}_3\text{OH} \)
  
  **Response**: equilibrium shifts to right
Effect of Changing the Volume

The equilibrium will shift to partially offset the change.

\[
\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)
\]

- A shift to the right reduces the pressure (replaces 3 moles of gas with 1 mole of gas).
- A shift to the left increases the pressure.

- **Change:** decreased volume (increased pressure)
  
  **Response:** equilibrium shifts to right

- **Change:** increased volume (decreased pressure)
  
  **Response:** equilibrium shifts to left
Effect of Inert Gas

CO(g) + 2H₂(g) ⇌ CH₃OH(g)

(1) Add He(g) while keeping the **volume fixed**.

- No effect on the reactants or products.
- No effect on the equilibrium.

(2) Add He(g) while keeping the **total pressure fixed**.

- Volume increases.
- Partial pressures of reactants and products decrease.
- Equilibrium shifts to left.
Exothermic and Endothermic Reactions

- Breaking chemical bonds requires **energy**. Forming bonds releases energy.

- Chemical reactions may **absorb or release** energy. This energy is often transferred as **heat**.

- **Exothermic** reactions **release** energy as heat:
  \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]
  \[ \text{H}_2\text{SO}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_3\text{O}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \]

- **Endothermic** reactions **absorb** energy as heat:
  \[ \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}) \]
  \[ \text{NaOH}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \]
Effect of Change in Temperature

The equilibrium will shift to partially offset the change.

- For **endothermic** reactions, the equilibrium constant **increases** when the temperature goes up.
- For **exothermic** reactions, the equilibrium constant **decreases** when the temperature goes up.

**Examples:**

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( K_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>( 1.0 \times 10^{-23} )</td>
</tr>
<tr>
<td>1200</td>
<td>1.0</td>
</tr>
</tbody>
</table>

- \( \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \)
  - This reaction is endothermic.

- \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \)
  - The equilibrium constant will be smaller at higher \( T \).
Effect of a Catalyst

A **catalyst** is a substance that increases the rate of a chemical reaction without being consumed by the reaction.

A catalyst:

- Does not change the position of equilibrium.
- Can decrease the time it takes to reach equilibrium.
- Will not make an unfavorable reaction occur.
- Can help a favorable reaction to proceed faster.
The Direction of Change - Summary

- Equilibrium is not achieved for just one set of concentrations. It is achieved for any concentrations that satisfy the *equilibrium constant*.

- The *reaction quotient*, $Q$, gives the direction of change from a specific set of initial conditions.

- **Le Châtelier’s Principle**: An equilibrium system responds to a change in conditions by partially offsetting the change.

- The effect of changes in amount, pressure, or volume can also be determined by using $Q$.

- The effect of temperature on $K$ depends on whether the reaction is *endothermic* or *exothermic*. 
Equilibrium Calculations

Many types of reactions rapidly reach equilibrium:
- acid/base reactions
- salts entering solution
- formation of complex ions

We need to learn how to calculate:
- equilibrium constants from composition data
- composition from equilibrium constants

Some of these calculations require the use of stoichiometry and mass balance.
Determining $K_C$ from Equilibrium Data

*Example*: $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

At equilibrium at 25°C, a 3.00 L vessel contains 7.64 g of $\text{N}_2\text{O}_4$ and 1.56 g of $\text{NO}_2$. Find $K_C$.

*Solution*:

Calculate the concentrations of reactants and products:

$$[\text{N}_2\text{O}_4] = 0.0277 \text{ M} \quad [\text{NO}_2] = 0.0113 \text{ M}$$

Evaluate the equilibrium constant:

$$K_C = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4] = 4.61 \times 10^{-3}$$
$K_P$ from Initial and Final Amounts of a Substance

*Example*: \[2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)\]

Initially, 0.0200 mol of SO$_3$ are put into an evacuated 1.52 L vessel. At equilibrium at 900 K, there are 0.0142 mol SO$_3$. Find $K_P$.

*Solution*:

(1) Calculate equilibrium moles of all reactants and products.

(2) Calculate partial pressures of all species.

(3) Evaluate the equilibrium constant: \[K_P = \frac{P^2_{\text{SO}_2}P_{\text{O}_2}}{P^2_{\text{SO}_3}}\]
**$K_P$ from Initial and Final Amounts - continued**

(1) The **ICE Table**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>$0.0200 \text{ mol}$ $0.0000 \text{ mol}$ $0.0000 \text{ mol}$</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>$-0.0058 \text{ mol}$ $0.0058 \text{ mol}$ $0.0029 \text{ mol}$</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>$0.0142 \text{ mol}$ $0.0058 \text{ mol}$ $0.0029 \text{ mol}$</td>
</tr>
</tbody>
</table>

(2) Partial pressures: $0.690 \text{ atm}$ $0.282 \text{ atm}$ $0.141 \text{ atm}$

This used the ideal gas law: $P = nRT/V = (48.6 \text{ atm mol}^{-1}) \times n$

(3) Evaluate $K_P = P_{\text{SO}_2}^2P_{\text{O}_2}/P_{\text{SO}_3}^2$

$$K_P = 0.0235 = \mathbf{0.024} \text{ (2 significant figures)}$$
Variations in the ICE Table

- The ICE table is based on moles.
- Other quantities (concentrations, partial pressures) may be used if they are strictly proportional to moles.

Examples:

Concentration = \( \frac{n}{V} \) may be used if \( V \) is fixed.

Partial pressure may be used if \( T \) and \( V \) are fixed:

\[ P = \frac{nRT}{V} \]
Equilibrium Partial Pressures from $K_p$

**Example:** \( \text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S(g)} \)

At 25 °C, \( K_P = 0.108 \)

Excess solid \( \text{NH}_4\text{HS} \) is placed in an evacuated flask. **Find the partial pressures of \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) at equilibrium.**

**Solution:** \( K_P = P_{\text{NH}_3} P_{\text{H}_2\text{S}} \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S(g)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
</tr>
<tr>
<td>Change</td>
<td>-</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-</td>
</tr>
</tbody>
</table>

\( x^2 = K_P = 0.108 \) \( \Rightarrow P_{\text{NH}_3} = 0.329 \text{ atm} \) and \( P_{\text{H}_2\text{S}} = 0.329 \text{ atm} \)
Equilibrium from Initial Conditions and \( K_C \)

**Example:** \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \)

At 25 °C, \( K_C = 4.61 \times 10^{-3} \)

0.0240 mole of \( \text{N}_2\text{O}_4 \) is placed in a 0.372 L flask.

**Find the moles of \( \text{N}_2\text{O}_4 \) at equilibrium.**

**Solution:** \( K_C = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4] \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0.0240 mol</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-x mol</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>(0.0240-x) mol</td>
</tr>
</tbody>
</table>

\[
K_C = \left( \frac{2x}{V} \right)^2 / \left( \frac{(0.0240-x)}{V} \right)
\]
Solving for the Unknown Concentration

From the previous slide: $VK_C (0.0240-x) = 4x^2$

**Method 1:** If only a little $N_2O_4$ dissociates, then

$x \ll 0.0240 \Rightarrow 0.0240-x \approx 0.0240 \Rightarrow 4x^2 \approx 0.0240VK_C$

So $x \approx 0.00321$ and $n_{N2O4} = 0.0240-x = 0.0208$ mol

Check: $x/0.0240 = 0.13$, so assumption may be OK.

**Method 2:** Use the result from Method 1 to improve the approximation: $0.0240-x \approx 0.0240-0.0032 = 0.0208$

So $4x^2 \approx 0.0208VK_C \Rightarrow x \approx 0.00299$ and $n_{N2O4} = 0.0210$ mol

Can repeat until a constant value is reached.
Method 3: Use quadratic equation.

If \( 0 = ax^2 + bx + c \) then 
\[
x = \frac{1}{2a} \left( -b \pm \sqrt{b^2 - 4ac} \right)
\]

\[
0 = 4x^2 + VK_Cx - 0.0240VK_C
\]

\[
a = 4 \quad b = VK_C \quad c = -0.0240VK_C
\]

\[
\Rightarrow x = 0.00300 \quad \text{and} \quad n_{N_2O_4} = 0.0210 \ \text{mol}
\]

Check result: \( K_C = [NO_2]^2 / [N_2O_4] \)

\[
[N_2O_4] = n_{N_2O_4}/V = 0.0564 \ \text{M}, \quad [NO_2] = 2x/V = 0.016 \ \text{M}
\]

\( K_C = 4.61 \times 10^{-3} \) which is what it should be
Initial Concentrations Given for Multiple Species

*Example:* \( V^{3+}(aq) + Cr^{2+}(aq) \rightleftharpoons V^{2+}(aq) + Cr^{3+}(aq) \)

\([V^{3+}] = [Cr^{2+}] = 0.0100 \text{ M} \quad [V^{2+}] = [Cr^{3+}] = 0.150 \text{ M}\)

\(K_C = 720\) 

Find the equilibrium concentrations.

*Solution:*

Decide in which direction the reaction will proceed:

\[ Q_C = \frac{[V^{2+}][Cr^{3+}]}{[V^{3+}][Cr^{2+}]} = \frac{(0.150)(0.150)}{(0.0100)(0.0100)} = 225 \]

Since \( Q_C < K_C \), the reaction will proceed to the right.
Initial Concen. for Multiple Species - continued

Reaction: \( V^{3+}(aq) + Cr^{2+}(aq) \rightleftharpoons V^{2+}(aq) + Cr^{3+}(aq) \)

Initial: 
- \( V^{3+} \): 0.0100 M
- \( Cr^{2+} \): 0.0100 M
- \( V^{2+} \): 0.150 M
- \( Cr^{3+} \): 0.150 M

Change: 
- \( -x \) M
- \( -x \) M
- \( +x \) M
- \( +x \) M

Equil.: 
- \( V^{3+} \): \( 0.0100 - x \) M
- \( Cr^{2+} \): \( 0.0100 - x \) M
- \( V^{2+} \): \( 0.150 + x \) M
- \( Cr^{3+} \): \( 0.150 + x \) M

\[ K_c = \frac{[V^{2+}][Cr^{3+}]}{[V^{3+}][Cr^{2+}]} = \frac{(0.150+x)(0.150+x)}{(0.0100-x)(0.0100-x)} = 720 \]

\[ \Rightarrow \frac{(0.150+x)}{(0.0100-x)} = \sqrt{720} \]

\[ \Rightarrow x(1+\sqrt{720}) = (0.0100)\sqrt{720} - 0.150 \Rightarrow x = 4.25 \times 10^{-3} \]

\[ \Rightarrow [V^{3+}] = [Cr^{2+}] = 0.0057 \text{ M} \quad [V^{2+}] = [Cr^{3+}] = 0.154 \text{ M} \]
Equilibrium Calculations - Summary

To calculate equilibrium constants from composition data:

- Calculate equilibrium amounts all species.
- Evaluate the equilibrium constant.

To calculate equilibrium composition from equilibrium constants and initial composition:

- Construct the ICE table to get the all the equilibrium amounts in terms of a single unknown, $x$.
- Substitute into the expression for $K$, then solve for $x$.
- Evaluate all the equilibrium amounts.

Amounts can be moles, concentrations, or partial pressures.