Chapter 15: Chemical Equilibrium: How Much Product Does a Reaction Really Make?


Example: Ice melting is a dynamic process: \( H_2O(s) \rightleftharpoons H_2O(l) \)

1. Under normal atmospheric conditions this occurs at what temperatures? _______

2. If a glass at room temperature is filled with ice cubes then water is added, can the reverse process occur? Explain.

3. Enough ice cubes are added to half fill each of three plastic jars then enough water is added to cover the ice cubes. Each jar is capped to be airtight. The first jar is placed in a refrigerator set at 38°F, the second in a freezer set at 0°F, and the third in a refrigerator set at 32°F.

Explain what you expect to find in each jar after 24 hours.

<table>
<thead>
<tr>
<th>1. The jar kept at 38°F</th>
<th>2. The jar kept at 0°F</th>
<th>3. The jar kept at 32°F</th>
</tr>
</thead>
</table>

Reactants are not always converted to products in a chemical reaction.

- When carrying out stoichiometry problems (e.g. “Calculate the mass of hydrogen gas produced when …”), we have assumed that reactions always proceed to completion.

In reality this is not always the case.

- Depending on the reaction and the conditions,
  1. In some reactions, all the reactants are converted to products.
     → The reaction proceeds essentially to completion.
     → The final composition consists mainly of products.
  2. In some reactions, very little of the reactants are converted to products.
     → The reaction occurs only to a slight extent.
     → The final composition consists mainly of reactants.
  3. In some reactions, some of the reactants are converted to products.
     → The reaction stops short of completion.
     → The final composition consists of appreciable amounts of reactants and products.
Case #1: a. Complete the following:  \[ \text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \]  

b. When 10.00 mL of 1.00M hydrochloric acid are added to a flask containing 10.50 mL of 1.00M sodium hydroxide,

The limiting reactant=______________, and the reactant in excess=______________.

c. Using phenolphthalein, how can you show that this reaction proceeds to completion—i.e., only products and the reactant in excess are present after the reagents mix?

Case #2: About 95% of dry eggshells consist of calcium carbonate, which decomposes as follows,

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

Given how quickly eggshells decompose at room temperature or even refrigerated temperatures, to what extent does this reaction occur at these temperatures?

Case #3: Consider the following reaction between the hexaaquacobalt(II) ion and chloride ion to form the tetrachlorocobalt(II) ion:

\[ [\text{Co(H}_2\text{O)}_6]^{2+}(aq) + 4 \text{Cl}^-(aq) \rightarrow \text{CoCl}_4^{2-}(aq) + 6 \text{H}_2\text{O}(l) \]

At room temperature the equilibrium mixture is purple. To what extent does the reaction occur? Explain.

In both the ice-water mixture and the examples above, some or all of the reactants react to form products, and when enough products form, the reverse reaction occurs. These are examples of reversible reactions—i.e., both the forward and reverse reactions take place.

Because the ice-water mixture and the reactions in Cases #2 and #3 above do not always go to completion, they are more correctly represented using a double-arrow (\( \rightleftharpoons \)):

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

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

\[ [\text{Co(H}_2\text{O)}_6]^{2+}(aq) + 4 \text{Cl}^-(aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) + 6 \text{H}_2\text{O}(l) \]
15.1 THE DYNAMICS OF CHEMICAL EQUILIBRIUM

vaporization: liquid $\rightarrow$ gas
- From a molecular viewpoint, a molecule “escapes” from the liquid state to the gaseous state

As the liquid evaporates, more molecules go into the gas phase.
$\rightarrow$ vapor: The gas above a liquid when the liquid and gaseous states are both present

vaporization: liquid + heat $\rightarrow$ vapor  condensation: vapor $\rightarrow$ liquid + heat

Liquid-Gas Equilibrium: liquid + heat $\xrightarrow{\text{vaporization}}$ vapor $\xleftarrow{\text{condensation}}$ liquid

When the molecules in the liquid have enough energy, they escape to the gas phase.
- In a closed system, when enough vapor exists above the liquid, some gaseous molecules condense back to the liquid.
- Ultimately, the rate of vaporization = the rate of condensation.
  $\rightarrow$ The system has reached a state of dynamic equilibrium in which the forward process occurs at the same rate as the reverse process.

In an open system, molecules in the liquid have enough energy to escape to the gas phase and continue to escape in a process called evaporation.

What is chemical equilibrium? TED ED talk - George Zaidan and Charles Morton
https://www.youtube.com/watch?v=dUMmoPdwBy4

Any chemical reaction in a closed vessel will eventually achieve chemical equilibrium—a state in which the concentrations of all reactants and products remain constant with time.
$\rightarrow$ At equilibrium, the rates of the forward and reverse reactions are equal.
Example: Sulfuryl chloride decomposes as follows: \( \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \)

The figures above show closed systems of \( \text{SO}_2\text{Cl}_2 \), \( \text{SO}_2 \), and \( \text{Cl}_2 \) at 375K.
- Initially, only \( \text{SO}_2\text{Cl}_2 \) molecules are present.
- When heated, the \( \text{SO}_2\text{Cl}_2 \) decomposes, and all three molecules are present.
- Given enough time, the system achieves equilibrium.

Ex. 1: Using the figures above, indicate the number of \( \text{SO}_2 \), \( \text{Cl}_2 \), and \( \text{SO}_2\text{Cl}_2 \) molecules at equilibrium at 375K.

\[
\begin{array}{ccc}
\_\_\_\_ & \_\_\_\_ & \_\_\_\_ \\
\text{SO}_2\text{Cl}_2 \text{ molecules} & \text{SO}_2 \text{ molecules} & \text{Cl}_2 \text{ molecules}
\end{array}
\]

Ex. 2: Indicate the number of \( \text{SO}_2 \), \( \text{Cl}_2 \), and \( \text{SO}_2\text{Cl}_2 \) molecules present 15 minutes after the equilibrium is initially achieved at the same temperature.

\[
\begin{array}{ccc}
\_\_\_\_ & \_\_\_\_ & \_\_\_\_ \\
\text{SO}_2\text{Cl}_2 \text{ molecules} & \text{SO}_2 \text{ molecules} & \text{Cl}_2 \text{ molecules}
\end{array}
\]

Ex. 3: If 9 \( \text{SO}_2 \) molecules and 9 \( \text{Cl}_2 \) molecules are placed in an empty container like those above, the container is closed, and the system once again achieves equilibrium at 375K, indicate the number of \( \text{SO}_2 \), \( \text{Cl}_2 \), and \( \text{SO}_2\text{Cl}_2 \) molecules present at equilibrium.

\[
\begin{array}{ccc}
\_\_\_\_ & \_\_\_\_ & \_\_\_\_ \\
\text{SO}_2\text{Cl}_2 \text{ molecules} & \text{SO}_2 \text{ molecules} & \text{Cl}_2 \text{ molecules}
\end{array}
\]

Ex. 4: In another experiment 9 \( \text{SO}_2\text{Cl}_2 \) are placed in an empty container like those described above and the container is closed. The system once again achieves equilibrium at 375K. Indicate the number of \( \text{SO}_2 \), \( \text{Cl}_2 \), and \( \text{SO}_2\text{Cl}_2 \) molecules present at equilibrium.

\[
\begin{array}{ccc}
\_\_\_\_ & \_\_\_\_ & \_\_\_\_ \\
\text{SO}_2\text{Cl}_2 \text{ molecules} & \text{SO}_2 \text{ molecules} & \text{Cl}_2 \text{ molecules}
\end{array}
\]

Thus, when a system achieves equilibrium, the equilibrium mixture (ratio of reactants to products) will be the same regardless of whether the system achieves equilibrium starting with only reactants, only products, or a combination of reactants and products.
Sulfuryl chloride decomposes as follows: \[ \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \]

Ex. 5: Consider the plot of concentrations of reactants and products over time for a closed chamber containing only \( \text{SO}_2\text{Cl}_2 \). Indicate on the plot below the approximate time when equilibrium is achieved.

15.2 WRITING EQUILIBRIUM CONSTANT EXPRESSIONS

Science is essentially *empirical*—i.e., it is based on experiment.

In 1864, Norwegian chemists Guldberg and Waage proposed the law of mass action to describe the equilibrium conditions for a system.

Consider the general reaction,

\[ j \text{A} + k \text{B} \rightleftharpoons l \text{C} + m \text{D} \]

where \( \text{A} \) and \( \text{B} \) are the reactants, \( \text{C} \) and \( \text{D} \) are the products, and \( j, k, l, \) and \( m \) are their respective coefficients in the balanced equation.

The law of mass action can be applied to this reaction to write the equilibrium expression (or equilibrium constant expression):

\[ K_c = \frac{[\text{C}]^l [\text{D}]^m}{[\text{A}]^j [\text{B}]^k} \]

where square brackets indicate the concentrations of reactants and products at equilibrium, and \( K_c \) is the equilibrium constant.

Example: Write the equilibrium expression for each of the following reactions:

a. \[ \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \quad K_c = \]

b. \[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \quad K_c = \]
Characteristics of the Equilibrium Expression

#1. The equilibrium constant, $K_c$, for a reaction will always be the same at a given temperature.

→ Within experimental error, at equilibrium the ratio of concentrations of products and reactants remain the same regardless of the initial concentrations.
→ The only factor that affects the equilibrium constant is temperature.

#2. The magnitude of the equilibrium constant indicates the extent of a reaction (the tendency for the reactants to be converted to products).

1. For large $K_c$ values ($K_c > 10^3$), the equilibrium mixture consists mostly of products.
   → The equilibrium lies to the right = products are favored.
      – These reactions essentially go to completion, with very few of the reactants in the equilibrium mixture.

2. For very small $K_c$ values ($K_c < 10^{-3}$), the equilibrium mixture consists mostly of reactants.
   → The equilibrium lies to the left = reactants are favored.
      – These reactions do not occur to any significant extent.

3. For intermediate $K_c$ values ($10^{-3} < K_c < 10^3$), the equilibrium mixture contains appreciable amounts of both reactants and products.
   → The reaction occurs but stops short of completion.
      → If $K_c > 1$, the equilibrium lies to the right.
      → If $K_c < 1$, the equilibrium lies to the left.

Consider again the reaction at $375 \text{K}$: \( \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \)

Ex. 1 For this reaction, the equilibrium lies to the _________, left right
favoring ____________.
reactants products neither

Consider again the following reaction: \( \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \)

Ex. 2 For this reaction, the equilibrium lies to the _________, left right
favoring ____________.
reactants products neither
15.4 Manipulating Equilibrium Constant Expressions

Ex. 1: Write the equilibrium expression for each of the following reactions:

a. \[ 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]

b. \[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \]

Ex. 2: How do these two compare with one another?

#3. The equilibrium expression for a reaction written in reverse is the reciprocal of that for the original reaction.
   - Equilibrium constants for forward and reverse reactions are reciprocals of one another.

Equilibrium Expressions Involving Partial Pressures

For reactions involving gases, concentrations are generally reported as partial pressures, so the equilibrium expression can be written in terms of the equilibrium partial pressures of gases.

Thus, for the general reaction, \[ j \text{A}(g) + k \text{B}(g) \rightleftharpoons l \text{C}(g) + m \text{D}(g) \]
the law of mass action can be applied to this reaction to write the equilibrium expression:

\[ K_p = \frac{(P_C)^l (P_D)^m}{(P_A)^j (P_B)^k} \]

where \( P_C, P_D, P_A, P_B \), are the partial pressures of gases C, D, A, and B, respectively, and \( K_p \) is the equilibrium constant in terms of partial pressures.

Example: Write the equilibrium expression in terms of partial pressures for each of the following reactions:

a. \[ 2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(g) \quad K_p = \]

b. \[ \text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{H}_2\text{O}(g) + 3 \text{CO}_2(g) \quad K_p = \]
15.3 RELATIONSHIPS BETWEEN $K_c$ AND $K_p$ VALUES

Using the ideal gas law, $PV=nRT$, and molar concentration (in $\frac{\text{mol}}{L}$), $M=\frac{n}{V}$, we can substitute for $P$ in terms of $M$, $R$, and $T$: $P=\frac{nRT}{V} = \frac{n}{V} RT = MRT$.

Thus, we can determine the relationship between $K_p$ and $K_c$ for the general reaction,

$$j \text{A}(g) + k \text{B}(g) \rightleftharpoons l \text{C}(g) + m \text{D}(g)$$

$$K_p = \frac{(P_C)^l (P_D)^m}{(P_A)^j (P_B)^k}$$

Relating $K_p$ to $K_c$: $K_p = K_c(RT)^\Delta n$ where $\Delta n = (l + m) - (j + k)$ for the general reaction

$$j \text{A} + k \text{B} \rightleftharpoons l \text{C} + m \text{D}$$

or the difference in the sums of the products’ and reactants’ coefficients.

Example: Determine $\Delta n$ for each of the following reactions:

a. $\text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g)$

b. $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$

c. $2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(g)$

d. $\text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{H}_2\text{O}(g) + 3 \text{CO}_2(g)$
Equilibrium Position: The set of concentrations of reactants and products at equilibrium.

- While there is only one equilibrium constant ($K_c$ or $K_p$) for a given reaction at a specific temperature, an infinite number of equilibrium positions is possible and depends only on the initial concentrations of reactants and products.

Example: Consider the following reaction, $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ and sets of initial and equilibrium concentrations for the reaction at 500°C:

<table>
<thead>
<tr>
<th>Trial</th>
<th>Initial Concentrations</th>
<th>Equilibrium Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$[N_2]=1.000M$, $[H_2]=1.000M$, $[NH_3]=0$</td>
<td>$[N_2]=0.921M$, $[H_2]=0.763M$, $[NH_3]=0.157M$</td>
</tr>
<tr>
<td>2</td>
<td>$[N_2]=0$, $[H_2]=0$, $[NH_3]=1.000M$</td>
<td>$[N_2]=0.399M$, $[H_2]=1.197M$, $[NH_3]=0.203M$</td>
</tr>
<tr>
<td>3</td>
<td>$[N_2]=2.00M$, $[H_2]=1.00M$, $[NH_3]=3.00M$</td>
<td>$[N_2]=2.59M$, $[H_2]=2.77M$, $[NH_3]=1.82M$</td>
</tr>
</tbody>
</table>

a. Calculate the equilibrium constant for each equilibrium system above.

b. Do the equilibrium constants vary for different sets of initial concentrations? Should they?

Note that while the concentrations of reactants and products at equilibrium are not the same, the equilibrium constant is about the same as long as the temperature is constant.
15.6 Heterogeneous Equilibria

The equilibria described thus far have been for reactions where all the reactants and products are gases. These represent **homogeneous equilibria** since only one phase is involved.

Equilibria involving more than one phase are called **heterogeneous equilibria**.

For example, \[ \text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{H}_2\text{O}(l) + \text{CO}(g) \]

\[ \text{I}_2(s) \rightleftharpoons \text{I}_2(g) \]

**For heterogeneous systems:**

1. Experimental data indicates that for heterogeneous systems, equilibrium does **NOT** depend on the amounts of pure solids or pure liquids present.
   - If enough of each pure solid or liquid is present, the system will achieve equilibrium regardless of the initial amounts of each pure solid or pure liquid in the reaction.

Consider the following reaction: \[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \]

The images show the **partial pressure of CO}_2 at equilibrium is the same** (for a given temperature) even for **two different initial amounts** of solid CaCO\(_3\) and solid CaO.

(a) At equilibrium the amount of CaO(s) exceeds the amount of CaCO\(_3\)(s) present, but the number of CO\(_2\) molecules is the same (for a given temperature).

(b) At equilibrium the amount of CaCO\(_3\)(s) exceeds the amount of CaO(s) present, but the number of CO\(_2\) molecules is the same (for a given temperature).

Thus, given enough of the pure liquids and solids are present, **only the concentrations of gases and aqueous species in solution will affect the equilibrium system.**
#2. The concentrations for pure solids and liquids are omitted from the equilibrium expression for a reaction.

Note that the molar concentration (in \( \frac{\text{mol}}{\text{L}} \)) of a pure solid or liquid is proportional to the density of the substance, which is constant.

\[ \text{Since a pure solid or pure liquid’s density is constant, its molar concentration is constant.} \]

Thus, for the decomposition of calcium carbonate, \( \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \), we can derive the equilibrium expression as follows:

\[
K' = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} = \frac{C_1}{C_2}
\]

where \( K' \) indicates an equilibrium constant that varies slightly from the accepted constant, \( K_c \). \( C_1 \) and \( C_2 \) are constants representing the “molar concentrations” of CaO and CaCO}_3, respectively.

Rearranging the equation gives

\[
\frac{K' C_2}{C_1} = [\text{CO}_2] \quad \text{and} \quad \frac{K' C_2}{C_1} = K_c = [\text{CO}_2]
\]

Thus, the equilibrium expression includes only the concentration for \( \text{CO}_2 \) (or only the partial pressure of \( \text{CO}_2 \) for the \( K_p \)).

Example: Write the equilibrium expressions for \( K_c \) and \( K_p \) for the following:

\[ \begin{align*}
\text{a. } & 2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(l) \\
\text{b. } & 4 \text{Al}(s) + 3 \text{O}_2(g) \rightleftharpoons 2 \text{Al}_2\text{O}_3(s) \\
\text{c. } & 2 \text{ZnS}(s) + 3 \text{O}_2(g) \rightleftharpoons 2 \text{ZnO}(s) + 2 \text{SO}_2(g)
\end{align*} \]
Note: Equilibrium constants, $K_c$ and $K_p$, are generally given without units!

- Equilibrium constants are actually based on the **activity** of the species in solution or in a gas. The activity of a species is a measure of its “effective concentration" in a mixture which determines its chemical potential or ability to alter a system.
- However, it’s easier to express the “effective concentration” of a species in terms of molar concentration or partial pressure, so in General Chemistry, we express equilibrium constants based on these quantities.
- But remember: Since these expressions and constants are actually based on activities which are unitless, the *equilibrium constants are also unitless*.

### 15.8 Calculations based on K

**Ex. 1:** For the following reaction at 1000K, \( \text{CH}_4(g) + 2 \text{H}_2\text{S}(g) \leftrightharpoons 4 \text{H}_2(g) + \text{CS}_2(g) \), the partial pressures of the equilibrium mixture are 0.20 atm, 0.25 atm, and 0.10 atm for methane, hydrogen sulfide, and hydrogen, respectively. The total pressure for the system at equilibrium is 1.07 atm.

a. Calculate the equilibrium constant, $K_p$, for the reaction.

b. Calculate the equilibrium constant, $K_c$, for the reaction.

**Ex. 2:** Carbonyl chloride (or phosgene) was used as a poisonous gas during World War I. The gas can be produced as follows: \( \text{CO}(g) + \text{Cl}_2(g) \leftrightharpoons \text{COCl}_2(g) \)

Calculate the concentration of chlorine at equilibrium given equilibrium concentrations of \([\text{CO}]=0.012\text{M}\) and \([\text{COCl}_2]=0.14\text{M}\), and $K_c=216$. 
Ex. 3: Ammonium carbamate decomposes, \[ \text{NH}_4\text{CO}_2\text{NH}_2(s) \rightleftharpoons \text{CO}_2(g) + 2 \text{NH}_3(g). \]

After a pure sample of ammonium carbamate decomposes at 40°C in an empty flask, the partial pressure of ammonia is 0.242 atm at equilibrium.

a. What is the partial pressure of carbon dioxide?

b. Solve for \( K_p \).

Ex. 4: Consider the following equilibrium system at 2200°C, \[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

a. Given that the system contains only reactants initially, complete the following ICE table.

<table>
<thead>
<tr>
<th>( \text{N}_2(g) )</th>
<th>+</th>
<th>3 ( \text{H}_2(g) )</th>
<th>( \rightleftharpoons )</th>
<th>2 ( \text{NH}_3(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.235M</td>
<td>2.285M</td>
<td>[ \rightleftharpoons ]</td>
<td>0.250M</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td>[ \rightleftharpoons ]</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td>0.250M</td>
</tr>
</tbody>
</table>

b. Solve for \( K_c \).
Ex. 5: Consider the equilibrium system at 300K, \( 2 \text{NO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{N}_2(g) + 2 \text{H}_2\text{O}(g) \)

a. A mixture of 0.100 mol of NO, 0.050 mol of H\(_2\), and 0.100 mol of H\(_2\)O is placed in a 1.00 L container. When equilibrium is established, [NO]=0.062M. Complete the following ICE table:

<table>
<thead>
<tr>
<th></th>
<th>2 \text{NO}(g)</th>
<th>+</th>
<th>2 \text{H}_2(g)</th>
<th>\rightleftharpoons</th>
<th>\text{N}_2(g)</th>
<th>+</th>
<th>2 \text{H}_2\text{O}(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b. Solve for \( K_c \).

Ex. 6: Consider again \( \text{SO}_2\text{Cl}_2(g) \) decomposing at 375K: \( \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \)

When a sample of \( \text{SO}_2\text{Cl}_2 \) decomposes and the system reaches equilibrium, the partial pressure of \( \text{SO}_2\text{Cl}_2 \) is 0.762 atm, and the total pressure of the system is 0.980 atm. Calculate the value of the equilibrium constant, \( K_p \), for this system at 375K.
Solving Equilibrium Problems given $K_c$ or $K_p$

1. Write the equilibrium expression.
2. Write the balanced chemical equation and list the initial concentrations or partial pressures in an ICE table.
3. Indicate the changes in concentrations or partial pressures in terms of a single unknown, $x$.
4. Define the equilibrium concentrations or partial pressures by applying the changes to the initial partial pressures.
5. Substitute the equilibrium concentrations or partial pressures into the equilibrium expression, then solve for $x$.
6. Substitute the value for $x$ to determine the equilibrium concentrations or partial pressures for the appropriate reactants and products.

Ex. 1: Consider the following equilibrium system at 1100K, $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$.

In an experiment, 0.831 g of SO$_3$ is placed in a 1.00 L flask and heated to 1100K. At equilibrium, the total pressure in the container is 1.300 atm.

a. Solve for $K_p$ at 1100K. (Use PV=nRT to solve for the initial pressure of SO$_3$.)

b. Calculate $K_c$ for the reaction.
Ex. 2: Consider the following reaction at equilibrium: \(2 \text{NOCl}(g) \rightleftharpoons 2 \text{NO}(g) + \text{Cl}_2(g)\).

When 2.50 moles of nitrosyl chloride, NOCl, is placed in a 1.50 L container at 400°C, the resulting equilibrium mixture indicates 28.0% dissociation for NOCl. Calculate \(K_c\) for the dissociation at this temperature.

Ex. 3: Consider the following equilibrium system at 2000°C, \(2 \text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)\).

Initially, only NO is present at a concentration of 0.200M. If \(K_c\) is \(2.4 \times 10^3\) at 2000°C, calculate the equilibrium concentrations of NO, N\(_2\), and O\(_2\) at 2000°C.
15.5 Equilibrium Constant and Reaction Quotients

The reaction quotient (Q) describes the system at a given instant—i.e., a “snapshot” of the system, which may or may not be at equilibrium.

The expression for the reaction quotient is also obtained using the law of mass action.

For the general reaction, \[ j\, A + k\, B \rightleftharpoons l\, C + m\, D \]

The reaction quotient, \( Q \) is as follows:
\[ Q = \frac{[C]^l\,[D]^m}{[A]^j\,[B]^k} \]

Predicting the Direction of the Reaction Using Q:

• If \( Q < K \), the reaction shifts to the right (or proceeds from left to right).
  – In the current system, there are too many reactants relative to the amount of products, so reactants must be converted to products to attain equilibrium.

• If \( Q > K \), the reaction shifts to the left (or proceeds from right to left).
  – In the current system, there are too many products relative to the amount of reactants, so products must be converted to reactants to attain equilibrium.

• If \( Q = K \), the system is already at equilibrium.

The figure below shows how the concentrations of reactants and products change for a system to establish equilibrium.
Ex. 1: At 250°C, \( K_p \) is 1.05 for the reaction, \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \).

a. Calculate the reaction quotient for a reaction mixture in which the partial pressures are 0.177 atm, 0.223 atm, and 0.111 atm for \( \text{PCl}_5 \), \( \text{PCl}_3 \), and \( \text{Cl}_2 \), respectively.

b. Is the system at equilibrium? Yes No

c. If the system is not at equilibrium, will the system shift left or shift right? Explain why.

Ex. 2: At 298K, \( K_p \) is 6.7 for the following reaction: \( 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \).

A 2.25 L container contains 0.055 mol of \( \text{NO}_2 \) and 0.082 mol of \( \text{N}_2\text{O}_4 \) at 298K.

a. Is the system at equilibrium? Yes No

c. If the system is not at equilibrium, will the system shift left or shift right? Explain why.
15.8 Calculations Based on $K$

Solving for $x$ using the quadratic method:

1. Rearrange the equation to the form: $ax^2 + bx + c = 0$

2. Apply the quadratic formula: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Since concentrations and partial pressures must always be positive, only one of the values is plausible.

Ex. 1: At 700K, $K_p=0.76$ for the decomposition of $\text{CCl}_4$: $\text{CCl}_4(g) \rightleftharpoons \text{C}(s) + 2 \text{Cl}_2(g)$

A flask is charged with 2.00 atm of carbon tetrachloride which then reaches equilibrium at 700K. What are the equilibrium partial pressures of carbon tetrachloride and chlorine in the flask?
Ex. 2: At 700K, $K_c$ is 57.0 for the reaction: \[ H_2(g) + I_2(g) \rightleftharpoons 2 HI(g). \]

A 10.00L flask is filled with 1.00 mol of hydrogen and 2.00 mol of iodine at 700K. Determine the equilibrium concentrations of the reactants and products for the reaction.
15.7 Le Châtelier’s Principle
Henri Louis Le Châtelier (1850-1936) proposed how equilibrium systems respond to changes.

**Le Châtelier’s Principle:** If a stress (e.g. change in concentration, pressure, or temperature) is imposed on a system at equilibrium, the system will (if possible) shift to minimize the change.

The Effect of a Change in Concentration
– Consider the synthesis of ammonia: \( \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \)

The plot of concentration versus time below shows how the concentrations of the reactants and products shift when \( \text{N}_2 \) is added to a system at equilibrium.

![Graph showing the effect of adding \( \text{N}_2 \) on concentrations of \( \text{H}_2, \text{NH}_3, \text{N}_2 \).](image)

a. After the \( \text{N}_2 \) is added, the concentration of \( \text{H}_2 \)_____.  ↑  ↓  stays the same
b. After the \( \text{N}_2 \) is added, the concentration of \( \text{N}_2 \)_____.  ↑  ↓  stays the same
c. After the \( \text{N}_2 \) is added, the concentration of \( \text{NH}_3 \)_____.  ↑  ↓  stays the same
d. Adding \( \text{N}_2 \) caused the equilibrium to __________.  shift left  shift right
Thus, when a species is added to a system at equilibrium, the system shifts to consume and reduce the concentration of the added species.

When a species is removed from a system at equilibrium, the system shifts to replace the species removed.

→ During industrial production, the desired product is often removed, so the system constantly shifts right to make more product.

Example: Given the following system at equilibrium, \(2 \text{NO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{N}_2(g) + 2 \text{H}_2\text{O}(g)\), predict how the system will shift given the following stresses and explain why:

a. When \(\text{H}_2\) is added to the system, the system shifts_____ left       right
   Why?

b. When \(\text{N}_2\) is added to the system, the system shifts_____ left       right
   Why?

c. When \(\text{NO}\) is removed from the system, the system shifts_____ left       right
   Why?

d. When steam is removed from the system, the system shifts_____ left       right
   Why?

Effects of Changes in Pressure and Volume

The volume of a system is directly related to the number of molecules,

Starting with \(PV=nRT\), solve for \(V\):

\[
V = \frac{nRT}{P} = \left(\frac{RT}{P}\right) \cdot n
\]

so at constant \(T\) and \(P\):

\(V \propto n\)
When the container volume decreases (pressure increases) → the system will shift to decrease its volume by decreasing the # of moles of gas.

When the container volume increases (pressure decreases) → the system will shift to increase its volume by increasing the # of moles of gas.

Ex. 1: Consider the following equilibrium system: \( \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) \).
Predict how the system will shift given the following stresses and explain why:

a. When the volume of the container changes from 1.0L to 2.0 L, the system shifts_______ left right Why?

b. When the volume of the container changes from 10.0L to 5.0 L, the system shifts_______ left right Why?

Ex. 2: Predict how the following systems will shift when the volume of the reaction container is increased.

a. \( 2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \) to the left to the right

b. \( \text{CCl}_4(\text{g}) \rightleftharpoons \text{C(s)} + 2 \text{Cl}_2(\text{g}) \) to the left to the right

c. \( 2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \) to the left to the right

d. \( \text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g}) \) to the left to the right

e. \( \text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{CO}(\text{g}) \) to the left to the right

f. \( \text{P}_4(\text{s}) + 6 \text{Cl}_2(\text{g}) \rightleftharpoons 4 \text{PCl}_3(\text{l}) \) to the left to the right

g. \( \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}) \) to the left to the right

Thus, for reactions where the number of moles of gaseous reactants equals the number of moles of gaseous products (i.e., \( \Delta n=0 \)), a change in volume will have no effect on the equilibrium position.
The Effect of Temperature Changes
- Consider heat a reactant or product in a reaction.

- When temperature increases
  → the system shifts to consume the heat added
  → the endothermic reaction occurs.
  → Increasing temperature causes an endothermic reaction to occur.

- When temperature decreases
  → the system shifts to replace the heat removed
  → the exothermic reaction occurs.
  → Decreasing temperature causes an exothermic reaction to occur.

Ex. 1: Consider the synthesis of ammonia at equilibrium:

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \quad \Delta H = -92.2 \text{ kJ} \]

a. Given the reaction's \( \Delta H \), add heat as a reactant or product in the equation.

b. Predict the direction the reaction will shift given the following stresses:
   i. The system is heated, the system shifts ____. left right
   ii. The system is cooled, the system shifts ____. left right

Ex. 2: Consider the equilibrium reaction:

\[ \text{N}_2\text{F}_4(g) \rightleftharpoons 2 \text{NF}_2(g) \quad \Delta H = 38.5 \text{kJ} \]

a. Given the reaction's \( \Delta H \), add heat as a reactant or product in the equation.

b. Predict the direction the reaction will shift given the following stresses:
   i. If temperature changes from 25°C to 375K, the system shifts ______. left right
   ii. If temperature changes from 25°C to 273K, the system shifts ______. left right

\( K_c \) and \( K_p \) Change with Temperature
- Note: Only temperature affects the equilibrium constant!
  → When temperature increases, \( K_c \) and \( K_p \) increase for endothermic reactions.
  → When temperature decreases, \( K_c \) and \( K_p \) increase for exothermic reactions.
Ex. 3: Consider the following reaction at equilibrium:

\[ \text{Co}^{2+}(aq) + 4 \text{Cl}^-(aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) \]

Consider the demo or youtube video of the reaction to explain the following:

a. What is the initial color of the solution before anything is added to it?

b. What happens to the color of the solution when concentrated HCl(aq) is added?

c. Use Le Châtelier’s Principle to explain the color change observed in part b.

d. The solution turns blue when the system is heated. Thus, when heated the system shifts _________. left right

e. Thus, heat can be considered a _________ reactant product in this reaction.

f. Given your answer in part e, this reaction must be ________. exothermic endothermic

Predict the direction the reaction will shift given the following stresses and explain why.

g. When the temperature changes from 25°C to 273K, the system shifts _____. left right

h. When the temperature changes from 25°C to 375K, the system shifts _____. left right
   – Explain why.

i. When temperature is increased, \( K_c \)__________ increases decreases for this reaction.
   – Explain why.
15.4 Manipulating Equilibrium Constant Expressions

Multiple Equilibria or \( K \) for Equations Multiplied by a Number

While most the chemical systems studied thus far have been relatively simple, many chemical reactions involve multiple equilibria in which the products of one equilibrium system are involved in a second equilibrium system.

Consider a general reaction in which the final products are \( E \) and \( F \). In the process, the products from the first equilibrium system (\( C \) and \( D \)) are consumed in the second equilibrium system. The corresponding equilibrium expression for each elementary step is also shown.

\[
A + B \rightleftharpoons C + D \quad K'_c = \frac{[C][D]}{[A][B]}
\]

\[
C + D \rightleftharpoons E + F \quad K''_c = \frac{[E][F]}{[C][D]}
\]

\[
A + B \rightleftharpoons E + F \quad K_c = \frac{[E][F]}{[A][B]} \times \frac{[C][D]}{[A][B]} = K'_c \cdot K''_c
\]

Thus, when a reaction can be expressed as a sum or two or more reactions, the equilibrium constant for the overall reaction is simply the product of the equilibrium constants for the individual reactions.

In some situations, one or more elementary steps may have to be manipulated in order to get the correct overall reaction mechanism. Knowing the following rules will help for these situations:

**Rule #3:** The equilibrium expression for a reaction written in reverse is the reciprocal of that for the original reaction.
- Equilibrium constants for forward and reverse reactions are reciprocals of one another.

\[
a. \quad 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \quad K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}
\]

\[
b. \quad \text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}
\]

**Rule #4:** If the coefficients in a balanced equation are multiplied by a factor, \( n \), the equilibrium constant is raised to the \( nth \) power.

\[
a. \quad 2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(g) \quad K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}
\]

\[
b. \quad 2 [2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(g)] \quad K_c = \frac{[\text{H}_2\text{O}]^4}{[\text{H}_2]^4[\text{O}_2]^2} = \left(\frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}\right)^2
\]
Ex. 1: Consider the following equilibrium systems and their corresponding equilibrium constants at 1123K:

\[ \text{C(s)} + \text{CO}_2(g) \rightleftharpoons 2 \text{CO}(g) \quad K_p' = 1.3 \times 10^{14} \]
\[ \text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \quad K_p'' = 6.0 \times 10^{-3} \]

Write the equilibrium expression for $K_p'$, and solve for $K_p'$ at 1123K for the overall reaction:

\[ \text{C(s)} + \text{CO}_2(g) + 2 \text{Cl}_2(g) \rightleftharpoons 2 \text{COCl}_2(g) \]

Ex. 2: At a given temperature the following equilibrium systems have the equilibrium constants shown below

\[ \text{S(s)} + \text{O}_2(g) \rightleftharpoons \text{SO}_2(g) \quad K_c' = 4.2 \times 10^{62} \]
\[ 2 \text{S(s)} + 3 \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \quad K_c'' = 9.8 \times 10^{128} \]

Write the equilibrium expression for $K_c'$, and solve for $K_c'$ at 1123K for the overall reaction:

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