Ch14 Chemical Equilibrium

Modified by Dr. Cheng-Yu Lai
Chemical Equilibrium

If the rate at which people move from the first floor to the second equals the rate at which people move from the second floor to the first, the number of people on each floor remains constant and the two populations are in dynamic equilibrium.

Chemical Equilibrium: The state reached when the concentrations of reactants and products remain constant over time.
Chemical Equilibrium

Chemical Equilibrium:

When the rate of the forward reaction equals the rate of the reverse reaction and the concentration of products and reactants remains unchanged.

\[ N_2O_4(g) \rightleftharpoons 2 NO_2(g) \]

Reaction occurs in both directions

Arrows going both directions (\( \rightleftharpoons \)) indicates equilibrium in a chemical equation

Reversible Reactions:

A chemical reaction in which the products can react to re-form the reactants

Eventually the rates are equal
TABLE 13.1 Concentration Data at 25 °C for the Reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Concentrations (M)</th>
<th>Equilibrium Concentrations (M)</th>
<th>Equilibrium Constant Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[N$_2$O$_4$] 0.0400</td>
<td>[N$_2$O$_4$] 0.0337</td>
<td>[NO$_2$] 0.0125</td>
</tr>
<tr>
<td>2</td>
<td>[NO$_2$] 0.0000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[N$_2$O$_4$] 0.0600</td>
<td>[N$_2$O$_4$] 0.0522</td>
<td>[NO$_2$] 0.0156</td>
</tr>
<tr>
<td>4</td>
<td>[NO$_2$] 0.0600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The expression [NO$_2$]$^2$/[N$_2$O$_4$] appears to be related to the balanced equation for the reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ in that the concentration of the product is in the numerator, raised to the power of its coefficient in the balanced equation, and the concentration of the reactant is in the denominator. Is there an analogous expression
Law of Mass Action

For the reaction, when \( \text{Rate}_{\text{for}} = \text{Rate}_{\text{rev}} \)

\[
\begin{align*}
  jA + kB & \rightleftharpoons lC + mD \\
  K &= \frac{[C]^l[D]^m}{[A]^j[B]^k}
\end{align*}
\]

Where \( K \) is the equilibrium constant
Writing an Equilibrium Expression

Write the equilibrium expression for the reaction:

$$2\text{NO}_2(g) \rightleftharpoons 2\text{NO}(g) + \text{O}_2(g)$$

$$K = ???$$

$$K = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2}$$
Playing with Equilibrium Expressions

\[ 2\text{NO}_2(\text{g}) \iff 2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \]

\[ K = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2} \]

- The equilibrium expression for a reaction is the reciprocal for a reaction written in reverse

\[ 2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \iff 2\text{NO}_2(\text{g}) \]

\[ K' = \frac{1}{K} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} \]
Playing with Equilibrium Expressions

\[ 2\text{NO}_2(g) \Leftrightarrow 2\text{NO}(g) + \text{O}_2(g) \]

\[ K = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2} \]

- When the balanced equation for a reaction is multiplied by a factor \( n \), the equilibrium expression for the new reaction is the original expression, raised to the \( nth \) power.

\[ \text{NO}_2(g) \Leftrightarrow \text{NO}(g) + \frac{1}{2}\text{O}_2(g) \]

\[ K' = K^{\frac{1}{2}} = \frac{\frac{1}{2}[\text{NO}][\text{O}_2]^2}{[\text{NO}_2]} \]
Playing with K

• If we multiply the equation by a constant, \( n \)

\[ njA + nkB \iff nC + nmD \]

• Then the equilibrium constant is

\[ K' = \frac{[A]^{nj}[B]^{nk}}{[C]^{nl}[D]^{nm}} = \frac{([A]^j[B]^k)^n}{([C]^l[D]^m)^n} = K^n \]
Adding Chemical Equations

The rule of multiple equilibria

- If a reaction can be expressed as the sum of two or more reactions, the K for the overall reaction is the product of the K values for the individual reactions.

- Consider
  - \( \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) \rightleftharpoons \text{SO}_3 (g) \quad K = 2.2 \)
  - \( \text{NO}_2 (g) \rightleftharpoons \text{NO} (g) + \frac{1}{2}\text{O}_2 (g) \quad K = 4.0 \)

- For
  - \( \text{SO}_2 (g) + \text{NO}_2 (g) \rightleftharpoons \text{SO}_3 (g) + \text{NO} (g) \quad K = 8.8 \)
Playing with K - Summary

### TABLE 12.3 Dependence of $K$ on the Form of the Chemical Reaction

$$R(g) \rightleftharpoons Y(g) \quad K = \frac{P_Y}{P_R}$$

<table>
<thead>
<tr>
<th>Form of Equation</th>
<th>$K$ Expression</th>
<th>Relation to $K$</th>
<th>Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y(g) \rightleftharpoons R(g)$</td>
<td>$K' = \frac{P_R}{P_Y}$</td>
<td>$K' = \frac{1}{K}$</td>
<td>Reciprocal Rule</td>
</tr>
<tr>
<td>$nR(g) \rightleftharpoons nY(g)$</td>
<td>$K'' = \frac{(P_Y)^n}{(P_R)^n}$</td>
<td>$K'' = K^n$</td>
<td>Coefficient Rule</td>
</tr>
<tr>
<td>$R(g) \rightleftharpoons A(g)$</td>
<td>$K_1 = \frac{P_A}{P_R}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A(g) \rightleftharpoons Y(g)$</td>
<td>$K_2 = \frac{P_Y}{P_A}$</td>
<td>$K = K_1 \times K_2$</td>
<td>Rule of Multiple Equilibria</td>
</tr>
<tr>
<td>$R(g) \rightleftharpoons Y(g)$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Equilibrium Expressions Involving Pressure

For the gas phase reaction:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2})^3}$$

$P_{NH_3}, P_{N_2}, P_{H_2}$ are equilibrium partial pressures

$$K_p = K(RT)^{\Delta n}$$
Equilibrium and Pressure – Kc and Kp

• $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$

• $K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2 (P_{\text{O}_2})}$

• $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$
Equilibrium and Pressure – Kc and Kp

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

\[ \begin{align*}
\bullet \quad \text{Kc} &= \frac{(P_{\text{SO}_3}/RT)^2}{(P_{\text{SO}_2}/RT)^2(P_{\text{O}_2}/RT)} \\
\bullet \quad \text{Kc} &= \frac{(P_{\text{SO}_3})^2(1/RT)^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})(1/RT)^3} \\
\bullet \quad \text{Kc} &= \text{Kp} \frac{(1/RT)^2}{(1/RT)^3} = \text{Kp} \frac{RT}{(RT)^{-1}} \\
\Rightarrow \quad \text{Kp} &= \text{kc} \quad (RT)^{-1}
\end{align*} \]
RELATING THE EQUILIBRIUM CONSTANTS $K_p$ AND $K_c$

Hydrogen is produced industrially by the steam–hydrocarbon re-forming process. The reaction that takes place in the first step of this process is

$$H_2O(g) + CH_4(g) \rightleftharpoons CO(g) + 3 H_2(g)$$

(a) If $K_c = 3.8 \times 10^{-3}$ at 1000 K, what is the value of $K_p$ at the same temperature?

(b) If $K_p = 6.1 \times 10^4$ at 1125 °C, what is the value of $K_c$ at 1125 °C?

**STRATEGY**

To calculate $K_p$ from $K_c$, or vice versa, use the equation $K_p = K_c(RT)^{\Delta n}$, where $R$ must be in units of (L·atm)/(K·mol), $T$ is the temperature in kelvin, and $\Delta n$ is the number of moles of gaseous products minus the number of moles of gaseous reactants.

**SOLUTION**

(a) For this reaction, $\Delta n = (1 + 3) - (1 + 1) = 2$. Therefore,

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^2 = (3.8 \times 10^{-3})\left[(0.08206)(1000)\right]^2 = 26$$

(b) Solving the equation $K_p = K_c(RT)^2$ for $K_c$ gives

$$K_c = \frac{K_p}{(RT)^2} = \frac{6.1 \times 10^4}{[(0.08206)(1398)]^2} = 4.6$$

Note that the temperature in these equations is the absolute temperature; 1125 °C corresponds to $1125 + 273 = 1398$ K.
Equilibrium Constant Expression

- For a reaction where
  
  \[ aA (g) + bB (g) \rightleftharpoons cC (g) + dD (g) \]
  
  - A, B, C, D all gases
  - a, b, c, d are the coefficients of the balanced equation

- \( K_p \) is the **equilibrium constant**

\[
K_p = \frac{(P_c)^c (P_d)^d}{(P_a)^a (P_b)^b}
\]

- All partial pressures must be expressed in **atm**.
- **Product** terms are in the **numerator**.
- **Reactant** terms are in the **denominator**.
- **Coefficients** of reactant and product are used as **powers**.
- This K can be termed \( K_p \) (pressure equilibrium constant)
The units for K

- Are determined by the various powers and units of concentrations.
- They depend on the reaction.
Product Favored Equilibrium

Large values for $K$ signify the reaction is “product favored”

When equilibrium is achieved, most reactant has been converted to product
Reactant Favored Equilibrium

Small values for $K$ signify the reaction is “reactant favored”

When equilibrium is achieved, very little reactant has been converted to product
Solving for Equilibrium Concentration

Consider this reaction at some temperature:
\[ H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) \quad K = 2.0 \]

Assume you start with 8 molecules of H\(_2\)O and 6 molecules of CO. How many molecules of H\(_2\)O, CO, H\(_2\), and CO\(_2\) are present at equilibrium?

Here, we learn about “ICE” – the most important problem solving technique in the second semester. You will use it for the next 4 chapters!
Solving for Equilibrium Concentration

\[ \text{H}_2\text{O}(g) + \text{CO}(g) \iff \text{H}_2(g) + \text{CO}_2(g) \quad K = 2.0 \]

**Step #1:** We write the law of mass action for the reaction:

\[ 2.0 = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} \]
Solving for Equilibrium Concentration

Step #2: We “ICE” the problem, beginning with the initial concentrations.

\[
H_2O(g) + CO(g) \leftrightarrow H_2(g) + CO_2(g)
\]

<table>
<thead>
<tr>
<th>Initial:</th>
<th>8</th>
<th>6</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change:</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium:</td>
<td>8-x</td>
<td>6-x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
Solving for Equilibrium Concentration

**Step #3:** We plug equilibrium concentrations into our equilibrium expression, and solve for \( x \)

\[
\begin{align*}
\text{Equilibrium:} & & 8-x & & 6-x & & x & & x \\
2.0 &= \frac{(x)(x)}{(8-x)(6-x)} \quad \boxed{x = 4}
\end{align*}
\]

Because the right side of this equation is not a perfect square, we must put the equation into the standard quadratic form, \( ax^2 + bx + c = 0 \), and then solve for \( x \) using the quadratic formula (Appendix A.4): 

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]
Solving for Equilibrium Concentration

Step #4: Substitute x into our equilibrium concentrations to find the actual concentrations

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

<table>
<thead>
<tr>
<th>Equilibrium:</th>
<th>8-x</th>
<th>6-x</th>
<th>x</th>
<th>x</th>
</tr>
</thead>
</table>

\[ x = 4 \]

| Equilibrium: | 8-4=4 | 6-4=2 | 4 | 4 |
Example 14.5 Finding Equilibrium Constants from Experimental Concentration Measurements

Consider the following reaction:

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

A reaction mixture at 780 °C initially contains [CO] = 0.500 M and [H\text{\textsubscript{2}}] = 1.00 M. At equilibrium, the CO concentration is found to be 0.15 M. What is the value of the equilibrium constant?

$$
\begin{array}{c|c|c|c}
\text{Initial} & \text{[CO]} & \text{[H\textsubscript{2}]} & \text{[CH\textsubscript{3}OH]} \\
\text{Change} & -0.35 & -0.70 & +0.35 \\
\text{Equil} & 0.15 & & \\
\end{array}
$$

The equilibrium constant is given by:

$$
K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{0.35}{(0.15)(0.30)^2} = 26
$$
Example 14.6 Finding Equilibrium Constants from Experimental Concentration Measurements

Consider the following reaction:

\[ 2 \text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_2(g) + 3 \text{H}_2(g) \]

A reaction mixture at 1700 °C initially contains [CH\(_4\)] = 0.115 M. At equilibrium, the mixture contains [C\(_2\)H\(_2\)] = 0.035 M. What is the value of the equilibrium constant?

\[
K_c = \frac{[\text{C}_2\text{H}_2][\text{H}_2]^3}{[\text{CH}_4]^2}
\]

\[
= \frac{(0.035)(0.105)^3}{(0.045)^2}
\]

\[
= 0.020
\]
For the system

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

\( K \) is 0.64 at 900 \( K \). Calculate the equilibrium partial pressures of all species, starting with

\( \text{a} \) \( P_{\text{CO}_2} = P_{\text{H}_2} = 1.00 \text{ atm}; P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0 \)

\( \text{b} \) \( P_{\text{CO}_2} = 2.00 \text{ atm}, P_{\text{H}_2} = 1.00 \text{ atm}; P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0 \)

**ANALYSIS**

Information given:
- initial partial pressures for \( \text{CO}_2 \) (1.00 atm), \( \text{H}_2 \) (1.00 atm), \( \text{CO} \) (0 atm), and \( \text{H}_2\text{O} \) (0 atm)
- \( K \) (0.64) at 900 \( K \)

Information implied:
- direction of the reaction

Asked for:
- equilibrium partial pressures of all species

**STRATEGY AND SOLUTION**

1. Create a table.

<table>
<thead>
<tr>
<th>( P_{\text{CO}_2} ) (atm)</th>
<th>( P_{\text{H}_2} ) (atm)</th>
<th>( P_{\text{CO}} ) (atm)</th>
<th>( P_{\text{H}_2\text{O}} ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0 )</td>
<td>( 0 )</td>
<td>( 0 )</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>
2. Choose $\Delta P$ for CO as $x$. Since all the coefficients of the reaction are 1, all the species have $x$ for $\Delta P$.

<table>
<thead>
<tr>
<th>Species</th>
<th>$P_0$ (atm)</th>
<th>$\Delta P$ (atm)</th>
<th>$P_{eq}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2(g)$</td>
<td>1.00</td>
<td>$x$</td>
<td>$1.00 - x$</td>
</tr>
<tr>
<td>$H_2(g)$</td>
<td>1.00</td>
<td>$x$</td>
<td>$1.00 - x$</td>
</tr>
<tr>
<td>$CO(g)$</td>
<td>0</td>
<td>$+x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$H_2O(g)$</td>
<td>0</td>
<td>$+x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

3. Direction of the reaction ($\rightarrow$)

<table>
<thead>
<tr>
<th>Species</th>
<th>$P_0$ (atm)</th>
<th>$\Delta P$ (atm)</th>
<th>$P_{eq}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2(g)$</td>
<td>1.00</td>
<td>$-x$</td>
<td>$1.00 - x$</td>
</tr>
<tr>
<td>$H_2(g)$</td>
<td>1.00</td>
<td>$-x$</td>
<td>$1.00 - x$</td>
</tr>
<tr>
<td>$CO(g)$</td>
<td>0</td>
<td>$+x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$H_2O(g)$</td>
<td>0</td>
<td>$+x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

4. Equilibrium partial pressures

<table>
<thead>
<tr>
<th>Species</th>
<th>$P_0$ (atm)</th>
<th>$\Delta P$ (atm)</th>
<th>$P_{eq}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2(g)$</td>
<td>1.00</td>
<td>$-x$</td>
<td>$1.00 - x$</td>
</tr>
<tr>
<td>$H_2(g)$</td>
<td>1.00</td>
<td>$-x$</td>
<td>$1.00 - x$</td>
</tr>
<tr>
<td>$CO(g)$</td>
<td>0</td>
<td>$+x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$H_2O(g)$</td>
<td>0</td>
<td>$+x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

5. $K$ expression

$$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(x)(x)}{(1.00 - x)(1.00 - x)} = 0.64$$

Solve for $x$

Take the square root of both sides: $0.80 = \frac{x}{1.00 - x} \Rightarrow x = 0.44$

6. $P_{eq}$

$$P_{CO} = P_{H_2O} = x = 0.44 \text{ atm}; \quad P_{CO_2} = P_{H_2} = 1.00 - x = (1.00 - 0.44) \text{ atm} = 0.56 \text{ atm}$$
ANALYSIS

Information given: initial partial pressures for CO$_2$ (2.00 atm), H$_2$ (1.00 atm), CO (0 atm), and H$_2$O (0 atm) $K$ (0.64) at 900 K

Information implied: direction of the reaction

Asked for: equilibrium partial pressures of all species

STRATEGY AND SOLUTION

1-4. The first four steps (shown in detail in part (a)) of the pathway give the following table:

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$(g)</th>
<th>+</th>
<th>H$_2$(g)</th>
<th>$\rightleftharpoons$</th>
<th>CO(g)</th>
<th>+</th>
<th>H$_2$O(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_0$ (atm)</td>
<td>2.00</td>
<td>1.00</td>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta P$ (atm)</td>
<td>$-x$</td>
<td>$-x$</td>
<td></td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_{eq}$ (atm)</td>
<td>2.00 $-x$</td>
<td>1.00 $-x$</td>
<td></td>
<td>$x$</td>
<td>$x$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. $K$ expression

$$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(x)(x)}{(2.00 - x)(1.00 - x)} = 0.64$$

It is not useful to take the square root of both sides, so rearrange the equation to the standard form for using the quadratic equation: $ax^2 + bx + c = 0 \rightarrow 0.36 x^2 + 1.92 x - 1.28 = 0$
Apply the quadratic formula: 
\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]
\[ x = 0.60 \text{ or } -5.93 \]

0.60 atm is plausible; -5.93 atm would imply a negative partial pressure.

6. \( P_{eq} \)

\[
\begin{align*}
P_{CO} &= P_{H_2O} = x = 0.60 \text{ atm} \\
P_{CO_2} &= 2.00 - 0.60 = 1.40 \text{ atm} \\
P_{H_2} &= 1.00 - 0.60 = 0.40 \text{ atm}
\end{align*}
\]

END POINT

Check your algebra by substituting the equilibrium partial pressures back into the expression for \( K \).

\[
K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(0.60)(0.60)}{(1.40)(0.40)} = 0.64 \quad \text{Voila!}
\]
Homogeneous Equilibria

• So far every example dealt with reactants and products where all were in the same phase.
• We can use K in terms of either concentration or pressure.
• Units depend on reaction.
Heterogeneous Equilibria

• If the reaction involves pure solids or pure liquids the concentration of the solid or the liquid doesn’t change.

• As long as they are not used up they are not used up we can leave them out of the equilibrium expression.

• For example
For Example

- \( \text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2\text{HI}(\text{g}) \)
- \( \text{K} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \)
- But the concentration of \( \text{I}_2 \) does not change. For example, \([\text{H}_2\text{O}] = 15.6 \text{ M}\)
- Combining \([\text{I}_2] \) into \( \text{K}_{c} \), then \( \text{K}[	ext{I}_2] = \frac{[\text{HI}]^2}{[\text{H}_2]} = \text{new K}' \)
HETEROGENEOUS EQUILIBRIA

CaCO₃(s) ⇌ CaO(s) + CO₂(g)
Limestone    Lime

\[ K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \]

The analogous equilibrium equation in terms of pressure is \( K_p = P_{\text{CO}_2} \) where \( P_{\text{CO}_2} \) is the equilibrium pressure of \( \text{CO}_2 \) in atmospheres:

\[ K_c = [\text{CO}_2] \quad K_p = P_{\text{CO}_2} \]

\[ K_p = K_c (RT)^{\frac{1}{2}} \]

---

(a) Small amount of \( \text{CaCO}_3 \); large amount of \( \text{CaO} \)

(b) Large amount of \( \text{CaCO}_3 \); small amount of \( \text{CaO} \)

At the same temperature, the equilibrium pressure of \( \text{CO}_2 \) is the same in (a) and (b), independent of how much solid \( \text{CaCO}_3 \) and \( \text{CaO} \) is present.
WRITING EQUILIBRIUM EQUATIONS FOR HETEROGENEOUS EQUILIBRIA

Write the equilibrium equation for each of the following reactions:

(a) \( \text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2 \text{CO}(g) \)

(b) \( \text{Hg}(l) + \text{Hg}^{2+}(aq) \rightleftharpoons \text{Hg}_2^{2+}(aq) \)

STRATEGY

Write the usual equilibrium constant expressions but omit the pure solid carbon in part (a) and the pure liquid mercury in part (b) because the ratio of their concentrations to their concentrations in the standard state is equal to 1.

SOLUTION

(a) \( K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} \)

Alternatively, because CO and CO\(_2\) are gases, the equilibrium equation can be written using partial pressures:

\[ K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} \]

The relationship between \( K_p \) and \( K_c \) is \( K_p = K_c(RT)^\Delta n = K_c(RT) \), because \( \Delta n = 2 - 1 = 1 \).

(b) \( K_c = \frac{[\text{Hg}_2^{2+}]}{[\text{Hg}^{2+}]} \)

In this case, it’s not appropriate to write an expression for \( K_p \) because none of the reactants and products is a gas.
In the equilibrium expression, always include:

- Partial pressures for gases, raised to the coefficient of each
- Molar concentrations for aqueous species (molecules or ions), raised to the coefficient of each

Always exclude:

- Terms for pure liquids and pure solids
- \( \text{Zn (s)} + 2\text{H}^+ (\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2 (\text{g}) \)

\[ K = \frac{[\text{Zn}^{2+}]p_{\text{H}_2}}{[\text{H}^+]^2} \]
Le Chatelier’s Principle
LeChatelier’s Principle

When a system at equilibrium is placed under stress, the system will undergo a change in such a way as to relieve that stress and restore a state of equilibrium.

Please see the link below:

http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/flash.mhtml
Le Chatelier Translated:

When you take something away from a system at equilibrium, the system shifts in such a way as to replace some what you’ve taken away.

When you add something to a system at equilibrium, the system shifts in such a way as to use up some of what you’ve added.
FACTORS THAT ALTER THE COMPOSITION OF AN EQUILIBRIUM MIXTURE: LE CHÂTELIER’S PRINCIPLE

Several factors can be exploited to alter the composition of an equilibrium mixture:

- The concentration of reactants or products can be changed.
- The pressure and volume can be changed.
- The temperature can be changed.

Case 1

Any of the changes marked in blue shifts the equilibrium to the left.

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

Any of the changes marked in red shifts the equilibrium to the right.

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

Figure 13.9

Effect of concentration changes on the equilibrium \( \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \). An increase in the \( \text{N}_2 \) or \( \text{H}_2 \) concentration or a decrease in the \( \text{NH}_3 \) concentration shifts the equilibrium from left to right. A decrease in the \( \text{N}_2 \) or \( \text{H}_2 \) concentration or an increase in the \( \text{NH}_3 \) concentration shifts the equilibrium from right to left.
Case 2

\[
\text{Fe}^{3+}(aq) + \text{SCN}^{-}(aq) \rightleftharpoons \text{FeNCS}^{2+}(aq)
\]

Pale yellow  Colorless  Red

(a) Original solution: Fe\(^{3+}\) (pale yellow), SCN\(^{-}\) (colorless), and FeNCS\(^{2+}\) (red).

(b) After adding FeCl\(_3\) to (a): [FeNCS\(^{2+}\)] increases.

(c) After adding KSCN to (a): [FeNCS\(^{2+}\)] increases.

Figure 13.10
Color changes produced by adding various reagents to an equilibrium mixture of Fe\(^{3+}\) (pale yellow), SCN\(^{-}\) (colorless), and FeNCS\(^{2+}\) (red).
When the pressure is decreased by increasing the volume, the position of equilibrium shifts toward the side with the greater number of molecules—the reactant side.
**ALTERING AN EQUILIBRIUM MIXTURE: CHANGES IN TEMPERATURE**

\[
\text{N}_2\text{O}_4(g) + 55.3 \text{ kJ} \rightleftharpoons 2 \text{NO}_2(g) \quad \Delta H^\circ = +55.3 \text{ kJ}
\]

Colorless \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad

In general, the temperature dependence of an equilibrium constant depends on the sign of $\Delta H^\circ$ for the reaction.

- The equilibrium constant for an exothermic reaction (negative $\Delta H^\circ$) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive $\Delta H^\circ$) increases as the temperature increases.

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g); \Delta H > 0
\]

The darker brown color of the sample at the highest temperature indicates that the equilibrium $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$ shifts from reactants to products with increasing temperature, as expected for an endothermic reaction.
APPLYING LE CHÂTELIER’S PRINCIPLE TO TEMPERATURE CHANGES

In the first step of the Ostwald process for the synthesis of nitric acid, ammonia is oxidized to nitric oxide by the reaction

$$4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g) \quad \Delta H^\circ = -901.2 \text{ kJ}$$

How does the equilibrium amount of NO vary with an increase in temperature?

STRATEGY

Le Châtelier’s principle predicts that the stress of added heat when the temperature is increased will be relieved by net reaction in the direction that absorbs the heat. It’s helpful to include the heat in the balanced equation—on the reactant side if the reaction is endothermic, or on the product side if the reaction is exothermic.

SOLUTION

Because the oxidation of ammonia is exothermic, we include the heat (901.2 kJ) on the product side:

$$4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g) + 901.2 \text{ kJ}$$

The stress of added heat when the temperature is increased will be relieved by net reaction from products to reactants, which absorbs the added heat. The equilibrium will therefore shift to the reactant side ($K_C$ will decrease) with an increase in temperature. Consequently, the equilibrium mixture will contain less NO at higher temperatures.
The Reaction Quotient

For some time, t, when the system is not at equilibrium, the reaction quotient, $Q$, takes the place of $K$, the equilibrium constant, in the law of mass action.

$$jA + kB \rightleftharpoons lC + mD$$

$$Q = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$
Significance of the Reaction Quotient

- If $Q = K$, the system is at equilibrium
- If $Q > K$, the system shifts to the left, consuming products and forming reactants until equilibrium is achieved
- If $Q < K$, the system shifts to the right, consuming reactants and forming products until equilibrium is achieved
Compare Q and K to predict the reaction Direction

\[ \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) \quad K_{eq} = 11 \text{ atm (T = 373 K)} \]

Mix 0.2 mol of \( \text{N}_2\text{O}_4 \) with 0.2 mol of \( \text{NO}_2 \) in a 4.0 L flask at 100°C.

\[ Q = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} \]

First find \( P_{\text{NO}_2} \) and \( P_{\text{N}_2\text{O}_4} \) using \( PV = nRT \)

\begin{align*}
P_{\text{NO}_2} &= P_{\text{N}_2\text{O}_4} = (0.20 \text{ mol})(0.0821 \text{ L atm/mol K})(373 \text{ K})/(4.0 \text{ L}) = 1.5 \text{ atm} \\
Q &= (1.5 \text{ atm})^2/1.5 \text{ atm} = 1.5 \text{ atm} < 11 \text{ atm} \\
Q < K, \text{ so the reaction will proceed in the forward direction,}
\end{align*}

\[ \text{N}_2\text{O}_4 (g) \rightarrow 2 \text{NO}_2 (g) \text{ until it reaches equilibrium.} \]