Chapter 14: Chemical Equilibrium

14.1 Fetal Hemoglobin and Equilibrium (Suggested Reading)

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Dynamic equilibrium in blood stream

- Hemoglobin protein (Hb) found in red blood cells reacts with $O_2$
  - enhances the amount of $O_2$ that can be carried through the bloodstream

  $$Hb + O_2 \rightleftharpoons HbO_2$$

  - The Hb represents the entire protein—it is not a chemical formula.
  - The $\rightleftharpoons$ represents that the reaction is in dynamic equilibrium.
Hemoglobin Equilibrium System

\[ \text{Hb} + \text{O}_2 \rightleftharpoons \text{HbO}_2 \]

- The concentrations of Hb, O\textsubscript{2}, and HbO\textsubscript{2} are all interdependent.
- The relative amounts of Hb, O\textsubscript{2}, and HbO\textsubscript{2} at equilibrium are related to a constant called the \textit{equilibrium constant}, \( K \).
  - The larger the value of \( K \), the more product is found at equilibrium.

In the lungs, with high concentration of O\textsubscript{2}, the equilibrium shifts to combine the Hb and O\textsubscript{2} together to make more HbO\textsubscript{2}.

In the cells, with low concentration of O\textsubscript{2}, the equilibrium shifts to break down the HbO\textsubscript{2} and increase the amount of free O\textsubscript{2}.

dynamic equilibrium in blood stream
Fetal Hemoglobin, HbF

\[ \text{HbF} + \text{O}_2 \rightleftharpoons \text{HbFO}_2 \]

- Fetal hemoglobin's equilibrium constant (\(K_F\)) is larger than adult hemoglobin (\(K_A\)).
- Because fetal hemoglobin is more efficient at binding \(\text{O}_2\), \(\text{O}_2\) is transferred to the fetal hemoglobin from the mother's hemoglobin in the placenta.

Dynamic equilibrium

**Equilibrium**

*The state reached by a reaction where the forward and reverse rates are equal.*

- When a reaction mixture reaches equilibrium there is no change in it's composition although the forward and reverse reactions are occurring (dynamic equilibrium).
- To show that a reaction involves equilibrium we place a double arrow (\(\rightleftharpoons\)) between the reactants and products in the chemical equation:

\[ \text{REACTANTS} \rightleftharpoons \text{PRODUCTS} \]
At time 32, there are now more products than reactants in the mixture—the forward reaction has slowed down as the reactants run out, and the reverse reaction accelerated.

\[ [\text{H}_2] = 4, \ [\text{I}_2] = 4, \ [\text{HI}] = 8 \]

At time 48, the amounts of products and reactants in the mixture haven’t changed—the forward and reverse reactions are proceeding at the same rate. It has reached dynamic equilibrium.

\[ [\text{H}_2] = 4, \ [\text{I}_2] = 4, \ [\text{HI}] = 8 \]
Reaching Equilibrium

• The rates of the forward and reverse reactions are equal at equilibrium.
• However, that does not mean the concentrations of reactants and products are equal.
• Some reactions reach equilibrium only after almost all the reactant molecules are consumed. We say the position of equilibrium favors the products.
• Other reactions reach equilibrium when only a small percentage of the reactant molecules are consumed. We say the position of equilibrium favors the reactants.

Equilibrium Constant (\(K\))

• The relationship between the chemical equation and the concentrations of reactants and products is called the Law of Mass Action.
• For the general equation \(\text{aA + bB} \rightleftharpoons \text{cC + dD}\)
  
  • the Law of Mass Action gives the relationship below.
  – The uppercase letters represent the coefficients of the balanced chemical equation.
  – always products over reactants
  
  • \(K\) is called the equilibrium constant.
    – unitless

\[
K = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]
Expressing Equilibrium Constants for Chemical Reactions

We can now represent the relationship between equilibrium and concentration for the reaction:

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

by an equilibrium expression:

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

Calculating Equilibrium Constants

Practice—
(a) When the reaction \(A(aq) \rightleftharpoons 2 B(aq)\) reaches equilibrium, \([A] = 1.0 \times 10^{-5}\) M and \([B] = 4.0 \times 10^{-1}\) M.

(b) When the reaction \(2 B(aq) \rightleftharpoons Z(aq)\) reaches equilibrium, \([B] = 4.0 \times 10^{-3}\) M and \([Z] = 2.0 \times 10^{-6}\) M.

Calculate the equilibrium constant for each of these reactions

\[
K_{rm1} = \frac{[B]^2}{[A]} = \frac{(4.0 \times 10^{-1})^2}{1.0 \times 10^{-5}} = 1.6 \times 10^4
\]

\[
K_{rm2} = \frac{[Z]}{[B]^2} = \frac{2.0 \times 10^{-6}}{(4.0 \times 10^{-3})^2} = 5.0 \times 10^{-1}
\]
Calculating Equilibrium Constants

**Problem 1**: Express the equilibrium constant for the following reactions:

(a) \( \text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightleftharpoons 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g}) \)

(b) \( 2 \text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \)

Equilibrium Constants for Chemical Reactions

**Problem 2**: The following equilibrium concentrations were measured at 800 K for the reaction:

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

\[ [\text{SO}_2] = 3.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \]
\[ [\text{O}_2] = 3.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \]
\[ [\text{SO}_3] = 5.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \]

Calculate the **equilibrium constant \( K \)** at 800 K.
The Significance of the Equilibrium Constant

If the equilibrium constant for a reaction is large, the equilibrium point of the reaction lies far to the right. That is, the concentration of products is large and the concentration of reactants is small.

\[ K = \frac{[HBr]^2}{[H_2][Br_2]} = \text{large number} \]

\[ K = 1.9 \times 10^{19} \text{ (at 25°C)} \]

If the equilibrium constant for a reaction is small, the equilibrium point of the reaction lies far to the left. That is, the concentration of products is small and the concentration of reactants is large.

\[ K = \frac{[NO]^2}{[N_2][O_2]} = \text{small number} \]

\[ K = 4.1 \times 10^{-31} \text{ (at 25°C)} \]
### The Significance of the Equilibrium Constant

If \( K \ll 1 \) (very small number) then the reverse reaction is favoured (the forward reaction does not proceed very far).

If \( K \gg 1 \) (very large number) then the forward reaction is favoured (the forward reaction will proceed essentially to completion).

If \( K \approx 1 \) then neither the forward, nor the reverse reaction is favoured. You may think of this as the forward reaction proceeding half-way.

### Manipulating Equilibrium Equations

- **If a chemical equation is modified in some way, \( K \) for the equation must be changed** to reflect the modification.

- **Three common modifications** are:
  1) If you **reverse the equation**, invert the equilibrium constant.
  2) If you **multiply the coefficients** in an equation by a factor, raise the equilibrium constant to the same factor.
  3) If you **add two or more individual chemical equations** to obtain an overall equation, multiply the corresponding equilibrium constants by each other to obtain the overall equilibrium constant.
Manipulating Equilibrium Equations

1) When the reaction is written backwards, $K$ is inverted.

For the reaction $aA + bB \rightleftharpoons cC + dD$
the equilibrium constant expression is:

$$K_{\text{forward}} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

For the reaction $cC + dD \rightleftharpoons aA + bB$
the equilibrium constant expression is:

$$K_{\text{backward}} = \frac{[A]^a \times [B]^b}{[C]^c \times [D]^d}$$

$$\therefore K_{\text{backward}} = \frac{1}{K_{\text{forward}}}$$

Manipulating Equilibrium Equations

2) When the coefficients of an equation are multiplied by a factor, $K$ is raised to that factor.

For the reaction $aA + bB \rightleftharpoons cC$
The equilibrium constant expression is:

$$K_{\text{original}} = \frac{[C]^c}{[A]^a \times [B]^b}$$

For the reaction $2aA + 2bB \rightleftharpoons 2cC$
The equilibrium constant expression is:

$$K_{\text{new}} = \frac{[C]^{2c}}{[A]^{2a} \times [B]^{2b}}$$

$$= \left( \frac{[C]^c}{[A]^a \times [B]^b} \right)^2$$

$$\therefore K_{\text{new}} = K_{\text{original}}$$
Manipulating Equilibrium Equations

3) When you **add equations to get a new equation**, $K$ of the new equation is the product of the equilibrium constants of the old equations.

For the reactions (1) $aA = bB$ and (2) $bB = cC$ the equilibrium constant expressions are:

\[
K_1 = \frac{[B]^p}{[A]^p} \\
K_2 = \frac{[C]^p}{[B]^p}
\]

For the reaction $aA = cC$ ($= \text{sum of 1 + 2}$)

the equilibrium constant expression is:

\[
K_{\text{new}} = \frac{[C]^p}{[A]^p} = \frac{[B]^p}{[A]^p} \times \frac{[C]^p}{[B]^p}
\]

\[\therefore K_{\text{new}} = K_1 \times K_2\]

---

**Problem 3:** Compute the equilibrium constant at 25 °C for the reaction $\text{NH}_3(g) \rightleftharpoons 0.5 \text{N}_2(g) + 1.5 \text{H}_2(g)$

**GIVEN:** $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g), K = 3.7 \times 10^8$ at 25 °C

**Solution:**

\[
\begin{align*}
K_1 &= 3.7 \times 10^8 \\
K_2 &= \frac{1}{K_1} = \frac{1}{3.7 \times 10^8} \\
K' &= (K_2)^{1/2} = \left(\frac{1}{3.7 \times 10^8}\right)^{1/2} \\
K' &= 5.2 \times 10^{-5}
\end{align*}
\]
Problem 4: Consider the following equations and equilibrium constants. Determine the value of the unknown equilibrium constants.

(a) \[2 \text{CO}_2(g) \rightleftharpoons \text{CO}_2(g) + \text{CF}_4(g) \quad K = 2.2 \times 10^6\]
\[2 \text{CO}_2(g) + 2 \text{CF}_4(g) = 4 \text{COF}_2(g) \quad K_{\text{new}} = ?\]

(b) \[\text{CO}_2(g) + 3 \text{H}_2(g) = \text{CH}_3\text{OH}(g) + \text{H}_2\text{O}(g) \quad K_1 = ?\]
\[\text{CO}(g) + \text{H}_2\text{O}(g) = \text{CO}_2(g) + \text{H}_2(g) \quad K_2 = 1.0 \times 10^5\]
\[\text{CO}(g) + 2\text{H}_2(g) = \text{CH}_3\text{OH}(g) \quad K_3 = 1.4 \times 10^7\]

Expressing the Equilibrium Constant in Terms of Pressure

The concentration of a gas in a mixture is proportional to its partial pressure. \([A] \propto P_A\)

- Therefore, the equilibrium constant can be expressed as the ratio of the partial pressures of the gases.
- For \(aA(g) + bB(g) = cC(g) + dD(g)\) the equilibrium constant can be expressed as \(K_c\) or \(K_p:\)

\[K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}\] or \[K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}\]

\([A]\) = concentration of A (mol/L), etc……
\(P_A = \) partial pressure of A (atm), etc…..
Expressing the Equilibrium Constant in Terms of Pressure

- In calculating $K_p$, the partial pressures are *always in atm*.

- The values of $K_p$ and $K_c$ are not necessarily the same
  - because of the difference in units
  - $K_p = K_c$ only when $\Delta n = 0$

- The relationship between them is:

$$K_p = K_c \times (RT)^{\Delta n}$$

Where $R = 0.08206 \text{ atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

$\Delta n$ is the difference between the number of moles of products - moles of reactants. $(n_{\text{products}} - n_{\text{reactants}})$

For the reaction:

$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$\Delta n = (c+d) - (a+b)$

---

Expressing the Equilibrium Constant in Terms of Pressure

- **Problem 5:**
  
  (a) Find $K_c$ for the reaction
  
  $2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g)$
  
  given $K_p = 2.2 \times 10^{12} \text{ at } 25 \degree \text{C}$.

  (b) Find $K_p$ for the reaction
  
  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$
  
  given $K_c = 6.2 \times 10^2 \text{ at } 25 \degree \text{C}$

---
Heterogeneous Equilibria: Reactions Involving Solids and Liquids

Note: Equilibrium constant expressions do not contain concentration terms for solid or liquid phases.

- Why? Because the concentration of a solid or liquid does not change during the course of a reaction.

- For the reaction:
  - \( aA(s) + bB(aq) \rightleftharpoons cC(l) + dD(aq) \)

  \[
  K_c = \frac{[D]^d}{[B]^b} \]

  A and C are not part of the equilibrium.

Heterogeneous Equilibria: Reactions Involving Solids and Liquids

The equilibrium position is independent of the amount of C (s) present.
Heterogeneous Equilibria: Reactions Involving Solids and Liquids

Problem 6:
Write the $K_c$ expression for the following:

(a) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

(b) $CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

Calculating the Equilibrium Constant from Measured Equilibrium Concentrations

The most direct way of finding the equilibrium constant is to measure the amounts of reactants and products in a mixture at equilibrium.

The equilibrium mixture may have different amounts of reactants and products, but the value of the equilibrium constant will always be the same.

See next Table that shows this.

The value of the equilibrium constant is independent of the initial amounts of reactants and products.
Calculating the Equilibrium Constant from Measured Equilibrium Concentrations

**Stoichiometry** can be used to determine the equilibrium concentrations of all reactants and products if you know initial concentrations and one equilibrium concentration.

**Suppose** you have a reaction \(2 \text{A(aq)} + \text{B(aq)} \rightleftharpoons 4 \text{C(aq)}\) with initial concentrations \([\text{A}] = 1.00 \text{ M}, [\text{B}] = 1.00 \text{ M},\) and \([\text{C}] = 0\). You then measure the equilibrium concentration of C as \([\text{C}] = 0.50 \text{ M}\).

This allows you to calculate A and B.
Calculating the **Equilibrium Constant** from Measured Equilibrium Concentrations

- This type of table is referred to as an **ICE** table
  \( \text{I} = \text{initial}, \text{C} = \text{change}, \text{E} = \text{equilibrium} \)

### Calculating the **Equilibrium Constant** from Measured Equilibrium Concentrations

**Example 14.6** Find the value of \( K_c \) for the reaction

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

at 1700 °C if the initial \([\text{CH}_4] = 0.115 \text{ M}\) and the equilibrium \([\text{C}_2\text{H}_2] = 0.035 \text{ M}\).

1) Construct an ICE table for the reaction.

<table>
<thead>
<tr>
<th></th>
<th>([\text{CH}_4])</th>
<th>([\text{C}_2\text{H}_2])</th>
<th>([\text{H}_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.115</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>change</td>
<td></td>
<td>+0.035</td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td></td>
<td>0.035</td>
<td></td>
</tr>
</tbody>
</table>
Calculating the **Equilibrium Constant** from Measured Equilibrium Concentrations

3) Use the known change to determine the change in the other materials.

4) Add the change to the initial concentration to get the equilibrium concentration in each column.

5) Use the equil. concentrations to calculate $K_c$.

<table>
<thead>
<tr>
<th></th>
<th>[CH$_4$]</th>
<th>[C$_2$H$_2$]</th>
<th>[H$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.115</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>change $\Delta$</td>
<td>$-2(0.035)$</td>
<td>$+0.035$</td>
<td>$+3(0.035)$</td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.045</td>
<td>0.035</td>
<td>0.105</td>
</tr>
</tbody>
</table>

$$K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} = \frac{(0.035)(0.105)^3}{(0.045)^2} = 0.020$$

**Problem 7:**

(a) Initially, $[CO] = 0.500$ M, $[H_2] = 1.00$ M, and the equilibrium $[CO] = 0.15$ M.

What is the value of $K$?

$CO(g) + 2 H_2(g) \rightleftharpoons CH_3OH(g)$

(b) Determine the equilibrium constant for the following reaction:

---initial $[SO_2Cl_2] = 0.020$ M, and the equilibrium $[Cl_2] = 1.2 \times 10^{-2}$ M.

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$
The Reaction Quotient: Predicting the Direction of Change

If a reaction is not at equilibrium we can predict the direction of the net reaction; that is, if the net reaction must proceed toward to reactants or products in order to establish equilibrium.

**Reaction Quotient (Q):** concentration ratio of the products (raised to the power of their coefficients) divided by the reactants (raised to the power of their coefficients)

\[
Q_c = \frac{[C]^r \times [D]^s}{[A]^t \times [B]^u}
\]

\[
Q_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}
\]

Very similar calculations to \( K_c \) and \( K_p \)

For the gas phase reaction \( aA + bB \leftrightarrow cC + dD \)
the reaction quotient is:

If \( Q_c = K_c \), then the reaction is at equilibrium.

If \( Q_c < K_c \), the net reaction proceeds from left to right (the forward reaction).

If \( Q_c > K_c \), the net reaction proceeds from right to left (the reverse reaction).
The Reaction Quotient: Predicting the Direction of Change

Determine if the reactions are at equilibrium, and if not, in which direction with the reaction proceed?

\[ \text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2 \text{HI} (g) \quad K_c = 57.0 \text{ at } 700 \text{ K} \]

If \([\text{H}_2]_t = 0.80 \text{ mol/L},\)

\([\text{I}_2]_t = 0.25 \text{ mol/L}, \text{ and} \]

\([\text{HI}]_t = 10.0 \text{ mol/L}\)

Answer next slide
The Reaction Quotient: Predicting the Direction of Change

\[ \text{H}_2 (g) + \text{I}_2 (g) \leftrightarrow 2 \text{HI} (g) \quad K_c = 57.0 \]

\[ Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(10.0)^2}{(0.80)(0.25)} = 500 \]

\( Q_c \neq K_c \), so the system is not at equilibrium.

\( Q_c > K_c \), the reaction will proceed from right to left.

---

The Reaction Quotient: Predicting the Direction of Change

**Problem 8:** Consider the following reactions and their equilibrium constants. Determine if the reactions are at equilibrium, and if not, in which direction will the reaction proceed?

(a) \( \text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g) \quad K_p = 81.9 \)

Reaction mixture contains: P (I\(_2\)) = 0.114 atm
P (Cl\(_2\)) = 0.102 atm, P (ICl) = 0.355 atm

(b) \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \quad K_c = 5.85 \times 10^{-3} \)

Reaction mixture contains: \([\text{NO}_2] = 0.0255 \, \text{M}\)
\([\text{N}_2\text{O}_4] = 0.0331 \, \text{M}\)
Finding Equilibrium Concentrations

• Finding Equilibrium Concentrations When You Are Given the Equilibrium Constant and All but One of the Equilibrium concentrations of the Reactants and Products

A sample of PCl₅(g) is placed in a 0.500-L container and heated to 160 °C. The PCl₅ is decomposed into PCl₃(g) and Cl₂(g). At equilibrium, 0.203 moles of PCl₃ and Cl₂ are formed. Determine the equilibrium concentration of PCl₅ if $K_c = 0.0635$

\[
\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2
\]

<table>
<thead>
<tr>
<th>equilibrium concentration, M</th>
<th>?</th>
<th>0.203 mol</th>
<th>0.203 mol</th>
<th>0.500 L</th>
<th>0.500 L</th>
</tr>
</thead>
</table>

\[
K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}
\]

\[
[\text{PCl}_5] = \frac{[\text{PCl}_3][\text{Cl}_2]}{K_c} = \frac{(0.406)(0.406)}{0.0635}
\]

\[
[\text{PCl}_5] = 2.60 \text{ M}
\]

Finding Equilibrium Concentrations

Problem 9:
Diatomic iodine (I₂) decomposes at high temperatures to form I atoms according to the reaction:

\[
\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)
\]

$K_c = 0.0110$ at 1,200 °C

In an equilibrium mixture, the concentration of I₂ is 0.0100 M. What is the equilibrium concentration of I?
• Most commonly, we know our initial concentrations, and the equilibrium constant ($K_c$), and want to determine our equilibrium concentrations.

Consider the reaction:

$$A(g) \rightleftharpoons 2 \text{B}(g) \quad K = 0.33$$

The initial concentration of $A = 1.0\text{ M}$.

Our ICE table will take the following form:

<table>
<thead>
<tr>
<th></th>
<th>$[A]$</th>
<th>$[B]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.0</td>
<td>0.00</td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+2x$</td>
</tr>
<tr>
<td>Equil</td>
<td>$1.0-x$</td>
<td>$2x$</td>
</tr>
</tbody>
</table>

Represent changes from initial conditions with the variable $x$.

Using the coefficient from the chemical equation for the coefficient of $x$.

$$K = \frac{[B]^2}{[A]} = 0.33$$

$$4x^2 = 0.33 \quad \rightarrow \quad \text{A quadratic equation! (Solve for $x$)}$$

We will learn how to do this later.
Steps in Finding Equilibrium Concentrations (the harder question)

1) decide which direction the reaction will proceed.
   – compare $Q$ to $K$

2) Define the changes of all materials in terms of $x$.
   – Use the coefficient from the chemical equation for the coefficient of $x$.
   – The $x$ change is (+) for materials on the side the reaction is proceeding toward.
   – The $x$ change is (-) for materials on the side the reaction is proceeding away from.

- For some calculations of $x$ you need to use:

\[
0 = ax^2 + bx + c;
\]
\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a};
\]

This will give two Answers for $x$; we are only interested in positive values for Equil. concentrations

Finding Equilibrium Concentrations

Problem:

\[
C(s) + H_2O (g) \rightleftharpoons CO (g) + H_2 (g)
\]

$K_p$ is 2.44

What are the equilibrium partial pressures of $H_2O$, $CO$, and $H_2$ if the initial partial pressures are $P_{H_2O} = 1.20$ atm, $P_{CO} = 1.00$ atm, and $P_{H_2} = 1.40$ atm?

Step 1) Use the initial concentrations to calculate the reaction quotient ($Q$) for the initial concentrations. Compare $Q$ to $K$ and predict the direction in which the reaction will proceed.

\[
Q_p = \frac{P_{CO}P_{H_2}}{P_{H_2O}^2} = \frac{(1.00)(1.40)}{(1.20)^2} = 1.17
\]

$Q_p < K_p$

Reaction proceeds to right
Finding Equilibrium Concentrations

**Step 2)** Set up an ICE table. Represent the change in the concentration of one of the reactants or products with the variable $x$. Define the changes in the concentrations of the other reactants or products in terms of $x$.

<table>
<thead>
<tr>
<th>(all in atm)</th>
<th>C(s)</th>
<th>$+$</th>
<th>H$_2$O (g)</th>
<th>$\rightleftharpoons$</th>
<th>CO (g)</th>
<th>$+$</th>
<th>H$_2$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial press.</td>
<td>N/A</td>
<td>1.20</td>
<td>1.00</td>
<td>1.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Press. change</td>
<td>N/A</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equil. press.</td>
<td>N/A</td>
<td>1.20$-x$</td>
<td>1.00$+x$</td>
<td>1.40$+x$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$K_p = \frac{P_{CO}}{P_{H_2O}}$$ at 1000K

so $$2.44 = \frac{(1.00+x)(1.40+x)}{(1.20-x)}$$

---

Finding Equilibrium Concentrations

**Step 3) Do the Math!**

Rearranging, we get

$$2.44(1.20-x) - [(1.00+x)(1.40+x)] = 0$$

$$[2.928-2.44x] - [1.40+2.40x+x^2] = 0$$

$$1.528-4.84x-x^2 = 0$$

This is a **quadratic equation** of the form

$$ax^2 + bx + c = 0$$

which has solutions given by
Finding Equilibrium Concentrations

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

so

\[ x = \frac{(-4.84) \pm \sqrt{(-4.84)^2 - 4(-1.00)(1.528)}}{2(-1.00)} \]

\[ x = \frac{(-4.84) + \sqrt{(-4.84)^2 - 4(-1.00)(1.528)}}{2(-1.00)} \quad \text{or} \quad x = \frac{(-4.84) - \sqrt{(-4.84)^2 - 4(-1.00)(1.528)}}{2(-1.00)} \]

\[ x = \frac{4.84 + \sqrt{29.538}}{-2.00} \quad \text{or} \quad x = \frac{4.84 - \sqrt{29.538}}{-2.00} \]

\[ x = 10.27 \quad \text{or} \quad x = -5.95 \]

so \( x = -5.14 \) atm or \( x = 0.30 \) atm

Finding Equilibrium Concentrations

**Step 4** Calculate the equilibrium pressures

\[ x = -5.14 \text{ atm or } x = 0.30 \text{ atm} \]  
*(which one!)*

Our equilibrium partial pressures must all be positive.

Select \( x = 0.30 \text{ atm at equilibrium} \)

\[ P_{H_2O} = (1.20 \text{ atm} - 0.30 \text{ atm}) = 0.90 \text{ atm}, \]
\[ P_{CO} = (1.00 \text{ atm} + 0.30 \text{ atm}) = 1.30 \text{ atm}, \]
\[ P_{H_2} = (1.40 \text{ atm} + 0.30 \text{ atm}) = 1.70 \text{ atm}. \]

All these equilibrium pressures are physically real. This is the correct equilibrium mixture!
Finding Equilibrium Concentrations

**Step 5)** We should check our answer:

\[
K_p = \frac{(P_{CO})(P_{H_2})}{(P_{H_2O})} = \frac{(1.30)(1.70)}{(0.90)} = 2.46
\]

which is the equilibrium constant we were given, within rounding errors.

Finding Equilibrium Concentrations

**Problem 10**: Consider the following reaction:

\[
N_2 (g) + O_2 (g) \rightleftharpoons 2 NO (g) \quad K_c = 0.10 \text{ (at 2000°C)}
\]

A reaction mixture (at 2000 °C) initially contains \([N_2] = 0.200 \text{ M}\) and \([O_2] = 0.200 \text{ M}\).

Find the equilibrium concentrations of the reactants and products at this temperature.

**Hint when calculating \([ \text{______} ]_{\text{equilibrium}}\)**: In this problem you can take the square root of both sides of the expression to solve for \(x\).
2) In other cases you need to use the quadratic equation (as in previous examples).
3) Except when $K$ is very small (next section) and you do an approximation.

Finding Equilibrium Concentrations

With Small Equilibrium Constants

- When the equilibrium constant is very small, the position of equilibrium favours the reactants.
- For relatively large initial concentrations of reactants, the reactant concentration will not change significantly when it reaches equilibrium.

\[ A_{\text{equilibrium}} = (A_{\text{initial}} - ax) \approx A_{\text{initial}} \]

We are approximating the equilibrium concentration of reactant to be the same as the initial concentration.

Finding Equilibrium Concentrations

With Small Equilibrium Constant

- We can check our approximation afterwards by comparing the approximate value of $x$ to the initial concentration.

- If the approximate value of $x$ is less than 5% of the initial concentration, the approximation is valid.

\[ \text{If } \frac{\text{approximate } x}{\text{initial concentration}} \times 100\% < 5\% \text{ the approximation is valid} \]
Practice: \( I_2(g) \rightleftharpoons 2 I(g) \)

With Small Equilibrium Constant

\[ K_c = 3.76 \times 10^{-5} \text{ at } 1000 \text{ K} \]

If 1.00 mole of \( I_2 \) is placed into a 2.00-L flask and heated, what will be the equilibrium concentrations of \([I_2] \) and \([I] \)?

<table>
<thead>
<tr>
<th></th>
<th>([I_2])</th>
<th>([I])</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.500</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>(-x)</td>
<td>+2x</td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.500-x</td>
<td>2x</td>
</tr>
</tbody>
</table>

Since \([I]_{\text{initial}} = 0\), \(Q = 0\) and the reaction must proceed forward.

\[ K_c = \frac{[I]^2}{[I_2]} \]

\[ 3.76 \times 10^{-5} = \frac{(2x)^2}{(0.500-x)(0.500)} \]

\[ 3.76 \times 10^{-5} \times 0.500 = 4x^2 \]

\[ x = 2.17 \times 10^{-3} \]

The approximation is valid!!
Find the equilibrium concentrations of $H_2$ and $S_2$. 

**Step 6** Calculate equilibrium concentrations

<table>
<thead>
<tr>
<th></th>
<th>$[I_2]$</th>
<th>$[I]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.500</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>$-x$</td>
<td>$+2x$</td>
</tr>
<tr>
<td>equilibrium</td>
<td>$0.500-x$</td>
<td>$2x$</td>
</tr>
</tbody>
</table>

$x = 0.00217$

$0.500 - 0.00217 = 0.498$

$[I_2] = 0.498 \text{ M}$

$2(0.00217) = 0.00434$

$[I] = 0.00434 \text{ M}$

**Step 7** Check

$K_c = \frac{[I]^2}{[I_2]} = \frac{(0.00434)^2}{(0.498)} = 3.78 \times 10^{-5}$

---

**Finding Equilibrium Concentrations**

**Problem 11** Finding Equilibrium Concentrations from Initial Concentrations

Consider the following reaction for the decomposition of hydrogen disulfide:

$$2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g) \quad @ \ 800 \ ^\circ \text{C}, \ K_c = 1.67 \times 10^{-7}$$

A 0.500-L reaction vessel initially contains 0.0125 mol of $\text{H}_2\text{S}$ at 800 °C. Find the equilibrium concentrations of $\text{H}_2$ and $\text{S}_2$. 

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Chem 1011 Winter 2012  R. Helleur
Le Chatelier’s Principle: How a System at Equilibrium Responds to Disturbances

• Le Chatelier's Principle states:

When an equilibrium system is subjected to a change in temperature, pressure or concentration of a reacting species, the system responds by attaining a new equilibrium that partially offsets the impact of the change.

The effect of a concentration change on equilibrium

• Increasing the concentration of a reacting species will shift the equilibrium in the opposite direction.

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

• Increasing the concentration of either $\text{SO}_2(g)$ or $\text{O}_2(g)$ will favour the forward reaction.
• Increasing the concentration of $\text{SO}_3(g)$ will favour the reverse reaction.
• Decreasing the concentration of either $\text{SO}_2 (g)$ or $\text{O}_2(g)$ will favour the reverse reaction.
• Decreasing the concentration of $\text{SO}_3(g)$ will favour the forward reaction.
The effect of a concentration change on equilibrium

Which way will the equilibrium below shift if we decrease the concentration of CH₄?

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

The equilibrium will shift to the products side to replace the lost CH₄.

Which way will the following equilibrium shift if we add Carbon?

\[
\text{C(s) + S}_2\text{(g)} \rightleftharpoons \text{CS}_2\text{(g)}
\]

Since carbon is a solid, adding it to the equilibrium mixture will have no effect.

The effect of a volume or pressure change

The pressure of a reaction system can be changed by:

1. **Add or remove a gaseous reactant**
   - This has the same effect as increasing or decreasing the pressure, (increasing or decreasing concentration).

2. **Add an inert gas to the constant-volume reaction mixture.**
   - This has the effect of increasing the total pressure of the system. It will not change the equilibrium position.

3. **Change the pressure by changing the volume of the system.**
   - When the volume of an equilibrium mixture of gases is reduced a net reaction occurs in the direction producing the fewer moles of gases.
   - When the volume is increased a net reaction occurs in the direction producing more moles of gases.
The effect of a volume or pressure change

In what direction will the equilibrium below shift if we increase the total pressure by adding helium gas?

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

**Answer:** Adding helium will not cause the partial pressures of any of the gases in the equilibrium mixture to change, therefore, it will have *no effect* (no shift will occur).
Problem 12
An equilibrium mixture of N$_2$(g), H$_2$(g), and NH$_3$(g) is transferred from a 1.50 L flask to a 5.00 L flask.
In which direction does a net reaction occur to restore equilibrium?
N$_2$(g) + 3 H$_2$(g) $\rightleftharpoons$ 2 NH$_3$(g)

Problem 13
Indicate whether an increase or decrease in pressure (by changing volume) would result in more products being formed in the following reactions:
1) CO(g) + 2 H$_2$(g) $\rightleftharpoons$ CH$_3$OH(g)
2) FeO(s) + CO(g) $\rightleftharpoons$ Fe(s) + CO$_2$(g)
3) N$_2$O$_4$(g) $\rightleftharpoons$ 2 NO$_2$(g)
The effect of a temperature change

- When considering this change we have to know if the equilibrium reaction is **endothermic** or **exothermic**.
- When temperature is lowered the equilibrium will shift so that heat is produced.
- When temperature is raised the equilibrium will shift so that the added heat is used up.

The effect of a temperature change

- In Chem. 1010 we learned about endothermic and exothermic reactions.
  - In an **endothermic** reaction heat is absorbed and acts like a **reactant**
    \[
    \text{REACTANTS} + \text{HEAT} \rightleftharpoons \text{PRODUCTS}
    \]
- In an **exothermic** reaction heat is given off and acts like a **product**
  \[
  \text{REACTANTS} \rightleftharpoons \text{PRODUCTS} + \text{HEAT}
  \]
The effect of a temperature change

- **Problem 14**
  Methanol is prepared industrially from synthesis gas (CO and H₂)
  \[ \text{CO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \quad \Delta H^0 = -21.7 \text{ kcal} \]

  Would the fraction of methanol obtained at equilibrium be increased by raising the temperature? Explain.

Problem 15—Le Châtelier’s Principle

- The reaction \( 2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \) with \( \Delta H^0 = -198 \text{ kJ} \) is at equilibrium. How will each of the following changes affect the equilibrium concentrations of each gas once equilibrium is re-established?
  - adding more \( \text{O}_2 \) to the container?
  - condensing and removing \( \text{SO}_3 \)?
  - compressing the gases?
  - cooling the container?
  - doubling the volume of the container?
  - warming the mixture?
  - adding the inert gas helium to the container?
  - adding a catalyst to the mixture?