Attention Online Users

- The font used to create the double arrows used in chemical equations to designate an equilibrium cannot be imbedded in an Acrobat document. Acrobat substitutes a comma or similar funny character wherever there should be double arrows.
- Keep tuned—we’ll try to solve the problem.

Properties of an Equilibrium

Equilibrium systems are

- DYNAMIC (in constant motion)
- REVERSIBLE
- can be approached from either direction

Pink to blue
Co(H\textsubscript{2}O\textsubscript{6})\textsubscript{2+}Cl\textsubscript{2} \rightarrow Co(H\textsubscript{2}O\textsubscript{4})Cl\textsubscript{2} + 2 H\textsubscript{2}O

Blue to pink
Co(H\textsubscript{2}O\textsubscript{4})Cl\textsubscript{2} + 2 H\textsubscript{2}O \rightarrow Co(H\textsubscript{2}O\textsubscript{6})\textsubscript{2+}Cl\textsubscript{2}

Examples of Chemical Equilibria

Phase changes such as
H\textsubscript{2}O(s) \rightleftharpoons H\textsubscript{2}O(liq)

Chemical Equilibrium

Fe\textsuperscript{3+} + SCN\textsuperscript{-} \rightleftharpoons FeSCN\textsuperscript{2+}

Fe(H\textsubscript{2}O\textsubscript{6})\textsuperscript{3+} + SCN\textsuperscript{-} \rightleftharpoons Fe(SCN)(H\textsubscript{2}O\textsubscript{5})\textsuperscript{3+} + H\textsubscript{2}O

- After a period of time, the concentrations of reactants and products are constant.
- The forward and reverse reactions continue after equilibrium is attained.
Examples of Chemical Equilibria

Formation of stalactites and stalagmites

\[ \text{CaCO}_3(s) + \text{H}_2\text{O(liq)} + \text{CO}_2(g) \rightarrow \text{Ca}^{2+}(aq) + 2 \text{HCO}_3^-(aq) \]

Chemical Equilibria

At a given T and P of CO\(_2\), [Ca\(^{2+}\)] and [HCO\(_3^-\)] can be found from the EQUILIBRIUM CONSTANT.

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**THE EQUILIBRIUM CONSTANT**

For any type of chemical equilibrium of the type

\[ a \text{ A} + b \text{ B} \rightarrow c \text{ C} + d \text{ D} \]

the following is a CONSTANT (at a given T)

\[ K = \frac{[	ext{C}]^c [	ext{D}]^d}{[	ext{A}]^a [	ext{B}]^b} \]

If K is known, then we can predict concs. of products or reactants.

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**Determining K**

Place 2.00 mol of NOCl in a 1.00 L flask. At equilibrium you find 0.66 mol/L of NO. Calculate K.

**Solution**

Set a table of concentrations

<table>
<thead>
<tr>
<th></th>
<th>[NOCl]</th>
<th>[NO]</th>
<th>[Cl(_2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>2.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-0.66</td>
<td>+0.66</td>
<td>+0.33</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.34</td>
<td>0.66</td>
<td>0.33</td>
</tr>
</tbody>
</table>

**K**

\[ K = \frac{[	ext{NO}]^2[	ext{Cl}_2]}{[	ext{NOCl}]^2} = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080 \]
Writing and Manipulating K Expressions

Solids and liquids NEVER appear in equilibrium expressions.

- \( S(s) + O_2(g) \ \rightarrow SO_2(g) \)

**The Meaning of K**

1. Can tell if a reaction is product-favored or reactant-favored.

For \( N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g) \)

\[
K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 3.5 \times 10^5
\]

Conc. of products is much greater than that of reactants at equilibrium.

The reaction is strongly product-favored.

For \( AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \)

\[ K_c = [Ag^+][Cl^-] = 1.8 \times 10^{-5} \]

Conc. of products is much less than that of reactants at equilibrium.

The reaction is strongly reactant-favored.
The Meaning of K

2. Can tell if a reaction is at equilibrium. If not, which way it moves to approach equilibrium.

\[
\begin{align*}
\text{n-butane} & \quad \text{iso-butane} \\
\text{H}_2\text{C} & \text{C} & \text{C} & \text{C} & \text{H} \\
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{H} & \text{C} & \text{H} & \text{H} & \text{H} \\
\end{align*}
\]

\[K = \frac{[\text{iso}]}{[\text{n}]} = 2.5\]

If \([\text{iso}] = 0.35 \text{ M} \) and \([\text{n}] = 0.15 \text{ M}\), are you at equilibrium? If not, which way does the reaction “shift” to approach equilibrium?

See Screen 16.9

In general, all reacting chemical systems are characterized by their REACTION QUOTIENT, \(Q\).

\[Q = \frac{\text{product concentrations}}{\text{reactant concentrations}}\]

If \(Q = K\), then system is at equilibrium.

\(Q (2.3) < K (2.5)\). Reaction is NOT at equilibrium, so \([\text{iso}]\) must become _____ and \([\text{n}]\) must become _____.

Typical Calculations

PROBLEM: Place 1.00 mol each of \(\text{H}_2\) and \(\text{I}_2\) in a 1.00 L flask. Calc. equilibrium concentrations.

\[
\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g), K_c = 55.3
\]

Step 1. Set up table to define EQUILIBRIUM concentrations.

\[
\begin{array}{ccc}
\text{[H}_2]\quad & \text{[I}_2]\quad & \text{[HI]} \\
\text{Initial} & 1.00 & 1.00 \\
\text{Change} & & 0 \\
\text{Equilib} & & \\
\end{array}
\]

\[K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 55.3\]
\[ H_2(g) + I_2(g) \rightarrow 2 HI(g), \ K_c = 55.3 \]

Step 1. Set up table to define EQUILIBRIUM concentrations.

<table>
<thead>
<tr>
<th></th>
<th>[H_2]</th>
<th>[I_2]</th>
<th>[HI]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.00</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-x</td>
<td>+2x</td>
</tr>
<tr>
<td>Equilib</td>
<td>1.00-x</td>
<td>1.00-x</td>
<td>2x</td>
</tr>
</tbody>
</table>

where \(x\) is defined as am’t of \(H_2\) and \(I_2\) consumed on approaching equilibrium.

\[ H_2(g) + I_2(g) \rightarrow 2 HI(g), \ K_c = 55.3 \]

Step 2. Put equilibrium concentrations into \(K_c\) expression.

\[ K_c = \frac{[2x]^2}{[1.00-x][1.00-x]} = 55.3 \]

\[ 7.44 = \frac{2x}{1.00-x} \]

\[ x = 0.79 \]

Therefore, at equilibrium

\[ [H_2] = [I_2] = 1.00 - x = 0.21 \text{ M} \]

\[ [HI] = 2x = 1.58 \text{ M} \]

\[ [H_2O_4] = [NO_2] = 0.0059 \text{ at 298 K} \]

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

If initial concentration of \(N_2O_4\) is 0.50 M, what are the equilibrium concentrations?

Step 1. Set up an equilibrium table

<table>
<thead>
<tr>
<th></th>
<th>[N_2O_4]</th>
<th>[NO_2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.50</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+2x</td>
</tr>
<tr>
<td>Equilib</td>
<td>0.50 - x</td>
<td>2x</td>
</tr>
</tbody>
</table>
Nitrogen Dioxide Equilibrium

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

Step 2. Substitute into \( K_c \) expression and solve.

\[ K_c = 0.0059 = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \]

Rearrange:

\[ 0.0059 (0.50 - x) = 4x \]
\[ 0.0029 - 0.0059x = 4x \]
\[ 4x^2 + 0.0059x - 0.0029 = 0 \]

This is a QUADRATIC EQUATION

\[ ax^2 + bx + c = 0 \]
\[ a = 4 \quad b = 0.0059 \quad c = -0.0029 \]

Solve the quadratic equation for \( x \).

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]
\[ x = \frac{-0.0059 \pm \sqrt{(0.0059)^2 - 4(4)(-0.0029)}}{2(4)} \]
\[ x = -0.00074 \pm 0.027 \]
\[ x = 0.026 \quad \text{or} \quad -0.028 \]

But a negative value is not reasonable.

Conclusion

\[ [\text{N}_2\text{O}_4] = 0.050 - x = 0.47 \text{ M} \]
\[ [\text{NO}_2] = 2x = 0.052 \text{ M} \]