**Ch. 13: Chemical Equilibrium**

13.5/6: Applications of Equilibrium Constant (K)
13.7: Le' Chatlier's Principle

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**Equilibrium Constant**

- if we know the value of K, we can predict:
  - tendency of a reaction to occur
  - if a set of concentrations could be at equilibrium
  - equilibrium position, given initial concentrations
- If you start a reaction with only reactants:
  - concentration of reactants will decrease by a certain amount
  - concentration of products will increase by a same amount

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**Example 1**

- The following reaction has a K of 16. You are starting reaction with 9 O₃ molecules and 12 CO molecules.
- Find the amount of each species at equilibrium.

  \[ \text{O}_3(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{O}_2(g) \]

  \[ K = \frac{[\text{O}_2][\text{CO}_2]}{[\text{O}_3][\text{CO}]} = \frac{N_{\text{O}_2} \cdot N_{\text{CO}_2}}{N_{\text{O}_3} \cdot N_{\text{CO}}} = 16 \]

<table>
<thead>
<tr>
<th></th>
<th>\text{O}_3(g)</th>
<th>+</th>
<th>\text{CO}(g)</th>
<th>\rightarrow</th>
<th>\text{O}_2(g)</th>
<th>+</th>
<th>\text{CO}_2(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>E</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Initial | 1 | 9 | 12 | 0 | 0 |
| Change  | C | -x| -x| +x| +x|
| Equilibrium | E | 9-x| 12-x| x | x |

\[ K = \frac{(x) \cdot (x)}{(9-x) \cdot (12-x)} = 16 \]

\[ x^2 = 16x^2 - 336x + 1728 \]

\[ 0 = 15x^2 - 336x + 1728 \]

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**Example 1**

- 0 = 3(5x² - 112x + 576)
- 0 = 3(5x - 72)(x - 8)
- x = 8 OR 14.4

<table>
<thead>
<tr>
<th>\text{O}_3(g)</th>
<th>+</th>
<th>\text{CO}(g)</th>
<th>\rightarrow</th>
<th>\text{O}_2(g)</th>
<th>+</th>
<th>\text{CO}_2(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1</td>
<td>9</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>E</td>
<td>9-(8)</td>
<td>12-(8)</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

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**Extent of a Reaction**

- If K >> 1:
  - mostly products
  - goes essentially to completion
  - lies far to right
- If K<< 1:
  - mostly reactants
  - reaction is negligible
  - lies far to left

- Size of K and time needed to reach equilibrium are NOT related
- Size of K and time required is determined by reaction rate (Ea)
**Example 2**

- For the synthesis of ammonia at 500°C, the equilibrium constant is $6.0 \times 10^{-2}$. Predict the direction the system will shift to reach equilibrium in the following case:

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

  $$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 6.0 \times 10^{-2}$$

**Example 3**

- In the gas phase, dinitrogen tetroxide decomposes to gaseous nitrogen dioxide:

  $$N_2O_4(g) \rightarrow 2NO_2(g)$$

- Consider an experiment in which gaseous $N_2O_4$ was placed in a flask and allowed to reach equilibrium at a T where $K_p = 0.133$. At equilibrium, the pressure of $N_2O_4$ was found to be 2.71 atm. Calculate the equilibrium pressure of $NO_2$.

  $$K_p = \frac{P_{NO_2}}{P_{N_2O_4}} = 0.133$$

  $$P_{NO_2} = K_p \cdot P_{N_2O_4} = (0.133)(2.71) = 0.360$$

  $$P_{N_2O_4} = \sqrt{0.360} = 0.600$$

**Example 4**

- At a certain temperature a 1.00 L flask initially contained 0.298 mol $PCl_3(g)$ and 8.70x$10^{-3}$ mol $PCl_5(g)$. After the system had reached equilibrium, 2.00x$10^{-3}$ mol $Cl_2(g)$ was found in the flask.

  $$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

- Calculate the equilibrium concentrations of all the species and the value of $K$. 

<table>
<thead>
<tr>
<th>PCl$_3$(g)</th>
<th>PCl$_5$(g)</th>
<th>Cl$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.70x$10^{-3}$</td>
<td>0.298</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>8.70x$10^{-3}$x = 0.298 + x = 0.298 + 2.00x$10^{-3}$ = x = 2.00x$10^{-3}$</td>
<td>6.70x$10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>6.70x$10^{-3}$</td>
<td>8.96x$10^{-2}$</td>
</tr>
</tbody>
</table>

$$K = \frac{(0.300)(2.00x10^{-3})}{6.70x10^{-3}} = 8.96 \times 10^{-2}$$
Approximations

- If K is very small, we can assume that the change (x) is going to be negligible compared to the initial concentration of the substances.
- Can be used to cancel out when adding or subtracting from a "normal" sized number.
- To simplify algebra.

\[ K = \frac{(x)(2x)^2}{(1.0-2x)^2} \approx (x)(2x)^2 = 4x^3 \]

Example 5

2.0 mol NOCl in 2.0 L flask

<table>
<thead>
<tr>
<th>2NOCl(g) → 2NO(g) + Cl₂(g)</th>
</tr>
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<tbody>
<tr>
<td>I</td>
</tr>
<tr>
<td>C</td>
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<tr>
<td>E</td>
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1.6x10⁻⁵ = \frac{(x)(2x)^2}{(1.0-2x)^2} \approx \frac{(x)(2x)^2}{(1.0)^2} = 4x^3, \ x = 0.016

\[ [\text{NOCl}] = 1.0 \cdot (2 \times 0.016) = 0.97 \text{ M} = 1.0 \text{ M}, \]
\[ [\text{NO}] = 0.032 \text{ M}, [\text{Cl}_2] = 0.016 \text{ M} \]

Example 5

1.0 mol NOCl and 1.0 mol NO in 1.0 L flask

<table>
<thead>
<tr>
<th>2NOCl(g) → 2NO(g) + Cl₂(g)</th>
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<td>E</td>
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1.6x10⁻⁵ = \frac{(x)(1.0+2x)^2}{(1.0-2x)^2} \approx \frac{(x)(1.0)^2}{(1.0)^2} = x

\[ [\text{NOCl}] = 1.0 \cdot (2 \times 1.6 \times 10⁻⁵) = 0.999968 \text{ M} = 1.0 \text{ M}, \]
\[ [\text{NO}] = 1.00 + (2 \times 1.6 \times 10⁻⁵) = 1.0 \text{ M}, [\text{Cl}_2] = 1.6 \times 10⁻³ \text{ M} \]

Example 5

2.0 mol NOCl and 1.0 mol Cl₂ in 1.0 L flask

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<td>C</td>
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<tr>
<td>E</td>
</tr>
</tbody>
</table>

1.6x10⁻⁵ = \frac{(1.0+x)(2x)^2}{(2.0-2x)^3} \approx \frac{(1.0)(2x)^2}{(2.0)^3} = x², \ x = 0.0040

\[ [\text{NOCl}] = 2.0 \cdot (2 \times 4.0 \times 10⁻³) = 1.992 \text{ M} = 2.0 \text{ M}, \]
\[ [\text{Cl}_2] = 1.0 + 4.0 \times 10⁻³ = 1.0 \text{ M}, [\text{NO}] = 0.0080 \text{ M} \]

Le Châtelier’s Principle

- Can predict how certain changes or stresses put on a reaction will affect the position of equilibrium.
- Helps us determine which direction the reaction will progress in to achieve equilibrium again.
- System will shift away from the added component or towards a removed component.
Changing Concentration
- equilibrium position can change but not K
- system will shift away from the added component or towards a removed component
- Ex: \( N_2 + 3H_2 \rightarrow 2NH_3 \)
  - if more \( N_2 \) is added, then equilibrium position shifts to right (creates more products)
  - if some \( NH_3 \) is removed, then equilibrium position shifts to right (creates more products)

Adding Gas
- adding or removing gaseous reactant or product is same as changing concentration
- adding inert or uninvolved gas
  - increase the total pressure
  - doesn’t effect the equilibrium position

Changing the Volume
- only important in gaseous reactions
- decrease V
  - requires a decrease in # gas molecules
  - shifts towards the side of the reaction with less gas molecules
- increase V
  - requires an increase in # of gas molecules
  - shifts towards the side of the reaction with more gas molecules

Changing the Volume
- all other changes alter the concentrations at equilibrium but don’t actually change value of K
- value of K does change with temperature
- if energy is added, the reaction will shift in direction that consumes energy
- treat energy as a
  - reactant: for endothermic reactions
  - product: for exothermic reactions

energy + \( N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \)
- endo or exo?
  - \( \Delta H = 181 \text{ kJ} \)
  - endothermic
- increase temp
  - to right
- remove \( O_2 \)
  - to left

Change in Temperature
- as the temperature increases, does the reaction make more reactants or products?
- Must the reaction be endothermic or exothermic?
- as the pressure increases, does the reaction make more reactants or products? Why?
<table>
<thead>
<tr>
<th>Effect on $\text{H}_2$O$_2$(g)</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of NO$_2$(g)</td>
<td>Right</td>
</tr>
<tr>
<td>Addition of $\text{H}_2$O(g)</td>
<td>Left</td>
</tr>
<tr>
<td>Removal of NO$_2$(g)</td>
<td>Left</td>
</tr>
<tr>
<td>Addition of $\text{O}_2$(g)</td>
<td>Right</td>
</tr>
<tr>
<td>Decrease reaction volume</td>
<td>None</td>
</tr>
<tr>
<td>Increase reaction volume</td>
<td>Right</td>
</tr>
<tr>
<td>Decrease temperature</td>
<td>None</td>
</tr>
<tr>
<td>Increase temperature</td>
<td>Left</td>
</tr>
</tbody>
</table>