My, I look presidential today!

Le Châtelier’s Principle

When a stress is applied to a system at equilibrium, the system will adjust so as to counteract the effect of the stress.

- Henri Le Châtelier
- 1850-1936
- Studied mining engineering.
- Interested in glass and ceramics.

Le Châtelier's Principle

Stress Factors

1. Change in concentration of reactants or products
2. Change in volume or pressure (for gases)
3. Change in temperature
4. Addition of a catalyst
5. Addition of a common ion

Some things just cause stress!

Responses to Stress

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

1. Change concentration
   - a. add H\textsubscript{2} or N\textsubscript{2}
   - b. remove NH\textsubscript{3}

Remember, equilibrium describes the system when there is no change in the concentration of reactants and products, and they exist in a specific ratio.

Throw Back Problem

Given the following:

\[
\text{C}_{10}\text{H}_{14}\text{N}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NicH}^+(\text{aq}) + \text{OH}^- (\text{aq})
\]

\[ K_1 = 7.0 \times 10^{-7} \]

\[
\text{NicH}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Nic H}_2\text{O}^2+(\text{aq}) + \text{OH}^- (\text{aq})
\]

\[ K_2 = 1.1 \times 10^{-10} \]

Calculate total [OH\textsuperscript{-}] at equilibrium if the solution is initially 0.020 M nicotine (C\textsubscript{10}H\textsubscript{14}N\textsubscript{2}(aq))
3 \( H_2(g) + N_2(g) \rightleftharpoons 2 \text{NH}_3(g) \)

So, if the ratio can not change and we
a. add \( H_2 \), what would happen?

b. remove \( \text{NH}_3 \)?

c. add \( \text{NH}_3 \)?

2. Change in volume or pressure
a. increase volume

A system at equilibrium will shift toward the side of the reaction that maintains the correct ratio of gas molecules

So, what would happen if we increased the volume of the reaction vessel?

3 \( H_2(g) + N_2(g) \rightleftharpoons 2 \text{NH}_3(g) \)

b. Increase pressure

A change in the pressure of a system follows the rules for change in volume. If there is no change in temperature or volume with the change in pressure, no change in the equilibrium exists.

So what would happen if we increased the pressure by compressing the gases?

c. add \( \text{He} \)

According to the effects of changing the pressure and volume, what would happen if we added \( \text{He} \) to the system without changing the volume of the container?

The \( \text{He} \) does not react with either the reactants or products.

3 \( H_2(g) + N_2(g) \rightleftharpoons 2 \text{NH}_3(g) \)

3 \( H_2(g) + N_2(g) \rightleftharpoons 2 \text{NH}_3(g) \Delta H = -92 \text{ kJ} \)

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3. Change in temperature
a. increase temperature

For a system in equilibrium where the temperature of the system increases, the equilibrium will shift in such a way as to absorb that energy.

So, if the temperature of the reaction vessel at equilibrium for the reaction above was increased, what shift would occur in the system?
4. Addition of a catalyst

The addition of a catalyst has no effect on a system at equilibrium. However, it may affect the rate at which a system that is not at equilibrium may attain an equilibrium.

2. For the following reaction:

\[ \text{AgNO}_3(s) \rightleftharpoons \text{Ag}^+(aq) + \text{NO}_3^-(aq) \]

Describe what would happen in each of the scenarios below:

a. add AgNO\(_3\)(s)
b. add H\(_2\)O
c. add Ag\(_2\)O
d. add NaCl

3. For the reaction above, what is the effect of:
   • increasing temp.
   • increasing volume
   • Adding NaCH\(_3\)CO\(_2\)

\[ \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CO}_2^- \quad \Delta H = - \]

Adding an ion “common” to an equilibrium causes the equilibrium to shift back to reactant.

The Common-Ion Effect

The dissociation of a weak electrolyte is decreased by adding a strong electrolyte having a common ion.

Examine:

\[ \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CO}_2^- \]

The addition of NaCH\(_3\)CO\(_2\) shifts the equilibrium to the left due to the competition between acetate ions.

Calculations involving the addition of a common ion are very similar to the procedures used to calculate concentrations for weak acid-base systems and saturated solutions.

The only difference is that the initial concentration of the anion (A\(^-\)) is not zero for the reaction.

\[ \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \]
4. Consider the equilibrium:

\[ \text{B}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HB}^+_{(aq)} + \text{OH}^-_{(aq)} \]

In terms of Le Chatelier’s Principle, explain the effect of the presence of salt \( \text{HB}^+ \) on the ionization of \( \text{B} \). Also, give an example of a salt that can decrease the ionization of \( \text{NH}_3 \) in the solution.

5. Give an example of a salt that can decrease the ionization of \( \text{NH}_3 \) in the solution.

6. Calculate the hydronium ion concentration of \( \text{HF} \) in a solution containing 1.0 \( M \) \( \text{HF} \) and 1.0 \( M \) \( \text{NaF} \) (\( K_a = 7.2 \times 10^{-4} \)) for the reaction:

\[ \text{HF}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{F}^-_{(aq)} \]

7. Using equilibrium constants from Appendix D, calculate the equilibrium concentrations for all species present in the following solutions.

a. 0.080 \( M \) in potassium propionate, \( \text{KC}_3\text{H}_5\text{O}_2 \), and 0.16 \( M \) in propanoic acid, \( \text{HC}_3\text{H}_5\text{O}_2 \)

b. 0.0750 \( M \) in pyridine, \( \text{C}_5\text{H}_5\text{N} \), and 0.0500 \( M \) in pyridinium chloride, \( \text{C}_5\text{H}_5\text{NHCl} \)