CHEM 116
Equilibrium Calculations

Lecture 17
Prof. Sevian

Today we will begin with the end of Lecture 16 notes that we didn't finish last week. If you have already printed Lecture 16, then bring it to lecture with you along with Lecture 17 here. The pages included here in Lecture 17 are what will be covered after we finish Lecture 16. If you didn't print Lecture 16 yet, you will need page 10 onward of that lecture.

Today's agenda

- Equilibrium (finish ch. 15)
  - Relationships among *K* expressions
    - Multiplying reactions by factors
    - Summing reactions
  - le Chatelier's principle
- Acids & bases (start ch. 16)
  - Arrhenius model
  - Bronsted-Lowry model
- Return Exam 2

What patterns do you recognize in these reactions?

1. $HCl\ (aq) + NaOH\ (aq) \leftrightarrows NaCl\ (aq) + H_2O\ (l)$
2. $2\ HNO_3\ (aq) + Ba(OH)_2\ (aq) \leftrightarrows Ba(NO_3)_2\ (aq) + 2\ H_2O\ (l)$
3. $CH_3COOH\ (aq) + KOH\ (aq) \leftrightarrows KCH_3COO\ (aq) + H_2O\ (l)$
4. $H_2SO_4\ (aq) + NaOH\ (aq) \leftrightarrows NaHSO_4\ (aq) + H_2O\ (l)$
5. $H_2C_2O_4\ (aq) + NaOH\ (aq) \leftrightarrows NaHC_2O_4\ (aq) + H_2O\ (l)$

Acid + Base ⇆ Salt + Water

This is the general Arrhenius acid-base reaction.

- **What do all Arrhenius acids have in common?**
- **What do all Arrhenius bases have in common?**

Arrhenius acids

What do all Arrhenius acids have in common?

1. $HCl\ (aq) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + Cl^-\ (aq)$
2. $HNO_3\ (aq) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + NO_3^-\ (aq)$
3. $CH_3COOH\ (aq) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + CH_3COO^-\ (aq)$
4. $H_2SO_4\ (aq) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + HSO_4^-\ (aq)$
5. $H_2C_2O_4\ (aq) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + HC_2O_4^-\ (aq)$

Arrhenius acids

What do all Arrhenius acids have in common?

1. $HCl\ (aq) \leftrightarrows H^+\ (aq) + Cl^-\ (aq)$
2. $HNO_3\ (aq) \leftrightarrows H^+\ (aq) + NO_3^-\ (aq)$
3. $CH_3COOH\ (aq) \leftrightarrows H^+\ (aq) + CH_3COO^-\ (aq)$
4. $H_2SO_4\ (aq) \leftrightarrows H^+\ (aq) + HSO_4^-\ (aq)$
5. $H_2C_2O_4\ (aq) \leftrightarrows H^+\ (aq) + HC_2O_4^-\ (aq)$

$HA \leftrightarrows H^+ + A^-$

Arrhenius bases

What do all Arrhenius bases have in common?

1. $NaOH\ (aq) \leftrightarrows Na^+\ (aq) + OH^-\ (aq)$
2. $Ba(OH)_2\ (aq) \leftrightarrows Ba^{2+}\ (aq) + 2\ OH^-\ (aq)$
3. $KOH\ (aq) \leftrightarrows K^+\ (aq) + OH^-\ (aq)$
4. Same as 1
5. Same as 1

$B(OH) \leftrightarrows B^+ + OH^-$

General Arrhenius acid-base reaction

$HA \leftrightarrows H^+ + A^-$

$B(OH) \leftrightarrows B^+ + OH^-$

$HA + B(OH) \leftrightarrows H^+ + A^- + B^+ + OH^-$

However, we also know that $H_2O \leftrightarrows H^+ + OH^-$ has

$$K_w = [H^+][OH^-] = 10^{-14}$$

Therefore, nearly all the $H^+ + OH^-$ converts to H_2O, so

$HA + B(OH) \leftrightarrows (B^+)(A^-) + H_2O$

Acid + Base ⇆ Salt + Water

What patterns do you recognize in these reactions?

1. $H_3O^+ (aq) + NH_3 (g) \leftrightarrows NH_4^+ (aq) + H_2O (l)$
2. $H_2SO_3 (aq) + HS^- (aq) \leftrightarrows H_2S (g) + HSO_3^- (aq)$
3. $CH_3COOH (aq) + NH_3 (aq) \leftrightarrows NH_4^+ (aq) + CH_3COO (aq)$
4. $HNO_2 (aq) + HPO_4^{2-} (aq) \leftrightarrows H_2PO_4^- (aq) + NO_2^- (aq)$
5. $NH_4^+ (aq) + CN^- (aq) \leftrightarrows HCN (aq) + NH_3 (g)$

Acid1 + Base2 ⇆ Acid2 + Base1

This is the general Bronsted-Lowry acid-base reaction.

- **What do all Bronsted acids have in common?**
- **What do all Bronsted bases have in common?**

Bronsted acids

What do all Bronsted acids have in common?

1. $H_3O^+ (aq) \leftrightarrows H^+ (aq) + H_2O (l)$
2. $H_2SO_3 (aq) \leftrightarrows H^+ (aq) + HSO_3^- (aq)$
3. $CH_3COOH (aq) \leftrightarrows H^+ (aq) + CH_3COO^- (aq)$
4. $HNO_2 (aq) \leftrightarrows H^+ (aq) + NO_2^- (aq)$
5. $NH_4^+ (aq) \leftrightarrows H^+ (aq) + NH_3 (g)$

   Acid1 $\leftrightarrows$ H^+ + Base1

   HA $\leftrightarrows$ H^+ + A^-

Bronsted bases

What do all Bronsted bases have in common?

1. $NH_3 (g) + H^+ (aq) \leftrightarrows NH_4^+ (aq)$
2. $HS^- (aq) + H^+ (aq) \leftrightarrows H_2S (g)$
3. Same as 1
4. $HPO_4^{2-} (aq) + H^+ (aq) \leftrightarrows H_2PO_4^- (aq)$
5. $CN^- (aq) + H^+ (aq) \leftrightarrows HCN (aq)$

   Base2 + H^+ $\leftrightarrows$ Acid2

   B + H^+ $\leftrightarrows$ HB^+

General Bronsted-Lowry acid-base reaction

Acid1 ⇆ H^+ + Base1	HA ⇆ H^+ + A^-
Base2 + H^+ ⇆ Acid2	B + H^+ ⇆ HB^+
Acid1 + Base2 + H^+ ⇆ H^+ + Acid2 + Base1	HA + B + H^+ ⇆ HB^+ + H^+ + A^-
Or simply,	Or simply,
Acid1 + Base2 ⇆ Acid2 + Base1	HA + B ⇆ HB^+ + A^-

Compare the two models of acids and bases

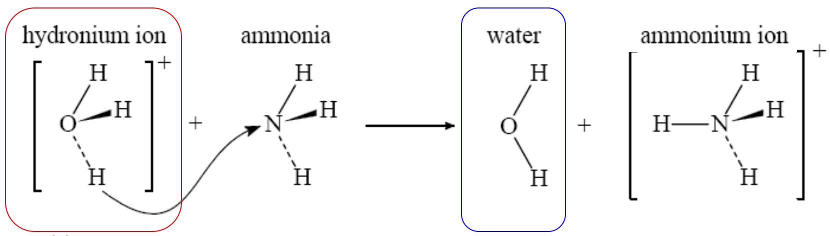
Arrhenius definition

- Acid is a substance that produces H^+ when added to water
  - HCl, H_2SO_4, HNO_3
  - CH_3COOH
- Base is a substance that produces OH^- when added to water
  - NaOH, $Ba(OH)_2$

Bronsted-Lowry definition

- Acid is a substance that donates protons (H^+)
  - HCl, H_2SO_4, HNO_3
  - CH_3COOH
  - H_3O^+, NH_4^+
- Base is a substance that accepts protons (H^+)
  - OH^-
  - NH_3, H_2O

Conjugate acid-base pairs

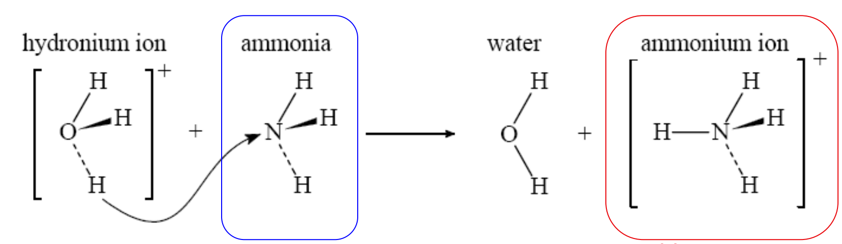


Acid #1
Proton donor

Base #1
After Acid #1 (H_3O^+) donated the proton

Pair #1: an acid on one side and its conjugate base on the other side

Conjugate acid-base pairs



Base #2
Proton acceptor

Acid #2
After Base #2 (NH_3) accepted the proton

Pair #2: a base on one side and its conjugate acid on the other side

Recognizing reactions by their patterns

Arrhenius acid-base reaction

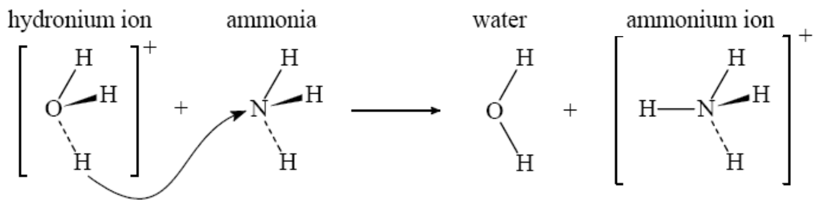
$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (l)$

$H_2SO_4\ (aq) + Ba(OH)_2\ (aq) \rightarrow BaSO_4\ (aq) + 2\ H_2O\ (l)$

Acid + Base → Salt + Water

Bronsted-Lowry acid-base reaction

$H_3O^+\ (aq) + NH_3\ (aq) \rightarrow H_2O\ (l) + NH_4^+\ (aq)$



$CH_3COOH\ (aq) + NH_3\ (aq) \rightarrow CH_3COO^-\ (aq) + NH_4^+\ (aq)$

Acid #1 + Base #2 → Base #1 + Acid #2

Amphiprotic substances

- Some chemicals can be an acid or a base
- Water is the most important amphiprotic substance (water can be the proton donor and its own proton acceptor)
- Autoionization of water is a fast equilibrium reaction that always is occurring wherever there is water present

$$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$$

Net: $2\ H_2O \leftrightarrows H_3O^+ + OH^-$

Shorthand: $H_2O \leftrightarrows H^+ + OH^-$

- Equilibrium constant

  $K_c = [H_3O^+]\,[OH^-]$ (or $K_c = [H^+]\,[OH^-]$ in shorthand)

  $= 1.0 \times 10^{-14}$ at 25ºC

You practice it

A Precursor to Practice Exercises on p. 673

Identify the acid on the left and its conjugate base on the right. Similarly, identify the base on the left and its conjugate acid on the right.

1. $HNO_3\ (aq) + NH_3\ (g) \leftrightarrows NH_4^+\ (aq) + NO_3^-\ (aq)$
2. $CN^-\ (aq) + HClO\ (aq) \leftrightarrows HCN\ (aq) + ClO^-\ (aq)$
3. $HCO_3^-\ (aq) + H_2O\ (l) \leftrightarrows CO_3^{2-}\ (aq) + H_3O^+\ (aq)$

Acid (or base) ionization constant K_a (or K_b)

Acid ionization (with water acting as the base):

- General form: $HA + H_2O \leftrightarrows A^- + H_3O^+$
- Examples
  - $\mathbf{HF + H_2O \leftrightarrows F^- + H_3O^+}$
  - $\mathbf{H_2S + H_2O \leftrightarrows HS^- + H_3O^+}$
  - $\mathbf{HSO_4^- + H_2O \leftrightarrows SO_4^{2-} + H_3O^+}$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Base ionization (with water acting as the acid):

- General form: $\mathbf{B} + H_2O \leftrightarrows HB^+ + OH^-$
- Examples
  - $\mathbf{NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-}$
  - $\mathbf{F^- + H_2O \leftrightarrows HF + OH^-}$
  - $\mathbf{HPO_4^{2-} + H_2O \leftrightarrows H_2PO_4^- + OH^-}$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$