CHEM 116

Acid-Base Systems

November 2, 2006
Prof. Sevian

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Agenda

- Equilibrium (end of ch. 15)
  - Le Chatelier's principle
- Acids and Bases (start of ch. 16)
  - Bronsted-Lowry model of acids and bases
  - Strong vs. weak acids and bases
  - Comparing strengths of weak acids or of weak bases
- Group problem #4
- The final exam is scheduled for Monday, December 18, 11:30AM-2:30PM. Location TBA.

Summary of le Chatelier's principle

If you take a system that is at equilibrium and then disturb it, it will come back to equilibrium in a special way: It will partially un-do the disturbance

- If you add a chemical that is involved in the equilibrium, the new equilibrium will be shifted toward the direction that uses up some of the new chemical that was added (K_{eq} will not change)
- If you change the pressure or the volume in a gas phase reaction, the new equilibrium will shift in the direction that reduces the disturbance (K_{eq} will not change)
- If you add heat, the new equilibrium will be shifted toward the direction that uses up some of the heat that was added and the value of K_{eq} will also change, since you changed T

Example: Disturbing a chemical equilibrium

Similar to Practice Exercises on pp. 655-656.

Explain the effect in each case. Assume each system is at equilibrium before the disturbance occurs.

a) $2\ NOCl\ (g) \leftrightarrows 2\ NO\ (g) + Cl_2\ (g) \quad \Delta H^o_{rxn} = +77.1\ kJ$
What would happen if the temperature were decreased?

b) $H_2\ (g) + CO_2\ (g) \leftrightarrows H_2O\ (g) + CO\ (g)$
What would happen if the volume were increased?

c) $C\ (s) + CO_2\ (g) \leftrightarrows 2\ CO\ (g)$
What would happen if suddenly more CO_2 were added? More C?

d) $C\ (s) + CO_2\ (g) \leftrightarrows 2\ CO\ (g)$
An increase in temperature causes the CO concentration to increase. What is the sign of ΔH?

Important equilibria

- Weak acids and weak bases (ch. 16)
- Buffers, acid-base titrations (ch. 17)
- Solubility equilibria (ch. 17)
- Oxidation-reduction, separated so as to generate voltage (ch. 20)

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. $H_2C_2O_4\ (aq) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + HC_2O_4^-\ (aq)$

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. $HCl\ (aq) \leftrightarrows H^+\ (aq) + Cl^-\ (aq)$
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 ⇆ 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^+ ⇆ Acid2

B + H^+ ⇆ HB^+

Definitions 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

General Bronsted-Lowry acid-base reaction

Acid1 ⇆ H^+ + Base1

Base2 + H^+ ⇆ Acid2

Acid1 + Base2 + H^+ ⇆ H^+ + Acid2 + Base1

Or simply,

Acid1 + Base2 ⇆ Acid2 + Base1

HA ⇆ H^+ + A^-

B + H^+ ⇆ HB^+

HA + B + H^+ ⇆ HB^+ + H^+ + A^-

Or simply,

HA + B ⇆ HB^+ + A^-

Recognizing reactions by their patterns

Arrhenius acid-base reaction

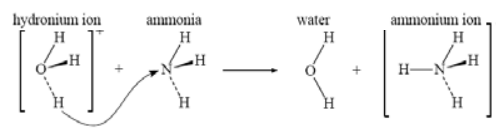
$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (l)$

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

Acid + Base → Salt + Water

Bronsted-Lowry acid-base reaction

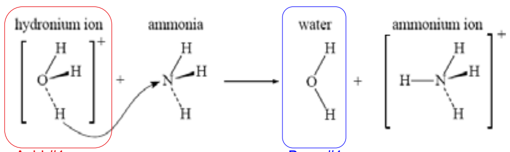
$H_3O^+\ (aq) + NH_3\ (aq) \rightarrow H_2O\ (l) + NH_4^+\ (aq)$



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

Acid #1 + Base #2 → Base #1 + Acid #2

Conjugate acid-base pairs



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

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

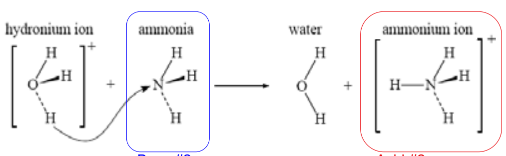
$$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$$

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

Conjugate acid-base pairs



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

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
  - $HF + H_2O \leftrightarrows F^- + H_3O^+$
  - $H_2S + H_2O \leftrightarrows HS^- + H_3O^+$
  - $HSO_4^- + H_2O \leftrightarrows SO_4^{2-} + H_3O^+$

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

Base ionization (with water acting as the acid):

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

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

Comparing Bronsted acids (see handout)

Table 17.3 • Ionization Constants for Some Acids and Their Conjugate Bases

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaqualuminum ion	$Al(H_2O)_6^{3+}$	7.9×10^{-6}	$Al(H_2O)_5OH^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$Cu(H_2O)_6^{2+}$	1.6×10^{-7}	$Cu(H_2O)_5OH^+$	6.25×10^{-8}	pentaaquahydroxocopper(II) ion

Increasing Acid Strength ↑ / Increasing Base Strength ↓

*The values of K_a for HS^- and K_b for S^{2-} are estimates.

Using the K_a values to predict the position of a proton-transfer equilibrium

Similar to Practice Exercise, p. 676

Use the table of ionization constants for acids and bases to answer the following questions.

1. Which is the stronger acid, H_2SO_4 or H_2SO_3?
2. To which direction does this equilibrium lie?
   $H_2SO_4 + HSO_3^- \leftrightarrows H_2SO_3 + HSO_4^-$
3. Is benzoic acid (C_6H_5COOH) stronger or weaker than acetic acid?
4. Which has the stronger conjugate base, acetic acid or boric acid?
5. Which is the stronger base, ammonia or the acetate ion?
6. Which has the stronger conjugate acid, ammonia or the acetate ion?

Group problem #4

At 400 K, the equilibrium constant K_c = 7.00 for the reaction

$$Br_2\,(g) + Cl_2\,(g) \leftrightarrows 2\,BrCl\,(g)$$

Consider a mixture of 0.122 mol of Br_2, 0.122 mol of Cl_2, and 0.982 mol of $BrCl$ (g) in a 1.00-liter vessel at 400 K.

- What is the value of the reaction quotient, Q, for this initial mixture?
- In what direction will the reaction proceed, *i.e.*, which chemicals will there be more made of?
- What are the final concentrations of all three chemicals when equilibrium is reached?