Chapter 16: Aqueous Equilibria: Acids and Bases

16.12 Equilibria in Solutions of Weak Bases

The equilibrium reaction of any general base B with water is characterized by the equilibrium equation and the equilibrium constant is called the base-dissociation constant, K_b

$$B(aq) + H_2O(l) \rightleftharpoons {}^{-}OH(aq) + BH^{+}(aq)$$

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

Table 16.4 Values for Some Weak Bases and Values for Their Conjugate Acids at 25 °C

Base	Formula, B	K_b	Conjugate Acid, BH^+	K_a
Ammonia	NH_3	1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Aniline	$C_6H_5NH_2$	4.3×10^{-10}	$C_6H_5NH_3^+$	2.3×10^{-5}
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	$(CH_3)_2NH_2^+$	1.9×10^{-11}
Hydrazine	N_2H_4	8.9×10^{-7}	$N_2H_5^+$	1.1×10^{-8}
Hydroxylamine	NH_2OH	9.1×10^{-9}	NH_3OH^+	1.1×10^{-6}
Methylamine	CH_3NH_2	3.7×10^{-4}	$CH_3NH_3^+$	2.7×10^{-11}

Many weak bases are organic compounds called amines, derivatives of ammonia in which one or more hydrogen atoms are replaced by an organic, carbon-based group, such as a methyl group (CH_3). Methylamine (CH_3NH_2) for example, is an organic amine responsible for the odor of rotting fish.

Example: Write a dissociation equation for methylamine in water, then write the equilibrium expression, K_b

<u>Equilibria in solutions of weak bases are treated by the same procedure used for solving problems involving weak acids.</u>

- Step 1: Write the balance equation for weak acid and water
- Step 2: Identify the principle reaction (the reaction that has larger K_b)
- Step 3: Generate an ICE table
- Step 4: Solve for x
- Step 5: Calculate pH and all other concentrations (B, ^{-}OH and BH^{+})

Example: Find the concentration of all species and pH in a 0.250 M solution of trimethylamine, $(CH_3)_3N$. K_b = 6.3×10^{-5}

Example: Lactated Ringer's solution is given intravenously to replenish fluids in patients who have experienced significant blood loss. The solution contains several different ions including sodium, potassium, chloride, calcium, and lactate ($C_3H_5O_3^-$). Lactate is the only species that affects the pH. The solution has a lactate concentration of 0.028 M and pH of 8.16. What is the value of K_b and pK_b for lactate?

16.13 Relation Between K_a and K_b

For any conjugate acid–base pair, the product of the acid-dissociation constant for the acid and the base-dissociation constant for the base always equals the ion-product constant for water:

$$\mathbf{K_a \times K_b = K_w}$$

Consider the ionization reactions for a conjugate acid-base pair, HA and A^-

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

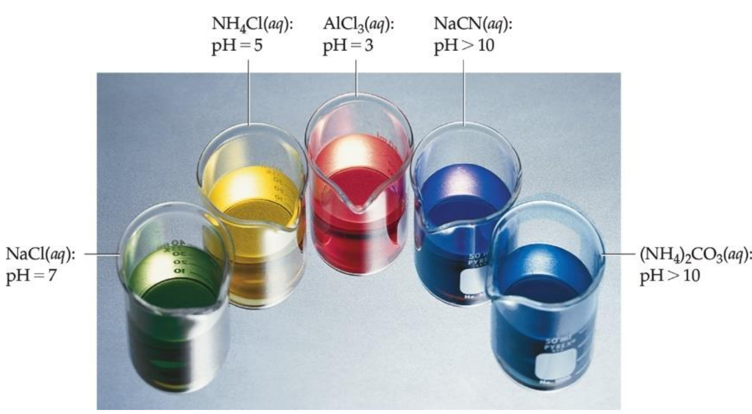
$$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons {}^-OH_{(aq)} + HA_{(aq)} \qquad K_b = \frac{[^-OH][HA]}{[A^-]}$$

Net equation:

Taking the negative base-10 logarithm of both sides of the equation $\mathbf{K_w = K_a \times K_b}$ gives another useful relationship:

$$\mathbf{pK_a + pK_b = 14.00}$$

16.14 Acid–Base Properties of Salts



pH of a salt solution is determined by the acid-base properties of the cations and anions. that when an acid neutralizes a base an ionic compound called a salt

Acid + Base → water + salt

In an acid-base reaction, the influence of the stronger partner is predominant

- Strong acid + Strong Base → Neutral solution
- Strong acid + Weak Base → Acidic solution
- Weak acid + Strong Base → Basic solution
- Weak acid + Weak base → either Acidic or Basic solution, depending on the strength of conjugates

Neutral Salt

- A salt of a strong base and a strong acid. E.g NaCl

Neutral cation + neutral anion → neutral salt

Na^+ Cl^- NaCl

$Na^+_{(aq)} + H_2O_{(l)} \rightarrow NR$

$Cl^-_{(aq)} + H_2O(l) \rightarrow NR$

- Cations from strong bases: group 1A and 2A metals (**Ca^{+2}, Sr^{2+}, Ba^{2+}**)
- Anions from strong monoprotic acids: **Cl^-, Br^-, I^-, NO_3^- and ClO_4^-**

Basic Salts

- A salt of a strong base and a weak acid. E.g NaCN

Neutral cation + basic anion → basic salt

Na^+ CN^- NaCN

$Na^+_{(aq)} + H_2O_{(l)} \rightarrow NR$

$CN^-_{(aq)} + H_2O_{(l)} \rightarrow HCN_{(aq)} + {}^-OH_{(aq)}$

Acidic Salts:

- A salt of a weak base and a strong acid. E.g NH_4Cl

Acidic cation + neutral anion → Acidic salt

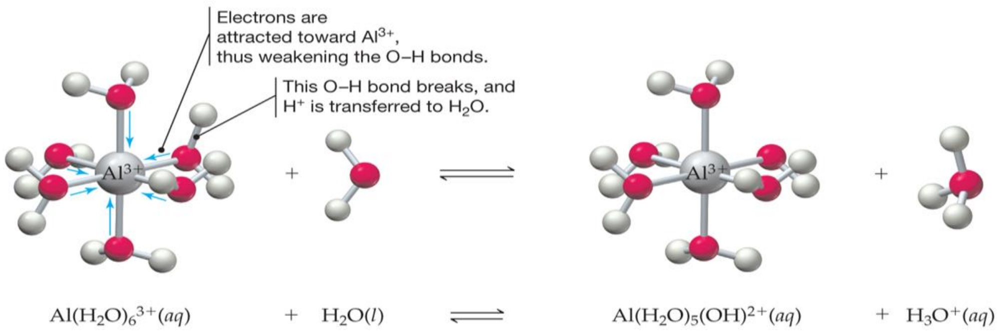
NH_4^+ + Cl^- NH_4Cl

$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)}$

$Cl^-{}_{(aq)} + H_2O_{(l)} \rightarrow NR$

Including those that are small, highly charged metal cations such as Al^{3+}

$Al^{3+}{}_{(aq)} + 6\ H_2O_{(l)} \rightarrow Al(H_2O)_6{}^{3+}{}_{(aq)}$



The acid-dissociation constant for $Al(H_2O)_6^{3+}$, is 14 x 10^{-5} much larger than , which means that the water molecules in the hydrated cation are much stronger proton donors than are free solvent water molecules. Transition metal cations, such as Zn^{2+}, Fe^{3+} and Cr^{3+}, also give acidic solutions; their K_a values are listed in Table C.2 of Appendix C.

<u>A salt of a weak base and a weak acid</u>

Acidic cation + basic anion (50 :50 mixture) must compare K_a and K_b

Recall, for acid-base conjugate pair,

$$\mathbf{K_a \times K_b = K_w}$$

Therefore

- $K_a > K_b$: The solution will contain an excess of H_3O^+ ions (pH < 7).
- $K_a < K_b$: The solution will contain an excess of ^-OH ions (pH > 7).
- $K_a = K_b$: The solution will contain approximately equal concentrations of H_3O^+ and ^-OH ions (pH ≈ 7).

Type of Salt	Examples	Ions That React with Water	pH of Solution
Cation from strong base; anion from strong acid	$NaCl$, KNO_3, BaI_2	None	~7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3, $[(CH_3)_3NH]Cl$	Cation	<7
Small, highly charged, cation; anion from strong acid	$AlCl_3$, $Cr(NO_3)_3$, $Fe(ClO_4)_3$	Hydrated cation	<7
Cation from strong base; anion from weak acid	$NaCN$, KF, Na_2CO_3	Anion	>7
Cation from weak base; anion from weak acid	NH_4CN, NH_4F, $(NH_4)_2CO_3$	Cation and anion	<7 if $K_a > K_b$ >7 if $K_a < K_b$ ~7 if $K_a \approx K_b$

Determine each of the following salt solutions as acidic, basic or neutral. Write the hydrolysis of the salt solution

KNO_2

$CaBr_2$

NH_4F

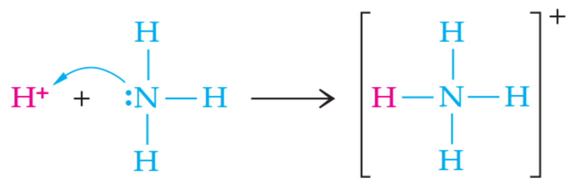
Determining the pH of a salt solution

E.g Predict whether 0.100 M $NaCHO_2$ salt is acidic, basic or neutral then find the pH. (K_a for $HCHO_2$ is 1.8×10^{-4})

Example: Predict whether 0.24M NH_4Br salt solution is acidic, basic or neutral then determine the pH of the salt solution.

16.15 Lewis Acids and Bases

In 1923, the same year in which Brønsted and Lowry defined acids and bases in terms of their proton donor/acceptor properties, the American chemist G. N. Lewis (1875–1946) proposed an even more general concept of acids and bases. Lewis noticed that when a base accepts a proton, it does so by sharing a lone pair of electrons with the proton to form a new covalent bond.



In this reaction, the proton behaves as an electron-pair acceptor and the ammonia molecule behaves as an electron-pair donor. Consequently, the Lewis definition of acids and bases states that a Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor.

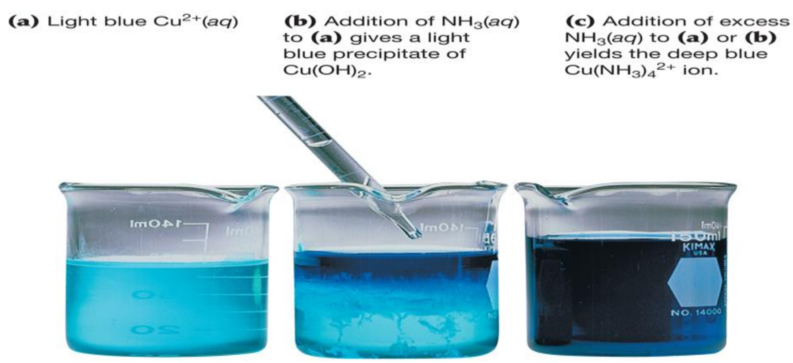
Lewis Acid: An electron-pair acceptor.

- Include cations and neutral molecule having vacant valence orbitals that can accept a share in a pair of electrons from a Lewis Base

Lewis Base: An electron-pair donor.

- All Lewis bases are Bronsted-Lowry bases

$$\underset{\text{Lewis acid}}{Cu^{2+}} + \underset{\text{Lewis base}}{4\,{:}NH_3} \longrightarrow Cu(NH_3)_4^{2+}$$



Example: Identify the Lewis acid and Lewis base in the reaction $AlCl_3 + Cl^- \rightarrow AlCl_4^-$.

A. $AgCl_4^-$ (Lewis acid), Cl^- (Lewis base)

B. $AlCl_3$ (Lewis acid), Cl^- (Lewis base)

C. $AgCl_4^-$(Lewis base), Cl^- (Lewis acid)

D. $AlCl_3$ (Lewis base), Cl^- (Lewis acid)

For the following Lewis acid–base reaction, draw electron-dot structures for the reactants and products, and use the curved arrow notation to represent the donation of a lone pair of electrons from the Lewis base to the Lewis acid.

$BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$