

pH of Salt Solutions

The ions composing salts may possess acidic or basic character, ionizing when dissolved in water to yield acidic or basic solutions. Acidic cations are typically the conjugate partners of weak bases, and basic anions are the conjugate partners of weak acids. Many metal ions bond to water molecules when dissolved to yield complex ions that may function as acids.

Learning Objectives

By the end of this section, you will be able to:

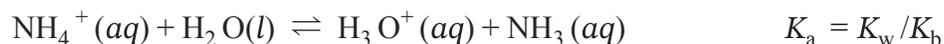
- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

25.1 Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation



The ammonium ion is the conjugate acid of the base ammonia, NH_3 ; its acid ionization (or acid hydrolysis) reaction is represented by



Since ammonia is a weak base, K_b is measurable and $K_a > 0$ (ammonium ion is a weak acid).

The chloride ion is the conjugate base of hydrochloric acid, and so its base ionization (or *base hydrolysis*) reaction is represented by



Since HCl is a strong acid, K_{a} is immeasurably large and $K_{\text{b}} \approx 0$ (chloride ions don't undergo appreciable hydrolysis).

Thus, dissolving ammonium chloride in water yields a solution of weak acid cations (



) and inert anions (Cl^{-}), resulting in an acidic solution.

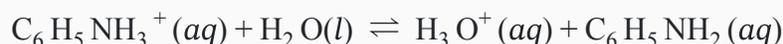
EXAMPLE 25.1.1

Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride,



a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 M solution of anilinium chloride



Solution

The K_a for anilinium ion is derived from the K_b for its conjugate base, aniline (see [Appendix H](#)):

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Using the provided information, an ICE table for this system is prepared:

	$\text{C}_6\text{H}_5\text{NH}_3^+$	+	H_2O	\rightleftharpoons	$\text{C}_6\text{H}_5\text{NH}_2$	+	H_3O^+
Initial concentration (M)	0.233				0		~0
Change (M)	-x				+x		+x
Equilibrium concentration (M)	0.233 - x				x		x

Substituting these equilibrium concentration terms into the K_a expression gives

$$K_a = [\text{C}_6\text{H}_5\text{NH}_2][\text{H}_3\text{O}^+]/[\text{C}_6\text{H}_5\text{NH}_3^+] \\ 2.3 \times 10^{-5} = (x)(x)/0.233 - x$$

Assuming $x \ll 0.233$, the equation is simplified and solved for x :

$$2.3 \times 10^{-5} = x^2/0.233 \\ x = 0.0023 \text{ M}$$

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0023) = 2.64$$

Check Your Learning

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3 , a salt composed of the ions



and



Which is the stronger acid



or



✓ Answer

$$[\text{H}_3\text{O}^+] = 7.5$$

×

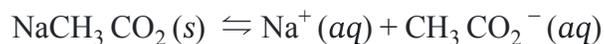
$$10^{-6} \text{ M},$$



is the stronger acid.

25.2 Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

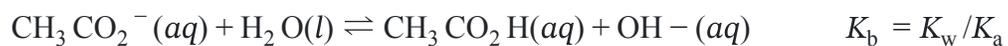


The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH. This may seem obvious from the ion's formula, which indicates no hydrogen or oxygen atoms, but some dissolved metal ions function as weak acids, as addressed later in this section.

The acetate ion,



is the conjugate base of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, and so its base ionization (or *base hydrolysis*) reaction is represented by



Because acetic acid is a weak acid, its K_a is measurable and $K_b > 0$ (acetate ion is a weak base).

Dissolving sodium acetate in water yields a solution of inert cations (Na^+) and weak base anions



resulting in a basic solution.

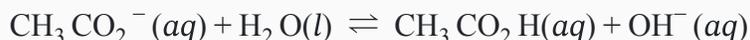
EXAMPLE 25.2.1

Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with

$$[\text{CH}_3\text{CO}_2^-] = 0.050\text{ M}$$

and $[\text{OH}^-] = 2.5 \times 10^{-6}\text{ M}$ at equilibrium. The reaction is:



Solution

The provided equilibrium concentrations and a value for the equilibrium constant will permit calculation of the missing equilibrium concentration. The process in question is the base ionization of acetate ion, for which

$$K_b(\text{for CH}_3\text{CO}_2^-) = \frac{K_w}{K_a(\text{for CH}_3\text{CO}_2\text{H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Substituting the available values into the K_b expression gives

$$\begin{aligned} K_b &= \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = 5.6 \times 10^{-10} \\ &= \frac{[\text{CH}_3\text{CO}_2\text{H}](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10} \end{aligned}$$

Solving the above equation for the acetic acid molarity yields $[\text{CH}_3\text{CO}_2\text{H}] = 1.1 \times 10^{-5}\text{ M}$.

Check Your Learning

What is the pH of a 0.083-M solution of NaCN?

✓ Answer

11.11

25.3 Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. Likewise, some salts contain a single ion that is amphiprotic, and so the relative strengths of this ion's acid and base character will determine its effect on solution pH. For both types of salts, a comparison of the K_a and K_b values allows prediction of the solution's acid-base status, as illustrated in the following example exercise.

EXAMPLE 25.3.1

Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- (a) KBr
- (b) NaHCO₃
- (c) Na₂HPO₄
- (d) NH₄F

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

(a) The K⁺ cation is inert and will not affect pH. The bromide ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

(b) The Na⁺ cation is inert and will not affect the pH of the solution; while the



anion is amphiprotic. The K_a of



is 4.7×10^{-11} , and its K_b is

$$\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}.$$

Since $K_b \gg K_a$, the solution is basic.

(c) The Na⁺ cation is inert and will not affect the pH of the solution, while the



anion is amphiprotic. The K_a of



is 4.2×10^{-13} ,

and its K_b is

$$\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}.$$

Because $K_b \gg K_a$, the solution is basic.

(d) The



ion is acidic (see above discussion) and the F^- ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of



is 5.6×10^{-10} and the K_b of F^- is 1.6×10^{-11} , so the solution is acidic, since $K_a > K_b$.

Check Your Learning

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) K_2CO_3

(b) CaCl_2

(c) KH_2PO_4

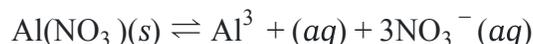
(d) $(\text{NH}_4)_2\text{CO}_3$

✓ Answer

(a) basic; (b) neutral; (c) acidic; (d) basic

25.4 The Ionization of Hydrated Metal Ions

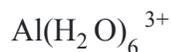
Unlike the group 1 and 2 metal ions of the preceding examples (Na^+ , Ca^{2+} , etc.), some metal ions function as acids in aqueous solutions. These ions are not just loosely solvated by water molecules when dissolved, instead they are covalently bonded to a fixed number of water molecules to yield a complex ion (see chapter on coordination chemistry). As an example, the dissolution of aluminum nitrate in water is typically represented as



However, the aluminum(III) ion actually reacts with six water molecules to form a stable complex ion, and so the more explicit representation of the dissolution process is



As shown in [Figure 25.1](#), the

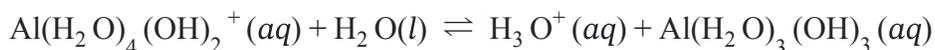
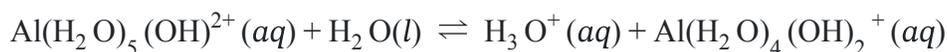
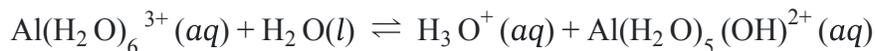


ions involve bonds between a central Al atom and the O atoms of the six water molecules. Consequently, the bonded water molecules' O–H bonds are more polar than in nonbonded water molecules, making the bonded molecules more

prone to donation of a hydrogen ion:



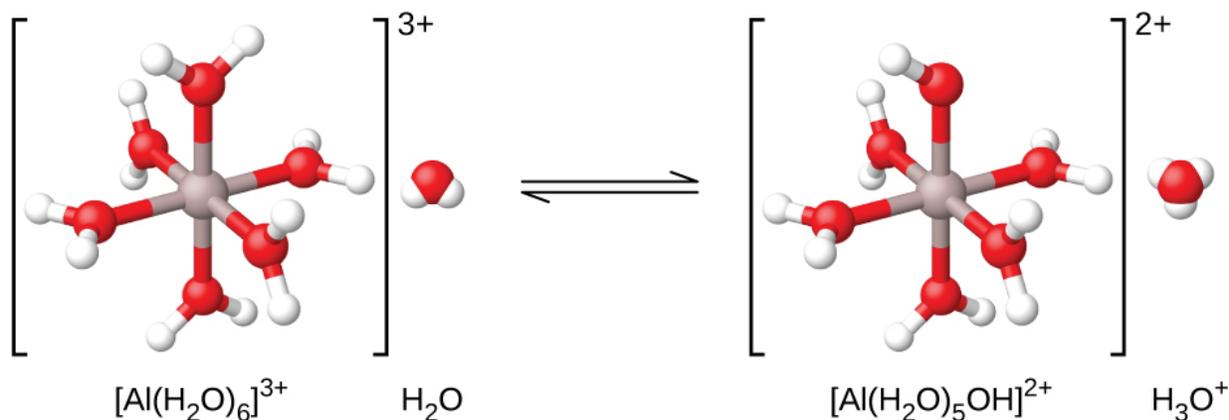
The conjugate base produced by this process contains five other bonded water molecules capable of acting as acids, and so the sequential or step-wise transfer of protons is possible as depicted in few equations below:



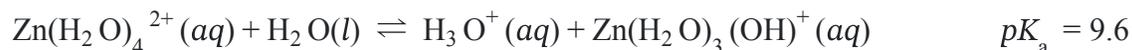
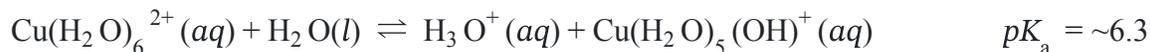
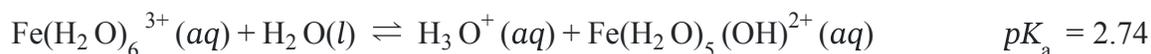
This is an example of a polyprotic acid, the topic of discussion in a later section of this chapter.

Figure 25.1

When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.



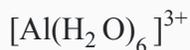
Aside from the alkali metals (group 1) and some alkaline earth metals (group 2), most other metal ions will undergo acid ionization to some extent when dissolved in water. The acid strength of these complex ions typically increases with increasing charge and decreasing size of the metal ions. The first-step acid ionization equations for a few other acidic metal ions are shown below:



EXAMPLE 25.4.1

Hydrolysis of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

Calculate the pH of a 0.10-*M* solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion



in solution.

Solution

The equation for the reaction and K_a are:



An ICE table with the provided information is

	$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$		
Initial concentration (M)	0.10	~0	0
Change (M)	-x	+x	+x
Equilibrium concentration (M)	0.10 - x	x	x

Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} \\ &= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5} \end{aligned}$$

Assuming $x \ll 0.10$ and solving the simplified equation gives:

$$x = 1.2 \times 10^{-3} \text{ M}$$

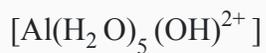
The ICE table defined x as equal to the hydronium ion concentration, and so the pH is calculated to be

$$[\text{H}_3\text{O}^+] = 0 + x = 1.2 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.92 \text{ (an acidic solution)}$$

Check Your Learning

What is



in a 0.15-M solution of $\text{Al}(\text{NO}_3)_3$ that contains enough of the strong acid HNO_3 to bring $[\text{H}_3\text{O}^+]$ to 0.10 M?

▼ Answer

2.1

×

10^{-5} M

Files

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