Al-Rasheed University College

Department of Medical Laboratory Technique

Medical Chemistry
Lecture 3

Prepared by

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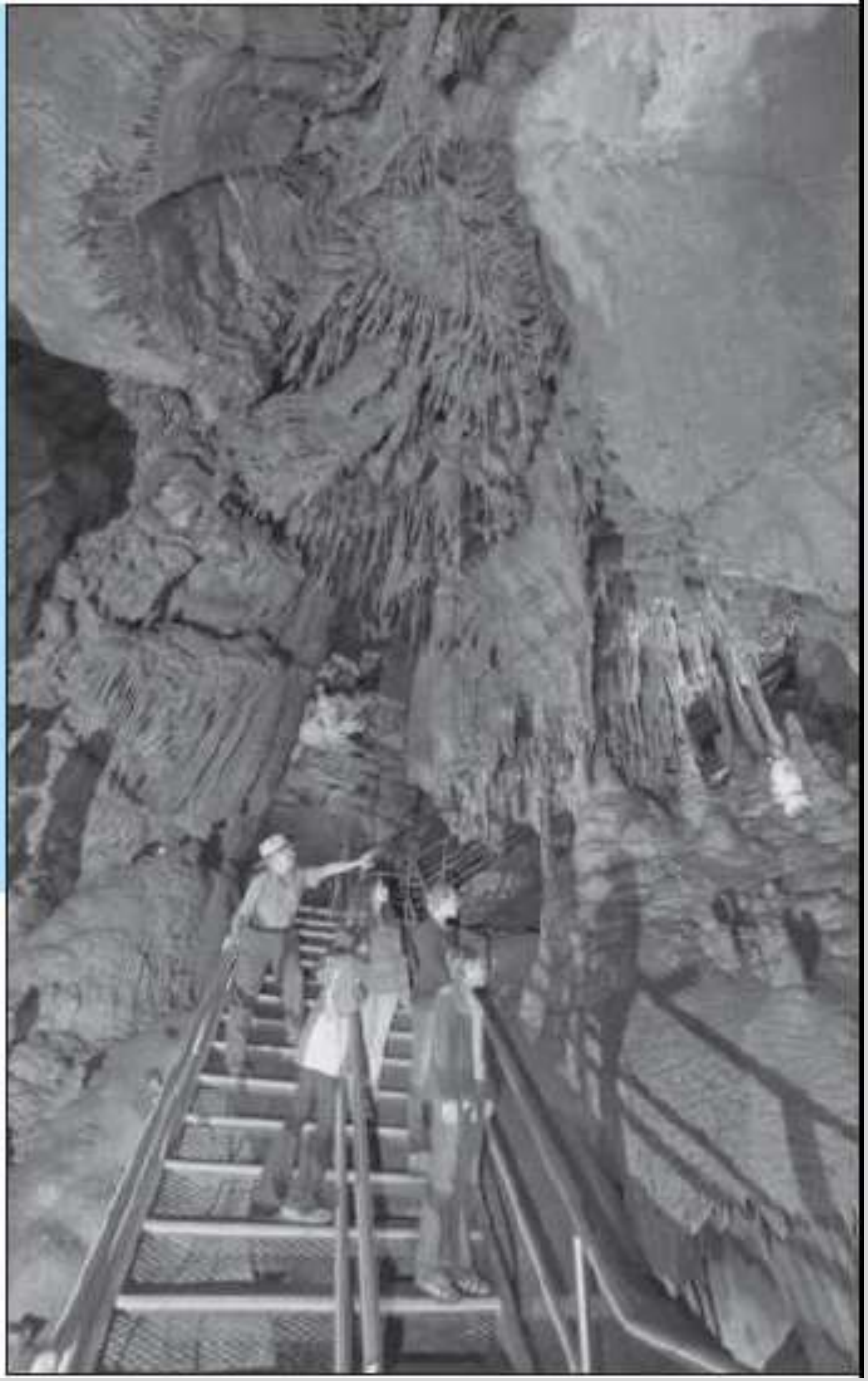
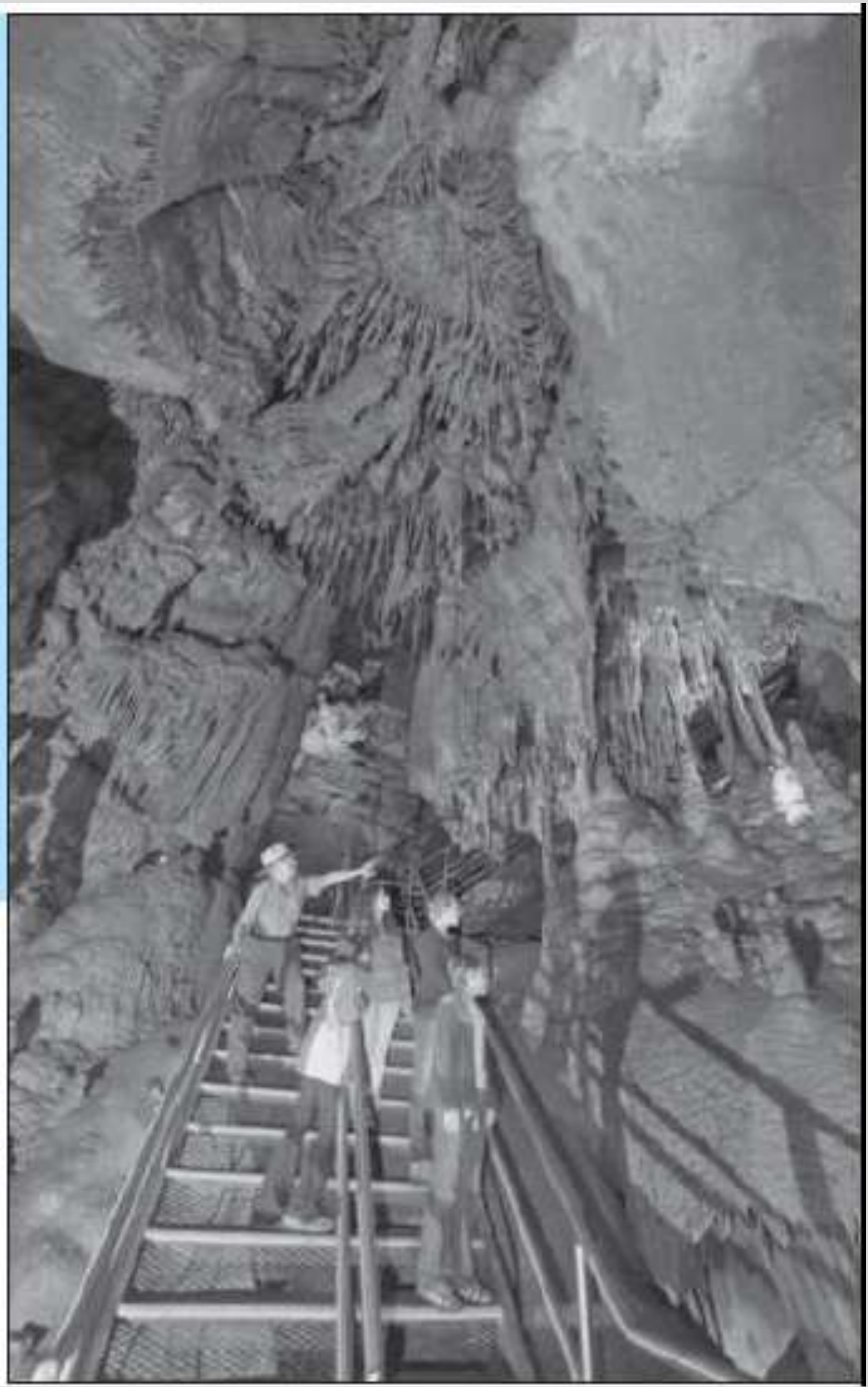


ACID–BASE EQUILIBRIA

This chapter presents a fundamental approach to chemical equilibrium, including calculations of chemical composition and of equilibrium concentrations for monoprotic acid/base systems. We also discuss buffer solutions, which are extremely important in many areas of science, and describe the properties of these solutions.



CHAPTER 2
ACID–BASE EQUILIBRIA

Acid–Base Theories

Several acid–base theories have been proposed to explain or classify acidic and basic properties of substances.

ARRHENIUS THEORY

an **acid** is any substance that ionizes (partially or completely) in water to give *hydrogen ions* (which associate with the solvent to give hydronium ions, H_3O^+):

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

A **base** ionizes in water to give *hydroxide ions*. Weak (partially ionized) bases generally ionize as follows:

$$B + H_2O \rightarrow BH^+ + OH^-$$

while strong bases such as metal hydroxides (e.g., NaOH) dissociate as

$$M(OH)_n \rightarrow M^{n+} + nOH^-$$

This theory is obviously restricted to water as the solvent.

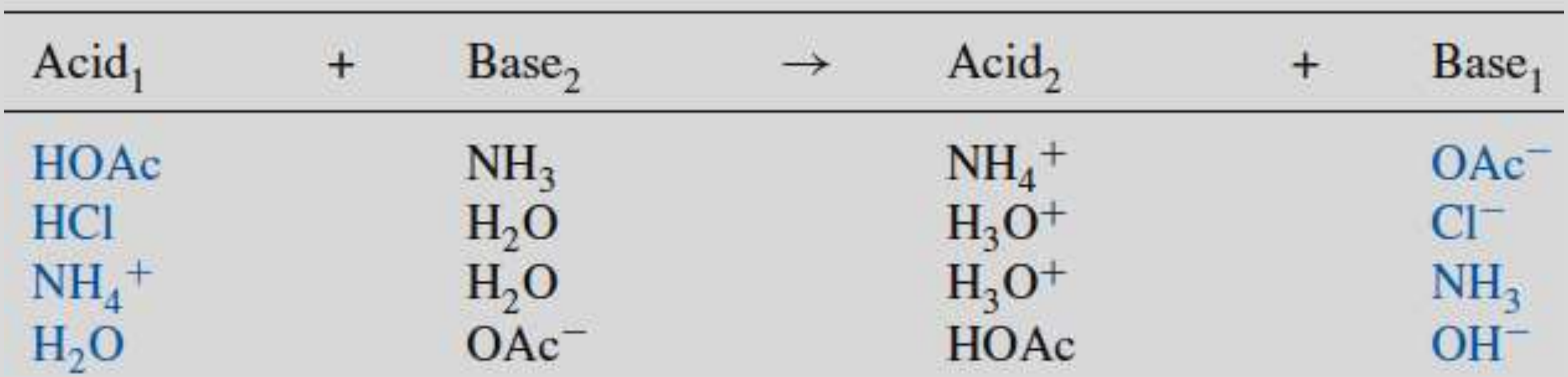
BRØNSTED—LOWRY THEORY

This theory states that an **acid** is any substance that can *donate a proton*, and a **base** is any substance that can *accept a proton*. Thus, we can write a “half reaction”a

$$\boxed{\text{acid} = H^+ + \text{base}}$$

The acid and base of a half-reaction are called **conjugate pairs**. A substance cannot act as an acid unless a base is present to accept the protons. Some acid–base reactions are illustrated below. In the first example, acetate ion is the conjugate base of acetic acid and ammonium ion is the conjugate acid of ammonia.

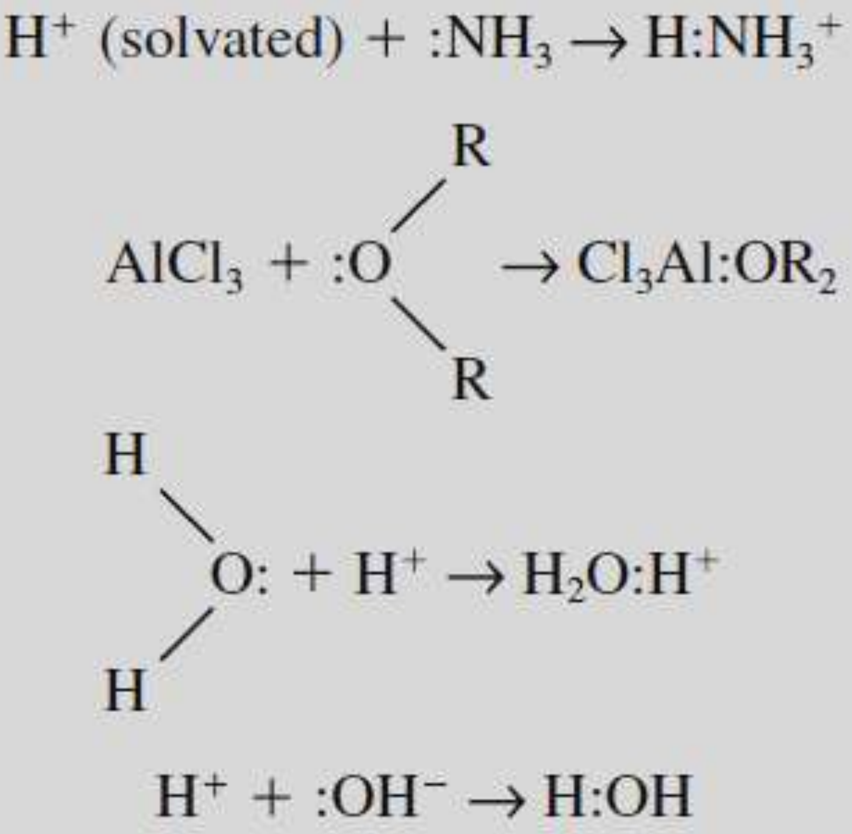
The BrØnsted–Lowry theory assumes a transfer of protons from an acid to a base, i.e., conjugate pairs.



$Acid_1$	+	$Base_2$	→	$Acid_2$	+	$Base_1$
HOAc		NH_3		NH_4^+		OAc^-
HCl		H_2O		H_3O^+		Cl^-
NH_4^+		H_2O		H_3O^+		NH_3
H_2O		OAc^-		HOAc		OH^-

LEWIS THEORY

In the **Lewis** theory, an **acid** is a substance that can accept an electron pair and a **base** is a substance that can donate an electron pair. The latter frequently contains an oxygen or a nitrogen as the electron donor. Examples of acid–base reactions in the Lewis theory are as follows:



$$H^+ \text{ (solvated)} + :NH_3 \rightarrow H:NH_3^+$$

$$AlCl_3 + :OR_2 \rightarrow Cl_3Al:OR_2$$

$$H_2O: + H^+ \rightarrow H_2O:H^+$$

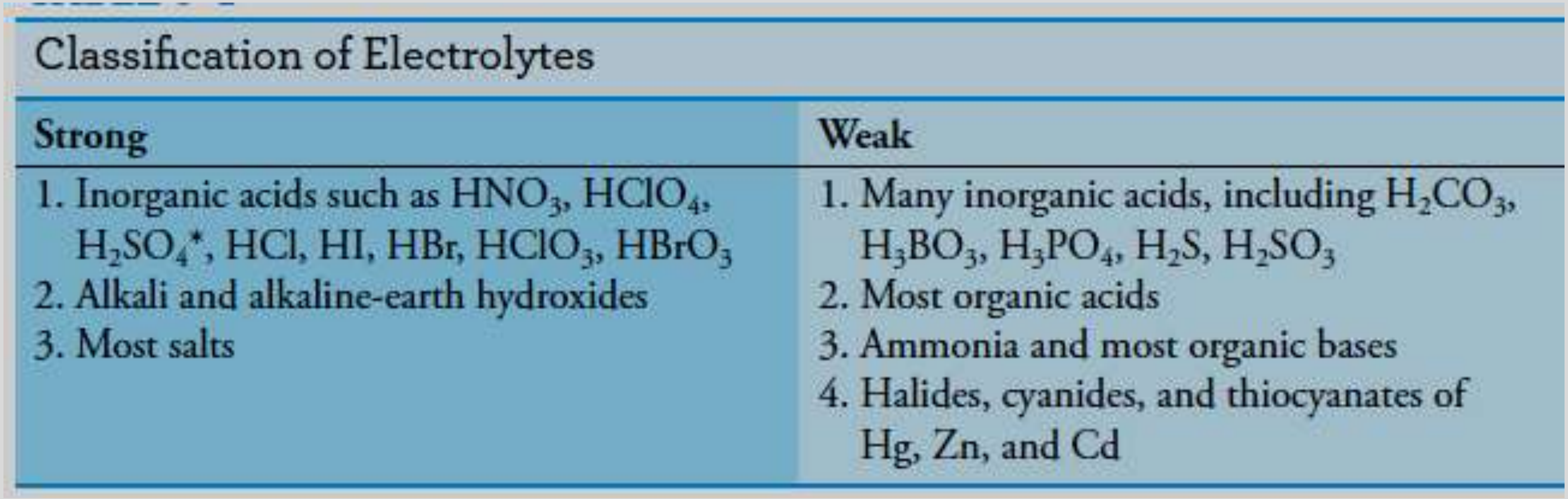
$$H^+ + :OH^- \rightarrow H:OH$$

The Lewis theory assumes a donation (sharing) of electrons from a base to an acid.

In the second example, aluminum chloride is an acid and ether is a base.

Acid–Base Equilibria in Water

When an acid or base is dissolved in water, it will dissociate, or **ionize**, the amount of ionization being dependent on the strength of the acid or the base. A **“strong” electrolyte** is completely dissociated, while a **“weak” electrolyte** is partially dissociated. Table below lists some common electrolytes, some strong and some weak.



Classification of Electrolytes

Strong	Weak
1. Inorganic acids such as HNO_3, $HClO_4$, H_2SO_4*, HCl, HI, HBr, $HClO_3$, $HBrO_3$	1. Many inorganic acids, including H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3
2. Alkali and alkaline-earth hydroxides	2. Most organic acids
3. Most salts	3. Ammonia and most organic bases
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

Hydrochloric acid is a strong acid, and in water, its ionization is complete:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

The proton H^+ exists in water as a hydrated ion, the **hydronium ion**, H_3O^+. Higher hydrates probably exist, particularly H_9O4^+.

Acetic acid is a weak acid, which ionizes only partially in water (a few percent):

$$\mathrm{HOAc} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OAc^-}$$

We can write an **equilibrium constant** for this reaction:

$$K_a^\circ = \frac{a_{\mathrm{H_3O^+}} \cdot a_{\mathrm{OAc^-}}}{a_{\mathrm{HOAc}} \cdot a_{\mathrm{H_2O}}}$$

where K_a is the **thermodynamic acidity constant** and a is the **activity** of the indicated species.

In dilute solutions, the activity of water remains essentially constant, and is taken as unity at standard state. Therefore, Equation above can be written as

$$K_a^\circ = \frac{a_{\mathrm{H_3O^+}} \cdot a_{\mathrm{OAc^-}}}{a_{\mathrm{HOAc}}}$$

Pure water ionizes slightly, or undergoes **autoprotolysis:**

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Autoprotolysis is the self-ionization of a solvent to give a characteristic cation and anion, e.g., $2CH_3OH \rightleftharpoons CH_3OH^+ + CH_3O^-$.

The equilibrium constant for this is

$$K_w^\circ = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O^2}}$$

Again, the activity of water is constant in dilute solutions (its concentration is essentially constant at ~55.5 *M), so*

$$K_w^\circ = a_{H_3O^+} \cdot a_{OH^-}$$

where K_w is the **thermodynamic autoprotolysis**, or **self-ionization, constant**.

We will use H^+ in place of H_3O^+, for simplicity. Also, molar concentrations will generally be used instead of activities.

Molar concentration will be represented by square brackets [ ] around the species. Simplified equations for the above reactions are

$$\mathrm{HCl} \rightarrow \mathrm{H^+ + Cl^-}$$

$$\mathrm{HOAc} \rightleftharpoons \mathrm{H^+ + OAc^-}$$

$$\boxed{K_a = \frac{[\mathrm{H^+}][\mathrm{OAc^-}]}{[\mathrm{HOAc}]}}$$

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+ + OH^-}$$

$$\boxed{K_w = [\mathrm{H^+}][\mathrm{OH^-}]}$$

K_a and K_w are the **molar equilibrium constants.**

The product of the hydrogen ion concentration and the hydroxide ion concentration in aqueous solution is *always* equal to 1.0 × 10^{-14} at room temperature:

$$\boxed{[\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}}$$

In pure water, then, the concentrations of these two species are equal since there are no other sources of H^+ or OH^- except H_2O dissociation:

$$[H^+] = [OH^-]$$

Therefore,

$$[H^+][H^+] = 1.0 \times 10^{-14}$$

$$[H^+] = 1.0 \times 10^{-7}\, M \equiv [OH^-]$$

Example 7.1

A $1.0 \times 10^{-3}\, M$ solution of hydrochloric acid is prepared. What is the hydroxide ion concentration?

Solution

Since hydrochloric acid is a strong electrolyte and is completely ionized, the H^+ concentration is $1.0 \times 10^{-3}\, M$. Thus,

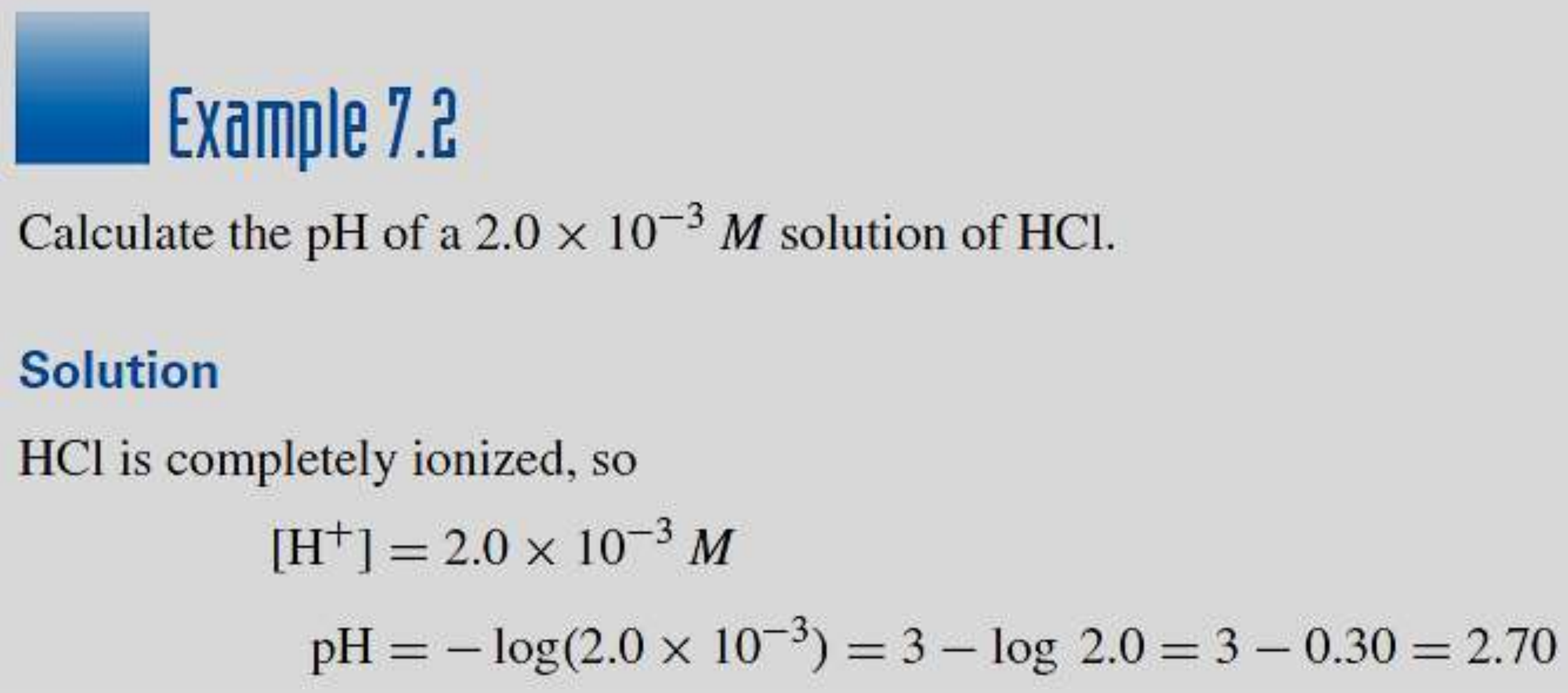
$$(1.0 \times 10^{-3})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = 1.0 \times 10^{-11}\, M$$

The pH Scale

The **pH** of a solution was defined by SØrenson as

$$\boxed{\mathrm{pH} = -\log[\mathrm{H}^+]}$$



Example 7.2

Calculate the pH of a $2.0 \times 10^{-3}\ M$ solution of HCl.

Solution

HCl is completely ionized, so

$$[\mathrm{H}^+] = 2.0 \times 10^{-3}\ M$$

$$\mathrm{pH} = -\log(2.0 \times 10^{-3}) = 3 - \log\ 2.0 = 3 - 0.30 = 2.70$$

A similar definition is made for the hydroxide ion concentration:

$$\boxed{\mathrm{pOH} = -\log[\mathrm{OH}^-]}$$

Equation below can be used to calculate the hydroxyl ion concentration if the hydrogen ion concentration is known, and vice versa. The equation in logarithm form for a more direct calculation of pH or pOH is

$$\boxed{K_w = [\mathrm{H}^+][\mathrm{OH}^-]}$$

$$-\log K_w = -\log[\mathrm{H}^+][\mathrm{OH}^-] = -\log[\mathrm{H}^+] - \log[\mathrm{OH}^-]$$

$$\boxed{\mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH}}$$

At 25°C,

$$\boxed{14.00 = \mathrm{pH} + \mathrm{pOH}}$$

A 1 M HCl solution has a pH of 0 and pOH of 14. A 1 M NaOH solution has a pH of 14 and a pOH of 0.

Example 7.3

Calculate the pOH and the pH of a 5.0×10^{-2} *M* solution of NaOH at 25°C.

Solution

$$[\text{OH}^-] = 5.0 \times 10^{-2}\ M$$

$$\text{pOH} = -\log(5.0 \times 10^{-2}) = 2 - \log\ 5.0 = 2 - 0.70 = 1.30$$

$$\text{pH} + 1.30 = 14.00$$

$$\text{pH} = 12.70$$

or

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13}\ M$$

$$\text{pH} = -\log(2.0 \times 10^{-13}) = 13 - \log\ 2.0 = 13 - 0.30 = 12.70$$

Example 7.4

Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution of pH 3.00 and 3.0 mL of a strong base of pH 10.00.

Solution

$$[\mathrm{H^+}] \text{ of acid solution} = 1.0 \times 10^{-3}\ M$$

$$\text{mmol } \mathrm{H^+} = 1.0 \times 10^{-3}\ M \times 2.0 \text{ mL} = 2.0 \times 10^{-3} \text{ mmol}$$

$$\text{pOH of base solution} = 14.00 - 10.00 = 4.00$$

$$[\mathrm{OH^-}] = 1.0 \times 10^{-4}\ M$$

$$\text{mmol } \mathrm{OH^-} = 1.0 \times 10^{-4}\ M \times 3.0 \text{ mL} = 3.0 \times 10^{-4} \text{ mmol}$$

There is an excess of acid.

$$\text{mmol } \mathrm{H^+} = 0.0020 - 0.0003 = 0.0017 \text{ mmol}$$

$$\text{Total Volume} = (2.0 + 3.0) \text{ mL} = 5.0 \text{ mL}$$

$$[\mathrm{H^+}] = 0.0017 \text{ mmol}/5.0 \text{ mL} = 3.4 \times 10^{-4}\ M$$

$$\text{pH} = -\log 3.4 \times 10^{-4} = 4 - 0.53 = 3.47$$

Example 7.5

The pH of a solution is 9.67. Calculate the hydrogen ion concentration in the solution.

Solution

$$-\log[\mathrm{H}^+] = 9.67$$

$$[\mathrm{H}^+] = 10^{-9.67} = 10^{-10} \times 10^{0.33}$$

$$[\mathrm{H}^+] = 2.1 \times 10^{-10}\,M$$

Remember, this answer is reported to two significant figures (2.1×10^{-10} M) because the mantissa of the pH value (9.67) has two significant figures.

$$[\mathrm{H}^+] = 10^{-\mathrm{pH}}.$$

1. When $[H^+] = [OH^-]$, then a solution is said to be **neutral**. If $[H^+] > [OH^-]$, then the solution is **acidic**. And if $[H^+] < [OH^-]$, the solution is **alkaline**.

1. The hydrogen ion and hydroxide ion concentrations in pure water at 25◦C are each 10^{-7} *M*, and the pH of water is 7. A pH of 7 is therefore neutral. Values of pH that are greater than this are alkaline, and pH values less than this are acidic. The reverse is true of pOH values. A pOH of 7 is also neutral.

1. Note that the product of $[H^+]$ and $[OH^-]$ is always 10^{-14} at 25◦C, and the sum of pH and pOH is always 14.

1. If the temperature is other than 25◦C, then K_w is different from 1.0×10^{-14}, and a neutral solution will have other than 10^{-7} *M* H^+ and OH^-.