

Acid-base Equilibria, Buffers and pH

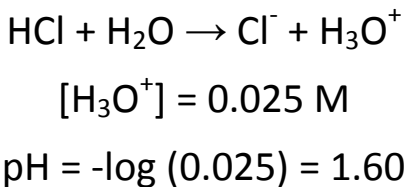
Introduction

This model focuses on approaches to estimating the pH of solutions of acids and bases. We will look at several cases; strong acids, strong bases, weak acids, weak bases and buffers.

Case 1: Strong Acids

Strong acids completely dissociate in water to form H_3O^+ . So, the $[\text{H}_3\text{O}^+]$ can be taken directly from the formal concentration (the concentration at which it was prepared) of the strong acid.

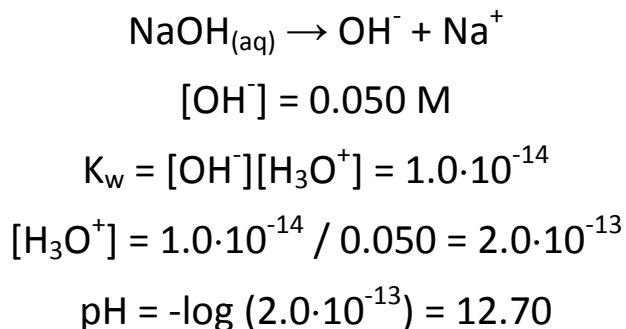
Example: A 0.025 M solution of HCl has a pH of 1.60



Case 2: Strong Bases

Strong bases completely dissociate in water to form OH^- . So, the $[\text{OH}^-]$ can be taken directly from the formal concentration (the concentration at which it was prepared) of the strong base.

Example: A 0.050 M solution of NaOH has a pH of 12.70

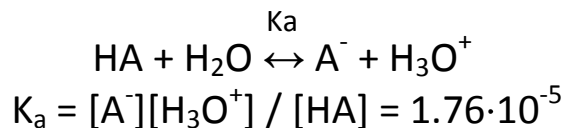


Case 3: Weak acids

Weak acids partially dissociate in water to form its conjugate base and H_3O^+ , as dictated by its acid dissociation constant. We can set up an ICE table, simplify and solve for the $[\text{H}_3\text{O}^+]$.

Example: A 0.10 M solution of acetic acid (CH_3COOH , represented as HA) has a pH of 2.88.

$$K_a(\text{acetic acid}) = 1.76 \cdot 10^{-5}$$



From ICE Table

$$K_a = x^2 / 0.100 - x = 1.76 \cdot 10^{-5}$$

$$x \ll 0.10, \text{ so}$$

$$[\text{H}_3\text{O}^+] = x = \{1.76 \cdot 10^{-5} \cdot 0.100\}^{1/2} = 0.00132 \text{ M}$$

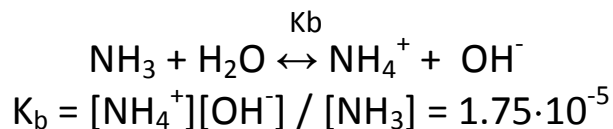
$$\text{pH} = -\log(0.00132) = 2.88$$

Case 4: Weak bases

Weak bases partially hydrolyze in water to form its conjugate acid and OH^- , as dictated by its base hydrolysis constant. We can set up an ICE table, simplify and solve for the $[\text{OH}^-]$.

Example: A 0.010 M solution of ammonia (NH_3) has a pH of 10.62.

$$K_b(\text{ammonia}) = 1.75 \cdot 10^{-5}$$



From ICE Table

$$K_b = x^2 \cdot 0.0100 - x = 1.75 \cdot 10^{-5}$$

$$x \ll 0.010, \text{ so}$$

$$[\text{OH}^-] = x = \{1.75 \cdot 10^{-5} \cdot 0.010\}^{1/2} = 0.0004184 \text{ M}$$

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \cdot 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 1.0 \cdot 10^{-14} / 0.0004184 = 2.390 \cdot 10^{-11}$$

$$\text{pH} = -\log(2.390 \cdot 10^{-11}) = 10.62$$

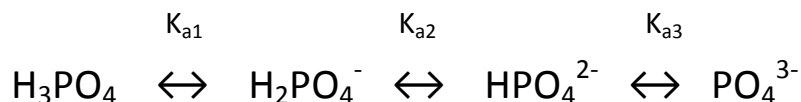
Case 5: Buffers

A buffer is a mixture of a weak acid and its conjugate base. These solutions are resistant to pH change. The capacity to resist pH change upon the addition of acid or base is maximized at a high concentration of an equal mixture of the weak acid and the conjugate base. When the concentration of the weak acid and its conjugate base are equal the pH equals the pKa of the conjugate pair. Out of convenience the Henderson-Hasselbalch Equation is often used to handle buffers.

$$\text{pH} = \text{pKa} + \log \left\{ \frac{\text{conjugate base}}{\text{conjugate acid}} \right\}$$

Example 1: A mixture that is 0.050 M H_2PO_4^- and 0.050 M HPO_4^{2-} has a pH of 7.20.

These two species are part of the phosphoric acid system. Phosphoric acid is a triprotic acid.



The acid dissociation reaction involving these two species is dictated by K_{a2} .

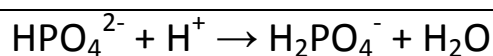
$$K_{a2} = 6.32 \cdot 10^{-8}$$



$$\text{pK}_{a2} = -\log(K_a) = 7.199$$

$$\text{pH} = 7.199 + \log \left\{ \frac{0.050}{0.050} \right\} = 7.20$$

Example 2: 20.0 mL of 0.100 M Na_2HPO_4 is mixed with 10.0 mL of 0.100 M HCl. The resulting pH is 7.20. The reaction of weak bases with strong acids goes to completion to produce its conjugate base and water.



Use a table to predict the mol ratio of the weak base and its conjugate.

	HPO_4^{2-}	H^+	H_2PO_4^-
Initial	2.00 mmol	1.00 mmol	0
Change	-1.00 mmol	-1.00 mmol	+1.00 mmol
Final	1.00 mmol	0	1.00 mmol

$$\text{pH} = 7.199 + \log \left\{ \frac{1.00}{1.00} \right\} = 7.199$$

Objectives and Success Criteria

- Understand and predict how different types of acids and bases will act in water

Prerequisites

- pH, acid-base reactions, equilibrium
- $\text{pH} = -\log [\text{H}_3\text{O}^+]$
- $\text{pK}_a = -\log K_a$

EXERCISES

1. Calculate the pH of a 0.10 M solution of HBr. (1.00)

The $[\text{OH}^-]$ of the solution is $1.0 \cdot 10^{-13}$ M. Explain the impact that adding a strong acid has on the K_w equilibrium in terms of LeChatlier's Principle.

2. Calculate the pH of a 0.0050 M solution of Ca(OH)_2 (it is completely soluble at this concentration and acts as a strong base). (12.000)

3. Construct the ICE Table for the Case 3 example.

4. Estimate the pH of a 0.020 M solution of ammonium chloride (NH_4Cl). This salt completely dissociates to produce NH_4^+ and Cl^- . NH_4^+ is the weak acid conjugate of ammonia (NH_3). Cl^- is just a spectator ion. (5.47)

$$(K_a(\text{NH}_4^+) = 5.77 \cdot 10^{-10})$$

5. Construct the ICE Table for the Case 4 example.

6. Estimate the pH of a 0.0015 M solution of sodium formate, HCOONa. The K_a of formic acid (HCOOH) is $1.8 \cdot 10^{-4}$. Sodium formate completely dissociates to produce Na^+ and the formate ion (HCOO^-), which is the conjugate base of formic acid. (7.46)
7. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.0100 M acetic acid (CH_3COOH) with 50.0 mL of 0.0100 M sodium acetate, the conjugate base of acetic acid. ($K_a(\text{acetic acid}) = 1.75 \cdot 10^{-5}$). Sodium acetate completely dissociates in water to form Na^+ and the acetate ion (CH_3COO^-). The Na^+ is a spectator ion. HINT: when you mix the solutions you are diluting the concentrations! (4.46)

8. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.0100 M sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$) with 50.0 mL of 0.0100 M HCl (a strong acid). $K_a(\text{benzoic acid, C}_6\text{H}_5\text{COOH}) = 6.28 \cdot 10^{-5}$ Hint: The reaction of weak bases with strong acids goes to completion. (4.20)
9. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.100 M sodium dihydrogen phosphate (NaH_2PO_4) with 50.0 mL of 0.0500 M NaOH (a strong base). Hint: The reaction of a weak acid with a strong base goes to completion. (6.722)