



ACID–BASE EQUILIBRIUM

Detailed Solutions

Part I – Strong Acid: HClO_4

Data: $C = 1.0 \times 10^{-2} \text{ mol L}^{-1}$, measured $\text{pH} = 2.00$.

1. **Degree of dissociation.** From the measured pH :

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.00} = 1.0 \times 10^{-2} \text{ mol L}^{-1}.$$

Reaction: $\text{HClO}_4 + \text{H}_2\text{O} \longrightarrow \text{ClO}_4^- + \text{H}_3\text{O}^+$, so

$$\alpha = \frac{[\text{H}_3\text{O}^+]}{C} = \frac{1.0 \times 10^{-2}}{1.0 \times 10^{-2}} = 1 \quad (100\%).$$

$\alpha = 1$: HClO_4 is completely dissociated.

2. **Theoretical pH .** If dissociation is complete, $[\text{H}_3\text{O}^+] = C$:

$$\text{pH}_{\text{th}} = -\log C = -\log(1.0 \times 10^{-2}) = 2.00.$$

This equals the measured value.

$\text{pH}_{\text{th}} = \text{pH}_{\text{meas}} = 2.00$: complete dissociation is confirmed.

3. **Can we conclude that an acid is strong from its pH alone? No.** The pH depends on both the strength of the acid *and* its concentration. A weak acid at a high enough concentration can also give $\text{pH} = 2$. We must compare the measured pH with $-\log C$:

- $\text{pH} = -\log C$ ($\alpha = 1$): strong acid;
- $\text{pH} > -\log C$ ($\alpha < 1$): weak acid.

4. K_a and $\text{p}K_a$.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_4^-]}{[\text{HClO}_4]} = \frac{(1.0 \times 10^{-2})(1.0 \times 10^{-2})}{1.0 \times 10^{-8}} = 1.0 \times 10^4,$$

$$\text{p}K_a = -\log K_a = -4.$$

$K_a = 1.0 \times 10^4$, $\text{p}K_a = -4$ (strong acid).

Part II – Weak Base and Mixture

Question 1: Weak Base

Data: $C_b = 0.10 \text{ mol L}^{-1}$, $\text{p}K_a = 9.25$, $\text{p}K_e = 14.00$.

a)

$$\text{p}K_a - \log C_b = 9.25 - \log(0.10) = 9.25 + 1 = 10.25.$$

$\text{p}K_a - \log C_b = 10.25$.

- b) **pH of the weak base.** Reaction: $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, with $pK_b = 14.00 - 9.25 = 4.75$. Assuming the base is weakly protonated:

$$\text{pOH} = \frac{1}{2} (pK_b - \log C_b) = \frac{1}{2} (4.75 + 1) = 2.875,$$

$$\text{pH} = 14.00 - 2.875 = 11.125.$$

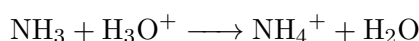
$$\text{Equivalent: } \text{pH} = \frac{1}{2} (pK_e + pK_a + \log C_b) = \frac{1}{2} (14.00 + 9.25 - 1) = 11.125.$$

Check: $[\text{OH}^-] = 10^{-2.875} = 1.3 \times 10^{-3} \text{ mol L}^{-1} \ll 0.10$, so the approximation is valid.

pH $\approx$ 11.13.

Question 2: Strong Acid + Weak Base

- a) **Reaction.**



Its equilibrium constant is

$$K = \frac{1}{K_a} = 10^{pK_a} = 10^{9.25} \approx 1.8 \times 10^9 \gg 10^4,$$

so the reaction is **quantitative (complete), from left to right.**

- b) **pH of the mixture.**

$$n(\text{HClO}_4) = 0.10 \times 50.0 \times 10^{-3} = 5.0 \times 10^{-3} \text{ mol},$$

$$n(\text{NH}_3)_0 = 0.10 \times 100.0 \times 10^{-3} = 1.0 \times 10^{-2} \text{ mol}.$$

	NH_3	H_3O^+	NH_4^+
Initial (mol)	1.0×10^{-2}	5.0×10^{-3}	0
Final (mol)	5.0×10^{-3}	≈ 0	5.0×10^{-3}

HClO_4 is the limiting reagent. The final mixture contains equal amounts of NH_3 and NH_4^+ : it is a **buffer solution**. Total volume = 150.0 mL:

$$[\text{NH}_3] = [\text{NH}_4^+] = \frac{5.0 \times 10^{-3}}{0.150} = 3.3 \times 10^{-2} \text{ mol L}^{-1}.$$

$$\text{pH} = pK_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.25 + \log(1) = 9.25.$$

pH = 9.25 (half-equivalence: pH = pK_a).

Part III – Ampholytes and Polyacids

- Ampholyte.** A species that can act both as an acid (proton donor) and as a base (proton acceptor); it belongs to two acid–base couples. *Example:* water ($\text{H}_3\text{O}^+/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{OH}^-$), or HCO_3^- , H_2PO_4^- .
- Behaviour of HCO_3^- in water.**
 - Acid (couple $\text{HCO}_3^-/\text{CO}_3^{2-}$): $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$
 - Base (couple $\text{CO}_2, \text{H}_2\text{O}/\text{HCO}_3^-$): $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2, \text{H}_2\text{O} + \text{OH}^-$



3. **Polyprotic acids.** An acid that can release more than one proton per molecule.

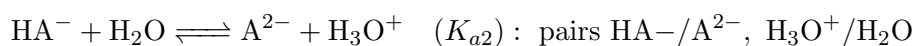
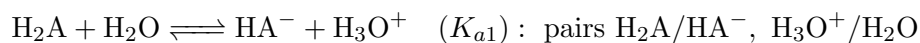
- **Diprotic:** 2 protons, e.g. H_2CO_3 , H_2SO_4 .
- **Triprotic:** 3 protons, e.g. H_3PO_4 .

4. **Several dissociation constants.** The protons are released one at a time, each step being a separate equilibrium with its own constant. For H_2A :

$$K_{a1} = \frac{[\text{HA}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}]} \quad (\text{1st proton}), \quad K_{a2} = \frac{[\text{A}^{2-}][\text{H}_3\text{O}^+]}{[\text{HA}^-]} \quad (\text{2nd proton}).$$

Generally $K_{a1} \gg K_{a2}$: it is harder to remove a proton from a negative ion than from a neutral molecule.

5. **Successive dissociations of H_2A .**



HA^- is an ampholyte: base of the first pair and acid of the second.