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4.2.10.4 Weak Base

Weak bases are weak electrolytes that ionize only partially in water. At equilibrium, an aqueous solution of a weak base contains a mixture of non-ionized base, OH^- ions, and molecules of the conjugate acid of the base. The strengths of weak bases vary considerably according to their degree of ionization.[33],[30] This limited ionization is governed by the equilibrium constant.

Caution

Important notes:

- Anions derived from weak acids are weak bases[6]
- The stronger the conjugate acid (K_a large), the weaker the base (K_b small)
- The relation: $K_a \times K_b = K_e = 10^{-14}$ at 25 °C[31]
- Example: For CH_3COOH/ CH_3COO^-, $K_a = 1.8 \times 10^{-5}$, therefore $K_b = \dfrac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

Example:

Table 4.12 Basicity constants (K_b) of weak bases and their conjugate acids at 25 °C.

Base	Conjugate Acid	pK_b	K_b
NH_3 (ammonia)	NH_4^+ (ammonium ion)	4.75	1.8×10^{-5}
CH_3NH_2 (methylamine)	$CH_3NH_3^+$ (methylammonium ion)	3.36	4.4×10^{-4}
$C_2H_5NH_2$ (ethylamine)	$C_2H_5NH_3^+$ (ethylammonium ion)	3.25	5.6×10^{-4}
C_5H_5N (pyridine)	$C_5H_5NH^+$ (pyridinium ion)	8.75	1.8×10^{-9}
$C_6H_5NH_2$ (aniline)	$C_6H_5NH_3^+$ (phenylammonium ion)	9.38	4.2×10^{-10}
CO_3^{2-} (carbonate ion)	HCO_3^- (bicarbonate ion)	3.67	2.1×10^{-4}
HCO_3^- (bicarbonate ion)	H_2CO_3 (carbonic acid)	7.65	2.2×10^{-8}
HPO_4^{2-} (hydrogen phosphate ion)	$H_2PO_4^-$ (dihydrogen phosphate ion)	6.80	1.6×10^{-7}
PO_4^{3-} (phosphate ion)	HPO_4^{2-} (hydrogen phosphate ion)	1.68	2.1×10^{-2}
F^- (fluoride ion)	HF (hydrofluoric acid)	10.32	4.8×10^{-11}
CH_3COO^- (acetate ion)	CH_3COOH (acetic acid)	9.25	5.6×10^{-10}
CN^- (cyanide ion)	HCN (hydrocyanic acid)	4.79	1.6×10^{-5}
NO_2^- (nitrite ion)	HNO_2 (nitrous acid)	10.65	2.2×10^{-11}
OH^- (hydroxide ion)	H_2O (water)	-1.74	5.5×10^{1}

The steps for solving a weak base ionization problem are the same as for a weak acid; we just need to use the basicity constant K_b as it is more appropriate. Otherwise, using K_a remains acceptable. Don't forget the reaction progress table:

Reaction Equation		$B + H_2O \rightleftharpoons BH^+ + OH^-$		
Initial state at t_0	$\alpha = 0$	C_b	0	0
Intermediate state at t	$0 < \alpha < 1$	$C_b - C_b\alpha$	$C_b\alpha$	$C_b\alpha$
Final state at t_{eq}	$\alpha \ll 1$	$C_b(1-\alpha) \simeq C_b$	$C_b\alpha$	$C_b\alpha$

The first approach we can take is to neglect the dissociation coefficient α, which gives this equation:

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(C_b\alpha)(C_b\alpha)}{C_b(1-\alpha)} = \frac{[OH^-]^2}{C_b} \Rightarrow [OH^-] = \sqrt{K_bC_b}$$

$$pOH = -\log\sqrt{K_bC_b} = \frac{1}{2}\Big(pK_b - \log C_b\Big)$$

Key takeaways

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 - \frac{1}{2}\Big(\mathrm{p}K_b - \log C_b\Big) \tag{4.9}$$

We can express the pH of a weak base using K_a:

$$K_b = \frac{[\mathrm{BH}^+][\mathrm{OH}^-]}{[\mathrm{B}]} = \frac{[\mathrm{OH}^-]^2}{C_b} \Leftrightarrow \frac{K_e}{K_a} = \frac{K_e^2}{[\mathrm{H_3O}^+]^2 C_b} \Rightarrow [\mathrm{H_3O}^+]^2 = \frac{K_e K_a}{C_b} \Rightarrow [\mathrm{H_3O}^+] = \sqrt{\frac{K_e K_a}{C_b}}$$

Key takeaways

$$\mathrm{pH} = -\frac{1}{2}\log\left(\frac{K_e K_a}{C_b}\right) = \frac{1}{2}\Big(14 + \mathrm{p}K_a + \log C_b\Big) \tag{4.10}$$

Caution

Condition of validity: $C_b \gg K_b$ (i.e., $\alpha \ll 1$, a coefficient too small compared to 1 and therefore negligible):[32]

- If: $\alpha < 0.05$: Excellent approximation
- If: $0.05 < \alpha < 0.1$: Acceptable approximation

Otherwise:

- $\alpha > 0.1$: Use the exact solution[32],[6]

The Exact Solution:

$$K_b = \frac{[\mathrm{BH}^+][\mathrm{OH}^-]}{[\mathrm{B}]} = \frac{(C_b\alpha)(C_b\alpha)}{C_b(1-\alpha)} = \frac{C_b^2\alpha^2}{C_b(1-\alpha)} = \frac{C_b\alpha^2}{1-\alpha}$$

Thus:

$$K_b = \frac{C_b\alpha^2}{1-\alpha} \Rightarrow K_b(1-\alpha) = C_b\alpha^2 \Leftrightarrow K_b - K_b\alpha = C_b\alpha^2 \Leftrightarrow \boxed{C_b\alpha^2 + K_b\alpha - K_b = 0}$$

This exact solution is always valid but requires solving a quadratic equation with α as the unknown.

$$\boxed{\alpha = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2C_b}}$$

We keep only the positive solution because a concentration cannot be negative.

$$[\mathrm{OH}^-] = C_b\alpha = C_b \cdot \frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2C_b} = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2} \tag{11}$$

$$\mathrm{pOH} = -\log\left(\frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2}\right)$$

Then:

Key takeaways

$$\mathrm{pH} = 14 + \log\left(\frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2}\right) \tag{4.11}$$

This exact solution can be written in terms of K_a; here is the demonstration:

$$K_b = \frac{K_e}{K_a} = \frac{10^{-14}}{K_a} = \frac{[\mathrm{BH}^+][\mathrm{OH}^-]}{[\mathrm{B}]} = \frac{(C_b\alpha)(C_b\alpha)}{C_b(1-\alpha)} = \frac{C_b^2\alpha^2}{C_b(1-\alpha)} = \frac{C_b\alpha^2}{1-\alpha}$$

Thus:

$$\frac{C_b\alpha^2}{1-\alpha} = \frac{10^{-14}}{K_a} \Rightarrow K_aC_b\alpha^2 = 10^{-14}(1-\alpha) \Leftrightarrow K_aC_b\alpha^2 = 10^{-14} - 10^{-14}\alpha \Leftrightarrow$$

$$K_a C_b \alpha^2 + 10^{-14}\alpha - 10^{-14} = 0$$

$$\boxed{K_a C_b \alpha^2 + K_e \alpha - K_e = 0}$$

This solution is always valid; we solve a quadratic equation with α as the unknown.

$$\boxed{\alpha = \frac{-K_e + \sqrt{(K_e)^2 + 4 \times K_e K_a C_b}}{2K_a C_b}}$$

We keep only the positive solution because a concentration cannot be negative.

$$[\mathrm{OH}^-] = C_b \alpha = C_b \cdot \frac{-K_e + \sqrt{K_e^2 + 4 \times K_e K_a C_b}}{2K_a C_b} = \frac{-K_e + \sqrt{K_e^2 + 4 \times K_e K_a C_b}}{2K_a}$$

$$\mathrm{pOH} = -\log\left(\frac{-K_e + \sqrt{K_e^2 + 4 \times K_e K_a C_b}}{2K_a}\right)$$

Then:

Key takeaways

$$\mathrm{pH} = 14 + \log\left(\frac{-K_e + \sqrt{K_e^2 + 4K_e K_a C_b}}{2K_a}\right) \tag{4.12}$$

Alternatively, we can perform a direct substitution from equation (11): By setting $K_b = 10^{-14}/K_a$ in the general solution:

$$[\mathrm{OH}^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_b C_b}}{2} = \frac{-\frac{10^{-14}}{K_a} + \sqrt{\left(\frac{10^{-14}}{K_a}\right)^2 + 4 \cdot \frac{10^{-14}}{K_a} \cdot C_b}}{2}$$

$$= \frac{-10^{-14} + \sqrt{10^{-28} + 4 \times 10^{-14} K_a C_b}}{2K_a}$$

$$\boxed{\mathrm{pH} = 14 + \log\left(\frac{-K_e + \sqrt{K_e^2 + 4 \times K_e K_a C_b}}{2K_a}\right)}$$

Special case: high dilution The question that now arises: if we have a solution with $C_b = 10^{-8.5}\mathrm{M}$, $K_b(\mathrm{NH_3}) \approx 1.8 \times 10^{-5}$. What is the pH of this solution?
Everything depends on the value of K_b. The base concentration (C_b) is of the same order of magnitude as the pure water contribution $[\mathrm{OH}^-]_{\text{water}} = 10^{-7}\,\mathrm{M}$. In this case, we must not neglect water and what it brings to the solution (the influence of water on pH is not negligible). In the general case, here is how to decide rigorously.

Simple and safe procedure

a) Calculate x, the positive solution of the exact equation (neglecting water autoprotolysis):

$$x = \frac{-K_b + \sqrt{K_b^2 + 4K_b C_b}}{2} \qquad (x \approx [\mathrm{OH}^-] \text{ from the base})$$

b) Calculate the degree of dissociation: $\alpha = \dfrac{x}{C_b}$

c) Interpretation:
- If $\alpha < 0.1$: the approximation $\alpha \ll 1$ is acceptable.
- If $\alpha > 0.1$: we must use the exact solution (quadratic equation).

d) Compare x to the water contribution ($10^{-7}\,\mathrm{M}$):

- If $x \ll 10^{-7}$: water dominates and the pH will be close to 7 (the small base contribution changes almost nothing).
- If $x \gtrsim 10^{-7}$: the base significantly influences the pH.

In summary: We must calculate x using the quadratic formula, then evaluate α and compare x to 10^{-7}. In this section we will treat both cases and see the difference.

Demonstration of pH for a very dilute weak base (ammonia):

Consider ammonia NH_3 in aqueous solution:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

- Initial concentration: $C_b = 10^{-8.5}$ M $\approx 3.16 \times 10^{-9}$ M
- Basicity constant: $K_b(NH_3) \approx 1.8 \times 10^{-5}$
- Degree of dissociation: $\alpha = \dfrac{[OH^-]}{C_b}$

Reaction Equation		NH_3 + H_2O $\rightleftharpoons$	NH_4^+ +	OH^-
Initial state at t_0	$\alpha = 0$	C_b	0	0
Intermediate state at t	$0 < \alpha < 1$	$C_b - C_b\alpha$	$C_b\alpha$	$C_b\alpha$
Final state at t_{eq}	$\alpha \ll 1$	$C_b(1-\alpha) \simeq C_b$	$C_b\alpha$	$C_b\alpha$

1. Dissociation equation The basicity constant is:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \approx \frac{(C_b\alpha)(C_b\alpha)}{C_b(1-\alpha)} = \frac{C_b^2\alpha^2}{C_b} \approx C_b\alpha^2$$

We obtain:

$$\alpha \approx \sqrt{\frac{K_b}{C_b}} \quad \Longrightarrow \quad [OH^-] = C_b\alpha \approx \sqrt{K_bC_b}.$$

2. Expression of pOH and pH

$$\text{pOH} = -\log[OH^-] = -\log\sqrt{K_bC_b} = -\frac{1}{2}\log(K_bC_b)$$

$$\text{pOH} = \frac{1}{2}(\text{p}K_b - \log C_b) = 6.62$$

$$\text{pH} = 14 - \text{pOH} = 14 - \frac{1}{2}(\text{p}K_b - \log_{10} C_b) = 7.38 \quad \text{Physically incorrect}$$

3. Note: For a very low concentration ($C_b \ll 10^{-7}$ M), the contribution of water to the OH^- concentration becomes dominant. In this case, the pH remains very close to 7, and the approximation $\alpha \ll 1$ is not appropriate (it is false).

Reaction Equation		NH_3 + H_2O $\rightleftharpoons$	NH_4^+ +	OH^-
Initial state at t_0	$\alpha = 0$	C_b	0	0
Intermediate state at t	$0 < \alpha < 1$	$C_b - C_b\alpha$	$C_b\alpha$	$C_b\alpha$
Final state at t_{eq}	$\alpha > 0.1$	$C_b(1-\alpha)$	$C_b\alpha$	$C_b\alpha$

1) Usual approximation (neglecting water autoprotolysis):
By setting $[OH^-] = C_b\alpha = y$ and neglecting K_e,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{y^2}{C_b - y} \quad \Longrightarrow \quad y^2 + K_by - K_bC_b = 0,$$

hence the positive solution

$$y = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_b}}{2} \approx 3.1617 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(3.1617 \times 10^{-9}) \approx 8.5 \quad \Rightarrow \quad \text{pH} = 14 - 8.5 = 5.5$$

Caution

Why is pH = 5.50 physically impossible?

- At pH = 5.50, $[H_3O^+] \approx 3.16 \times 10^{-9}$ M
- This concentration comes **solely** from ammonia
- But pure water at 25 °C already provides $[H_3O^+] = 10^{-7}$ M
- Ammonia, being a **base**, cannot **acidify** the solution!

Note: this result (pH = 5.50) is counterintuitive; it corresponds to taking into account **only** the dissociation of the base without water autoprotolysis. For such dilute solutions, we must imperatively take K_e into account.
2) Exact solution (taking water autoprotolysis K_e into account): Ammonia is a weak base, but here $C_b \ll K_b$, which means it is very dilute. In this case, the pH is mainly influenced by water, but the base provides a slight contribution.

a) **Equilibria to consider are**:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$\text{With: } K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \tag{1}$$

And:

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^- \quad \text{(autoprotolysis)}$$

$$\text{With: } K_e = [H_3O^+][OH^-] = 10^{-14}$$

b) **Species balance**:

- Conservation of matter: $[NH_3]_{eq} + [NH_4^+]_{eq} = [NH_3]_0 = C_b$ (2)
- Electroneutrality: $[NH_4^+] + [H_3O^+] = [OH^-]$

c) **Approximation**: Since C_b is very small, we expect the pH to be close to 7.

$$\text{From electroneutrality: } [NH_4^+] + [H_3O^+] = [OH^-] \tag{3}$$

Now, $[NH_4^+]$ can be expressed as a function of K_b and C_b. For a very dilute weak base, we use:

$$[NH_4^+] \approx \frac{K_bC_b}{K_b + [OH^-]} \tag{4}$$

Where does this equation (4) come from?

$$\text{With (1) and (2) we obtain: } K_b = \frac{[NH_4^+][OH^-]}{C_b - [NH_4^+]}$$

$$K_b(C_b - [NH_4^+]) = [NH_4^+][OH^-]$$

$$K_bC_b - K_b[NH_4^+] = [NH_4^+][OH^-]$$

$$K_bC_b = [NH_4^+]([OH^-] + K_b)$$

$$\boxed{[NH_4^+] = \frac{K_bC_b}{[OH^-] + K_b}}$$

But since C_b is very small and $[OH^-] \approx 10^{-7}$, we have $K_b \gg [OH^-]$ (because $K_b = 1.8 \times 10^{-5}$ and $[OH^-] \approx 10^{-7}$), therefore:

$$[NH_4^+] \approx \frac{K_bC_b}{K_b} = C_b$$

This is not entirely exact because $[OH^-]$ is not negligible compared to K_b. In fact, we must solve exactly.

d) **Exact resolution method**: From electroneutrality with substitution (4) into (3):

$$[NH_4^+] + [H_3O^+] = [OH^-]$$

$$\frac{K_b C_b}{[OH^-] + K_b} + \frac{K_e}{[OH^-]} = [OH^-]$$

Let $[OH^-] = y$, and solve:

$$y = \frac{K_b C_b}{y + K_b} + \frac{K_e}{y}$$

Since $K_b \gg y$ (because $y \approx 10^{-7}$, $K_b = 1.8 \times 10^{-5}$), we approximate $y + K_b \approx K_b$, therefore:

$$y \approx \frac{K_b C_b}{K_b} + \frac{K_e}{y} = C_b + \frac{K_e}{y}$$

$$y \approx C_b + \frac{K_e}{y}$$

$$y^2 \approx C_b y + K_e$$

$$y^2 - C_b y - K_e = 0$$

This is a quadratic equation: $y^2 - C_b y - K_e = 0$ With $C_b = 3.1623 \times 10^{-9}$, $K_e = 10^{-14}$.
Let us solve:

$$\boxed{y = \frac{C_b + \sqrt{C_b^2 + 4K_e}}{2}} = 1.0158 \times 10^{-7}$$

Thus, $[OH^-] \approx 1.0158 \times 10^{-7}$ **M**, therefore $\text{pOH} = -\log(1.0158 \times 10^{-7}) \approx 6.993$.

$$\text{pH} = 14 - 6.993 = 7.007$$

Key takeaways

$$\text{pH} = 14 + \log\left(\frac{C_b + \sqrt{C_b^2 + 4K_e}}{2}\right) \tag{4.13}$$

The pH is very slightly above 7 due to the presence of the weak base.

$$\boxed{\textbf{pH} \approx 7.007}$$

Caution

Notes and practical conditions:

- The quadratic approximation (without K_e) gives pH ≈ 5.50 here, clearly physically incorrect: water dominates at these dilutions and makes the solution practically neutral.
- For $C_b \lesssim 10^{-7}\,\text{mol} \cdot \text{L}^{-1}$ we must always solve the cubic (or include K_e) to obtain a reliable result.
- If $C_b \gtrsim 10^{-6}\,\text{mol} \cdot \text{L}^{-1}$, the quadratic generally suffices.

We also sometimes find demonstrations using K_a:
1) Usual approximation (neglecting water autoprotolysis):
By setting $[OH^-] = C_b\alpha = y$ and neglecting K_e,

$$K_b = \frac{K_e}{K_a} = \frac{10^{-14}}{K_a} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{y^2}{C_b - y}$$

$$\Rightarrow \frac{y^2}{C_b - y} = \frac{K_e}{K_a} \quad \Longrightarrow \quad K_a y^2 = K_e(C_b - y)$$

$$K_a y^2 + K_e y - K_e C_b = 0,$$

hence the positive solution

$$\boxed{y = \frac{-K_e + \sqrt{K_e^2 + 4K_eK_aC_b}}{2K_a}}$$

Numerical substitution with $K_a(NH_4^+) = 5.56 \times 10^{-10}$:

$$y \approx 3.1617 \times 10^{-9}\ \text{mol} \cdot \text{L}^{-1} \quad \Rightarrow \quad \text{pOH} = -\log y \approx 8.5 \quad \Rightarrow \quad \text{pH} = 14 - 8.5 = 5.5$$

Note: this result (pH = 5.50) is counterintuitive; it corresponds to taking into account **only** the dissociation of the base without water autoprotolysis; for such dilute solutions we must imperatively take K_e into account.
2) Exact solution (taking water autoprotolysis K_e into account): Ammonia is a weak base, but here $C_b \ll K_b$, which means it is very dilute. In this case, the pH is mainly influenced by water, but the base provides a slight contribution.

a) **Equilibria to consider**:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$\text{With: } K_b = \frac{K_e}{K_a} = \frac{10^{-14}}{K_a} = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{1}$$

And:

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^- \quad \text{(autoprotolysis)} \quad K_e = [H_3O^+][OH^-] = 10^{-14}$$

b) **Species balance**:

- Conservation of matter: $[NH_3]_{eq} + [NH_4^+]_{eq} = C_b$ (2)
- Electroneutrality: $[NH_4^+] + [H_3O^+] = [OH^-]$

c) **Approximation**: Since C_b is very small, we expect the pH to be close to 7.

$$\text{From electroneutrality:} [NH_4^+] + [H_3O^+] = [OH^-] \tag{3}$$

Now, $[NH_4^+]$ can be expressed as a function of K_a and C_b. For a very dilute weak base:

$$[NH_4^+] \approx \frac{K_bC_b}{K_b + [OH^-]} = \frac{\frac{K_e}{K_a}C_b}{\frac{K_e}{K_a} + [OH^-]} = \frac{K_eC_b}{K_e + K_a[OH^-]} \tag{4}$$

d) **Exact method**: From electroneutrality with substitution of (4) into (3):

$$[NH_4^+] + [H_3O^+] = [OH^-]$$

$$\frac{K_eC_b}{K_e + K_ay} + \frac{K_e}{y} = y$$

Since $K_a = 5.56 \times 10^{-10}$ and $y \approx 10^{-7}$, we have $K_ay \approx 5.56 \times 10^{-17} \ll 10^{-14}$, therefore:

$$\frac{10^{-14}C_b}{K_e} + \frac{K_e}{y} \approx y$$

$$y^2 - C_by - K_e = 0$$

Resolution:

$$y = \frac{C_b + \sqrt{C_b^2 + 4K_e}}{2} = 1.0158 \times 10^{-7}$$

Thus, $[OH^-] \approx 1.0158 \times 10^{-7}$ **M**, therefore $\text{pOH} = -\log(1.0158 \times 10^{-7}) \approx 6.993$.

$$\text{pH} = 14 - 6.993 = 7.007$$

The pH is very slightly above 7 due to the presence of the weak base.

$$\boxed{\textbf{pH} \approx 7.007}$$

For the more curious: detailed mathematical approach:

a) **Species balance**:
- **Conservation of matter:** $[NH_3]_{eq} + [NH_4^+]_{eq} = [NH_3]_0 = C_b$
- **Electroneutrality:** $[NH_4^+] + [H_3O^+] = [OH^-]$

b) **Approximation and development**: Since C_b is very small, we expect the pH to be close to 7.
From electroneutrality:

$$[NH_4^+] = [OH^-] - [H_3O^+] = [OH^-] - \frac{K_e}{[OH^-]}$$

From conservation of matter:

$$[NH_3]_{eq} = C_b - [NH_4^+]_{eq} = C_b - \left([OH^-] - \frac{K_e}{[OH^-]}\right)$$

Expression of K_b as a function of $[OH^-]$:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{\left([OH^-] - \frac{K_e}{[OH^-]}\right)[OH^-]}{C_b - [OH^-] + \frac{K_e}{[OH^-]}} = \frac{[OH^-]\left([OH^-]^2 - K_e\right)}{C_b[OH^-] - [OH^-]^2 + K_e}$$

Final cubic equation:

$$\begin{aligned} K_b\left(C_b[OH^-] - [OH^-]^2 + K_e\right) &= [OH^-]\left([OH^-]^2 - K_e\right) \\ K_bC_b[OH^-] - K_b[OH^-]^2 + K_bK_e &= [OH^-]^3 - K_e[OH^-] \\ [OH^-]^3 + K_b[OH^-]^2 - (K_bC_b + K_e)[OH^-] - K_bK_e &= 0 \end{aligned}$$

For a very dilute weak base, the hydroxide ion concentration is the solution of the cubic equation:[31]

$$[OH^-]^3 + K_b[OH^-]^2 - (K_bC_b + K_e)[OH^-] - K_bK_e = 0$$

Approximate resolution:
The cubic equation can be simplified by neglecting the terms in $[OH^-]^3$ and $[OH^-]^2$ because $[OH^-]$ is small for a dilute weak base.
We then obtain:

$$-(K_bC_b + K_e)[OH^-] - K_bK_e \approx 0$$

That is:

$$[OH^-]^2 = K_bC_b + K_e$$

Hence the solution:

$$\boxed{[OH^-] = \sqrt{K_bC_b + K_e}}$$

$$\text{pH} = 14 + \log(\sqrt{1.8 \cdot 10^{-5} \cdot 10^{-8.5} + 10^{-14}}) = 7.5$$

Special case of very dilute solutions

When acid or base solutions are extremely dilute ($C < 10^{-6}$ M), water autoprotolysis becomes significant[31],[34] and can no longer be neglected. The pH approaches slightly 7. In very dilute solutions, water is no longer a simple solvent but actively participates in the acid-base equilibrium. Its influence becomes predominant when concentrations become comparable to 10^{-7} M.

The logic of pH calculations

In acid-base chemistry, a fundamental truth emerges: every aqueous solution contains a **constant dialogue** between acidic and basic species. This dialogue follows precise rules that we have explored:

- **Two major families** oppose and complement each other: **acids** (proton donors) and **bases** (proton acceptors)
- **Two personalities** characterize each family: **strong** ones that commit completely to the reaction, and

weak ones that hesitate and establish a delicate equilibrium

- **Two master factors** determine the final pH:
  - The **amount** present (the concentration C): the more acid or base we add, the more pronounced the effect
  - The **intrinsic strength** (K_a or K_b): the natural ability to release or capture protons

The beauty of this system lies in its **dynamic equilibrium**: when a weak acid is very concentrated, it can influence the pH almost like a strong acid. Conversely, a very dilute strong acid approaches the pH of pure water.
This understanding allows us to **predict** and **calculate** the pH in varied situations, from ultra-acidic to ultra-basic solutions, passing through all intermediate nuances. Each pH calculation thus tells the story of this subtle balance between concentration and strength, between total commitment and measured hesitation.

To better grasp a problem and find the pH, I present the golden rule:

a) **I choose my side:** Acid or Base?
b) **I choose my weapon: Strong** (simple) or **Weak** (calculation)?
c) **I check the concentration:** Is it **Normal** or **Very dilute**? **Water intervenes** (look for the term K_e or $\sqrt{... + K_e}$).

The table below summarizes the main equations for calculating the pH of acidic and basic solutions. The formulas are chosen according to the type of solute and its degree of dissociation α as well as cases of high dilution.
Note: For weak bases, the two formulas in each case are mathematically equivalent. The first uses the basicity constant K_b, while the second uses the acidity constant K_a.

Conclusion

The determination of pH in aqueous solution constitutes a fundamental exercise in chemical thermodynamics, requiring the judicious selection of an **appropriate level of approximation** contingent upon three interdependent parameters: the nature of the electrolyte (strong versus weak), the analytical concentration C, and the degree of dissociation α. This methodological hierarchy reflects the underlying thermodynamic reality that proton transfer equilibria are governed by relative magnitudes rather than absolute values.
For **strong electrolytes** ($\alpha \simeq 1$), complete dissociation renders the pH a straightforward function of the stoichiometric concentration, with activities often approximated by concentrations in dilute media ($\gamma_i \approx 1$). The pH is then obtained directly from the logarithmic relation $\mathrm{pH} = -\log[\mathrm{H^+}]$ for strong acids, or via $p\mathrm{OH}$ for strong bases.
For **weak electrolytes**, the situation demands a more nuanced treatment. The relationship between $[\mathrm{H^+}]$ and the acidity constant K_a (or K_b for bases) is governed by the equilibrium expression:

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

The **weak dissociation approximation** ($\alpha \ll 1$) remains valid provided that the extent of ionization does not exceed approximately 5% of the initial concentration — a criterion often formalized as the "5% rule." This approximation yields the simplified expression:

$$[\mathrm{H^+}] \approx \sqrt{K_a C_a}$$

When this condition is violated, the exact quadratic equation must be solved:

$$[\mathrm{H^+}]^2 + K_a[\mathrm{H^+}] - K_a C_a = 0$$

which admits the physically meaningful solution:

$$[\mathrm{H^+}] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_a}}{2}$$

For **extremely dilute solutions** (typically $C \lesssim 10^{-6}\ \mathrm{mol\,L^{-1}}$), the autoprotolysis of water can no longer be neglected. This fundamental equilibrium:

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-} \qquad K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 10^{-14} \quad \text{at } 25^\circ\mathrm{C}$$

must be incorporated into the charge balance, leading to the general expression:

$$[\mathrm{H}^+] = \frac{K_w}{[\mathrm{OH}^-]} \quad \text{or} \quad [\mathrm{H}^+]^2 - K_a C_a - K_w = 0$$

depending on the system.
This progressive refinement — from the strong electrolyte simplification to the weak dissociation approximation, and finally to the full treatment incorporating water autoprotolysis — constitutes a coherent and pedagogical framework for mastering acid-base equilibria. Such a systematic approach is indispensable not only for fundamental chemistry but also for applications in biochemistry, pharmaceutical sciences, and environmental chemistry, where proton transfer processes are ubiquitous.[31],[32]

Table 4.13 pH calculation formulas in aqueous solution (at 25 °C).

Solution Type	Conditions	pH Equation (mnemonic)
Strong acid	$\alpha = 1$	$\mathrm{pH} = -\log C_A$ (Strong = Simple)
Strong base		$\mathrm{pH} = 14 + \log C_B$ (Base = Bonus +14)
Weak acid	$\alpha < 0.1$	$\mathrm{pH} = \frac{1}{2}\left(\mathrm{p}K_a - \log C_a\right)$ (weak = half-formula)
Weak base		$\mathrm{pH} = \frac{1}{2}\left(14 + \mathrm{p}K_a + \log C_b\right)$
		$\mathrm{pH} = 14 - \frac{1}{2}\left(\mathrm{p}K_b - \log C_b\right)$
Weak acid	$\alpha > 0.1$	$\mathrm{pH} = -\log\left(\frac{-K_a + \sqrt{K_a^2 + 4K_a C_a}}{2}\right)$
Weak base		$\mathrm{pH} = 14 + \log\left(\frac{-K_e + \sqrt{K_e^2 + 4K_e K_a C_b}}{2K_a}\right)$
		$\mathrm{pH} = 14 + \log\left(\frac{-K_b + \sqrt{K_b^2 + 4K_b C_b}}{2}\right)$
Ultra-dilute strong acid	$C < 10^{-6}$	$\mathrm{pH} = -\log\left(\frac{C_a + \sqrt{C_a^2 + 4K_e}}{2}\right)$
Ultra-dilute strong base		$\mathrm{pH} = 14 + \log\left(\frac{C_b + \sqrt{C_b^2 + 4K_e}}{2}\right)$
Ultra-dilute weak acid	$C_a \ll K_a$	$\mathrm{pH} = -\frac{1}{2}\log\left(K_a C_a + K_e\right)$
	general solution	$\mathrm{pH} = -\log\left(\frac{-K_a + \sqrt{K_a^2 + 4K_a C_a + 4K_e}}{2}\right)$
Ultra-dilute weak base	$C_b \ll K_b$	$\mathrm{pH} = 14 + \frac{1}{2}\log\left(K_b C_b + K_e\right)$
	general solution	$\mathrm{pH} = 14 + \log\left(\frac{-K_b + \sqrt{K_b^2 + 4K_b C_b + 4K_e}}{2}\right)$

Chapter 5

Acid-Base Titration

In chemistry, it is not enough to know which substances are present in a sample (qualitative analysis); it is often crucial to know in what quantity they are present (quantitative analysis). Think of a recipe: saying "add some salt" is very different from prescribing "5 grams of salt." The first is qualitative (identifying the ingredient), the second is quantitative (measuring its amount). Titration, or quantification, is precisely the transition from theory ("iron is present in this water") to practice ("there is 0.2 milligrams of iron per liter of water"). Without this precise measurement, chemistry would remain a descriptive science. Titration allows us to make rapid decisions: a physician can diagnose a disease through blood glucose levels, or adjust a drug dosage based on its pKa to optimize intestinal absorption.[(35)] An engineer can check if river water is drinkable, and an industrial pharmacist can ensure that a medication contains the correct dose of active ingredient. In short, titrating means giving meaning and value to our chemical observations in order to act on the real world.

From theory to practice: why titrate?

Imagine a physician receiving the results of a blood test. Knowing that "glucose is present" in the sample is qualitatively interesting, but clinically useless. On the other hand, knowing that the glucose concentration is 1.2 grams per liter is a quantitative, objective datum that allows a diagnosis of diabetes and a treatment decision. This is the whole difference between describing and acting. Titration, or quantification, is the essential bridge between the presence of a molecule and its biological impact. As future healthcare professionals, you will be confronted every day with titration results: to prescribe the right drug at the right dosage, to monitor the progression of a disease, or to guarantee the purity of a compound in pharmacy. Titrating is therefore translating the language of chemistry into a relevant medical, pharmaceutical, or biological decision.

The importance of titrations in analytical chemistry

If analytical chemistry is the art of investigation in the service of life sciences, titration is its irrefutable proof. It is the tool that transforms a suspicion into a measurable fact, the foundation of evidence-based medicine. Its importance is omnipresent and critical in your future professions:

- In medicine, titration is the key to diagnosis and monitoring. It allows evaluation of renal function through creatinine assays, confirmation of myocardial infarction by measuring troponin, or adjustment of drug doses such as the anticoagulant warfarin to avoid hemorrhages or thromboses.
- In pharmacy, it is essential at every stage of the drug lifecycle: from manufacturing, where the exact dose of active ingredient is verified, to pharmacovigilance, where blood assays allow monitoring of drug pharmacokinetics and anticipation of side effects.[(35)]
- In dental surgery, titrations guarantee the safety of care, whether it involves controlling the concentration of local anesthetic or verifying the biocompatibility and composition of filling materials or prostheses.
- In life sciences, titration is a fundamental research tool for quantifying gene expression, measuring enzyme activity, or monitoring nutrient consumption by cell cultures.

Without titration, clinical practice would be nothing but a series of conjectures. Titration provides the numbers, the thresholds, the evidence that allow moving from uncertainty to an informed and safe decision for the patient.

Overview of the approach

Performing a reliable titration, especially on a complex biological sample such as blood or saliva, is not improvised. It follows a rigorous methodology in four steps, which you must master to guarantee the validity of your results.

1) Define the analytical problem: This is the clinical or biological starting point. The question is not "what are we measuring?" but "why are we measuring this and in which matrix?" For example: "What is the LDL

(low-density lipoprotein) cholesterol level in this patient at cardiovascular risk?" or "What is the fluoride concentration in this toothpaste?" This definition conditions everything else.

2) Choose and prepare: Select the most appropriate assay method (spectrophotometry, chromatography, immunoassay...) based on the analyte, the complexity of the sample (blood, urine, saliva), and the required precision. The sample often must be prepared: centrifugation of blood to isolate plasma, dilution, filtration... This is a crucial step to avoid interferences.

3) Measure: This is the experimental phase, where the chosen technique is implemented. Whether with a clinical chemistry analyzer or a laboratory spectrophotometer, this step requires extreme rigor in reagent handling and signal recording (a color, a light, a current...).

4) Interpret and conclude: The raw signal is translated into concentration by calculation. But the work does not stop there. The result must be compared to reference intervals (the "normal values") to be interpreted. The conclusion is not "the concentration is X", but "the concentration is X, which is above normal, suggesting such pathology." This is the return to the initial question to provide useful and actionable information.

Definition and objectives

A **titration**, or quantitative analysis, is the set of operations that allow the precise determination of the quantity of a specific chemical substance, called the **analyte**, present in a sample. It is not about knowing *if* a molecule is present (qualitative analysis), but answering the question: "**How much?**" This "how much" can be expressed in different ways: a mass (in grams, milligrams), a concentration (in moles per liter, grams per liter), or even a volume.

The objectives of a titration are varied but always centered on decision-making. In life sciences and healthcare, a titration allows:

- **Diagnose:** The concentration of a biological marker (such as troponin for a heart attack) allows confirmation of a pathology.
- **Monitor:** Track the progression of a disease or the effectiveness of a treatment by regularly assaying a molecule in the blood.
- **Define a dosage:** Adjust the dose of a drug so that it is therapeutic without being toxic.
- **Quality control:** Verify that a medication, cosmetic, or medical device contains the promised amount of active ingredient and complies with safety standards.
- **Detect toxicity:** Measure the concentration of a poison or pollutant in a biological or environmental medium.

In summary, titration transforms a chemical presence into a quantitative datum, essential for any reasoning and action in medicine, pharmacy, and biology.

Analogy: The mystery recipe

To understand the principle, imagine you are a chef and you find an exceptional cake recipe... but a crucial piece of information is missing. For the sugar, it simply says: "Add sugar." If you add a pinch, the cake will be bland. If you add the whole bag, it will be inedible. The recipe is unusable without the **exact quantity** of sugar.

In this situation:

- Your cake batter: is the **sample** to be analyzed (e.g., a patient's blood or a medication vial).
- The sugar: is the **analyte**, the substance being quantified (e.g., glucose or the active ingredient of an antibiotic).
- Your question "How much sugar did I put in?" is **the objective of the titration**: determining the **concentration** $\left(c = \frac{n}{V} \text{ in mol/L}\right)$.
- Your precision scale and graduated measuring cup: are the **laboratory instruments** (analytical balance, UV-Vis spectrophotometer).
- Your method: prepare **standards** (reference batters with 0 g, 5 g, 10 g of sugar per L), measure the "taste" (or absorbance in the lab), plot the **calibration curve** (taste vs. dose), then estimate the unknown dose by interpolation.

Clinical example: Blood glucose assay by UV spectroscopy (821 nm). Standards: 0–20 mmol/L. Result: $c = 5.2 \pm 0.1$ mmol/L.

Titration is exactly that: it is the operation that allows you to go from "add sugar" (vague and useless information) to "add **exactly 150 grams of sugar**" (precise and actionable information). In the same way,

a physician cannot treat a patient knowing only that they have "cholesterol"; they need to know that they have 2.5 g/L to prescribe the right treatment.

Essential vocabulary

To master titrations, you must first speak the same language. Some terms are fundamental, and their distinction is crucial for understanding the approach and avoiding interpretation errors.

Titrand and titrant solutions

Imagine you are an investigator facing a suspicious blood sample. You want to know if it contains substance X and in what quantity.

The titrand solution (or titrated solution) is your **unknown sample**. It is the solution that contains the analyte whose quantity you are trying to determine. In our analogy, it is the vial of blood taken from the patient. Its concentration in substance X is the "mystery" to be solved.

The titrant solution is your **measuring tool**. It is a solution whose concentration is known **very precisely**. It is added progressively (drop by drop) to the titrand solution. It is the "revealing reagent" that will react in a predictable way with substance X.

In summary: we have a known volume of the **titrand solution** (the unknown) and we add a measured volume of the **titrant solution** (the known) to find the unknown.

Equivalence point and endpoint

This is the most important distinction, and often the most confusing. Think of a GPS.

The equivalence point is a **theoretical, perfect** concept. It is the exact, mathematical instant when the reactants have been introduced in ideal stoichiometric proportions. That is, the amount of substance (in moles) of titrant added is perfectly sufficient to consume all the amount of substance of the analyte in the titrand solution. Neither remains. It is like the exact GPS coordinates of the address you are aiming for.

The endpoint is an **experimental, concrete** notion. It is the instant you observe and that indicates you have reached (or very slightly exceeded) the equivalence point. Most often, this signal is a **sudden color change** of a colored indicator added to the mixture. It is the moment when your GPS announces: "You have arrived." In practice, you may be a few meters from the door, but it is enough to know you are at your destination.

The objective of any titration is to choose a method and an indicator such that the **endpoint** (what you see) is as close as possible to the **equivalence point** (what really happens).

pH jump

The pH jump is not a concept, but an **observable phenomenon**. It is the signature, the alarm signal that warns us that we have just crossed the equivalence point. During an acid-base titration, just before the equivalence point, the solution still contains some acid (or base) that "buffers" the system and prevents the pH from varying much. At the precise moment of the equivalence point, all the acid (or base) has been neutralized. If you add a single additional drop of titrant (strong), this drop finds itself "alone" in a neutral medium and causes a **sudden and immense** variation in pH. This is the almost vertical spike on a titration curve called the **pH jump**. It is this jump that causes the color change of the indicator and allows us to locate the endpoint.

5.1 The titration reaction

Titration does not work with just any chemical reaction. For a reaction to serve as the basis for a reliable titration, it must imperatively meet three conditions, which Skoog et al. describe as the fundamental criteria of any analytical titration:[(36)] the "three pillars" of titration.

Characteristics (complete, specific, rapid)

a) **Complete (or quantitative):** The reaction must be complete. At the end, there must be no reactants left (or a negligible amount). If the reaction is an equilibrium, part of the reactants remains in solution

and it is impossible to know when we have added "just enough" titrant.
    - **Analogy:** It is like filling a bucket that has no hole. We know that once full, all the water poured in will overflow. If the bucket has a hole (non-complete reaction), it will never fill completely.
b) **Specific (or univocal):** The titrant must react **only** with the analyte of interest. If it also reacts with other compounds present in the sample (impurities, solvent...), the measurement will be skewed because we will be titrating several things at once without knowing it.
    - **Analogy:** It is like having a key that only opens one lock. If your key also opens your neighbor's door, you will never know which door you actually opened.
c) **Rapid:** The reaction must be instantaneous, or at least very fast. If the reaction is slow, you will add titrant while waiting for the previous reaction to finish, and you will largely exceed the equivalence point without even realizing it.
    - **Analogy:** It is like driving a car with brakes that react immediately. If you press the pedal and the car takes 10 seconds to stop, you will always overshoot your stopping point.

How to choose the right reaction?

The choice of reaction is not random; it follows from the nature of the analyte. The approach is as follows:
a) **Identify the chemical family** of the analyte: is it an acid? a base? an oxidant? a reductant? a metal ion?
b) **Select the corresponding type of reaction:**
    - Acid + Base → Acid-base reaction
    - Oxidant + Reductant → Oxidation-reduction (redox) reaction
    - Metal ion + Ligand → Complexation reaction
    - Two ions that form a precipitate → Precipitation reaction
c) **Verify that the chosen reaction** respects the three pillars (complete, specific, rapid). For this, we rely on known data (equilibrium constants, redox potentials, etc.) and experience.

Correction elements for the exercise:
a) **Yes.** The reaction is complete (strong acid/strong base), specific (no other reactants), and instantaneous. It is the perfect titration.
b) **No, or it is complicated.** The problem is the **specificity** criterion. Sodium hydroxide will react with acetic acid but also with amino acids. We will not be titrating only the vinegar.
c) **No.** The problem is the **completeness** criterion. The double arrow ($\rightleftharpoons$) indicates an equilibrium. The reaction is not complete; there will always be free Cu^{2+} ions, making it impossible to determine a clear equivalence point.

5.2 pH-metric Monitoring: Theory

5.2.1 The principle of pH-metric monitoring

Why measure pH?

During an acid-base titration, the molecules (acid and base) are invisible. How do we know where we are in the reaction? How do we know when we have reached the equivalence point without a color indicator that would change imprecisely? The answer is to follow a **signal** that directly depends on the reaction. pH is this signal.
By continuously measuring the pH of the solution with an electrode, we have a "thermometer" of acidity. Each drop of titrant added modifies the concentration of H_3O^+ (or OH^-) ions, and therefore the pH. By following this evolution, we are not just reading numbers: we are observing in real time the "battle" between the acid and the base. The pH meter is our eye, the one that allows us to see the invisible and transform a chemical reaction into a curve, a concrete and analyzable object of study.

The pH = f(V) curve: the "identity card" of the titration

If the pH meter is our eye, the titration curve, which plots pH as a function of the volume of titrant added (noted pH = f(V)), is the brain that interprets the information. This curve is not just a simple graph; it is the true **identity card** of the titration. For this "identity card" to be usable, the pH = f(V) curve must

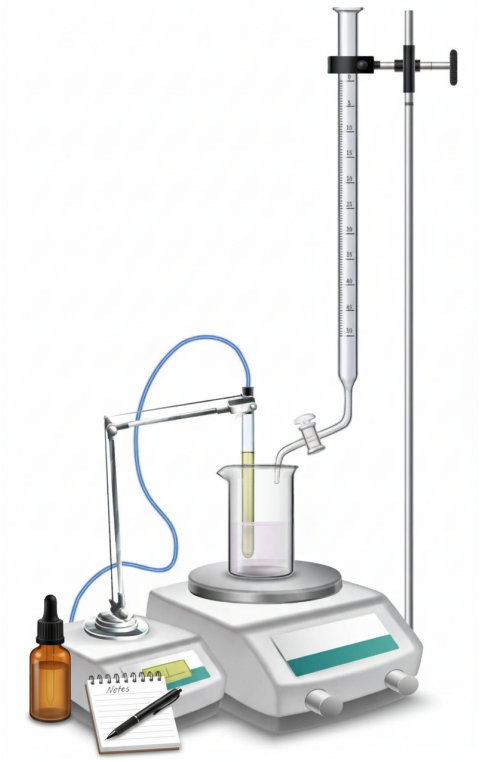


Figure 5.1 pH-metry setup

be constructed from reliable measurements: for each volume V of titrant added, the pH is recorded after stabilization, with additions tightened near the pH jump to determine V_{eq} precisely.

Experimental protocol: The protocol described below follows Harris's recommendations for pH-metric titrations:[37]

1. Set up the apparatus as shown in Figure 5.1.
2. Rinse then fill the graduated burette with the titrant solution.
3. Pipette **10.0 mL** of the titrand solution using a volumetric pipette and a propipette, then introduce it into the beaker.
4. Place a magnetic stir bar in the beaker, place it on the magnetic stirrer, then immerse the pH meter electrode (without touching the stir bar).
5. Start the magnetic stirrer, turn on the pH meter, and record the initial pH (V=0).
6. Add a volume ΔV of titrant solution, wait for the display to stabilize, then record the pH and the total volume V added.
7. Repeat the previous step, recording the (V,pH) pair after each addition.
8. Near the pH jump, perform additions in 0.5 mL increments, recording (V,pH) after each addition.
9. When the pH no longer varies significantly, resume additions in 1.0 mL increments, recording (V, pH) after each addition.
10. Plot the curve pH = f(V) to determine V_{eq} (equivalence volume).

Think of an electrocardiogram (ECG) for a heart. For a physician, the peaks and troughs of the ECG tell a complete story: the rhythm, the strength of contractions, possible pathologies. Similarly, the pH = f(V) curve tells the complete story of our reaction:

- The **starting point** (initial pH) tells us whether we are dealing with a strong or weak acid.
- The **general shape** of the curve before the jump informs us about the strength of the acid or base we are titrating.
- The **position** of the large pH jump gives us the volume of titrant needed to neutralize the analyte, and therefore its quantity: this is the goal of the titration!
- A very precise point on the curve, which we will see later, even gives us the **pKa** of the acid, a fundamental datum in pharmacy.

Learning to read this curve is like learning to read an ECG: it is acquiring the ability to diagnose a chemical reaction with precision and confidence.

5.2.2 The four characteristic zones

The theoretical analysis of acid-base titration curves is developed in detail by Atkins and de Paula.[38] The titration curve is not monotonic: it can be divided into four distinct zones, like the four acts of a play. Understanding each zone means understanding the chemistry happening at each moment of the titration.

Phase 1: Before the equivalence point

- **What happens:** We add the titrant (for example, a strong base) to our titrand solution (an acid). But there is still a large **excess of acid** in the beaker.
- **Curve appearance:** The pH increases, but very slowly. The curve has a gentle slope.
- **Why?** We are in the presence of a **buffer solution**. The large amount of remaining acid "absorbs" the base we add, limiting the pH variation. It is like trying to heat a huge swimming pool with a single kettle: the water temperature (the pH) will barely increase. The solution resists change.

Phase 2: The half-equivalence point

- **What happens:** We have added **exactly half** the volume of titrant needed to reach the equivalence point. At this precise instant, the amount of remaining acid (HA) is equal to the amount of its conjugate base formed (A^-).
- **Curve appearance:** This is a particular point located in the middle of the buffer zone. The curve is often the "flattest" there.
- **Why is this a key point?** At this instant, a fundamental relationship appears: **the pH of the solution is equal to the pKa of the titrated acid** (pH = pK_a), a direct consequence of the Henderson-Hasselbalch equation.[38] This is an extremely powerful experimental method for determining the pKa of a molecule, which is crucial for understanding the behavior of a drug in the body (its absorption, membrane passage, etc.).[35]

Phase 3: The equivalence point (the key point!)

- **What happens:** This is the pivotal moment. All the initial acid has been neutralized. There is no more acid HA, nor titrant base. The solution contains only water and the conjugate base A^-.
- **Curve appearance:** This is the famous **pH jump**. The curve is almost vertical. The pH changes by several units in a single drop of titrant.
- **Why?** The buffer capacity has disappeared! There is no more acid to neutralize the base we continue to add. The drop of strong base "falls" into a solution that can no longer counter it, causing a pH explosion. The center of this vertical jump corresponds to the **equivalence volume ($\mathbf{V_{eq}}$)**, the most important data of the titration.

Phase 4: After the equivalence point

- **What happens:** We continue to add the titrant base, but now it is in **excess**. The pH of the solution is no longer controlled by the initial acid (which has disappeared) but by the base we are adding.
- **Curve appearance:** After the jump, the pH increases again, but slowly, gradually stabilizing towards the pH of the pure titrant solution.
- **Why?** The situation is symmetric to **Phase 1**. We are progressively diluting our excess base in an increasingly larger volume of water. The pH variation becomes moderate again. The curve joins an asymptote corresponding to the pH of the sodium hydroxide solution we are adding.

5.2.3 Titration of a Strong Acid with a Strong Base: The Perfect Duel

Acid-base titration is one of the most classic and pedagogical methods in analytical chemistry. It is based on the neutralization reaction between oxonium ions H_3O^+ provided by an acid and hydroxide ions OH^- provided by a base. This reaction is complete, rapid, and stoichiometric:

$$H_3O^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,H_2O\,(l)$$

In this specific case, we consider the titration of a **strong acid** (e.g., HCl) with a **strong base** (e.g., NaOH). A strong acid is completely dissociated in aqueous solution, as is a strong base. Thus, the initial concentration of the acid directly corresponds to the concentration of H_3O^+ ions, and that of the base corresponds to the concentration of OH^- ions.

To better understand:

Imagine a duel between two fighters of absolute power and honesty. Every blow struck is effective, every defense is transparent. There is no trickery, no hidden strategy, just a pure and predictable confrontation. This is exactly what happens during the titration of a strong acid with a strong base. It is the textbook case, the reference model that allows us to understand all the others, more complex ones.

Principle of the experiment

A volume V_a of strong acid of concentration C_a is placed in a beaker. A solution of strong base of concentration C_B is progressively added using a graduated burette. With each addition, the solution reacts immediately: OH^- ions neutralize part of the H_3O^+ ions. The titration can be monitored either by a color indicator (such as phenolphthalein) or by pH measurement with a probe.

Imagine a duel between two fighters of absolute power. Every blow struck is effective, a transparent defense. There is no trickery, no hidden strategy, just a pure and predictable confrontation. This is exactly what happens during the titration of a strong acid with a strong base. It is the reference model that allows us to understand all the other, more complex cases.

To master this titration, we must answer four fundamental questions: Who are the fighters? What remains after the battle? How does the battle unfold, step by step? And how do we know when the battle is over?

5.2.4 The Fighters: "Honest" Actors

A strong acid (such as hydrochloric acid, HCl) and a strong base (such as sodium hydroxide, NaOH) are called "strong" because, once in water, they make no mystery of their identity. They dissociate **completely and immediately** into ions.

$$HCl_{(aq)} \longrightarrow {H^+}_{(aq)} + {Cl^-}_{(aq)} \quad \text{(in reality, } H_3O^+\text{)}$$

$$NaOH_{(aq)} \longrightarrow {Na_{(aq)}}^+ + OH-_{(aq)}$$

There is no equilibrium, no acid or base molecules "waiting." From the moment they are in the solution, they are 100% present as ions, ready to react. This transparency is the first key to the simplicity of this titration.

5.2.5 The Aftermath: Harmless "Spectators"

The reaction between the ions is just as direct:

$${H_{(aq)}}^+ + {OH^-}_{(aq)} \longrightarrow H_2O_{(l)}$$

What happens to the other ions, Na^+ and Cl^-? They do not participate in the reaction. They are called **spectator ions**. They are like spectators in a stadium: they are present, but they do not play the match. More importantly, these ions are chemically inert towards water. The Na^+ ion is such a weak acid that it is incapable of removing a proton from a water molecule. The Cl^- ion is such a weak base that it never captures a proton.

The product of their "association," sodium chloride (NaCl), is therefore a **neutral salt**. Dissolved in water, it does not modify the pH. This is the second key, the most important one: at the precise moment when all the acid has reacted with all the base (the equivalence point), the solution contains only water and neutral spectator ions. The pH is therefore that of pure water: **7**.

5.2.6 The Battle, Step by Step: The Anatomy of the Curve

To visualize this duel, let us follow a concrete example: we titrate 10 mL of hydrochloric acid (HCl) $C_A = 0.1$ M with sodium hydroxide (NaOH) at a concentration of $C_B = 0.1$ M. Note that it is the same concentration, so the volume needed to neutralize all the acid is 10 mL.

Reaction Equation	HCl	+ NaOH	$\rightleftharpoons$	NaCl	+ H_2O
Initial state at t_0	n_A	n_B		0	–
	C_AV_A	C_BV_B		0	–
Equilibrium state at t_{eq}	$C_AV_A - C_BV_B$	0		C_BV_B	–

Phase 1: The Reign of the Acid (Before the equivalence point)

At the beginning of the titration, the strong acid reigns supreme in the beaker. Each drop of base added is immediately neutralized by the excess of H_3O^+ ions present. The balance still tilts largely in favor of the acid: the pH increases, but very slowly. The solution retains a strongly acidic character.

Calculation at V = 1 mL of NaOH added

Reaction Equation	HCl	+ NaOH	$\longrightarrow$	NaCl	+ H_2O
Initial state (mol)	n_A	n_B		0	solvent
	$1.0 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$		0	–
Final state (mol)	$9.0 \cdot 10^{-4}$	0		$0.1 \cdot 10^{-3}$	–
	Strong acid	Strong base		Neutral salt	

Why reason in terms of amount of matter?

Imagine you are preparing a cocktail: if you pour some syrup into a glass, then add water, the sweet taste becomes weaker. The **concentration** of sugar has changed, but the **total amount** of sugar in the glass has remained the same.

This is exactly what happens during a titration:

- When the base solution is added, **the total volume increases**.
- All **concentrations** are therefore **diluted** and change constantly.
- On the other hand, the **amounts of matter (in moles)** are not affected by this dilution.

Step-by-step calculation method

1. Calculate the initial amounts of matter:

$$\text{Moles of acid: } n_A = C_AV_A = 0.1 \cdot 10 \cdot 10^{-3} = 1.0 \cdot 10^{-3} \text{ mol}$$
$$\text{Moles of base added: } n_B = C_BV_B = 0.1 \cdot 1 \cdot 10^{-3} = 1.0 \cdot 10^{-4} \text{ mol}$$

2. Identify the species determining the pH:

The final mixture contains:

- **Remaining strong acid**: active species that imposes acidity
- **Neutral salt (NaCl)**: spectator ions that do not influence the pH

Analysis of the mixture at t_{eq}: what determines the pH? Before any calculation, it is essential to identify the chemical species present in the beaker **after** the reaction, i.e., at equilibrium, and to understand their role.

In our case (before the equivalence point), the mixture consists of:

- **Remaining strong acid (HCl)**: This is the **active** species.
  - It is completely dissociated into H_3O^+ ions.
  - It is a powerful **proton donor**.
  - It **imposes** an acidic medium.
- **Salt (NaCl) formed**: This is a **spectator** species.
  - It comes from the Cl^- anion (conjugate base of a strong acid, extremely weak).
  - It comes from the Na^+ cation (conjugate acid of a strong base, extremely weak).
  - These two ions are **totally stable** in water and **do not interact** with H_3O^+ or OH^-.

– They **do not influence** the pH of the medium.

Conclusion: The pH of the mixture is **solely and entirely** controlled by the **remaining strong acid**. The salt, being neutral, only "dilutes" the solution without participating in the acid-base equilibrium.

The appropriate equation for calculating the H_3O^+ concentration is therefore the one that describes the **complete dissociation of a strong acid**:

3. Calculate the pH:

- Amount of remaining acid: $n_{\text{remaining}} = n_A - n_B = 9.0 \cdot 10^{-4}$ mol
- Total volume: $V_{\text{total}} = V_A + V_B = 11.0$ mL
- H_3O^+ concentration:

$$[H_3O^+] = \frac{n_{\text{remaining}}}{V_{\text{total}}} = \frac{9.0 \cdot 10^{-4}}{11.0 \cdot 10^{-3}} = 8.18 \cdot 10^{-2} \text{ mol/L}$$

- pH calculation:

$$\text{pH} = -\log[H_3O^+] = -\log(8.18 \cdot 10^{-2}) \approx \boxed{1.09}$$

Interpretation

The initial pH was 1.00. After adding 1 mL of base, the pH only increases very slightly to 1.09. This small variation confirms that:

- The mixture remains very acidic
- We are still far from the equivalence point
- The remaining strong acid still dominates the medium

In summary

By reasoning with amounts of matter, you follow the real evolution of the reactants, independently of dilution. This approach is essential for accurately calculating the pH at each step of the titration.

Phase 2: At Half-Equivalence (V_B = 5 mL)

We are approaching the middle of the titration. The strong base is gaining ground, but the battle is still tight. At this stage, half of the initial acid has been neutralized, while the other half remains present. This particular situation creates a characteristic equilibrium.

Calculation at V = 5 mL of NaOH added

Reaction Equation	HCl	+ NaOH	⟶ NaCl	+ H_2O
Initial state (mol)	n_A	n_B	0	solvent
	$1.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-4}$	0	–
Final state (mol)	$5.0 \cdot 10^{-4}$	0	$5.0 \cdot 10^{-4}$	–
	Strong acid	Strong base	Neutral salt	

Step-by-step calculation method

1. Calculate the initial amounts of matter:

$$\text{Moles of acid: } n_A = 1.0 \cdot 10^{-3} \text{ mol}$$
$$\text{Moles of base added: } n_B = C_B V_B = 0.1 \cdot 5 \cdot 10^{-3} = 5.0 \cdot 10^{-4} \text{ mol}$$

2. Identify the species determining the pH:

The final mixture contains:

- **Remaining strong acid**: $5.0 \cdot 10^{-4}$ mol
- **Neutral salt (NaCl)**: $5.0 \cdot 10^{-4}$ mol
- **No strong base**: all the added base has reacted

Particular situation of the half-equivalence At this strategic point, we observe that:

- The amount of remaining acid **equals** the amount of salt formed
- Exactly half of the initial acid has been neutralized
- The medium remains acidic, but much less than at the beginning

3. Calculate the pH:

- Amount of remaining acid: $n_{\text{remaining}} = n_A - n_B = 5.0 \cdot 10^{-4}$ mol
- Total volume: $V_{\text{total}} = V_A + V_B = 15.0$ mL
- H_3O^+ concentration:

$$[H_3O^+] = \frac{n_{\text{remaining}}}{V_{\text{total}}} = \frac{5.0 \cdot 10^{-4}}{15.0 \cdot 10^{-3}} = 3.33 \cdot 10^{-2} \text{ mol/L}$$

- pH calculation:

$$\text{pH} = -\log[H_3O^+] = -\log(3.33 \cdot 10^{-2}) \approx \boxed{1.48}$$

In summary

The half-equivalence represents a pivotal point where exactly half of the initial acid has been consumed. The pH has significantly increased compared to the beginning of the titration, announcing the approach of the equivalence point.

Phase 3: The Equivalence Point ($V_B = 10$ mL)

Here we are at the crucial moment of the titration: the equivalence point. This is the instant when the acid and base have been mixed in the exact stoichiometric proportions of the reaction. There is neither excess acid nor excess base. The two armies have annihilated each other in a perfectly balanced battle.

Calculation at V = 10 mL of NaOH added

Reaction Equation	HCl	+ NaOH	⟶ NaCl	+ H_2O
Initial state (mol)	n_A	n_B	0	solvent
	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	0	–
Final state (mol)	0	0	$1.0 \cdot 10^{-3}$	–
	Strong acid	Strong base	Neutral salt	

Step-by-step calculation method

1. Calculate the initial amounts of matter:

$$\text{Moles of acid: } n_A = C_A V_A = 0.1 \cdot 10 \cdot 10^{-3} = 1.0 \cdot 10^{-3} \text{ mol}$$
$$\text{Moles of base added: } n_B = C_B V_B = 0.1 \cdot 10 \cdot 10^{-3} = 1.0 \cdot 10^{-3} \text{ mol}$$

Crucial observation: At equivalence, $n_A = n_B$. The reactants are in the exact stoichiometric proportions.

2. Qualitative analysis of the mixture at equivalence

What do we find in the beaker after the reaction?

- Strong acid (HCl): completely consumed, not a single mole of acid remains.
- Strong base (NaOH): with the same number of molecules as the acid, it will also be absent in the final mixture, so not a single mole of base remains.
- Water (H_2O): formed by the reaction, but it is the solvent
- Salt (NaCl): $1.0 \cdot 10^{-3}$ mol of sodium chloride

Who determines the pH now? NaCl salt is composed of:

- **Na^+ ion**: conjugate acid of NaOH (strong base), therefore **extremely weak acid**
- **Cl^- ion**: conjugate base of HCl (strong acid), therefore **extremely weak base**

These two ions are **totally spectator**. Neither reacts significantly with water. They have **no influence** on the pH.

pH calculation at equivalence

3. What is the determining species?
Since there is neither strong acid nor strong base left, and the salt is neutral, the pH is controlled by... **pure water!**

- Total volume: $V_{\text{total}} = V_A + V_B = 20.0$ mL
- In aqueous solution, water autoprotolyzes:

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

- At 25 °C, the ionic product of water is:

$$K_e = [H_3O^+][OH^-] = 1.0 \cdot 10^{-14}$$

- In pure water, $[H_3O^+] = [OH^-]$, therefore:

$$[H_3O^+]^2 = 1.0 \cdot 10^{-14}$$

$$[H_3O^+] = \sqrt{1.0 \cdot 10^{-14}} = 1.0 \cdot 10^{-7} \text{ mol/L}$$

- pH calculation:

$$\text{pH} = -\log[H_3O^+] = -\log(1.0 \cdot 10^{-7}) = \boxed{7.00}$$

In summary

The equivalence point represents the perfect completion of the neutralization reaction. It is the instant when the acid and base, having been added in stoichiometrically equivalent amounts, have completely reacted to give a neutral salt and water. The pH at equivalence for a strong acid/strong base pair is always 7.00 at 25 °C.

Phase 4: The Reign of the Base (After the equivalence point)

We have now passed the equivalence point. The strong base, which was previously the limiting reactant, becomes the species in excess. This is a complete reversal of the situation: the base takes control of the medium and imposes its basic character.

Calculation at V = 15 mL of NaOH added

Reaction Equation	HCl	+	NaOH	⟶	NaCl	+	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$		$1.5 \cdot 10^{-3}$		0		–
Final state (mol)	0 Strong acid		$0.5 \cdot 10^{-3}$ Strong base		$1.0 \cdot 10^{-3}$ Neutral salt		–

Step-by-step calculation method

1. Calculate the initial amounts of matter:

$$\text{Moles of acid: } n_A = 1.0 \cdot 10^{-3} \text{ mol}$$
$$\text{Moles of base added: } n_B = C_B V_B = 0.1 \cdot 15 \cdot 10^{-3} = 1.5 \cdot 10^{-3} \text{ mol}$$

Crucial observation: After equivalence, $n_B > n_A$. The base is now in excess.
2. Qualitative analysis of the mixture
What do we find in the beaker after the reaction?

- **Strong acid (HCl)**: total dissociation
- **Strong base (NaOH)**: in excess ($0.5 \cdot 10^{-3}$ mol)
- **Neutral salt (NaCl)**: $1.0 \cdot 10^{-3}$ mol
- The OH^- ions from the strong base impose the basic character

Who determines the pH now?

- The **strong base in excess**: it is completely dissociated and produces OH^- ions
- The **neutral salt (NaCl)**: remains spectator, without influence on pH
- The **strong acid**: has completely disappeared

pH calculation after equivalence

3. Calculation of OH^- ion concentration

- Amount of base in excess: $n_{\text{base excess}} = n_B - n_A = 0.5 \cdot 10^{-3}$ mol
- Total volume: $V_{\text{total}} = V_A + V_B = 25.0$ mL
- OH^- concentration:

$$[OH^-] = \frac{n_{\text{base excess}}}{V_{\text{total}}} = \frac{0.5 \cdot 10^{-3}}{25.0 \cdot 10^{-3}} = 2.0 \cdot 10^{-2} \text{ mol/L}$$

4. pH calculation

- First calculate pOH:

$$\text{pOH} = -\log[OH^-] = -\log(2.0 \cdot 10^{-2}) \approx 1.70$$

- Then deduce pH:

$$\text{pH} = 14 - \text{pOH} = 14 - 1.70 = \boxed{12.30}$$

Interpretation

Complete pH evolution:

- At $V_B = 0$ mL: pH = 1.00 (reign of acid)
- At $V_B = 1$ mL: pH = 1.09 (acid dominant)
- At $V_B = 5$ mL: pH = 1.48 (half-equivalence)
- At $V_B = 10$ mL: pH = 7.00 (equivalence - neutrality)
- At $V_B = 15$ mL: pH = 12.30 (base dominant)

Characteristics of the zone after equivalence:

- The strong base in excess imposes a **basic** pH
- The pH increases **much more slowly** than around equivalence
- Each additional base addition dilutes the solution, limiting the pH increase
- The neutral salt present only slightly attenuates the basicity by dilution

In summary

After equivalence, we witness a complete reversal: the strong base, now in excess, dominates the medium and imposes a basic pH. The pH calculation is done by determining the concentration of the remaining strong base, exactly as we did for the strong acid before equivalence, but reasoning with OH^- ions and pOH.

5.2.7 Titration of a Strong Base with a Strong Acid: The Reverence

5.2.7.1 An Elegant Symmetry

If the titration of a strong acid with a strong base was a duel between two equal fighters, the titration of a strong base with a strong acid is its **reverence**, the same battle, but seen from the other side of the mirror.
For the astute student: You already master the essentials. The titration curve is the **perfect mirror** of the previous one, symmetric with respect to the point ($V_{eq} = 10$ mL, pH = 7).

5.2.7.2 The Reversed Scenario

Our new protagonist:

- **In the beaker:** Volume V_b of strong base (e.g., NaOH 0.1 M)
- **In the burette:** Strong acid (e.g., HCl 0.1 M)
- **Reaction:** Identical! $OH^- + H_3O^+ \longrightarrow 2\,H_2O$

5.2.7.3 The Four Phases

a) **Phase 1 - The Reign of the Base** (Before equivalence)
   - Initial pH **high** (≈13 for NaOH 0.1 M)

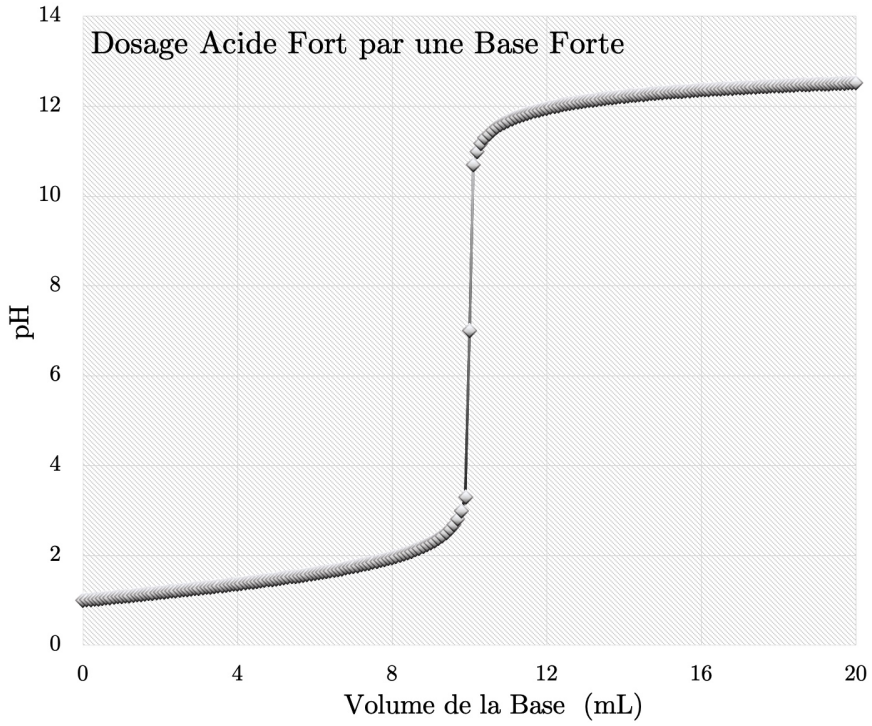


Figure 5.2 Titration of HCl with NaOH

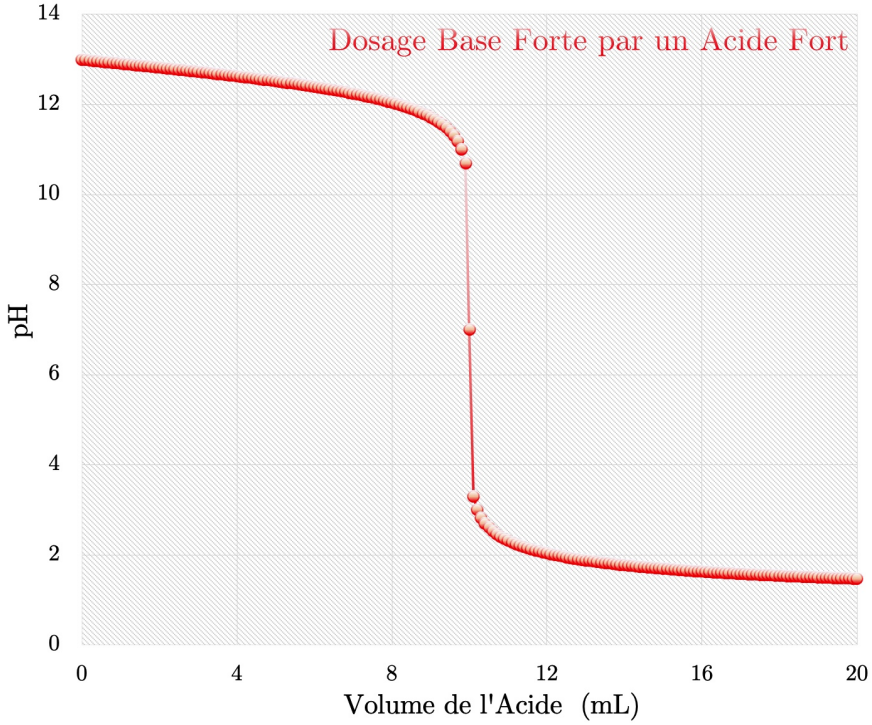


Figure 5.3 Titration of NaOH with HCl

- Each drop of acid neutralizes part of the OH^-
- **pH decreases slowly**

b) **Phase 2 - Half-Equivalence**

- Pivotal moment where half of the base has been neutralized
- pH = ? **Your turn!** (Hint: pOH = -log[remaining OH^-])

c) **Phase 3 - Equivalence**

- **Same point!** $V_{eq} = V_b$, pH = 7.00
- Neutral solution: only salt + water
- **Sudden pH jump**

d) **Phase 4 - The Reign of the Acid** (After equivalence)
- The strong acid in excess imposes acidity
- **pH decreases slowly** towards 1-2

5.2.7.4 The Mirror Curve

Point	**Acid→Base Titration** (Figure 5.2)	**Base→Acid Titration** (Figure 5.3)
Start	pH ≈ 1	pH ≈ 13
Half-eq.	pH ≈ 1.5	pH ≈ 12.5
Equivalence	pH = 7	pH = 7
End	pH ≈ 12-13	pH ≈ 1-2

5.2.8 Titration of a Weak Acid with a Strong Base

Unlike the strong acid-strong base titration which was a "perfect duel" between two transparent fighters, the titration of a weak acid with a strong base introduces an additional strategic dimension. The weak acid, like acetic acid CH_3COOH, does not immediately reveal all its strength. It conceals part of its potential, creating complex equilibria and buffer zones that make this titration more subtle and richer in lessons.

5.2.8.1 The Fighters: A "Strategic" Acid and a "Brutal" Base

The weak acid (CH_3COOH): a balanced fighter A weak acid is only partially dissociated in aqueous solution. It establishes a dynamic equilibrium:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

This equilibrium is characterized by its acidity constant K_a:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8 \times 10^{-5} \quad \text{with} \quad pK_a = 4.74$$

The strong base (NaOH): transparent force As before, the strong base dissociates completely:

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

5.2.8.2 The Reaction Mechanism: "A Progressive Neutralization"

The titration reaction is written:

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow (CH_3COO^-, Na^+)_{(aq)} + H_2O_{(l)}$$

This reaction is complete ($K \gg 1$), but its progress is more complex than in the strong acid-strong base case. This complexity comes from the **equilibrium nature** of the weak acid. Unlike a strong acid that delivers all its protons instantly, acetic acid maintains a dynamic equilibrium that evolves progressively during the titration. Each addition of strong base does not only neutralize free protons, but **shifts this equilibrium** according to Le Chatelier's principle, forcing the dissociation of new acid molecules. This sequential mechanism creates an **extended buffer zone** where pH varies little, and inevitably leads to a **basic pH at equivalence** due to the hydrolysis of the acetate formed CH_3COO^-. It is this continuous progression of equilibria that we will now analyze in detail through the different characteristic zones of the titration.

5.2.8.3 Detailed Study of the Different Titration Phases

Consider the titration of $V_a = 10$ mL of acetic acid $C_a = 0.1$ M with sodium hydroxide $C_B = 0.1$ M.

Phase 1: Before Equivalence

The zone before equivalence is characterized by an excess of weak acid. It can be divided into two distinct sub-phases:

First sub-phase: Pure weak acid solution ($V_B = 0$ mL) At this initial stage, we have a pure acetic acid solution. The pH is determined solely by the dissociation equilibrium of the weak acid. The pH is calculated by:

$$[\mathrm{H_3O^+}] = \sqrt{K_a C_A} = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3} \text{ mol/L}$$

$$\mathrm{pH} = -\log(1.34 \times 10^{-3}) = \boxed{2.87}$$

Second sub-phase: The buffer zone ($0 < V_B < V_{eq}$) From the first drop of base added ($V_B > 0$), the situation changes radically. We enter the domain of the buffer solution, where the remaining weak acid and its formed conjugate base coexist. This zone, which extends until equivalence, presents remarkable properties of resistance to pH variations that we will explore in detail.

Situation at $V_B = 1$ mL (Beginning of titration)

Reaction Equation	$\mathrm{CH_3COOH}$ +	NaOH	$\longrightarrow$ $\mathrm{CH_3COONa}$ +	$\mathrm{H_2O}$
Initial state (mol)	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$	0	–
Final state (mol)	$9.0 \cdot 10^{-4}$	0	$1.0 \cdot 10^{-4}$	–
	Weak acid	Strong base	Basic salt	

At this early stage of the titration, we are in the presence of a mixture of the weak acid $\mathrm{CH_3COOH}$ and sodium acetate $\mathrm{CH_3COONa}$. This salt, in aqueous solution, provides:

- A spectator ion $\mathrm{Na^+}$ that does not influence pH
- The acetate ion $\mathrm{CH_3COO^-}$, the conjugate base of acetic acid

So, in summary, we have a weak acid and its conjugate base, and this is exactly the definition of a buffer solution:

Summary of active species:

- Remaining weak acid: 9.0×10^{-4} mol
- Conjugate base formed: 1.0×10^{-4} mol
- Total volume: $V_{\text{total}} = 11.0$ mL

Then the application of the Henderson-Hasselbalch relation is paramount:

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}\right) = 4.74 + \log\left(\frac{0.1}{0.9}\right) = 4.74 - 0.95 = \boxed{3.79}$$

Interpretation The pH has increased from 2.87 to 3.79, and the solution is beginning to develop buffer properties. Before moving to the next phase, it is very important to make a brief acquaintance with buffer solutions:

Buffer Solutions: Origin and Properties

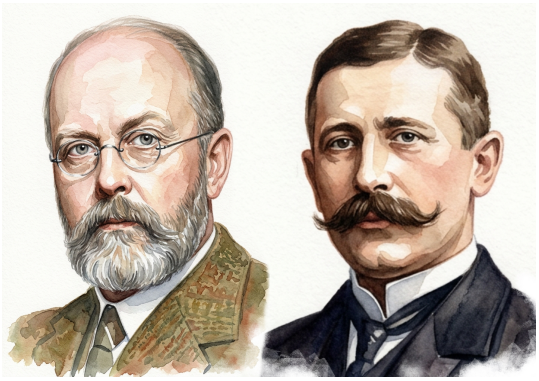
Definition Buffer Solution: The Wise Equilibrium

A buffer solution is a mixture of a weak acid and its conjugate base, or a weak base with its conjugate acid, which coexist in harmony, forming a complementary duo. Like a wise regulator, it maintains the pH relatively constant. Its secret lies in its dual capacity to neutralize acidic attacks with its conjugate base and basic attacks with its weak acid, thus maintaining a remarkably stable pH through this calculated dynamic equilibrium. The properties and applications of buffer solutions are exhaustively treated by Perrin and Dempsey.[39]

Origin of the Henderson-Hasselbalch equation: The equation owes its name to two scientists who, independently, marked the beginning of the 20th century with their foundational work:

Lawrence Joseph Henderson (1908) - American biochemist who first formulated an equation describing acid-base equilibrium in blood. Working on blood pH regulation and the role of bicarbonate, he established the fundamental relationship between acid and conjugate base concentrations.

Karl Albert Hasselbalch (1916) - Danish physician and chemist who, building on Henderson's work, had the brilliant idea of applying the logarithm function to the original equation. This transformation gave the relationship its modern and practical form that we use today.



Henderson & Hasselbalch

Mathematical evolution: Consider the generic acid-base equilibrium:

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

$$\text{The acidity constant is written} : \quad K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$\text{Henderson's original equation (1908)} : \quad [H^+] = K_a \frac{[HA]}{[A^-]}$$

$$\text{Hasselbalch's transformation (1916)} : \quad pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Key takeaways

$$pH = pK_a + \log\left(\frac{[\text{Base}]}{[\text{Acid}]}\right) \tag{5.1}$$

This equation, born from physiological concerns about blood pH regulation, has become a universal tool in solution chemistry, finding applications far beyond the medical field that saw its birth. For a complete mathematical demonstration, the reader may refer to Perrin and Dempsey.[39]

Conditions for forming an effective buffer solution For a buffer solution to deploy its protective shield, four essential conditions must be met:

- **The right team**: Simultaneous presence of both partners of the conjugate acid-base pair. Significant concentrations of both forms, acid (HA) and base (A^-), are required. This team can be formed in four ways:
  - **Direct mixing** of a weak acid with its conjugate base.
  - **Direct mixing** of a weak base with its conjugate acid.
  - **Partial neutralization of a weak acid with a strong base**: A limited amount of strong base is added to an excess of weak acid. The strong base is completely consumed (limiting reactant), generating the conjugate base, while part of the weak acid remains unneutralized. Such as:

$$CH_3COOH + NaOH \longrightarrow CH_3COO{-}Na^+ + H_2O$$

  - **Partial neutralization of a weak base with a strong acid**: A limited amount of strong acid is added to an excess of weak base. The strong acid is completely consumed (limiting reactant), generating the conjugate acid, while part of the weak base remains unneutralized. Such as:

$$NH_3 + HCl \longrightarrow {NH_4}^+Cl^-$$

- **Perfect harmony**: A balanced concentration ratio. The buffer capacity is maximal when $[A^-] = [HA]$ ($pH = pK_a$). The buffer remains effective for ratios between 0.1 and 10, i.e., for a pH range of $pK_a \pm 1$.
- **Numerical strength**: Sufficient absolute concentrations. High concentrations (typically 0.01 M to 1

M) ensure better buffer capacity, like a more numerous army can better resist attacks.
- **Favorable terrain**: An appropriate pK_a. The pK_a of the acid must be close to the desired pH for the buffer zone, ensuring that both forms are present in significant quantities.

In summary: An effective buffer solution requires the right chemical team, in numerical harmony, sufficiently concentrated, and operating on its preferred terrain!

Buffer action mechanism The buffer's effectiveness relies on its dual capacity to neutralize:
- **Strong base additions**:
$$HA + OH^- \longrightarrow A^- + H_2O$$
The weak acid consumes the added OH^- ions.
- **Strong acid additions**:
$$A^- + H_3O^+ \longrightarrow HA + H_2O$$
The conjugate base consumes the added H_3O^+ ions.

Application to our acetic acid/sodium hydroxide titration In our case, the buffer pair is CH_3COOH/CH_3COO^- with p$K_a = 4.74$. Throughout the phase before equivalence ($0 < V_B < 10$ mL), we naturally create a buffer solution whose properties explain:
- The small pH variation in this zone
- The characteristic curvature of the titration curve
- The particular importance of the half-equivalence

Buffer capacity and efficiency zone The buffer capacity is maximal at half-equivalence and decreases as we move away from this condition. In our titration, the effective buffer zone extends approximately from pH = 3.74 to pH = 5.74 (p$K_a \pm 1$).
This in-depth understanding of buffer solutions now allows us to analyze with more relevance the particular point of half-equivalence.

Phase 2 at $V_B = 5$ mL (Half-Equivalence)

Reaction Equation	CH_3COOH +	$NaOH$ $\longrightarrow$	CH_3COONa +	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-4}$	0	–
Final state (mol)	$5.0 \cdot 10^{-4}$	0	$5.0 \cdot 10^{-4}$	–
	Weak acid	Strong base	Basic salt	

Important correction: In the "Final state" row, it should read "Weak acid" and "Basic salt" to be consistent with the chemistry of acetic acid.

Detailed analysis of this remarkable point At half-equivalence, we reach a perfect equilibrium situation with exceptional characteristics:
- **Perfect stoichiometric equality**:
$$[CH_3COOH] = [CH_3COO^-] = 5.0 \times 10^{-4} \text{ mol}$$
Exactly half of the initial acid has been converted to its conjugate base.
- **Simplified Henderson-Hasselbalch relation**:
$$\text{pH} = \text{p}K_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log(1) = \boxed{4.74}$$
The logarithm of 1 being zero, the pH becomes **independent of absolute concentrations** and exactly equals pK_a.
- **Maximum buffer capacity**: The solution exhibits **optimal** buffer properties. The capacity to resist pH variations is at its maximum because any addition of acid or base will be neutralized with equal efficiency by both forms of the pair.

- **Experimental importance**: This point is crucial in the laboratory because it allows experimental determination of the pK_a of a weak acid with great precision, simply by measuring the pH at half-equivalence.
- **Perfect dynamic equilibrium**: The system reaches an equilibrium state where the protonation and deprotonation rates are perfectly balanced, creating remarkable pH-metric stability.

Fundamental consequence The half-equivalence represents the **inflection point** of the titration curve where the derivative of the pH $= f(\text{V})$ curve changes behavior. It is the moment when the buffer system exhibits all its protective efficiency.
At half-equivalence, we observe a remarkable situation:

- $[CH_3COOH] = [CH_3COO^-]$
- The pH is equal to the pK_a of the acid
- The solution exhibits **optimal** buffer properties

Situation at $V_B = 8$ mL

Reaction Equation	CH_3COOH +	NaOH	$\longrightarrow$ CH_3COONa +	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-4}$	0	–
Final state (mol)	$0.2 \cdot 10^{-3}$	0	$8 \cdot 10^{-4}$	–
	Weak acid	Strong base	Basic salt	

Detailed quantitative analysis

- Matter balance after reaction:

$$\begin{aligned} \text{Remaining acetic acid} &: 2.0 \times 10^{-4} \text{ mol} \\ \text{Sodium acetate formed} &: 8.0 \times 10^{-4} \text{ mol} \\ \text{Ratio } \frac{[CH_3COO^-]}{[CH_3COOH]} &= \frac{8.0}{2.0} = 4.0 \\ \text{Total volume} &: V_{\text{total}} = 10 + 8 = 18 \text{ mL} = 0.018 \text{ L} \end{aligned}$$

- **Application of the Henderson-Hasselbalch relation**:

$$\text{pH} = \text{p}K_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log \left(\frac{4.44 \times 10^{-2}}{1.11 \times 10^{-2}} \right) = 4.74 + 0.60 = \boxed{5.34}$$

Physical and chemical interpretation

- **Departure from half-equivalence**: We are now in a situation where the conjugate base largely dominates ($[CH_3COO^-] = 4 \times [CH_3COOH]$).
- **Still effective buffer capacity**: Although diminished compared to half-equivalence, the buffer capacity remains significant because the concentration ratio (4:1) is still in the efficiency zone (between 0.1 and 10).
- **pH evolution**: Compared to half-equivalence (pH = 4.74), the pH has increased by 0.60 unit, which corresponds exactly to the logarithm of the concentration ratio.
- **Approaching equivalence**: At $V_B = 8$ mL, we have consumed 80% of the initial acid. Only 20% of the acid remains to be neutralized to reach the equivalence point.

Perspective This situation illustrates how the Henderson-Hasselbalch relation allows us to accurately predict pH evolution in the buffer zone, even when we move away from the optimal conditions of half-equivalence.

Phase 3: The Equivalence Point ($V_B = 10$ mL)

Reaction Equation	CH_3COOH +	$NaOH$	$\longrightarrow$	CH_3COONa +	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$		0	–
Final state (mol)	0	0		$1.0 \cdot 10^{-3}$	–
	Weak acid	Strong base		Basic salt	

The Reversal of Situation At equivalence, we witness a fundamental transformation:

- Complete disappearance of the initial acetic acid.
- Total consumption of the added strong base.
- Exclusive appearance of sodium acetate CH_3COONa.

Why a Basic pH at Equivalence? Unlike the strong acid-strong base titration where the pH at equivalence is neutral (pH = 7), here the equivalence gives a **basic** pH (pH > 7), for the simple reason that the acetate ion CH_3COO^- is the **conjugate base** of a weak acid. In aqueous solution, it undergoes a hydrolysis reaction with water:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

This reaction releases OH^- ions, making the solution basic.

Detailed pH Calculation

a) **Acetate concentration**:

$$[CH_3COO^-] = \frac{n_{\text{salt formed}}}{V_{\text{total}}} = \frac{1.0 \times 10^{-3}}{20 \times 10^{-3}} = 0.05 \text{ mol/L}$$

b) **Basicity constant K_b**:

$$K_b = \frac{K_e}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

This fundamental relation links the basicity of acetate to the acidity of acetic acid.

c) **OH^- concentration**:

$$[OH^-] = \sqrt{K_b \times C} = \sqrt{5.56 \times 10^{-10} \times 0.05} = 5.27 \times 10^{-6} \text{ mol/L}$$

Application of the weak base formula at concentration C.

d) **pOH and pH**:

$$\text{pOH} = -\log(5.27 \times 10^{-6}) = 5.28$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.28 = \boxed{8.72}$$

Conclusion The equivalence point marks the end of the buffer zone and the beginning of a basic dominance. The pH of 8.72 testifies to the hydrolysis of the acetate ion and constitutes experimental proof of the weakness of the initial acetic acid.

Phase 4: After Equivalence ($V_B = 15$ mL)

Reaction Equation	CH_3COOH +	$NaOH$	$\longrightarrow$	CH_3COONa +	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$		0	–
Final state (mol)	0	$5.0 \cdot 10^{-4}$		$1.0 \cdot 10^{-3}$	–
	Weak acid	Strong base		Basic salt	

The Complete Reversal of Situation After equivalence, we witness a fundamental regime change:

- Total disappearance of the initial acetic acid
- Appearance of an excess of strong base NaOH

- Residual presence of the sodium acetate formed

Why Does the Strong Base Dominate? In this zone, two basic species coexist:
- The strong base NaOH: Completely dissociated, it imposes its basicity
- The acetate ion CH_3COO^-: Weak base, its influence is negligible compared to the strong base.

The pH is therefore **exclusively controlled or imposed** by the excess of strong base, according to the same principle as in the strong acid-strong base titration.

Detailed pH Calculation

$$\begin{aligned} \text{OH}^- \text{ concentration} &: [\text{OH}^-] = \frac{n_{\text{OH}^-}}{V_{\text{total}}} = \frac{5.0 \times 10^{-4}}{0.025} = 0.020 \text{ mol/L} \\ \text{pOH calculation} &: \text{pOH} = -\log(0.020) = -\log(2.0 \times 10^{-2}) = 1.70 \\ \text{pH calculation} &: \text{pH} = 14.00 - \text{pOH} = 14.00 - 1.70 = \boxed{12.30} \end{aligned}$$

Conclusion After equivalence, the system loses its complexity and behaves like a simple strong base solution. The titration curve asymptotically joins that of the strong acid-strong base titration, marking the end of the specific behavior of weak acids.

Remarkable Characteristics of Weak Acid-Strong Base Titration

- **Buffer zone**: Between the beginning of the titration and equivalence, the weak acid/its conjugate base mixture constitutes a buffer solution
- **Half-equivalence**: Point where pH = pK_a, crucial for experimental determination of pK_a
- **Basic equivalence**: The pH at equivalence is greater than 7 due to the hydrolysis of the acetate ion
- **Less marked pH jump**: The pH variation around equivalence is less abrupt than in the strong acid-strong base case

Weak acid	Conjugate base	pK_a	K_a
CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)	4.76	1.8×10^{-5}
HCOOH (formic acid)	$HCOO^-$ (formate ion)	3.75	1.8×10^{-4}
HF (hydrofluoric acid)	F^- (fluoride ion)	3.17	6.8×10^{-4}

Behavior of weak acids in a titration with a strong base: This comparative graph reveals several fundamental lessons about the titration of weak acids:
- **Impact of pK_a on curve position**: The lower the pK_a, the more the curve is shifted towards low pH at the beginning of titration. Hydrofluoric acid (HF, pK_a = 3.17) starts at pH ≈ 2.0 while acetic acid (CH_3COOH, pK_a = 4.76) begins at pH ≈ 2.9.
- **Characteristic buffer zones**: Each curve presents a **plateau** centered on its respective pK_a. It is in this zone that the buffer capacity is maximal, where pH varies little despite base addition.
- **Half-equivalence points**: The **inflection point** of each curve corresponds exactly to the pKa of the acid (pH = pK_a when $V_B = \frac{V_{eq}}{2}$). This point is crucial for the experimental determination of acidity constants.
- **pH at equivalence**: Unlike strong acids, all pH values at equivalence are **greater than 7**. The weaker the acid (higher pK_a), the more basic the pH at equivalence: HF (≈ 8.2) < HCOOH (≈ 8.5) < CH_3COOH (≈ 8.7).
- **pH jump at equivalence**: The amplitude of the pH-metric jump decreases as pK_a increases. Weaker acids give **more gradual** transitions, making the location of the equivalence point more delicate.

Important remarks:
- **Titration precision**: Acids with higher pKa (CH_3COOH) present less sharp pH jumps, reducing the precision of equivalence point location.
- **Experimental validation**: These curves confirm the fundamental relation pH = pK_a at half-equivalence, allowing verification of the consistency of experimental measurements.

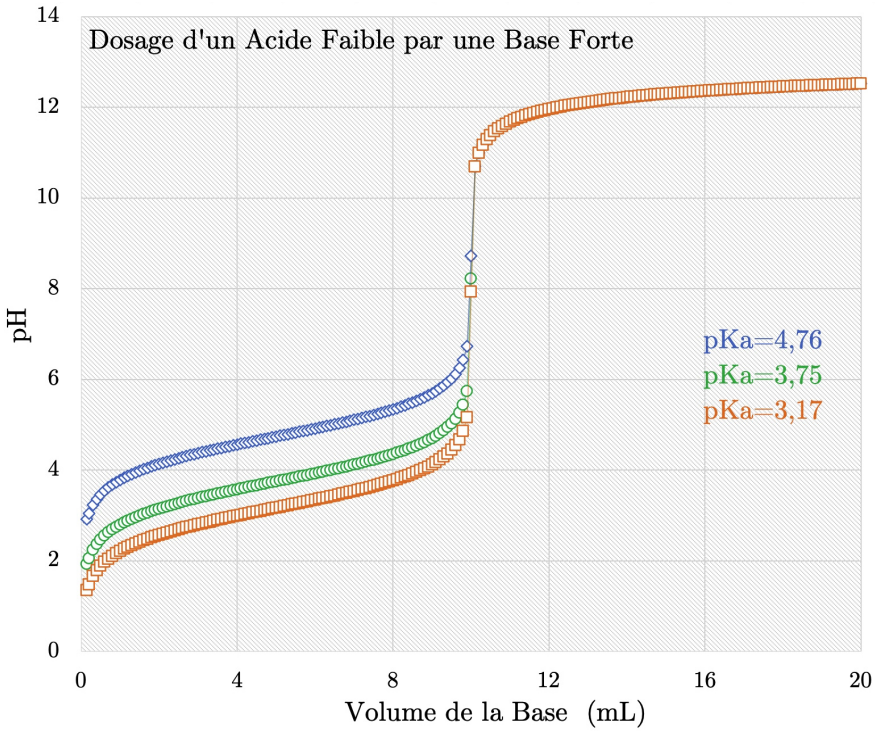


Figure 5.4 Titration of weak acids (CH_3COOH, HCOOH and HF) with NaOH

This visual comparison perfectly illustrates how the acidity constant K_a influences all the characteristics of an acid-base titration: initial position, buffer zone, pH at equivalence, and sharpness of the jump. It underlines the importance of knowing the pKa to optimize the operating conditions of a titration.

Conclusion

The titration of a weak acid with a strong base perfectly illustrates the importance of acid-base equilibria and buffer solutions. Unlike the strong acid-strong base case where the pH at equivalence is always 7, here the pH at equivalence depends on the strength of the weak acid used. This study shows the richness and complexity of acid-base systems in aqueous solution.

Acid titration phases with strong base	V_B (mL)	**pH Strong Acid**	**pH Weak Acid**
Initial	0	1.00	2.87
Half-equivalence	5	1.48	4.74
Equivalence	10	7.00	8.72
After equivalence	15	12.30	12.30

Table 5.1 Comparison of pH during the titration of a strong acid and a weak acid with a strong base.

5.2.9 Titration of a Weak Base with a Strong Acid: The Inverted Symmetry

Unlike the previous titration where the weak acid dictated its law, we now reverse the roles: the weak base reigns supreme in the beaker, and the strong acid plays the role of the progressive assailant. This apparent symmetry nevertheless hides a unique dynamic where the weak base, such as ammonia NH_3, reveals its strategy sparingly, creating subtle equilibria and basic buffer zones that make this titration equally fascinating.

5.2.9.1 The Fighters: A "Strategic" Base and a "Brutal" Acid

The weak base (NH_3): a balanced strategist A weak base is only partially protonated in aqueous solution. It establishes a dynamic equilibrium:

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

This equilibrium is characterized by its basicity constant K_b:

$$K_b = \frac{[{NH_4}^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \quad \text{with} \quad pK_b = 4.74$$

So for the conjugate acid-base pair (${NH_4}^+/NH_3$): $pK_a = 9.26$

The strong acid (HCl): transparent force As before, the strong acid dissociates completely:

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

5.2.9.2 The Reaction Mechanism: "A Progressive Neutralization"

The titration reaction is written:

$$NH_{3(aq)} + HCl_{(aq)} \longrightarrow ({NH_4}^+, Cl^-)_{(aq)}$$

This reaction is complete ($K \gg 1$), but its progress presents the same strategic complexity as the previous case.
The complexity of this titration does not come from a "slow progression," but from the superposition of two acid-base equilibria that interact. Let us analyze it mechanistically:

a) **The Fundamental Equilibrium of the Weak Base:** The initial ammonia solution is not a simple solution of OH^- ions. It is governed by the dissociation equilibrium of the weak base:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons {NH_4}^+_{(aq)} + OH^-_{(aq)} \quad \text{with } K_b$$

The initial concentration of OH^- ions is therefore low and depends on this constant K_b.

b) **The Neutralization Mechanism and Equilibrium Shift:** When strong acid (H_3O^+) is added, the OH^- ions present in solution are the first to be neutralized:

$$H_3O^+ + OH^- \longrightarrow 2\,H_2O$$

This consumption of OH^- ions **shifts equilibrium (1) to the right**, according to Le Chatelier's principle. To compensate for the loss of OH^-, new ammonia molecules NH_3 are protonated, generating both ${NH_4}^+$ ions and OH^- ions.

c) **Consequence: The Basic Buffer Zone:** This compensation mechanism is the very definition of the buffer effect. The $NH_3/{NH_4}^+$ pair absorbs the added H_3O^+ ions, which explains why the pH varies very little over a wide range of added acid volume. The system resists pH change.

d) **The Equivalence Point: A Reversal of Situation:** At equivalence, all the initial weak base (NH_3) has been converted to its conjugate acid (${NH_4}^+$). The solution therefore no longer contains base, but only the weak acid ${NH_4}^+$ and spectator ions. This ${NH_4}^+$ ion is now the major species and imposes its own equilibrium:

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

Since ${NH_4}^+$ is an acid (even weak), it releases H_3O^+ ions into the solution. Consequently, **the pH at equivalence is necessarily acidic**.

It is therefore the succession of these two regimes — a first buffer regime dominated by the $NH_3/{NH_4}^+$ pair, followed by a second acidic regime dominated by the hydrolysis of ${NH_4}^+$ — that defines the pH curve of this titration.

5.2.9.3 Detailed Study of the Different Titration Phases

Consider the titration of $V_B = 10$ mL of ammonia $C_B = 0.1$ M with hydrochloric acid $C_A = 0.1$ M.

Phase 1: Before Equivalence

The zone before equivalence is characterized by an excess of weak base. It can be divided into two distinct sub-phases:

First sub-phase: Pure weak base solution ($V_A = 0$ mL) At this initial stage, we have a pure ammonia solution. The pH is determined solely by the basicity equilibrium of the weak base. The pH is calculated by:

$$[\text{OH}^-] = \sqrt{K_b C_B} = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3} \text{ mol/L}$$

$$\text{pOH} = -\log(1.34 \times 10^{-3}) = 2.87 \quad \Rightarrow \quad \text{pH} = 14.00 - 2.87 = \boxed{11.13}$$

Second sub-phase: The buffer zone ($0 < V_A < V_{eq}$) From the first drop of acid added ($V_A > 0$), the situation changes radically. We enter the domain of the basic buffer solution, where the remaining weak base and its formed conjugate acid coexist. This zone, which extends until equivalence, presents remarkable properties of resistance to pH variations.

Situation at $V_A = 1$ mL (Beginning of titration)

Reaction Equation	NH_3	+	HCl	$\longrightarrow$	NH_4Cl	+	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$		$1.0 \cdot 10^{-4}$		0		–
Final state (mol)	$9.0 \cdot 10^{-4}$ Weak base		0 Strong acid		$1.0 \cdot 10^{-4}$ Acidic salt		–

At this early stage of the titration, we are in the presence of a mixture of the weak base NH_3 and ammonium chloride NH_4Cl. This salt, in aqueous solution, provides:

- A spectator ion Cl^- that does not influence pH
- The ammonium ion $NH_4{}^+$, the conjugate acid of ammonia

We therefore have a weak base and its conjugate acid, which constitutes exactly the definition of a buffer solution:

Summary of active species:

- Remaining weak base: 9.0×10^{-4} mol
- Conjugate acid formed: 1.0×10^{-4} mol
- Total volume: $V_{\text{total}} = 11.0$ mL

Then the application of the Henderson-Hasselbalch relation is paramount:

$$\text{pH} = \text{p}K_{a\,(\text{NH4+/NH3})} + \log\left(\frac{[NH_3]}{[NH_4{}^+]}\right) = 9.26 + \log\left(\frac{0.9}{0.1}\right)$$

$$\text{pH} = 9.26 + \log(9) = 9.26 + 0.95 = \boxed{10.21}$$

Interpretation

- The pH has decreased from 11.13 to 10.21
- The solution develops buffer properties in basic medium
- The ratio $[NH_3]/[NH_4{}^+]$ is still high (9.0)
- The weak base largely dominates the medium

Phase 2 at $V_A = 5$ mL (Half-Equivalence)

Reaction Equation	NH_3	+	HCl	$\longrightarrow$	NH_4Cl	+	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$		$5.0 \cdot 10^{-4}$		0		–
Final state (mol)	$5.0 \cdot 10^{-4}$ Weak base		0 Strong acid		$5.0 \cdot 10^{-4}$ Acidic salt		–

Detailed analysis of this remarkable point At half-equivalence, we reach a perfect equilibrium situation:

- **Perfect stoichiometric equality**:

$$[NH_3] = [NH_4^+] = 5.0 \times 10^{-4} \text{ mol}$$

  Exactly half of the initial base has been converted to its conjugate acid.
- **Simplified Henderson-Hasselbalch relation**:

$$\text{pH} = \text{p}K_a + \log \frac{[NH_3]}{[NH_4^+]} = 9.26 + \log(1) = \boxed{9.26}$$

  The pH becomes **independent of absolute concentrations** and exactly equals the pK_a of the pair.
- **Maximum buffer capacity**: The solution exhibits **optimal** buffer properties in basic medium.

Phase 3: The Equivalence Point ($V_A = 10$ mL)

Reaction Equation	NH_3 +	HCl ⟶	NH_4Cl +	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	0	–
Final state (mol)	0	0	$1.0 \cdot 10^{-3}$	–
	Weak base	Strong acid	Acidic salt	

Why an Acidic pH at Equivalence? Unlike the strong base-strong acid titration where the pH at equivalence is neutral (pH = 7), here the equivalence gives an **acidic** pH (pH < 7), because the ammonium ion NH_4^+ is the **conjugate acid** of a weak base. In aqueous solution, it undergoes hydrolysis:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

This reaction releases H_3O^+ ions, making the solution acidic.

Detailed pH Calculation

a) **Ammonium concentration**:

$$[NH_4^+] = \frac{1.0 \times 10^{-3}}{20 \times 10^{-3}} = 0.05 \text{ mol/L}$$

b) **H_3O^+ concentration**:

$$[H_3O^+] = \sqrt{K_a \times C} = \sqrt{5.56 \times 10^{-10} \times 0.05} = 5.27 \times 10^{-6} \text{ mol/L}$$

c) **pH calculation**:

$$\text{pH} = -\log(5.27 \times 10^{-6}) = 5.28$$

Phase 4: After Equivalence ($V_A = 15$ mL)

Reaction Equation	NH_3 +	HCl ⟶	NH_4Cl +	H_2O
Initial state (mol)	$1.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0	–
Final state (mol)	0	$5.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	–
	Weak base	Strong acid	Acidic salt	

The pH is controlled by the excess of strong acid:

$$[H_3O^+] = \frac{5.0 \times 10^{-4}}{0.025} = 0.020 \text{ M}$$

$$\text{pH} = -\log(0.020) = \boxed{1.70}$$

Comparison of Strong Base / Weak Base Titrations with Strong Acid

Base titration phases with strong acid	V_A (mL)	pH Strong Base	pH Weak Base
Initial	0	13.00	11.13
Half-equivalence	5	12.52	9.26
Equivalence	10	7.00	5.28
After equivalence	15	1.70	1.70

Table 5.2 Comparison of pH during the titration of a strong base and a weak base with a strong acid

Remarkable Characteristics of Weak Base-Strong Acid Titration

- **Basic buffer zone**: Between the beginning of the titration and equivalence
- **Half-equivalence**: Point where pH = pK_a of the acid-base pair
- **Acidic equivalence**: The pH at equivalence is less than 7
- **Perfect symmetry** with the weak acid-strong base titration

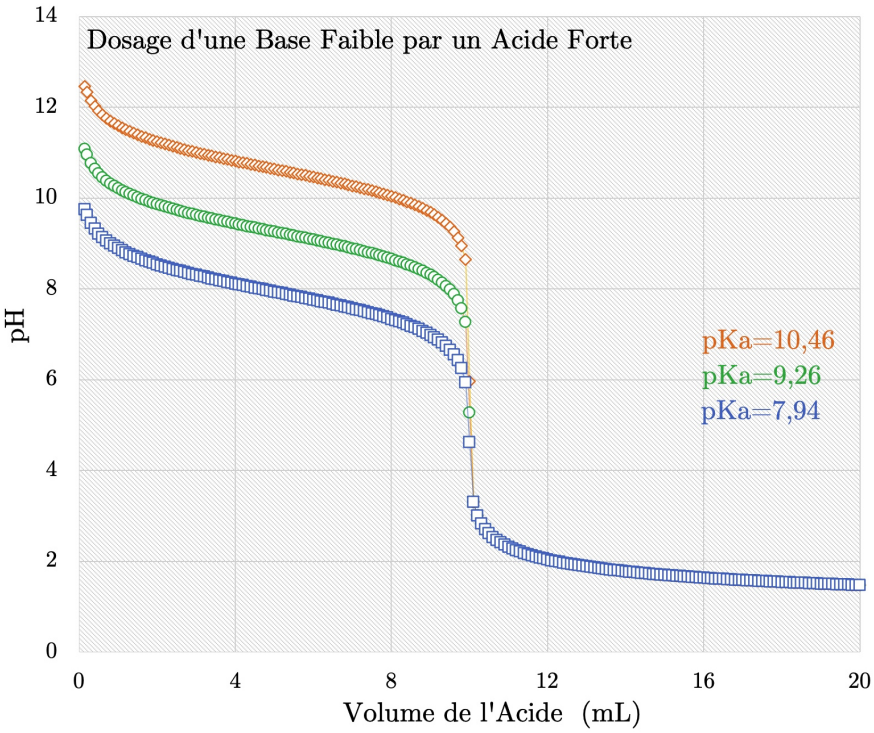


Figure 5.5 Titration of weak bases (N_2H_4, NH_3 and CH_3NH_2) with HCl

Weak base	Conjugate acid	pK_a	K_a
CH_3NH_2 (methylamine)	$CH_3NH_3^+$ (methylammonium ion)	10.64	2.3×10^{-11}
NH_3 (ammonia)	NH_4^+ (ammonium ion)	9.26	5.6×10^{-10}
N_2H_4 (hydrazine)	$N_2H_5^+$ (hydrazinium ion)	7.94	1.2×10^{-8}

Fundamental characteristics of weak base - strong acid titration

The titration of a weak base with a strong acid presents remarkable particularities that distinguish it from the strong base-strong acid case:

- **Buffer solution**: Before equivalence, the weak base/its conjugate acid mixture forms a buffer system that resists pH variations
- **Half-equivalence**: Characteristic point where pH = pK_a, allowing experimental determination of the acidity constant of the acid-base pair

- **Equivalence**: The pH at the equivalence point is less than 7 due to the hydrolysis of the formed conjugate acid
- **Progressive transition**: The pH variation around equivalence is less abrupt than in the strong base-strong acid case

Conclusion

The weak base-strong acid titration beautifully completes our panorama. It illustrates the beautiful symmetry of acid-base phenomena while maintaining the richness of chemical equilibria that make these titrations so instructive.

5.2.10 Titration of a Weak Acid with a Weak Base: The Duel of Strategists

We arrive at the most sophisticated and instructive case: the encounter of two "strategist" fighters. Unlike previous titrations where one protagonist imposed its law by brute force, here we witness a truly tactical duel where the weak acid and the weak base deploy all their subtlety. Each added drop triggers a cascade of intertwined equilibria, creating a chemical choreography of fascinating complexity.

5.2.10.1 The Fighters: Two Strategists in Equilibrium

The weak acid (CH_3COOH): As we already know, acetic acid maintains its characteristic equilibrium:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

with $K_a = 1.8 \times 10^{-5}$ and $pK_a = 4.74$
The weak base (CH_3NH_2) methylamine: Ammonia deploys its own equilibrium strategy:

$$CH_3NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons {CH_3NH_3}^+_{(aq)} + OH^-_{(aq)}$$

with $K_b = 4.4 \times 10^{-4}$ and $pK_b = 3.36$ $\Rightarrow$ $pK_a = 10.64$

The Reaction Mechanism: A Dance of Intertwined Equilibria The overall reaction is written:

$$CH_3COOH_{(aq)} + CH_3NH_{2(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + {CH_3NH_3}^+_{(aq)}$$

Unlike previous titrations where one reactant was always limiting, here we constantly navigate in an **equilibrium regime**. The reaction never reaches completion because the acidity and basicity constants are of the same order of magnitude.

Detailed Study of the Different Situations Consider the titration of $V_A = 10$ mL of acetic acid $C_A = 0.1$ M with methylamine $C_B = 0.1$ M.

Phase 1: Before Equivalence

First sub-phase ($V_B = 0$ mL) Only acetic acid is present. So it is very simple; the pH is that of acetic acid CH_3COOH:

$$[H_3O^+] = \sqrt{K_a C_A} = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3} \text{ mol/L}$$

$$\boxed{\text{pH} = 2.87}$$

Second sub-phase ($V_B = 1$ mL) The buffer zone ($0 < V_a < V_{eq}$) is exactly the same as the second sub-phase of the weak acid-strong base titration, a domain of the acidic buffer solution, where two species of different nature coexist forming a conjugate acid/base pair. This continues in the same rhythm until equivalence.

Equation	CH_3COOH	+	CH_3NH_2	$\rightleftharpoons$	CH_3COO^-	+	${CH_3NH_3}^+$
Initial state (mol)	1.0×10^{-3}		0.1×10^{-3}		0		0
Final state (mol)	$(1.0 \times 10^{-3}) - x$		$(0.1 \times 10^{-3}) - x$		x		x

Important

The General Rule and the Spectrum of Possibilities: For the reaction: $\mathrm{HA} + \mathrm{B} \rightleftharpoons \mathrm{A}^- + \mathrm{HB}^+$

$$K = \frac{[\mathrm{A}^-][\mathrm{HB}^+]}{[\mathrm{HA}][\mathrm{B}]} \times \frac{[\mathrm{H_3O}^+]}{[\mathrm{H_3O}^+]} = \left(\frac{[\mathrm{A}^-][\mathrm{H_3O}^+]}{[\mathrm{HA}]}\right) \times \left(\frac{[\mathrm{HB}^+]}{[\mathrm{B}][\mathrm{H_3O}^+]}\right)$$

$$K = K_a(\mathrm{HA}) \times \frac{1}{K_a(\mathrm{HB}^+)} = \frac{K_a(\mathrm{HA})}{K_a(\mathrm{HB}^+)}$$

Conversion to logarithmic notation (pK) Taking the decimal logarithm of the expression:

$$\log K = \log K_a(\mathrm{HA}) - \log K_a(\mathrm{HB}^+) \quad \Rightarrow \quad \mathrm{p}K = \mathrm{p}K_a(\mathrm{HA}) - \mathrm{p}K_a(\mathrm{HB}^+)$$

And thus, returning to the exponential:

$$K = 10^{\mathrm{p}K_a(\mathrm{HA}) - \mathrm{p}K_a(\mathrm{HB}^+)} = 10^{\mathrm{p}K_a(\text{conjugate acid of the base}) - \mathrm{p}K_a(\text{acid})}$$

Physical interpretation:

- $\Delta\mathrm{p}K_a = \mathrm{p}K_a(\mathrm{HB}^+) - \mathrm{p}K_a(\mathrm{HA})$
- $\Delta\mathrm{p}K_a = 0 : K = 1$ (perfect equilibrium)
- $\Delta\mathrm{p}K_a = 1 : K = 10$ (slightly favored)
- $\Delta\mathrm{p}K_a = 2 : K = 100$ (clearly favored)
- $\Delta\mathrm{p}K_a = 3 : K = 1000$ (highly favored)
- $\Delta\mathrm{p}K_a = 4 : K = 10^4$ (almost complete)
- $\Delta\mathrm{p}K_a = -1 : K = 0.1$ (slightly unfavorable)
- $\Delta\mathrm{p}K_a = -2 : K = 0.01$ (clearly unfavorable)

Detailed calculation of equilibrium quantities Total volume: $V = 11$ mL $= 0.011$ L
Resolution: Let x be the extent of reaction at equilibrium (in mol). The concentrations are written:

$$[\mathrm{CH_3COOH}] = [\mathrm{CH_3NH_2}] = \frac{1.0 \times 10^{-3} - x}{0.011}$$

$$[\mathrm{CH_3NH_2}] = \frac{0.1 \times 10^{-3} - x}{0.011}$$

$$[\mathrm{CH_3COO}^-] = [\mathrm{CH_3NH_3}^+] = \frac{x}{0.011}$$

The expression of the equilibrium constant:

$$K = \frac{[\mathrm{CH_3COO}^-][\mathrm{CH_3NH_3}^+]}{[\mathrm{CH_3COOH}][\mathrm{CH_3NH_2}]} = \frac{\left(\frac{x}{0.011}\right)^2}{\left(\frac{1.0 \times 10^{-3} - x}{0.011}\right)\left(\frac{0.1 \times 10^{-3} - x}{0.011}\right)}$$

The Spectrum of Possibilities:

- **Extremely unfavorable reaction ($\Delta\mathrm{p}K_a = -6$):**

$$\mathrm{HCN}\ (\mathrm{p}K_a = 9.2) \quad \text{with} \quad \mathrm{C_6H_5NH_2}\ (\mathrm{p}K_a = 4.6)$$

$$\Delta\mathrm{p}K_a = 4.6 - 9.2 = -4.6 \quad \Rightarrow \quad K = 10^{-4.6} \approx 2.5 \times 10^{-5}$$

- **Equilibrated reaction ($\Delta\mathrm{p}K_a \approx 0$)** The 4 species coexist in comparable proportions.

$$\mathrm{CH_3COOH}\ (\mathrm{p}K_a = 4.74) \quad \text{with} \quad \mathrm{C_6H_5NH_2}\ (\mathrm{p}K_a = 4.6)$$

$$\Delta\mathrm{p}K_a = 4.6 - 4.74 = -0.14 \quad \Rightarrow \quad K = 10^{-0.14} \approx 0.72$$

- **Our case ($\Delta \mathrm{p}K_a = 5.9$)**

$$\mathrm{p}K_a(\mathrm{CH_3COOH}) = 4.74 \quad \text{and} \quad \mathrm{p}K_a(\mathrm{CH_3NH_3}^+) = 10.64$$

$$\Delta \mathrm{p}K_a = 10.64 - 4.74 = 5.90 \quad \Rightarrow \quad \boxed{K = 10^{5.90} \approx 7.94 \times 10^5}$$

$$K \approx 8 \times 10^5 \quad \text{(very strongly favored)}$$

- **Extremely favored reaction ($\Delta \mathrm{p}K_a = 6$)**

$$\mathrm{HF}\ (\mathrm{p}K_a = 3.17) \quad \text{with} \quad \mathrm{NH_3}\ (\mathrm{p}K_a(\mathrm{NH_4}^+) = 9.26)$$

$$\Delta \mathrm{p}K_a = 9.26 - 3.17 = 6.09 \quad \Rightarrow \quad K = 10^{6.09} \approx 1.2 \times 10^6$$

This is one of the most favored cases between common weak acids/bases.

Practical rule for titrations:

- $\Delta \mathrm{p}K_a > 4$: Titration possible with clear pH jump
- $2 < \Delta \mathrm{p}K_a < 4$: Difficult titration, unclear pH jump
- $\Delta \mathrm{p}K_a < 2$: Practically impossible titration

Resolution of the equilibrium equation Consider the equation:

$$7.94 \times 10^5 = \frac{x^2}{(1.0 \times 10^{-3} - x)(0.1 \times 10^{-3} - x)}.$$

1. Conversion to polynomial form Setting:

$$a = 1.0 \times 10^{-3}, \qquad b = 0.1 \times 10^{-3}, \qquad K = 7.94 \times 10^5,$$

we expand:

$$K(ab - (a+b)x + x^2) = x^2.$$

2. Reorganization of the equation

$$K\,ab - K(a+b)x + Kx^2 = x^2 \quad \Rightarrow \quad (K-1)x^2 - K(a+b)x + Kab = 0.$$

3. Numerical substitution

$$A = K - 1 = 7.94 \times 10^5 - 1 \approx 7.94 \times 10^5$$
$$B = -K(a+b) = -7.94 \times 10^5 \times (1.1 \times 10^{-3}) = -873.4$$
$$C = Kab = 7.94 \times 10^5 \times (1.0 \times 10^{-7}) = 0.0794$$

We thus obtain:

$$7.94 \times 10^5 x^2 - 873.4x + 0.0794 = 0$$

4. Calculation of the discriminant

$$\Delta = B^2 - 4AC = (-873.4)^2 - 4 \times (7.94 \times 10^5) \times 0.0794$$

$$\Delta = 7.626 \times 10^5 - 2.522 \times 10^5 = 5.104 \times 10^5$$

$$\sqrt{\Delta} \approx 714.4$$

5. Calculation of the roots

$$x = \frac{-B \pm \sqrt{\Delta}}{2A} = \frac{873.4 \pm 714.4}{1.588 \times 10^6}$$

$$\Rightarrow \begin{cases} x_1 = \dfrac{873.4 - 714.4}{1.588 \times 10^6} = 1.00 \times 10^{-4} \\ x_2 = \dfrac{873.4 + 714.4}{1.588 \times 10^6} = 9.99 \times 10^{-4} \end{cases}$$

6. Choice of the physical solution The extent x cannot exceed the smallest initial quantity ($n_{CH_3NH_2} = 0.1 \times 10^{-3}$ mol). Thus, $x_2 > 0.1 \times 10^{-3}$ is impossible.

$$\boxed{x = 1.00 \times 10^{-4} \text{ mol}}$$

7. Balance of equilibrium quantities

$$\Rightarrow \begin{cases} n^{\text{final}}_{CH_3COOH} = 1.0 \times 10^{-3} - 1.00 \times 10^{-4} = 9.00 \times 10^{-4} \text{ mol} \\ n^{\text{final}}_{CH_3NH_2} = 0.1 \times 10^{-3} - 1.00 \times 10^{-4} = 0 \text{ mol} \\ n^{\text{final}}_{CH_3COO^-} = n^{\text{final}}_{CH_3NH_3^+} = 1.00 \times 10^{-4} \text{ mol} \end{cases}$$

Calculation of concentrations and pH The total volume $V = 11$ mL gives:

$$[CH_3COOH] = \frac{9.00 \times 10^{-4}}{0.011} = 8.18 \times 10^{-2} \text{ mol/L}$$
$$[CH_3COO^-] = \frac{1.00 \times 10^{-4}}{0.011} = 9.09 \times 10^{-3} \text{ mol/L}$$

pH calculation using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a(CH_3COOH) + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.74 + \log\left(\frac{9.09 \times 10^{-3}}{8.18 \times 10^{-2}}\right) = 4.74 + \log(0.111).$$

$$\boxed{\text{pH} = 3.79}$$

Verification of the approximation validity

$$[CH_3NH_2] = \frac{[CH_3COO^-][CH_3NH_3^+]}{K[CH_3COOH]} = \frac{(9.09 \times 10^{-3})^2}{(7.94 \times 10^5)(8.18 \times 10^{-2})} \approx 1.3 \times 10^{-9} \text{ mol/L}$$

This value is completely negligible, confirming the validity of the complete reaction approximation.

Important observation At $V_B = 1$ mL:

- **Ratio [base]/[acid] = 0.111**: the buffer system is beginning to form.
- **pH = 3.79**: moderate increase compared to the initial pH (2.87).
- **Nearly complete reaction**: the added methylamine is entirely converted.
- **Emerging buffer regime**: coexistence of weak acid and its conjugate base.

This situation illustrates the typical behavior of a titration in **buffer regime**, where the pH evolves slowly thanks to the stabilizing effect of the conjugate acid/base pair.

Phase 2: Half-Equivalence at $V_B = 5$ mL: Complexity Revealed

Equation	CH_3COOH +	CH_3NH_2 $\rightleftharpoons$	CH_3COO^- +	$CH_3NH_3^+$
Initial state (mol)	$1.0 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	0	0
Final state (mol)	$(1.0 \cdot 10^{-3}) - x$	$(0.5 \cdot 10^{-3}) - x$	x	x

Detailed calculation of equilibrium quantities Total volume: $V = 15$ mL $= 0.015$ L
Resolution:
Let x be the extent at equilibrium (in mol). The concentrations are written:

$$[CH_3COOH] = \frac{1.0 \times 10^{-3} - x}{0.015}$$
$$[CH_3NH_2] = \frac{0.5 \times 10^{-3} - x}{0.015}$$
$$[CH_3COO^-] = [CH_3NH_3{}^+] = \frac{x}{0.015}$$

The expression of the equilibrium constant:

$$K = \frac{[CH_3COO^-][CH_3NH_3{}^+]}{[CH_3COOH][CH_3NH_2]} = \frac{\left(\frac{x}{0.015}\right)^2}{\left(\frac{1.0 \times 10^{-3} - x}{0.015}\right)\left(\frac{0.5 \times 10^{-3} - x}{0.015}\right)}$$

Resolution of the equilibrium equation Consider the equation:

$$7.94 \times 10^5 = \frac{x^2}{(1.0 \times 10^{-3} - x)(0.5 \times 10^{-3} - x)}$$

We thus obtain:

$$7.94 \times 10^5 x^2 - 1191x + 0.397 = 0.$$

Discriminant:

$$\Delta = B^2 - 4AC = (-1191)^2 - 4 \times (7.94 \times 10^5) \times 0.397 = 1.576 \times 10^5$$
$$\sqrt{\Delta} \approx 397.0$$

Calculation of the roots: $x = \dfrac{-B \pm \sqrt{\Delta}}{2A}$

$$\Rightarrow \begin{cases} x_1 = \dfrac{1191 - 397.0}{1.587998 \times 10^6} = 5.00 \times 10^{-4} \\ x_2 = \dfrac{1191 + 397.0}{1.587998 \times 10^6} = 1.00 \times 10^{-3} \end{cases}$$

6. Choice of the physical solution The extent x cannot exceed the smallest initial quantity ($n_{CH_3NH_2} = 0.5 \times 10^{-3}$ mol). Thus, $x_2 > 0.5 \times 10^{-3}$ is impossible.

$$\boxed{x = 5.00 \times 10^{-4} \text{ mol}}$$

7. Verification of chemical consistency

$$\Rightarrow \begin{cases} n^{\text{final}}_{CH_3COOH} = 1.0 \times 10^{-3} - x = 5.0 \times 10^{-4} \\ n^{\text{final}}_{CH_3NH_2} = 0.5 \times 10^{-3} - x \approx 0. \\ n^{\text{final}}_{CH_3COO^-} = n^{\text{final}}_{CH_3NH_3{}^+} = x = 5.0 \times 10^{-4} \end{cases}$$

The total volume $V = 15$ mL gives:

$$[CH_3COOH] = [CH_3COO^-] = \frac{5.0 \times 10^{-4}}{0.015} = 3.33 \times 10^{-2} \text{ mol/L}$$

$$\Rightarrow \frac{[CH_3COO^-]}{[CH_3COOH]} \approx 1 \quad \Rightarrow \quad \text{pH} \approx \text{p}K_a = 4.74$$

The extent $x \approx 5.0 \times 10^{-4}$ mol confirms that the reaction is **nearly complete** ($K = 7.9 \times 10^5$), and that the mixture at half-titration forms an **acetic acid / ammonium acetate buffer**.

Verification of the approximation validity: At equilibrium the constant is written

$$K = \frac{[\mathrm{A}^-][\mathrm{BH}^+]}{[\mathrm{HA}][\mathrm{B}]}$$

hence

$$[\mathrm{B}] = [\mathrm{CH_3NH_2}] = \frac{[\mathrm{A}^-][\mathrm{BH}^+]}{K\,[\mathrm{HA}]}$$

Under the half-titration conditions we have approximately

$$[\mathrm{A}^-] \approx [\mathrm{BH}^+] \approx \frac{5.00 \times 10^{-4}}{0.015} = 3.33 \times 10^{-2}\ \text{mol/L}$$

therefore

$$[\mathrm{CH_3NH_2}] \approx \frac{0.03333}{7.94 \times 10^5} \approx 4.2 \times 10^{-8}\ \text{mol/L}$$

The corresponding residual quantity is

$$n^{final}_{\mathrm{CH_3NH_2}} = [\mathrm{CH_3NH_2}] \times V \approx 4.2 \times 10^{-8} \times 0.015 \approx 6.3 \times 10^{-10}\ \text{mol},$$

which is negligible compared to the other quantities present. This value confirms that the "nearly complete reaction" approximation is perfectly valid for this case.

Fundamental observation: At half-way ($V_B = 5$ mL), the ratio $[\mathrm{A}^-]/[\mathrm{HA}] \approx 1$, hence

$$\boxed{\mathrm{pH} \approx \mathrm{p}K_a(\mathrm{CH_3COOH}) = 4.74}$$

"The question that now arises is: at the half-equivalence point, we obtain pH = pKa, which was predictable for a buffer system. However, this situation is different from the first sub-phase where we had a pure weak acid. Does the calculation method remain the same for all points before equivalence?"

Phase 3: Equivalence at $V_B = 10$ mL

Equation	$\mathrm{CH_3COOH}$ +	$\mathrm{CH_3NH_2}$ $\rightleftharpoons$	$\mathrm{CH_3COO^-}$ +	$\mathrm{CH_3NH_3^+}$
Initial state (mol)	1.0×10^{-3}	1.0×10^{-3}	0	0
Final state (mol)	$(1.0 \times 10^{-3}) - x$	$(1.0 \times 10^{-3}) - x$	x	x

Detailed calculation of equilibrium quantities Total volume: $V = 20$ mL $= 0.020$ L
Resolution:
Let x be the extent at equilibrium (in mol). The concentrations are written:

$$[\mathrm{CH_3COOH}] = \frac{1.0 \times 10^{-3} - x}{0.020}$$
$$[\mathrm{CH_3NH_2}] = \frac{1.0 \times 10^{-3} - x}{0.020}$$
$$[\mathrm{CH_3COO^-}] = [\mathrm{CH_3NH_3^+}] = \frac{x}{0.020}$$

The expression of the equilibrium constant:

$$K = \frac{[\mathrm{CH_3COO^-}][\mathrm{CH_3NH_3^+}]}{[\mathrm{CH_3COOH}][\mathrm{CH_3NH_2}]} = \frac{\left(\frac{x}{0.020}\right)^2}{\left(\frac{1.0 \times 10^{-3} - x}{0.020}\right)^2}$$

Resolution of the equilibrium equation Consider the equation:

$$7.94 \times 10^5 = \frac{x^2}{(1.0 \times 10^{-3} - x)^2} \Rightarrow \sqrt{7.94 \times 10^5} = \frac{x}{1.0 \times 10^{-3} - x} \Leftrightarrow 891.1 = \frac{x}{1.0 \times 10^{-3} - x}$$

Resolution

$$891.1(1.0 \times 10^{-3} - x) = x$$
$$8.911 \times 10^{-1} - 891.1x = x$$
$$8.911 \times 10^{-1} = 892.1x$$
$$x = \frac{8.911 \times 10^{-1}}{892.1} = 9.99 \times 10^{-4} \text{ mol}$$

$$x \approx 1.0 \times 10^{-3} \text{ mol}$$

Balance of equilibrium quantities

Equation	CH_3COOH +	CH_3NH_2 $\rightleftharpoons$	CH_3COO^- +	$CH_3NH_3^+$
Initial state (mol)	1.0×10^{-3}	1.0×10^{-3}	0	0
Final state (mol)	0	0	1.0×10^{-3}	1.0×10^{-3}

pH calculation at equivalence At equivalence, we essentially have a solution of **methylammonium acetate** $CH_3COO^-CH_3NH_3^+$, which is a salt of a weak acid and a weak base.

Calculation method: For a salt A^-B^+ of a weak acid and weak base, the pH is given by:

$$\text{pH} = \frac{\text{p}K_a(\text{HA}) + \text{p}K_a(\text{BH}^+)}{2}$$

Demonstration of the formula: pH $= \dfrac{\mathbf{p}K_a(\text{HA}) + \mathbf{p}K_a(\text{BH}^+)}{2}$

Context: We have a salt A^-B^+ in solution, resulting from the reaction between the acid HA and the base B.

Equilibria involved:

(1) $A^- + H_2O \rightleftharpoons HA + OH^-$ (basicity of A^-)
(2) $B^+ + H_2O \rightleftharpoons B + H_3O^+$ (acidity of B^+)

Equilibrium constants:

$$K_b(A^-) = \frac{[HA][OH^-]}{[A^-]} = \frac{K_e}{K_a(HA)}$$
$$K_a(B^+) = \frac{[B][H_3O^+]}{[B^+]}$$

Electroneutrality equation:

$$[B^+] + [H_3O^+] = [A^-] + [OH^-]$$

Conservation of matter:

$$[HA] + [A^-] = C \quad \text{and} \quad [B] + [B^+] = C$$

Approximations for a concentrated salt: For C sufficiently large, we can neglect $[H_3O^+]$ and $[OH^-]$ compared to $[A^-]$ and $[B^+]$:

$$[B^+] \approx [A^-] \approx C$$

Expression of the concentrations of minor species: From the equilibrium constants, we obtain:

$$[HA] = \frac{[A^-][OH^-]}{K_b(A^-)} \approx \frac{C[OH^-]}{K_e/K_a(HA)} = \frac{CK_a(HA)[OH^-]}{K_e}$$
$$[B] = \frac{[B^+][H_3O^+]}{K_a(B^+)} \approx \frac{C[H_3O^+]}{K_a(B^+)}$$

Fundamental equation: From the conservation of matter, we also have:

$$[HA] \approx [B]$$

Because the protons "lost" by B^+ are "gained" by A^-.
Therefore:

$$\frac{CK_a(HA)[OH^-]}{K_e} \approx \frac{C[H_3O^+]}{K_a(B^+)}$$

Simplification: We simplify by C:

$$\frac{K_a(HA)[OH^-]}{K_e} \approx \frac{[H_3O^+]}{K_a(B^+)}$$

But $[OH^-] = \frac{K_e}{[H_3O^+]}$, therefore:

$$\frac{K_a(HA) \cdot \frac{K_e}{[H_3O^+]}}{K_e} \approx \frac{[H_3O^+]}{K_a(B^+)}$$

Elimination of K_e:

$$\frac{K_a(HA)}{[H_3O^+]} \approx \frac{[H_3O^+]}{K_a(B^+)}$$

Final relation:

$$[H_3O^+]^2 \approx K_a(HA) \cdot K_a(B^+)$$

$$[H_3O^+] \approx \sqrt{K_a(HA) \cdot K_a(B^+)}$$

Conversion to pH:

$$pH = -\log[H_3O^+] = -\log\sqrt{K_a(HA) \cdot K_a(B^+)}$$

$$pH = -\frac{1}{2}\left[\log K_a(HA) + \log K_a(B^+)\right]$$

$$pH = \frac{1}{2}\left[-\log K_a(HA) - \log K_a(B^+)\right]$$

Key takeaways

$$pH = \frac{pK_a(HA) + pK_a(B^+)}{2} \tag{5.2}$$

Validity conditions:

- Salt concentration sufficiently high ($C > 10^{-2}$ M)
- The approximations $[H_3O^+] \ll C$ and $[OH^-] \ll C$ are valid
- The salt is perfectly dissociated
- No other parasitic equilibria

Therefore our case:

$$\text{pH} = \frac{4.74 + 10.64}{2} = \frac{15.38}{2} = \boxed{7.69}$$

Phase 4: After Equivalence at $V_B = 15$ mL: The Basic Regime

Equation	CH_3COOH +	CH_3NH_2 $\rightleftharpoons$	CH_3COO^- +	$CH_3NH_3^+$
Initial state (mol)	$1.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0	0
Final state (mol)	$(1.0 \cdot 10^{-3}) - x$	$(1.5 \cdot 10^{-3}) - x$	x	x

Detailed calculation of equilibrium quantities **Data:**

- Total volume: $V = 25$ mL $= 0.025$ L
- Equilibrium constant: $K = 7.94 \times 10^5$

Resolution:

Let x be the extent at equilibrium. The equilibrium equation is written:

$$7.94 \times 10^5 = \frac{x^2}{(1.0 \times 10^{-3} - x)(1.5 \times 10^{-3} - x)}$$

Let us expand the equation:

Resolution of the Equation for $V_B = 15$ mL

Consider the equilibrium equation:

$$7.94 \times 10^5 = \frac{x^2}{(1.0 \times 10^{-3} - x)(1.5 \times 10^{-3} - x)}$$

1. Conversion to polynomial form Setting $a = 1.0 \times 10^{-3}$ and $b = 1.5 \times 10^{-3}$, we expand:

$$\begin{aligned} 7.94 \times 10^5 (ab - (a+b)x + x^2) &= x^2 \\ 7.94 \times 10^5 (1.5 \times 10^{-6} - 2.5 \times 10^{-3} x + x^2) &= x^2 \\ 1.191 - 1985x + 7.94 \times 10^5 x^2 &= x^2 \end{aligned}$$

Grouping the terms:

$$(7.94 \times 10^5 - 1)x^2 - 1985x + 1.191 = 07.94 \times 10^5 x^2 - 1985x + 1.191 = 0$$

2. Calculation of the discriminant

$$\begin{aligned} \Delta = B^2 - 4AC &= (-1985)^2 - 4 \times (7.94 \times 10^5) \times 1.191 \\ &= 1.56825 \times 10^5 \Rightarrow \sqrt{\Delta} \approx 396.01 \end{aligned}$$

3. Calculation of the roots

$$x = \frac{-B \pm \sqrt{\Delta}}{2A} \Rightarrow \begin{cases} x_1 = \dfrac{1985 - 396.01}{1.58798 \times 10^6} = \dfrac{1588.99}{1.58798 \times 10^6} \approx 1.00 \times 10^{-3} \text{ mol} \\ x_2 = \dfrac{1985 + 396.01}{1.58798 \times 10^6} = \dfrac{2381.01}{1.58798 \times 10^6} \approx 1.50 \times 10^{-3} \text{ mol} \end{cases}$$

4. Choice of the physical solution The extent x cannot exceed the smallest initial quantity. Here, acetic acid CH_3COOH is the limiting reactant with $n = 1.0 \times 10^{-3}$ mol.

- $x_2 = 1.50 \times 10^{-3}$ mol is impossible.
- $x_1 = 1.00 \times 10^{-3}$ mol is the physically acceptable solution.

$$x \approx 1.00 \times 10^{-3} \text{ mol}$$

Final quantities at equilibrium:

$$n^{\text{eq}}_{CH_3COOH} = 1.0 \times 10^{-3} - 1.00 \times 10^{-3} = 0 \text{ mol}$$
$$n^{\text{eq}}_{CH_3NH_2} = 1.5 \times 10^{-3} - 1.00 \times 10^{-3} = 0.50 \times 10^{-3} \text{ mol}$$
$$n^{\text{eq}}_{CH_3COO^-} = n^{\text{eq}}_{CH_3NH_3^+} = 1.00 \times 10^{-3} \text{ mol}$$

Equilibrium concentrations:

$$[CH_3COOH] = 0 \text{ mol/L}$$
$$[CH_3NH_2] = \frac{0.50 \times 10^{-3}}{0.025} = 2.00 \times 10^{-2} \text{ mol/L}$$
$$[CH_3COO^-] = \frac{1.00 \times 10^{-3}}{0.025} = 4.00 \times 10^{-2} \text{ mol/L}$$
$$[CH_3NH_3^+] = \frac{1.00 \times 10^{-3}}{0.025} = 4.00 \times 10^{-2} \text{ mol/L}$$

Analysis of the system:
We have two acid-base pairs:

- Pair 1: CH_3COOH/CH_3COO^- with $K_{a1} = 1.74 \times 10^{-5}$
- Pair 2: $CH_3NH_3^+/CH_3NH_2$ with $K_{a2} = 1.26 \times 10^{-11}$

The major species are:

- CH_3COO^-: 4.00×10^{-2} mol/L (weak base)
- $CH_3NH_3^+$: 4.00×10^{-2} mol/L (very weak acid)
- CH_3NH_2: 2.00×10^{-2} mol/L (weak base)

pH calculation by the competitive equilibria method:
The system is complex because we have several acids and bases in competition. However, we can observe that:

- $CH_3NH_3^+$ is a very weak acid ($K_a = 1.26 \times 10^{-11}$)
- CH_3COO^- is a weak base ($K_b = 5.75 \times 10^{-10}$)
- CH_3NH_2 is a weak base ($K_b = 7.94 \times 10^{-4}$)

The most basic species is CH_3NH_2 (highest K_b). The pH will therefore be controlled mainly by the equilibrium:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

Calculation with the modified Henderson-Hasselbalch equation:
For a complex mixture, we can use the approximation:

$$\text{pH} \approx pK_a(CH_3NH_3^+) + \log \frac{[CH_3NH_2]}{[CH_3NH_3^+]}$$

$$\text{pH} = 10.90 + \log\left(\frac{2.00 \times 10^{-2}}{4.00 \times 10^{-2}}\right) = 10.90 + \log(0.5) = 10.90 - 0.301 = 10.60$$

Verification with the second pair:

$$\text{pH} \approx pK_a(CH_3COOH) + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

But here $[CH_3COOH] = 0$, so this formula is not directly applicable. This confirms that the acetic acid has completely reacted.
Conclusion:

The pH is mainly controlled by the methylamine/methylammonium pair, with an excess of weak base.

$$\boxed{\text{pH} = 10.6}$$

The medium is basic, dominated by free methylamine and its conjugate acid in comparable proportions.

Special Case:

We will now analyze a case where the two strategists are perfectly balanced, a "duel of masters." This case illustrates the limits of titration and the crucial importance of the equilibrium constant.
The weak acid (acetic acid): $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$ with $pK_a = 4.74$

The weak base (aniline): $C_6H_5NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons {C_6H_5NH_3}^+{}_{(aq)} + OH^-_{(aq)}$ with $pK_a({C_6H_5NH_3}^+) = 4.6$

The overall reaction is: $CH_3COOH_{(aq)} + C_6H_5NH_{2(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + {C_6H_5NH_3}^+{}_{(aq)}$
Equilibrium constant:

$$K = 10^{pK_a(\text{conjugate acid of the base}) - pK_a(\text{acid})} = 10^{4.6-4.74} = 10^{-0.14} \approx \mathbf{0.72}$$

Note: A constant $K \approx 0.72$ is less than 1. This is the crucial point: the reaction is **slightly unfavorable**. The reactants are a little "stronger" than the products. At equilibrium, a non-negligible amount of reactants will remain. **We CANNOT consider it as complete.**

Practical consequence: Such a titration is **very difficult, even impossible to carry out experimentally**. The pH jump at equivalence will be very small and gradual, making the detection of the equivalence point imprecise. This is an excellent theoretical example for understanding the limits of the method.

Detailed Study of the Titration (Equilibrium Method): Consider the titration of $V_A = 15$ mL of acetic acid $C_a = 0.1$ M with aniline $C_b = 0.15$ M. The theoretical equivalence volume is $V_{eq} = 10$ mL.

Phase-1: Before Equivalence ($0 < V_B < 10$ mL) Since the reaction is not complete, we cannot use a simple reaction progress table. We must solve the complete equilibrium. The system will always contain all 4 species in non-negligible quantities. The calculation is complex and requires solving a system of equations (electroneutrality, equilibrium constant). The pH will evolve very slowly, without forming an effective buffer zone.

Before equivalence at $V_B = 2.0$ mL:

Equation	CH_3COOH +	$C_6H_5NH_2$ $\rightleftharpoons$	CH_3COO^- +	$C6H5NH3^+$
Initial state (mol)	$1.50 \cdot 10^{-3}$	$0.3 \cdot 10^{-3}$	0	0
Final state (mol)	$(1.50 \cdot 10^{-3}) - x$	$(0.3 \cdot 10^{-3}) - x$	x	x

Equilibrium equation

$$K = \frac{[CH_3COO^-][{C_6H_5NH_3}^+]}{[CH_3COOH][C_6H_5NH_2]} = \frac{\left(\frac{x}{0.0170}\right)^2}{\left(\frac{1.50 \cdot 10^{-3} - x}{0.0170}\right)\left(\frac{0.30 \cdot 10^{-3} - x}{0.0170}\right)}$$

$$0.72 = \frac{x^2}{(1.50 \cdot 10^{-3} - x)(0.30 \cdot 10^{-3} - x)}$$

Resolution of the equation

$$-0.28x^2 - 1.296 \cdot 10^{-3}x + 3.24 \cdot 10^{-7} = 0$$

Discriminant:

$$\Delta = (1.296 \cdot 10^{-3})^2 - 4 \times (-0.28) \times (3.24 \cdot 10^{-7})$$

$$\sqrt{\Delta} = 1.429 \cdot 10^{-3}$$

Roots:

$$x_1 = \frac{1.296 \cdot 10^{-3} - 1.429 \cdot 10^{-3}}{-0.56} = \frac{-1.33 \cdot 10^{-4}}{-0.56} = 2.38 \cdot 10^{-4} \text{ mol}$$

$$x_2 = \frac{1.296 \cdot 10^{-3} + 1.429 \cdot 10^{-3}}{-0.56} = \frac{2.725 \cdot 10^{-3}}{-0.56} = -4.87 \cdot 10^{-3} \text{ mol (impossible)}$$

$$\boxed{x = 2.38 \cdot 10^{-4} \text{ mol}}$$

Balance of quantities

$$\begin{cases} n^{\text{final}}_{CH_3COOH} = 1.50 \cdot 10^{-3} - 2.38 \cdot 10^{-4} = 1.262 \cdot 10^{-3} \text{ mol} \\ n^{\text{final}}_{C_6H_5NH_2} = 0.30 \cdot 10^{-3} - 2.38 \cdot 10^{-4} = 0.062 \cdot 10^{-3} \text{ mol} \\ n^{\text{final}}_{CH_3COO^-} = n^{\text{final}}_{C_6H_5NH_3^+} = 2.38 \cdot 10^{-4} \text{ mol} \end{cases}$$

Concentrations and pH:

$[CH_3COOH] = \dfrac{1.262 \cdot 10^{-3}}{0.0170} = 7.42 \cdot 10^{-2}$ mol/L and $[CH_3COO^-] = \dfrac{2.38 \cdot 10^{-4}}{0.0170} = 1.40 \cdot 10^{-2}$ mol/L

Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a(CH_3COOH) + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log\left(\frac{1.40 \cdot 10^{-2}}{7.42 \cdot 10^{-2}}\right) = 4.74 - 0.724 = \boxed{4.02}$$

Verification of residual aniline concentration:

$$[C_6H_5NH_2] = \frac{0.062 \cdot 10^{-3}}{0.0170} = 3.65 \cdot 10^{-3} \text{ mol/L}$$

This value is **not negligible**, confirming that all 4 species coexist ($K \approx 1$).

Important

Interpretation: We are in the **unbalanced buffer zone**, with a ratio [base]/[acid] = 0.189, which explains why the pH is slightly below the pKa.

Phase-2: Half-equivalence at $V_B = 5.0$ mL:

Initial data

- Acetic acid volume: $V_A = 15.0$ mL, $C_A = 0.100$ mol/L
- Aniline volume added: $V_B = 5.0$ mL, $C_B = 0.150$ mol/L
- Equilibrium constant: $K = 0.72$
- Total volume: $V = 20.0$ mL $= 0.0200$ L

Equation	CH_3COOH	+	$C_6H_5NH_2$	$\rightleftharpoons$	CH_3COO^-	+	$C_6H_5NH_3^+$
Initial state (mol)	$1.50 \cdot 10^{-3}$		$0.75 \cdot 10^{-3}$		0		0
Final state (mol)	$(1.50 \cdot 10^{-3}) - x$		$(0.75 \cdot 10^{-3}) - x$		x		x

$$0.72 = \frac{x^2}{(1.50 \cdot 10^{-3} - x)(0.75 \cdot 10^{-3} - x)}$$

$$\boxed{x = 4.63 \cdot 10^{-4} \text{ mol}}$$

Final concentrations

$$[CH_3COOH] = \frac{1.037 \cdot 10^{-3}}{0.0200} = 5.19 \cdot 10^{-2} \text{ mol/L}, \quad [CH_3COO^-] = \frac{4.63 \cdot 10^{-4}}{0.0200} = 2.32 \cdot 10^{-2} \text{ mol/L}$$
$$[C_6H_5NH_2] = \frac{2.87 \cdot 10^{-4}}{0.0200} = 1.44 \cdot 10^{-2} \text{ mol/L}, \quad [C_6H_5NH_3^+] = \frac{4.63 \cdot 10^{-4}}{0.0200} = 2.32 \cdot 10^{-2} \text{ mol/L}$$

Analysis of characteristic ratios

- Acetic acid ratio: $\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{2.32}{5.19} = 0.447$
- Aniline ratio: $\frac{[C_6H_5NH_2]}{[C_6H_5NH_3^+]} = \frac{1.44}{2.32} = 0.621$
- Extent of reaction: $\alpha = \frac{x}{n^0_{C_6H_5NH_2}} = \frac{4.63}{7.50} = 0.617$

pH calculation by dominant equilibrium:

The CH_3COOH/CH_3COO^- pair ($pK_a = 4.74$) slightly dominates because it is more concentrated.

$$pH = pK_a(CH_3COOH) + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log(0.447) = \boxed{4.39}$$

Verification with the second pair:

$$pH = pK_a(C_6H_5NH_3^+) + \log \frac{[C_6H_5NH_2]}{[C_6H_5NH_3^+]}$$
$$pH = 4.60 + \log(0.621) = 4.60 - 0.207 = 4.39$$

Important

Validation: Both pairs give the same pH (4.39), confirming the internal consistency of the calculation and the equilibrium state of the system. In a classical titration ($K \gg 1$), at half-equivalence we would have pH = pKa = 4.74. Here, the pH is lower (4.39) because the incomplete reaction leaves less conjugate base formed. As physical interpretation we have:

- **Moderate extent:** $\alpha = 61.7\%$ only, due to $K < 1$
- **Marked coexistence:** All 4 species are present in significant proportions
- **Intermediate pH:** 4.39 between the two pKa values (4.60 and 4.74)
- **Limiting reactant:** Aniline is almost completely consumed

Conclusion:

The half-equivalence point reveals all the complexity of a titration with $K \approx 1$. Unlike usual titrations, we do not observe pH = pKa, but a lower value reflecting the incomplete equilibrium and the coexistence of the four chemical species.

Phase-3: After equivalence at $V_B = 20.0$ mL

Equation	CH_3COOH +	$C_6H_5NH_2$ $\rightleftharpoons$	CH_3COO^- +	$C_6H_5NH_3^+$
Initial state (mol)	$1.50 \cdot 10^{-3}$	$3.00 \cdot 10^{-3}$	0	0
Final state (mol)	$(1.50 \cdot 10^{-3}) - x$	$(3.00 \cdot 10^{-3}) - x$	x	x

Complete equilibrium equation

$$K = \frac{[CH_3COO^-][C_6H_5NH_3^+]}{[CH_3COOH][C_6H_5NH_2]} = \frac{\left(\frac{x}{0.0350}\right)^2}{\left(\frac{1.50 \cdot 10^{-3} - x}{0.0350}\right)\left(\frac{3.00 \cdot 10^{-3} - x}{0.0350}\right)} = 0.72$$

Solutions:

$$x_1 = \frac{3.24 \cdot 10^{-3} - 3.759 \cdot 10^{-3}}{-0.56} = 9.27 \cdot 10^{-4} \text{ mol}$$
$$x_2 = \frac{3.24 \cdot 10^{-3} + 3.759 \cdot 10^{-3}}{-0.56} = -1.250 \cdot 10^{-2} \text{ mol (rejected)}$$

$$\boxed{x = 9.27 \cdot 10^{-4} \text{ mol}}$$

Complete material balance at equilibrium

$$\begin{cases} n^{\text{eq}}_{CH_3COOH} = 1.50 \cdot 10^{-3} - 9.27 \cdot 10^{-4} = 5.73 \cdot 10^{-4} \text{ mol} \\ n^{\text{eq}}_{C_6H_5NH_2} = 3.00 \cdot 10^{-3} - 9.27 \cdot 10^{-4} = 2.073 \cdot 10^{-3} \text{ mol} \\ n^{\text{eq}}_{CH_3COO^-} = n^{\text{eq}}_{C_6H_5NH_3^+} = 9.27 \cdot 10^{-4} \text{ mol} \end{cases}$$

Final concentrations

$$[CH_3COOH] = \frac{5.73 \cdot 10^{-4}}{0.0350} = 1.64 \cdot 10^{-2} \text{ mol/L}, \quad [CH_3COO^-] = \frac{9.27 \cdot 10^{-4}}{0.0350} = 2.65 \cdot 10^{-2} \text{ mol/L}$$
$$[C_6H_5NH_2] = \frac{2.073 \cdot 10^{-3}}{0.0350} = 5.92 \cdot 10^{-2} \text{ mol/L}, \quad [C_6H_5NH_3^+] = \frac{9.27 \cdot 10^{-4}}{0.0350} = 2.65 \cdot 10^{-2} \text{ mol/L}$$

Corrected pH calculation: Treat the aniline excess as a weak base.

$$K_b(C_6H_5NH_2) = \frac{K_e}{K_a(C_6H_5NH_3^+)} = \frac{10^{-14}}{10^{-4.60}} = 10^{-9.40} = 4.0 \cdot 10^{-10}$$

Effective base concentration:

$$[C_6H_5NH_2] \approx 5.92 \cdot 10^{-2} \text{ mol/L}$$

Basicity calculation:

$$[OH^-] = \sqrt{K_b \times [C_6H_5NH_2]} = \sqrt{4.0 \times 10^{-10} \times 5.92 \times 10^{-2}} = \sqrt{2.37 \times 10^{-11}}$$

$$[OH^-] = 4.87 \cdot 10^{-6} \text{ mol/L}$$

$$\text{pOH} = -\log(4.87 \times 10^{-6}) = 5.31$$

$$\boxed{\text{pH} = 14.00 - 5.31 = 8.69}$$

Validation and interpretation

Important

Validated result: pH = 8.69 corresponds well to a **basic** medium, consistent with the presence of an aniline excess.
Conclusion: Despite the low basicity of aniline ($K_b = 4.0 \times 10^{-10}$), the high concentration ($5.92 \cdot 10^{-2}$ mol/L) leads to a clearly basic pH.

System summary

- **Limited reaction:** Extent $x = 9.27 \cdot 10^{-4}$ mol only (out of $1.50 \cdot 10^{-3}$ mol possible)
- **Coexistence:** All 4 species are present in significant concentrations
- **Net excess:** Aniline in large excess ($2.073 \cdot 10^{-3}$ mol)
- **Final pH:** 8.69 - basic as expected

5.2.11 Application Exercises:

Exercise

pH Calculation

Calculate the pH of the following solutions:

a) Acetic acid: mixture of 50 mL of 1.0 mol/L acetic acid solution with 150 mL of water. Data: $pK_a = 4.76$.
b) Ammonia: mixture of 50 mL of 0.100 mol/L ammonia solution with 150 mL of 0.200 mol/L ammonia solution. Data: $pK_a = 9.25$.
c) Mixture of 50 mL of HI 0.050 mol/L with 50 mL of HBr 0.75 mol/L.
d) Mixture of 500 mL of HCl 0.10 mol/L and 500 mL of NaOH 0.050 mol/L.
e) Mixture of 500 mL of HCl 0.10 mol/L and 100 mL of NH_3 0.20 mol/L.
f) Mixture of 500 mL of CH_3COOH 0.10 mol/L and 500 mL of NaOH 0.20 mol/L.

Solution

a) Acetic acid: mixture of 50 mL (1.0 mol/L) with 150 mL of water

Data:

- Initial volume: $V_a = 50$ mL $= 0.050$ L
- Initial concentration: $C_a = 1.0$ mol/L
- $pK_a = 4.76$
- Water volume: $V_{\text{water}} = 150$ mL

1. Concentration after dilution

Total volume: $V_{\text{total}} = 50 + 150 = 200$ mL $= 0.200$ L
Amount of acid: $n_a = C_a \times V_a = 1.0 \times 0.050 = 0.050$ mol
Concentration after dilution:

$$C'_a = \frac{n_a}{V_{\text{total}}} = \frac{0.050}{0.200} = 0.250 \text{ mol/L}$$

2. pH calculation (weak acid)

For a weak acid: $\text{pH} = \frac{1}{2}pK_a - \frac{1}{2}\log C$
Verification: $C = 0.250 \text{ mol/L} \gg 10^{-4.76} \approx 1.74 \times 10^{-5}$ (approximation valid)
Calculation:

$$\begin{aligned}\text{pH} &= \frac{1}{2} \times 4.76 - \frac{1}{2}\log(0.250) \\ &= 2.68\end{aligned}$$

Answer: pH = 2.68

Why verify with $C \gg 10^{-pK_a}$?

This condition guarantees the validity of the approximation $x \ll C$ to avoid the quadratic equation. Butler[40] proposes a rigorous approach for treating cases where this approximation is not valid, particularly for very weak acids or very dilute solutions.

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \quad \text{with:} \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

	HA	+	H_2O	$\rightleftharpoons$	H_3O^+	+	A^-
$t = 0$	C		–		10^{-7}		10^{-7}
adv	$-x$		–		$+x$		$+x$
equil	$C - x$		–		$10^{-7} + x$		$10^{-7} + x$

Approximation: $10^{-7} \ll x$ and $x \ll C$

$$K_a = \frac{x^2}{C-x} \approx \frac{x^2}{C} \quad \Rightarrow \quad x = \sqrt{K_a C}$$

Condition of validity: $\frac{x}{C} < 0.05$ (dissociation $< 5\%$)

$$x = \sqrt{K_a C} \quad \Rightarrow \quad \frac{\sqrt{K_a C}}{C} < 0.05 \quad \Rightarrow \quad \frac{K_a}{C} < 2.5 \times 10^{-3}$$

$$\frac{C}{K_a} > 400 \quad \text{(practical rule: often simplified to 100)}$$

$$\boxed{C \gg 10^{-pK_a} \quad \text{or} \quad \frac{C}{K_a} \geq 100}$$

Exact equation (if condition not met):

$$K_a = \frac{x^2}{C-x} \quad \Rightarrow \quad x^2 = K_a(C-x)$$

$$x^2 + K_a x - K_a C = 0 \quad \text{we use:} \quad \Delta = K_a^2 + 4K_a C$$

$$x = \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2}$$

Practical verification: After approximation.

$$\frac{[\mathrm{H_3O^+}]_{\text{approx}}}{C} \times 100 < 5\%$$

Conclusion

$C \gg 10^{-pK_a}$ is the mathematical consistency test. It guarantees that the approximation reflects the chemical reality of weak dissociation.

b) Ammonia: mixture of 50 mL (0.100 mol/L) with 150 mL (0.200 mol/L)

Data:

- Solution 1: $V_1 = 50$ mL $= 0.050$ L, $C_1 = 0.100$ mol/L
- Solution 2: $V_2 = 150$ mL $= 0.150$ L, $C_2 = 0.200$ mol/L
- $pK_a(\mathrm{NH_4^+}) = 9.25$ (conjugate acid of $\mathrm{NH_3}$)

1. Calculation of total concentration

Total amount of ammonia:

$$n_{\mathrm{NH_3}} = C_1 \times V_1 + C_2 \times V_2 = (0.100 \times 0.050) + (0.200 \times 0.150)$$

$$n_{\mathrm{NH_3}} = 0.00500 + 0.0300 = 0.0350 \text{ mol}$$

Total volume:

$$V_{\text{total}} = V_1 + V_2 = 0.050 + 0.150 = 0.200 \text{ L}$$

Total concentration:

$$C = \frac{n_{\mathrm{NH_3}}}{V_{\text{total}}} = \frac{0.0350}{0.200} = 0.175 \text{ mol/L}$$

2. Calculation with pK_a

For a weak base NH_3 using the pK_a of its conjugate acid NH_4^+:

$$\text{pH} = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

Verification of the approximation:

$$C = 0.175 \text{ mol/L} \gg 10^{-(14-9.25)} = 10^{-4.75} \approx 1.78 \times 10^{-5}$$

Calculation:

$$\begin{aligned}\text{pH} &= 7 + \frac{1}{2} \times 9.25 + \frac{1}{2}\log(0.175) \\ &= \boxed{11.24}\end{aligned}$$

Alternative method: Calculation with pK_b
First, calculate pK_b:

$$pK_b = 14 - pK_a = 14 - 9.25 = 4.75$$

Formula for a weak base with pK_b:

$$\text{pH} = 14 - \left[\frac{1}{2}pK_b - \frac{1}{2}\log C\right] = 14 - \frac{1}{2}pK_b + \frac{1}{2}\log C$$

Same verification:

$$C = 0.175 \text{ mol/L} \gg 10^{-pK_b} = 10^{-4.75} \approx 1.78 \times 10^{-5}$$

Calculation:

$$\begin{aligned}\text{pH} &= 14 - \frac{1}{2} \times 4.75 + \frac{1}{2}\log(0.175) \\ &= \boxed{11.24}\end{aligned}$$

Verification of the equivalence of the two methods:
Method 1: $\text{pH} = \frac{1}{2}\left(14 + pK_a + \frac{1}{2}\log C\right)$
Method 2: $\text{pH} = 14 - \frac{1}{2}\left(pK_b - \frac{1}{2}\log C\right)$
Substituting $pK_b = 14 - pK_a$ into method 2:

$$\begin{aligned}\text{pH} &= 14 - \frac{1}{2}(14 - pK_a) + \frac{1}{2}\log C \\ &= 14 - 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C \\ &= 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C\end{aligned}$$

Which is exactly the formula from method 1.
Answer: $\boxed{\text{pH} = 11.24}$

c) Mixture of 50 mL of HI 0.050 mol/L with 50 mL of HBr 0.75 mol/L

Data:

- HI: $V_1 = 0.050$ L, $C_1 = 0.050$ mol/L
- HBr: $V_2 = 0.050$ L, $C_2 = 0.75$ mol/L

1. Amounts of matter
$n_{\text{HI}} = C_1 \times V_1 = 0.050 \times 0.050 = 0.00250$ mol
$n_{\text{HBr}} = C_2 \times V_2 = 0.75 \times 0.050 = 0.0375$ mol
2. Total H^+ concentration

Total amount of H^+:

$$n_{H^+} = n_{HI} + n_{HBr} = 0.00250 + 0.0375 = 0.0400 \text{ mol}$$

Total volume:

$$V_{total} = V_1 + V_2 = 0.050 + 0.050 = 0.100 \text{ L}$$

H^+ concentration:

$$[H^+] = \frac{n_{H^+}}{V_{total}} = \frac{0.0400}{0.100} = 0.400 \text{ mol/L}$$

3. pH calculation

$$\text{pH} = -\log[H^+] = -\log(0.400) = 0.3979 \approx 0.40$$

Answer: pH = 0.40

d) Mixture of 500 mL of HCl 0.10 mol/L and 500 mL of NaOH 0.050 mol/L

Data:

- HCl: $V_a = 0.500$ L, $C_a = 0.10$ mol/L
- NaOH: $V_b = 0.500$ L, $C_b = 0.050$ mol/L

1. Amounts of matter

$n_{H^+} = 0.10 \times 0.500 = 0.0500$ mol

$n_{OH^-} = 0.050 \times 0.500 = 0.0250$ mol

2. Reaction:

Reaction Equation	HCl	+	NaOH	⟶	NaCl	+	H_2O
Initial state (mol)	n_A		n_B		0		solvent
	0.05		0.025		0		–
Final state (mol)	0.025		0		0.025		–
	Strong acid		Strong base		Neutral salt		

3. H^+ concentration

Total volume: $V_{total} = 1.000$ L

$$[H^+] = \frac{0.0250}{1.000} = 0.0250 \text{ mol/L}$$

4. pH calculation

$$\text{pH} = -\log(0.0250) = 1.6021 \approx 1.60$$

Answer: pH = 1.60

e) Mixture of 500 mL of HCl 0.10 mol/L and 100 mL of NH_3 0.20 mol/L

Data:

- HCl: $V_a = 0.500$ L, $C_a = 0.10$ mol/L
- NH_3: $V_b = 0.100$ L, $C_b = 0.20$ mol/L
- $pK_a(NH_4^+) = 9.25$

1. Initial quantities

$n_{H^+} = 0.10 \times 0.500 = 0.0500$ mol

$n_{NH_3} = 0.20 \times 0.100 = 0.0200$ mol

2. Reaction:

Reaction Equation	HCl	+	NH_3	$\longrightarrow$	NH_4Cl
Initial state (mol)	n_A		n_b		
	0.05		0.02		0
Final state (mol)	0.03		0		0.02
	Strong acid		Weak base		Acidic salt

3. H^+ concentration
Total volume: $V_{\text{total}} = 0.600$ L
$[H^+] = \dfrac{0.0300}{0.600} = 0.0500$ mol/L
4. pH calculation

$$\text{pH} = -\log(0.0500) \approx 1.30$$

Answer: pH = 1.30

f) Mixture of 500 mL of CH_3COOH 0.10 mol/L and 500 mL of NaOH 0.20 mol/L

Data:
- CH_3COOH: $V_a = 0.500$ L, $C_a = 0.10$ mol/L
- NaOH: $V_b = 0.500$ L, $C_b = 0.20$ mol/L
- $pK_a(CH_3COOH) = 4.76$

1. Initial quantities
$n_{CH_3COOH} = 0.10 \times 0.500 = 0.0500$ mol
$n_{NaOH} = 0.20 \times 0.500 = 0.100$ mol
2. Reaction:

Reaction Equation	CH_3COOH	+	NaOH	$\longrightarrow$	CH_3COONa	+	H_2O
Initial state (mol)	n_a		n_B		0		solvent
	0.05		0.1		0		–
Final state (mol)	0		0.05		0.05		–
	Weak acid		Strong base		Basic salt		

3. OH^- concentration Total volume: $V_{\text{total}} = 1.000$ L $[OH^-] = \dfrac{0.0500}{1.000} = 0.0500$ mol/L
4. pH calculation

$$\text{pOH} = -\log(0.0500) = 1.3010$$

$$\text{pH} = 14 - 1.3010 \approx 12.70$$

Answer: pH = 12.70
Verification with H^+ concentration (via ionic product of water)
Total volume: $V_{\text{total}} = 1.000$ L
$[OH^-] = \dfrac{0.0500}{1.000} = 0.0500$ mol/L

$$K_w = [H^+][OH^-] = 10^{-14} \quad \text{at } 25°C$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.0500} = 2.00 \times 10^{-13} \text{ mol/L}$$

pH calculation:

$$\text{pH} = -\log[H^+] = -\log(2.00 \times 10^{-13}) = 12.70$$

Answer: pH = 12.70

Exercise

pH Calculation - Advanced Level

Calculate the pH of the following solutions (systematically verify the approximations):

a) **Dilution of a weak acid**: 30 mL of a 0.15 mol/L hydrocyanic acid HCN solution is diluted with 120 mL of water. Data: $pK_a(\text{HCN}) = 9.21$. (Verify the condition $C \gg 10^{-pK_a}$)

b) **Aniline/anilinium buffer mixture**: mix 80 mL of a 0.060 mol/L aniline solution with 120 mL of a 0.040 mol/L anilinium chloride solution. Data: $pK_a(\text{C}_6\text{H}_5\text{NH}_3{}^+) = 4.63$.

c) **Mixture of acids**: 60 mL of a 0.085 mol/L hydrochloric acid HCl solution is mixed with 40 mL of a 0.35 mol/L phosphoric acid H_3PO_4 solution. We consider that the first acidity of H_3PO_4 is completely dissociated.

d) **Weak acid-weak base reaction**: mix 400 mL of a 0.12 mol/L acetic acid CH_3COOH solution with 400 mL of a 0.12 mol/L ammonia NH_3 solution. Data: $pK_a(\text{CH}_3\text{COOH}) = 4.76$, $pK_a(\text{NH}_4{}^+) = 9.25$.

e) **Partial neutralization of an ammonium salt**: 350 mL of a 0.14 mol/L sodium hydroxide NaOH solution is added to 250 mL of a 0.20 mol/L ammonium chloride NH_4Cl solution. Data: $pK_a(\text{NH}_4{}^+) = 9.25$.

f) **Partial titration of a weak acid**: mix 200 mL of a 0.25 mol/L formic acid HCOOH solution with 300 mL of a 0.18 mol/L potassium hydroxide KOH solution. Data: $pK_a(\text{HCOOH}) = 3.75$. Verify the validity of the approximations.

Solution

pH Calculation (Advanced Level)

Conventions: we work at 25 °C (so $pK_e = 14$). We denote C as the analytical concentration after mixing. We systematically verify the approximation conditions (for example if $x \ll C$).

a) **Hydrocyanic acid HCN**: 30 mL of 0.15 mol/L + 120 mL of water, $pK_a = 9.21$.
Concentration after dilution:

$$n_0(\text{HCN}) = C_i V_i = 0.15 \text{ mol/L} \times 0.030 \text{ L} = 4.50 \cdot 10^{-3} \text{ mol}$$

$$V_f = 0.030 \text{ L} + 0.120 \text{ L} = 0.150 \text{ L} \quad \Rightarrow \quad C = \frac{n_0}{V_f} = \frac{4.50 \cdot 10^{-3}}{0.150} = 3.0 \cdot 10^{-2} \text{ mol/L}$$

Setting up the equation:

$$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^- \qquad K_a = 10^{-pK_a} = 10^{-9.21} = 6.2 \cdot 10^{-10}$$

If $x = [\text{H}^+] = [\text{CN}^-]$ at equilibrium, then

$$K_a = \frac{x^2}{C - x} \quad \Rightarrow \quad x^2 + K_a x - K_a C = 0.$$

Approximation and check: We propose $x \ll C$ (very weak acid):

$$x \simeq \sqrt{K_a C} = \sqrt{(6.2 \cdot 10^{-10})(3.0 \cdot 10^{-2})} = 4.3 \cdot 10^{-6} \text{ mol/L}.$$

Check: $x/C \approx 1.4 \cdot 10^{-4} \ll 5\%$ so the approximation is excellent.

$$\boxed{\text{pH} = -\log x \simeq 5.37}$$

Note: $C \gg 10^{-pK_a}$ because $3.0 \cdot 10^{-2}$ mol/L $\gg 6.2 \cdot 10^{-10}$.

b) **Aniline**: 80 mL of 0.060 mol/L mixed with 120 mL of 0.040 mol/L. Data: $pK_a(\text{C}_6\text{H}_5\text{NH}_3{}^+) = 4.63$.
Interpretation of the statement: The statement indicates "solution 0.040 mol/L" without specification. The data $pK_a(\text{C}_6\text{H}_5\text{NH}_3{}^+)$ suggests we are working with the aniline/anilinium pair. **We therefore interpret the second solution as anilinium chloride $\mathbf{C_6H_5NH_3Cl}$.**

Amounts of matter:

$$n(C_6H_5NH_2) = 0.080 \times 0.060 = 4.8 \cdot 10^{-3} \text{ mol}$$

$$n(C_6H_5NH_3^+) = 0.120 \times 0.040 = 4.8 \cdot 10^{-3} \text{ mol}$$

Concentrations after mixing:

$$V_f = 0.200 \text{ L} \qquad \Rightarrow \qquad [C_6H_5NH_2] = \frac{4.8 \cdot 10^{-3}}{0.200} = 2.4 \cdot 10^{-2} \text{ mol/L}$$

$$[C_6H_5NH_3^+] = \frac{4.8 \cdot 10^{-3}}{0.200} = 2.4 \cdot 10^{-2} \text{ mol/L}$$

pH of a buffer (Henderson-Hasselbalch):

$$\boxed{\text{pH} = pK_a + \log \frac{[C_6H_5NH_2]}{[C_6H_5NH_3^+]}} = 4.63 + \log\left(\frac{2.4 \cdot 10^{-2}}{2.4 \cdot 10^{-2}}\right)$$

$$\boxed{\text{pH} = 4.63}$$

c) **Mixture of:** 60 mL of HCl 0.085 mol/L with 40 mL of H_3PO_4 0.35 mol/L. We assume: first dissociation of H_3PO_4 complete.
Amounts of matter introduced:

$$n(\text{HCl}) = 0.060 \text{ L} \times 0.085 \text{ mol/L} = 5.10 \cdot 10^{-3} \text{ mol}$$

$$n(H_3PO_4) = 0.040 \text{ L} \times 0.35 \text{ mol/L} = 1.40 \cdot 10^{-2} \text{ mol}$$

Calculation of total protons: First acidity complete: each H_3PO_4 releases 1 proton.

$$H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$$

$$n(H^+)_{\text{total}} = 5.10 \cdot 10^{-3} + 1.4 \cdot 10^{-2} = 1.91 \cdot 10^{-2} \text{ mol}$$

Concentration and pH:

$$V_f = 0.100 \text{ L} \qquad [H^+] \approx \frac{1.91 \cdot 10^{-2}}{0.1} = 0.191 \text{ mol/L}$$

The second and third dissociations of H_3PO_4 are very limited at such acidic pH.

$$\boxed{\text{pH} = -\log(0.191) = 0.72}$$

d) **Equimolar mixture**: 400 mL of CH_3COOH 0.12 mol/L and 400 mL of NH_3 0.12 mol/L. Data: $pK_a(CH_3COOH) = 4.76$, $pK_a(NH_4^+) = 9.25$.
Dominant acid-base reaction:

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

We compare pK_a: the strongest acid is CH_3COOH (4.76) and the conjugate acid of NH_3 is NH_4^+ (9.25). The reaction is therefore very strongly shifted to the right.
Equimolar case:

$$n(CH_3COOH) = n(NH_3) = 0.400 \text{ L} \times 0.12 \text{ mol/L} = 4.8 \cdot 10^{-2} \text{ mol}$$

They are almost completely consumed: essentially the salt CH_3COONH_4 remains. For a salt of

a weak acid and a weak base, a good approximation is

$$\boxed{\text{pH} \simeq \frac{1}{2}(pK_a(\text{CH}_3\text{COOH}) + pK_a(\text{NH}_4{}^+))}$$

$$\boxed{\text{pH} \simeq \frac{1}{2}(4.76 + 9.25) = 7.01}$$

e) **Mixture of:** 350 mL of NaOH 0.14 mol/L + 250 mL of NH_4Cl 0.20 mol/L, $pK_a(\text{NH}_4{}^+) = 9.25$.
Stoichiometry:

$$n(\text{OH}^-) = 0.350 \times 0.14 = 4.9 \cdot 10^{-2} \text{ mol}$$

$$n(\text{NH}_4{}^+) = 0.250 \times 0.20 = 5.0 \cdot 10^{-2} \text{ mol}$$

$$\text{NH}_4{}^+ + \text{OH}^- \longrightarrow \text{NH}_3 + \text{H}_2\text{O}$$

OH^- is limiting: it is completely consumed. Remaining:

$$n(\text{NH}_4{}^+)_{\text{remaining}} = 5.0 \cdot 10^{-2} - 4.9 \cdot 10^{-2} = 1.0 \cdot 10^{-3} \text{ mol}$$

and $n(\text{NH}_3) = 4.9 \cdot 10^{-2}$ mol has been formed.

$$V_f = 0.600 \text{ L} \Rightarrow [\text{NH}_3] = \frac{4.9 \cdot 10^{-2}}{0.6} = 8.17 \cdot 10^{-2} \text{ mol/L}$$

$$[\text{NH}_4{}^+] = \frac{1.0 \cdot 10^{-3}}{0.6} = 1.67 \cdot 10^{-3} \text{ mol/L}$$

Buffer $\text{NH}_4{}^+/\text{NH}_3$ (Henderson–Hasselbalch):

$$\boxed{\text{pH} = pK_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4{}^+]}}$$

$$\text{pH} = 9.25 + \log\left(\frac{8.17 \cdot 10^{-2}}{1.67 \cdot 10^{-3}}\right) = 9.25 + \log(49)$$

$$\boxed{\text{pH} = 11.20}$$

f) **Mixture of:** 200 mL of HCOOH 0.25 mol/L + 300 mL of KOH 0.18 mol/L. Data: $pK_a(\text{HCOOH}) = 3.75$.
Stoichiometry:

$$n(\text{HCOOH}) = 0.200 \times 0.25 = 5.0 \cdot 10^{-2} \text{ mol}$$

$$n(\text{OH}^-) = 0.300 \times 0.18 = 5.4 \cdot 10^{-2} \text{ mol}$$

$$\text{HCOOH} + \text{OH}^- \longrightarrow \text{HCOO}^- + \text{H}_2\text{O}$$

The base is in excess: $n_{\text{excess}}(\text{OH}^-) = 0.004$ mol.

$$V_f = 0.500 \text{ L} \Rightarrow [\text{OH}^-] \approx \frac{0.004}{0.500} = 8.0 \cdot 10^{-3} \text{ mol/L}$$

pH governed by the excess of strong base:

$$\text{pOH} = -\log(8.0 \cdot 10^{-3}) = 2.10 \qquad \Rightarrow \qquad \boxed{\text{pH} = 14 - 2.10 = 11.90}$$

Verification of the approximation: We neglect the hydrolysis of formate HCOO^- because the solution already contains $[\text{OH}^-] = 8 \cdot 10^{-3}$ mol/L. Formate is a weak base ($pK_b = 14 - pK_a = 10.25 \Rightarrow K_b \approx 5.6 \cdot 10^{-11}$), so its contribution to $[\text{OH}^-]$ is much smaller than the calculated excess.

Exercise

pH Calculation - (New Context)

Calculate the pH of the following solutions at 25 °C ($pK_w = 14$):

a) **Dilution of benzoic acid**: mixture of 40 mL of a 0.30 mol/L benzoic acid C_6H_5COOH solution with 160 mL of water. Data: $pK_a(C_6H_5COOH) = 4.20$.

b) **Trimethylamine/trimethylammonium buffer mixture**: mixture of 60 mL of a 0.12 mol/L trimethylamine $(CH_3)_3N$ solution with 140 mL of a 0.08 mol/L trimethylammonium chloride $(CH_3)_3NHCl$ solution. Data: $pK_a((CH_3)_3NH^+) = 9.80$.

c) **Mixture of strong acids**: mixture of 90 mL of a 0.06 mol/L sulfuric acid H_2SO_4 solution with 60 mL of a 0.22 mol/L hydrochloric acid HCl solution. We consider that H_2SO_4 releases 2 H^+ per molecule (first acidity completely dissociated).

d) **Strong acid - strong base neutralization**: mixture of 450 mL of a 0.09 mol/L nitric acid HNO_3 solution and 300 mL of a 0.12 mol/L barium hydroxide $Ba(OH)_2$ solution. Recall that $Ba(OH)_2$ releases 2 OH^- per formula unit.

e) **Strong acid - weak base reaction**: mixture of 320 mL of a 0.14 mol/L hydroiodic acid HI solution and 180 mL of a 0.25 mol/L pyridine C_5H_5N solution. Data: $pK_a(C_5H_5NH^+) = 5.25$.

f) **Weak acid - strong base titration**: mixture of 280 mL of a 0.16 mol/L hydrofluoric acid HF solution and 220 mL of a 0.20 mol/L sodium hydroxide NaOH solution. Data: $pK_a(HF) = 3.17$.

Solution

pH Calculation (New Context)

Conventions: we work at 25 °C (so $pK_e = 14$). We denote C as the analytical concentration after mixing. We systematically verify the approximation conditions.

a) **Benzoic acid C_6H_5COOH**: 40 mL of 0.30 mol/L + 160 mL of water, p$K_a = 4.20$.

Concentration after dilution:

$$n_0(C_6H_5COOH) = C_iV_i = 0.30 \times 0.040 = 1.20 \cdot 10^{-2} \text{ mol}$$

$$V_f = 0.040 + 0.160 = 0.200 \text{ L} \quad \Rightarrow \quad C = \frac{n_0}{V_f} = \frac{1.20 \cdot 10^{-2}}{0.200} = 6.0 \cdot 10^{-2} \text{ mol/L}$$

Setting up the equation:

$$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^- \qquad K_a = 10^{-pK_a} = 10^{-4.20} = 6.3 \cdot 10^{-5}$$

If $x = [H^+]$ at equilibrium, then

$$K_a = \frac{x^2}{C - x} \quad \Rightarrow \quad x^2 + K_a x - K_a C = 0$$

Exact resolution:

$$x = \frac{-K_a + \sqrt{K_a^2 + 4K_aC}}{2} = \frac{-6.3 \cdot 10^{-5} + \sqrt{(6.3 \cdot 10^{-5})^2 + 4 \times 6.3 \cdot 10^{-5} \times 6.0 \cdot 10^{-2}}}{2}$$

$$x \simeq 1.91 \cdot 10^{-3} \text{ mol/L}$$

Verification of the approximation: If we had used the approximation $x \ll C$:

$$x \simeq \sqrt{K_aC} = \sqrt{(6.3 \cdot 10^{-5})(6.0 \cdot 10^{-2})} = 1.94 \cdot 10^{-3} \text{ mol/L}$$

$$\frac{x}{C} \approx \frac{1.91 \cdot 10^{-3}}{6.0 \cdot 10^{-2}} \approx 3.2\% < 5\% \quad \text{(acceptable)}$$

$$\boxed{\text{pH} = -\log(1.91 \cdot 10^{-3}) \simeq 2.72}$$

b) **Trimethylamine/trimethylammonium**: 60 mL of $(CH_3)_3N$ 0.12 mol/L + 140 mL of

$(CH_3)_3NHCl$ 0.08 mol/L. Data: $pK_a((CH_3)_3NH^+) = 9.80$.
Amounts of matter:

$$n((CH_3)_3N) = 0.060 \times 0.12 = 7.2 \cdot 10^{-3} \text{ mol}$$

$$n((CH_3)_3NH^+) = 0.140 \times 0.08 = 1.12 \cdot 10^{-2} \text{ mol}$$

Concentrations after mixing:

$$V_f = 0.200 \text{ L}$$

$$[(CH_3)_3N] = \frac{7.2 \cdot 10^{-3}}{0.200} = 3.6 \cdot 10^{-2} \text{ mol/L}$$

$$[(CH_3)_3NH^+] = \frac{1.12 \cdot 10^{-2}}{0.200} = 5.6 \cdot 10^{-2} \text{ mol/L}$$

pH of the buffer (Henderson-Hasselbalch):

$$\boxed{\text{pH} = pK_a + \log \frac{[(CH_3)_3N]}{[(CH_3)_3NH^+]}}$$

$$\text{pH} = 9.80 + \log\left(\frac{3.6 \cdot 10^{-2}}{5.6 \cdot 10^{-2}}\right) = 9.80 + \log(0.643)$$

$$\boxed{\text{pH} \simeq 9.80 - 0.192 \simeq 9.61}$$

c) **Mixture of strong acids**: 90 mL of H_2SO_4 0.06 mol/L + 60 mL of HCl 0.22 mol/L.
Amounts of protons:

$$n(H^+)_{H_2SO_4} = 2 \times (0.090 \times 0.06) = 2 \times 5.4 \cdot 10^{-3} \text{ mol} = 1.08 \cdot 10^{-2} \text{ mol}$$

$$n(H^+)_{HCl} = 0.060 \times 0.22 = 1.32 \cdot 10^{-2} \text{ mol}$$

$$n(H^+)_{\text{total}} = 1.08 \cdot 10^{-2} \text{ mol} + 1.32 \cdot 10^{-2} \text{ mol} = 2.40 \cdot 10^{-2} \text{ mol}$$

Concentration and pH:

$$V_f = 0.150 \text{ L} \qquad [H^+] = \frac{2.40 \cdot 10^{-2} \text{ mol}}{0.150 \text{ L}} = 0.160 \text{ mol/L}$$

$$\boxed{\text{pH} = -\log(0.160) \simeq 0.80}$$

d) **Strong acid - strong base neutralization**: 450 mL of HNO_3 0.09 mol/L + 300 mL of $Ba(OH)_2$ 0.12 mol/L.
Stoichiometry:

$$n(H^+) = 0.450 \text{ L} \times 0.09 \text{ mol/L} = 4.05 \cdot 10^{-2} \text{ mol}$$

$$n(OH^-) = 2 \times (0.300 \times 0.12) = 2 \times 3.6 \cdot 10^{-2} \text{ mol} = 7.20 \cdot 10^{-2} \text{ mol}$$

Excess of base:

$$n_{\text{excess}}(OH^-) = 7.20 \cdot 10^{-2} \text{ mol} - 4.05 \cdot 10^{-2} \text{ mol} = 3.15 \cdot 10^{-2} \text{ mol}$$

Concentration in OH^- and pH:

$$V_f = 0.750 \text{ L} \qquad [OH^-] = \frac{3.15 \cdot 10^{-2}}{0.750} = 4.20 \cdot 10^{-2} \text{ mol/L}$$

$$\text{pOH} = -\log(4.2 \cdot 10^{-2}) = 1.38$$

$$\boxed{\text{pH} = 14.00 - 1.38 = 12.62}$$

e) **Strong acid - weak base reaction**: 320 mL of HI 0.14 mol/L + 180 mL of pyridine 0.25 mol/L. Data: $pK_a(C_5H_5NH^+) = 5.25$.

Stoichiometry:

$$n(H^+) = 0.320 \times 0.14 = 4.48 \cdot 10^{-2} \text{ mol}$$

$$n(C_5H_5N) = 0.180 \times 0.25 = 4.50 \cdot 10^{-2} \text{ mol}$$

$$C_5H_5N + H^+ \longrightarrow C_5H_5NH^+$$

Situation after reaction: The acid is slightly limiting:

$$n(C_5H_5N)_{\text{remaining}} = 4.50 \cdot 10^{-2} \text{ mol} - 4.48 \cdot 10^{-2} \text{ mol} = 2.0 \cdot 10^{-4} \text{ mol}$$

$$n(C_5H_5NH^+)_{\text{formed}} = 4.48 \cdot 10^{-2} \text{ mol}$$

Concentrations and pH of the buffer:

$$V_f = 0.500 \text{ L}$$

$$[C_5H_5N] = \frac{2.0 \cdot 10^{-4} \text{ mol}}{0.500 \text{ L}} = 4.0 \cdot 10^{-4} \text{ mol/L}$$

$$[C_5H_5NH^+] = \frac{4.48 \cdot 10^{-2} \text{ mol}}{0.500 \text{ L}} = 8.96 \cdot 10^{-2} \text{ mol/L}$$

$$\boxed{\text{pH} = pK_a + \log \frac{[C_5H_5N]}{[C_5H_5NH^+]}}$$

$$\text{pH} = 5.25 + \log\left(\frac{4.0 \cdot 10^{-4}}{8.96 \cdot 10^{-2}}\right) = 5.25 + \log(4.46 \times 10^{-3})$$

$$\boxed{\text{pH} \simeq 5.25 - 2.35 \simeq 2.90}$$

f) **Weak acid - strong base titration**: 280 mL of HF 0.16 mol/L + 220 mL of NaOH 0.20 mol/L. Data: $pK_a(HF) = 3.17$.

Stoichiometry:

$$n(HF) = 0.280 \text{ L} \times 0.16 \text{ mol/L} = 4.48 \cdot 10^{-2} \text{ mol}$$

$$n(OH^-) = 0.220 \text{ L} \times 0.20 \text{ mol/L} = 4.40 \cdot 10^{-2} \text{ mol}$$

$$HF + OH^- \longrightarrow F^- + H_2O$$

Situation after reaction: The base is slightly limiting:

$$n(HF)_{\text{remaining}} = 4.48 \cdot 10^{-2} \text{ mol} - 4.40 \cdot 10^{-2} \text{ mol} = 8.0 \cdot 10^{-4} \text{ mol}$$

$$n(F^-)_{\text{formed}} = 4.40 \cdot 10^{-2} \text{ mol}$$

Concentrations and pH of the buffer:

$$V_f = 0.500 \text{ L}$$

$$[HF] = \frac{8.0 \cdot 10^{-4} \text{ mol}}{0.500 \text{ L}} = 1.60 \cdot 10^{-3} \text{ mol/L}$$

$$[F^-] = \frac{4.40 \cdot 10^{-2} \text{ mol}}{0.500 \text{ L}} = 8.80 \cdot 10^{-2} \text{ mol/L}$$

$$\boxed{\text{pH} = pK_a + \log \frac{[F^-]}{[HF]}}$$

$$\text{pH} = 3.17 + \log\left(\frac{8.80 \cdot 10^{-2}}{1.60 \cdot 10^{-3}}\right) = 3.17 + \log(55.0)$$

$$\text{pH} \simeq 3.17 + 1.74 \simeq 4.91$$

Exercise

pH Calculation - (New Systems)

Calculate the pH of the following solutions:

a) Propionic acid: mixture of 25 mL of a 0.80 mol/L solution with 125 mL of water. Data: $\text{p}K_a = 4.87$.
b) Methylamine: mixture of 120 mL of a 0.035 mol/L solution with 80 mL of a 0.095 mol/L solution. Data: $\text{p}K_a(\text{CH}_3\text{NH}_3^+) = 10.64$.
c) Mixture of 120 mL of HClO_4 0.045 mol/L with 80 mL of HNO_3 0.18 mol/L.
d) Mixture of 600 mL of HI 0.07 mol/L and 400 mL of LiOH 0.12 mol/L.
e) Mixture of 180 mL of H_2SO_4 0.09 mol/L and 320 mL of aniline 0.11 mol/L. ($pK_a(\text{C}_6\text{H}_5\text{NH}_3^+) = 4.63$)
f) Mixture of 150 mL of H_3PO_4 0.24 mol/L and 250 mL of KOH 0.16 mol/L. ($pK_{a1} = 2.14$)

Solution

pH Calculation - Solution (New Systems)

Conventions: we work at 25 °C (so $\text{p}K_e = 14$). We systematically verify the approximation conditions.

a) **Propionic acid**: 25 mL of 0.80 mol/L + 125 mL of water, $\text{p}K_a = 4.87$.

Concentration after dilution:

$$n_0(\text{CH}_3\text{CH}_2\text{COOH}) = C_i V_i = 0.80 \text{ mol/L} \times 0.025 \text{ L} = 0.0200 \text{ mol}$$

$$V_f = 0.025 \text{ L} + 0.125 \text{ L} = 0.150 \text{ L}$$

$$C = \frac{n_0}{V_f} = \frac{0.0200 \text{ mol}}{0.150 \text{ L}} = 0.1333 \text{ mol/L}$$

Dissociation equilibrium:

$$\text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CH}_2\text{COO}^- \qquad K_a = 10^{-4.87} = 1.35 \cdot 10^{-5}$$

Approximate resolution:

$$[\text{H}^+] \approx \sqrt{K_a C} = \sqrt{1.35 \cdot 10^{-5} \cdot 0.1333}$$

$$[\text{H}^+] = \sqrt{1.800 \times 10^{-6}} = 1.342 \cdot 10^{-3} \text{ mol/L}$$

Verification:

$$\frac{[\text{H}^+]}{C} = \frac{1.342 \times 10^{-3}}{0.1333} \approx 0.0101 = 1.01\% < 5\%$$

$$\text{pH} = -\log(1.342 \cdot 10^{-3}) \approx 2.87$$

b) **Methylamine**: 120 mL of 0.035 mol/L + 80 mL of 0.095 mol/L. Data: $\text{p}K_a(\text{CH}_3\text{NH}_3^+) = 10.64$.

Interpretation: The second solution is interpreted as methylammonium chloride $\text{CH}_3\text{NH}_3\text{Cl}$ to form a buffer.

Amounts of matter:

$$n(\text{CH}_3\text{NH}_2) = 0.120 \text{ L} \times 0.035 \text{ mol/L} = 4.20 \cdot 10^{-3} \text{ mol}$$

$$n(\text{CH}_3\text{NH}_3^+) = 0.080 \text{ L} \times 0.095 \text{ mol/L} = 7.60 \cdot 10^{-3} \text{ mol}$$

Concentrations after mixing:

$$V_f = 0.200 \text{ L}$$

$$[\mathrm{CH_3NH_2}] = \frac{4.20 \cdot 10^{-3}\ \mathrm{mol}}{0.200\ \mathrm{L}} = 2.10 \cdot 10^{-2}\ \mathrm{mol/L}$$

$$[\mathrm{CH_3NH_3^+}] = \frac{7.60 \cdot 10^{-3}\ \mathrm{mol}}{0.200\ \mathrm{L}} = 3.80 \cdot 10^{-2}\ \mathrm{mol/L}$$

pH of the buffer:

$$\boxed{\mathrm{pH} = pK_a + \log \frac{[\mathrm{CH_3NH_2}]}{[\mathrm{CH_3NH_3^+}]}}$$

$$\mathrm{pH} = 10.64 + \log\left(\frac{2.1 \cdot 10^{-2}}{3.8 \cdot 10^{-2}}\right) = 10.64 + \log(0.5526)$$

$$\boxed{\mathrm{pH} \approx 10.64 - 0.257 = 10.38}$$

c) **Mixture of strong acids**: 120 mL of $\mathrm{HClO_4}$ 0.045 mol/L + 80 mL of $\mathrm{HNO_3}$ 0.18 mol/L.
Amounts of matter:

$$n(\mathrm{H^+})_{\mathrm{HClO_4}} = 0.120\ \mathrm{L} \times 0.045\ \mathrm{mol/L} = 5.40 \cdot 10^{-3}\ \mathrm{mol}$$

$$n(\mathrm{H^+})_{\mathrm{HNO_3}} = 0.080\ \mathrm{L} \times 0.18\ \mathrm{mol/L} = 1.44 \cdot 10^{-2}\ \mathrm{mol}$$

$$n(\mathrm{H^+})_{\mathrm{total}} = 5.40 \cdot 10^{-3}\ \mathrm{mol} + 1.44 \cdot 10^{-2}\ \mathrm{mol} = 1.98 \cdot 10^{-2}\ \mathrm{mol}$$

Concentration and pH:

$$V_f = 0.200\ \mathrm{L}$$

$$[\mathrm{H^+}] = \frac{1.98 \cdot 10^{-2}\ \mathrm{mol}}{0.200\ \mathrm{L}} = 0.0990\ \mathrm{mol/L}$$

$$\boxed{\mathrm{pH} = -\log(0.0990) \approx 1.00}$$

d) **Strong acid - strong base neutralization**: 600 mL of HI 0.07 mol/L + 400 mL of LiOH 0.12 mol/L.
Stoichiometry:

$$n(\mathrm{H^+}) = 0.600\ \mathrm{L} \times 0.07\ \mathrm{mol/L} = 4.20 \cdot 10^{-2}\ \mathrm{mol}$$

$$n(\mathrm{OH^-}) = 0.400\ \mathrm{L} \times 0.12\ \mathrm{mol/L} = 4.80 \cdot 10^{-2}\ \mathrm{mol}$$

Excess of base:

$$n_{\mathrm{excess}}(\mathrm{OH^-}) = 4.80 \cdot 10^{-2}\ \mathrm{mol} - 4.20 \cdot 10^{-2}\ \mathrm{mol} = 6.00 \cdot 10^{-3}\ \mathrm{mol}$$

Concentration and pH:

$$V_f = 1.000\ \mathrm{L}$$

$$[\mathrm{OH^-}] = \frac{6.00 \cdot 10^{-3}\ \mathrm{mol}}{1.000\ \mathrm{L}} = 6.00 \cdot 10^{-3}\ \mathrm{mol/L}$$

$$\mathrm{pOH} = -\log(6.00 \cdot 10^{-3}\ \mathrm{mol/L}) = 2.22$$

$$\boxed{\mathrm{pH} = 14.00 - 2.22 = 11.78}$$

e) **Strong acid - weak base reaction**: 180 mL of $\mathrm{H_2SO_4}$ 0.09 mol/L + 320 mL of aniline 0.11 mol/L. Data: $pK_a(\mathrm{C_6H_5NH_3^+}) = 4.63$.
Important: $\mathrm{H_2SO_4}$ releases 2 $\mathrm{H^+}$ per molecule.
Amounts of matter:

$$n(\mathrm{H^+}) = 2 \times (0.180\ \mathrm{L} \times 0.09\ \mathrm{mol/L}) = 2 \times 1.62 \cdot 10^{-2}\ \mathrm{mol} = 3.24 \cdot 10^{-2}\ \mathrm{mol}$$

$$n(\mathrm{C_6H_5NH_2}) = 0.320\ \mathrm{L} \times 0.11\ \mathrm{mol/L} = 3.52 \cdot 10^{-2}\ \mathrm{mol}$$

Reaction: $\mathrm{C_6H_5NH_2 + H^+ \longrightarrow C_6H_5NH_3^+}$

Situation after reaction: The acid is slightly limiting:

$$n(\mathrm{C_6H_5NH_2})_{\text{remaining}} = 3.52 \cdot 10^{-2}\ \text{mol} - 3.24 \cdot 10^{-2}\ \text{mol} = 2.80 \cdot 10^{-3}\ \text{mol}$$

$$n(\mathrm{C_6H_5NH_3^+})_{\text{formed}} = 3.24 \cdot 10^{-2}\ \text{mol}$$

Concentrations and pH:

$$V_f = 0.500\ \text{L}$$

$$[\mathrm{C_6H_5NH_2}] = \frac{2.80 \cdot 10^{-3}\ \text{mol}}{0.500\ \text{L}} = 5.60 \cdot 10^{-3}\ \text{mol/L}$$

$$[\mathrm{C_6H_5NH_3^+}] = \frac{3.24 \cdot 10^{-2}\ \text{mol}}{0.500\ \text{L}} = 6.48 \cdot 10^{-2}\ \text{mol/L}$$

$$\boxed{\mathrm{pH} = pK_a + \log \frac{[\mathrm{C_6H_5NH_2}]}{[\mathrm{C_6H_5NH_3^+}]}}$$

$$\mathrm{pH} = 4.63 + \log\left(\frac{5.60 \cdot 10^{-3}}{6.48 \cdot 10^{-2}}\right) = 4.63 + \log(0.0864)$$

$$\boxed{\mathrm{pH} \approx 4.63 - 1.063 = 3.57}$$

f) **Phosphoric acid - potassium hydroxide titration**: 150 mL of $\mathrm{H_3PO_4}$ 0.24 mol/L + 250 mL of KOH 0.16 mol/L. Data: $pK_{a1} = 2.14$.
Initial amounts of matter:

$$n(\mathrm{H_3PO_4}) = 0.150\ \text{L} \times 0.24\ \text{mol/L} = 3.60 \cdot 10^{-2}\ \text{mol}$$

$$n(\mathrm{OH^-}) = 0.250\ \text{L} \times 0.16\ \text{mol/L} = 4.00 \cdot 10^{-2}\ \text{mol}$$

Step-by-step reaction:
Step 1: Neutralization of the first acidity

$$\mathrm{H_3PO_4 + OH^- \longrightarrow H_2PO_4^- + H_2O}$$

After this step:

$$n(\mathrm{H_3PO_4})_{\text{remaining}} = 0 \quad \text{(completely consumed)}$$

$$n(\mathrm{H_2PO_4^-})_{\text{formed}} = 3.60 \cdot 10^{-2}\ \text{mol}$$

$$n(\mathrm{OH^-})_{\text{remaining}} = 4.00 \cdot 10^{-2}\ \text{mol} - 3.60 \cdot 10^{-2}\ \text{mol} = 4.00 \cdot 10^{-3}\ \text{mol}$$

Step 2: Partial neutralization of the second acidity

$$\mathrm{H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O}$$

After this step:

$$n(\mathrm{H_2PO_4^-})_{\text{remaining}} = 3.60 \cdot 10^{-2}\ \text{mol} - 4.00 \cdot 10^{-3}\ \text{mol} = 3.20 \cdot 10^{-2}\ \text{mol}$$

$$n(\mathrm{HPO_4^{2-}})_{\text{formed}} = 4.00 \cdot 10^{-3}\ \text{mol}$$

$$n(\mathrm{OH^-})_{\text{remaining}} = 0$$

Final concentrations:

$$V_f = 0.400\ \text{L}$$

$$[\mathrm{H_2PO_4^-}] = \frac{3.20 \cdot 10^{-2}\ \text{mol}}{0.400\ \text{L}} = 8.00 \cdot 10^{-2}\ \text{mol/L}$$

$$[\mathrm{HPO_4^{2-}}] = \frac{4.00 \cdot 10^{-3}\ \text{mol}}{0.400\ \text{L}} = 1.00 \cdot 10^{-2}\ \text{mol/L}$$

pH of the $H_2PO_4^-/HPO_4^{2-}$ buffer:

$$\boxed{\text{pH} = \text{p}K_{a2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}}$$

Attention: We need $\text{p}K_{a2}$, not $\text{p}K_{a1}$! For H_3PO_4: $\text{p}K_{a2} = 7.20$ (standard value).

$$\text{pH} = 7.20 + \log\left(\frac{1.00 \cdot 10^{-2}}{8.00 \cdot 10^{-2}}\right) = 7.20 + \log(0.125)$$

$$\boxed{\text{pH} \approx 7.20 - 0.903 = 6.30}$$

Note: The given $\text{p}K_{a1} = 2.14$ is not used directly because we are beyond the first equivalence point.

Exercise

Exercise 2: NH_3/NH_4^+ Buffer Solutions

I) Mixing 500 mL of NH_3 0.20 mol/L with 500 mL of NH_4Cl(aq) produces a solution with pH = 9.0. Calculate the mass of ammonium chloride used.

II) To prepare 500 mL of a buffer solution with concentration 0.10 mol/L and pH = 9.0, we have available:
- NH_3 1.0 mol/L (with $pK_a = 9.25$),
- HCl 0.50 mol/L.

Calculate the volumes needed to prepare this solution.

Solution

I) Mixing 500 mL of NH_3 0.20 mol/L with NH_4Cl to obtain pH = 9.0

Context and objective:
- We have 500 mL of an ammonia NH_3 solution at 0.20 mol/L
- We want to add ammonium chloride NH_4Cl to form an NH_3/NH_4^+ buffer
- The desired pH for this buffer is 9.0
- We know the $\text{p}K_a$ of the pair: $\text{p}K_a(NH_4^+/NH_3) = 9.25$

Given data:
- Volume of NH_3 solution: $V_{NH_3} = 500$ mL $= 0.500$ L
- Concentration of NH_3: $C_{NH_3} = 0.20$ mol/L
- Target buffer pH: 9.0
- $\text{p}K_a$ of the NH_4^+/NH_3 pair: $pK_a = 9.25$
- Molar mass of NH_4Cl:

$$M = 14.01\ (\text{N}) + 4 \times 1.008\ (\text{H}) + 35.45\ (\text{Cl}) = 53.49\ \text{g/mol}$$

Step 1: Understanding the buffer system
We will form a buffer by mixing: - The weak base NH_3 already present in solution - Its conjugate acid NH_4^+ which we will add as the salt NH_4Cl
Ammonium chloride NH_4Cl dissociates completely in solution:

$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Step 2: Application of the Henderson-Hasselbalch equation
For a weak acid/weak base buffer, the fundamental relationship is:

$$\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

In our case: - Base: NH_3 - Acid: NH_4^+
Therefore:

$$9.0 = 9.25 + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

Step 3: Determination of the concentration ratio

$$\log\frac{[NH_3]}{[NH_4^+]} = 9.0 - 9.25 = -0.25$$
$$\frac{[NH_3]}{[NH_4^+]} = 10^{-0.25}$$

Numerical value:

$$10^{-0.25} = \approx 0.5623$$

Interpretation: The NH_3 concentration must be approximately 0.56 times that of NH_4^+.
Step 4: Conversion to amounts of matter
Since the final volume will be the same for both species (we add NH_4Cl to the existing solution), the concentration ratio equals the amount of matter ratio:

$$\frac{[NH_3]}{[NH_4^+]} = \frac{n_{NH_3}}{n_{NH_4^+}} = 0.5623$$

Let us first calculate the amount of NH_3 already present:

$$n_{NH_3} = C_{NH_3} \times V_{NH_3} = 0.20 \times 0.500 = 0.100 \text{ mol}$$

Step 5: Calculation of the required NH_4^+ amount
From the relation $\frac{n_{NH_3}}{n_{NH_4^+}} = 0.5623$, we deduce:

$$n_{NH_4^+} = \frac{n_{NH_3}}{0.5623} = \frac{0.100}{0.5623} = 0.1778 \text{ mol}$$

Step 6: Calculation of the corresponding NH_4Cl mass
The required NH_4^+ amount comes from the dissolution of NH_4Cl. Each mole of NH_4Cl provides one mole of NH_4^+.
Therefore:

$$n_{NH_4Cl} = n_{NH_4^+} = 0.1778 \text{ mol}$$

Mass of NH_4Cl to weigh:

$$m_{NH_4Cl} = n_{NH_4Cl} \times M_{NH_4Cl} = 0.1778 \times 53.49$$

Rounded to 3 significant figures (as the data):

$$\boxed{m_{NH_4Cl} = 9.51 \text{ g}}$$

Step 7: Preparation protocol

a) Precisely weigh 9.51 g of solid ammonium chloride NH_4Cl
b) Dissolve this solid in the 500 mL of NH_3 0.20 mol/L solution
c) Stir until complete dissolution
d) Check the pH with a pH meter

Theoretical pH verification: Using the calculated values:

$$\begin{aligned} \text{pH} &= 9.25 + \log\left(\frac{0.100}{0.1778}\right) \\ &= 9.25 + (-0.25) = 9.00 \quad \text{(exactly the target value)} \end{aligned}$$

Final answer:
To prepare 500 mL of NH_3/NH_4^+ buffer at pH = 9.0 from 500 mL of NH_3 0.20 mol/L, dissolve:

$$\boxed{m_{NH_4Cl} = 9.51 \text{ g}}$$

of ammonium chloride in the ammonia solution.

II) Preparation of 500 mL of a 0.10 mol/L buffer solution at pH = 9.0

Data and objective:

- We want to prepare 500 mL of an NH_3/NH_4^+ buffer solution
- Total concentration (NH_3 + NH_4^+): $C_{tot} = 0.10$ mol/L
- Desired pH: 9.0
- pK_a of the NH_4^+/NH_3 pair: $pK_a = 9.25$
- Available solutions:
  - Concentrated NH_3 solution: 1.0 mol/L
  - HCl solution: 0.50 mol/L
- Strategy: We will add HCl to the NH_3 solution to form the buffer according to the reaction:

$$NH_3 + H^+ \rightarrow NH_4^+$$

Step 1: Calculation of the total amount of buffer species
Final desired volume: $V_f = 0.500$ L
Total amount of buffer species (NH_3 + NH_4^+):

$$n_{tot} = C_{tot} \times V_f = 0.10 \times 0.500 = 0.0500 \text{ mol}$$

This amount will be distributed between NH_3 and NH_4^+.
Step 2: Application of the Henderson-Hasselbalch equation
For a weak base/salt of its conjugate acid buffer:

$$\text{pH} = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

Since the volume is the same for both species, we can work with amounts of matter:

$$9.0 = 9.25 + \log\left(\frac{n_{NH_3}}{n_{NH_4^+}}\right)$$

Step 3: Solving for the quantity ratio

$$\begin{aligned} \log\left(\frac{n_{NH_3}}{n_{NH_4^+}}\right) &= 9.0 - 9.25 = -0.25 \\ \frac{n_{NH_3}}{n_{NH_4^+}} &= 10^{-0.25} = 0.5623 \end{aligned}$$

This ratio means that for each mole of NH_4^+, we need 0.5623 moles of NH_3.
Step 4: Determination of the exact amounts
We have two equations with two unknowns:
a) Conservation of matter: $n_{NH_3} + n_{NH_4^+} = 0.05$

b) Quantity ratio: $n_{NH_3} = 0.5623 \times n_{NH_4^+}$

Substitute the second equation into the first:

$$\begin{aligned} 0.5623 \times n_{NH_4^+} + n_{NH_4^+} &= 0.05 \\ (0.5623 + 1) \times n_{NH_4^+} &= 0.05 \\ 1.5623 \times n_{NH_4^+} &= 0.05 \\ n_{NH_4^+} &= \frac{0.05}{1.5623} = 0.032 \text{ mol} \end{aligned}$$

Deduce n_{NH_3}:

$$n_{NH_3} = 0.0500 - 0.03200 = 0.018 \text{ mol}$$

Step 5: Chemical interpretation

- NH_4^+ comes from the reaction: $NH_3 + H^+ \rightarrow NH_4^+$
- To obtain 0.032 mol of NH_4^+, we must add 0.032 mol of HCl to the NH_3 solution
- Initially, we therefore need a total amount of NH_3 equal to:

$$n_{NH_3\,\text{initial}} = n_{NH_3} + n_{NH_4^+} = 0.018 + 0.032 = 0.05000 \text{ mol}$$

Step 6: Calculation of volumes to be taken

- **Volume of NH_3** 1.0 mol/L:

$$V_{NH_3} = \frac{n_{NH_3\,\text{initial}}}{C_{NH_3}} = \frac{0.05}{1.0} = 0.05 \text{ L} = \boxed{50.0 \text{ mL}}$$

- **Volume of HCl** 0.50 mol/L:

$$V_{HCl} = \frac{n_{HCl}}{C_{HCl}} = \frac{0.032}{0.50} = 0.06400 \text{ L} = \boxed{64.0 \text{ mL}}$$

Step 7: Preparation protocol

a) Take 50.0 mL of the NH_3 1.0 mol/L solution

b) Add 64.0 mL of the HCl 0.50 mol/L solution

- **Warning:** Always pour the acid into the base, not the reverse

c) Transfer to a 500 mL volumetric flask

d) Make up to volume with distilled water

e) Homogenize by several inversions

Verification: Total volume of concentrated solutions: $50.0 + 64.0 = 114$ mL Volume of water to add: $500 - 114 = \boxed{386 \text{ mL}}$

Answer:

- $\boxed{V_{NH_3} = 50.0 \text{ mL}}$ of 1.0 mol/L solution
- $\boxed{V_{HCl} = 64.0 \text{ mL}}$ of 0.50 mol/L solution
- Dilute to 500 mL with distilled water in a volumetric flask

Note: The final pH of the solution should be verified with a pH meter after preparation.

Exercise

Exercise: Buffer Solution and Vitamin C

Ascorbic acid (vitamin C) presents, in aqueous solution, an acidic function with $pK_a = 4.17$. Some pharmaceutical forms offer buffered vitamin C by preparing a mixture of ascorbic acid and monosodium ascorbate.

A tablet of mass 0.500 g contains only these two molecules. It is dissolved in 0.100 L of pure water. The pH of the resulting solution is 4.50.

Given molar masses:

- Ascorbic acid: 176 g/mol

- Monosodium ascorbate: 198 g/mol

What are the respective molar concentrations of ascorbic acid and monosodium ascorbate in the resulting solution?

Solution

Data:

- $pK_a(\text{HA}) = 4.17$ where HA = ascorbic acid, A^- = ascorbate
- pH of the solution: 4.50
- Total mass of the tablet: $m_{\text{tot}} = 0.50$ g
- Volume of dissolution: $V = 0.10$ L
- $M(\text{HA}) = 176$ g/mol, $M(\text{A}^-\text{Na}^+) = 198$ g/mol

1. Use of the Henderson-Hasselbalch relationship

For an acid-base pair HA/A^-, we have:

$$\text{pH} = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Numerical application:

$$4.50 = 4.17 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\log \frac{[\text{A}^-]}{[\text{HA}]} = 4.50 - 4.17 = 0.33$$

$$\boxed{\frac{[\text{A}^-]}{[\text{HA}]} = 10^{0.33} \approx 2.14}$$

2. Expression of concentrations in terms of amounts of matter

Let:

- n_{HA} = amount of ascorbic acid (in mol)
- n_{A^-} = amount of monosodium ascorbate (in mol)

The concentrations are:

$$[\text{HA}] = \frac{n_{\text{HA}}}{V} = \frac{n_{\text{HA}}}{0.10 \text{ L}}$$

$$[\text{A}^-] = \frac{n_{\text{A}^-}}{V} = \frac{n_{\text{A}^-}}{0.10 \text{ L}}$$

The concentration ratio becomes:

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{n_{\text{A}^-}}{n_{\text{HA}}} = 2.14$$

$$\boxed{n_{\text{A}^-} = 2.14 \times n_{\text{HA}}}$$

3. Mass balance of the tablet

The total mass of the tablet is the sum of the masses of the two compounds:

$$m_{\text{HA}} + m_{\text{A}^-} = 0.5 \text{ g}$$

With $m_{\text{HA}} = M(\text{HA}) \times n_{\text{HA}}$ and $m_{\text{A}^-} = M(\text{A}^-\text{Na}^+) \times n_{\text{A}^-}$:

$$176 \times n_{\text{HA}} + 198 \times n_{\text{A}^-} = 0.5$$

Substituting n_{A^-} with its expression in terms of n_{HA}:

$$176 n_{\text{HA}} + 198 \times (2.14 \times n_{\text{HA}}) = 0.5$$

$$176 n_{\text{HA}} + 423.72 n_{\text{HA}} = 0.5$$

$$599.72 n_{\text{HA}} = 0.5$$

$$n_{\text{HA}} = \frac{0.5}{599.72} \approx 8.34 \cdot 10^{-4} \text{ mol}$$

We deduce:

$$n_{\text{A}^-} = 2.14 \times 8.34 \cdot 10^{-4} \text{ mol} \approx 1.78 \cdot 10^{-3} \text{ mol}$$

4. Calculation of concentrations

$$[\text{HA}] = \frac{n_{\text{HA}}}{V} = \frac{8.34 \cdot 10^{-4} \text{ mol}}{0.10 \text{ L}} = 8.34 \cdot 10^{-3} \text{ mol/L}$$

$$[\text{A}^-] = \frac{n_{\text{A}^-}}{V} = \frac{1.78 \cdot 10^{-3} \text{ mol}}{0.10 \text{ L}} = 1.78 \cdot 10^{-2} \text{ mol/L}$$

5. Verification

- Concentration ratio: $\dfrac{1.78 \cdot 10^{-2}}{8.34 \cdot 10^{-3}} \approx 2.13$
- Total mass: $176 \times 8.34 \times 10^{-4} + 198 \times 1.78 \times 10^{-3} \approx 0.147 + 0.352 = 0.499$ g

Final results:

$\boxed{[\text{HA}] = 8.3 \cdot 10^{-3} \text{ mol/L}}$ and $\boxed{[\text{A}^-] = 1.8 \cdot 10^{-2} \text{ mol/L}}$

Concentrations in the solution after dissolution of the tablet

Interpretation: The solution is indeed a buffer since $[\text{A}^-] > [\text{HA}]$, which corresponds to a pH (4.50) greater than the pK_a (4.17). The concentration ratio is approximately 2.1, which is typical of an effective buffer.

Exercise

pH Calculations

Three aqueous solutions:

- **A** contains 0.03 mol · L^{-1} of $\text{ClCH}_2\text{CH}_2\text{–COOH}$ (1-chloropropanoic acid) ($K_a = 7.94 \times 10^{-5}$)
- **B** contains 0.007 mol · L^{-1} of HCl
- **C** contains $2 \cdot 10^{-2}$ mol · L^{-1} of ammonium chloride NH_4Cl ($K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$)

a) What is the pH of A, B and C?

b) We mix 25 mL of a 0.5 mol · L^{-1} NH_4Cl solution with 50 mL of a 0.5 mol · L^{-1} NH_3 solution. Calculate the pH of this buffer solution.

Solution

Conventions: We work at 25 °C ($pK_e = 14$).

1. pH of solutions A, B and C

a) **Solution A: 1-Chloropropanoic acid $\text{ClCH}_2\text{CH}_2\text{COOH}$**

Data:

$$C_A = 0.03 \text{ mol} \cdot \text{L}^{-1}, \quad K_a = 7.94 \times 10^{-5} \quad (pK_a \approx 4.10)$$

Verification of the approximation:

$$C_A \gg K_a \quad \text{because} \quad 0.03 \text{ mol} \cdot \text{L}^{-1} \gg 7.94 \times 10^{-5}$$

We can therefore use the approximation $x \ll C_A$.

Calculation:

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{x^2}{C_A - x} \approx \frac{x^2}{C_A}$$

$$x = [\text{H}^+] \approx \sqrt{K_a C_A} = \sqrt{(7.94 \times 10^{-5}) \times 0.03}$$

$$x = \sqrt{2.382 \times 10^{-6}} = 1.544 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

Verification:

$$\frac{x}{C_A} = \frac{1.544 \times 10^{-3}}{0.03} \approx 0.0515 = 5.15\%$$

The approximation is borderline but acceptable. For a more rigorous analysis of critical cases, the reader may refer to Butler.[40]

$$\boxed{\text{pH}_A = -\log(1.544 \times 10^{-3}) \approx 2.81}$$

b) **Solution B: Hydrochloric acid HCl**
Data:

$$C_B = 0.007 \text{ mol} \cdot \text{L}^{-1}$$

HCl is a strong acid, therefore completely dissociated:

$$\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$$

$$[\text{H}^+] = C_B = 0.007 \text{ mol} \cdot \text{L}^{-1}$$

$$\boxed{\text{pH}_B = -\log(0.007) \approx 2.15}$$

c) **Solution C: Ammonium chloride NH_4Cl**
Data:

$$C_C = 2 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}, \quad K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$$

NH_4^+ is a weak acid:

$$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$$

Verification of the approximation:

$$C_C \gg K_a \quad \text{because} \quad 2 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1} \gg 5.6 \times 10^{-10}$$

Calculation:

$$[\text{H}^+] \approx \sqrt{K_a C_C} = \sqrt{(5.6 \times 10^{-10}) \times 0.02}$$

$$[\text{H}^+] = \sqrt{1.12 \times 10^{-11}} = 3.346 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

Verification:

$$\frac{[\text{H}^+]}{C_C} = \frac{3.346 \times 10^{-6}}{0.02} \approx 1.67 \times 10^{-4} \ll 5\%$$

The approximation is excellent.

$$\boxed{\text{pH}_C = -\log(3.346 \times 10^{-6}) \approx 5.48}$$

2. Ammonia/ammonium chloride buffer solution
Data:

- Solution 1: 25 mL of NH_4Cl 0.5 $\text{mol} \cdot \text{L}^{-1}$
- Solution 2: 50 mL of NH_3 0.5 $\text{mol} \cdot \text{L}^{-1}$
- $K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$ therefore $pK_a = 9.25$

Calculation of amounts of matter:

$$n(\text{NH}_4^+) = C \times V = 0.5 \times 0.025 = 0.0125 \text{ mol}$$

$$n(\text{NH}_3) = 0.5 \times 0.050 = 0.0250 \text{ mol}$$

Concentrations after mixing:

$$V_{\text{total}} = 0.025 + 0.050 = 0.075 \text{ L}$$

$$[NH_4^+] = \frac{0.0125}{0.075} = 0.1667 \text{ mol} \cdot \text{L}^{-1}$$

$$[NH_3] = \frac{0.0250}{0.075} = 0.3333 \text{ mol} \cdot \text{L}^{-1}$$

Application of the Henderson-Hasselbalch formula:

$$\text{pH} = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$\text{pH} = 9.25 + \log\left(\frac{0.3333}{0.1667}\right)$$

$$\text{pH} = 9.25 + \log(2.00)$$

$$\boxed{\text{pH} = 9.25 + 0.3010 \approx 9.55}$$

Interpretation: This is an effective buffer because the ratio $[NH_3]/[NH_4^+] = 2$ is close to 1, and the pH is close to the pK_a.

Exercise

Exercise on the CH_3COOH / NH_3 → CH_3COO^- / NH_4^+ System

Consider the following acid-base equilibrium in aqueous solution at 25 °C:

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

Data: $pK_a(CH_3COOH) = 4.76$, $pK_a(NH_4^+) = 9.25$, $pK_w = 14.00$.

I) **Thermodynamic study: direction of the reaction**

a) Write the expression for the equilibrium constant K associated with: $CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$.

b) Show that K can be expressed in terms of the acidity constants:

$$K = \frac{K_a(CH_3COOH)}{K_a(NH_4^+)}$$

then calculate K numerically.

c) Conclude on the favored direction of the reaction (strongly shifted or not?).

II) **Case 1: equimolar mixture (formation of a salt)**

We mix 400 mL of CH_3COOH 0.12 mol · L^{-1} and 400 mL of NH_3 0.12 mol · L^{-1}.

a) Make the reaction progress table (in moles) of the acid-base reaction. Identify the limiting reactant and the final quantities (before taking hydrolysis into account).

b) What is the main nature of the resulting solution? (*salt of weak acid/weak base*, *buffer*, etc.)

c) Show (without differential calculus) that, for a salt $BH^+\,A^-$ derived from a weak base B and a weak acid HA, we can obtain:

$$\text{pH} \simeq \frac{1}{2}\left(pK_a(HA) + pK_a(BH^+)\right)$$

then calculate the pH of the mixture.

d) **Critical verification:** discuss the validity of this relationship. (Hint: write the equilibria

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

and comment on why the dependence on C may disappear.)

III) **Case 2: non-equimolar mixture (CH_3COOH/CH_3COO^- buffer)**
We mix 250 mL of CH_3COOH 0.20 mol · L^{-1} with 150 mL of NH_3 0.20 mol · L^{-1}.
a) Make the reaction progress table and determine the major species after the quasi-total reaction.
b) Show that we obtain a CH_3COOH/CH_3COO^- buffer. Give the appropriate Henderson-Hasselbalch expression and calculate the pH.
c) **Approximation test:** justify that we can neglect the autoprotolysis of water and the contribution of NH_4^+/NH_3 to the pH, to first order.
d) Calculate the ratio $\frac{[CH_3COO^-]}{[CH_3COOH]}$ and deduce whether the buffer is "good" (efficient zone).

IV) **Case 3: Acetic acid - ammonia titration: characteristic points**
We titrate 50 mL of CH_3COOH 0.10 mol · L^{-1} with a 0.10 mol · L^{-1} NH_3 solution. (We consider that the reaction $CH_3COOH + NH_3 \longrightarrow CH_3COO^- + NH_4^+$ is quasi-total.)
a) Calculate the equivalence volume V_{eq}.
b) Calculate the initial pH (weak acid alone) justifying the approximation $x \ll C$.
c) Calculate the pH at half-equivalence. (*Hint:* which buffer pair dominates? What remarkable value do we obtain?)
d) Calculate the pH at equivalence.
e) Calculate the pH after adding 60 mL of the ammonia solution.

Solution

Conventions: $T = 25$ °C, $pK_e = 14.00$.

I. Thermodynamic study: direction of the reaction

a) **Expression of the equilibrium constant K:**

$$K = \frac{[CH_3COO^-][NH_4^+]}{[CH_3COOH][NH_3]}$$

b) **Relationship with the acidity constants:** We have two acid/base pairs:

$$CH_3COOH/CH_3COO^- : \quad K_a(CH_3COOH) = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$NH_4^+/NH_3 : \quad K_a(NH_4^+) = \frac{[H^+][NH_3]}{[NH_4^+]}$$

Dividing member by member:

$$\frac{K_a(CH_3COOH)}{K_a(NH_4^+)} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \times \frac{[NH_4^+]}{[H^+][NH_3]} = \frac{[CH_3COO^-][NH_4^+]}{[CH_3COOH][NH_3]}$$

$$\boxed{K = \frac{K_a(CH_3COOH)}{K_a(NH_4^+)}}$$

Numerical calculation:

$$K_a(CH_3COOH) = 10^{-4.76} = 1.74 \cdot 10^{-5}$$

$$K_a(NH_4^+) = 10^{-9.25} = 5.62 \cdot 10^{-10}$$

$$K = \frac{1.74 \times 10^{-5}}{5.62 \times 10^{-10}} = 3.10 \cdot 10^4$$

$$\boxed{K \approx 3.1 \cdot 10^4}$$

c) **Direction of the reaction:** $K \gg 1$ (approximately 31000), therefore the reaction is **very**

strongly shifted to the right.

$$CH_3COOH + NH_3 \longrightarrow CH_3COO^- + NH_4^+ \quad \text{(quasi-total)}$$

II. Case 1: equimolar mixture (formation of a salt)

a) **Reaction progress table:**

Initial quantities:

$$n_0(CH_3COOH) = 0.400 \times 0.12 = 4.80 \cdot 10^{-2} \text{ mol}$$

$$n_0(NH_3) = 0.400 \times 0.12 = 4.80 \cdot 10^{-2} \text{ mol}$$

	CH_3COOH +	NH_3 $\rightleftharpoons$	CH_3COO^- +	NH_4^+
Initial	4.80×10^{-2}	4.80×10^{-2}	0	0
Final	~ 0	~ 0	4.80×10^{-2}	4.80×10^{-2}

The reactants are in stoichiometric proportions, so neither is limiting. After the quasi-total reaction, we essentially obtain CH_3COONH_4.

b) **Nature of the solution:** This is a salt of a weak acid (CH_3COOH) and a weak base (NH_3). The salt formula is CH_3COONH_4 (ammonium acetate).

c) **Derivation of the approximate formula:**

Consider the two equilibria in solution:

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad K_a(NH_4^+) = \frac{[H^+][NH_3]}{[NH_4^+]} \tag{1}$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad K_a(CH_3COOH) = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \tag{2}$$

In the salt CH_3COONH_4, we have approximately:

$$[NH_4^+] \approx [CH_3COO^-] \quad \text{and} \quad [NH_3] \approx [CH_3COOH]$$

(the two pairs are linked by the autoprotolysis of water).

Dividing (2) by (1):

$$\frac{K_a(CH_3COOH)}{K_a(NH_4^+)} = \frac{[CH_3COOH]}{[NH_3]} \times \frac{[NH_4^+]}{[CH_3COO^-]}$$

With the above approximations:

$$\frac{K_a(CH_3COOH)}{K_a(NH_4^+)} \approx 1$$

Taking $-\log$ of both sides:

$$pK_a(CH_3COOH) - pK_a(NH_4^+) \approx 0$$

This is not exact. In reality, we obtain a better approximation by writing:

$$[H^+]^2 \approx K_a(CH_3COOH) \cdot K_a(NH_4^+)$$

$$\text{pH} \approx \frac{1}{2}\left(pK_a(CH_3COOH) + pK_a(NH_4^+)\right)$$

Numerical application:

$$\text{pH} \approx \frac{1}{2}(4.76 + 9.24) = \frac{14.}{2}$$

$$\boxed{\text{pH} \approx 7}$$

d) **Validity of the formula:**

This formula is valid when:

- The concentration C of the salt is not too low
- The approximations $[NH_4^+] \approx C$ and $[CH_3COO^-] \approx C$ are good
- The hydrolysis is limited (no extreme pH values)

The dependence on C disappears because the two pairs mutually equilibrate: the acidity of NH_4^+ is compensated by the basicity of CH_3COO^-.

III. Case 2: non-equimolar mixture (CH_3COOH/CH_3COO^- buffer)

a) **Reaction progress table:**

Initial quantities:

$$n_0(CH_3COOH) = 0.250 \times 0.20 = 5.00 \cdot 10^{-2} \text{ mol}$$

$$n_0(NH_3) = 0.150 \times 0.20 = 3.00 \cdot 10^{-2} \text{ mol}$$

Reaction: $CH_3COOH + NH_3 \longrightarrow CH_3COO^- + NH_4^+$

	CH_3COOH	+	NH_3	$\rightleftharpoons$	CH_3COO^-	+	NH_4^+
Initial	5.00×10^{-2}		3.00×10^{-2}		0		0
Final	2.00×10^{-2}		~ 0		3.00×10^{-2}		3.00×10^{-2}

NH_3 is limiting. After reaction:

- CH_3COOH in excess: $2.00 \cdot 10^{-2}$ mol
- CH_3COO^- formed: $3.00 \cdot 10^{-2}$ mol
- NH_4^+ formed: $3.00 \cdot 10^{-2}$ mol

b) **CH_3COOH/CH_3COO^- buffer:**

Total volume: $V_f = 0.250 + 0.150 = 0.400$ L

$$[CH_3COOH] = \frac{2.00 \times 10^{-2}}{0.400} = 5.00 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$[CH_3COO^-] = \frac{3.00 \times 10^{-2}}{0.400} = 7.50 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

Henderson-Hasselbalch formula:

$$\boxed{\text{pH} = pK_a(CH_3COOH) + \log \frac{[CH_3COO^-]}{[CH_3COOH]}}$$

$$\text{pH} = 4.76 + \log\left(\frac{7.50 \times 10^{-2}}{5.00 \times 10^{-2}}\right) = 4.76 + \log(1.50)$$

$$\text{pH} = 4.76 + 0.176$$

$$\boxed{\text{pH} \approx 4.94}$$

c) **Justification of the approximations:**

- **Autoprotolysis of water:** negligible because $[H^+] \approx 10^{-4.94} \approx 1.1 \cdot 10^{-5}$ mol $\cdot$ L^{-1} $\gg 10^{-7}$
- **Contribution of NH_4^+/NH_3:** the NH_4^+/NH_3 pair has $pK_a = 9.25$, so at pH = 4.94, the NH_3 form is negligible. Moreover, $[NH_4^+] \approx 7.5 \cdot 10^{-2}$ mol $\cdot$ L^{-1} is of the same order as the acetic buffer species.

d) **Quality of the buffer:**

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 1.50$$

A buffer is effective when $0.1 < \frac{[\text{base}]}{[\text{acid}]} < 10$. Here, 1.50 is in this interval, so it is a **good buffer**.

IV. Case 3: Acetic acid - ammonia titration: characteristic points

a) **Equivalence volume:**

At equivalence: $n(CH_3COOH) = n(NH_3)$

$$C_{CH_3COOH} \times V_{CH_3COOH} = C_{NH_3} \times V_{eq}$$

$$0.10 \times 0.050 = 0.10 \times V_{eq}$$

$$\boxed{V_{eq} = 50.0 \text{ mL}}$$

b) **Initial pH ($V = 0$ mL):**
Acetic acid solution alone:

$$C_0 = 0.10 \text{ mol} \cdot \text{L}^{-1}, \quad K_a = 1.74 \times 10^{-5}$$

Approximation $x \ll C_0$:

$$[\text{H}^+] \approx \sqrt{K_a C_0} = \sqrt{1.74 \times 10^{-5} \times 0.10} = \sqrt{1.74 \times 10^{-6}}$$

$$[\text{H}^+] \approx 1.32 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

Verification: $\dfrac{1.32 \times 10^{-3}}{0.10} = 1.32\% < 5\%$

$$\text{pH} = -\log(1.32 \times 10^{-3})$$

$$\boxed{\text{pH}_{\text{initial}} \approx 2.88}$$

c) **pH at half-equivalence ($V = 25.0$ mL):**
At half-equivalence: $[CH_3COOH] = [CH_3COO^-]$

$$\text{pH} = pK_a(CH_3COOH) + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a(CH_3COOH) + \log(1)$$

$$\boxed{\text{pH}_{\text{half-eq}} = 4.76}$$

d) **pH at equivalence ($V = 50.0$ mL):**
At equivalence, we obtain the salt CH_3COONH_4. Total volume: $V_f = 50.0 + 50.0 = 100.0$ mL $= 0.100$ L
Amount of salt formed:

$$n_{\text{salt}} = 0.050 \times 0.10 = 5.00 \cdot 10^{-3} \text{ mol}$$

$$C_{\text{salt}} = \frac{5.00 \times 10^{-3}}{0.100} = 5.00 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

For a salt of a weak acid and weak base:

$$\text{pH} \approx \frac{1}{2}\left(pK_a(CH_3COOH) + pK_a(NH_4^+)\right)$$

$$\text{pH} \approx \frac{1}{2}(4.76 + 9.25) = \frac{14.01}{2}$$

$$\boxed{\text{pH}_{\text{eq}} \approx 7.01}$$

e) **pH after adding 60 mL of ammonia:**
Total volume: $V_f = 50.0 + 60.0 = 110.0$ mL $= 0.110$ L
Initial amounts:

$$n(CH_3COOH) = 0.10 \times 0.050 = 5.00 \cdot 10^{-3} \text{ mol}$$

$$n(NH_3) = 0.10 \times 0.060 = 6.00 \cdot 10^{-3} \text{ mol}$$

Reaction: $CH_3COOH + NH_3 \longrightarrow CH_3COO^- + NH_4^+$ CH_3COOH is limiting, so after reaction:

$$n(CH_3COO^-) = n(NH_4^+) = 5.00 \cdot 10^{-3} \text{ mol}$$

$$n(NH_3)_{\text{remaining}} = 6.00 \times 10^{-3} - 5.00 \times 10^{-3} = 1.00 \cdot 10^{-3} \text{ mol}$$

We have a buffer NH_4^+/NH_3:

$$[NH_4^+] = \frac{5.00 \times 10^{-3}}{0.110} = 4.55 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$[NH_3] = \frac{1.00 \times 10^{-3}}{0.110} = 9.09 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

pH of the buffer:

$$\text{pH} = pK_a(NH_4^+) + \log \frac{[NH_3]}{[NH_4^+]}$$

$$\text{pH} = 9.25 + \log\left(\frac{9.09 \times 10^{-3}}{4.55 \times 10^{-2}}\right) = 9.25 + \log(0.200)$$

$$\text{pH} \approx 9.25 - 0.699 = 8.55$$

Summary of results:

- Equilibrium constant: $K \approx 3.1 \cdot 10^4$
- Case 1 (equimolar): pH ≈ 7.01
- Case 2 (acetic buffer): pH ≈ 4.94
- Case 3 (titration):
  - Initial pH: 2.88
  - pH at half-equivalence: 4.76
  - pH at equivalence: 7.01
  - pH after adding 60 mL: 8.55

Bibliography

(1) H. Geiger and E. Marsden. “On a Diffuse Reflection of the α-Particles”. In: *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 82.557 (1909). Article original rapportant les résultats de l’expérience de diffusion des particules alpha par la feuille d’or, pp. 495–500.

(2) R. Chang and K. A. Goldsby. *Chimie générale*. French. Trans. by A. Arpin and L. Papillon. 4th ed. Traduction et adaptation française. Chenelière Éducation / McGraw-Hill Education, 2013.

(3) E. Rutherford. “The Scattering of α and β Particles by Matter and the Structure of the Atom”. In: *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* 21.125 (1911). Article fondateur du modèle nucléaire de l’atome interprétant les résultats de l’expérience de la feuille d’or, pp. 669–688.

(4) J. Chadwick. “Possible Existence of a Neutron”. In: *Nature* 129.3252 (1932), p. 312.

(5) J. J. Thomson. “Cathode Rays”. In: *Philosophical Magazine* 44.269 (1897), pp. 293–316.

(6) M. Silberberg. *Chimie : La mole et les transformations de la matière*. 3rd ed. Chapitre 16 : Approche pédagogique des calculs de pH. Cas standards avec nombreuses applications. De Boeck, 2018 (cit. on pp. 137, 138).

(7) R. A. Millikan. “The Isolation of an Ion, a Precise Measurement of its Charge”. In: *Physical Review* 32 (1911), pp. 349–397.

(8) H. Becquerel. “Sur les radiations émises par phosphorescence”. In: *Comptes Rendus de l’Académie des Sciences* 122 (1896), pp. 420–421.

(9) W. C. Röntgen. “Über eine neue Art von Strahlen”. In: *Sitzungsberichte der Würzburger Physik-medic. Gesellschaft* (1895).

(10) P. Villard. “Sur la réflexion et la réfraction des rayons cathodiques”. In: *Comptes Rendus de l’Académie des Sciences* 130 (1900), pp. 1010–1012.

(11) E. Rutherford and F. Soddy. “The Cause and Nature of Radioactivity”. In: *Philosophical Magazine*. 6th ser. 4.21 (Oct. 1902), pp. 370–396.

(12) Nobel Foundation. *The Nobel Prize in Chemistry 1908*. https://www.nobelprize.org/prizes/chemistry/1908/summary/. Consulté le 4 mai 2026. 1908.

(13) A. S. Eve. *Rutherford: Being the Life and Letters of the Rt. Hon. Lord Rutherford, O.M.* Cambridge: Cambridge University Press, 1939.

(14) Nobel Foundation. *The Nobel Prize in Chemistry 1921*. https://www.nobelprize.org/prizes/chemistry/1921/summary/. Consulté le 4 mai 2026. 1921.

(15) N. Bohr. “On the Constitution of Atoms and Molecules”. In: *Philosophical Magazine* 26.151 (1913), pp. 1–25.

(16) J. J. Balmer. “Notiz über die Spectrallinien des Wasserstoffs”. In: *Annalen der Physik und Chemie* 25 (1885), pp. 80–87.

(17) J. Rydberg. “Recherches sur la constitution des spectres d’émission des éléments chimiques”. In: *Kongliga Svenska Vetenskaps-Akademiens Handlingar* 23.11 (1888), pp. 1–155.

(18) W. Ritz. “Recherches critiques sur les séries spectrales”. In: *Annales de Chimie et de Physique* 24 (1908), pp. 293–406.

(19) J. C. Slater. “Atomic Shielding Constants”. In: *Physical Review* 36 (1930), pp. 57–64.

(20) L. De Broglie. “Recherches sur la théorie des quanta”. In: *Annales de Physique* 10.3 (1925), pp. 22–128.

(21) V. M. Klechkowski. “Justification of the Rule for the Sequence of Filling of Electron Shells in Atoms”. In: *Zhurnal Eksperimental’noi i Teoreticheskoi Fiziki* 41 (1962), p. 1659.

(22) W. Pauli. “Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren”. In: *Zeitschrift für Physik* 31 (1925), pp. 765–783.

(23) F. Hund. “Zur Deutung verwickelter Spektren, insbesondere der Elemente Scandium bis Nickel”. In: *Zeitschrift für Physik* 33 (1925), pp. 345–371.

(24) D. Mendeleev. “On the Relationship of the Properties of the Elements to their Atomic Weights”. In: *Zeitschrift für Chemie* 12 (1869), pp. 405–406.

(25) IUPAC. *Periodic Table of Elements*. https://iupac.org/what-we-do/periodic-table-of-elements/. 2016.

(26) G. N. Lewis. “The Atom and the Molecule”. In: *Journal of the American Chemical Society* 38 (1916), pp. 762–785.

(27) N. V. Sidgwick and H. M. Powell. “Stereochemical Types and Valency Groups”. In: *Proceedings of the Royal Society A* 176 (1940), pp. 153–180.

(28) R. J. Gillespie and R. S. Nyholm. “Inorganic Stereochemistry”. In: *Quarterly Reviews, Chemical Society* 11 (1957), pp. 339–380.

(29) P. Atkins and J. de Paula. *Atkins' Physical Chemistry*. 11th ed. Règle de Hund et application de la théorie des orbitales moléculaires à O2 : ordre de liaison 2 et deux électrons non appariés. Oxford University Press, 2018.

(30) P. Atkins and J. de Paula. *Chimie Physique*. 5th ed. Pages 245–268 : Fondements théoriques des équilibres acide-base. Équations générales pour acides/bases forts et faibles. De Boeck, 2021 (cit. on p. 137).

(31) J. N. Butler. *Ionic Equilibrium: Solubility and pH Calculations*. Chapitre 4 : Traitement complet des solutions ultra-diluées. Équations exactes pour tous les cas limites. Référence majeure pour les cas complexes. Wiley, 1998 (cit. on pp. 137, 144, 146).

(32) D. C. Harris. *Quantitative Chemical Analysis*. 9th ed. Chapitre 9 : Approche analytique avec critères de validité. Seuil typique : alpha < 0.1 pour les approximations. W. H. Freeman, 2016 (cit. on pp. 138, 146).

(33) M. J. F. Leroy. *Chimie des solutions aqueuses*. Chapitre 3 : Approche progressive avec exercices corrigés. Tableaux récapitulatifs similaires. Ellipses, 2000 (cit. on p. 137).

(34) V. L. Snoeyink and D. Jenkins. *Water Chemistry*. Pages 145–167 : Traitement des solutions très diluées. Influence de l'autoprotolyse de l'eau. Wiley, 1980 (cit. on p. 144).

(35) J. G. Hardman and L. E. Limbird. *Goodman & Gilman : Les bases pharmacologiques de la thérapeutique*. pKa et absorption des médicaments. De Boeck, 2001 (cit. on pp. 147, 152).

(36) D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch. *Fundamentals of Analytical Chemistry*. 10th. Cengage Learning, 2021 (cit. on p. 149).

(37) D. C. Harris. *Quantitative Chemical Analysis*. 9th ed. Chapitre 9 : Dosages acido-basiques, pH-métrie et indicateurs. W. H. Freeman, 2016 (cit. on p. 151).

(38) P. Atkins and J. de Paula. *Chimie Physique*. 5th ed. Pages 245–268 : Fondements théoriques des équilibres acide-base. De Boeck, 2021 (cit. on p. 152).

(39) D. D. Perrin and B. Dempsey. *Buffers for pH and Metal Ion Control*. Appendice A : Dérivation mathématique complète des formules. Chapman and Hall, 1974 (cit. on pp. 161, 162).

(40) J. N. Butler. *Ionic Equilibrium: Solubility and pH Calculations*. Chapitre 4 : Équations exactes pour tous les cas limites. Wiley, 1998 (cit. on pp. 186, 206).

(41) F. L. Coe, A. P. Evan, and E. M. Worcester. “Kidney stone disease”. In: *The Journal of Clinical Investigation* 115.10 (2005). Physiopathologie des calculs rénaux et rôle de la sursaturation, pp. 2598–2608.

(42) J. D. B. Featherstone. “Prevention and reversal of dental caries: role of low level fluoride”. In: *Community Dentistry and Oral Epidemiology* 27.1 (1999). Mécanisme d'action du fluor : formation de CaF2 et fluorapatite, pp. 31–40.

(43) G. L. Amidon, H. Lennernäs, V. P. Shah, and J. R. Crison. “A theoretical basis for a biopharmaceutic drug classification: the correlation of in vitro drug product dissolution and in vivo bioavailability”. In: *Pharmaceutical Research* 12.3 (1995). Article fondateur du système BCS (Biopharmaceutics Classification System), pp. 413–420.

(44) W. Stumm and J. J. Morgan. *Aquatic Chemistry*. 3rd ed. Pages 112–135 : Approche rigoureuse des équilibres en solution diluée. Cas environnementaux réels. Wiley-Interscience, 1996.

(45) Haute Autorité de Santé. *Guide du bon usage des produits de contraste en radiologie*. https://www.has-sante.fr. Recommandations françaises pour l'utilisation du sulfate de baryum. 2018.

(46) D. R. Lide. *CRC Handbook of Chemistry and Physics*. 85th ed. Valeurs de Ks, pKa, et constantes thermodynamiques de référence. CRC Press, 2004.

(47) G. Khorasani, S. J. Hosseinimehr, and A. H. Kashi. "The effect of silver sulfadiazine on burn wound infection". In: *Burns* 35.5 (2009). Utilisation des ions argent en cicatrisation (pansements), pp. 713–716.

(48) R. Chang and J. Overby. *General Chemistry: The Essential Concepts*. 6th ed. McGraw-Hill, 2011.

(49) F. L. Coe, A. P. Evan, and E. M. Worcester. "Pathophysiology-based treatment of idiopathic calcium kidney stones". In: *Clinical Journal of the American Society of Nephrology* 6.8 (2011). Traitement basé sur la physiopathologie, lien avec Q et Ks, pp. 2083–2092.

(50) J. M. ten Cate. "Contemporary perspective on the use of fluoride products in caries prevention". In: *British Dental Journal* 214 (2013). Utilisation clinique du fluor en dentisterie, pp. 161–167.

(51) D. D. Perrin and B. Dempsey. *Buffers for pH and Metal Ion Control*. Appendice A : Dérivation mathématique complète des formules. Conditions de validité détaillées. Chapman and Hall, 1974.

(52) G. Pocock, C. D. Richards, and D. A. Richards. *Human Physiology*. 5th ed. Chapitre sur l'équilibre acido-basique sanguin et le tampon bicarbonate. Oxford University Press, 2018.

(53) M. Faraday. "Experimental Researches in Electricity. Seventh Series". In: *Philosophical Transactions of the Royal Society* 124 (1834). Établissement des lois de l'électrolyse, pp. 77–122.

(54) L. Galvani. "De Viribus Electricitatis in Motu Musculari Commentarius". In: *De Bononiensi Scientiarum et Artium Instituto atque Academia Commentarii* 7 (1791). Découverte de l'électricité animale (contraction des grenouilles), pp. 363–418.

(55) A. Volta. "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds". In: *Philosophical Transactions of the Royal Society* 90 (1800). Invention de la pile voltaïque, pp. 403–431.

(56) J. F. Daniell. "On the Voltaic Combination". In: *Philosophical Transactions of the Royal Society* 126 (1836). Invention de la pile de Daniell à compartiments séparés, pp. 107–124.

(57) G. Planté. "Recherches sur les phénomènes électriques produits dans les accumulateurs". In: *Comptes Rendus de l'Académie des Sciences* 49 (1859). Invention de la batterie au plomb rechargeable, pp. 936–939.

(58) R. A. Day and A. L. Underwood. *Quantitative Analysis*. 4th. Ouvrage de référence en chimie analytique. Il utilise la valeur (0.059) dans ses exemples d'application de l'équation de Nernst. Prentice Hall Inc., 1980.

(59) Wase. *Chem One*. Extrait d'un manuel de chimie américain. À 25°C, la constante de Nernst est présentée comme (0.0592) V en valeur exacte et (0.06) V en approximation. [Éditeur inconnu], 2021.

(60) W. Nernst. "Die elektromotorische Wirksamkeit der Jonen". In: *Zeitschrift für Physikalische Chemie* 4 (1889). Établissement de l'équation de Nernst, pp. 129–181.

(61) Nobel Foundation. *The Nobel Prize in Chemistry 1920*. https://www.nobelprize.org/prizes/chemistry/1920/summary/. Prix Nobel de Walther Nernst. 1920.

(62) D. C. Harris. *Quantitative Chemical Analysis*. 9th ed. Chapitre sur les méthodes électrochimiques et les électrodes de référence. W. H. Freeman, 2016.

(63) P. Atkins and J. de Paula. *Chimie Physique*. 5th ed. Chapitre sur l'électrochimie : potentiels standards, équation de Nernst. De Boeck, 2021.

(64) A. J. Bard and L. R. Faulkner. *Electrochemical Methods: Fundamentals and Applications*. 2nd ed. Référence majeure en électrochimie. Wiley, 2001.

(65) A. A. Ravdel' and A. M. Ponomareva, eds. *Kratkii spravochnik fiziko-khimicheskikh velichin*. 10th ed. Sankt-Peterburg: Ivan Fedorov, 2003, p. 149.

(66) P. Atkins and J. de Paula. *Elements of Physical Chemistry*. USA: Oxford University Press, 2017.

(67) S. S. Zumdahl and S. A. Zumdahl. *Chemistry: An Atoms First Approach*. Cengage Learning, 2016.

(68) P. W. Atkins, L. Jones, and L. Laverman. *Chemical Principles: The Quest for Insight*. 6th ed. W. H. Freeman, 2013.

(69) M. S. Silberberg and P. G. Amateis. *Chemistry: The Molecular Nature of Matter and Change*. 10th. McGraw Hill, 2023.

(70) C. H. McQuarrie, D. A. McQuarrie, P. A. Rock, P. Depovere, and C. G. Jung. *Chimie générale*. 3rd ed. Bruxelles: De Boeck Université, 1992.

(71) D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch. *Fundamentals of Analytical Chemistry*. 10th. Cengage Learning, 2021.

(72) European Association of Urology. *EAU Guidelines on Urolithiasis*. https://uroweb.org/guidelines/urolithiasis. Recommandations cliniques pour la prise en charge des calculs urinaires. 2023.