

Recipes for acid-base titration*

General Chemistry

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Contents

Introduction

Here is everything you need to do simple calculations of pH in acid-base titrations. For each kind of titration, there are four circumstances that need to be handled differently, according to whether you are at

- the start of the titration,
- before the equivalence point,
- at the equivalence point, or
- after the equivalence point.

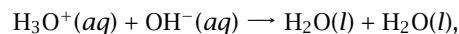
It is crucial that you first calculate the reaction of the acid and base as a **limiting reagent problem**, using **moles** of acid and base, to determine which of these four circumstances you have. Then, you need to set up and solve the **equilibrium equations** for that circumstance, using **concentrations**.

As you study these notes, try to master the method rather than to memorize formulas. It is easy to write down the formulas you need once you understand the method.

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1 Titration of strong acid with strong base

The first thing to do — **always** — is to calculate the reaction of the acid and base,



as a **limiting reagent problem** (ignore the anion of the acid and the cation of the base). Do this by computing the number n_a of moles of acid and the number n_b of moles of base. Then,

- If $n_b = 0$, we have **pure strong acid**. The pH is

$$\text{pH} = -\log c_a.$$

- If $n_b \neq 0$ but $n_b < n_a$, we have a **unreacted acid**. The reaction of the base leaves $n_a - n_b$ moles of unreacted acid, so that

$$c_a = \frac{n_a - n_b}{V_a + V_b}$$

and hence

$$\text{pH} = -\log c_a.$$

- If $n_b = n_a$, we have a **pure water**. The reaction of the base produces $n_a - n_b = 0$ moles of unreacted acid and $n_b - n_a = 0$ moles of unreacted base, so that

$$\text{pH} = 7.$$

- If $n_b > n_a$, we have a **excess base**. The reaction of the base consumes all of the acid and leaves $n_b - n_a$ moles of unreacted base, so that

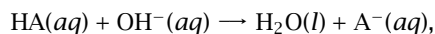
$$c_b = \frac{n_b - n_a}{V_a + V_b}$$

and hence

$$\text{pH} = 14 + \log c_b.$$

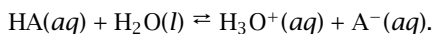
2 Titration of weak acid with strong base

The first thing to do — **always** — is to calculate the reaction of the acid and base,



as a **limiting reagent problem** (ignore the cation of the strong base). Do this by computing the number n_a of moles of acid and the number n_b of moles of base. Then,

- If $n_b = 0$, we have **pure weak acid**. The equilibrium relation is



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

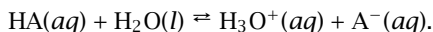
and so

$$\text{pH} = -\log x = -\frac{1}{2} \log (K_a c_a).$$

- If $n_b \neq 0$ but $n_b < n_a$, we have a **buffer**. The reaction of the strong base produces n_b moles of the conjugate base, A^- , of the weak acid and leaves $n_a - n_b$ moles of unreacted weak acid, so that

$$c_a = \frac{n_a - n_b}{V_a + V_b} \quad \text{and} \quad c_{cb} = \frac{n_b}{V_a + V_b}.$$

The equilibrium relation is



$$K_a = \frac{x(c_{cb} + x)}{c_a - x} \approx \frac{x c_{cb}}{c_a} \Rightarrow x \approx \frac{K_a c_a}{c_{cb}}$$

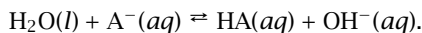
and so

$$\text{pH} = -\log x = -\log \left(\frac{K_a c_a}{c_{cb}} \right).$$

- If $n_b = n_a$, we have **hydrolysis**. The reaction of the strong base produces $n_b = n_a$ moles of the conjugate base, A^- , of the weak acid and leaves $n_a - n_b = 0$ moles of unreacted weak acid, so that

$$c_{cb} = \frac{n_b}{V_a + V_b}.$$

The equilibrium relation is



$$K_{cb} = \frac{K_w}{K_a} = \frac{x^2}{c_{cb} - x} \approx \frac{x^2}{c_{cb}} \Rightarrow x \approx \sqrt{\frac{K_w c_{cb}}{K_a}}$$

and so

$$\text{pH} = 14 + \log x = 14 + \frac{1}{2} \log \left(\frac{K_w c_{cb}}{K_a} \right)$$

- If $n_b > n_a$, we have a **excess strong base**. The reaction of the strong base produces n_a moles of the conjugate base, A^- , of the weak acid, leaves 0 moles of unreacted acid (since $n_a - n_b < 0$) and leaves $n_b - n_a$ moles of unreacted strong base, so that

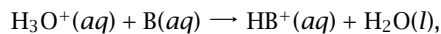
$$c_b = \frac{n_b - n_a}{V_a + V_b}.$$

The excess strong base overwhelms the OH^- from the hydrolysis of the conjugate base, A^- , of the weak acid, so we can **ignore hydrolysis** and compute

$$\text{pH} = 14 + \log c_b.$$

3 Titration of weak base with strong acid

The first thing to do — **always** — is to calculate the reaction of the acid and base,



as a **limiting reagent problem** (ignore the anion of the strong acid). Do this by computing the number n_a of moles of acid and the number n_b of moles of base. Then,

- If $n_a = 0$, we have **pure weak base**. The equilibrium relation is



$$K_b = \frac{x^2}{c_b - x} \approx \frac{x^2}{c_b} \Rightarrow x \approx \sqrt{K_b c_b}$$

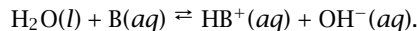
and so

$$\text{pH} = 14 + \log x = 14 + \frac{1}{2} \log (K_b c_b).$$

- If $n_a \neq 0$ but $n_a < n_b$, we have a **buffer**. The reaction of the strong acid produces n_a moles of the conjugate acid, HB^+ , of the weak base and leaves $n_b - n_a$ moles of unreacted weak base, so that

$$c_b = \frac{n_b - n_a}{V_a + V_b} \quad \text{and} \quad c_{ca} = \frac{n_a}{V_a + V_b}.$$

The equilibrium relation is



$$K_b = \frac{x(c_{ca} + x)}{c_b - x} \approx \frac{x c_{ca}}{c_b} \Rightarrow x \approx \frac{K_b c_b}{c_{ca}}$$

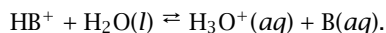
and so

$$\text{pH} = 14 + \log x = 14 + \log \left(\frac{K_b c_b}{c_{ca}} \right).$$

- If $n_a = n_b$, we have **hydrolysis**. The reaction of the strong acid produces $n_a = n_b$ moles of the conjugate acid, HB^+ , of the weak base and leaves $n_b - n_a = 0$ moles of unreacted weak base base, so that

$$c_{ca} = \frac{n_a}{V_a + V_b}.$$

The equilibrium relation is



$$K_{ca} = \frac{K_w}{K_b} = \frac{x^2}{c_{ca} - x} \approx \frac{x^2}{c_{ca}} \Rightarrow x \approx \sqrt{\frac{K_w c_{ca}}{K_b}}$$

and so

$$\text{pH} = -\log x = -\frac{1}{2} \log \left(\frac{K_w c_{ca}}{K_b} \right)$$

- If $n_a > n_b$, we have a **excess strong acid**. The reaction of the strong acid produces n_b moles of the conjugate acid, HB^+ , of the weak base leaves 0 moles of unreacted weak base (since $n_b - n_a < 0$), and leaves $n_a - n_b$ moles of unreacted strong acid, so that

$$c_a = \frac{n_a - n_b}{V_a + V_b}.$$

The excess strong acid overwhelms the H_3O^+ from the hydrolysis of the conjugate acid of the weak base, so HB^+ , we can **ignore hydrolysis** and compute

$$\text{pH} = -\log c_a.$$