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,

\[ H_3O^+(aq) + OH^-(aq) \rightarrow H_2O(l) + H_2O(l), \]

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
  \[ pH = -\log c_a. \]

- If \( n_b \neq 0 \) but \( n_b < n_a \), we have an 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
  \[ pH = -\log c_a. \]

- 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
  \[ pH = 7. \]

- If \( n_b > n_a \), we have an 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
  \[ pH = 14 + \log c_b. \]
2 Titration of weak acid with strong base

The first thing to do — always — is to calculate the reaction of the acid and base, \( \text{HA(aq)} + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O(l)} + \text{A}^-(aq) \), 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

  \[
  \text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{A}^- (aq).
  \]

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

  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, \( \text{A}^- \), 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

  \[
  \text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{A}^- (aq).
  \]

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

  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 \( n_b \) moles of the conjugate base, \( \text{A}^- \), 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

  \[
  \text{H}_2\text{O(l)} + \text{A}^- (aq) \rightleftharpoons \text{HA(aq)} + \text{OH}^- (aq).
  \]

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

  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 \( n_b \) moles of the conjugate base, \( \text{A}^- \), 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 \( \text{OH}^- \) from the hydrolysis of the conjugate base, \( \text{A}^- \), 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,

\[ \text{H}_3\text{O}^+(aq) + \text{B}(aq) \rightarrow \text{HB}^+(aq) + \text{H}_2\text{O}(l), \]

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
  
  \[ \text{H}_2\text{O}(l) + \text{B}(aq) \rightarrow \text{HB}^+(aq) + \text{OH}^-(aq). \]

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

  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, \( \text{HB}^+ \), 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

  \[ \text{H}_2\text{O}(l) + \text{B}(aq) \rightarrow \text{HB}^+(aq) + \text{OH}^-(aq). \]

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

  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, \( \text{HB}^+ \), of the weak base and leaves \( n_b - n_a = 0 \) moles of unreacted weak base, so that

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

  The equilibrium relation is

  \[ \text{HB}^+ + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{B}(aq). \]

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

  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, \( \text{HB}^+ \), 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 \( \text{H}_3\text{O}^+ \) from the hydrolysis of the conjugate acid of the weak base, so \( \text{HB}^+ \), we can ignore hydrolysis and compute

  \[ \text{pH} = -\log c_a. \]