Acid-base titrations (Ch. 12-1 to 12-4)

- Titration of strong acid with strong base
- Titration of weak acid with strong base
- Titration of weak base with strong acid
- Titrations in diprotic systems

Titration of strong acid with strong base

Titration of 50.00 mL of 0.02000 M KOH with 0.1000M HBr.

There are 3 different regions.

1. Before EP (e.g. v = 3.00 mL)

new volume = 0.05000 L + 0.00300 L = 0.05300 L

excess moles of OH^- = 0.02000 M × 0.05000 L - 0.1000 M × 0.00300 L = 0.00070

$[OH^-]=\frac{0.00070}{0.05300L}=0.0132M$ $pOH=-\log(0.01321)=1.88$ $\boxed{pH=14.00-1.88=12.12}$

2. At EP (i.e. v_e = 10.00 mL)

0.1000 M × v_e = 0.02000 M × 0.05000 L v_e = 0.01000 L

There is no excess OH^- from KOH and no excess H^+ from HBr, and Br^- is a strong conjugate base without hydrolysis. Therefore, only the dissociation of H_2O is considered.

$[H^+]=\sqrt{1.00\times10^{-14}}=1.00\times10^{-7}M$ $\boxed{pH=-\log1.00\times10^{-7}=7.00}$

Note that pH= 7.00 at EP is only valid in a strong acid-strong base titration.

Titration of strong acid with strong base

3. After EP (i.e. v = 10.50 mL)

new volume = 0.05000 L + 0.01050 L
= 0.06050 L

excess moles of H^+
= 0.1000M × 0.01050L - 0.0200M × 0.05000L
or 0.1000 M × (0.01050 - 0.0100)L
= 0.00005

$[H^+]=\frac{0.00005}{0.06050L}=8.26\times10^{-4}M$

$\boxed{pH=-\log(8.26\times10^{-4})=3.08}$

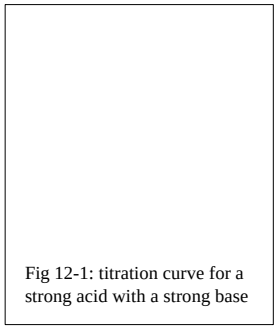


Fig 12-1: titration curve for a strong acid with a strong base

Titration of weak acid with strong base

Titration of 50.00 mL of 0.02000 M MES with 0.10000 M NaOH. MES is 2-(N-morpholino)ethanesulfonic acid with pK_a = 6.15.

There are 4 different regions.

1. Before base is added (i.e. v = 0) This is a calculation of a weak acid.

$HA \rightleftharpoons H^+ + A^-$

F-x x x

$\frac{x^2}{0.02000-x}=K_a=10^{-6.15}$ $[H^+]=x=1.19\times10^{-4}$ $\boxed{pH=-\log(1.19\times10^{-4})=3.93}$

2. Before EP (e.g. v = 3.00 mL) This is a buffer containing HL and L^-.

$HA + OH^- \rightarrow A^- + H_2O$

0.05000×0.020000-0.00300×0.10000 =0.0007 0.00300×0.10000 =0.0003

$\therefore pH=pK_a+\log\frac{[A^-]}{[HA]}\approx6.15+\log\frac{0.0003/0.05300}{0.0007/0.05300}=5.78$

Note that pH=pK_a when $[A^-]=[HA]$ or when v=½Ve.

If activity coefficients are considered, pH=pK_a only when $\gamma_{A^-}[A^-]=\gamma_{HA}[HA]$

Titration of weak acid with strong base

3. At EP (i.e. v_e = 10.00 mL) This is a solution of weak base A^-.

0.1000 M × v_e = 0.02000 M × 0.05000 L v_e = 0.01000 L

$c_{A^-}=\frac{0.05000L\times0.02000M}{(0.05000+0.01000)L}=0.0167M$

$\frac{x^2}{0.0167-x}=K_b=\frac{K_w}{K_a}=\frac{10^{-14.00}}{10^{-6.15}}$ $[OH^-]=x=1.54\times10^{-5}M$

$\boxed{pH=14.00-pOH=14.00+\log(1.54\times10^{-5})=9.18}$

Note that pH at EP is higher than 7.00 for a titration of a weak acid with a strong base because the solution contains a weak base, A^-.

Titration of weak acid with strong base

4. After EP (e.g. v = 10.10 mL)

There is an excess of OH^-.

new volume = 0.05000 L + 0.01010 L
= 0.06010 L

excess moles of OH^-
= 0.1000M × 0.01010L - 0.0200M × 0.05000L
or 0.1000 M × (0.01010 - 0.0100)L
= 0.00001

$[OH^-]=\frac{0.00001}{0.06010L}=1.66\times10^{-4}M$

$\boxed{pH=14.00-pOH=14.00+\log(1.66\times10^{-4})=10.22}$

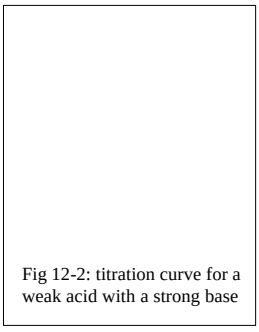


Fig 12-2: titration curve for a weak acid with a strong base

Titration of weak base with strong acid

The titration of a weak base with a strong acid is just like the reverse of the titration of a weak acid with a strong base.

There are 4 different regions.

1. Before acid is added (i.e. v = 0) This is a calculation of a weak base.
2. Before EP This is a buffer containing B & BH^+.
3. At EP This is a solution of weak acid BH^+.
4. After EP There is an excess of H^+.

Note that the pH at EP is below 7.00 because the solution contains the weak acid BH^+.

Titrations in diprotic systems

Titration of 10.0 mL of 0.100 M of base B with a strong acid (0.100 M HCl) base B is a weak diprotic base with pK_{b1}=4.00 and pK_{b2}=9.00.

There are 6 different regions.

1. Point A (i.e. v = 0) This is a solution of weak base B.

$$\frac{x^2}{0.100-x}=10^{-4.00} \qquad [OH^-]=x=3.1_1\times10^{-3}M$$

$$\boxed{pH=14.00-pOH=14.00+\log(3.1_1\times10^{-3})=11.49}$$

We assume that the second association of B (I.e. from BH^+ to BH_2^{2+}) is negligible.

2. Point B', before 1st EP (e.g. v = 1.5 mL)

This is a buffer solution containing B and BH^+.

$$c_B=\frac{0.100M\times0.0100L-0.100M\times0.0015L}{(0.0100+0.0015)L} \qquad c_{BH^+}=\frac{0.100M\times0.0015L}{(0.0100+0.0015)L} \qquad \therefore\frac{c_B}{c_{BH^+}}=\frac{8.5}{1.5}$$

$$\therefore pH=pK_2+\log\frac{[B]}{[BH^+]}=(14.00-4.00)+\log\frac{8.5}{1.5}=10.75$$

Note that, at point B, pH=pK_2 when [B]=[BH^+] or when v = 5.0 mL.

Titrations in diprotic systems

3. Point C, at 1st EP (e.g. v_{e1} = 10.0 mL)

This is a solution with all B converted to the intermediate form: BH^+.

$$[H^+]=\sqrt{\frac{K_1K_2[HL]+K_1K_W}{K_1+[HL]}}\approx\sqrt{\frac{K_1K_2F_{HL}+K_1K_W}{K_1+F_{HL}}}$$

$$F_{BH^+}=0.100M\times\frac{0.0100L}{(0.0100+0.0100)L}=0.050M \qquad K_1=\frac{K_W}{K_{b_2}}=\frac{10^{-14.00}}{10^{-9.00}}=10^{-5.00} \qquad K_2=\frac{K_W}{K_{b_1}}=\frac{10^{-14.00}}{10^{-4.00}}=10^{-10.00}$$

$$\therefore[H^+]\approx\sqrt{\frac{10^{-5.00}10^{-10.00}(0.050)+10^{-5.00}10^{-14.00}}{10^{-5.00}+0.050}}=3.1_6\times10^{-8}M$$

$$\boxed{\therefore pH=7.50}=\frac{1}{2}(pK_1+pK_2)$$

Note that point C is the least-buffered point on the whole titration curve (see Fig. 12-4).

The intermediate form of a diprotic acid or base is a worst choice of a buffer.

Titrations in diprotic systems

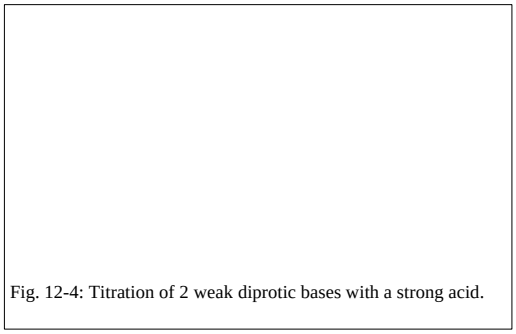


Fig. 12-4: Titration of 2 weak diprotic bases with a strong acid.

Titrations in diprotic systems

4. Point D', between EP1 and EP2 (e.g. v = 17.2 mL)

This is a buffer containing BH^+ and BH_2^{2+}.

$$c_{BH^+}=\frac{0.100M\times0.0100L-0.100M\times0.0072L}{(0.0100+0.0172)L}$$

Note that 10.0 mL HCl has been used to form 0.100×0.0100 mole of BH^+ at EP1.

$$c_{BH_2^{2+}}=\frac{0.100M\times0.0072L}{(0.0100+0.0172)L} \qquad \therefore\frac{c_{BH^+}}{c_{BH_2^{2+}}}=\frac{2.8}{7.2}$$

$$\therefore pH=pK_1+\log\frac{[BH^+]}{[BH_2^{2+}]}\approx(14.00-9.00)+\log\frac{2.8}{7.2}=4.59$$

Note that, at point D, pH=pK_1 when [BH^+]=[BH_2^{2+}] or when v = 15.0 mL.

Titrations in diprotic systems

5. Point E, at EP2 (i.e. v_{e2} = 20.0 mL)

This is a solution with all BH^+ converted to the weak acid BH_2^{2+}.

$$F_{BH_2^{2+}}=0.100M\times\frac{0.0100L}{(0.0100+0.0200)L}=0.033M$$

$$\frac{x^2}{0.033-x}=10^{-5.00} \qquad [H^+]=x=5.7_2\times10^{-4}M \qquad \boxed{pH=3.24}$$

We assume that the second dissociation of BH_2^{2+} (I.e. from BH^+ to B) is negligible.

6. Point F, after EP2 (e.g. v = 25.0 mL) There is an excess of 5.0 mL of HCl.

$$[H^+]=0.100M\times\frac{0.0050L}{(0.0100+0.0250)L}=1.4_3\times10^{-2}M \qquad \boxed{pH=1.85}$$

Note that there is no perceptible transition at EP when pH is too low or too high or when pK_a values are too close together.

Titrations in diprotic systems

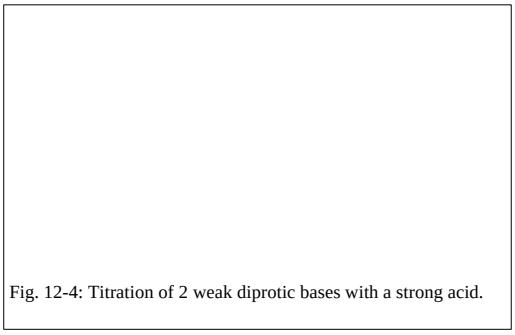
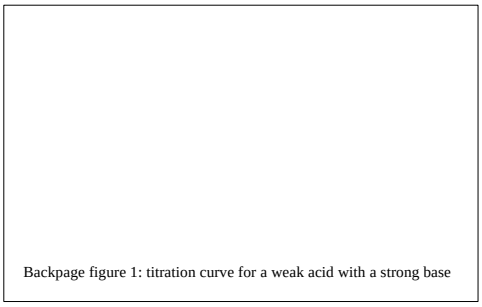


Fig. 12-4: Titration of 2 weak diprotic bases with a strong acid.

Summary: Acid-base titrations

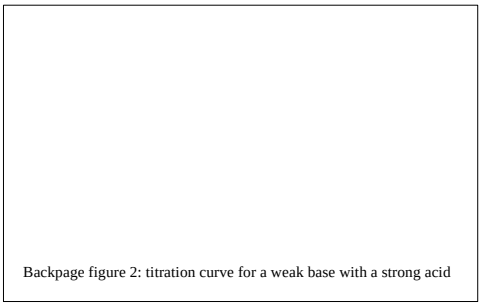
- To determine the points on a curve for the titration of strong acid with strong base (Do Exercise 12-2)
- To determine the points on a curve for the titration of weak acid with strong base (Do Exercise 12-6)
- To determine the points on a curve for the titration of weak base with strong acid (Do Exercise 12-12)
- To determine the points on a curve for the titrations in diprotic systems (Do Exercise 12-25)

Summary: Acid-base titrations



Backpage figure 1: titration curve for a weak acid with a strong base

Summary: Acid-base titrations



Backpage figure 2: titration curve for a weak base with a strong acid