

4 – Titrations

1] A common primary standard for the standardization of bases is

_____ ¹

2] Solutions of NaOH(aq) titrant must be re-standardized frequently because

_____ ²

3] Which of the following is not a primary standard? ³

- a) Potassium Hydrogen Phthalate (KHP)
- b) Benzoic Acid
- c) Potassium Hydrogen Iodate
- d) NaOH
- e) NaHCO₃

4] Why would KHP (MW = 204.22) be preferred over NaHCO₃ (MW = 84.007g/mol) as primary standard? ⁴

5] What is the difference between the end point and equivalence point for a monobasic-monoacid titration? ⁵

6] What is the final pH if solutions of 200.0-mL of 0.0500 M NaOH(aq) and 75.0-mL of 0.100 M CH₃COOH(aq) are added together? ⁶

7] When titrating a weak acid with a strong base it is expected that the equivalence point will be ⁷

- a) Slightly acidic, since the equilibrium $HA = H^+ + A^-$ predominates.
- b) Neutral since $[OH^-] = [H^+]$
- c) Slightly basic since the equilibrium $A^- + H_2O = HA + OH^-$ predominates.
- d) It is impossible to know since it could be acidic or basic depending on the K_a of the acid.
- e) Strongly basic since excess OH^- is present.

8] What is the pH of the solution that results from mixing of 25.00 mL of 0.250 M of a weak acid H₂A with 25.00 mL of 0.250 M NaOH?⁸



$$K_{a1} = 1.00e-4$$



9] A sample solution of 50.00 mL 0.0500 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is titrated with 50.00 mL of 0.1000 M of NaOH. Which of the following is true after the two solutions are mixed? ⁹

- a) This is the first equivalence point.
- b) This a pH buffer region where $[\text{H}_2\text{C}_2\text{O}_4] = [\text{HC}_2\text{O}_4^-]$
- c) This is a metal buffer region
- d) This is the second equivalence point.
- e) This is the excess OH^- region where the pH is strongly alkaline.

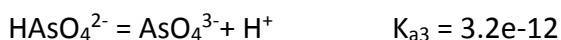
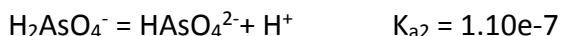
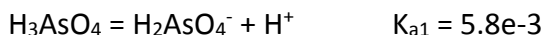
10] A sample solution of 50.00 mL 0.0500 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is titrated with 35.00 mL of 0.1000 M of NaOH. Which of the following is true after the two solutions are mixed? ¹⁰

- a) There is 2.50 mmol of $\text{H}_2\text{C}_2\text{O}_4$ present.
- b) There is 1.50 mmol of OH^- present.
- c) There is 2.50 mmol of HC_2O_4^- present.
- d) There is 1.00 mmol of $\text{H}_2\text{C}_2\text{O}_4$ present.
- e) There is 1.00 mmol of $\text{C}_2\text{O}_4^{2-}$ present

11] What is the pH of a titration solution that consists of 0.100 M CH_3COOH ($K_a = 1.75\text{e-}5$) and 0.050 M NaOH? ¹¹

12] What is the pH of a titration solution that has 10.00 mL of 0.100 M HA with 15.00 mL of 0.100 M NaOH added titrant? $K_a(\text{HA}) = 9.22\text{e-}5$ ¹²

13] Calculate the pH of a mixture of 25.00 mL of 0.500 M NaOH and 25.00 mL of 0.250 M H_3AsO_4 (arsenic acid). ¹³



14] A sample solution of 50.00 mL 0.0500 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is titrated with 50.00 mL of 0.1000 M of NaOH. Which of the following is true after the two solutions are mixed? ¹⁴

- a) This is the first equivalence point.
- b) This a pH buffer region where $[H_2C_2O_4] = [HC_2O_4^-]$
- c) This is a metal buffer region
- d) This is the second equivalence point.

This is the excess OH^- region where the pH is strongly alkaline.

15] A solution of 50.00 mL 0.0500 M oxalic acid ($H_2C_2O_4$) is mixed with 60.00 mL of 0.1000 M of NaOH. What is the pH of the final solution? ¹⁵

- a) 2.04
- b) 3.55
- c) 13.00
- d) 11.96
- e) 12.52

16] 75.0-mL of 0.100 M $CH_3COOH(aq)$ ($pK_a = 4.757$) is titrated with 0.0500 M NaOH(aq). What is the volume of NaOH solution required to reach the equivalence point?

What is the pH of the equivalence point? ¹⁶

17] A) Calculate pH of 50.00 mL of 0.0200 M HA with $pK_a = 6.15$ before any base is added.

B) pH when 3.00 mL of 0.100 M NaOH is added.

C) pH when 10.00 mL of 0.100 M NaOH is added.

D) pH when 10.10 mL of 0.100 M NaOH is added. ¹⁷

18] A 50.0-mL, 0.150 M solution of $CH_3COOH(aq)$ is titrated with 0.25 M NaOH(aq). Calculate the volume of titrant and the pH's needed to reach ϕ of 0.75, 1.00, and 1.25. ¹⁸

19] A 0.527 g sample of a mixture of Na_2CO_3 , $NaHCO_3$, and inert impurities was titrated with 0.109 M HCl, requiring 15.7 mL to reach the first end point and a total of 43.8 mL to reach the second endpoint. What is the percent Na_2CO_3 and $NaHCO_3$ in the mixture? ¹⁹

Answers

¹ Potassium Hydrogen Phthalate

² solvation of CO_2 from the atmosphere producing H_2CO_3

³ NaOH

⁴ The higher MW gives more accuracy in weighing out stoichiometric quantities of KHP.

⁵ The equivalence point is where mol acid = mol base and the end point is where indicator changes color.

⁶ mol CH₃COOH = 75.0-mL*0.100 M = 7.50 mmol

mol OH⁻ = 200.0-mL*0.0500 M = 10.0 mmol

excess OH⁻ = 10.0 – 7.50 mmol = 2.50 mmol

[OH⁻] = 2.50 mmol/275-mL = 9.09e-3

pOH = 2.041

pH = 11.959

⁷ C

⁸ 1 eq pt, therefore mol HA⁻ = 25.00 mL (0.250 M) = 6.25 mmol
[HA⁻] = 6.25 mmol/50.00 mL = 0.125 M

Note that: HA⁻ + H₂O = H₂A + OH⁻
 HA⁻ = H⁺ + A²⁻ are both possible therefore amphoteric

Amphoteric pH = ½ (pK_{a1} + pK_{a2}) = ½ (-log(1.00e-4) + -log(1.00e-7)) = ½ (4.000 + 7.000) = **5.500**

⁹ D

¹⁰ e: 1.00 mmol past 1st eq. pt. Initial HA⁻ = 2.5 mmol

HA⁻ + OH⁻ = A²⁻ + H₂O

2.50 1.00 0

-1.00 -1.00 +1.00

1.50 0 1.00

1.00 mmol A²⁻

¹¹ $\text{pH} = \text{pK}_a = 4.76$

¹² Amount of HA = 10.00 mL (0.100 M) = 1.00 mmoles

Amount OH⁻ = 15.00 mL (0.100 M) = 1.50 mmoles

Excess OH⁻ = 1.50 – 1.00 mmoles = 0.50 mmoles [OH⁻] = 0.50 mmoles / 25.00 mL = 2.0e-2 M

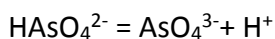
$\text{pOH} = 1.70$ **$\text{pH} = 12.30$**

¹³ 2nd eq. pt where all H₃AsO₄ is titrated to HAsO₄²⁻ which is intermediate of H₂AsO₄⁻ and AsO₄³⁻.

These two equilibria become important:



$$K_{a2} = 1.10\text{e-}7$$



$$K_{a3} = 3.2\text{e-}12$$

$$\text{Therefore pH} = \frac{1}{2}(\text{pK}_{a2} + \text{pK}_{a3})$$

$$= \frac{1}{2} (6.9586 + 11.495) = 9.23$$

¹⁴ This is the second equivalence point.

¹⁵ $2 * 0.05 * 50 = 5 \text{ mmol H}_2\text{C}_2\text{O}_4$

$$0.10 * 60 = 6 \text{ mmol NaOH}$$

$$\text{excess OH}^- = 6 - 5 \text{ mmol} = 1 \text{ mmol}$$

$$[\text{OH}^-] = 1\text{mmol}/110 \text{ mL} = 9.09\text{e-}3$$

$$\text{pOH} = 2.0413$$

$$\text{pH} = 11.96$$

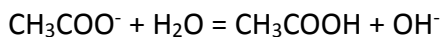
¹⁶ eq. pt. mol CH₃COOH = mol OH⁻

$$\text{mol CH}_3\text{COOH} = 75.0\text{-mL} * 0.100 \text{ M} = 7.50 \text{ mmol}$$

$$\text{vol NaOH} = 7.50 \text{ mmol}/0.0500 \text{ M} = 150\text{-mL}$$

total volume = 150-mL+75.0-mL = 225-mL

$$[\text{CH}_3\text{COO}^-] = 7.50 \text{ mmol}/225\text{-mL} = 3.33\text{e-}2 \text{ M}$$



$$3.33\text{e-}2 \quad \quad \quad -- \quad \quad \quad 0 \quad \quad \quad 0$$

$$-x \quad \quad \quad \quad \quad -- \quad \quad \quad +x \quad \quad \quad +x$$

$$K_b = K_w/K_a = 5.71\text{e-}10$$

$$= x^2/(3.33\text{e-}2-x) \approx x^2/(3.33\text{e-}2)$$

$$x = 4.36\text{e-}6$$

$$\text{pOH} = 5.360$$

$$\text{pH} = 8.640$$



$$0.020 \quad 0 \quad 0$$

$$-x \quad +x \quad +x \quad \quad \quad x^2 / 0.0200-x = 7.08\text{e-}7 \quad \quad \quad x = 1.19\text{e-}4$$

$$[\text{H}^+] = 3.92$$

B] Initial HA = 50.00 * 0.0200 = 1.00 mmol

OH⁻ added = 0.300 mmol

Rxn:



$$1.00 \text{ mmol} \quad \quad 0.300 \quad 0$$

$$\underline{-0.300} \quad \quad \quad \underline{-0.300} \quad \underline{+0.300}$$

$$0.700 \quad \quad \quad 0 \quad \quad 0.300$$

Buffer system $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$

$$[\text{H}^+] = K_a [\text{HA}] / [\text{A}^-] = 7.08\text{e-}7 * 0.700 / 0.300$$

$$\text{pH} = 5.78$$

C] OH⁻ added = 1.00 mmol we are at the eq. pt.

Rxn:

HA+	OH ⁻	A ⁻	H ₂ O
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1.00	1.00	0 mmol	
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-1.00	-1.00	+1.00 mmol	
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0	0	1.00 mmol	
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$[A^-] = 1.00 \text{ mmol} / 60.00 \text{ mL} = 0.01667 \text{ M}$

Rxn:

A ⁻	H ₂ O	HA+	OH ⁻
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0.01667	--	0	0
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-x		+x	+x
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$K_b = K_w / K_a = 1.41e-8 = x^2 / (0.01667-x)$

$x = 1.533e-5$

pH = 9.19

D] Excess OH⁻ = 0.10 mL * 0.100 M = 0.010 mmol

$[OH^-] = 0.010 \text{ mmol} / 60.10 \text{ mL} = 1.66e-4 \text{ M}$

pH = 10.22

¹⁸ $\phi = C_b/C_a = \text{mol}_b/\text{mol}_a$

$\text{mol}_a = 0.0500\text{-L} * 0.150\text{M}$

$= 7.50e-3 \text{ mol CH}_3\text{COOH}$

for $\phi = 0.75$ $\text{mol}_b = 5.63e-3 \text{ mol}$

$\text{vol NaOH} = 5.63e-3 \text{ mol} * 1/0.25 \text{ M}$

$= 2.25e-2 \text{ L} = 23\text{-mL}$

for pH Rxn:

$\text{CH}_3\text{COOH} + \text{OH}^- = \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$

7.50e-3	5.63e-3	0mol	
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$$\underline{-5.63e-3 \quad -5.63e-3 \quad +5.63e-3 \text{ mol}}$$

$$1.87e-3 \quad 0 \quad 5.63e-3 \text{ mol}$$

$$[\text{CH}_3\text{COOH}] = 1.87e-3 \text{ mol}/0.073 \text{ L} = 2.6e-2 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 5.63e-3 \text{ mol}/0.073 \text{ L} = 7.7e-2 \text{ M}$$

$$K_a = 1.75e-5 = [\text{H}^+][7.7e-2]/[2.6e-2] \quad [\text{H}^+] = 5.9e-6$$

$$\text{pH} = 5.23$$

for $\phi = 1.00$ $\text{mol}_b = 7.5e-3 \text{ mol}$

all HA is consumed since $\text{mol}_b = \text{mol}_a$ therefore vol NaOH

$$= 7.5e-3 \text{ mol} \cdot (1/0.25 \text{ M}) = 3.0e-2 \text{ L or 30-mL}$$

$$[\text{A}^-] = 7.5e-3 \text{ mol}/0.0800 \text{ L} = 0.094 \text{ M}$$



$$0.094 - x \quad x \quad x$$

$$x^2/0.094 - x = K_b = K_w/K_a$$

$$= 1e-14/1.75e-5 = 5.71e-10$$

$$x = 7.3e-6$$

$$\text{pOH} = 5.14 \quad \text{pH} = 8.86$$

for $\phi = 1.25$ $\text{mol}_b = 9.4e-3 \text{ mol}$

$$\text{vol NaOH} = 9.4e-3 \text{ mol} \cdot (1/0.25 \text{ M}) = 38\text{-mL}$$

region of excess OH^-

$$\text{mol OH}^- = 9.4e-3 - 7.5e-3 = 1.9e-3$$

$$[\text{OH}^-] = 1.9e-3 \text{ mol}/0.088 \text{ L} = 2.2e-2 \text{ M} \quad \text{pOH} = 1.67 \quad \text{pH} = 12.33$$

¹⁹ The first end point is due to: $\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$

$$\text{mol of CO}_3^{2-} = 0.109 \text{ mol/L} \cdot 15.7 \text{ mL} = 1.71 \text{ mmols}$$

The 2nd endpoint is due to: $\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3$

Remember that the second endpoint is due to HCO_3^- from the first endpoint (Na_2CO_3) and from HCO_3^- from NaHCO_3 .

Therefore HCO_3^- from NaHCO_3 is calculated as:

$$0.109 \text{ mol/L} * 43.8 \text{ mL} - 2 * 1.71 \text{ mmols} = 1.35 \text{ mmol}$$

$$\% \text{ Na}_2\text{CO}_3 = 1.71\text{e-}3 \text{ mol} * 106.0 \text{ g/mol} * 100/0.527\text{g} = 34.4\%$$

$$\% \text{ NaHCO}_3 = 1.35\text{e-}3 \text{ mol} * 84.0 \text{ g/mol} * 100/0.527\text{g} = 21.5\%$$