

Lecture three

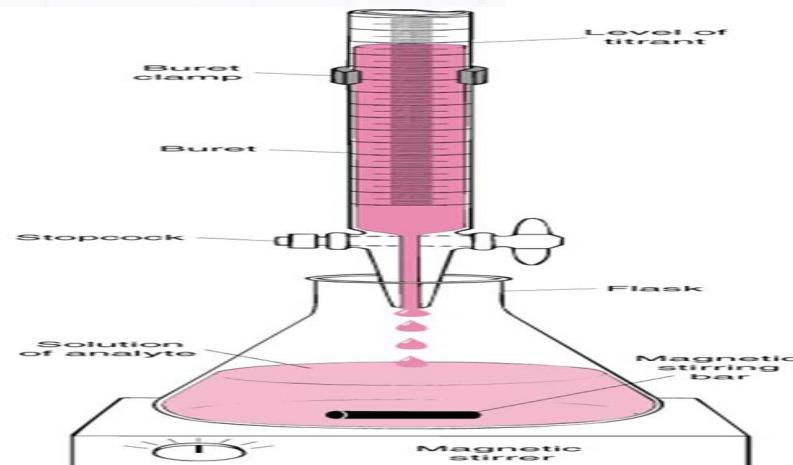
Volumetric Analysis

Titrimetric Methods

Titrimetric methods include a large and powerful group of quantitative procedures that are based on measuring the amount of a reagent of known concentration that is consumed by an analyte.

Titrations are widely used in analytical chemistry to determine acids, bases, oxidants, reductants, metal ions, proteins, and many other species. Titrations are based on a reaction between the analyte and a standard reagent known as the titrant. The reaction is of known and reproducible stoichiometry.

Volumetric titrimetry involves measuring the volume of a solution of known concentration that is needed to react essentially completely with the analyte.



Types of Titrimetric Methods

neutralization titrations

precipitation titrimetry

redox titrations

Complexometric titrations

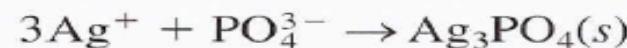
SOME TERMS USED IN VOLUMETRIC TITRIMETRY¹

A standard solution: is a reagent of exactly known concentration that is used in a titrimetric analysis

Titration: is a process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is judged to be complete.

Back-titration : is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution. Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

example, the amount of phosphate in a sample can be determined by adding a measured excess of standard silver nitrate to a solution of the sample, which leads to the formation of insoluble silver phosphate:



The excess silver nitrate is then back-titrated with a standard solution of potassium thiocyanate:



Here, the amount of silver nitrate is chemically equivalent to the amount of phosphate ion plus the amount of thiocyanate used for the back-titration.

The **equivalence point** in a titration is a theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample. For example, the equivalence point in the titration of sodium chloride with silver nitrate occurs after exactly 1 mol of silver ion has been added for each mole of chloride ion in the sample.

End point: is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence. In volumetric methods, the titration error E_t is given by

$$E_t = V_{ep} - V_{eq}$$

where (V_{ep}) is the actual volume of reagent required to reach the end point and (V_{eq}) is the theoretical volume to reach the equivalence point.

Indicators: are organic materials (almost weak acid or weak base) are often added to the analyte solution to produce an observable physical change (the end point) at or near the equivalence point.

example, the behavior of an acid-type indicator



The equilibrium for a base-type indicator



The equilibrium-constant expression for the dissociation of an acid-type indicator takes the form

$$K_a = \frac{[\text{H}_3\text{O}^+] [\text{In}^-]}{[\text{HIn}]} \quad (14-1)$$

Rearranging leads to

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HIn}]}{[\text{In}^-]} \quad (14-2)$$

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In⁻, particularly when the ratio [HIn]/[In⁻] is greater than about 10 or smaller than about 0.1. Consequently, the color change detected by an average observer occurs within a limited range of concentration ratios from about 10 to about 0.1. At greater or smaller ratios, the color appears essentially constant to the eye and is independent of the ratio. As a result, we can write that the average indicator, HIn, exhibits its pure acid color when

$$\frac{[\text{HIn}]}{[\text{In}^-]} \geq \frac{10}{1}$$

and its base color when

$$\frac{[\text{HIn}]}{[\text{In}^-]} \leq \frac{1}{10}$$

So, for the full acid color,

$$[\text{H}_3\text{O}^+] = 10K_a$$

and in the same way, for the full base color,

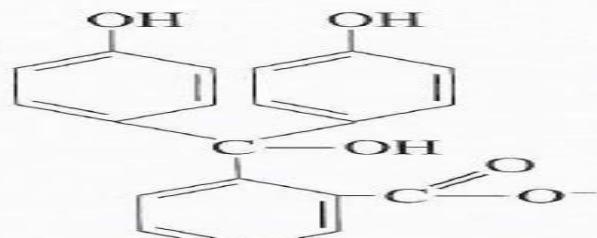
$$[\text{H}_3\text{O}^+] = 0.1K_a$$

To obtain the indicator pH range, we take the negative logarithms of the two expressions:

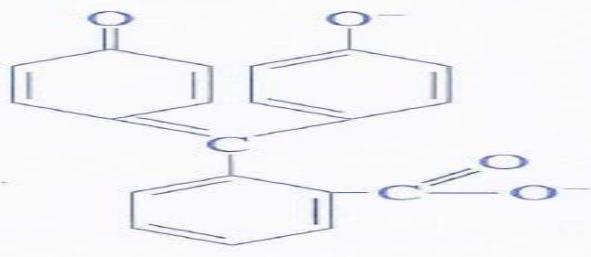
$$\text{pH}(\text{acid color}) = -\log (10K_a) = \text{p}K_a + 1$$

$$\text{pH}(\text{basic color}) = -\log (0.1K_a) = \text{p}K_a - 1$$

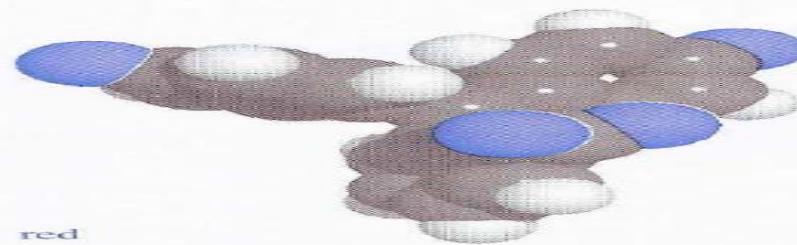
$$\text{indicator pH range} = \text{p}K_a \pm 1 \quad (14-3)$$



↓



+
H₃O⁺



Ph.ph Indicator for acid – base titration

TABLE 14-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK _a *	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R–Y	1
	8.0–9.6	8.96§	Y–B	
Methyl yellow	2.9–4.0		R–Y	2
Methyl orange	3.1–4.4	3.46§	R–O	2
Bromocresol green	3.8–5.4	4.66§	Y–B	1
Methyl red	4.2–6.3	5.00§	R–Y	2
Bromocresol purple	5.2–6.8	6.12§	Y–P	1
Bromothymol blue	6.2–7.6	7.10§	Y–B	1
Phenol red	6.8–8.4	7.81§	Y–R	1
Cresol purple	7.6–9.2		Y–P	1
Phenolphthalein	8.3–10.0		C–R	1
Thymolphthalein	9.3–10.5		C–B	1
Alizarin yellow GG	10–12		C–Y	2

13B STANDARD SOLUTIONS

Standard solutions play a central role in all titrimetric methods of analysis. Therefore, we need to consider the desirable properties for such solutions, how they are prepared, and how their concentrations are expressed. The ideal standard solution for a titrimetric method will

1. be sufficiently stable so that it is necessary to determine its concentration only once;
2. react rapidly with the analyte so that the time required between additions of reagent is minimized;
3. react more or less completely with the analyte so that satisfactory end points are realized; and
4. undergo a selective reaction with the analyte that can be described by a balanced equation.

A primary standard: is an **ultrapure compound** that serves as the reference material for a titrimetric method of analysis.

A primary standard should fulfill these requirements:

1. It should be *100.00% pure*, although 0.01 to 0.02% impurity is tolerable if it is accurately known.
2. It should be *stable to drying temperatures*, and it should be stable indefinitely at room temperature. The primary standard is always dried before weighing.³
3. It should be *readily available* and fairly inexpensive.
4. Although not necessary, it should have a *high formula weight*. This is so that a relatively large amount of it will have to be weighed to get enough to titrate. The relative error in weighing a greater amount of material will be smaller than that for a small amount.
5. If it is to be used in titration, it should possess the *properties required for a titration* listed above. In particular, the equilibrium of the reaction should be far to the right so that a very sharp end point will be obtained.

A secondary standard: is a compound whose **purity has been established by chemical analysis** and that serves as the **reference material for a titrimetric method of analysis**.

In a standardization, the concentration of a volumetric solution is determined by titrating it against a carefully measured quantity of a primary or secondary standard or an exactly known volume of another standard solution.

The requirements of a titration are as follows:

1. The reaction must be **stoichiometric**. That is, there must be a well-defined and known reaction between the analyte and the titrant. In the titration of acetic acid in vinegar with sodium hydroxide, for example, a well-defined reaction takes place:



2. The reaction should be *rapid*. Most ionic reactions, as above, are very rapid.
3. There should be *no side reactions*, and the reaction should be specific. If there are interfering substances, these must be removed. In the above example, there should be no other acids present.

4. There should be a *marked change in some property of the solution when the reaction is complete*. This may be a change in color of the solution or in some electrical or other physical property of the solution. In the titration of acetic acid with sodium hydroxide, there is a marked increase in the pH of the solution when the reaction is complete. A color change is usually brought about by addition of an **indicator**, whose color is dependent on the properties of the solution, for example, the pH.
5. The point at which an equivalent or stoichiometric amount of titrant is added is called the **equivalence point**. The point at which the reaction is *observed* to be complete is called the **end point**, that is, when a change in some property of the solution is detected. The end point should coincide with the equivalence point or be at a reproducible interval from it.
6. The reaction should be **quantitative**. That is, the equilibrium of the reaction should be far to the right so that a sufficiently *sharp* change will occur at the end point to obtain the desired accuracy. If the equilibrium does not lie far to the right, then there will be gradual change in the property marking the end point (e.g., pH) and this will be difficult to detect precisely.

Titer or Chemical Factor:

titer is the weight of analyte that is chemically equivalent to 1 mL of the titrant, usually expressed in milligrams. For example, if a potassium dichromate solution has a titer of 1.267 mg Fe, each milliliter potassium dichromate will react with 1.267 mg iron, and the weight of iron titrated is obtained by simply multiplying the volume of titrant used by the titer. The titer can be expressed in terms of any form of the analyte desired, for example, milligrams FeO or Fe₂O₃.

**Titer = milligrams analyte that react
with 1 mL of titrant.**



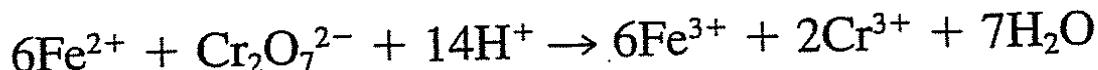
Titer of A = Molarity of T(mmole / ml) x mole ratio(mmole A / mmole T) x M.WT (A)

Example 5.37

A standard solution of potassium dichromate contains 5.442 g/L. What is its titer in terms of milligrams Fe_3O_4 ?

Solution

The iron is titrated as Fe^{2+} and each $\text{Cr}_2\text{O}_7^{2-}$ will react with 6 Fe^{2+} or the iron from $2\text{Fe}_3\text{O}_4$:



The molarity of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution is

$$M_{\text{Cr}_2\text{O}_7^{2-}} = \frac{\text{g/L}}{\text{f wt}_{\text{K}_2\text{Cr}_2\text{O}_7}} = \frac{5.442 \text{ g/L}}{294.19 \text{ g/mol}} = 0.01850 \text{ mol/L}$$

Therefore the titer is

$$\begin{aligned} 0.01850 & \left(\frac{\text{mmol K}_2\text{Cr}_2\text{O}_7}{\text{mL}} \right) \times \frac{2}{1} \left(\frac{\text{mmol Fe}_3\text{O}_4}{\text{mmol K}_2\text{Cr}_2\text{O}_7} \right) \times 231.54 \left(\frac{\text{mg Fe}_3\text{O}_4}{\text{mmol Fe}_3\text{O}_4} \right) \\ & = 8.567 \text{ mg Fe}_3\text{O}_4/\text{mL K}_2\text{Cr}_2\text{O}_7 \end{aligned}$$

Titration Curve

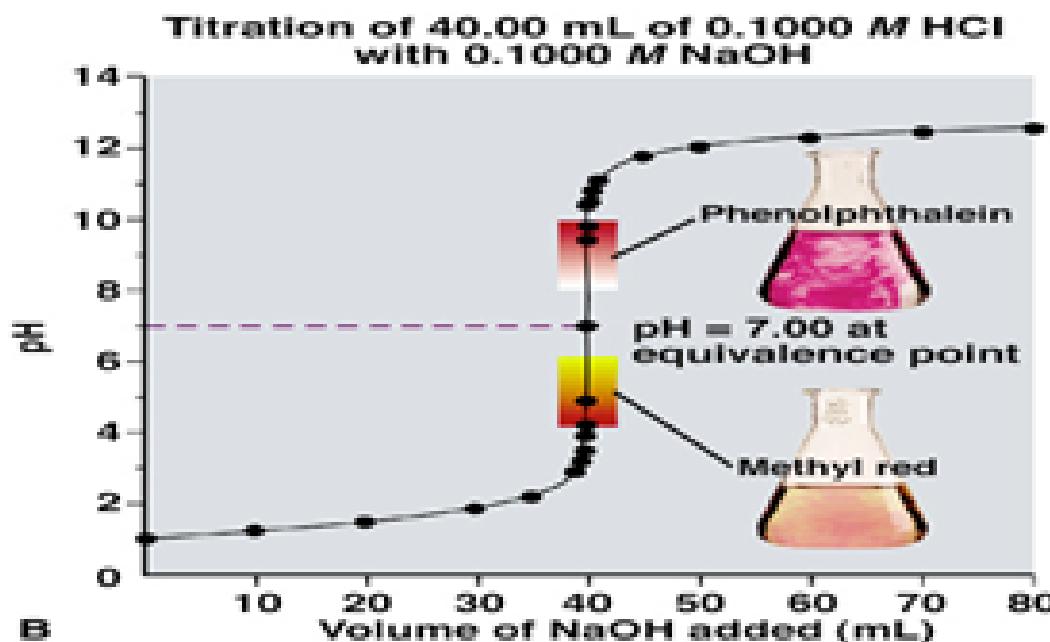
A titration curve is a plot of pH vs. the amount of titrant added. Typically the titrant is a strong (completely) dissociated acid or base. Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.

Martin S. Silbergberg, Chemistry: The Molecular Nature of Matter and Change, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

Strong Acid-Base Titration Curve

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

A



ACID—BASE TITRATIONS

Strong Acid versus Strong Base—The Easy Titrations

In the case of a strong acid versus a strong base, both the titrant and the analyte are completely ionized. An example is the titration of hydrochloric acid with sodium hydroxide:



Example 8.1

Calculate the pH at 0, 10, 90, 100, and 110% titration for the titration of 50.0 mL of 0.100 *M* HCl with 0.100 *M* NaOH.

Solution

At 0% $\text{pH} = -\log 0.100 = 1.00$

At 10%, 5.0 mL NaOH is added. We start with $0.100 \text{ M} \times 50.0 \text{ mL} = 5.00 \text{ mmol H}^+$. Calculate the concentration of H^+ after adding the NaOH:

$$\begin{array}{lcl} \text{mmol H}^+ \text{ at start} & & = 5.00 \text{ mmol H}^+ \\ \text{mmol OH}^- \text{ added} = 0.100 \text{ M} \times 5.0 \text{ mL} & = \underline{\underline{0.500 \text{ mmol OH}^-}} \\ \text{mmol H}^+ \text{ left} & & = 4.50 \text{ mmol H}^+ \text{ in } 55.0 \text{ mL} \end{array}$$

$$[\text{H}^+] = 4.50 \text{ mmol}/55.0 \text{ mL} = 0.0818 \text{ M}$$

$$\text{pH} = -\log 0.0818 = 1.09$$

At 90%

$$\begin{array}{ll} \text{mmol H}^+ \text{ at start} & = 5.00 \text{ mmol H}^+ \\ \text{mmol OH}^- \text{ added} = 0.100 M \times 45.0 \text{ mL} & = \frac{4.50 \text{ mmol OH}^-}{\text{mmol H}^+ \text{ left}} \\ & = 0.50 \text{ mmol H}^+ \text{ in } 95.0 \text{ mL} \end{array}$$

$$[\text{H}^+] = 0.00526 M$$

$$\text{pH} = -\log 0.00526 = 2.28$$

At 100%: All the H^+ has been reacted with OH^- , and we have a $0.0500 M$ solution of NaCl. Therefore, the pH is 7.00.

At 110%: We now have a solution consisting of NaCl and excess added NaOH.

$$\text{mmol OH}^- = 0.100 M \times 5.00 \text{ mL} = 0.50 \text{ mmol OH}^- \text{ in } 105 \text{ mL}$$

$$[\text{OH}^-] = 0.00476 M$$

$$\text{pOH} = -\log 0.00476 = 2.32; \text{pH} = 11.68$$

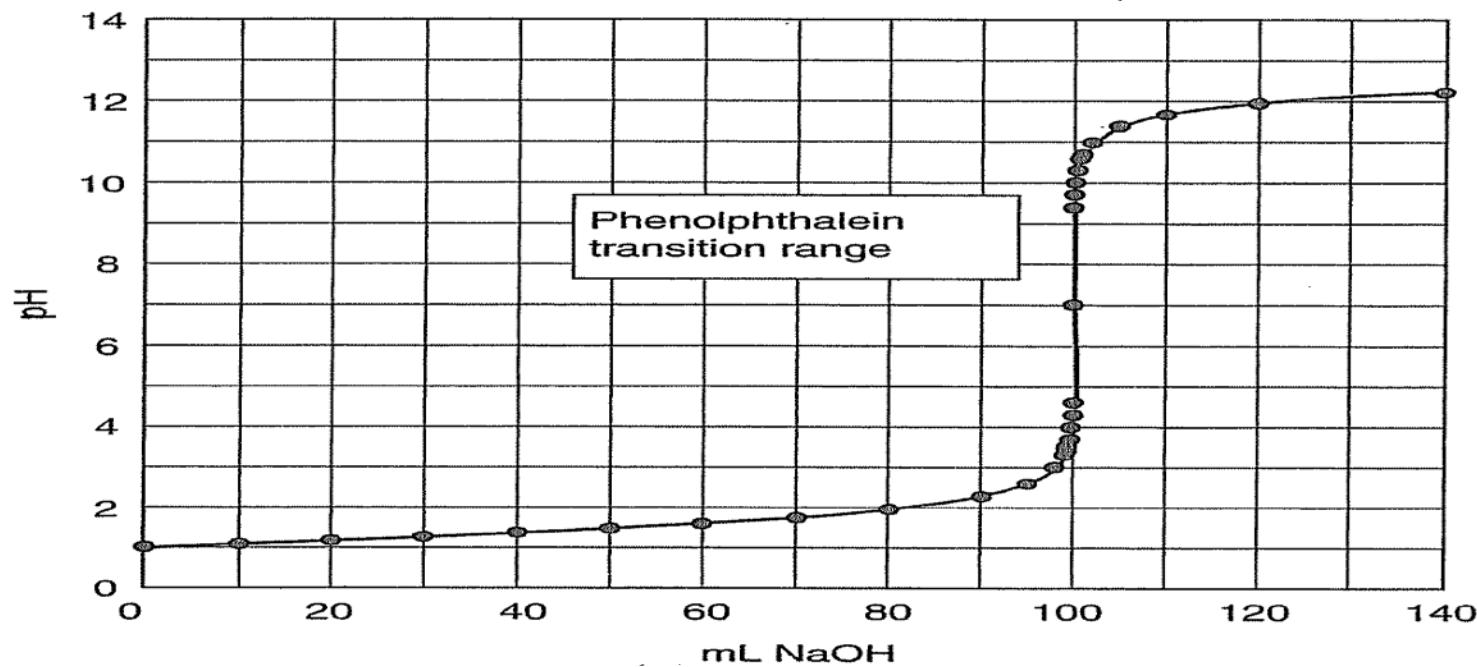


Fig. 8.1. Titration curve for 100 mL of 0.1 *M* HCl versus 0.1 *M* NaOH.

Table 8.1

Equations Governing a Strong-Acid (HX) or Strong-Base (BOH) Titration

Fraction F Titrated	Strong Acid		Strong Base	
	Present	Equation	Present	Equation
$F = 0$	HX	$[H^+] = [HX]$	BOH	$[OH^-] = [BOH]$
$0 < F < 1$	$HX X^-$	$[H^+] = [\text{remaining HX}]$	BOH/B^+	$[OH^-] = [\text{remaining BOH}]$
$F = 1$	X^-	$[H^+] = \sqrt{K_w}$ (Eq. 7.13)	B^+	$[H^+] = \sqrt{K_w} [Eq. 7.13]$
$F > 1$	OH^-/X^-	$[OH^-] = [\text{excess titrant}]$	H^+/B^+	$[H^+] = [\text{excess titrant}]$

EXAMPLE 14-1

Generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH.

Titrating a Strong Base with a Strong Acid

Titration curves for strong bases are derived in an analogous way to those for strong acids. Short of the equivalence point, the solution is highly basic, the hydroxide ion concentration being numerically related to the analytical molarity of the base. The solution is neutral at the equivalence point and becomes acidic in the region beyond the equivalence point; then the hydronium ion concentration is equal to the analytical concentration of the excess strong acid.

EXAMPLE 14-2

Calculate the pH during the titration of 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl after the addition of the following volumes of reagent: (a) 24.50 mL, (b) 25.00 mL, (c) 25.50 mL.

- (a) At 24.50 mL added, $[\text{H}_3\text{O}^+]$ is very small and cannot be computed from stoichiometric considerations but can be obtained from $[\text{OH}^-]$

$$[\text{OH}^-] = c_{\text{NaOH}} = \frac{\text{original no. mmol NaOH} - \text{no. mmol HCl added}}{\text{total volume of solution}}$$
$$= \frac{50.00 \times 0.0500 - 24.50 \times 0.100}{50.00 + 24.50} = 6.71 \times 10^{-4} \text{ M}$$

$$[\text{H}_3\text{O}^+] = K_w / (6.71 \times 10^{-4}) = 1.00 \times 10^{-14} / (6.71 \times 10^{-4})$$
$$= 1.49 \times 10^{-11} \text{ M}$$

$$\text{pH} = -\log(1.49 \times 10^{-11}) = 10.83$$

(b) This is the equivalence point where $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

$$[\text{H}_3\text{O}^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(1.00 \times 10^{-7}) = 7.00$$

(c) At 25.50 mL added,

$$\begin{aligned} [\text{H}_3\text{O}^+] &= c_{\text{HCl}} = \frac{(25.50 \times 0.100 - 50.00 \times 0.0500)}{75.50} \\ &= 6.62 \times 10^{-4} \text{ M} \end{aligned}$$

$$\text{pH} = -\log(6.62 \times 10^{-4}) = 3.18$$

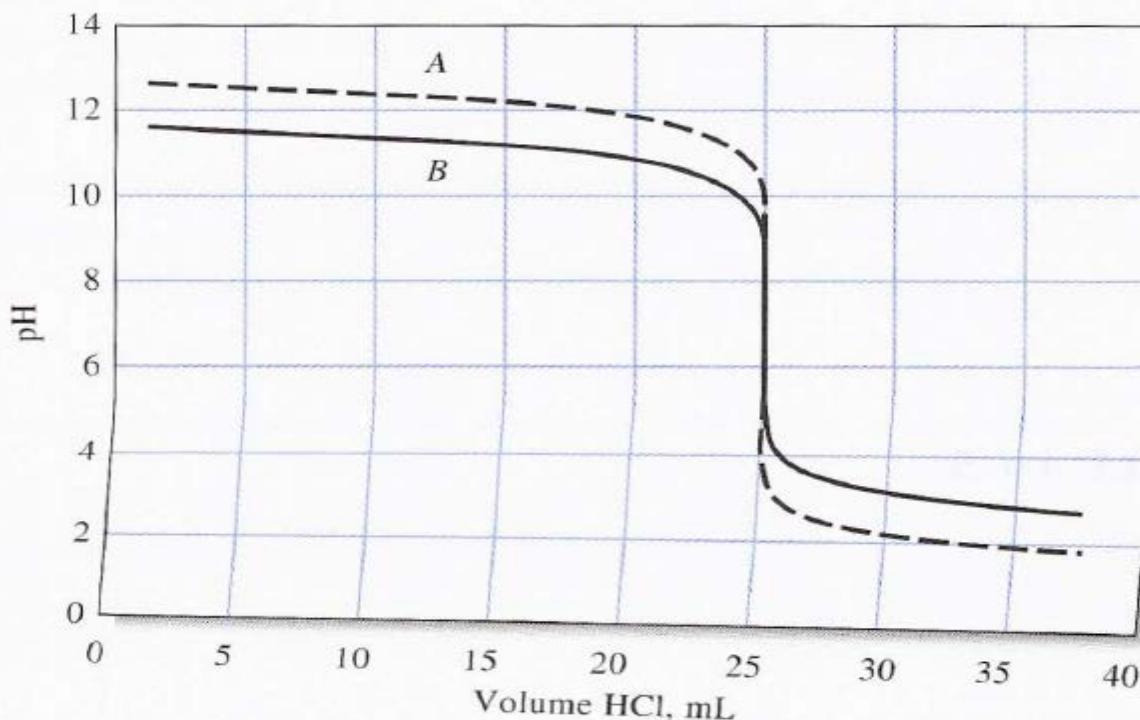


Figure 14-4 Titration curves for NaOH with HCl. Curve A: 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl. Curve B: 50.00 mL of 0.00500 M NaOH with 0.0100 M HCl.

Four distinctly different types of calculations are needed to derive a titration curve for a weak acid (or a weak base):

1. At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that solute and its dissociation constant.
2. After various increments of titrant have been added (in quantities up to, but not including, an equivalent amount), the solution consists of a series of buffers. The pH of each buffer can be calculated from the analytical concentrations of the conjugate base or acid and the residual concentrations of the weak acid or base.
3. At the equivalence point, the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.
4. Beyond the equivalence point, the excess of strong acid or base titrant represses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.

Weak Acid versus Strong Base—A Bit Less Straightforward



Table 8.2

Equations Governing a Weak-Acid (HA) or Weak-Base (B) Titration

Fraction <i>F</i>	Weak Acid			Weak Base	
	Titrated	Present	Equation	Present	Equation
<i>F</i> = 0	HA		$[\text{H}^+] = \sqrt{K_a \cdot C_{\text{HA}}}$ (Eq. 7.20)	B	$[\text{OH}^-] = \sqrt{K_b \cdot C_B}$ (Example 7.8)
$0 < F < 1$	HA/A ⁻		$\text{pH} = \text{p}K_a + \log \frac{C_{\text{A}^-}}{C_{\text{HA}}}$ (Eq. 7.45)	B/BH ⁺	$\text{pH} = (\text{p}K_w - \text{p}K_b) + \log \frac{C_B}{C_{\text{BH}^+}}$ (Eq. 7.56)
<i>F</i> = 1	A ⁻		$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{\text{A}^-}}$ (Eq. 7.32)	BH ⁺	$[\text{H}^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{\text{BH}^+}}$ (Eq. 7.39)
<i>F</i> > 1	OH ⁻ /A ⁻		$[\text{OH}^-] = [\text{excess titrant}]$	H ⁺ /BH ⁺	$[\text{H}^+] = [\text{excess titrant}]$

Example 8.2

Calculate the pH at 0, 10.0, 25.0, 50.0, and 60.0 mL titrant in the titration of 50.0 mL of 0.100 M acetic acid with 0.100 M NaOH.

Solution

At 0 mL, we have a solution of only 0.100 M HOAc:

$$\frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$[H^+] = x = 1.32 \times 10^{-3} M$$

$$pH = 2.88$$

At 10.0 mL, we started with $0.100 M \times 50.0 \text{ mL} = 5.00 \text{ mmol HOAc}$; part has reacted with OH^- and has been converted to OAc^- :

mmol HOAc at start

= 5.00 mmol HOAc

mmol OH^- added = $0.100 M \times 10.0 \text{ mL} = 1.00 \text{ mmol OH}^-$

= mmol OAc^- formed in 60.0 mL

mmol HOAc left

= 4.00 mmol HOAc in 60.0 mL

We have a buffer. Since volumes cancel, use millimoles:

$$pH = pK_a + \log \frac{[\text{OAc}^-]}{[\text{HOAc}]}$$

$$pH = 4.76 + \log \frac{1.00}{4.00} = 4.16$$

At 25.0 mL, one-half the HOAc has been converted to OAc⁻, so pH = pK_a:

$$\begin{array}{ll} \text{mmol HOAc at start} & = 5.00 \text{ mmol HOAc} \\ \text{mmol OH}^- = 0.100 M \times 25.0 \text{ mL} & = \frac{2.50 \text{ mmol OAc}^- \text{ formed}}{\text{mmol HOAc left}} \\ & = 2.50 \text{ mmol HOAc} \end{array}$$

$$\text{pH} = 4.76 + \log \frac{2.50}{2.50} = 4.76$$

At 50.0 mL, all the HOAc has been converted to OAc⁻ (5.00 mmol in 100 mL, or 0.0500 M):

$$\begin{aligned} [\text{OH}^-] &= \sqrt{\frac{K_w}{K_a} [\text{OAc}^-]} \\ &= \sqrt{\frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} \times 0.0500} = 5.35 \times 10^{-6} M \end{aligned}$$

$$\text{pOH} = 5.27 \quad \text{pH} = 8.73$$

At 60.0 mL, we have a solution of NaOAc and excess added NaOH. The hydrolysis of the acetate is negligible in the presence of added OH⁻. So the pH is determined by the concentration of excess OH⁻:

$$\text{mmol OH}^- = 0.100 \text{ M} \times 10.0 \text{ mL} = 1.00 \text{ mmol in } 110 \text{ mL}$$

$$[\text{OH}^-] = 0.00909 \text{ M}$$

$$\text{pOH} = -2.04; \text{pH} = 11.96$$

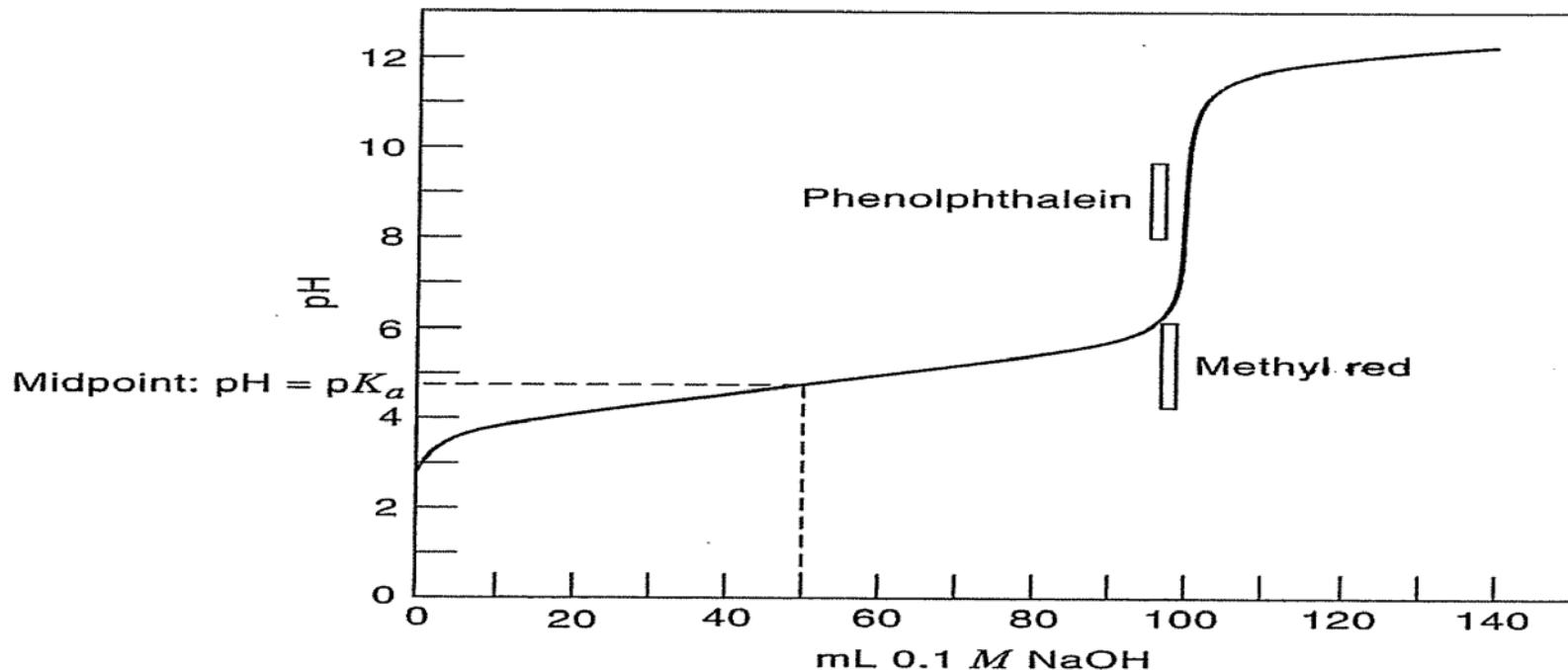


Fig. 8.5. Titration curve for 100 mL 0.1 M HOAc versus 0.1 M NaOH.

EXAMPLE 14-3

Generate a curve for the titration of 50.00 mL of 0.1000 M acetic acid with 0.1000 M sodium hydroxide.

Weak Base versus Strong Acid

The titration of a weak base with a strong acid is completely analogous to the above case, but the titration curves are the reverse of those for a weak acid versus a strong base.

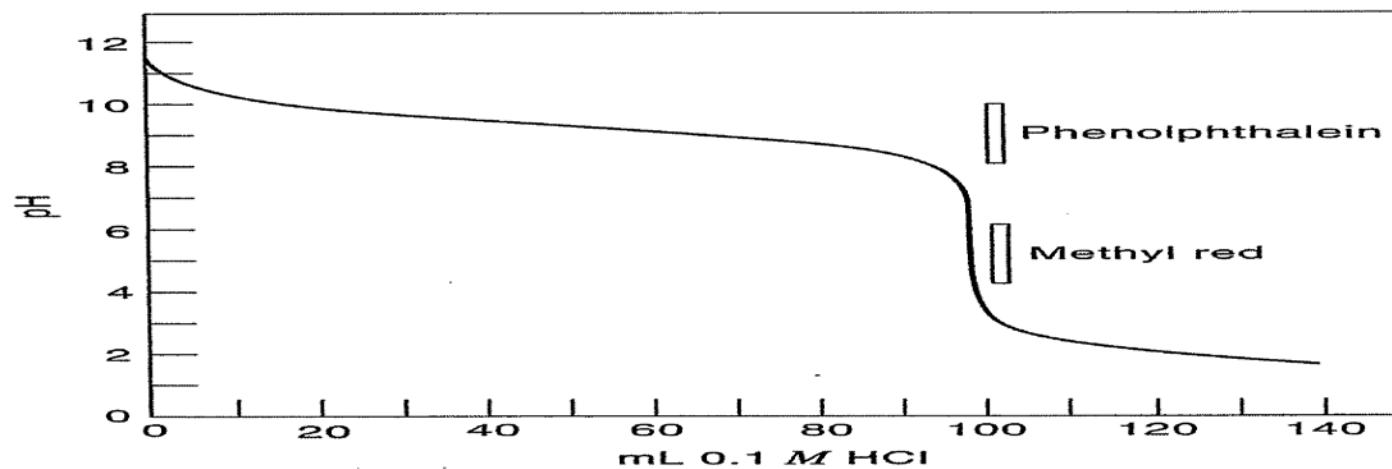
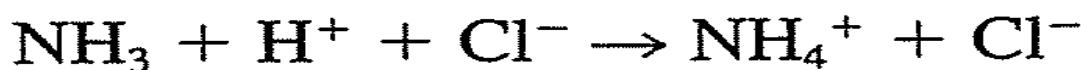


Fig. 8.8. Titration curve for 100 mL $0.1 \text{ M} \text{ NH}_3$ versus $0.1 \text{ M} \text{ HCl}$.

Example: Generate the hypothetical titration curve and calculate the pH for the titration 0.1M from HCl with 25ml (0.1M) Ammonia?

$$K_b = 1.75 \times 10^{-5}$$



a) Before addition HCl ($V=0$ ml)



$$K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$[\text{OH}^-] = [\text{NH}_4^+]$$

$$[\text{OH}^-]^2 = K_b \times 0.1 \\ = 1.75 \times 10^{-5} \times 0.1 = 1.75 \times 10^{-6}$$

$$[\text{OH}^-] = \sqrt{1.75 \times 10^{-6}} = 1.32 \times 10^{-3} \text{ mol/L}$$

$$\text{pOH} = -\log 1.32 \times 10^{-3} = 2.88$$

$$\text{pH} = 14 - 2.88 = 11.12$$

b) Before the equivalent point (V = 10ml from HCl)

After addition 10ml from HCl , ammonium chloride NH₄Cl will formed and excess from ammonia. Which is buffer solution and in this case we can calculate pOH and then pH as.

$$[\text{OH}^-] = K_b \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$[\text{NH}_4^+] = \frac{10 \times 0.1}{25 + 10} = 0.029 \text{ mol/L} = [\text{NH}_4\text{Cl}] \text{ salt}$$

$$[\text{NH}_4\text{OH}] = \frac{25 \times 0.1 - 10 \times 0.1}{25 + 10} = 0.043 \text{ mol/L} = \text{Residual of Ammonia}$$

$$\text{pOH} = 4.76 + \log \frac{0.029}{0.043} = 4.58$$

$$\text{pH} = 14 - 4.58 = 9.42$$

c) At the equivalent point:

Which is mean addition equal volume (25m) from HCl to 25ml(0.1M) Ammonia to form salt of weak base only NH₄Cl and we can calculate the pH to the salt of weak base as.

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

$$[NH_4^+] \approx [NH_4^+] = \frac{25 \times 0.1}{25 + 25} = 0.05 \text{ mol/L}$$

$$\begin{aligned} pH &= \frac{1}{2} \times 14 - \frac{1}{2} \times 4.79 - \frac{1}{2} \log 0.05 \\ &= 7 - 2.38 + 0.65 = 5.25 \end{aligned}$$

d) Post equivalent point:

This case mean addition from HCl, like addition 26ml. We can calculate the pH from the excess of HCl as.

$$[H^+] = \frac{26 \times 0.1 - 25 \times 0.1}{25 + 26} = 2 \times 10^{-3} \text{ mol/L} \quad pH = -\log 2 \times 10^{-3} = 2.71$$

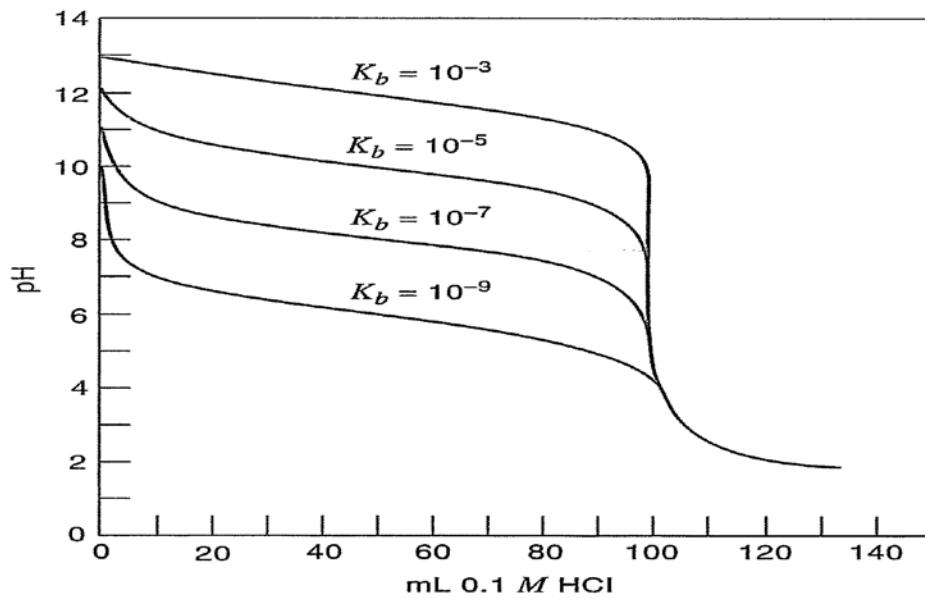
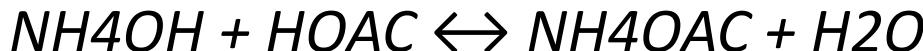


Fig. 8.9. Titration curves for 100 mL 0.1 *M* weak bases of different K_b values versus 0.1 *M* HCl.

- 14-42.** Calculate the pH after addition of 0.00, 5.00, 15.00, 25.00, 40.00, 45.00, 49.00, 50.00, 51.00, 55.00, and 60.00 mL of 0.1000 M HCl in the titration of 50.00 mL of
 *(a) 0.1000 M ammonia.
- 14-38.** A 50.00-mL aliquot of 0.1000 M NaOH is titrated with 0.1000 M HCl. Calculate the pH of the solution after the addition of 0.00, 10.00, 25.00, 40.00, 45.00, 49.00, 50.00, 51.00, 55.00, and 60.00 mL of acid, and prepare a titration curve from the data.

Weak acid versus Weak base:

In this type of titration the change in the pH at the equivalent point is very small, no suitable simple indicator is used to determine the eq.point.



Example: Titration 0.1M NH₄OH with 50ml(0.1M) CH₃COOH.

a) Before the addition of NH₄OH.

$$\begin{aligned}\text{pH} &= \frac{1}{2} \text{ pK}_a = \frac{1}{2} \log [\text{acid}] \\ &= \frac{1}{2} \times 4.74 = \frac{1}{2} \log [10^{-1}] \\ &= 2.37 + 0.5 = 2.87\end{aligned}$$

b) After addition 10ml NH₄OH.

Buffer solution from HOAc/ OAC- will formed.



$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$[\text{salt}] = \frac{10 \times 0.1}{50 + 10} = 0.017 \text{ mol/L}$$

$$[\text{acid}] = \frac{50 \times 0.1 - 10 \times 0.1}{50 + 10} = 0.067 \text{ mol/L}$$

$$\text{pH} = 4.74 + \log \frac{0.017}{0.067} = 4.14$$

c) At the equivalent point, addition 50ml from NH₄OH, and Ammonium acetate will formed, salt of both weak acid and weak base.

$$\begin{aligned}\text{pH} &= \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b \\ &= 7.0\end{aligned}$$

d) Post equivalent point , after addition 60ml from ammonia. That is mean another buffer solution will form that produce all HOAc were convert to Ammonium acetate , and the excess of ammonia.

$$\text{pH} = \text{pK}_w - \text{pK}_b - \log \frac{[\text{salt}]}{[\text{base}]}$$

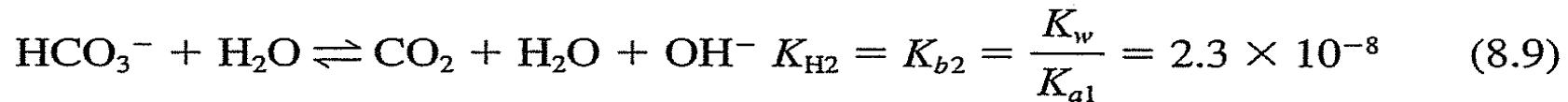
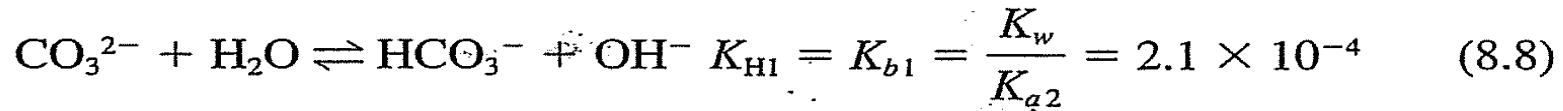
$$[\text{salt}] = \frac{50 \times 0.1}{50 + 60} = 0.045 \text{ mol/L}$$

$$[\text{base}] = \frac{60 \times 0.1 - 50 \times 0.1}{50 + 60} = 9.1 \times 10^{-3} \text{ mol/L}$$

$$\text{pH} = 14 - 4.75 - \log \frac{0.045}{9.1 \times 10^{-3}} = 7.56$$

Titration of Sodium Carbonate—A Diprotic Base

- 1- Sodium carbonate is a Brønsted base that is used as a primary standard for the standardization of strong acids. It hydrolyzes in two steps:



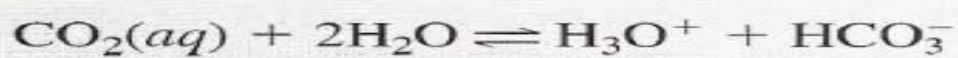
$$K_b 1 = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

- 2- *K_b values should differ by at least 10⁴ to obtain good separation of the equivalence point breaks in a case such as this.*

3-where K_{a1} and K_{a2} refer to the K_a values of H_2CO_3 ; HCO_3^- is the conjugate acid of CO_3^{2-} and H_2CO_3 is the conjugate acid of HCO_3^-

$$K_{a2} = K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

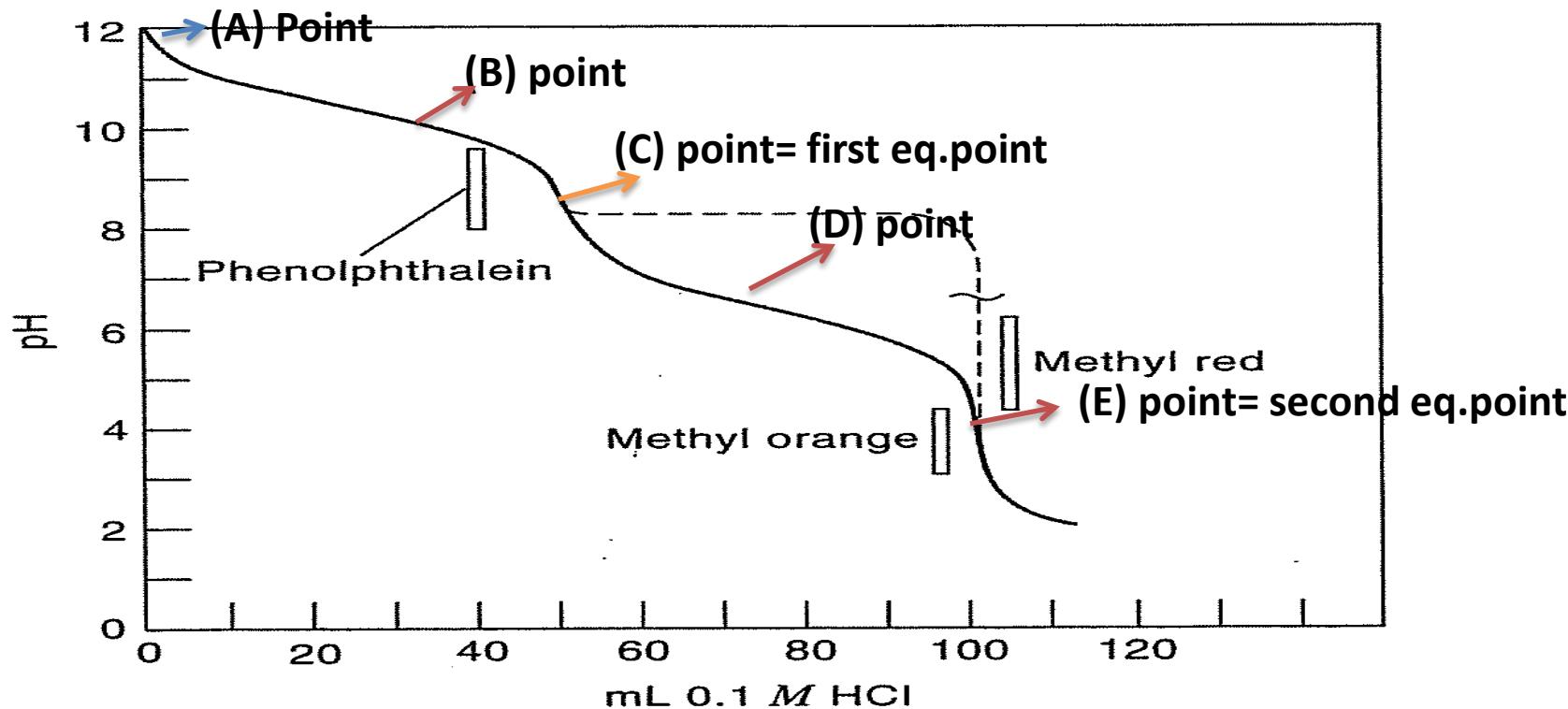
$$K_{a1} = K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2(aq)]}$$
$$= 4.2 \times 10^{-7}$$

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$
$$= 4.69 \times 10^{-11}$$

4- A titration curve for Na_2CO_3 versus HCl is shown in Figure 8.10 (solid line).



(A) point: before any addition(at 0.0ml volume from HCl)

In this case we have only sodium carbonate CO_3^{2-} and the pH is determined from the hydrolysis of Bronsted base as:

$$K_{\text{b}1} = \frac{[\text{HCO}_3^-] [\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

$$[\text{HCO}_3^-] = [\text{OH}^-]$$

$$\frac{10^{-14}}{5 \times 10^{-11}} = \frac{[\text{OH}^-]^2}{0.1} \quad [\text{OH}^-] = 4.5 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.34$$

$$\text{pH} = 14 - \text{pOH} = 11.7$$

(B) point: After addition 25ml HCl:

In this case a part from carbonate CO_3^{2-} is converted to HCO_3^- and $\text{CO}_3^{2-}/\text{HCO}_3^-$ buffer region is established.

$$K_{\text{a}2} = \frac{[\text{H}_3\text{O}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\text{CO}_3^{2-} = (50-25) \times 0.1 / VT(75\text{ml}) = 2.5 \text{ mmole} / 75\text{ml}$$

$$\text{HCO}_3^- = 25 \times 0.1 / Vt(75\text{ml}) = 2.5\text{mmole}/75\text{ml}$$

$$[\text{H}^+] = 4.69 \times 10^{-11} \quad \text{pH} = 10.32$$

(C) point: first eq.point(addition 50ml HCl):

In this case all were CO_3^{2-} -converted to HCO_3^- and we calculate the pH for mono-protanted salt HCO_3^- from K_{a1} and K_{a2} as.

$$\text{CO}_3^{2-} = (50-50) \times 0.1 / Vt(100\text{ml}) = 0.0\text{mmole}/100\text{ml}$$

$$\text{HCO}_3^- = 50 \times 0.1 / Vt(100\text{ml}) = 5\text{mmole} / 100\text{ml}$$

$$[\text{H}^+] = \sqrt{K_1 K_2} \quad [\text{H}^+] \approx \sqrt{K_{a1} K_{a2}}.$$

$$\text{pH} = 8.3$$

(D) point: After first eq.point (addition 75ml HCl):

Beyond the first equivalence point, the HCO_3^- is partially converted to $\text{H}_2\text{CO}_3(\text{CO}_2)$ and a second buffer region is established, the pH being established by $[\text{HCO}_3^-]/[\text{CO}_2]$.

$$\text{HCO}_3^- = 50 \times 0.1 / Vt(125\text{ml}) = 5\text{mmole} / 125\text{ml} \quad \text{will formed}$$

$$\text{HCO}_3^- = (50 - 25) \times 0.1 \text{ M} / 125\text{ml} = 2.5\text{mmole} / 125\text{ml} \quad \text{residual concentration}$$

H_2CO_3 (= 25 x 0.1 / Vt) = 2.5 mmole / 125ml will formed from

$$K_a = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$[\text{H}_3\text{O}^+] = 4.2 \times 10^{-7} \quad \text{pH} = 6.37$$

(E) point: second eq.point(addition 100ml HCl):

At the second equivalence point (E) the pH is determined by the extent of dissociation of carbonic acid, the principal species present, and $[\text{H}^+]$ is calculated from Equation.

$$K_{a1} = K_1 = \frac{[\text{H}_3\text{O}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.2 \times 10^{-7}$$

$$[\text{H}_2\text{CO}_3] = 50 \times 0.1 / Vt(150\text{ml}) = 0.0333$$

$$4.2 \times 10^{-7} = \frac{[\text{H}^+] [\text{HCO}_3^-]}{(0.1) [50/(50 + 100)]} = \frac{[\text{H}^+]^2}{0.033}$$

$$[\text{H}^+] = 1.177 \times 10^{-4} \text{ M} \quad \text{pH} = 3.92$$

Important notes:

- 1- Phenolphthalein is used to detect the first end point, and methyl orange is used to detect the second one.
- 2- Neither end point, however, is very sharp.
- 3- phenolphthalein is colorless beyond the first end point and does not interfere.
- 4- The second equivalence point, which is used for accurate titrations, is normally not very accurate with methyl orange indicator because of the gradual change in the color of the methyl orange. This is caused by the gradual decrease in the pH due to the $\text{HCO}_3^-/\text{CO}_2$ buffer system beyond the first end point.
- 5- If beyond the first equivalence point we were to boil the solution after each addition of HCl to remove the CO_2 from the solution, the buffer system of $\text{HCO}_3^-/\text{CO}_2$ would be removed, leaving only HCO_3^- in solution.

Titration of Polyprotic Acids

- 1-** Compounds with two or more acid functional groups yield multiple end points in a titration provided that the functional groups differ sufficiently in strength as acids.
For example of diprotic acids are H₂A, H₃PO₄, Malonic acid = HOOC-CH₂-COOH
And maleic acid, HOOC-CH=CH-COOH
- 2-** In order to obtain good end point breaks for titration of the first proton, K_{a1} should be at least $10^4 \times K_{a2}$.
- 3-** If this ratio is smaller, the error becomes excessive, particularly in the region of the first equivalence point, and a more rigorous treatment of the equilibrium relationships is required.
- 4-** Two indicators must be used to detect the equivalent points in the titration of diprotic acid H₂A with sodium hydroxide NaOH.

5- Figure 8.12 illustrates the titration curve for a diprotic acid H_2A , and Table 8.3 summarizes the equations governing the different portions of the titration curve.

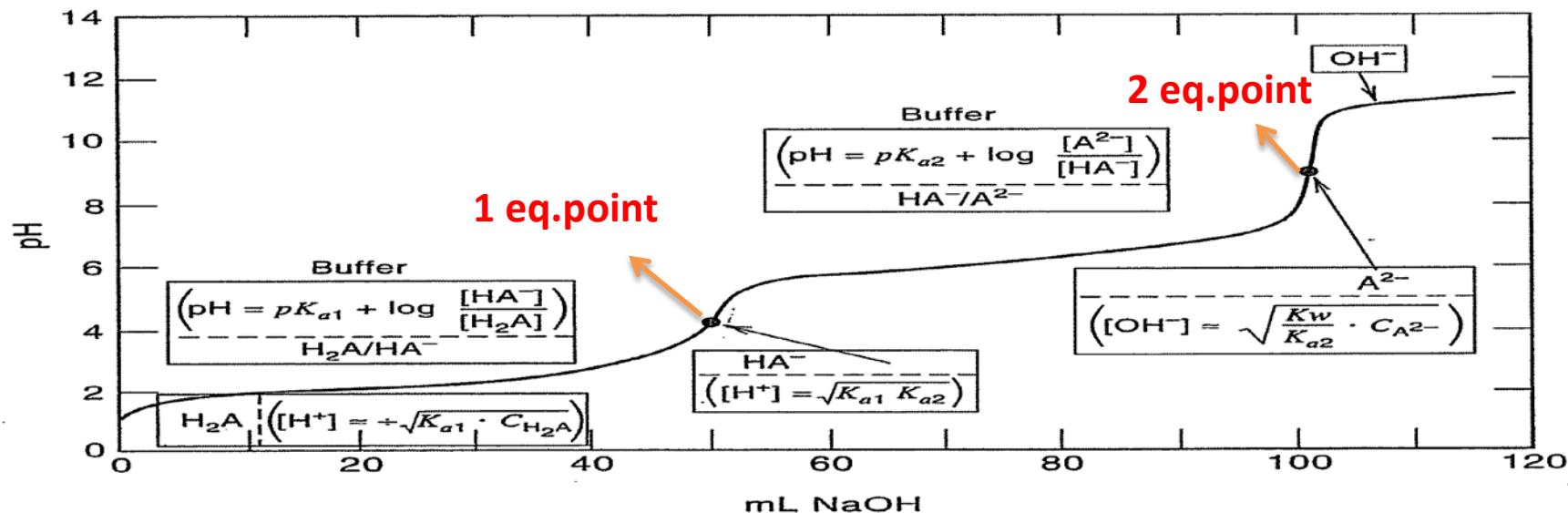
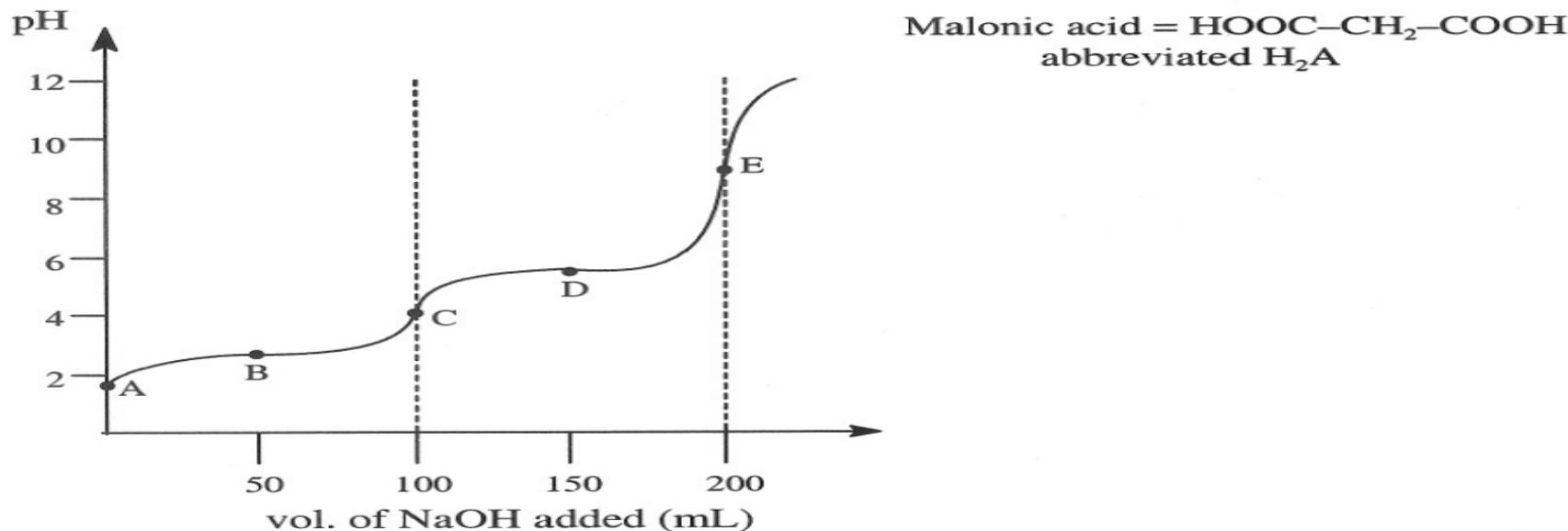


Table 8.3
Equations Governing Diprotic Acid (H_2A) Titration

Fraction F Titrated	Present	Equation
$F = 0$ (0%)	H_2A	$[\text{H}^+] \approx \sqrt{K_{a1} C_{\text{H}_2\text{A}}}$ (Example 7.7) (or Eq. 7.20; Ex. 7.17, quadratic, if \sim strong acid)
$0 < F < 1$ (>0 to <100%)	$\text{H}_2\text{A}/\text{HA}^-$	$\text{pH} = \text{p}K_{a1} + \log \frac{C_{\text{HA}^-}}{C_{\text{H}_2\text{A}}}$ (Eq. 7.45) (or $C_{\text{HA}^-} + [\text{H}^+]$ and $C_{\text{H}_2\text{A}} - [\text{H}^+]$ if a strong acid)
$F = 1$ (100%) (1st eq. pt.)	HA^-	$[\text{H}^+] \approx \sqrt{K_{a1} K_{a2}}$ (Eq. 7.84) (or Eq. 7.83 if H_2A \sim strong acid)
$1 < F < 2$ (>100 to <200%)	$\text{HA}^-/\text{A}^{2-}$	$\text{pH} = \text{p}K_{a2} + \log \frac{C_{\text{A}^{2-}}}{C_{\text{HA}^-}}$ (Eq. 7.45, Ex. 7.16, 7.22)
$F = 2$ (200%) (2nd eq. pt.)	A^{2-}	$[\text{OH}^-] \approx \sqrt{\frac{K_w}{K_{a2}}} \cdot C_{\text{A}^{2-}}$ (Eq. 7.32) (or Eq. 7.29, Ex. 7.19, quadratic if A^{2-} \sim strong base)
$F > 2$ (>200%)	$\text{OH}^-/\text{A}^{2-}$	$[\text{OH}^-] = [\text{excess titrant}]$

Example:

When 100.0 mL of 0.10 M malonic acid is titrated with 0.10 M NaOH the following titration curve is observed:



Given that $K_{a_1} = 1.5 \times 10^{-3}$ and $K_{a_2} = 2.0 \times 10^{-6}$ for malonic acid, answer the following questions:

- A. Write out the reactions and the equilibrium expressions associated with K_{a_1} and K_{a_2} .
- B. Calculate the pH at:
- 1) point A (pH = 1.94)
 - 2) point B
 - 3) point C
 - 4) point D
 - 5) point E

Solution



$$K_{a1} = \frac{[\text{H}^+][\text{HOOCCH}_2\text{COO}^-]}{[\text{HOOCCH}_2\text{COOH}]} = 1.5 \times 10^{-3}$$



$$K_{a2} = \frac{[\text{H}^+][\text{OOCCH}_2\text{COO}^{2-}]}{[\text{HOOCCH}_2\text{COO}^-]} = 2.0 \times 10^{-6}$$

B. Point A: 100 mL of 0.10 M H_2A (Addition 0.0ml from NaOH)

	H_2A	\rightleftharpoons	H^+	$+$	HA^-	$K_{a1} = 1.5 \times 10^{-3}$
I	0.10 M		0		0	
C	-x		+x		+x	
E	0.10 - x		x		x	

$$K_{a1} = 1.5 \times 10^{-3} = \frac{x^2}{0.10 - x}$$

The 5% rule fails. $x = 1.15 \times 10^{-2} \text{ M}$ by successive approximations.

Ignore the amount of $[\text{H}^+]$ released by 2nd dissociation (it will be negligible).

$$\text{pH} = -\log(1.15 \times 10^{-2}) = 1.94$$

Point B: halfway to first equivalence point where $[H_2A] = [HA^-]$

$$pH = pK_{a1} = -\log (1.5 \times 10^{-3}) = 2.82$$

(After addition 50ml from NaOH), in this case the solution contains both HA- and H₂A which is buffer solution:

$$[HA^-] = 50 \times 0.1 / V_t(150\text{ml}) = 0.033\text{Molar}$$

$$[H_2A] = (100 - 50) \times 0.1 / V_t(150\text{ml}) = 0.033\text{M}$$

$$[HA^-] = [H_2A]$$

$$pH = pK_{a1} + \log HA^- / H_2A \quad pH = pK_{a1} = 2.82$$

Point C: first equivalence point

(After addition 100ml from NaOH)

Major species is HA⁻ which is both an acid

and a base (amphoteric species).

$$pH = \frac{pK_{a1} + pK_{a2}}{2} = \frac{2.82 + 5.70}{2} = 4.26$$

In this case all H₂A was converted to HA-, which is **mono-protic salt** and we can calculate the pH from the above law or .

$$[H^+] \approx \sqrt{K_{a1}K_{a2}}.$$

Point D: halfway to second equivalence point where $[HA^-] = [A^{2-}]$.

$$pH = pK_{a2} = -\log K_{a2} = -\log (2.0 \times 10^{-6}) = 5.70$$

After addition 150ml from NaOH, in this case 100ml from NaOH will convert all H₂A to HA⁻, and the other 50ml will convert an equal amount from HA⁻ to A²⁻. Which is buffer solution contains A²⁻ / HA⁻ and we can calculate the pH as:

$$[HA^-] \text{ formed} = 100\text{ml} \times 0.1 / Vt(250\text{ml}) = 0.04M$$

$$[HA^-] \text{ remaining or residual} = (100 - 50) \times 0.1 / Vt(250\text{ml}) = 0.02M$$

$$[A^{2-}] \text{ formed} = 50 \times 0.1 / Vt(250\text{ml}) = 0.02M$$

$$[HA^-] = [A^{2-}]$$

$$pH = pK_{a2} + \log [A^{2-}] / [HA^-] = 5.70$$

Point E: second equivalence point; only A²⁻ present (a weak base).

	A ²⁻ + H ₂ O ⇌ HA ⁻ + OH ⁻	K _b = K _w /K _{a2} = 5.0 × 10 ⁻⁹
I	10 mmol/300 mL	0
C	-x	+x
E	0.033 M - x	x

$$5.0 \times 10^{-9} = \frac{x^2}{0.033 - x} \approx \frac{x^2}{0.033}$$

$$x = 1.3 \times 10^{-5} M = [OH^-]$$

Check assumption: $\frac{1.3 \times 10^{-5}}{0.033} \times 100\% = 0.04\% < 5\%$ so assumption good

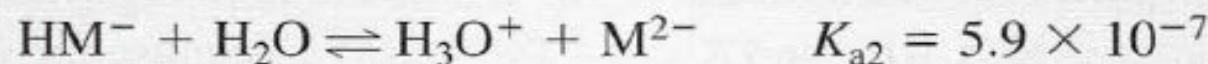
$$pOH = -\log [OH^-] = 4.89$$

$$pH = 14.00 - pOH = 9.11$$

EXAMPLE 15-9

Construct a curve for the titration of 25.00 mL of 0.1000 M maleic acid, HOOC—CH=CH—COOH, with 0.1000 M NaOH.

Symbolizing the acid as H₂M, we can write the two dissociation equilibria as

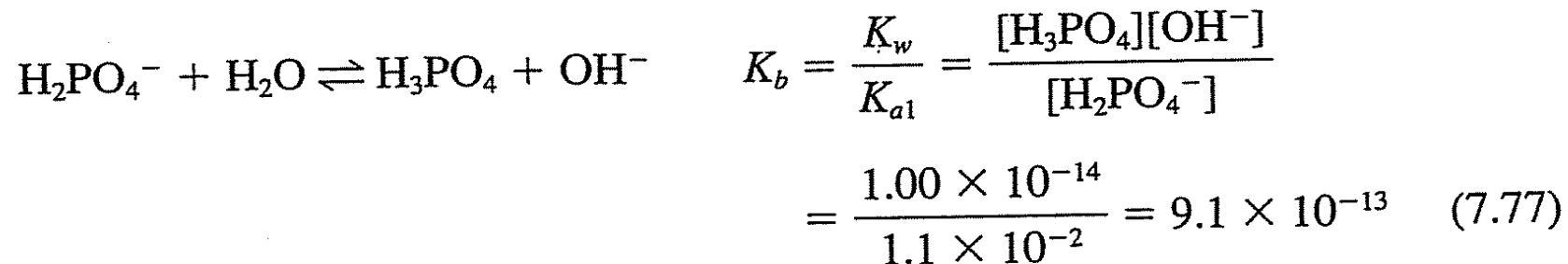
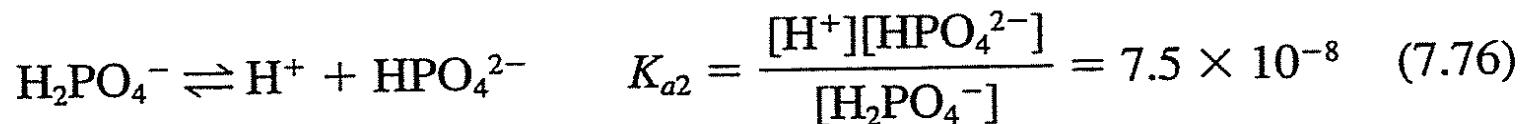


After addition : 0.0ml , 5ml, 24.9ml, 25ml(first eq.point), 25.01ml , 25.5ml , 49.9ml and 50ml(second eq.point) from NaOH.

SALTS OF POLYPROTIC ACIDS—ACID OR BASE?

Salts of acids such as H_3PO_4 may be acidic or basic. The protonated salts possess both acidic and basic properties (H_2PO_4^- , HPO_4^{2-}), while the unprotonated salt is simply a Brønsted base that hydrolyzes (PO_4^{3-}).

1. Amphoteric Salts. H_2PO_4^- possesses both acidic and basic properties. That is, it is amphoteric. It ionizes as a weak acid and it also is a Brønsted base that hydrolyzes:



The solution could, hence, be either alkaline or acidic, depending on which ionization is more extensive. Since K_{a2} for the first ionization is nearly 10^5 greater than K_b for the second ionization, the solution in this case will obviously be acidic.

An expression for the hydrogen ion concentration in a solution of an ion such as H_2PO_4^- can be obtained as follows.

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a2}c_{\text{NaHA}} + K_w}{1 + c_{\text{NaHA}}/K_{a1}}}$$

So when:

1- If $\frac{C_{\text{HA}^-}}{K_{a1}} \gg 1$, $K_{a2}C_{\text{NaHA}} \gg K_w$

$$[\text{H}_3\text{O}^+] \approx \sqrt{K_{a1}K_{a2}}$$

2- If $K_{a2} \times C_{\text{HA}^-} \gg K_w$ K_w is negligible

and $[\text{HA}^-] / K_{a1} \leq 1$...is not negligible

$$[H^+] = \sqrt{\frac{C_{\text{HA}^-} \times K_{a2}}{1 + \frac{C_{\text{HA}^-}}{K_{a1}}}}$$

**3- If $K_{a2} \times [HA^-] \leq K_w$ K_w is not negligible
and $[HA^-] / K_{a1} >> 1$ 1 is negligible**

$$[H^+] = \sqrt{\frac{C_{HA^-} \times K_{a2} + K_w}{\frac{C_{HA^-}}{K_{a1}}}}$$

EXAMPLE 15-6

Calculate the hydronium ion concentration of a 1.00×10^{-3} M Na_2HPO_4 solution.

The pertinent dissociation constants are K_{a2} and K_{a3} , which both contain $[\text{HPO}_4^{2-}]$. Their values are $K_{a2} = 6.32 \times 10^{-8}$ and $K_{a3} = 4.5 \times 10^{-13}$. Considering again the assumptions that led to Equation 15-16, we find that $(1.0 \times 10^{-3})/(6.32 \times 10^{-8})$ is much larger than 1, so that the denominator can be simplified. The product $K_{a2}c_{\text{Na}_2\text{HPO}_4}$ is by no means much larger than K_w , however. We therefore use a partially simplified version of Equation 15-15:

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{4.5 \times 10^{-13} \times 1.00 \times 10^{-3} + 1.00 \times 10^{-14}}{(1.00 \times 10^{-3})/(6.32 \times 10^{-8})}} = 8.1 \times 10^{-10} \text{ M}$$

EXAMPLE 15-7

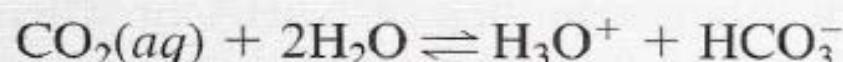
Find the hydronium ion concentration of a 0.0100 M NaH_2PO_4 solution.

The two dissociation constants of importance (those containing $[\text{H}_2\text{PO}_4^-]$) are $K_{\text{a}1} = 7.11 \times 10^{-3}$ and $K_{\text{a}2} = 6.32 \times 10^{-8}$. We see that the denominator of Equation 15-15 cannot be simplified, but the numerator reduces to $K_{\text{a}2}c_{\text{NaH}_2\text{PO}_4}$. Thus, Equation 15-15 becomes

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{6.32 \times 10^{-8} \times 1.00 \times 10^{-2}}{1.00 + (1.00 \times 10^{-2})/(7.11 \times 10^{-3})}} = 1.62 \times 10^{-5} \text{ M}$$

EXAMPLE 15-8

Calculate the hydronium ion concentration of a 0.100 M NaHCO₃ solution. We assume, as we have earlier (page 400), that [H₂CO₃] << [CO₂(aq)] and that the following equilibria describe the system adequately:



$$K_{\text{a}1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]} \\ = 4.2 \times 10^{-7}$$



$$K_{\text{a}2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \\ = 4.69 \times 10^{-11}$$

$$[\text{H}_3\text{O}^+] \approx \sqrt{K_{\text{a}1} K_{\text{a}2}}$$

Clearly, $c_{\text{NaHA}}/K_{\text{a}1}$ in the denominator of Equation 15-15 is much larger than unity; in addition, $K_{\text{a}2}c_{\text{NaHA}}$ has a value of 4.69×10^{-12} , which is substantially greater than K_w . Thus, Equation 15-16 applies, and

$$[\text{H}_3\text{O}^+] = \sqrt{4.2 \times 10^{-7} \times 4.69 \times 10^{-11}} = 4.4 \times 10^{-9}\text{M}$$

Volumetric apparatus

