

Ch. 10: Acid-Base Titrations

Outline:

- 10-1 Titration of Strong Base with Strong Acid
- 10-2 Titration of Weak Acid with Strong Base
- 10-3 Titration of Weak Base with Strong Acid
- 10-4 Titrations in Diprotic Systems
- 10-5 Finding the End Point with a pH Electrode
- 10-6 Finding the End Point with Indicators
- 10-7 Practical Notes
- 10-9 The Levelling Effect

Updated Oct. 31, 2011: minor edits: 2, 5; new slides 22-27

Strong Acid-Strong Base Titrations

Each type of titration:

1. Write the involved chemical reactions/equilibria.
2. Measure pH values with a pH electrode (or sometimes an indicator).
3. Construct a pH curve.

e.g., Titration of 50.00 mL of 0.02000 M KOH with 0.1000 M HBr. The equilibrium is:



meaning any amount of H^+ which is added will be consumed by OH^- stoichiometrically, until all of the OH^- is consumed (after which H^+ is in excess).

What volume of HBr, (V_e) is needed to reach the *equivalence point*?

$$\underbrace{(V_e \cancel{\text{L}}) \left(0.1000 \frac{\text{mol}}{\cancel{\text{L}}} \right)}_{\text{mol of HBr at equivalence point}} = \underbrace{(0.05000 \cancel{\text{L}}) \left(0.02000 \frac{\text{mol}}{\cancel{\text{L}}} \right)}_{\text{mol of OH}^- \text{ being titrated}} \Rightarrow V_e = 0.01000 \text{ L}$$

$V_e = 10.00 \text{ mL}$, which means that after 10.00 mL of HBr solution has been added, the titration is complete.

1. **Prior to e.p.:** OH^- in XS.
2. **At the e.p.:** H^+ and OH^- react completely, pH dependent upon water dissociation.
3. **After the e.p.:** H^+ in XS

Equivalence point vs. End point

Equivalence Point:

The *equivalence point* occurs when added titrant is exactly enough for stoichiometric reaction with the analyte. The equivalence point is the ideal result we seek in a titration.

End Point:

What we actually measure is the *end point*, which is marked by a sudden physical change, such as indicator colour or an electrode potential (i.e., we take the system past the end point).



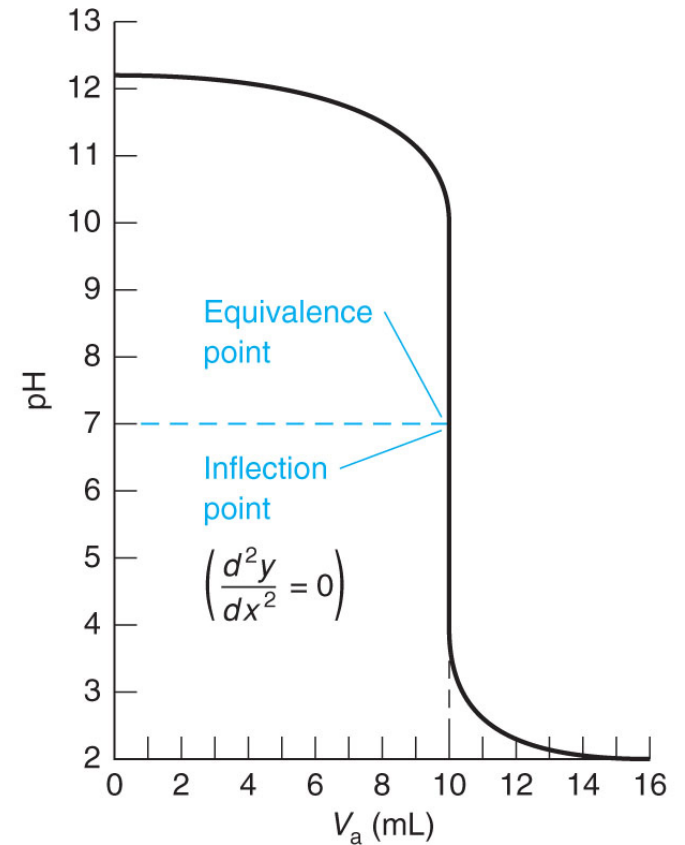
Good Endpoint



Bad Endpoint (Overly Titrated)

pH curves

	mL HBr added (V_a)	Concentration of unreacted OH^- (M)	Concentration of excess H^+ (M)	pH
Region 1 (excess OH^-)	0.00	0.020 0		12.30
	1.00	0.017 6		12.24
	2.00	0.015 4		12.18
	3.00	0.013 2		12.12
	4.00	0.011 1		12.04
	5.00	0.009 09		11.95
	6.00	0.007 14		11.85
	7.00	0.005 26		11.72
	8.00	0.003 45		11.53
	9.00	0.001 69		11.22
	9.50	0.000 840		10.92
Region 2	9.90	0.000 167		10.22
	9.99	0.000 016 6		9.22
	10.00	—	—	7.00
Region 3 (excess H^+)	10.01		0.000 016 7	4.78
	10.10		0.000 166	3.78
	10.50		0.000 826	3.08
	11.00		0.001 64	2.79
	12.00		0.003 23	2.49
	13.00		0.004 76	2.32
	14.00		0.006 25	2.20
	15.00		0.007 69	2.11
	16.00		0.009 09	2.04



Calculated titration curve, showing how pH changes as 0.1000 M HBr is added to 50.00 mL of 0.02000 M KOH. The equivalence point is an inflection point at which the second derivative is zero.

Region I: Before the E.P.

When 3.00 mL of HBr have been added, the total volume is 53.00 mL. HBr is consumed by NaOH, leaving excess NaOH. **Detailed (but easy) calculation follows:**

Moles of added HBr: $(0.1000 \text{ M})(0.00300 \text{ L}) = 0.300 \times 10^{-3} \text{ mol HBr} = 0.300 \text{ mmol HBr}$.

Initial moles of NaOH: $(0.02000 \text{ M})(0.05000 \text{ L}) = 1.000 \times 10^{-3} \text{ mol NaOH} = 1.000 \text{ mmol NaOH}$.

Unreacted OH⁻ is the difference: $1.000 \text{ mmol} - 0.300 \text{ mmol} = 0.700 \text{ mmol}$.

The concentration of unreacted OH⁻: $(0.700 \text{ mmol})/(53.00 \text{ mL}) = 0.0132 \text{ M}$.

Therefore, $[\text{H}^+] = K_w/[\text{OH}^-] = 7.57 \times 10^{-13} \text{ M}$ and $\text{pH} = -\log[\text{H}^+] = 12.12$.

Streamlined calculation:

3.00 mL of HBr added, the reaction is **3/10** complete, since because $V_e = 10.00 \text{ mL}$. The fraction of OH⁻ left unreacted is **7/10**. The concentration of remaining OH⁻ is the product of the fraction remaining, the initial concentration, and a dilution factor:

$$[\text{OH}^-] = \underbrace{\left(\frac{10.00 - 3.00}{10.00}\right)}_{\text{Fraction of OH}^- \text{ remaining}} \underbrace{(0.02000 \text{ M})}_{\text{Initial concentration of OH}^-} \underbrace{\left(\frac{50.00}{50.00 + 3.00}\right)}_{\text{Dilution factor}} = 0.0132 \text{ M}$$

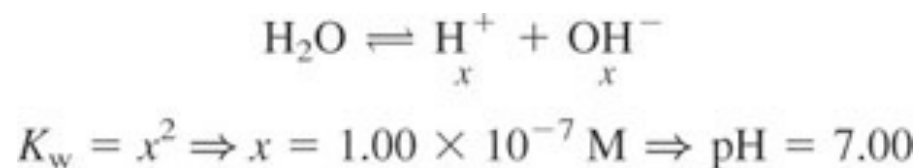
Initial volume of OH⁻

Total volume of solution

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0132} = 7.57 \times 10^{-13} \text{ M} \Rightarrow \text{pH} = 12.12$$

Region II: At the E.P.

Region 2 is the equivalence point, where just enough H^+ has been added to consume OH^- . pH is determined by dissociation of water:



The pH at the equivalence point in the titration of any strong base (or acid) with strong acid (or base) will be 7.00 at 25°C.

We will soon discover that the pH is not 7.00 at the equivalence point in the *titrations of weak acids or bases*. The pH is 7.00 only if the titrant and analyte are both strong.

Region III: After the E.P.

After the equivalence point, excess HBr is added to the solution. The concentration of excess H^+ at, say, 10.50 mL is given by

$$[H^+] = \underbrace{(0.1000 \text{ M})}_{\text{Initial concentration of } H^+} \underbrace{\left(\frac{0.50}{50.00 + 10.50} \right)}_{\text{Dilution factor}} = 8.26 \times 10^{-4} \text{ M}$$

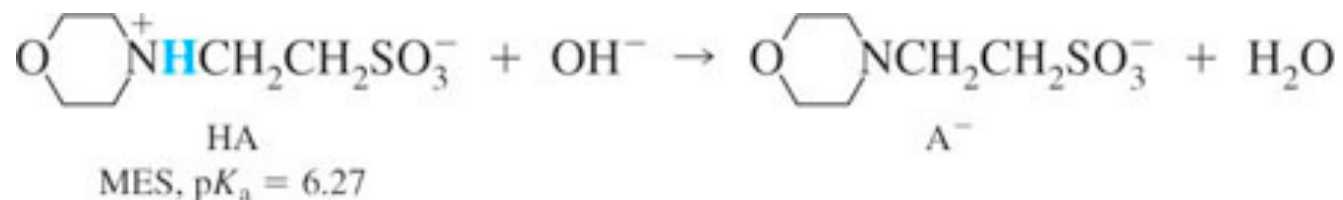
Total volume of solution

$$\text{pH} = -\log[H^+] = 3.08$$

At $V_a = 10.50$ mL, there is an excess of just $V_a - V_e = 10.50 - 10.00 = 0.50$ mL of HBr. That is the reason why 0.50 appears in the dilution factor.

Titration: Weak Acid with Strong Base

We will consider the titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH. MES is an abbreviation for *2-(N-morpholino)ethanesulfonic acid*, which is a weak acid with $pK_a = 6.27$.



This is the reverse of the K_b reaction for the base A^- . Therefore, the equilibrium constant for is $K = 1/K_b = 1/(K_w/K_a \text{ (for HA)}) = 5.4 \times 10^7$. K is very large, indicating that strong plus weak react completely (i.e., after each addition of OH^-).

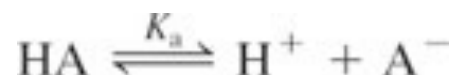
The volume of base, V_b , needed to reach the equivalence point:

$$\underbrace{(V_b \text{ (mL)})(0.1000 \text{ M})}_{\text{mmol of base}} = \underbrace{(50.00 \text{ mL})(0.02000 \text{ M})}_{\text{mmol of HA}} \Rightarrow V_b = 10.00 \text{ mL}$$

Titration: Weak Acid with Strong Base, 2

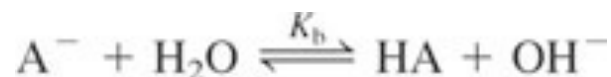
There are four types of titration calculations for this sort of problem:

1. **Before any base is added**, the solution contains just HA in water. This is a weak acid whose pH is determined by the equilibrium.



2. From the **first addition of NaOH** until **immediately before the equivalence point**, there is a mixture of unreacted HA plus the A⁻: i.e., a buffer! We can use the Henderson-Hasselbalch equation to find the pH.

3. **At the equivalence point**, “all” HA has been converted into A⁻. The same solution could be made by dissolving A⁻ in water. A⁻ is a weak base with pH determined by the reaction:



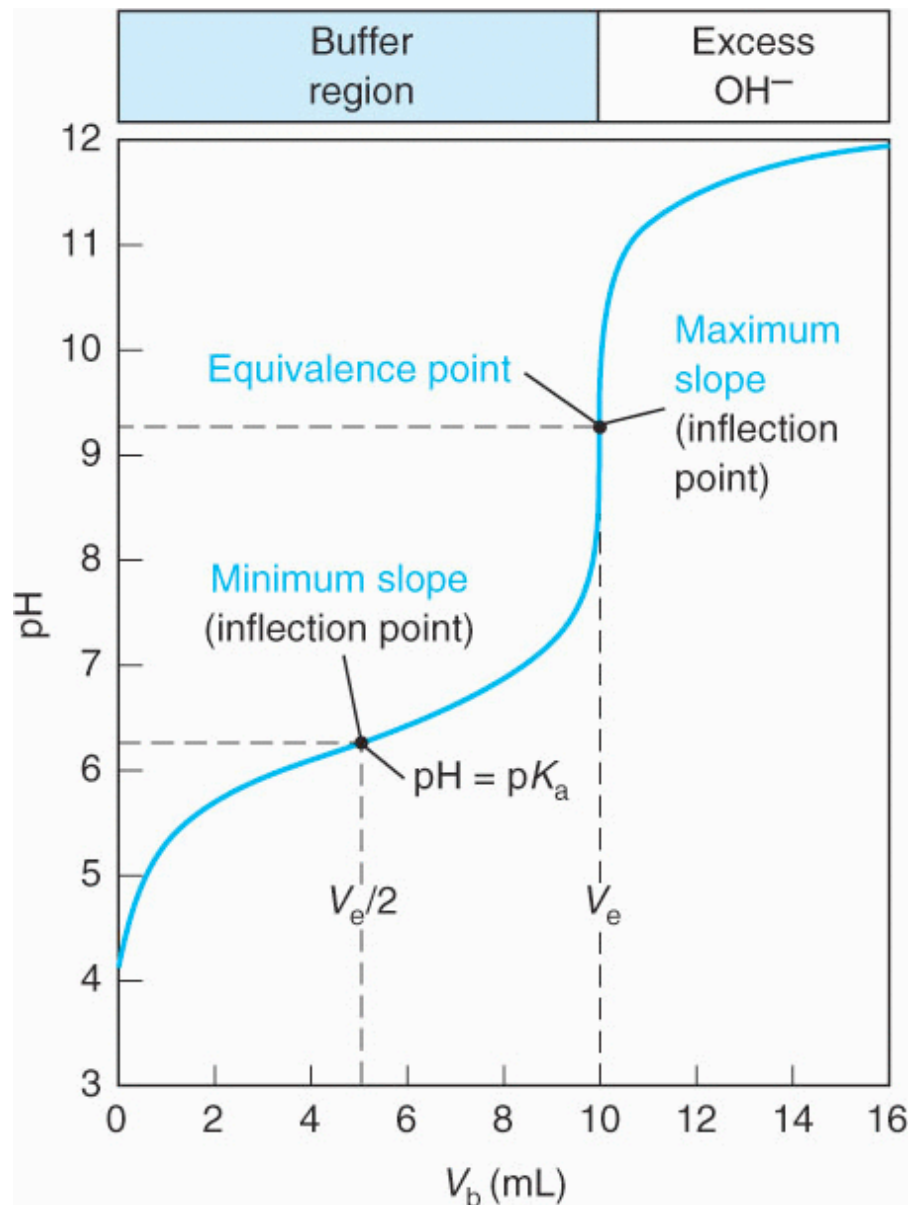
4. **After the equivalence point**, excess NaOH is being added to a solution of A⁻. To a good approximation, pH is determined by the strong base. Calculate the pH as if excess NaOH is added to water, neglecting the tiny effect of the weak base, A⁻.

Try *written example* covering all four steps!

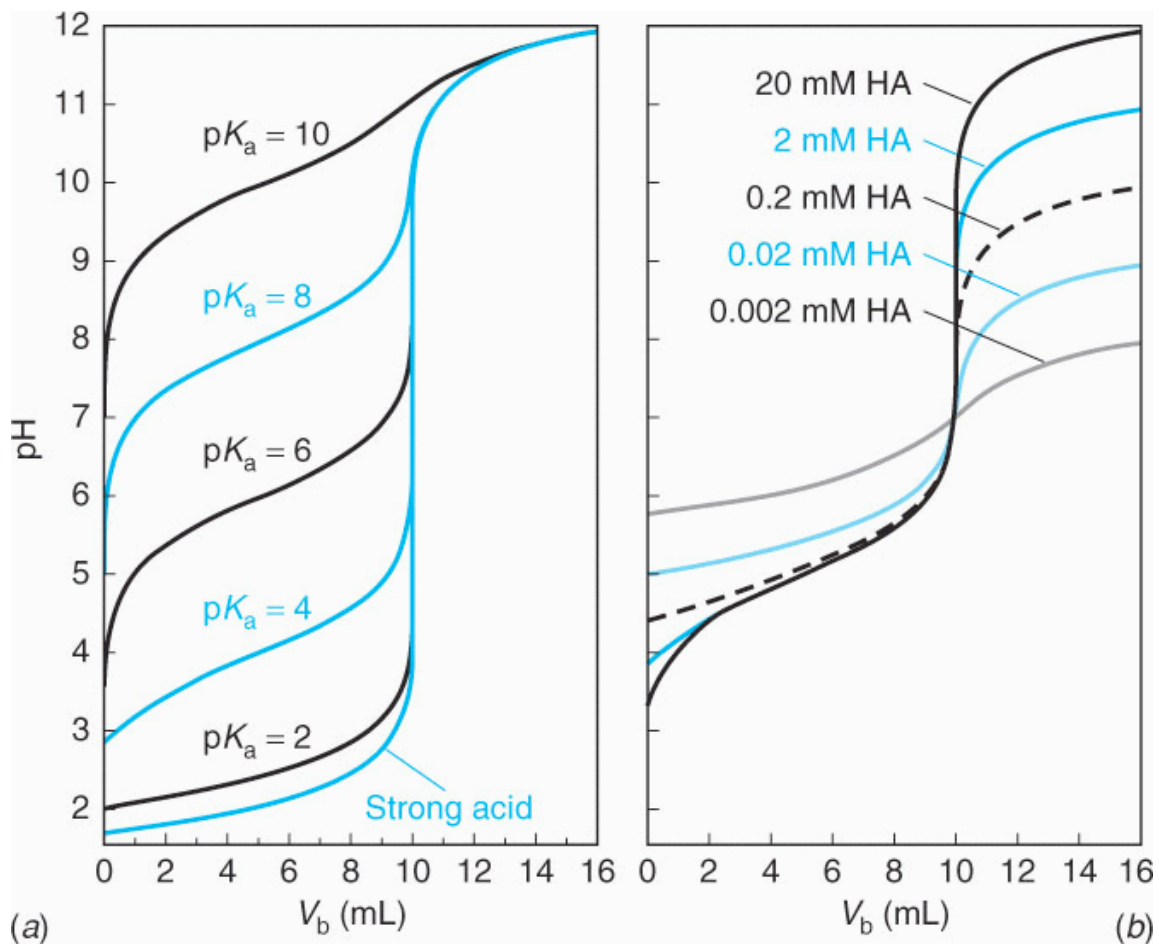
Titration Curve: WA titrated with SB

	mL base added (V_b)	pH
Region 1 (weak acid)	0.00	3.99
	0.50	4.99
	1.00	5.32
	2.00	5.67
	3.00	5.90
Region 2 (buffer)	4.00	6.09
	5.00	6.27
	6.00	6.45
	7.00	6.64
	8.00	6.87
	9.00	7.22
	9.50	7.55
Region 3 (weak base)	9.90	8.27
	10.00	9.25
	10.10	10.22
	10.50	10.91
Region 4 (excess OH^-)	11.00	11.21
	12.00	11.50
	13.00	11.67
	14.00	11.79
	15.00	11.88
	16.00	11.95

Calculated titration curve for the reaction of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH. Landmarks occur at half of the equivalence volume ($\text{pH} = \text{p}K_a$ - also point of maximum buffer capacity) and at the equivalence point (mol OH^- = mol HA, only A^- in solution), which is the steepest part of the curve.



Titration Curve: WA titrated with SB, 2



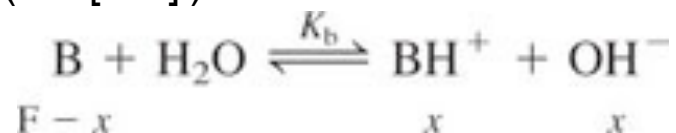
(a) Calculated curves showing the titration of 50.0 mL of 0.0200 M HA with 0.100 M NaOH. (b) Calculated curves showing the titration of 50.0 mL of HA ($pK_a = 5$) with NaOH whose concentration is five times greater than that of HA. As HA becomes a weaker acid, or as the concentrations of analyte and titrant decrease, the inflection near the equivalence point decreases, until the equivalence point becomes too shallow to detect - not practical to titrate with very weak acids or very dilute concentrations!

Titration: Weak Base with Strong Acid

This is the reverse of the WA with SB titration. The titration reaction goes to completion after each addition of the strong acid (since B is a weak base):



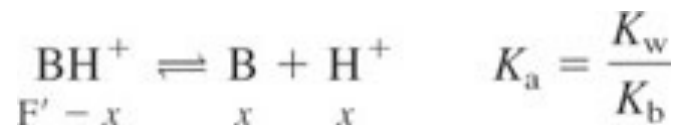
1. **Before any acid is added**, the solution contains just the weak base, B, in water. The pH is determined by the K_b reaction ($x = [OH^-]$).



2. Between the first addition of acid and the equivalence point, mixture of B and BH^+ (i.e., a **buffer!**) There is special point where $V_a = 0.5V_e$ and $pH = pK_a$ (for BH^+).

$$pH = pK_a (\text{for } BH^+) + \log\left(\frac{[B]}{[BH^+]}\right)$$

3. **At the equivalence point**, “all” B has been converted into BH^+ . The same solution could be made by dissolving BH^+ in water. BH^+ is a weak acid with pH determined by the reaction:

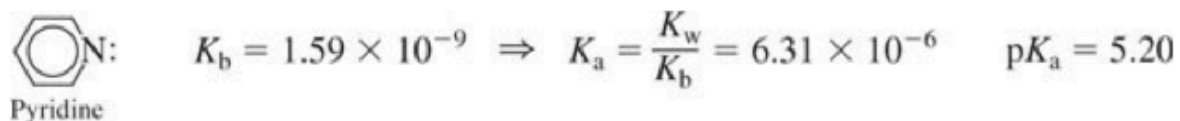


4. **After the equivalence point**, the excess strong acid determines the pH. We neglect the contribution of weak acid, BH^+ .

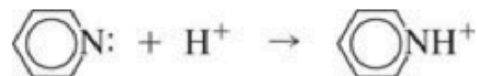
Titration: Weak Base with Strong Acid, 2

EXAMPLE Titration of Pyridine with HCl

Consider the titration of 25.00 mL of 0.083 64 M pyridine with 0.106 7 M HCl.



The titration reaction is



and the equivalence point occurs at 19.60 mL:

$$\underbrace{(V_e \text{ (mL)})(0.1067 \text{ M})}_{\text{mmol of HCl}} = \underbrace{(25.00 \text{ mL})(0.08364 \text{ M})}_{\text{mmol of pyridine}} \Rightarrow V_e = 19.60 \text{ mL}$$

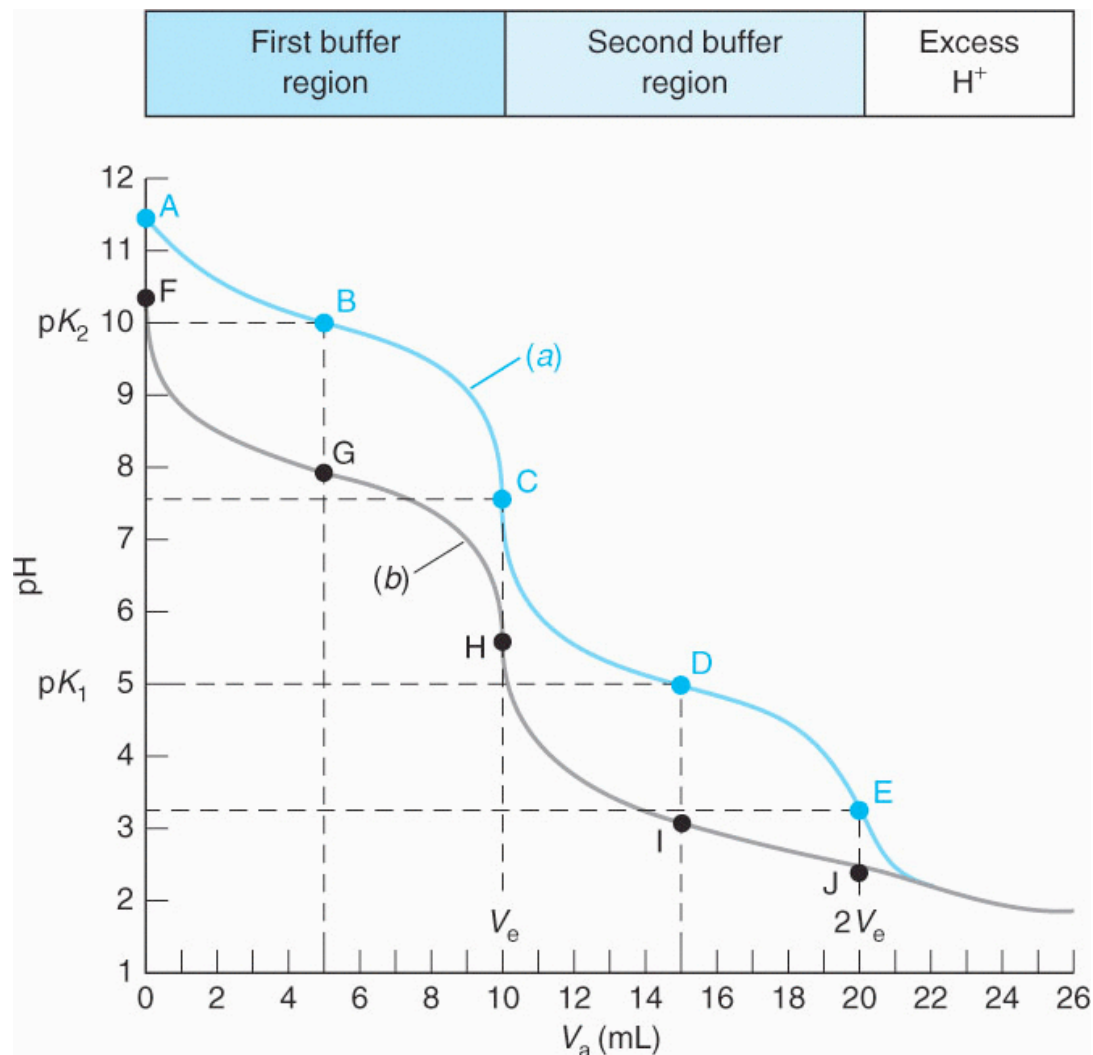
Find the pH when $V_a = 4.63$ mL.

Solution Part of the pyridine has been neutralized, so there is a mixture of pyridine and pyridinium ion—*Aha! A buffer!* The fraction of pyridine that has been titrated is $4.63/19.60 = 0.236$, because it takes 19.60 mL to titrate the whole sample. The fraction of pyridine remaining is $1 - 0.236 = 0.764$. The pH is

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{B}]}{[\text{BH}^+]}\right) \\ &= 5.20 + \log\frac{0.764}{0.236} = 5.71 \end{aligned}$$

Titrations in Diprotic Systems

The **upper curve** is calculated for the titration of 10.0 mL of 0.100 M base (B) with 0.100 M HCl. The base is **dibasic**, with $pK_{b1} = 4.00$ and $pK_{b2} = 9.00$.

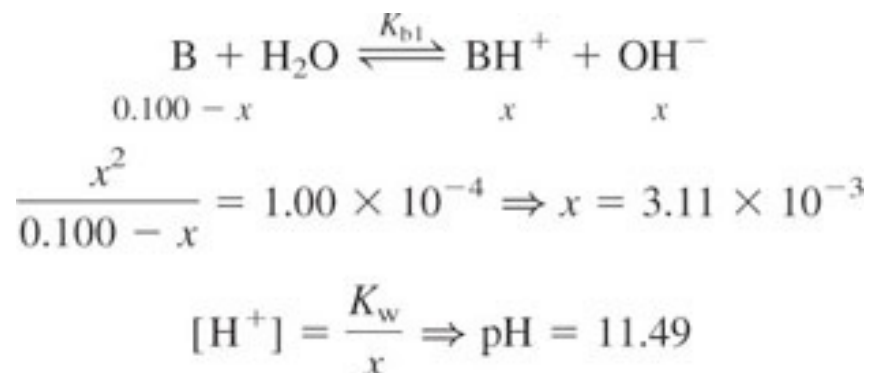


(a) Titration of 10.0 mL of 0.100 M base ($pK_{b1} = 4.00$, $pK_{b2} = 9.00$) with 0.100 M HCl. The two equivalence points are C and E. Points B and D are the *half-neutralization points*, whose pH values equal pK_{a2} and pK_{a1} , respectively.

(b) Titration of 10.0 mL of 0.100 M nicotine ($pK_{b1} = 6.15$, $pK_{b2} = 10.85$) with 0.100 M HCl. There is no sharp break at the second equivalence point, J, because the pH is too low.

Titrations in Diprotic Systems, 2

A. Before acid is added, the solution contains just weak base, B, whose pH comes from



B. At any point between A (the initial point) and C (the first E.P.), we have a buffer containing B and BH⁺. Point B is halfway to the equivalence point, so [B] = [BH⁺]. The pH is calculated from the HH equation for the weak acid, BH⁺, with K_{a2} (for BH²⁺) = $K_w/K_{b1} = 10^{-10.00}$.

$$\text{pH} = \text{p}K_{a2} + \log \frac{[\text{B}]}{[\text{BH}^+]} = 10.00 + \log 1 = 10.00$$

To calculate the quotient [B]/[BH⁺] at any point in the buffer region, just find what fraction of the way from point A to point C the titration has progressed. For example, if V_a (volume of titrant acid) = 1.5 mL, and V_e (amount of acid to reach the first E.P.) = 10 mL, then

$$\text{pH} = 10.00 + \log \frac{8.5}{1.5} = 10.75$$

Titration in Diprotic Systems, 3

C. At the first E.P., B has been converted into BH^+ , the intermediate form of the diprotic acid, and BH^+ is both an acid and a base.

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

where K_1 and K_2 are the acid dissociation constants of BH_2^{2+} . The formal concentration of BH^+ is calculated by considering dilution of the original solution of B.

$$F = \underbrace{(0.100 \text{ M})}_{\substack{\text{Original} \\ \text{concentration} \\ \text{of B}}} \underbrace{\left(\frac{10.0}{20.0}\right)}_{\substack{\text{Dilution} \\ \text{factor}}} = 0.0500 \text{ M}$$

↙ Initial volume of B
↖ Total volume of solution

Plugging in all of this data yields:

$$[H^+] = \sqrt{\frac{(10^{-5})(10^{-10})(0.0500) + (10^{-5})(10^{-14})}{10^{-5} + 0.0500}} = 3.16 \times 10^{-8}$$

$$\text{pH} = 7.50$$

Point C is the *least buffered* point on the whole curve (pH changes the most) - worst choice for buffer conditions!

Titrations in Diprotic Systems, 4

D. At any point between C and E, there is a buffer containing BH^+ (the base) and BH_2^{2+} (the acid). When $V_a = 15.0 \text{ mL}$, $[\text{BH}^+] = [\text{BH}_2^{2+}]$ and

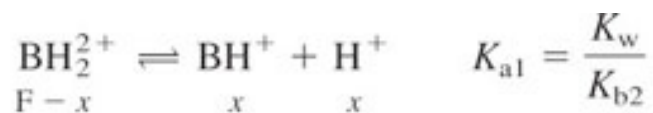
$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{BH}^+]}{[\text{BH}_2^{2+}]} = 5.00 + \log 1 = 5.00$$

E. Point E is the second E.P. (i.e., $V_a = 20.0 \text{ mL}$), at which the solution is formally the same as one prepared by dissolving BH_2Cl_2 in water. The formal concentration of BH_2^{2+} is

$$F = (0.100 \text{ M}) \left(\frac{10.0}{30.0} \right) = 0.0333 \text{ M}$$

Original volume of B
Total volume of solution

The pH is determined by the weak acid dissociation reaction of BH_2^{2+}



$$\frac{x^2}{0.0333 - x} = 1.0 \times 10^{-5} \Rightarrow x = 5.72 \times 10^{-4} \Rightarrow \text{pH} = 3.24$$

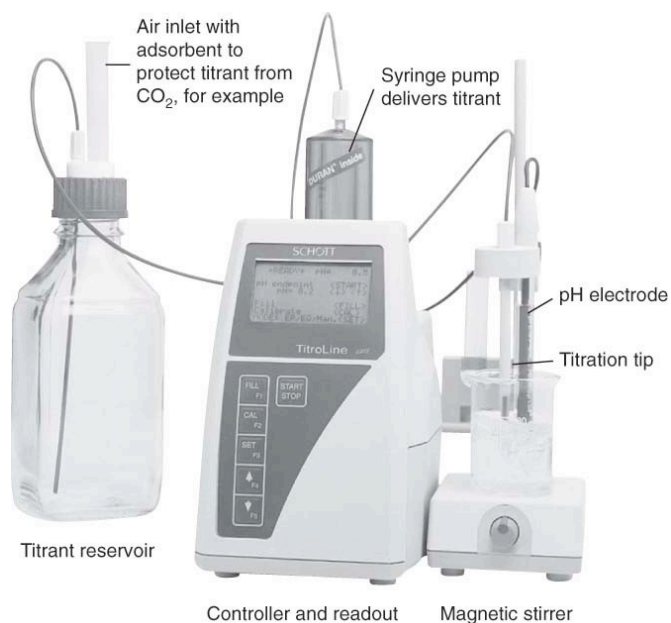
Beyond the second equivalence point ($V_a > 20.0 \text{ mL}$), the pH of the solution can be calculated from the volume of strong acid added to the solution.

Finding the end point with a pH electrode

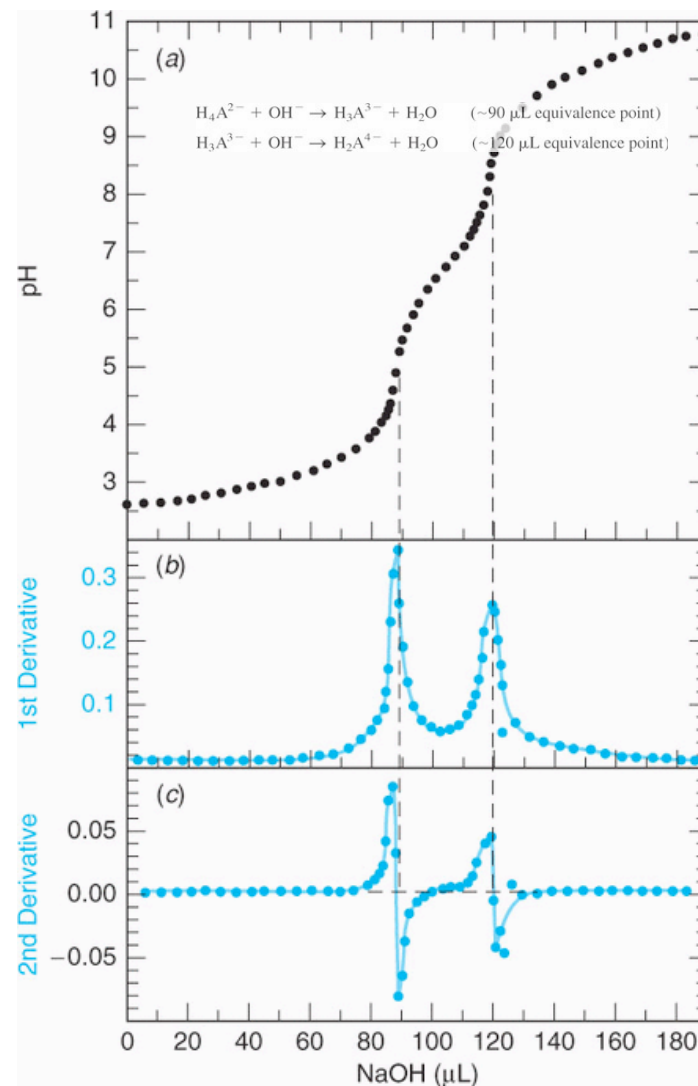
Titrations are commonly performed to find out how much analyte is present or to measure equilibrium constants. We can obtain the information necessary for both purposes by monitoring pH during the titration.

Autotitrators

automatically produce very nice pH curves. The instrument waits for pH to stabilize after each addition of titrant, before adding the next increment. The end point is computed automatically by finding the maximum slope in the titration curve.



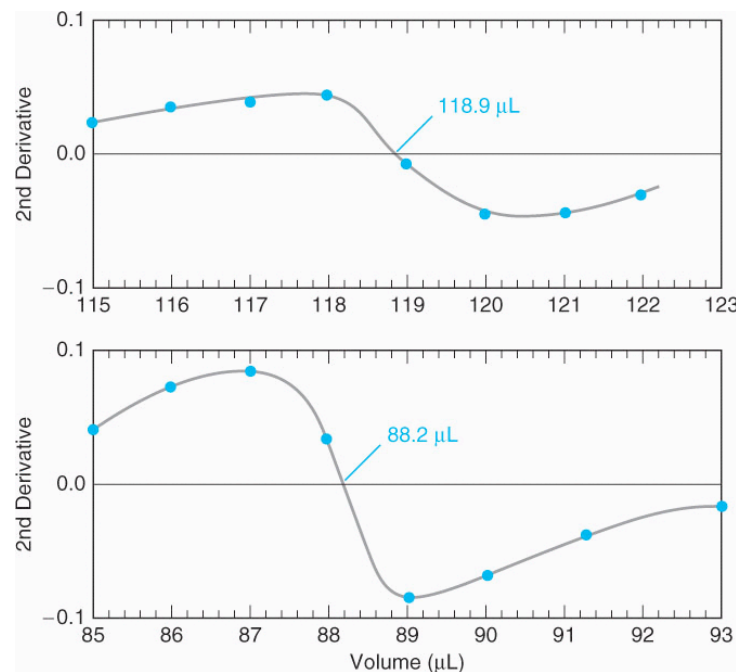
(a) Experimental points in the titration of 1.430 mg of xylene orange, a hexaprotic acid, dissolved in 1.000 mL of aqueous 0.10 M NaNO₃. The titrant was 0.06592 M NaOH. (b) The first derivative, $\Delta\text{pH}/\Delta V$, of the titration curve. (c) The second derivative, $\Delta(\Delta\text{pH}/\Delta V)/\Delta V$, which is the derivative of the curve in panel b. End points are taken as *maxima* in the derivative curve and *zero crossings* of the second derivative.



Using derivatives to find the end point

The end point is taken as the volume where the slope (dpH/dV) of the titration curve is greatest.

	A	B	C	D	E	F
1	Derivatives of a Titration Curve					
2	Data		1st derivative		2nd derivative	
3	$\mu\text{L NaOH}$	pH	μL	$\Delta\text{pH}/\Delta\mu\text{L}$	μL	$\Delta(\Delta\text{pH}/\Delta\mu\text{L})$
4	85.0	4.245	85.5	0.155	86.0	0.0710
5						
6	86.0	4.400				
7			86.5	0.226		
8	87.0	4.626			87.0	0.0810
9			87.5	0.307		
10	88.0	4.933			88.0	0.0330
11			88.5	0.340		
12	89.0	5.273			89.0	-0.0830
13			89.0	0.257		
14	90.0	5.530			90.0	-0.0680
15			90.5	0.189		
16	91.0	5.719			91.25	-0.0390
17			92.0	0.131		
18	93.0	5.980				
19	Representative formulas:					
20	$C5 = (A6 + A4)/2$		$E6 = (C7 + C5)/2$			
21	$D5 = (B6 - B4)/(A6 - A4)$		$F6 = (D7 - D5)/(C7 - C5)$			

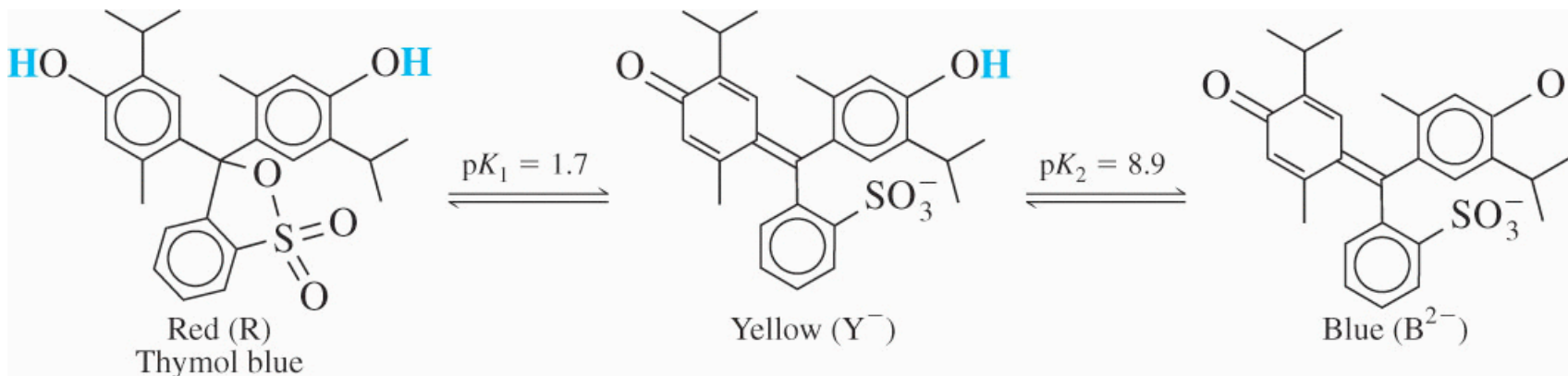


Above: enlargements of the 1st and 2nd derivative regions of the plot on the previous slide.

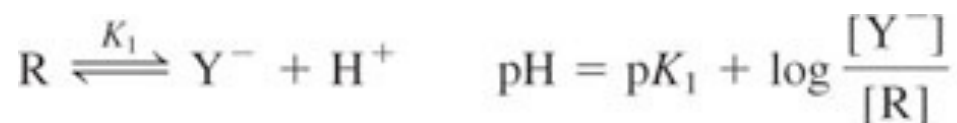
It is trivial to use Excel spreadsheets to calculate first and second derivatives, as shown above.

Using indicators to find the end point

An acid-base indicator is itself an acid or base whose various protonated species have different colours. An example is *thymol blue*.



The equilibrium between R and Y^- can be written as



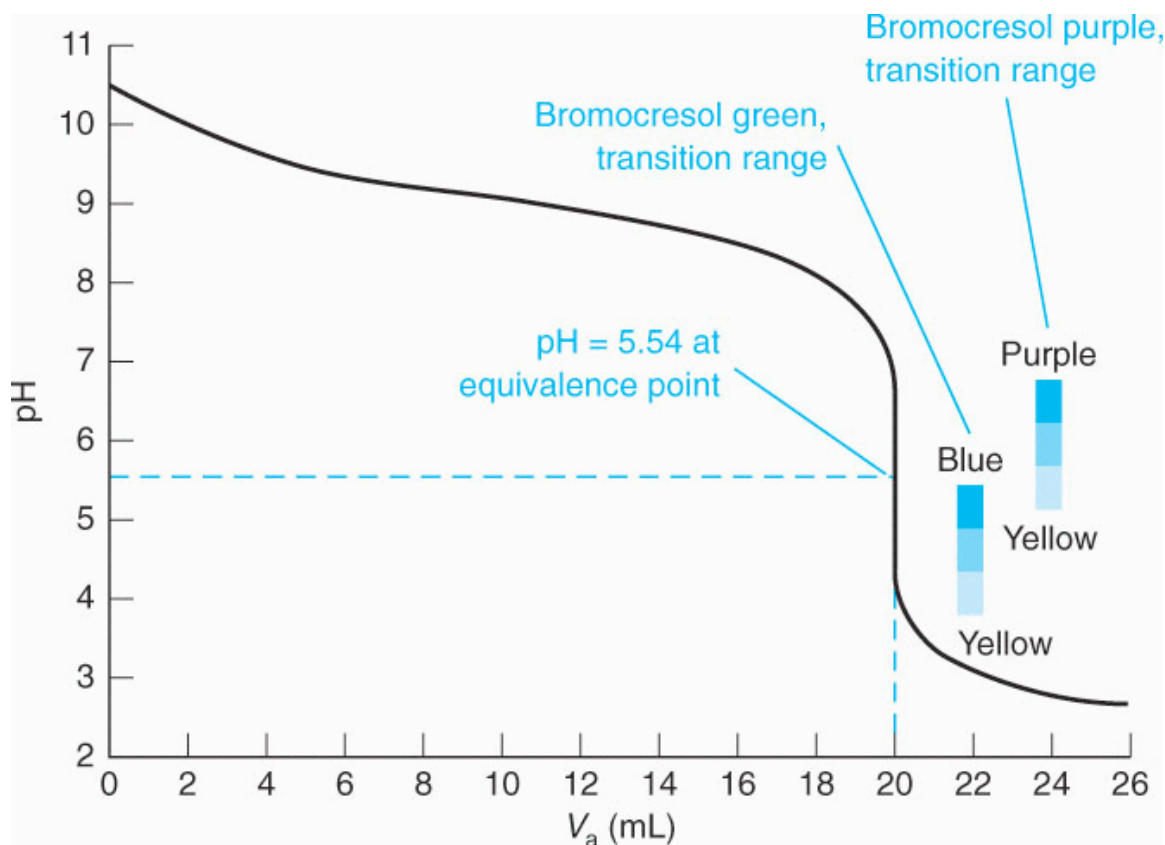
pH	$[Y^-]:[R]$	Color
0.7	1:10	red
1.7	1:1	orange
2.7	10:1	yellow

At pH 1.7 (= $\text{p}K_1$), there will be a 1:1 mixture of the yellow and red species, which appears orange. As a crude rule of thumb, we can say that the solution will appear red when $[Y^-]/[R] \leq 1/10$, and yellow when $[Y^-]/[R] \geq 10/1$. The pH range (1.2 to 2.8) over which the colour changes is called the transition range.

Choosing an indicator

A titration curve for which $\text{pH} = 5.54$ at the equivalence point would work best with an indicator with a colour change near this pH . The pH drops steeply (from 7 to 4) over a small volume interval. Therefore, any indicator with a colour change in this pH interval would provide a fair approximation to the equivalence point.

The closer the point of colour change is to $\text{pH} 5.54$, the more accurate the end point. The difference between the observed end point (colour change) and the true equivalence point is called the *indicator error*.



Calculated titration curve for the reaction of 100 mL of 0.0100 M base ($\text{p}K_b = 5.00$) with 0.0500 M HCl. The moles of indicator must be negligible relative to the moles of analyte: **never** use more than a few drops of dilute indicator solution!

Practical Notes

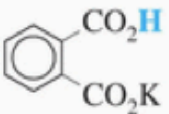
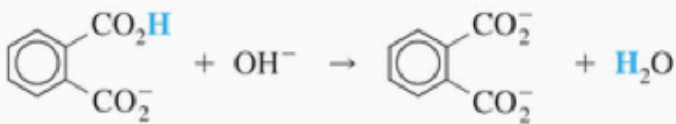
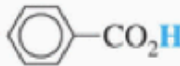
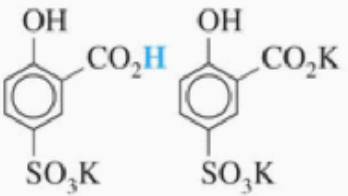
Acids and bases in the tables on the following slides (Table 10-4, 8th edition) can be obtained pure enough to be *primary standards*.

Alkaline solutions: NaOH and KOH are not primary standards because they contain carbonate (from reaction with atmospheric CO₂) and adsorbed water. Solutions of NaOH and KOH must be standardized against a primary standard such as potassium hydrogen phthalate. Solutions of NaOH for titrations are prepared by diluting a stock solution of 50 wt% aqueous NaOH. Sodium carbonate is insoluble in this stock solution and settles to the bottom. Alkaline solutions must also be protected from atmosphere, as they absorb CO₂ to form HCO₃⁻, which serves to reduce the pH of the solution over time.

Storage: Standard solutions are commonly stored in high-density polyethylene bottles with screw caps. Evaporation from the bottle slowly changes the reagent concentration. The chemical supplier *Sigma-Aldrich* reports that an aqueous solution stored in a tightly capped bottle became 0.2% more concentrated in 2 years at 23°C and 0.5% more concentrated in 2 years at 30°C. Enclosing the bottle in a sealed, aluminized bag reduced evaporation by a factor of 10. The lesson is that a standard solution has a finite shelf life.

Strongly basic solutions should always be stored in plastic bottles, as the OH⁻ tends to attack the surface of the glass (never keep strongly basic solutions in burets for a long time!)

Practical Notes, 2

Compound	Density (g/mL) for buoyancy corrections	Notes
<p>ACIDS</p>  <p>Potassium hydrogen phthalate FM 204.221</p>	1.64	<p>The pure commercial material is dried at 105°C and used to standardize base. A phenolphthalein end point is satisfactory.</p> 
<p>HCl Hydrochloric acid FM 36.461</p>	—	<p>HCl and water distill as an <i>azeotrope</i> (a mixture), whose composition (~6 M) depends on pressure and is tabulated as a function of the pressure during distillation. See Problem 10-56 for more information.</p>
<p>KH(IO₃)₂ Potassium hydrogen iodate FM 389.912</p>	—	<p>This is a strong acid, so any indicator with an end point between ~5 and ~9 is adequate.</p>
 <p>Benzoic acid FM 122.121</p>	1.27	<p>Primary standard for nonaqueous titrations in solvents such as ethanol. A glass electrode is used to find the end point.</p>
 <p>Sulfosalicylic acid double salt FM 550.639</p>	—	<p>1 mol of commercial grade sulfosalicylic acid is combined with 0.75 mol of reagent-grade KHCO₃, recrystallized several times from water, and dried at 110°C to produce the double salt with 3 K⁺ ions and one titratable H⁺.¹⁶ Phenolphthalein is used as the indicator for titration with NaOH.</p>

Practical Notes, 3

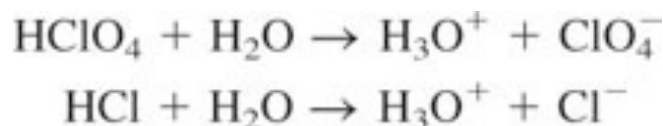
Compound	Density (g/mL) for buoyancy corrections	Notes
H_3NSO_3^+ Sulfamic acid FM 97.094	2.15	Sulfamic acid is a strong acid with one acidic proton, so any indicator with an end point between ~5 and ~9 is suitable.
BASES		
$\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3$ Tris(hydroxymethyl)aminomethane (also called tris or tham) FM 121.135	1.33	<p>The pure commercial material is dried at 100°–103°C and titrated with strong acid. The end point is in the range pH 4.5–5.</p> $\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3 + \text{H}^+ \rightarrow \text{H}_3\text{N}^+\text{C}(\text{CH}_2\text{OH})_3$
HgO Mercuric oxide FM 216.59	11.1	<p>Pure HgO is dissolved in a large excess of I^- or Br^-, whereupon 2 OH^- are liberated:</p> $\text{HgO} + 4\text{I}^- + \text{H}_2\text{O} \rightarrow \text{HgI}_4^{2-} + 2\text{OH}^-$ <p>The base is titrated, using an indicator end point.</p>
Na_2CO_3 Sodium carbonate FM 105.988	2.53	<p>Primary-standard-grade Na_2CO_3 is commercially available. Alternatively, recrystallized NaHCO_3 can be heated for 1 h at 260°–270°C to produce pure Na_2CO_3. Sodium carbonate is titrated with acid to an end point of pH 4–5. Just before the end point, the solution is boiled to expel CO_2.</p>
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Borax FM 381.372	1.73	<p>The recrystallized material is dried in a chamber containing an aqueous solution saturated with NaCl and sucrose. This procedure gives the decahydrate in pure form.¹⁷ The standard is titrated with acid to a methyl red end point.</p> $\text{“B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}^{2-}\text{”} + 2\text{H}^+ \rightarrow 4\text{B}(\text{OH})_3 + 5\text{H}_2\text{O}$

The Levelling Effect

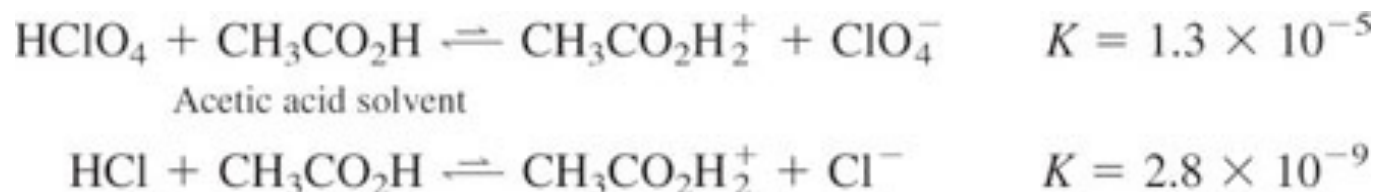
The strongest acid that can exist in water is H_3O^+ and the strongest base is OH^- .

- If an acid stronger than H_3O^+ is dissolved in water, it protonates H_2O to make H_3O^+ .
- If a base stronger than OH^- is dissolved in water, it deprotonates H_2O to make OH^- .

Because of this levelling effect, HClO_4 and HCl behave as if they had the same acid strength; both are levelled to H_3O^+ :

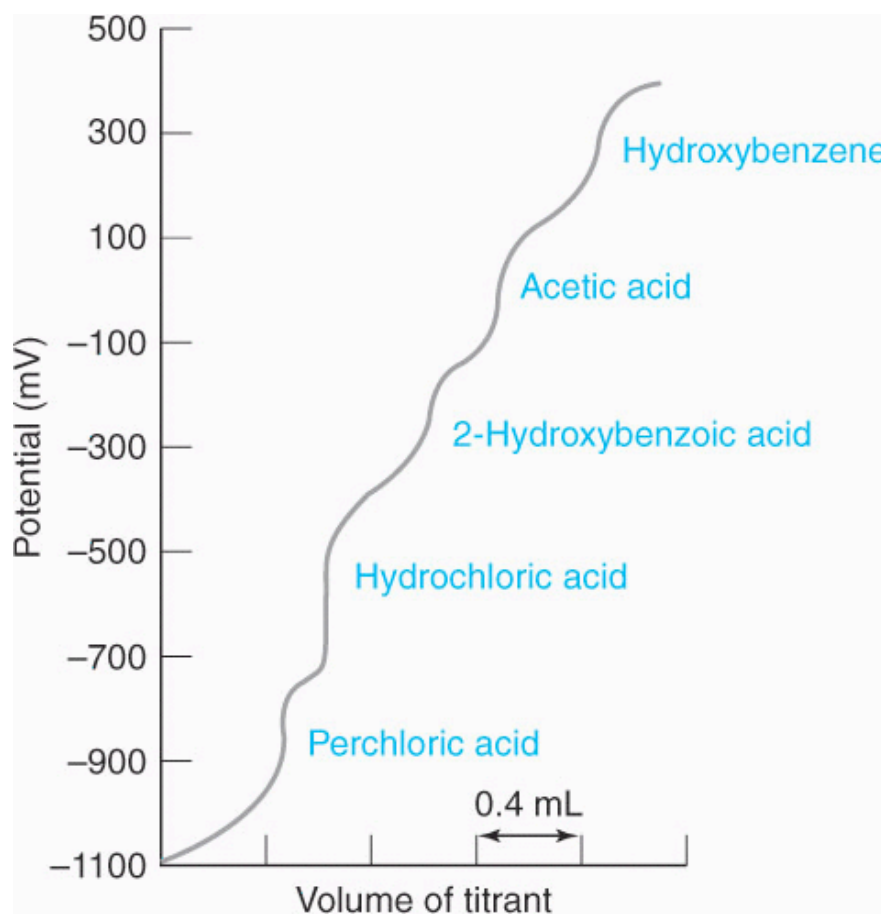


However, in acetic acid solvent, which is less basic than H_2O , HClO_4 and HCl are not levelled to the same strength (HClO_4 is a stronger acid in this case):



The Levelling Effect, 2

Titration of a mixture of acids with tetrabutylammonium hydroxide in methyl isobutyl ketone solvent shows that the order of acid strength is $\text{HClO}_4 > \text{HCl} > 2\text{-hydroxybenzoic acid} > \text{acetic acid} > \text{hydroxybenzene}$.



Titration of a mixture of acids with 0.2 M tetrabutylammonium hydroxide in methyl isobutyl ketone solvent (which is not protonated to any great extent) shows that the order of acid strength is $\text{HClO}_4 > \text{HCl} > 2\text{-hydroxybenzoic acid} > \text{acetic acid} > \text{hydroxybenzene}$.

Measurements were made with a glass electrode and a platinum reference electrode. The ordinate is proportional to pH, with increasing pH as the potential becomes more positive.

The Levelling Effect, 3

The levelling effect is useful in considering the titrations of weak acids or bases which may be too weak to give a distinct endpoint in a water solution.

Consider a base such as *urea*, $(\text{H}_2\text{N})_2\text{C}=\text{O}$ ($K_b = 1.3 \times 10^{-14}$), that is too weak to give a distinct end point when titrated with a strong acid in water.

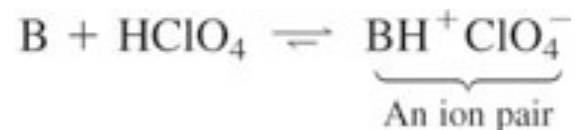
Titration with HClO_4 in H_2O :



The endpoint cannot be recognized, since the K_b is not large enough. However, if a stronger acid were available, the K_b might be large enough to give an endpoint.

If the same base were dissolved in acetic acid and titrated with HClO_4 dissolved in acetic acid:

Titration with HClO_4 in $\text{CH}_3\text{CO}_2\text{H}$:



(The product in this reaction is written as an ion pair because the dielectric constant of acetic acid is too low to allow ions to separate extensively.)

This reaction may have a larger K_b , since HClO_4 is a stronger acid than H_3O^+ . Hence, titrations that may not be feasible in water can always be attempted in other solvents.