Chapter 11 (9th Edition)

Chapter 10 (8th Edition)

Acid-Base Titrations

Objectives

11-1 Titration of Strong Base with Strong Acid

11-2 Titration of Weak Acid with Strong Base

11-3 Titration of Weak Base with Strong Acid

11-4 Titrations in Diprotic Systems

11-5 Finding the End Point with a pH Electrode

11-6 Finding the End Point with Indicators

11-7 Practical Notes

~~11-8 Kjeldahl Nitrogen Analysis~~

11-9 The Leveling Effect

~~11-10 Calculating Titration Curves with Spreadsheets~~

11-1: Titration of Strong Base with Strong Acid

Strong acid/strong base titration: pH is determined by the concentration of excess unreacted H^+ or OH^-.

1. Before the equivalence point, pH is determined by excess OH^- in the solution.
2. At the equivalence point, H^+ is just sufficient to react with all OH^- to make H_2O. The pH is determined by dissociation of water.
3. After the equivalence point, pH is determined by excess H^+ in the solution.

11-1: Titration of Strong Base with Strong Acid

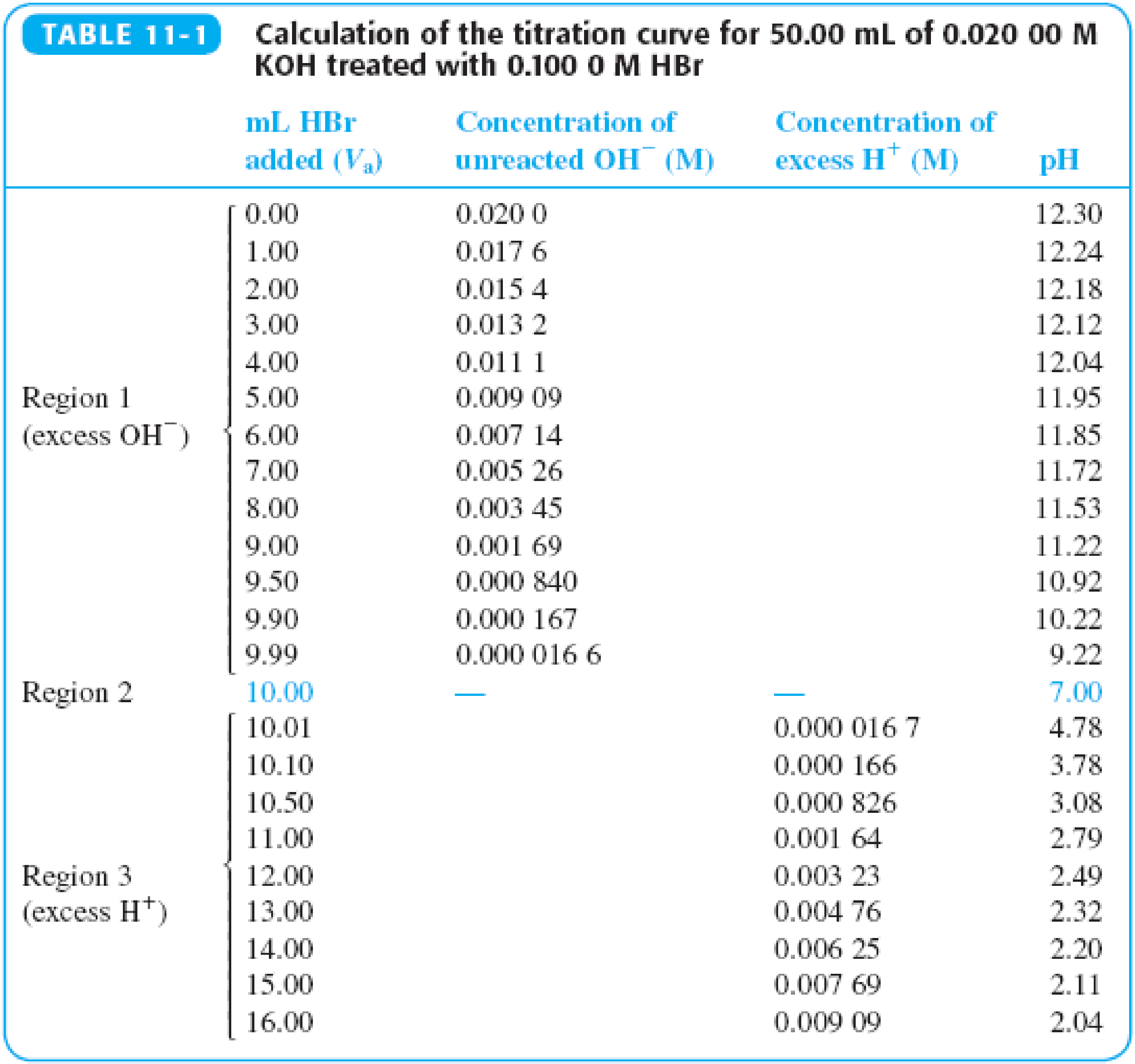
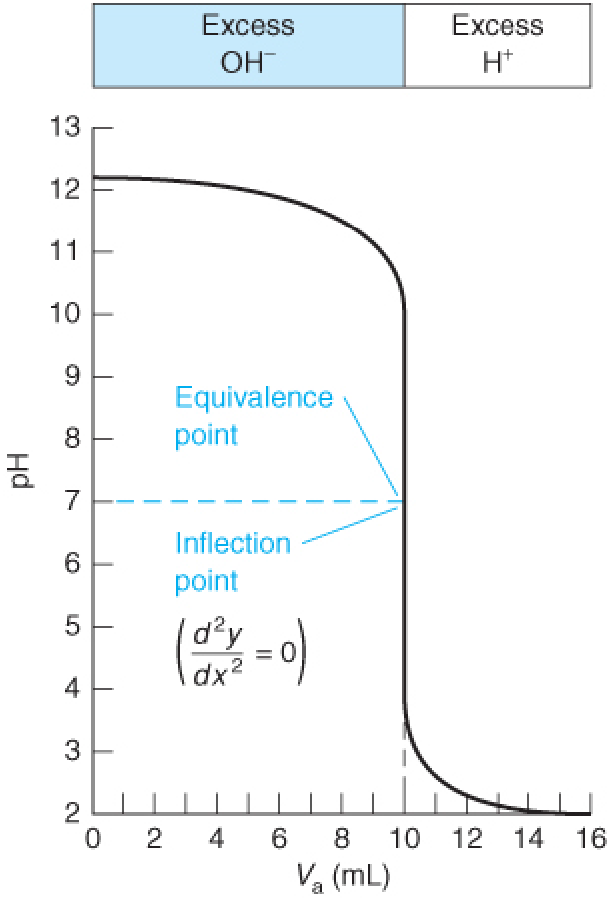


TABLE 11-1 Calculation of the titration curve for 50.00 mL of 0.020 00 M KOH treated with 0.100 0 M HBr

	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
	9.90	0.000 167		10.22
	9.99	0.000 016 6		9.22
Region 2	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



11-2: Titration of Weak Acid with Strong Base

Four distinct regions of the titration curve:

1. Before base added, the solution contains just the weak acid, HA, in water. $HA \rightleftharpoons H^+ + A^-$

2. Between the initial point and the equivalence point, there is a mixture of HA and A^-. Buffer!

3. At the equivalence point, HA has been converted into A^-, a weak base. The pH is calculated by considering the base hydrolysis reaction of A^-.

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

4. After the equivalence point, the excess strong base

   determines the pH.

11-3: Titration of Weak Base with Strong Acid

- The titration of a weak base with a strong acid is the reverse of the titration of a weak acid with a strong base.
- Because the reactants are a weak base and a strong acid, the reaction goes essentially to completion after each addition of acid.

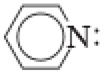
11-3: Titration of Weak Base with Strong Acid

Four distinct regions of the titration curve:

1. Before acid is added, the solution contains just the weak base, B, in water.
2. Between the initial point and the equivalence point, there is a mixture of B and BH^+.
3. At the equivalence point, B has been converted into BH^+, a weak acid. The pH is calculated by considering the acid dissociation reaction of BH^+.
4. After the equivalence point, the excess strong acid determines the pH.

EXAMPLE Titration of Pyridine with HCl

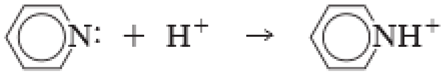
Consider the titration of 25.00 mL of 0.083 64 M pyridine with 0.106 7 M HCl.



Pyridine

$$K_b = 1.59 \times 10^{-9} \quad \Rightarrow \quad K_a = \frac{K_w}{K_b} = 6.31 \times 10^{-6} \qquad pK_a = 5.20$$

The titration reaction is



and the equivalence point occurs at 19.60 mL:

$$\underbrace{(V_e(\text{mL}))(0.106\,7\text{ M})}_{\text{mmol of HCl}} = \underbrace{(25.00\text{ mL})(0.083\,64\text{ M})}_{\text{mmol of pyridine}} \Rightarrow V_e = 19.60\text{ mL}$$

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

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

$$= 5.20 + \log\frac{0.764}{0.236} = 5.71$$

TEST YOURSELF Find the pH when $V_a = 14.63$ mL. (***Answer:*** 4.73)

11-4: Titrations in Diprotic Systems

The principles developed for titrations of monoprotic acids and bases extend directly to titrations of polyprotic acids and bases.

Consider 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. The equivalence points correspond to the reactions below:

$$B + H^+ \rightarrow BH^+$$

$$BH^+ + H^+ \rightarrow BH_2^{2+}$$

11-4: Titrations in Diprotic Systems

1. Find the first and second equivalence points.

- The volume at the first equivalence point is 10.00 mL because

  $(V_e(\text{mL}))(0.100\text{ M}) = (10.00\text{ mL})(0.100\,0\text{ M}) \rightarrow V_e = 10.00\text{ mL}$

  mmol of HCl = mmol of B

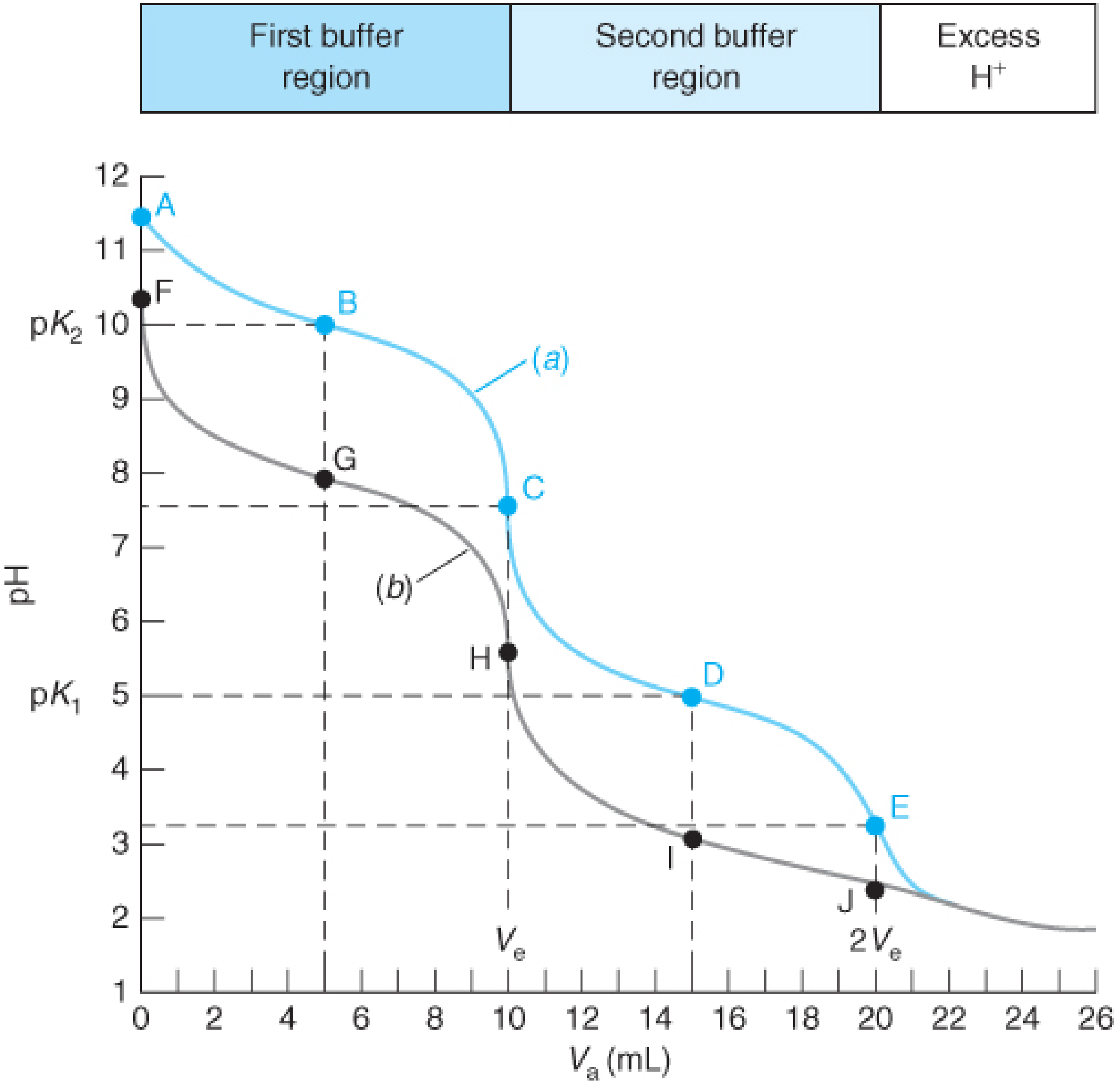
- The volume at the second equivalence point must be $2V_e$, because the second reaction requires the same number of moles of HCl as the first reaction. $2V_e = 20.0$ mL.

2. Before acid is added, the solution contains just weak base, B, whose pH is governed by base hydrolysis. The fully basic form of a dibasic compound can be treated as if it were monobasic.

11-4: Titrations in Diprotic Systems

3. At any point between $V_a = 0$ and V_e, we have a buffer containing B and BH^+. Use the Henderson-Hasselbalch equation to calculate the pH.
4. At the first equivalence point, Ve, B has been converted into BH^+. The intermediate form of the diprotic acid, BH_2^+, BH^+ is both an acid and a base.
5. At any point between Ve and 2Ve, the pH is governed by the buffer containing BH^+ and BH_2^+. Again the Henderson-Hasselbalch equation is used.
6. After the second equivalence point, 2Ve, the pH is governed by the excess strong acid in solution, H^+.

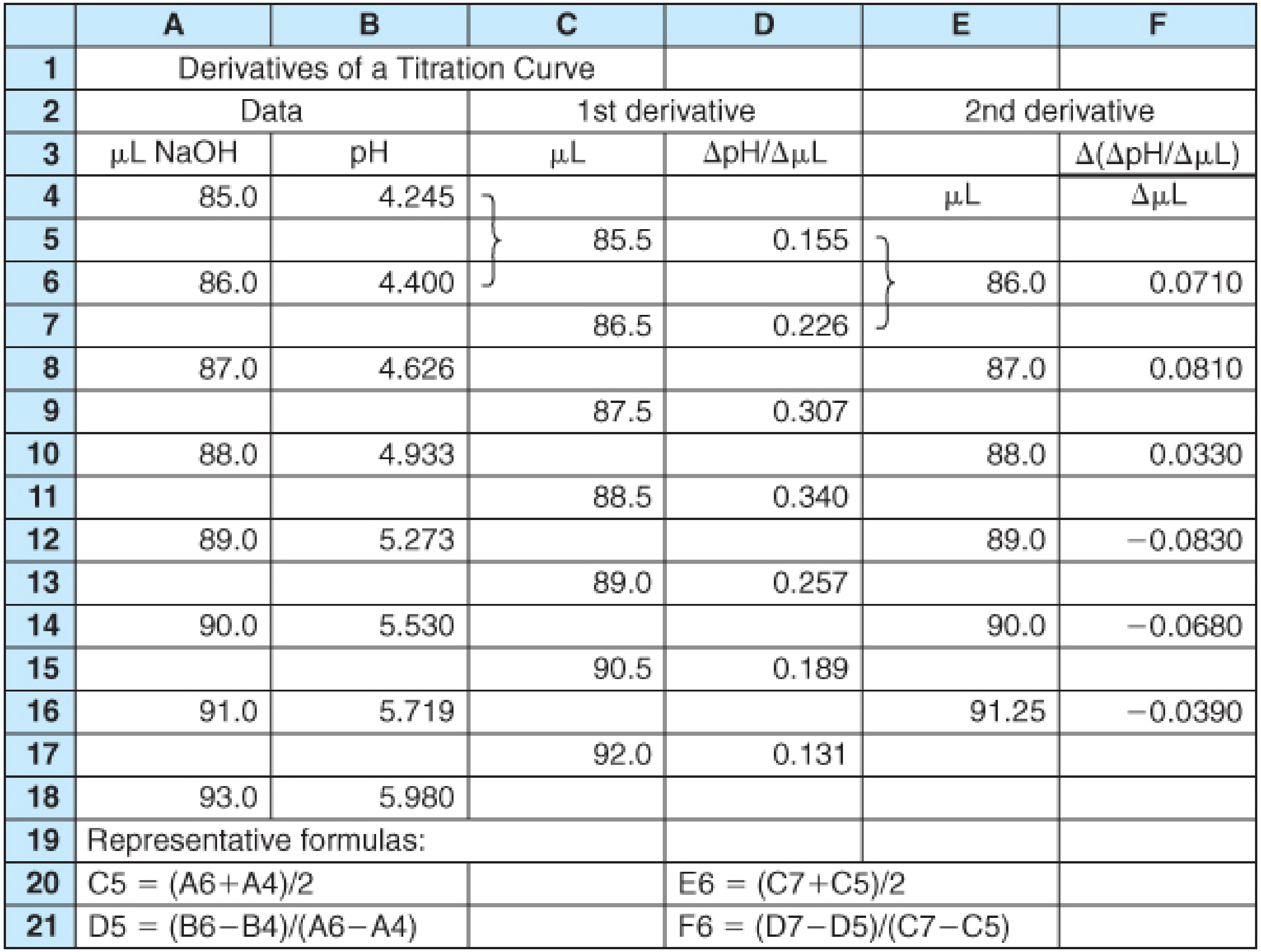
11-4: Titrations in Diprotic Systems



11-5: Finding the End Point with a pH Electrode

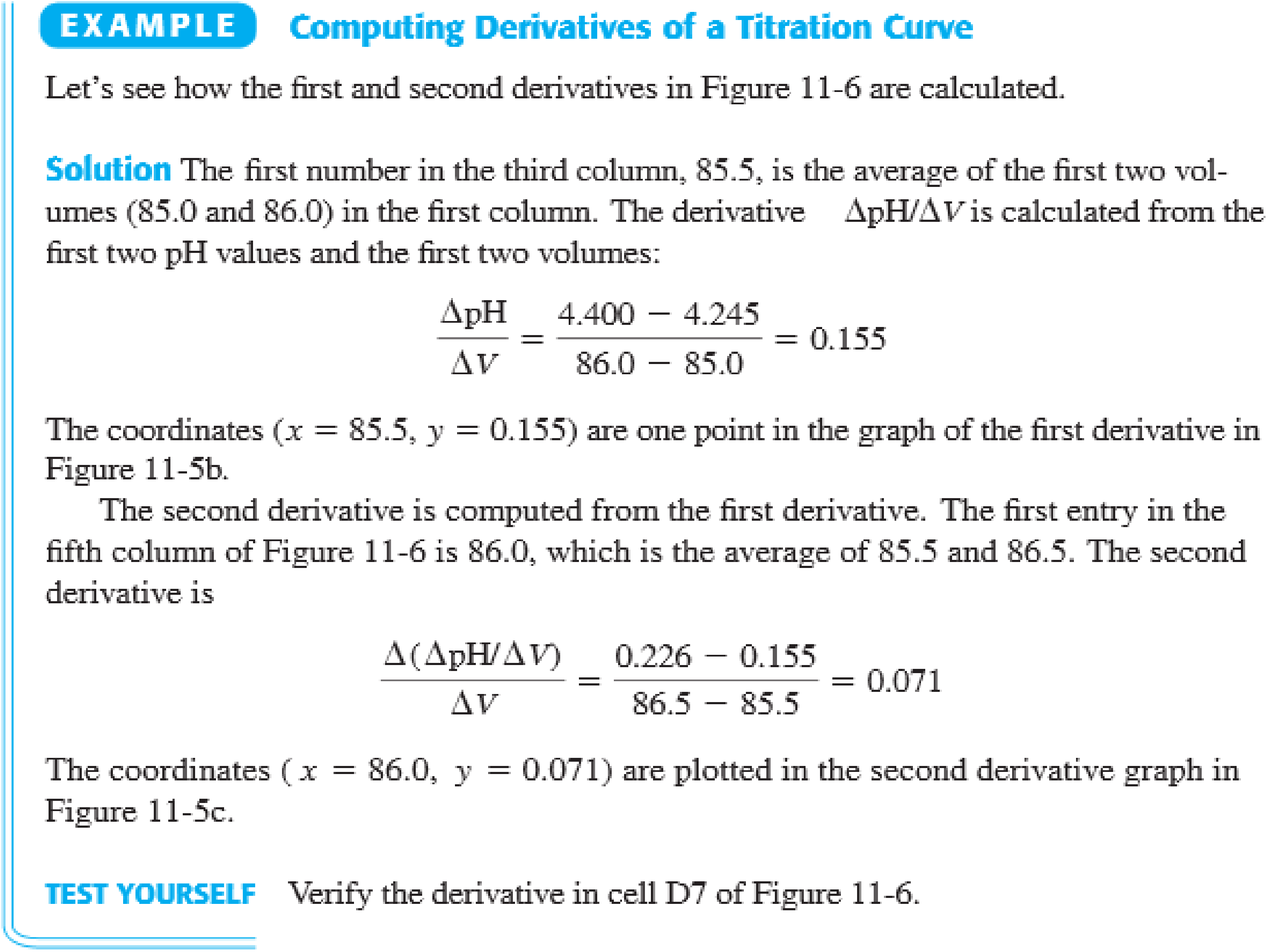
- Titrations are commonly performed to find out how much analyte is present or to measure equilibrium constants.
- We can obtain the information necessary for both purposes by monitoring pH during the titration.
- An *autotitrator* performs the entire operation automatically. The instrument waits for 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.

11-5: Finding the End Point with a pH Electrode



	A	B	C	D	E	F
1	Derivatives of a Titration Curve					
2	Data		1st derivative		2nd derivative	
3	μL NaOH	pH	μL	ΔpH/ΔμL		Δ(ΔpH/ΔμL)
4	85.0	4.245			μL	ΔμL
5			85.5	0.155		
6	86.0	4.400			86.0	0.0710
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)		

11-5: Finding the End Point with a pH Electrode



EXAMPLE **Computing Derivatives of a Titration Curve**

Let's see how the first and second derivatives in Figure 11-6 are calculated.

Solution The first number in the third column, 85.5, is the average of the first two volumes (85.0 and 86.0) in the first column. The derivative $\Delta pH/\Delta V$ is calculated from the first two pH values and the first two volumes:

$$\frac{\Delta pH}{\Delta V} = \frac{4.400 - 4.245}{86.0 - 85.0} = 0.155$$

The coordinates ($x = 85.5$, $y = 0.155$) are one point in the graph of the first derivative in Figure 11-5b.

The second derivative is computed from the first derivative. The first entry in the fifth column of Figure 11-6 is 86.0, which is the average of 85.5 and 86.5. The second derivative is

$$\frac{\Delta(\Delta pH/\Delta V)}{\Delta V} = \frac{0.226 - 0.155}{86.5 - 85.5} = 0.071$$

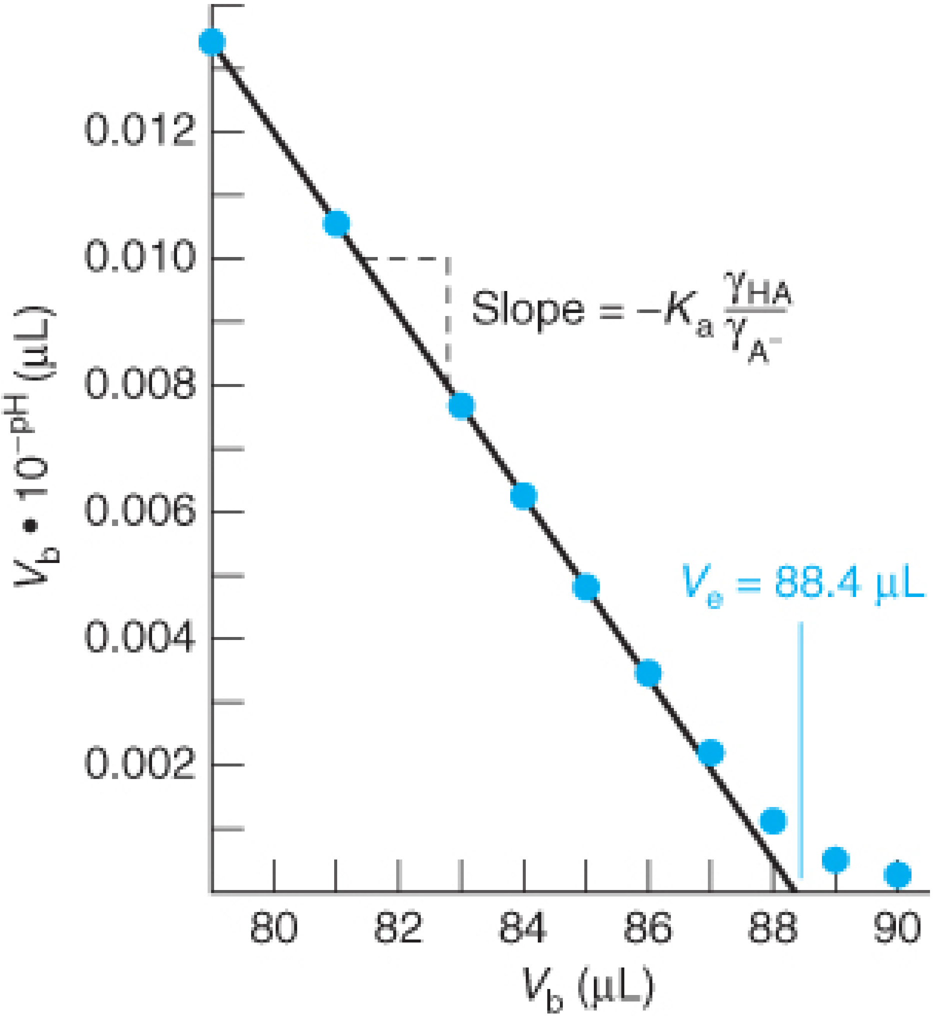
The coordinates ($x = 86.0$, $y = 0.071$) are plotted in the second derivative graph in Figure 11-5c.

TEST YOURSELF Verify the derivative in cell D7 of Figure 11-6.

11-5: Finding the End Point with a pH Electrode

- A problem with using derivatives to find the end point is that titration data are least accurate right near the end point (buffering is minimal and electrode response is sluggish).
- A **Gran plot** is a graph of $V_b \times 10^{-pH}$ versus V_b.
- A Gran plot uses data from before the end point to locate the end point.
- The slope of the linear portion of the graph is K_a and the x-intercept is V_e.

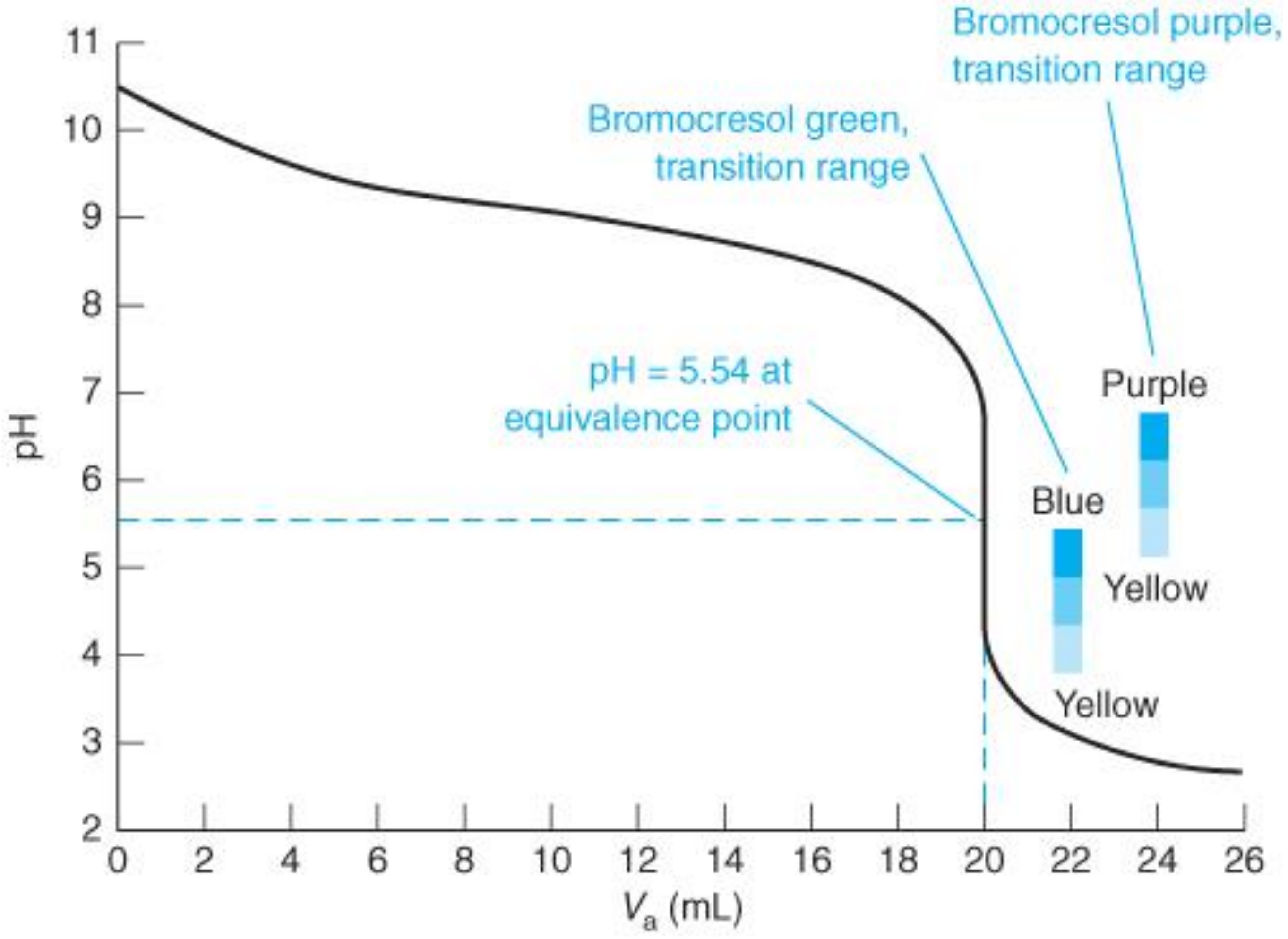
11-5: Finding the End Point with a pH Electrode



11-6: Finding the End Point with Indicators

- An acid-base **indicator** is itself an acid or base whose various protonated species have different colors.
- One of the most common indicators is **phenolphthalein**, usually used for its colorless-to-pink transition at pH 8.0–9.6.
- In strong acid, the colorless form of phenolphthalein turns orange-red. In strong base, the red species loses its color.
- Choose an indicator whose transition range overlaps the steepest part of the titration curve.
- **Indicator error** is the difference between the observed end point (color change) and the true equivalence point.

11-6: Finding the End Point with Indicators



11-7: Practical Notes

- Acids and bases in Table 11-4 can be obtained pure enough to be **primary standards.**
- NaOH and KOH are not primary standards because they contain carbonate and adsorbed water. Solutions of NaOH and KOH must be standardized.
- Alkaline solutions (e.g., 0.1 M NaOH) must be protected from the atmosphere; otherwise, they absorb CO_2. Standard solutions are commonly stored in high-density polyethylene bottles with screw caps.

$$OH^- + CO_2 \rightarrow HCO_3^-$$

- Strongly basic solutions attack glass and are best stored in plastic containers.

~~11-8: Kjeldahl Nitrogen Analysis~~

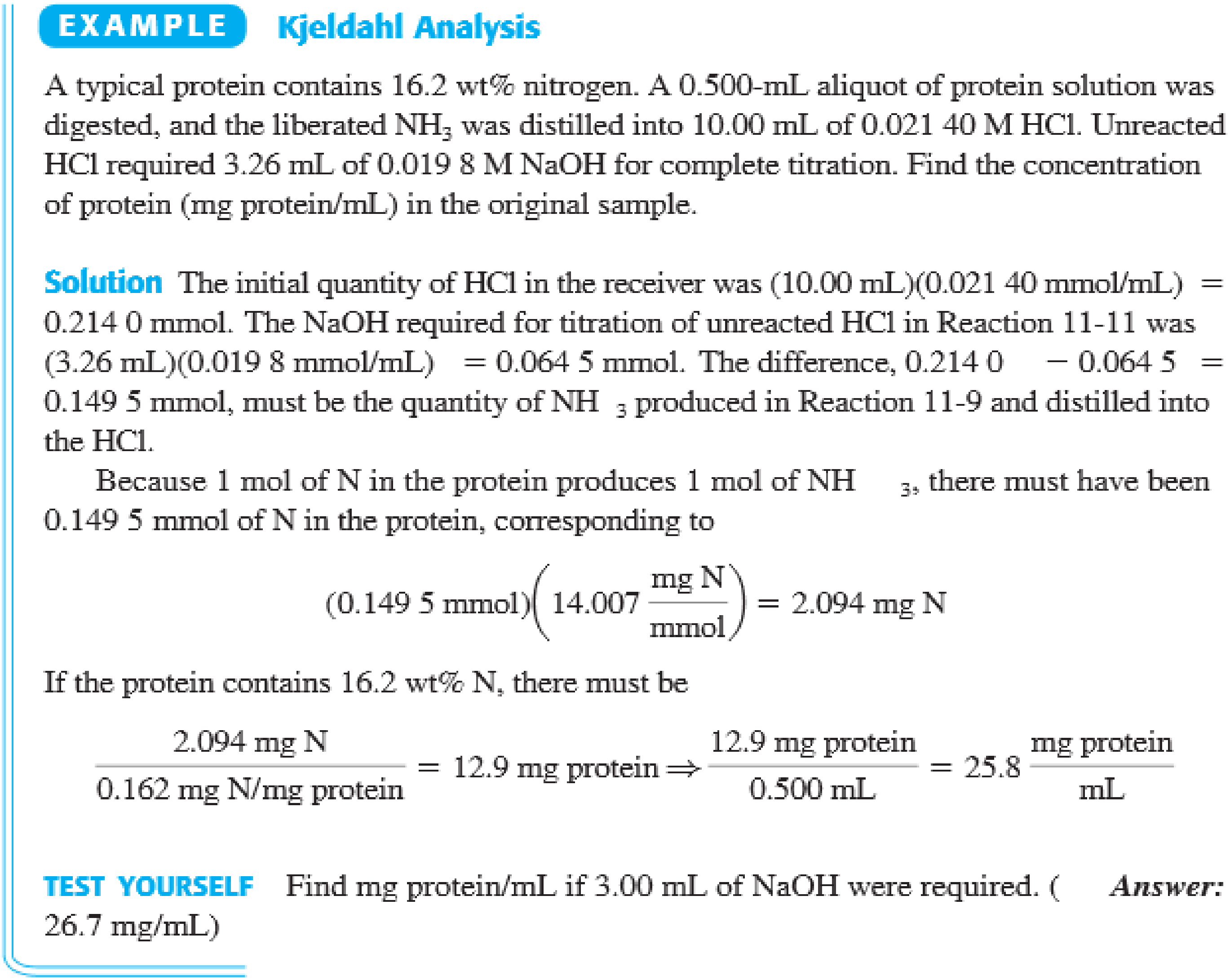
Kjeldahl nitrogen analysis:

- One of the most widely used methods for determining nitrogen in organic substances, especially for proteins (~16 wt% nitrogen).
- A sample is first **digested** (decomposed and dissolved) in boiling sulfuric acid, which converts amine and amide nitrogen into ammonium ion, NH_4^+, and oxidizes other elements present.
- To speed the reaction, the boiling point of concentrated (98 wt%) sulfuric acid is raised by adding K_2SO_4.
- Digestion is carried out in a long-neck **Kjeldahl flask** that prevents loss of sample from spattering.

~~11-8: Kjeldahl Nitrogen Analysis~~

- After digestion is complete, the solution containing NH_4^+ is made basic, and the liberated NH_3 is steam distilled (with a large excess of steam) into a receiver containing a **known amount** of HCl.
- Excess, unreacted HCl is then titrated with standard NaOH to determine how much HCl was consumed by NH_3.

~~11-8: Kjeldahl Nitrogen Analysis~~



EXAMPLE **Kjeldahl Analysis**

A typical protein contains 16.2 wt% nitrogen. A 0.500-mL aliquot of protein solution was digested, and the liberated NH_3 was distilled into 10.00 mL of 0.021 40 M HCl. Unreacted HCl required 3.26 mL of 0.019 8 M NaOH for complete titration. Find the concentration of protein (mg protein/mL) in the original sample.

Solution The initial quantity of HCl in the receiver was (10.00 mL)(0.021 40 mmol/mL) = 0.214 0 mmol. The NaOH required for titration of unreacted HCl in Reaction 11-11 was (3.26 mL)(0.019 8 mmol/mL) = 0.064 5 mmol. The difference, 0.214 0 − 0.064 5 = 0.149 5 mmol, must be the quantity of NH_3 produced in Reaction 11-9 and distilled into the HCl.

Because 1 mol of N in the protein produces 1 mol of NH_3, there must have been 0.149 5 mmol of N in the protein, corresponding to

$$(0.149\,5\ \text{mmol})\left(14.007\ \frac{\text{mg N}}{\text{mmol}}\right) = 2.094\ \text{mg N}$$

If the protein contains 16.2 wt% N, there must be

$$\frac{2.094\ \text{mg N}}{0.162\ \text{mg N/mg protein}} = 12.9\ \text{mg protein} \Rightarrow \frac{12.9\ \text{mg protein}}{0.500\ \text{mL}} = 25.8\ \frac{\text{mg protein}}{\text{mL}}$$

TEST YOURSELF Find mg protein/mL if 3.00 mL of NaOH were required. (*Answer:* 26.7 mg/mL)

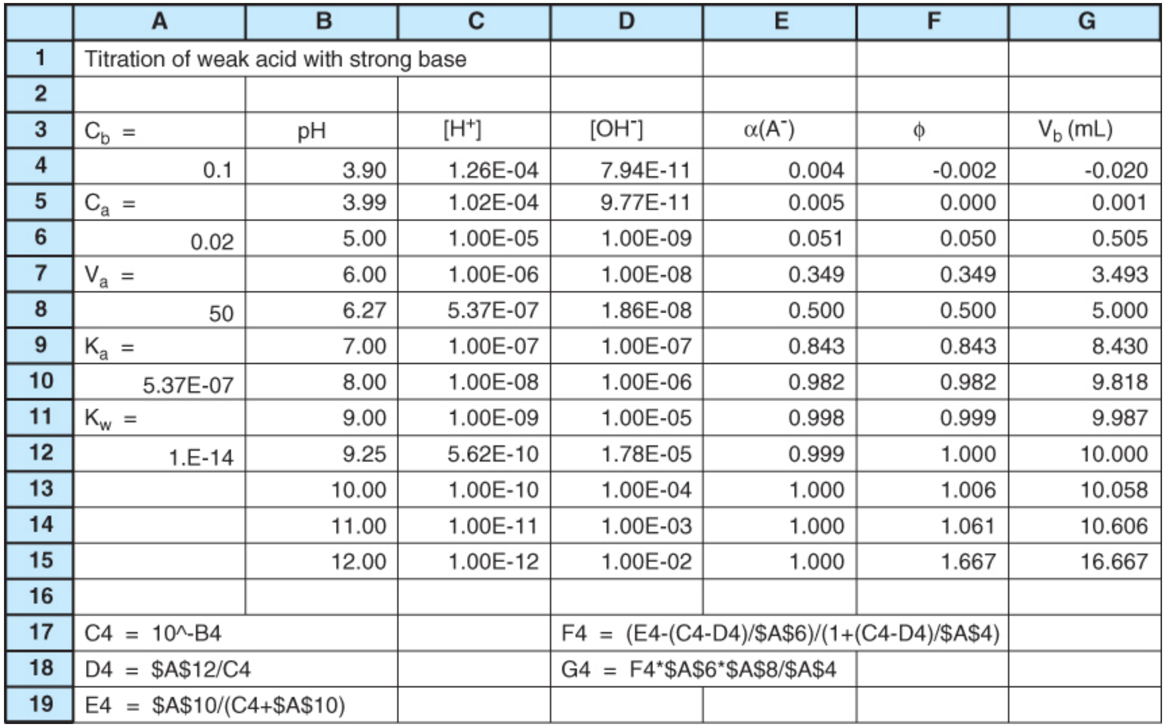
11-9: The Leveling Effect

Acid strength: Expect $HClO_4$ (aq) > HCl (aq)

- 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 **leveling effect,** $HClO_4$ and HCl behave as if they had the same acid strength; both are leveled to H_3O^+.

~~11-10: Calculating Titration Curves with~~ Spreadsheets

- The approximations used previously are of limited value when concentrations are too dilute or equilibrium constants are not of the right magnitude or K_a values are too closely spaced, like those in a protein.
- Spreadsheets can be used to deal with titrations in a general manner.



	A	B	C	D	E	F	G
1	Titration of weak acid with strong base						
2							
3	C_b =	pH	$[H^+]$	$[OH^-]$	$\alpha(A^-)$	ϕ	V_b (mL)
4	0.1	3.90	1.26E-04	7.94E-11	0.004	-0.002	-0.020
5	C_a =	3.99	1.02E-04	9.77E-11	0.005	0.000	0.001
6	0.02	5.00	1.00E-05	1.00E-09	0.051	0.050	0.505
7	V_a =	6.00	1.00E-06	1.00E-08	0.349	0.349	3.493
8	50	6.27	5.37E-07	1.86E-08	0.500	0.500	5.000
9	K_a =	7.00	1.00E-07	1.00E-07	0.843	0.843	8.430
10	5.37E-07	8.00	1.00E-08	1.00E-06	0.982	0.982	9.818
11	K_w =	9.00	1.00E-09	1.00E-05	0.998	0.999	9.987
12	1.E-14	9.25	5.62E-10	1.78E-05	0.999	1.000	10.000
13		10.00	1.00E-10	1.00E-04	1.000	1.006	10.058
14		11.00	1.00E-11	1.00E-03	1.000	1.061	10.606
15		12.00	1.00E-12	1.00E-02	1.000	1.667	16.667
16							
17	C4 = 10^-B4			F4 = (E4-(C4-D4)/$A$6)/(1+(C4-D4)/$A$4)			
18	D4 = $A$12/C4			G4 = F4*$A$6*$A$8/$A$4			
19	E4 = $A$10/(C4+$A$10)						