

The hydrolysis of a weak base is discussed on page 594 of PoC and demonstrated in Example 16-6.

As in Exercises 26 through 31, the same three systems ( $\text{CH}_2\text{ClCOO}^-/\text{CH}_2\text{ClCOOH}$ ,  $\text{C}_6\text{H}_5\text{COO}^-/\text{C}_6\text{H}_5\text{COOH}$ , and  $\text{CN}^-/\text{HCN}$ ) will continue to provide a consistent set of examples.

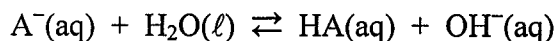
32.  $\text{NaCH}_2\text{ClCOO}$  is the salt of  $\text{CH}_2\text{ClCOOH}$  (a weak acid) and  $\text{NaOH}$  (a strong base). The cation  $\text{Na}^+$ , conjugate to  $\text{NaOH}$ , does not affect the concentrations of hydronium or hydroxide ion. The chloroacetate anion, however, undergoes hydrolysis (reacts with water) to produce a solution with excess hydroxide ion:



$$K_b = \frac{[\text{CH}_2\text{ClCOOH}][\text{OH}^-]}{[\text{CH}_2\text{ClCOO}^-]} = 7.1 \times 10^{-12}$$

The value of  $K_b$ , equal to  $K_w/K_a$ , is obtained from the ionization constant of the corresponding acid. See the preceding exercise.

For convenience in solving the next several problems, we shall henceforth refer to a general hydrolysis reaction involving  $\text{A}^-$ ,  $\text{HA}$ , and  $\text{OH}^-$ . The symbol  $c$  will be used interchangeably with  $[\text{A}^-]_0$  for the initial concentration of the conjugate base:



Initial concentration	$c$	0	0
Change	$-x$	$x$	$x$
Equilibrium concentration	$c - x$	$x$	$x$

The mass-action equation that results is of exactly the same form used to describe the equilibrium of a weak acid,

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{K_w}{K_a}$$

$$= \frac{x^2}{c - x}$$

and therefore we can carry over the procedures outlined in Exercise 26. Our choice is

between a simplified expression with an approximate (often very accurate) solution,

$$K_b = \frac{x^2}{c-x} \approx \frac{x^2}{c} \quad \text{if } x \ll c$$

$$x = \sqrt{K_b c} \quad (\text{approximate solution})$$

or the unmodified quadratic equation (more complicated, but always reliable):

$$0 = x^2 + K_b x - K_b c$$

$$x = \frac{-K_b \pm \sqrt{(K_b)^2 - 4(1)(-K_b c)}}{2(1)} \quad (\text{quadratic formula})$$

For example, both the simplified form and the full quadratic equation yield effectively the same root when  $c = 0.010 \text{ M}$ :

$$x = \sqrt{K_b c} = \sqrt{(7.14 \times 10^{-12})(0.010)} = 2.67 \times 10^{-7} \text{ M} \quad (\text{approximate solution})$$

$$x_+ = \frac{-(7.14 \times 10^{-12}) + \sqrt{(7.14 \times 10^{-12})^2 + 4(7.14 \times 10^{-12})(0.010)}}{2(1)} = 2.67 \times 10^{-7} \text{ M}$$

(quadratic formula)

Note that we show the value of  $K_b$  with an extra (nonsignificant) digit,

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.14 \times 10^{-12}$$

as a reminder not to round off intermediate values in the calculation.

The final step is to solve for  $[\text{H}_3\text{O}^+]$  and pH, taking  $[\text{OH}^-] = x$ :

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]}$$

$$= -\log \frac{1.0 \times 10^{-14}}{2.67 \times 10^{-7}}$$

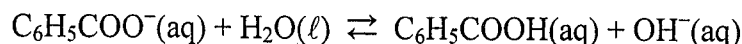
$$= 7.43 \quad (2 \text{ sig fig})$$

Since the approximate equation proves mathematically sound when  $c = 0.010 M$ , we can justifiably use it for any higher initial concentration:

	$c (M)$	pH
(a)	1.000	8.43
(b)	0.500	8.28
(c)	0.100	7.93
(d)	0.010	7.43

CAUTION: The accuracy of our whole approach starts to become questionable at  $\text{OH}^-$  concentrations noticeably less than  $10^{-6} M$ , as happens in this system when  $c = 0.010 M$ . Under such conditions, we cannot properly neglect the water autoionization reaction as a source of  $\text{OH}^-$ . An exact treatment, taking into account all competing equilibria, requires the solution of a cubic equation (which yields a corrected pH of 7.46 for  $c = 0.010 M$ ).

33. The calculations are done in exactly the same way as in the preceding exercise, this time with a base ionization constant of  $1.5 \times 10^{-10}$  (from Exercise 31b):



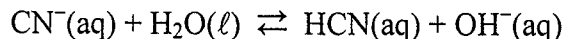
$$K_b = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.5 \times 10^{-5}} = 1.5 \times 10^{-10}$$

Again, we expect a basic solution after hydrolysis:

	$c (M)$	pH
(a)	1.000	9.09
(b)	0.500	8.94
(c)	0.100	8.59
(d)	0.010	8.09

The symbol  $c$  denotes the initial concentration of conjugate base,  $[\text{C}_6\text{H}_5\text{COO}^-]_0$ .

34. The computation follows the same pattern established in the preceding two exercises. Here the base ionization constant is  $1.6 \times 10^{-5}$  (from Exercise 31c),



$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

and we obtain basic solutions with the highest pH values so far:

	$c$ (M)	pH
(a)	1.000	11.60
(b)	0.500	11.45
(c)	0.100	11.10
(d)	0.010	10.60

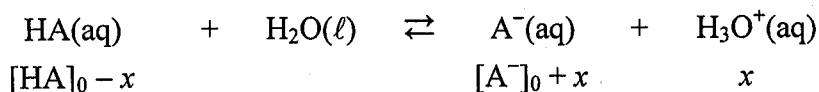
The symbol  $c$  denotes the initial concentration of conjugate base,  $[\text{CN}^-]_0$ .

*Buffers (Exercises 35 through 41) are covered in Section 16-5 of PoC and demonstrated in Example 16-5.*

*As before, we use chloroacetic acid, benzoic acid, and hydrocyanic acid to establish a standard for comparison. The series begins with Exercise 35.*

**35.** This exercise, together with those immediately following, considers a *buffer solution*—a mixture in which substantial concentrations of both a weak acid (HA) and its conjugate base ( $\text{A}^-$ ) are present.

Inserting the initial values  $[\text{HA}]_0$  and  $[\text{A}^-]_0$  into our standard acid–base equilibrium,



we obtain the full mass-action expression connecting  $\text{H}_3\text{O}^+$ ,  $\text{A}^-$ , and HA:

$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{A}^-]_{\text{eq}}}{[\text{HA}]_{\text{eq}}} = \frac{x([\text{A}^-]_0 + x)}{[\text{HA}]_0 - x}$$

If, however, the change in concentration ( $x$ ) is small compared with  $[\text{A}^-]_0$  and  $[\text{HA}]_0$ , then we can solve the simpler *Henderson-Hasselbalch* equation instead:

$$K_a \approx \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{A}^-]_0}{[\text{HA}]_0}$$

$$-\log K_a = -\log [\text{H}_3\text{O}^+]_{\text{eq}} - \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

The buffer equation is usually reasonable for swings within a factor of 10 on either side:

$$0.1 \leq \frac{[\text{A}^-]_0}{[\text{HA}]_0} \leq 10$$

If now we introduce a small concentration ( $\delta$ ) of  $\text{H}_3\text{O}^+$ , the anion-to-acid ratio becomes

$$\frac{[\text{A}^-]_0 - \delta}{[\text{HA}]_0 + \delta}$$

and the pH decreases slightly to

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0 - \delta}{[\text{HA}]_0 + \delta}$$

Similarly, introduction of a small concentration of  $\text{OH}^-$  will increase the pH slightly to

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0 + \delta}{[\text{HA}]_0 - \delta}$$

SAMPLE CALCULATION: The conditions specified in (a) will serve as a sufficiently general example for the long series of calculations requested:

$$\frac{[\text{A}^-]_0}{[\text{HA}]_0} = \frac{[\text{CH}_2\text{ClCOO}^-]_0}{[\text{CH}_2\text{ClCOOH}]_0} = \frac{0.500 \text{ M}}{0.500 \text{ M}} = 1.00$$

With  $[\text{A}^-]_0 = [\text{HA}]_0$ , the value of  $\text{p}K_a$  (equal to 2.85) establishes the central pH of the buffer:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0} = -\log(1.4 \times 10^{-3}) + \log 1.00 \\ &= 2.85 + 0 = 2.85 \end{aligned}$$

Addition of 0.005 M hydronium ion to this system will decrease the pH by 0.009 unit:

$$\text{pH} = 2.85 + \log \frac{0.500 - 0.005}{0.500 + 0.005} = 2.85 - 0.009$$

Addition of 0.005 M hydroxide ion will produce the same change in the opposite direction:

$$\text{pH} = 2.85 + \log \frac{0.500 + 0.005}{0.500 - 0.005} = 2.85 + 0.009$$

The remaining computations, here and in Exercises 36 and 37, are all handled identically. In the summary table that follows, the last column reports the approximate change in pH caused by injection of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  at a level of  $0.005\text{ M}$ :

	$[\text{HA}]_0\text{ (M)}$	$[\text{A}^-]_0\text{ (M)}$	$\frac{[\text{A}^-]_0}{[\text{HA}]_0}$	$\text{p}K_a$	pH	$\Delta\text{pH} (\delta = 0.005\text{ M})$
(a)	0.500	0.500	1.00	2.85	2.85	$\pm 0.009$
(b)	1.000	0.500	0.500	2.85	2.55	$\pm 0.007$
(c)	0.500	1.000	2.00	2.85	3.15	$\pm 0.007$
(d)	1.000	1.000	1.000	2.85	2.85	$\pm 0.004$
(e)	1.000	0.100	0.100	2.85	1.85	$\pm 0.024$
(f)	0.100	1.000	10.0	2.85	3.85	$\pm 0.024$

Note that the variation in pH is smallest when  $[\text{A}^-]_0$  and  $[\text{HA}]_0$  are individually largest, thereby ensuring that the ratios

$$\frac{[\text{A}^-]_0 + \delta}{[\text{HA}]_0 - \delta} \quad \text{and} \quad \frac{[\text{A}^-]_0 - \delta}{[\text{HA}]_0 + \delta}$$

are altered least by the value  $\delta$ . A buffer in which  $[\text{A}^-]_0 = [\text{HA}]_0 = 1.000\text{ M}$ , for example, is better able to withstand  $\delta = 0.005\text{ M}$  than one in which  $[\text{A}^-]_0 = [\text{HA}]_0 = 0.500\text{ M}$ :

$$\log \frac{1.000 \pm 0.005}{1.000 \mp 0.005} = \pm 0.004$$

$$\log \frac{0.500 \pm 0.005}{0.500 \mp 0.005} = \pm 0.009$$

Both solutions tend to maintain  $\text{pH} = \text{p}K_a$ , but the buffer with the greater reserves does so more robustly.

**36.** The method here is the same as in the preceding exercise. This time the buffer operates around a  $\text{p}K_a$  of 4.19:

$$\text{p}K_a = -\log K_a = -\log(6.5 \times 10^{-5}) = 4.19$$

In the accompanying table, observe how the range of values is similar to that obtained in Exercise 35. The deviations of pH from  $\text{p}K_a$ ,

$$\text{pH} - \text{p}K_a = \log \frac{[\text{A}^-]_0 \pm \delta}{[\text{HA}]_0 \mp \delta}$$

are all determined by the same sets of sets of initial conditions (specified by  $[\text{HA}]_0$  and  $[\text{A}^-]_0$ ):

	$[\text{HA}]_0 (M)$	$[\text{A}^-]_0 (M)$	$\frac{[\text{A}^-]_0}{[\text{HA}]_0}$	$\text{p}K_a$	pH	$\Delta\text{pH} (\delta = 0.005 M)$
(a)	0.500	0.500	1.00	4.19	4.19	$\pm 0.009$
(b)	1.000	0.500	0.500	4.19	3.89	$\pm 0.007$
(c)	0.500	1.000	2.00	4.19	4.49	$\pm 0.007$
(d)	1.000	1.000	1.000	4.19	4.19	$\pm 0.004$
(e)	1.000	0.100	0.100	4.19	3.19	$\pm 0.024$
(f)	0.100	1.000	10.0	4.19	5.19	$\pm 0.024$

37. Aside from a different central pH,

$$\text{p}K_a = -\log K_a = -\log(6.2 \times 10^{-10}) = 9.21$$

the calculation for a  $\text{CN}^-/\text{HCN}$  buffer is the same as those undertaken in the two preceding exercises:

	$[\text{HA}]_0 (M)$	$[\text{A}^-]_0 (M)$	$\frac{[\text{A}^-]_0}{[\text{HA}]_0}$	$\text{p}K_a$	pH	$\Delta\text{pH} (\delta = 0.005 M)$
(a)	0.500	0.500	1.00	9.21	9.21	$\pm 0.009$
(b)	1.000	0.500	0.500	9.21	8.91	$\pm 0.007$
(c)	0.500	1.000	2.00	9.21	9.51	$\pm 0.007$
(d)	1.000	1.000	1.000	9.21	9.21	$\pm 0.004$
(e)	1.000	0.100	0.100	9.21	8.21	$\pm 0.024$
(f)	0.100	1.000	10.0	9.21	10.21	$\pm 0.024$

38. The pH of a buffer solution is approximated to reasonable accuracy by the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

See Table C-20 in Appendix C of *PoC* (pages A98–A99) for a selection of  $\text{p}K_a$  values.

(a) Hypochlorous acid ( $pK_a = 7.52$ ) will produce a buffer solution with  $pH = 7.52$  when equal concentrations of  $HClO$  (the acid  $HA$ ) and  $ClO^-$  (the conjugate base  $A^-$ ) are on hand:

$$pH = pK_a + \log \frac{[ClO^-]_0}{[HClO]_0} = 7.52 + \log 1 = 7.52$$

The initial concentrations of acid and base should be sufficiently large to preserve the anion-to-acid ratio

$$\frac{[ClO^-]_0}{[HClO]_0} = 1.00$$

in the presence of any stray concentration  $\delta$  of  $OH^-$  or  $H_3O^+$  ions:

$$pH = pK_a + \log \frac{[ClO^-]_0 \pm \delta}{[HClO]_0 \mp \delta} \approx pK_a + \log \frac{[ClO^-]_0}{[HClO]_0}$$

(b) The variation in  $pH$  is equal to  $\pm \log 4$  over the specified interval:

$$\text{Minimum: } pH - pK_a = \log \frac{[A^-]_0}{[HA]_0} = \log \frac{1}{4} = -\log 4$$

$$\text{Maximum: } pH - pK_a = \log \frac{[A^-]_0}{[HA]_0} = \log 4$$

Values range from  $pH = 6.92$  at the low end to  $8.12$  at the high end. See Figure 16.3.

(c) A solution prepared so that

$$\frac{[ClO^-]_0}{[HClO]_0} = 1.55$$

will have a buffered  $pH$  of  $7.71$ :

$$\log \frac{[ClO^-]_0}{[HClO]_0} = pH - pK_a = 7.71 - 7.52 = 0.19$$

$$\frac{[ClO^-]_0}{[HClO]_0} = 10^{0.19} = 1.55$$



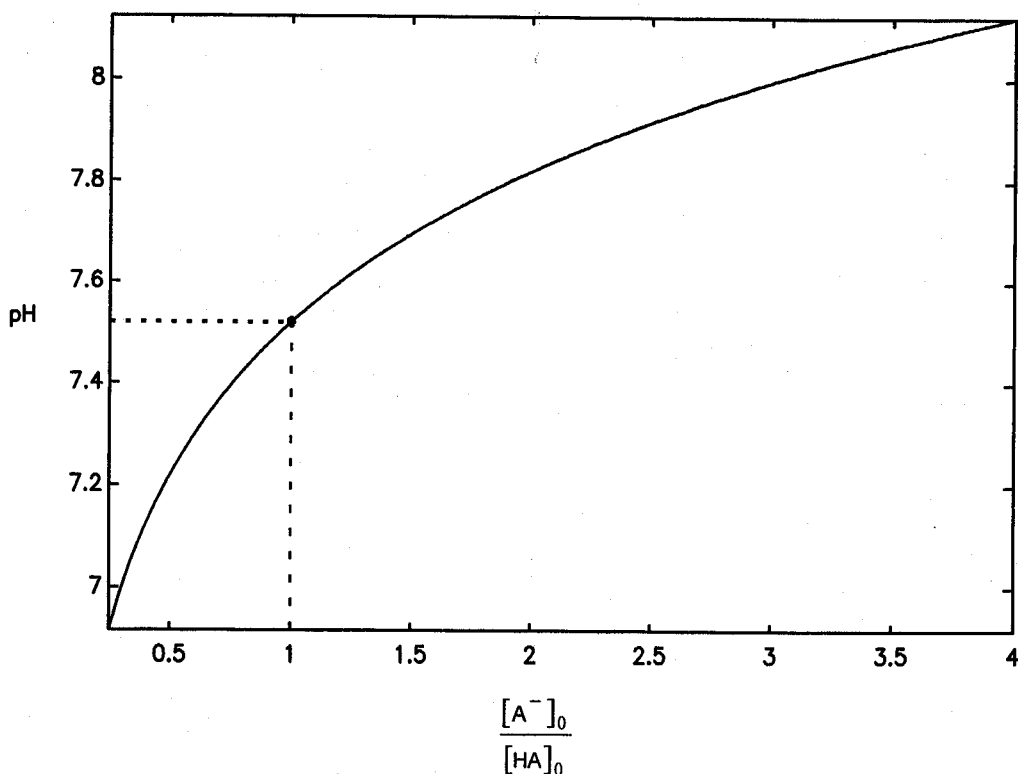


FIGURE 16.3 Variation of pH for a  $\text{ClO}^-/\text{HClO}$  buffer, plotted for anion-to-acid ratios ranging from 0.25 to 4. The point  $\text{pH} = \text{p}K_a$ , corresponding to a ratio of 1, is marked by the intersection of the dashed lines.

39. Use the same reasoning as in the preceding exercise. Values of  $\text{p}K_a$  are listed in Table C-20 of Appendix C (*PoC*, pages A98–A99).

(a) Fluoroacetic acid ( $\text{p}K_a = 2.59$ ) will produce a buffer solution with

$$\text{pH} = \text{p}K_a = 2.59$$

when equal concentrations of  $\text{CH}_2\text{FCOOH}$  (the acid) and  $\text{CH}_2\text{FCOO}^-$  (the conjugate base) are present. The concentrations should be large enough to withstand any anticipated intrusion of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions.

(b) Figure 16.4 shows the titration curve over the requested interval. The variation of pH around  $\text{p}K_a$  is equal to  $\pm \log 4$ , just as in Exercise 38:

$$\text{pH} - \text{p}K_a = \pm \log 4 = \pm 0.60$$

Values range from  $\text{pH} = 1.99$  to  $\text{pH} = 3.19$ .

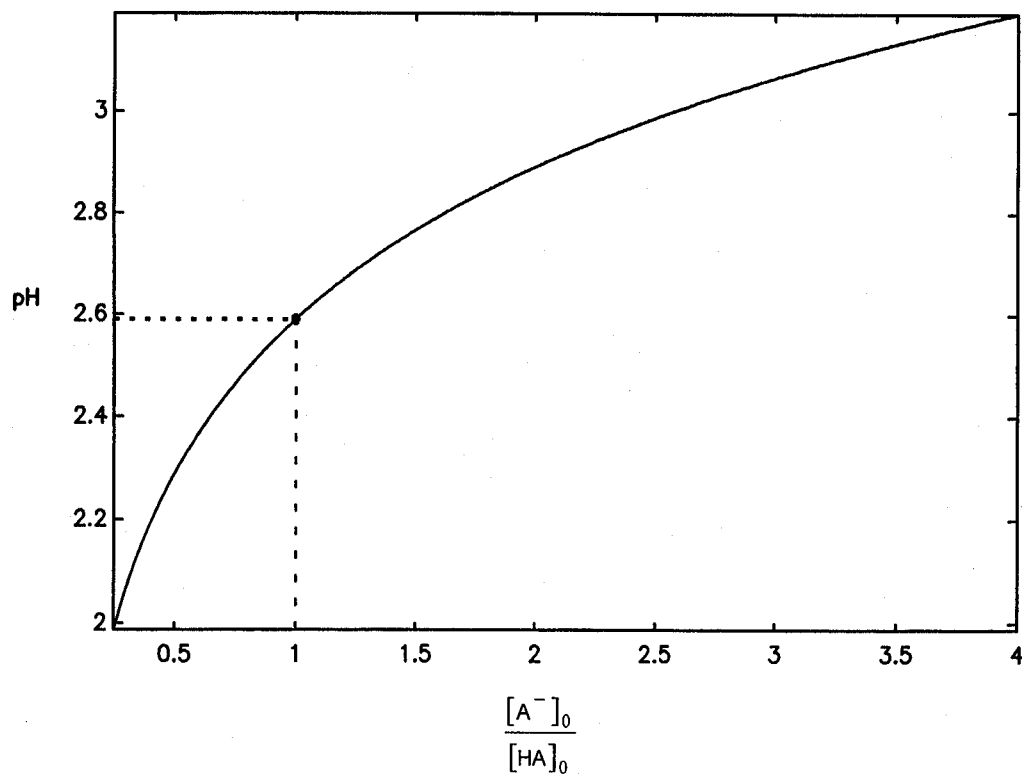


FIGURE 16.4 Variation of pH for a  $\text{CH}_2\text{FCOO}^-/\text{CH}_2\text{FCOOH}$  buffer, plotted for anion-to-acid ratios ranging from 0.25 to 4. The point  $\text{pH} = \text{p}K_a$ , corresponding to a ratio of 1, is marked by the intersection of the dashed lines. Note the similarity to Figure 16.3.

(c) A solution prepared so that

$$\frac{[\text{CH}_2\text{FCOO}^-]_0}{[\text{CH}_2\text{FCOOH}]_0} = 0.65$$

will have a buffered pH of 2.40:

$$\log \frac{[\text{CH}_2\text{FCOO}^-]_0}{[\text{CH}_2\text{FCOOH}]_0} = \text{pH} - \text{p}K_a = 2.40 - 2.59 = -0.19$$

$$\frac{[\text{CH}_2\text{FCOO}^-]_0}{[\text{CH}_2\text{FCOOH}]_0} = 10^{-0.19} = 0.65$$

40. As in the preceding exercises, we apply the Henderson-Hasselbalch equation to a buffer solution:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

(a) Since we have equimolar amounts of  $\text{A}^-$  and  $\text{HA}$  in the same volume, the anion-to-acid ratio is 1.00 and thus the pH is equal to  $\text{p}K_a$ :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0} = 4.86 + \log 1.00 = 4.86$$

(b) Adding equal amounts (moles) of both  $\text{A}^-$  and  $\text{HA}$  does not change the ratio of concentrations in this system:

$$\frac{[\text{A}^-]_0}{[\text{HA}]_0} = \frac{\frac{0.100 \text{ mol} + 0.010 \text{ mol}}{0.500 \text{ L}}}{\frac{0.100 \text{ mol} + 0.010 \text{ mol}}{0.500 \text{ L}}} = \frac{0.110}{0.110} = 1.00$$

The pH remains fixed at its original value:

$$\text{pH} = \text{p}K_a = 4.86$$

(c) A change in volume (here, a doubling) does not change the ratio of concentrations:

$$\frac{[\text{A}^-]_0}{[\text{HA}]_0} = \frac{\frac{0.100 \text{ mol}}{2 \times 0.500 \text{ L}}}{\frac{0.100 \text{ mol}}{2 \times 0.500 \text{ L}}} = \frac{0.100}{0.100} = 1.00$$

The pH remains constant at 4.86, as it will for all such changes—provided that the solution does not become overly dilute.

41. The pH is determined not by the ratio of masses but rather by the ratio of *moles*:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

Assume, therefore, that we start with some arbitrary mass  $m$  of  $\text{HCOOH}$  and  $\text{NaHCOO}$  in a common volume  $V$ , from which we compute the ratio of moles (and hence concentrations):

$$\frac{[A^-]_0}{[HA]_0} = \frac{m \text{ g NaHCOO} \times \frac{1 \text{ mol NaHCOO}}{68.008 \text{ g}} \times \frac{1 \text{ mol HCOO}^-}{\text{mol NaHCOO}}}{\frac{m \text{ g HCOOH} \times \frac{1 \text{ mol HCOOH}}{46.026 \text{ g}}}{V}} = \frac{46.026}{68.008} = 0.67677$$

The pH then follows directly from the Henderson-Hasselbalch equation:

$$\text{pH} = 3.75 + \log 0.67677 = 3.58$$

Note that the result is independent of the common volume,  $V$ .

*Various mixtures of acids and bases, strong and weak, are analyzed in Exercises 42 through 45—a lead-in to titration (beginning with Exercise 46).*

**42.** The initial amount of  $\text{HNO}_3$  (and therefore the initial amount of  $\text{H}_3\text{O}^+$ ) is the same in each mixture:

$$\frac{0.100 \text{ mol HNO}_3}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HNO}_3} \times 0.100 \text{ L} = 0.0100 \text{ mol H}_3\text{O}^+$$

Nitric acid,  $\text{HNO}_3$ , is a strong acid.

**(a)** Add an equimolar amount of strong base:

$$\frac{0.050 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.200 \text{ L} = 0.010 \text{ mol OH}^-$$

The hydronium ions (0.0100 mol) are neutralized completely by an equal number of hydroxide ions (0.010 mol), leaving a solution with  $\text{pH} = 7.00$  at  $25^\circ\text{C}$ . Neither  $\text{Na}^+$  nor  $\text{NO}_3^-$  affects the  $\text{pH}$ , and we have the equilibrium concentrations

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

arising solely from the autoionization of water. See *PoC*, pages 581–582 and 584–589.

**(b)** Similar to (a). Add an equivalent amount of strong base:

$$\frac{0.100 \text{ mol KOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol KOH}} \times 0.100 \text{ L} = 0.0100 \text{ mol OH}^-$$

Again, 0.0100 mol  $\text{H}_3\text{O}^+$  neutralizes 0.0100 mol  $\text{OH}^-$ . The solution is neutral, just as it is in (a):  $\text{pH} = 7.00$ .

(c) The concentration and volume of NaOH are different from what we had in (a), but the molar *amount* of strong base is the same:

$$\frac{0.200 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.050 \text{ L} = 0.010 \text{ mol OH}^-$$

The outcome is necessarily the same as well: a neutral solution, with pH = 7.00 at 25°C.

(d) Once more. Whether supplied by NaOH, KOH, Ca(OH)<sub>2</sub>, or any other Arrhenius base, the addition of 0.010 mol OH<sup>-</sup> will neutralize the 0.0100 mol H<sub>3</sub>O<sup>+</sup> already present:

$$\frac{0.100 \text{ mol Ca(OH)}_2}{\text{L}} \times \frac{2 \text{ mol OH}^-}{\text{mol Ca(OH)}_2} \times 0.050 \text{ L} = 0.010 \text{ mol OH}^-$$

Again, pH = 7.00.

(e) Pure H<sub>2</sub>O is added. The solution now contains the original 0.0100 mol H<sub>3</sub>O<sup>+</sup> in a total volume of 1.000 L:

$$[\text{H}_3\text{O}^+] = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 1.00 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-2}) = 2.000$$

43. The initial amount of HCl (and therefore the initial amount of H<sub>3</sub>O<sup>+</sup>) is the same in each mixture:

$$\frac{0.100 \text{ mol HCl}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} \times 0.100 \text{ L} = 0.0100 \text{ mol H}_3\text{O}^+$$

Hydrochloric acid, HCl, is a strong acid.

(a) Add an excess of strong base:

$$\frac{0.100 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.200 \text{ L} = 0.0200 \text{ mol OH}^-$$

Neutralization of 0.0100 mol OH<sup>-</sup> by 0.0100 mol H<sub>3</sub>O<sup>+</sup> leaves 0.0100 mol OH<sup>-</sup> remaining in a total volume of 1.000 L:

$$[\text{OH}^-] = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 1.00 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{1.00 \times 10^{-2}} = 12.00$$

(b) Add *less* than an equivalent amount of strong base:

$$\frac{0.100 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.050 \text{ L} = 0.0050 \text{ mol OH}^-$$

Neutralization of 0.0050 mol  $\text{H}_3\text{O}^+$  by 0.0050 mol  $\text{OH}^-$  leaves 0.0050 mol  $\text{H}_3\text{O}^+$  dissolved in 1.000 L:

$$[\text{H}_3\text{O}^+] = \frac{0.0050 \text{ mol}}{1.000 \text{ L}} = 5.0 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(5.0 \times 10^{-3}) = 2.30$$

(c) Sodium chloride, NaCl, is the salt of a strong acid (HCl) and a strong base (NaOH). Neither  $\text{Na}^+$  nor  $\text{Cl}^-$  reacts with  $\text{H}_2\text{O}$  to produce excess hydronium or hydroxide ions. The amount of  $\text{H}_3\text{O}^+$  originally contributed by the acid remains unchanged, and the pH is determined only by the existing hydronium ions present in the new volume:

$$[\text{H}_3\text{O}^+] = \frac{\text{original amount}}{\text{new volume}} = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 1.00 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-2}) = 2.000$$

(d) Add excess strong acid:

$$\frac{0.100 \text{ mol HNO}_3}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HNO}_3} \times 0.100 \text{ L} = 0.0100 \text{ mol H}_3\text{O}^+$$

$$[\text{H}_3\text{O}^+] = \frac{0.0100 \text{ mol} + 0.0100 \text{ mol}}{1.000 \text{ L}} = 0.0200 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.00 \times 10^{-2}) = 1.699$$

The total amount of  $\text{H}_3\text{O}^+$  is the sum of the amounts contributed separately by HCl and  $\text{HNO}_3$ .

(e) Similar to (c). The addition of pure water leaves the original amount of  $\text{H}_3\text{O}^+$  unchanged:

$$[\text{H}_3\text{O}^+] = \frac{\text{original amount}}{\text{new volume}} = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 1.00 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-2}) = 2.000$$

44. The initial amount of  $\text{HCOOH}$ , a weak acid, is the same in each mixture:

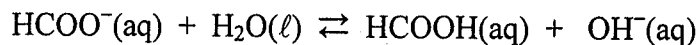
$$\frac{0.100 \text{ mol HCOOH}}{\text{L}} \times 0.100 \text{ L} = 0.0100 \text{ mol HCOOH}$$

The subsequent pH is determined by an equilibrium involving  $\text{HCOOH}$ ,  $\text{HCOO}^-$ ,  $\text{H}_3\text{O}^+$ , and  $\text{OH}^-$ .

(a) Add an equivalent amount of strong base:

$$\frac{0.100 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.100 \text{ L} = 0.0100 \text{ mol OH}^-$$

Neutralization of 0.0100 mol  $\text{HCOOH}$  by 0.0100 mol  $\text{OH}^-$  creates 0.0100 mol of the conjugate base,  $\text{HCOO}^-$ , in a volume of 1.000 L. Starting from this initial concentration of 0.0100 M, the formate ion then undergoes hydrolysis to produce a basic solution:



Initial concentration	0.0100	0	0
Change	-x	x	x
Equilibrium concentration	0.0100 - x	x	x

Solving for  $x = [\text{OH}^-]$ , we obtain the pH of the basic mixture that develops at the equivalence point:

$$K_b = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{K_w}{K_a}$$

$$\frac{x^2}{0.0100 - x} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}}$$

$$x \approx \sqrt{\frac{(0.0100)(1.0 \times 10^{-14})}{(1.8 \times 10^{-4})}} = 7.45 \times 10^{-7} \text{ M} = [\text{OH}^-] \quad (x \ll 0.0100)$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{7.45 \times 10^{-7}} = 7.87$$

We continue to neglect the autoionization of water as a source of  $\text{OH}^-$ , an assumption that must be reconsidered in systems where hydronium and hydroxide ions are present in nearly equal amounts. Difficulties may arise when either the concentration of  $\text{H}_3\text{O}^+$  (in an acidic ionization reaction) or the concentration of  $\text{OH}^-$  (in a basic ionization reaction) falls below  $10^{-6} \text{ M}$ . In such cases, not treated explicitly in *PoC*, an exact formulation generally involves five equations in five unknowns. The solution is one of the roots of a cubic equation.

In the present example, the correction proves modest and well within our tolerance limits: a 1% change in  $[\text{OH}^-]$ , from  $7.45 \times 10^{-7} \text{ M}$  to  $7.52 \times 10^{-7} \text{ M}$  (indistinguishable through two significant figures). The resulting pH increases only slightly, from 7.87 to 7.88.

(b) The environment is exactly the same as in (a). We add an equivalent amount of strong base,

$$\frac{0.050 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.200 \text{ L} = 0.010 \text{ mol OH}^-$$

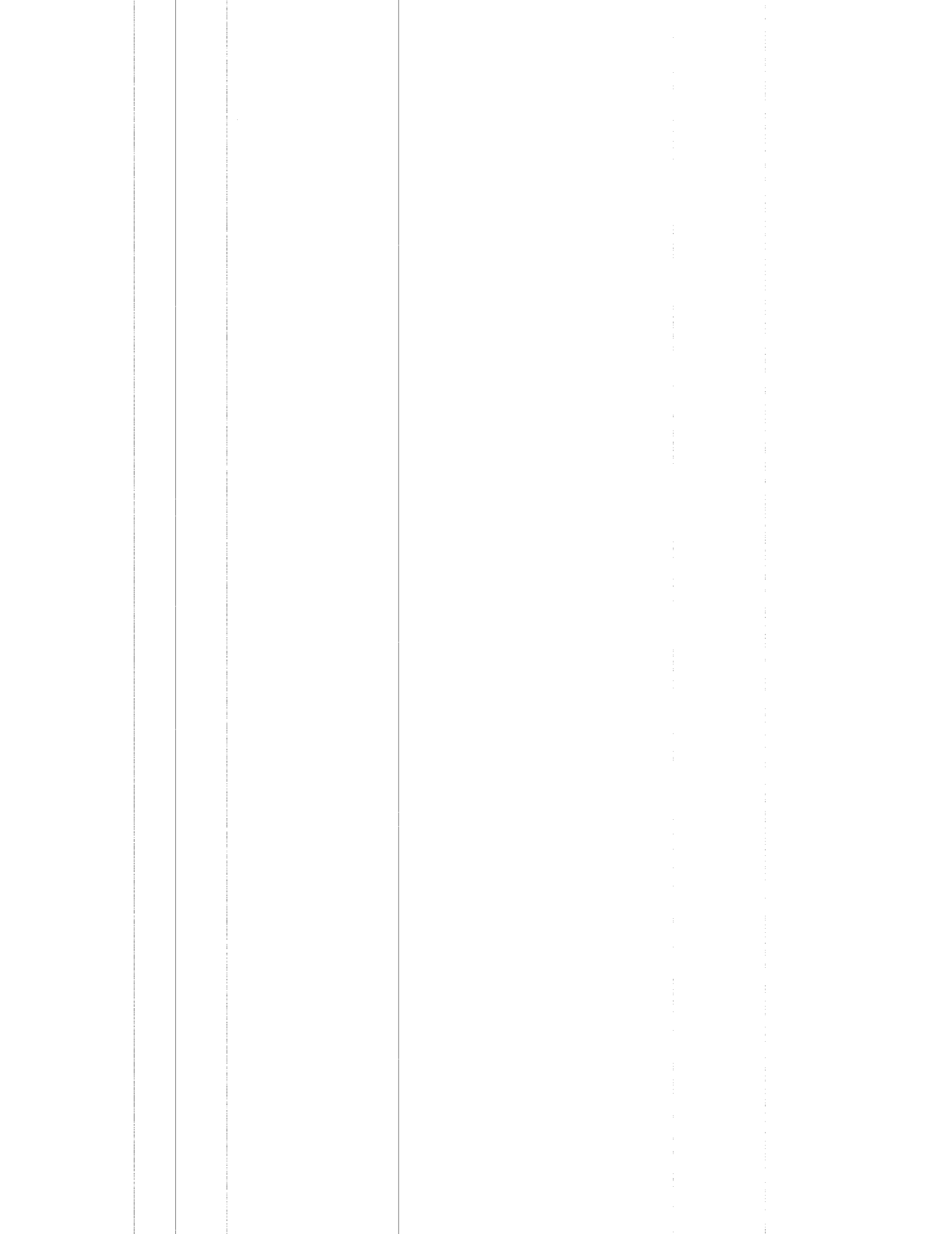
and the resulting pH is approximately 7.87.

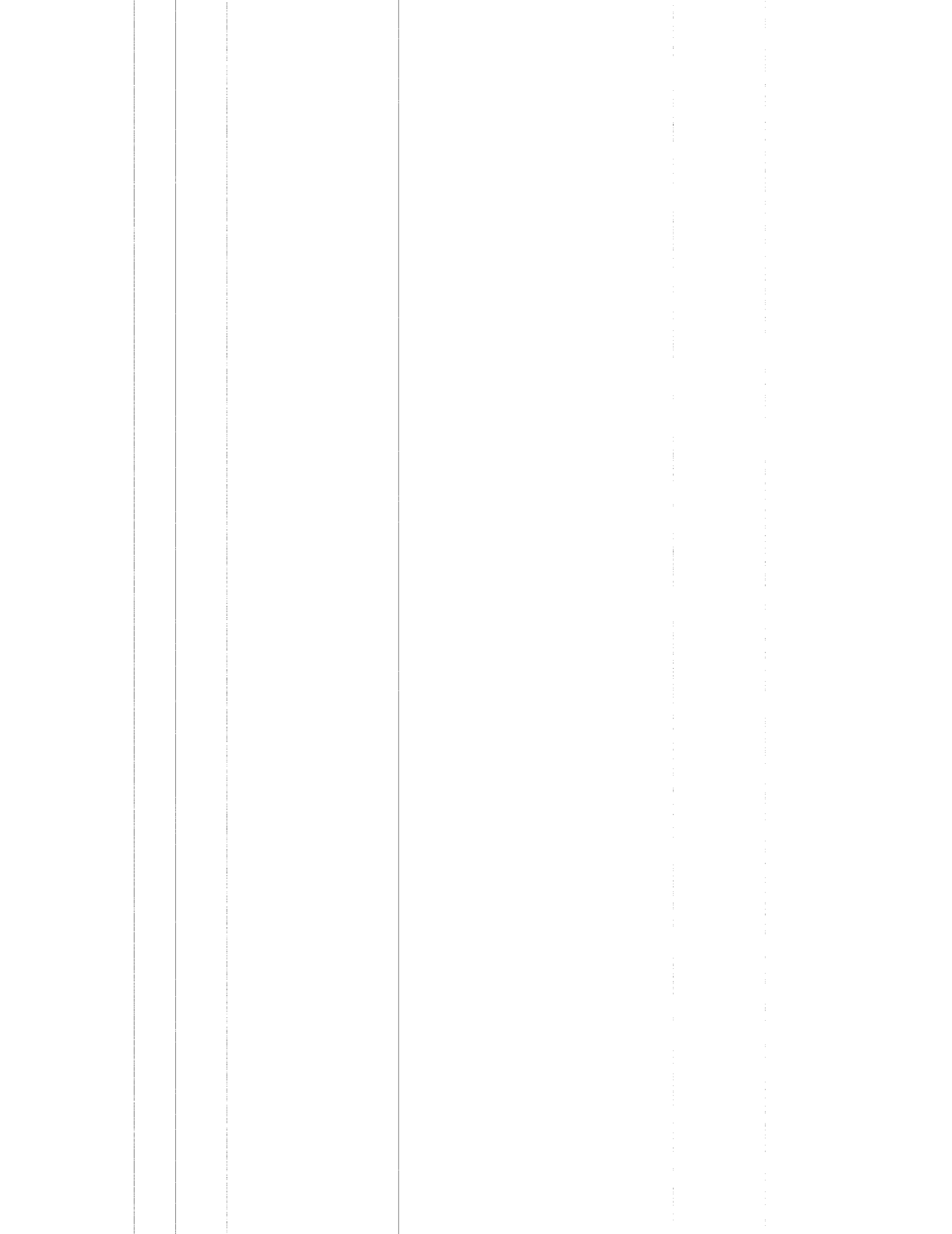
(c) Add *half* an equivalent amount of strong base:

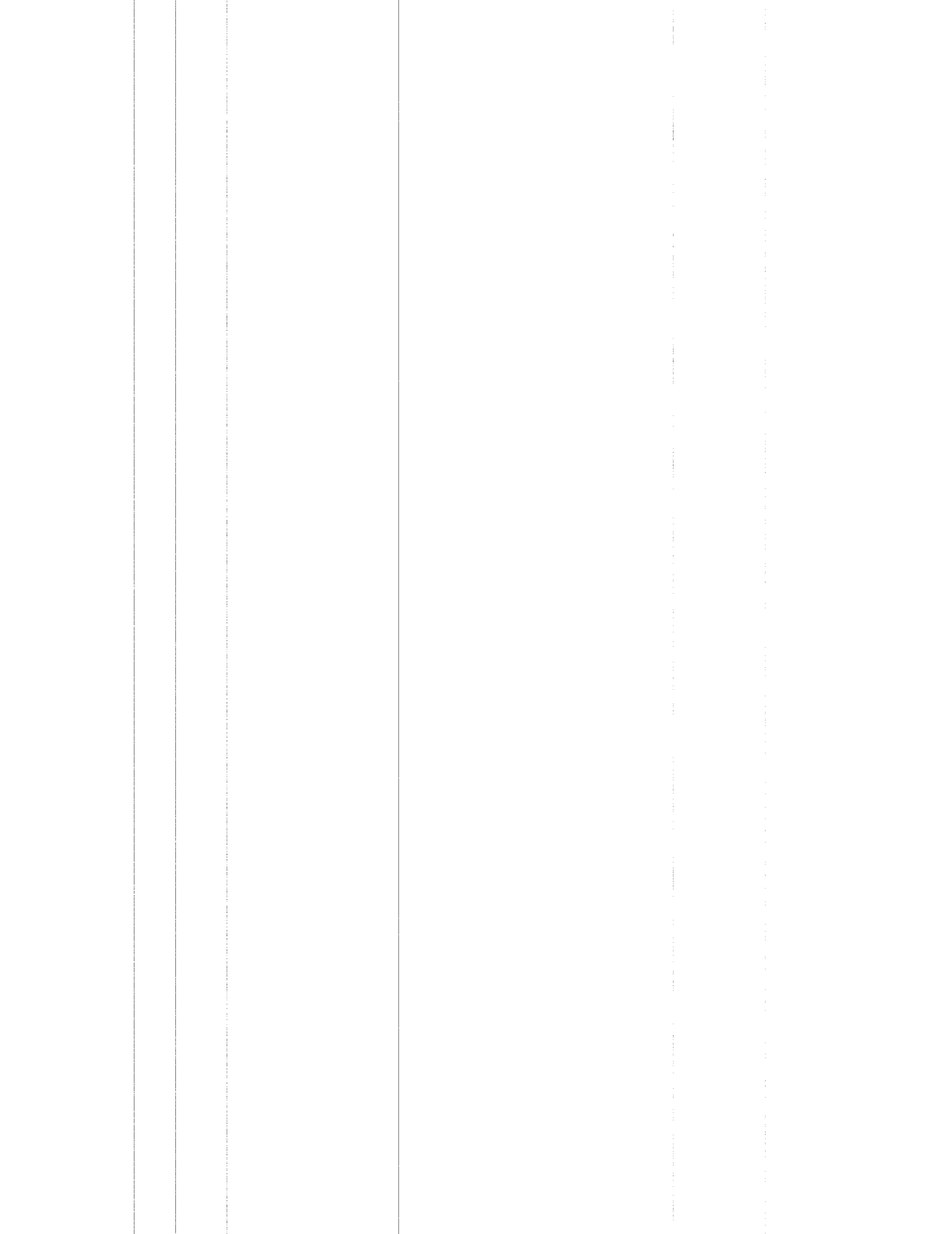
$$\frac{0.100 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.050 \text{ L} = 0.0050 \text{ mol OH}^-$$

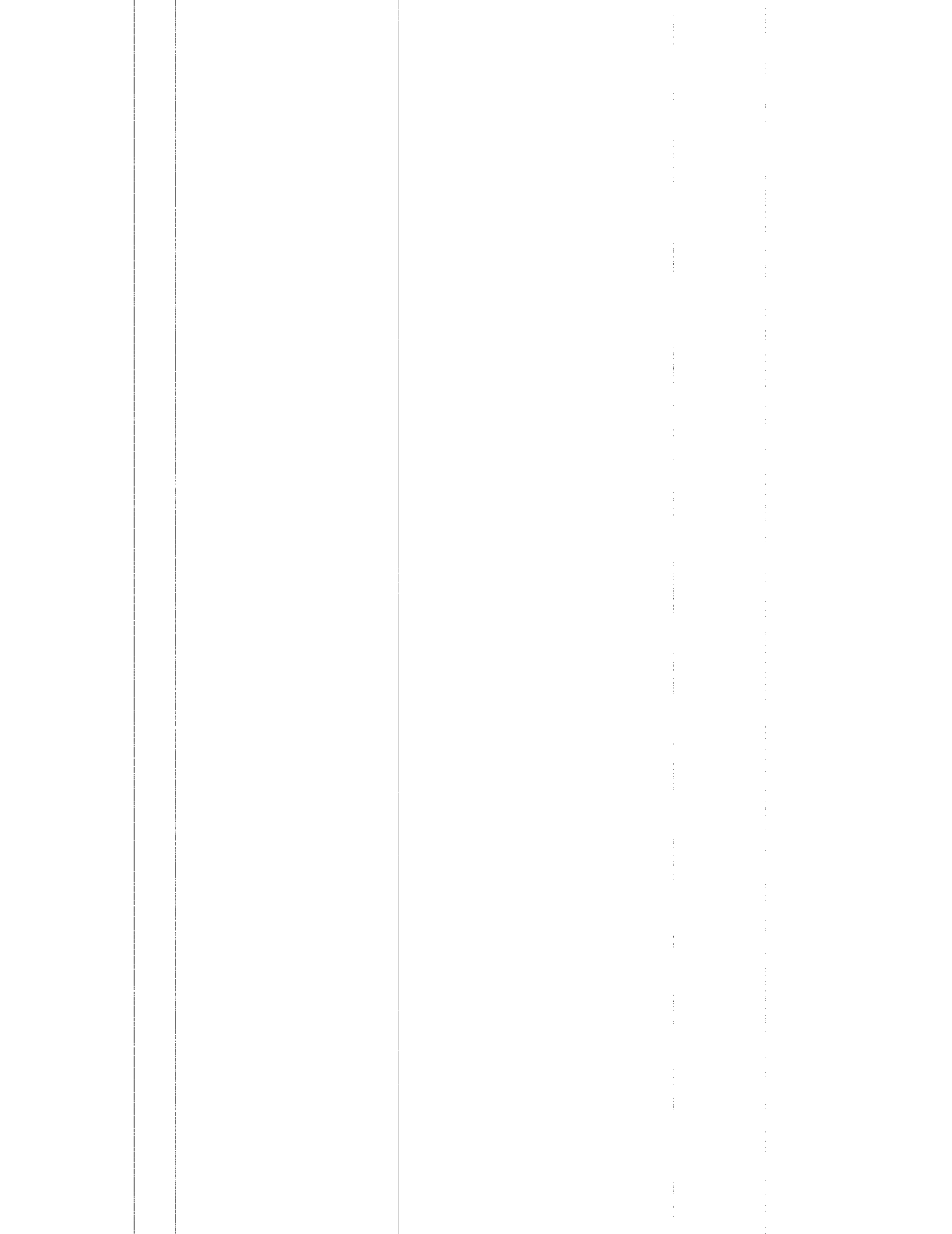
This entire quantity, 0.0050 mol, reacts with the 0.0100 mol of  $\text{HCOOH}$  on hand, producing 0.0050 mol  $\text{HCOO}^-$  and leaving 0.0050 mol of  $\text{HCOOH}$  unconverted. The resulting mixture is a buffer solution in which the concentrations of weak acid and conjugate base are equal:

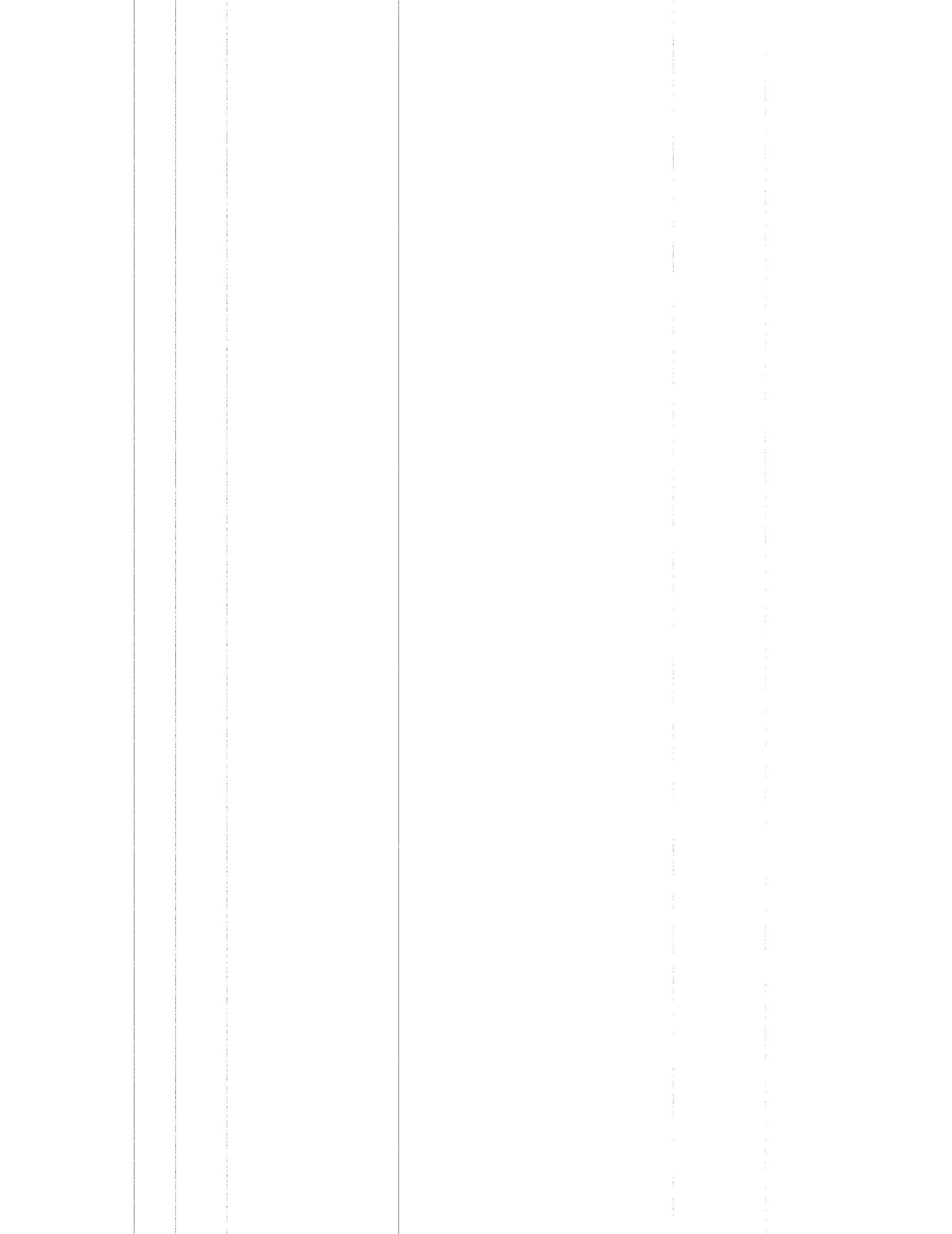


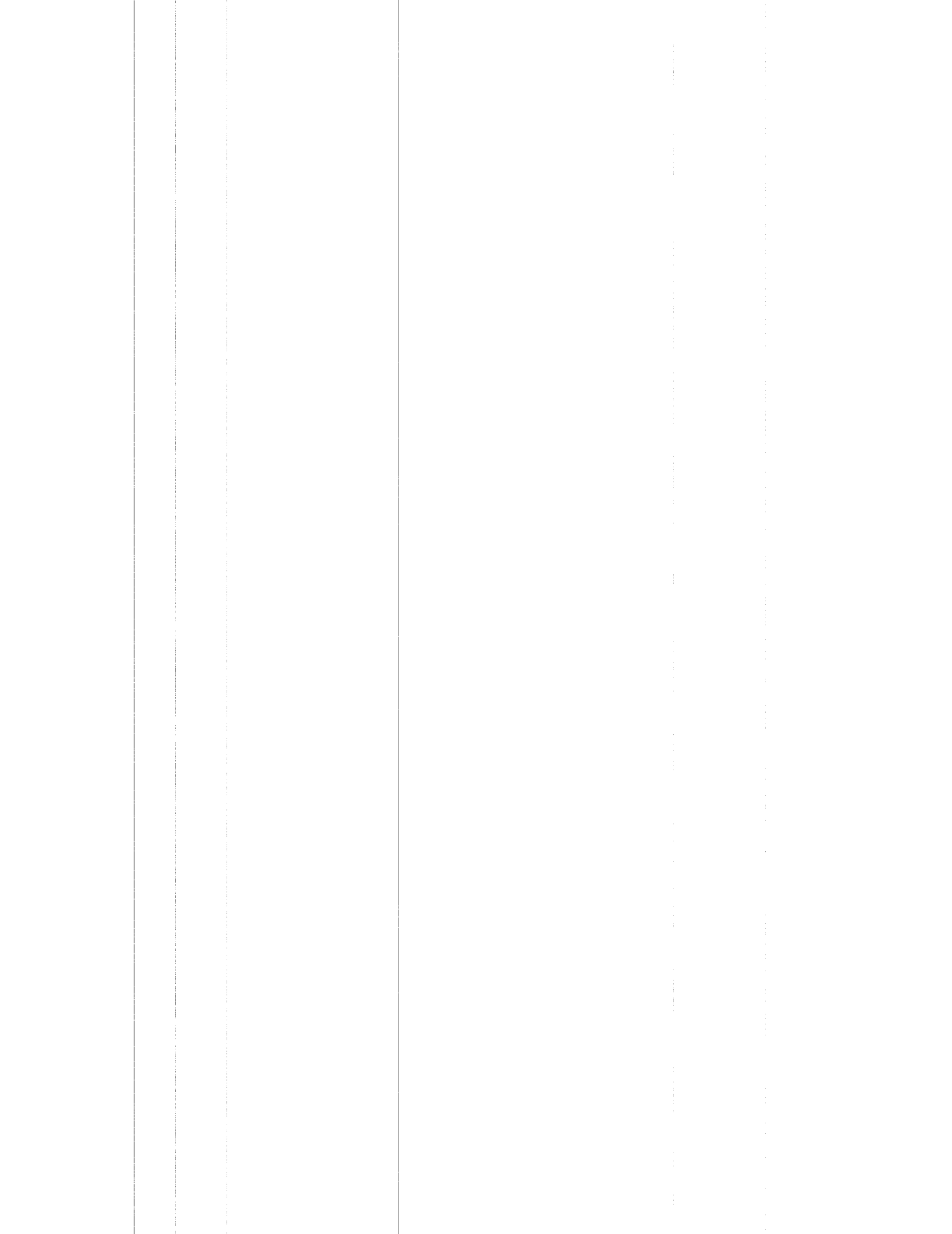


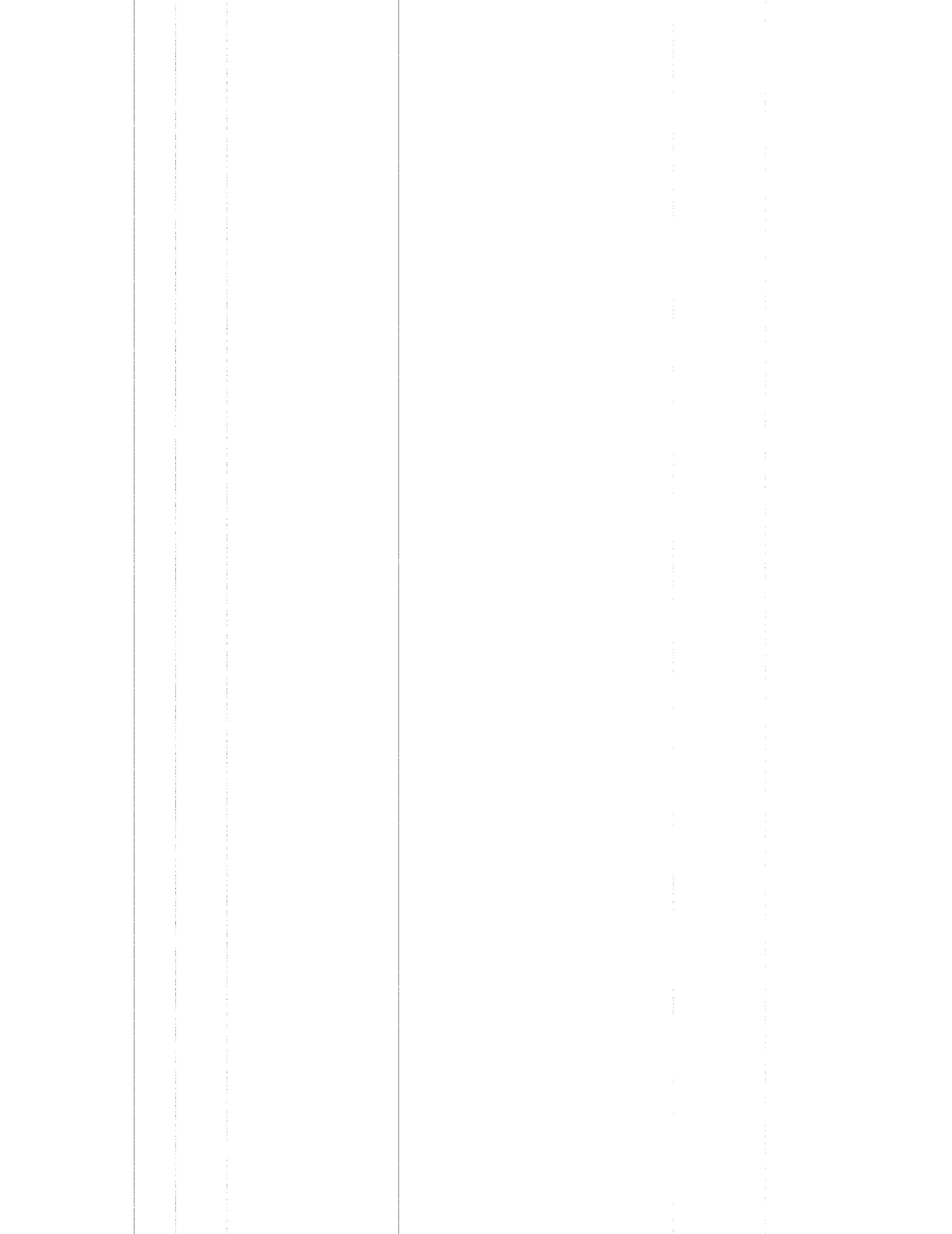


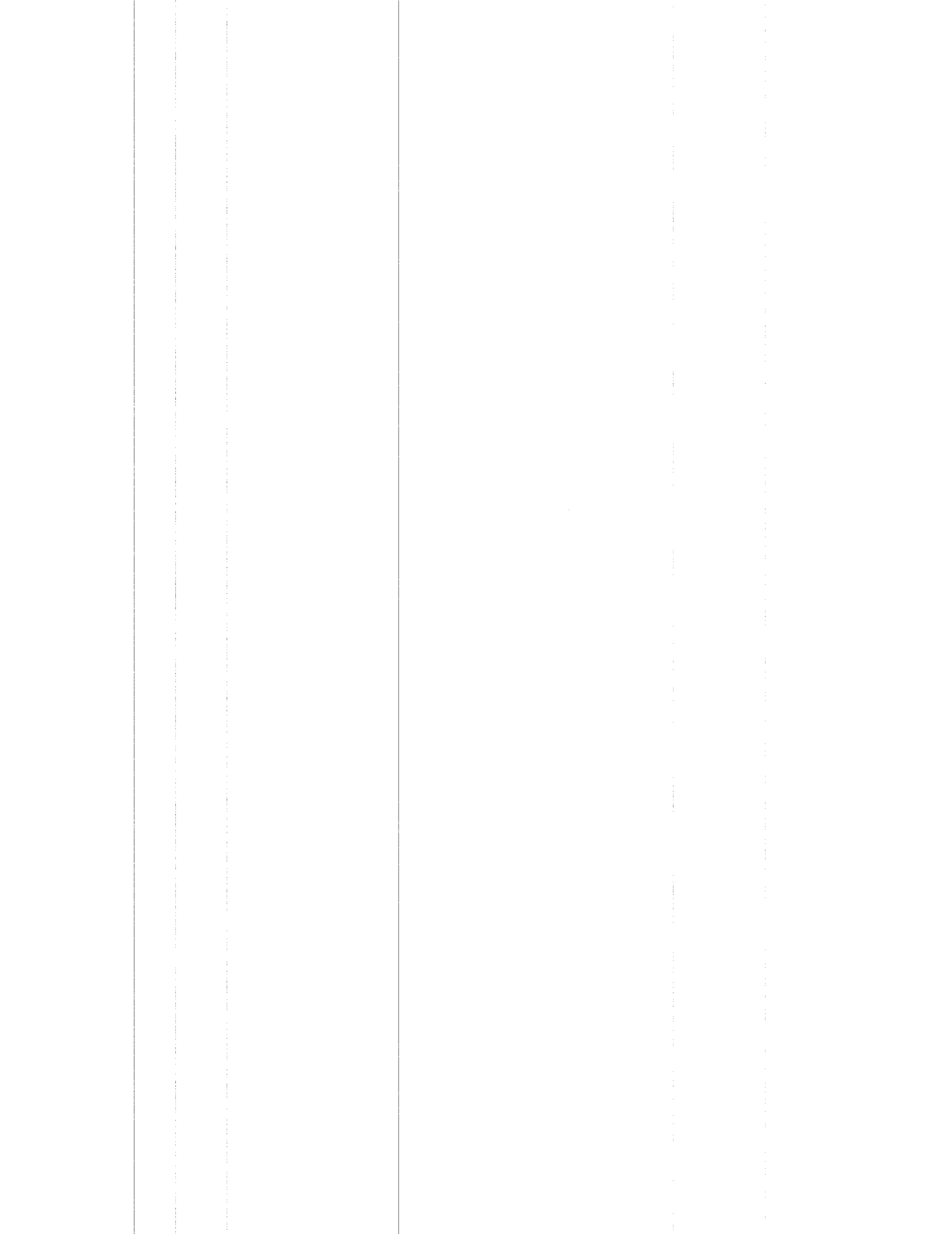




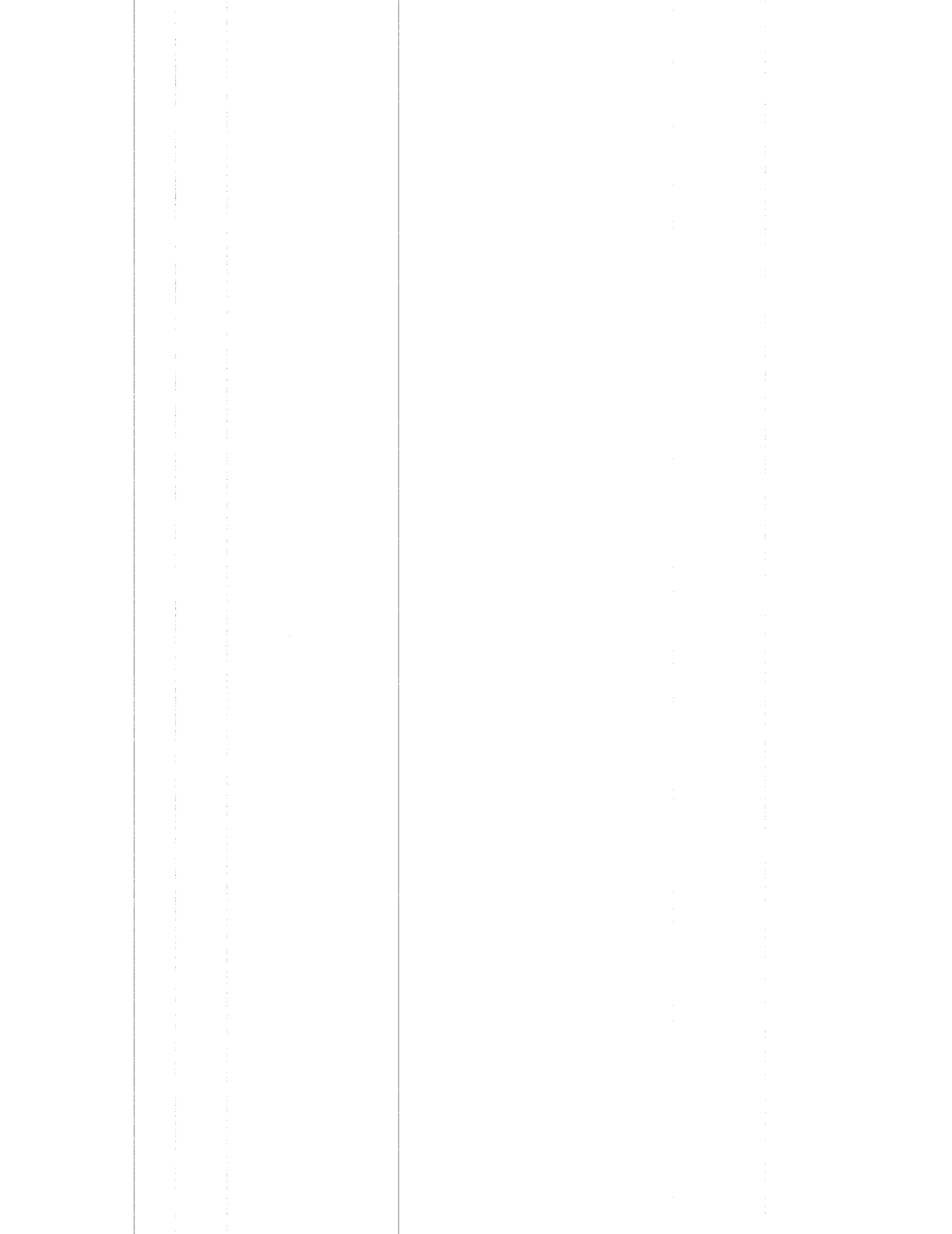


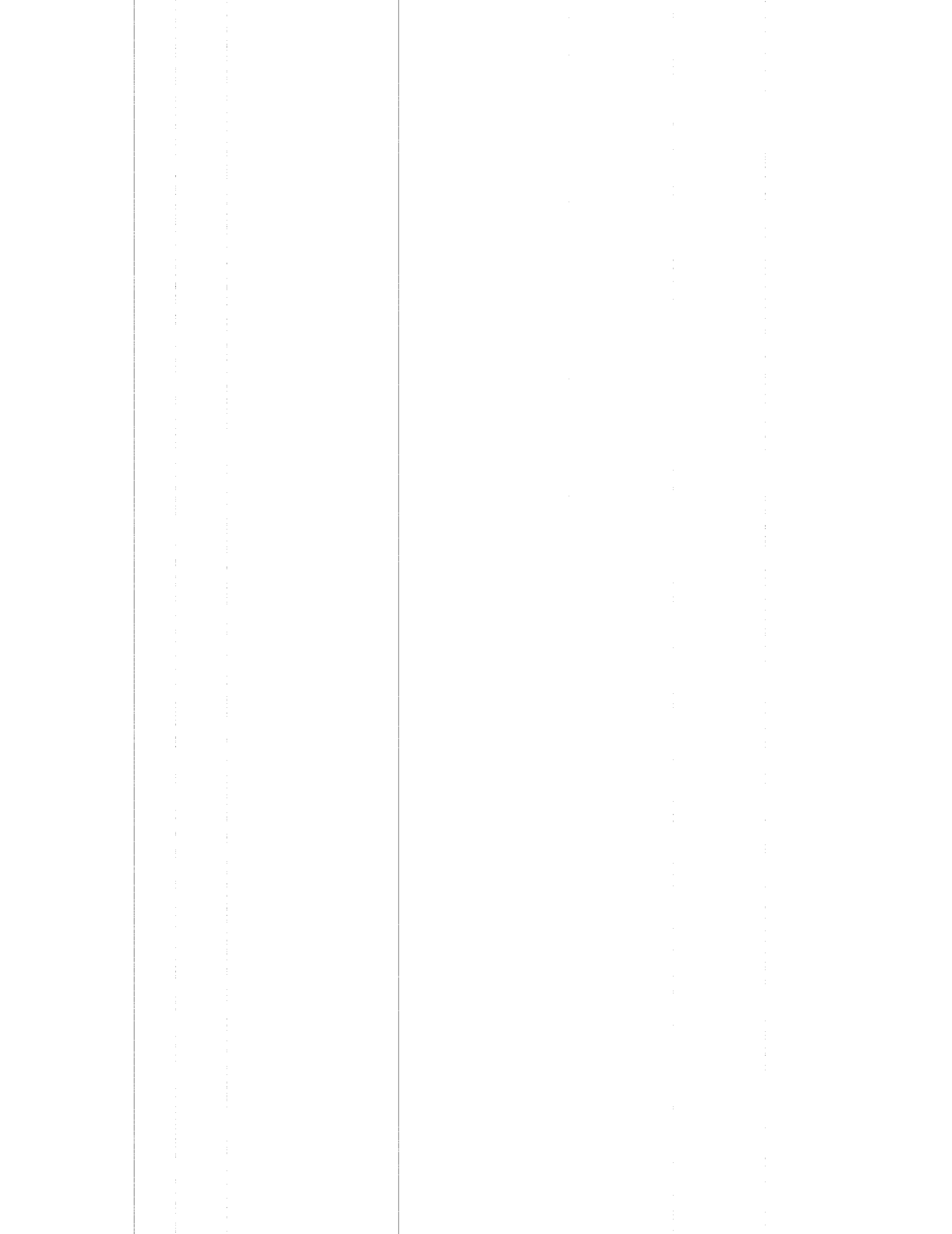






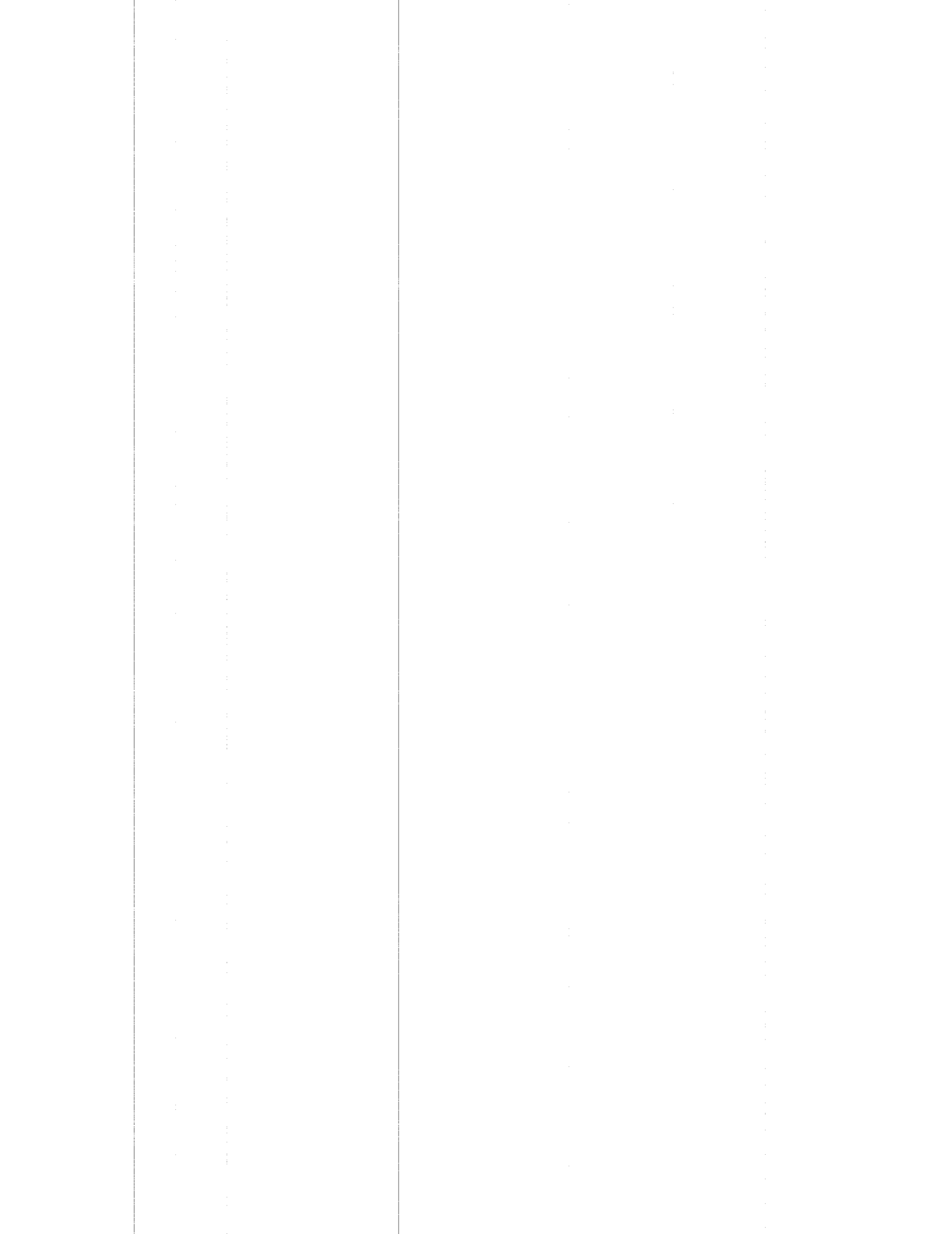


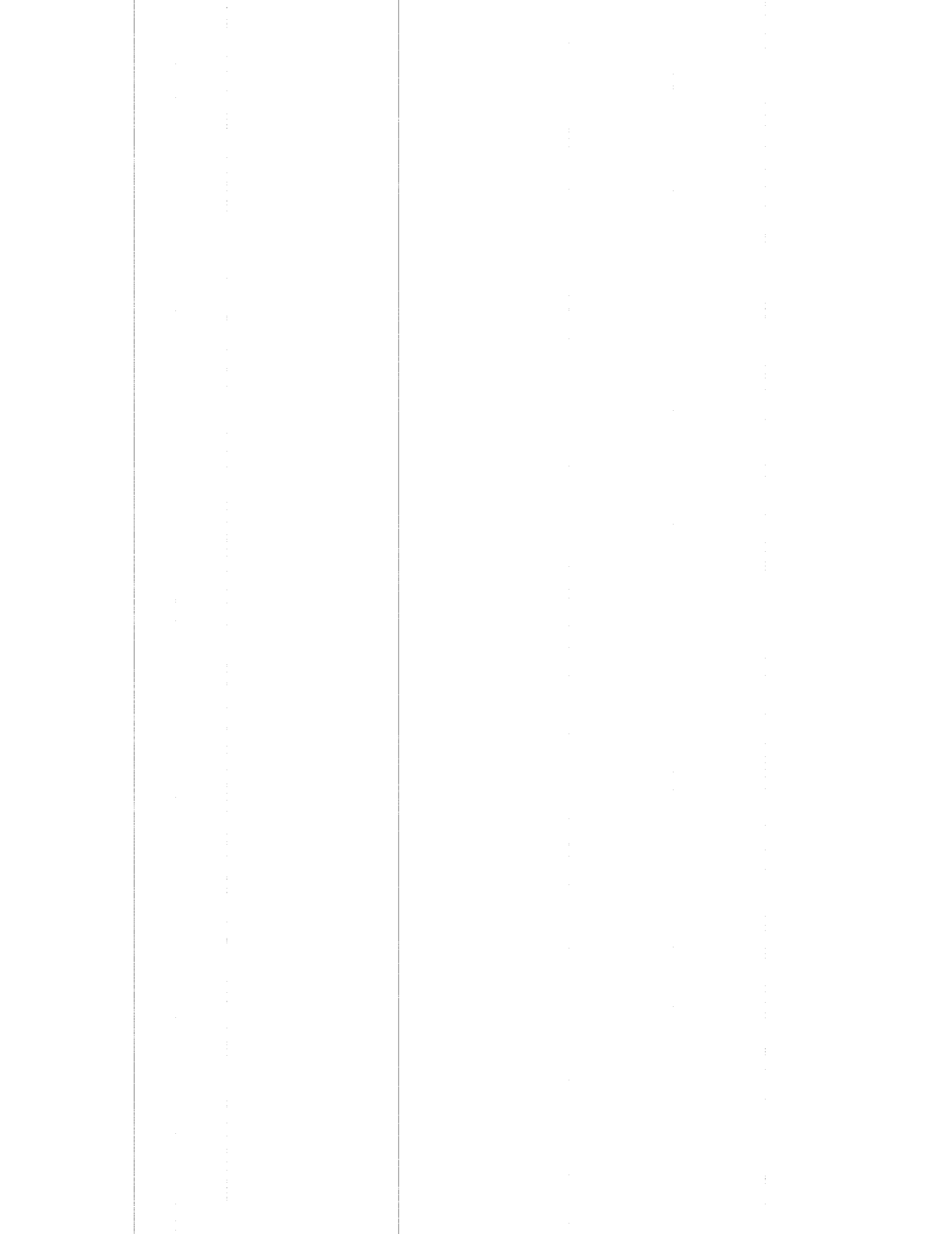




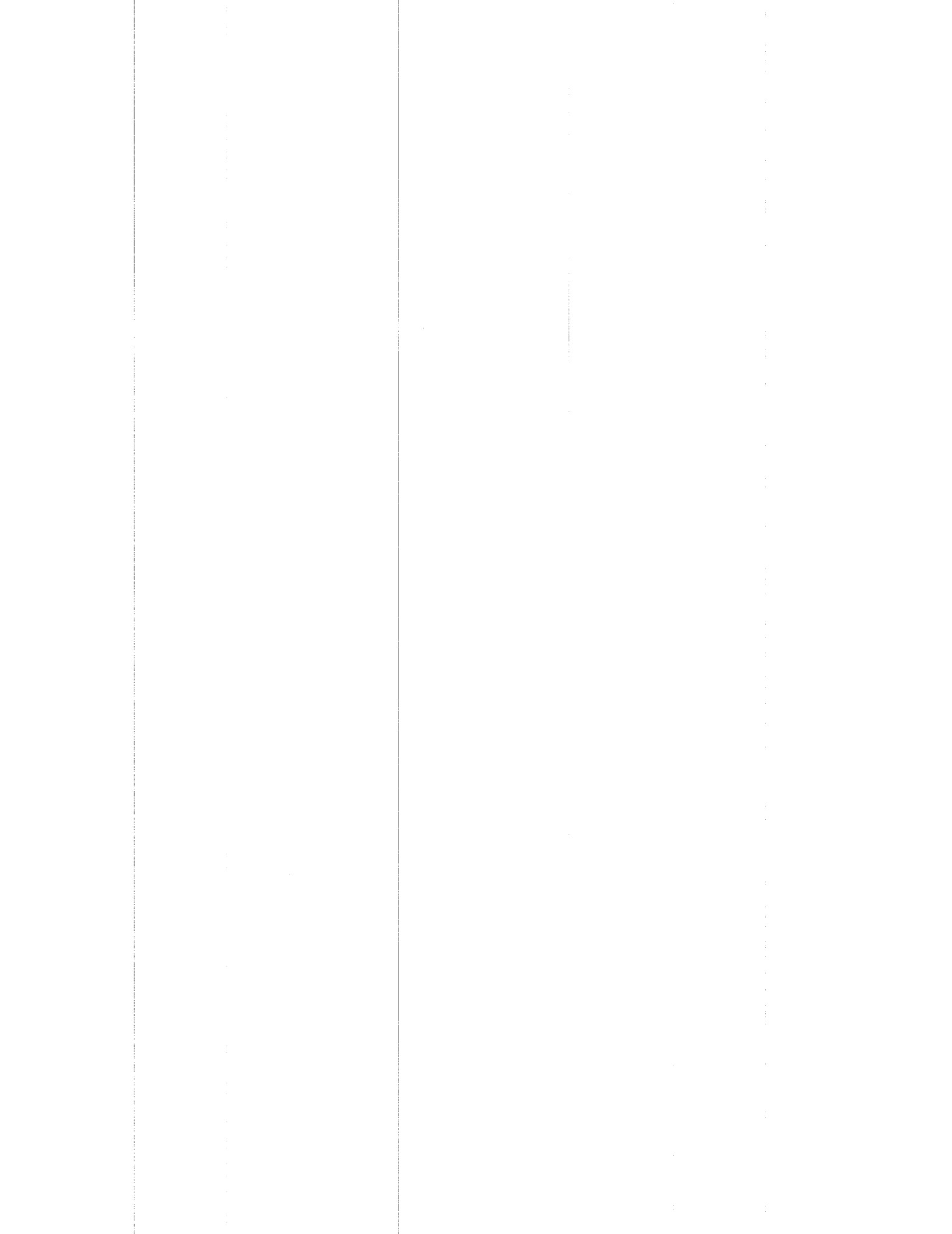














$$[\text{HCOO}^-]_0 = \frac{0.0050 \text{ mol}}{1.000 \text{ L}} = 0.0050 \text{ M}$$

$$[\text{HCOOH}]_0 = \frac{0.0050 \text{ mol}}{1.000 \text{ L}} = 0.0050 \text{ M}$$

The pH is given by the Henderson-Hasselbalch equation:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{HCOO}^-]_0}{[\text{HCOOH}]_0} \\ &= -\log(1.8 \times 10^{-4}) + \log 1.0 \\ &= 3.74 \end{aligned}$$

(d) The environment is identical to the one in (c). We add half an equivalent of strong base,

$$\frac{0.050 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.100 \text{ L} = 0.0050 \text{ mol OH}^-$$

and produce an equilibrium pH of 3.74. The system behaves as a 1:1 buffer.

(e) Add excess strong acid:

$$\frac{0.100 \text{ mol HCl}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} \times 0.100 \text{ L} = 0.0100 \text{ mol H}_3\text{O}^+$$

The high concentration of hydronium ion suppresses the weak ionization of HCOOH, leaving the pH to be determined by the concentration of the strong acid alone:

$$[\text{H}_3\text{O}^+] = \frac{\text{original amount of HCl}}{\text{new volume}} = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 1.00 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-2}) = 2.000$$

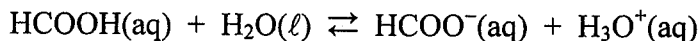
(f) Adding extra formic acid,

$$\frac{0.100 \text{ mol HCOOH}}{\text{L}} \times 0.100 \text{ L} = 0.0100 \text{ mol HCOOH}$$

we have an initial concentration of 0.0200 M:

$$[\text{HCOOH}]_0 = \frac{0.0100 \text{ mol} + 0.0100 \text{ mol}}{1.000 \text{ L}} = 0.0200 \text{ M}$$

Ionization of the weak acid then establishes the equilibrium pH:



Initial concentration	0.0200	0	0
Change	$-x$	$x$	$x$
Equilibrium concentration	$0.0200 - x$	$x$	$x$

We solve the mass-action equation for  $x$ , the final concentration of  $\text{H}_3\text{O}^+$ :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{0.0200 - x} = 1.8 \times 10^{-4}$$

Approximate solution:

$$x \approx \sqrt{(0.0200)(1.8 \times 10^{-4})} = 1.9 \times 10^{-3}$$

Quadratic formula:

$$0 = x^2 + (1.8 \times 10^{-4})x - (3.6 \times 10^{-6})$$

$$x = \frac{-(1.8 \times 10^{-4}) \pm \sqrt{(1.8 \times 10^{-4})^2 - 4(1)(-3.6 \times 10^{-6})}}{2(1)} = 1.81 \times 10^{-3}, -1.99 \times 10^{-3}$$

Taking the more accurate solution,

$$x_+ = [\text{H}_3\text{O}^+] = 1.81 \times 10^{-3} \text{ M}$$

we have the pH:

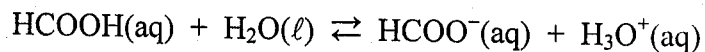
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.81 \times 10^{-3}) = 2.74$$

The final result is stated to two significant figures, consistent with the value of  $K_a$ .

(g) Following the addition of pure water, the original 0.0100 mol HCOOH is now dissolved in a total volume of 1.000 L:

$$[\text{HCOOH}]_0 = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 0.0100 \text{ M}$$

The equilibrium pH is determined, in the usual way, by ionization of the weak acid:



Initial concentration	0.0100	0	0
Change	-x	x	x
Equilibrium concentration	0.0100 - x	x	x

Under these particular conditions, solution of the mass-action equation

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{0.0100 - x} = 1.8 \times 10^{-4}$$

is best accomplished with the quadratic formula.

Approximate solution:

$$x \approx \sqrt{(0.0100)(1.8 \times 10^{-4})} = 1.34 \times 10^{-3}$$

Quadratic formula:

$$0 = x^2 + (1.8 \times 10^{-4})x - (1.8 \times 10^{-6})$$

$$x = \frac{-(1.8 \times 10^{-4}) \pm \sqrt{(1.8 \times 10^{-4})^2 - 4(1)(-1.8 \times 10^{-6})}}{2(1)} = 1.25 \times 10^{-3}, -1.43 \times 10^{-3}$$

Taking the physically valid solution,

$$x_+ = [\text{H}_3\text{O}^+] = 1.25 \times 10^{-3} \text{ M}$$

we have the pH:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.25 \times 10^{-3}) = 2.90$$

The final value is limited to two significant figures by the stated accuracy of  $K_a$ .

45. The initial amount of  $\text{NH}_3$ , a weak base, is the same in each mixture:

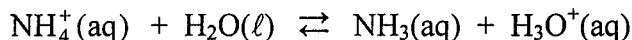
$$\frac{0.100 \text{ mol NH}_3}{\text{L}} \times 0.100 \text{ L} = 0.0100 \text{ mol NH}_3$$

The subsequent pH is determined by an equilibrium involving  $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ , and  $\text{OH}^-$ .

(a) Add an equivalent amount of strong acid:

$$\frac{0.100 \text{ mol HCl}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} \times 0.100 \text{ L} = 0.0100 \text{ mol H}_3\text{O}^+$$

The amount of  $\text{H}_3\text{O}^+$  (0.0100 mol) is just enough to convert all 0.0100 mol  $\text{NH}_3$  into its conjugate acid,  $\text{NH}_4^+$ . Subsequent hydrolysis in a volume of 1.000 L yields an acidic solution:



Initial concentration	0.0100	0	0
Change	$-x$	$x$	$x$
Equilibrium concentration	$0.0100 - x$	$x$	$x$

Solution of the mass-action equation, facilitated by the (good) assumption that  $x \ll 0.100$ , gives us  $[\text{H}_3\text{O}^+]$  and the associated pH:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{K_w}{K_b}$$

$$\frac{x^2}{0.0100 - x} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$x \approx \sqrt{\frac{(0.0100)(1.0 \times 10^{-14})}{1.8 \times 10^{-5}}} = 2.36 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.36 \times 10^{-6}) = 5.63$$

(b) Again, add an equivalent amount of strong acid:

$$\frac{0.050 \text{ mol HCl}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} \times 0.200 \text{ L} = 0.010 \text{ mol H}_3\text{O}^+$$

The environment is exactly the same as in (a):  $\text{pH} = 5.63$ .

(c) Add half the equivalent amount of strong acid:

$$\frac{0.100 \text{ mol HCl}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} \times 0.050 \text{ L} = 0.0050 \text{ mol H}_3\text{O}^+$$

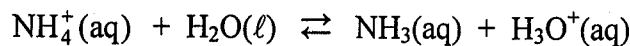
This entire quantity, 0.0050 mol, reacts with the 0.0100 mol of  $\text{NH}_3$  on hand, producing 0.0050 mol  $\text{NH}_4^+$  and leaving 0.0050 mol of  $\text{NH}_3$  unconverted. The resulting mixture is a buffer solution in which the conjugate species have equal initial concentrations:

$$[\text{NH}_3]_0 = [\text{NH}_4^+]_0 = \frac{0.0050 \text{ mol}}{1.000 \text{ L}} = 0.0050 \text{ M}$$

Coming to equilibrium under conditions that justify the Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]_0}{[\text{NH}_4^+]_0}$$

the system finally attains a pH equal to the  $\text{p}K_a$  of the ammonium ion:



$$K_a = \frac{K_w}{K_b} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{NH}_3]_{\text{eq}}}{[\text{NH}_4^+]_{\text{eq}}} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}([\text{NH}_3]_0 + x)}{[\text{NH}_4^+]_0 - x} \approx \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{NH}_3]_0}{[\text{NH}_4^+]_0}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]_0}{[\text{NH}_4^+]_0} = -\log \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} + \log \frac{1.0}{1.0} = 9.26$$

(d) Adding half an equivalent amount of strong acid, as in (c) above, we create exactly the same environment:

$$\frac{0.050 \text{ mol HCl}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} \times 0.100 \text{ L} = 0.0050 \text{ mol H}_3\text{O}^+$$

The pH is necessarily the same as well: 9.26.

(e) Add excess strong base:

$$\frac{0.100 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times 0.100 \text{ L} = 0.0100 \text{ mol OH}^-$$

The high concentration of hydroxide ion suppresses the weak ionization of  $\text{NH}_3$ , leaving the pH to be determined by the concentration of the strong base alone:

$$[\text{OH}^-] = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 1.00 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{1.00 \times 10^{-2}} = 12.00$$

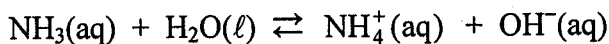
(f) Adding extra ammonia,

$$\frac{0.100 \text{ mol NH}_3}{\text{L}} \times 0.100 \text{ L} = 0.0100 \text{ mol NH}_3$$

we have an initial concentration of  $0.0200 \text{ M}$ :

$$[\text{NH}_3]_0 = \frac{0.0100 \text{ mol} + 0.0100 \text{ mol}}{1.000 \text{ L}} = 0.0200 \text{ M}$$

Ionization of the weak base then establishes the equilibrium pH:



Initial concentration	0.0200	0	0
Change	$-x$	$x$	$x$
Equilibrium concentration	$0.0200 - x$	$x$	$x$

We solve the mass-action equation for  $x$ , the final concentration of  $\text{OH}^-$ :

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.0200 - x} = 1.8 \times 10^{-5}$$

Approximate solution:

$$x \approx \sqrt{(0.0200)(1.8 \times 10^{-5})} = 6.0 \times 10^{-4}$$

Quadratic formula:

$$0 = x^2 + (1.8 \times 10^{-5})x - (3.6 \times 10^{-7})$$

$$x = \frac{-(1.8 \times 10^{-5}) \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-3.6 \times 10^{-7})}}{2(1)} = 5.91 \times 10^{-4}, -6.09 \times 10^{-4}$$

Accepting the physically valid root,

$$x_+ = [\text{OH}^-] = 5.91 \times 10^{-4} \text{ M}$$

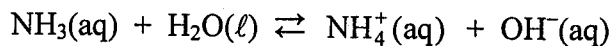
we calculate the corresponding pH to two significant figures:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{5.91 \times 10^{-4}} = 10.77$$

(g) With the addition of pure water, the original 0.0100 mol  $\text{NH}_3$  is now dissolved in a total volume of 1.000 L:

$$[\text{NH}_3]_0 = \frac{0.0100 \text{ mol}}{1.000 \text{ L}} = 0.0100 \text{ M}$$

The equilibrium concentration of  $\text{OH}^-$  is determined by ionization of the weak base:



Initial concentration	0.0100	0	0
Change	-x	x	x
Equilibrium concentration	0.0100 - x	x	x

Solution of the mass-action equation

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.0100 - x} = 1.8 \times 10^{-5}$$

yields  $x = [\text{OH}^-] = 4.15 \times 10^{-4} \text{ M}$  as the best root.

Approximate solution:

$$x \approx \sqrt{(0.0100)(1.8 \times 10^{-5})} = 4.24 \times 10^{-4}$$

Quadratic formula:

$$0 = x^2 + (1.8 \times 10^{-5})x - (1.8 \times 10^{-7})$$

$$x = \frac{-(1.8 \times 10^{-5}) \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-1.8 \times 10^{-7})}}{2(1)} = 4.15 \times 10^{-4}, -4.33 \times 10^{-4}$$

The corresponding pH is 10.62:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{4.15 \times 10^{-4}} = 10.62$$

*Titration is covered in Section 16-6 and Examples 16-7 and 16-8 of PoC. The exercises in the next group are intended to highlight the symmetrical relationships connecting the various possibilities: titration of strong acid by strong base, titration of strong base by strong acid, titration of weak acid by strong base, titration of weak base by strong acid.*

**46.** The titrations described here and in the next exercise are identical. Only the roles of acid and base are interchanged.

**(a)** We use the relationship

$$\text{Concentration} \times \text{volume} = \text{amount}$$

and set the amount of  $\text{OH}^-$  equal to the amount of  $\text{H}_3\text{O}^+$ :

$$c_a V_a = c_b V_b$$

$$c_a = c_b \frac{V_b}{V_a} = 0.100 \text{ M} \times \frac{0.0762 \text{ L}}{0.0500 \text{ L}} = 0.152 \text{ M}$$

Symbols are defined as in Example 16-8:

$$c_a = \text{concentration of acid} \quad V_a = \text{volume of acid}$$

$$c_b = \text{concentration of base} \quad V_b = \text{volume of base}$$

**(b)** Titration of a strong acid by a strong base yields a neutral solution:  $\text{pH} = 7.00$ .

**47.** The titration of a strong base by a strong acid mirrors the titration of a strong acid by a strong base.



(a) At the equivalence point, the amount of  $\text{H}_3\text{O}^+$  added is exactly equal to the original amount of  $\text{OH}^-$ :

moles acid = moles base

$$\frac{\text{mol}}{\text{L}} \times \text{L} = \frac{\text{mol}}{\text{L}} \times \text{L}$$

Converting dimensions into symbols, we recover the fundamental titration equation already introduced in Example 16-8:

$$c_a V_a = c_b V_b$$

concentration of acid  $\nearrow$   $c_a V_a = c_b V_b$   $\nwarrow$  volume of base  
 volume of acid  $\nearrow$   $\nwarrow$  concentration of base

Given three of the four variables, we then solve for the fourth:

$$c_b = c_a \frac{V_a}{V_b} = 0.100 \text{ M} \times \frac{0.0762 \text{ L}}{0.0500 \text{ L}} = 0.152 \text{ M}$$

(b) Titration of a strong base by a strong acid yields a neutral solution:  $\text{pH} = 7.00$ . The outcome is identical to that reached when a strong acid is titrated by a strong base.

48. Titration of a weak acid by a strong base.

(a) Weak acid or strong, complete neutralization demands equimolar amounts of acid and base:

$$c_a V_a = c_b V_b$$

$$c_a = c_b \frac{V_b}{V_a} = 0.100 \text{ M} \times \frac{0.0762 \text{ L}}{0.0500 \text{ L}} = 0.1524 \text{ M} = 0.152 \text{ M} \quad (3 \text{ sig fig})$$

The required concentrations, volumes, and amounts are exactly the same as those obtained in the two preceding exercises.

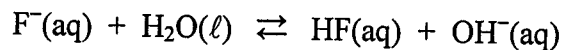
(b) Before titration, we had 0.00762 mol HF in a volume of 50.0 mL:

CONCENTRATION	VOLUME	AMOUNT
$\frac{0.1524 \text{ mol HF}}{\text{L}}$	$\times 0.0500 \text{ L}$	$= 0.00762 \text{ mol HF}$

After neutralization, the same number of moles (0.00762) exists as the conjugate base,  $F^-$ . The total volume, however, is 126.2 mL (the original 50.0 mL plus the 76.2 mL added), and therefore the concentration of  $F^-$  before equilibration is diluted to 0.0604 M:

$$[F^-]_0 = \frac{0.00762 \text{ mol}}{0.0500 \text{ L} + 0.0762 \text{ L}} = 0.0604 \text{ M}$$

Subsequent hydrolysis of  $F^-$  produces excess  $OH^-$  and yields a basic solution:



Initial concentration	0.0604	0	0
Change	-x	x	x
Equilibrium concentration	0.0604 - x	x	x

From these stoichiometric relationships we then construct and solve the mass-action equation (making the simplifying assumption that  $x \ll 0.0604$ ):

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{K_w}{K_a}$$

$$\frac{x^2}{0.0604 - x} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}}$$

$$x \approx \sqrt{\frac{(0.0604)(1.0 \times 10^{-14})}{6.8 \times 10^{-4}}} = 9.42 \times 10^{-7} \text{ M}$$

The concentration of  $OH^-$  is thus  $9.42 \times 10^{-7} \text{ M}$ , and the pH (limited to two significant figures by  $K_a$  and  $K_w$ ) is 7.97:

$$\text{pH} = -\log[H_3O^+] = -\log \frac{K_w}{[OH^-]} = -\log \frac{1.0 \times 10^{-14}}{9.42 \times 10^{-7}} = 7.97$$

Throughout, we neglect any small contribution of  $H_3O^+$  and  $OH^-$  arising from the autoionization of water.

#### 49. Titration of a weak base by a strong acid.

(a) Weak base or strong, complete neutralization demands equimolar amounts of acid and base:

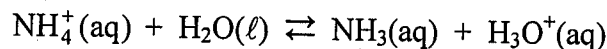
$$c_a V_a = c_b V_b$$

$$c_b = c_a \frac{V_a}{V_b} = 0.100 \text{ M} \times \frac{0.0762 \text{ L}}{0.0500 \text{ L}} = 0.1524 \text{ M} = 0.152 \text{ M} \quad (3 \text{ sig fig})$$

The required concentrations, volumes, and amounts are identical to those obtained in Exercises 46 through 48. For each titration—strong acid against strong base, strong base against strong acid, weak acid against strong base, weak base against strong acid—the equivalence point is reached only when the target species has been converted fully into its conjugate partner:

moles acid = moles base

(b) What differs, though, is the pH of the system after equilibration at the equivalence point. Neutralization of a weak base by a strong acid yields an acidic solution when the conjugate acid (here,  $\text{NH}_4^+$ ) partially ionizes in the presence of water:



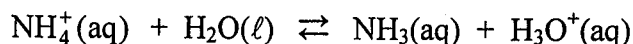
Analyzing the process step by step, we begin with 0.00762 mol  $\text{NH}_3$  in a volume of 50.0 mL *before* titration:

CONCENTRATION	VOLUME	AMOUNT
$\frac{0.1524 \text{ mol NH}_3}{\text{L}}$	$\times 0.0500 \text{ L}$	$= 0.00762 \text{ mol NH}_3$

After neutralization, the same number of moles (0.00762) exists as the conjugate acid,  $\text{NH}_4^+$ . The total volume, however, is 126.2 mL (the original 50.0 mL plus the 76.2 mL added), and therefore the nonequilibrium initial concentration of  $\text{NH}_4^+$  is diluted to 0.0604 M:

$$[\text{NH}_4^+]_0 = \frac{0.00762 \text{ mol}}{0.0500 \text{ L} + 0.0762 \text{ L}} = 0.0604 \text{ M}$$

Subsequent ionization of  $\text{NH}_4^+$  yields excess  $\text{H}_3\text{O}^+$  and hence a mixture with a pH less than 7:



Initial concentration	0.0604	0	0
Change	$-x$	$x$	$x$
Equilibrium concentration	$0.0604 - x$	$x$	$x$

Solution of the mass-action equation is simplified by the assumption that  $x \ll 0.0604$ :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{K_w}{K_b}$$

$$\frac{x^2}{0.0604 - x} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

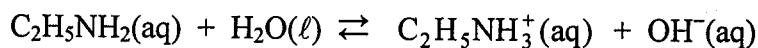
$$x \approx \sqrt{\frac{(0.0604)(1.0 \times 10^{-14})}{1.8 \times 10^{-5}}} = 5.79 \times 10^{-6} \text{ M}$$

The concentration of  $\text{H}_3\text{O}^+$  is thus  $5.79 \times 10^{-6} \text{ M}$ , and the pH (limited to two significant figures by  $K_b$  and  $K_w$ ) is 5.24:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(5.79 \times 10^{-6}) = 5.24$$

**50.** The titration of a weak base by a strong acid is conceptually analogous to the titration of a weak acid by a strong base.

**(a)** Before any strong acid is introduced, the system contains only weak base in aqueous solution:



Initial concentration	0.100	0	0
Change	$-x$	$x$	$x$
Equilibrium concentration	$0.100 - x$	$x$	$x$

The resulting mass-action expression

$$K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]} = \frac{x^2}{0.100 - x} = 6.4 \times 10^{-4}$$

may be solved either approximately or by use of the full quadratic formula.

Approximate solution:

$$x \approx \sqrt{(0.100)(6.4 \times 10^{-4})} = 8.0 \times 10^{-3}$$

Quadratic formula:

$$0 = x^2 + (6.4 \times 10^{-4})x - (6.4 \times 10^{-5})$$

$$x = \frac{-(6.4 \times 10^{-4}) \pm \sqrt{(6.4 \times 10^{-4})^2 - 4(1)(-6.4 \times 10^{-5})}}{2(1)} = 7.69 \times 10^{-3}, -8.33 \times 10^{-3}$$

The physically valid root,  $x_+ = [\text{OH}^-] = 7.69 \times 10^{-3} \text{ M}$ , translates into a pH of 11.89:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{7.69 \times 10^{-3}} = 11.89$$

(b) Originally we had 0.00500 mole of weak base in 0.0500 L (50.0 mL):

$$\frac{0.100 \text{ mol C}_2\text{H}_5\text{NH}_2}{\text{L}} \times 0.0500 \text{ L} = 0.00500 \text{ mol C}_2\text{H}_5\text{NH}_2$$

At the half-equivalence point, exactly half this amount has reacted with strong acid. The volume of HCl required is therefore 0.0100 L:

$$\frac{0.00500 \text{ mol C}_2\text{H}_5\text{NH}_2}{2} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol C}_2\text{H}_5\text{NH}_2} \times \frac{1 \text{ mol HCl}}{\text{mol H}_3\text{O}^+} \times \frac{1 \text{ L HCl}}{0.250 \text{ mol HCl}}$$

$$= 0.0100 \text{ L HCl}$$

The solution, now a buffer, contains 0.00250 mol  $\text{C}_2\text{H}_5\text{NH}_2$  and 0.00250 mol  $\text{C}_2\text{H}_5\text{NH}_3^+$  in a total volume of 0.0600 L (60.0 mL):

$$[\text{C}_2\text{H}_5\text{NH}_2]_0 = [\text{C}_2\text{H}_5\text{NH}_3^+]_0 = \frac{0.00250 \text{ mol}}{0.0600 \text{ L}} = 0.0417 \text{ M}$$

Since  $[\text{C}_2\text{H}_5\text{NH}_2]_0 = [\text{C}_2\text{H}_5\text{NH}_3^+]_0$ , we have

$$K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}}}{[\text{C}_2\text{H}_5\text{NH}_2]_{\text{eq}}} = \frac{([\text{C}_2\text{H}_5\text{NH}_3^+]_0 + x) [\text{OH}^-]_{\text{eq}}}{[\text{C}_2\text{H}_5\text{NH}_2]_0 - x}$$

$$\approx \frac{[\text{C}_2\text{H}_5\text{NH}_3^+]_0 [\text{OH}^-]_{\text{eq}}}{[\text{C}_2\text{H}_5\text{NH}_2]_0} = [\text{OH}^-]_{\text{eq}} = 6.4 \times 10^{-4} \quad (\text{half-equivalence point})$$

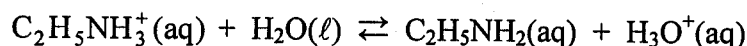
and a corresponding pH of 10.81:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-4}} = 10.81$$

Our simplifying assumption is that  $x$ , the equilibrium concentration of  $\text{OH}^-$ , is small relative to the initial concentrations of the conjugate species:

$$x = [\text{OH}^-]_{\text{eq}} \ll [\text{C}_2\text{H}_5\text{NH}_2]_0, [\text{C}_2\text{H}_5\text{NH}_3^+]_0$$

The result is the same as that obtained from the Henderson-Hasselbalch equation for the dissociation of the conjugate acid:



$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{C}_2\text{H}_5\text{NH}_2]_{\text{eq}}}{[\text{C}_2\text{H}_5\text{NH}_3^+]_{\text{eq}}} \approx \frac{[\text{H}_3\text{O}^+]_{\text{eq}}[\text{C}_2\text{H}_5\text{NH}_2]_0}{[\text{C}_2\text{H}_5\text{NH}_3^+]_0} = \frac{K_w}{K_b} = 1.56 \times 10^{-11}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_5\text{NH}_2]_0}{[\text{C}_2\text{H}_5\text{NH}_3^+]_0} = -\log(1.56 \times 10^{-11}) + \log 1.00 = 10.81$$

Note, as well, the general condition for half-equivalence in a titration of any kind, whether acid is added to base (left) or base is added to acid (right):

$$\text{moles acid} = \frac{\text{moles base}}{2} \quad \text{or} \quad \text{moles base} = \frac{\text{moles acid}}{2} \quad (\text{half-equivalence})$$

$$c_a V_a = \frac{c_b V_b}{2} \quad c_b V_b = \frac{c_a V_a}{2}$$

(c) In all, we need to add 20.0 mL of HCl to reach the equivalence point:

$$\text{moles acid} = \text{moles base} \quad (\text{equivalence})$$

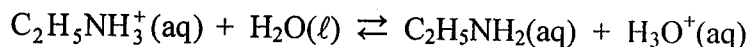
$$c_a V_a = c_b V_b$$

$$V_a = \frac{c_b}{c_a} V_b = \frac{0.100 \text{ M}}{0.250 \text{ M}} \times 50.0 \text{ mL} = 20.0 \text{ mL}$$

Neutralization of 0.00500 mol  $\text{C}_2\text{H}_5\text{NH}_2$  by 0.00500 mol  $\text{H}_3\text{O}^+$  produces 0.00500 mol  $\text{C}_2\text{H}_5\text{NH}_3^+$  in a total volume of 70.0 mL (50.0 mL of original base plus 20.0 mL of added acid). The initial concentration of  $\text{C}_2\text{H}_5\text{NH}_3^+$  is thus

$$[\text{C}_2\text{H}_5\text{NH}_3^+]_0 = \frac{0.00500 \text{ mol}}{0.0700 \text{ L}} = 0.0714 \text{ M}$$

before the conjugate species undergoes acidic hydrolysis:



Initial concentration	0.0714	0	0
Change	-x	x	x
Equilibrium concentration	0.0714 - x	x	x

Solving the mass-action equation, we have the equilibrium concentration of  $\text{H}_3\text{O}^+$  and its associated pH:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_5\text{NH}_2]}{[\text{C}_2\text{H}_5\text{NH}_3^+]} = \frac{K_w}{K_b}$$

$$\frac{x^2}{0.0714 - x} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-4}}$$

$$x \approx \sqrt{(0.0714) \left( \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-4}} \right)} = 1.06 \times 10^{-6} \quad (x \ll 0.0714)$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.06 \times 10^{-6}) = 5.97 \quad (2 \text{ sig fig})$$

Observe that  $[\text{H}_3\text{O}^+]$  is only 10 times greater than  $10^{-7} M$ .

(d) At a volume 2.0 mL past the equivalence point, the pH is determined mostly by the  $\text{H}_3\text{O}^+$  coming from the excess HCl:

$$\frac{0.250 \text{ mol HCl}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{O}^+}{\text{mol HCl}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 2.0 \text{ mL} = 0.00050 \text{ mol H}_3\text{O}^+$$

Since the total volume is 72.0 mL (50.0 mL of original base plus 20.0 mL of acid to reach equivalence plus 2.0 mL of acid beyond), the concentration of  $\text{H}_3\text{O}^+$  is 0.0069 M:

$$[\text{H}_3\text{O}^+] = \frac{0.00050 \text{ mol}}{0.0720 \text{ L}} = 0.0069 M$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0069 = 2.16$$

(e) See Figure 16.5 (overleaf) for a plot of the full titration curve.

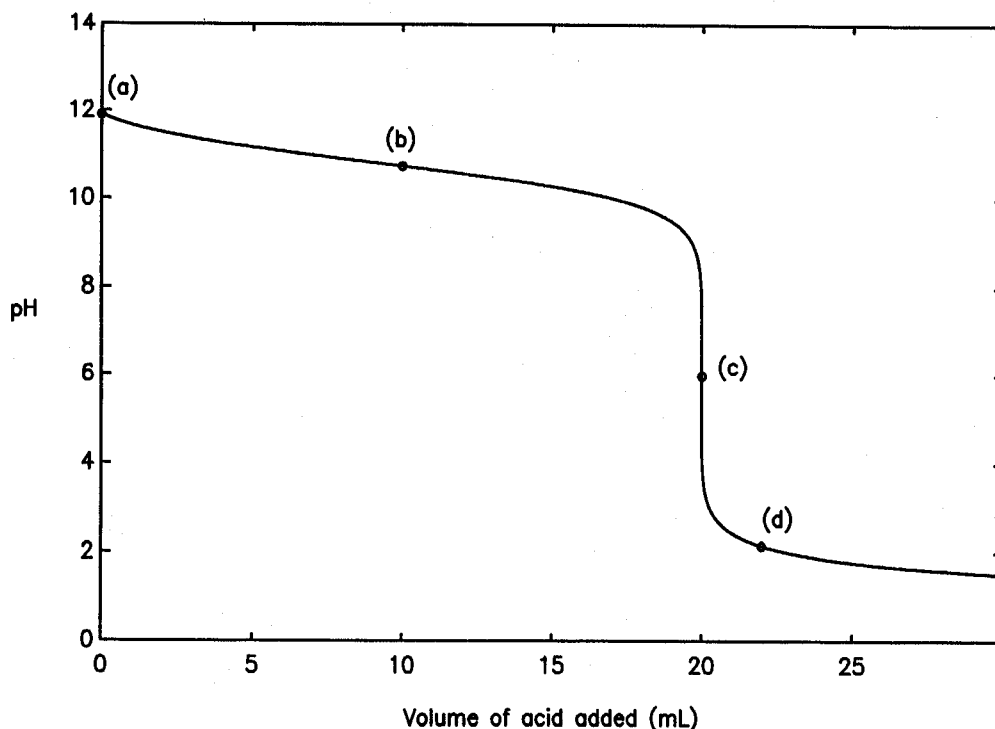


FIGURE 16.5 Titration of 50.0 mL of 0.100  $M$   $C_2H_5NH_2$  by 0.250  $M$   $HCl$ . (a) Before strong acid is added ( $V_a = 0$ ), the system consists entirely of the weak base ethylamine in aqueous solution. The pH is 11.89. (b) *Half-equivalence point*: Addition of 10.0 mL of hydrochloric acid converts half the original amount of weak base into its conjugate acid, leaving the system with equal concentrations of each species. The solution stands at the center of the comparatively flat buffer region, with a pH of 10.81. (c) *Equivalence point*: Upon addition of 20.0 mL of  $HCl$ , all of the original base has been converted into its conjugate acid. The ensuing hydrolysis reaction leaves the solution acidic, its pH near 6. (d) Beyond the equivalence point, the system is dominated by unbuffered hydrochloric acid. The pH falls to 2.16 after addition of 2.0 mL of excess  $HCl$ .

51. For a similar calculation, see Example 16-7 in *PoC* (beginning on page R16.16).

(a) At the half-equivalence point, exactly one-half the original amount of propionic acid ( $CH_3CH_2COOH$ ) has been converted into the propionate anion ( $CH_3CH_2COO^-$ ). A corresponding amount of strong base ( $OH^-$ ) is required:

$$\text{moles base} = \frac{\text{moles acid}}{2}$$

$$c_b V_b = \frac{c_a V_a}{2}$$

The specific volume of  $NaOH$  needed here is 10.0 mL:

$$V_b = \frac{1}{2} \left( \frac{c_a}{c_b} \right) V_a = \frac{1}{2} \left( \frac{0.100 M}{0.250 M} \right) \times 50.0 \text{ mL} = 10.0 \text{ mL} \quad (\text{half-equivalence point})$$



To achieve full equivalence,

moles base = moles acid

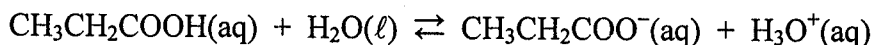
$$c_b V_b = c_a V_a$$

we need an additional 10.0 mL of NaOH:

$$V_b = \frac{c_a}{c_b} V_a = \frac{0.100 \text{ M}}{0.250 \text{ M}} \times 50.0 \text{ mL} = 20.0 \text{ mL} \quad (\text{equivalence point})$$

The complete titration curve is plotted in Figure 16.6 and explained further in parts (b), (c), (d), and (e) below.

(b) Before any NaOH is introduced, the 0.100 M CH<sub>3</sub>CH<sub>2</sub>COOH solution is initially governed by the ionization equilibrium of a weak acid:



Initial conc.	0.100	0	0
Change	-x	x	x
Equilibrium conc.	0.100 - x	x	x

We set up and solve the mass-action equation in the usual way, approximating the denominator (0.100 - x) as simply 0.100:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]} = 1.4 \times 10^{-5}$$

$$\frac{x^2}{0.100 - x} = 1.4 \times 10^{-5}$$

$$x \approx \sqrt{(0.100)(1.4 \times 10^{-5})} = 1.18 \times 10^{-3} \text{ M}$$

The corresponding pH is 2.93:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.18 \times 10^{-3}) = 2.93$$

(c) The concentrations [CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup>]<sub>0</sub> and [CH<sub>3</sub>CH<sub>2</sub>COOH]<sub>0</sub> are equal at the half-equivalence point, where pH = pK<sub>a</sub>:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{CH}_3\text{CH}_2\text{COO}^-]_0}{[\text{CH}_3\text{CH}_2\text{COOH}]_0} = -\log(1.4 \times 10^{-5}) + \log 1.00 \\ &= 4.85 + 0 = 4.85 \end{aligned}$$

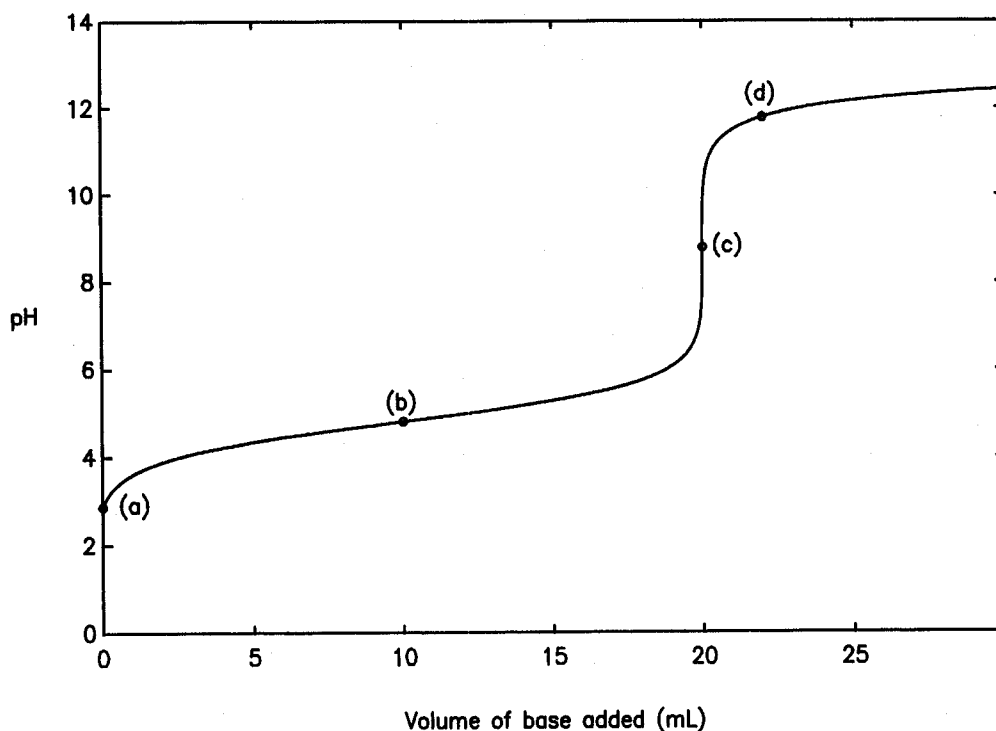


FIGURE 16.6 Titration of 50.0 mL of 0.100  $M$   $\text{CH}_3\text{CH}_2\text{COOH}$  by 0.250  $M$   $\text{NaOH}$ . (a) Before strong base is added ( $V_b = 0$ ), the system consists entirely of the weak acid in aqueous solution. The pH is 2.93. (b) Addition of 10.0 mL of sodium hydroxide converts half the original amount of propionic acid into sodium propionate. At this *half-equivalence point*, midway through the buffer region, the ratio of conjugate base to weak acid is 1 and hence pH is equal to  $\text{p}K_a$ : 4.85. (c) All of the original acid has been converted into its conjugate base at the *equivalence point*, reached upon addition of 20.0 mL of 0.250  $M$   $\text{NaOH}$ . Hydrolysis of the conjugate base,  $\text{CH}_3\text{CH}_2\text{COO}^-$ , produces a basic solution with a pH of 8.85. (d) Further addition of  $\text{NaOH}$  past the equivalence point converts the system into an uncomplicated strong base. The pH rises sharply to 11.84 after only 2.0 mL of excess  $\text{NaOH}$  are introduced.

(d) The following conditions prevail at the equivalence point:

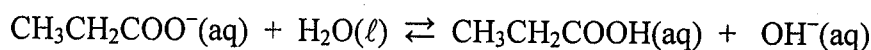
1. The total volume is 70.0 mL, arising from the original 50.0 mL of acid plus the additional 20.0 mL of base needed for complete neutralization (see above, part a).
2. The initial amount of conjugate base,  $\text{CH}_3\text{CH}_2\text{COO}^-$ , is equal to the amount of acid originally contained in 50.0 mL:

$$\frac{0.100 \text{ mol } \text{CH}_3\text{CH}_2\text{COOH}}{\text{L}} \times \frac{1 \text{ mol } \text{CH}_3\text{CH}_2\text{COO}^-}{\text{mol } \text{CH}_3\text{CH}_2\text{COOH}} \times 0.0500 \text{ L} \\ = 0.00500 \text{ mol } \text{CH}_3\text{CH}_2\text{COO}^-$$

3. The concentration of  $\text{CH}_3\text{CH}_2\text{COO}^-$  before equilibration is therefore 0.0714 M, arising from 0.00500 mol in a volume of 0.0700 L:

$$[\text{CH}_3\text{CH}_2\text{COO}^-]_0 = \frac{0.00500 \text{ mol}}{0.0700 \text{ L}} = 0.0714 \text{ M}$$

The conjugate base undergoes hydrolysis, and the system eventually comes to equilibrium:



Initial conc.	0.0714	0	0
Change	-x	x	x
Equilibrium conc.	0.0714 - x	x	x

Solving for  $x = [\text{OH}^-]$ , we obtain the pH of the basic mixture that develops at the equivalence point:

$$K_b = \frac{[\text{CH}_3\text{CH}_2\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{COO}^-]} = \frac{K_w}{K_a}$$

$$\frac{x^2}{0.0714 - x} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-5}}$$

$$x \approx \sqrt{\frac{(0.0714)(1.0 \times 10^{-14})}{1.4 \times 10^{-5}}} = 7.14 \times 10^{-6} \text{ M} \quad (x \ll 0.0714)$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{7.14 \times 10^{-6}} = 8.85$$

(e) Past the equivalence point there is excess strong base, and the pH of the solution is determined largely by the hydroxide ions coming from NaOH. The amount of  $\text{OH}^-$  contributed by hydrolysis of  $\text{CH}_3\text{CH}_2\text{COO}^-$  is negligible in the presence of a far larger concentration of strong base.

Specifically, at 2.0 mL beyond the equivalence point, we have 0.00050 mole of excess  $\text{OH}^-$  in a total volume of 72.0 mL:

$$\frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 2.0 \text{ mL} = 0.00050 \text{ mol OH}^-$$

$$\text{Volume} = 50.0 \text{ mL} + 20.0 \text{ mL} + 2.0 \text{ mL}$$

$\uparrow$                        $\uparrow$                        $\uparrow$   
 original acid                      equivalent volume of base                      excess base

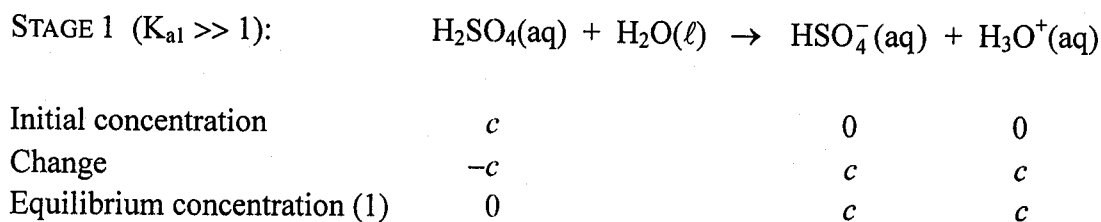
The concentration of  $\text{OH}^-$  is  $0.0069 \text{ M}$ , and the corresponding pH is 11.84:

$$[\text{OH}^-] = \frac{0.00050 \text{ mol}}{0.0720 \text{ L}} = 0.0069 \text{ M}$$

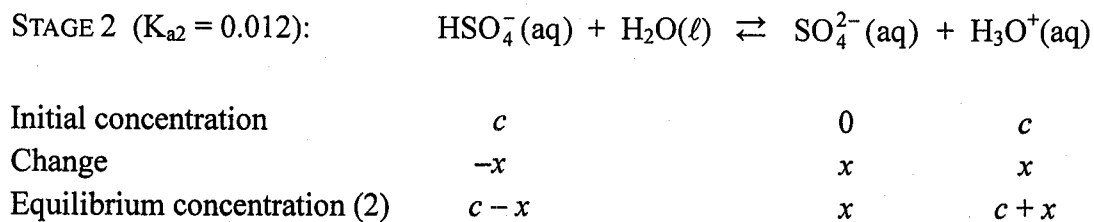
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{1.0 \times 10^{-14}}{6.9 \times 10^{-3}} = 11.84$$

See Examples 16-9 and 16-10 in PoC for calculations dealing with polyprotic acids.

52. Assume that the first ionization goes to completion, producing aqueous concentrations of  $\text{H}_3\text{O}^+$  and  $\text{HSO}_4^-$  equal to the initial concentration ( $c$ ) of  $\text{H}_2\text{SO}_4$ :



The second ionization is then governed by the following equilibrium:



From there, we set up the mass-action equation

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(c+x)x}{c-x}$$

and either obtain an approximate solution for small  $x$ ,

$$K_{a2} = \frac{(c+x)x}{c-x} \approx \frac{cx}{c} = x \quad (x \ll c)$$

or else expand the expression in full:

$$\begin{aligned} x^2 + cx &= K_{a2}c - K_{a2}x \\ x^2 + (c + K_{a2})x - K_{a2}c &= 0 \end{aligned}$$

The latter option, valid for all the initial concentrations we shall consider, produces a quadratic equation of the form

$$px^2 + qx + r = 0$$

with coefficients  $p$ ,  $q$ , and  $r$ :

$$p = 1 \quad q = c + K_{a2} \quad r = -K_{a2}c$$

Its solution is given by the quadratic formula (*PoC*, pages A50–A54):

$$x = \frac{-q \pm \sqrt{q^2 - 4pr}}{2p}$$

Solving for  $x$ , we reject the negative root and use just the positive root to calculate the pH after stage 2 (final equilibrium):

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(c + x)$$

Note that the pH after stage 1 is equal to  $-\log c$ , which differs increasingly from  $-\log(c + x)$  as the solution becomes more dilute.

SAMPLE CALCULATION: As an example, consider the initial conditions specified in (a):

$$c = 1.000 \text{ M} \quad K_{a2} = 0.012$$

$$p = 1 \quad q = c + K_{a2} = 1.012 \quad r = -K_{a2}c = -0.012$$

Setting up and solving the quadratic equation, we obtain a final concentration ( $c + x$ ) greater than 1 M and hence a pH less than 0:

$$x = \frac{-q + \sqrt{q^2 - 4pr}}{2p} = \frac{-1.012 + \sqrt{(1.012)^2 - 4(1)(-0.012)}}{2(1)} = 0.0117 = 0.012 \text{ M}$$

$$\text{pH} = -\log(c + x) = -\log 1.0117 = -0.0051$$

ALTERNATIVE SOLUTION: Since  $x$  proves to be relatively small compared with  $c = 1.000 \text{ M}$ , we obtain effectively the same result by using the approximate formulation:

$$K_{a2} = \frac{(c+x)x}{c-x} \approx \frac{cx}{c} = x \quad (x \ll c)$$

$$x = K_{a2} = 0.012$$

$$\text{pH} = -\log(c + x) = -\log 1.012 = -0.0052$$

This simplification, although welcome, becomes less reliable as  $c$  decreases. The results below were all calculated using the quadratic formula. See also Example 16-10 in *PoC*.

	$c$ (M)	pH (STAGE 1)	pH (STAGE 2)
(a)	1.000	0.00	-0.0051
(b)	0.500	0.30	0.29
(c)	0.100	1.00	0.96
(d)	0.010	2.00	1.84

53. Hydrosulfuric acid dissociates in two stages, yielding first the anion  $\text{HS}^-$ :



Initial concentration	$c$	0	0
Change	$-x$	$x$	$x$
Equilibrium concentration (1)	$c - x$	$x$	$x$

Expressing the equilibrium constant symbolically,

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{x^2}{c-x}$$

we obtain our usual approximate solution for this first stage:

$$x \approx \sqrt{K_{a1}c} \quad (x \ll c)$$

The approximation is reasonable since  $c - x \approx c$  in each of the requested calculations.

The second ionization produces the sulfide ion,  $\text{S}^{2-}$ :

STAGE 2 ( $K_{a2} = 1 \times 10^{-19}$ ):	$\text{HS}^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{S}^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial concentration	$x$	0	$x$
Change	$-y$	$y$	$y$
Equilibrium concentration (2)	$x-y$	$y$	$x+y$

In solving the corresponding mass-action equation,

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{(x+y)y}{x-y} = 1 \times 10^{-19}$$

we now substitute the concentration  $x$  previously determined for stage 1:

$$x = \sqrt{K_{a1}c}$$

Further, expecting  $y$  to be small relative to  $x$ , we make the approximation

$$x \pm y \approx x$$

and thereby simplify the equation for  $K_{a2}$  considerably:

$$y \approx K_{a2} = 1 \times 10^{-19}$$

With  $y$  so small, the pH is then determined only by the first ionization:

$$\text{pH} = -\log(x+y) \approx -\log x = -\log \sqrt{K_{a1}c} \quad (y = K_{a2} \ll \sqrt{K_{a1}c})$$

In (a), for example, we find that an initial concentration of 1.000 *M* yields a pH of 3.53:

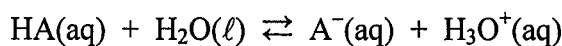
$$\begin{aligned}
 c &= 1.000 \text{ M} & K_{a1} &= 8.9 \times 10^{-8} \\
 \text{pH} &= -\log x \\
 &= -\log \sqrt{K_{a1}c} \\
 &= -\log \sqrt{(8.9 \times 10^{-8})(1.000)} \\
 &= 3.53
 \end{aligned}$$

The other calculations are done in exactly the same way. See also Example 16-9 in *PoC*.

	<i>c</i> ( <i>M</i> )	pH
(a)	1.000	3.53
(b)	0.500	3.68
(c)	0.100	4.03
(d)	0.010	4.53

**54.** A reminder that a particular equilibrium *concentration* (such as represented by pH) is not the same as an equilibrium *constant* (such as represented by  $pK_a$ ).

(a) The pH is a measure of the hydronium ion concentration at equilibrium, not an intrinsic property of an acid. It depends on both the value of  $K_a$  and the initial values  $[HA]_0$ ,  $[A^-]_0$ , and  $[H_3O^+]_0$  in the ionization reaction:

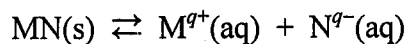


$$K_a = \frac{[H_3O^+]_{eq}[A^-]_{eq}}{[HA]_{eq}} = \text{constant}$$

The same acid will produce different values of pH under different conditions.

(b) The logarithmic quantity  $pK_a$  is a measure of the equilibrium constant  $K_a(T)$ , an intrinsic parameter of the acid.

(c) Similar to  $K_a$ , the solubility-product constant  $K_{sp}$  (an equilibrium constant) is a fixed number at a given temperature. Consider, for example, the arbitrary ionic compound MN:



$$K_{sp}(T) = [M^{q+}]_{eq}[N^{q-}]_{eq} = \text{constant}$$



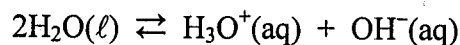
Like pH, the concentrations of  $M^{q+}$  and  $N^{q-}$  are variable within the limits imposed by an equilibrium constant. The equilibrium values  $[M^{q+}]_{\text{eq}}$  and  $[N^{q-}]_{\text{eq}}$  depend on both the magnitude of  $K_{\text{sp}}$  and the initial concentrations  $[M^{q+}]_0$  and  $[N^{q-}]_0$ .

**55.** A strong Arrhenius base (B) produces one mole of  $\text{OH}^-$  for every mole of B dissolved. Unionized species B(aq) are unlikely to be found in solution. If the base is poorly soluble, then only a relatively small amount of B will dissolve in water—but nearly 100% of the dissolved material will exist in ionic form.

**56.** A solution need not have a pH of 7 to be neutral. The autoionization constant varies with temperature, and the equilibrium concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  follow suit. It is the *equality* of  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ , not the particular numerical value, that determines acid–base neutrality.

See pages 450–452 and 456–457 in *PoC*, along with Examples 12-15 and 15-9, for the dependence of an equilibrium constant on temperature.

(a) The reaction



is presumably endothermic, since the equilibrium constant

$$K_w(T) = [\text{H}_3\text{O}^+][\text{OH}^-]$$

increases with temperature. A larger concentration of  $\text{H}_2\text{O}$  is dissociated at equilibrium when the temperature is higher. Heat functions as a reactant, driving the process forward toward the formation of hydronium and hydroxide ions.

(b) Pure water is neutral at all temperatures. Equal concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are produced in the autoionization reaction:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = x$$

$$x^2 = K_w(T)$$

$$x = \sqrt{K_w(T)}$$

(c) Neutral. See part (b) above.

(d) At 70°C, we know that  $K_w(T) = 1.5 \times 10^{-13}$  and thus  $\text{pH} = 6.41$ :

$$x^2 = 1.5 \times 10^{-13}$$

$$x = 3.87 \times 10^{-7}$$

$$\text{pH} = -\log x = 6.41$$

Given that the autoionization reaction is endothermic, we then assume that  $K_w(90^\circ\text{C})$  is greater than  $K_w(70^\circ\text{C})$ . The concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  increase equally at the higher temperature, rising to a value greater than  $x = 3.87 \times 10^{-7} \text{ M}$ . In turn, the pH falls to a value less than 6.41—probably only slightly less. Of the choices provided,  $\text{pH} = 6.2$  is the only one consistent with these requirements.