Acid-Base Equilibria

Section 97 – Buffers

97-1 Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

Solution

OH^- is a base, and NH_4^+ is a weak acid. They react with one another to form NH_3, thereby setting up the equilibrium $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$. Because both the base (NH_3) and the conjugate acid (NH_4^+) are present, a buffer is formed. However, in the second case, NH_3 and OH^- are both bases, so no buffer is possible.

97-2 Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

Solution

Excess H_3O^+ is removed primarily by the reaction:

$$H_3O^+(aq) + H_2PO_4^-(aq) \rightarrow H_2O(l) + H_3PO_4(aq)$$

Excess base is removed by the reaction:

$$OH^-(aq) + H_3PO_4(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$$

97-3 Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

Solution

A mixture of NH_3 and NH_4Cl is a buffer because it contains a weak base and its conjugate acid (the salt). If hydroxide ions are added, the ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration toward its original value: $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$.

If hydronium ions are added, the ammonia molecules in the buffer react with them to form ammonium ions, reducing the hydronium ion concentration toward its original value:
$NH_3(aq) + H_3O^+(aq) \rightleftharpoons NH_4^+(aq) + H_2O(l)$.

97-4 What is $[H_3O^+]$ in a solution of 0.25 *M* acetic acid (CH_3CO_2H) and 0.030 *M* sodium acetate ($NaCH_3CO_2$)?

Solution

The Ka for the weak acid acetic acid is $K_a = 1.8 \times 10^{-5}$. The equilibrium involved is as follows:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

The equilibrium expression is:

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \text{ x } 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2H]$	$[H_3O^+]$	$[CH_3CO_2^-]$
Initial concentration (*M*)	0.25	0	0.030
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.25 - x$	x	$0.030 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that (0.25 – x ≈ 0.25 and 0.030 + x ≈ 0.030.

$$\frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = \frac{(x)(0.030 + x)}{(0.25 - x)} \approx \frac{(x)(0.030)}{0.25} = 1.8 \text{ x } 10^{-5}$$

Solving for x gives $1.50 \times 10^{-4} M$. Because this value is less than 5% of both 0.25 and 0.030, our assumptions are correct. Therefore, $[H_3O^+] = 1.5 \times 10^{-4}\ M$.

This problem more easily be solved using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pKa} + \log\frac{[\text{base}]}{[\text{acid}]}$$

We can determine the pKa value from $pK_a = -\log(K_a) = -\log(1.8 \times 10^{-5}) = 4.74$

The [acid] ≈ 0.25M (since CH_3CO_2H is a weak acid, it does not significantly dissociate).
The [base] = 0.030 M (since $CH_3CO_2^-$ is a weak base, it does not significantly accept protons).
Thus,

$$\text{pH} = 4.74 + \log\frac{0.030 \text{ M}}{0.25 \text{ M}} = 4.74 + \log(0.12) = 4.74 + (-0.92) = 3.82$$

This number for the pH makes sense since [acid] > [base], and so the pH should be more acidic (lower) than the pKa value.

Since pH = -log $[H_3O^+]$,
3.82 = -log $[H_3O^+]$ and thus $[H_3O^+] = 10^{-3.82} = 1.5 \text{ x } 10^{-4}$ M.

97-5 What is $[H_3O^+]$ in a solution of 0.075 *M* nitric acid (HNO_2) and 0.030 *M* sodium nitrite ($NaNO_2$)?

Solution
The Ka for nitric acid can be obtained in Appendix H: Ka = $4.6 \text{ x } 10^{-5}$. The equilibrium involved is as follows:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

This is another example of a problem that is easily solved using the Henderson-Hasselbach equation. We are provided with significant concentrations of both a weak acid, HNO_2, and its conjugate base, NO_2^-. (We know that HNO_2 is a weak acid since we are given its Ka value).

$$\mathrm{pH} = \mathrm{pKa} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

We can determine the pKa value from $pK_a = -\log(K_a) = -\log(4.6 \times 10^{-5}) = 4.34$

The [acid] ≈ 0.75M (since HNO_2 is a weak acid, it does not significantly dissociate); the [base] = 0.030 M (since NO_2^- is a weak base, it does not significantly accept protons).
Thus,

$$\mathrm{pH} = 4.34 + \log\frac{0.030\ \mathrm{M}}{0.75\ \mathrm{M}} = 4.34 + \log(0.040) = 4.34 + (-1.40) = 2.94$$

This number for the pH makes sense since [acid] > [base], and so the pH should be more acidic (lower) than the pKa value.

Since pH = -log $[H_3O^+]$,
2.94 = -log $[H_3O^+]$ and thus $[H_3O^+] = 10^{-2.94} = 1.1 \times 10^{-3}$ M.

(Note that, depending on how many significant figures you carried through your calculations, you may obtain numbers such as 1.2×10^{-3} M which is fine).

97-6 What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

Solution:
The equilibrium involved is as follows:

$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$ Kb = 4.4×10^{-4}

The equilibrium expression is:

$$K_b = \frac{[\mathrm{CH_3NH_3^+}][\mathrm{OH^-}]}{[\mathrm{CH_3NH_2}]} = 4.4 \times 10^{-4}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3NH_2]$	$[CH_3NH_3^+]$	$[OH^-]$
Initial concentration (*M*)	0.125	0.130	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.125 - x$	$0.130 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that (0.125 – *x*) ≈ 0.125 and (0.130 – *x*) ≈ 0.130, gives:

$$4.4 \times 10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

$$4.4 \times 10^{-4} = \frac{[0.130 + x][x]}{[0.125 - x]}$$

$$4.4 \times 10^{-4} \approx \frac{[0.130][x]}{[0.125]}$$

$$x \approx \frac{(4.4 \times 10^{-4})(0.125)}{(0.130)}$$

$x \approx 4.2 \times 10^{-4}$ *M*, thus $[OH^-] = 4.2 \times 10^{-4}$ *M*

Solving for *x* gives 4.23×10^{-4} *M*. Because this value is less than 5% of both 0.125 and 0.130, our assumptions are correct.

97-7 What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

Solution

The equilibrium involved is:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ $K_b = 1.8 \times 10^{-5}$

The equilibrium expression is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	1.25	0.78	0
Change (*M*)	−*x*	+*x*	+*x*
Equilibrium (*M*)	0.125 – *x*	0.78 + *x*	*x*

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that (1.25 – *x*) ≈ 1.25 and (0.78 + *x*) ≈ 0.78, gives:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.78 - x)(x)}{(1.25 - x)} \approx \frac{(0.78)(x)}{(1.25)} = 1.8 \times 10^{-5}$$

Solving for *x* gives $2.88 \times 10^{-5} M$. Because this value is less than 5% of both 1.25 and 0.78, our assumptions are correct. Therefore, $[OH^-] = 2.9 \times 10^{-5}\ M$.

This problem can also be solved using the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{pKa} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

Caution is required: the H-H equation is written with respect to the pKa of the weak ACID. You cannot simply substitute with the pKb value; it is also important to assign the base and its conjugate acid properly. The solution contains 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3. Since NO_3^- is simply a “spectator ion”, there are appreciable quantities of both the acid (NH_4^+) and the conjugate base (NH_3) present. Let us rewrite the reaction in terms of the behaviour of the acid in aqueous solution:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

Note that the base is NH_3 and the conjugate acid is NH_4^+. Thus, [base] = $[NH_3]$ ≈1.25 M; [acid] = $[NH_4^+]$ ≈ 0.78 *M*.

The H-H equation requires the pKa value for the acid NH_4^+] is related to the pKb of the conjugate base: pKa = pKw – pKb. The pKb = –logKb = –log (1.8×10^{-5}) = – (4.74) = 4.74.
Thus the pKa = 14.00 – 4.74 = 9.26.

The Henderson-Hasselbalch equation becomes:

$$\mathrm{pH} = \mathrm{pKa} + \log\frac{[\ NH_3]}{[NH_4^+]}$$
$$\mathrm{pH} = 9.26 + \log\frac{(1.25)]}{(0.78)} = 9.26 + \log(1.60) = 9.26 + (0.20)$$
pH = 9.46

We are asked for $[OH^-]$ (not pH), so the last step is to convert pH into $[OH^-]$. Recall that

pKw = pH + pOH.

Thus,

pOH = pKw – pH
pOH = 14.00 – 9.46 = 4.54
$[OH^-] = 10^{-4.54} = 2.9 \times 10^{-5}$ M

97-8 What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

(a) HCl
(b) KCH_3CO_2

(c) NaCl
(d) KOH
(e) CH_3CO_2H

Solution
The equilibrium reaction and equilibrium constant are as follows:

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq) \qquad Ka = 1.8 \times 10^{-5}$$

(a) HCl is a strong acid, and so will dissociate to form H^+ and Cl^- in aqueous solution. Thus the addition of HCl will increase the $[H^+]$. This will shift the equilibrium reaction indicated above to the left: i.e., the H^+ will react with the acetate ($CH_3CO_2^-$), thus producing more acetic acid (CH_3CO_2H). Thus, $[CH_3CO_2^-]$ decreases and $[CH_3CO_2H]$ increases.
(b) Potassium salts are extremely soluble in water, so the added KCH_3CO_2 will dissociate to form K^+ and $CH_3CO_2^-$ ions, thus increasing the $[CH_3CO_2^-]$. This will shift the equilibrium above to the left: the extra $CH_3CO_2^-$ will react with H^+, thus $[H^+]$ decreases slightly, while $[CH_3CO_2H]$ increases.
(c) The added NaCl will have no effect on the concentration of the ions. The NaCl will dissolve in the aqueous solution to form Na^+ and Cl^- ions, but these are not involved in the equilibrium above.
(d) The KOH is a strong base, and the ions will dissociate in aqueous solution to form K^+ and OH^- ions. The hydroxide ions will react with H^+ according to the neutralization reaction

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

Thus the $[H^+]$ will decrease. This will pull the equilibrium reaction above to the right: some CH_3CO_2H will dissociate to attempt to replenish the H^+, also producing more $CH_3CO_2^-$ in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[CH_3CO_2^-]$ increases.
(e) The addition of more CH_3CO_2H will shift the equilibrium above to the right. As some of the CH_3CO_2H dissociates, more H^+ and $CH_3CO_2^-$ will be produced. Thus both $[CH_3CO_2^-]$ and $[H^+]$ will increase.

97-9 What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

(a) KI
(b) NH_3
(c) HI
(d) NaOH
(e) NH_4Cl

Solution
The equilibrium reaction and equilibrium constant are as follows:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad Kb = 1.8 \times 10^{-5}$$

(a) The added KI will dissociate into K^+ and I^- ions in aqueous solution, but since neither ion is involved in the equilibrium, there will be no effect on the concentrations of the ammonia, hydroxide ions, or ammonium ions.
(b) The added NH_3 will increase its concentration, which will shift the equilibrium above to the right, producing more OH^- and NH_4^+. Thus, $[OH^-]$ and $[NH_4^+]$ both increase.

(c) The HI is a strong acid, and would dissociate completely in aqueous solution to form H^+ and I-. However, the H^+ will not persist since it will immediately react with OH- in a neutralization reaction according to

$$OH^-(aq) + H^+(aq) \rightleftharpoons H_2O(l)$$

Since the OH^- is, thus, being used in this neutralization reaction, the $[OH^-]$ decreases, pulling the equilibrium reaction above to the right. Thus some NH_3 will react with water in order to attempt to partially replenish the OH^-, forming more NH_4^+ in the process. Thus $[NH_3]$ decreases and $[NH_4^+]$ increases.

(d) NaOH is a strong base and will completely dissociate in aquaeous solution to form Na+ and OH^- ions. Thus the $[OH^-]$ will increase, pushing the equilibrium above to the left. The OH- will react with some NH_4^+, forming NH_3 in the process. Thus the of $[NH_4^+]$ decreases and $[NH_3]$ increases.

(e) Ammonium salts are very soluble in water and will ionize to form NH_4^+ and Cl^- ions. Thus the $[NH_4^+]$ will increase, pushing the equilibrium above to the left. The NH_4^+ will react with some OH^-, forming some NH_3 will form in the process. Thus, $[OH^-]$ decreases and $[NH_3]$ increases.

97-10 What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

Solution

Nitrates are highly soluble in water, and ammonium nitrate (NH_4NO_3) will dissociate into the complex ions NH_4^+ and NO_3^- immediately in aqueous solution. The nitrate is a spectator ion and does not affect the pH; the ammonium (NH_4^+) is the conjugate acid of the weak base ammonia (NH_3). The reaction and equilibrium constant are:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad Kb = 1.8 \times 10^{-5}$$

The equilibrium expression is:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The initial concentrations of NH_3 and NH_4^+ are 0.20 *M* and 0.40 *M*, respectively. The equilibrium concentrations for this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	0.20	0.40	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.20 - x$	$0.40 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.20 - x) \approx 0.20$ and $(0.40 + x) \approx 0.40$, gives:

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{(0.40 + x)(x)}{(0.20 - x)}$$

$$1.8 \times 10^{-5} \approx \frac{(0.40)(x)}{(0.20)}$$

$$x = \frac{(1.8 \times 10^{-5})(0.20)}{(0.40)}$$

x = 9.00 x 10^{-6} M

Solving for x gives 9.00 × 10^{-6} M. Because this value is less than 5% of both 0.20 and 0.40, our assumptions are correct. Therefore, $[OH^-]$ = 9.00 × 10^{-6} M. Thus:

pOH = –log(9.00 × 10^{-6}) = 5.046

pH = 14.000 – pOH = 14.000 – 5.046 = 8.954 = 8.95

97-11 Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

Solution

The reaction and equilibrium constant are:

$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$ Ka = 7.5 x 10^{-3}

The equilibrium expression is

$$K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

The initial concentration of $H_2PO_4^-$ = 0.250 mol / 0.500 L = 0.500 M; that of H_3PO_4= 0.155 mol / 0.500 L = 0310 M. The equilibrium concentrations for this system can be written as follows:

	$[H_3PO_4]$	$[H_3O^+]$	$[H_2PO_4^-]$
Initial concentration (*M*)	0.310	0	0.500
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.310 - x$	x	$0.500 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that (0.310 – x) ≈ 0.310 and (0.500 + x) ≈ 0.500, gives:

$$K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$7.5 \times 10^{-3} = \frac{(x)(0.500 + x)}{(0.310 - x)} \approx \frac{(x)(0.500)}{(0.310)}$$

$$x = \frac{(7.5 \times 10^{-3})(0.310)}{(0.0.500)} \approx 7.5 \text{ x } 10^{-3}$$

Solving for *x* gives 4.65×10^{-3} *M*. Because this value is less than 5% of both 0.310 and 0.500, our assumptions are correct. Therefore, $[H_3O^+] = 4.65 \times 10^{-3}$ *M*. Thus:

$$pH = -\log(4.65 \times 10^{-3}) = 2.333 = 2.33$$

97-12 How much solid $NaCH_3CO_2{\bullet}3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

Solution

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log [base] / [acid]$$

where the base is acetate ion and the acid is acetic acid.

The pK_a for acetic acid is

$$pK_a = -\log K_a = -\log 1.8 \times 10^{-5} = 4.74$$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$$[C_2H_3O_2^-] / [HC_2H_3O_2] = 10^{(5.00 - 4.74)} = 10^{0.26} = 1.82$$

The small K_a for acetic acid means very little will undergo acid ionization, and so its concentration will be ~0.50 M. The molarity of acetate ion required is therefore

$$[C_2H_3O_2^-] = [HC_2H_3O_2] \times 1.82 = 0.50 \times 1.82 = 0.91 \text{ M}$$

The mass of sodium acetate trihydrate required is then

$$0.91 \text{ mol/L} \times 136.1 \text{ g/mol} \times 0.300 \text{ L} = 37 \text{ g}$$

97-13 What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

Solution

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log [base] / [acid]$$

where the base is ammonia and the acid is ammonium ion.

The pK_a for ammonium ion is

$$pK_a = pK_w - pK_b = 14.00 - (-\log K_b) = 14.00 - 4.74 = 9.26$$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$$[NH_3] / [NH_4^+] = 10^{(9.26 - 9.26)} = 10^{0.00} = 1.0$$

The small K_b for ammonia means very little will undergo base ionization, and so its concentration will be ~0.100 M. The molarity of ammonium ion required is therefore

$[NH_4^+]$ = $[NH_3]$ / 1.0 = 0.100 / 1.00 = 0.10 M

The mass of ammonium chloride required is then

0.10 mol/L × 53.49 g/mol × 0.750 L = 4.0 g

97-14 A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

(a) What is the pH of the solution?
(b) Is the solution acidic or basic?
(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

Solution

(a) The reaction and equilibrium constant are:

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq) \qquad Ka = 1.8 \times 10^{-5}$$

The pH of the solution can be readily determined using the H-H equation. The acid is acetic acid, and its concentration was 0.200 M before dilution; the base is acetate and its concentration was 0.600 M before dilution. We do not know the actual volumes of the two solutions added, but since equal volumes were added, the concentrations would be divided by 2. Since acetic acid and acetate are a weak acid and its conjugate base, we know that the final concentrations are about the same as the initial concentrations.

$$\text{pH} = \text{pKa} + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log\frac{0.600\ \text{M}/2}{0.200\ \text{M}/2}$$

pH = 3.74 + log 3.000

pH = 3.74 + (0.477) = 4.22

(b) The solution is acidic (since the pH is less than neutral).

(c) When 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer, the moles of H+ added are as follows:

$$\text{Moles H}^+ = 3.00\ \text{mL} \times \frac{1\ L}{1000\ mL} \times \frac{0.034\ mol}{L}$$

moles H^+ = 1.02×10^{-4} mol

This added H^+ will react with the base (acetate) to shift the equilibrium to the left

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$$

resulting in the formation of more acetic acid. This changes the ratio of [acetate]:[acetic acid], and thus changes the pH. We can determine the exact ratio through stoichiometry: the extra 1.02×10^{-4} mol of H^+ will react with the same amount of acetate, forming 1.02×10^{-4} mol of acetic acid. We just need to first calculate how much acetate and acetic acid are initially present in 0.200 L of buffer:

For the acetic acid, the initial moles present equal 0.1000 *M* × 0.200 L = 0.0200 mol, and for acetate ion, 0.300 *M* × 0.200 L = 0.0600 mol. Thus:

	CH_3CO_2H *(aq)* ⇌	H^+*(aq)*	$CH_3CO_2^-$ *(aq)*
I	0.0200 mol	0.000102 mol	0.0600 mol
C	+0.000102 mol	-0.000102 mol	-0.000102 mol
E	0.020102	~0	0.059898 mol

$$\text{pH} = \text{pKa} + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = 3.74 + \log\frac{0.059898\ \text{mol}/0.200\ \text{L}}{0.020102\ \text{mol}/0.200\text{L}}$$

pH = 3.74 + log 2.9797
pH = 3.74 + (0.474) = 4.22

You can see that the addition of a relatively small amount of extra acid has a negligible effect on the pH of the buffer solution: if we use the appropriate number of significant figures, the pH of the buffer is the same as it was before the HCl was added. This is to be expected of a buffer solution: it will resist a change in pH when extra acid or base is added.

97-15 A 5.36 g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution diluted to 0.100 L.

(a) What is the pH of this buffer solution?
(b) Is the solution acidic or basic?
(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

Solution

(a) Ammonium chloride (NH_4Cl) will dissolve in aqueous solution to form ammonium (NH_4^+) and chloride (Cl^-) ions. Chloride ions are pH neutral (they do not affect the pH), but ammonium is a weak acid. It cannot form a buffer on its own, but since some strong base NaOH is also added to the solution, the OH^- ions will react with the NH_4^+ to form some ammonia (NH_3) in the solution. Then, since both NH_4^+ and its conjugate base are present, the solution is a buffer.

Thus, the approach to the problem is to first determine the stoichiometry of the reaction between the NH_4^+ and the OH^-, in order to determine the ratio between the NH_4^+ and it conjugate base, in order to determine the pH of the solution.

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$

The MW of NH_4Cl is 53.4912 g/mol. Thus, the moles of NH_4^+ originally added can be determined as follows:

$$\text{mol } NH_4^+ = 5.36\text{ g } NH_4Cl \times \frac{1\ \text{mol NH}_4\ \text{Cl}}{53.4912\ \text{g NH}_4\ \text{Cl}} \times \frac{1\ \text{mol NH}_4^+}{1\ \text{mol NH}_4\ \text{Cl}} = 0.1002\text{ mol}$$

The moles of OH- added can be determined as follows:

mol OH^- = 1.00 M x 0.0250 L = 0.0250 mol.

We can use an ICE table to determine the amounts of NH_4^+ and its conjugate base left after reaction:

	NH_4^+ *(aq)*	+ OH^-*(aq)* →	NH_3*(aq)*	+ H_2O*(l)*
I	0.1002 mol	0.0250 mol	0	
C	-0.0250 mol	-0.0250 mol	+0.0250 mol	
E	0.0752 mol	~0	0.0250 mol	

The equilibrium between ammonia and ammonium can be represented as below:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ Kb = 1.8×10^{-5}

It is easiest to solve for pH using the H-H equation, so we need to consider the equilibrium with the ammonium as the acid. We can determine the Ka from the Kb using either Ka x Kb = Kw, or else pKa + pKb = pKw. Since we ultimately need the pKa for the H-H equation, it is easier to use the latter approach.

pKb = -log(Kb) = -log (1.8×10^{-5}) = 4.74
pKa = pKw – pKb = 14.00 – 4.74 = 9.26

Thus,

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$ pKa = 9.26

$$\mathrm{pH} = \mathrm{pKa} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

$$\mathrm{pH} = 9.26 + \log\frac{0.0250/0.100\mathrm{L}}{0.0752\ \mathrm{mol}/0.100\mathrm{L}}$$

pH = 9.26 + log0.332 = 9.26 + (-0.48) = 8.78

Note that we were told in the problem that the final volume of the buffer was 0.100 L. The volumes actually cancel out when we are using the H-H equation, the pH is determined by the ratio of [base]:[acid].