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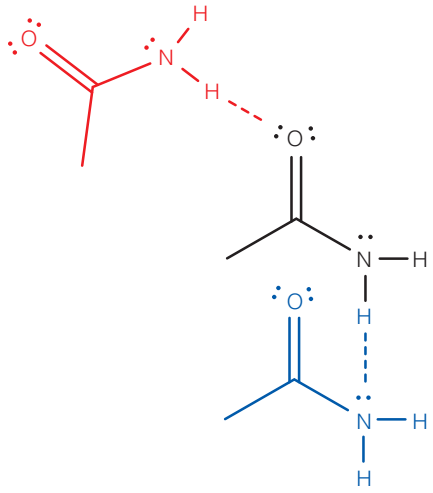
Chapter 02

1. a. Equation 2.3 predicts that the interaction energy between the ions will be greater in the lower dielectric medium; thus, the attraction between the Na^+ and Cl^- will be greater in pentane.

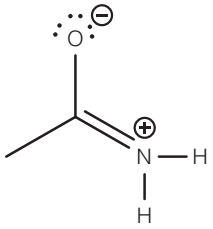
b. Since the length of the ionic bonds is 2 × 1.16 Å in each case (i.e., the value of r is the same for Ca-F and Na-F), Equation 2.3 predicts that the interaction energy between the ion will be greater as the values of q increase; thus, the attraction between the Ca^{2+} ($q = 2$) and F^- ($q = -1$) will be greater than the attraction between the Na^+ ($q = 1$) and F^- ($q = -1$).

c. Ca^{2+} will be bound more tightly by a –COOH group that is fully deprotonated. At pH = 3 the –COOH form will predominate. At pH = 4.2 the –COOH and $–COO^-$ forms will be in equal concentration. At pH 8 the $–COO^-$ will predominate; thus, expect the greatest Ca^{2+} binding at pH = 8.

2. In the red/black pair, NH is the donor and O is the acceptor. This is the more likely interaction. In the blue/black pair, the black NH is the donor and the blue N is the acceptor.



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The resonance structure for formamide makes H-bonding to oxygen more likely than H-bonding to nitrogen because the nitrogen lone pair is partially tied up in a double bond as shown.

3. The curve shown in the question describes the situation where the water dipoles are parallel and side by side. Assuming the antiparallel dipoles are also side by side (rather than head to tail), the curve would be the mirror image reflected across the Energy = 0 line on the y-axis.

4. a. HCl is a strong acid; thus, [HCl] ≈ [H^+] and pH = –log[H^+] = –log[0.35] = 0.456.

b. Acetic acid is a weak acid with $K_a = 1.74 \times 10^{-5}$; thus, use ICE table to solve this problem:

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$$H_2O + CH_3COOH \rightleftarrows H_3O^+ + CH_3COO^-$$

	NH_4^+	H^+	NH_3
Initial	1 M	0 M	0 M
Change	−x	+x	+x
Equilibrium	1−x M	x M	x M

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{[CH_3COOH]-x}$$

Assume $[CH_3COO^-] = [H_3O^+]$ and $[CH_3COOH] >> x$; therefore:

$$1.74 \times 10^{-5} = \frac{x^2}{0.35 - x}$$
$$x = 2.47 \times 10^{-3} = [H_3O^+]$$

$pH = -\log(2.47 \times 10^{-3}) = 2.61$
This answer verifies the initial assumption that $[CH_3COOH] >> x$.

c. Here $[CH_3COOH] >> x$ cannot be assumed, so use the ICE table approach with the quadratic equation to solve this problem:

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$$K_a = \frac{x^2}{0.035 - x}$$

Rearrange to $0 = x^2 + K_a x - 0.035K_a = x^2 + (1.74 \times 10^{-5})x - (6.09 \times 10^{-7})$

Solve using the quadratic equation:

$$x = \frac{-(1.74 \times 10^{-5}) \pm \sqrt{(1.74 \times 10^{-5})^2 - (4 \times -6.09 \times 10^{-7})}}{2}$$

$x = 7.717 \times 10^{-4} = [H^+]$; thus, $pH = -\log[7.717 \times 10^{-4}] = 3.11$

d. pH is lowest for the strongest acid (HCl) because it completely dissociates into H^+ and conjugate base (i.e., Cl^-). For acetic acid more H^+ dissociates as the concentration of HA increases. This follows from Le Chatelier's principle for the equilibrium: $HA \rightleftarrows H^+ + A^-$.

5. a. See Table 2.6, which indicates that NH_4^+ is a weak acid with $K_a = 5.62 \times 10^{-10}$; thus, use the ICE table to solve this problem:

$$HA \rightleftarrows H^+ + A^-$$

	NH_4^+	H^+	NH_3
Initial	1 M	0 M	0 M
Change	−x	+x	+x
Equilibrium	1−x M	x M	x M

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$$K_a = \frac{x^2}{1-x} = 5.62 \times 10^{-10}$$

Solve for x = 2.371×10^{-5} = $[H^+]$; thus, pH = $-\log(2.371 \times 10^{-5})$ = 4.63

b. NH_4^+ is a weak acid with pK_a = 9.25. Here, NaOH is consuming H^+ from the NH_4^+ thus, use this alternate version of the ICE table to solve for [HA] and $[A^-]$ after addition of NaOH (a source of ^-OH). Note: the activity of H_2O is assumed to be unity (see Equation 2.7), so it does not appear in these calculations.

$$HA + {}^-OH \rightleftarrows A^- + H_2O$$

	NH_4^+	^-OH	NH_3
Initial	0.040 mol	0.010 mol	~ 0
Change	–0.010 mol	–0.010 mol	+0.010 mol
Equilibrium	0.030 mol	0	0.010 mol

Solve for $[H^+]$ using the Henderson–Hasselbalch equation:

$$pH = pK_a + log\frac{[A^-]}{[HA]} = 9.25 + log\left(\frac{\left(\frac{0.010\,mol}{0.050\,L}\right)}{\left(\frac{0.040\,mol}{0.050\,L}\right)}\right) = 9.25 + -0.602 = 8.85$$

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c. Solve as in part (b)

$$HA + {}^-OH \rightleftarrows A^- + H_2O$$

	NH_4^+	^-OH	NH_3
Initial	0.040 mol	0.030 mol	~ 0
Change	–0.030 mol	–0.030 mol	+0.030 mol
Equilibrium	0.010 mol	0	0.030 mol

Solve for $[H^+]$ using the Henderson–Hasselbalch equation:

$$pH = pK_a + log\frac{[A^-]}{[HA]} = 9.25 + log\left(\frac{\left(\frac{0.030\,mol}{0.070\,L}\right)}{\left(\frac{0.010\,mol}{0.070\,L}\right)}\right) = 9.25 + 0.477 = 9.73$$

6. a.

$$HA \rightleftarrows H^+ + A^-$$

Initial []	0.2M	0	0
Change []	–x	+x	+x
Equilibrium []	0.2M–x	+x	+x

$$x = 0.2M \times 2\% = 0.004M$$

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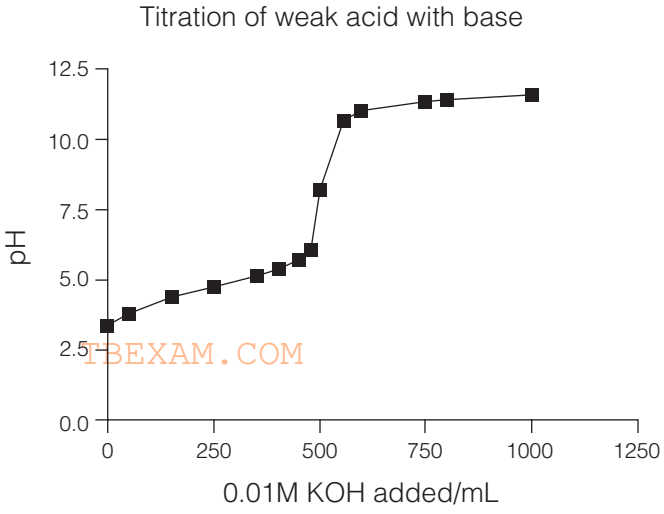
And

$$K_a = \frac{x^2}{0.2 - x} = \frac{0.004^2}{0.2 - 0.004} = 8.2 \times 10^{-5}$$

6. b. $\text{pH} = -\log[\text{H}^+] = -\log[0.004] = 2.40$

7. The titration curve can be generated using a spreadsheet to perform multiple calculations of pH as a function of added titrant (as was done in problems 5b and 5c). The calculated pH values can then be plotted as a function of added titrant. For Example:

Total volume of KOH added	pH
0mL	3.38
50mL	3.80
150mL	4.38
250mL	4.76
350mL	5.14
400mL	5.36
450mL	5.71
475mL	6.04
500mL	8.23
550mL	10.63
600mL	10.96
750mL	11.30
800mL	11.41
1000mL	11.52



8. a. Moles of acetic acid = (1 *M*) × (0.100 L) = 0.10 mol
Moles of acetate = (0.5 *M*) × (0.100 L) = 0.050 mol
Total volume = 0.200 L; thus, [acetic acid] = 0.50 *M*, and [acetate] = 0.25 *M*

$$pH = pK_a + log\left(\frac{[A^-]}{[HA]}\right) = 4.76 + log\left(\frac{0.25}{0.50}\right) = 4.46$$

8. b. Moles of H_3PO_4 = (0.3 *M*) × (0.250 L) = 0.075 mol
Moles of $H_2PO_4^-$ = (0.8 *M*) × (0.250 L) = 0.20 mol
Total volume = 0.500 L; thus, $[H_2PO_4^-]$ = 0.150 *M*, and $[HPO_4^{2-}]$ = 0.40 *M*

$$pH = pK_a + log\left(\frac{[A^-]}{[HA]}\right) = 2.14 + log\left(\frac{0.40}{0.150}\right) = 2.57$$

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9. a.

$H_2PO_4^- + H_2O \rightleftarrows \quad HPO_4^{-2} + H_3O^+$

$pK_a = 6.86$

$pH = 7.00$

$[H_2PO_4^-] = 0.1M$

$$pH = pK_a + \log\left[\frac{A^-}{HA}\right] = 7.0$$

$$7.0 = 6.86 + \log\left[\frac{A^-}{0.1}\right]$$

$$0.14 = \log\left[\frac{A-}{0.1}\right]$$

$$[A^-] = 0.138M$$

9. b.

$[H_2PO_4^-] + [HPO_4^{-2}] = 0.3M$

$[H_2PO_4^-] = 0.3M - [HPO_4^{-2}]$

$$7.00 = pK_a + \log\left[\frac{HPO_4^{-2}}{H_2PO_4^-}\right] = 6.86 + \log\left[\frac{0.3 - H_2PO_4^-}{H_2PO_4^-}\right]$$

$$\log\left[\frac{0.3 - H_2PO_4^-}{H_2PO_4^-}\right] = 0.14$$

$$10^{0.14} = \left[\frac{0.3 - H_2PO_4^-}{H_2PO_4^-}\right] = 1.38$$

$$1.38 = \frac{0.3 - x}{x}$$

$solve: x$

$x = 0.126M = [KH_2PO_4]$

$[Na_2HPO_4] = 0.174M$

10. Formic acid is a weak acid with pK_a = 3.75. Since the formate buffer is at pH = pK_a, [HA]=[A^-] initially. Here, KOH is consuming H^+ from the HCOOH; thus, use this alternate version of the ICE table to solve for [HA] and [A^-] after addition of KOH (a source of $^-$OH). Note: the activity of H_2O is assumed to be unity (see Equation 2.7), so it does not appear in these calculations.

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$$HA + {}^{-}OH \rightleftarrows A^{-} + H_2O$$

	HCOOH	$^{-}$OH	HCOO^{-}
Initial	0.025 mol	0.005 mol	0.025 mol
Change	–0.005 mol	–0.005 mol	+0.005 mol
Equilibrium	0.020 mol	0	0.030 mol

Solve for [H^{+}] using the Henderson–Hasselbalch equation:

$$pH = pK_a + log\frac{[A^-]}{[HA]} = 3.75 + log\left(\frac{\left(\frac{0.030\,mol}{0.505\,L}\right)}{\left(\frac{0.020\,mol}{0.505\,L}\right)}\right) = 3.75 + 0.176 = 3.93$$

11. The best choice would be a buffer of $H_2PO_4^-$ and HPO_4^{2-} because the pK_a for this conjugate acid/base pair is 6.86, which is close to the target pH of 7.0.

12. Glycine is a zwitterion at pH 7, so upon dissolving neutral solid glycine in water we have almost entirely $NH_3^+CH_2COO^-$. This species is "HA" in the Henderson–Hasselbalch equation used below. Moles of glycine = (0.100 *M*) × (2.00 L) = 0.200 mol → 15.02 g of glycine required for 2 L of 0.100 *M* buffer.

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$$9.0 = 9.6 + log\left(\frac{[A^-]}{[HA]}\right) \rightarrow \frac{[A^-]}{[HA]} = 0.251$$

Thus, at pH = 9.0, for every 1 mol of HA, there are 0.251 mol of A^{-}. With this information the mole fractions of A^{-} and HA can be calculated:

$$mole\ fraction\ A^- = \frac{mol\ A^-}{mol\ A^- + mol\ HA} = \frac{0.251}{0.251+1} = 0.201$$

$$mole\ fraction\ HA = \frac{mol\ HA}{mol\ A^- + mol\ HA} = \frac{1}{0.251+1} = 0.799$$

Thus, of the 0.200 mol of glycine in the buffer, 20.1% will be in the A^{-} form and 79.9% will be in the HA form. At pH 9.0, there will be (0.200 mol glycine) × (0.201) = 0.040 mol A^{-} and (0.200 mol glycine) × (0.799) = 0.160 mol HA. The source of A^{-} is the titration of HA with NaOH; thus, to generate 0.040 mol of A^{-}, 0.040 mol of NaOH are need. Since the molarity of NaOH is 1 *M*, 40 mL of NaOH are needed.

In summary, 15.02 g of glycine would be dissolved in water, 40 mL of 1 *M* NaOH would be added, then more water would be added to bring the final volume to 2.00 L. In practice, the glycine would be added to ~ 1.8 L water, and the 1 *M* NaOH would be added while monitoring the pH with a pH meter. Once pH 9.0 was achieved, water would be added to bring the final volume to 2.00 L.

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13. The relevant describes the dissociation of carbonic acid to bicarbonate ion and H^+: pK_a = 6.3.

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$$

From the Henderson–Hasselbalch equation:

$$7.4 = 6.3 + log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right) \rightarrow \frac{[HCO_3^-]}{[H_2CO_3]} = 12.56$$

$$mole\ fraction\ H_2CO_3 = \frac{mol\ H_2CO_3}{mol\ HCO_3^- + mol\ H_2CO_3} = \frac{1}{12.56+1} = 0.0737$$

Thus ~ 7.4% is H_2CO_3 and ~ 92.6% is HCO_3^- (as expected when pH > pK_a). Since the pK_a for dissociation of HCO_3^- is 10.25, we expect the $[CO_3^{2-}]$ to be negligible at pH = 7.4.

14. Protein molecules in aqueous solution become increasingly protonated as the pH decreases. Thus, proteins become more positively charged because carboxylic acids become *less negatively charged* as pH drops, whereas amines become *more positively charged*. Proteins become more negatively charged as pH increases, because acidic groups become more negatively charged while the basic groups become less positively charged.

15. a. Species III is the isoelectric species (not net charge); thus, the pK_as that describe ionization events that include this species will be used to calculate the pI. Since Species I is not one of these (and Species I is present at an insignificant concentration), we can ignore it for this simple case (i.e., a molecule with only three ionizable groups).

$$pI = \left(\frac{pK_{a1} + pK_{a2}}{2}\right) = \left(\frac{8.99 + 12.5}{2}\right) = 10.75$$

15. b. At pH = 9.20 the deprotonation of the α–carboxylic acid will be essentially 100% (pK_a = 1.82 is >7 pH units below the pH 9.20; thus, the deprotonated form will predominate by 7 orders of magnitude). Thus, it is safe to assume a charge of –1 on the α–carboxylate at pH 9.20.

At pH = 9.20 the deprotonation of the α–amino group will be closer to 50% (pK_a = 8.99 is close to the pH 9.20; thus, the [HA] and $[A^-]$ will be within a factor of ten). The fractional charge on the α–amino group can be calculated using the Henderson–Hasselbalch equation:

$$9.20 = 8.99 + log\left(\frac{[A^-]}{[HA]}\right) \rightarrow \frac{[A^-]}{[HA]} = 1.62$$

Thus, at pH = 9.2, for every 1 mol of HA, there are 1.62 mol of A^-. With this information the mole fractions of A^- (i.e., $–NH_2$) and HA (i.e., $–NH_3^+$) can be calculated:

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$$mole\ fraction\ A^- = \frac{mol\ A^-}{mol\ A^- + mol\ HA} = \frac{1.62}{1.62+1} = 0.618$$

$$mole\ fraction\ HA = \frac{mol\ HA}{mol\ A^- + mol\ HA} = \frac{1}{1.62+1} = 0.382$$

Since the A^- form is uncharged (i.e., $-NH_2$), it will not contribute to the overall molecular charge. However, at pH 9.20, 38.2% of the α–amino groups are in the positively charged ($-NH_3^+$) form. Thus, the average charge on this group is +0.382 at pH 9.20.

At pH = 9.20 the deprotonation of the side chain guanidinium group will be negligible (pK_a = 12.5 is more than 3 pH units above the pH 9.20; thus, the [HA] form will predominate by three orders of magnitude). Thus, it is safe to assume a charge of +1 on the side-chain guanidinium group at pH 9.20.

The average molecular charge at pH 9.20 is the sum of the average charges on each ionizable group: (−1) + (+0.382) + (+1) = + 0.382.

15. c. Yes. When pH < pI the molecule is predicted to carry a positive charge.

16. Successive deprotonations increase the (−) charge density on the resulting anion. This results in unfavorable electrostatic repulsions between the carboxylate anions, which reduces the likelihood that a proton would dissociate. It is more favorable for the proton to remain bound to reduce unfavorable charge repulsion. In fact, the citrate dianion has a pK_a of 6.86. Note that the pK_a of the citrate hydroxyl group is high; thus it remains in the –OH form at physiologically relevant values of pH.

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17. Use Equation 2.31 to calculate the differences in ionic strength for these two salts:

$$I_{NaCl} = 0.5 \times \sum m_i Z_i^2 = 0.5[1.0 \times (+1)^2 + 1.0 \times (-1)^2] = 1.0$$

Where $NaCl \longrightarrow Na^+ + Cl^-$

For

$(NH_4)_2SO_4 \longrightarrow 2NH_4^{1+} + SO_4^{2-}$

$$I_{(NH_4)_{2SO_4}} = 0.5 \times \sum m_i z_i^2 = [2.0 \times (+1)^2 + 1.0 \times (-2)^2] = 3.0$$

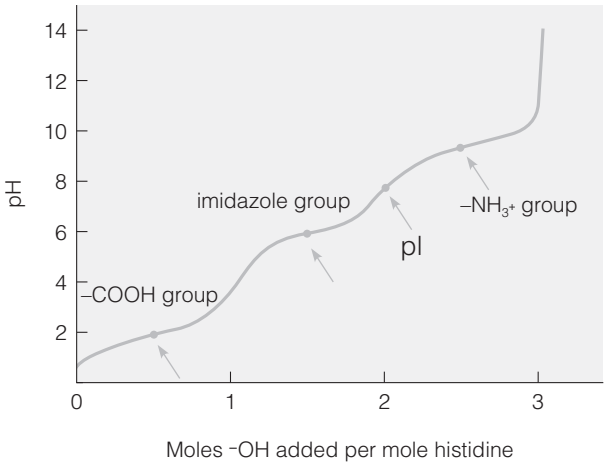
Thus, the ionic strength of 1 M $(NH_4)_2SO_4$ is three times greater than the ionic strength of NaCl.

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18. a.



18. b. See Figure 5.7 which shows the charges on each ionic species. Follow the strategy of identifying the isoelectric species to find the relevant pK_as to average (see Problem 15a).
pI = (6 + 9.2)/2 = 7.6.

19. a. The enzyme will be more active at pH = 3.5 because the –COOH group will be more protonated at that pH (protonation is favored when pH < pK_a).

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b. When pH = pK_a the ionizable group is 50% protonated; thus, 50% of the enzymes will be in an active state.

c. The enzyme will be 78% active when 78% of the –COOH groups are protonated, or when the mole fraction of –COOH vs. $-COO^-$ is 0.78. The ratio of COOH: COO^- can be calculated by setting mol COOH to an arbitrary value and solving for mol COO^-. For this purpose setting mol COOH = 1 is convenient:

$$mole\ fraction\ \mathrm{COOH} = \frac{mol\,\mathrm{COOH}}{mol\,\mathrm{COO^-} + mol\,\mathrm{COOH}} = \frac{1}{x+1} = 0.78 \rightarrow x = 0.282$$

Now use the Henderson–Hasselbalch equation to solve for pH:

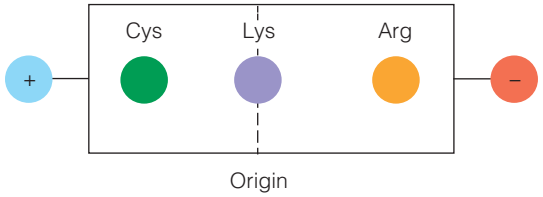
$$pH = 4.07 + log\left(\frac{[0.282]}{[1]}\right) = 4.07 + -0.55 = 3.52$$

20. Lysine has a pI of 9.5; thus, when pH = 9.5 it will carry no net charge and will not migrate in an electric field. At this pH, cystein carries a net charge of –0.99; thus, it will migrate toward the anode. At pH = 9.5, arginine carries a net charge of +0.24 and will migrate toward the cathode. Since the migration of each amino acid is different at pH = 9.5, that is a good choice to achieve the desired separation.

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21. a. Isoelectric focusing. The single-charge difference would make little difference in mobility in a normal gel electrophoresis experiment (which separates chains based on size), but would make a detectable difference in pI.

b. At a pH below 6.4 (e.g., pH 5) such that the His side chain is highly (+) charged, this will distinguish the His variant from the Val variant since the Val side chain carries no charge.

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