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Chapter 2

Water: The Solvent for Biochemical Reactions

SUMMARY

Section 2.1

- Water is a polar molecule, with a partial negative charge on the oxygen and partial positive charges on the hydrogens.
- There are forces of attraction between the unlike charges.
- Polar substances tend to dissolve in water, but nonpolar substances do not.
- The properties of water have a direct effect on the behavior of biomolecules.
- There are several different types of forces based on charge that will be seen frequently in this book. These include, from strongest to weakest, ionic bonds, ion-dipole bonds, dipole-dipole bonds, dipole-induced dipole bonds, induced dipole-induced dipole bonds.

Section 2.2

- A hydrogen bond is a special example of a dipole-dipole bond.
- Water molecules are extensively hydrogen bonded.
- The ability to form strong hydrogen bonds is responsible for the many unique characteristics of water, such as its very high melting point and boiling point for a molecule of its size.
- The three dimensional structures of many important biomolecules, including proteins and nucleic acids, are stabilized by hydrogen bonds.

Section 2.3

- Acids are proton donors, and bases are proton acceptors.
- Water can accept or donate protons.
- The strength of an acid is measured by its acid dissociation constant, K_a . The larger the K_a , the stronger the acid and the more H^+ dissociates.
- The concentration of H^+ is expressed conveniently as the pH, which is the negative log of the hydrogen ion concentration.
- A similar expression, pK_a , can be used in place of the K_a . $pK_a = -\log K_a$.
- The pH of a solution of a weak acid and its conjugate base is related to the concentration of the acid and base and the pK_a by the Henderson-Hasselbalch equation.

Section 2.4

- In aqueous solution, the relative concentrations of a weak acid and its conjugate base can be related to the titration curve of the acid.
- In the region of the titration curve in which the pH changes very little upon addition of acid or base, the acid/base ratio varies within a narrow range (10:1 at one extreme and 1:10 at the other extreme).

Water: The Solvent for Biochemical Reactions Chapter 2

Section 2.5

- Buffer solutions are characterized by their tendency to resist pH change when small amounts of strong acid or strong base are added.
- Buffers work because the concentration of the weak acid and base is kept in the narrow window of the acid titration curve.
- Many experiments must have a buffered system to keep a stable pH.
- There are many physiological buffers, such as the bicarbonate blood buffer or the phosphate buffer that help maintain physiological pH.

LECTURE NOTES

The material in this chapter is often overlooked nowadays to make room for more exciting and timely topics, like molecular biology. However, many of the concepts here are critical to understanding much of what is to come. Without a thorough understanding of electronegativity and hydrogen bonds, the student cannot later understand most of the structural analysis of biomolecules. The material best fits into two lectures, with the first covering through acids and bases. The second should focus on buffers and include enough examples and mathematical problems so it will eventually be second nature. Buffers are extremely challenging to many students, and they need to understand more than just how to use the Henderson-Hasselbalch equation.

LECTURE OUTLINE

- I. Polarity of water
 - A. Electronegativity
 - B. Polar bonds vs. polar molecules — dipoles
 - C. Solvent properties of water
 1. Hydrophilic molecules
 2. Hydrophobic molecules
 3. Types of bonds based on charges
 4. Amphipathic molecules, micelles
- II. Hydrogen Bonds
 - A. Donors and acceptors
 - B. Geometric arrangements
 - C. Strength compared to covalent bonds
 - D. Physical and chemical consequences
 1. melting and boiling points
 2. density of ice vs. liquid water
 3. solvent properties
 - E. Other biologically important hydrogen bonds
- III. Acids and bases
 - A. Definitions
 - B. Acid strength, dissociation constants
- IV. Dissociation of water and pH
 - A. Derivation of K_w
 - B. Relationship of pH to K_w , and pKa to K_a
 - C. Henderson-Hasselbalch equation

Water: The Solvent for Biochemical Reactions Chapter 3

V. Titrations and equivalence points

VI. Buffers

- A. What a buffer is
- B. Relationship between buffering and Henderson-Hasselbalch equation
- C. Buffering capacity
- D. How to make a buffer
- E. Physiologically important buffers

ANSWERS TO PROBLEMS

2.1 Water and Polarity

1. The unique fitness of water for forming hydrogen bonds determines the properties of many important biomolecules. Water can also act as an acid and as a base, giving it great versatility in biochemical reactions.
2. If atoms did not differ in electronegativity, there would be no polar bonds. This would drastically affect all reactions that involve functional groups containing oxygen or nitrogen—that is, most biochemical reactions.
3. Van der Waals forces are weak intermolecular forces that do not involve a full ionic interaction, such as dipole-dipole, and dipole –induced dipole interactions.
4. An induced dipole is a momentary dipole created by the transient distortion of an electron cloud of one atom due to the proximity of another atom.
5. A salt bridge refers to electrostatic attractions of parts of molecules with others. An example would be a negatively charged side-chain from an aspartate residue in a protein with a positively charged lysine residue.
6. If the dipole is cancelled out by another of equal and opposite orientation. The classic example is CO₂. Each carbon-oxygen bond is a dipole, but the two cancel each other out and the molecule is nonpolar.
7. The sodium ion is a fully charged anion. Therefore its interaction with the partial negative charge on the oxygen of ethanol would be stronger than the interaction of the same oxygen with a partially positive charge from the hydrogen of another ethanol molecule.
8. Dipole – dipole > dipole – induced dipole > induced dipole – induced dipole

2.2 Hydrogen Bonds

9. Dipole –dipole bond.
10. A hydrogen bond is a type of dipole-dipole bond, and a dipole-dipole bond is a type of Van der Waals force. However, hydrogen bonds are particularly strong examples of a dipole-dipole bond, sometimes approaching the strength of an ion – dipole bond. For this reason most people do not classify a hydrogen bond as a Van der Waals force.
11. Proteins and nucleic acids have hydrogen bonds as an important part of their structures.
12. Replication of DNA and its transcription to RNA requires hydrogen bonding of complementary bases to the DNA template strand.
13. The C-H bond is not sufficiently polar for greatly unequal distribution of electrons at its two ends. Also, there are no unshared pairs of electrons to serve as hydrogen bond acceptors.

Water: The Solvent for Biochemical Reactions Chapter 2

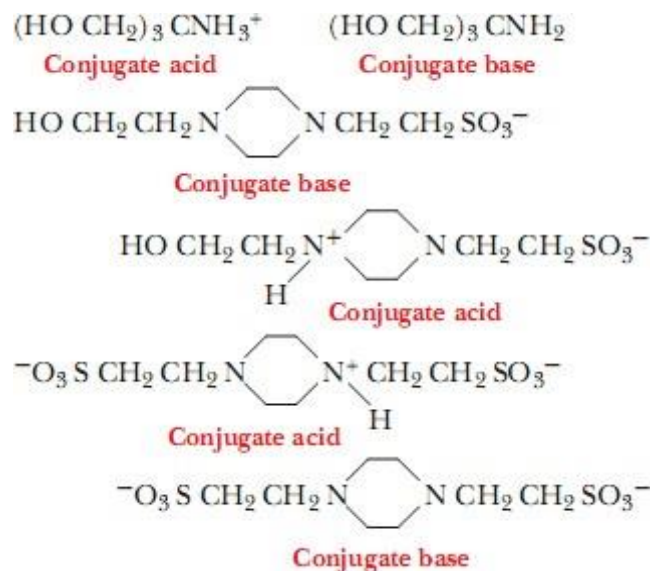
14. Many molecules can form hydrogen bonds. Examples might be H₂O, CH₃OH, or NH₃.
15. For a bond to be called a hydrogen bond, it must have a hydrogen covalently bonded to O, N, or F. This hydrogen then forms a hydrogen bond with another O, N, or F.
16. In a hydrogen-bonded dimer of acetic acid the -OH portion of the carboxyl group on molecule 1 is hydrogen-bonded to the -C=O portion of the carboxyl group on molecule 2, and vice versa.
17. Glucose = 17 and sorbitol = 18, ribitol = 15; each alcohol group can bond to three water molecules and the ring oxygen binds to two. The sugar alcohols bind more than the corresponding sugars.
18. Positively charged ions will bind to nucleic acids as a result of electrostatic attraction to the negatively charged phosphate groups.

2.3 Acids, Bases, and pH

19.

	Conjugate Acid	Conjugate Base
(a)	(CH ₃) ₃ NH ⁺	(CH ₃) ₃ N
(b)	⁺ H ₃ N-CH ₂ -COOH	⁺ H ₃ N-CH ₂ -COO ⁻
(c)	⁺ H ₃ N-CH ₂ -COO ⁻	H ₂ N-CH ₂ -COO ⁻
(d)	⁻ OOC-CH ₂ -COOH	⁻ OOC-CH ₂ -COO ⁻
(e)	HOOC-CH ₂ -COOH	⁻ OOC-CH ₂ -COOH

20.



21. Aspirin is electrically neutral at the pH of the stomach and can pass through the membrane more easily than in the small intestine.
22. The definition of pH is $-\log[\text{H}^+]$. Due to the log function, a change in concentration of 10 will lead to a change in pH of 1. The log of 10 is 1, the log of 100 is 2, etc.

Water: The Solvent for Biochemical Reactions Chapter 2

23.23.

Blood plasma, pH 7.4	$[H_+] = 4.0 \times 10^{-8} \text{ M}$
Orange juice, pH 3.5	$[H_+] = 3.2 \times 10^{-4} \text{ M}$
Human urine, pH 6.2	$[H_+] = 6.3 \times 10^{-7} \text{ M}$
Household ammonia, pH 11.5	$[H_+] = 3.2 \times 10^{-12} \text{ M}$
Gastric juice, pH 1.8	$[H_+] = 1.6 \times 10^{-2} \text{ M}$

24.24.

Saliva, pH 6.5	$[H_+] = 3.2 \times 10^{-7} \text{ M}$
Intracellular fluid (liver), pH 6.9	$[H_+] = 1.6 \times 10^{-7} \text{ M}$
Tomato juice, pH 4.3	$[H_+] = 5.0 \times 10^{-5} \text{ M}$
Grapefruit juice, pH 3.2	$[H_+] = 6.3 \times 10^{-4} \text{ M}$

25.25.

Saliva, pH 6.5	$[OH^-] = 3.2 \times 10^{-8} \text{ M}$
Intracellular fluid (liver), pH 6.9	$[OH^-] = 7.9 \times 10^{-8} \text{ M}$
Tomato juice, pH 4.3	$[OH^-] = 2.0 \times 10^{-10} \text{ M}$
Grapefruit juice, pH 3.2	$[OH^-] = 1.6 \times 10^{-11} \text{ M}$

2.4 Titration Curves

26. (a) The numerical constant equal to the concentration of the products of the dissociation divided by the concentration of the undissociated acid form:

$$\frac{[H_+][A^-]}{[HA]}$$
 (b) The qualitative or quantitative description of how much acid (HA) dissociates to hydrogen ion.
 (c) The property of a molecule that has both a polar region and a nonpolar region.
 (d) The amount of acid or base that can be added to a buffer before experiencing a sharp pH change.
 (e) The point in a titration curve at which the added acid or base equals the amount of buffer originally present.
 (f) The property of a molecule that is readily soluble in water (i.e., water loving).
 (g) The property of a molecule that is insoluble in water (i.e., water hating).
 (h) The property of a molecule that is not soluble in water. The property of a covalent bond in which there is even sharing of electrons and no dipole moments (partial charges).
 (i) The property of a molecule that is soluble in water. The property of a covalent bond in which the electrons are not shared evenly and dipole moments (partial charges) exist.
 (j) An experiment in which acid or base is added stepwise to a solution of a compound and the pH is measured as a function of the added substance.
27. To get a titration curve most like the one in Figure 2.15, we have to titrate a compound with a pK_a as close as possible to that of $H_2PO_4^-$. According to Table 2.8, MOPS has a pK_a of 7.2, which is the closest value.
28. The titration curve for TRIS would be shifted to the right compared to that of phosphate. The crossover point would be at pH 8.3, rather than pH 7.2.

Water: The Solvent for Biochemical Reactions Chapter 8

2.5 Buffers

29. The pK of the buffer should be close to the desired buffer pH, and the substance chosen should not interfere with the reaction being studied.
30. The useful pH range of a buffer is one pH unit above and below its pK_a .
31. Use the Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$5.00 = 4.76 + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$0.24 = \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = \text{inverse log of } 0.24 = \frac{1.7}{1}$$

32. Use the Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$4.00 = 4.76 + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$-0.76 = \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = \text{inverse log of } -0.76 = \frac{0.17}{1}$$

33. Use the Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[TRIS]}{[TRIS-H^+]}\right)$$

$$8.7 = 8.3 + \log\left(\frac{[TRIS]}{[TRIS-H^+]}\right)$$

$$0.4 = \log\left(\frac{[TRIS]}{[TRIS-H^+]}\right)$$

$$\frac{[TRIS]}{[TRIS-H^+]} = \text{inverse log of } 0.4 = \frac{2.5}{1}$$

34. Use the Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[HEPES]}{[HEPES-H^+]}\right)$$

$$7.9 = 7.55 + \log\left(\frac{[HEPES]}{[HEPES-H^+]}\right)$$

$$0.35 = \log\left(\frac{[HEPES]}{[HEPES-H^+]}\right)$$

$$\frac{[HEPES]}{[HEPES-H^+]} = \text{inverse log of } 0.35 = \frac{2.2}{1}$$

35. At pH 7.5, the ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ is 2/1 (pK_a of $H_2PO_4^- = 7.2$), as calculated using the Henderson–Hasselbalch equation. K_2HPO_4 is a source of the base form, and HCl must be added to convert one-third of it to the acid form,

Water: The Solvent for Biochemical Reactions Chapter 2

according to the 2/1 base/acid ratio. Weigh out 8.7 grams of K_2HPO_4 (0.05 mol, based on a formula weight of 174 g/mol), dissolve in a small quantity of distilled water, add 16.7 mL of 1 M HCl (gives 1/3 of 0.05 mol of hydrogen ion, which converts 1/3 of the 0.05 mol of HPO_4^{2-} to $H_2PO_4^-$) and dilute the resulting mixture to 1 L.

36. A 2/1 ratio of the base form to acid form is still needed, because the pH of the buffer is the same in both problems. NaH_2PO_4 is a source of the acid form, and NaOH must be added to convert two-thirds of it to the base form. Weigh out 6.0 g of NaH_2PO_4 (0.05 mol, based on a formula weight of 120 g/mol), dissolve in a small quantity of distilled water, add 33.3 mL of 1 M NaOH (gives 2/3 of 0.05 mol of hydroxide ion, which converts 2/3 of the 0.05 mol of $H_2PO_4^-$ to HPO_4^{2-}) and dilute the resulting mixture to 1 L.
37. After mixing, the buffer solution (100 mL) contains 0.75 M lactic acid and 0.25 M sodium lactate. The pK_a of lactic acid is 3.86. Use the Henderson–Hasselbalch equation

$$pH = pK_a + \log\left(\frac{[CH_3CHOHCOO^-]}{[CH_3CHOHCOOH]}\right)$$

$$pH = 3.86 + \log\left(\frac{[CH_3CHOHCOO^-]}{[CH_3CHOHCOOH]}\right)$$

$$pH = 3.86 + \log(0.25\text{ M}/0.75\text{ M})$$

$$pH = 3.86 + (-0.48)$$

$$pH = 3.38$$

38. After mixing, the buffer solution (100 mL) contains 0.25 M lactic acid and 0.75 M sodium lactate. The pK_a of lactic acid is 3.86. Use the Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[CH_3CHOHCOO^-]}{[CH_3CHOHCOOH]}\right)$$

$$pH = 3.86 + \log\left(\frac{[CH_3CHOHCOO^-]}{[CH_3CHOHCOOH]}\right)$$

$$pH = 3.86 + \log(0.75\text{ M}/0.25\text{ M})$$

$$pH = 3.86 + (0.48)$$

$$pH = 4.34$$

39. Use the Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$pH = 4.76 + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$pH = 4.76 + \log(0.25\text{ M}/0.10\text{ M})$$

$$pH = 4.76 + 0.40$$

$$pH = 5.16$$

Water: The Solvent for Biochemical Reactions Chapter 8

40. Yes, it is correct, calculate the molar amounts of the two forms and insert into the Henderson–Hasselbalch equation. (2.02 g = 0.0167 mol and 5.25 g = 0.0333 mol.)
41. The solution is a buffer because it contains equal concentrations of TRIS in the acid and free amine forms. When the two solutions are mixed, the concentrations of the resulting solution (in the absence of reaction) are 0.05 M HCl and 0.1 M TRIS because of dilution. The HCl reacts with half the TRIS present, giving 0.05 M TRIS (protonated form) and 0.05 M TRIS (free amine form).
42. Any buffer that has equal concentrations of the acid and basic forms will have a pH equal to its pK_a . Therefore, the buffer from Question 33 will have a pH of 8.3.
43. First calculate the moles of buffer that you have: 100 mL = 0.1 L, and 0.1 L of 0.1 M TRIS buffer is 0.01 mol. Since the buffer is at its pK_a , there are equal concentrations of the acid and basic form, so the amount of TRIS is 0.005 mol, and the amount of TRIS- H^+ is 0.005 mol. If you then add 3 mL of 1 M HCl, you will be adding 0.003 mol of H^+ . This will react as shown: $TRIS + H^+ \rightarrow TRIS-H^+$ until you run out of something, which will be the H^+ , since it is the limiting reagent. The new amounts can be calculated as shown below: $TRIS-H^+ = 0.005 \text{ mol} + 0.003 \text{ mol} = 0.008 \text{ mol}$
 $TRIS = 0.005 \text{ mol} - 0.003 \text{ mol} = 0.002 \text{ mol}$
Now plug these values into the Henderson–Hasselbalch equation:
 $pH = 8.3 + \log ([TRIS]/[TRIS-H^+]) = 8.3 + \log(0.002/0.008)$
 $pH = 7.70$
44. First calculate the mol of buffer that you have (we are going to do some rounding off): 100 mL = 0.1 L, and 0.1 L of 0.1 M TRIS buffer is 0.01 mol. Since the buffer is at pH 7.70, we saw in Question 25 that the amount of TRIS is 0.002 mol, and the amount of TRIS- H^+ is 0.008 mol. If you then add 1 mL of 1 M HCl, you will be adding 0.001 mol of H^+ . This will react as shown: $TRIS + H^+ \rightarrow TRIS-H^+$ until you run out of something, which will be the TRIS, since it is the limiting reagent. All the TRIS is converted to TRIS- H^+ : $TRIS-H^+ = 0.01 \text{ mol}$, $TRIS = \sim 0 \text{ mol}$. We have used up the buffer capacity of the TRIS. We now have 0.001 mol of H^+ in approximately 0.1 L of solution. This is approximately 0.01 M H^+ .
 $pH = -\log 0.01$, $pH = 2.0$.
45. $[H^+] = [A^-]$ for pure acid, thus $K_a = [H^+]^2/[HA]$
 $[H^+]^2 = K_a \times [HA]$, $-2 \log [H^+] = pK_a - \log [HA]$
 $pH = 1/2 \{pK_a - \log [HA]\}$
46. Use the Henderson–Hasselbalch equation. $[Acetate \text{ ion}]/[acetic \text{ acid}] = 2.3/1$
47. A substance with a pK_a of 3.9 has a buffer range of 2.9 to 4.9. It will not buffer effectively at pH 7.5.
48. Use the Henderson–Hasselbalch equation. The ratio of A-/HA would be 3981 to 1.
49. In all cases, the suitable buffer range covers a pH range of $pK_a \pm 1$ pH units.
(a) Lactic acid ($pK_a = 3.86$) and its sodium salt. pH 2.86–4.86.
(b) Acetic acid ($pK_a = 4.76$) and its sodium salt, pH 3.76–5.76.
(c) TRIS (see Table 3.4, $pK_a = 8.3$) in its protonated form and its free amine form, pH 7.3–9.3.

Water: The Solvent for Biochemical Reactions Chapter 2

- (d) HEPES (see Table 3.4, $pK_a = 7.55$) in its zwitterionic and its anionic form, pH 6.55–8.55.
50. Several of the buffers would be suitable, namely TES, HEPES, MOPS, and PIPES; but the best buffer would be MOPS, because its pK_a of 7.2 is closest to the desired pH of 7.3.
 51. The solution is called 0.0500 M, even though the concentration of neither the free base nor the conjugate acid is 0.0500 M. Why is 0.0500 M the correct concentration to report? (Buffer concentrations are typically reported to be the sum of the two ionic forms.)
 52. At the equivalence point of the titration, a small amount of acetic acid remains because of the equilibrium $\text{CH}_3\text{COOH} \rightarrow \text{H}^+ + \text{CH}_3\text{COO}^-$. There is a small, but nonzero, amount of acetic acid left.
 53. Buffering capacity is based upon the amounts of the acid and base forms present in the buffer solution. A solution with a high buffering capacity can react with a large amount of added acid or base without drastic changes in pH. A solution with a low buffering capacity can react with only comparatively small amounts of acid or base before showing changes in pH. The more concentrated the buffer, the higher is its buffering capacity. Buffer (a) has one-tenth the buffering capacity of buffer (b), which in turn has one-tenth the buffering capacity of buffer (c). All three buffers have the same pH, because they all have the same relative amounts of the acid and base form.
 54. It would be more effective to start with the HEPES base. You want a buffer at a pH above the pK_a , which means that the base form will predominate when you have finished preparing it. It is easier to convert some of the base form to the acid form than most of the acid form to the base form.
 55. In a buffer with the pH above the pK_a , the base form predominates. This would be useful as a buffer for a reaction that produces H^+ because there will be plenty of the base form to react with the hydrogen ion produced.
 56. Zwitterions tend not to interfere with biochemical reactions.
 57. It is useful to have a buffer that will maintain a stable pH even if assay conditions change. Dilution is one such possible change.
 58. It is useful to have a buffer that will maintain a stable pH even if assay conditions change. Temperature variation is one such possible change.
 59. The only zwitterion is $^+\text{H}_3\text{N}-\text{CH}_2-\text{COO}^-$.
 60. Hypoventilation decreases the pH of blood.