

BCH 4053—Summer 2001—Chapter 2 Lecture Notes

Slide
1

Chapter 2

Water, pH and Ionic Equilibria

Slide
2

Physical Properties of Water

- High boiling point
- High melting point
- High heat of vaporization
- High heat of fusion

Slide
3

Physical Properties of Water

- High specific heat
 - good heat exchange medium
- High surface tension
- High dielectric constant
- Density of ice < density of liquid
 - (Ice floats)

Slide
4

Structure of Water

- Bent Polar Molecule (Fig 2.1)
- Tetrahedral ice structure (Fig 2.2)
 - hydrogen bonding
- Liquid still highly hydrogen bonded
 - “Flickering Cluster” 10 psec (Fig 2.3)

Slide
5

Interaction with Solutes

- Solvation of ions (Fig 2.4)
 - Dielectric constant of water
- Hydrogen bonding with polar molecules

Slide
6

Interaction with Solutes, (con't)

- Non-polar solutes—“Hydrophobic Effect”
 - Clathrate “ice-like” structure around non-polar molecule (Fig 2.5)
 - Water becomes “more ordered”, therefore entropy disfavors solubility
 - “attraction” between non-polar molecules is really an “expulsion” from water

Slide
7

Interaction with Solutes, (con't)

- Amphipathic molecules (Fig 2.6)
 - Micelles (Fig 2.7)
 - Bilayers (Fig 9.2)
 - lamellar structures (Fig 9.4)
 - protein folding
 - base stacking in DNA
- Chaotropic Agents
 - urea and guanidinium ion disrupt ordered structure

Slide
8

Interaction with Solutes, (con't)

- Colligative Properties (depends on # of solute particles)
 - freezing point depression
 - boiling point elevation
 - vapor pressure lowering
 - osmotic pressure increase (Fig 2.8)

Slide
9

Acids and Bases

- Definition of Acid and Base
 - Arrhenius—effect on $[H^+]$
 - Bronsted-Lowery—proton donor/acceptor
 - Lewis—electron pair donor/acceptor
- The hydrated proton $[H_3O^+]$ (Fig 2.10)

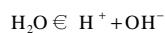
Slide
10

Auto-ionization of water



$$K_{\text{a1}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

or



$$K_{\text{a1}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

or

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

Slide
11

Range of $[\text{H}^+]$ and $[\text{OH}^-]$

- $[\text{H}_2\text{O}] = 55.5 \text{ M}$
- Therefore for Acids
 - $[\text{H}_3\text{O}^+] \ll 55.5 \text{ M}$
 - $[\text{OH}^-] \gg 10^{-14}/55.5 \text{ M}$
- Or for Bases
 - $[\text{OH}^-] \ll 55.5 \text{ M}$
 - $[\text{H}_3\text{O}^+] \gg 10^{-14}/55.5 \text{ M}$

Slide
12

Definitions of pH and pOH

- Because of large concentration range (between about 10 M and 10^{-15} M) a logarithmic scale of concentrations is defined:
 - $\text{pH} = -\log[\text{H}^+]$
 - $\text{pOH} = -\log[\text{OH}^-]$

Slide
13

Relationship of pH and pOH

Since $[H^+][OH^-] = 10^{-14}$

$-\log[H^+] + -\log[OH^-] = -\log[10^{-14}]$

$pH + pOH = 14$

So $pH = 14 - pOH$ and $pOH = 14 - pH$

Neutral solution, $pH = pOH = 7$

Acid solutions, $[H^+] > [OH^-]$, $pH < 7$

Basic solutions, $[H^+] < [OH^-]$, $pH > 7$

(See Table 2.2)

Slide
14

Review of Logarithmic Calculations

- What is pH if $[H^+]$ is 3.2×10^{-4} M?

$$\begin{aligned}\log 3.2 \times 10^{-4} &= \log 3.2 + \log 10^{-4} \\ &= 0.51(\text{the mantissa}) - 4(\text{the characteristic}) \\ &= -3.49 \\ \text{so } pH &= -(-3.49) = 3.49\end{aligned}$$

- What is $[H^+]$ if pH is 8.56?

$$\begin{aligned}[H^+] &= 10^{-pH} = 10^{-8.56} = 10^{0.44} \times 10^{-9} \\ &= 2.75 \times 10^{-9}\end{aligned}$$

Slide
15

Need Review in such calculations?

- Visit the [pH drill](#) web site
- Visit your [textbook](#) web site

Slide
16

Strong Acids versus Weak Acids

- Strong acids completely dissociate
 - $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
 - $[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-]$
- concentration will be given by HCl concentration unless it is low enough that OH^- cannot be ignored.
- Weak acids partly dissociate. The extent of dissociation can be expressed by an equilibrium constant, K_a

Other strong acids are HNO_3 , HBr , HI , H_2SO_4 (first proton dissociation), HClO_3 , and HClO_4 . Note that a 10^{-9} M solution of HCl would **not** have a pH of 9! You could not ignore the hydroxide concentration then, and would need to solve the equation $[\text{H}^+] = [\text{Cl}^-] + K_w/[\text{H}^+]$, where you substitute $K_w/[\text{H}^+]$ for $[\text{OH}^-]$.

Slide
17

Weak Acid Dissociation

$$\begin{array}{ccccccc}
 \text{HA} & + & \text{H}_2\text{O} & \rightleftharpoons & \text{H}_3\text{O}^+ & + & \text{A}^- \\
 \text{acid} & & \text{base} & & \text{conjugate} & & \text{conjugate} \\
 & & & & \text{acid} & & \text{base}
 \end{array}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

or

$$\begin{array}{ccc}
 \text{HA} & \rightleftharpoons & \text{H}^+ + \text{A}^- \\
 & & \text{K}_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}
 \end{array}$$

Slide
18

Calculation of $[\text{H}^+]$ for a Weak Acid ($[\text{HA}] = c$)

$$\begin{array}{ccc}
 \text{HA} & \rightleftharpoons & \text{H}^+ + \text{A}^- \\
 c-x & & x \quad x
 \end{array}$$

$$K_a = \frac{x^2}{(c-x)}$$

if $x < 0.05c$, $K_a = \frac{x^2}{c}$ and $x = \sqrt{K_a c}$

if $x \geq 0.05c$, $x^2 + K_a x - K_a c = 0$

and $x = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a c}}{2}$

Try the formula $(K_a c)^{1/2}$ first to see if x is small enough relative to c to ignore. If not, then you need to use the quadratic equation. Note we are assuming that $[\text{H}^+] = [\text{A}^-]$, when actually $[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$. But if the solution is acidic, $[\text{H}^+] \gg [\text{OH}^-]$ and the hydroxide term can be ignored. That might not be the case for very dilute solutions, or for K_a 's approaching 7 and above. For K_a 's above 7, the calculation should probably be done using K_b

Slide
19

Henderson-Hasselbalch Equation

- Rearrange K_a expression

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

- Take logarithm

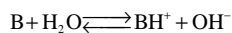
$$\log[H^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

$$-\log[H^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$pH = pK + \log \frac{[A^-]}{[HA]}$$

Slide
20

A Base Can Be Treated As an Acid



$$K_b = \frac{[BH^+][OH^-]}{[B][H_2O]} = \frac{[BH^+][OH^-]}{[B]}$$

can also be written as: $BH^+ \rightleftharpoons B + H^+$

$$K_a = \frac{[B][H^+]}{[BH^+]}$$

$$\text{and } K_a \times K_b = \frac{[B][H^+]}{[BH^+]} \times \frac{[BH^+][OH^-]}{[B]} = [H^+][OH^-] = K_w$$

Slide
21

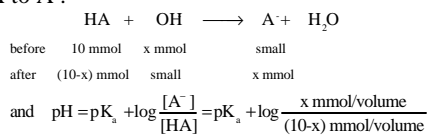
Difference in an “Acid” and a “Base” Dissociation

- $HA \rightarrow H^+ + A^-$
 - Charge separation; dielectric constant affects K_a
- $BH^+ \rightarrow H^+ + B$
 - No charge separation; no dielectric constant affect on K_a

Slide
22

Titration of a Weak Acid with a Strong Base

- A strong base added to the equilibrium solution of the weak acid will consume the H^+ , converting HA to A^- .



- This equation leads to the graph of Figure 2.12

Slide
23

Distinguish Between *Fraction* of Base Form and *Ratio* of Base/Acid

HA	A^-	A^-/HA	$A^-/(HA+A^-)$
90 mmol	10 mmol	10/90=0.11	10/100=0.10
75 mmol	25 mmol	25/75=0.33	25/100=0.25
50 mmol	50 mmol	50/50=1.0	50/100=0.50
25 mmol	75 mmol	75/25=3.0	75/100=0.75
10 mmol	90 mmol	90/10=9.0	90/100=0.90

Slide
24

Sketching Titration Curves

- According to **ratio** of A^-/HA

Fraction	Ratio	Log(ratio)	pH
0.10	0.11	-0.96	$pK_a - 0.96$
0.25	0.33	-0.48	$pK_a - 0.48$
0.50	1.0	0.0	pK_a
0.75	3.0	0.48	$pK_a + 0.48$
0.90	9.0	0.95	$pK_a + 0.95$

Rough rule of thumb:

- 1% titration, $pH = pK - 2$
- 10% titration, $pH = pK - 1$
- 50% titration, $pH = pK$
- 90% titration, $pH = pK + 1$
- 99% titration, $pH = pK + 2$

These calculations assume that $[A^-]$ = concentration of hydroxide added. That is not necessarily the case for acids with very low pK 's, because you also have to take into account the A^- formed in the dissociation of the acid before you started adding base.

Slide
25

Sketching Titration Curves (con't)

- The **shape** of all curves are the same
- The **position** of the curves varies with pK_a
 - See Figure 2.13
- Curves for **diprotic** and **triprotic** acids can be laid from end to end
 - See Figure 2.14

Slide
26

Buffers

- A weak acid and its conjugate base constitute a **buffer**
- Buffers resist change in pH
- Buffers are most effective at the pK of the weak acid
- Buffer *capacity* depends on concentration
- Refer to Figure 2.15
- See [Textbook website](#) discussion of buffers

Slide
27

Phosphate Buffer

- Best buffer at its pK 's; pK_2 most physiologically relevant
 - $pK_1=2.15$, $pK_2=7.20$, $pK_3=12.40$
- As your first group exercise, calculate the concentration of all ionic species of phosphate in 0.01 M total phosphate at pH 7.0
 - (i.e. $[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$, and $[PO_4^{3-}]$)

Slide
28

Hint for Phosphate Calculation

- You have three equilibrium equations
 - For K_1 , K_2 , and K_3
- You have one conservation equation
 - $[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = 0.01 \text{ M}$
- Four equations and four unknowns can be solved by simultaneous equations. There are several algebraic ways to proceed.

Slide
29

Bicarbonate Buffer

- A major buffer in blood
- Also in equilibrium with gaseous CO_2
- Relevant equations:
$$CO_{2(g)} \rightleftharpoons CO_{2(d)}$$
$$CO_{2(d)} + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Slide
30

Bicarbonate Buffer, (con't)

- The pK_1 recorded for bicarbonate depends on whether you are referring to $[H_2CO_3]$ alone, or "total dissolved CO_2 " which is $[H_2CO_3] + [CO_{2(d)}]$
 - Where $[CO_{2(d)}] = 500 [H_2CO_3]$
$$pH = pK_1 + \log \frac{[HCO_3^-]}{[H_2CO_3] + [CO_{2(d)}]}$$
, then $pK_1 = 3.57$
$$pH = pK_{1(overall)} + \log \frac{[HCO_3^-]}{[H_2CO_3 + CO_{2(d)}]}$$

then $pK_{1(overall)} = 6.1$

While a normal titration is plotting the curve for $pH = pK + \log(x/c - x)$, when carbonic acid is titrated the concentration of the acid does not decrease because it is replenished by the gaseous CO_2 in equilibrium with the solution. So the equation becomes $pH = pK + \log(x/c)$, and this curve does not turn up, but keeps getting flatter. Hence bicarbonate is a better buffer at 7.4 than at 6.1, even though that is more than one pH unit above the pK

Slide
31

Laboratory Buffers

- Most laboratory experiments require the use of buffers to control the pH. Phosphate buffer is often used, but a number of other buffers referred to as the “Good” buffers (after N.E.Good) have been developed for experimental use. (See Fig. 2.18)

Slide
32

Some Calculations Involving pH

- Ratio and Fraction of protonated species
- Preparation of buffers
 - From mixture of weak acid and its salt
 - From mixture of weak acid and strong base
- Change in buffer pH with strong acid or base

Don't try to memorize a set series of steps for solving buffer and pH problems. Try to remember the general principles, then think about what you are being asked. Then apply the mathematical relationships you know about the system.

Slide
33

Ratio and Fraction of Protonated Species

- Acetic acid has a pK of 4.76. What would be the ratio of [OAc⁻]/[HOAc] in a solution of pH 5.2?

$$\frac{[\text{OAc}^-]}{[\text{HOAc}]} = 10^{\text{pH}-\text{pK}} = 10^{5.2-4.76} = 10^{0.44} = 2.75$$

Slide
34

Con't.

- What is the fraction of the acetic acid that is protonated in this solution?

$$\frac{[\text{OAc}^-]}{[\text{HOAc}]} = 2.75 \text{ or } \frac{2.75}{1}$$

therefore the fraction of HOAc is

$$\frac{[\text{HOAc}]}{[\text{HOAc}] + [\text{OAc}^-]} = \frac{1}{1 + 2.75} = \frac{1}{3.75} = 0.27 \text{ (or 27\%)}$$

Read the problem carefully.
Determine whether it is asking for a *ratio* or a *fraction* (or a percentage).
Remember there is a difference.

Slide
35

Con't.

- The imidazole side chain of histidine has a pK of 6.0. What fraction of the side chain is protonated at pH 7.0?

$$\frac{[\text{his}^0]}{[\text{his}^+]} = 10^{7.0-6.0} = 10$$

$$\text{fraction of his}^+ = \frac{1}{1+10} = \frac{1}{11} = 0.091$$

The same question in a different guise. Here the unprotonated form is neutral, and the protonated form is positive charged.

Slide
36

Con't.

- An unknown substance was shown to be positively charged at low pH and neutral at high pH. Electrophoresis experiments showed it had a relative charge of 0.25 at pH 7.0 (it was 25% protonated). What is its pK?

Okay, now you have data presented in an unfamiliar way. You have to stop and think what you need and how you put the numbers together.

Slide
37

Con't.

- This one is a bit different. There are several steps to think about.
- Which is the protonated form?
- The positively charged species (call it XH^+)
- What is the ratio of $[X]/[XH^+]$?

$$\frac{[X]}{[XH^+]} = \frac{0.75}{0.25} = 3.0$$

Slide
38

Con't.

- Okay, then how do I calculate the pK?
- From the Henderson-Hasselbalch, of course.

$$pH = pK + \log \frac{[X]}{[XH^+]} \text{ so } pK = pH - \log \frac{[X]}{[XH^+]}$$

$$pK = 7.0 - \log(3.0) = 7.0 - (+0.48) = 6.52$$

Slide
39

Preparation of Buffers From a Weak Acid and its Salt

- Let's take for example, problem 5, page 55. "From 0.1 M solutions of acetic acid and sodium acetate, prepare 1 L of a buffer with pH of 5.4.
- What is the acetate/acetic acid ratio needed?

$$\frac{[OAc^-]}{[HOAc]} = 10^{5.44-7.6} = 10^{-2.16} = 4.37$$

Now lets turn to some practical applications for the laboratory. A common practice in the laboratory is to make up **stock solutions** of an acid and its salt, so simply mixing together the proper ratio of the solutions produces the correct salt/acid ratio. A dilution calculation might be called for if the stock solutions are concentrated.

Slide
40

Con't.

- Okay, what do I do with the ratio?
- You want 1 L of solution. Therefore you need to know what *fraction* of this liter should come from the acetic acid solution, and what fraction from the sodium acetate solution.

$$\text{fraction OAc}^- = \frac{4.37}{1+4.37} = \frac{4.37}{5.37} = 0.81$$

Slide
41

Con't.

- 1 L of solution x 0.81 = 810 mL of sodium acetate
- How much acetic acid solution?
- This leaves 1000-810 mL = 190 mL of 0.1M acetic acid solution
 - Or 1 L x (1.0-0.81) = 1 L x 0.19

Since both the acid and salt solutions were 1 M, there is no need to calculate a dilution. Notice that you can get the amount of acetic acid either by simply subtracting the volume of sodium acetate from one liter, or first calculating the fraction of acetic acid (1-fr. Sodium acetate), and multiplying by 1 L.

Slide
42

Preparation of Buffers From a Weak Acid and a Strong Base

- You have as **stock solutions** 1 M H_3PO_4 and 1 M NaOH. How would you prepare a 0.015 M phosphate buffer with a pH of 7.4?
- How can I break this problem down?
- Major phosphate species at 7.4?
- H_2PO_4^- and HPO_4^{2-}
- Ratio? $\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{7.4-7.2} = 10^{0.2} = 1.58$

Now we reach a problem where memorizing a series of steps doesn't help. You have to stop and think about the information you have and how to proceed.

Slide
43

Con't.

- Concentration of each species in a 0.015 M solution?

$$[\text{HPO}_4^{2-}] = 0.015 \text{ M} \frac{1.58}{1+1.58} = 0.015 \times 0.61 \text{ M} = 0.0092 \text{ M}$$

$$[\text{H}_2\text{PO}_4^-] = 0.015 \text{ M} \frac{1}{1+1.58} = 0.015 \times 0.387 = 0.0058 \text{ M}$$

$$\text{or } [\text{H}_2\text{PO}_4^-] = 0.015 \text{ M} - [\text{HPO}_4^{2-}] = 0.015 - 0.0092 = 0.0058 \text{ M}$$

Notice you need to calculate the fraction of each species in order to decide of the 0.015 M solution, how much is from each species.

Slide
44

Con't.

- How much solution do you want to make?
- That wasn't given in the problem. Let's calculate 1 L for simplicity, then we could modify that for any volume.
- What next?
- You are essentially doing a titration. You need to change from *concentrations* to *quantities*.

In using the Henderson Hasselbalch, one could use either a *concentration* ratio or a *quantity* ratio, since both the acid and its salt is in the same volume. But to calculate changes in a titration, you need to work with *quantity*. It is often convenient to consider quantity in **mmoles**.

Slide
45

Con't.

- What *quantity* of HPO_4^{2-} and H_2PO_4^- ?
- $\text{HPO}_4^{2-} = 0.0092 \text{ mol/L} \times 1 \text{ L} = 0.0092 \text{ mol}$ (or 9.2 mmol)
- $\text{H}_2\text{PO}_4^- = 0.0058 \text{ mol/L} \times 1 \text{ L} = 0.0058 \text{ mol}$ (or 5.8 mmol)
- What quantity of H_3PO_4 do you need to start with?
- You need to start with 0.015 mol (or 15 mmol), which would be 15 mL of the 1 M solution

Now we are taking the quantity of the final species and back calculating to the quantity of reagents needed.

Slide
46

Con't.

- So how much NaOH is needed in the titration?
- To convert H_3PO_4 to H_2PO_4^- ?
- 15 mmol, or 15 mL
- To convert H_2PO_4^- to HPO_4^{2-} ?
- An additional 9.2 mmol or 9.2 mL, for a total of 24.2 mL of 1 M NaOH

Slide
47

Con't.

Summary:

- Reagents
 - 15 mL of 1 M H_3PO_4
 - 24.2 mL of 1 M NaOH
- How much water to dilute?
- 1000 mL total - 15 mL - 24.2 mL = 960.8 mL

You assume in these volume calculations that all volumes are additive.

Slide
48

Change in Buffer pH with Strong Acid or Strong Base

- Lets take problem 11a, page 55, as an example. Add 50 mL of 0.01 M HCl to 100 mL of 0.05 M phosphate at pH 7.2. What is new pH?

Slide
49

Problem 11 a. Con't.

- Strategy?
- Calculate quantity of major phosphate species at 7.2 (similar to previous problem)
- Calculate quantity of acid added
- Calculate **new** quantity of major phosphate species
- Calculate pH from new quantity

Remember, you don't want to follow a set formula of steps. Break the problem down.

Slide
50

Problem 11 a. Con't.

- Quantity of major species?

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{7.2-7.2} = 10^0 = 1$$

fraction of each = 0.5, so

$$\text{HPO}_4^{2-} = \text{H}_2\text{PO}_4^- = 0.5(100 \text{ mL})(0.05 \text{ mmol/mL}) = 2.5 \text{ mmol}$$

This is a bit easier, since you are at the pK, and there is an equal amount of each form.

Slide
51

Problem 11 a. Con't.

- How much acid is added?
- $50 \text{ mL} \times 0.01 \text{ mmol/mL} = 0.5 \text{ mmol}$
- New quantities of phosphate species?
- $\text{H}_2\text{PO}_4^- = 2.5 \text{ mmol} + 0.5 \text{ mmol} = 3.0 \text{ mmol}$
- $\text{HPO}_4^{2-} = 2.5 \text{ mmol} - 0.5 \text{ mmol} = 2.0 \text{ mmol}$
- New pH?
$$\text{pH} = \text{pK} + \log \frac{2.0 \text{ mmol}/150 \text{ mL}}{3.0 \text{ mmol}/150 \text{ mL}} = 7.2 - 0.17 = 7.02$$