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Chapter 2

Water, pH and Ionic Equilibria

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Physical Properties of Water

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

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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)

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### 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)

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### Interaction with Solutes

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

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### 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

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## 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

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## 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)

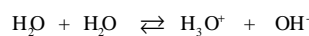
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## Acids and Bases

- 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)

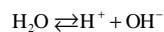
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### Auto-ionization of water



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

or



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

or

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

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### 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
  - $[\text{OH}^-] \ll 55.5 \text{ M}$
  - $[\text{H}_3\text{O}^+] \gg 10^{-14}/55.5 \text{ M}$

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### Definitions of pH and pOH

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

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## 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)

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## Review of Logarithmic Calculations

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

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

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## Need Review in such calculations?

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

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### 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  $\text{OH}^-$  cannot be ignored.
- Weak acids partly dissociate. The extent of dissociation can be expressed by an equilibrium constant,  $K_a$

Other strong acids are  $\text{HNO}_3$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{SO}_4$  (first proton dissociation),  $\text{HClO}_3$ , and  $\text{HClO}_4$ . Note that a  $10^{-9}$  M solution of  $\text{HCl}$  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  $[\text{OH}^-]$ .

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### 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

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

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### 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  $K_b$

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## Henderson-Hasselbalch Equation

- Rearrange  $K_a$  expression

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

- Take logarithm

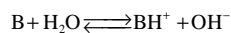
$$\log[H^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

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

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

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## 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:  $BH^+ \rightleftharpoons B + H^+$

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

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

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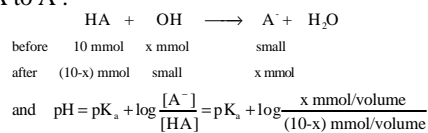
## Difference in an “Acid” and a “Base” Dissociation

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

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## 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

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## 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

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## 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.



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## 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

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## 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

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## 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  $[PO_4^{3-}]$ )

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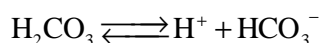
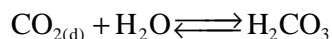
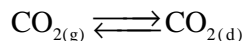
### Hint for Phosphate Calculation

- 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.

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### Bicarbonate Buffer

- A major buffer in blood
- Also in equilibrium with gaseous  $CO_2$
- Relevant equations:



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### 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  $[CO_{2(d)}] = 500 [H_2CO_3]$

$$pH = pK_1 + \log \frac{[HCO_3^-]}{[H_2CO_3]}, \text{ then } pK_1 = 3.57$$

$$pH = pK_{1(\text{overall})} + \log \frac{[HCO_3^-]}{[H_2CO_3 + CO_{2(d)}]}$$

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

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

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## 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)

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## 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.

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## Ratio and Fraction of Protonated Species

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

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

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### 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.

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### 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.

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### 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.

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### 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  $\text{XH}^+$ )
- What is the ratio of  $[\text{X}]/[\text{XH}^+]$ ?

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

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### Con't.

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

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

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

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### 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?

$$\frac{[\text{OAc}^-]}{[\text{HOAc}]} = 10^{5.4-4.76} = 10^{0.64} = 4.37$$

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.

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### 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.

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

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### 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.

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### Preparation of Buffers From a Weak Acid and a Strong Base

- You have as **stock solutions** 1 M  $\text{H}_3\text{PO}_4$  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?
- $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$
- 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.

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### 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.

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### 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**.

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### Con't.

- What *quantity* of  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ ?
- $\text{HPO}_4^{2-} = 0.0092 \text{ mol/L} \times 1 \text{ L} = 0.0092 \text{ mol}$  (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  $\text{H}_3\text{PO}_4$  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.

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### Con't.

- So how much NaOH is needed in the titration?
- To convert  $\text{H}_3\text{PO}_4$  to  $\text{H}_2\text{PO}_4^-$ ?
- 15 mmol, or 15 mL
- To convert  $\text{H}_2\text{PO}_4^-$  to  $\text{HPO}_4^{2-}$ ?
- An additional 9.2 mmol or 9.2 mL, for a total of 24.2 mL of 1 M NaOH

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### Con't.

#### Summary:

- Reagents
  - 15 mL of 1 M  $\text{H}_3\text{PO}_4$
  - 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.

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### 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?



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### 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.

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### 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.

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### 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?  $\text{pH} = \text{pK} + \log \frac{2.0 \text{ mmol}/150 \text{ mL}}{3.0 \text{ mmol}/150 \text{ mL}} = 7.2 - 0.17 = 7.02$