29. (a) Calculate the pH of a 0.20 M solution of benzoic acid at 25°C.

(b) How many moles of acetic acid must be dissolved per liter of water to obtain the same pH as that from part (a)?

(a)

	$C_6H_5COOH(aq)$	$+H_2O(l) \rightleftharpoons$	$C_6H_5COO^-(aq) +$	$H_3O^+(aq)$
Init. Conc. (M)	0.20	—	0	small
Change in Conc. (M)	$-x$	—	$+x$	$+x$
Equil. Conc. (M)	$0.20 - x$	—	x	x

$$K_a = 6.46 \times 10^{-5} = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]} = \frac{x^2}{0.20 - x}$$

$x = 0.0036$, The $\,$ pH is $-\log[H_3O^+] = \boxed{2.45}$.

(b)

$$K_a = \frac{x^2}{[HOAc]_0 - x} \quad \text{hence} \quad 1.76 \times 10^{-5} = \frac{(3.56 \times 10^{-3})^2}{[HOAc]_0 - 3.56 \times 10^{-3}}$$

Solving gives $[HOAc]_0 = 0.72$ M. This means $\boxed{0.72 \text{ mol}}$ of acetic acid must be dissolved per liter of solution.

42. Suppose a 0.100 M solution of each of the following substances is prepared. Rank the pH of the resulting solutions from lowest to highest: KF, NH_4I, HBr, NaCl, LiOH.
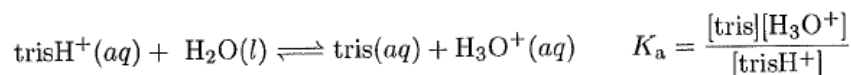
Low pH: HBr < NH_4I < NaCl < KF < LiOH :High pH

43. "Tris" is short for tris(hydroxymethyl)aminomethane. This weak base is widely used in biochemical research for the preparation of buffers. It offers low toxicity and a pK_b (5.92 at 25°C) that is convenient for the control of pH in clinical applications. A buffer is prepared by mixing 0.050 mol of tris with 0.025 mol of HCl in a volume of 2.00 L. Compute the pH of the solution.

The addition of HCl converts some tris to its conjugate acid

$$\text{tris}(aq) + \text{HCl}(aq) \rightleftharpoons \text{trisH}^+(aq) + \text{Cl}^-(aq)$$
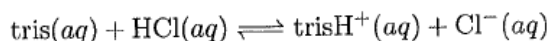
The resulting solution is a mixture of a weak acid (trisH$^+$) and its conjugate base (tris). It is a buffer by virtue of the reaction

$$\text{trisH}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{tris}(aq) + \text{H}_3\text{O}^+(aq) \qquad K_\text{a} = \frac{[\text{tris}][\text{H}_3\text{O}^+]}{[\text{trisH}^+]}$$

Compute the concentrations of the tris and trisH$^+$ after complete reaction with the HCl but before the preceding equilibrium is established

$$[\text{tris}]_0 = \frac{(0.050 - 0.025 \text{ mol})}{2.00 \text{ L}} = 0.0125 \text{ M} \qquad \text{and} \qquad [\text{trisH}^+]_0 = \frac{0.025 \text{ mol}}{2.00 \text{ L}} = 0.0125 \text{ M}$$

The equilibrium now reduces the concentration of the trisH$^+$ as it forms H$_3$O$^+$ and tris in equal amounts. If x is the equilibrium concentration of H$_3$O$^+(aq)$ ion, then

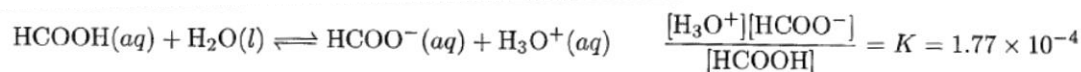|	trisH$^+(aq)$	$+\text{H}_2\text{O}(aq) \rightleftharpoons$	tris$(aq) +$	H$_3$O$^+(aq)$
Init. Conc. (M)	0.0125	—	0.0125	small
Change in Conc. (M)	$-x$	—	$+x$	$+x$
Equil. Conc. (M)	$0.0125 - x$	—	$0.0125 + x$	x

$$K_\text{a} = \frac{[\text{tris}][\text{H}_3\text{O}^+]}{[\text{trisH}^+]} = \frac{(0.0125 + x)x}{(0.0125 - x)}$$

Assume that x is small compared to 0.0125. Then the 0.0125's cancel out and

$$[\text{H}_3\text{O}^+] = K_\text{a} \quad \text{so that} \quad \text{pH} = pK_\text{a} = \boxed{8.08}$$

Clearly x is less than 10^{-7}, so the assumption was justified.

49. You have at your disposal an ample quantity of a solution of 0.0500 M NaOH and 500 mL of a solution of 0.100 M formic acid (HCOOH). How much of the NaOH solution should be added to the acid solution to produce a buffer of pH 4.00?

$$\text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCOO}^-(aq) + \text{H}_3\text{O}^+(aq) \qquad \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = K = 1.77 \times 10^{-4}$$

At pH $= 4.00$, $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-4}$ M. Inserting this value into the K_a expression gives:

$$1.77 \times 10^{-4} = \frac{(1.0 \times 10^{-4})[\text{HCOO}^-]}{[\text{HCOOH}]} \qquad \text{which gives} \qquad 1.77 = \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$$

Let the volume of 0.0500 M NaOH that is needed to raise the pH to 4.00 equal V mL. The final volume of the mixture at pH 4.00 then equals $(500 + V)$ mL. Each millimole of NaOH that is added converts one millimole of $HCOOH(aq)$ to $HCOO^-(aq)$. Assume that this acid-base reaction is the only significant source of $HCOO^-(aq)$. After $0.0500\,V$ mmol of NaOH has been added

$$[HCOO^-] = \frac{0.0500V \text{ mmol}}{(500 + V) \text{ mL}}$$

in which the numerator is the chemical amount of $HCOO^-(aq)$ produced by the reaction and the denominator is the final volume of the solution. Also

$$[HCOO^-] + [HCOOH] = \frac{50.0 \text{ mmol}}{(500 + V) \text{ mL}}$$

Solve the second of the preceding equations for [HCOOH] and insert the expression for [HCOO⁻]

$$[HCOOH] = \frac{50.0}{500 + V} - [HCOO^-] = \frac{50.0}{500 + V} - \frac{0.0500\,V}{500 + V}$$
$$= \frac{50.0 - 0.0500\,V}{500 + V} \text{ M}$$

Substitute the expressions for [HCOOH] and [HCOO⁻] into the equation for their ratio

$$1.77 = \frac{[HCOO^-]}{[HCOOH]} = \frac{0.0500\,V/(500 + V)}{(50.0 - 0.0500\,V)/(500 + V)}$$
$$= \frac{0.0500\,V}{50.0 - 0.0500\,V} = \frac{0.0500\,V}{0.0500\,(1000 - V)}$$
$$1.77 = \frac{V}{1000 - V}$$

It is now easy to solve for V, which equals $\boxed{639 \text{ mL}}$. The final volume of the solution is 1139 mL and the concentrations of $HCOOH(aq)$ and $HCOO^-(aq)$ are 0.0158 and 0.0280 M respectively. Both are large in comparison to the final H_3O^+ concentration, 1.0×10^{-4} M. This means that the ionization equilibrium affects these two concentrations only negligibly.

56. Ammonia is a weak base with a K_b of 1.8×10^{-5}. A 140.0-mL sample of a 0.175 M solution of aqueous ammonia is titrated with a 0.106 M solution of the strong acid HCl. The reaction is

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

Compute the pH of the titration solution before any acid is added, when the titration is at the half-equivalence point, when the titration is at the equivalence point, and when the titration is 1.00 mL past the equivalence point.

The original solution (before any titrating acid is added) is 0.175 M aqueous NH_3. Ammonia acts as a base in water

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad \frac{[NH_4^+][OH^-]}{[NH_3]} = K_b = 1.8 \times 10^{-5}$$
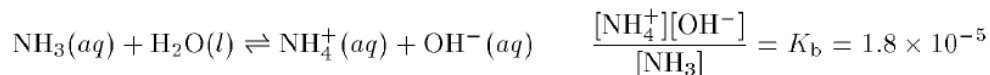
If the equilibrium concentration of NH_4^+ is x, then the equilibrium concentration of NH_3 is $0.175 - x$ and that of OH^- is x. The other sources of OH^- are negligible. Substitution and solving for x (by iteration) gives $[OH^-] = 1.766 \times 10^{-3}$ M and a pH of 11.25.

Text section 15.6 shows that in the titration of a weak acid with a strong base, the pH at the half-equivalence point is very close to the pK_a of the weak acid: $pK_a = pH$. Construct the analogous relationship $pK_b = pOH$ to apply to the titration of a weak base with a strong acid. Then, $pH = 14.00 - pOH = 14.00 - 4.745 = 9.26$

It requires $(0.175/0.106)(140.0) = 231.13$ mL to titrate the solution to the equivalence point, at which point the total volume of the solution is 371.13 mL. The solution is in effect dilute aqueous NH_4Cl in which the concentration of the NH_4^+ ion is nominally $0.175(140.00/371.13) = 0.0660$ M. This concentration is lowered slightly by the reaction of the NH_4^+ ion with water to generate H_3O^+ and NH_3. The K_a for this reaction is

$$\frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

Substituting in the usual way into the equilibrium expression for this acid ionization gives $[H_3O^+] = 6.06 \times 10^{-6}$ M, pH $= 5.22$.

When the titration is 1.00 mL past the equivalence point, the NH_4^+ is still present but is completely overshadowed as a source of H_3O^+ by the excess $HCl(aq)$. Consider only the HCl. The first 231.13 mL of 0.106 M HCl were neutralized, so the effective concentration of HCl in the solution is the amount of HCl contributed by the last 1.00 mL divided by the total volume of the solution. This is $(1.00/372.13)(0.106) = 2.85 \times 10^{-4}$ M. This is also the concentration of H_3O^+ so the pH is 3.55.

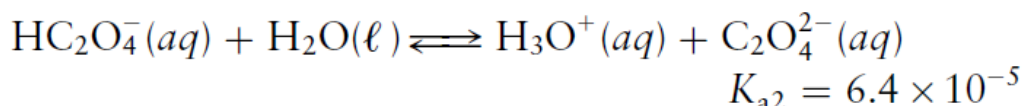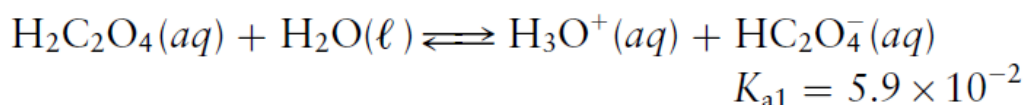## 58. An antacid tablet (such as Tums or Rolaids) weighs 1.3259 g. The only acid-neutralizing ingredient in this brand of antacid is $CaCO_3$. When placed in 12.07 mL of 1.070 M HCl, the tablet fizzes merrily as $CO_2(g)$ is given off. After all of the CO_2 has left the solution, an indicator is added, followed by 11.74 mL of 0.5310 M NaOH. The indicator shows that at this point the solution is definitely basic. Addition of 5.12 mL of 1.070 M HCl makes the solution acidic again. Then 3.17 mL of the 0.5310 M NaOH brings the titration exactly to an endpoint, as signaled by the indicator. Compute the percentage by mass of $CaCO_3$ in the tablet.

The total chemical amount of HCl added is 18.393 mmol; the total chemical amount of NaOH added is 7.917 mmol. These numbers, which come from multiplying the concentrations of the acid and base by their respective total volumes in mL, are not equal. The tablet supplies the base needed to neutralize $18.393 - 7.917 = 10.476$ mmol of H_3O^+. The reaction is
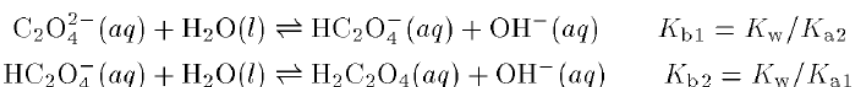
$$CaCO_3(s) + 2\,H_3O^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + 3\,H_2O(l)$$

Each mole of $CaCO_3$ takes up 2 mol of H_3O^+ so there is in the tablet $((10.476/2) = 5.238)$ mmol of $CaCO_3$. The molar mass of $CaCO_3$ is 100.09 g mol^{-1} so the tablet contains 0.5243 g of $CaCO_3$. This is 39.54% of its total mass.

66. Oxalic acid ionizes in two stages in aqueous solution:

$$H_2C_2O_4(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-(aq)$$
$$K_{a1} = 5.9 \times 10^{-2}$$

$$HC_2O_4^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq)$$
$$K_{a2} = 6.4 \times 10^{-5}$$

Calculate the equilibrium concentrations of $C_2O_4^{2-}$, $HC_2O_4^-$, $H_2C_2O_4$, and OH^- in a 0.10 M solution of sodium oxalate ($Na_2C_2O_4$).

$$C_2O_4^{2-}(aq) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + OH^-(aq) \qquad K_{b1} = K_w/K_{a2}$$
$$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons H_2C_2O_4(aq) + OH^-(aq) \qquad K_{b2} = K_w/K_{a1}$$

Let the final concentration of $HC_2O_4^-$ equal y. This is also the final concentration of OH^- because the first reaction is the only important source of OH^-. The concentration of $C_2O_4^{2-}$ ion at equilibrium is then $0.10 - y$. Therefore

$$\frac{y^2}{0.10 - y} = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}}$$

Thus, $y = 4.0 \times 10^{-6}$, and $[OH^-] = [HC_2O_4^-] = 4.0 \times 10^{-6}$ M. The hydrogen oxalate ion ($HC_2O_4^-$) itself can serve as a weak base, as represented in the second chemical equation above. For that equation

$$\frac{[OH^-][H_2C_2O_4]}{[HC_2O_4^-]} = K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-2}}$$

Insertion of the known equilibrium concentrations of OH^- and $HC_2O_4^-$ gives $[H_2C_2O_4] = 1.7 \times 10^{-13}$ M.

At the moment of mixing, the concentration of the oxalate ion was 0.10 M. Some of this oxalate then reacted, but not much—there is only a tiny concentration of hydrogen oxalate ion (4.0×10^{-6} M) and an incredibly tiny concentration of oxalic acid (1.7×10^{-13} M). The final concentration of oxalate ion is still 0.10 M.

73. Which will be the stronger acid: benzene (C_6H_6) or cyclo-hexane (C_6H_{12})? Explain by using resonance Lewis structures.

Neither is a very strong acid, but ⟦benzene⟧ should be a stronger acid than cyclohexane. In benzene the negative charge left after the loss of a hydrogen ion is delocalized on the benzene ring; in cyclohexane, the negative charge is substantially constrained to reside on a single carbon atom.

75. For each of the following pairs of molecules, predict which is the stronger acid.
(a) CF_3COOH or CCl_3COOH.
(b) $CH_2FCH_2CH_2COOH$ or $CH_3CH_2CHFCOOH$
(c)
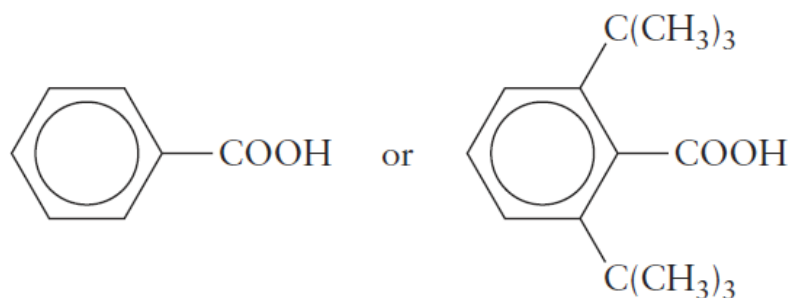
a) ⟦Trifluoroacetic acid⟧ is stronger than trichloroacetic acid. The high electronegativity of the F's stabilizes the trifluoroacetate ion compared to the trichloroacetate ion.

b) ⟦2-Fluorobutyric acid⟧ (which has the second structure given in the problem) is a stronger acid than 4-fluorobutyric acid. The F atom is closer to the carboxylic acid group and so is better able to accommodate some of the negative charge left by the loss of the hydrogen ion on the carboxylic acid group.

c) ⟦Benzoic acid⟧ (the left-hand structure in the problem) is stronger than 2,6-di(t-butyl)benzoic acid because the t-butyl groups tend to push electron density onto the benzene ring, making it less able to accommodate the negative charge left by the loss of the hydrogen ion on the carboxylic acid group.

78. A sample of vinegar contains 40.0 g of acetic acid (CH_3-COOH) per liter of solution. Suppose 1.00 mL is removed and diluted to 1.00 L, and 1.00 mL of *that* solution is removed and diluted to 1.00 L. Calculate the pH of the resulting solution. (*Hint:* This is a sufficiently dilute solution that the autoionization of water cannot be neglected.)

Figure out the original concentration of the acetic acid

$$c_a = \frac{40.0 \text{ g L}^{-1}}{60.05 \text{ g mol}^{-1}} = 0.666 \text{ M}$$

The million-to-one dilution reduces this concentration to $c_a = 6.66 \times 10^{-7}$ M. Substitute in the cubic equation in text Section 15.8 with c_b equal to zero

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - (K_w + c_aK_a)[H_3O^+] - K_aK_w = 0$$

$$[H_3O^+]^3 + 1.76 \times 10^{-5}[H_3O^+]^2 - 1.173 \times 10^{-11}[H_3O^+] - 1.76 \times 10^{-19} = 0$$

A scientific calculator quickly gives the roots of this equation

$$[H_3O^+] = -1.824 \times 10^{-5}, \qquad 6.572 \times 10^{-7}, \qquad -1.468 \times 10^{-8}$$

The physically correct answer cannot be negative. This eliminates the first and third roots.

$$[H_3O^+] = 6.57 \times 10^{-7} \text{ M} \quad pH = 6.18$$