

Solutions to Homework Assignment #8
CHM 152
Spring 2002

15.22 (a) acidic (b) neutral (c) basic

15.23 The pH can be found using Equation (15.5) of the text.

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 9.40 = 4.60$$

The hydrogen ion concentration can be found as in Example 15.4 of the text.

$$4.60 = -\log[\text{H}^+]$$

Taking the antilog of both sides:

$$[\text{H}^+] = 2.5 \times 10^{-5} M$$

$$15.24 \quad 5.50 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.360 \text{ mol}}{1 \text{ L}} \right) = 1.98 \times 10^{-3} \text{ mol KOH}$$

KOH is a strong base and therefore ionizes completely. The OH^- concentration equals the KOH concentration, because there is a 1:1 mole ratio between KOH and OH^- .

$$[\text{OH}^-] = 0.360 M$$

$$\text{pOH} = -\log[\text{OH}^-] = 0.444$$

15.25 We can calculate the OH^- concentration from the pOH.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.00 = 4.00$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 1.0 \times 10^{-4} M$$

Since NaOH is a strong base, it ionizes completely. The OH^- concentration equals the initial concentration of NaOH.

$$[\text{NaOH}] = 1.0 \times 10^{-4} \text{ mol/L}$$

So, we need to prepare 546 mL of $1.0 \times 10^{-4} M$ NaOH.

This is a factor-label problem. We need to perform the following unit conversions.

$$\text{mol/L} \rightarrow \text{mol NaOH} \rightarrow \text{grams NaOH}$$

$$546 \text{ mL} = 0.546 \text{ L}$$

$$\begin{aligned} ? \text{ g NaOH} &= \left(\frac{1.0 \times 10^{-4} \text{ mol NaOH}}{1 \text{ L soln}} \right) \times (0.546 \text{ L soln}) \times \left(\frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}} \right) \\ &= 2.2 \times 10^{-3} \text{ g NaOH} \end{aligned}$$

15.34 (a) false, they are equal (b) true, find the value of $\log(1.00)$ on your calculator
(c) true (d) false, if the acid is strong, $[\text{HA}] = 0.00 M$

15.42 Step 1: Calculate the concentration of acetic acid before ionization.

$$0.0560 \text{ g acetic acid} \times \frac{1 \text{ mol acetic acid}}{60.05 \text{ g acetic acid}} = 9.33 \times 10^{-4} \text{ mol acetic acid}$$

$$\frac{9.33 \times 10^{-4} \text{ mol}}{0.0500 \text{ L soln}} = 0.0187 \text{ M acetic acid}$$

Step 2: Next, recognize that acetic acid is a weak, monoprotic acid. It is not one of the six strong acids, so it must be a weak acid. Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown x , that represents the change in concentration. Let $(-x)$ be the depletion in concentration (mol/L) of CH_3COOH . From the stoichiometry of the reaction, it follows that the increase in concentration for both H^+ and CH_3COO^- must be x . Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

	$\text{CH}_3\text{COOH} (aq)$	\rightleftharpoons	$\text{H}^+ (aq)$	$+$	$\text{CH}_3\text{COO}^- (aq)$
Initial (M):	0.0187		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$0.0187 - x$		x		x

Step 3: Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant (K_a), solve for x .

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

You can look up the K_a value for acetic acid in Table 15.3 of your text.

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.0187 - x)}$$

At this point, we can make an assumption that x is very small compared to 0.0187. Hence,

$$0.0187 - x \approx 0.0187$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.0187}$$

Solving for x .

$$x = 5.8 \times 10^{-4} \text{ M} = [\text{H}^+] = [\text{CH}_3\text{COO}^-]$$

$$[\text{CH}_3\text{COOH}] = (0.0187 - 5.8 \times 10^{-4})\text{M} = 0.0181 \text{ M}$$

Checking the validity of the assumption,

$$\frac{5.8 \times 10^{-4}}{0.0187} \times 100\% = 3.1\% < 5\%$$

The assumption is valid.

15.43 First we find the hydrogen ion concentration.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-6.20} = 6.3 \times 10^{-7} \text{ M}$$

Substituting into the acid ionization constant expression:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(6.3 \times 10^{-7})(6.3 \times 10^{-7})}{(0.010 - 6.3 \times 10^{-7})} = 4.0 \times 10^{-11}$$

We have omitted the contribution to $[\text{H}^+]$ due to water.

15.44 A pH of 3.26 corresponds to a $[\text{H}^+]$ of $5.5 \times 10^{-4} \text{ M}$. Let the original concentration of formic acid be x so that:

	$\text{HCOOH} (aq)$	\rightleftharpoons	$\text{H}^+ (aq)$	$+$	$\text{HCOO}^- (aq)$
Initial (M):	x		0		0
Change (M):	-5.5×10^{-4}		5.5×10^{-4}		5.5×10^{-4}
Equilibrium (M):	$x - 5.5 \times 10^{-4}$		5.5×10^{-4}		5.5×10^{-4}

Substitute K_a and the equilibrium concentrations into the ionization constant expression to solve for x .

$$\frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.7 \times 10^{-4}$$

$$\frac{(5.5 \times 10^{-4})^2}{(x - 5.5 \times 10^{-4})} = 1.7 \times 10^{-4}$$

$$x = [\text{HCOOH}] = 2.3 \times 10^{-3} \text{ M}$$

15.46 Percent ionization is defined as:

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\%$$

For a monoprotic acid, HA, the concentration of acid that undergoes ionization is equal to the concentration of H^+ ions or the concentration of A^- ions at equilibrium. Thus, we can write:

$$\text{percent ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\%$$

(a) First, recognize that hydrofluoric acid is a weak acid. It is not one of the six strong acids, so it must be a weak acid.

Step 1: Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown x , that represents the change in concentration. Let $(-x)$ be the depletion in concentration (mol/L) of HF. From the stoichiometry of the reaction, it follows that the increase in concentration for both H^+ and F^- must be x . Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

	$\text{HF} (aq)$	\rightleftharpoons	$\text{H}^+ (aq)$	$+$	$\text{F}^- (aq)$
Initial (M):	0.60		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$0.60 - x$		x		x

Step 2: Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant (K_a), solve for x .

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

You can look up the K_a value for hydrofluoric acid in Table 15.3 of your text.

$$7.1 \times 10^{-4} = \frac{(x)(x)}{(0.60 - x)}$$

At this point, we can make an assumption that x is very small compared to 0.60. Hence,

$$0.60 - x \approx 0.60$$

Oftentimes, assumptions such as these are valid if K is very small. A very small value of K means that a very small amount of reactants go to products. Hence, x is small. If we did not make this assumption, we would have to solve a quadratic equation.

$$7.1 \times 10^{-4} = \frac{(x)(x)}{0.60}$$

Solving for x .

$$x = 0.021 \text{ M} = [\text{H}^+]$$

Step 3: Having solved for the $[\text{H}^+]$, calculate the percent ionization.

$$\begin{aligned} \text{percent ionization} &= \frac{[\text{H}^+]}{[\text{HF}]_0} \times 100\% \\ &= \frac{0.021 \text{ M}}{0.60 \text{ M}} \times 100\% = \mathbf{3.5\%} \end{aligned}$$

(b) – (c) are worked in a similar manner to part (a). However, as the initial concentration of HF becomes smaller, the assumption that x is very small compared to this concentration will no longer be valid. You must solve a quadratic equation.

$$\text{(b)} \quad K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{(0.0046 - x)} = 7.1 \times 10^{-4}$$

$$x^2 + (7.1 \times 10^{-4})x - (3.3 \times 10^{-6}) = 0$$

$$x = 1.5 \times 10^{-3} \text{ M}$$

$$\text{Percent ionization} = \frac{1.5 \times 10^{-3} \text{ M}}{0.0046 \text{ M}} \times 100\% = \mathbf{33\%}$$

$$\text{(c)} \quad K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{(0.00028 - x)} = 7.1 \times 10^{-4}$$

$$x^2 + (7.1 \times 10^{-4})x - (2.0 \times 10^{-7}) = 0$$

$$x = 2.2 \times 10^{-4} \text{ M}$$

$$\text{Percent ionization} = \frac{2.2 \times 10^{-4} \text{ M}}{0.00028 \text{ M}} \times 100\% = \mathbf{79\%}$$

As the solution becomes more dilute, the percent ionization increases.

15.51 (a) We construct the usual table.

	$\text{NH}_3(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{NH}_4^+(aq)$	+	$\text{OH}^-(aq)$
Initial (M):	0.10				0.00		0.00
Change (M):	-x				+x		+x
Equilibrium (M):	(0.10 - x)				x		x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{(0.10 - x)} = 1.8 \times 10^{-5}$$

Assuming $(0.10 - x) \approx 0.10$, we have:

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

$$x = 1.3 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log(1.3 \times 10^{-3}) = 2.89$$

$$\text{pH} = 14.00 - 2.89 = 11.11$$

By following the identical procedure, we can show: (b) **pH = 8.96**.

15.53 A pH of 11.22 corresponds to a $[\text{H}^+]$ of $6.03 \times 10^{-12} \text{ M}$ and a $[\text{OH}^-]$ of $1.66 \times 10^{-3} \text{ M}$.

The equilibrium is: $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$

The concentration of $[\text{OH}^-] = [\text{NH}_4^+]$ (why?) If we let x equal the original concentration of ammonia

$$K_b = 1.8 \times 10^{-5} = \frac{(1.66 \times 10^{-3})(1.66 \times 10^{-3})}{x - 1.66 \times 10^{-3}}$$

Assuming 1.66×10^{-3} is small relative to x , then

$$x = 0.15 \text{ M} = [\text{NH}_3]$$

15.62 For the first stage of ionization:

	$\text{H}_2\text{CO}_3(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{HCO}_3^-(aq)$
Initial (M):	0.025		0.00		0.00
Change (M):	-x		+x		+x
Equilibrium (M):	(0.025 - x)		x		x

$$K_{a_1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{(0.025 - x)} = 4.2 \times 10^{-7}$$

Assuming $(0.025 - x) \approx 0.025$,

$$x = 1.0 \times 10^{-4} \text{ M}$$

For the second ionization,

	$\text{HCO}_3^- (aq) \rightleftharpoons \text{H}^+ (aq) + \text{CO}_3^{2-} (aq)$	
Initial (M):	1.0×10^{-4}	1.0×10^{-4} 0.00
Change (M):	$-x$	$+x$ $+x$
Equilibrium (M):	$1.0 \times 10^{-4} - x$	$1.0 \times 10^{-4} + x$ x

$$K_{a_2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.8 \times 10^{-11}$$

$$4.8 \times 10^{-11} = \frac{(1.0 \times 10^{-4} - x)(x)}{1.0 \times 10^{-4} - x} \approx \frac{(1.0 \times 10^{-4})(x)}{1.0 \times 10^{-4}}$$

$$x = [\text{CO}_3^{2-}] = 4.8 \times 10^{-11}$$

Since HCO_3^- is a very weak acid, there is little ionization at this stage. Therefore we have:

$$[\text{H}^+] = [\text{HCO}_3^-] = 1.0 \times 10^{-4} \text{ M and } [\text{CO}_3^{2-}] = 4.8 \times 10^{-11} \text{ M}$$

- 15.76** There is an inverse relationship between acid strength and conjugate base strength. As acid strength decreases, the proton accepting power of the conjugate base increases. In general the weaker the acid, the stronger the conjugate base. All three of the potassium salts ionize completely to form the conjugate base of the respective acid. The greater the pH, the stronger the conjugate base, and therefore, the weaker the acid.

The order of increasing acid strength is **HZ < HY < HX**.

- 15.77** The salt sodium acetate completely dissociates upon dissolution, producing $0.36 \text{ M } [\text{Na}^+]$ and $0.36 \text{ M } [\text{CH}_3\text{COO}^-]$ ions. The $[\text{CH}_3\text{COO}^-]$ ions will undergo hydrolysis because they are a weak base.

	$\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^- (aq)$	
Initial (M):	0.36	0.00 0.00
Change (M):	$-x$	$+x$ $+x$
Equilibrium (M):	$(0.36 - x)$	$+x$ $+x$

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{(0.36 - x)} = 5.6 \times 10^{-10}$$

Assuming $(0.36 - x) \approx 0.36$, then

$$x = [\text{OH}^-] = 1.4 \times 10^{-5}$$

$$\text{pOH} = -\log(1.4 \times 10^{-5}) = 4.85$$

$$\text{pH} = 14.00 - 4.85 = \mathbf{9.15}$$

- 15.78** The salt ammonium chloride completely ionizes upon dissolution, producing $0.42\text{ M} [\text{NH}_4^+]$ and $0.42\text{ M} [\text{Cl}^-]$ ions. NH_4^+ will undergo hydrolysis because it is a weak acid (NH_4^+ is the conjugate acid of the weak base, NH_3).

Step 1: Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown x , that represents the change in concentration. Let $(-x)$ be the depletion in concentration (mol/L) of NH_4^+ . From the stoichiometry of the reaction, it follows that the increase in concentration for both H_3O^+ and NH_3 must be x . Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

	$\text{NH}_4^+ (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{NH}_3 (aq) + \text{H}_3\text{O}^+ (aq)$		
Initial (M):	0.42	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$(0.42 - x)$	x	x

Step 2: You can calculate the K_a value for NH_4^+ from the K_b value of NH_3 . The relationship is

$$K_a \times K_b = K_w$$

or

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Step 3: Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant (K_a), solve for x .

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.42 - x} = 5.6 \times 10^{-10}$$

Assuming $(0.42 - x) \approx 0.42$,

$$x = [\text{H}^+] = 1.5 \times 10^{-5}\text{ M}$$

$$\text{pH} = -\log(1.5 \times 10^{-5}) = \mathbf{4.82}$$

Since NH_4Cl is the salt of a weak base (aqueous ammonia) and a strong acid (HCl), we expect the solution to be slightly acidic, which is confirmed by the calculation.