Chapter 6

Acids and Bases

1. **Define a conjugate acid-base pair.**
   A conjugate acid-base pair is a weak acid and a weak base that differ by only one proton.
2. **Indicate the conjugate acid for each of the following:**
   a) **OH^{1-}** H_2O b) **NO_2^{1-}** HNO_2 c) **NH_2^{1-}** NH_3
   d) **PO_4^{3-}** HPO_4^{2-} e) **HSO_3^{1-}** H_2SO_3
3. **Indicate the conjugate base for each of the following:**
   a) **OH^{1-}** O^{2-} b) **H_2O_2** HO_2^{1-} c) **$H_2PO_4^{1-}$** HPO_4^{2-}
   d) **H_3O^{1+}** H_2O e) **H_2SO_3** HSO_3^{1-}
4. **Define a Lewis acid and a Brønsted acid. Give an example of a Lewis acid that is not a Brønsted acid.**
   A Lewis acid can accept a pair of electrons from a Lewis base to form a covalent bond. A Brønsted acid is a proton donor. $AlCl_3$, SO_3, and BF_3 are Lewis acids but not Brønsted acids.
5. **Are all Brønsted bases also Lewis bases? Explain.**
   Yes! Both types of base must have a lone pair to form a covalent bond to an acid.
6. **What distinguishes a weak acid from a strong one?**
   Strong acids are characterized by $K_a > 1$, while weak acids are characterized by $K_a < 1$.
7. **Which of the following are Brønsted bases?**
   a) **NaOH** yes b) **NaCl** not in water c) **CH_3OH** no
   d) **KCN** yes e) **KH_2PO_4** yes
8. **Which of the following are Brønsted acids?**
   a) **HClO** yes b) **CaH_2** no c) **CH_3CO_2H** yes
   d) **$KHSO_3$** yes e) **NH_4Cl** yes
9. **Explain how the reaction $Ag^{1+} + Cl^{1-} \rightarrow AgCl$ is a Lewis acid-base reaction. Is it a Brønsted acid-base reaction?**
   Ag^{1+} is a Lewis acid that accepts a lone pair on Cl^{1-} to form a bond that has substantial covalent character. It is not a Brønsted acid-base reaction because no proton is transferred.
10. **Write Brønsted acid-base reactions or indicate no reaction if K << 1.**
    a) **Hydrochloric acid and aqueous sodium hydroxide are mixed.**
    $H_3O^{1+} + OH^{1-} \rightarrow 2H_2O$ (strong acid + weak acid)
    b) **Aqueous potassium fluoride is added to perchloric acid.**
    $F^{1-} + H_3O^{1+} \rightarrow HF + H_2O$ (weak base + strong acid)
    c) **Aqueous NH_4Cl is added to aqueous $KHSO_4$.**
    $NH_4^{1+} + HSO_4^{1-} \rightarrow$ no reaction (HSO_4^{1-} is much too weak a base to react with NH_4^{1+})
    d) **Aqueous ammonia is added to hydrofluoric acid.**
    $NH_3 + HF \rightarrow NH_4^{1+} + F^{1-}$ (weak acid + weak base, but produced acid is weaker than reacting acid)
    e) **HNO_2 is added to aqueous KF.**
    $HNO_2 + F^{1-} \rightarrow NO_2^{1-} + HF$ (weak acid + weak base, produced acid and reacting acid of similar strengths)
11. **Write Brønsted acid-base reactions or indicate no reaction if K << 1.**
    a) **Aqueous sodium sulfate is added to hydrobromic acid.**
    $SO_4^{2-} + H_3O^{1+} \rightarrow HSO_4^{1-} + H_2O$ (weak base + strong acid)
    b) **Aqueous NH_4Cl and aqueous KF are mixed.**
    $NH_4^{1+} + F^{1-} \rightarrow$ no reaction (HF, the produced acid, is much stronger than the reacting acid)
    c) **Aqueous sodium cyanide is added a large excess of sulfurous acid.**
    $CN^{1-} + H_2SO_3 \rightarrow HSO_3^{1-} + HCN$
    d) **Acetic acid and aqueous sodium hypochlorite are mixed.**
    $CH_3COOH + OCl^{1-} \rightarrow CH_3COO^{1-} + HOCl$ (produced acid is weaker than reacting acid)

e) Hydrogen sulfide is bubbled into water.

$H_2S + H_2O \rightarrow$ no reaction (this is the K_a reaction of a weak acid and the extent is very small)

12. Explain why $HClO_4$ is a strong acid, but HClO is a weak acid.

Additional oxygens withdraw electron density from the chlorine and weaken the O-H bond, making for a stronger acid. Alternatively, the oxidation state of Cl is +7 in $HClO_4$ and only +1 in HClO. The higher oxidation state removes electron density from the O-H bond and makes the acid stronger.

13. Explain why HCl is a strong acid, but HF is a weak acid.

The HF bond is much stronger than the HCl bond.

14. What is the predominate phosphorus containing species in a solution prepared by adding some sodium phosphate to a large excess of carbonic acid?

H_2CO_3 is strong enough to protonate PO_4^{3-} and HPO_4^{2-}, but it is too weak to react with $H_2PO_4^{1-}$. Thus, most of the phosphorus is in the form of $H_2PO_4^{1-}$.

15. What is the predominate phosphorus containing species in a solution prepared by adding some phosphoric acid to a solution containing a large excess of ammonia?

NH_3 is strong enough to remove a proton from H_3PO_4 and $H_2PO_4^{1-}$, but it is too weak to react with HPO_4^{2-}. Therefore, the predominant phosphorus containing species is HPO_4^{2-}.

16. Define the term *amphiprotic*. Identify the amphiprotic substances in Exercises 2 and 3.

An amphiprotic substance can behave as either an acid or a base. Thus, it must contain both a proton that can be transferred (usually attached to an oxygen) and a lone pair. The amphiprotic substances in Exercise 2 are OH^{1-}, NH_2^{1-}, and HSO_3^{1-}, where only HSO_3^{1-} would be amphiprotic in water because the bases O^{2-} and NH^{2-} are far too strong to exist in water. The amphiprotic substances in Exercise 3 are OH^{1-} and $H_2PO_4^{1-}$. As above, OH^{1-} is not amphiprotic in water because it cannot function like an acid to produce O^{2-} in water.

17. What is an *autoionization* reaction? Write the chemical equation for the autoionization of ammonia. H_3O^{1+} and OH^{1-} are the strongest acid and base that can exist in aqueous solutions because water reacts with any acids or bases that are stronger than these acids. This is known as the *leveling effect.* What are the strongest acid and base that can exist in liquid ammonia?

Autoionization reactions are reactions between two identical molecules that produce ion. The autoionization of ammonia is $NH_3 + NH_3 \rightarrow NH_2^{1-} + NH_4^{1+}$. The strongest acid that can exist in liquid ammonia is NH_4^{1+} and the strongest base is NH_2^{1-}.

18. Determine the hydronium and hydroxide ion concentrations in the following solutions:

All of these problems can be solved using the following equations: $[H_3O^{1+}] = 10^{-pH}$ & $[OH^{1-}] = \frac{K_w}{[H_3O^{1+}]}$

a) rainwater; pH = 5.3

$[H_3O^{1+}] = 10^{-pH} = 10^{-5.3} = 5 \times 10^{-6}$ M $\rightarrow$ $[OH^{1-}] = \frac{1.0 \times 10^{-14}}{[H_3O^{1+}]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-6}} = 2.0 \times 10^{-9}$ M

b) household ammonia; pH = 11.9	$[H_3O^{1+}] = 1 \times 10^{-12}$ M	$[OH^-] = 8 \times 10^{-3}$ M
c) vinegar; pH = 2.7	$[H_3O^{1+}] = 2 \times 10^{-3}$ M	$[OH^-] = 5 \times 10^{-12}$ M
d) seawater; pH = 7.6	$[H_3O^{1+}] = 3 \times 10^{-8}$ M	$[OH^-] = 4 \times 10^{-7}$ M

19. Determine the hydronium and hydroxide ion concentrations in the following solutions:

a) detergent; pH = 10.3	$[H_3O^{1+}] = 5 \times 10^{-11}$ M	$[OH^-] = 2 \times 10^{-4}$ M
b) stomach acid; pH = 2.4	$[H_3O^{1+}] = 4 \times 10^{-3}$ M	$[OH^-] = 3 \times 10^{-12}$ M
c) beer; pH = 4.2	$[H_3O^{1+}] = 6 \times 10^{-5}$ M	$[OH^-] = 2 \times 10^{-10}$ M
d) milk of magnesia; pH = 10.5	$[H_3O^{1+}] = 3 \times 10^{-11}$ M	$[OH^-] = 3 \times 10^{-4}$ M

20. Determine the pK_a of each of the following acids:

a) hypoiodous acid	HOI	$K_a = 2.3 \times 10^{-11}$	$pK_a = -\log(2.3 \times 10^{-11}) = 10.64$
b) iodic acid	HIO_3	$K_a = 0.16$	$pK_a = -\log(0.16) = 0.80$

21. Determine the pK_a of each of the following acids:

a) tartaric acid	$H_2C_4H_4O_6$	$K_a = 1.0 \times 10^{-3}$	$pK_a = -\log(1.0 \times 10^{-3}) = 3.00$
b) boric acid	H_3BO_3	$K_a = 5.8 \times 10^{-10}$	$pK_a = -\log(5.8 \times 10^{-10}) = 9.24$

22. Determine the K_a of each of the following acids:

a) phenol	C_5H_5OH	$pK_a = 10.00$	$K_a = 10^{-10.00} = 1.0 \times 10^{-10}$
b) ascorbic acid	$H_3C_6H_6O_6$	$pK_a = 4.10$	$K_a = 10^{-4.10} = 7.9 \times 10^{-5}$

23. Determine the K_a of each of the following acids:

a) hypobromous acid	HOBr	$pK_a = 8.64$	$K_a = 10^{-8.64} = 2.3 \times 10^{-9}$
b) saccharin	$H_3NC_7H_4SO_3$	$pK_a = 11.68$	$K_a = 10^{-11.68} = 2.1 \times 10^{-12}$

24. What is the pK_b of the conjugate base of each of the acids in Exercise 20:

a) hypoiodous acid	$pK_a = 10.64$	$pK_b = 14.00 - 10.64 = 3.36$
b) iodic acid	$pK_a = 0.80$	$pK_b = 14.00 - 0.80 = 13.20$

25. What is the pK_b of the conjugate base of each of the acids in Exercise 21:

a) tartaric acid	$pK_a = 3.00$	$pK_b = 14.00 - 3.00 = 11.00$
b) boric acid	$pK_a = 9.24$	$pK_b = 14.00 - 9.24 = 4.76$

26. Determine the pH of solutions with the following pOH's:

Use the expression $pH = pK_W - pOH$ and assume a temperature of 25 °C where $pK_W = 14.00$.

a) 12.32	pH = 14.00 - 12.32 = 1.68
b) 1.86	pH = 14.00 - 1.86 = 12.14
c) 4.37	pH = 14.00 - 4.37 = 9.63

27. What is the K_a of the acids whose conjugate bases have the following pK_b's?

Use the expression $pK_a = pK_W - pK_b$ and assume a temperature of 25 °C where $pK_W = 14.00$.

a) 8.37	$pK_a = 14.00 - 8.37 = 5.63$	$K_a = 10^{-5.63} = 2.3\text{x}10^{-6}$
b) 12.66	$pK_a = 14.00 - 12.66 = 1.34$	$K_a = 10^{-1.34} = 4.6\text{x}10^{-2}$
c) 0.22	$pK_a = 14.00 - 0.22 = 13.78$	$K_a = 10^{-13.78} = 1.7\text{x}10^{-14}$

28. Determine the pH and pOH of solutions with the following hydronium ion concentrations:

Use the expression $pH = -\log[H_3O^{1+}]$ and $pOH = pK_W - pH$ and assume a temperature of 25 °C where $pK_W = 14.00$.

a) $3.4\text{x}10^{-6}$ M	$pH = -\log(3.4 \times 10^{-6}) = 5.47$	pOH = 14.00 - 5.47 = 8.53
b) $4.7\text{x}10^{-3}$ M	$pH = -\log(4.7 \times 10^{-3}) = 2.33$	pOH = 14.00 - 2.33 = 11.67
c) $8.8\text{x}10^{-10}$ M	$pH = -\log(8.8 \times 10^{-10}) = 9.06$	pOH = 14.00 - 9.06 = 4.94

29. Determine the pH and pOH of solutions with the following hydroxide ion concentrations:

Use the expression $pOH = -\log[OH^{11}]$ and $pH = pK_W - pOH$ and assume a temperature of 25 °C where $pK_W = 14.00$.

a) $7.5\text{x}10^{-8}$ M	$pOH = -\log(7.5 \times 10^{-8}) = 7.12$	pH = 14.00 - 7.12 = 6.88
b) $3.9\text{x}10^{-4}$ M	$pOH = -\log(3.9 \times 10^{-4}) = 3.41$	pH = 14.00 - 3.41 = 10.59
c) $1.0\text{x}10^{-12}$ M	$pOH = -\log(1.0 \times 10^{-12}) = 12.00$	pH = 14.00 - 12.00 = 2.00

30.* What is the pH of $1.0\text{x}10^{-8}$ M HCl at 25 °C?

At first glance, the pH might be assumed to $-\log(1.0 \times 10^{-8}) = 8.0$, but a hydrochloric acid solution must have a pH less than 7. Thus, HCl is not the only source of H_3O^{1+} in this solution; the other source is water. Consider the autoionization of water in the presence of $1.0\text{x}10^{-8}$ M HCl

	$2H_2O$	$\rightleftharpoons$	H_3O^{1+} +	OH^{1-}
initial			$1.0\text{x}10^{-8}$	0
Δ			+x	+x
Eq			$1.0\text{x}10^{-8}$ + x	x

The K_w expression is $K_w = (1.0\text{x}10^{-8}+x)(x)$ or $1.0 \times 10^{-14} = 1.0\text{x}10^{-8}x + x^2$.

Putting the Kw expression in the format of the quadratic equation, $1x^2 + 1.0 \times 10^{-8}x - 1.0 \times 10^{-14} = 0$

Solving for x with the quadratic equation, $x = \dfrac{-1.0\times10^{-8} \pm \sqrt{(1.0\times10^{-8})^2 + 4(1)(1.0\times10^{-14})}}{2} = 9.5\times10^{-8}$ M

Nine times more H_3O^{1+} ion is produced by the water than is added.

$[H_3O^{1+}] = 1.0 \times 10^{-8} + 9.5 \times 10^{-8} = 10.5 \times 10^{-8}$ M, so the pH is 6.98.

31.* The solubility of $Al(OH)_3$ in water is $2.9\text{x}10^{-9}$ M at 25 °C. What is the pH of a saturated solution of $Al(OH)_3$?

$[OH^{1-}] = 3\,(2.9 \times 10^{-9}) = 8.7 \times 10^{-9}$ M, but a hydroxide must produce an basic solution, so $[OH^{1-}] > 1.0 \times 10^{-7}$ M. Consequently, the hydroxide produced by the water must exceed that produced by such an insoluble hydroxide.

	$2H_2O$	$\rightleftharpoons$	OH^{1-} +	H_3O^{1+}
initial			$8.7\text{x}10^{-9}$	0
Δ			+x	+x
Eq			$8.7\text{x}10^{-9}$ + x	x

The K_w expression is $K_w = (8.7\text{x}10^{-9}+x)(x)$ or $1.0\text{x}10^{-14} = 8.7\text{x}10^{-9}x + x^2$.

Putting the K_w expression in the form of the quadratic equation, $1x^2 + 8.7\text{x}10^{-9}x - 1.0\text{x}10^{-14} = 0$

Solving for x with the quadratic equation, $x = \dfrac{-8.7\times10^{-9} \pm \sqrt{(8.7\times10^{-9})^2 + 4(1)(1.0\times10^{-14})}}{2} = 9.6\times10^{-8}$ M

Nine times more OH^{1-} ion is produced by the water than is added.

$[OH^{1-}] = 8.7 \times 10^{-9} + 9.6 \times 10^{-8} = 10.5 \times 10^{-8}$ M, so the pOH is 6.98, and pH = 7.02.

32. The pH of pure water at 100 °C is 6.13. What is the value of K_w at 100 °C?

In pure water, $[H_3O^{1+}] = [OH^{1-}]$.

At 100 °C, pH = 6.13, so $[H_3O^{1+}] = [OH^{1-}] = 10^{-pH} = 10^{-6.13} = 7.4 \times 10^{-7}$ M

$K_w = [H_3O^{1+}][OH^{1-}] = (7.4 \times 10^{-7})^2 = 5.5 \times 10^{-13}$

33. What is pH of a neutral solution at 37 °C?

$[H_3O^{1+}] = [OH^{1-}]$ in a neutral solution, and $K_w = [H_3O^{1+}][OH^{1-}] = 2.42 \times 10^{-14}$

so, $[H_3O^{1+}] = \sqrt{K_w} = \sqrt{2.42\times10^{-14}} = 1.56\times10^{-7}$ M

pH = $-\log(1.56 \times 10^{-7}) = 6.81$

34. The K_a of a weak acid at 37 °C is $5.0\text{x}10^{-10}$. What is the K_b of its conjugate base?

$K_w = 2.42 \times 10^{-14}$, so $K_b = \dfrac{K_w}{K_a} = \dfrac{2.42\times10^{-14}}{5.0\times10^{-10}} = 4.8\times10^{-5}$

35. The pK_a of a weak acid is 5.21 at 37 °C. What is the pK_b of its conjugate base?

$pK_w = -\log K_w = -\log(2.42\text{x}10^{-14}) = 13.62$

$pK_b = pK_w - pKa = 13.62 - 5.21 = 8.41$

36. The hydroxide ion concentration in a weak base solution at 37 °C is 0.024. What is the pH of the solution?

pH = pK_w – pOH = $-\log(2.42\text{x}10^{-14}) + \log(0.024) = 13.62 - 1.62 = 12.00$

37. What is the pH of each of the following aqueous solutions?

a) **0.066 M HCl** pH = -log 0.066 = 1.18

b) **0.21 M KOH** pOH = -log 0.21 = 0.68 pH = 14.00 - 0.68 = 13.32

c) **0.11 M $Ba(OH)_2$** $[OH^{1-}] = 2(0.11) = 0.22$ M
pOH = -log 0.22 = 0.66 pH = 14.00 - 0.66 = 13.34

38. What is the pH of each of the following aqueous solutions?

a) 0.57 M NaOH pOH = -log 0.57 = 0.24 pH = 14.00 - 0.24 = 13.76

b) $1.3x10^{-4}$ M HNO_3 pH = - log (1.3×10^{-4}) = 3.89

c) 2.1 M KOH pOH = -log 2.1 = -0.32 pH = 14.00 + 0.32 = 14.32

39. To what volume must 5.0 mL of 6.0 M HCl be diluted to prepare a solution with pH = 1.22?

The final concentration of hydronium ion is $10^{-1.22}$ = 0.060 M. Using the dilution expression from Chapter 2, we solve for the final volume,

$$V_f = \frac{M_iV_i}{M_f} = \frac{(6.0\text{ mmol/mL})(5.0\text{ mL})}{0.060\text{ mmol/mL}} = 5.0 \times 10\text{ mL} = 0.50\text{ L}$$

40. How much water must be added to 25 mL of an HCl solution with a pH = 2.46 to produce a solution with a pH = 4.00? Assume the volumes are additive.

The initial concentration of hydronium ion is $10^{-2.46} = 3.5 \times 10^{-3}$ M, and the final concentration is 1.0×10^{-4} M. Using the dilution expression from Chapter 2, we solve for the final volume,

$$V_f = \frac{M_iV_i}{M_f} = \frac{(3.5 \times 10^{-3}\text{ mmol/mL})(25\text{ mL})}{1.0 \times 10^{-4}\text{ mmol/mL}} = 8.7 \times 10^2\text{ mL} = 0.87\text{ L}$$

The original volume of 25 mL is insignificant given the number of significant figures in the problem. Thus, we cannot distinguish of the final volume from the volume of water.

41. What volume of HCl gas measured at 300. K and 1 atm is required to prepare 5.0 L of hydrochloric acid with a pH of 3.84?

$[H_3O^{1+}] = 10^{-3.84} = 1.5 \times 10^{-4}$ M

The number of moles of HCl required is (5.0 L)(1.5×10^{-4} M) = 7.2×10^{-4} mol

Use the ideal gas law to determine the volume of gas

$$V = \frac{nRT}{P} = \frac{(7.2 \times 10^{-4}\text{ mol})(0.0821\text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(300\text{ K})}{1.0\text{ atm}} = 0.018\text{ L}$$

42. 512 mL of HCl gas at 300. K and 886 torr is dissolved in water. What is the pH of the resulting solution if the total volume is 653 m?

Use the ideal gas law to determine the number of moles of HCl.

$$n = \frac{PV}{RT} = \frac{(886/760\text{ atm})(0.512\text{ L})}{(0.0821\text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(300\text{ K})} = 0.0242\text{ mol} = 24.2\text{ mmol}$$

$$[H_3O^{1+}] = \frac{24.2\text{ mmol }H_3O^{1+}}{653\text{ mL}} = 0.0371\text{ M; pH} = -\log(0.0371) = 1.430$$

43. How many grams of $Ba(OH)_2$ would have to be dissolved in water to prepare 500.0 mL of a pH= 9.80 solution?

pOH = 14.00 – 9.80 = 4.20; $[OH^{1-}] = 10^{-4.20} = 6.3x10^{-5}$ M

$$0.5000\text{ L solution} \times \frac{6.5 \times 10^{-5}\text{ mol OH}^{1-}}{1\text{ L solution}} \times \frac{1\text{ mol Ba(OH)}_2}{2\text{ mol OH}^{1-}} \times \frac{171.3\text{ g Ba(OH)}_2}{1\text{ mol Ba(OH)}_2} = 2.8 \times 10^{-3}\text{ g} = 2.8\text{ mg}$$

44. To what volume should 2.6 mL of 0.11 M NaOH be diluted in order to make a pH = 12.00 solution?

pOH = 14.00 – 12.00 = 2.00; $[OH^{-1}] = 10^{-2.00} = 0.010$ M

$$(2.6\text{ mL})(0.11\text{ M}) = V(0.010\text{ M});\quad V = \frac{(2.6\text{ mL})(0.11\text{ M})}{0.010\text{ M}} = 29\text{ mL}$$

45. What is the 5% rule?

The amount of acid that reacts can be assumed negligible in the subtraction from the original amount of acid if no more than 5% of the acid reacts.

46 Use the 5% rule to determine whether the equilibrium concentration of the acid can be approximated by its makeup concentration.

The percent dissociation is approximated as % = $\sqrt{\frac{K_a}{c_o}} \times 100\%$. If this is less than 5% then the approximation is acceptable.

a) 2.0 M HF $\sqrt{\frac{7.2 \times 10^{-4}}{2.0}} \times 100\% = 1.9\%$ approximation is valid

b) 2.0×10^{-4} M H_2S $\sqrt{\dfrac{1.0\times10^{-7}}{2.0\times10^{-4}}}\times100\% = 2.2\%$ approximation is valid

c) 0.10 M HNO_2 $\sqrt{\dfrac{4.0\times10^{-4}}{0.10}}\times100\% = 6.3\%$ approximation is NOT valid

47. Use the 5% rule to determine whether the equilibrium concentration of the acid can be approximated by its makeup concentration.

Proceed as in Exercise 41 after converting the pK_a of the acid into its K_a.

a) 0.80 M cyanic acid (HCNO, pK_a = 3.46)

$K_a = 10^{-3.46} = 3.5 \times 10^{-4}$ $\sqrt{\dfrac{3.5\times10^{-4}}{0.80}}\times100\% = 2.1\%$ approximation is valid

b) 4.4×10^{-3} M hydrazoic acid (HN_3, pK_a = 4.6)

$K_a = 10^{-4.6} = 3 \times 10^{-5}$ $\sqrt{\dfrac{3\times10^{-5}}{4.4\times10^{-3}}}\times100\% = 8\%$ approximation is NOT valid

c) 3.0 M arsenic acid (H_3AsO_4, pK_a = 2.26)

$K_a = 10^{-2.26} = 5.5 \times 10^{-3}$ $\sqrt{\dfrac{5.5\times10^{-3}}{3.0}}\times100\% = 4.3\%$ approximation is valid

48. Calculate the pH of a 0.25 M phenol (C_6H_5OH, $K_a = 1.0 \times 10^{-10}$), which is often used as an antiseptic.

The acid dissociation reaction of penol is:

	C_6H_5OH	+ H_2O	⇌	H_3O^{1+} +	$C_6H_5O^{1-}$
Initial	0.25			0	0
Δ	- x			+ x	+ x
Equilibrium	0.25 - x			+ x	+ x

$$K_a = \frac{[H_3O^{1+}][A^{1-}]}{[HA]} = 1.0\times10^{-10} = \frac{x^2}{0.25\text{-}x} = \frac{x^2}{0.25}$$

K_a is so small that it can be safely assumed that the change in the initial concentration (x) of the weak acid is negligible. Therefore, the denominator can be simplified.

$x = [H^{1+}] = 5.0 \times 10^{-6}$ → pH = -log[H^{1+} = -log(5.0×10^{-6}) = 5.3

49. What is the pH of vinegar, a 4.5% solution of acetic acid?

First, determine the concentration of acetic acid in a 4.5% solution.

$$\frac{4.5\text{ g }CH_3COOH}{100\text{ g sol'n}}\times\frac{1\text{ mol }CH_3COOH}{60.054\text{ g }CH_3COOH}\times\frac{1.0\text{ g sol'n}}{1.0\text{ mLsol'n}}\times\frac{1000\text{ mL}}{1\text{ L}} = 0.75\text{ M }CH_3COOH$$

Next, set up the dissociation reaction:

	CH_3COOH +	H_2O	⇌	CH_3COO^{1-} +	H_3O^{1+}
Initial:	0.75	-		0	0
Δ	- x			+ x	+ x
Final:	0.75 -x			x	x

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{0.75\text{-}x} = 1.8 \times 10^{-5}\text{; from Appendix H ;}$$

K_a is small, so we can simplify the above relationship

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.75}\text{, so } x = [H_3O^{1+}] = \sqrt{K_a c} = \sqrt{(1.8\times10^{-5})(0.75)} = 3.7\times10^{-3}\ M$$

pH = -log[H_3O^+] = 2.44 when extra figures are kept from previous calculations

50. The pH of a 0.030 M benzoic acid solution is 2.85.

a) What are K_a and pK_a of benzoic acid?

$$K_a = \frac{[H^{1+}][A^{1-}]}{[HA]} = \frac{x^2}{0.030 - x}$$

In this case, x is known because the pH of the solution is given: $x = [H^{1+}] = [A^{1-}] = 10^{-pH} = 10^{-2.85} = 1.4 \times 10^{-3}$
The change in concentration on the initial benzoic acid concentration can not be ignored in this problem.

Calculate the disassociation constant, K_a: $K_a = \frac{(1.4\times10^{-3})^2}{0.029} = 7.0\times10^{-5}$ $pK_a = -\log K_a = -\log(6.8 \times 10^{-5}) = 4.16$

b) What are K_b and pK_b of the benzoate ion?

$pK_b = pK_w - pK_a = 14.00 - 4.16 = 9.84$
$K_b = 10^{-pKb} = 1.4 \times 10^{-10}$

51. What is the hypochlorite ion concentration in a 0.14 M-solution of HOCl? What is the pH of the solution?

	HOCl	+	H_2O	$\rightleftharpoons$	OCl^{1-}	+	H_3O^{1+}
Eq	0.14 – x				x		x

Assume x is negligible, then $x = [OCl^{1-}] = \sqrt{K_a c} = \sqrt{(3.5\times10^{-8})(0.14)} = 7.0 \times 10^{-5}$ M $= [H_3O^{1+}]$

$pH = -\log[H_3O^{1+}] = -\log 7.0\times10^{-5} = 4.15$

52 What is the fluoride ion concentration in 2.0 M HF?

	HF	+	H_2O	$\rightleftharpoons$	F^{1-}	+	H_3O^{1+}
Eq	2.0 – x				x		x

Assume x is negligible, then $x = [F^{1-}] = \sqrt{(7.2\times10^{-4})(2.0)} = 0.038$ M, which is negligible

53. What is the pH of 0.044 M HF?

$HF + H_2O \rightleftharpoons H_3O^{1+} + F^{1-}$ $K = 7.2\times10^{-4}$ If $x = [H_3O^{1+}] = [F^{1-}]$, then $[HF] = 0.044 - x$. Setup K_a expression and solve for x.

$$\frac{x^2}{0.044-x} = 7.2\times10^{-4}; \qquad x^2 + 7.2\times10^{-4}x - 3.2\times10^{-5} = 0$$

$$x = \frac{-7.2\times10^{-4} + \sqrt{(7.2\times10^{-4})^2 - 4(1)(-3.2\times10^{-5})}}{2(1)} = 5.3\times10^{-3}\ M = [H_3O^{1+}];\ pH = -\log(5.3\times10^{-3}) = 2.28$$

54. What is the phosphate ion concentration in 0.066 M H_3PO_4?

Phosphate is not produced until the third dissociation, which includes H_3O^{1+} and HPO_4^{2-}. We determine $[H_3O^{1+}]$ from the first ionization and use the fact that $[HPO_4^{2-}] = K_2 = 6.2\times10^{-8}$ M. Phosphoric is much stronger than acetic, so the quadratic formula must be used to determine $[H_3O^{1+}]$ in the first step.

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^{1-} + H_3O^{1+}$ $K_1 = 0.0075$; $x = [H_2PO_4^{1-}] = [H_3O^{1+}]$; $0.066 - x = [H_3PO_4]$

$$\frac{x^2}{0.066-x} = 0.0075; \qquad x^2 + 0.0075x - 5.0\times10^{-4} = 0$$

$$x = \frac{-0.0075 + \sqrt{(0.0075)^2 - 4(1)(-5.0\times10^{-4})}}{2(1)} = 0.019\ M = [H_3O^{1+}]$$

The third dissociation: $HPO_4^{1-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^{1+}$ At equilibrium, $[HPO_4^{2-}] = K_2 = 6.2\times10^{-8}$ M and $[H_3O^{1+}] = 0.019$ M

$$K_3 = 4.8\times10^{-13} = \frac{[PO_4^{3-}][H_3O^{1+}]}{[HPO_4^{2-}]} = \frac{[PO_4^{3-}](0.019)}{6.2\times10^{-8}}; \quad [PO_4^{3-}] = \frac{(4.8\times10^{-13})(6.2\times10^{-8})}{0.019} = 1.6\times10^{-18}\ M$$

55. What is the K_a of chloroacetic acid, $ClCH_2COOH$, if a 0.085-M solution has a pH of 2.00?

$[H_3O^{1+}] = 10^{-pH} = 0.010\ M = [ClCH_2COO^{1-}]$

	$ClCH_2COOH$	+	H_2O	$\rightleftharpoons$	$ClCH_2COO^{1-}$	+	H_3O^{1+}
Eq	0.085 – 0.010				0.010		0.010

$$K_a = \frac{[ClCH_2COO^{1-}][H_3O^{1+}]}{[ClCH_2COOH]} = \frac{(0.010)(0.010)}{0.075} = 1.3\times10^{-3}$$

56. What is the K_a of an acid if a 0.21-M solution is 3.4% dissociated?

The concentrations of the hydronium ion and the conjugate base are obtained by multiplying the fraction that reacts times the initial concentration: (0.034)(0.21) = 0.00714 M. (Carry an extra significant figure.)

	HA	+	H_2O	$\rightleftharpoons$	A^{1-}	+	H_3O^{1+}
Eq	0.21 – 0.007				0.00714		0.00714

$$K_a = \frac{[A^{1-}][H_3O^{1+}]}{[HA]} = \frac{(0.00714)(0.00714)}{0.21} = 2.5\times10^{-4}$$

57 What is the pK_a of iodic acid if the iodate ion concentration in a 0.066-M solution of HIO_3 is 0.050 M?

	HIO_3	+	H_2O	$\rightleftharpoons$	IO_3^{1-}	+	H_3O^{1+}
Eq	0.066 - 0.050				0.050		0.050

$$K_a = \frac{[IO_3^{1-}][H_3O^{1+}]}{[HIO_3]} = \frac{(0.050)(0.050)}{0.016} = 0.16\text{ ; } pK_a = -\log 0.16 = 0.81$$

58. What is the percent dissociation of 0.048 M propanoic acid (pK_a = 4.86)?

Use Equation 6.6, but realize that the equation is only good if less than 5% dissociates.

$K_a = 10^{-pK_a} = 10^{-4.86} = 1.4 \times 10^{-5}$ $\quad \sqrt{\frac{K_a}{c_o}}\times100\% = \sqrt{\frac{1.4\times10^{-5}}{0.048}}\times100\% = 1.7\%$

59. What is the percent dissociation of 0.26 M uric acid (pK_a = 3.89)?

Use Equation 6.6, but realize that the equation is only good if less than 5% dissociates.

$K_a = 10^{-pK_a} = 10^{-3.89} = 1.3 \times 10^{-4}$ $\quad \sqrt{\frac{K_a}{c_o}}\times100\% = \sqrt{\frac{1.3\times10^{-4}}{0.26}}\times100\% = 2.2\%$

60. What is the percent dissociation of 0.15 M iodic acid?

Apply Equation 6.7: $\% = \sqrt{\frac{0.17}{0.15}}\times100\% = 107\%$. Clearly Iodic acid is too strong and Equation 6.7 cannot be used.

Instead, we must use the quadratic formula to solve for the amount that reacts.
$HIO_3 + H_2O \rightleftharpoons IO_3^{1-} + H_3O^{1+}$ K_a = 0.17. Let x = $[IO_3^{1-}] = [H_3O^{1+}]$ then $[HIO_3]$ = 0.15 – x

$$0.17 = \frac{x^2}{0.15 - x};\quad x^2 + 0.17x - 0.0255 = 0;\quad x = \frac{-0.17 + \sqrt{0.17^2 - 4(1)(-0.0255)}}{2(1)} = 0.096\text{ M}$$

$$\% = \frac{x}{c_o}\times100\% = \frac{0.096}{0.15}\times100\% = 64\%$$

61. What mass of ammonium chloride is required to prepare 500. mL of a solution with a pH of 4.62?

$$NH_4^{1+} + H_2O \rightleftharpoons NH_3 + H_3O^{1+} \qquad K_a = 5.6 \times 10^{-10}$$

$[NH_3] = [H_3O^{1+}] = 10^{-pH} = 10^{-4.62} = 2.4\text{x}10^{-5}$ M $\quad [NH_4^{1+}] = c - 2.4\text{x}10^{-5} \sim c$

Substituting the above equilibrium concentrations into the Ka expression, we obtain

$$K = 5.6\times10^{-10} = \frac{[NH_3][H_3O^{1+}]}{[NH_4^{1+}]} = \frac{(2.4\times10^{-5})(2.4\times10^{-5})}{c}\text{ or } c = \frac{(2.4\times10^{-5})(2.4\times10^{-5})}{5.6\times10^{-10}} = 1.03\text{ M}$$

500 mL of solution must contain (0.50 L)(1.03 mol/L) = 0.51 mol, which has a mass of 0.51 mol x 53.5 g/mol = 27.5 g (between 27 g and 28 g).

62. What mass of potassium hydrogensulfate is required to make 350. mL of a solution with a pH of 2.50?

$$HSO_4^{1-} + H_2O \rightleftharpoons SO_4^{2-} + H_3O^{1+} \qquad K_a = 0.012$$

$[SO_4^{2-}] = [H_3O^{1+}] = 10^{-pH} = 10^{-2.50} = 3.2\text{x}10^{-3}$ M $\quad [HSO_4^{1-}] = c_o - 3.2\text{x}10^{-3} = c'$.

Substituting the above equilibrium concentrations into the K_a expression, we obtain

$$K = 0.012 = \frac{[SO_4^{2-}][H_3O^{1+}]}{[HSO_4^{1-}]} = \frac{(3.2\times10^{-3})(3.2\times10^{-3})}{[HSO_4^{1-}]}\text{ or } [HSO_4^{1-}] = \frac{(3.2\times10^{-3})(3.2\times10^{-3})}{0.012} = 8.3\times10^{-4}\text{ M}$$

The question asks for the makeup makeup amount. $c_o = [HSO_4^{1-}] + x = 3.2\text{x}10^{-3} + 0.8\text{ x}10^{-3} = 4.0\text{x}10^{-3}$ M

350 mL of solution must contain (350 mL)($4.0\text{x}10^{-3}$ mmol/mL) = 1.4 mmol, which has a mass of 1.4 mmol x 136.2 mg/mmol = 190 mg = 0.19 g

63. Vitamin C is ascorbic acid, $H_2C_6H_8O_6$. Calculate the pH, $[H_2C_6H_6O_6]$, $[HC_6H_6O_6^{1-}]$ and $[C_6H_6O_6^{2-}]$ in a 0.075-M solution of ascorbic acid.

From Appendix C, $K_1 = 8.0\text{x}10^{-5}$ and $K_2 = 1.6\text{x}10^{-12}$. K_2 is much smaller, so concentrations achieved in the first deprotonation are not affected by the second. The reaction table for the first ionization is

	$C_6H_8O_6$	+	H_2O	$\rightleftharpoons$	$HC_6H_6O_6^{1-}$	+	H_3O^{1+}
Initial:	0.075 M		-		0		0
Δ	- x		-		+x		+x
Final:	0.075 - x		0		x		x

Assuming the extent of reaction is negligible,

$[H_3O^{1+}] = [HC_6H_6O_6^{1}] = \sqrt{K_a c_o} = \sqrt{(8.0\times10^{-5})(0.075)} = 0.0024$ M , which is less than 5% of 0.075 M, so the approximation is acceptable. $[C_6H_8O_6] = 0.075 – 0.002 = 0.073$ M. pH = –log (0.0022) = 2.66

The concentration of the ion produced in the second ionization equals K_2, so the final concentration is $[C_6H_6O_6^{2}] = 1.6 \times 10^{-12}$ M.

64. Oxalic acid is a diprotic acid that occurs naturally in some plants. Calculate the pH and the concentrations of all species present in a 0.25-M solution. The acid dissociation constants are $K_1 = 5.9\text{x}10^{-2}$ and $K_2 = 6.4\text{x}10^{-5}$.

Consider oxalic acid as a generic diprotic acid, H_2A.

	H_2A	+ H_2O	$\rightleftharpoons$	H_3O^{1+} +	HA^{1-}
Initial	0.25			0	0
Δ	- x			+ x	+ x
Equilibrium	0.25 - x			+ x	+ x

$$K_1 = \frac{[H_3O^{1+}][HA^{1-}]}{[H_2A]} = 5.9 \text{ x } 10^{-2} = \frac{x^2}{0.25 - x} \quad \text{or} \quad x^2 + 0.059x - 0.147 = 0$$

Use the *quadratic formula* to calculate the value of *x*: $x = \dfrac{-0.059+\sqrt{(0.059)^2 - 4\times1\times-0.0147}}{2\times1} = 0.096$ M

$[H_3O^{1+}] = [HA^{1-}] = 0.096$ M and $[H_2A] = 0.25 – 0.096 = 0.15$ M.

For the second equilibrium

	HA^{1-}	+ H_2O	$\rightleftharpoons$	H_3O^{1+} +	A^{2-}
Initial	0.096			0.096	0
Δ	- x			+ x	+ x
Equilibrium	0.096 - x			0.096 + x	+ x

$$K_2 = \frac{[A^{1-}][H_3O^{1+}]}{[HA^{1-}]} = 6.4 \text{ x } 10^{-5} = \frac{(0.096+x)x}{0.096 - x}$$

If x is negligible compared to 0.096, then $x = K_2 = 6.4 \times 10^{-5}$ M.
$[A^{2-}] = 6.4 \text{ x } 10^{-5}$ M, $[HA^{1-}] = [H_3O^{1+}] = 0.096$ M, so pH = 1.02

65. What are concentrations of all species in a 0.16-M solution of malonic acid ($H_2C_3H_2O_4$)? $K_1 = 1.5\text{x}10^{-3}$ and $K_2 = 2.0\text{x}10^{-6}$

$H_2C_3H_2O_4 + H_2O \rightleftharpoons HC_3H_2O_4^{1-} + H_3O^{1+}$ let $x = [HC_3H_2O_4^{1-}] = [H_3O^{1+}]$ then $[H_2C_3H_2O_4] = 0.16 – x$

$$\frac{x^2}{0.16-x} = 0.0015; \qquad x^2 + 0.0015x - 2.4\times10^{-4} = 0$$

$$x = \frac{-0.0015 + \sqrt{(0.0015)^2 - 4(1)(-2.4\times10^{-4})}}{2(1)} = 0.015 \text{ M} = [H_3O^{1+}] = [HC_3H_2O_4^{1-}]$$

$[H_2C_3H_2O_4] = 0.16 - 0.015 = 0.15$ M; $[C_3H_2O_4^{2-}] = K_2 = 2.0\times10^{-6}$ M

The concentration of $C_3H_2O_4^{2-}$ produced in the second step is negligible compared to 0.015 M, so the assumption that $[C_3H_2O_4^{2-}] = K_2$ is valid.

66. Calculate the pH of a 0.50-M solution of pyridine (C_6H_5N, $K_b = 1.7\text{x}10^{-9}$).

Set up Reaction Table. Note the lone pair on the nitrogen atom is basic (Py = C_6H_5N and $HPy^{1+} = C_6H_5NH^{1+}$).

	Py	+	H_2O	$\rightleftharpoons$	HPy^{1+}	+	OH^{1-}
Initial:	0.50		-		0		0
Δ	- x				+ x		+ x
Final:	0.50 -x				x		x

$K_b = 1.7 \times 10^{-9} = \frac{[HPy^{1+}][OH^{1-}]}{[Py]} = \frac{[x][x]}{[0.50\text{-}x]}$

Again, this problem can be simplified to: $K_b = \frac{[x][x]}{[0.50]}$ or x = $[OH^{1-}] = \sqrt{K_b c} = \sqrt{(1.7\times10^{-9})(0.50)} = 2.9\times10^{-5}$ M

pOH = -log(2.9 x 10^{-5}) = 4.54; pH = 14.00 – 4.54 = 9.46

67. The hypochlorite ion is the active ingredient in bleach.

a) Industrial bleach is 15% NaOCl by mass. What is the hypochlorous acid concentration in industrial bleach?

First, convert the mass percent to a molarity

$$\frac{15\text{ g NaOCl}}{100\text{ g sol'n}} = \frac{15\text{ g NaOCl}\times\frac{1\text{ mol NaOCl}}{74.5\text{ g NaOCl}}}{100\text{ g sol'n}\times\frac{1\text{ mL sol'n}}{1\text{ g sol'n}}\times\frac{1\text{ L sol'n}}{1000\text{ mL sol'n}}} = \frac{0.20\text{ mol NaOCl}}{0.10\text{ L sol'n}} = 2.0\text{ M}$$

The hypochlorite ion is a weak base

	OCl^{1-}	+	H_2O	$\rightleftharpoons$	HOCl	+	OH^{1-}
Eq	2.0 – x				x		x

Assume that $[OCl^{1-}]$ = 2.0 M at equilibrium because c_o is very large and OCl^{1-} is a weak base.

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{3.5\times10^{-8}} = 2.9\times10^{-7} = \frac{[HOCl][OH^{1-}]}{[HOCl]} = \frac{x^2}{2.0}$$

x = $\sqrt{(2.9\times10^{-7})(2.0)} = 7.6\times10^{-4}$ M = [HOCl], which is negligible compared to 2.0 M.

b) Household bleach is a 5.25% solution of NaOCl. What is its pH?

Determine the molar concentration of the NaOCl. Assuming a 100. g solution (also 100. mL solution since the density is 1.0 g/mL), 5.25% translates to 5.25 g.

$$\frac{5.25\text{ g NaOCl}}{0.100\text{ L}}\times\frac{1\text{ mol}}{74.44\text{ g}} = 0.705\text{ M NaOCl}$$

K_b =2.9 x 10^{-7} from part a, so the hydroxide ion concentration is

$\left[OH^{1-}\right] = \sqrt{K_b\times c_o} = \sqrt{\left(2.9\times10^{-7}\right)\times\left(0.70\right)} = 4.5\times10^{-4}$ M, so pOH = -log $[OH^{1-}]$ = 3.35 and pH = 14.00 - 3.35 = 10.65

68. What are the HF concentration and pH of 0.32 M KF?

	F^{1-}	+	H_2O	$\rightleftharpoons$	HF	+	OH^{1-}
Eq	0.32 - x				x		x

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4\times10^{-11}.$$

Fluoride ion is so weak that we can neglect x in the subtraction. Thus, Equation 6.7 can be used.

[HF] = $[OH^{1-}] = \sqrt{K_b c_o} = \sqrt{(1.4\times10^{-11})(0.32)} = 2.1\times10^{-6}$ M

pOH = -log 2.1 x 10^{-6} = 5.68, so pH = 14.00 – 5.68 = 8.32

69. What are the NH_4^{1+} concentration and pH of a 0.16-M solution of NH_3?

	NH_3	+	H_2O	$\rightleftharpoons$	NH_4^{1+}	+	OH^{1-}
Eq	0.16 - x				x		x

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{5.6\times10^{-10}} = 1.8\times10^{-5}.$$

Assume that x is negligible in the subtraction, so Equation 6.7 can be used.

$[NH_4^{1+}] = [OH^{1-}] = \sqrt{K_b c_o} = \sqrt{(1.8\times10^{-5})(0.16)} = 1.7\times10^{-3}$ M (which is less than 5% reaction)

pOH = -log 1.7 x 10^{-3} = 2.77, so pH = 14.00 – 2.77 = 11.23

70. The pH of a 0.068-M solution of methyl amine (CH_3NH_2) is 11.72.

a) What are the K_b and pK_b of methylamine?

Methyl amine is a weak base, so we start with the K_b reaction.

$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^{1+} + OH^{1-}$

The concentrations of both the methyl ammonium ion and the hydroxide ion equal and are determined as 10^{-pOH}. We get the pOH from the pH: pOH = 14.00 - pH = 14.00 - 11.72 = 2.28

$[OH^{1-}] = [CH_3NH_3^{1+}] = 10^{-pOH} = 10^{-2.28} = 0.0052$ M

The equilibrium concentration of the methyl amine is obtained by difference to be

$[CH_3NH_2] = c_o - x = 0.068 - 0.005 = 0.063$ M

$K_b = \frac{[CH_3NH_3^{1+}][OH^{1-}]}{[CH_3NH_2]} = \frac{[0.0053][0.0053]}{[0.063]} = 4.4\times10^{-4}$; $pK_b = -\log K_b = 3.36$

b) What are the K_a and pK_a of the methylammonium ion?

$K_a = 1.0 \times 10^{-14}/K_b = (1.0 \times 10^{-14})/(4.4 \times 10^{-4}) = 2.3 \times 10^{-11}$ $\rightarrow$ $pK_a = -\log K_a = 10.64$

71. The pH of 0.083 M aniline ($C_6H_5NH_2$) is 8.76. What are its K_b and pK_b?

pOH = 14.00 – 8.76 = 5.24 $\rightarrow$ $[OH^{1-}] = [C_6H_5NH_3^{1+}] = 10^{-pOH} = 10^{-5.24} = 5.8 \times 10^{-6}$ M

	$C_6H_5NH_2$	+	H_2O	$\rightleftharpoons$	$C_6H_5NH_3^{1+}$	+	OH^{1-}
Eq	0.083				5.8×10^{-6}		5.8×10^{-6} M

$K_b = \frac{[C_6H_5NH_3^{1+}][OH^{1-}]}{[C_6H_5NH_2]} = \frac{(5.8\times10^{-6})^2}{0.083} = 4.1\times10^{-10}$ $\rightarrow$ $pK_b = -\log 4.1 \times 10^{-5} = 9.39$

72. How many grams of KCN are required to prepare 250. mL of a pH = 11.15 solution.

pOH = 14.00 – 11.15 = 2.85 $\rightarrow$ $[OH^{1-}] = [CN^{1-}] = 10^{-pOH} = 10^{-2.85} = 0.0014$ M

	CN^{1-}	+	H_2O	$\rightleftharpoons$	HCN	+	OH^{1-}
Eq	$c_o - 0.0014$				0.0014		0.0014

$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.0\times10^{-10}} = 2.5\times10^{-5} = \frac{(0.0014)^2}{c_o - 0.0014} \Rightarrow c_o = \frac{(0.0014)^2}{2.5\times10^{-5}} + 0.0014 = 0.080$ M

$0.25\text{ L}\times\frac{0.080\text{ mol}}{\text{L}}\times\frac{65.1\text{ g KCN}}{\text{mol}} = 1.3$ g KCN

73. What percent of the ammonia molecules in a 0.12-M solution have reacted to produce ammonium ions?

Modify Equation 6.6 for bases. $\% = \sqrt{\frac{K_b}{c_o}}\times100\% = \sqrt{\frac{1.8\times10^{-5}}{0.12}}\times100\% = 1.2\%$ (less than 5% so assumption valid)

74. What percent of the acetate ions in a 0.060-M solution of potassium acetate react to produce acetic acid molecules?

Modify Equation 6.6 for bases. Carrying extra figures in the K_b value in the calculation.

$\% = \sqrt{\frac{K_b}{c_o}}\times100\% = \sqrt{\frac{5.56\times10^{-10}}{0.060}}\times100\% = 9.6\times10^{-3}$ % (less than 5% so assumption valid)

75. What are the concentrations of all P containing species in 0.084 M K_3PO_4? What is the pH of the solution?

1) $PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^{1-}$ $K = K_w/K_a = 1.0\times10^{-14}/4.8\times10^{-13} = 0.021$; Let $x = [HPO_4^{2-}]=[OH^{1-}]$ & $0.084-x = [PO_4^{3-}]$

$\frac{x^2}{0.084-x} = 0.021$; $x^2 + 0.021x - 1.75\times10^{-3} = 0$

$x = \frac{-0.021 + \sqrt{(0.021)^2 - 4(1)(-1.75\times10^{-3})}}{2(1)} = 0.033\text{ M} = [OH^{1-}] = [HPO_4^{1-}]$

$[PO_4^{3-}] = 0.084 - 0.033 = 0.051$ M

2) $HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^{1-} + OH^{1-}$ $K_2 = K_w/K_a = 1.0\times10^{-14}/6.2\times10^{-8} = 1.6\times10^{-7}$

Small K, so assume x is negligible, which means that $[H_2PO_4^{1-}] = K_2 = 1.6\times10^{-7}$ M

3) $H_2PO_4^{2-} + H_2O \rightleftharpoons H_3PO_4 + OH^{1-}$ $K_3 = 1.0\times10^{-14}/7.5\times10^{-3} = 1.3\times10^{-12}$; $[OH^{1-}] = 0.033$ M & $[H_2PO_4^{1-}] = 1.6\times10^{-7}$ M

$$1.3\times10^{-12} = \frac{[H_3PO_4](0.033)}{1.6\times10^{-7}}; \quad [H_3PO_4] = \frac{(1.3\times10^{-12})(1.6\times10^{-7})}{0.033} = 6.5\times10^{-18}\ M$$

pOH = -log(0.033) = 1.48; pH = 14.00 – 1.48 = 12.52

76. What are the concentrations of all carbon-containing species in 0.041-M K_2CO_3?

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^{1-} + OH^{1-}$ $K_1 = K_w/K_a = 1.0x10^{-14}/4.7x10^{-11} = 2.1x10^{-4}$; Let x = $[HCO_3^{1-}]=[OH^{1-}]$ & 0.041-x = $[CO_3^{2-}]$

$$\frac{x^2}{0.041-x} = 2.1\times10^{-4}; \qquad x^2 + 2.1\times10^{-4}\ x - 8.7\times10^{-6} = 0$$

$$x = \frac{-2.1\times10^{-4} + \sqrt{(2.1\times10^{-4})^2 - 4(1)(-8.7\times10^{-6})}}{2(1)} = 0.0028\ M = [OH^{1-}] = [HCO_3^{1-}]$$

$[CO_3^{2-}]$ = 0.041 - 0.003 = 0.038 M

$HCO_3^{1-} + H_2O \rightleftharpoons H_2CO_3 + OH^{1-}$ $K_2 = 1.0x10^{-14}/4.3x10^{-7} = 2.3x10^{-8}$

If x is negligible, $[HCO_3^{1-}]=[OH^{1-}]$ and $[H_2CO_3] = K_2 = 2.3x10^{-8}$ M

77. Define the term salt. Given an example of a neutral, a basic, and an acidic salt.

A salt is an ionic compound formed in an acid-base reaction. Neutral: $KClO_4$; Basic: KCN; Acidic: NH_4NO_3.

78. Explain why all anions are not bases in water. Give examples of two anions that are not bases for different reasons.

Some anions are protonated and are acids. Others conjugate bases of strong acids, which means that they are simply too weak to react with water. Examples: HSO_4^{1-}, NO_3^{1-}

79. Indicate whether each of the following is an acidic, a basic, or a neutral salt.

a) K_2SO_4	neutral	**b) K_2SO_3**	basic	**c) $KHSO_4$**	acidic
d) K_2CO_3	basic	**e) KOCl**	basic	**f) NH_4OCl**	basic ($K_b > K_a$)

80. Indicate whether each of the following is an acidic, a basic, or a neutral salt.

a) NH_4F	acidic ($K_a>K_b$)	**b) NH_4HSO_4**	acidic (two acids)	**c) $(NH_4)_3PO_4$**	basic ($K_b>K_a$)
d) KNO_3	neutral	**e) $(NH_4)_2CO_3$**	basic	**f) NaF**	basic

81. What is the pH of each of the following salt solutions?

a) 0.12 M NH_4Cl

NH_4^{1+} is acidic, while Cl^{1-} is neutral, so NH_4Cl is an acidic salt: $[H_3O^{1+}] = \sqrt{(5.6\times10^{10})(0.12)} = 8.2\times10^{-6}$ M; pH = 5.09

b) 0.096 M KCN

K^{1+} is neutral, but CN^{1-} is basic, so KCN is a basic salt: $K_b = \frac{1.0\times10^{-14}}{4.0\times10^{-10}} = 2.5\times10^{-5}$

$[OH^{1-}] = \sqrt{(2.5\times10^{-5})(0.096)} = 1.55\times10^{-3}$ M; pOH = 2.81; pH = 11.19

c) 0.10 M $KHSO_3$

K^{1+} is neutral, and HSO_3^{1-} is amphiprotic, so use Equation 6.12. pH = ½($pK_1 + pK_2$) = ½(1.82 + 7.00) = 4.41

82. What is the pH of each of the following salt solutions?

a) 0.12 M KCl

Both ions are neutral, so KCl is a neutral salt with pH = 7.0

b) 0.086 M KH_2PO_4

K^{1+} is neutral, and $H_2PO_4^{1-}$ is amphiprotic, so use Equation 6.12. pH = ½($pK_1 + pK_2$) = ½(2.12 + 7.21) = 4.67

c) 0.096 M Na_2SO_3

Na_2SO_3 is a basic salt. $K_b = \frac{1.0\times10^{-14}}{1.0\times10^{-7}} = 1.0\times10^{-7}$

$[OH^{1-}] = \sqrt{(1.7\times10^{-7})(0.088)} = 9.38\times10^{-5}$ M; pOH = 4.03; pH = 9.97