

## Chapter 6

### Acids and Bases

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**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)  $\text{OH}^{1-}$     $\text{H}_2\text{O}$                       b)  $\text{NO}_2^{1-}$     $\text{HNO}_2$                       c)  $\text{NH}_2^{1-}$     $\text{NH}_3$   
d)  $\text{PO}_4^{3-}$     $\text{HPO}_4^{2-}$                       e)  $\text{HSO}_3^{1-}$     $\text{H}_2\text{SO}_3$

**3. Indicate the conjugate base for each of the following:**

- a)  $\text{OH}^{1-}$     $\text{O}^{2-}$                       b)  $\text{H}_2\text{O}_2$     $\text{HO}_2^{1-}$                       c)  $\text{H}_2\text{PO}_4^{1-}$     $\text{HPO}_4^{2-}$   
d)  $\text{H}_3\text{O}^{1+}$     $\text{H}_2\text{O}$                       e)  $\text{H}_2\text{SO}_3$     $\text{HSO}_3^{1-}$

**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.  $\text{AlCl}_3$ ,  $\text{SO}_3$ , and  $\text{BF}_3$  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)  $\text{NaOH}$  yes                      b)  $\text{NaCl}$  not in water                      c)  $\text{CH}_3\text{OH}$  no  
d)  $\text{KCN}$  yes                      e)  $\text{KH}_2\text{PO}_4$  yes

**8. Which of the following are Brønsted acids?**

- a)  $\text{HClO}$  yes                      b)  $\text{CaH}_2$  no                      c)  $\text{CH}_3\text{CO}_2\text{H}$  yes  
d)  $\text{KHSO}_3$  yes                      e)  $\text{NH}_4\text{Cl}$  yes

**9. Explain how the reaction  $\text{Ag}^{1+} + \text{Cl}^{1-} \rightarrow \text{AgCl}$  is a Lewis acid-base reaction. Is it a Brønsted acid-base reaction?**

$\text{Ag}^{1+}$  is a Lewis acid that accepts a lone pair on  $\text{Cl}^{1-}$  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  $K \ll 1$ .**

- a) **Hydrochloric acid and aqueous sodium hydroxide are mixed.**  
 $\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$  (strong acid + weak acid)
- b) **Aqueous potassium fluoride is added to perchloric acid.**  
 $\text{F}^{1-} + \text{H}_3\text{O}^{1+} \rightarrow \text{HF} + \text{H}_2\text{O}$  (weak base + strong acid)
- c) **Aqueous  $\text{NH}_4\text{Cl}$  is added to aqueous  $\text{KHSO}_4$ .**  
 $\text{NH}_4^{1+} + \text{HSO}_4^{1-} \rightarrow$  no reaction ( $\text{HSO}_4^{1-}$  is much too weak a base to react with  $\text{NH}_4^{1+}$ )
- d) **Aqueous ammonia is added to hydrofluoric acid.**  
 $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^{1+} + \text{F}^{1-}$  (weak acid + weak base, but produced acid is weaker than reacting acid)
- e)  **$\text{HNO}_2$  is added to aqueous  $\text{KF}$ .**  
 $\text{HNO}_2 + \text{F}^{1-} \rightarrow \text{NO}_2^{1-} + \text{HF}$  (weak acid + weak base, produced acid and reacting acid of similar strengths)

**11. Write Brønsted acid-base reactions or indicate no reaction if  $K \ll 1$ .**

- a) **Aqueous sodium sulfate is added to hydrobromic acid.**  
 $\text{SO}_4^{2-} + \text{H}_3\text{O}^{1+} \rightarrow \text{HSO}_4^{1-} + \text{H}_2\text{O}$  (weak base + strong acid)
- b) **Aqueous  $\text{NH}_4\text{Cl}$  and aqueous  $\text{KF}$  are mixed.**  
 $\text{NH}_4^{1+} + \text{F}^{1-} \rightarrow$  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.**  
 $\text{CN}^{1-} + \text{H}_2\text{SO}_3 \rightarrow \text{HSO}_3^{1-} + \text{HCN}$
- d) **Acetic acid and aqueous sodium hypochlorite are mixed.**  
 $\text{CH}_3\text{COOH} + \text{OCl}^{1-} \rightarrow \text{CH}_3\text{COO}^{1-} + \text{HOCl}$  (produced acid is weaker than reacting acid)

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- e) **Hydrogen sulfide is bubbled into water.**

$\text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow$  no reaction (this is the  $K_a$  reaction of a weak acid and the extent is very small)

12. **Explain why  $\text{HClO}_4$  is a strong acid, but  $\text{HClO}$  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  $\text{HClO}_4$  and only +1 in  $\text{HClO}$ . The higher oxidation state removes electron density from the O-H bond and makes the acid stronger.

13. **Explain why  $\text{HCl}$  is a strong acid, but  $\text{HF}$  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?**

$\text{H}_2\text{CO}_3$  is strong enough to protonate  $\text{PO}_4^{3-}$  and  $\text{HPO}_4^{2-}$ , but it is too weak to react with  $\text{H}_2\text{PO}_4^{1-}$ . Thus, most of the phosphorus is in the form of  $\text{H}_2\text{PO}_4^{1-}$ .

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?**

$\text{NH}_3$  is strong enough to remove a proton from  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^{1-}$ , but it is too weak to react with  $\text{HPO}_4^{2-}$ . Therefore, the predominant phosphorus containing species is  $\text{HPO}_4^{2-}$ .

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  $\text{OH}^{1-}$ ,  $\text{NH}_2^{1-}$ , and  $\text{HSO}_3^{1-}$ , where only  $\text{HSO}_3^{1-}$  would be amphiprotic in water because the bases  $\text{O}^{2-}$  and  $\text{NH}_2^{2-}$  are far too strong to exist in water. The amphiprotic substances in Exercise 3 are  $\text{OH}^{1-}$  and  $\text{H}_2\text{PO}_4^{1-}$ . As above,  $\text{OH}^{1-}$  is not amphiprotic in water because it cannot function like an acid to produce  $\text{O}^{2-}$  in water.

17. **What is an *autoionization* reaction? Write the chemical equation for the autoionization of ammonia.  $\text{H}_3\text{O}^{1+}$  and  $\text{OH}^{1-}$  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  $\text{NH}_3 + \text{NH}_3 \rightarrow \text{NH}_2^{1-} + \text{NH}_4^{1+}$ . The strongest acid that can exist in liquid ammonia is  $\text{NH}_4^{1+}$  and the strongest base is  $\text{NH}_2^{1-}$ .

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

All of these problems can be solved using the following equations:  $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}}$  &  $[\text{OH}^{1-}] = \frac{K_w}{[\text{H}_3\text{O}^{1+}]}$

- a) **rainwater; pH = 5.3**

$$[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-5.3} = 5 \times 10^{-6} \text{ M} \rightarrow [\text{OH}^{1-}] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^{1+}]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-6}} = 2.0 \times 10^{-9} \text{ M}$$

- b) **household ammonia; pH = 11.9**

$$[\text{H}_3\text{O}^{1+}] = 1 \times 10^{-12} \text{ M} \quad [\text{OH}^-] = 8 \times 10^{-3} \text{ M}$$

- c) **vinegar; pH = 2.7**

$$[\text{H}_3\text{O}^{1+}] = 2 \times 10^{-3} \text{ M} \quad [\text{OH}^-] = 5 \times 10^{-12} \text{ M}$$

- d) **seawater; pH = 7.6**

$$[\text{H}_3\text{O}^{1+}] = 3 \times 10^{-8} \text{ M} \quad [\text{OH}^-] = 4 \times 10^{-7} \text{ M}$$

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

- a) **detergent; pH = 10.3**

$$[\text{H}_3\text{O}^{1+}] = 5 \times 10^{-11} \text{ M} \quad [\text{OH}^-] = 2 \times 10^{-4} \text{ M}$$

- b) **stomach acid; pH = 2.4**

$$[\text{H}_3\text{O}^{1+}] = 4 \times 10^{-3} \text{ M} \quad [\text{OH}^-] = 3 \times 10^{-12} \text{ M}$$

- c) **beer; pH = 4.2**

$$[\text{H}_3\text{O}^{1+}] = 6 \times 10^{-5} \text{ M} \quad [\text{OH}^-] = 2 \times 10^{-10} \text{ M}$$

- d) **milk of magnesia; pH = 10.5**

$$[\text{H}_3\text{O}^{1+}] = 3 \times 10^{-11} \text{ M} \quad [\text{OH}^-] = 3 \times 10^{-4} \text{ M}$$

20. **Determine the  $\text{p}K_a$  of each of the following acids:**

- a) **hypoiodous acid**

$\text{HOI}$

$$K_a = 2.3 \times 10^{-11}$$

$$\text{p}K_a = -\log(2.3 \times 10^{-11}) = 10.64$$

- b) **iodic acid**

$\text{HIO}_3$

$$K_a = 0.16$$

$$\text{p}K_a = -\log(0.16) = 0.80$$

**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        | $C_6H_5OH$     | $pK_a = 10.00$ | $K_a = 10^{-10.00} = 1.0 \times 10^{-10}$ |
| 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  | $pK_a = 14.00 - 8.37 = 5.63$  | $K_a = 10^{-5.63} = 2.3 \times 10^{-6}$   |
| b) 12.66 | $pK_a = 14.00 - 12.66 = 1.34$ | $K_a = 10^{-1.34} = 4.6 \times 10^{-2}$   |
| c) 0.22  | $pK_a = 14.00 - 0.22 = 13.78$ | $K_a = 10^{-13.78} = 1.7 \times 10^{-14}$ |

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

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

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

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

**30.\* What is the pH of  $1.0 \times 10^{-8} \text{ M HCl}$  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  $1.0 \times 10^{-8} \text{ M HCl}$



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

- a) **0.57 M NaOH**       $\text{pOH} = -\log 0.57 = 0.24$        $\text{pH} = 14.00 - 0.24 = 13.76$   
 b)  **$1.3 \times 10^{-4}$  M HNO<sub>3</sub>**       $\text{pH} = -\log (1.3 \times 10^{-4}) = 3.89$   
 c) **2.1 M KOH**       $\text{pOH} = -\log 2.1 = -0.32$        $\text{pH} = 14.00 + 0.32 = 14.32$

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,

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

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  $1.0 \times 10^{-4}$  M. Using the dilution expression from Chapter 2, we solve for the final volume,

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

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?

$$[\text{H}_3\text{O}^{1+}] = 10^{-3.84} = 1.5 \times 10^{-4} \text{ M}$$

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

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 mL?

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

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

$$[\text{H}_3\text{O}^{1+}] = \frac{24.2 \text{ mmol H}_3\text{O}^{1+}}{653 \text{ mL}} = 0.0371 \text{ M}; \text{pH} = -\log (0.0371) = 1.430$$

43. How many grams of Ba(OH)<sub>2</sub> would have to be dissolved in water to prepare 500.0 mL of a pH= 9.80 solution?

$$\text{pOH} = 14.00 - 9.80 = 4.20; [\text{OH}^{1-}] = 10^{-4.20} = 6.3 \times 10^{-5} \text{ M}$$

$$0.5000 \text{ L solution} \times \frac{6.3 \times 10^{-5} \text{ mol OH}^{1-}}{1 \text{ L solution}} \times \frac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol OH}^{1-}} \times \frac{171.3 \text{ g Ba(OH)}_2}{1 \text{ mol Ba(OH)}_2} = 2.8 \times 10^{-3} \text{ g} = 2.8 \text{ mg}$$

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

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

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

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

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b)  $2.0 \times 10^{-4} \text{ M H}_2\text{S}$   $\sqrt{\frac{1.0 \times 10^{-7}}{2.0 \times 10^{-4}}} \times 100\% = 2.2\%$  approximation is valid

c)  $0.10 \text{ M HNO}_2$   $\sqrt{\frac{4.0 \times 10^{-4}}{0.10}} \times 100\% = 6.3\%$  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  $\text{pK}_a$  of the acid into its  $\text{K}_a$ .

a)  $0.80 \text{ M cyanic acid (HCNO, pK}_a = 3.46)$

$$\text{K}_a = 10^{-3.46} = 3.5 \times 10^{-4} \quad \sqrt{\frac{3.5 \times 10^{-4}}{0.80}} \times 100\% = 2.1\% \quad \text{approximation is valid}$$

b)  $4.4 \times 10^{-3} \text{ M hydrazoic acid (HN}_3, \text{pK}_a = 4.6)$

$$\text{K}_a = 10^{-4.6} = 3 \times 10^{-5} \quad \sqrt{\frac{3 \times 10^{-5}}{4.4 \times 10^{-3}}} \times 100\% = 8\% \quad \text{approximation is NOT valid}$$

c)  $3.0 \text{ M arsenic acid (H}_3\text{AsO}_4, \text{pK}_a = 2.26)$

$$\text{K}_a = 10^{-2.26} = 5.5 \times 10^{-3} \quad \sqrt{\frac{5.5 \times 10^{-3}}{3.0}} \times 100\% = 4.3\% \quad \text{approximation is valid}$$

48. Calculate the pH of a  $0.25 \text{ M phenol (C}_6\text{H}_5\text{OH, K}_a = 1.0 \times 10^{-10})$ , which is often used as an antiseptic.

The acid dissociation reaction of phenol is:

	$\text{C}_6\text{H}_5\text{OH}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^{1+}$	+	$\text{C}_6\text{H}_5\text{O}^{1-}$
Initial	0.25				0		0
$\Delta$	-x				+x		+x
Equilibrium	$0.25 - x$				+x		+x

$$\text{K}_a = \frac{[\text{H}_3\text{O}^{1+}][\text{A}^{1-}]}{[\text{HA}]} = 1.0 \times 10^{-10} = \frac{x^2}{0.25-x} = \frac{x^2}{0.25}$$

$\text{K}_a$  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.

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

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.

$$\frac{4.5 \text{ g CH}_3\text{COOH}}{100 \text{ g sol'n}} \times \frac{1 \text{ mol CH}_3\text{COOH}}{60.054 \text{ g CH}_3\text{COOH}} \times \frac{1.0 \text{ g sol'n}}{1.0 \text{ mL sol'n}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.75 \text{ M CH}_3\text{COOH}$$

Next, set up the dissociation reaction:

	$\text{CH}_3\text{COOH}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CH}_3\text{COO}^{1-}$	+	$\text{H}_3\text{O}^{1+}$
Initial:	0.75		-		0		0
$\Delta$	-x				+x		+x
Final:	$0.75 - x$				x		x

$$\text{K}_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.75-x} = 1.8 \times 10^{-5}; \text{ from Appendix H;}$$

$\text{K}_a$  is small, so we can simplify the above relationship

$$\text{K}_a = 1.8 \times 10^{-5} = \frac{x^2}{0.75}, \text{ so } x = [\text{H}_3\text{O}^{1+}] = \sqrt{\text{K}_a c} = \sqrt{(1.8 \times 10^{-5})(0.75)} = 3.7 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.44 \text{ when extra figures are kept from previous calculations}$$

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.

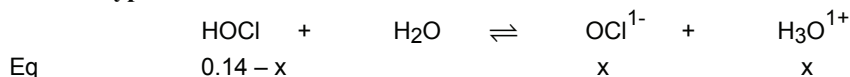
$$\text{Calculate the disassociation constant, } K_a: K_a = \frac{(1.4 \times 10^{-3})^2}{0.029} = 7.0 \times 10^{-5} \quad pK_a = -\log K_a = -\log(7.0 \times 10^{-5}) = 4.16$$

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

$$pK_b = pK_w - pK_a = 14.00 - 4.16 = 9.84$$

$$K_b = 10^{-pK_b} = 1.4 \times 10^{-10}$$

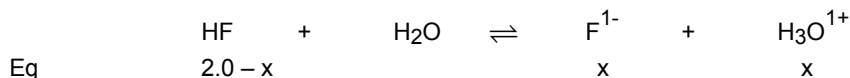
51. What is the hypochlorite ion concentration in a 0.14 M-solution of HOCl? What is the pH of the solution?



Assume x is negligible, then  $x = [\text{OCl}^{1-}] = \sqrt{K_a c} = \sqrt{(3.5 \times 10^{-8})(0.14)} = 7.0 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^{1+}]$

$$\text{pH} = -\log[\text{H}_3\text{O}^{1+}] = -\log 7.0 \times 10^{-5} = 4.15$$

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



Assume x is negligible, then  $x = [\text{F}^{1-}] = \sqrt{(7.2 \times 10^{-4})(2.0)} = 0.038 \text{ M}$ , which is negligible

53. What is the pH of 0.044 M HF?

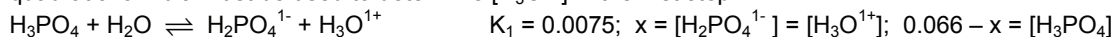
$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{1+} + \text{F}^{1-}$   $K = 7.2 \times 10^{-4}$  If  $x = [\text{H}_3\text{O}^{1+}] = [\text{F}^{1-}]$ , then  $[\text{HF}] = 0.044 - x$ . Setup  $K_a$  expression and solve for x.

$$\frac{x^2}{0.044 - x} = 7.2 \times 10^{-4}; \quad x^2 + 7.2 \times 10^{-4} x - 3.2 \times 10^{-5} = 0$$

$$x = \frac{-7.2 \times 10^{-4} + \sqrt{(7.2 \times 10^{-4})^2 - 4(1)(-3.2 \times 10^{-5})}}{2(1)} = 5.3 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^{1+}]; \text{pH} = -\log(5.3 \times 10^{-3}) = 2.28$$

54. What is the phosphate ion concentration in 0.066 M  $\text{H}_3\text{PO}_4$ ?

Phosphate is not produced until the third dissociation, which includes  $\text{H}_3\text{O}^{1+}$  and  $\text{HPO}_4^{2-}$ . We determine  $[\text{H}_3\text{O}^{1+}]$  from the first ionization and use the fact that  $[\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ M}$ . Phosphoric is much stronger than acetic, so the quadratic formula must be used to determine  $[\text{H}_3\text{O}^{1+}]$  in the first step.



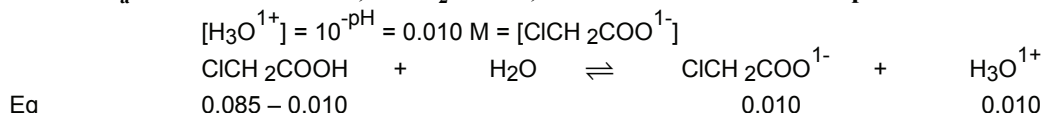
$$\frac{x^2}{0.066 - x} = 0.0075; \quad x^2 + 0.0075 x - 5.0 \times 10^{-4} = 0$$

$$x = \frac{-0.0075 + \sqrt{(0.0075)^2 - 4(1)(-5.0 \times 10^{-4})}}{2(1)} = 0.019 \text{ M} = [\text{H}_3\text{O}^{1+}]$$

The third dissociation:  $\text{HPO}_4^{1-} + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{O}^{1+}$  At equilibrium,  $[\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ M}$  and  $[\text{H}_3\text{O}^{1+}] = 0.019 \text{ M}$

$$K_3 = 4.8 \times 10^{-13} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^{1+}]}{[\text{HPO}_4^{2-}]} = \frac{[\text{PO}_4^{3-}](0.019)}{6.2 \times 10^{-8}}; \quad [\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.019} = 1.6 \times 10^{-18} \text{ M}$$

55. What is the  $K_a$  of chloroacetic acid,  $\text{ClCH}_2\text{COOH}$ , if a 0.085-M solution has a pH of 2.00?

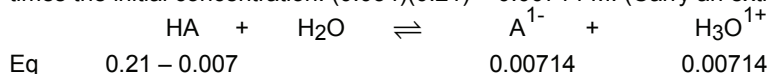


$$K_a = \frac{[\text{ClCH}_2\text{COO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{ClCH}_2\text{COOH}]} = \frac{(0.010)(0.010)}{0.075} = 1.3 \times 10^{-3}$$

# Acids and Bases

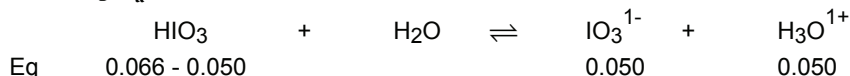
## 56. What is the $K_a$ of an acid if a 0.21-M solution is 3.4% dissociated?

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.)



$$K_a = \frac{[\text{A}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HA}]} = \frac{(0.00714)(0.00714)}{0.21} = 2.5 \times 10^{-4}$$

## 57. What is the $pK_a$ of iodic acid if the iodate ion concentration in a 0.066-M solution of $\text{HIO}_3$ is 0.050 M?



$$K_a = \frac{[\text{IO}_3^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HIO}_3]} = \frac{(0.050)(0.050)}{0.016} = 0.16; \quad pK_a = -\log 0.16 = 0.81$$

## 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.

$$K_a = 10^{-pK_a} = 10^{-4.86} = 1.4 \times 10^{-5} \quad \sqrt{\frac{K_a}{c_0}} \times 100\% = \sqrt{\frac{1.4 \times 10^{-5}}{0.048}} \times 100\% = 1.7\%$$

## 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.

$$K_a = 10^{-pK_a} = 10^{-3.89} = 1.3 \times 10^{-4} \quad \sqrt{\frac{K_a}{c_0}} \times 100\% = \sqrt{\frac{1.3 \times 10^{-4}}{0.26}} \times 100\% = 2.2\%$$

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

Apply Equation 6.7:  $\% = \sqrt{\frac{0.17}{0.15}} \times 100\% = 107\%$ . Clearly iodic acid is too strong and Equation 6.7 cannot be used.

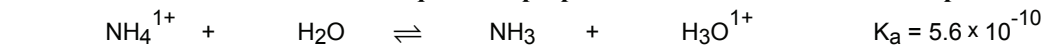
Instead, we must use the quadratic formula to solve for the amount that reacts.

$\text{HIO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{IO}_3^{1-} + \text{H}_3\text{O}^{1+}$   $K_a = 0.17$ . Let  $x = [\text{IO}_3^{1-}] = [\text{H}_3\text{O}^{1+}]$  then  $[\text{HIO}_3] = 0.15 - x$

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

$$\% = \frac{x}{c_0} \times 100\% = \frac{0.096}{0.15} \times 100\% = 64\%$$

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



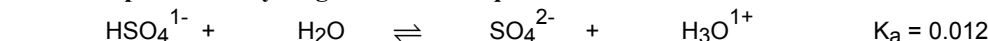
$$[\text{NH}_3] = [\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-4.62} = 2.4 \times 10^{-5} \text{ M} \quad [\text{NH}_4^{1+}] = c - 2.4 \times 10^{-5} \sim c$$

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

$$K = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^{1+}]}{[\text{NH}_4^{1+}]} = \frac{(2.4 \times 10^{-5})(2.4 \times 10^{-5})}{c} \quad \text{or } c = \frac{(2.4 \times 10^{-5})(2.4 \times 10^{-5})}{5.6 \times 10^{-10}} = 1.03 \text{ M}$$

500 mL of solution must contain  $(0.50 \text{ L})(1.03 \text{ mol/L}) = 0.51 \text{ mol}$ , which has a mass of  $0.51 \text{ mol} \times 53.5 \text{ g/mol} = 27.5 \text{ g}$  (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?



$$[\text{SO}_4^{2-}] = [\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-2.50} = 3.2 \times 10^{-3} \text{ M} \quad [\text{HSO}_4^{1-}] = c_0 - 3.2 \times 10^{-3} = c'$$

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

$$K = 0.012 = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{HSO}_4^{1-}]} = \frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{[\text{HSO}_4^{1-}]} \quad \text{or } [\text{HSO}_4^{1-}] = \frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{0.012} = 8.3 \times 10^{-4} \text{ M}$$

The question asks for the makeup amount.  $c_0 = [\text{HSO}_4^{1-}] + x = 3.2 \times 10^{-3} + 0.8 \times 10^{-3} = 4.0 \times 10^{-3} \text{ M}$

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

63. Vitamin C is ascorbic acid,  $\text{H}_2\text{C}_6\text{H}_8\text{O}_6$ . Calculate the pH,  $[\text{H}_2\text{C}_6\text{H}_8\text{O}_6]$ ,  $[\text{HC}_6\text{H}_7\text{O}_6^-]$  and  $[\text{C}_6\text{H}_6\text{O}_6^{2-}]$  in a 0.075-M solution of ascorbic acid.

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

	$\text{C}_6\text{H}_8\text{O}_6$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HC}_6\text{H}_7\text{O}_6^-$	+	$\text{H}_3\text{O}^{1+}$
Initial:	0.075 M		-		0		0
$\Delta$	-x		-		+x		+x
Final:	0.075 - x		0		x		x

Assuming the extent of reaction is negligible,

$[\text{H}_3\text{O}^{1+}] = [\text{HC}_6\text{H}_7\text{O}_6^-] = \sqrt{K_a c_0} = \sqrt{(8.0 \times 10^{-5})(0.075)} = 0.0024 \text{ M}$ , which is less than 5% of 0.075 M, so the approximation is acceptable.  $[\text{C}_6\text{H}_8\text{O}_6] = 0.075 - 0.0024 = 0.073 \text{ M}$ .  $\text{pH} = -\log(0.0024) = 2.66$

The concentration of the ion produced in the second ionization equals  $K_2$ , so the final concentration is  $[\text{C}_6\text{H}_6\text{O}_6^{2-}] = 1.6 \times 10^{-12} \text{ M}$ .

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  $K_1 = 5.9 \times 10^{-2}$  and  $K_2 = 6.4 \times 10^{-5}$ .

Consider oxalic acid as a generic diprotic acid,  $\text{H}_2\text{A}$ .

	$\text{H}_2\text{A}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^{1+}$	+	$\text{HA}^{1-}$
Initial	0.25				0		0
$\Delta$	-x				+x		+x
Equilibrium	0.25 - x				+x		+x

$$K_1 = \frac{[\text{H}_3\text{O}^{1+}][\text{HA}^{1-}]}{[\text{H}_2\text{A}]} = 5.9 \times 10^{-2} = \frac{x^2}{0.25 - x} \quad \text{or} \quad x^2 + 0.059x - 0.147 = 0$$

Use the *quadratic formula* to calculate the value of x:  $x = \frac{-0.059 + \sqrt{(0.059)^2 - 4 \times 1 \times -0.147}}{2 \times 1} = 0.096 \text{ M}$

$$[\text{H}_3\text{O}^{1+}] = [\text{HA}^{1-}] = 0.096 \text{ M} \quad \text{and} \quad [\text{H}_2\text{A}] = 0.25 - 0.096 = 0.15 \text{ M}$$

For the second equilibrium

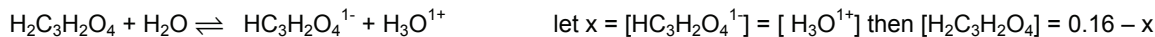
	$\text{HA}^{1-}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^{1+}$	+	$\text{A}^{2-}$
Initial	0.096				0.096		0
$\Delta$	-x				+x		+x
Equilibrium	0.096 - x				0.096 + x		+x

$$K_2 = \frac{[\text{A}^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{HA}^{1-}]} = 6.4 \times 10^{-5} = \frac{(0.096 + x)x}{0.096 - x}$$

If x is negligible compared to 0.096, then  $x = K_2 = 6.4 \times 10^{-5} \text{ M}$ .

$[\text{A}^{2-}] = 6.4 \times 10^{-5} \text{ M}$ ,  $[\text{HA}^{1-}] = [\text{H}_3\text{O}^{1+}] = 0.096 \text{ M}$ , so  $\text{pH} = 1.02$

65. What are concentrations of all species in a 0.16-M solution of malonic acid ( $\text{H}_2\text{C}_3\text{H}_2\text{O}_4$ )?  $K_1 = 1.5 \times 10^{-3}$  and  $K_2 = 2.0 \times 10^{-6}$



$$\frac{x^2}{0.16 - x} = 0.0015; \quad x^2 + 0.0015x - 2.4 \times 10^{-4} = 0$$

$$x = \frac{-0.0015 + \sqrt{(0.0015)^2 - 4(1)(-2.4 \times 10^{-4})}}{2(1)} = 0.015 \text{ M} = [\text{H}_3\text{O}^{1+}] = [\text{HC}_3\text{H}_2\text{O}_4^-]$$

$$[\text{H}_2\text{C}_3\text{H}_2\text{O}_4] = 0.16 - 0.015 = 0.15 \text{ M}; \quad [\text{C}_3\text{H}_2\text{O}_4^{2-}] = K_2 = 2.0 \times 10^{-6} \text{ M}$$

The concentration of  $\text{C}_3\text{H}_2\text{O}_4^{2-}$  produced in the second step is negligible compared to 0.015 M, so the assumption that  $[\text{C}_3\text{H}_2\text{O}_4^{2-}] = K_2$  is valid.

66. Calculate the pH of a 0.50-M solution of pyridine ( $\text{C}_6\text{H}_5\text{N}$ ,  $K_b = 1.7 \times 10^{-9}$ ).

Set up Reaction Table. Note the lone pair on the nitrogen atom is basic ( $\text{Py} = \text{C}_6\text{H}_5\text{N}$  and  $\text{HPy}^{1+} = \text{C}_6\text{H}_5\text{NH}^{1+}$ ).

	Py	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HPy}^{1+}$	+	$\text{OH}^{1-}$
Initial:	0.50		-		0		0
$\Delta$	-x				+x		+x
Final:	0.50 - x				x		x

## Acids and Bases

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

Again, this problem can be simplified to:  $K_b = \frac{[x][x]}{[0.50]}$  or  $x = [\text{OH}^{1-}] = \sqrt{K_b c} = \sqrt{(1.7 \times 10^{-9})(0.50)} = 2.9 \times 10^{-5} \text{ M}$

$$\text{pOH} = -\log(2.9 \times 10^{-5}) = 4.54; \text{pH} = 14.00 - 4.54 = 9.46$$

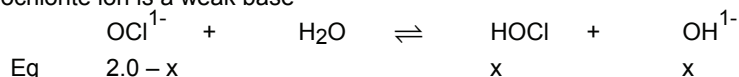
### 67. The hypochlorite ion is the active ingredient in bleach.

#### 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



Assume that  $[\text{OCl}^{1-}] = 2.0 \text{ M}$  at equilibrium because  $c_0$  is very large and  $\text{OCl}^{1-}$  is a weak base.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7} = \frac{[\text{HOCl}][\text{OH}^{1-}]}{[\text{OCl}]} = \frac{x^2}{2.0}$$

$$x = \sqrt{(2.9 \times 10^{-7})(2.0)} = 7.6 \times 10^{-4} \text{ M} = [\text{HOCl}], \text{ which is negligible compared to } 2.0 \text{ M.}$$

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

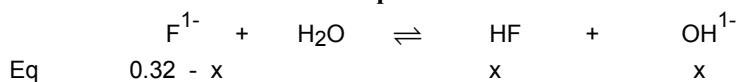
Determine the molar concentration of the NaOCl. Assuming a 100. g solution (also 100. mL solution since the density is 1.0 g/mL), 5.25% translates to 5.25 g.

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

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

$$[\text{OH}^{1-}] = \sqrt{K_b \times c_0} = \sqrt{(2.9 \times 10^{-7})(0.70)} = 4.5 \times 10^{-4} \text{ M, so } \text{pOH} = -\log [\text{OH}^{1-}] = 3.35 \text{ and } \text{pH} = 14.00 - 3.35 = 10.65$$

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



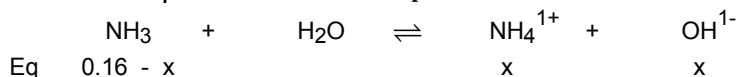
$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

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

$$[\text{HF}] = [\text{OH}^{1-}] = \sqrt{K_b c_0} = \sqrt{(1.4 \times 10^{-11})(0.32)} = 2.1 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log 2.1 \times 10^{-6} = 5.68, \text{ so } \text{pH} = 14.00 - 5.68 = 8.32$$

### 69. What are the $\text{NH}_4^{1+}$ concentration and pH of a 0.16-M solution of $\text{NH}_3$ ?



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

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

$$[\text{NH}_4^{1+}] = [\text{OH}^{1-}] = \sqrt{K_b c_0} = \sqrt{(1.8 \times 10^{-5})(0.16)} = 1.7 \times 10^{-3} \text{ M (which is less than 5% reaction)}$$

$$\text{pOH} = -\log 1.7 \times 10^{-3} = 2.77, \text{ so } \text{pH} = 14.00 - 2.77 = 11.23$$

70. The pH of a 0.068-M solution of methyl amine ( $\text{CH}_3\text{NH}_2$ ) is 11.72.

a) What are the  $K_b$  and  $\text{p}K_b$  of methylamine?

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



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

$$[\text{OH}^{1-}] = [\text{CH}_3\text{NH}_3^{1+}] = 10^{-\text{pOH}} = 10^{-2.28} = 0.0052 \text{ M}$$

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

$$[\text{CH}_3\text{NH}_2] = c_0 - x = 0.068 - 0.005 = 0.063 \text{ M}$$

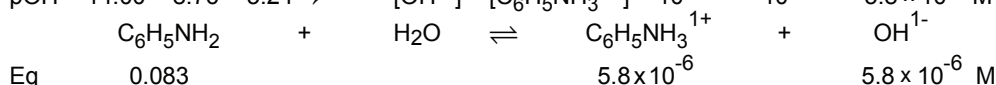
$$K_b = \frac{[\text{CH}_3\text{NH}_3^{1+}][\text{OH}^{1-}]}{[\text{CH}_3\text{NH}_2]} = \frac{[0.0053][0.0053]}{[0.063]} = 4.4 \times 10^{-4}; \quad \text{p}K_b = -\log K_b = 3.36$$

b) What are the  $K_a$  and  $\text{p}K_a$  of the methylammonium ion?

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

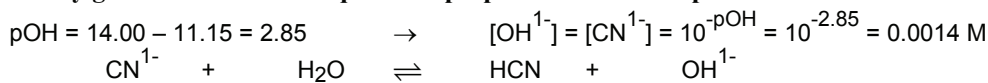
71. The pH of 0.083 M aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) is 8.76. What are its  $K_b$  and  $\text{p}K_b$ ?

$$\text{pOH} = 14.00 - 8.76 = 5.24 \rightarrow [\text{OH}^{1-}] = [\text{C}_6\text{H}_5\text{NH}_3^{1+}] = 10^{-\text{pOH}} = 10^{-5.24} = 5.8 \times 10^{-6} \text{ M}$$



$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^{1+}][\text{OH}^{1-}]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(5.8 \times 10^{-6})^2}{0.083} = 4.1 \times 10^{-10} \quad \rightarrow \quad \text{p}K_b = -\log 4.1 \times 10^{-5} = 9.39$$

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



$$\begin{array}{ccccccc} \text{Eq} & c_0 - 0.0014 & & & 0.0014 & & 0.0014 \\ K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5} = \frac{(0.0014)^2}{c_0 - 0.0014} \Rightarrow c_0 = \frac{(0.0014)^2}{2.5 \times 10^{-5}} + 0.0014 = 0.080 \text{ M} \end{array}$$

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

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

$$\text{Modify Equation 6.6 for bases. } \% = \sqrt{\frac{K_b}{c_0}} \times 100\% = \sqrt{\frac{1.8 \times 10^{-5}}{0.12}} \times 100\% = 1.2\% \text{ (less than 5\% so assumption valid)}$$

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.

$$\% = \sqrt{\frac{K_b}{c_0}} \times 100\% = \sqrt{\frac{5.56 \times 10^{-10}}{0.060}} \times 100\% = 9.6 \times 10^{-3} \% \text{ (less than 5\% so assumption valid)}$$

75. What are the concentrations of all P containing species in 0.084 M  $\text{K}_3\text{PO}_4$ ? What is the pH of the solution?

$$1) \text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^{1-} \quad K = K_w/K_a = 1.0 \times 10^{-14} / 4.8 \times 10^{-13} = 0.021; \quad \text{Let } x = [\text{HPO}_4^{2-}] = [\text{OH}^{1-}] \text{ \& } 0.084 - x = [\text{PO}_4^{3-}]$$

$$\frac{x^2}{0.084 - x} = 0.021; \quad x^2 + 0.021x - 1.75 \times 10^{-3} = 0$$

$$x = \frac{-0.021 + \sqrt{(0.021)^2 - 4(1)(-1.75 \times 10^{-3})}}{2(1)} = 0.033 \text{ M} = [\text{OH}^{1-}] = [\text{HPO}_4^{2-}]$$

$$[\text{PO}_4^{3-}] = 0.084 - 0.033 = 0.051 \text{ M}$$

$$2) \text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^{1-} + \text{OH}^{1-} \quad K_2 = K_w/K_a = 1.0 \times 10^{-14} / 6.2 \times 10^{-8} = 1.6 \times 10^{-7}$$

Small  $K$ , so assume  $x$  is negligible, which means that  $[\text{H}_2\text{PO}_4^{1-}] = K_2 = 1.6 \times 10^{-7} \text{ M}$

$$3) \text{H}_2\text{PO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_4 + \text{OH}^{1-} \quad K_3 = 1.0 \times 10^{-14} / 7.5 \times 10^{-3} = 1.3 \times 10^{-12}; \quad [\text{OH}^{1-}] = 0.033 \text{ M} \text{ \& } [\text{H}_2\text{PO}_4^{1-}] = 1.6 \times 10^{-7} \text{ M}$$

## Acids and Bases

$$1.3 \times 10^{-12} = \frac{[\text{H}_3\text{PO}_4](0.033)}{1.6 \times 10^{-7}}; \quad [\text{H}_3\text{PO}_4] = \frac{(1.3 \times 10^{-12})(1.6 \times 10^{-7})}{0.033} = 6.5 \times 10^{-18} \text{ M}$$

$$\text{pOH} = -\log(0.033) = 1.48; \quad \text{pH} = 14.00 - 1.48 = 12.52$$

### 76. What are the concentrations of all carbon-containing species in 0.041-M $\text{K}_2\text{CO}_3$ ?

$$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^{-} + \text{OH}^{-} \quad K_1 = K_w/K_a = 1.0 \times 10^{-14}/4.7 \times 10^{-11} = 2.1 \times 10^{-4}; \quad \text{Let } x = [\text{HCO}_3^{-}] = [\text{OH}^{-}] \text{ \& } 0.041 - x = [\text{CO}_3^{2-}]$$

$$\frac{x^2}{0.041 - x} = 2.1 \times 10^{-4}; \quad x^2 + 2.1 \times 10^{-4}x - 8.7 \times 10^{-6} = 0$$

$$x = \frac{-2.1 \times 10^{-4} + \sqrt{(2.1 \times 10^{-4})^2 - 4(1)(-8.7 \times 10^{-6})}}{2(1)} = 0.0028 \text{ M} = [\text{OH}^{-}] = [\text{HCO}_3^{-}]$$

$$[\text{CO}_3^{2-}] = 0.041 - 0.003 = 0.038 \text{ M}$$

$$\text{HCO}_3^{-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^{-} \quad K_2 = 1.0 \times 10^{-14}/4.3 \times 10^{-7} = 2.3 \times 10^{-8}$$

$$\text{If } x \text{ is negligible, } [\text{HCO}_3^{-}] = [\text{OH}^{-}] \text{ and } [\text{H}_2\text{CO}_3] = K_2 = 2.3 \times 10^{-8} \text{ M}$$

### 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:  $\text{KClO}_4$ ; Basic:  $\text{KCN}$ ; Acidic:  $\text{NH}_4\text{NO}_3$ .

### 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:  $\text{HSO}_4^{-}$ ,  $\text{NO}_3^{-}$

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

- a)  $\text{K}_2\text{SO}_4$  neutral                      b)  $\text{K}_2\text{SO}_3$  basic                      c)  $\text{KHSO}_4$  acidic  
d)  $\text{K}_2\text{CO}_3$  basic                      e)  $\text{KOCl}$  basic                      f)  $\text{NH}_4\text{OCl}$  basic ( $K_b > K_a$ )

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

- a)  $\text{NH}_4\text{F}$  acidic ( $K_a > K_b$ )                      b)  $\text{NH}_4\text{HSO}_4$  acidic (two acids)                      c)  $(\text{NH}_4)_3\text{PO}_4$  basic ( $K_b > K_a$ )  
d)  $\text{KNO}_3$  neutral                      e)  $(\text{NH}_4)_2\text{CO}_3$  basic                      f)  $\text{NaF}$  basic

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

#### a) 0.12 M $\text{NH}_4\text{Cl}$

$\text{NH}_4^{1+}$  is acidic, while  $\text{Cl}^{1-}$  is neutral, so  $\text{NH}_4\text{Cl}$  is an acidic salt:  $[\text{H}_3\text{O}^{1+}] = \sqrt{(5.6 \times 10^{-10})(0.12)} = 8.2 \times 10^{-6} \text{ M}$ ;  $\text{pH} = 5.09$

#### b) 0.096 M $\text{KCN}$

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

$$[\text{OH}^{1-}] = \sqrt{(2.5 \times 10^{-5})(0.096)} = 1.55 \times 10^{-3} \text{ M}; \quad \text{pOH} = 2.81; \quad \text{pH} = 11.19$$

#### c) 0.10 M $\text{KHSO}_3$

$\text{K}^{1+}$  is neutral, and  $\text{HSO}_3^{1-}$  is amphiprotic, so use Equation 6.12.  $\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) = \frac{1}{2}(1.82 + 7.00) = 4.41$

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

#### a) 0.12 M $\text{KCl}$

Both ions are neutral, so  $\text{KCl}$  is a neutral salt with  $\text{pH} = 7.0$

#### b) 0.086 M $\text{KH}_2\text{PO}_4$

$\text{K}^{1+}$  is neutral, and  $\text{H}_2\text{PO}_4^{1-}$  is amphiprotic, so use Equation 6.12.  $\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) = \frac{1}{2}(2.12 + 7.21) = 4.67$

#### c) 0.096 M $\text{Na}_2\text{SO}_3$

$\text{Na}_2\text{SO}_3$  is a basic salt.  $K_b = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}$

$$[\text{OH}^{1-}] = \sqrt{(1.7 \times 10^{-7})(0.088)} = 9.38 \times 10^{-5} \text{ M}; \quad \text{pOH} = 4.03; \quad \text{pH} = 9.97$$