

*Chapter 16*  
*Acid-Base Equilibria*

- Acids and bases are found in many common substances and are important in life processes.
- Group Work: Make a list of some common acids and bases. How do we know which is which?
- There are several models for what constitutes an acid or a base -- three models to be discussed.

*16.1 Acids and Bases: A Brief Review*

- |  |                            |
|--|----------------------------|
| • Acid:  | Base:                      |
| • tastes sour  | tastes bitter              |
| • stings skin  | feels slippery             |
| • corrosive to metals  |                            |
| • releases CO <sub>2</sub> from carbonates   |                            |
| • turns litmus red   | turns litmus blue          |
| • turns phenolphthalein colorless  | turns phenolphthalein pink |
| • React together to form a salt with loss of the characteristic acid/base properties |                            |

*Arrhenius Theory*

- Acid: substance that produces H<sup>+</sup> in aqueous solution
- Base: substance that produces OH<sup>-</sup> in aqueous solution
- Not realistic: H<sup>+</sup> has a radius of 10<sup>-13</sup> cm, which gives a very concentrated charge, so it associates with H<sub>2</sub>O as H(H<sub>2</sub>O)<sub>4</sub><sup>+</sup>, which we usually simplify to H<sub>3</sub>O<sup>+</sup> or H<sup>+</sup>(aq)
- OH<sup>-</sup> is also associated with H<sub>2</sub>O as OH(H<sub>2</sub>O)<sub>3</sub><sup>-</sup> which we usually write as OH<sup>-</sup>(aq).
- Limited to aqueous solutions, but we find acid-base behavior with other solvents as well.

*16.2 Bronsted-Lowrey Acids and Bases*

- Acid: donates a proton to another substance
- Base: accepts a proton from another substance
- Acids:
 
$$\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$

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

$$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{OH}^-(\text{aq}) + \text{HCO}_3^-(\text{aq})$$

*Acid-Base Neutralization Reaction*

- Transfer of a proton (hydrogen ion)

*Conjugate Acids and Bases*

- Pair of substances differing only by one H<sup>+</sup>

- $\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$   
acid 1    base 2    acid 2    base 1
- Acid-Base Neutralization
- $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l})$   
acid 1    base 2    acid 2    base 1
- Write a balanced equation showing how the following substances behave as acids in water and identify the conjugate acid-base pairs.
- $\text{HNO}_3$      $\text{HCO}_3^-$      $\text{H}_3\text{PO}_4$      $\text{H}_2\text{PO}_4^-$

#### *Amphoterism*

- Amphoteric substances can act as either an acid or a base.  $\text{H}_2\text{O}$  is the most important example.
- $\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- Other examples are  $\text{HCO}_3^-$  and  $\text{HSO}_3^-$
- $\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- $\text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- Another example is  $\text{Al}(\text{OH})_3$ , which can react with acid to give  $\text{Al}^{3+}(\text{aq})$ , or with base to give  $\text{Al}(\text{OH})_4^-(\text{aq})$ .

#### *Polyprotic Acids*

- Some acids can donate more than one proton.
- Mono-    di-    tri-    ...    poly-
- Diprotic:
- $\text{H}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + 2\text{H}_3\text{O}^+(\text{aq})$
- Not all H atoms are acidic. Example: acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$
- In oxoacids, the acidic hydrogens are bonded to oxygen.

#### *Polyprotic Acids*

- How many acidic hydrogens?
- $\text{H}_2\text{SO}_4$
- $\text{H}_3\text{PO}_4$
- $\text{H}_3\text{PO}_3$
- $\text{H}_3\text{PO}_2$
- $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$

#### *Acid Strengths*

- We can measure the relative tendency for acids to donate protons (usually relative to the solvent). Acids are rated from strong to weak.
- Strong acid: complete donation of proton to water
- $\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- Proton always transfers from the stronger acid to the stronger base to form a weaker acid and a weaker base.

*Strong Acid: HNO<sub>3</sub>*

- HNO<sub>3</sub> is completely dissociated into the ions, H<sub>3</sub>O<sup>+</sup> and NO<sub>3</sub><sup>-</sup>

*Acid Strengths*

- In the HCl example,
- acid HCl > H<sub>3</sub>O<sup>+</sup>
- base H<sub>2</sub>O > Cl<sup>-</sup>
- Any acid that is stronger than H<sub>3</sub>O<sup>+</sup> (the conjugate acid of the solvent) will dissociate completely to form H<sub>3</sub>O<sup>+</sup>
- H<sub>3</sub>O<sup>+</sup> is the strongest acid we can find in H<sub>2</sub>O; this is called the leveling effect of the solvent.
- Weak acid: partial donation of protons to water.
- HF(aq) + H<sub>2</sub>O(l) ⇌ H<sub>3</sub>O<sup>+</sup>(aq) + F<sup>-</sup>(aq)
- weaker weaker stronger stronger
- acid base acid base
- The reaction reaches a state of equilibrium in which the relative acid strengths determine the degree of dissociation.
- By examining the position of equilibrium, we can rank acids and bases.
- HF is only partially dissociated into H<sub>3</sub>O<sup>+</sup> and F<sup>-</sup>

## ACID STRENGTHS:

	Acid	Base	
Strongest acids	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	Weakest bases
	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	
	HI	I <sup>-</sup>	
	HBr	Br <sup>-</sup>	
	HCl	Cl <sup>-</sup>	
	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	
	<b>H<sub>3</sub>O<sup>+</sup></b>	<b>H<sub>2</sub>O</b>	
	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	
	H <sub>2</sub> SO <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	
	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	
	HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	
	HF	F <sup>-</sup>	
	CH <sub>3</sub> CO <sub>2</sub> H	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	
	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	
	H <sub>2</sub> S	HS <sup>-</sup>	
	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	
	HCN	CN <sup>-</sup>	
	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	
	HS <sup>-</sup>	S <sup>2-</sup>	
	<b>H<sub>2</sub>O</b>	<b>OH<sup>-</sup></b>	
Weakest acids	NH <sub>3</sub>	NH <sub>2</sub> <sup>-</sup>	Strongest bases
	OH <sup>-</sup>	O <sup>2-</sup>	

*Leveling Effect*

- All acids above  $\text{H}_3\text{O}^+$  in the table are strong acids, which dissociate completely in aqueous solution.
- All bases below  $\text{OH}^-$  in the table are strong bases, which dissociate completely in aqueous solution.
- The table can be used to make predictions, based on the principle that the stronger acid reacts with the stronger base to form a weaker acid and a weaker base.

*Predicting Acid-Base Reactions*

- $\text{HCl} + \text{HSO}_3^- \rightleftharpoons \text{H}_2\text{SO}_3 + \text{Cl}^-$   
 stronger acid    stronger base    weaker acid    weaker base
- We must also consider  $\text{H}_2\text{O}$  as a possible acid or base. Thus,  $\text{HNO}_3$  will transfer its proton to  $\text{H}_2\text{O}$ , not to  $\text{Cl}^-$  because  $\text{H}_2\text{O}$  is a stronger base than  $\text{Cl}^-$ .
- Write an equation showing the position of equilibrium for the following mixtures. Remember that  $\text{H}_2\text{O}$  can also be either an acid or a base.
- $\text{HSO}_4^-$  and  $\text{F}^-$
- $\text{HS}^-$  and  $\text{HCO}_3^-$

*16.3 Autoionization of Water*

- Water undergoes autoionization:
- $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
- $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  at  $24^\circ\text{C}$
- Called the ion product of water
- By convention,  $[\text{H}_2\text{O}]$  is omitted.
- In pure water,  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$
- Add an acid,  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$
- 0.10 M HCl (strong acid, completely ionized)
- $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$
- $(0.10)[\text{OH}^-] = 1.0 \times 10^{-14}$
- $[\text{OH}^-] = 1.0 \times 10^{-14} / 0.10 = 1.0 \times 10^{-13} \text{ M}$
- Add a base,  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$
- 0.010 M NaOH (strong base, completely ionized)
- $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$
- $[\text{H}_3\text{O}^+](0.010) = 1.0 \times 10^{-14}$
- $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 0.010 = 1.0 \times 10^{-12} \text{ M}$

*The pH Scale*

- pH scale defined to make it easier to refer to relative  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  values
- $\text{pH} = -\log [\text{H}_3\text{O}^+]$ ,  $\text{pOH} = -\log [\text{OH}^-]$
- $\text{pH} = 0$ ,  $[\text{H}_3\text{O}^+] = 1.0 \text{ M}$
- $\text{pH} = 14$ ,  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}$
- $\text{pH} = 7$ ,  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$
- $\text{pH} + \text{pOH} = 14 = \text{p}K_w$

- neutral:  $\text{pH} = \text{pOH} = 7$
- acidic:  $\text{pH} < 7$   $\text{pOH} > 7$
- basic:  $\text{pH} > 7$   $\text{pOH} < 7$

### *Measuring pH*

- litmus or pH paper
- color changes of indicators
- voltage generated by electrodes (pH meter)

### *Changes in pH with Dilution*

- pH for factors of 10 dilution?
- What is the pH of 1.0 M HCl?
- $\text{pH} = 0.00$
- What is the pH of 0.10 M HCl (a 1:10 dilution)?
- $\text{pH} = 1.00$
- What is the pH of 0.010 M HCl?
- $\text{pH} = 2.00$
- What is the pH of  $1.0 \times 10^{-3}$  M HCl?
- $\text{pH} = 3.00$
- What is the pH of  $1.0 \times 10^{-4}$  M HCl?
- $\text{pH} = 4.00$
- What is the pH of  $1.0 \times 10^{-5}$  M HCl?
- $\text{pH} = 5.00$
- What is the pH of  $1.0 \times 10^{-6}$  M HCl?
- $\text{pH} = 5.996$
- What is the pH of  $1.0 \times 10^{-7}$  M HCl?
- $\text{pH} = 6.791$
- What is the pH of  $1.0 \times 10^{-8}$  M HCl?
- $\text{pH} = 6.996$
- Why does the pH stop changing at a value of about 7?
- Water has a pH of 7 due to autodissociation, so it is never possible to get a pH higher than 7 by addition of water.

## *16.5 Strong Acids and Bases*

### *Strong Acids*

- The strongest common acids are HCl, HBr, HI,  $\text{HNO}_3$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$ .
- Strong acids are strong electrolytes.
- All strong acids ionize completely in solution:
- $\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
- Since  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  are used interchangeably, we write
- $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
- In solutions the strong acid is usually the only source of  $\text{H}^+$ . (If the molarity of the acid is less than  $10^{-6}$  M then the autoionization of water needs to be taken into account.)
- Therefore, the pH of the solution is the initial molarity of the acid.

*Strong Bases*

- Most ionic hydroxides are strong bases (e.g. NaOH, KOH, and Ca(OH)<sub>2</sub>).
- Strong bases are strong electrolytes and dissociate completely in solution.
- The pOH (and hence pH) of a strong base is given by the initial molarity of the base. Be careful of stoichiometry.
- In order for a hydroxide to be a base, it must be soluble.
- Bases do not have to contain the OH<sup>-</sup> ion:
- $O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$
- $H^-(aq) + H_2O(l) \rightarrow H_2(g) + OH^-(aq)$
- $N_3^-(aq) + H_2O(l) \rightarrow HN_3(aq) + OH^-(aq)$

*16.6 Weak Acids*

- Except for the strong acids, most acids do not ionize completely. These acids are called weak acids.
- $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- We can write an equilibrium expression for this reaction, just like for gaseous equilibrium reactions. We call the constant the acid ionization constant,  $K_a$ . As usual, we omit water:
- $$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$
- Values are summarized for several acids in Table 16.2
- Note that polyprotic acids have more than one value and each successive value decreases, often by a factor of about  $10^{-4}$  or  $10^{-5}$ .
- $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \quad K_a = 4.45 \times 10^{-7}$
- $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \quad K_a = 4.7 \times 10^{-11}$
- The larger the value of  $K_a$ , the more ionization occurs in solution. For a given initial concentration, a larger  $K_a$  gives a larger  $[H_3O^+]$  and a lower pH.

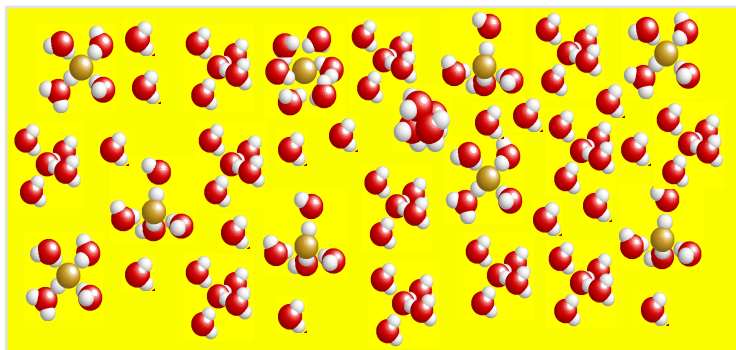
*Calculation of pH*

- Use the same procedure as for gaseous equilibria described in Chapter 15.
- Example: What is the pH of a 0.100 M HF solution?  $K_a = 7.0 \times 10^{-4}$
- $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- $K_a = [H_3O^+][F^-]/[HF] = 7.0 \times 10^{-4}$
- Substance            HF                     $H_3O^+$                      $F^-$
- Initial                0.100                    0                            0
- Change                -x                        +x                        +x
- Equilibrium           0.100 - x                x                            x
- $(x)(x)/(0.100 - x) = 7.0 \times 10^{-4}$
- Assume  $x \ll 0.100$
- $x^2/0.100 = 7.0 \times 10^{-4}$
- $x^2 = 7.0 \times 10^{-5}$
- $x = 8.4 \times 10^{-3}$ , which is 8% of initial concentration, so assumption was not very good, and we must solve the quadratic equation.

- $(x)(x)/(0.100 - x) = 7.0 \times 10^{-4}$
- $x^2 = 7.0 \times 10^{-5} - 7.0 \times 10^{-4} x$
- $x^2 + 7.0 \times 10^{-4} x - 7.0 \times 10^{-5} = 0$
- $x = \frac{-7.0 \times 10^{-4} \pm [(7.0 \times 10^{-4})^2 - (4)(1)(-7.0 \times 10^{-5})]^{1/2}}{(2)(1)}$
- $x = 0.00802$
- $[\text{H}_3\text{O}^+] = [\text{F}^-] = 8.02 \times 10^{-3} \text{ M}$
- $[\text{HF}] = 0.100 - 0.00802 = 0.0920 \text{ M}$
- $[\text{H}_3\text{O}^+][\text{F}^-]/[\text{HF}] = (8.02 \times 10^{-3})^2/0.0920 = 6.99 \times 10^{-4}$  which compares well to  $K_a = 7.0 \times 10^{-4}$ , so the calculation is correct
- $\text{pH} = -\log(8.02 \times 10^{-3}) = 2.096$  (or 2.10)
- What is the pH of 1.00 M HF solution?  $K_a = 7.0 \times 10^{-4}$
- $x = 0.0265$  when we assume that  $x \ll 1.00$ , so the assumption is okay.
- $\text{pH} = 1.577$

#### *pH and $K_a$*

- Should be able to work back from a pH value to a value of  $K_a$ . Generally simpler than calculating pH.
- The pH of 0.500 M  $\text{HNO}_2$  is 1.827. What is  $K_a$  of  $\text{HNO}_2$ ?
- $[\text{H}_3\text{O}^+] = 10^{-1.827} = 0.0149 \text{ M}$
- $[\text{NO}_2^-] = [\text{H}_3\text{O}^+] = 0.0149 \text{ M}$
- $[\text{HNO}_2] = 0.500 - 0.0149 = 0.485 \text{ M}$
- $K_a = [\text{H}_3\text{O}^+][\text{NO}_2^-]/[\text{HNO}_2]$
- $K_a = (0.0149)^2/0.485 = 4.58 \times 10^{-4}$
- Examine this picture of a solution of 0.0515 M HF and determine the value of  $K_a$  for these conditions.



#### *Calculations for Polyprotic Weak Acids*

- Because  $K_{a1}/K_{a2}$  is usually  $> 10^5$ , we can treat successive ionizations as separate steps. Solve the first one, then use the results from it to solve the second. We won't worry too much about these calculations, except to illustrate the result of such a wide difference in ionization constants.
- $\text{H}_2\text{S}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HS}^-(\text{aq}) \quad K_{a1} = 5.7 \times 10^{-8}$

- $\text{HS}^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{S}^{2-}(\text{aq}) \quad K_{a2} = 1.2 \times 10^{-13}$
- 0.100 M  $\text{H}_2\text{S}$  (saturated solution often used in qualitative analysis where  $[\text{S}^{2-}]$  controls the precipitation of metal sulfide salts)
- $[\text{H}_2\text{S}] = 0.100 \text{ M}$
- $[\text{H}_3\text{O}^+] = [\text{HS}^-] = 7.55 \times 10^{-5} \text{ M}$
- $[\text{S}^{2-}] = 1.2 \times 10^{-13} \text{ M}$
- Is the value of  $[\text{S}^{2-}]$  dependent on pH?

### 16.7 Weak Bases

- Concepts and calculations are similar to those for weak acids.
- $\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- $K_b = [\text{BH}^+][\text{OH}^-]/[\text{B}]$
- Most common weak bases are amines ( $\text{NH}_3$ ) or conjugate bases of weak acids.
- See Table 16.4 for some representative values of  $K_b$ .
- Calculations are the same as for weak acids, except we solve for  $[\text{OH}^-]$  and pOH, then convert to pH by using  $\text{p}K_w$ .
- For 0.100 M  $\text{NH}_3$ ,  $K_b = 1.76 \times 10^{-5}$ , which leads to  $\text{pOH} = 2.877$  and  $\text{pH} = 11.123$

### 16.8 Relationship Between $K_a$ and $K_b$

- $K_a$  and  $K_b$  for a conjugate acid-base pair are related by  $K_w$
- $K_a K_b = K_w$
- $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
- $K_b = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$
- $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- $K_a = [\text{NH}_3][\text{H}_3\text{O}^+]/[\text{NH}_4^+]$
- $K_a K_b = [\text{NH}_4^+][\text{OH}^-][\text{NH}_3][\text{H}_3\text{O}^+]/[\text{NH}_3][\text{NH}_4^+]$
- $= [\text{OH}^-][\text{H}_3\text{O}^+] = K_w$
- $K_a K_b = K_w$
- $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00$

### 16.9 Acid-Base Properties of Salt Solutions

- Ions are often modified when dissolved in solution. Examine the photos of Fe(III) salts and solutions. Why do they have different colors?
- $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  contains pink  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$
- Solutions may hydrolyze to give yellow  $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$  or even reddish brown  $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3$
- $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  contains ions such as yellow  $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$

#### Hydrolysis

- Hydrolysis is more important for more highly charged ions
- Highly charged metal ions ( $\geq +3$ ) cause pH shifts due to hydrolysis:
- $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+} + \text{H}_3\text{O}^+$
- Many other salts also cause pH shifts when dissolved in water. These salts contain



the conjugate acid or base of a weak base or acid.

- $\text{NH}_4\text{Cl}$ :  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$   $\text{pH} < 7$
- $\text{NaCH}_3\text{CO}_2$ :  $\text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} + \text{OH}^-$   $\text{pH} > 7$
- These reactions are called hydrolysis.
- Hydrolysis is not observed with ions derived from strong acids or bases:
- Cations of group I and II (except  $\text{Be}^{2+}$ )
- Anions:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$
- Hydrolysis is observed for:
- Cations with charge  $\geq +3$
- Transition metal +2 ions
- Some post-transition metal ions with high charge
- Common for  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Pb}^{4+}$
- See table below for values of  $K_a$  for metal ions. Greater values of  $K_a$  for ions with larger charge and smaller size.

$\text{Na}^+$	95 pm	$3.3 \times 10^{-15}$
$\text{Li}^+$	60 pm	$1.5 \times 10^{-14}$
$\text{Be}^{2+}$	31 pm	$3.2 \times 10^{-7}$
$\text{Mg}^{2+}$	65 pm	$3.8 \times 10^{-12}$
$\text{Ba}^{2+}$	135 pm	$1.5 \times 10^{-14}$
$\text{Cr}^{3+}$	69 pm	$9.8 \times 10^{-5}$
$\text{Zr}^{4+}$	78 pm	$6.0 \times 10^{-1}$

#### *Hydrolysis of Salts*

- Cation/Anion from:
  - Strong base,  
strong acid
  - Strong base,  
weak acid
  - Weak base,  
strong acid
  - Weak base,  
weak acid
- |                             |                        |   |
|-----------------------------|------------------------|---|
|                             | $\text{NaCl}$          | $\text{pH} = 7$                                 |
| no hydrolysis               |                        |   |
|                             | $\text{LiCN}$          | $\text{pH} > 7$                                 |
| anion hydrolysis            |                        |   |
|                             | $\text{NH}_4\text{Cl}$ | $\text{pH} < 7$                                 |
| cation hydrolysis           |                        |   |
|                             | $\text{NH}_4\text{CN}$ | $\text{pH}$ depends on relative $K_a$ and $K_b$ |
| cation and anion hydrolysis |                        |   |

#### *Hydrolysis Constant*

- The equilibrium constant,  $K_h$ , for hydrolysis is just a  $K_a$  or  $K_b$ , depending on the type of hydrolysis.
- $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
- $K_h = K_a$  of  $\text{NH}_4^+ = K_w/K_b$  of  $\text{NH}_3$
- $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$
- $K_h = K_b$  of  $\text{F}^- = K_w/K_a$  of  $\text{HF}$
- Calculate the pH of a solution the same as for any weak acid or weak base, using  $K_h$  for the equilibrium constant.

*Weak Acid/Weak Base Hydrolysis*

- Is a solution of  $\text{NH}_4\text{OCN}$  acidic or basic?
- $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
- $K_h = K_a = 1.0 \times 10^{-14} / 1.76 \times 10^{-5}$   
 $= 5.7 \times 10^{-10}$
- $\text{OCN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HO CN} + \text{OH}^-$
- $K_h = K_b = 1.0 \times 10^{-14} / 3.46 \times 10^{-4} = 2.9 \times 10^{-11}$
- Produces more  $\text{H}_3\text{O}^+$  than  $\text{OH}^-$ , so the solution is acidic.

*16.10 Acid-Base Behavior and Chemical Structure*

## Factors That Affect Acid Strength

- Consider H-X. For this substance to be an acid we need:
- H-X bond to be polar with  $\text{H}^{\delta+}$  and  $\text{X}^{\delta-}$  (if X is a metal then the bond polarity is  $\text{H}^{\delta-}$ ,  $\text{X}^{\delta+}$  and the substance is a base).
- the H-X bond must be weak enough to be broken.
- the conjugate base,  $\text{X}^-$ , must be stable.

*Structure and Bonding Effects on Acid Strength*

- *Binary acids*:  $K_a$  increases with electronegativity and with size.
- For E-H, a higher electronegativity results in a more ionic bond. Larger size gives a more ionic bond.
- These factors don't always work in the same direction.
- $\chi$  increases across a period,  $K_a$  increases
- $\chi$  increases up a group, but  $K_a$  decreases due to a larger size at the bottom of the group; a more diffuse charge has a lower attraction for  $\text{H}^+$ .

*Oxoacids,  $\text{EO}_n\text{H}$* 

- For constant E, an increase in oxidation number results in an increase in  $K_a$ .
- Greater charge of E in E-O-H pulls electrons from O-H and ionizes this bond more.
- +1     +3     +5     +7
- $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$
- $3 \times 10^{-8} \quad 1 \times 10^{-2} \quad 5 \times 10^2 \quad \sim 10^8$

- When E is not constant,  $K_a$  varies with electronegativity of E.

$\text{H}_3\text{BO}_3$	$\text{H}_2\text{CO}_3$	$\text{HNO}_3$
$6 \times 10^{-10}$	$4 \times 10^{-7}$	large
		$\text{H}_3\text{PO}_4$
		$8 \times 10^{-3}$
		$\text{H}_3\text{AsO}_4$
		$6 \times 10^{-3}$

- In E-O-H, larger electronegativity of E makes the O-H bond easier to ionize by attracting electrons towards E

- Polyprotic acids: successive  $K_a$  values decrease by about  $10^5$ .
 

$H_3PO_4$	$7.5 \times 10^{-3}$
$H_2PO_4^-$	$6.2 \times 10^{-8}$
$HPO_4^{2-}$	$2.2 \times 10^{-13}$
- It is easier to pull  $H^+$  away from a neutral molecule than from an anion and the difficulty increases with increasing negative charge.

#### *Oxides and Hydroxides*

- Oxides and hydroxides also act as acids or bases. They are the anhydrides (without water) of acids or bases.
- $H_2SO_4 - H_2O = SO_3$
- $2H_3PO_4 - 3H_2O = P_2O_5$  (or  $P_4O_{10}$ )
- $Ca(OH)_2 - H_2O = CaO$
- Keep removing water until there is no H in the formula.
- Metal oxides are usually bases.
- metal oxide + water  $\rightarrow$  hydroxide base
- Nonmetal oxides are usually acids.
- nonmetal oxide + water  $\rightarrow$  oxoacid
- Neutralization reactions:
  - $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$
  - $SO_3 + Ca(OH)_2 \rightarrow CaSO_4 + H_2O$
  - $H_2SO_4 + CaO \rightarrow CaSO_4 + H_2O$
  - $SO_3 + CaO \rightarrow CaSO_4$

#### *Why are metal oxides bases?*

- In both metal and nonmetal oxides, hydration produces E-O-H, which can either be an oxoacid or a hydroxide base. The difference arises from the identity of the bond that is most ionic, E-O or O-H.
- Base:  $E-O-H(aq) \rightleftharpoons E^+(aq) + OH^-(aq)$
- Acid:  $E-O-H(aq) \rightleftharpoons EO^-(aq) + H^+(aq)$
- The greatest electronegativity difference (E-O or O-H) determines which is the most ionic.  $\Delta\chi$  of O-H is 1.4; if  $\Delta\chi$  of E-O is greater than 1.4, we have a base. This is found for metals.

#### *Electronegativity Differences*

- Metals have low  $\chi$ ; nonmetals have high  $\chi$ 

$Al-O$	$\Delta\chi = 2.0$	$N-O$	$\Delta\chi = 0.5$
$Mg-O$	$2.3$	$C-O$	$1.0$
$Li-O$	$2.5$	$B-O$	$1.5$
$Na-O$	$2.6$	$F-O$	$0.5$
$Cr-O$	$1.9$	$Cl-O$	$0.5$
$Fe-O$	$1.7$	$S-O$	$1.0$
$Cu-O$	$1.6$	$P-O$	$1.4$

*Periodicity of Acidity*

- Acid character of oxides increases from left to right and bottom to top of the periodic table.

*16.11 Lewis Acids and Bases*

- Proton transfer also involves transfer of a share in an electron pair
- $\text{H}_3\text{N:} + \text{H}_2\text{O:H}^+ \rightleftharpoons \text{H}_3\text{N:H}^+ + \text{H}_2\text{O}$
- Lewis base: electron pair donor
- Lewis acid: electron pair acceptor
- Applies as well to systems that don't have protons
- acid + base:  $\rightleftharpoons$  acid:base (adduct or coordination compound or complex ion)
- $\text{BF}_3 + \text{:NH}_3 \rightleftharpoons \text{F}_3\text{B:NH}_3$
- Identify the Lewis acid and the Lewis base:
- $\text{Co}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{CoCl}_4^{2-}$
- $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$
- The metal ion in each case is the acid and the nonmetal species is the base. The products are called complex ions.