

Chemistry 132 NT

It is the mark of an instructed mind to rest satisfied with the degree of precision that the nature of a subject permits, and not to seek exactness where only an approximation of the truth is possible.

Aristotle

1



2

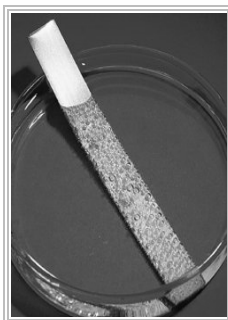
Chem 132 NT

Acid-Base Equilibria

Module 2

Solutions of a Weak Base

- Base-Ionization Equilibria
- Acid-Base Properties of Salt Solutions



Reaction of zinc metal with hydrochloric acid.

3

Review

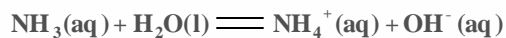
- ✎ Determining K_a (or K_b) from the solution pH
- ✎ Calculating the concentration of a species in a weak acid solution using K_a
- ✎ Calculating concentrations of species in a solution of a diprotic acid.

4

Base-Ionization Equilibria

- ✎ Equilibria involving **weak bases** are treated similarly to those for weak acids.

◆ Ammonia, for example, ionizes in water as follows.



◆ The corresponding equilibrium constant is:

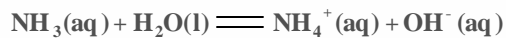
$$K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}$$

5

Base-Ionization Equilibria

- ✎ Equilibria involving **weak bases** are treated similarly to those for weak acids.

◆ Ammonia, for example, ionizes in water as follows.



◆ The concentration of water is nearly constant.

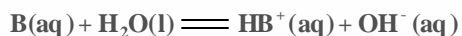
$$K_b = [\text{H}_2\text{O}]K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

6

Base-Ionization Equilibria

Equilibria involving **weak bases** are treated similarly to those for weak acids.

In general, a weak base B with the base ionization



has a base ionization constant equal to

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

A table in your text lists ionization constants for some weak bases.

7

A Problem To Consider

What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

As before, we will follow the three steps in solving an equilibrium.

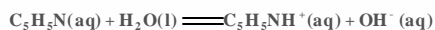
1. Write the **equation** and make a **table** of concentrations.
2. Set up the **equilibrium constant expression**.
3. Solve for $x = [OH^-]$.

8

A Problem To Consider

What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

Pyridine ionizes by picking up a proton from water (as ammonia does).



Starting	0.20
Change	-x
Equilibrium	0.20-x

0	0
+x	+x
x	x

9

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

Note that

$$\frac{C_b}{K_b} = \frac{0.20}{1.4 \times 10^{-9}} = 1.4 \times 10^8$$

which is much greater than 100, so we may use the simplifying assumption that $(0.20 - x) \approx (0.20)$.

10

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

The equilibrium expression is

$$\frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]} = K_b$$

11

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

If we substitute the equilibrium concentrations and the K_b into the equilibrium constant expression, we get

$$\frac{x^2}{(0.20 - x)} = 1.4 \times 10^{-9}$$

12

A Problem To Consider

◆ What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

◆ Using our simplifying assumption that the x in the denominator is negligible, we get

$$\frac{x^2}{(0.20)} \approx 1.4 \times 10^{-9}$$

13

A Problem To Consider

◆ What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

◆ Solving for x we get

$$x^2 \approx (0.20) (1.4 \times 10^{-9})$$

$$x = [OH^-] \approx \sqrt{(0.20) (1.4 \times 10^{-9})} \approx 1.7 \times 10^{-5}$$

14

A Problem To Consider

◆ What is the pH of a 0.20 M solution of pyridine, C_5H_5N , in aqueous solution? The K_b for pyridine is 1.4×10^{-9} .

◆ Solving for pOH

$$pOH = -\log[OH^-] = -\log(1.7 \times 10^{-5}) = 4.8$$

◆ Since $pH + pOH = 14.00$

$$pH = 14.00 - pOH = 14.00 - 4.8 = 9.2$$

15

Acid-Base Properties of a Salt Solution

☛ One of the successes of the Brønsted-Lowry concept of acids and bases was in pointing out that some **ions can act as acids or bases**.

◆ Consider a solution of sodium cyanide, NaCN.



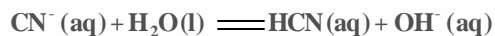
◆ A 0.1 M solution has a pH of 11.1 and is therefore fairly basic.

16

Acid-Base Properties of a Salt Solution

☛ One of the successes of the Brønsted-Lowry concept of acids and bases was in pointing out that some **ions can act as acids or bases**.

◆ Sodium ion, Na^+ , is un-reactive with water, but the cyanide ion, CN^- , reacts to produce HCN and OH^- .

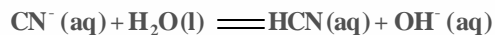


17

Acid-Base Properties of a Salt Solution

☛ One of the successes of the Brønsted-Lowry concept of acids and bases was in pointing out that some **ions can act as acids or bases**.

◆ From the Brønsted-Lowry point of view, the CN^- ion acts as a base, because it accepts a proton from H_2O .

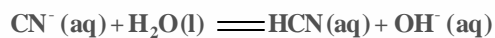


18

Acid-Base Properties of a Salt Solution

☛ One of the successes of the Brønsted-Lowry concept of acids and bases was in pointing out that some **ions can act as acids or bases**.

◆ You can also see that OH^- ion is a product, so you would expect the solution to have a basic pH. This explains why NaCN solutions are basic.



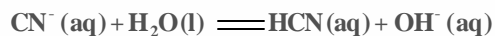
◆ The reaction of the CN^- ion with water is referred to as the **hydrolysis** of CN^- .

19

Acid-Base Properties of a Salt Solution

☛ The **hydrolysis** of an ion is the reaction of an ion with water to produce the **conjugate acid and hydroxide ion** or the **conjugate base and hydronium ion**.

◆ The CN^- ion **hydrolyzes** to give the conjugate acid, HCN, and hydroxide.

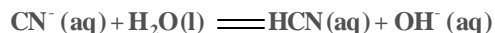


20

Acid-Base Properties of a Salt Solution

☛ The **hydrolysis** of an ion is the reaction of an ion with water to produce the **conjugate acid and hydroxide ion** or the **conjugate base and hydronium ion**.

◆ The hydrolysis reaction for CN^- has the form of a **base ionization** so you write the K_b expression for it.

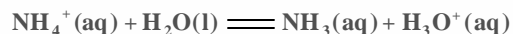


21

Acid-Base Properties of a Salt Solution

✎ The **hydrolysis** of an ion is the reaction of an ion with water to produce the **conjugate acid and hydroxide ion** or the **conjugate base and hydronium ion**.

◆ The NH_4^+ ion **hydrolyzes** to the conjugate base (NH_3) and hydronium ion.

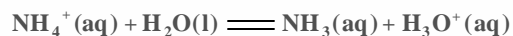


22

Acid-Base Properties of a Salt Solution

✎ The **hydrolysis** of an ion is the reaction of an ion with water to produce the **conjugate acid and hydroxide ion** or the **conjugate base and hydronium ion**.

◆ This equation has the form of an acid ionization so you write the K_a expression for it.



23

Predicting Whether a Salt is Acidic, Basic, or Neutral

✎ How can you predict whether a particular salt will be acidic, basic, or neutral?

◆ The Brønsted-Lowry concept illustrates the inverse relationship in the strengths of conjugate acid-base pairs.

◆ Consequently, **the anions of weak acids (poor proton donors) are good proton acceptors.**

◆ **Anions of weak acids therefore, are basic.**

24

Predicting Whether a Salt is Acidic, Basic, or Neutral

How can you predict whether a particular salt will be acidic, basic, or neutral?

- One the other hand, the **anions of strong acids (good proton donors) have virtually no basic character**, that is, they do not hydrolyze.
- For example, the Cl^- ion, which is conjugate to the strong acid HCl, shows no appreciable reaction with water.



25

Predicting Whether a Salt is Acidic, Basic, or Neutral

How can you predict whether a particular salt will be acidic, basic, or neutral?

- Conversely, the **cations of weak bases are acidic**.
- One the other hand, the **cations of strong bases have virtually no acidic character**, that is, they do not hydrolyze. For example,



26

Predicting Whether a Salt is Acidic, Basic, or Neutral

To predict the acidity or basicity of a salt, you must examine the acidity or basicity of the ions composing the salt.

- Consider potassium acetate, $\text{KC}_2\text{H}_3\text{O}_2$.
The potassium ion is the cation of a strong base (KOH) and does not hydrolyze.



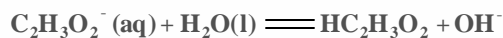
27

Predicting Whether a Salt is Acidic, Basic, or Neutral

☛ To predict the acidity or basicity of a salt, you must examine the acidity or basicity of the ions composing the salt.

◆ Consider potassium acetate, $\text{KC}_2\text{H}_3\text{O}_2$.

The acetate ion, however, is the anion of a weak acid ($\text{HC}_2\text{H}_3\text{O}_2$) and is basic.



A solution of potassium acetate is predicted to be **basic**.

28

Predicting Whether a Salt is Acidic, Basic, or Neutral

☛ These rules apply to normal salts (those in which the anion has no acidic hydrogen)

1. A salt of a **strong base** and a **strong acid**.

The salt has **no hydrolyzable ions** and so gives a **neutral** aqueous solution.

An example is NaCl.

29

Predicting Whether a Salt is Acidic, Basic, or Neutral

☛ These rules apply to normal salts (those in which the anion has no acidic hydrogen)

2. A salt of a **strong base** and a **weak acid**.

The anion of the salt is the conjugate of the weak acid. It hydrolyzes to give a **basic** solution.

An example is NaCN .

30

Predicting Whether a Salt is Acidic, Basic, or Neutral

⚠ These rules apply to normal salts (those in which the anion has no acidic hydrogen)

3. A salt of a **weak base** and a **strong acid**.

The cation of the salt is the conjugate of the weak base. It hydrolyzes to give an **acidic** solution.

An example is NH_4Cl .

31

Predicting Whether a Salt is Acidic, Basic, or Neutral

⚠ These rules apply to normal salts (those in which the anion has no acidic hydrogen)

4. A salt of a **weak base** and a **weak acid**.

Both ions hydrolyze. You must compare the K_a of the cation with the K_b of the anion.

If the K_a of the cation is larger the solution is **acidic**.

If the K_b of the anion is larger, the solution is **basic**.

32

The pH of a Salt Solution

⚠ To calculate the **pH of a salt solution** would require the **K_a of the acidic cation** or the **K_b of the basic anion**.

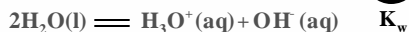
◆ The ionization constants of ions are not listed directly in tables because the values are easily related to their conjugate species.

◆ Thus the K_b for CN^- is related to the K_a for HCN .

33

The pH of a Salt Solution

✎ To see the relationship between K_a and K_b for conjugate acid-base pairs, consider the acid ionization of HCN and the base ionization of CN^- .

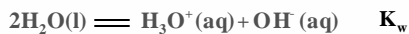


◆ When these two reactions are added you get the **ionization of water.**

34

The pH of a Salt Solution

✎ To see the relationship between K_a and K_b for conjugate acid-base pairs, consider the acid ionization of HCN and the base ionization of CN^- .

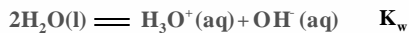


◆ When two reactions are added, their **equilibrium constants are multiplied**

35

The pH of a Salt Solution

✎ To see the relationship between K_a and K_b for conjugate acid-base pairs, consider the acid ionization of HCN and the base ionization of CN^- .



◆ Therefore,

$$\text{For HCN} \rightarrow K_a \cdot K_b = K_w \leftarrow \text{For CN}^-$$

36

A Problem To Consider

◆ Use the tables in your text to obtain the following at 25°C.: (a) K_b for CN^- and (b) K_a for NH_4^+ .

(a) The conjugate acid of CN^- is HCN, whose K_a is 4.9×10^{-10} (from table in text). Therefore,

$$K_b (\text{for } \text{CN}^-) = \frac{K_w}{K_a (\text{for HCN})}$$

37

A Problem To Consider

◆ Use the tables in your text to obtain the following at 25°C.: (a) K_b for CN^- and (b) K_a for NH_4^+ .

(a) The conjugate acid of CN^- is HCN, whose K_a is 4.9×10^{-10} (from table in text). Therefore,

$$K_b (\text{for } \text{CN}^-) = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$

◆ Note that the K_b for CN^- is approximately equal to K_b for ammonia, NH_3 (1.8×10^{-5}).

38

A Problem To Consider

◆ Use the tables in your text to obtain the following at 25°C.: (a) K_b for CN^- and (b) K_a for NH_4^+ .

(a) The conjugate acid of CN^- is HCN, whose K_a is 4.9×10^{-10} (from table in text). Therefore,

$$K_b (\text{for } \text{CN}^-) = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$

◆ This means the base strength of CN^- is comparable with that of NH_3 .

39

A Problem To Consider

◆ Use the tables in your text to obtain the following at 25°C.: (a) K_b for CN^- and (b) K_a for NH_4^+ .

(b) The conjugate base of NH_4^+ is NH_3 , whose K_b is 1.8×10^{-5} (from table in text). Therefore,

$$K_a (\text{for } \text{NH}_4^+) = \frac{K_w}{K_b (\text{for } \text{NH}_3)}$$

40

A Problem To Consider

◆ Use the tables in your text to obtain the following at 25°C.: (a) K_b for CN^- and (b) K_a for NH_4^+ .

(b) The conjugate base of NH_4^+ is NH_3 , whose K_b is 1.8×10^{-5} (from table in text). Therefore,

$$K_a (\text{for } \text{NH}_4^+) = \frac{1.0 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} = 5.6 \cdot 10^{-10}$$

◆ NH_4^+ is a relatively weak acid. Acetic acid, by comparison has a K_a equal to 1.8×10^{-5} .

41

The pH of a Salt Solution

◆ For a solution of a salt in which **only one ion hydrolyzes**, the calculation of equilibrium composition follows that of weak acids and bases.

◆ The only difference is first obtaining the K_a or K_b for the ion that hydrolyzes.

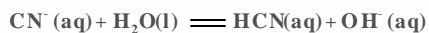
◆ The next example illustrates the reasoning and calculations involved.

42

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C?
The K_a for HCN is 4.9×10^{-10} .

- Sodium cyanide gives Na^+ ions and CN^- ions in solution.
- Only the CN^- ion hydrolyzes.



43

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C?
The K_a for HCN is 4.9×10^{-10} .

- The CN^- ion is acting as a base, so first, we must calculate the K_b for CN^- .

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$

- Now we can proceed with the equilibrium calculation.

44

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C?
The K_a for HCN is 4.9×10^{-10} .

- Let $x = [\text{OH}^-] = [\text{HCN}]$, then substitute into the equilibrium expression.

$$\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = K_b$$

45

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C? The K_a for HCN is 4.9×10^{-10} .

◆ This gives

$$\frac{x^2}{(0.10 - x)} = 2.0 \times 10^{-5} \quad @ \quad \frac{x^2}{(0.10)}$$

↗
We can use our simplifying assumption to ignore this “x”

46

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C? The K_a for HCN is 4.9×10^{-10} .

◆ Solving the equation, you find that

$$x = [\text{OH}^-] = 1.4 \times 10^{-3}$$

◆ Hence,

$$\text{pH} = 14.00 - \text{pOH} = 14.00 + \log(1.4 \times 10^{-3}) = 11.2$$

◆ As expected, the solution has a pH greater than 7.0.

47

Operational Skills

- Calculating the concentration of a species in a weak base solution using K_b
- Predicting whether a salt solution is acidic, basic, or neutral
- Obtaining K_a from K_b or K_b from K_a
- Calculating concentrations of species in a salt solution

Time for a few review questions

48



49
