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Chapter 15: Acids and Bases

Section 15.1: Brønsted-Lowry Acids and Bases

According to Brønsted-Lowry, an **acid** is a proton donor and a **base** is a proton acceptor. Therefore, in an **acid**-**base** reaction, a proton (H^+) is transferred from an **acid** to a **base**.

Example: $HCl_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + Cl^-_{(aq)}$

In this reaction: HCl is an **acid**
H_2O is a **base**
H_3O^+ is the conjugate **acid**
Cl^- is the conjugate **base**

Conjugate **acid**: The species formed when a proton is added to a **base** is called the conjugate **acid**.
Conjugate **base**: The species formed when a proton is removed from an **acid** is called the conjugate **base**.
The conjugate **acid**-**base** pair consists of the two substances related to each other by the donation and acceptance of a single proton.

Example: In the following aqueous reaction, identify the **acid**, the **base**, the conjugate **acid** and the conjugate **base**.

$$H_2O_{(l)} + HONH_3^+{}_{(aq)} \rightleftarrows HONH_{2\,(aq)} + H_3O^+_{(aq)}$$

Looking at the equation, one can conclude that H_2O has accepted a proton from $HONH_3^+$ to form H_3O^+.

Thus, $HONH_3^+$ is a proton donor (the **acid**).
H_2O is the proton acceptor (the **base**).
H_3O^+ is the species formed when the proton is added to the **base** (the conjugate **acid**).
$HONH_2$ is the species formed when a proton is removed from the **acid** (the conjugate **base**).

In this section, practice the Interactive Problems.

Section 15.2: The Autoionization of Water

Pure liquid water has a very low electrical conductivity. This is because water is ionized to a very small extent.

$$H_2O_{(l)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + OH^-_{(aq)}$$

In this reaction, H_2O behaves as an **acid** as well as a **base**. Substances acting as either an **acid** or a **base** are said to be **amphoteric**.

The above reaction is called the **autoionization** of water. The equilibrium constant for the autoionization of water is written as:

$$K_C = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

H_2O is the solvent and its concentration (~ 56 M) is much larger than that of any of the solutes. Thus, $[H_2O]$ can be considered constant. We can therefore define a new equilibrium constant, K_w, called the **ion product constant**.

$$K_w = [H_3O^+][OH^-]$$

$$\text{In pure water } [H_3O^+] = [OH^-]$$

$$\text{At } 25^oC,\ [H_3O^+] = [OH^-] = 1.0 \times 10^{-7}\ \text{mol.L}^{-1}$$

$$\begin{aligned}\text{Hence, } K_w &= [H_3O^+]\,[OH^-] \\ &= (1.0 \times 10^{-7})\,(1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14}\end{aligned}$$

$$\text{Thus, } K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14} \text{ at } 25^oC$$

The value of K_w increases slightly with temperature.

Recall: The magnitude of an equilibrium constant often depends on temperature.

In this section, practice the Interactive Problems.

Section 15.3: Amphoteric Substances

A substance that can behave either as an **acid** or a **base** is called an **amphoteric** substance.

Example: Consider the formation of an aqueous solution of H_2SO_4.

$$H_2O_{(l)} + H_2SO_{4\,(aq)} \leftrightarrows HSO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$$

In this reaction H_2O has accepted a proton from H_2SO_4 to form H_3O^+.

Thus, H_2SO_4 is an **acid** since it donates a proton.
H_2O is a **base** since it accepts a proton.
H_3O^+ is the the conjugate **acid** since it forms when a proton is added to the **base**.
HSO_4^- is the conjugate **base** of the **acid** H_2SO_4.

But, HSO_4^- can also donate a proton according to the reaction:

$$HSO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+{}_{(aq)} + SO_4^{-2}{}_{(aq)}$$

Thus, according to this reaction, HSO_4^- is an **acid**. HSO_4^- can behave as an **acid** and a **base**, so it is an amphoteric substance.

HSO_4^- is the **acid** because it donates a proton.
H_2O is the **base** because it accepts a proton.
H_3O^+ is the conjugate **acid**, because it is formed when a proton is added to the **base**.
SO_4^{-2} is the conjugate **base**, because it is formed when a proton is removed from the **acid**.

Since, H_2SO_4 can donate two protons, it is called a **diprotic acid**.

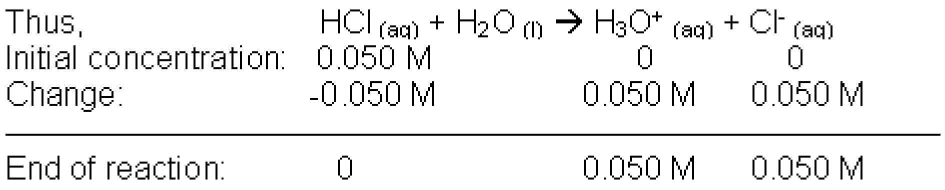
In this section, practice the Interactive Problems.

Section 15.4: Calculations of Ion Concentrations

At 25 °C, $K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$

Example: Calculate $[H_3O^+]$ and $[OH^-]$ in a 0.050 M HCl aqueous solution.

HCl is a strong **acid**. A strong **acid** is defined as one that is completely dissociated in water.



Thus,	$HCl_{(aq)}$ + $H_2O_{(l)}$ →	$H_3O^+{}_{(aq)}$ +	$Cl^-{}_{(aq)}$
Initial concentration:	0.050 M	0	0
Change:	-0.050 M	0.050 M	0.050 M
End of reaction:	0	0.050 M	0.050 M

This means that: $[H_3O^+] = [Cl^-] = 0.050\ mol.L^{-1}$

We know that: $[H_3O^+]\ [OH^-] = 1.0 \times 10^{-14}$

$(0.050) \times [OH^-] = 1.0 \times 10^{-14}$ Hence, $[OH^-] = 2.0 \times 10^{-13}\ mol.L^{-1}$

Thus, $[H_3O^+] = 0.050\ mol.L^{-1}$ and $[OH^-] = 2.0 \times 10^{-13}\ mol.L^{-1}$

Hence, in a 0.050 M HCl solution: $[H_3O^+] >> [OH^-]$

In this section, practice the Interactive Problems.

Section 15.5: The pH Scale

The pH scale provides a convenient way to express the acidity of dilute aqueous solutions. The pH is calculated using a decimal logarithm or log base 10.

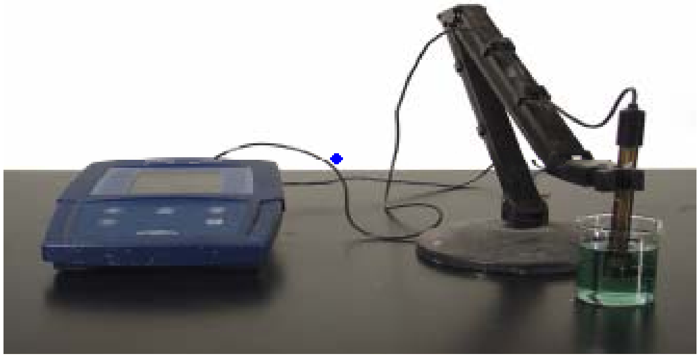
$pH = - \log [H^+]$ or $pH = - \log [H_3O^+]$

Remember that you can write $[H^+] = [H_3O^+]$

Thus, $[H^+] = 10^{-pH}$

Similarly, $pOH = - \log [OH^-]$

The pH of a solution is usually measured using a pH meter. A pH meter is an electronic device with an electrode that can be inserted into the solution of unknown pH.



The electrode contains an **acidic** aqueous solution enclosed in a special glass membrane that allows H^+ ions to migrate. The difference in pH between the solution in the electrode and the solution of unknown pH generates an electrical potential which is registered on the pH meter.

We know, $K_w = [H^+] [OH^-]$

Take the log of both sides: $\log K_w = \log [H^+] + \log [OH^-]$

Multiply both sides by - 1:

$$- \log K_w = - \log [H^+] - \log [OH^-]$$

Define pK_w by: $pK_w = - \log K_w$

$$pK_w = pH + pOH$$

At 25 ^oC $K_w = 1.0 \times 10^{-14}$ $pK_w = 14.00$

Thus, pH + pOH = 14.00

A neutral solution has pH = 7.

A solution having pH < 7 is called an **acidic** solution.

A solution having pH > 7 is called a **basic** solution.

Note: You should know the rule on significant figures for logarithms.

Rule: The number of decimal places in the log is equal to the number of significant figures in the original number.

Example: Calculate the pH of a solution for which $[H^+] = 1.0 \times 10^{-7}$ mol.L^{-1}

Thus, $[H^+] = 1.0 \times 10^{-7}$ mol.L^{-1}. This number has 2 significant figures.

$pH = - \log (1.0 \times 10^{-7}) = 7.00$. This number has 2 decimal places.

Example: Calculate pH and pOH for the following solutions at 25 ^oC

a) 2.0×10^{-3} mol.L^{-1} OH^-

$pOH = - \log [OH^-] = - \log (2.0 \times 10^{-3}) = 2.70$
pH + pOH = 14.00
pH + 2.70 = 14.00
pH = 11.30

b) 3.2 $mol.L^{-1}$ H^+

pH = - log [H^+]

= - log (3.2) = 0.51

pH + pOH = 14.00

pOH = 13.49

In this section, practice the Interactive Problems.

Section 15.6: Calculating the pH of Strong Monoprotic Acid Solutions.

Earlier, in Chapter 2, we discussed the definition of strong **acids**. There are relatively few strong **acids**. Consider an aqueous solution of 1.0 M HCl. We know that HCl is a strong **acid** since it dissociates completely in water. Thus,

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Note: This reaction reaches a chemical equilibrium, in which the HCl solution contains only an extremely small number of HCl molecules and consists mostly of H^+ and Cl^- ions. Hence, while the reverse arrow could be shown in the above reaction, it is generally ignored. Hence, for strong **acids**, we normally do not represent this reaction with two anti-parallel arrows.

Hence, the equilibrium reaction for a strong **acid** is expressed as above:

Whenever we deal with the **acid**-**base** equilibrium it is important to understand the solution components. In a 1.0 M HCl solution, there will mostly be H^+ and Cl^- ions.

Therefore, [H^+] = 1.0 M and [Cl^-] = 1.0 M

Thus, pH of a 1.0 M HCl solution would be: pH = - log (1.0)

pH = 0

Since 0 < 7, the solution is **acidic**.

In this section, practice the Interactive Problems.

Section 15.7: Weak Acid Solutions

Recall the definition of a weak **acid**: "A weak **acid** does not ionize completely when dissolved in water." Consider a general weak **acid**, HA. According to the definition:

$$HA_{(aq)} \leftrightarrows H^{+}_{(aq)} + A^{-}_{(aq)}$$

In solution, there are H^+ and A^- ions and HA molecules. Thus, the ionization reaction of a weak **acid** is represented by forward and reverse arrows. The forward and reverse arrows indicate that the ions and molecules are at equilibrium at a given temperature. Hence, the equilibrium constant is expressed as:

$$K_{eq} = \frac{[H^+]\,[A^-]}{[HA]}$$

Here, K_{eq} is the same as K_c, discussed in the previous chapter. Since the reaction depicts the dissociation of a weak **acid**, the equilibrium constant is often expressed as K_a.

$$\text{Thus,}\quad K_a = \frac{[H^+][A^-]}{[HA]}$$

Let us examine the differences between a strong and weak **acid**:

.

(1) Consider a strong **acid**, HA.

The ionization reaction is expressed as: $HA_{(aq)} \leftrightarrows H^{+}_{(aq)} + A^{-}_{(aq)}$

The equilibrium constant is:

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

Note: The value of K_a is very large, since strong acids are almost fully dissociated ($[HA] \cong 0$). Hence, this expression is not often used for strong **acids**.

(2) Consider a weak **acid**, HA.

The ionization reaction is expressed as: $HA_{(aq)} \leftrightarrows H^{+}_{(aq)} + A^{-}_{(aq)}$

The equilibrium constant is:

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

Note: The value of K_a is very small. The smaller the K_a value, the weaker the **acid**.

Acids (HA)

Strong	**Weak**
$HA_{(aq)} \rightarrow H^{+}_{(aq)} + A^{-}_{(aq)}$	$HA_{(aq)} \leftrightarrows H^{+}_{(aq)} + A^{-}_{(aq)}$

In both equations, A^{-} is the conjugate **base**.

The stronger the **acid**, the weaker the conjugate **base**.
or
The weaker the **acid**, the stronger the conjugate **base**.

The K_a values at 25 °C for some weak **acids** are given in the table on the DVD.
Note: The smaller K_a, the weaker the **acid**, but the stronger the conjugate **base**.

Example: Consider an aqueous solution of HF, $K_a = 7.2 \times 10^{-4}$ at 25 °C.

(a) Write the ionization reaction.

$$HF_{(aq)} \rightarrow H^{+}_{(aq)} + F^{-}_{(aq)}$$

(b) Write the equilibrium constant expression.

$$K_a = \frac{[H^{+}][F^{-}]}{[HF]} = 7.2 \times 10^{-4}$$

(c) Identify the conjugate base.

$F^{-}_{(aq)}$ is the conjugate **base**.

Remember: Since only one proton is released in the ionization reaction, the **acid** is generally called a **monoprotic acid**.

In this section, practice the Interactive Problems.

Sections 15.8 - 15.10: Calculating the pH of Weak Monoprotic Acid Solutions.

Example: Calculate the pH of 1.0 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$).

Step 1. Write the ionization reaction of the **acid**.

$CH_3COOH_{(aq)} \leftrightarrows H^+_{(aq)} + CH_3COO^-_{(aq)}$ $\qquad$ $K_a = 1.8 \times 10^{-5}$

Step 2. Write the K_a value of the **acid** (given in the problem).

$$K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

Step 3. Write the autoionization equation for H_2O.

$H_2O_{(l)} \leftrightarrows H^+_{(aq)} + OH^-_{(aq)}$ $\qquad$ $K_w = 1.0 \times 10^{-14}$

Step 4. Compare K_a to K_w.

If $K_a > K_w$, we conclude that CH_3COOH is the dominant source for H^+. Note, if $K_a < K_w$, we cannot ignore H^+ from H_2O. In this case, the pH is 7.00.

Step 5. Assume x amount of the **acid** dissociates

	$CH_3COOH_{(aq)}$ $\leftrightarrows$	$H^+_{(aq)}$ +	$CH_3COO^-_{(aq)}$
Initial	1.0 M	0 M	0 M
Change	- x	x	x

Note: According to the stoichiometry, if x mol.L^{-1} CH_3COOH **acid** dissociates then, x mol.L^{-1} H^+ and x mol.L^{-1} CH_3COO^- are formed.

Step 6. The equilibrium mole fractions are:

	$CH_3COOH_{(aq)}$ $\leftrightarrows$	$H^+_{(aq)}$ +	$CH_3COO^-_{(aq)}$
Initial	1.0 M	0 M	0 M
Change	- x	x	x
Equilibrium	(1.0 – x)	x	x

Step 7. Write the equilibrium constant expression and substitute the respective values.

$$K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(1.0 - x)} = \frac{x^2}{(1.0 - x)}$$

Step 8. Assumption: Since the K_a value for the **acid** is small, assume only a very small amount of the **acid** ionizes. Therefore, one can assume x to be negligible in (1.0 - x). Thus, the equilibrium constant expression becomes

$$1.8 \times 10^{-5} = \frac{x^2}{1.0} \quad \text{or}$$

$$x = \sqrt{1.8 \times 10^{-5}} = 4.2 \times 10^{-3} \text{ mol.L}^{-1}$$

Step 9. Examine the equilibrium concentrations

	$CH_3COOH_{(aq)}$ ⇆	$H^+_{(aq)}$ +	$CH_3COO^-_{(aq)}$
Initial	1.0 M	0 M	0 M
Change	- x	x	x
Equilibrium	(1.0 – x)	x	x

$$[H^+] = x = 4.2 \times 10^{-3} \text{ mol.L}^{-1}$$

$$pH = - \log [H^+]$$

$$pH = - \log (4.2 \times 10^{-3})$$

$$pH = 2.37$$

Typically, K_a values for **acids** are known with an accuracy of ± 5%. Hence, one can check the validity of the assumption made in Step 8. The concentration of x we calculated is 4.2×10^{-3} mol.L^{-1} and the initial concentration of the **acid** is 1.0 M.

$$\text{Recall}: \% = \frac{\text{Part}}{\text{Whole}} \times 100$$

$$\% \text{ dissociated} = \frac{4.2 \times 10^{-3}}{1.0} \times 100 = 0.42\,\%$$

$$0.42\,\% < 5\,\%$$

Therefore, the assumption is valid. If this assumption was not valid, then x should be obtained by solving the quadratic equation in step 8.

In Sections 15.9 and 15.10, practice the Interactive Problems.

Section 15.11: Calculating the pH of Strong Base Solutions

By definition, a strong **base** is completely dissociated in water. Therefore, the formation of a 0.10 M NaOH solution is expressed as:

$$\begin{array}{lll} NaOH_{(aq)} \rightarrow & Na^{+}_{(aq)} + & OH^{-}_{(aq)} \\ & 0.10\ M & 0.10\ M \end{array}$$

The concentrations of Na^+ and OH^- ions are 0.10 M.

Recall: $pH = -\log [H^+]$ and $pH = -\log [OH^-]$

Hence, the pH of a 0.10 M NaOH solution is calculated as:

$$pOH = -\log (0.10)$$
$$pOH = 1.00$$
$$pH + pOH = 14.00$$
$$pH = 13.00$$

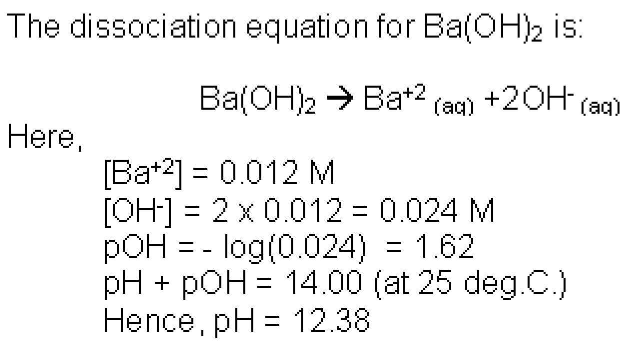
Example: Calculate the pH of a solution prepared by dissolving 2.0 g of $Ba(OH)_2$ in 1.0 L of H_2O.

The molar mass of $Ba(OH)_2$ = 171.3 g/mol

$$\text{moles of } Ba(OH)_2 = \frac{2.0\ g}{171.3\ g.mol^{-1}} = 0.012\ mol$$

$$\text{Molarity (M)} = \frac{\text{moles}}{\text{liters}} = \frac{0.012\ mol}{1.0\ L} = 0.012\ M$$

Thus, the concentration of $Ba(OH)_2$ = 0.012 M



The dissociation equation for $Ba(OH)_2$ is:

$$Ba(OH)_2 \rightarrow Ba^{+2}{}_{(aq)} + 2OH^-{}_{(aq)}$$

Here,

$[Ba^{+2}] = 0.012$ M
$[OH^-] = 2 \times 0.012 = 0.024$ M
$pOH = -\log(0.024) = 1.62$
$pH + pOH = 14.00$ (at 25 deg.C.)
Hence, $pH = 12.38$

Remember: Alkali metal and alkaline earth metal hydroxides are strong **bases** except $Be(OH)_2$ and $Mg(OH)_2$.

In this section, practice the Interactive Problems.

Section 15.12: Weak Base Solutions

By definition, a weak **base** does not dissociate completely when dissolved in water. When a weak **base** (B) dissolves in H_2O, it accepts a proton from H_2O according to the reaction:

$$B_{(aq)} + H_2O_{(l)} \leftrightarrows BH^+{}_{(aq)} + OH^-{}_{(aq)}$$

Ignoring water, the expression for the equilibrium constant is written as:

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

Note: $[H_2O]$ is assumed to be constant. Here, K_b is defined as the **base** dissociation constant. The relationship between K_b and pK_b is:

$$pK_b = -\log K_b$$

According to this equation, as the value of K_b increases, the value of pK_b decreases. A larger value of K_b indicates a stronger **base**.

In aqueous solution, the two large classes of weak **bases** are:

1) Nitrogen-containing molecules such as NH_3 and amines.
2) The anions of weak **acids**.

Remember: The weaker the **acid**, the stronger the conjugate **base**.

Note: The statement “stronger conjugate **base**” does not mean that the conjugate **base** of a weak **acid** is strong (i.e. fully dissociated). The conjugate **base** of a weak **acid** is a weak **base**.

The table on the DVD lists the name, formula, K_b and pK_b values of common weak **bases**. You can see that the weaker the **base**, the smaller the K_b value and the larger the pK_b value.

Sections 15.13 - 15.14: Calculating the pH of Weak Base Solutions

Example: **Calculate the pH of 1.5 M solution of NH_3 ($K_b = 1.8 \times 10^{-5}$).**

Step 1. Write the reaction between the **base** and H_2O along with the K_b value.

$$NH_{3\,(aq)} + H_2O_{\,(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K_b = 1.8 \times 10^{-5}$$

Step 2. Write the equation for the autoionization for H_2O along with the K_w value.

$$H_2O_{\,(l)} \leftrightarrows H^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K_w = 1.0 \times 10^{-14}$$

Step 3. Compare K_w to K_b.
If $K_b > K_w$, then consider that OH^- comes principally from the reaction of the **base** with H_2O.
If $K_b < K_w$, assume the pH of the solution to be 7.00.
In this example, $K_b > K_w$. Therefore OH^- comes primarily from the reaction of NH_3 with H_2O.

Step 4. Write the initial concentration of all species in the reaction.

$$NH_{3\,(aq)} + H_2O_{\,(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

Initial	1.5 M	0 M	0 M

Step 5. Consider x to be the change in $[NH_3]$ due to reaction with water.

$$NH_{3\,(aq)} + H_2O_{(l)} \leftrightarrows NH_{4\,(aq)}^{+} + OH^{-}_{(aq)}$$

Initial	1.5 M	0 M	0 M
Change	- x	x	x
Equilibrium	(1.5 – x)	x	x

Step 6. Write the equilibrium constant expression for this reaction.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

$$K_b = \frac{(x)(x)}{(1.5 - x)} = 1.8 \times 10^{-5} = \frac{x^2}{(1.5 - x)}$$

Step 7. Assume x to be negligible in (1.5 - x).Thus,

$$\frac{x^2}{1.5} = 1.8 \times 10^{-5} \qquad x = 5.2 \times 10^{-3}$$

Note**:** 5.2×10^{-3} is less than 5% of 1.5 M. Thus, the assumption is valid.

Remember: $[OH^-] = x = 5.2 \times 10^{-3}$ mol.L^{-1}
$pOH = -\log [OH^-]$
$pOH = -\log (5.2 \times 10^{-3})$
pOH = 2.28

Step 8. pH + pOH = 14.00
Thus, pH = 14.00 - 2.28
pH = 11.72

In Section 15.14, practice the Interactive Problems.

Section 15.15: Calculating pH of Sulfuric Acid

Sulfuric **acid**, H_2SO_4, can release two protons when dissolved in water. Hence, it is called a diprotic **acid** and has two equilibrium constants. The first dissociation reaction for H_2SO_4, ignoring water, is written as:

$$H_2SO_{4\,(aq)} \rightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)} \quad K_{a1} = \text{very large}$$

Since the K_{a1} value is very large, H_2SO_4 behaves like a strong **acid** in the first dissociation step.

$$\text{Then, } HSO_4^-{}_{(aq)} \leftrightarrows H^+_{(aq)} + SO_4^{-2}{}_{(aq)} \qquad K_{a2} = 1.2 \times 10^{-2}$$

Note: In the second dissociation step, H_2SO_4 behaves like a weak **acid**.

Example: Calculate the pH of a 2.0 M H_2SO_4 solution.

Step 1: Write the equation for the first dissociation of H_2SO_4.

$$H_2SO_{4\,(aq)} \rightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)}$$

Remember that for H_2SO_4, K_{a1} is very large. The first dissociation reaction is that of a strong **acid**. Thus, $[H^+]$ = 2.0 M and $[HSO_4^-]$ = 2.0 M.

Step 2: Write the equation for the second dissociation of H_2SO_4.

$$HSO_4^-{}_{(aq)} \leftrightarrows H^+_{(aq)} + SO_4^{-2}{}_{(aq)} \qquad K_{a2} = 1.2 \times 10^{-2}$$

Step 3: Write the initial concentrations of all the species.

$$HSO_4^-{}_{(aq)} \leftrightarrows H^+_{(aq)} + SO_4^{-2}{}_{(aq)} \qquad K_{a2} = 1.2 \times 10^{-2}$$

Initial	2.0 M	2.0 M	0 M

Step 4: Consider x to the change in $[H^+]$ due to the dissociation of HSO_4^-.

$$HSO_4^-{}_{(aq)} \leftrightarrows H^+_{(aq)} + SO_4^{-2}{}_{(aq)} \qquad K_{a2} = 1.2 \times 10^{-2}$$

Initial	2.0 M	2.0 M	0 M
Change	- x M	x M	x M
Equilibrium	(2.0 – x)	(2.0 + x)	x

Step 5: Write the expression of the equilibrium constant for the second dissociation reaction.

$$K_{a_2} = \frac{[H^+][SO_4^{-2}]}{[HSO_4^-]} = 1.2 \times 10^{-2}$$

$$\frac{(2.0 + x)(x)}{(2.0 - x)} = 1.2 \times 10^{-2}$$

Step 6: Assume x to be negligible in comparison to 2.0 in (2.0 - x).

$$\frac{(2.0)(x)}{(2.0)} = 1.2 \times 10^{-2}$$

Hence, $x = 1.2 \times 10^{-2}$ M

Step 7: Calculate the % dissociation of HSO_4^-.

$$\% \text{ dissociation} = \frac{1.2 \times 10^{-2} \text{ M}}{2.0 \text{ M}} \times 100 = 0.6 \%$$

$0.6\% < 5\%$

The assumption that "x is negligible in comparison to 2.0" is valid.

Step 8: Calculate the overall concentration of H^+.

$[H^+]_{\text{Overall}} = [H^+]_{\text{1st dissociation}} + [H^+]_{\text{2nd dissociation}}$

$[H^+]_{\text{Overall}} = 2.0 \text{ M} + 1.2 \times 10^{-2} \text{ M}$

$[H^+]_{\text{Overall}} \sim 2.0 \text{ M}$

Step 9: Calculate the pH.

pH = - log $[H^+]$
pH = - log (2.0)
pH = 0.30

Section 15.16: Acid-Base Properties of Salts

Ionic compounds are called salts. Salts that dissolve in water break into ions. These ions move about independently in dilute solutions. Sometimes, these ions can behave as **acids** or **bases**.

Now, it is important that you know the definitions of **acids** and **bases**. Remember, weak **acids** and **bases** are always associated with relatively low K_a and K_b values, respectively.

Salts that dissolve in water can produce **acidic**, neutral or **basic** solutions. First, we examine salts that produce neutral solutions.

Section 15.17: Salts that Produce Neutral Solutions

Consider the dissolution of solid sodium chloride, $NaCl_{(s)}$ in water. The dissociation reaction for NaCl is expressed as:

$$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

$Na^+_{(aq)}$ is the cation of a strong **base**, NaOH. The dissociation reaction for NaOH is expressed as:

$$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

Thus, $Na^+_{(aq)}$ is the very weak conjugate **acid** of the strong **base**, NaOH. Hence, $Na^+_{(aq)}$ has no affinity for $OH^-_{(aq)}$ and cannot produce $H^+_{(aq)}$. Thus, the formation of $Na^+_{(aq)}$ from NaCl has no effect on the pH.

$Cl^-_{(aq)}$ is the anion of the strong **acid**, HCl. The dissociation reaction for HCl is expressed as:

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Thus, $Cl^-_{(aq)}$ is the very weak conjugate **base** of the strong **acid**, HCl. Hence, $Cl^-_{(aq)}$ has no affinity for $H^+_{(aq)}$ nor can it produce $OH^-_{(aq)}$. Thus, the formation of $Cl^-_{(aq)}$ from NaCl has no effect on the pH.

Therefore, the dissolution in water of a salt consisting of a cation from a strong **base** and an anion from a strong **acid** has no effect on the concentration of H^+. Since $[H^+]$ is not affected, the pH does not change. Recall that the pH of water is 7.00 at 25°C. Hence, these salts produce a neutral solution when dissolved in water. Other examples of salts that produce neutral aqueous solutions are KCl, KNO_3, $NaNO_3$, NaBr, NaI.

Sections 15.18 - 15.19: Salts that Produce Basic Solutions

Consider sodium acetate, $NaC_2H_3O_2$. The dissociation reaction for $NaC_2H_3O_2$, ignoring water, is written as:

$$NaC_2H_3O_2 \rightarrow Na^+{}_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

$Na^+{}_{(aq)}$ is the cation of a strong **base** (NaOH). $Na^+{}_{(aq)}$ has no affinity for $OH^-{}_{(aq)}$, nor can it produce $H^+{}_{(aq)}$. Thus, $Na^+{}_{(aq)}$ has no effect on the pH.

$C_2H_3O_2^-{}_{(aq)}$ is the anion of the weak **acid**, $HC_2H_3O_2$ (acetic **acid**). The dissociation of $HC_2H_3O_2$ is given as:

$$HC_2H_3O_{2\,(aq)} \rightleftarrows H^+{}_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

$C_2H_3O_2^-{}_{(aq)}$ is the weak conjugate **base** of the weak **acid**, $HC_2H_3O_2$. According to the Brønsted-Lowry definition, a **base** is a proton acceptor. Hence, $C_2H_3O_2^-{}_{(aq)}$ has some affinity for $H^+{}_{(aq)}$. $C_2H_3O_2^-{}_{(aq)}$ accepts $H^+{}_{(aq)}$ from H_2O to form $HC_2H_3O_2$ by the reaction:

$$C_2H_3O_2^-{}_{(aq)} + H_2O_{(l)} \rightleftarrows HC_2H_3O_{2\,(aq)} + OH^-{}_{(aq)}$$

$C_2H_3O_2^-{}_{(aq)}$ has some affinity for $H^+{}_{(aq)}$ resulting in the formation of $OH^-{}_{(aq)}$ and thus, producing a **basic** solution.

Therefore, the dissolution in water of a salt consisting of a cation from a strong **base** and an anion from a weak **acid**; results in the formation of $OH^-{}_{(aq)}$. Hence, these salts produce a **basic** solution when dissolved in water. Other examples of salts that produce **basic** solutions include KNO_2, KF, KCN, etc…

Example: **Calculate the pH of a 0.25 M aqueous solution of $NaC_2H_3O_2$. K_a for $HC_2H_3O_2$ = 1.8×10^{-5}**

Recall that $NaC_2H_3O_2$ is a salt which is soluble in water. Ignoring water, the dissociation reaction for $NaC_2H_3O_2$ is written as:

$$NaC_2H_3O_2 \rightarrow Na^+{}_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

Here, $[Na^+]$ = 0.25 M and $[C_2H_3O_2^-]$ = 0.25 M. $Na^+{}_{(aq)}$ has no effect on the pH of the solution.

	$C_2H_3O_2^-{}_{(aq)}$ +	$H_2O_{(l)} \rightleftarrows$	$HC_2H_3O_{2\,(aq)}$ +	$OH^-{}_{(aq)}$
Initial	0.25 M		0 M	0 M

Consider x, the amount of $H^+{}_{(aq)}$, that is donated by water to the acetate ion.

	$C_2H_3O_2^{-}{}_{(aq)} + H_2O_{(l)}$ ⇆	$HC_2H_3O_2{}_{(aq)}$ +	$OH^{-}{}_{(aq)}$
Initial	0.25 M	0 M	0 M
Change	- x	x	x
Equilibrium	(0.25 – x)	x	x

In this problem, we are given $K_a = 1.8 \times 10^{-5}$ for $HC_2H_3O_2$. $C_2H_3O_2^{-}{}_{(aq)}$ is the conjugate **base** of $HC_2H_3O_2$. The above equation describes the reaction of a **base** with water. Hence, to solve this problem, we need to use the expression for K_b.

Recall that $K_a \times K_b = K_w$ $\quad K_w = 1.0 \times 10^{-14}$ at 25 deg. C

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

The equilibrium constant for this reaction is expressed as:

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} \quad \text{or} \quad 5.6 \times 10^{-10} = \frac{(x)(x)}{(0.25 - x)}$$

Assume x is negligible when compared to 0.25.

$$5.6 \times 10^{-10} = \frac{x^2}{0.25}$$

or $x = 1.2 \times 10^{-5}$ M

This is the concentration of OH^-. Note that x is indeed much smaller than 0.25. Thus, $[OH^-] = 1.2 \times 10^{-5}$ M and pOH = 4.93.

pH + pOH = 14.00

pH = 14.00 - 4.93

pH = 9.07

In Section 15.19, practice the Interactive Problem.

Sections 15.20 - 15.21: Salts that Produce Acidic Solutions.

Consider ammonium chloride, NH_4Cl. Ignoring water, the dissociation reaction for NH_4Cl is:

$$NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$Cl^-{}_{(aq)}$ is the conjugate **base** of the strong **acid**, HCl. $Cl^-{}_{(aq)}$ is a very weak **base** (weaker than H_2O). Hence, $Cl^-{}_{(aq)}$ does not affect the pH. $NH_4^+{}_{(aq)}$ is the weak conjugate **acid** of the weak **base** NH_3. An **acid**, by definition, is a proton donor. Thus, $NH_4^+{}_{(aq)}$ reacts with water as follows:

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrows NH_{3\,(aq)} + H_3O^+{}_{(aq)}$$

Ignoring water, the reaction can be simply written as:

$$NH_4^+{}_{(aq)} \leftrightarrows NH_{3\,(aq)} + H^+{}_{(aq)}$$

Formation of $H^+{}_{(aq)}$ implies that an **acidic** solution is produced.

Therefore, dissolution in water of salts consisting of an anion from a strong **acid** and a cation that is the conjugate **acid** of a weak **base**, results in the formation of an **acidic** solution.

Note: In principle, all metal ions react with water to produce **acidic** solutions. Furthermore, the higher the charge of the metal ions (Al^{+3}, Cr^{+3}, Fe^{+3}, etc), the more **acidic** the aqueous solution produced by the corresponding salts.

Example: **Calculate the pH of a 0.15 M aqueous solution of NH_4Cl ,($K_b = 1.8 \times 10^{-5}$ for NH_3).**

The dissociation reaction for NH_4Cl is: $NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

Here, $[NH_4^+] = 0.15$ M and $[Cl^-] = 0.15$ M

$Cl^-{}_{(aq)}$ has no effect on pH, since it is the very weak conjugate **base** of a strong **acid**, HCl. NH_4^+ is the weak conjugate **acid** of the weak **base** NH_3. Hence, $NH_4^+{}_{(aq)}$ reacts with water to form $H^+{}_{(aq)}$ and $NH_{3\,(aq)}$.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrows NH_3{}_{(aq)} + H_3O^+{}_{(aq)}$$

Ignoring water:

	$NH_4^+{}_{(aq)}$	$\leftrightarrows$	$NH_3{}_{(aq)}$	+	$H^+{}_{(aq)}$	$K_a = 5.6 \times 10^{-10}$
Initial	0.15 M		0 M		0 M	
Change	- x		x		x	
Equilibrium	(0.15 –x)		x		x	

In this problem, we are given $K_b = 1.8 \times 10^{-5}$ for NH_3. We are interested in the reaction of NH_4^+ (conjugate **acid** of NH_3) with H_2O. This reaction is the dissociation reaction of an **acid** in water. Hence, to solve this problem we need the K_a value for this **acid**.

Recall that $K_a \times K_b = K_w$

$K_w = 1.0 \times 10^{-14}$ at 25 °C

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

	$NH_4^+{}_{(aq)}$	$\leftrightarrows$	$NH_3{}_{(aq)}$	+	$H^+{}_{(aq)}$	$K_a = 5.6 \times 10^{-10}$
Initial	0.15 M		0 M		0 M	
Change	- x		x		x	
Equilibrium	(0.15 –x)		x		x	

The equilibrium constant for this reaction is expressed as:

$$K_a = \frac{[NH_3]\,[H^+]}{[NH_4{}^+]}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{(0.15 - x)}$$

Assume x to be negligible in comparison to 0.15 in 0.15 – x.:

$$5.6 \times 10^{-10} = \frac{x^2}{0.15}$$

$$\text{or} \qquad x = 9.2 \times 10^{-6}\ \text{M}$$

This is the concentration of H^+. **Note** that x is indeed much smaller than 0.15!

$$\text{Thus, } [H^+] = 9.2 \times 10^{-6}$$

$$pH = -\log(9.2 \times 10^{-6})$$

$$pH = 5.04$$

In Section 15.21, practice the Interactive Problem.

Section 15.22: Acid - Base Properties of Oxides.

Oxides can be classified as **acidic**, **basic** or amphoteric.

All alkali metal oxides are **basic**. **Basic** metal oxides react with water to form metal hydroxides. The general reaction of alkali metal oxide with water is:

$$M_2O + H_2O \rightarrow 2\ MOH$$

All alkaline earth metal oxides, except BeO, are **basic**. BeO is amphoteric. Amphoteric substances can behave as an **acid** or as a **base**. The general reaction of an alkaline earth metal oxide with water is:

$$MO + H_2O \rightarrow M(OH)_2$$

Oxides of Al (i.e. Al_2O_3), Ga (i.e. Ga_2O_3), Sn (i.e. SnO_2) and Pb (i.e. PbO_2) are also amphoteric.

Non-metal oxides in which the oxidation number of the non-metal is high are **acidic**. For example, considering CO and CO_2, CO_2 is **acidic**. Some examples of reaction between non-metal oxides and water are given below:

$CO_{2\ (g)} + H_2O_{\ (l)} \rightarrow H_2CO_{3\ (aq)}$ H_2CO_3 is carbonic **acid**.

$SO_{3\ (g)} + H_3O_{\ (l)} \rightarrow H_2SO_{4\ (aq)}$ H_2SO_4 is sulfuric **acid**.

$N_2O_{5\ (g)} + H_2O_{\ (l)} \rightarrow 2\ HNO_{3\ (aq)}$ HNO_3 is nitric **acid**.

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