



Acids, Bases and Salts

Acids, Bases and Salts
(Hebden Unit 4 – page 109-182)

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

We will cover the following topics:

1. Definition of Acids and Bases
2. Bronsted-Lowry Acids and Bases

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Arrhenius Definition of Acids and Bases

An acid is a substance that reacts with water to produce hydronium ions, H_3O^+ .

A base is a substance that produces hydroxide ions, OH^- , in water.



When an acid and base reacts, an ionic compound is produced as one of the products. We call ionic compounds “salts”.

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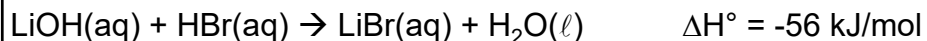
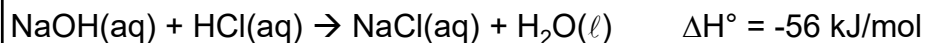
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Acids, Bases and Salts

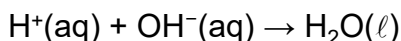
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Arrhenius Theory of Acid and Bases

Support for the Arrhenius concept comes from measurements of ΔH° of neutralization of any strong acid and base. Consider the following reactions:



If we write the net ionic equation for both of these reactions we see that they are the same



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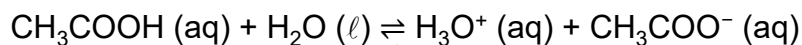
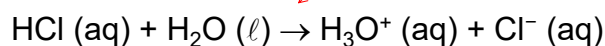
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Monoprotic and Polyprotic acids

1. Monoprotic acids – capable of ionizing 1 H⁺ ion per molecule of acid.

Example:

Strong acid = 100% dissociation into ions



Weak acid = partial dissociation into ions

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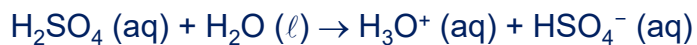
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Monoprotic and Polyprotic acids

2. Polyprotic acids – capable of ionizing more than one H⁺ ion per molecule of acid.

Example of a Diprotic acid:



Example of a Triprotic acid:



You should be able to write acid dissociation reactions.

Pay attention to the charges on all the ions, and balance the reactions.

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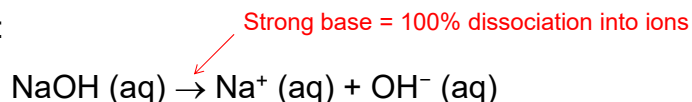
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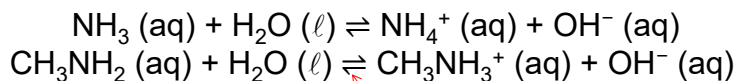
Monoprotic and Polyprotic bases

1. Monoprotic bases – capable of ionizing 1 OH⁻ ion per molecule of base.

Example:



Organic nitrogen compounds, amines, are bases because they dissolve in water to produce OH⁻ ions.



Weak base = partial dissociation into ions

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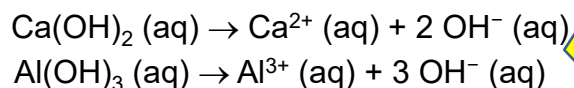
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Monoprotic and Polyprotic bases

2. Polyprotic bases – capable of ionizing more than one OH⁻ ion per molecule of base.

Example:



You should be able to write base dissociation reactions.

Pay attention to the charges on all the ions, and balance the reactions.

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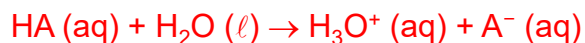
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In general,

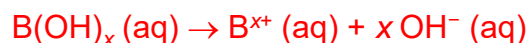
1. Ionization of an acid in water



2. Ionization of a base in water



or



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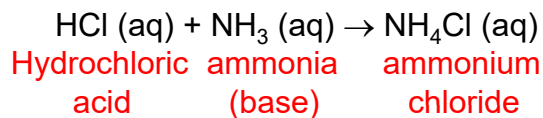
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Brønsted-Lowry Acids and Bases

When neutralization reaction occurs in aqueous solution, Arrhenius' definition of acid and base works well.



Recall that
Arrhenius Definition of
Acid and Base

An **acid** as a substance
that reacts with water
to produce H_3O^+ .

A **base** that reacts
with water to produce
 OH^- .

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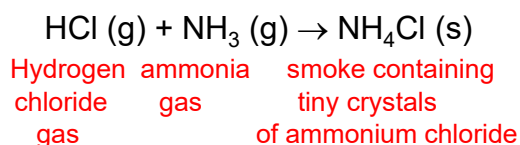
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Brønsted-Lowry Acids and Bases

This same neutralization reaction can occur when it is not in an aqueous medium. Therefore, Arrhenius's definition of an acid and a base is too restrictive.

Example: Neutralization reaction of reactants in gas phase



We need a broader definition!

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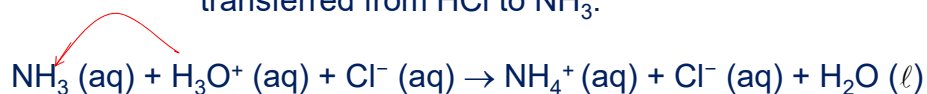
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Brønsted-Lowry Acids and Bases

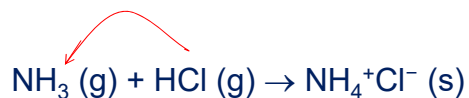
What is in common between the gaseous and aqueous reactions?

1. Both involve a transfer of a H^+ from one reactant to another.

In solution, HCl is completely ionized and the H^+ ion is transferred from HCl to NH_3 .



In gas phase,



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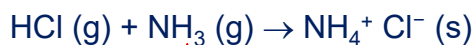
Brønsted-Lowry Acids and Bases

- View acid-base reactions as simply the transfer of H⁺ (protons) from one species to another.

Brønsted-Lowry Acids and Bases Definitions

Acid is a proton donor.

Base is a proton acceptor.



This species donates a proton to NH₃, therefore, it is an acid.

This species accepts a proton, therefore, it is a base.

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Brønsted-Lowry Acids and Bases

In general,



CONJUGATE ACID-BASE PAIRS

Two species that differ by H⁺ are called a *conjugate pair*.

There is a whole table of Brønsted-Lowry Acids and Bases.

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Brønsted-Lowry Acids and Bases

RELATIVE STRENGTHS OF BRØNSTED-LOWRY ACIDS AND BASES
in aqueous solution at room temperature.

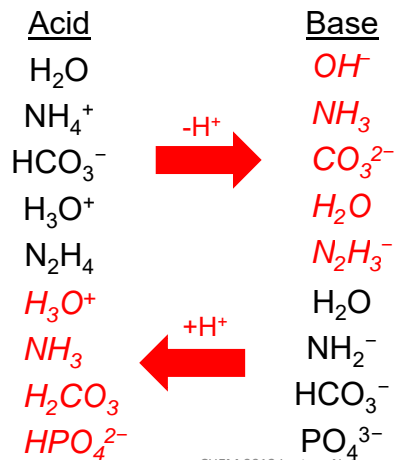
Name of Acid	Acid	Base	K_a
Perchloric	HClO_4	$\rightarrow \text{H}^+ + \text{ClO}_4^-$	very large
Hydriodic	HI	$\rightarrow \text{H}^+ + \text{I}^-$	very large
Hydrobromic	HBr	$\rightarrow \text{H}^+ + \text{Br}^-$	very large
Hydrochloric	HCl	$\rightarrow \text{H}^+ + \text{Cl}^-$	very large
Nitric	HNO_3	$\rightarrow \text{H}^+ + \text{NO}_3^-$	very large
Sulphuric	H_2SO_4	$\rightarrow \text{H}^+ + \text{HSO}_4^-$	very large
Hydronium Ion	H_3O^+	$\rightleftharpoons \text{H}^+ + \text{H}_2\text{O}$	1.0
Iodic	HIO_3	$\rightleftharpoons \text{H}^+ + \text{IO}_3^-$	1.7×10^{-1}
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	$\rightleftharpoons \text{H}^+ + \text{HC}_2\text{O}_4^-$	5.9×10^{-2}
Sulphurous ($\text{SO}_2 + \text{H}_2\text{O}$)	H_2SO_3	$\rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	1.5×10^{-2}
Hydrogen sulphate ion	HSO_4^-	$\rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	1.2×10^{-2}
Phosphoric	H_3PO_4	$\rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	7.5×10^{-3}

↓

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Brønsted-Lowry Conjugate Acids-Bases Pairs



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We will cover the following topics:

1. Amphiprotic Substance
2. Amphoteric Compounds

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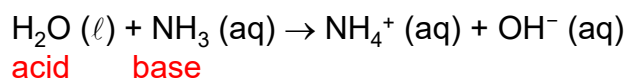
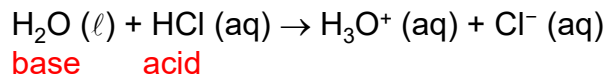
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1. Amphiprotic Substance

A substance that can act either as a proton acceptor or a proton donor.

All amphiprotic substances contain a hydrogen atom.

Example 1 – Water, H₂O



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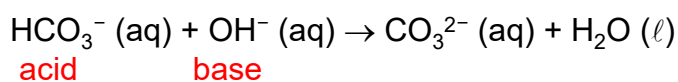
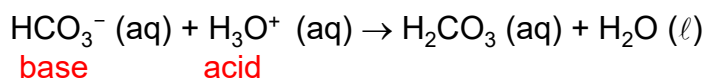
1. Amphiprotic Substance

A substance that can act either as a proton acceptor or a proton donor.

All amphiprotic substances contain a hydrogen atom.

Example 2 – Bicarbonate, HCO_3^-

You should be able to write these equations.



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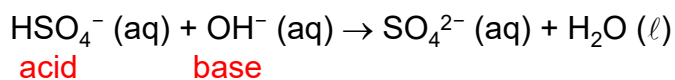
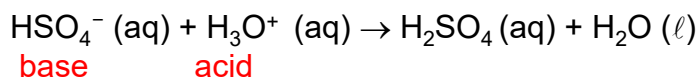
1. Amphiprotic Substance

A substance that can act either as a proton acceptor or a proton donor.

All amphiprotic substances contain a hydrogen atom.

Example 3 – hydrogen sulfate ion, HSO_4^-

You should be able to write these equations.



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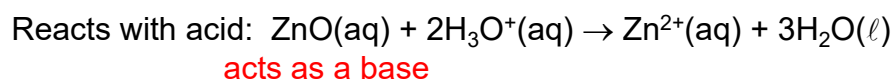
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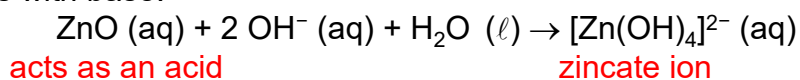
2. Amphoteric Substance

- A compound that can react as either an acid or a base.
- “Ampho-” is Greek, it means “both”.
- Metals have amphoteric oxides. (eg – ZnO, Al(OH)₃)

Example 1 – Zinc oxide, ZnO



Reacts with base:



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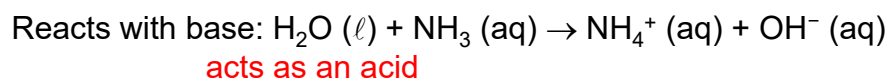
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2. Amphoteric Substance

- A compound that can react as either an acid or a base.
- “Ampho-” is Greek, it means “both”.
- Metals have amphoteric oxides. (eg – ZnO, Al(OH)₃)

Example 2 – Water, H₂O



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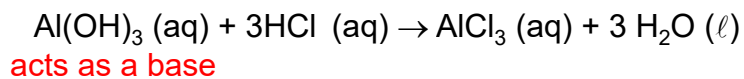
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2. Amphoteric Substance

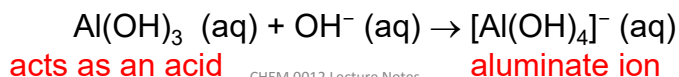
- A compound that can react as either an acid or a base.
- “Ampho-” is Greek, it means “both”.
- Metals have amphoteric oxides. (eg – ZnO, Al(OH)₃)

Example 3 – Aluminum hydroxide, Al(OH)₃

Reacts with acid:



Reacts with base:



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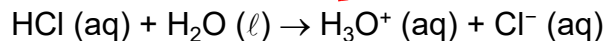
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Strong acids

An acid which dissociates 100% into its ions in a water solution.

Strong acid = 100% dissociation into ions



The [H⁺] (or [H₃O⁺]) concentration of a 0.10 M HCl solution is 0.10 M.

For monoprotic strong acids [acid]_{initial} = [H⁺]

A common notation to express [H⁺] is pH, where

$$\text{pH} = -\log [\text{H}^+] = -\log 0.10 = 1.00$$

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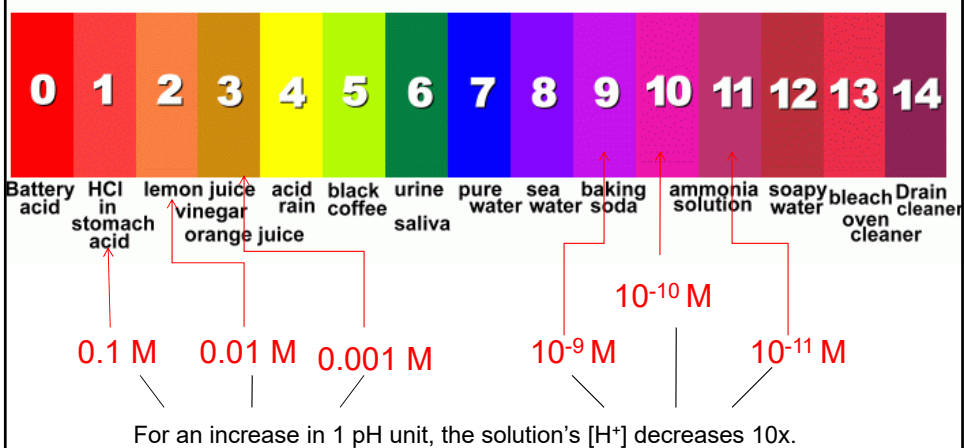
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Recall the pH scale

$$\text{pH} = -\log [\text{H}^+]$$



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Strong acids

K_a

Perchloric	HClO_4	$\rightarrow \text{H}^+ + \text{ClO}_4^-$	very large
Hydriodic	HI	$\rightarrow \text{H}^+ + \text{I}^-$	very large
Hydrobromic	HBr	$\rightarrow \text{H}^+ + \text{Br}^-$	very large
Hydrochloric	HCl	$\rightarrow \text{H}^+ + \text{Cl}^-$	very large
Nitric	HNO_3	$\rightarrow \text{H}^+ + \text{NO}_3^-$	very large
Sulphuric	H_2SO_4	$\rightarrow \text{H}^+ + \text{HSO}_4^-$	very large

These are strong acids.

Dissociation is a single arrow to produce ions.

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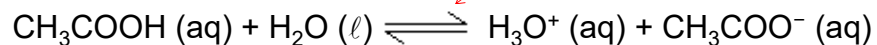
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Weak acids

An acid which dissociates **less than 100%** into its ions in a water solution.

Weak acid = < 100% dissociation into ions.
Use double arrows to indicate this.



The $[\text{H}^+]$ (or $[\text{H}_3\text{O}^+]$) concentration of a **0.10 M** CH_3COOH solution is **LESS THAN 0.10 M**.

Therefore,

$$\text{pH} > 1.00$$

In weak acids $[\text{acid}]_{\text{initial}} \neq [\text{H}^+]$, $[\text{acid}]_{\text{initial}} > [\text{H}^+]$

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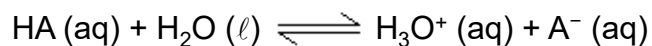
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Weak acids

An acid which dissociates **less than 100%** into its ions in a water solution.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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Weak acids

K_a

Hydronium Ion	$\text{H}_3\text{O}^+ \rightleftharpoons \text{H}^+ + \text{H}_2\text{O}$	1.0
Iodic	$\text{HIO}_3 \rightleftharpoons \text{H}^+ + \text{IO}_3^-$	1.7×10^{-1}
.	.	.
.	.	.
Water	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	1.0×10^{-14}
Hydroxide ion	$\text{OH}^- \leftarrow \text{H}^+ + \text{O}^{2-}$	very small
Ammonia	$\text{NH}_3 \leftarrow \text{H}^+ + \text{NH}_2^-$	very small

These are weak acids except the bottom two.

These last two are too weak to act as acids in water.

Note the single arrows pointing backward because the forward dissociation never occurs.

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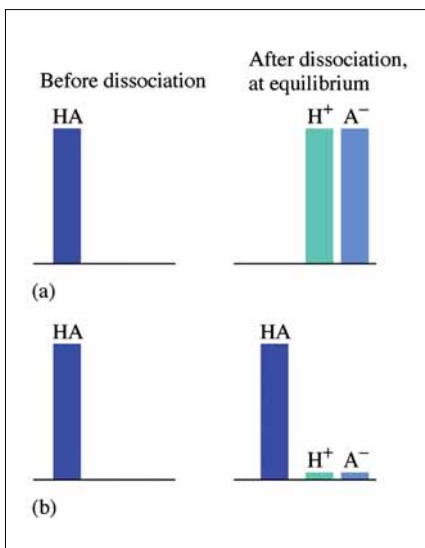
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Illustration of Strong and Weak Acids

Graphic representation of the behavior of acids of different strengths in aqueous solution.

- (a) A strong acid.
- (b) A weak acid.



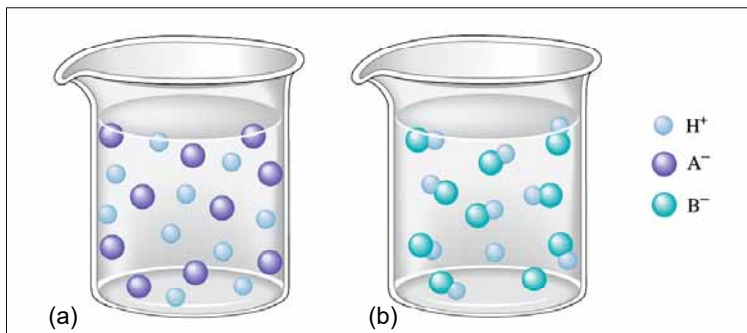
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Illustration of Strong and Weak Acids



(a) A strong acid HA is completely ionized in water.

(b) A weak acid HB exists mostly as undissociated HB molecules in water.

Note that the water molecules are not shown in this figure.

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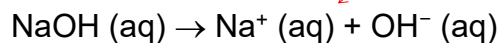
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Strong bases

A base which dissociates 100% into its ions in a water solution.

Strong base = 100% dissociation into ions



The [OH⁻] concentration of a 0.10 M NaOH solution is 0.10 M.

For NaOH, [base]_{initial} = [OH⁻]

A common notation to express [OH⁻] is pOH, where

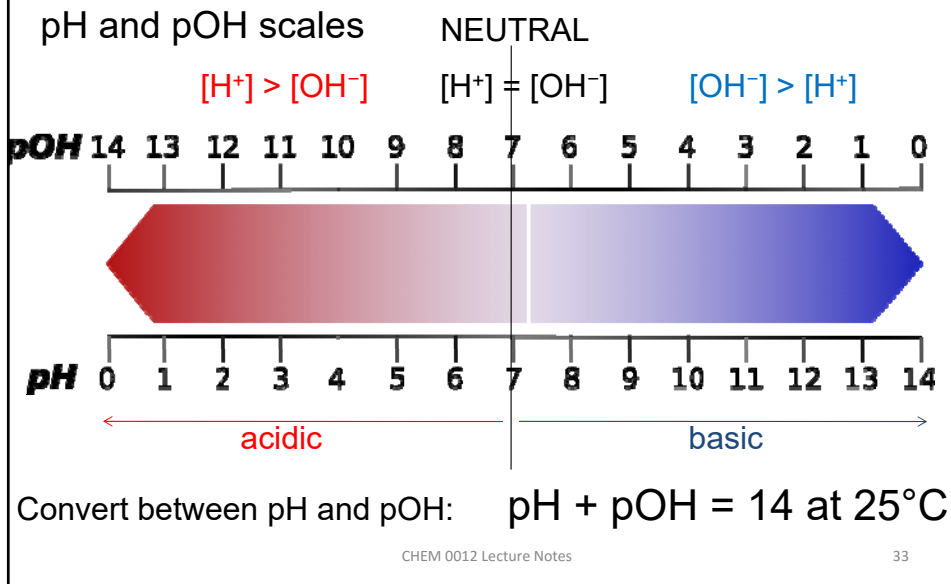
$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.10 = 1.00$$

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Acids, Bases and Salts

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Strong bases

Water	$H_2O \rightleftharpoons H^+ + OH^-$	1.0×10^{-14}
Hydroxide ion	$OH^- \leftarrow H^+ + O^{2-}$	very small
Ammonia	$NH_3 \leftarrow H^+ + NH_2^-$	very small

↑
These are strong bases.

Any substance which dissociates completely to produce OH^- , O^{2-} , or NH_2^- is a strong base.

Examples: Group 1 hydroxides: $LiOH$, $NaOH$, KOH , $RbOH$, $CsOH$
 Group 2 hydroxides: $Mg(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$

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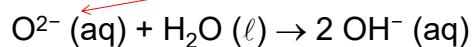
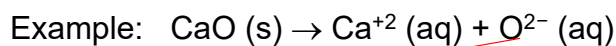
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Strong bases

- For NaOH, $[\text{OH}^-] = [\text{base}]$
- For $\text{Ba}(\text{OH})_2$, $[\text{OH}^-] = 2 \times [\text{base}]$

Salts which produce O^{2-} are strong bases.



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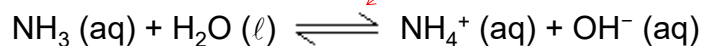
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Weak bases

A base which dissociates **less than 100%** into its ions in a water solution.

Weak bases = < 100% dissociation into ions.
Use double arrows to indicate this.



The $[\text{OH}^-]$ concentration of a **0.10 M** NH_3 solution is **LESS THAN 0.10 M**.

Therefore,

$$\text{pOH} > 1.00$$

In weak bases $[\text{base}]_{\text{initial}} \neq [\text{OH}^-]$, $[\text{base}]_{\text{initial}} > [\text{OH}^-]$

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Weak bases

A base which dissociates **less than 100%** into its ions in a water solution.



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

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Weak bases

K_a

Perchloric	HClO ₄ → H ⁺ + ClO ₄ ⁻	very large
Hydriodic	HI → H ⁺ + I ⁻	very large
Hydrobromic	HBr → H ⁺ + Br ⁻	very large
Hydrochloric	HCl → H ⁺ + Cl ⁻	very large
Nitric	HNO ₃ → H ⁺ + NO ₃ ⁻	very large
Sulphuric	H ₂ SO ₄ → H ⁺ + HSO ₄ ⁻	very large

Conjugate bases of strong acids are **VERY** weak bases.

⋮

These are weak bases, found on the right side of the table.

Hydronium Ion	H ₃ O ⁺ ⇌ H ⁺ + H ₂ O	1.0
Iodic	HIO ₃ ⇌ H ⁺ + IO ₃ ⁻	1.7 × 10 ⁻¹

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Amphiprotic Species

- Found on both sides of the table (eg – HCO_3^-)
- Can act as acids or as bases
- When found on the **left**, it is an acid.

			K_a
Phenol	$\text{C}_6\text{H}_5\text{OH}$	$\rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{O}^-$	1.3×10^{-10}
Hydrogen carbonate ion	HCO_3^-	$\rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	5.6×10^{-11}
Hydrogen peroxide	H_2O_2	$\rightleftharpoons \text{H}^+ + \text{HO}_2^-$	2.4×10^{-12}


Acid
Strength
increases

HCO_3^- is a weaker acid than phenol and a stronger acid than hydrogen peroxide.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Amphiprotic Species

- Found on both sides of the table (eg – HCO_3^-)
- Can act as acids or as bases
- When found on the **right**, it is a base.

			K_a
Hexaquoaluminum ion, aluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{3+}$	$\rightleftharpoons \text{H}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	1.4×10^{-5}
Carbonic ($\text{CO}_2 + \text{H}_2\text{O}$)	H_2CO_3	$\rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	4.3×10^{-7}
Monohydrogen citrate ion	$\text{HC}_6\text{H}_5\text{O}_7^{2-}$	$\rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-}$	4.1×10^{-7}


Base
Strength
increases

HCO_3^- is a weaker base than citrate ion and a stronger base than $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Brønsted-Lowry Acids and Bases

RELATIVE STRENGTHS OF BRØNSTED-LOWRY ACIDS AND BASES
in aqueous solution at room temperature.

Name of Acid	Acid	Base	K_a
Perchloric	HClO_4	$\rightarrow \text{H}^+ + \text{ClO}_4^-$	very large
Hydriodic	HI	$\rightarrow \text{H}^+ + \text{I}^-$	very large
Hydrobromic	HBr	$\rightarrow \text{H}^+ + \text{Br}^-$	very large
Hydrochloric	HCl	$\rightarrow \text{H}^+ + \text{Cl}^-$	very large
Nitric	HNO_3	$\rightarrow \text{H}^+ + \text{NO}_3^-$	very large
Sulphuric	H_2SO_4	$\rightarrow \text{H}^+ + \text{HSO}_4^-$	very large
Hydronium Ion	H_3O^+	$\rightleftharpoons \text{H}^+ + \text{H}_2\text{O}$	1.0
Iodic	HIO_3	$\rightleftharpoons \text{H}^+ + \text{IO}_3^-$	1.7×10^{-1}
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	$\rightleftharpoons \text{H}^+ + \text{HC}_2\text{O}_4^-$	5.9×10^{-2}
Sulphurous ($\text{SO}_2 + \text{H}_2\text{O}$)	H_2SO_3	$\rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	1.5×10^{-2}
Hydrogen sulphate ion	HSO_4^-	$\rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	1.2×10^{-2}
Phosphoric	H_3PO_4	$\rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	7.5×10^{-3}

↑ **STRENGTH OF ACID** (left side) ↓ **STRENGTH OF BASE** (right side)

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

We will work with the reference table

RELATIVE STRENGTHS OF BRØNSTED-LOWRY ACIDS AND BASES

to determine the Acid-Base Equilibria and Relative Strengths of Acids and Bases.

By examining the relative strengths of the acids on both sides of the equilibrium, we can determine which side of the equilibrium is favoured.

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

1. When H_2CO_3 and SO_3^{2-} are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



This can only donate a H^+ ion. It is an **ACID**.

This ion can only act as a **BASE**, accept a H^+ ion.

As a result ...

HCO_3^- is the **conjugate base** of H_2CO_3 .

HSO_3^- is the **conjugate acid** of SO_3^{2-} .

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Acids, Bases and Salts

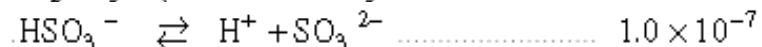
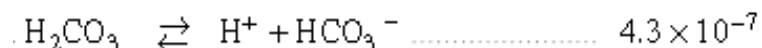
Hebden – Unit 4 (page 109-182)

1. When H_2CO_3 and SO_3^{2-} are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



acid
base
conjugate base
conjugate acid

Compare the K_a of the two acids



H_2CO_3 is a slightly stronger acid than HSO_3^- .
The equilibrium will favour the products.

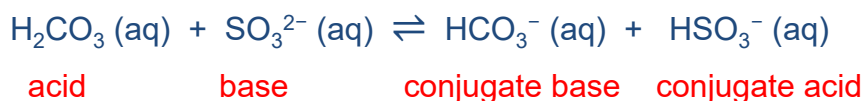
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

1. When H_2CO_3 and SO_3^{2-} are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



What is the value of K for this equilibrium?

$$K = \frac{K_a (\text{H}_2\text{CO}_3)}{K_a (\text{HSO}_3^-)} = \frac{4.3 \times 10^{-7}}{1.0 \times 10^{-7}} = 4.3 > 1$$

Since $K > 1$, equilibrium favors products

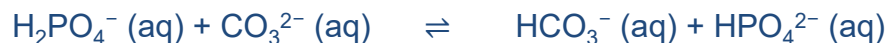
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

2. When H_2PO_4^- and CO_3^{2-} are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



This is an amphiprotic ion. It can donate or accept a H^+ ion.

This ion can only act as a **BASE**, accept a H^+ ion.

After considering, in this mixture, H_2PO_4^- will act as an **acid**.

As a result ...

HCO_3^- is the **conjugate acid** of CO_3^{2-} .

HPO_4^{2-} is the **conjugate base** of H_2PO_4^- .

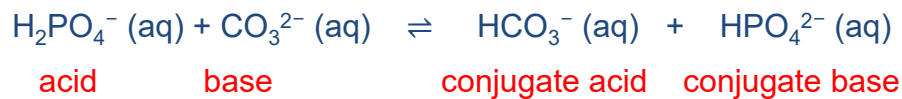
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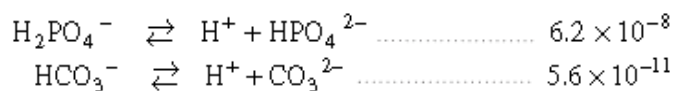
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

2. When H_2PO_4^- and CO_3^{2-} are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



Compare the K_a of the two acids



H_2PO_4^- is a stronger acid than HCO_3^- .
The equilibrium will favour the products.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

3. When HSO_4^- and NH_3 are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



This is an amphiprotic ion. It can donate or accept a H^+ ion.

This can only act as a **BASE**, accept a H^+ ion.

After considering, in this mixture, HSO_4^- will act as an **acid**.

As a result ...

NH_4^+ is the **conjugate acid** of NH_3 .

SO_4^{2-} is the **conjugate base** of HSO_4^- .

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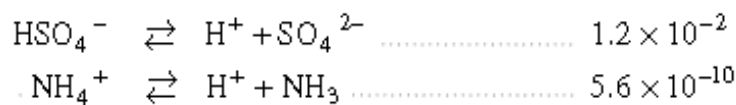
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

3. When HSO_4^- and NH_3 are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



Compare the K_a of the two acids



HSO_4^- is a stronger acid than NH_4^+ .

The equilibrium will favour the products.

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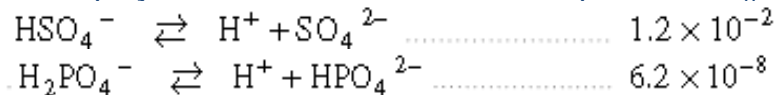
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

4. When HSO_4^- and H_2PO_4^- are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

Both HSO_4^- and H_2PO_4^- are amphiprotic ions.

Which will play the role of an acid? Let's compare their K_a values.



HSO_4^- is a stronger acid than H_2PO_4^- .

HSO_4^- will act as an acid donating protons to H_2PO_4^- .

After considering, in this mixture, HSO_4^- will act as an **acid**. $\text{H}_2\text{PO}_4^{2-}$ will act as the **base**.

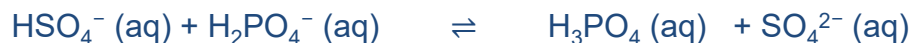
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

4. When HSO_4^- and H_2PO_4^- are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



K_a of HSO_4^- is bigger. It has the higher tendency to donate H^+ .

K_a of H_2PO_4^- is smaller. Comparatively, it has less tendency to donate H^+ .

As a result ...

H_3PO_4 is the conjugate acid of H_2PO_4^- .

SO_4^{2-} is the conjugate base of HSO_4^- .

After considering, in this mixture, HSO_4^- will act as an acid.

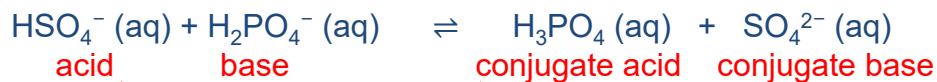
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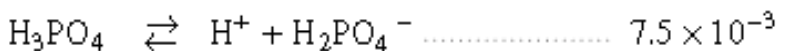
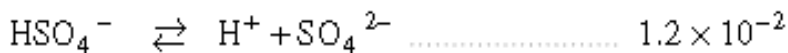
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

4. When HSO_4^- and H_2PO_4^- are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



Compare the K_a of the two acids



HSO_4^- is a stronger acid than H_3PO_4 .
The equilibrium will favour the products.

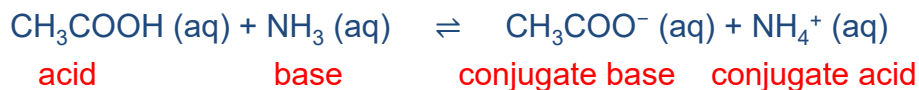
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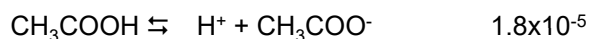
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

5. When CH_3COOH and NH_3 are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?



Compare the K_a of the two acids



CH_3COOH is a stronger acid than NH_4^+ .
The equilibrium will favour the products.

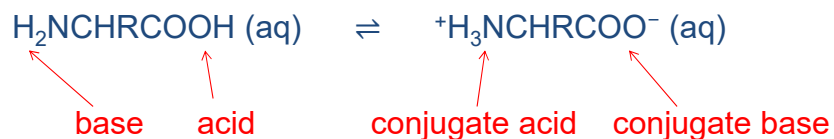
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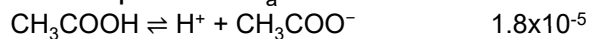
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

6. Consider an amino acid, an equilibrium is set up between the amine group, R-NH_2 , and the carboxylic acid group, R-COOH . Which side of the equilibrium is favoured?



Compare the K_a of the two acids



CH_3COOH is a stronger acid than NH_4^+ .
The equilibrium will favour the products
(i.e. a double charged species).

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Direction of Reaction Example

Predict the direction favored in each of the following acid-base reactions. That is, does the reaction tend to go more in the forward or in the reverse direction?

- a) $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3$ Forward
- b) $\text{HSO}_4^- + \text{NO}_3^- \rightleftharpoons \text{HNO}_3 + \text{SO}_4^{2-}$ Reverse
- c) $\text{HSO}_3^- + \text{CH}_3\text{COO}^- \rightleftharpoons \text{SO}_3^{2-} + \text{CH}_3\text{COOH}$ Reverse
- d) $\text{CH}_3\text{COOH} + \text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+} \rightleftharpoons \text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{CH}_3\text{COO}^-$ Reverse
- e) $\text{HNO}_2 + \text{ClO}_4^- \rightleftharpoons \text{HClO}_4 + \text{NO}_2^-$ Reverse
- f) $\text{H}_2\text{CO}_3 + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{HCO}_3^-$ Forward

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

- In aqueous solutions, H_3O^+ (aq) & OH^- (aq) are the strongest acids and bases that exist.

Stronger bases react with water to form OH^- (aq)
 O^{2-} (aq) + H_2O (l) \rightarrow OH^- (aq) + OH^- (aq)

Stronger acids react with water to form H_3O^+ (aq).
 HCl (aq) + H_2O (l) \rightarrow H_3O^+ (aq) + Cl^- (aq)

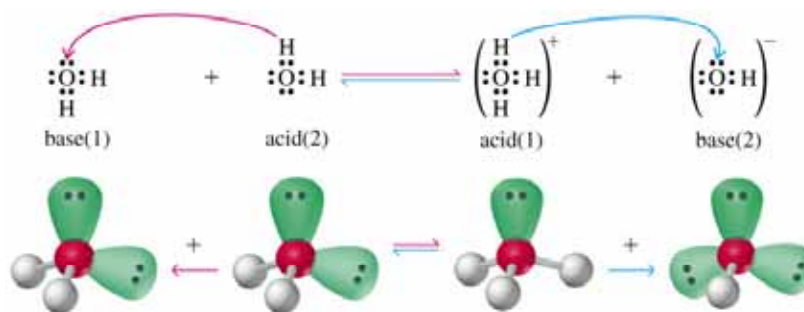
This is known as the **Leveling Effect**

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

The Self-Ionization of Water

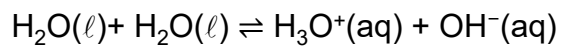


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Acids, Bases and Salts

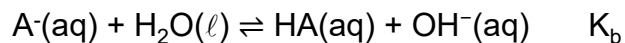
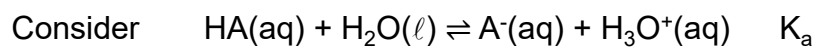
Hebden – Unit 4 (page 109-182)

Ion Product of Water



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}$$



$$K_a K_b = \left(\frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \right) \left(\frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \right) = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

$$K_w = K_a K_b$$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

pH and pOH

- The potential of the hydrogen ion was defined in 1909 as *the negative of the logarithm of [H⁺]*.

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad \text{pOH} = -\log[\text{OH}^-]$$

$$K_{\text{W}} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$-\log K_{\text{W}} = -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] = -\log(1.0 \times 10^{-14})$$

$$\text{p}K_{\text{W}} = \text{pH} + \text{pOH} = -(-14)$$

$$\text{p}K_{\text{W}} = \text{pH} + \text{pOH} = 14 \text{ at } 25^\circ\text{C}$$

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Concentration and pH and pOH Examples at 25°C

	[H ⁺]	[OH ⁻]	pH	pOH	Acidic/Basic
pH = 5.52					
0.15 M HNO ₃					
0.0100 M Ca(OH) ₂					
1.0 × 10 ⁻¹⁰ M Ca(OH) ₂					

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Concentration and pH and pOH Examples at 25°C

	[H ⁺]	[OH ⁻]	pH	pOH	Acidic/Basic
pH = 5.52	3.0x10 ⁻⁶ M	3.3x10 ⁻⁹ M	5.52	8.48	Acidic
0.15 M HNO ₃	0.15 M	6.7x10 ⁻¹⁴ M	0.82	13.18	Acidic
0.0100 M Ca(OH) ₂	5.00x10 ⁻¹³ M	2.00x10 ⁻² M	12.301	1.699	Basic
1.0x10 ⁻¹⁰ M Ca(OH) ₂	1x10 ⁻⁷ M	1x10 ⁻⁷ M	7	7	Neutral

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Strong Acid and Bases Examples

1. Calculate the pH of a solution of 0.400 g of HI in 500. ml of solution.

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Strong Acid and Bases Examples

1. Calculate the pH of a solution of 0.400 g of HI in 500. ml of solution.

$$[H^+] = \frac{(0.400 \text{ g HI}) \left(\frac{\text{mol HI}}{127.9 \text{ g HI}} \right) \left(\frac{\text{mol H}^+}{\text{mol HI}} \right)}{0.500 \text{ L}} = 6.25 \times 10^{-3} \text{ M}$$

$$pH = -\log[H^+] = -\log(6.25 \times 10^{-3}) = 2.204$$

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Strong Acid and Bases Examples

2. Calculate the mass of $\text{Sr}(\text{OH})_2$ which must be dissolved in 600. ml of solution to make a pH of 12.00.

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Strong Acid and Bases Examples

- Calculate the mass of $\text{Sr}(\text{OH})_2$ which must be dissolved in 600. ml of solution to make a pH of 12.00.

$$[\text{OH}^-] = 10^{-(\text{pOH})} = 10^{(\text{pH}-14.00)} = 10^{-2.00} = 1.0 \times 10^{-2} \text{ M}$$

$$n_{\text{OH}^-} = (1.0 \times 10^{-2} \text{ M})(0.600 \text{ l}) = 6.0 \times 10^{-3} \text{ mol OH}^-$$

$$\text{g Sr}(\text{OH})_2 = (6.0 \times 10^{-3} \text{ mol OH}^-) \left(\frac{\text{mol Sr}(\text{OH})_2}{2 \text{ mol OH}^-} \right) \left(\frac{121.6 \text{ g Sr}(\text{OH})_2}{\text{mol Sr}(\text{OH})_2} \right)$$

$$\text{g Sr}(\text{OH})_2 = 0.36 \text{ g Sr}(\text{OH})_2$$

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Weak Acid and Bases Examples

- Butyric acid, $\text{HC}_4\text{H}_7\text{O}_2$ (or $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$) is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of $\text{HC}_4\text{H}_7\text{O}_2$ is found to have a pH of 2.72. Determine K_A for butyric acid.

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Weak Acid and Bases Examples

1. Butyric acid, $\text{HC}_4\text{H}_7\text{O}_2$ (or $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$) is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of $\text{HC}_4\text{H}_7\text{O}_2$ is found to have a pH of 2.72. Determine K_a for butyric acid.



I	0.250	0	0
C	$-10^{-2.72}$	$10^{-2.72}$	$10^{-2.72}$
E	$0.250 - 10^{-2.72}$	$10^{-2.72}$	$10^{-2.72}$

$$K_a = \frac{[\text{C}_4\text{H}_7\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_4\text{H}_7\text{O}_2]} = \frac{(10^{-2.72})(10^{-2.72})}{0.250 - 10^{-2.72}} = 1.5 \times 10^{-5}$$

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Weak Acid and Bases Examples

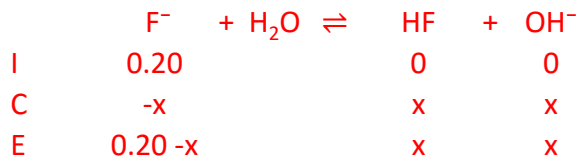
2. Calculate the pH of a 0.20 M solution of KF, K_b for F^- is 1.5×10^{-11} .

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Weak Acid and Bases Examples

2. Calculate the pH of a 0.20 M solution of KF, K_b for F^- is 1.5×10^{-11} .



$$K_b = 1.5 \times 10^{-11} = \frac{[HF][OH^-]}{[F^-]} = \frac{(x)(x)}{0.20 - x}$$

K_b is small x is probably small, thus $0.20 - x \approx 0.20$

$$\therefore 1.5 \times 10^{-11} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20} \quad \text{or} \quad x = \sqrt{(0.20)(1.5 \times 10^{-11})} = 1.7 \times 10^{-6}$$

so $x = [OH^-] = 1.7 \times 10^{-6} \ll 0.20 \therefore$ assumption is OK

$$pOH = -\log[OH^-] = -\log(1.7 \times 10^{-6}) = 5.77$$

$$pH = 14.00 - pOH = 14.00 - 5.77 = 8.23$$

Acids, Bases and Salts

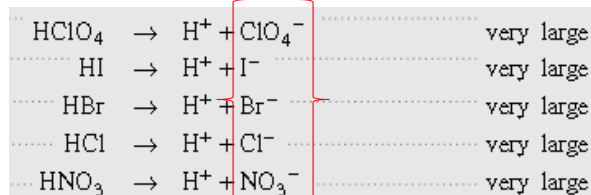
Hebden – Unit 4 (page 109-182)

Hydrolysis

is the reaction between water and the ions contained in the water solution. When this occurs, this could result in producing an acidic or basic solution.

Spectator ions do **NOT** undergo hydrolysis. They are:

- Group 1 (alkali metals): Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+
- Group 2 (alkaline-earth metals): Be^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+}
- Conjugate bases of strong acids: ClO_4^- , I^- , Br^- , Cl^- , NO_3^-



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Acids, Bases and Salts

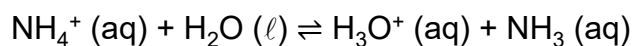
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Cation that undergo hydrolysis

- NH_4^+ , ammonia



Hydrolysis equation:



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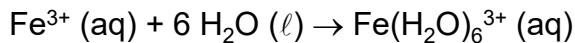
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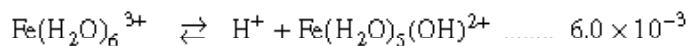
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Hydrated cations that undergo hydrolysis

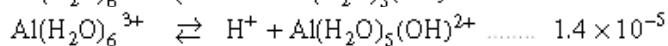
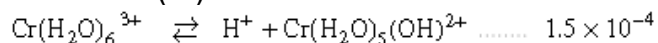
- Transition metals have smaller ions and bigger charges
- This attracts H_2O molecules
- Example – Fe^{3+} or iron (III) ions forms



Hexaquoiron, or iron (III) ion is a weak acid.



- Other hydrated ions are chromium (III) and aluminum (III) ions



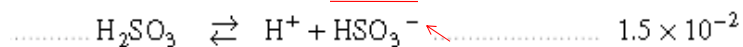
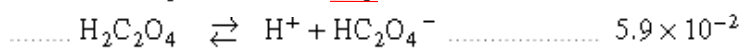
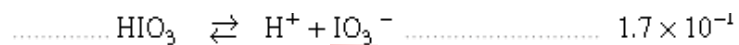
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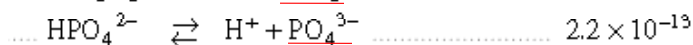
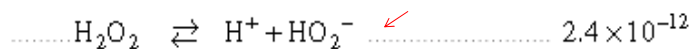
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Anions that undergo hydrolysis



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All ions in this section can undergo hydrolysis.



Anions that are not amphiprotic will act as weak bases in water.

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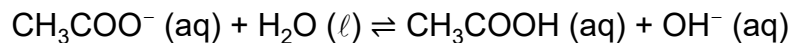
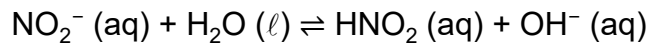
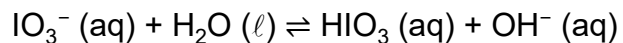
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Acids, Bases and Salts

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Anions that undergo hydrolysis

Examples of net ionic hydrolysis equations are:



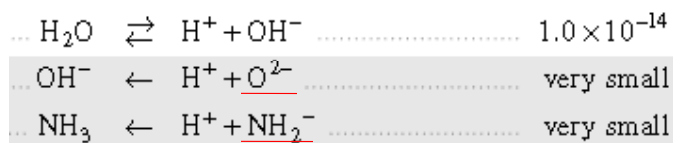
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Anions that undergo hydrolysis



These 2 ions act as STRONG Bases. They undergo 100% hydrolysis to form OH^- ions.

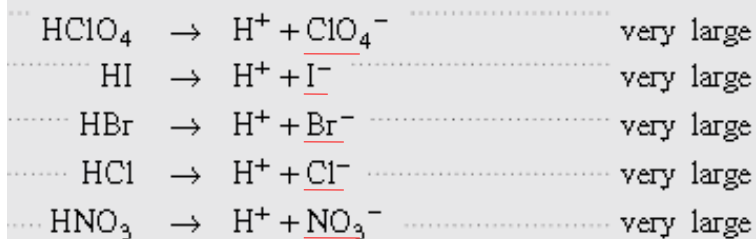
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Anions that do not undergo hydrolysis



These 5 ions do NOT undergo hydrolysis. They are spectators.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Amphiprotic anions that undergo hydrolysis

These anions start with “H” and have a “-” charge.

Examples: HSO_4^- , HSO_3^- , H_2PO_4^- , HPO_4^{2-} , HS^- etc.

Amphiprotic anions hydrolyze as **acids** to produce H_3O^+ , but they also hydrolyze as **bases** to produce OH^- . Compare the K_a and K_b values to determine the predominant hydrolysis.

Find the K_a of the ion by looking for the ion on the LEFT side of the acid table.

Find the K_b of the ion by looking for the ion on the RIGHT side of the acid table. ($K_b = K_w/K_a$ (conjugate acid))

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

1. Is the salt NaCl acidic, basic or neutral in water?



Na^+ and Cl^- ions are spectator ions.

As a result ...

No hydrolysis reaction occurs.
Solution is neutral.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

2. Is the salt NaF acidic, basic or neutral in water?
What is the net ionic equation?



Na⁺ ions are spectator ions.
F⁻ ions are found on the right side of the acid table.
It is a weak base.



As a result ...

F⁻ undergoes hydrolysis reaction.
F⁻ (aq) + H₂O (ℓ) ⇌ HF (aq) + OH⁻ (aq)
Solution is basic.

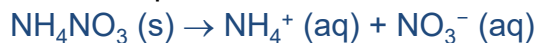
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

3. Is the salt NH₄NO₃ acidic, basic or neutral in water?
What is the net ionic equation?



NO₃⁻ ions are spectator ions.
NH₄⁺ ions are found on the left side of the acid table.
It is a weak acid.



As a result ...

NH₄⁺ undergoes hydrolysis reaction.
NH₄⁺ (aq) + H₂O (ℓ) ⇌ NH₃ (aq) + H₃O⁺ (aq)
Solution is acidic.

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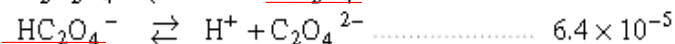
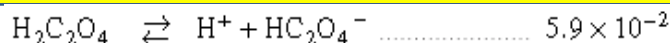
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

4. Is the salt NaHC_2O_4 acidic, basic or neutral in water?
What is the net ionic equation?



Na^+ ions are spectator ions.
 HC_2O_4^- ions are found on the right and left side of the acid table.
It can either be a weak acid or a weak base.



As a result, compare K_a and K_b values of HC_2O_4^- .

$$K_a = 6.4 \times 10^{-5}; \quad K_b = \frac{10^{-14}}{5.9 \times 10^{-2}} = 1.7 \times 10^{-13}$$

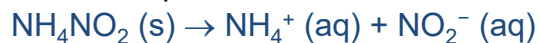
$K_a > K_b$.
 $\text{HC}_2\text{O}_4^- (\text{aq}) + \text{H}_2\text{O} (\ell) \rightleftharpoons \text{C}_2\text{O}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$
Solution is acidic.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

5. Is the salt NH_4NO_2 acidic, basic or neutral in water?
Write the net ionic equation.



NH_4^+ ions are found on the left side of the acid table.
 NO_2^- ions are found on the right side of the acid table.



As a result, compare K_a of NH_4^+ K_b of NO_2^- .

$$K_a = 5.6 \times 10^{-10}; \quad K_b = \frac{10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-11}$$

$K_a > K_b$. Solution is acidic.

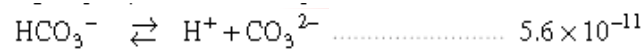
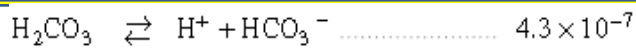
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

6. Is the HCO_3^- ion acidic, basic or neutral in water?

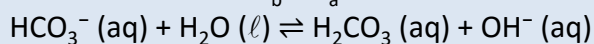
HCO_3^- ions are found on the right and left side of the acid table.



As a result, compare K_a and K_b of HCO_3^- .

$$K_a = 5.6 \times 10^{-11}; \quad K_b = \frac{10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

$$K_b > K_a.$$



Solution is basic.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Salt Examples

Predict whether the following solutions are acidic or basic?

a) NaCN Na^+ no hydrolysis, CN^- is conjugate base of HCN.

Therefore solution is basic.

b) KCl K^+ no hydrolysis, Cl^- no hydrolysis.

Therefore solution is neutral.

c) NH_4Br Br^- no hydrolysis (HBr is strong acid) ,

NH_4^+ is a weak acid. Therefore solution is acidic.

d) NH_4CN Both NH_4^+ and CN^- hydrolyze in aqueous solutions.

Must compare the values of $K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$

and $K_b(\text{CN}^-) = 2.0 \times 10^{-5}$. Since $K_b > K_a$ the solution

is basic.

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

TABLE 14.6 Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO ₃ , NaCl, NaNO ₃	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	NaC ₂ H ₃ O ₂ , KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH ₄ Cl, NH ₄ NO ₃	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	NH ₄ C ₂ H ₃ O ₂ , NH ₄ CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	Al(NO ₃) ₃ , FeCl ₃	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

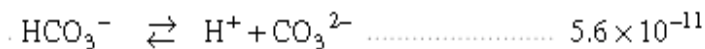
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Is the salt Na₂CO₃ acidic, basic or neutral in water?
Write the net ionic equation.



Na⁺ ions are spectator ions.
CO₃²⁻ ions are found on the right side of the acid table.
It is a weak base.



As a result ...

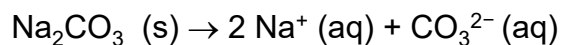
CO₃²⁻ undergoes hydrolysis reaction. The net ionic equation is
CO₃²⁻ (aq) + H₂O (ℓ) ⇌ HCO₃⁻ (aq) + OH⁻ (aq)
Solution is basic.

Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na_2CO_3 .

Step 1: Identify the ions involved.



Spectator ion

Found on the right side of the acid table; undergo base hydrolysis

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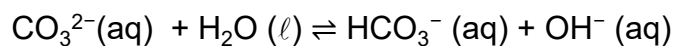
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na_2CO_3 .

Step 2: Write the net ionic equation for the hydrolysis. Set up ICE table.



	$\text{CO}_3^{2-} (\text{aq}) + \text{H}_2\text{O} (\ell) \rightleftharpoons \text{HCO}_3^- (\text{aq}) + \text{OH}^- (\text{aq})$			
[I]	0.30		0	0
[C]	- x		+ x	+ x
[E]	0.30 - x		x	x

Stoichiometric ratio

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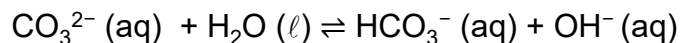
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Acids, Bases and Salts

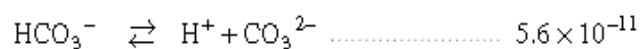
Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na_2CO_3 .

Step 3: Determine the K_b for the base hydrolysis.



Look up in the acid table the K_a for HCO_3^-



$$K_b = \frac{K_w}{K_a(\text{HCO}_3^-)} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.786 \times 10^{-4}$$

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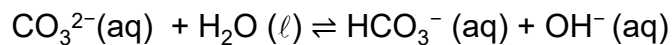
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na_2CO_3 .

Step 4: Write the K_b expression for the base hydrolysis.



$$K_b = \frac{[\text{HCO}_3^-] \cdot [\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na_2CO_3 .

Step 5: Substitute in the equilibrium concentrations from the ICE table.

	$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$			
[I]	0.30		0	0
[C]	-x		+x	+x
[E]	0.30 - x		x	x

$$K_b = \frac{[\text{HCO}_3^-] \cdot [\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{x^2}{0.30 - x} = 1.786 \times 10^{-4}$$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na_2CO_3 .

Step 6: Solve for x, where $x = [\text{OH}^-]$.

$$K_b = \frac{[\text{HCO}_3^-] \cdot [\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{x^2}{0.30 - x} = 1.786 \times 10^{-4}$$

$$\frac{x^2}{0.30} = 1.786 \times 10^{-4}$$

Use assumption $0.30 - x \cong 0.30$
because
 $[0.30] > 1000 \times 1.786 \times 10^{-4}$

$$[\text{OH}^-] = x = 7.319 \times 10^{-3} \text{ M}$$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na_2CO_3 .

Step 7: From the $[\text{OH}^-]$, calculate the pOH.

$$\text{pOH} = -\log (7.319 \times 10^{-3}) = 2.1355$$

Step 8: Convert pOH to pH.

$$\text{pH} = 14 - \text{pOH} = 14 - 2.1355 = 11.86$$

Step 9: Check that your answer makes sense.

We expect CO_3^{2-} ions will undergo base hydrolysis. $\text{pH} > 7$.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 1: Determine the concentration of the solution.

$$\frac{45.0 \text{ g}}{53.5 \text{ g/mole}} = 0.841 \text{ mole}$$

$$\frac{0.841 \text{ mole}}{1.50 \text{ L}} = 0.561 \text{ M } \text{NH}_4\text{Cl}$$

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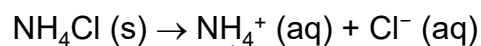
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 2: Identify the ions involved.



Found on the left side of the acid table; undergo acid hydrolysis

Spectator ion

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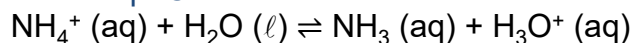
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 3: Write the net ionic equation for the hydrolysis.

Set up ICE table.



	$\text{NH}_4^+ (\text{aq}) + \text{H}_2\text{O} (\ell) \rightleftharpoons \text{NH}_3 (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$		
[I]	0.561		0 0
[C]	- x		+ x + x
[E]	0.561 - x		x x

Stoichiometric ratio

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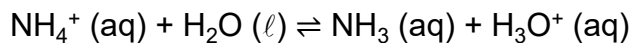
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 4: Determine the K_a for the acid hydrolysis.



Look up in the acid table the K_a for NH_4^+



K_a

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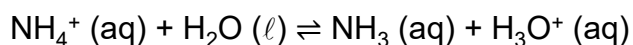
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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 5: Write the K_a expression for the acid hydrolysis.



$$K_a = \frac{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 6: Substitute in the equilibrium concentrations from the ICE table.

	$\text{NH}_4^+ (\text{aq}) + \text{H}_2\text{O} (\ell) \rightleftharpoons \text{NH}_3 (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$			
[I]	0.561		0	0
[C]	- x		+ x	+ x
[E]	0.561 - x		x	x

$$K_a = \frac{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.561 - x} = 5.6 \times 10^{-10}$$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 7: Solve for x, where $x = [\text{H}_3\text{O}^+]$.

$$K_a = \frac{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.561 - x} = 5.6 \times 10^{-10}$$

Make assumption: $0.561 - x \cong 0.561$

$$K_a = \frac{x^2}{0.561} = 5.6 \times 10^{-10}$$

$$[\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-5} \text{ M}$$

Check assumption:
[Initial] > 1000 x K_a

Assumption is valid because
 $0.561 > 1000 \times 5.6 \times 10^{-10}$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH_4Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH_4Cl is 53.5 g/mole.

Step 8: Convert to pH.

$$[\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Titration

- Equivalence point:
 - The point in the reaction at which both acid and base have been consumed.
 - Neither acid nor base is present in excess.
- End point:
 - The point at which the indicator changes color.
- Titrant:
 - The solution added to the solution in the flask.
- Titration Curve:
 - A plot of pH of the solution being analyzed as a function of the amount of titrant added.

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Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

Acid-Base Indicators

- Color of some substances depends on the pH.
$$\text{HIn}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{In}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
 - >90% acid form the color appears to be the acid color
 - >90% base form the color appears to be the base color
 - Intermediate color is seen in between these two states.
- Complete color change occurs over 2 pH units
- Marks the **end point** of a titration by changing color.
- The **equivalence point** is **not** necessarily the same as the **end point**.

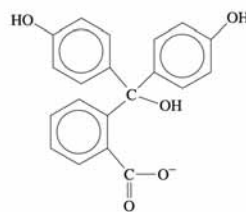
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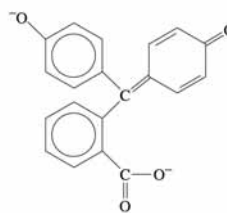
Acids, Bases and Salts

Hebden – Unit 4 (page 109-182)

The acid and base forms of the indicator phenolphthalein. In the acid form (HIn), the molecule is colorless. When a proton (plus H_2O) is removed to give the base form (In^-), the color changes to pink.



(Colorless acid form, HIn)



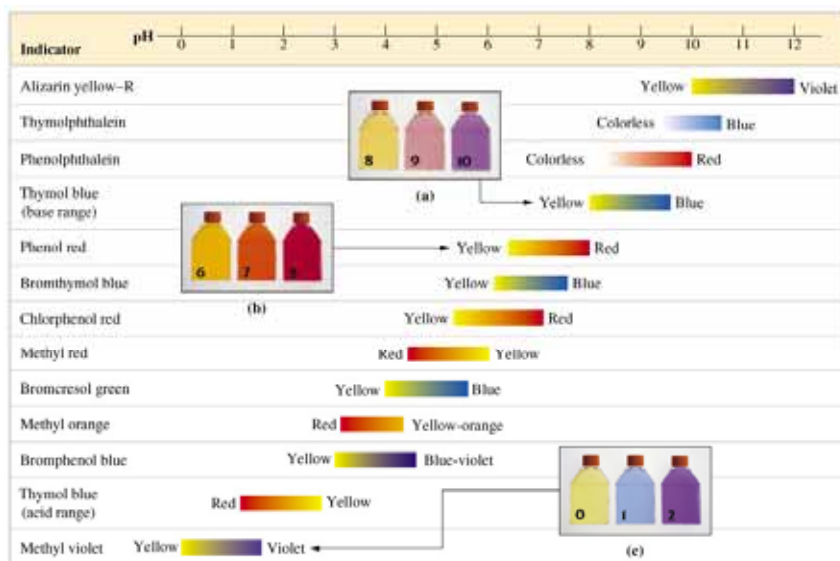
(Pink base form, In^-)

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Acids, Bases and Salts

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Acids, Bases and Salts

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Titration of a Strong Acid with a Strong Base

- The pH has a low value at the beginning.
- The pH changes slowly
 - until just before the equivalence point.
- The pH rises sharply
 - perhaps 6 units per 0.1 mL addition of titrant.
- The pH rises slowly again.
- Any Acid-Base Indicator will do.
 - As long as color change occurs between pH 4 and 10.

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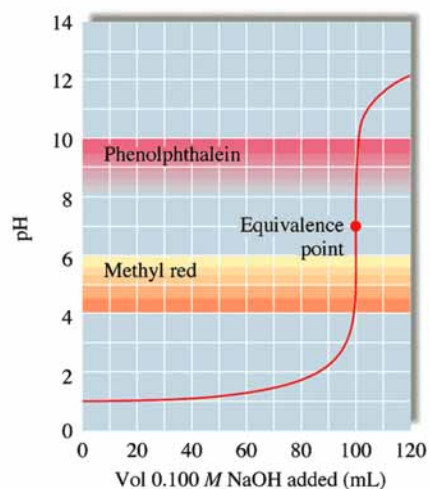
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The pH curve for the titration of 100.0 mL of 0.10 M HCl with 0.10 M NaOH.

Note:

- At the equivalence point $\text{pH} = 7$
- Either indicator will give a fairly accurate result



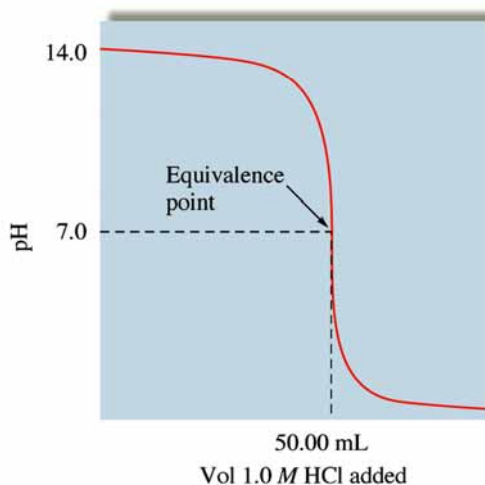
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Acids, Bases and Salts

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For the titration of a strong base with a strong acid the titration curve is just flipped over.

The pH curve for the titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl.



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Acids, Bases and Salts

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Weak Acid - Strong Base Titration

- Step 1 - A **stoichiometry problem** - reaction is assumed to run to completion - then determine remaining species.
- Step 2 - An **equilibrium problem** - determine position of weak acid equilibrium and calculate pH.

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Acids, Bases and Salts

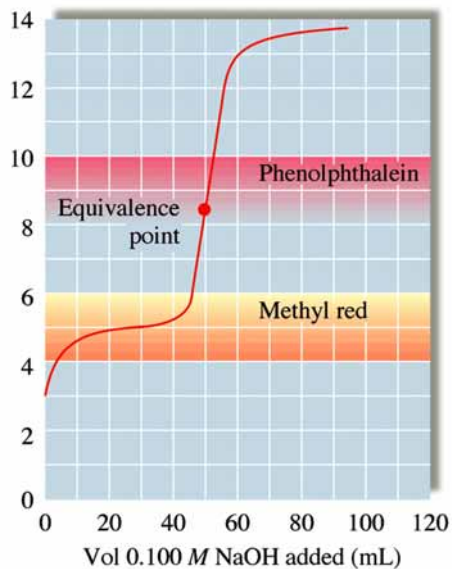
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Weak Acid - Strong Base Titration

The pH curve for the titration of 50.0 mL of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.100 M NaOH.

Note:

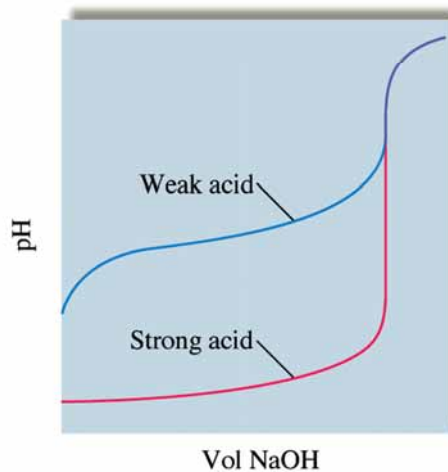
- At the equivalence point $\text{pH} > 7$
- Choice of indicator is important
- $\text{pK}_a = \text{pH}$ at the point halfway to the equivalence point
- The pH is fairly constant around halfway to the equivalence point i.e it is a buffer solution



Acids, Bases and Salts

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Comparison of strong and weak acid titration curves.



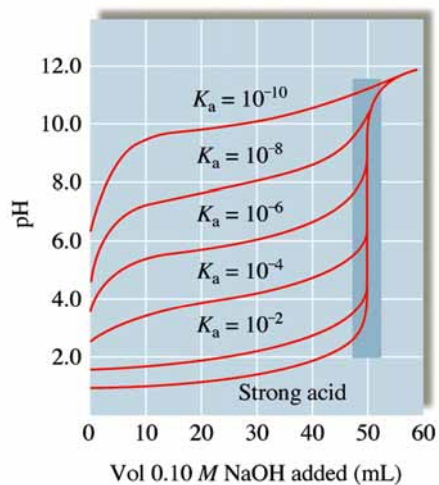
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The pH curves for the titrations of 50.0-mL samples of 0.10 M acids with various K_a values with 0.10 M NaOH.



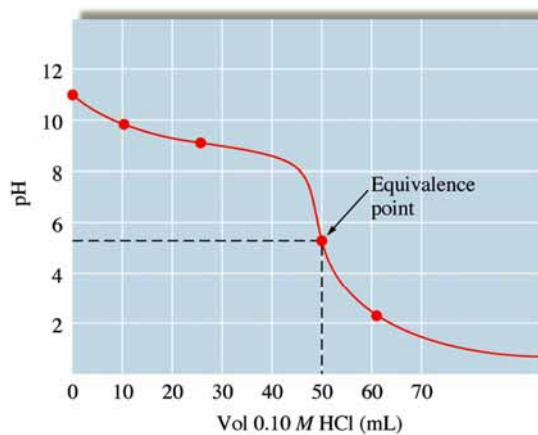
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For the titration of a weak base with a strong acid the titration curve is just flipped over.

The pH curve for the titration of 100.0 mL of 0.050 M NH_3 with 0.10 M HCl.

Note at equivalence point $\text{pH} < 7$



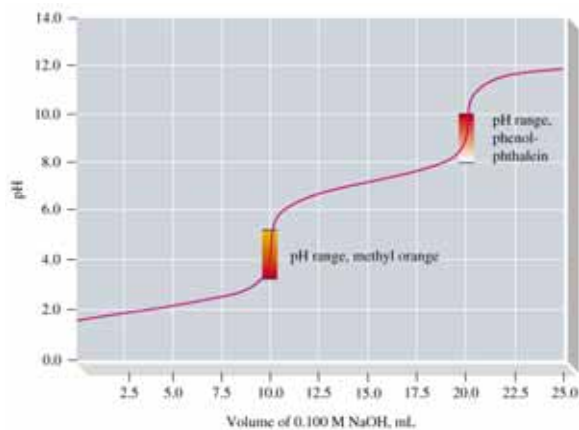
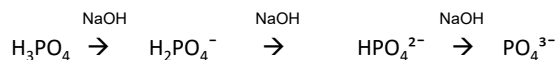
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Titration of a Weak Polyprotic Acid



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Buffer Solutions

- Two component systems that change pH only slightly on addition of acid or base.
 - The two components must not neutralize each other but must neutralize strong acids and bases.
- A weak acid and its conjugate base.
- A weak base and its conjugate acid
- After addition of strong acid or base, deal with **stoichiometry first**, then equilibrium.

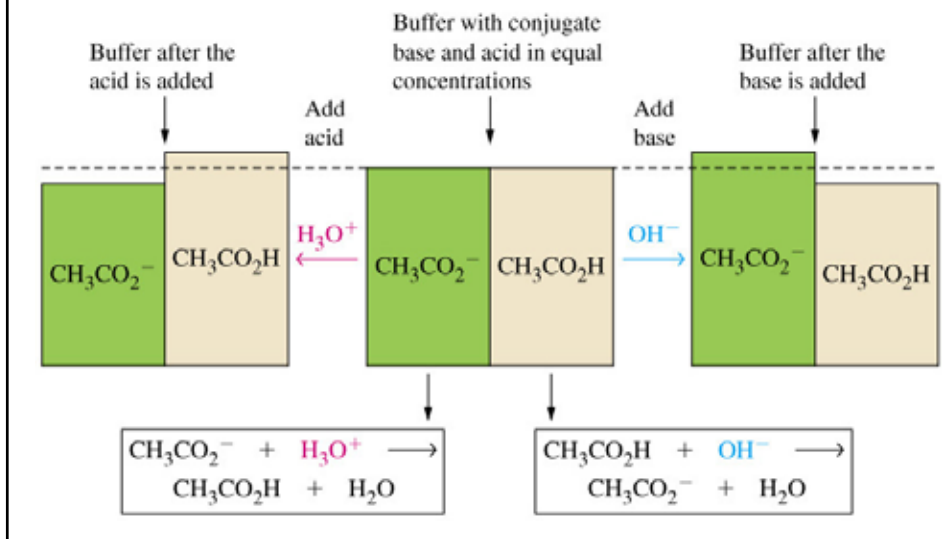
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How A Buffer Works



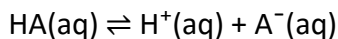
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The Henderson-Hasselbalch Equation

A variation of the ionization constant expression.

Consider a hypothetical weak acid, HA, and its salt NaA:



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow -\log(K_a) = -\log[\text{H}^+] - \log\left[\frac{[\text{A}^-]}{[\text{HA}]}\right]$$

$$\text{p}K_a = \text{pH} - \log\left[\frac{[\text{A}^-]}{[\text{HA}]}\right] \quad \text{or} \quad \text{pH} = \text{p}K_a + \log\left[\frac{[\text{A}^-]}{[\text{HA}]}\right]$$

$$\text{pH} = \text{p}K_a + \log\left[\frac{\text{conjugate base}}{\text{conjugate acid}}\right]$$

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The Henderson-Hasselbalch Equation

- Only useful when you can use *initial* concentrations of acid and salt.
 - This limits the validity of the equation.

- Limits can be met by:

$$0.1 < \frac{[A^-]}{[HA]} < 10$$

$$\text{and both } [A^-] > 10K_a \text{ and } [HA] > 10K_a$$

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Characteristics of the Henderson-Hasselbalch Equation

- pH depends only on the ratio $[A^-]/[HA]$
 - This means that the pH of a buffer solution does not change on dilution.
- When $[A^-] = [HA]$ then $pH = pK_a$. This is also the point where the ratio changes least upon the addition of either acid or base. Therefore a system is best at buffering at a $pH = pK_a$.
- pH changes as the Log of the ratio $[A^-]/[HA]$. Therefore pH is not very sensitive to the value of $[A^-]/[HA]$
- The larger the value of $[A^-]$ and $[HA]$ the more acid or base that can be added without significantly changing the pH (i.e. the greater the buffering capacity of the solution).

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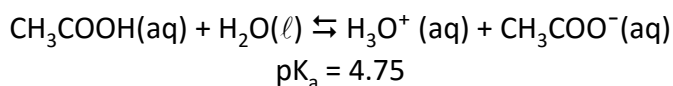
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Buffer Solutions

Consider the case of acetic acid



$[\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$	pH
0.1	3.75
0.5	4.45
1	4.75
2	5.05
10	5.75

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Preparing a Buffer Solution of a Desired pH

- What mass of $\text{NaC}_2\text{H}_3\text{O}_2$ must be dissolved in 0.300 L of 0.25 M $\text{HC}_2\text{H}_3\text{O}_2$ ($K_a = 1.8 \times 10^{-5}$) to produce a solution with pH = 5.09? (Assume that the solution volume is constant at 0.300 L)



$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$\Rightarrow [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{K_a[\text{HC}_2\text{H}_3\text{O}_2]}{[\text{H}^+]} = \frac{(1.8 \times 10^{-5})(0.25)}{(10^{-5.09})} = 0.553 \text{ M } \text{C}_2\text{H}_3\text{O}_2^-$$

$$\Rightarrow 0.553 \text{ M } \text{NaC}_2\text{H}_3\text{O}_2$$

$$(0.553 \text{ M } \text{NaC}_2\text{H}_3\text{O}_2) \left(\frac{82.0 \text{ g } \text{NaC}_2\text{H}_3\text{O}_2}{\text{mol } \text{NaC}_2\text{H}_3\text{O}_2} \right) (0.300 \text{ L}) = 14 \text{ g } \text{NaC}_2\text{H}_3\text{O}_2$$

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