MACQUARIE University

CBMS107: Acids and Bases

LEWIS ACIDS AND BASES

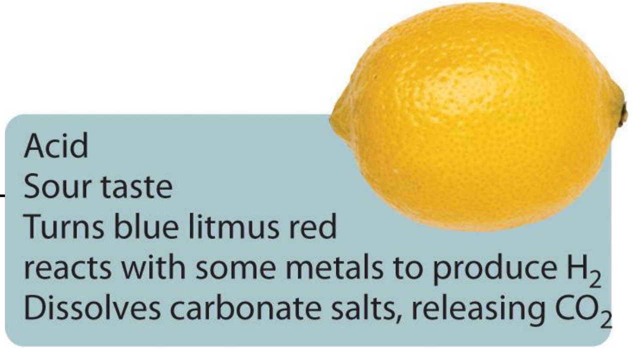
MOLARITY

ION PRODUCT OF WATER, Kw

pH AND pOH

Note2: brackets **[ ]** indicate that we are referring to the concentration of species. For example, when we write **[H^+]**, we mean concentration of H^+.

Acids and Bases (AB)



- A further important concept qualitatively related to electronegativity and bond polarity is that of **acidity** and **basicity**.

- For example, the acid-base behaviour of many organic molecules helps to explain why and how they react with other molecules.

- We characterise acids and bases as either "**strong**" or "**weak**".

	Weak AB		*Strong AB*
Acid	$H_2O(l)$ $HCOOH(aq)$	*Acid*	$HCl(aq)$ $HNO_3(aq)$
Base	$H_2O(l)$ $NH_3(aq)$	*Base*	$LiOH(aq)$ $NaOH(aq)$

Acids and Bases

ARRHENIUS MODEL

- The simplest definition for AB is the Arrhenius model, which while useful, has limited interpretative value, especially in organic chemistry. In aqueous solution:
    - Acids dissociate to form **hydrogen ions (H^+)**

$$HCl(g) \xrightarrow{\text{water}} \boxed{H^+(aq)} + Cl^-(aq)$$

    - Bases dissociate to form **hydroxide ions (OH^-)**

$$NaOH(s) \xrightarrow{\text{water}} Na^+(aq) + \boxed{OH^-(aq)}$$

- Note: a **solution** is a homogeneous mixture composed of a **solvent** and one or more **solutes**. If the solvent is water, we say that the solution is an aqueous solution and use the symbol **(aq)**.

- For example, sea water is a liquid solution, composed of water and dissolved substances (eg Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, etc).

Acids and Bases

BRØNSTED-LOWRY MODEL

- The Brønsted-Lowry model defines:
  - acid as a substance (molecule or ion) that **donates** H^+ to another substance
  - base as a substance that **accepts** H^+

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- In the Brønsted-Lowry model, an acid and base always work together to transfer a H^+.

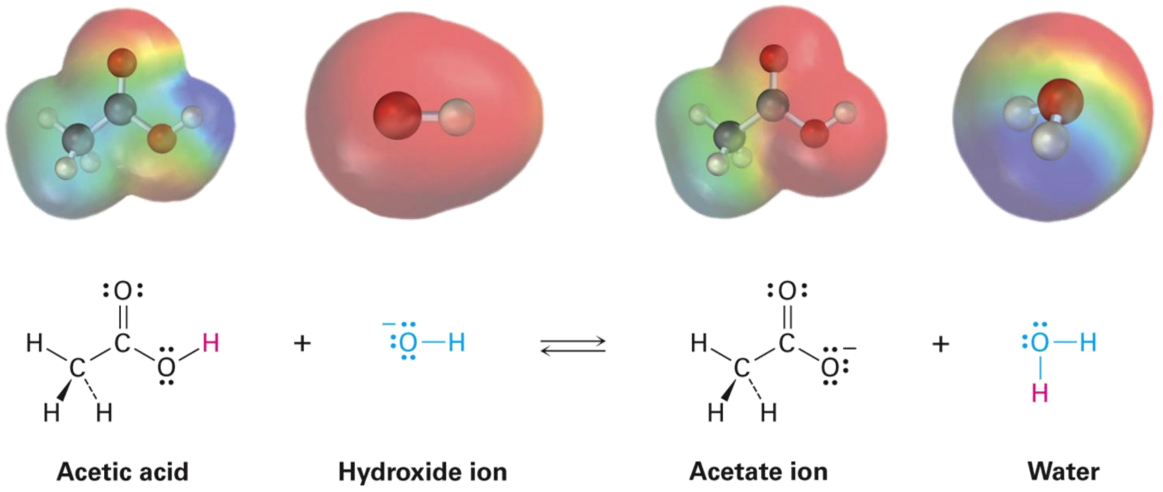
- Note that water acts as either an acid or base. **Amphiprotic** substances act as a:
  - **base** when **combined with** something more **strongly acidic** than itself
  - **acid** when **combined with** something more **strongly basic** than itself

Acids and Bases

LEWIS MODEL

- Many of the organic reactions considered in CBMS107, including essentially all biological reactions, involve organic acids and organic bases.

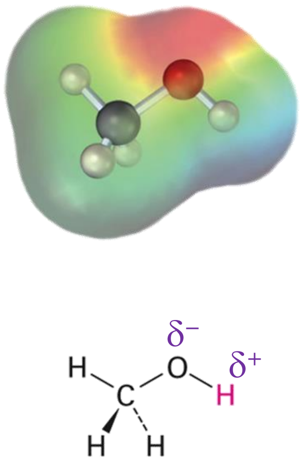
- Compounds that **lose a H^+ from O–H** are very common examples of organic acids.



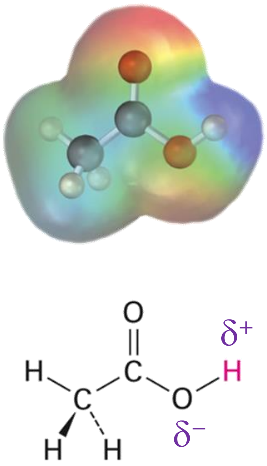
Acids and Bases

LEWIS MODEL

- Organic acids are characterized by the presence of **positively polarized** hydrogen atom.

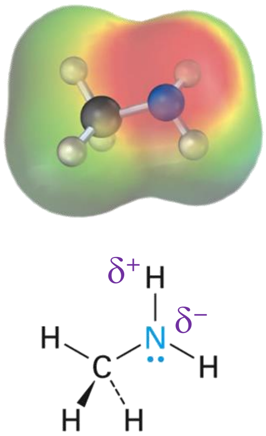


Methanol

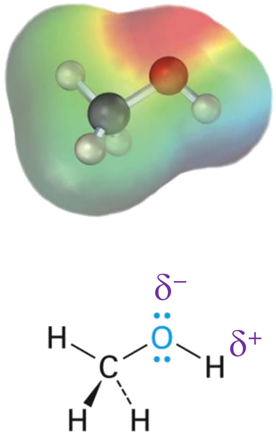


Acetic acid

- Organic bases are characterized by the presence of an **atom with a lone pair of electrons** that can bond to H^+.



Methylamine

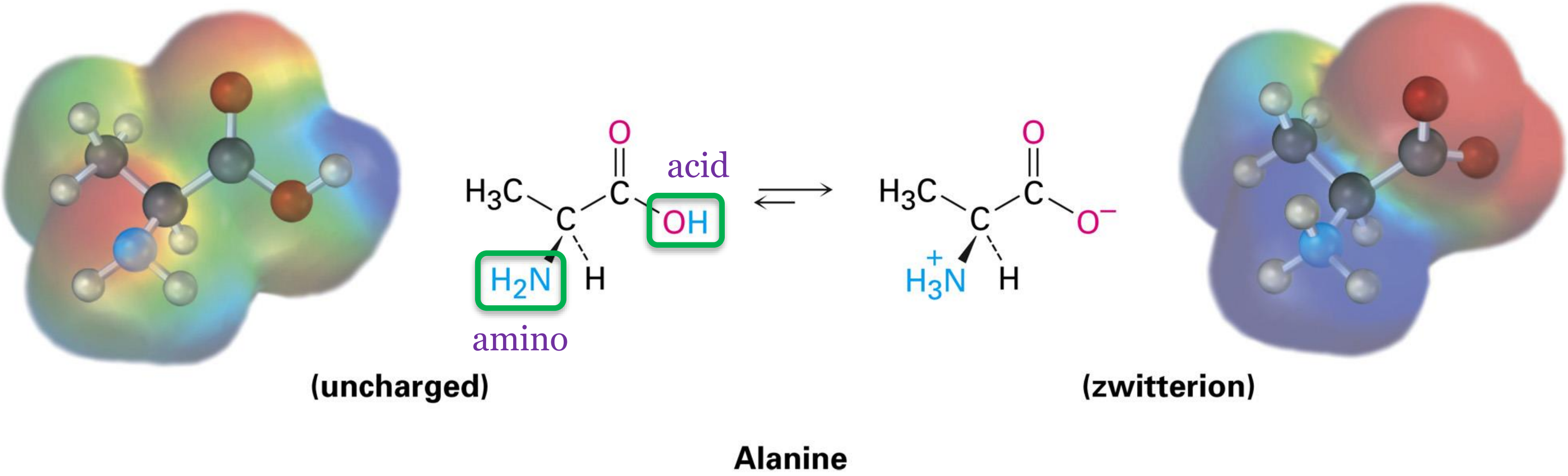


Methanol

Acids and Bases

LEWIS MODEL

- **Amino acids** are the building blocks of proteins. They are both an acid and a base, in the same molecule.



Acids and Bases

LEWIS MODEL

- **Lewis acids are electron pair acceptors** and **Lewis bases are electron pair donors.**
- The Lewis model for AB is broader than the Brønsted-Lowry model, as it is not limited by H^+ exchange.
- **Lewis bases** can accept protons as do Brønsted-Lowry bases.
- However, not all Brønsted-Lowry acids are **Lewis acids**, as they cannot accept an electron pair directly.

NOTE: The Lewis definition leads to a general description of many reaction patterns but there is no scale of strengths, as in the Brønsted-Lowry model (eg K_a).

Some Lewis acids

CH_3CH_2OH alcohol

HNO_3 nitric acid

$CH_3C(=O)\text{-}OH$ carboxylic acid

Mg^{2+} magnesium dication

Some Lewis bases

CH_3CH_2OH alcohol

CH_3OCH_3 ether

$CH_3C(=O)CH_3$ ketone

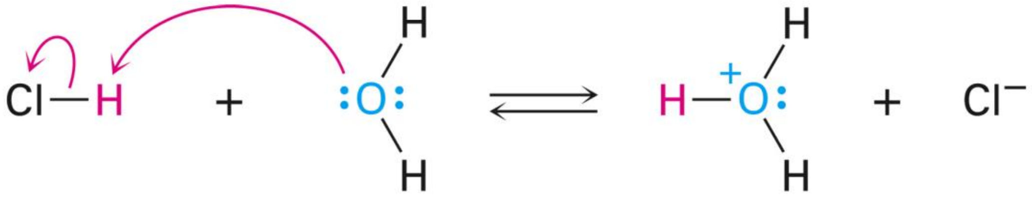
$CH_3N(CH_3)CH_3$ amine

Acids and Bases

LEWIS MODEL

- The Lewis AB definition can be used to explore reaction processes. For example, water (a **Lewis base**) **donating a pair of nonbonding electrons to** the hydrogen of hydrogen chloride (a **Lewis acid**).

The magenta arrow shown is an example of “arrow pushing”, a topic you will discuss in detail with Joanne Jamie.



Hydrogen chloride (Lewis acid)

Water (Lewis base)

Hydronium ion

Acids and Bases

MODELS

- **Arrhenius model**
  - Acids dissociate to produce hydrogen ions (H^+) and bases dissociate to produce hydroxide ions (OH^-)

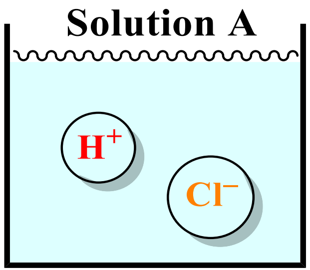
- **Brønsted-Lowry model** – good for quantifying relative AB strength
  - An acid is a substance that donates H^+ to another substance and a base is a substance that accepts H^+.

- **Lewis model** – most general definition and good for studying reactions
  - Acids are electron pair acceptors and bases are electron pair donors.

Molarity

SOLUTION ACIDITY AND BASICITY

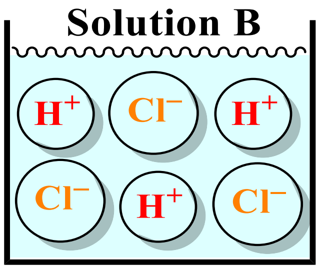
- To describe the acidity or basicity of a solution, we need to know the **concentration** of the species present.



$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Which HCl solution is more acidic?

Both solutions have a total volume of 100 mL.



- Solutions A and B are both made from the same strong acid, HCl. However, solution **B (right) is more acidic**, as it contains more H^+ ions. As both solutions have the same volume, solution **B is also is more concentrated**.

Molarity

CONCENTRATION

- As we noted, the acidity (basicity) of a solution depends not only on the nature of the acid (base), but also its **concentration**.

- The concept of concentration is used to specify the amount of **solute dissolved in a given quantity of solution (solvent)**.

- The concept is intuitive: the greater the amount of solute dissolved in a certain amount of solvent, the more concentrated the resulting solution.

- To express the concentrations of solutions **quantitatively**, we use the quantity **molarity**.

Molarity

DEFINITION

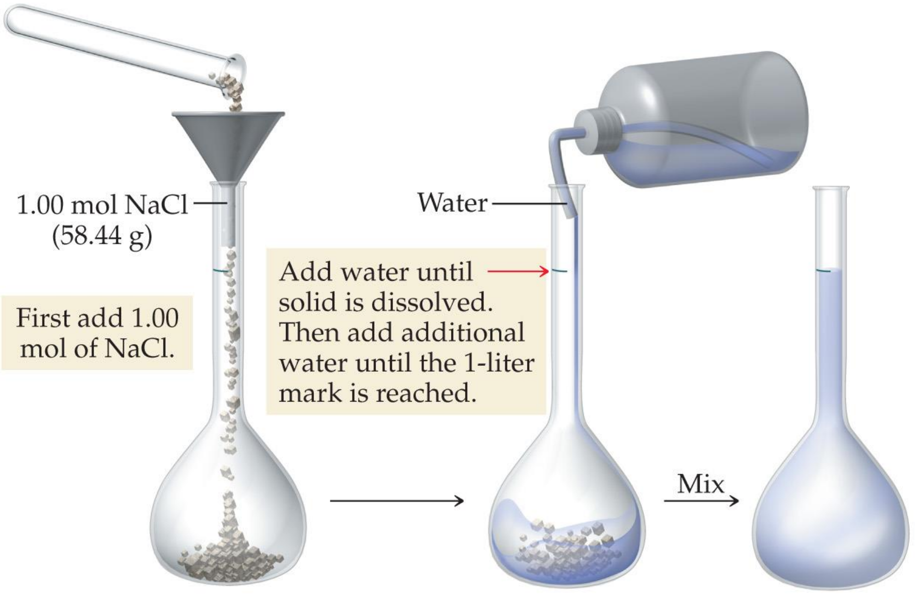
$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution in litres}} = \frac{n}{V}$$

- Molarity (M) expresses the concentration of a solution as the number of moles of solute in a litre of solution:

$$1\ M\ \text{NaCl} = \frac{1\ \text{mol of NaCl}}{1\ \text{litre of water}}$$

$$\text{Moles } (n) = \text{molarity x volume}$$
$$= \text{M x } V$$
$$\text{Volume } (V) = \frac{\text{moles}}{\text{molarity}}$$
$$= \frac{n}{\text{M}}$$

How to prepare a 1.00 molar NaCl solution.



A 1.00 molar NaCl solution

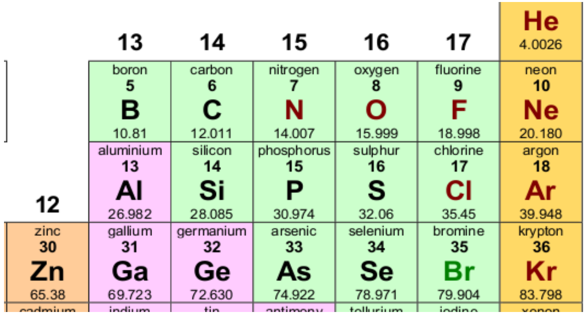
Molarity

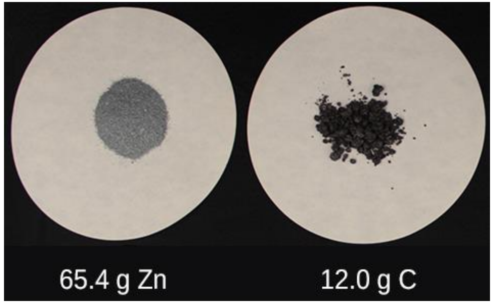
MOLE CONCEPT

- The periodic table includes **weights**, which enable us to convert between two of the **SI base units**, mole and kilogram. For chemists, this is a very important function.

- A mole of any substance contains **6.022×10^{23}** elementary particles. This is Avogadro's constant (NA).

- It is very important that you understand that mass and moles are connected. Eg, one mole of carbon weighs 12.011 g, which we can write as **12.011 g mol^{-1}**.





Source: https://opentextbc.ca

Molarity

MOLE CONCEPT

- Question: I have 27.91 g of calcium metal. How many moles of calcium do I have? How many calcium atoms do I have? Round values to two decimal places (2dp).
  - molar mass Ca = 40.078 g mol^{-1}
  - mole Ca = 27.91 g / 40.078 g mol^{-1}
    = 0.70 mol
  - atom Ca = 0.7 mol × (6.022×10^{23} atoms mol^{-1})
    = 4.19×10^{23} atoms

Did you get exactly the same answer? Why not?

$$\text{mole} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1})}$$

The mass of one mole of a substance is called the molar mass.

Molarity

EXAMPLES

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution in litres}} = \frac{n}{V}$$

- Question: 0.380 g solid $NaNO_3$ is made up to exactly 50.0 mL with water. What is the molarity of the $NaNO_3$ solution?
  - mole $NaNO_3$ = mass / molar mass
    = (0.380 g) / ((22.990 + 14.007 + (3 × 15.999)) g mol^{-1})
    = 4.47×10^{-3} mol
  - molarity $NaNO_3$ = mole / volume
    = (4.47×10^{-3} mol) / ((50.0 / 1000) L)
    = 0.0894 mol L^{-1}

$$\text{mole} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1}\text{)}}$$

Molarity

EXAMPLES

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution in litres}} = \frac{n}{V}$$

- Question: How many moles of solute are there in 25.0 mL 0.106 M NaOH solution?

  - mole NaOH = molarity × volume

    $= (0.106 \text{ mol L}^{-1}) \times ((25 / 1000) \text{ L})$

    $= 2.65 \times 10^{-3}$ mol

Molarity

EXAMPLES

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution in litres}} = \frac{n}{V}$$

- Question: What mass of $Ba(OH)_2$ is required to make a 500 mL solution of 0.060 M Ba(OH)2? What is the molarity of hydroxide ions in this solution?

$$\text{mole} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1}\text{)}}$$

  - mole $Ba(OH)_2$ = molarity × volume
    $= (0.060 \text{ mol L}^{-1}) \times ((500 / 1000) \text{ L})$
    $= 3.0 \times 10^{-2}$ mol

  - mass $Ba(OH)_2$ = mole x molar mass
    $= (3.0 \times 10^{-2} \text{ mol}) \times ((137.33 + (2 \times 17.007)) \text{ g mol}^{-1})$
    $= 5.14$ g

  - ~~molarity OH^- = molarity $Ba(OH)_2$~~ wrong OH^- molarity!!!

Molarity

EXAMPLES

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution in litres}} = \frac{n}{V}$$

- Question: What mass of $Ba(OH)_2$ is required to make a 500 mL solution of 0.060 M Ba(OH)2? **What is the molarity of hydroxide ions in this solution?**

The relative ion concentrations following dissolution depend on the chemical formula of the species present.

Molarity in 1 L of water

$NaCl(s)$	$\longrightarrow$	$Na^+(aq)$ +	$Cl^-(aq)$	$Na^+(aq)$	$Cl^-(aq)$
1.0 mol		1.0 mol	1.0 mol	**1 mol L⁻¹**	**1 mol L⁻¹**
$Ba(OH)_2(s)$	$\longrightarrow$	$Ba^{2+}(aq)$ +	$2\ OH^-(aq)$	$Ba^{2+}(aq)$	$OH^-(aq)$
1.0 mol		1.0 mol	2.0 mol	**1 mol L⁻¹**	**2 mol L⁻¹**

Molarity

EXAMPLES

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution in litres}} = \frac{n}{V}$$

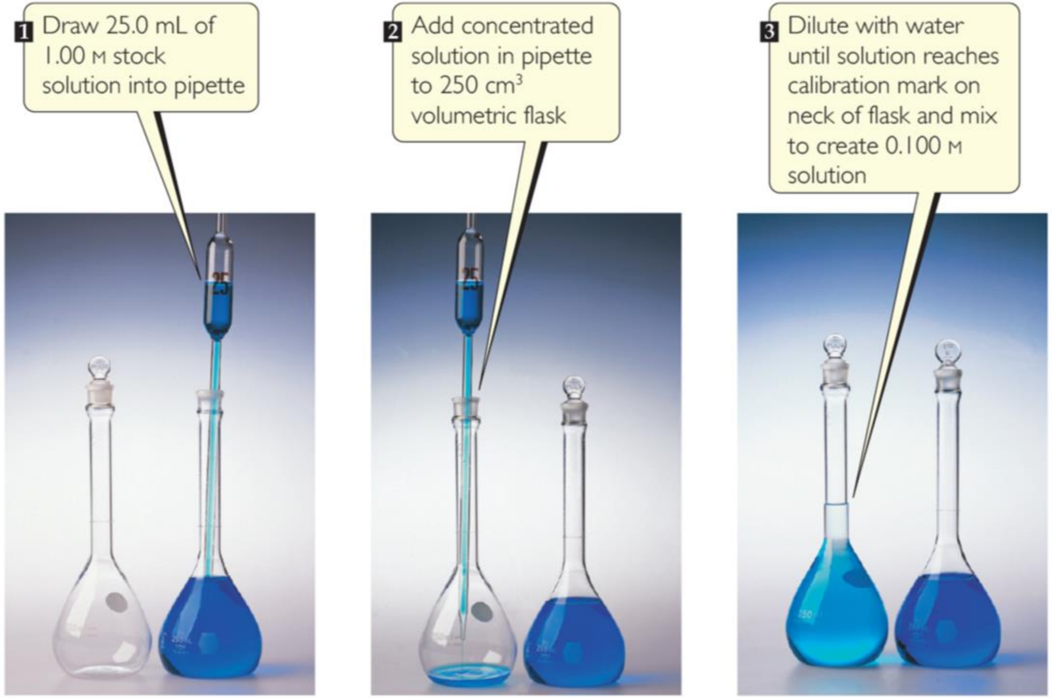
- Question: What mass of $Ba(OH)_2$ is required to make a 500 mL solution of 0.060 M Ba(OH)2? What is the molarity of hydroxide ions in this solution?
  - mole $Ba(OH)_2$ = molarity × volume
    $= (0.060 \text{ mol L}^{-1}) \times ((500 / 1000) \text{ L})$
    $= 3.0 \times 10^{-2}$ mol
  - mass $Ba(OH)_2$ = mole x molar mass
    $= (3.0 \times 10^{-2} \text{ mol}) \times ((137.33 + (2 \times 17.007)) \text{ g mol}^{-1})$
    $= 5.14$ g
  - molarity OH^- $= \boxed{2} \times$ molarity $Ba(OH)_2$
    $= 2 \times (0.060 \text{ mol L}^{-1})$
    $= 0.12 \text{ mol L}^{-1}$

$$Ba(OH)_2(s) \longrightarrow Ba^{2+}(aq) + \boxed{2}OH^-(aq)$$

Molarity

DILUTION

http://cottees.com.au/our-product-range



▲ **FIGURE 4.18** **Procedure for preparing 250 dm^3 of 0.100 M $CuSO_4$ by dilution of 1.00 M $CuSO_4$.** (1) Draw 25.0 cm^3 of the 1.00 M solution into a pipette. (2) Add this to a 250 cm^3 volumetric flask. (3) Add water to dilute the solution to a total volume of 250 cm^3.

- Solutions that are used routinely in the laboratory are often purchased or prepared in concentrated form (called ***stock solutions***).

- Solutions of lower concentrations can then be obtained by adding water, a process called **dilution**.

Molarity

DILUTION

Moles solute before dilution	=	Moles solute after dilution

- When solvent is added to dilute a solution, the number of moles of solute remains unchanged.

- Change in concentration (volume) with dilution:

$$V_{conc} = \frac{M_{dil} \text{ x } V_{dil}}{M_{conc}} \qquad M_{dil} = \frac{M_{conc} \text{ x } V_{conc}}{V_{dil}}$$

$$M_{conc} \text{ x } V_{conc} = M_{dil} \text{ x } V_{dil}$$

$$\frac{\text{mol}}{\cancel{\text{L}}} \text{ x } \cancel{\text{L}} = \frac{\text{mol}}{\cancel{\text{L}}} \text{ x } \cancel{\text{L}}$$

$$\text{mol} = \text{mol}$$

Question: What is the molarity of a solution of NaCl if 25.0mL of 0.657 M solution is diluted to 275 mL?

Acids and Bases

ACID AND BASE MODELS

- **Arrhenius model**
  - Acids dissociate to produce hydrogen ions (H^+) and bases dissociate to produce hydroxide ions (OH^-)
- **Brønsted-Lowry model** – good for quantifying relative AB strength
  - An acid is a substance that donates H^+ to another substance and a base is a substance that accepts H^+.
- **Lewis model** – most general definition and good for studying reactions
  - Acids are electron pair acceptors and bases are electron pair donors.

Acids and Bases

STRONG AND WEAK ACIDS

- In aqueous solution, the distinction between strong and weak acids reflects produced $[H_3O^+]$.

What is the $[H_3O^+]$ of a 0.150 M HCl solution?

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Strong acid → 100% ionisation

$[H_3O^+]$ = 0.150 M

What is the $[H_3O^+]$ of 0.150 M CH_3COOH solution which is 1.42% ionised?

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Weak acid → 1.42% ionised

$[H_3O^+] = 0.150\ M \times 1.42/100$

$= 2.13 \times 10^{-3}\ M$

Acids and Bases

AUTOIONISATION OF WATER

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- As we have seen, water can act as either an acid or a base. As a result, it can react with itself in an *acid-base reaction*. This process is called water autoionization.

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

- The process is reversible and the equilibrium constant for the autoionisation of water is K_w, also known as the ion product of water.
  - By experiment at 25 ^oC: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M
  - Therefore, at 25 ^oC: $K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$ M^2

$$\boxed{K_w = [H_3O^+]\,[OH^-]}$$

Acids and Bases

ION PRODUCT OF WATER, K_W

$K_w = [H_3O^+][OH^-]$
$= 1.0 \times 10^{-14}\ M^2$

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- For example, calculate $[OH^-]$ of a solution of 0.245 M nitric acid.

Nitric acid, HNO_3, is a strong acid.

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$

$[H^+] = 0.245$ M

Substituting in $[H_3O^+][OH^-] = 1.0 \times 10^{-14}\ M^2$

$$[OH^-] = \frac{1.0 \times 10^{-14}\ M^2}{0.245\ M} = 4.08 \times 10^{-14}\ M$$

- For example, calculate $[H_3O^+]$ of a 0.331 M NaOH solution.

NaOH is a strong base.

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

$[OH^-] = 0.331$ M

Substituting in $[H_3O^+][OH^-] = 1.0 \times 10^{-14}\ M^2$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}\ M^2}{0.331\ M} = 3.02 \times 10^{-14}\ M$$

Acids and Bases

H_3O^+ VERSUS OH^- IN WATER

$$K_w = [H_3O^+]\,[OH^-]$$
$$= 1.0 \times 10^{-14}\ M^2$$

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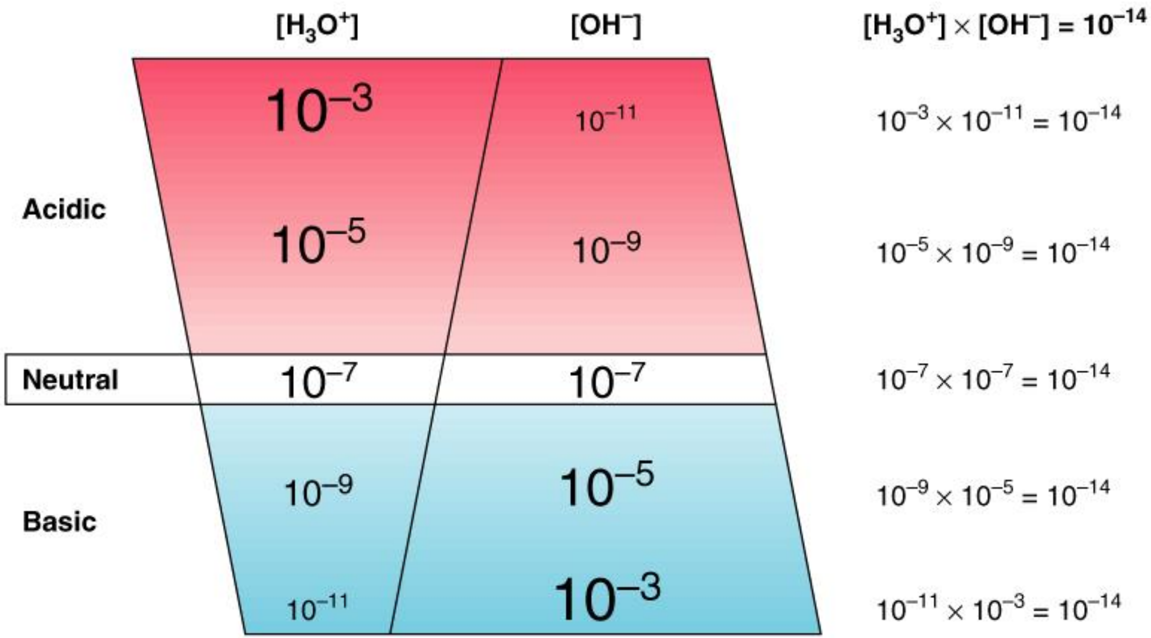

Figure 12-5 The Relationship Between H_3O^+ and OH^- in Water. A large concentration of H_3O^+ corresponds to a low concentration of OH^- in a solution, and vice versa.

Acidic solution:
$[H_3O^+] > 1.0 \times 10^{-7}$ M
and $[OH^-] < 1.0 \times 10^{-7}$ M

Neutral solution:
$[H_3O^+] = [OH^-]$
$= 1.0 \times 10^{-7}$ M

Basic solution:
$[OH^-] > 1.0 \times 10^{-7}$ M and
$[H_3O^+] < 1.0 \times 10^{-7}$ M

Acids and Bases

PH SCALE

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\ M^2$$

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- $[H3O^+]$ and $[OH^-]$ concentrations tend to be relatively small numbers (eg 1.0×10^{-7} M)

- We use the **pH** and **pOH** scale, as among others things, it enables us to avoid working with small numbers. The operator **"p"** means **"-log of"** the concentration.

Acid: $pH = -\log_{10}[H_3O^+]$

(rearranging): $[H_3O^+] = 10^{-pH}$

If $[H_3O^+] = 1.0 \times 10^{-7}$ M in a **neutral** solution, then:

$pH = -\log_{10}[\ 1.0 \times 10^{-7}\ ]$

$= \mathbf{7.00}$

Base: $pOH = -\log_{10}[OH^-]$

(rearranging): $[H_3O^+] = 10^{-pH}$

If $[OH^-] = 1.0 \times 10^{-7}$ M in a **neutral** solution, then:

$pOH = -\log_{10}[\ 1.0 \times 10^{-7}\ ]$

$= \mathbf{7.00}$

Acids and Bases

PH AND POH SCALES

$$K_w = [H_3O^+][OH^-]$$
$$= 1.0 \times 10^{-14}\ M^2$$

	$[H_3O^+]$	$[OH^-]$	pH	pOH
Acidic	10^{-3}	10^{-11}	3	11
	10^{-5}	10^{-9}	5	9
Neutral	10^{-7}	10^{-7}	7	7
Basic	10^{-9}	10^{-5}	9	5
	10^{-11}	10^{-3}	11	3

Acidic solution:
pH < 7 & pOH > 7

Neutral solution:
pH = pOH = 7

Basic solution:
pH > 7 & pOH < 7

Acids and Bases

EXAMPLES

$$K_w = [H_3O^+]\,[OH^-]$$
$$= 1.0 \times 10^{-14}\ M^2$$

- ***Calculate the pH of a 0.037 M hydrochloric acid solution.***

HCl is a strong acid.

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

$[H^+] = 0.037\ M$

$pH = -\log_{10}[H^+] = -\log_{10}0.037 = 1.43$

- ***What is the pOH of the above solution?***

$pOH + pH = 14.00$

$pOH = 14.00 - 1.43 = 12.57$

- ***Calculate [H+] in a solution with a pH of 5.92.***

$pH = 5.92 = -\log_{10}[H^+]$

$[H^+] = 10^{-5.92} = 1.2 \times 10^{-6}\ M$

- ***Calculate the pH of a 0.016 M solution of calcium hydroxide.***

$Ca(OH)_2$ is a strong base.

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

$[OH^-] = 2 \times 0.016\ M = 0.032\ M$

$pOH = -\log_{10}[OH^-] = -\log_{10}0.032$

$= 1.49$

$pH = 14.00 - pOH = 12.51$

Stop